LATVIJAS
UNIVERSITĀTE

ĶĪMIJAS FAKULTĀTE

**Aleksandrs Aršaņica**

# RŪPNIECISKAI RAŽOŠANAI PIEMĒROTI RISINĀJUMI BIORAFINĒŠANAS CEĻĀ IEGŪTU LIGNĪNU KĀ ATJAUNOJAMO IZEJVIELU IZMANTOŠANAI POLIMĒRU SASTĀVĀ

PROMOCIJAS DARBS

Doktora grāda iegūšanai ķīmijas nozarē

Apakšnozare: fizikālā ķīmija

Darba vadītāja

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Rīga, 2021

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# ANOTĀCIJA

Rūpnieciskai ražošanai piemēroti risinājumi biorafinēšanas ceļā iegūtu lignīnu kā atjaunojamo izejvielu izmantošanai polimēru sastāvā. Aršaņica, Aleksandrs. Darba vadītāja: prof. *Dr. habil. chem*. Gaļina Teliševa. Rakstu kopas kopsavilkums, 33 lapaspuses, 18 attēli, 6 tabulas, 59 literatūras avoti. Latviešu valodā.

BIORAFINĒŠANA, LIGNĪNS, BIOPLASTMASA, FRAKCIONĒŠANA AR ORGANISKAJIEM ŠĶĪDINĀTĀJIEM, OKSIALKILĒŠANA, GLICIDILĒŠANA, MAKROMONOMĒRS, AKTĪVA PILDVIELA, POLIURETĀNI, EPOKSĪDI.

Darba mērķis ir teorētiskās bāzes izveide un tehnoloģiskās koncepcijas izstrāde biorafinēšanas procesos radīto tehnisko lignīnu izmantošanai par biobāzētu materiālu sastāvdaļām. Galvenie uzdevumi ir metožu izstrāde lignīnu mehāniski ķīmiskai aktivācijai, lignīnu ķīmiskai modifikācijai, veicot frakcionēšanu ar organiskajiem šķīdinātājiem, modifikācijai ar oksirāna gredzenu saturošiem monomēriem savienojumiem un iegūto produktu izmantošana par hidroksilu un epoksīdu saturošiem makromonomēriem vai aktīvām pildvielām polimēru materiālos.

Izmantojot izstrādāto metodiku, tika modificēts un poliuretāna materiālos ievietots jaunais organiskajos šķīdinātājos šķīstošais lignīns *Organosolv* (OSL), kas izstrādāts kviešu salmu biorafinēšanas procesā *Compagnie Industrielle de la Matierre Vegetale* (CIMV) uzņēmumā Francijā.

Lignīna modifikācijas pirmā pieeja ļauj iegūt makromonomēru poliuretāna elastomēriem, un tas ietver lignīna frakcionēšanu, secīgi ekstrahējot to ar organiskajiem šķīdinātājiem. Poliuretāna (PU) plēves tika sintezētas no trim komponentiem – lignīna frakcijas, polietilēnglikola (PEG) un polimēra metildiizocianāta (PMDI) –, izmantojot liešanas metodi. Atkarībā no lignīna frakcijas veida un tā daudzuma materiāla sastāvā, tika iegūti augstas elastības PU elastomēri ar augstām elastības īpašībām istabas temperatūrā vai stingras stiklveida šķērssaistītas PU putas ar stiklošanās temperatūru virs 100 °C. Apstrādājot PU 200–600 °C temperatūrā skābekļa klātbūtnē (gaisā), lignīna frakcijas darbojas kā antioksidanti, kā arī veicina ogļu veidošanos.

Cita pieeja paredz lignīna modifikāciju, kas piemērota cietu, uz lignīna bāzes veidotu poliuretāna putu iegūšanai, un šis risinājums ietver lignīna pārveidošanu šķidros lignopoliolos reakcijā ar propilēna oksīdu (PO). Tika pētīta sākotnējā reakcijas maisījuma lignīna (L) satura ietekme uz oksipropilēšanas procesu un lignopoliolu īpašībām, kā arī uz L/PO kopolimēru īpašībām. Ja lignīna saturs sākotnējā reakcijas maisījumā ir 15–30%, iegūto lignopoliolu īpašības atbilst cietu poliuretāna putu ražošanai izmantojamo poliolēteru prasībām. Komerciālā uz glicerīna bāzes veidotā poliola poliētera aizstāšana ar lignopoliolu uzlabo PU putu šūnu struktūras viendabīgumu, izmēru stabilitāti, samazina ūdens absorbcijas spēju, uzlabojot materiāla fizikāli mehāniskās īpašības. Lignīns pēc tā mehāniski ķīmiskās aktivācijas tika ievadīts PU putu sistēmā arī kā pildviela, un tika pētīta lignīna ievadīšanas metodes ietekme uz iegūto materiālu īpašībām. Iekļaujot lignīnu poliuretāna putās, tika novērota termodegradācijas ātruma maksimālo vērtību samazināšanās.

Vēl cita pieeja bija saistīta ar lignīna ievadīšanu epoksīdsveķos, un tā tika testēta, izmantojot *LignoBoost*™ skujkoku kraftlignīnu, kas iegūts biorafinēšanas procesā

komerciālā mērogā. Epoksīdsveķi uz lignīna bāzes tika iegūti, ekstrahējot glicidilētu lignīnu ar acetonu vai glicidilējot acetonā šķīstošo lignīna frakciju. Tika pētīta glicidilēšanas režīmu ietekme uz acetonā šķīstošo frakciju iznākumu, to funkcionālo sastāvu un fizikāli ķīmiskajām īpašībām. Daļēja komerciālo fosilo sveķu aizstāšana ar glicidilēta lignīna frakciju pozitīvi ietekmē cietināto epoksīdu īpašības.

# SATURS / CONTENTS

# SAĪSINĀJUMU SARAKSTS

| | |
|---|---|
| BPA | bisfenols A |
| DCM | dihlormetāns |
| DTG | atvasinātā termogravimetrija |
| DSC | diferenciālās skenēšanas kalorimetrija |
| ECH | epihlorhidrīns |
| EEW | epoksīda ekvivalentais svars |
| F | frakcija |
| FTIR spektroskopija | Furjē transformācijas infrasarkanā spektroskopija |
| GC | gāzes hromatogrāfija |
| GLAF | acetonā šķīstošā glicidilētā lignīna sveķu frakcija |
| KL | kraftlignīns |
| LPU | lignopoliuretāni |
| L3300 | *Lupranol 3300*, komerciālais poliola poliēteris uz glicerīna bāzes |
| L3422 | *Lupranol 3422*, komerciālais poliola poliēteris uz sorbitola bāzes |
| MET | metanols |
| MDI | 4,4'-metilēndifenildiizocianāts |
| PMDI | polimērs metilēndifenildiizocianāts |
| MMD | molekulārās masas sadalījums |
| MW | molmasa |
| NMR | kodolmagnētiskā rezonanse |
| OHV | hidroksilvērtība |
| OSL | organiskajos šķīdinātājos šķīstošais lignīns, *Organosolv* |
| PEG | polietilēnglikols |
| PO | propilēnoksīds |
| PU | poliuretāns |
| PUR | cietas poliuretāna putas |
| TBAB | tetrabutilamonija bromīds |
| TG | termogravimetrija |
| SEC | gelfiltrācijas hromatogrāfija |

# IEVADS

Biomasas atjaunojamo resursu izmantošanu ķīmiskajā rūpniecībā līdz šim kavēja fosilo izejvielu (naftas, gāzes, akmeņogļu) pieejamība ķīmiskās rūpniecības vajadzībām, kā arī to standartizācijas vieglums, daudzu gadu pieredze pārstrādē, izveidotā efektīvā tehnoloģisko procesu kontrole un attīstītā loģistika. Tomēr jāņem vērā, ka pasaulē fosilo resursu rezervju krājumi samazinās, tie neatjaunojas un ar katru gadu saasinās vides piesārņojuma problēmas, ko rada to izmantošana. Minētie faktori nosaka nepieciešamību aktīvi attīstīt pētījumus, kas saistīti ar atjaunojamās, videi draudzīgās biomasas izmantošanu ķīmiskajā rūpniecībā (Hu *et al.*, 2002, Lampinen *et al.*, 2011). Patlaban noteiktais mērķis ir līdz 2030. gadam vismaz 30% esošo naftas produktu aizstāt ar augstvērtīgākiem, ilgtspējīgākiem un ekonomiski dzīvotspējīgākiem produktiem, tādējādi samazinot kaitīgo izmešu emisiju par 50%. Polimērķīmijas un tehnoloģijas mūsdienu attīstības virzienus nosaka resursu bāzes paplašināšana, izmantojot atjaunojamus izejmateriālus, palielinot "zaļās" sastāvdaļas īpatsvaru, un materiālu bioloģiskās noārdīšanās uzlabošana.

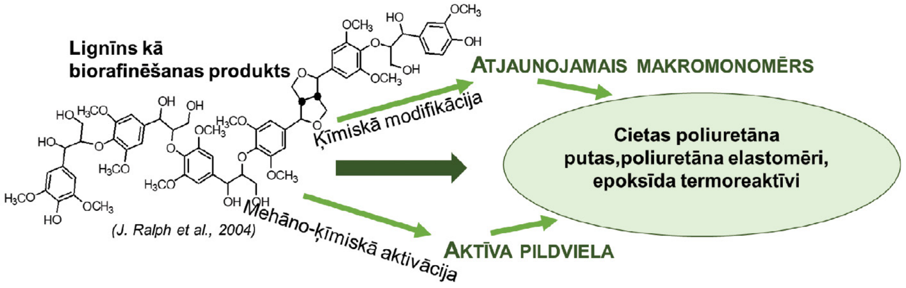
Ligno-ogļhidrātu biomasas delignifikācija un hidrolīze joprojām ir vislielākā mēroga augu biomasas ķīmiskās pārstrādes tehnoloģijas, kuru mērķis ir izmantot šos ogļhidrātu komponentus celulozes, papīra un bioetanola ražošanā. Lignīns ir visizplatītākais aromātiskais atjaunojamais biopolimērs, tomēr tas tiek nepietiekami novērtēts un izmantots. Tehniskā lignīna iznākums iepriekšminētajos rūpnieciskās ražošanas procesos atkarībā no izejmateriāla veida un izvēlētās tehnoloģijas ir 30–50% (no izejmateriāla sausās masas). Pasaules rūpniecība katru gadu rada apmēram 55 miljonus tonnu lignīna (Calvo-Flores *et al.,* 2010). Pašlaik aptuveni 98% no iegūtā lignīna tiek sadedzināti, lai iegūtu enerģiju galvenajiem tehnoloģiskajiem procesiem (Lampinen *et al.,* 2011). Saskaņā ar Eiropas Savienības pamatnostādņu tehnoloģisko platformu attīstības plānu mūsdienīgu, augsti efektīvu ražošanas objektu izveides pamatprasība ir bezatkritumu tehnoloģiskie procesi, kas tiek īstenoti saskaņā ar biorafinēšanas shēmu, kuras ietvaros visu veidu atkritumi tiek izmantoti kā izejvielas jauna mērķa produkta iegūšanai (Bozell *et al.,* 2007). Pasaules visizplatītāko bioaromātisko savienojumu pārdomāta izmantošana varētu ievērojami palielināt nākotnes lignocelulozes biorafinēšanas uzņēmumu rentabilitāti. Šajā sakarā tiek izstrādātas jaunas biofinansēšanas shēmas, kurās lignīna valorizācija tiek uzskatīta par vienu no galvenajiem mērķiem (Renders *et al.,* 2017).

Daudzsološākie potenciālie dažādas izcelsmes lignīnu izmantošanas veidi ir vērtīgu ķīmisko vielu, tādu kā fenols, benzols, toluols un ksilols (Zakzeski *et al.*, 2010), ražošana, kā arī lignīna izmantošana polimēru kompozītmateriālos pildvielas un makromonomēra bloka veidā, pēdējā gadījumā mērķtiecīgi iekļaujot to kopolimēru struktūrā caur kovalentajām saitēm. Ir pētīta lignīna izmantošana dažādos materiālos, piemēram, fenola sveķos (Da Silva *et al.*, 2013; Lora un Stiklers, 2002; Stjuarts, 2008), poliuretānos (Lora un Glasser, 2002; Pan un Saddler, 2013), epoksīdsveķos (Lora un Glasser, 2002; Stewart, 2008) un oglekļa šķiedrās (Hu, 2002; Pan, 2013). Lignīna pievienošana samazina iegūtā materiāla izmaksas, turklāt palielina tā elastību un arī tā siltuma, gaismas un sala izturību. Lignīnu var izmantot arī kā antioksidantu dažādos kompozītmateriālos (Pan *et al.*, 2006, El Hage *et al.*, 2020).

Jaunu biomasas pārstrādes tehnoloģiju izstrāde ļauj radīt tehniskus lignīnus ar uzlabotām īpašībām un paver jaunas iespējas izmantot tos kā biobāzētu materiālu sastāvdaļas (Renckens, 2017). Celulozes un papīra rūpniecībā tradicionālo delignifikācijas procesu mērķis ir izšķīdināt lignīnu, kas tiek uzskatīts par atkritumu. Visizplatītākajā krafta delignifikācijas procesā sārmu un nātrija sulfīdu izmanto kā reaģentus un koksni kā izejvielu. Attīstāmā CIMV delignifikācija ar organiskajiem šķīdinātājiem atbilst biorafinēšanas koncepcijai, un tā ļauj izdalīt un izmantot galvenos komponentus: lignīnu, celulozes pulpu un pentožu cukuru sīrupu. Šajā procesā trīs komponentu maisījumu, kas sastāv no etiķskābes, skudrskābes un ūdens, izmanto kā reaģentu, un kviešu salmus – kā izejvielu. Tā kā delignifikācijas tehnoloģijas, kurās izmanto organiskos šķīdinātājus, būtiski atšķiras no tradicionālajām tehnoloģijām, un lignīnu struktūra ir labila, iepriekš iegūtās zināšanas par tehnisko lignīnu valorizāciju nevar pārnest uz jaunajiem tehniskajiem lignīniem. CIMV lignīna izmantošana PU sastāvā veicinātu šīs biorafinēšanas tehnoloģijas komercializēšanu. Pašlaik vienīgais biorafinēšanā izmantotais lignīna izdalīšanas process, kas realizēts komerciālā mērogā, ir *Innventia AB* un Čalmersa Tehniskās universitātes (*Chalmers University of Technology*, Zviedrija) izstrādātā *LignoBoost* koncepcija (Tomani, 2010). *LignoBoost* lignīns ir jauna modificēta krafta procesa produkts. Šī tehniskā lignīna īpašības un lietošanas iespējas tiek aktīvi pētītas visā pasaulē.

Šī **darba mērķis** ir teorētiskās bāzes izveide un tehnoloģiskās koncepcijas izstrāde biorafinēšanas procesos radīto tehnisko lignīnu izmantošanai biobāzētu materiālu sastāvā.

**Galvenie uzdevumi** ir izstrādāt lignīnu mehāniski ķīmiskās aktivācijas metodes; izstrādāt lignīnu ķīmiskās modifikācijas metodes, izmantojot frakcionēšanu ar organiskajiem šķīdinātājiem; izstrādāt metodes lignīnu modifikācijai ar oksirāna gredzenu saturošiem monomēriem savienojumiem, lai iegūtu produktus, ko var izmantot par hidroksilu un epoksīdu saturošiem makromonomēriem vai aktīvām pildvielām polimēru materiālos (1. att.).



*1. attēls.* **Darba galveno uzdevumu shematisks attēlojums**

## Promocijas darba mērķa sasniegšanai ir izvirzīti šādi uzdevumi:

1. Raksturot un salīdzinoši analizēt tehnisko lignīnu un to komponentu funkcionālo sastāvu, to struktūras fizikāli ķīmiskos parametrus.
2. Novērtēt ar dažādas polaritātes šķīdinātājiem veiktas frakcionēšanas ietekmi uz *Organosolv* lignīna molekulāro un funkcionālo neviendabīgumu.
3. Izpētīt *Organosolv* lignīna reakciju ar propilēna oksīdu dažādos apstākļos un raksturot iegūto lignopoliolu ķīmiskās un fizikāli ķīmiskās īpašības.
4. Izmantot lignopoliolu kā hidroksilu saturošu makromonomēru cietajās poliuretāna putās un izpētīt iegūto materiālu fizikālās, mehāniskās un termiskās īpašības.
5. Veikt lignīna mehāniski ķīmisko aktivāciju, iekļaut to kā aktīvo pildvielu cieto poliuretāna putu sastāvā un izpētīt iegūto materiālu īpašības.
6. Dažādos apstākļos izpētīt nefrakcionēta un frakcionēta lignīna reakciju ar epihlorhidrīnu, izmantot iegūto produktu kā epoksīdu saturošu makromonomēru un izpētīt tā ietekmi uz komerciālo, ar amīnu cietināto epoksīda sveķu stiepes un termiskajām īpašībām.

## Rezultātu zinātniskā nozīme un novitāte

1. Iegūtās *Organosolv* lignīna frakcijas ir derīgas izmantošanai hidroksilu saturošu makromonomēru poliuretāna elastomēros, un tās vienlaikus spēj regulēt poliuretāna tīkla šķērssaistīšanos un darboties kā tehniski antioksidanti.
2. Tika noteikti *Organosolv* lignīna oksipropilēšanas procesa optimālie apstākļi un izejvielu optimālās attiecības.
3. Iegūtie lignopolioli sastāv no diviem galvenajiem komponentiem: no *Organosolv* lignīna ar propilēnoksīdu mijiedarbības produkta un propilēnglikola atvasinājumiem ar dažādām molekulmasām. Iegūtajiem lignopolioliem ir ievērojami augstāka reaģētspēja ar MDI dioksānā salīdzinājumā ar komerciālajiem uz glicerīna bāzes sintezētiem poliēteriem, kurus plaši izmanto PUR putu iegūšanai. *Organosolv* lignīna oksipropilēšana ievērojami samazināja tā polidispersitāti un palielināja segmentu kustīgumu.
4. Daļēja komerciālā poliētera aizstāšana ar lignopoliolu uzlaboja PU putu izmēru stabilitāti un hidrofobitāti, kā arī to termisko stabilitāti, pazemināja uzliesmojamību un neietekmēja tā spiedes īpašības.
5. Ievadot kviešu salmu *Organosolv* lignīnu poliuretānā vienlaikus kā lignopoliolu un pildvielu, cietā lignīna pildviela labāk savienojas ar poliuretāna putu komponentiem salīdzinājumā ar poliuretāna putu sistēmu, kas nesatur lignopoliolu.
6. *LignoBoost* kraftlignīna epoksīdiem ir šaurs molekulmasu sadalījums un epoksīda funkcionalitāte diapazonā no 3,1 līdz 4,5. Lignīns, kas ir ķīmiski iestrādāts cietināto komerciālo epoksīdsveķu matricā, augstā temperatūrā palielina to ogļu iznākumu un samazina degradācijas ātrumu salīdzinājumā ar references materiālu, un tas liecina par lignīna epoksīdu potenciālo izmantošanu liesmas izturīgu epoksīdu ražošanā.

## Rezultātu praktiskā nozīme

1. Kompozītmateriālu, kas satur modificētus lignīnus kā makromonomērus, uzlabotās īpašības (termiskā stabilitāte, izmēru stabilitāte, hidrofobitāte, stiepes izturība, Junga modulis, mazāka uzliesmojamība) salīdzinājumā ar komerciālajiem references materiāliem paver jaunas iespējas biobāzētu polimēru izstrādei.
2. Ir izstrādāta metodoloģija polimēru sintēzei izmantojamo hidroksilu saturošo makromonomēru iegūšanai uz dažādu tehnisko lignīnu bāzes. Metodoloģija ir aprobēta rūpniecības apstākļos pētniecības un ražošanas asociācijas eksperimentālajā rūpnīcā "Polymersintez" (Vladimira, Krievija).
3. Šo pētījumu rezultāti ļauj ražot lignopoliuretāna putas, kuras var izmantot, lietojot formēšanas un izsmidzināšanas metodes, un kuru īpašības atbilst tām putām, ko izmanto kā siltumizolējošus un vieglus celtniecības materiālus.
4. Formējot lignopoliuretāna putu sistēmu, pētniecības un ražošanas asociācijā "Gauja" (Rīga, Latvija) eksperimentāli tika izgatavoti sarežģītas konfigurācijas mīksto mēbeļu rāmja elementi.
5. Sadarbībā ar Latvijas Valsts būvniecības un eksperimentālo tehnoloģiju zinātnisko institūtu (Rīga, Latvija) un Latvijas Valsts koksnes ķīmijas institūta Polimēru laboratoriju (Rīga, Latvija) tika saražoti siltumizolācijas pārklājumi un "sendviča" tipa paneļi ar poliuretāna putu izolācijas slāni uz lignosulfonāta un *Organosolv* kviešu salmu lignīna bāzes.

## Iegūtie rezultāti sniedz nozīmīgu ieguldījumu šādu projektu īstenošanā:

1) H2020 projekts US4 GREENCHEM "Kombinēta lignocelulozes izejvielu ultraskaņas un enzīmu apstrāde cukura iegūšanai biotehnoloģiskām vajadzībām" (2015.–2019. g.);
2) līgums Nr. 13-46 ar MetGen Oy (Somija). Uzdevums: "MetGen pārstrādē izdalīto lignīna frakciju raksturojums, to oksipropilēšana un cieto PU putu iegūšana uz iegūto lignopoliolu bāzes" (2018). Izejas lignīns tika atdalīts ar METNIN™ valorizācijas tehnoloģiju biobāzētu rūpniecību kopuzņēmuma ietvaros saskaņā ar pētniecības un inovācijas programmu "Horizon 2020" projektam SWEETWOODS saskaņā ar grantu Nr. 792061. Līguma vadītājs no KĶI – A. Aršanitca;
3) Valsts pētījumu programmas *ResProd* projekts Nr. 3 "Meža un zemes dzīļu resursu izpēte, ilgtspējīga izmantošana – jauni produkti un tehnoloģijas" (2014.–2018. g.);
4) sadarbības projekts "BIOCORE" ("Biocommodity refinery") ES 7. programmas ietvaros. Līgums Nr. 241566 (2010.–2014. g.).

**Rezultāti ir izklāstīti 9 publikācijās recenzētos žurnālos, grāmatā "Cellulosics: Chemical, Biochemical and Material Aspects", 10 starptautiskās zinātniskās konferencēs, un uz to pamata ir izstrādāts Eiropas patents.**

## Pilna teksta zinātniskās publikācijas

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3. **Arshanitsa, A**., Vevere, L., Telysheva, G., Dizhbite T., Gosselink, R. J. A., Bikovens, O., Jablonski, A. Functionality and physico-chemical characteristics of wheat straw lignin, Biolignin™ derivatives formed in the oxypropylation process. *Holzforschung* (**IF 1.875**). 2015, vol. 69, no. 6, pp. 785–793. Available from: doi: 10.1515/hf-2014-0274 (P-3)
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6. **Arshanitsa, A.**, Ponomarenko J., Dizbite, T., Andersone, A., Gosselink, R. J. A., van der Putten, J., Laubert, M., Telysheva, G. Fractionationation of technical lignin as a tool for improvement of their antioxidant properties. *Journal of Analytical and Applied Pyrolysis* (**IF 3.91**). 2013, vol. 103, pp. 78–85. Available from: doi: 10.1016/j.jaap.2012.12.023 (P-6)
7. Dizhbite, T., Telysheva, G., Dobele, G., **Arshanitsa, A**., Andersone, A., Kampars, V. Py-GC/MS for characterization of non-hydrolyzed residues from bioethanol production from softwood. *Journal of Analytical and Applied Pyrolysis* (**IF 3.91**). 2011, vol. 90, no. 2, pp. 126–132. Available from: doi: 10.1016/j.jaap.2010.11.004 (P-7)
8. **Arshanitsa, A**., Paberza, A., Vevere, L., Cabulis, U., Telysheva, G. Two approaches for introduction of wheat straw lignin into rigid polyurethane foams. *AIP Conference Proceedings* (**IF 0.4**). 2014, pp. 388–391. Available from: doi:10.1063/1.4873806 (P-8)
9. **Arshanitsa, A. S.**, Gromova, M. F., Ioelovich, M. Y., Chirkova, E. A., Sisask, U. O. Vliyanie mehanicheskoj obrabotki na svojstva gidroliznogo lignina kak napolnitelya elastomerov [Influence of mechanical treatment on the properties of hydrolysis lignin as a filler for elastomers]. *Khimiya drevisini [Wood chemistry]*. 1990, no. 3, pp. 76–80 (P-9)

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Latvian State Institute of Wood Chemistry. *Method for production of heat-insulating materials [Verfahren zur Herstellung von Warmedammaterialien, Siltumizolācijas materiālu iegūšanas paņēmiens].* **A. Arshanitsa**, G. Telysheva, A. Paberza, U. Cabulis, L. Vevere, T. Dizhbite**.** Data of submission 2013-30-09. Pat. EP 2816052 A1, C 08G18/76, C 08G18/64, C 08L97/00, C 08H7/00, C 07G1/00. 2014-12-24. Available: https://www.google.com/patents/EP2816052A1?cl=en; https://register.epo.org/application?lng=de&tab=main&number=EP1318678; https://worldwide.espacenet.com. (P-11)

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## Lignīnu modifikācijas metodikas izstrāde un pielietošana polimēru kompozīcijās ir aprakstīta arī citās publikācijās un patentos, kas nav iekļauti šajā darbā

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8. Institute of General and Inorganic Chemistry of National Academy of Sciences of Belarus, Latvian State Institute of Wood Chemistry. *Sposob flotacii glinistih kalijnih rud [Clay potash ore flotation method].* A. Markin, L. Zhibul, N. Makarevich, G. Telysheva, M. Gromova, **A. Arshanitsa**. Data of submission 1989-12-12. SU 1704835, МПК B3D 1/012. 1992-01-15. Available: http://patents.su/2-1704835-sposob-flotacii-glinistykh-kalijjnykh-rud; http://www.findpatent.ru/patent/170/1704835.
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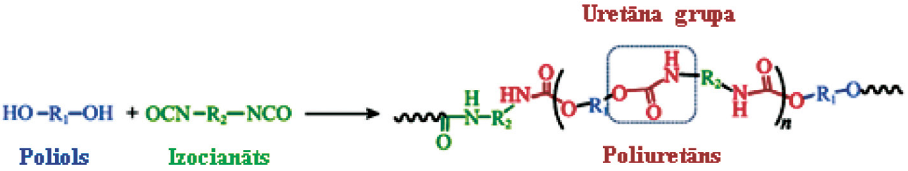
# 1. LITERATŪRAS APSKATS

Bioplastmasas tirgus ir viens no visstraujāk augošajiem tirgiem mūsdienās. Pēdējos gados tā vidējie pieauguma tempi pastāvīgi ir bijuši raksturojami ar divciparu skaitļiem (Storz and Viorlop, 2013, Zhao *et al.*, 2020). Eiropas Bioplastmasas asociācija bioplastmasu definē kā biobāzētu vai bioloģiski noārdāmu materiālu, vai gan pirmo, gan otro (European bioplastic, 2015). Termins "biobāzēts" nozīmē, ka materiāls tiek iegūts (pilnībā vai daļēji) no biomasas. Atjaunojamā oglekļa saturs bioplastmasā svārstās no 20% līdz 100% (Biron, 2020).

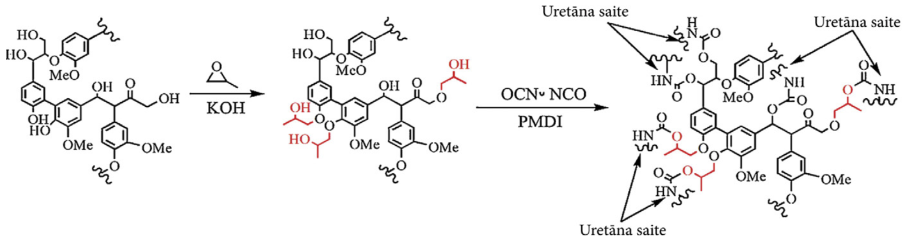
Poliuretāni (PU) ir visdaudzpusīgāk izmantojamais polimēru veids. Uz to pamata tiek iegūti visi zināmie materiālu veidi, kurus izmanto visās rūpniecības nozarēs bez izņēmuma. PU putas ir viens no vissvarīgākajiem siltumizolācijas materiāliem, ko izmanto būvniecības nozarē, un galvenais izolācijas materiāls, izmantojams izplatītajās ierīcēs (ledusskapji, saldētavas utt.). Viens no noteicošiem mūsdienu ķīmijas un PU tehnoloģijas attīstības virzieniem ir resursu bāzes paplašināšana, izmantojot atjaunojamus izejmateriālus, tādā veidā palielinot "zaļās" sastāvdaļas daļu, kopā ar iespēju uzlabot materiāla ekspluatācijas īpašības (Vahabi *et al.*, 2020). Saskaņā ar neseno ziņojumu globālais PU tirgus pieauguma temps ir sasniedzis 6,0%, un tiek lēsts, ka līdz 2026. gadam tas sasniegs 88 miljardus ASV dolāru lielu apgrozījumu (Sonnenschein *et al.*, 2014, Polyurethane (PU) market 2020, Grand view research 2020).

No ķīmijas viedokļa PU var definēt kā organiskus polimērus ar uretāna saitēm, kuras veidojas ķīmiskas reakcijas rezultātā starp izocianātiem un polioliem (2. att.).



*2. attēls.* **Poliuretānu veidošanās reakcija (Li, H., Liang. Y.** ***et al.*****, 2020)**

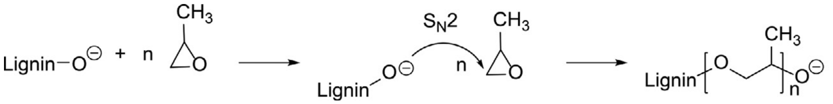
Aptuveni 30–40% no PU sastāva pēc masas veido polioli vai poliolu maisījumi (Grand view research, 2020, Ionescu 2005). Paredzams, ka pasaulē poliolu tirgus apjoms līdz 2025. gadam sasniegs 45,17 miljardus ASV dolāru ar kopējo gada pieauguma tempu – 8,5% (Research and markets, 2020). OH grupu saturs lignīnā (10–12% pēc svara) atbilst prasībām (11–15% pēc svara) (Ionescu, 2005), kas izvirzītas komerciāliem polioliem, kurus izmanto PU ražošanai. Lignīna izmantošana var uzlabot PU mehāniskās īpašības, termisko stabilitāti un palielināt to bioloģisko noārdīšanos (Hu *et al.*, 2002). Lignīnu saturoša PU materiāla īpašības ir atkarīgas no lignīna ievadīšanas metodes.



*3. attēls.* **Poliuretānu veidošanās no lignopolioliem (Li, B., Zhou, M.** ***et al.*****, 2020)**

Iespējamie tehnoloģiskie ceļi lignīna ievadīšanai PU materiālos ir šādi: tos pievieno kā inertu pulverveida pildvielu, kā ar hidroksiliem bagātinātu aktīvi reaģējošu pulverveida pildvielu vai šķīduma veidā kā hidroksilfunkcionālu monomēru, kas iegūts ķīmiskās modifikācijas ceļā, piemēram, veicot lignīna alkoksilēšanu (3. att.) (Hu *et al.*, 2002, Brodin *et al.*, 2009).

Galvenās grūtības, izstrādājot tirgum paredzētus lignīnu saturošus polimēru kompozītmateriālus, ieskaitot PU, ir šādas: tehnisko lignīnu neviendabīgums, funkcionālo grupu satura un veidu variācijas, kā arī atšķirības molekulmasas sadalījumā (MMD) lignīna fragmentu struktūrās, kas izveidojušās biomasas pārstrādes laikā, lignīnu veidojošo fenilpropāna vienību struktūru un saišu neviendabīgums, atšķirīga un ierobežota šķīdība organiskajos šķīdinātājos, ierobežota izocianātu reaģētspējīgo vietu pieejamība lignīna struktūrā telpisku traucējumu dēļ (Gosselink *et al.,* 2010, Mahmood *et al.,* 2016). Lai samazinātu iepriekš minētos lignīna trūkumus un uzlabotu tehnisko lignīnu kā makromonomēru īpašības, īpaši spēju piedalīties polimēru struktūru veidošanā, tiek izmantotas dažādas lignīna priekšapstrādes metodes. Daudzas metodes ir balstītas uz lignīna matricas depolimerizāciju, sašķeļot ētera saites un veidojot viendabīgākus oligomērus vai samazinātas molekulmasas produktus ar uzlabotu funkcionālo grupu pieejamību reakcijā ar izocianātiem (Mahmood *et al.,* 2016, Wang *et al.,* 2013). Depolimerizētos lignīnus veiksmīgi izmanto kā biopoliolus, aizstājot līdz 50% komerciālo poliolu cieto PU putu iegūšanai (Mahmood *et al.,* 2016). Tehnisko lignīnu oksipropilēšana sārmu katalizatoru klātbūtnē tiek atzīta par vēl vienu perspektīvu metodi lignīnu molekulārā un funkcionālā neviendabīguma pārvarēšanai un cieto PU putu sintēzei derīgu lignopoliolu iegūšanai (Cateto *et al.,* 2009, Ionescu, 2005) (1).

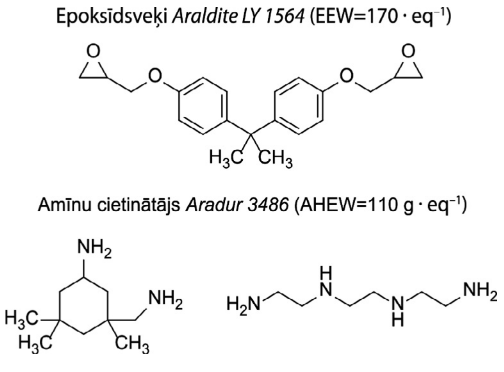


(1)

Šinī gadījumā lignīna noārdīšanos pavada oksipropila vienību piesaiste pie lignīna OH grupām, kas skābās grupas (fenola, karboksilgrupas) pārveido alifātiskajās, kurām piemīt lielāka spēja reaģēt ar izocianātu (Gandini *et al.,* 2002). Literatūrā ir aprakstīti vairāki skujkoku, lapkoku un zālaugu komerciālo tehnisko lignīnu oksipropilēšanas aspekti (Nadji *et al.,* 2005, Belgacem and Gandini, 2008, Cateto *et al.,* 2009, Ahvazi *et al.,* 2011, Li and Ragauskas, 2012). Neapšaubāmi, iepriekš minētie procesi ir izaicinoši sarežģītu reakcijas apstākļu dēļ (220–300 °C temperatūra un 5–30 bāru spiediens) (Mahmood *et al.,* 2016).

Tehnisko lignīnu frakcionēšana ar organiskajiem šķīdinātājiem, veicot ekstrakciju atmosfēras spiedienā un istabas vai paaugstinātā temperatūrā, varētu būt perspektīva iespēja paaugstināt lignīna kā makromonomēra izmantošanas efektivitāti PU materiālu ražošanā. Dažādu komerciālo krafta un organiskajos šķīdinātājos šķīstošo (etanols-ūdens) *Organosolv* lignīnu frakcionēšana ar dietilēteri, n-propanolu, metanolu un dihlormetāna/metanola maisījumu ļauj iegūt lignīna produktus ar mazāku molekulmasu (MM), vienmērīgākus pēc molekulārās masas sadalījuma un pilnīgi šķīstošus organiskajos šķīdinātājos, kurus lieto PU ķīmijā. Iegūtie modificētie lignīni ir piemēroti, lai veiksmīgi izpildītu makromonomēru lomu PU materiālu sintēzē (Gosselink *et al.,* 2010, Li and McDonald, 2014, Yoshida *et al.,* 1987). Šāda pieeja ļauj iegūt PU elastomērus ar paredzamām termiskām un mehāniskām īpašībām, kuras var variēt plašā diapazonā atkarībā no lignīna frakciju MM, to satura PU un izmantotā mīkstā segmenta veida (Yoshida *et al.,* 1990, Reiman *et al.,* 1991). Metiltetrahidrofurānā šķīstošai kraftlignīnu frakcijai (Indulin AT) pievienojot toluoldiizocianāta-trimetilolpropānu aduktu, var iegūt PU kompozītmateriālus, kurus var izmantot kā augstas kvalitātes pārklājumus un līmes (Griffini *et al.,* 2015).

Cietināti epoksīdsveķi parasti ir termoreaktīvi termiski izturīgi polimēri ar labām mehāniskajām īpašībām un augstu ķīmisko izturību (Abdurahman *et al.,* 2020; He *et al.,* 2014). Epoksīdsveķu pārklājumus, adhezīvus un armētus kompozītmateriālus plaši izmanto daudzās rūpniecības nozarēs, tostarp elektrotehnikā, elektronikā, automobiļu un gaisa kuģu rūpniecībā u. c. (Wanga *et al.,* 2016, Katunina *et al.,* 2016). Pašlaik komerciālos epoksīdsveķus galvenokārt (gandrīz 90%) ražo no naftas atvasinātām ķīmiskām vielām: bisfenola A (BPA) un epihlorhidrīna (ECH) (Khalil *et al.,* 2011). 4. attēlā ir parādīti komponenti, kas veido komerciālās, uz BPA pamata veidotās ar amīnu cietinātās epoksīdsistēmas. BPA nodrošina daudzas iegūtā produkta vērtīgās īpašības, taču diemžēl tas negatīvi ietekmē cilvēka veselību (Sasaki *et al.,* 2013). BPA un tā atvasinājumi negatīvi ietekmē cilvēka organisma endokrīno sistēmu. BPA iedarbība var izraisīt reprodukcijas, attīstības un vielmaiņas traucējumus (Fischnaller *et al.*, 2016).

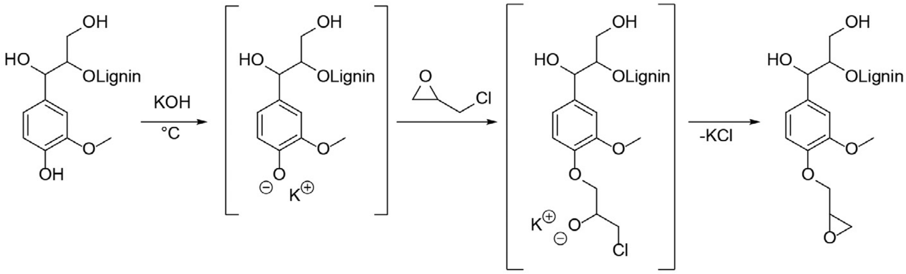

Epoksīdsveķi *Araldite LY 1564* (EEW=170 · $eq^{-1}$)

Amīnu cietinātājs *Aradur 3486* (AHEW=110 g · $eq^{-1}$)

*4. attēls.* **Komerciālās, ar amīnu cietinātās epoksīda sistēmas *Araldite LY 1564/Aradur  486* (HUNTSMAN) komponenti**

Nesen tika ziņots par vairākiem pētījumiem saistībā ar bioepoksīdsveķu sintēzi no dažādiem atjaunojamiem resursiem, piemēram, no vanilīna (Fache *et al.*, 2014), galluskābes un katehīna (Aouf *et al.*, 2013), izosorbīda (Lukaszczyk *et al.*, 2011), tannīniem (Benyahya *et al.*, 2014), augu eļļām (Shah and Ahmad, 2012 *et al.*) un lignīniem (Delmas *et al.*, 2013).

Lignīna aromātiskā struktūra un ievērojamā OH grupu (fenola, alifātisku, karboksilgrupu) daudzuma klātbūtne padara tehniskos lignīnus par perspektīvu izejvielu BPA aizvietošanai. Lignīnu var modificēt, panākot tā OH grupu reakciju ar epihlorhidrīnu. Lignīnam reaģējot ar epihlorhidrīnu (lignīna glicidilēšana), sārma katalizatora klātbūtnē notiek divi galvenie procesi (Nieh and Glasser, 1989). Viens no tiem ir hidroksilgrupu jonizācija, kas noved pie anjona nukleofilā "uzbrukuma" oksirāna gredzena ogleklim, pie tā atvēršanās un hloroglicerilētera veidošanās. Pēc tam notiek dehlorhidrogenēšana un oksirāna gredzena veidošanās. (5. att.)



*5. attēls.* **Lignīna fenola OH grupas glicidilēšanas shēma**

No lignīna OH grupām fenola grupas, salīdzinot ar alifātiskajām un karboksilgrupām, iepriekš minētajos apstākļos ir vispieejamākās glicidilēšanai, jo tiek panākts vispiemērotākais līdzsvars starp fenolātu skābumu un nukleofilitāti (Wu and Glasser, 1984).

Lai piemērotu lignīnu epoksīdsveķu ieguvei, tiek izmantotas dažādas pieejas, ieskaitot lignīna depolimerizāciju un ķīmisko modifikāciju. Ir pierādīts, ka cietināto epoksīdsveķu, kas ir iegūti uz depolimerizētu kraftlignīnu, hidrolīzes vai organiskajos šķīdinātājos šķīstošo (*Organosolv)* lignīnu bāzes, mehāniskās un termiskās īpašības ir labākas salīdzinājumā ar references komerciālajiem epoksīdsveķiem (Wang *et al.,* 2013). Vēl viena pieeja ir lignīna demetilēšana un lignīna produktu iegūšana ar brīvām fenola grupām 3 un 5 gredzena pozīcijās. Šos lignīnus varētu izmantot kā izejvielu stipri sazarotu epoksīdu ražošanā. Tomēr patlaban nav katalītiskās sintēzes metožu šī procesa realizācijai un plaši izmantotie reaģenti (alkilhalogenīdi) ir videi kaitīgi un nav piemēroti liela mēroga ražošanai (Ferhan *et al.,* 2013, Hu *et al.,* 2014). Fenolēšana ir vēl viena lignīna modifikācijas metode fenola grupu satura palielināšanai lignīnā, kura var radīt labvēlīgākus apstākļus lignīna reakcijai ar ECH. Tomēr šinī procesā tika konstatēta formaldehīda izdalīšanās un ciklizācija, fenolam eterificējoties ar lignīna sānu ķēdes oglekļiem, un tas samazina šīs pieejas priekšrocības (Podschun *et al.*, 2015). Hofmans un Glāzers ieguva epoksīda sveķus no hidroksialkillignīna (ar sārmu ekstrahēts lignīns no dzeltenās papeles, kas hidrolizēta ar tvaika sprādziena tehnoloģiju) atvasinājumiem ar dažādu alkoksilēšanas pakāpi. Lai iegūtu lignīna atvasinājumus, kas satur tikai ļoti aktīvas OH grupas, pirms reakcijas ar ECH tika veikta lignīna modifikācija ar alkilēnoksīdiem. Sagatavotos epoksīda prepolimērus sacietināja termoreaktīvos kompozītos ar augstu stiklošanās temperatūru (Hofmann and Glasser, 1993).

Tā kā lignīna īpašības un iespējas to modificēt ir ļoti atkarīgas no biomasas izcelsmes un lignīna izdalīšanas tehnoloģijas (Gosselink *et al.*, 2010), ir nepieciešams veikt pētījumus ar katru lignīna veidu, kuru plāno valorizēt.

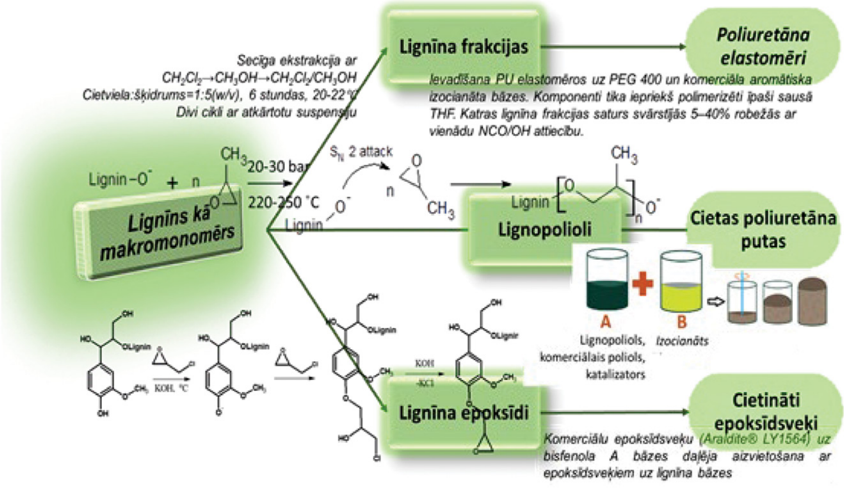
# 2. MATERIĀLI UN METODES

## 2.1. Pētāmie lignīni

Pieeja lignīna ievadīšanai poliuretāna materiālos ir parādīta piemērā ar kviešu salmu *Organosolv* lignīnu. Šo lignīnu ieguva, ekstrahējot to 3,5 stundas no kviešu salmiem ar etiķskābes, skudrskābes, ūdens maisījumu (30/55/15) atmosfēras spiedienā 105 °C temperatūrā CIMV izmēģinājumu rūpnīcā (Pomacle, Francija) (Delmas *et al.*, 2008). CIMV piegādāja lignīnu, kura aptuvenais ūdens saturs bija 48% (2015. gada 9. septembris). Materiāls tika mazgāts ar dejonizētu ūdeni līdz pH 4,4, lai atdalītu atlikušās brīvās skābes, pēc tam tas tika žāvēts gaisā līdz mitruma saturam 5% un samalts laboratorijas mēroga dezintegratorā DESI-11 ar ātrumu 10 000 apgr./min. Epoksīdsveķu iegūšana uz lignīna bāzes ir parādīta piemērā ar komerciālo *LignoBoost*™ skujkoku kraftlignīnu, kas ir izolēts no oriģinālā melnā atsārma, izmantojot jaunu *LignoBoost* tehnoloģiju. Šis lignīns ir iegūts no *Innventia AB* (uzdāvināts).

## 2.2. Lignīna modifikācija un ievadīšana polimēru kompozīcijās

- Izstrādātā koncepcija lignīnu kā makromonomēru izmantošanai polimēru kompozīcijās ir atspoguļota shēmā (6. att.).
- Lignīnu frakcionēšana ar organiskajiem šķīdinātājiem ir aprakstīta P-6.
- Lignīnu ievadīšana PU elastomēru sastāvā ir aprakstīta P-2.
- Lignīnu oksialkilēšana ir aprakstīta P-3 un P-10.



*Secīga ekstrakcija ar $CH_2Cl_2 \rightarrow CH_3OH \rightarrow CH_2Cl_2/CH_3OH$ Cietviela:šķidrums=1:5(w/v), 6 stundas, 20-22 °C Divi cikli ar atkārtotu suspensiju*

*Ievadīšana PU elastomēros uz PEG 400 un komerciāla aromātiska izocianāta bāzes. Komponenti tika iepriekš polimerizēti īpaši sausā THF. Katras lignīna frakcijas saturs svārstījās 5–40% robežās ar vienādu NCO/OH attiecību.*

*Komerciālu epoksīdsveķu (Araldite® LY1564) uz bisfenola A bāzes daļēja aizvietošana ar epoksīdsveķiem uz lignīna bāzes*

*6. attēls.* **Shēma, kas attēlo izstrādātās pieejas lignīnu modifikācijai un izmantošanai kā makromonomērus polimēru kompozīcijās**

- Lignopoliolu ievadīšana PU putu sastāvā ir aprakstīta P-8.
- Lignīnu ievadīšana cietinātos epoksīdsveķu sastāvā ir aprakstīta P-1.
- Turklāt lignīni tika mehanoķīmiski aktivizēti un ievadīti poliuretāna putu sistēmā arī kā pildviela. Tehnisko lignīnu mehanoķīmiskā aktivācija ir aprakstīta P-9. Lignīnu kā pildvielu ievadīšana PUR putu sistēmā ir aprakstīta P-5 un P-8.

## 2.3. Tehnisko lignīnu un to modifikācijas produktu komponentu analīze, strukturālā analīze un fizikāli ķīmiskā raksturošana

Izejmateriāla lignīni un to modifikācijas produkti tika izvērtēti pēc Klasona lignīna satura (TAPPI T222:2006 standarts), pelnu satura (LVS EN 14775:2016 standarts) un C, H, N satura (LVS EN 15104:2011 standarts). Pētāmiem paraugiem tika veikta funkcionālā analīze – tika noteikts metoksilgrupu (OCH3) saturs, fenola un alifātisko OH grupu saturs, karboksilgrupu saturs (Zakis, 1994). Struktūras informācija tika iegūta un lignīnu modifikācijas efektivitāte tika novērtēta, izmantojot FTIR spektroskopiju, $^{31}$P NMR spektroskopiju (Granata and Argyropoulos,1995), $^{1}$H-NMR spektroskopiju (Glasser *et al.,* 1984), analītisko pirolīzi (Py-GC/MS), gel-filtrācijas hromatogrāfiju (SEC). Stiklošanās temperatūras (Tg) tika noteiktas ar diferenciālās skenējošās kalorimetrijas (DSC) palīdzību (DIN standard 53765:1994). TGA analīze tika veikta slāpekļa un gaisa atmosfērā, tika izmantots pirmais termogravimetriskās līknes atvasinājums (diferenciālā termogravimetrija, DTG). Izstrādātā metodoloģija tehnisko lignīnu raksturošanai ir aprakstīta P-4 un P-7.

Ar secīgu ekstrakciju iegūtu lignīna frakciju kā PU tīklu makromonomēru pētījumi, ieskaitot to reakcijas ar 4,4'-metilēndifenildiizocianātu kinētiku, ir aprakstīti P-2 un P-6.

Oksipropilēšanas procesa izpēte un iegūto lignopoliolu specifiskais raksturojums ir aprakstīts P-3.

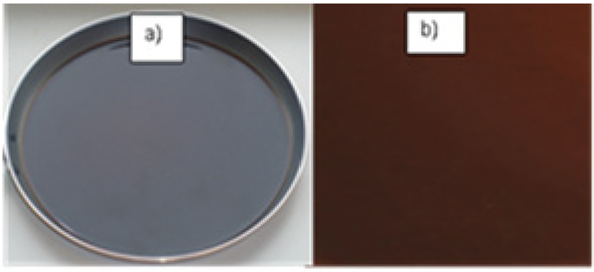
## 2.4. Iegūto polimēru kompozīciju raksturojums

Iegūtas lignopoliuretānu (LPU) plēves bija gludas un caurspīdīgas (7. att.). LPU plēvju stiepes testi tika veikti saskaņā ar ASTMD 882-10:2010 standartiem, izmantojot Zwick/Roell Z100 testēšanas mašīnu.

Poliuretāna putas (8. attēls) tika iegūtas ar brīvās putošanās metodi un testētas.

Putu saspiešanas izturības, blīvuma, slēgto šūnu satura, izmēru stabilitātes un ūdens absorbcijas mērījumi tika veikti atbilstoši attiecīgi DIN EN 826:1996, ISO 4590:2016, DIN 53420:1978, ISO 2796:1986 un DIN 53428:2017. Šūnu struktūras izpētei tika izmantots skenējošais elektronu mikroskops SEM TESCAN TS 5136 MM. Siltumvadītspēja diapazonā no 10 līdz 30 °C tika mērīta ar Linseis HFM 200 (siltuma plūsmas mērītāju) saskaņā ar ISO 8301:1991.

Stiepes testi sākotnējiem komerciālajiem epoksīdsveķiem, kas izstrādāti uz glicidilēta bisfenola A (BPA) bāzes Araldite LY 1564, un no tiem iegūtajiem epoksīdsveķiem ir veikti saskaņā ar ASTM D638:2014 standartu, izmantojot Zwick/Roell 2.5 testēšanas mašīnu.



*7. attēls.* **Lignopoliuretānu plēve, kas satur 20% lignīna metanolā šķīstošās frakcijas: a) cietēšana veidnē; b) gatavais paraugs**

*8. attēls.* **Lignopoliuretānu putas, kas iegūtas uz oksipropilētu kviešu salmu lignīnu bāzes**

*9. attēls.* **Cietinātie komerciālie epoksīdsveķi Araldite LY 1564: sākotnējais paraugs (1) un paraugs, kurā 10% glicidilēta BPA aizvietoti ar lignīna epoksīdu (2)**

Lignīna produktu ietekme uz materiālu termisko noārdīšanos tika pētīta ar termiskās analīzes (DTG un DTA) metodēm oksidatīvās (gaisa) un inertās (N2) vidēs, kā aprakstīts P-2.

# 3. REZULTĀTI UN DISKUSIJA

## 3.1. Lignīna īpašību pielāgošana, tos frakcionējot ar organiskajiem šķīdinātājiem

Galvenie rezultāti, kas attiecas uz *Organosolv* lignīna frakcionēšanu, ir parādīti P-2. Kviešu salmu *Organosolv* lignīnam (OSL) piemīt vāja šķīdība šķīdinātajos vai poiolos, kurus izmanto PU tīkla veidošanai. OSL lignīna secīga frakcionēšana ar dihlormetānu, metanolu un abu šķīdinātāju maisījumu ir perspektīvs modifikācijas paņēmiens OSL kā makromonomēra izmantošanai PU sastāvā. Iegūtajām frakcijām ir mazāka molekulmasa un mazāka polidispersitāte salīdzinājumā ar izejmateriāla lignīnu (1. tabula), kā arī pilnīga šķīdība cikliskajos ēteros, ieskaitot tetrahidrofurānu un dioksānu, un augstāka molekulāro ķēžu mobilitāte, par ko liecina stiklošanās temperatūras (Tg) vērtības (izejas lignīna Tg ir 177 °C, bet lignīna dihlormetānā šķīstošās frakcijas Tg ir 14 °C) (1. tabula). Tas uzlabo lignīna OH grupu pieejamību uretāna veidošanās reakcijā. Izocianātu un hidroksilus saturošu savienojumu mijiedarbība ir nukleofila pievienošanās reakcija.

Sakarā ar to, ka fenoli ir daudz skābāki savienojumi nekā alifātiskie spirti, tie ar izocianātiem reaģē daudz lēnāk [Saunders *et al.* 1962]. Relatīvais fenola OH reakcijas ātrums ir aptuveni 300 reižu mazāks nekā sekundāro OH grupu reakcijas ātrums (Ionescu, 2005). Arī karbonskābju reaktivitāte ar izocianātu ir daudz zemāka nekā spirtiem (Ionescu, 2005). Tāpēc kopējais OH grupu saturs un to sadalījums starp alifātiskajām un skābajām grupām (fenola un karboksilgrupām) ir nozīmīgi parametri, kas raksturo lignīna frakcijas kā makromonomērus LPU sintēzei (Kelley *et al.* 1989). Zemākais kopējais OH grupu saturs, 4,30 mmol·g$^{-1}$, ir dihlormetānā šķīstošajā frakcijā (DCM-F). Izejmateriāla lignīnā, metanolā šķīstošajā frakcijā (MET-F) un abu šķīdinātāju maisījumā šķīstošajā frakcijā (MET/DCM-F) to saturs attiecīgi ir 5,94, 7,71 un 6,83 mmol·g$^{-1}$. Ar organiskajiem šķīdinātājiem iegūtajās lignīna frakcijās relatīva alifātisko OH grupu daļa, kas visvairāk reaģē ar izocianātu, palielinās šādā vielu secībā: DCM < MET < MET/DCM (1. tabula). Attiecība starp fenola un benzola atvasinājumu summāro saturu pret gvajakola un siringola atvasinājumu summāro saturu lignīna frakciju pirolīzes produktos norāda, ka lignīna kondensācijas pakāpe palielinās jau minētās rindas secībā.

Palielinoties iegūto frakciju lignīna sastāvdaļu molekulārajam svaram un kondensācijas pakāpei, to Tg palielinās no 14 °C DCM-F līdz 160 °C MET/DCM-F (1. tabula).

Poliolu vidējo OH funkcionalitāti definē kā OH grupu skaitu vienā molekulā (Ionescu, 2005). Šīs vērtības ir 1,4, 4,2 un 7,5 attiecīgi DCM-F, MET-F un MET/DCM-F frakcijām. Tādēļ var sagaidīt atšķirīgu šķērssaistīšanās efektu, ja PU matricā iekļauj vienādu daudzumu dažādu lignīna frakciju ar vienādu NCO/OH attiecību.

Šie rezultāti parāda, ka uretāna veidošanās process, kurā lignīns tiek izmantots kā hidroksilgrupas saturošs komponents, norisinās saskaņā ar spirtu un izocianātu katalītiskās mijiedarbības pamatnostādnēm. Pētāmo lignīna frakciju reaģētspēja ar MDI dioksāna šķīdumā palielinās šādā secībā: DCM-F <MET/DCM-F <MET-F (1. tabula).

*1. tabula*

***Organosolv* lignīna un tā frakciju molekulmasas, funkcionālo grupu saturs, Tg un to reaģētspēja ar 4,4'-metilēndifenildiizocianātu (MDI) dioksāna šķīdumā**

| **Rādītājs** | **Lignīns un tā frakcijas** | | | |
|---|---|---|---|---|
| | **Lignīns** | **DCM-F** | **MET-F** | **MET/DCM-F** |
| Iznākums (%)* | – | 7,4±0,2 | 14,5±0,7 | 18,2±0,9 |
| Mw ($g{\cdot}mol^{-1}$) | 11100 | 1970 | 2200 | 5300 |
| Mn ($g{\cdot}mol^{-1}$) | 1050 | 334 | 540 | 1100 |
| $Mw{\cdot}Mn^{-1}$ | 10,6 | 5,9 | 4,1 | 4,8 |
| $OCH_3$ grupu saturs (mmol $g^{-1}$) | 3,12±0,03 | 2,96±0,03 | 3,55±0,06 | 3,67±0,03 |
| Acetilēto OH grupu saturs (mmol $g^{-1}$) | 4,53±0,15 | 3,24±0,06 | 5,30±0,10 | 5,00±0,10 |
| Alifātisko OH grupu saturs (mmol $g^{-1}$) | 3,76±0,28 | 1,65±0,19 | 4,5±0,3 | 4,35±0,23 |
| Fenola OH grupu saturs (mmol $g^{-1}$) | 1,47±0,08 | 2,12±0,10 | 2,06±0,10 | 1,60±0,08 |
| COOH grupu saturs (mmol $g^{-1}$) | 0,71±0,05 | 0,53±0,03 | 1,18±0,10 | 0,88±0,05 |
| Kopējais OH grupu saturs (mmol $g^{-1}$) | 5,94±0,25 | 4,30±0,12 | 7,7±0,3 | 6,83±0,20 |
| $OH_{aliph}/OH_{total}$ | 0,63 | 0,38 | 0,58 | 0,64 |
| Vidēja OH funkcionalitāte | 6,2 | 1,4 | 4,2 | 7,5 |
| Tg (°C) | 177 | 14 | 121 | 160 |
| Kondensācijas pakāpe (B+Ph)/(G+S) | 0,15±0,02 | 0,100±0,001 | 0,16±0,01 | 0,24±0,02 |
| $k{\times}10^4$ ($L{\cdot}mol^{-1}{\cdot}s^{-1}$)** | – | 2,30±0,15 | 4,7±0,4 | 3,9±0,4 |

* no krāsnī žāvēta sausa izejmateriāla lignīna masas bez pelniem

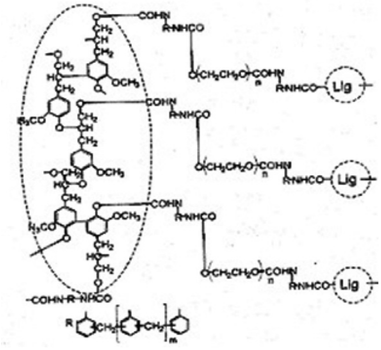
** otrās kārtas konstante reakcijai ar MDI dioksāna šķīdumā

MET-F frakcijas augstāko reaģētspēju var izskaidrot ar augstāku alifātisko OH grupu saturu tajā un to telpisko pieejamību ne pārāk augstas lignīna kondensācijas pakāpes dēļ (1. tabula).

## 3.2. Lignīna frakciju kā makromonomēru ietekme uz poliuretāna elastomēru īpašībām

Rezultāti par kviešu salmu *Organosolv* lignīna frakciju ietekmi uz PU elastomēru īpašībām ir atspoguļoti P-2 un P-6.

Iegūtās lignīna frakcijas, kas aktīvi reaģē ar izocianātu, iekļaujoties trīs komponentu poliuratāna sistēmā (šie komponenti ir lignīns (5–40 %), PEG (MW = 400 $g{\cdot}mol^{-1}$) un PMDI), darbojas kā šķērssaistīšanās aģenti (10. attēls).



*10. attēls.* **Lignopoliuretāna struktūra ar mīkstiem PEG segmentiem** (Hu, 2002)

Lignīna ievadīšana PU plēvju sastāvā paaugstina to:
- stiklošanās temperatūru;
- stiepes izturību;
- Junga moduli.

Pateicoties lignīna antioksidatīvai aktivitātei, lignopoliuretānos (LPU) ar mazu lignīna saturu (5%) tika novērota termooksidēšanās stabilitātes palielināšanās (2. tabula). Ja PU sintēzei izmantoja sastāvu ar lignīna frakciju saturu 30%, lignopoliuretānos tika novērta šķērssaistīšanās un tajos palielinājās termostabilu aromātisko komponentu saturs, un tā rezultātā savukārt tālāk palielinājās termooksidēšanās stabilitāte un augstā temperatūrā veidoto ogļu daudzums.

*2. tabula*

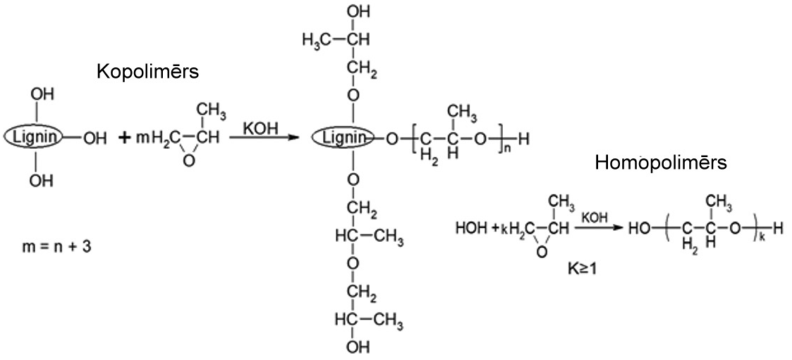
**OSL frakciju ietekme uz PU plēvju termooksidēšanās destrukcijas rādītājiem**

| **Frakcija** | **Saturs LPU (%)** | **$T_{start}$ (°C) (5% masas zudums)** | **$T_{50\%}$ (°C) (50% masas zudums)** | **Maksimālais degradācijas ātrums ($mg{\cdot}min^{-1}$)** | **Maksimālā degradācijas ātruma temperatūra (°C)** | **Ogles 500 °C (%)** |
|---|---|---|---|---|---|---|
| PU bez lignīna | 0 | 274 | 365 | 0,94 | 307 | 27,0 |
| DCM-F | 5 | 281 | 367 | 0,56 | 331 | 33,7 |
|  | 30 | 238 | 427 | 0,21 | 325 | 42,2 |
| MET-F | 5 | 279 | 403 | 0,44 | 331 | 32,4 |
|  | 30 | 205 | 442 | 0,30 | 360 | 44,5 |
| DCM/ MET-F | 5 | 286 | 402 | 0,27 | 331 | 35,7 |
|  | 30 | 225 | 499 | 0,18 | 324 | 50,0 |

Vēl viena priekšrocība lignīna izmantošanai PU ražošanā ir frakcionēto tehnisko lignīnu augstā antioksidatīvā aktivitāte, jo atšķirībā no komerciālajiem fenola antioksidantiem, kas ievērojami kavē kompozītmateriālu bioloģisko noārdīšanos, no lignīniem iegūtie antioksidanti ir ne tikai bioloģiski noārdāmi, bet tie var arī katalizēt tā materiāla bioloģisko sadalīšanos, kurā tiek ievadīti (Domenek *et al.,* 2013).

## 3.3. Organiskajos šķīdinātājos šķīstoša (*Organosolv*) lignīna oksialkilēšanas procesa izpēte un iegūto lignopoliolu raksturošana

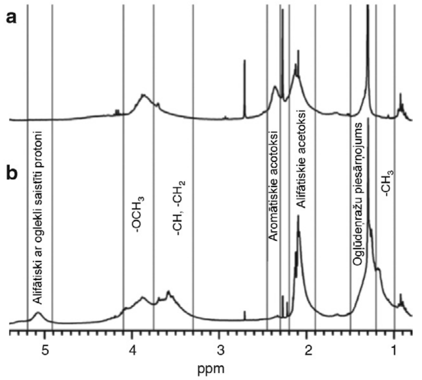
Rezultāti, kas attiecas uz *Organosolv* lignīna oksialkilēšanu, ir parādīti P-3. Nefrakcionēta OSL modifikācija ar propilēna oksīdu, kas veikta, izmantojot anjonu polimerizācijas mehānismu, ir perspektīva pieeja cieto lignīnu sašķidrināšanai un skābo lignīna grupu pārveidošanai alifātiskās OH grupās, kas aktīvi reaģē uretāna veidošanās reakcijās.



*11. attēls.* **Galveno produktu veidošanās shēma lignīna oksipropilēšanas procesā**

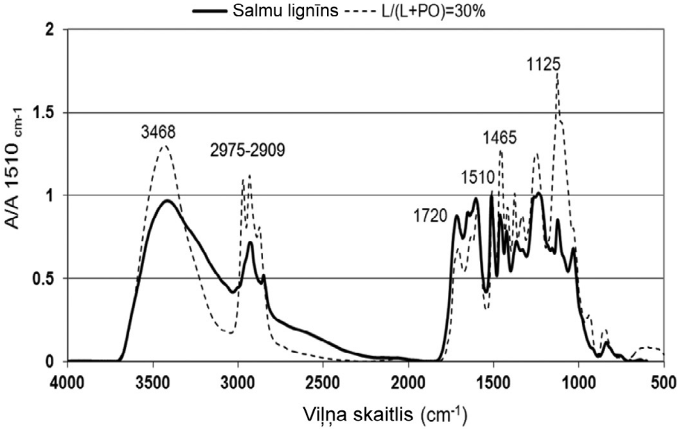
Oksialkilēšanas rezultātā zūd lignīna hidroksilgrupu struktūru ierobežojumi un tiek pārvarēti telpiskie traucējumi.

Lignīna un propilēna oksīda (PO) kopolimerizēšanas procesu pavada oksipropilēna homopolimerizācija un propilēnglikolu veidošanās (11. att.). $^1$H NMR spektroskopijā iegūtie dati apstiprina lignīna kopolimerizāciju ar PO (12. att.). Alifātisko protonu signālu (CH, $CH_2$, $CH_3$) intensitāte palielinās, savukārt metoksilgrupu intensitāte samazinās, atšķaidoties aromātiskajai sastāvdaļai PO pievienošanas dēļ. Aromātisko acetoksigrupu signāls pazūd un alifātisko acetoksigrupu signāls pastiprinās (12. att.).



*12. attēls.* **Salmu lignīna (a) un tā oksipropilētā atvasinājuma 1H KMR spektri (L/(L + PO) = 30%) (b)**

FTIR spektri apstiprina lignīna ķīmisko modifikāciju – OH grupu mijiedarbību ar PO, jo CH, $CH_2$, $CH_3$ grupu absorbcija pie 2975, 1465 $cm^{-1}$ un ētera saišu absorbcija pie 1125 $cm^{-1}$ palielinājās, bet nekonjugēto karbonilgrupu absorbcija pie 1720 $cm^{-1}$ samazinājās (13. attēls).



*13. attēls.* **OSL un tā oksipropilētā atvasinājuma normalizētie (1510 $cm^{-1}$) FTIR spektri**

OH grupas OSL-PO kopolimēros ir galvenokārt sekundāras spirta grupas, tā kā, apstrādājot oksipropilēto lignīna atvasinājumu ar HI un veicot iegūtu produktu GC analīzi, hromatogrammās dominē izopropiljodīda signāls un parādās n-propiljodīda pēdas.

Kopolimēru molekulmasas sadalījuma dati ļauj raksturot lignīna makromolekulas transformāciju oksipropilēšanas procesā un iegūto lignopoliolu fizikāli ķīmiskās īpašības. Kviešu salmu lignīna oksipropilēšanas rezultātā izveidojušies kopolimēri ir stipri viendabīgāki molekulmasas sadalījuma ziņā salīdzinājumā ar sākotnējo lignīnu (3. tabula). OSL oksipropilēšana ļāva pārvarēt divus galvenos šī lignīna kā atjaunojamā makromonomēra trūkumus (tie bija augsts molekulārais neviendabīgums un hidroksilfunkciju daudzveidība), tādējādi tika uzlabota poliuretāna tīklu formēšanas kontrole PU putu ražošanā. Visu kopolimēru paraugu brīvās fenola grupas atrodas galvenokārt kondensētās struktūrās (OHcond) acīmredzot to zemās telpiskās pieejamības dēļ oksipropilēšanas gaitā. Ir novērots neliels brīvo fenola hidroksilgrupu satura pieaugums kopolimēriem, kas ir iegūti ar lielāku (30–40%) sākuma OSL daudzumu reakcijas maisījumā (3. tabula).

Telpiski traucētie fenoli ir visizplatītākā antioksidantu klase, un tie tiek izmantoti nevēlamo ar brīvajiem radikāļiem saistīto procesu izbeigšanai/ierobežošanai. Šos antioksidantus plaši izmanto putu poliuretānu sastāvā, lai uzlabotu to izturību pret oksidatīvo noārdīšanos (Gray *et al.,* 1996). Brīvo fenola grupu klātbūtne OSL-PO kopolimēros 0,10–0,17 mmol $g^{-1}$ daudzumā var nodrošināt to funkcionālo iekļaušanu antioksidantu PUR putu sastāvos. PUR putu sistēmās lignīns var būt gan aktīvi reaģējošs aromātiskais makromonomērs, gan biobāzēts tehniskais antioksidants. Nesen šajā virzienā ir sākti pētījumi, un ir iegūti pirmie pozitīvie rezultāti par OSL-PO kopolimēru antioksidatīvo aktivitāti PUR putās.

*3. tabula*

**Salmu lignīna un tā oksipropilēto atvasinājumu funkcionālo grupu saturs un molekulmasas sadalījums**

| L/ (L+PO) (%) | OH (mmol·g$^{-1}$)* | | | | OH$_{alif}$ /OH | OH$_{cond}$/ ΣOH$_{pfen}$ | OCH$_3$ (mmol·g$^{-1}$) | Molekulmasa (g·mol$^{-1}$) | | M$_w$·M$_n^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | OH$_{alif}$ | ΣOH$_{pfen}$ | COOH | ΣOH | | | | M$_n$ | M$_w$ | |
| 15 | 2,26 | 0,10 | 0,03 | 2,39 | 0,95 | 0,62 | 1,39±0,03 | 8200 | 30000 | 3,7 |
| 20 | 2,53 | 0,10 | 0,04 | 2,67 | 0,95 | 0,65 | 1,66±0,01 | 4900 | 16300 | 3,3 |
| 25 | 2,56 | 0,12 | 0,05 | 2,73 | 0,94 | 0,63 | 1,77±0,01 | 4100 | 16900 | 4,1 |
| 30 | 2,59 | 0,14 | 0,05 | 2,78 | 0,93 | 0,63 | 1,97±0,01 | 4200 | 21500 | 5,1 |
| 35 | 2,59 | 0,14 | 0,07 | 2,80 | 0,93 | 0,63 | 2,29±0,06 | 3600 | 19700 | 5,5 |
| 40 | 2,65 | 0,17 | 0,06 | 2,88 | 0,92 | 0,56 | 2,39±0,06 | 3800 | 25700 | 6,8 |
| 100 | 1,39 | 1,62 | 0,50 | 3,51 | 0,40 | 0,32 | 3,69±0,10 | 2200 | 54000 | 24,5 |

* NMR $^{31}$P dati

Aprakstošā statistiskā analīze parādīja normālu izmērīto parametru sadalījumu atkārtotiem eksperimentiem un augstu oksipropilēšanas parametru un pētāmo lignopoliuolu īpašību atkārtojamību. Tas parāda, ka OSL oksipropilēšanas procesu potenciāli var veikt rūpnieciskā mērogā (4. tabula).

*4. tabula*

**Organosolv kviešu salmu lignīna oksipropilēšanas parametru un iegūto lignopoliolu raksturlielumus aprakstošā statistika (*n* = 25)**

| Statistiskie parametri | OP parametri | | | | Lignopoliolu raksturlielumi | |
|---|---|---|---|---|---|---|
| | T$_{onset}$ (°C) | T$_{maks.}$ (°C) | P$_{maks.}$ (bar) | OHV (mg KOH·g$^{-1}$) | Viskozitāte 20 °C (Pa·s) | Ūdens saturs K.F. (%)** |
| Vidējais | 164 | 241 | 24,7 | 447,3 | 57,5 | 0,05 |
| Mediāna | 164 | 241 | 24,6 | 450,1 | 56,2 | 0,50 |
| Minimums | 161 | 235 | 24,0 | 409,2 | 50,1 | 0,03 |
| Maksimums | 167 | 248 | 26,0 | 471,6 | 70,2 | 0,14 |
| Standartkļūda | 0,35 | 0,64 | 0,10 | 2,80 | 1,11 | 0,02 |
| Standartnovirze | 1,7 | 3,2 | 0,47 | 14,0 | 5,6 | 0,02 |
| Koef. VA (%)* | 1,0 | 1,3 | 1,9 | 3,1 | 9,7 | 40,0 |

* variācijas koeficients

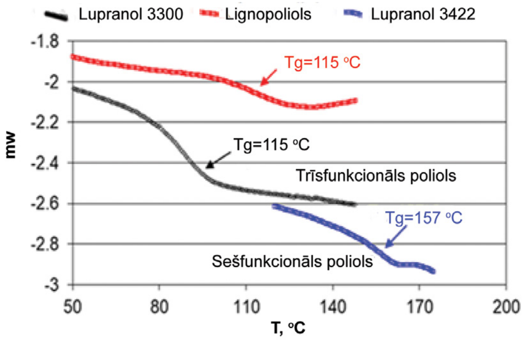
** lignopoliolu mitrums noteikts, izmantojot Karla Fišera titrēšanu ar kulonometrisko KF titratoru 275 KF

## 3.4. Lignopoliolu kā makromonomēru un lignīna kā pildvielas ietekme uz cieto poliuretāna putu īpašībām

Šajā darbā ir izpētīta *Organosolv* lignīna (OSL) izmantošana poliuretāna (PUR) putu ražošanai derīgo lignopoliolu sintēzē. Tajā pašā laikā nemodificēts lignīns tika izmantots kā pildviela cietajām PUR putām, kas ir iegūtas no iepriekšminētajiem lignopolioliem, palielinot atjaunojamo komponentu saturu polimēra materiālā. Ir izpētītas lignīnu saturošu putu termiskās, fizikāli mehāniskās un morfoloģiskās īpašības salīdzinājumā ar putām, kas iegūtas no komerciāliem poliēteriem. Rezultāti ir parādīti P-5 un P-8.

Tā kā lignopolioli satur arī kālija acetātu, kas darbojas kā izocianātu konversijas katalizators, oksipropilēšana ir labāk piemērota poliuretānu putu ražošanai, jo šī procesa realizācijai ir nepieciešama ātra mijiedarbība starp polioliem un izocianātiem. Komerciālais poliols poliēteris Lupranol 3300 tika pakāpeniski (25%, 50%, 75%, 100%) aizvietots ar lignopoliolu uz OSL bāzes (L/(L+PO) = 30%; OHV = 450 mg KOH·g$^{-1}$). Sastāvs, kas satur 30% OSL, ir optimāls attiecībā uz tā īpašībām un lignīna valorizāciju. Komerciālā poliētera aizstāšana ar lignopoliolu uzlaboja putu izmēru stabilitāti un hidrofobitāti un neietekmēja to saspiešanas izturību. OSL kā pildvielas ieviešana references lignopoliolu nesaturošā sastāvā pasliktina putu īpašības. Materiāla labākās īpašības tika sasniegtas, kad OSL ievadīja putu sastāvā vienlaikus gan kā poliolu, gan kā pildvielu.

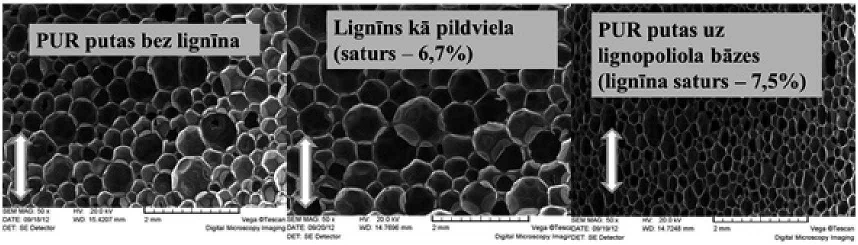
Uz lignopoliola bāzes veidotu PUR putu (bez Lupranola) stiklošanās temperatūra ir starp vērtībām, kas raksturīgas putām uz trīs- un seš-funkcionālo komerciālo poliolu bāzes (14. att.).



*14. attēls.* **Komerciālo poliēteru un lignopoliola poliuretāna putu DSC līknes**

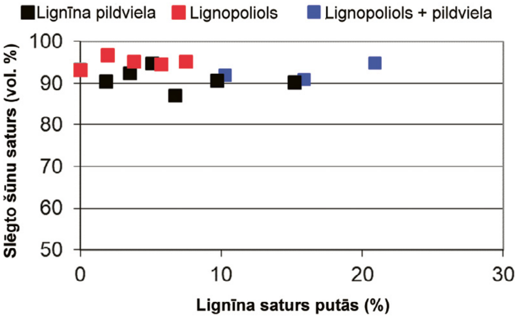
References PUR putu un putu ar 6–25% lignopoliola Tg vērtības atradās temperatūrā no 110 līdz 119 °C. Tāpēc lignopoliols var veiksmīgi aizvietot trīsfunkcionālo komerciālo uz glicerīna bāzes veidoto poliolu PUR putu sistēmā, nesamazinot materiāla siltumnoturību.

Ir parādīts, ka oksipropilētais lignīns darbojas kā virsmaktīvā viela PUR putu kompozīcijās, uzlabojot PUR šūnu struktūras vienmērīgumu un samazinot šūnu izmērus (15. att.).



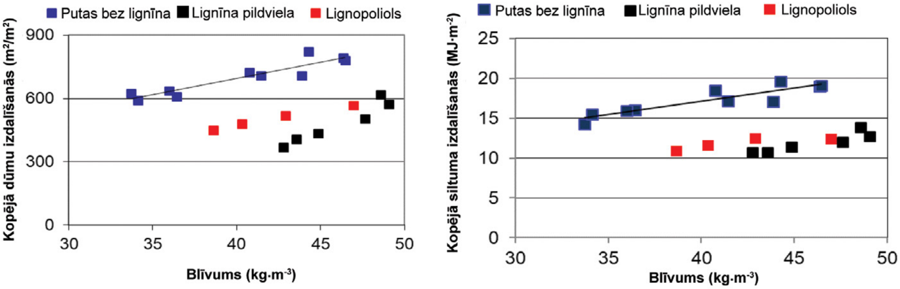
*15. attēls.* **Lignīna ietekme uz PUR putu šūnu morfoloģiju**

Lignīna pildvielai un lignopoliolam nav negatīvas ietekmes uz slēgto šūnu saturu PUR putās (16. att.).



*16. attēls.* **Lignīna ietekme uz PUR putu slēgto šūnu saturu**

Ir novērots lignopoliolu saturošu PUR putu maksimālā termiskās noārdīšanās ātruma ievērojams samazinājums no 1,20 mg/min lignopoliolu nesaturošām PUR putām līdz 0,54–0,93 mg/min PUR putām ar dažādu lignopoliola saturu. Nemodificēta lignīna pildvielai ir mazāk izteikta pozitīva ietekme uz materiāla termiskās degradācijas ātrumu, jo PUR putām ar lignīna piedevu tas ir 0,60–1,16 mg/min atkarībā no lignīna satura. Saskaņā ar kalorimetra testu, ievadot lignīnu kā lignopoliolu un pildvielu PUR putu sastāvā, ievērojami uzlabojas materiāla ugunsizturības rādītāji (17. att.). To var izskaidrot ar dažu faktoru kombināciju, ieskaitot lignīna brīvo radikāļu dezaktivēšanās un ogļu veidošanās veicināšanu.



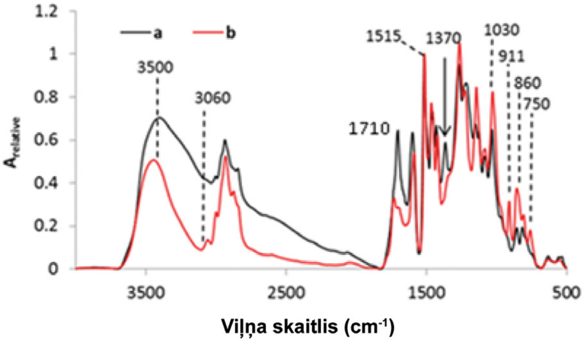
*17. attēls.* **Lignopoliola un lignīna pildvielas ietekme uz PUR putu degšanas parametriem**

Uz lignopoliola bāzes veidoto PUR putu izmērītās īpašības atbilst ES standarta prasībām attiecībā uz siltumizolācijas materiālu. Balstoties uz iepriekšminētajiem rezultātiem, ir izstrādāta siltumizolācijas materiālu ražošanas metode uz PUR putu bāzes, izmantojot izocianāta komponentu un poliola komponentu, kas sastāv no oksipropilēta lignīna un nemodificēta lignīna. Šī metode ir patentēta Eiropas Savienībā un aprakstīta P-11.

## 3.6. Lignīna epoksīdu ietekme uz komerciālo, uz bisfenola A bāzes izstrādāto epoksīdsveķu īpašībām

Rezultāti par *LignoBoost* kraftlignīna izmantošanu epoksīda sveķos ir parādīti P-1.

Kraftlignīna (KL) acetonā šķīstošas frakcijas un tā glicidilētā atvasinājuma FTIR spektri (18. att.) apstiprina veiksmīgu lignīna glicidilēšanu, jo kopolimēru spektros parādījās jaunas oksirāna gredzena absorbcijas joslas (3060, 750, 850, 910 cm$^{-1}$). Turklāt pēc lignīna glicidilēšanas alifātiskās grupas absorbcija (2975–2900 cm$^{-1}$) un ēteru saites absorbcija (1030 cm$^{-1}$) paaugstinās, bet OH grupu absorbcija (3480 cm$^{-1}$) un karbonilgrupu absorbcija (1710 cm$^{-1}$) samazinās salīdzinājumā ar nemodificēta KL acetonā šķīstošo frakciju. Absorbcijas joslas pie 1370 cm$^{-1}$ pazušana liecina par veiksmīgu fenola OH grupas glicidilēšanu. Tai pašā laikā būtiska absorbcijas intensitāte aptuveni pie 3500 cm$^{-1}$ apstiprina novērojumus, ka daļa nefenola OH grupu netiek glicidilēta jau minēto iemeslu dēļ. KOH/TBAB katalītiskās sistēmas izmantošana veicināja lignīna modeļvielas gan fenola, gan alifātisko OH grupu glicidilēšanu. Šiem katalizatoriem ir potenciāls pilnīgākā lignīnā glicidilēšanā.



*18. attēls.* **Nemodificēta KL (a) un tā glicidilēta atvasinājuma (b) normalizēti (1515 cm$^{-1}$) FTIR spektri**

Komerciālo epoksīdsveķu *Araldite LY 1524* aizvietošana ar lignīna epoksīdu (EEW = 368 g·eq$^{-1}$), kas ir iegūts, glicidilētu KL lignīnu ekstrahējot ar acetonu (GLAF), palielina Junga moduli ar amīnu cietinātiem kompozītiem stiepes laikā, nesamazinot to izturību. Lignīna epoksīdu ievadīšana stipri palielina komerciālo epoksīdsveķu viskozitāti (5. tabula).

*5. tabula*

**Necietinātu epoksīdsveķu viskozitāte un cietināto komerciālo epoksīdsveķu stiepes īpašības atkarībā no *Araldite*LY1564* aizvietošanas pakāpes ar GLAF**

| Aizvietošanas pakāpe (%) | Viskozitāte (mPa·s) 25 °C | Pārrāvuma izturība (MPa) | Junga modulis (GPa) | Pārrāvuma deformācija (%) |
|---|---|---|---|---|
| Reference | 1230 | 63,1±2,7 | 2,91±0,16 | 4,9±0,3 |
| 2 | 1420 | 61,3±1,8 | 3,13±0,19 | 4,8±0,9 |
| 5 | 2052 | 67,1±2,2 | 3,09±0,21 | 5,5±0,7 |
| 10 | 3580 | 66,2±1,3 | 3,36±0,22 | 4,9±0,5 |

Viskozitātes palielināšanās padara lignīna epoksīdu par nederīgu tehnoloģijām, kurās materiālam nepieciešama zema viskozitāte. Tādēļ lignīnu saturošus epoksīdus varētu izmantot līmju, mastikas vai plaisu pildvielu veidā.

Termiskā noturība ir viena no sacietējušo epoksīdsveķu priekšrocībām. Cietinātiem epoksīdiem, kas satur lignīnu, ir augstāks ogļu iznākums un zemāks degradācijas ātrums augstā temperatūras iedarbībā, un tas liecina par lignīna epoksīdu potenciālu liesmas izturīgu materiālu ražošanā (6. tabula).

*6. tabula*

**Daļējas *Araldite LY1564* aizvietošanas ar lignīna epoksīdu ietekme uz cietinātu sveķu termodegradācijas rādītājiem**

| Aizvietošanas pakāpe (%) | $T_{5\%}$ (°C) | dm/dt (mg·min$^{-1}$) | $T_{max}$ (°C) | Ogles atlikums 500 °C (%) |
|---|---|---|---|---|
| References paraugs | 338 | 1,6 | 336 | 10,5 |
| 2 | 325 | 1,4 | 368 | 13,7 |
| 5 | 320 | 1,4 | 363 | 17,6 |
| 10 | 303 | 1,2 | 365 | 22,6 |

$T_{5\%}$ – temperatūra, kurā tika sasniegts 5% svara zudums
dm/dt – maksimālais degradācijas ātrums
$T_{max}$ – temperatūra, kurā tika sasniegts maksimālais degradācijas ātrums

# SECINĀJUMI

1. Ir izstrādāta koncepcija lignīna kā makromonomēra izmantošanai dažādās poliuretānu un epoksīda sistēmās. Tā ietver dažādus risinājumus lignīna modifikācijai un iekļaušanai polimēra sastāvā, kuri paredz iekļaut līdz 40% biobāzētu sastāvdaļu, kas vienlaikus ļauj uzlabot materiālu mehānisko un termisko stabilitāti.
2. Frakcionēšana ar organiskajiem šķīdinātājiem ir perspektīvs risinājums, kas ļauj iegūt poliuretānu elastomēriem derīgus lignīna izcelsmes makromonomērus. Iegūtās lignīna frakcijas šķīst šķīdinātājos, kurus izmanto PU tīkla veidošanai, tās ir viendabīgākas salīdzinājumā ar izejmateriāla lignīnu un reaģē ar izocianātu. To ievadīšana PU sistēmā palielina PU plēvju stiklošanās temperatūru, stiepes izturību un Junga moduli.
3. Oksipropilēšana novērš lignīna hidroksilgrupu struktūras ierobežojumus un telpiskos traucējumus, stipri samazinot lignīna molekulmasas polidispersitāti. Oksialkilēšana ir efektīva metode lignīnu kā šķidro lignopoliolu ievadīšanai cieto poliuretānu putu sastāvā, kuras var pārstrādāt formējot un izsmidzinot.
4. Lignopoliola un cieta lignīna vienlaicīga ievadīšana cieto poliuretāna putu sastāvā ļauj ievērojami palielināt materiāla izmēru stabilitāti un samazināt ūdens absorbcijas rādītājus salīdzinājumā ar references sastāvu un ar poliuretāna putu sastāviem, kurās lignopoliols un cietais lignīns tika ievadīti atsevišķi.
5. Acetonā šķīstošās kraftlignīna un epihlorhidrīna reakcijas produktu frakcijas ir uz lignīna bāzes sintezēti makromonomēri ar šauru molekulmasas sadalījumu un vidēju epoksīda funkcionalitāti 3,1–4,5, tādējādi ir iespējams palielināt komerciālā bifunkcionālā uz bisfenola A bāzes sintezētā Araldite LY 1564 diglicidilētera epoksīda funkcionalitāti.
6. Fosilo resursu izcelsmes komerciālo epoksīdsveķu *Araldite LY 1564* daļēja aizvietošana ar glicidilēta lignīna frakciju divu komponentu ar amīnu cietināto epoksīdu sastāvā palielina cietināto epoksīdu stiepes moduli un termisko stabilitāti, jo lignīna makromonomēriem raksturīga augsta funkcionalitāte un tie palielina termostabilu aromātisko komponentu saturu cietinātos epoksīdos.

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UNIVERSITY
OF LATVIA

FACULTY OF CHEMISTRY

**Alexandr Arshanitsa**

# DEVELOPMENT OF APPROACHES FOR APPLICATION OF BIOREFINERY LIGNINS AS A RENEWABLE RAW MATERIAL FOR THE PRODUCTION OF POLYMERS COMPOSITIONS SUITABLE FOR INDUSTRIAL USE

SERIES OF ARTICLES

Submitted for the degree of Doctor of Philosophy (PhD) in Chemistry

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Supervisor:

Dr. habil. chem., Prof. **Galina Telysheva**

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# ANNOTATION

Development of approaches for application of biorefinery lignins as a renewable raw material for the production of polymers compositions suitable for industrial use. Arshanitsa, A., supervisor: Dr. habil. chem., Prof. Telysheva, G. Summary of a series of articles, 33 pages, 18 figures, 6 tables, 60 literature references. In English.

BIOREFINERY, LIGNIN, BIOPLASTICS, FRACTIONATION BY ORGANIC SOLVENTS, OXYALKYLATION, GLYCIDYLATION, MACROMONOMER, ACTIVE FILLER, POLYURETHANES, EPOXIDES

The aim of the work is the formation of a theoretical base and the development of a technological concept for application of technical lignins formed in biorefineries as components of bio-based materials. The main objectives include the implementation of lignins' mechano-chemical activation, chemical modification by fractionation with organic solvents, modification with oxirane ring bearing monomeric compounds and use of the products as hydroxyl- and epoxy-containing macromonomers or active fillers in polymeric materials.

Using the developed methodology, the novel organosolv lignin (OSL) produced by the wheat straw biorefinery elaborated by Compagnie Industrielle de la Matierre Vegetale (CIMV) (France) was modified and introduced into polyurethane materials. The first lignin's modification approach is suitable for obtaining a macromonomer for polyurethane elastomers and includes the fractionation of lignin by sequential extraction with organic solvents. Polyurethane (PU) films were synthesized by casting the three component systems: lignin fraction – polyethylene glycol (PEG) – polymeric 4,4'-diphenyl methane diisocyanate (PMDI). Depending on the lignin fraction type and its content in the composition, the tensile properties of PU elastomers in a high elastic state at room temperature or rigid and glassy crosslinked PU with the glass transition temperature above 100 °C were obtained. The lignin fractions act as antioxidants and charcoal formation promoters in the case of the 200–600 °C temperature treatment of PU in air. Another approach of lignin modification suitable for obtaining rigid polyurethane foams includes its conversion into liquid lignopolyols via a batch reaction with propylene oxide (PO). The effects of the lignin (L) content in the initial reaction mixture on the oxypropylation process and the properties of lignopolyols and L/PO copolymers were studied. At a lignin content of 15–30%, the lignopolyols fulfil the requirements of polyolpolyethers for rigid PU foam production. It was shown that the substitution of commercial polyether polyol based on glycerine by lignopolyol enhances the PU foam cell structure uniformity, dimensional stability, and decreases the water absorbtion capacity, improving its physico-mechanical properties. Lignin was introduced into the PU foam system also as a filler after its mechano-chemical activation, and the influence of the lignin introduction method on the properties of the obtaind materials was studied. It was shown that the incorporation of lignin into polyurethane foam leads to the decreasing of the maximum values of thermodegradation rates.

The approach for introduction of lignin into epoxy resins was tested using LignoBoost™ softwood kraft lignin, isolated in the framework of the biorefinery approach realized on a commercial scale. Lignin-based epoxy resins were obtained by

acetone extraction of glycidylated lignin or glycidylation of the acetone-soluble lignin fraction. The effect of glycidylation regimes on the yields of acetone-soluble fractions, their functional composition and physico-chemical characteristics was investigated. Partial substitution of commercial fossil derived resin with the glycidylated lignin fraction positively influences the properties of cured epoxides.

# LIST OF ABBREVIATIONS

| | |
|---|---|
| BPA | bisphenol A |
| DCM | Dichlrormethane |
| DTG | derivative thermogravimetry |
| DSC | differential scanning calorimetry |
| ECH | epichlorhydrin |
| EEW | epoxide equivalent weight |
| F | fraction |
| FTIR spectroscopy | Fourier-transform infrared spectroscopy |
| GC | gas chromatography |
| GLAF | acetone-soluble fraction of glycidylated lignin resin |
| KL | kraft lignin |
| LPU | lignopolyurethanes |
| L3300 | Lupranol 3300, glycerol based commercial polyol polyethers |
| L3422 | Lupranol 3422, sorbitol based commercial polyol polyethers |
| MET | methanol |
| MDI | 4,4’-diphenyl methane diisocyanate |
| PMDI | polymeric MDI |
| MMD | molecular mass distribution |
| MW | molecular weight |
| NMR | nuclear magnetic resonance |
| OHV | hydroxyl value |
| OSL | organosolv lignin |
| PEG | polyethylene glycol |
| PO | propylene oxide |
| PU | polyurethane |
| PUR | rigid polyurethane foam |
| TBAB | tetrabutylammonium bromide |
| TG | thermogravimetry |
| SEC | size exclusion chromatography |

# INTRODUCTION

The availability of fossil raw materials (oil, gas, coal) for the needs of the chemical industry, as well as the ease of their standardization, and many years of processing experience, including the effective control of technological processes and developed logistics, are the constraining factors of the use of biomass as a raw material for the chemical industry. However, the reduction in the world's reserves of non-renewable fossil resources, as well as the aggravated environmental problems arising from the use of fossil resources-based products, predetermine the need for an active development of research on biomass as a renewable raw material (Hu *et al.,* 2002, Lampinen *et al.,* 2011). For today, the aim is to replace at least 30% of the existing petroleum-based products with a better, more sustainable economically viable version by 2030, leading to a reduction in GHG emissions by 50%. Expanding the resource base through the use of renewable raw materials and increasing the share of the "green" component along with the possibility of improving the biodegrability of the material are defining directions of the modern development of polymer chemistry and technology.

Delignification and hydrolysis of ligno-carbohydrates biomass are still the most large-scale technologies for the chemical processing of plant biomass, aimed at using its carbohydrate component for the production of cellulose, paper and bioethanol. At the same time, lignin, which is the most widely spread renewable biopolymer of aromatic nature, is underutilized. The yield of technical lignin in the above processes, depending on the type of the raw material and the selected technology, is 30-50% of the dry mass of the raw material. The world industry generates about 55 million tons of lignin each year (Calvo-Flores *et al.,* 2010). Currently, about 98% of the extracted lignin is burned to generate energy for the main technological process (Lampinen *et al.,* 2011). According to the EU Technological platform, the basic requirement for the creation of modern highly efficient production facilities is waste-free technological processes, which are implemented according to the "biorefinery" scheme, when each waste is used as a raw material for obtaining a new target product (Bozell *et al.,* 2007). Thought-out utilization of the world's most abundant resource of bio-aromatics could substantially augment the profitability of future lignocellulosic biorefineries. In this regard, new biorefinery schemes are being developed, wherein the valorization of lignin is regarded as one of the primary targets (Renders *et al.,* 2017).

The most promising potential applications of lignins from various sources include the production of chemicals such as phenol(ics) and BTX (benzene, toluene and xylene) (Zakzeski *et al.,* 2010), as well as the use of lignin for the production of polymer composite materials, both as a filler and as a macromonomer block, which is purposefully incorporated into the structure of the copolymer via covalent bonds. The use of lignin in various material applications such as phenolic resins (Da Silva *et al.,* 2013), polyurethanes (Lora and Glasser, 2002, Pan and Saddler, 2013), epoxy resins (Lora and Glasser, 2002, Stewart, 2008), and carbon fibers (Hu, 2002, Pan, 2013) has been studied. Along with lowering the cost of the composition, the introduction of lignin increases the modulus of elasticity of the material, as well as its thermal, light and frost resistance. The use of lignin as an antioxidant for composite materials has been reported (Pan *et al.,* 2006, El Hage *et al.*, 2020).

The development of new biomass processing technologies produces technical lignins with improved properties and opens new opportunities for their application as components of bio-based materials (Renckens, 2017). The main traditional delignification process in the pulp and paper industry, aimed at the dissolution of lignin as a waste compound, is the kraft process, where alkali and sodium sulfide are used as reagents and wood as a feedstock. The developed organosolv delignification CIMV is a biorefinery concept, which can separate and promote the main components: lignin, pulp, and pentoses sugars syrop. The three components' mixture including acetic, formic acids and water is the reagent and wheat straw is a feedstock. Due to the principal difference of the delignification technologies using organic solvents and the lability of the native lignins' structure, the previously obtained knowledge concerning technical lignins' valorization cannot be transferred to the novel ones. The CIMV lignin application in PU compositions would promote the commercial implementation of the biorefinery technology. Now the only process of lignin isolation in the framework of the biorefinery approach realized on a commercial scale is the LignoBoost concept developed by Innventia AB and Chalmers University of Technology (Sweden) (Tomani, 2010). LignoBoost lignin is the product of the novel modified kraft process. The properties and application possibilities of this technical lignin are under active studies worldwide.

**The aim of this work is** the formation of a theoretical base and the development of a technological concept for application of technical lignins formed in biorefineries as components of bio-based materials. **The main objectives** of the work include: development and implementation of lignins' mechano-chemical activation, chemical modification by fractionation with organic solvents, modification with oxirane ring bearing monomeric compounds and use of the products as hydroxyl- and epoxy-containing macromonomers or active fillers in polymeric materials (Fig. 1).

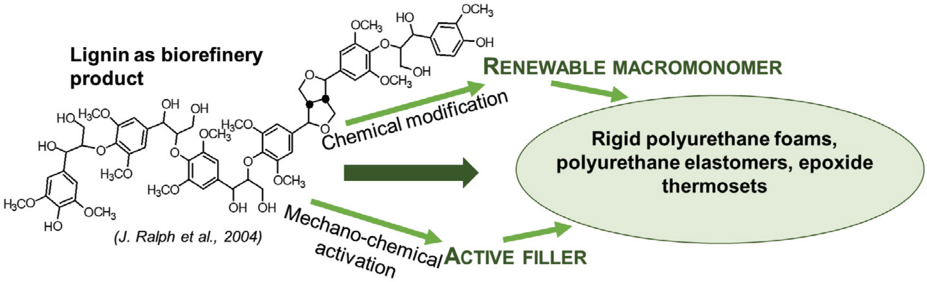

*Figure 1.* **Schematic representation of the main objectives of the work**

## The following tasks have been set to achieve the goal of the Doctoral thesis

1. Characterization and comparative analysis of the component and functional composition, and physico-chemical parameters of the structure of technical lignins.
2. Assessment of the effect of fractionation with solvents of different polarity on the molecular and functional heterogeneity of organosolv lignin in terms of its activity as polyurethanes macromonomer.
3. Incorporation of organosolv lignin fractions as hydroxyl-containing macromonomers in polyurethane elastomers and studies of the structure, mechanical and thermal properties of the obtained materials.
4. Study of the organosolv lignin's reaction with propylene oxide in different conditions, characterization of the chemical and physico-chemical properties of the obtained lignopolyos.
5. Application of the lignopolyols as hydroxyl-containing macromonomers in rigid polyurethane foams and studies of the physical, mechanical and thermal properties of the obtained materials.
6. Mechano-chemical activation of lignins, their incorporation as active fillers in the composition of rigid polyurethane foams and studies of the properties of the obtained materials.
7. Investigation of non-fractionated and fractionated lignins' reaction with epichlorhydrin in different conditions, application of the obtained products as epoxy containing macromonomers and their influence on the tensile and thermal properties of commercial amine cured epoxide resin.

## Scientific novelty and significance of the results

1. The obtained organosolv lignin's fractions are suitable for application as hydroxyl-containing macromonomers in polyurethane elastomers and are simultaneously capable to regulate the crosslinking of the polyurethane network and to act as technical antioxidants.
2. The optimal conditions of the organosolv lignin's oxypropylation process and optimal ratios of the raw materials were determined.
3. The obtained lignopolyols consist of two main constituents: the product of the interaction of organosolv lignin with propylene oxide and derivatives of propylene glycol of different molecular weights and have significantly higher reactivity towards MDI in dioxane in comparison with the commercial glycerol-based polyether widely used in PUR foam recipes. The oxypropylation of organosolv lignin decreases its polydispersity and increases segmental mobility.
4. The partial substitution of commercial polyether by lignopolyol improves the dimensional stability and hydrophobicity of PU foam, enhances its thermal stability, lowers its flammability and does not affect its compressive characteristics.
5. Simultaneous incorporation of organosolv wheat straw lignin as lignopolyol and filler allows to achieve a better compatibility of the solid lignin filler with the components of the polyurethane foam recipe in comparison with the case of the lignopolyol free reference polyurethane foam system.

6. LignoBoost kraft lignin epoxies have narrow molecular mass distribution and epoxy functionalities varying in the range of 3.1–4.5. Lignin, chemically incorporated into the matrix of cured commercial epoxy resin, increases their charcoal yield and decreases the degradation rate at the high temperature impact in comparison to the reference material, suggesting the lignin epoxies' potential for fabrication of flame-resistant epoxides.

## Practical importance

1. The improved properties (thermal stability, dimensional stability, hydrophobicity, tensile strength, Young's modulus, lower flammability) of composite materials containing modified lignins as macromonomers, in comparison to those of the commercial materials used as a reference, opens new opportunities for designing bio-based polymers.
2. The methodology for obtaining hydroxyl-containing macromonomers for polymers synthesis on the basis of different technical lignins was developed and approbated in industrial conditions (experimental plant of the Research-and-Production Association "Polymersintez" (Vladimir, Russia)).
3. The results of these studies allow to produce lignopolyurethane foams processed by molding and spraying, with properties that correspond to those of foams used as heat-insulating and lightweight construction materials.
4. The frame elements of upholstered furniture of complex configuration were produced (experimental lines) by molding of the lignopolyurethane foam system at the Research-and-Production Association "Gauja" (Riga, Latvia).
5. Heat-insulating coatings and "sandwich"-type building panels with a layer of lignosulphonate and organosolv wheat straw lignin-based polyurethane foam insulation were produced in collaboration with the Latvian State Scientific Institute of Building and Experimental Technologies (Riga, Latvia) and the Polymer Laboratory of the Latvian State Institute of Wood Chemistry (Riga, Latvia).

## The results make an important contribution to the implementation of the following projects

1. Horizon 2020 Project US4 GREENCHEM "Combined ultrasonic and enzyme treatment of lignocellulosic feedstock as substrate for sugar-based biotechnological applications" (2015–2019);
2. Contract No. 13–46 with MetGen Oy (Finland). Mission: "Characterization of lignin fractions separated by MetGen processing, their oxypropylation and development of rigid PU foams on the basis of lignopolyols obtained" (2018). Starting lignin was separated by the METNIN™ valorization technology in the framework of Bio-Based Industries Joint Undertaking under the European Horizon 2020 research and innovation programme for the SWEETWOODS project under grant agreement No. 792061. Contract leader from LS IWC – A. Arshanitsa;
3. National Research Programme ResProd project No. 3 "Research and sustainable use of forest and subsoil resources – new products and technologies" (2014–2018);

4. Cooperation project "BIOCORE" ("Biocommodity refinery") in the framework of the ES 7th Framework Programme. Contract No. 241566 (2010–2014).

**The results are presented in 9 publications in reviewed journals, in the book *"Cellulosics: Chemical, Biochemical and Material Aspects"*, at 10 international scientific conferences, and a European patent is developed on their basis.**

## Full text scientific publications

1. Jablonskis, A., **Arshanitsa, A**., Arnautov, A., Telysheva, G., Evtuguin, D. Evaluation of LignoBoost$^{TM}$ softwood kraft lignin epoxidation as an approach for its application in cured epoxy resin. *Industrial Crops and Products* (**IF 4.63**). 2018, vol. 115, pp. 225–235. Available from: doi: 10.1016/j.indcrop.2017.12.003 (P-1)
2. **Arshanitsa, A**., Krumina, L., Telysheva, G., Dizhbite, T. Exploring the application potential of incompletely soluble organosolv lignin as a macromonomer for polyurethane synthesis. *Industrial Crops and Products* (**IF 4.63**). 2016, vol. 92, pp. 1–12. Available from: doi: 10.1016/j.indcrop.2016.07.050 (P-2)
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9. **Arshanitsa, A. S**., Gromova, M. F., Ioelovich, M. Y., Chirkova, E. A., Sisask, U. O. Vliyanie mehanicheskoj obrabotki na svojstva gidroliznogo lignina kak napolnitelya elastomerov [Influence of mechanical treatment on the properties of hydrolysis lignin as a filler for elastomers]. *Khimiya drevisini [Wood chemistry]*. 1990, no. 3, pp. 76–80 (P-9)

## The book

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## European patent

Latvian State Institute of Wood Chemistry. *Method for production of heat-insulating materials [Verfahren zur Herstellung von Warmedammaterialien, Siltumizolācijas materiālu iegūšanas paņēmiens].* **A. Arshanitsa**, G. Telysheva, A. Paberza, U. Cabulis, L. Vevere, T. Dizhbite**.** Data of submission 2013-30-09. Pat. EP 2816052 A1, C 08G18/76, C 08G18/64, C 08L97/00, C 08H7/00, C 07G1/00. 2014-12-24. Available: https://www.google.com/patents/EP2816052A1?cl=en;https://register.epo.org/application?lng=de&tab=main&number=EP1318678;https://worldwide.espacenet.com. (P-11)

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2. **Arshanitsa, A**., Paberza, A., Vevere, L., Cabulis, U., Telysheva, G. Two approaches for introduction of wheat straw lignin into rigid polyurethane foams. **In:** *Abstract book of the 29th International Conference of the Polymer-Processing-Society (PPS).* Nuremberg, Germany, July 15–19, 2013, p. 129
3. **Arshanitsa, A**., Krumina, L., Gosselink, R., van der Putten, J., Telysheva, G. Fractionation of CIMV wheat straw lignin as an approach for promoting its interaction with isocyanates and chracteristic of products obtained. **In:** *Final program & Abstract book of the 8th International Conference on Renewable Resource & Biorefineries.* Toulouse, France, June 4–6, 2012, p. 100
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7. Cabulis, U., Pabeza, A., **Arshanitsa, A**. Wheat straw lignin as additive filler for rigid polyurethane foams on the basis of tail oil amide. **In:** *Proceeding of the 3rd*

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8. Paberza, A., **Arshanitsa, A.**, Cabulis, U. Thermal degradation and physical-mechanical properties of lignin-filled rigid polyurethane foam. **In:** *Proceeding of the Baltic Polymer Symposium.* Liepaja, Latvia, September 19–22, 2012, p. 155
9. **Arshanitsa, A.**, Krumina, L., Janceva, S., Telysheva, G. Study of the reactivity of kraft and organosolv lignins with 4,4'-diphenylmethane diisocyanate and characterization of the obtained products. **In:** *Proceedings of the Third Nordic Wood Biorefinery Conference.* Stockholm, Sweden, March 22-24, 2011, pp.348-350
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## The development of the methodology of lignins' modification and application in polymers compositions is described also in other publications and patents not included in this thesis:

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4. Gromova, M. F., **Arshanitsa, A. S.**, Sergeeva, V. N., Shishlo, R. Yu. Sintez i svojstva ligolov – prostih oligoefirov na osnove tehnicheskih lignosulfonatov [Synthesis and properties of ligols – simple oligoesters based on technical lignosulfonates]. *Rukopis dep. v VINITI [Manuscript dep. at VINITI].* 1988, no. 312-B88.
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7. Latvian State Institute of Wood Chemistry. *Sposob polucheniya gidroksilsoderzaschego sirya dlya zhestkih zalivochnih penopoliuretanov [Method of obtaining of hydroxyl-containing raw materials for rigid polyurethane moulding foams].* **A. Arshanitsa**, M. Gromova, G. Telysheva, G. Tarakanov, A. Sevastyanova. Data of submission 1991-01-02. МПК C08K 11/00, C07G 1/00. 1993-07-02. Available: http://patents.

su/3-1792941-sposob-polucheniya-gidroksilsoderzhashhego-syrya-dlya-zhestkikh-zalivochnykh-penopoliuretanov.html; http://www.findpatent.ru/patent/179/1792941.html

8. Institute of General and Inorganic Chemistry of the National Academy of Sciences of Belarus, Latvian State Institute of Wood Chemistry. *Sposob flotacii glinistih kalijnih rud [Method of flotation of clay potash ores].* A. Markin, L. Zhibul, N. Makarevich, G. Telysheva, M. Gromova, **A. Arshanitsa**. Data of submission 1989-12-12. SU 1704835, МПК B3D 1/012. 1992-01-15. Available: http://patents.su/2-1704835-sposob-flotacii-glinistykh-kalijjnykh-rud; http://www.findpatent.ru/patent/170/1704835.html
9. Research Institute for Chemistry of the Lobachevsky State University of Nizhni Novgorod, Latvian State Institute of Wood Chemistry. Geleobrazujuschaya kompoziciya dla obrabotki neftyanih skvazin *[Gel-forming composition for treating oil wells]*. N. Ryabokon, N. Myasnikova, M. Gromova, **A. Arshanitsa**, G. Telysheva, M. Prokofjeva, N. Kubareva. Data of submission 1988. A.c. SU 1548415, C09K 8/10, C09K 8/588, E21B 43/27. 1990. Available: //worldwide.espacenet.com [Gel-forming composition for treating oil wells]

# 1. LITERATURE OVERVIEW

Bioplastics represent one of the fastest growing markets today. The average growth rates over the past years have constantly been double-digit (Storz and Viorlop, 2013, Zhao *et al.,* 2020). The European Bioplastic Association defines bioplastic material as biobased, biodegradable, or both (European bioplastic, 2015). The term "biobased" means that material is derived (fully or partially) from biomass. The renewable carbon content of bioplastics ranges from 20% to 100% (Biron, 2020).

Polyurethanes (PU) are the most versatile type of polymers on the basis of which all known types of materials used in all, without exception, industries are obtained. PU foam is one of the most important thermal insulation materials used in the construction industry and as the main insulation material used in the global appliences (refrigerators, freezers, etc.) industry. Expanding the resource base through the use of renewable raw materials, increasing the share of the "green" component, along with the possibility of improving the operational characteristics of the material, are one of the defining directions of the modern development of chemistry and PU technology (Vahabi *et al.,* 2020). According to a recent report, the global PU market with a compound annual growth rate of 6.0% is estimated to reach USD 88 billion by 2026 (Sonnenschein *et al.,* 2014, Polyurethane (PU) market 2020, Grand view research 2020). From a chemistry standpoint, PUs are identified as organic polymers with urethane links, which are the result of a chemical reaction between isocyanates and polyols (Fig. 2).

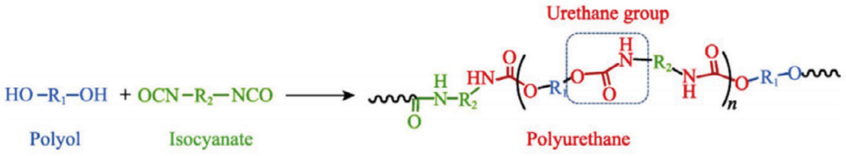


*Figure 2.* **Reaction of polyurethanes formation (Li, H., Liang. Y.** ***et al.*****, 2020)**

About 30–40% of the PU composition by weight consists of polyol or polyol blends (Grand view Research, 2020, Ionescu, 2005). The global polyol market size is expected to reach USD 45.17 billion by 2025 at an 8.5% compound annual growth rate during the forecast period (Research and markets, 2020). The content of OH-groups in lignin (10–12% by weight) meets the requirements (11–15% by weight) (Ionescu, 2005) for commercial polyols used for rigid PU production. The use of lignin can improve the mechanical characteristics and thermal stability of PU, and increase biodegradability (Hu *et al.,* 2002). The properties of lignin-containing PU depend on the method of lignin incorporation.

The possible synthetic routes for lignin incorporation into PU materials are the following: as an additive filler in the form of powder, as a hydroxyl enriched reactive filler in the form of powder, and as a hydroxyl functional monomer in a liquid form obtained by chemical modification, for example, by alkoxylation of lignin (Fig. 3) (Hu *et al.*, 2002, Brodin *et al.,* 2009).

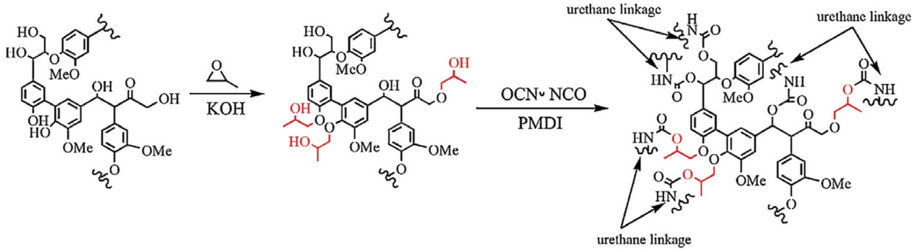
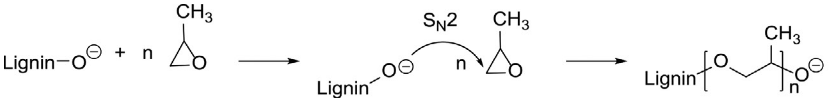


*Figure 3.* **Polyurethanes formation from lignopolyols** (Li, B., Zhou, M. *et al.,* 2020)

The main difficulties in working out market-oriented lignin-containing polymeric composite materials are as follows: heterogeneity of technical lignins, variation in the functional groups' content, their types and proportion in lignins, as well as the difference in the molecular mass distribution (MMD) of the lignin fragments formed during the biomass processing, the structure of lignin-forming phenyl propane units, links between them, the solubility in organic solvents that varies in a wide range and restricted accessibility of reactive sites towards isocyanate due to their steric hindrance (Gosselink *et al.,* 2010, Mahmood *et al.,* 2016). Various pretreatments are used to decrease the above-mentioned disadvantages of lignin and to enhance the efficiency of technical lignins' application as a macromonomer capable of taking part in the formation of polymeric structures. Numerous methods are based on the depolymerization of the lignin matrix via the cleavage of ether linkages into more uniform oligomeric or reduced molecular weight products with enhanced accessibility of functional groups in reactions with isocyanates (Mahmood *et al.,* 2016, Wang *et al.,* 2013). The produced depolymerized lignins were successfully utilized as bio-polyols replacing up to 50% of commercial polyols for the preparation of rigid PU foams (Mahmood *et al.,* 2016). Oxypropylation of technical lignins in the presence of alkali catalysts is recognized as another approach to overcome the molecular and functional heterogeneity of lignins, and to obtain lignopolyols for the formation of rigid PU foams (Cateto *et al.,* 2009, Ionescu, 2005) (1).

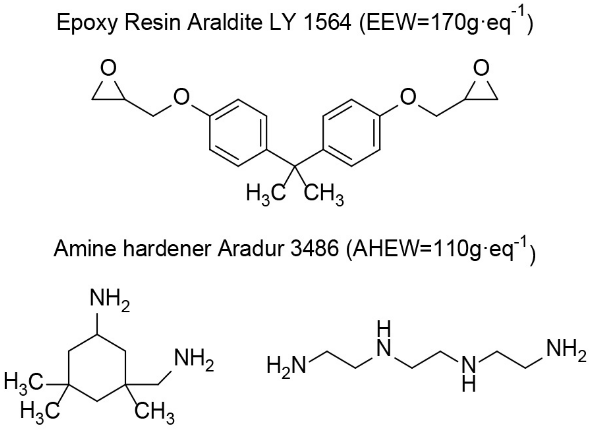


(1)

In this case, the degradation of the lignin core is accompanied by the attachment of oxypropyl units towards the OH groups of lignins, those converting the acidic groups (phenolic, carboxylic) into aliphatic ones with higher reactivity towards isocyanate (Gandini *et al.,* 2002). Several aspects of the oxypropylation of commercial technical lignins from softwood, hardwood, and grasses are described in the literature (Nadji *et al.,* 2005, Belgacem and Gandini, 2008, Cateto *et al.,* 2009, Ahvazi *et al.,* 2011, Li and Ragauskas, 2012). Undoubtedly, the above-mentioned processes are challenging due to the severity of reaction conditions (220–300 °C, and a pressure of 5–30 bar) (Mahmood *et al.,* 2016).

The fractionation of technical lignins by organic solvents extraction at atmospheric pressure and room or refluxing temperature could be a prospective opportunity, increasing the efficiency of lignin application as a macromonomer for PU materials' fabrication. Fractionation of different unmodified commercial kraft and organosolv (ethanol-water) lignins by diethyl ether, n-propanol, methanol and the dichloromethane/methanol mixtures allows obtaining of lignin samples with a lower molecular weight (MW), more uniform by MMD, completely soluble in organic solvents commonly used in PU chemistry and suitable to fulfill successfully the role of macromonomers in PU material synthesis (Gosselink *et al.,* 2010, Li and McDonald, 2014, Yoshida *et al.,* 1987). Such an approach permits obtaining of PU elastomers with predictable thermal and mechanical properties, which can be varied in a wide range depending on the lignin fractions' MW, their content in PU and the type of the used soft segment (Yoshida *et al.,* 1990, Reiman *et al.,* 1991). PU composites that have a potential for application in the field of high-performance coatings and adhesives are obtained also on the basis of the methyltetrahydrofuran soluble fraction of kraft lignin Indulin AT and toluene diisocyanate-trimethylolpropane adduct (Griffini *et al.,* 2015).

Cured epoxy resins usually are thermosetting heat-stable polymers with high mechanical properties and chemical resistance (Abdurahman *et al.,* 2020, He *et al.,* 2014). The coatings, adhesives and reinforced composites on the basis of epoxy resins are widely used in many industrial applications, including electrical engineering, electronics, automobile and aircraft industries, etc. (Wanga *et al.,* 2016, Katunina *et al.,* 2016). Commercial epoxy resins are currently produced mainly (almost 90%) from petroleum-derived chemicals: bisphenol A (BPA) and epichlorhydrin (ECH) (Khalil *et al.*, 2011). Figure 4 shows the components of the commercial BPA-based amine cured epoxy system. BPA is responsible for numerous favorable properties of the final material, but unfortunately, it exhibits an estrogenic activity and, therefore, is referred to as an environmental hormone that negatively influences the human health (Sasaki *et al.,* 2013). BPA and its derivatives possess high potential as an endocrine disruptor. Exposure to BPA may induce harmful, reproductive, developmental and metabolic disorders (Fischnaller *et al.*, 2016).


Epoxy Resin Araldite LY 1564 (EEW=170g·eq$^{-1}$)

Amine hardener Aradur 3486 (AHEW=110g·eq$^{-1}$)

*Figure 4.* **Components of the commercial amine cured epoxy system Araldite LY 1564/ Aradur 3486 (HUNTSMAN)**

Recently, several researches have been reported on the synthesis of bio-based epoxy resins from various renewable resources such as vanillin (Fache *et al.,* 2014), gallic acid and catechin (Aouf *et al.*, 2013), isosorbide (Lukaszczyk *et al.,* 2011), tannins (Benyahya *et al.,* 2014), vegetable oils (Shah and Ahmad, 2012) and lignins (Delmas *et al.,* 2013).

The aromatic structure of lignins and the presence of a significant amount of OH groups (phenolic, aliphatic and carboxylic) make technical lignins an attractive raw material for BPA substitution, capable of modification via the reaction of OH groups with epichlorohydrin. Two major processes take place during the lignin's reaction with epichlorohydrin in the presence of the alkaline catalyst (lignin's glycidylation) (Nieh and Glasser, 1989). One of them is the ionization of hydroxyl groups, leading to the nucleophilic attack of the anion on the carbon of the oxirane ring, and its opening and chloroglyceryl ether formation (Fig. 5). This is followed by dechlorohydrogenation and oxirane ring formation (Fig. 5).

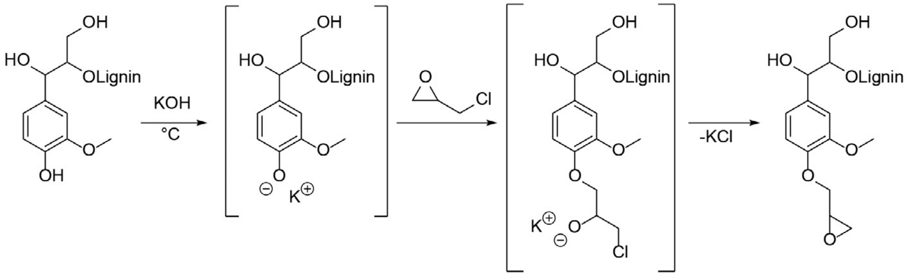


*Figure 5.* **Schematic view of OH phenolic glycidylation**

The phenolic groups of lignin, in comparison with aliphatic and carboxylic OH groups, are the most accessible ones for the glycidylation in these conditions, because a more suitable balance between the acidity and nucleophilicity of phenolates is achieved (Wu and Glasser, 1984).

Different approaches have been used for utilization of lignin for the synthesis of epoxy resins, including the depolymerization and chemical modification of lignin. The mechanical and thermal properties of cured epoxy resins on the basis of depolymerized kraft, hydrolysis and organosolv lignins were found to be inferior to those for reference commercial epoxy resins (Wang *et al.,* 2013). Another approach is demethylation of lignin and obtaining of lignin products with free phenolic groups in the 3 and 5 ring positions; these lignins could be used as a feedstock for lignin-based hyperbranched epoxy production. However, at the moment, catalytic pathways do not exist, and the widely used reagents (alkyl halides) are harmful and undesirable for large scale production (Ferhan *et al.,* 2013, Hu *et al.,* 2014). Phenolation, as another modification method for increasing the content of phenolic groups in lignin, has a potential for making more favorable conditions for lignin reaction with ECH. However, the release of formaldehyde to generate new reactive sites and cyclization via etherification of phenol with lignin side chain carbons was also detected, that diminished the advantages of this approach (Podschun *et al.*, 2015). Hofmann and Glasser prepared epoxy resins from hydroxyalkyl lignin (alkali extracted lignin from steam exploded yellow poplar) derivatives with varying degrees of alkoxylation. To obtain lignin derivatives, containing only high reactive aliphatic OH groups, the consequent modification of lignin was performed before glycidylation. The prepared epoxy prepolymers were cured into stiff thermosets having a high glass transition temperature (Hofmann and Glasser, 1993).

As lignin properties and its ability towards various chemical modifications depend strongly on the biomass origin and the technology of lignin isolation (Gosselink *et al.,* 2010), it is nesesarry to conduct studies with each lignin type intended for valorization.

# 2. MATERIALS AND METHODS

## 2.1. Lignins under study

The approach for introduction of lignin into polyurethane materials is exemplified by organosolv lignin of wheat straw. It was extracted from straw using a mixture of acetic acid/formic acid/water (30/55/15) at atmospheric pressure, time of reaction 3.5 h, 105 °C at the CIMV pilot plant (Pomacle, France) (Delmas *et al.*, 2008). The lignin was supplied with the water content of about 48% by CIMV (09. 2015). The material was washed with deionized water up to pH 4.4 to remove the residual free acids, then air-dried up to the moisture content of 5% and ground in a laboratory-scale disintegrator DESI-11 at 10000 rpm. The introduction of lignin into epoxy resins is exemplified by commercial LignoBoost™ softwood kraft lignin isolated from the original black liquor using the novel LignoBoost process. It was kindly gifted by Innventia AB.

## 2.2. Lignin modification and incorporation in polymers compositions

- The developed concept for application of lignins as macronomers of polymers compositions is represented by the scheme (Fig. 6).
- Lignins' fractionation by organic solvents is described in P-6.
- The incorporation of lignins in the composition of PU elastomers is described in P-2.
- The details of lignins' oxyalkylation are described in P-3 and P-10.
- The incorporation of lignopolyols in the composition of RPU foams is described in P-8.

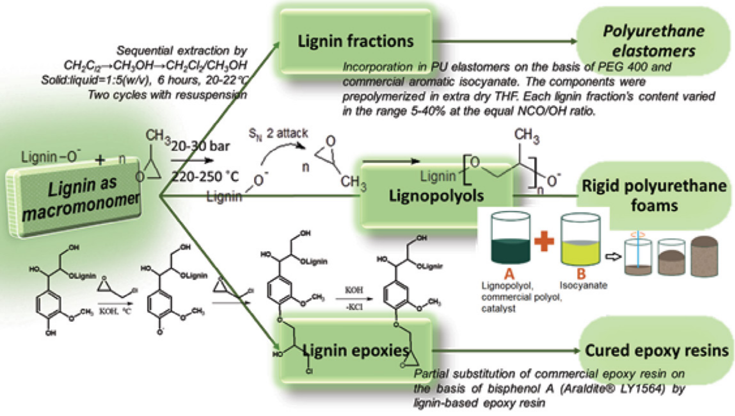


*Figure 6.* **Scheme representing the developed approaches for lignins modification and use as macromonomers in polymers compositions**

- The incorporation of lignins in the composition of cured epoxy resins is described in P-1.
- Besides, lignins were mechano-chemically activated and introduced in the composition of polyurethane foams as a filler. The mechano-chemical activation of technical lignins is described in P-9. The introduction of lignins as fillers in the composition of RPU foams is described in P-5, P-8.

## 2.3. Component analysis, structural analysis and physico-chemical characterization of technical lignins and products of their modification

The parent lignin and products of its modification were characterized in terms of Klason lignin content (TAPPI T222:2006 Standard), ash content (LVS EN 14775:2016 standard) and C,H,N content (LVS EN 15104:2011 standard, functional analysis: methoxyl groups' ($OCH_3$) content, phenolic and aliphatic OH groups' content, carboxylic groups' content (Zakis, 1994). Structural information was obtained and the efficiency of lignins modification was evaluated by FTIR spectroscopy, $^{31}P$ NMR spectroscopy (Granata and Argyropoulos,1995), $^{1}H$-NMR spectroscopy (Glasser *et al.*,1984), analytical pyrolysis (Py-GC/MS), size-exclusion chromatography (SEC). Glass transition temperatures (Tg) were determined by differential scanning calorimetry (DSC) (DIN standard 53765, 1994). TGA analysis was performed in nitrogen and air atmosphere and the first derivative of the thermogravimetric curve (differential thermogravimetric, DTG) was used for discussion. The developed methodology for characterization of technical lignins is described in P-4, P-7.

The study of the lignin fractions separated by sequential extraction as macromonomers of PU networks, including kinetics of their interaction with 4,4-methylene diphenylene diisocyanate (MDI) in dioxane solution, is described in P-2, P-6.

The study of the oxypropylation process and specific characterization of the obtained lignopolyols is described in P-3.

## 2.4. Characterization of the obtained polymers compositions

The prepared lignopolyurethane (LPU) films were smooth and translucent (Fig. 7). The tensile tests of LPU films were performed according to ASTMD 882-10:2010 standards using a Zwick/Roell Z100 testing machine.

Polyurethane foams (Fig. 8) were obtained by the free rising method and tested.

Measurements of compression strength, apparent density, closed cell content, dimensional stability, and water absorption of foams were performed according to DIN EN 826:1996, ISO 4590:2016, DIN 53420:1978, ISO 2796:2017 and DIN 53428:2017, respectively. A scanning electron microscope SEM TESCAN TS 5136 MM was used to study the cell structure. The thermal conductivity in the range between 10 and 30°C was tested with Linseis HFM (Heat Flow Meter) 200 was measured according to ISO 8301:1991.

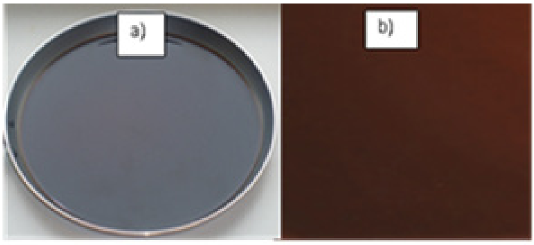


*Figure 7.* **Lignopolyurethane film, containing 20% of lignin's methanol fraction: a) under curing in a mold; b) cured and eliminated sample**

*Figure 8.* **Lignopolyurethane foams derived on the basis of oxypropylated wheat straw lignin**

*Figure 9.* **Amine cured commercial epoxy resin Araldite LY 1564: initial (1) and with 10% substitution of glycidylated BPA by lignin epoxy (2)**

Tensile tests of cured commercial glycidylated bisphenol A (BPA)-based epoxy resin Araldite LY 1564, initial and with partial substitution of BPA by lignin epoxy, were performed according to the ASTM D638:2014 plastics standard, using a Zwick/Roell 2.5 testing machine.

The effect of lignin products on the thermal degradation of materials was studied by thermal analysis (DTG and DTA) methods in oxidative (air) and inert ($N_2$) media as described in P-2.

# 3. RESULTS AND DISCUSSION

## 3.1. Tuning of lignin properties by fractionation with organic solvents

The main results concerning organosolv lignin fractionation are presented in: P-2. Organsolv lignin of wheat straw (OSL) shows weak solubility in the solvents or polyols used for PU network formation. The sequential fractionation of OSL by dichlorormethane, methanol and a mix of both is a promising modification for application of OSL as a macromonomer of PU compositions. The obtained fractions have lower molecular mass and lower polydispersity in comparison to parent lignin (Table 1), as well as complete solubility in cyclic ethers including tetrahydrofurane and dioxane, and higher mobility of the molecular chains as evidenced by the values of the glass transition temperature (Tg) (Tg of initial lignin is 177 °C, but Tg of dichlomethane soluble fraction is 14 °C) (Table 1). It enhances the availability of the OH groups of lignin in the urethane's formation reaction.

*Table 1*

**Molecular weights, functional groups' content, Tg of organosolv lignin and its fractions, and their ractivity towards 4,4-methylene diphenylene diisocyanate (MDI) in dioxane solution**

| Index | Lignin and its fractions | | | |
|---|---|---|---|---|
| | Lignin | DCM-F | MET-F | MET/ DCM-F |
| Yield (%)* | – | 7.4±0.2 | 14.5±0.7 | 18.2±0.9 |
| Mw ($g{\cdot}mol^{-1}$) | 11100 | 1970 | 2200 | 5300 |
| Mn ($g{\cdot}mol^{-1}$) | 1050 | 334 | 540 | 1100 |
| $Mw{\cdot}Mn^{-1}$ | 10.6 | 5.9 | 4.1 | 4.8 |
| $OCH_3$ content (mmol $g^{-1}$) | 3.12±0.03 | 2.96±0.03 | 3.55±0.06 | 3.67±0.03 |
| OH acetylated content (mmol $g^{-1}$) | 4.53±0.15 | 3.24±0.06 | 5.30±0.10 | 5.00±0.10 |
| OH aliphatic content (mmol $g^{-1}$) | 3.76±0.28 | 1.65±0.19 | 4.5±0.3 | 4.35±0.23 |
| OH phenolic content (mmol $g^{-1}$) | 1.47±0.08 | 2.12±0.10 | 2.06±0.10 | 1.60±0.08 |
| COOH content (mmol $g^{-1}$) | 0.71±0.05 | 0.53±0.03 | 1.18±0.10 | 0.88±0.05 |
| Total OH groups content (mmol $g^{-1}$) | 5.94±0.25 | 4.30±0.12 | 7.7±0.3 | 6.83±0.20 |
| $OH_{aliph}/OH_{total}$ | 0.63 | 0.38 | 0.58 | 0.64 |
| Average OH functionality | 6.2 | 1.4 | 4.2 | 7.5 |
| Tg (°C) | 177 | 14 | 121 | 160 |
| Condensation degree (B+Ph)/(G+S) | 0.15±0.02 | 0.100±0.001 | 0.16±0.01 | 0.24±0.02 |
| $k{\times}10^4$ ($L{\cdot}mol^{-1}{\cdot}s^{-1}$)** | - | 2.30±0.15 | 4.7±0.4 | 3.9±0.4 |

* – on the oven-dry ash-free matter of non-extracred lignin

** – second order constant of the reaction with MDI in dioxane solution

The interaction of isocyanates and hydroxyl containing compounds is the nucleophilic addition reaction. Due to that, phehols, being more acidic compounds than aliphatic alcohols, react with isocyanates much slower (Saunders *et al.,* 1962). The realative reaction rates of phenolic OH are about 300 times lower in comparison with those of secondary OH groups (Ionescu, 2005). The reactivity of carboxylic acids with isocyanate is also much lower than the one for alcohols (Ionescu, 2005). Therefore, the total content of OH groups and their allocation between aliphatic and acidic (phenolic plus carboxylic) groups are significant parameters, characterizing the lignin fractions as a macromonomer aimed at LPU synthesis (Kelley *et al.,* 1989). The lowest total content of OH groups, namely, 4.30 $\text{mmol}\cdot\text{g}^{-1}$ was determined in dichlormethane soluble fraction (DCM-F) vs 5.94, 7.71 and 6.83 $\text{mmol}\cdot\text{g}^{-1}$ in lignin, methanol soluble fraction (MET-F) and in a mix of both solvents soluble fraction (MET/DCM-F), respectively. The relative portion of the aliphatic OH groups, most reactive towards isocyanates for lignin fractions obtained, increased in the following row of solvents used: DCM < MET < MET/DCM (Table 1).

The ratio of the sum of the portions of phenol and benzene derivatives to the sum of guaiacol and syringol derivatives in pyrolysis products of lignin fractions indicates that the degree of lignin condensation is increased in the same row. The increasing molecular weights and increasing degree of condensation of lignin constituents led to the increase of the Tg of fractions from 14 °C for DCM-F to 160 °C for MET/DCM-F (Table 1). The average OH functionality of polyols is defined as a number of OH groups per one molecule (Ionescu, 2005). These values are equal to 1.4, 4.2 and 7.5 for DCM-F, MET-F and MET/DCM-F, respectively. Therefore, the different crosslinking effect can be expected from the incorporation of the same amounts of different lignin fractions at an equal NCO/OH ratio into the PU matrix.

The results show that the process of urethane formation using lignin as a hydroxyl-containing component proceeds in accordance with the basic positions of the catalytic interaction of alcohols and isocyanates. The reactivity of the investigated lignin fractions with MDI in dioxane solution increased in the following order: DCM-F < MET/DCM-F < MET-F (Table 1). The highest reactivity of the MET-F fraction could be explained by its higher content of aliphatic OH groups (Table 1) and their steric availability due to the not-too-high degree of lignin condensity.

## 3.2. Influence of lignin fractions as macromonomers on the properties of polyurethane elastomers

The results concerning the influence of the wheat straw organosolv lignins fractions on the properties of PU elastomers are presented in P-2, P-6.

The obtained lignin fractions, reactive towards isocyanate, act as a crosslinking agent being incorporated in the model three components: lignin (5–40%) – PEG (MW = 400 $\text{g}\cdot\text{mol}^{-1}$) – PMDI polyurethane system.

The incorporation of lignin in the composition of PU films enhances their:

- glass transition temperature;
- tensile strength;
- Young’s modulus.

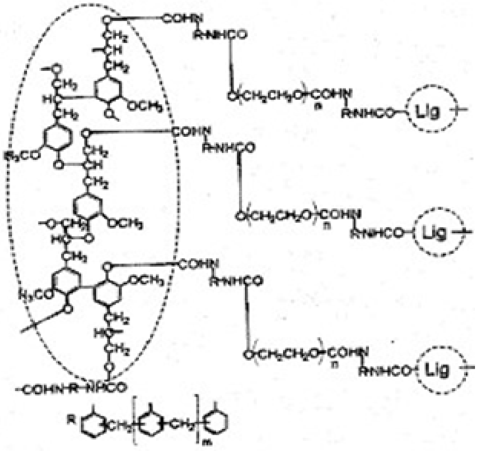


*Figure 10.* **Structure of lignopolyurethane with soft PEG segments (Hu, 2002)**

The increase of the thermo-oxidative stability of lignopolyurethanes (LPU) was observed at a minor (5%) content of lignins in LPU, when they revealed antioxidative activity (Table 2). At a 30% content of fractions in the compositions used for PU synthesis, the crosslinking effect and an increase in the thermostable aromatic constituents' content in lignopolyurethanes were revealed, leading to the further enhancement of their thermo-oxidative stability and charcoal yield under the impact of high temperature.

*Table 2*

**Effect of OSL fractions on the characteristics of the thermo-oxidative destruction of PU films**

| Fraction | Content in LPU (%) | Tstart (°C) (5% of weight loss) | $T_{50\%}$ (˚C) (50% of weight loss) | Maximal degradation rate (mg·min$^{-1}$) | Temperature of maximal degradation rate (°C) | Char residue at 500°C (%) |
|---|---|---|---|---|---|---|
| Lignin free PU | 0 | 274 | 365 | 0.94 | 307 | 27.0 |
| DCM-F | 5 | 281 | 367 | 0.56 | 331 | 33.7 |
| | 30 | 238 | 427 | 0.21 | 325 | 42.2 |
| MET-F | 5 | 279 | 403 | 0.44 | 331 | 32.4 |
| | 30 | 205 | 442 | 0.30 | 360 | 44.5 |
| DCM/ MET-F | 5 | 286 | 402 | 0.27 | 331 | 35.7 |
| | 30 | 225 | 499 | 0.18 | 324 | 50.0 |

The revealed high antioxidant activity of fractionated technical lignin is another advantage for lignin application in PU production, because, unlike commercial phenolic antioxidants, which significantly inhibit the biodegradation of the composite materials, the antioxidants derived from lignins are not only biodegradable, but they can also catalyze the biological decomposition of the material into which they are incorporated (Domenek *et al.,* 2013).

## 3.3. Study of the wheat straw organosolv lignin oxyalkylation process and characterization of the obtained polyols

The results concerning organosolv lignin oxyalkylation are presented in: P-3. Modification of non-fractionated OSL by propylene oxide using the anionic polymerization mechanism is a promising approach for the liquification of solid lignins and for the transformation of acidic lignin groups into aliphatic OH groups, highly active in urethane formation reactions.

Oxyalkylation leads to the disappearance of the electronic constraints and steric hindrance of lignin hydroxyl groups. The process of copolymerization of lignin and propylene oxide (PO) is accompanied by oxypropylene homopolymerization and the formation of propylene glycols (Fig. 11).

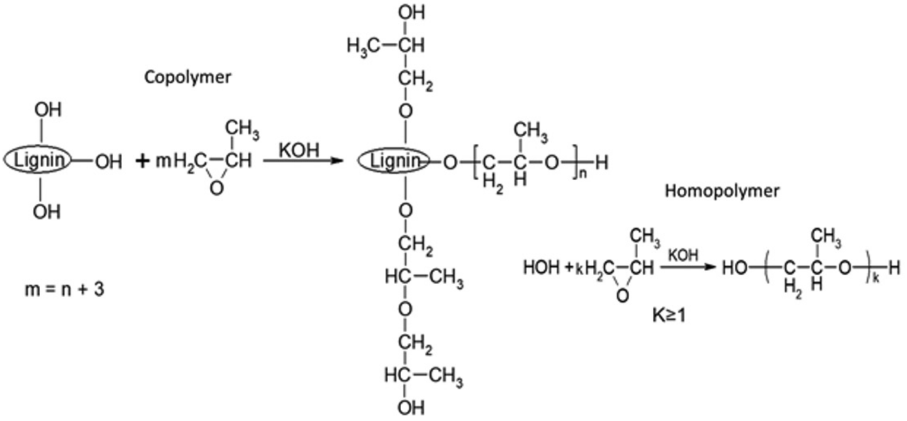


*Figure 11.* **Sheme of the formation of the main products in the straw lignin oxypropylation process**

The data obtained by $^1$H NMR spectroscopy confirms the copolymerization of lignin with PO (Fig. 12). The intensity of aliphatic proton signals (CH, $CH_2$, $CH_3$) is increasing while that of methoxy groups is decreasing due to the dilution of aromatic constituents by PO grafting. The aromatic acetoxy signal disappears, and the aliphatic acetoxy signal is elevated (Fig. 12).

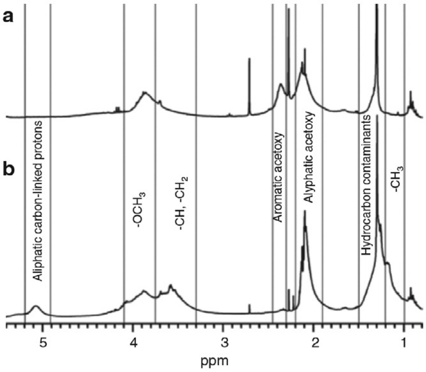


*Figure 12.* **1H NMR spectra of straw lignin (a) and its oxypropylated derivative (L/(L+PO) = 30%) (b)**

FTIR spectra confirm the chemical modification of lignin via the interaction of its OH groups with PO as CH, $CH_2$, $CH_3$ groups' absorbance at 2975, 1465 $cm^{-1}$ has increased, ether bonds' absorbance at 1125 $cm^{-1}$ has increased and unconjugated carbonyl moieties' absorbance at 1720 $cm^{-1}$ has decreased (Fig. 13).

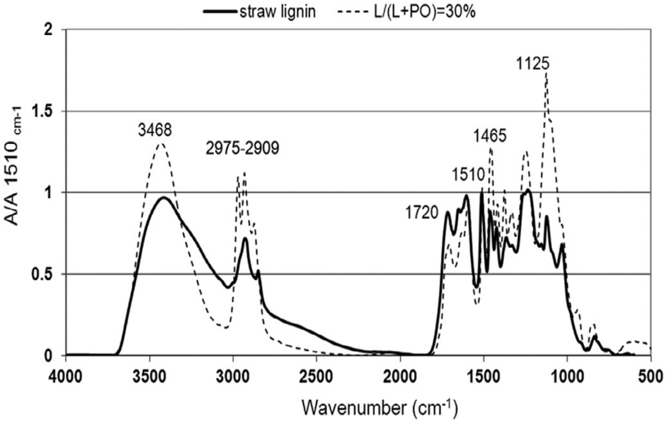


*Figure 13.* **Normalized (1510 cm-1) FTIR spectra of wheat straw lignin and its oxypropylated derivative**

OH groups in OSL-PO copolymers are presented mainly by secondary alcohol groups, as the HI treatment of the oxypropylated lignin derivative followed by the GC analysis of the reaction products led to the domination of the isopropyl iodide signal in the chromatogramm and appearance of the traces of n-propyl iodide.

The data of the molecular weight distribution of copolymers are other parameters that allow characterizing the transformation of the lignin macromolecule at oxypropylation and the physico-chemical properties of lignopolyols obtained. A drastic increase in the uniformity of copolymers in terms of molecular weight distribution was observed (Table 3).

*Table 3*

**Content of the functional groups and molecular mass distribution of wheat straw lignin and its oxypropylated derivatives**

| L/(L+PO) (%) | OH (mmol·$g^{-1}$)* | | | | $OH_{alif}$/ΣOH | $OH_{cond}$/$ΣOH_{pfen}$ | $OCH_3$ (mmol·$g^{-1}$) | Molecular mass (g·$mol^{-1}$) | | $M_w$·$M_n^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | $OH_{alif}$ | $ΣOH_{pfen}$ | COOH | ΣOH | | | | $M_n$ | $M_w$ | |
| 15 | 2.26 | 0.10 | 0.03 | 2.39 | 0.95 | 0.62 | 1.39±0.03 | 8200 | 30000 | 3.7 |
| 20 | 2.53 | 0.10 | 0.04 | 2.67 | 0.95 | 0.65 | 1.66±0.01 | 4900 | 16300 | 3.3 |
| 25 | 2.56 | 0.12 | 0.05 | 2.73 | 0.94 | 0.63 | 1.77±0.01 | 4100 | 16900 | 4.1 |
| 30 | 2.59 | 0.14 | 0.05 | 2.78 | 0.93 | 0.63 | 1.97±0.01 | 4200 | 21500 | 5.1 |
| 35 | 2.59 | 0.14 | 0.07 | 2.80 | 0.93 | 0.63 | 2.29±0.06 | 3600 | 19700 | 5.5 |
| 40 | 2.65 | 0.17 | 0.06 | 2.88 | 0.92 | 0.56 | 2.39±0.06 | 3800 | 25700 | 6.8 |
| 100 | 1.39 | 1.62 | 0.50 | 3.51 | 0.40 | 0.32 | 3.69±0.10 | 2200 | 54000 | 24.5 |

* – NMR $^{31}P$ data

The batch oxypropylation of OSL allowed the overpassing of two main disadvantages of this lignin as a renewable macromonomer: high molecular heterogeneity and diversity of hydroxyl functionalities, thus improving the control over the gelation of polyurethane networks at PU foams' processing.

Free phenolic groups for all copolymers samples are located mainly in condensed structures ($OH_{cond}$), obviously due to their lower steric ability at oxypropylation. Some increase in the free phenolic groups content was determined for copolymers obtained at a higher amount (30–40%) of the starting OSL in the reaction mixture (Table 3).

Hindered phenols are the most common class of antioxidants for the dermination of the processes with the participation of free radicals. This class of antioxidants is widely used in polyurethane foam compositions to enhance their resistance towards oxidative degradation (Gray *et al.,* 1996). The existence of free phenolic groups in OSL-PO copolymers in the amount of 0.10-0.17 mmol·$g^{-1}$ can provide their functional assignment in PUR foams compositions. Both the roles of lignin as a high reactive aromatic macromonomer and a bio-based technical antioxidant in PUR foam systems can be realized. Recently, investigations in this direction have been started and the first positive results of the antioxidant activity of OSL-PO copolymers in PUR foams have been obtained.

The descriptive statistical analysis showed a normal distribution of the measured parameters for repeated experiments and a high repeatability of the oxypropylation parameters and the properties of the lignopolyols under study. The data presented above show good potential for upscaling the OSL oxypropylation process (Table 4).

*Table 4*

**Descriptive statistics of the parameters of organosolv wheat straw lignin oxypropylation and characteristics of lignopolyols obtained (*n* = 25)**

| Statistical parameters | Parameters of OP | | | | Lignopolyol characteristics | |
|---|---|---|---|---|---|---|
| | Tonset (°C) | Tmax (°C) | Pmax (bar) | OHV (mg KOH·g$^{-1}$) | Viscosity at 20 °C (Pa·s) | Water cont. K.F. (%)** |
| Mean | 164 | 241 | 24.7 | 447.3 | 57.5 | 0.05 |
| Median | 164 | 241 | 24.6 | 450.1 | 56.2 | 0.50 |
| Minimum | 161 | 235 | 24.0 | 409.2 | 50.1 | 0.03 |
| Maximum | 167 | 248 | 26.0 | 471.6 | 70.2 | 0.14 |
| Standard error | 0.35 | 0.64 | 0.10 | 2.80 | 1.11 | 0.02 |
| Standard deviation | 1.7 | 3.2 | 0.47 | 14.0 | 5.6 | 0.02 |
| Coef. VA (%)* | 1.0 | 1.3 | 1.9 | 3.1 | 9.7 | 40.0 |

* – variation coefficient

** – the moisture of lignopolyols was determined by Karl Fisher titration using culonometric KF titrator 275 KF

## 3.4. Influence of lignopolyols as macromonomers and lignin as a filler on the properties of rigid polyurethane foams

In this work, the potential application of wheat straw organosolv lignin (OSL) for lignopolyols synthesis, capable of rigid polyurethane (PUR) foam production, was studied. At the same time, non-modified lignin was used as a filler of rigid PUR foams obtained from the above-mentioned lignopolyols, those increasing the content of the renewable component in the polymeric material. The thermal, physico-mechanical and morphological properties of lignin-containing foams vs those of the foams obtained from commercial polyethers were in focus. The results are presented in P-5, P-8.

Due to the presence of potassium acetate in lignopolyols, acting as a catalyst of isocyanate conversion, oxypropylation is more suitable for polyurethane foam production as a high-rate interaction of polyols with isocyanate is necessary for the realization of this process. Commercial polyol polyether Lupranol 3300 was gradually (by 25%, 50%, 75%, and 100%) substituted with OSL-based lignopolyol (L/(L+PO) = 30%; OHV = 450 mg KOH·g$^{-1}$). The composition containing 30% of OSL is optimal in terms of its properties and the relevance of lignin beyond energy utilization. The substitution of commercial polyether by lignopolyol improved the dimensional stability and hydrophobicity of foam and did not affect its compressive characteristics. The introduction of OSL as a filler into the reference lignopolyol free composition led to the decrease of the main characteristics of foam. The best characteristics of the material were achieved when OSL was simultaneously introduced into the foam composition, both as a polyol and a filler.

The glass transition temperature of Lignopolyol-based PUR foam (Lupranol free) is between the data of foams on the basis of three functional and six functional commercial polyols (Fig. 14).

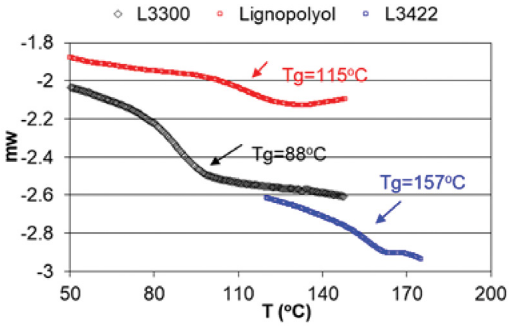


*Figure 14.* **DSC curves of polyurethane foams from commercial polyethers and lignopolyol**

The Tg values of the reference PUR foam and the foam with 6–25% of lignopolyol were in the range of 110–119 °C. Therefore, lignopolyol can successfully substitute the three functional glycerol-based commercial polyol in PUR foam systems without decreasing the heat resistance of the material.

It was shown that oxypropylated lignin acts as a surfactant in PUR foam compositions, improving the uniformity of the PUR cell structure and decreasing cell sizes (Fig. 15).

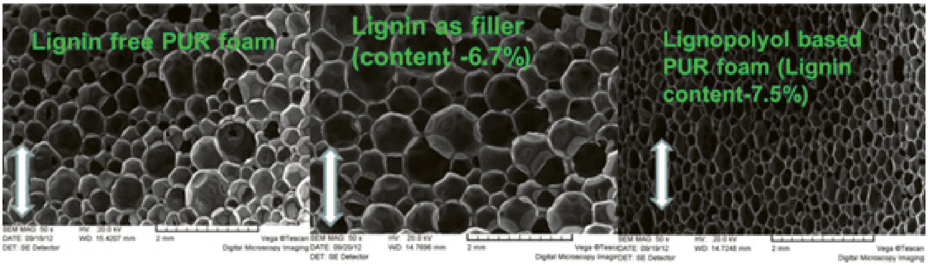


*Figure 15.* **Effect of lignin on the cell morphology of PUR foam**

There were no negative effects of the lignin filler and lignopolyol on the closed cell content in PUR foams (Fig. 16). A significant decrease in the maximum thermal degradation rate of lignopolysol-containing PUR foams has been observed from 1.20 mg/min. of lignopolysol-free PUR foams up to 0.54–0.93 mg/min. of PUR foams with different lignopolyol content.

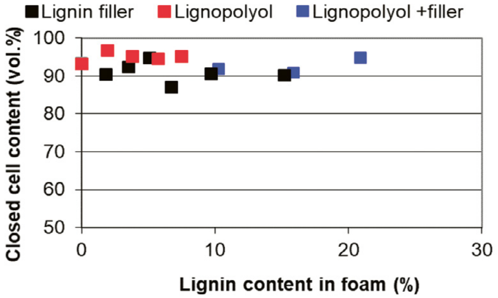


*Figure 16.* **Effect of lignin on the closed cell content of PUR foams**

Unmodified lignin filler has a less pronounced positive effect on the rate of thermal degradation of the material, as for PUR foams with lignin additive it is 0.60–1.16 mg/min. depending on the lignin content. In accordance with the cone calorimeter test, a significant fire retardation effect of the lignin introduced in the PUR foam composition as lignopolyols and a filler was observed. This can be explained by the combination of some factors including the free radical scavenging activity of lignin, and its charcoal formation promoting activity (Fig. 17).

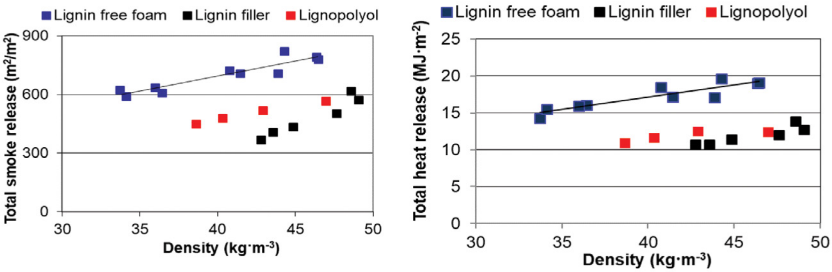


*Figure 17.* **Effect of lignopolyol and lignin filler on the combustion parameters of PUR foams**

The measured properties of the lignopolyol based PUR foams meet the requirements of the EU standard for heat insulating material. Based on the above mentioned results the method for production of heat insulation materials based on PUR foam by combination of isocyanate with polyol component, consisting of oxypropylated lignin an non – modified lignin was developed. This method is patented in the European Union and is described in P11.

## 3.6. Effect of lignin epoxies on the characteristics of bisphenol A-based commercial epoxy resin

The results concerning LignoBoost kraft lignin application in epoxy resins are presented in P-1.

The FTIR spectrum of the acetone-soluble fractions of kraft lignin (KL) and its glycidylated derivative (Fig. 18) confirms that glycidylation of lignin was realized, because new absorbance bands of the oxirane ring (3060, 750, 850, 910 $cm^{-1}$) appeared in the spectra of copolymers. Besides, the aliphatic groups (absorbance at 2975-2900 $cm^{-1}$) and ethers bonds (absorbance at 1030 $cm^{-1}$) were elevated, but the band of OH groups (absorbance at 3480 $cm^{-1}$) and carbonyl moieties (absorbance at 1710 $cm^{-1}$) decreased in comparison with the case of the acetone-soluble fraction of KL. The disappearance of the absorbance band at 1370 $cm^{-1}$ also testified that the successful glycidylation of phenolic OH took place. At the same time, the presence of a significant absorbance intensity at around 3500 $cm^{-1}$ confirmed that a portion of non-phenolic OH groups were not converted for the reason discussed above. The application of the KOH/TBAB catalytic system promoted the glycidylation of both phenolic and aliphatic OH groups of the lignin model compound. It has a potential for more complete glycidylation of lignin.

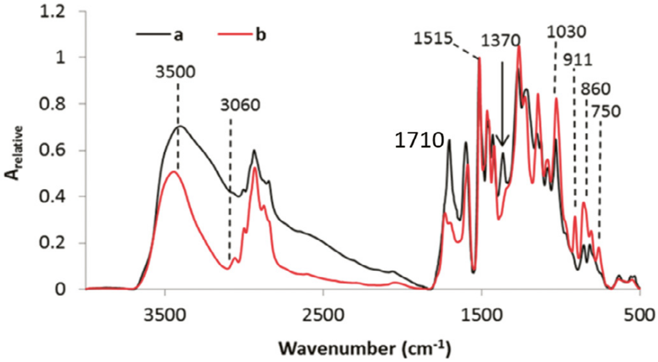


*Figure 18.* **Normalized (1515 cm-1) FTIR spectra of non-modified KL (a) and its glycidylated derivative (b)**

Substitution of commercial epoxy resin Araldite LY 1524 by lignin epoxy (EEW = 368 g·eq$^{-1}$) obtained by acetone extraction of glycidylated KL lignin (GLAF) leads to the increasing of Young's modulus at tensile for amine cured composites without decreasing of strength and strain. A drastic increase in the viscosity of commercial epoxy resin due to the incorporation of lignin epoxies was observed (Table 5).

**Table 5**

**Viscosity of non-cured epoxy resins and tensile properties of cured commercial epoxy resins vs the level of substitution of Araldite®LY1564 by GLAF**

| Level of substitution (%) | Viscosity (mPa·s) at 25 °C | Stress at break (MPa) | Young's modulus (GPa) | Strain at break (%) |
|---|---|---|---|---|
| Reference | 1230 | 63.1±2.7 | 2.91±0.16 | 4.9±0.3 |
| 2 | 1420 | 61.3±1.8 | 3.13±0.19 | 4.8±0.9 |
| 5 | 2052 | 67.1±2.2 | 3.09±0.21 | 5.5±0.7 |
| 10 | 3580 | 66.2±1.3 | 3.36±0.22 | 4.9±0.5 |

It makes lignin epoxy not suitable for technologies where the low viscosity of a composition is needed. Therefore, the possible practical application of lignin-containing epoxies as adhesive, mastic or crack filler instead of binder for fiber reinforced composites can be considered.

Thermal resistance is one of the advantages of cured epoxy resin. The lignin-containing cured epoxies demonstrated a higher charcoal yield and a lower degradation rate at high temperature treatment, suggesting that lignin epoxies have a potential for fabrication of flame-resistant epoxides (Table 6).

*Table 6*

**Effect of the partial substitution of Araldite LY1564 by lignin epoxy on the thermodegradation parameters of cured resins**

| Level of substitution (%) | $T_{5\%}$ (oC) | dm/dt (mg·min$^{-1}$) | Tmax (°C) | Char residue at 500 °C (%) |
|---|---|---|---|---|
| Reference | 338 | 1.6 | 336 | 10.5 |
| 2 | 325 | 1.4 | 368 | 13.7 |
| 5 | 320 | 1.4 | 363 | 17.6 |
| 10 | 303 | 1.2 | 365 | 22.6 |

$T_{5\%}$ – the temperature when 5% of weight loss was achieved
dm/dt – the maximum degradation rate
$T_{max}$ – the temperature when the maximum degradation rate was achieved

# CONCLUSIONS

1. The developed concept of lignin application as macromonomers of different polyurethane and epoxides systems, which includes different approaches of lignin modification and incorporation into the polymeric composition, allowed to introduce up to 40% of a bio-based component, simultaneously improving the mechanical and thermal stability of materials.
2. The fractionation with organic solvents is a perspective approach for obtaining lignin-derived macromonomers for polyurethane elastomers. The obtained lignin's fractions are soluble in solvents used for PU network formation, have decreased heterogeneity in comparison to parent lignin and are reactive towards isocyanate. Their introduction into the PU system enhances the glass transition temperature, tensile strength and Young's modulus of PU films.
3. Oxypropylation leads to the disappearance of the electronic constraints and steric hindrance of lignin hydroxyl groups, highly decreasing the molecular mass polydespersity of lignin. Oxyalkylation is effective for incorporation of lignins as liquid polyols in the composition of rigid polyurethane foam suitable for mold and spray processing.
4. Simultaneous incorporation of lignopolyol and solid lignin into the rigid polyurethane foam composition allows to significantly increase the dimensional stability and decrease the water absorption characteristics of the material in comparison with the case of the reference composition, and polyurethane foam compositions in which lignopolyol and solid lignin were incorporated separately.
5. The acetone-soluble fractions of kraft lignin-epichlorhydrine reaction products represent lignin based macromonomers with a narrow molecular mass distribution and the average epoxy functionality of 3.1–4.5 such increasing that of commercial bifunctional bisphenol A-based diglycydyl ethers Araldite LY 1564.
6. Partial substitution of commercial fossil derived epoxy resin Araldite LY 1564 in a two components amine cured epoxy composition with the glycidylated lignin fraction enhances the tensile modulus and thermal stability of cured epoxides due to the realization of the favorable effects of the high functionality of lignin macromonomers and the increase of the thermostable aromatics content in cured epoxides.

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## P-1

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# Evaluation of Ligno Boost™ softwood kraft lignin epoxidation as an approach for its application in cured epoxy resins

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## ABSTRACT

In this study, modification of LignoBoost™ softwood kraft lignin with epichlorhydrin in water-organic solvents media was realized. Lignin-based epoxy resins were obtained by two ways: acetone extraction of glycidylated lignin or glycidylation of the acetone soluble lignin fraction. The effect of glycidylation regimes on the yields of acetone soluble fractions, their functional composition and physical-chemical characteristics was investigated using wet chemistry methods, FTIR spectroscopy, size exclusion chromatography (SEC) and differential scanning calorimetry (DSC). The positive effect of the biphasic phase transfer catalytic system – KOH/quaternary ammonium salt – on glycidylation of both phenolic and aliphatic hydroxyl groups was testified, exemplified using a lignin-like model compound – 4-hydroxy-3-methoxylbenzyl alcohol (vanillyl alcohol). The partial substitution (up to 10%) of commercial epoxy resin on the basis of bisphenol A (Araldite® LY1564) by lignin-based epoxy resin significantly increased the viscosity of resin. Therefore, the possible practical application of lignin-containing epoxies as adhesive, mastic or crack filler instead of binder for fiber reinforced composites was considered. A tendency towards increasing Young's modulus of cured lignin-containing epoxies, compared with the case of the reference composition, was observed. The lignin chemically incorporated into the matrix of cured commercial epoxy resin acts as a charcoal formation promoter in high temperature treatment.

## 1. Introduction

Cured epoxy resins are thermosetting heat-stable polymers with high mechanical properties and chemical resistance (He et al., 2014). The coatings, adhesives and reinforced composites on the basis of epoxy resins are widely used in many industrial applications, including electrical engineering, electronics, automobile and air craft industries, etc. (Wanga et al., 2016; Katunina et al., 2017; Çakır et al., 2014; Murakami et al., 2016).

Commercial epoxy resins are currently produced mainly (almost 90%) from petroleum-derived chemicals: bisphenol A (BPA) and epichlorhydrin (ECH) (Abdul Khalil et al., 2011).

BPA is responsible for numerous favorable properties of the final material, but unfortunately, it exhibits an estrogenic activity and, therefore, is referred to as an environmental hormone that negatively influences the human health (Sasaki et al., 2013). BPA and its derivatives possess high potential as an endocrine disruptor. Exposure to BPA may induce harmful, reproductive, developmental and metabolic disorders (Fischnaller et al., 2016).

Besides, the depletion of fossil resources and the environmental problems induced by their processing and extensive utilization have encouraged the industry and science all over the world to seek for renewable resources for the production of bio-based polymerics, particularly epoxy resins (Ferdosian et al., 2016).

Recently, several researches have been reported on the synthesis of bio-based epoxy resins from various renewable resources such as vanillin (Fache et al., 2014), gallic acid and catechin (Aouf et al., 2013), isosorbide (Lukaszczyk et al., 2011), tannins (Aouf et al., 2014; Benyahya et al., 2014), vegetable oils (Shah and Ahmad, 2012) and lignins (Delmas et al., 2013; Hirose et al., 2012).

Nowadays, cellulose and other carbohydrates, derived from plant biomass, are successfully used in the paper industry and as a feedstock for bioethanol production. However, only 2% of the lignin obtained as by-products in pulp and fuel ethanol processing is used commercially (Li et al., 2012). The biorefinery conception assumes the most profitable usage of all components extracted from the lignocarbohydrate

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complex at its processing. Therefore, lignin utilization for the fabrication of value added products is a worldwide bio economic task.

Lignin in situ is a three-dimensional amorphous biopolymer formed by three major monolignols: *p*-coumaryl (P), coniferyl (C) and sinapyl (S) alcohols with different ratios, linked together by various types of ether and carbon−carbon bonds (Laurichesse and Avérous, 2014). The technical lignins extracted from plant biomass as by-products differ from native lignins; however, the aromatic structure of lignins and the presence of a significant amount of OH groups (phenolic, aliphatic and carboxylic) make technical lignins an attractive raw material for BPA substitution, capable of modification via the reaction of OH groups with epichlorohydrin.

The direct utilization of lignin for the synthesis of epoxy resins is challenging due to the large molecular weight and heterogeneity of lignins, their restricted solubility in common organic solvents, different electronic constraints and steric hindrance of the available OH groups. Overcoming these challenges, different approaches have been used, including the de-polymerization and chemical modification of lignin.

In recent decades, different lignin de-polymerization methods have been introduced. Base and acid catalyzed reactions at high temperatures and pressure were performed on a laboratory scale. The mechanical and thermal properties of cured epoxy resins on the basis of depolymerized kraft, hydrolysis and organosolv lignins were found to be inferior to those for reference commercial epoxy resins (Wang et al., 2013).

Another approach is demethylation of lignin and obtaining of lignin products with free phenolic groups in the 3 and 5 ring positions; these lignins could be used as a feedstock for lignin based hyperbranched epoxy production. However, at the moment, catalytic pathways do not exist, and the widely used reagents (alkyl halides) are harmful and undesirable for large scale production (Ferhan et al., 2013; Hu et al., 2014).

Phenolation, as another modification method for increasing the content of phenolic groups in lignin, has a potential for making more favorable conditions for lignin reaction with ECH. However, the release of formaldehyde to generate new reactive sites and cyclization via etherification of phenol with lignin side chain carbons was also detected, that diminished the advantages of this approach (Podschun et al., 2015).

Hofmann and Glasser prepared epoxy resins from hydroxyalkyl lignin (alkali extracted lignin from steam exploded yellow poplar) derivatives with varying degrees of alkoxylation. To obtain lignin derivatives, containing only high reactive primary OH groups, the consequent modification of lignin with propylene oxide and ethylene oxide was performed before glycidylation. The prepared epoxy prepolymers were cured into stiff thermosets having a high glass transition temperature (Hofmann and Glasser, 1993).

The complexity and labor expensive processing can be considered as the disadvantages of this modification from the viewpoint of its practical application.

It is known that lignin properties and its ability towards various chemical modifications depend strongly on the biomass origin and the technology of lignin isolation (Gosselink et al., 2010).

Different novel processes of lignin isolation in the framework of the biorefinery approach are currently under development, although only single of them are realized on a commercial scale. The LignoBoost concept developed by Innventia AB and Chalmers University (Sweden) is one of them (Tomani, 2010). LignoBoost lignin meets the requirements for a material pure enough to be used as a chemical feedstock for green chemicals and for quality fuel production.

The objectives of the present work were: (i) to provide the controlled covalent incorporation of the epoxy function in the LignoBoost™ softwood lignin structure via the glycidylation reaction, (ii) to investigate the tensile and thermal characteristics of cured lignin containing epoxy resins, (iii) to study the effect of quaternary ammonium salt as a phase transfer catalyst, combined with an alkali catalyst, on the glycidylation of both phenolic and aliphatic OH groups using vanillyl alcohol as a lignin-like model compound (LMC).

To obtain a lignin-based epoxy resin prospective for substitution of commercial BPA-based epoxy resin in amine cured composites, two pathways were used, i.e. extraction of glycidylated LignoBoost™ softwood lignin with acetone and glycidylation of the acetone soluble lignin fraction.

## 2. Experimental

### 2.1. Materials

LignoBoost™ softwood kraft lignin (KL), isolated from the original black liquor using the LignoBoost process, was kindly presented by Innventia AB.

Epichlorohydrin (ECH), acetone, dichloromethane, vanillyl alcohol, potassium hydroxide, dimethyl sulfoxide and sodium dihydrogen phosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$) were all of analytical grade and were sourced from Sigma Aldrich Company Ltd. and Lach-Ner Ltd. 2-Methoethanol was gas chromatographic grade from Fluka. Commercial BPA-based epoxy resin Araldite® LY1564 (epoxy equivalent weight, EEW = 170 g $eq^{-1}$), cured by the amine hardener Aradur®3486 (amine hydrogen equivalent weight, AHEW = 111 g $eq^{-1}$) containing cycloaliphatic polyamines: 5-amino-1,3,3-trimethyl isophoronediamine cyclohexanamine, cyclohexanemethanamine, 4,4′-methylenebis(2-methylcyclohexylamine) and polyoxy(methyl-1,2-ethanediyl), was sourced from Huntsman Chemical Company.

### 2.2. Klasson lignin content and functional characteristics of KL

Klasson lignin (96 ± 1%) was determined according to the TAPPI T222 Standard.

The content of total OH groups in KL was determined via acetylation of samples with acetic anhydride followed by potentiometric titration of free acetic acid in excess with 0.1 N NaOH in water. The content of phenolic and carboxylic OH groups in KL was determined by acid-base conductometric titration using an automatic titration device ABU901, coupled with a Conductometer CDM 210 and a titration manager TIM 900. The methoxyl groups ($OCH_3$) content was measured according to the Viebock-Schwappach method (Zakis, 1994). The functional composition of KL is shown in Table 1.

### 2.3. Extraction of non-modified KL and glycidylated lignin with acetone

The acetone soluble fraction of kraft lignin (KLAF) was isolated by double solid-liquid extraction of 10 g of KL with 100 mL of acetone in a round flask at room temperature. Each extraction step was done by vigorous stirring of the suspension for 60 min. The undissolved material was filtered off and resuspended for a second identical extraction. The acetone solutions of each extraction step were collected. After filtration, the acetone was distilled off in a rotary evaporator and the residue was oven dried in vacuum at 50 °C. Three replicate fractionations were made.

The acetone soluble fraction of lignin-based epoxy resin (GLAF) was isolated from glycidylated lignin (GL) by two times solid-liquid extraction with 100 mL of acetone in a round flask at room temperature.

**Table 1**
Functional groups of KL.

| Functional group | Content (mmol $g^{-1}$) |
|---|---|
| OH, total | 7.3 ± 0.3 |
| OH, phenolic | 1.4 ± 0.2 |
| COOH | 2.4 ± 0.3 |
| $OCH_3$ | 4.1 ± 0.1 |

The fractionation procedure was the same as for non-modified KL. GLAFs were used for further analysis by the FTIR spectroscopy, DSC and wet chemistry methods (functional analysis). The yield of the acetone soluble fraction was expressed in percentage from the dry weight of the non-extracted sample.

### 2.4. *KL and KLAF glycidylation*

The necessary amount of ECH (10–20 mol of ECH per each mole of lignin OH groups) was mixed with 5 g of KL or KLAF. In the case of using dimethylsulfoxide (DMSO) as a solvent, lignin had been previously dissolved in 30 mL of DMSO. The mixture was heated up to 65 °C and stirred up to complete KL dissolution. Then, a 30% solution of KOH in water (0.25–1.25 mol of KOH per each mole of lignin OH groups) was added dropwise. After that, the mixture was stored at mixing and heating during 2 h, and the next portion of KOH was added using the above mentioned ratio and mixed for the next 2 h, and then cooled (Table 1). After cooling, the reaction mixture was neutralized with $NaH_2PO_4 \cdot 2H_2O$ up to pH = 7.5–8.0 and precipitated in deionized cool water (T = 4–5 °C). The excess of ECH existed in the reaction mixture till the moment when the precipitation of lignin epoxy in cool water was done. After that the precipitate was filtrated, washed with warm water to remove the traces of ECH and oven dried at 50 °C. The schematic view of glycidylation is presented in Fig. 1.

### 2.5. *Glycidylation of LMC*

A biphasic transfer catalytic system, including ammonium salt – tetrabutylammonium bromide (TBAB) and KOH, was used. Vanillyl alcohol (0.033 mol), ECH (0.66 mol) and TBAB (0.008–0.033 mol) were placed in a round bottom flask and stirred for 2–6 h at 65 °C and 98 °C, respectively. After cooling, 0.132 mol of KOH (30% water solution) was added and the mixture was stirred for 8 h at 20–25 °C. Then, the mixture was neutralized with $NaH_2PO_4 \cdot 2H_2O$ and extracted twice with 100 mL of dichloromethane. Dichloromethane was dried under $Na_2SO_4$. The solvent was distilled in a rotary evaporator and oven dried in vacuum at 50 °C. The products obtained were analyzed by GC/MS. For comparison, the single KOH catalyzed glycidylation of vanillyl alcohol was performed. The reaction conditions for each of experiments are presented in Table 4.

### 2.6. *Characteristics of glycidylated products*

#### 2.6.1. *FTIR spectroscopy*

A Spectrum One (Perkin-Elmer) FTIR spectrometer was used to analyze the chemical structure of the KL, GL and GLAF by scanning from 500 to 4000 $cm^{-1}$; scan resolution and the number of scans were 4 $cm^{-1}$ and 64, respectively. The KBr technique was used.

#### 2.6.2. *UV spectroscopy*

Two weights (20 mg) of each lignin sample, including acetone soluble fractions of non-modified and glycidylated lignin were dissolved in 15 mL of 2-Metoxyethanol using two 25 mL flasks. 5 mL of 0.1 N NaOH and 5 mL of deionized water were added in first and second flask respectively. Both flasks were filled with 2-Metoxyethanol up to mark point. The difference UV spectrum was determined by measuring of absorbance of lignin alkali solution using Lambda 25 Perkin Elmer Instruments (Goldschmid, 1954).

#### 2.6.3. *Chemical analysis*

The EEW of lignin-based epoxies was measured by treatment of the sample with 0.2 N HCL in acetone, followed by the titration of the HCL excess by 0.1 N NaOH using a potentiometric titrator manager Radiometer analytical TIM 840 (GB/T 1677–2008).

#### 2.6.4. *SEC analysis of KL and its glycidylated derivatives*

Lignins were analyzed by SEC using a PL-GPC 110 apparatus (Polymer Laboratories, Shropshire, UK), equipped with a pre-column, 10 µm, Plgel and two 300 mm × 7.5 mm columns, 10 µm, Plgel MIXED D (Polymer Laboratories, Shropshire, UK) and a refraction index detector. The columns and the injection system were maintained at a temperature of 70 °C. The eluent flow (0.1 M LiCl in DMF) was 0.9 mL/min. The lignin solutions (1%) were prepared just before the analysis by dissolution in eluent solution (0.1 M LiCl in DMF). The column calibration was carried out using lignin model compounds (monomers, dimers and tetramers) and selected lignin samples (Mp = 950–3200 Da)

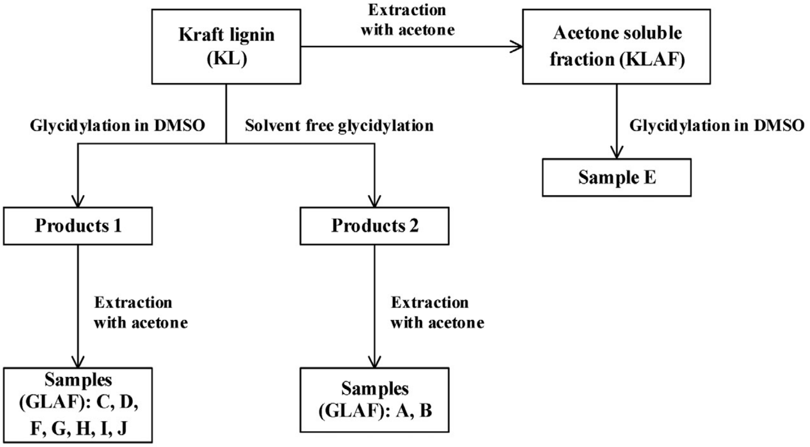

**Fig. 1.** Scheme of lignins glycidylation.

previously characterized by (electro spray ionization mass spectroscopy) ESI-MS.

### 2.6.5. *Thermal analysis*

The measurements of glass transition temperature (Tg) for non- and modified lignins were performed by a Metler ToledoStarDSC 823 instrument with a heating rate of 10 °C/min in a temperature range of 20–200 °C in a nitrogen atmosphere. Two scans were done. The second scan was used for calculation of Tg (the temperature at which specific heat capacity achieved a half of its change during the transition) (Affolte et al., 2001).

The thermal gravimetric analysis (TG/DTG) of cured epoxy resins was performed by a Metler Toledo Stare System TOA/ADTA 851e device in a nitrogen atmosphere between 20 °C and 650 °C at a heating rate of 10 °C/min. Each thermal analysis under study was performed in duplicate.

### 2.6.6. *GC/MS chromatography*

The GC/MS analysis of glycidylated LMC, dissolved in acetone, was done by a Shimadzu GC/MS-QP2010 device equipped with a capillary column Agilent, RTX-1701 (60 m × 0.25 mm × 0.2 µm film). FID and MS quadrupole detectors (detectable range: 15–370 *m/z*) were used. The temperature regimes were: injector – 270 °C, detector – 250 °C. The content of different compounds was expressed in percent from the total chromatogram area. Averaged data of two replicated measurements were presented.

### 2.6.7. *Curing of lignin-containing epoxy resins*

Lignin-containing epoxy resins were prepared by consequential substitution of 2.0%, 5.0% and 10% of commercial BPA-based Araldite® LY1564 epoxy resin with GLAF (EEW = 367.5 g eq$^{-1}$), followed by mixing the blends obtained with the Aradur® 3486 amine hardener at a constant equivalent ratio of 2:1, which agreed with the Araldite® LY1564 specification.

Then, the mixture was poured into a metal mold for two step curing: 12 h at 25 °C and 8 h at 80 °C. Six dog-bone specimens with a weight of ~8 g (per each) were obtained for the given composition.

The viscosities of GLAF – Araldite® LY1564 epoxy mixtures were determined by rotation viscosimetry using a HAAKE Viscotester 6L/R plus at 25 °C.

### 2.6.8. *Acetone extraction of cured resin*

Cured epoxies (~10 g) were crushed and extracted with acetone (200 mL) for 8 h in soxhlet. The solid residues were dried at 100 °C for 4 h.

The yield of sol fractions was shown in percentage from the weight of the non-extracted sample. Three replicates for each composition were made.

### 2.6.9. *Tensile characteristics of cured resins*

Tensile tests were performed according to the ASTM 638 plastics standard, using a Zwick/Roell 2.5 testing machine. A 250-kN dynamometer was used. Six dog-bone specimens were tested for each composition. Gage zone – 2 × 10 × 50 mm, crosshead rate – 2.0 mm/min. Stress and strain at break, and Young's modulus were calculated using Zwick/Roell software.

## 3. Results and discussion

### 3.1. *KL glycidylation*

The three primary classes of epoxies used for composite application are phenolic glycidyl ethers, aromatic glycidyl amines and cycloaliphatic epoxy resins (Boyle et al., 2001). Among them, the first commercial BPA-based epoxy resins remain the most widely used ones today. Within each class of epoxy resins, the structure of the glycidylated component, the type and content of the catalyst, and the excess of ECH in the reaction mixture will influence the key characteristics of epoxy resins: EEW, molecular weight (MW), physical state (liquid or solid), and Tg. Taking into account the above mentioned positions, the effect of the reaction media and the OH/KOH/ECH molar ratio on the yield of GLAF, their EEW, molecular mass distribution (MMD), average functionality, FTIR spectra and Tg were studied.

### 3.1.1. *Effect of reaction media*

Two different reaction media were used for KL glycidylation: ECH and ECH-DMSO (Fig. 1 and Table 2). In the first case, ECH acted as both a solvent and a reagent. In both cases, water alkali solution (30 wt%) was used to incorporate the alkali catalyst into the reaction media.

KL was found to be particularly soluble in ECH at elevated temperature, but when the alkali water solution was added into the reaction mixture, lignin solubility drastically decreased, and lignin lumps of different size were formed.

Therefore, an alternative method was used by the previous complete solubilization of lignin in alkali solution of water (30 wt.%), followed by its dropwise feeding into the bulb, containing an excess of ECH (Table 2, samples A and B). In this case, no lignin lump formation was observed. The yields of GL varied in the range 112–120% on dry weight of lignin. An incomplete solubility of unfractionated GL in commercial resin was observed. To obtain lignin derived epoxies, completely soluble in commercial epoxy resins, GLs were extracted with acetone, a widely used solvent for epoxy resins. The yield of the isolated acetone soluble fraction was about 80% from the weight of the GLs synthesized in ECH, and their EEW were in a range of 780–1075 g eq$^{-1}$ (Table 2, samples A and B).

A significantly higher content of epoxy groups (EEW = 330–368 g eq$^{-1}$) in GLAF was determined in the products synthesized in the presence of DMSO (Table 2, samples C and D). However, the yield of the acetone soluble fraction was about twice lower in comparison with that for the GLAF synthesized in ECH (Table 2, samples A and B). The highest content of the epoxy groups (EEW = 300 g eq$^{-1}$) was achieved for the glycidylated lignin fraction, which had been previously isolated from the initial KL by acetone extraction (yield = 65 ± 2%). These products were also completely soluble in acetone. The rather low yields of the GLAF isolated from the products obtained in ECH-DMSO media can be probably explained by the reaction of the epoxy groups in GL with the unmodified aliphatic OH groups remaining in the lignin macromolecule (Fig. 2). As a result, partial crosslinking of lignin-based epoxies took place and their solubility in acetone decreased. At the same time, the acetone soluble non-crosslinking fraction of GL, synthesized in ECL-DMSO media, was enriched with oxirane rings. In contrast, obviously, the low conversion of OH groups into glycidyl ethers arms in lignin modified in ECH media is not favorable for self-condensation performance. The use of the acetone soluble fraction of KL instead of the initial KL allowed avoiding self-condensation, and epoxy lignin, completely soluble in acetone, with

**Table 2**
Effect of the reaction media type and the molar ratio of reagents on the yield and EEW of GLAF.

| Sample | Reaction conditions[a] | | Yield (%) | EEW (g eq$^{-1}$) |
|---|---|---|---|---|
| | Organic media | OH/KOH/ECH (molar ratio) | | |
| A | ECH | 1/1.2/10 | 80.4 ± 1.8 | 1075 ± 135 |
| B | ECH | 1/2/10 | 81.1 ± 1.5 | 780 ± 71 |
| C | DMSO-ECH | 1/2/10 | 44.3 ± 1.3 | 330 ± 13 |
| D | DMSO-ECH | 1/2/20 | 36.7 ± 1.4 | 368 ± 9 |
| E[b] | DMSO-ECH | 1/2/20 | 100.0 ± 0.0[c] | 300 ± 5 |

[a] T = 65 °C, t = 4 h.
[b] The acetone soluble fraction of KL was used for glycidylation.
[c] The glycidylated product was fully soluble in acetone.

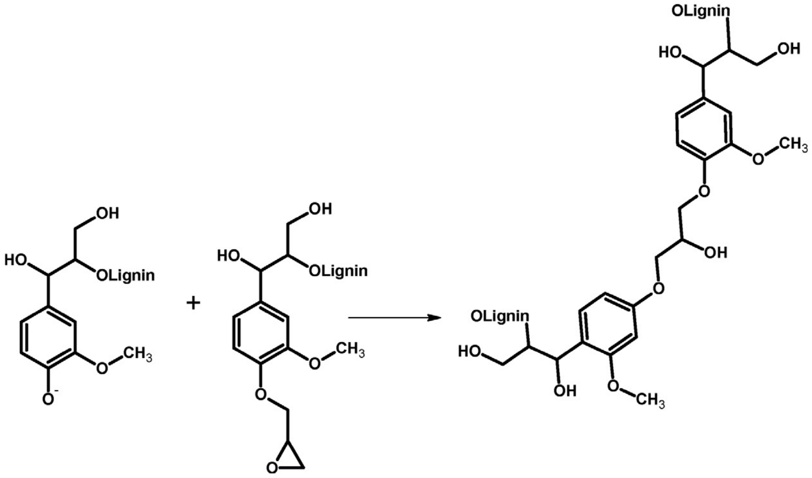

**Fig. 2.** Schematic view of the self-condensation of lignin-based epoxies.

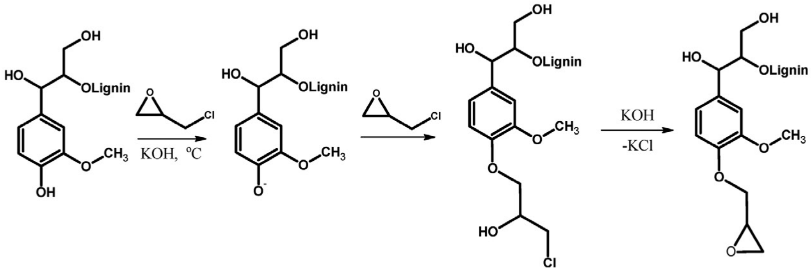

**Fig. 3.** Schematic view of OH phenolic glycidylation.

**Table 3**
Effect of the KOH content on the yield of GLAF and their EEW.

| Sample | Reaction conditions[a] | Yield (%) | EEW (g $eq^{-1}$) |
|---|---|---|---|
| | OH/KOH/ECH molar ratio | | |
| F | 1/0.5/10 | 44.2 ± 1.1 | 439 ± 13 |
| G | 1/0.75/10 | 43.3 ± 1.3 | 398 ± 11 |
| H | 1/1/10 | 39.5 ± 0.9 | 380 ± 10 |
| I | 1/1.5/10 | 41.2 ± 1.0 | 339 ± 13 |
| J | 1/2.5/10 | 46.3 ± 1.2 | 309 ± 12 |

[a] T = 65 °C, T = 4 h, organic media: ECH-DMSO.

low EEW, was obtained. The acetone soluble fractions isolated from different GL were completely soluble at elevated (80 °C) temperature in the commercial epoxy resin Araldite® LY1564 independently of the glycidylation regimes.

### *3.1.2. Effect of catalysts*

Two major processes take place under the effect of the alkaline catalyst of the glycidylation reaction (Nieh and Glasser, 1989). One of them is the ionization of hydroxyl groups, leading to the nucleophilic attack of the anion on the carbon of the oxirane ring, and its opening and chloroglyceryl ether formation (Fig. 3). This is followed by dechlorohydrogenation and oxirane ring formation (Fig. 3). In this reaction, KOH is consumed and additional KOH input is necessary to compensate for this consumption.

The phenolic groups of lignin, in comparison with aliphatic and carboxylic OH groups, are the most accessible ones for the glycidylation in these conditions, because a more suitable balance between the acidity and nucleophilicity of phenolates is achieved (Wu and Glasser, 1984; Alelio Gaetano, 1975). The glycidylation of both phenolic and non-phenolic OH groups in lignin has to increase the epoxy groups' content in the product. It is shown that the increase of the alkali content in the reaction mixture leads to some decrease of the EEW of products (Table 3). We can assume that the portion of glycidylated non-phenolic OH groups in lignin is increased with increasing alkali content.

**Table 4**
Effect of the biphasic phase transfer catalysis system on the content of glycidyl (2) and diglycidyl (3) ethers of LMC in products of the glycidylation reaction.

| No. | Reaction conditions | | | | Content of products[a] (%) | | |
|---|---|---|---|---|---|---|---|
| | T (°C) | t (h) | TBAB/LMC (molar ratio) | LMC/KOH/EC (molar ratio) | (2) | (3) | Side products |
| 1 | 65 | 4 | 0 | 1/4/20 | 69.3 | 2.6 | 28.1 |
| 2 | 65 | 4 | 0.25 | 1/4/20 | 57.2 | 18.6 | 24.2 |
| 3 | 65 | 6 | 0.25 | 1/4/20 | 58.8 | 20.1 | 21.1 |
| 4 | 98 | 4 | 0.25 | 1/4/20 | 48.9 | 22.4 | 28.7 |
| 5 | 98 | 6 | 0.25 | 1/4/20 | 16.0 | 44.0 | 40.0 |
| 6 | 98 | 2 | 1.0 | 1/4/20 | 11.6 | 55.0 | 33.4 |
| 7 | 98 | 4 | 1.0 | 1/4/20 | 13.5 | 51.8 | 34.7 |
| 8 | 98 | 6 | 1.0 | 1/4/20 | 14.3 | 48.4 | 33.4 |

[a] From the total area of the chromatogram.

## 3.2. Structural characterization of lignin-based epoxies by FTIR and UV spectroscopies, SEC and DSC

### 3.2.1. FTIR and UV spectroscopy

As an example, the FTIR spectrum of the acetone soluble fractions of KL and its glycidylated derivative (Fig. 4) confirms that glycidylation of lignin was realized, because new absorbance bands of the oxirane ring (3060, 750, 850, 910 cm$^{-1}$) appeared in the spectra of copolymers. Besides, the aliphatic groups (absorbance at 2975–2900 cm$^{-1}$) and ethers bonds (absorbance at 1030 cm$^{-1}$) were elevated, but the band of OH groups (absorbance at 3480 cm$^{-1}$) and carbonyl moieties (absorbance at 1710 cm$^{-1}$) decreased in comparison with the case of the acetone soluble fraction of KL. The disappearance of the absorbance band at 1370 cm$^{-1}$ also testified that the successful glycidylation of phenolic OH took place (Malutan et al., 2008; El Mansouri et al., 2011). The disappearance of phenolic groups in glycidylated KL due to their etherification was confirmed also by differential UV spectroscopy. The method is based on the bathachrome shift of the characteristic maximum of the lignin UV spectra at 280 nm due to phenolic groups' ionization in alkali media and is widely used in the analytical chemistry of lignin (Goldschmid, 1954; Zakis, 1994). As a result of ionization, the difference in the UV spectra of non-modified lignin has two distinguished absorption maxima at 300 and 370 nm (Fig. 5). This clear effect observed for non-modified lignin was not observed for glycidylated lignin samples due to the complete disappearance of phenolic groups in them, which coincides with FTIR data.

At the same time, the presence of significant absorbance intensity at around 3500 cm$^{-1}$ confirmed that a portion of non-phenolic OH groups were not converted for the reason discussed above (Fig. 4). Besides, we can assume that, at a low catalyst content, the dechlorohydrogenation and oxirane ring formation did not proceed completely although the formation of chlorglycerol ethers took place (Fig. 3).

The FTIR spectra show that the increase of the KOH/OH molar ratio at a given ECH content decreased the content of non-converted OH groups in lignin, which agrees with the data presented in Table 3 (Fig. 4b). Nevertheless, a lot of thenon-phenolic OH groups of KL remained free. It means that lignin's potential as an aromatic OH enriched renewable feedstock for obtaining high branched epoxy resins was not fully realized. The presence of significant absorption of O—H stretching

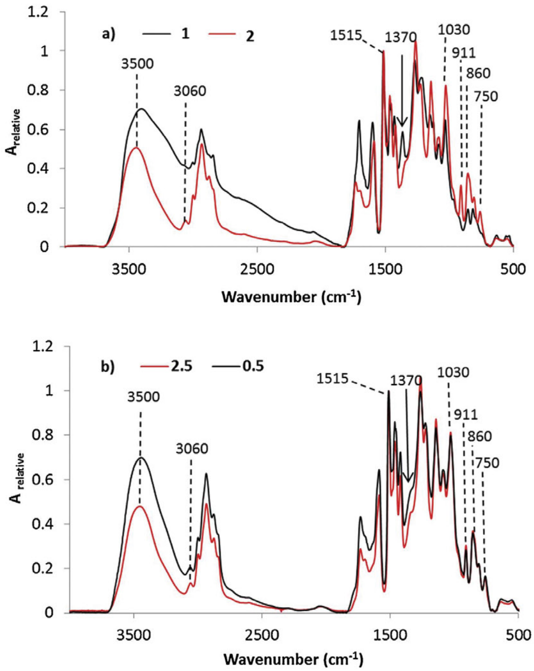

**Fig. 4.** Normalized (1515 cm$^{-1}$) FTIR spectra: a) the acetone soluble fraction of non-modified KL (1) and its glycidylated derivative (2); b) GLAF, obtained at different (2.5; 0.5) KOH/OH molar ratios.

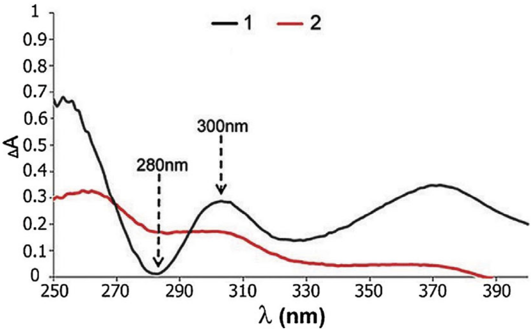

**Fig. 5.** Difference UV spectra of the acetone soluble fraction of non-modified KL (1) and its glycidylated derivative (2).

at 3400–3500 $cm^{-1}$ in FTIR spectra of glycidylated steam explosion lignin was reported also by Asada et al. (2015).

### 3.2.2. SEC analysis

The SEC data testified a well-formed decrease of MW and an increase of the uniformity of the acetone soluble lignin fraction in comparison with the case of the initial KL (Table 5). A marked increase of MW and some increase of polydispersity in comparison with KLAF was observed for all lignin epoxies under study, which testified the covalent incorporation of ECH into the lignin macromolecule. The calculated average epoxy functionalities for lignin derived epoxies varied in the range of 3.1–4.5. Therefore, an increase in the crosslinking density of cured lignin epoxies in comparison with that of cured bifunctional BPA derived commercial epoxy resins can be proposed, with appropriate influence on the mechanical properties of composites. The correlation of MMD and EEW data for lignin epoxies was not observed, because not the whole glycidylated KL but only its acetone soluble fractions differing by yields were analyzed.

### 3.2.3. DSC of glycidylated lignins

The $T_g$ of polymers depends on the heat mobility of the main polymeric chains and therefore is a physicochemical parameter, reflecting the structural changes in the polymeric matrix (Boyle et al., 2001).

The $T_g$ of acetone soluble fractions of all GL samples under study is lower compared to the unmodified acetone soluble fraction of KL, testifying the modification of the lignin matrix by ECH (Fig. 6). Firstly, this can be explained by the weakening of the hydrogen bond network due to the disappearance of phenolic OH. Besides, the incorporation of aliphatic glycidyl ethers chains into the lignin aromatic structure promotes the free molecular motion in modified lignin.

**Table 5**
MMD of non-modified and modified lignins, and average functionality of glycidylated derivatives.

| Sample | Mw (g $mol^{-1}$) | Mn (g $mol^{-1}$) | Mw $Mn^{-1}$ | Average epoxy functionality[a] |
|---|---|---|---|---|
| KL | 2840 | 1680 | 1.7 | /-/ |
| KLAF | 1510 | 1160 | 1.3 | /-/ |
| E | 1840 | 1295 | 1.4 | 4.3 |
| F | 1965 | 1370 | 1.4 | 3.1 |
| G | 2135 | 1480 | 1.4 | 3.7 |
| H | 1920 | 1380 | 1.4 | 3.8 |
| I | 1940 | 1400 | 1.4 | 4.1 |
| J | 1960 | 1370 | 1.4 | 4.5 |

[a] Mn $EEW^{-1}$.

The decrease of the $T_g$ of GLAF with increasing KOH/OH ratio is observed, which confirms the FTIR data and testifies that more complete glycidylation of lignin with increasing KOH content takes place (Table 3, Fig. 4). For example, the increase of the KOH/OH molar ratio from 0.5 (sample F) up to 2.5 (sample J) leads to the decrease of $T_g$ for lignin epoxies from 84 °C to 74 °C (Fig. 6).

### 3.3. Glycidylation of vanillyl alcohol in the presence of biphasic catalyst

To promote the ionization of not only phenolic but also aliphatic OH that are less acidic, the biphasic phase transfer catalytic system, including quaternary ammonium salt (TBAB) and alkali (KOH), was tested. Vanillyl alcohol, containing both aliphatic and phenolic groups, was used as LMC (Fig. 7). It was shown that the content of diglycidyl ethers of LMC in reaction products was only 2.6% when single KOH was used as a catalyst (Table 4). This testified that predominantly phenolic OH groups were modified in this case confirming the results of alkali catalyzed KL glycidylation. The content of diglycidylated ethers in reaction products was increased significantly (up to 55%) when TBAB in combination with KOH was used. The increase of the TBAB content and the reaction temperature were favorable factors, promoting the glycidylation of both phenolic and aliphatic OH groups. The results obtained confirmed the data reported in (Fache et al., 2014). Thus, the biphasic catalyst phase transfer catalytic system, including TBAB and alkali KOH, can be a prospective catalytic system for KL glycidylation, including its oxypropylated derivatives in which phenolic and acidic groups were transformed into aliphatic ones with similar electronic constrains. When vanillic alcohol was used as a model compound, the main products of the reaction were mono-and di-glycidyl ethers of vanillic alcohol, while significant amounts of side products were also indentified by GC/MS. Most of side products consisted of epichlorohydrin transformation products (1,3-dichloropropanol-2, glycerol, glycerol derivatives, diepoxyglycidyl ether and other epoxy groups containing ethers). However, in some cases, minor amounts of dimerized glycidilated vanillic alcohol derivatives were also observed. With increasing reaction temperature from 65 °C to 98 °C, the total yield of side products increased from 21 to 28% to 30–40% (Table 4). Probably, the side reactions of lignin modification with epichlorohydrin in the presence of alkali also occurred. Taking into account the results of vanillic acohol glycidylation, we can assume that the major portion of side products, due to their polarity, remains in the decantated ECH-water solution. The lignin washing with warm water will remove the epichlorohydrin derived side products absorbed by glycidylated lignin. Therefore, only traces of epichlorohydrin derived side products in glycidylated lignin could occur.

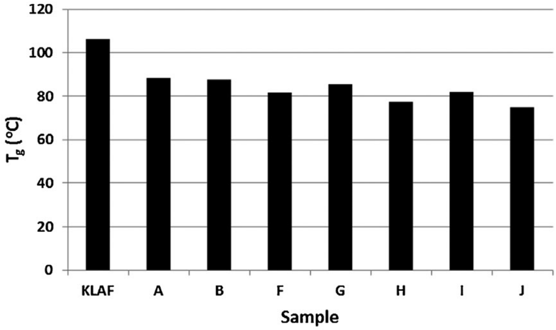

**Fig. 6.** The $T_g$ of the acetone soluble fractions of kraft lignin (KLAF), and its glycidylated derivatives synthesized in different conditions. (The abbreviations of samples are the same as in Tables 2 and 3).

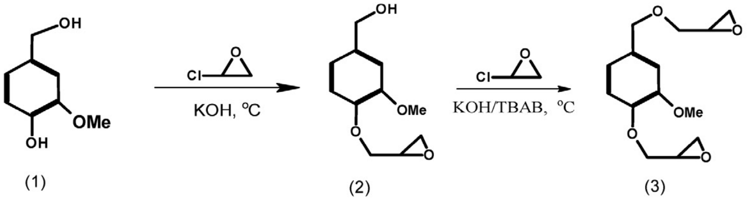

**Fig. 7.** Schematic view of glycidyl (2) and diglycidyl (3) ethers formation from vanillyl alcohol (1).

### 3.4. Effect of lignin epoxies on the characteristics of bisphenol a – based commercial epoxy resin

The acetone soluble fraction of glycidylated KL (Table 2, sample D), with EEW equal to 368 g $eq^{-1}$, was used for partial substitution of commercial epoxy resin (Araldite® LY1564).

It was shown that at 80 °C and the substitution level up to 10%, lignin epoxy was completely solubilized in commercial resin. After cooling, the lignin was not precipitated and uniform Newtonian fluids were obtained. At the same time, a drastic increase in the dynamic viscosity of the mixed resins was observed (Fig. 8).

For example, at 10% of the substitution level, the viscosity of the resin obtained exceeded threefold the viscosity of the reference lignin free epoxy resin. This can be explained by the branched/cross-linked and high molecular structure of the lignin core in lignin epoxy vs the low molecular (340 g $mol^{-1}$) and linear structure of the diglycidyl ethers of bisphenol A. Hence, the incorporation of lignin epoxy into BPA-based resin leads to the increase of the intrinsic friction between

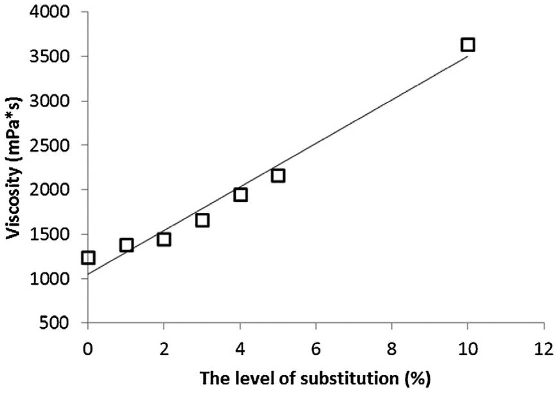

**Fig. 8.** Effect of the level substitution of commercial epoxy resin Araldite® LY1564 by lignin epoxy on the dynamic viscosity of the resulting mix at 25 °C.

**Table 6**
Tensile properties of cured commercial epoxy resins vs the level of substitution of Araldite® LY1564 by GLAF.

| Level of substitution (%) | Stress at break (MPa) | Young's modulus (GPa) | Strain at break (%) |
|---|---|---|---|
| Reference | 63.1 ± 2.7 | 2.91 ± 0.16 | 4.9 ± 0.3 |
| 2 | 61.3 ± 1.8 | 3.13 ± 0.19 | 4.8 ± 0.9 |
| 5 | 67.1 ± 2.2 | 3.09 ± 0.21 | 5.5 ± 0.7 |
| 10 | 66.2 ± 1.3 | 3.36 ± 0.22 | 4.9 ± 0.5 |

**Table 7**
Effect of the partial substitution of Araldite® LY1564 by lignin epoxy on the thermo-degradation parameters of cured resins.

| Level of substitution (%) | $T_{5\%}$ (°C) | $\frac{dm}{dt}$ (mg min − 1) | $T_{max}$ (°C) | Char residue at 500 °C (%) |
|---|---|---|---|---|
| Reference | 338 | 1.6 | 366 | 10.5 |
| 2 | 325 | 1.4 | 368 | 13.7 |
| 5 | 320 | 1.4 | 363 | 17.6 |
| 10 | 303 | 1.2 | 365 | 22.6 |

$T_{5\%}$. – the temperature when 5% of weight loss was achieved.
$\frac{dm}{dt}$ – the maximum degradation rate.
$T_{max}$ – the temperature when the maximum degradation rate was achieved.

the fluids' molecules despite the same aromatic origin of both – lignin and BPA. It can be assumed that the increase of the content of flexible oxirane-bearing polyether arms in modified lignin because of the complete glycidylation of all OH moieties in the lignin macromolecule will improve the compatibility of lignin-based epoxies with commercial epoxies.

The amounts of the non-cross-linked fraction extracted by acetone from cured reference and lignin-containing resins was similar, namely, 0.1–0.2%. This demonstrated that epoxy lignin had completely reacted with the amine hardener, being incorporated in the common epoxy network.

The analysis of the tensile characteristics of cured reference and lignin-containing resins showed similar strength and strain parameters (Table 6). A linear tendency towards increasing Young's modulus with increasing lignin epoxy content in epoxy blends was observed.

Thermal resistance is one of the advantages of cured epoxy resin. The results revealed that the lignin-containing cured resins, in comparison with the reference resins, started to degrade at a slightly lower temperature (Fig. 9). This can be explained by the intra-chain dehydration (so-called primary condensation) of the lignin structure at a temperature lower than 300 °C because of the presence of free OH groups (Arshanitsa et al., 2016).

The results of thermogravimetric analysis are presented in Table 7. The temperature at which a 5% weight loss is achieved is decreased from 338 °C (reference resin) to 303–325 °C for lignin-containing resins. At higher temperatures (330–400 °C), the favorable effects of the increase in crosslink density as well as the increase in the content of thermostable aromatics and condensed units in the molecular matrix of lignin-containing epoxides were realized.

As a result, the maximum degradation rate value achieved at a similar temperature of about 365 °C is decreased but the char residue is significantly increased with increasing lignin epoxy content. This testifies that modified lignin, present in the epoxy polymer, acts as a charcoal formation promoter, influencing the pyrolysis mechanism of cured epoxides. In the presence of char, the heat transfers from the flame to the condensed phase and the emission of gases, hazardous for human health, are decreased (Morgan and Gilman, 2013). The positive correlation between char yield and flame retardant properties of different polymers was established (Chattopadhyay and Webster, 2009). Above mentioned allow to propose that the incorporation of lignin epoxies into the compositions of traditional epoxy resins could be a valuable pathway for increasing the fire retardancy of the epoxide material. The performance of cone calorimeter tests for cured lignin containing epoxies is planned.

Taking into account the above results, we can conclude that lignin epoxies, being added into the BPA-based commercial resin, could find practical application as a constituent for adhesive, mastic, crack filler, etc. At the same time, the lignin epoxies obtained are not convenient for technologies where a low viscosity of the composition is needed, for example, injecting of an epoxy resin composition into a reinforcing fiber substrate.

It can be assumed that the increase of the content of flexible oxirane-bearing polyether arms in LignooBoost™ lignin and avoiding the self-condensation because of the complete glycidylation of OH moieties in the lignin macromolecule will improve the compatibility of lignin-based epoxies with commercial epoxies. This will prevent the drastic

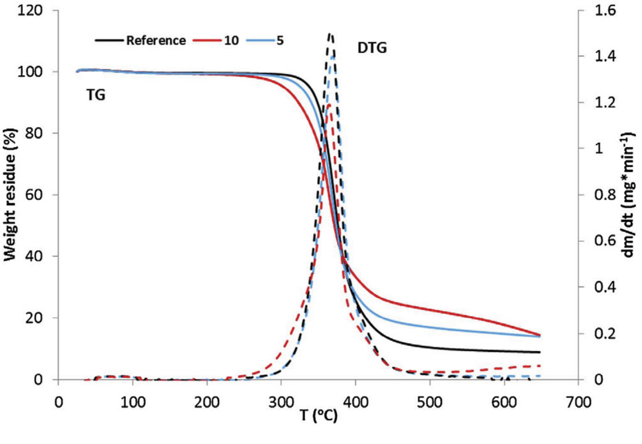

**Fig. 9.** TG/DTG curves of amine cured epoxy resins: referred and partly (5% and 10%) substituted by lignin epoxy.

increasing of the viscosity of non-cured epoxy blends and will increase the level of substitution of commercial epoxies by lignin-based epoxies. In this context, one batch high pressure oxypropylation (Arshanitsa et al., 2015) of LignooBoost ™ lignin, followed by its glycidylation using a biphasic phase transfer catalysis system – KOH/quaternary ammonium, could be considered as a suitable approach for obtaining liquid lignin-based epoxies in which the complete substitution of OH groups by glycidyl ethers arms takes place. Such a modification is under study.

## 4. Conclusions

Unmodified LignooBoost™ softwood kraft lignin was glycidylated in single epichlorhydrin and epichlorhydrin – dimethyl sulfoxide media in the presence of KOH as a catalyst. The lignin epoxies isolated from glycidylated KL by its acetone extraction or the glycidylated acetone soluble fraction of KL were soluble in commercial bisphenol A – based epoxy resin. The increase of the alkali catalyst content and the use of dimethyl sulfoxide led to the increase of the epoxy groups' content in lignin epoxies. However, in any case, in the presence of a single alkali catalyst, the glycidylation of phenolic OH predominantly took place, while the other OH functions were not modified completely. Application of the biphasic phase transfer catalysis system – KOH/quaternary ammonium salt – promoted the glycidylation of aliphatic OH groups, which was testified using vanillyl alcohol as a model lignin-like compound. The lignin epoxies were characterized by narrow MMD and epoxy functionalities varying in the range of 3.1–4.5. As a result, the partial substitution (up to 10%) of commercial resin by lignin epoxy revealed the increasing of Young's modulus for amine cured resins. The lignin-containing cured epoxies demonstrated also a higher charcoal yield and a lower degradation rate at the high temperature impact, suggesting the lignin epoxies' potential for fabrication of flame resistant epoxides. A drastic increase in the viscosity of commercial epoxy resin due to the incorporation of lignin epoxies therein was observed, which restricted the extent of commercial epoxy resin substitution. Therefore, the obtained KL-based epoxies could be suitable in compositions of adhesive and crack filler, but are not convenient for technologies where the low viscosity of a composition is needed. The batch oxypropylation of KL, followed by the glycidylation of the products obtained employing the two-component catalytic system – KOH/quaternary ammonium salt – was assumed as a suitable approach for obtaining liquid KL-based epoxies and more effective use of LignooBoost ™ lignin as a precursor of epoxy resins.

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# Exploring the application potential of incompletely soluble organosolv lignin as a macromonomer for polyurethane synthesis

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## ABSTRACT

A new type of organosolv wheat straw lignin, so-called Biolignin™, was studied. It is obtained according to the biomass processing in water diluted organic acid media and is not completely soluble in conventional organic solvents traditionally applied for polyurethanes (PU) synthesis. The fractionation of the lignin by sequential extraction with dichloromethane, methanol and a mixture of both solvents was performed. The total yield of the separated soluble fractions was 40%. The separated fractions were characterized, and preliminary kinetic investigations were used to reveal the reactivity of fractions obtained towards 4,4′-methylene diphenylene diisocyanate (MDI) in dioxane media. PU films were synthesized by casting the three component systems: lignin fraction – polyethylene glycol with a molecular weight of 400 g $mol^{-1}$ – polymeric methyl diisocyanate prepolymerized in tetrahydrofurane solution at a constant NCO/OH ratio of 1.05. The content of lignin in PU compositions was varied in a range of 5–40%. The PU films were characterized in terms of crosslink density, tensile properties, glass transition temperature and thermal stability. The obtained results show that the isolated fractions of Biolignin™ act as a crosslinking macromonomer in the PU network. Depending on the lignin fraction type and its content in the composition, the tensile properties of PU films with a high elastic state at room temperature or the tensile properties of glassy cross-linked films were obtained. Evidence for the activity of lignin fractions as antioxidants of PU compositions and charcoal formation promoters in the case of the high temperature treatment of PU in air was obtained.

## 1. Introduction

Lignin is a unique polyphenolic renewable raw material available as a by-product of the existing chemical processing of plant biomass that has an excellent capability for producing a value-added polymeric material, characterized by competitive mechanical and thermal properties, and chemical stability (Belgacem and Gandini, 2008; Hu, 2002). Nowadays, the annual industrial output of lignin is about 50 million tons, which are used primarily for energy production by combustion. Only a small amount (1–2%) is used for manufacture of a wide range of value-added products (Lora and Glasser, 2002). However, this approach disagrees with the main principle of the modern biorefinery conception – achievement of the most profitable usage of all components of the lignocellulosic complex.

All known technical lignins, irrespective of how they have been obtained and from what plant sources, are amorphous heterogenic aromatic polymers with glass transition in a range of 70–170 °C, containing a significant amount of functional groups and reactive sites, namely, phenolic, aliphatic, carboxylic OH groups, substituted aromatic sites and C=C bonds (Belgacem and Gandini, 2008). These chemical feasibilities allow considering lignin as a prospective building block for different polymeric compositions: phenol- and urea-formaldehyde resins, polyester resins, epoxy resins, polyurethanes etc. (Hu, 2002). In the broad spectrum of modern industrially produced polymers, PU are considered as a most versatile materials (Ionescu, 2005). Free aliphatic and phenolic OH groups are the most important functional groups opening up considerable opportunities for lignins' application as an aromatic polyol building block, capable of forming a number of covalent bonds with isocyanates in PU compositions. Although different technical lignins (kraft lignin, lignosulfonates, some organosolv lignins) have been successfully tested for obtaining PU materials on a laboratory scale (Belgacem and Gandini, 2008; Hu, 2002; Hatakeyama et al., 2004), lignin-containing PU materials have not yet been manufactured on an industrial scale. The main difficulties in working out market-oriented lignin-containing polymeric composite materials are as follows: heterogeneity of technical lignins,

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variation in the functional groups' content, their types and proportion in lignins, as well as the difference in molecular mass distribution (MMD) of the lignin fragments formed during the biomass processing, the structure of lignin-forming phenyl propane units, links between them, the solubility in organic solvents that varies in a wide range and restricted accessibility of reactive sites towards isocyanate due to their steric hindrance (Gosselink et al., 2010; Kelley et al., 1989; Lora and Glasser, 2002; Mahmood et al., 2016).

Various pretreatments are used to decrease the above-mentioned disadvantages of lignin and to enhance the efficiency of technical lignins' application as a macromonomer capable of taking part in the formation of polymeric structures that have to improve the target properties of polymeric materials. These methods are based on the depolymerization of the lignin matrix via the cleavage of ether linkages into more uniform oligomeric or reduced molecular weight products with enhanced accessibility of functional groups in reactions with isocyanates (Mahmood et al., 2016). Acid -, base- and metal-catalyzed as well as ionic liquids-assisted, and sub- and supercritical fluids-assisted depolymerizations of lignins have been investigated (Wang et al., 2013). The produced depolymerized lignins were successfully utilized as bio-polyols replacing up to 50% of commercial polyols for the preparation of rigid PU foams (Mahmood et al., 2016). Oxypropylation of technical lignins at ambient pressure in the presence of alkali catalysts is recognized as another approach to overcome the molecular and functional heterogeneity of lignins, and obtain lignopolyols for the formation of rigid PU foams that meet the requirements of commercial standards (Arshanitsa et al., 2015; Cateto et al., 2009; Li and Ragauskas, 2012). In this case, the degradation of the lignin core is accompanied by the attachment of oxypropyl units towards the OH groups of lignins, thus converting the acidic groups (phenolic, carboxylic) into aliphatic ones with higher reactivity towards isocyanate. Undoubtedly, the above mentioned processes are challenging due to the severity of reaction conditions (220–300 °C, and a pressure of 5–30 bar) (Mahmood et al., 2016; Arshanitsa et al., 2015). The fractionation of technical lignins by organic solvents extraction at atmospheric pressure and room or refluxing temperature could be a prospective opportunity, increasing the efficiency of lignin application as a macromonomer for PU materials' fabrication. Fractionation of different unmodified commercial kraft and organosolv (ethanol – water) lignins by diethyl ether, *n*-propanol, methanol and the dichloromethane/methanol mix allows obtaining of lignin samples with a lower molecular weight (MW), more uniform by MMD, completely soluble in organic solvents commonly used in PU chemistry and suitable to fulfill successfully the role of macromonomers in PU material synthesis (Gosselink et al., 2010; Kelley et al., 1989; Li and McDonald, 2014; Morck et al., 1986; Vanderlaan and Thring, 1998; Yoshida et al., 1987a). Fractionation is not an exclusive technique for obtaining a more uniform raw material for further processing but is used as an approach to elucidate the mechanism of the process, to gain new knowledge about the integral impact of different lignin characteristics on the properties of PU materials and, finally, to reveal a new application potential of non-modified lignins. Such an approach permits obtaining of PU elastomers with predictable thermal and mechanical properties, which can be varied in a wide range depending on the lignin fractions' MW, their content in PU and the type of the used soft segment (Yoshida et al., 1987b; Yoshida et al., 1990; Reiman et al., 1990). PU composites that have a potential for application in the field of high performance coatings and adhesives are obtained also on the basis of the methyltetrahydrofuran soluble fraction of kraft lignin Indulin AT and toluene diisocyanate-trimethylolpropane adduct (Griffini et al., 2015).

Today, the production of bioethanol as an alternative to fossil gasoline can be performed by acid and enzymatic hydrolysis of various pretreated plant biomasses. Therefore, various processes are currently under development. This leads to a new type of technical lignins, the properties of which are strongly dependent on the biomass origin and the pretreatment technology (Zhao et al., 2009). This is a challenge for the synthesis of novel lignin-containing polyols for application in different PU materials.

In this work, the object of investigation was a novel organosolv lignin of wheat straw, Biolignin$^{TM}$, obtained as a product of the technology developed by Compagnie Industrielle de la Matiere Vegetale (CIMV, France). This technology allows separating all the three main plant polymeric biomass components – cellulose, hemicellulose and lignin – without their significant degradation using a mix of water diluted acetic and formic acids and represents the first biomass refinery technology (Delmas et al., 2011).

The objective of the present study was to evaluate the suitability of application of the novel wheat straw lignin, Biolignin$^{TM}$, as a hydroxyl-containing macromonomer for PU films' synthesis. The poor solubility in organic media and the high polydispersity eliminate the use of Biolignin$^{TM}$ as a macromonomer in a lignopolyurethane (LPU) system. To avoid this disadvantage, Biolignin$^{TM}$ was fractionated by sequential extraction using solvents of different polarity and their mixture. Each fraction was characterized in terms of the composition, MMD, functionality and reactivity with MDI. The effects of the incorporation of each fraction on the structure, and tensile and thermal characteristics of model LPU systems on the basis of polyether diol and aromatic polyisocyanate were studied and discussed. The valorization of the fractionated novel lignin as an antioxidant and a charcoal formation promoter in PU systems was discussed.

## 2. Materials and methods

### 2.1. Lignin sample

Biolignin$^{TM}$ (further "lignin") was extracted from wheat straw using a mixture of acetic acid/formic acid/water at the CIMV pilot plant (Pomacle, France). Klason lignin (89.0 ± 1.0%) was determined according to TAPPI T222 standard. Ash content (1.0 ± 0.1%) was measured according to LVS EN 14775, 2010. Before fractionation, lignin was washed with deionized water up to pH 4.4, then air dried up to a moisture content of 5% and ground using a disintegrator DESI-11 (DESINTEGRAATOR Tootmise OU). The particle size of the ground lignin was $\leq$0.1 mm.

The chemicals used for analyses, including solvents, were of analytical grade (Sigma–Aldrich, Karl Rotch GmbH) with the exception of dioxane and tetrahydrofuran, which were extra-dry (Fluka).

### 2.2. Solvent fractionation

Lignin was fractionated by successive extraction with a dichloromethane, methanol, and methanol/dichloromethane mixture (7:3 v/v), differing by their polarity. The fractions obtained were abbreviated as DCM-F, MET-F and MET/DCM-F, respectively. The choice of solvents was conditioned by their proven efficiency for fractionation by molar mass and purification of different wood and grass lignins, targeted for application in binder compositions (Gosselink et al., 2010). Lignin (20 g) was suspended in 100 mL of the respective solvent and continuously stirred using a laboratory shaker at room temperature for 6 h. The undissolved material was filtered off and resuspended for a second identical extraction. The fractions from both steps were combined. The collected dissolved material was filtered over a glass filter (pore size 40–100 μm) and vacuum dried. The yields of the fractions were shown in percentage on oven dry ash-free non-extracted lignin. Three replicates of each fractionation were made.

### 2.3. FTIR spectroscopy

A Spectrum One (Perkin Elmer) FTIR spectrometer was used for the measurements. The KBr pellet technique for preparing lignin samples was employed. The spectral range was 4000–500 $cm^{-1}$; scan resolution and the number of scans were 4 $cm^{-1}$ and 64, respectively. Baseline correction was carried out by the Spectrum version 5.0 software (Perkin-Elmer) and the resulting spectra were normalized to an intensity of the band of 1510 $cm^{-1}$. Analysis was performed in duplicate. Average data were used for discussion. In the case of LPU, the Universal ATR Sampling Accessory was used.

### 2.4. Functional analysis

The functional groups' (methoxyl, carboxylic OH plus phenolic OH, carboxylic OH, acetylated OH) content was determined by wet chemistry methods. The procedures and calculations are described in detail elsewhere (Zakis, 1994). For each analysis, 5 repeated measurements were performed. All air dried samples were vacuum dried at 50 °C for 48 h before analysis. The results are expressed on a dry-weight and ash free basis.

The methoxyl groups' ($OCH_3$) content in lignin samples was determined according to the

Viebock-Schwappach method in a Zeisel apparatus (domestic glassware). The 57% HI was used for splitting of the ether bond in methoxyl groups and obtaining $CH_3I$. This procedure was followed by three subsequent quantitative reactions yielding free $I_2$ and its titrating with thiosulfate.

The total contents of phenolic OH and carboxylic OH groups were determined by two independent methods. Acid-base conductometric titration under $N_2$ using an automatic titration device ABU901, coupled with a Conductometer CDM 210 and a Titration manager TIM 900, and $BaCl_2$-based chemisorption were used. Similar data differing by 2.5–3.5% were obtained by different methods. The content of carboxylic OH groups in lignins was examined by chemisorption with calcium acetate in water solution. The liberated free acetic acid was determined by potentiometric titration with 0.05 M NaOH solution in water. The content of phenolic groups was calculated from the difference of both chemisorption methods.

The sum content of phenolic and aliphatic OH groups in lignin samples was determined by the modified Verley's method. Subsequently, the lignin samples were acetylated at 50 °C for 24 h using acetic anhydride and pyridine as a catalyst. The excess of acetic anhydride was decomposed by water into free acetic acid, which was titrated with 0.1 M NaOH. Because of the presence of carboxylic groups in lignin samples, the total content of phenolic and aliphatic OH groups was calculated as the sum of OH groups determined by the acetylation procedure, and carboxylic OH groups determined by the chemisorption method. The content of aliphatic OH groups ($OH_{aliph.}$) was calculated as acetylated OH + carboxylic OH − phenolic OH.

### 2.5. SEC analysis

The alkaline SEC analysis of lignin and fractions obtained was performed according to the procedure described in (Gosselink et al., 2010). The solution of the lignin sample in 0.5 M NaOH (1 mg $mL^{-1}$) was injected into a column (4.6 × 30 cm) packed manually with ethylene glycolmethacrylate copolymer TSK gel Toyoperl HW-55F, eluted with the same solvent and detected at 280 nm. Standards for calibration of the molar mass distribution were sodium–polystyrene sulfonates (Mw range: 891–976000 g $mol^{-1}$) and phenol.

### 2.6. Kinetic study

The chemical interaction of separated lignin fractions with MDI was realized in extra dry dioxane solution in a dry argon atmosphere at 25 °C in a glass reactor (50 $cm^3$) equipped with a thermostatic jacket in argon media. The initial concentration of OH groups and NCO groups was 0.3 mol $L^{-1}$ for all experiments. The concentration of dibutyltin dilaurate (DBTD) used as a catalyst was 0.0075 mol $L^{-1}$. FTIR spectroscopy Perkin-Elmer Spectrum One equipped with ATR mode was applied for monitoring the NCO groups' disappearance during the reaction (300 min). For this purpose, the ratio of absorbance at 2273 $cm^{-1}$ (NCO groups) to that of 2853 $cm^{-1}$ ($CH_2$ groups, used as an internal standard) was calculated (Cateto et al., 2008). To determine the absolute value of the NCO groups' concentrations, the calibration $A_{NCO}/A_{CH2}$ vs the concentration of NCO groups in dioxane solution was plotted ($R^2$ = 0.9995). Experiments were performed in triplicate for each type of lignin. The experimental data were inspected according to the second order kinetics:

$1/C = 1/C_0 + kt$(Cordeiroet al., 1997; Evtiouginaet al., 2001).

where C is the concentration of unreacted NCO groups in any moment of time, mol $L^{-1}$; $C_0$ is the starting concentration of NCO groups, 0.3 mol $L^{-1}$; t is the time of reaction, s; and k is the second order rate constant, L $mol^{-1}$ $s^{-1}$.

The reaction products were stored in a closed reactor at 25 °C under argon for 24 h to achieve ~ 100% NCO conversion. Then, the solvent was removed under vacuum and the products were extracted in a Soxhlet apparatus with dichloromethane for 8 h to remove the soluble non-crosslinking constituent (Evtuguin et al., 1998). The yield of the cross-linked polymer was determined by weight.

### 2.7. LPU films' synthesis

Model LPU films with a thickness of 0.150–0.200 mm were obtained by pre-polymerization of polyethylene glycol (Mn = 400 g $mol^{-1}$, [OH] = 5.0 mmol $g^{-1}$), lignin fractions, and commercial polymeric methylene diphenyl diisocyanate (PMDI) VORATEC SD 100 ([NCO] = 7.3 mmol $g^{-1}$) in extra dry tetrahydrofuran (THF) according to Ni and Thring (2003). The content of the lignin constituent in LPU varied in a range of 5–40% for each fraction, at a constant NCO/OH ratio equal to 1.05. DBTD at a concentration of 3% in terms of total solids was used as a catalyst. PEG, lignin, PMDI, and DBTD were dissolved each in THF. The obtained solutions were combined and mixed at room temperature for 20 min. In order to avoid the appearance of bubbles in LPU films, the pre-polymerized system was treated in an ultrasound bath Cole Parmer 8891 for 5 min 48 g of the pre-polymerized mixture, containing 9.5 g of prepolymer, was then poured into a disk mold with a flat bottom covered by polytetrafluorethylene (Teflon) for curing. To avoid the presence of small voids caused by rapid solvent evaporation, the mold was covered by flat glass. After the formation of gel, the glass was placed back and slower evaporation proceeded in a hood overnight. After 24 h, the cast films were peeled and dried in a desiccator above $P_2O_5$ at 20 °C for 7 days, followed by thermal curing at a temperature of 90 °C for 8 h. All lignin fractions were completely soluble in THF and the prepared LPU films were smooth and translucent (Fig. 1).

### 2.8. Swelling test

The experimental measurement of the crosslink density of LPU films was done by the swelling method (Yoshida et al., 1987b; Ni and Thring, 2003; Kurimoto et al., 2001). Five replicates of oven-

**Fig. 1.** LPU film, containing 20% of MET-F: a) under curing in a mold; b) cured and eliminated sample.

dried species with a weight of about 0.3500 g for each LPU film were placed in five weighing vessels, containing 20 mL of dimethylformamide (DMFA), and were stored at 20 °C for 7 days. The crosslink density of LPU films ($\upsilon_c/V_0$, unit: mol cm$^{-3}$) was calculated using the Flory–Rethner equation (Yoshida et al., 1987b):

$$\upsilon_c/V_0 = -2\left(\upsilon + \chi\upsilon^2 + \ln(1-\upsilon)\right)/V_1(2\upsilon^{1/3} - \upsilon)$$

where $\upsilon_c$ is the effective number of crosslink chains (mol), $V_0$ is the volume of dry polymer (cm$^3$),

$V_1$ is DMFA molar volume (76.87 mL mol$^{-1}$), $\chi$ is the polyurethane–DMFA interaction parameter (0.40) (Yoshida et al., 1987b), $\upsilon$ is the volume fraction of polyurethane in swollen gel ($\upsilon = V_0/V$) and V is the volume of swollen gel at equilibrium (cm$^3$).

25 mL of liquid pycnometers was used to determine the dry films' densities according to EN ISO 1183-1, 2004.

The yield of the sol fraction (Sol) and weight gain (WG) as a result of LPU swelling were determined by the corresponding equations:

$$Sol = (m_0 - m_D)/m_0 \times 100\%$$

$$WG = (m_s - m_D)/m_D \times 100\%$$

where $m_o$ is the mass of the dry LPU sample before swelling (g), $m_D$ is the mass of the dry LPU after swelling (g) and $m_s$ is the mass of the swollen gel (g).

### 2.9. UV spectroscopy

The quantities of the lignin removed from LPU films at swelling were determined using an UV spectrometer PerkinElmer Lambda 25 UV–vis (cuvette thickness 2.0 mm). The dependences of absorbance at 316 nm on the concentration of each lignin fraction (in a range of 50–250 mg $L^1$) in DMFA were plotted for calibration. The absorbance intensity at 316 nm of DMFA solutions after 7-day swelling of each LPU film therein was measured using pure DMFA as a reference. The amount of dissolved lignin was computed using the corresponding calibration graph.

### 2.10. Tensile tests

The tensile tests of LPU films were performed according to ASTM D 882-10 standards using a Zwick/Roell Z100 testing machine. The tensile tests were carried out at 22 °C and $\phi$ = 55%. The samples were stored in these conditions for 24 h prior to the test. The cross-head distance was 70 mm. The dimensions of samples were: length 100 mm, width 5 mm and thickness 150–200 µm. Five to seven specimens were tested per each sample. Tensile strength (stress at break), elastic modulus (Young's modulus) and percent elongation at break (ultimate strain) were computed using the software testXpert.

### 2.11. Differential scanning calorimetry (DSC)

DSC analysis of PU films was carried out using a calorimeter Metler Toledo Star DSC 823$^e$. To eliminate the effect of enthalpy relaxation, the starting lignin and its fractions obtained were first scanned from +20 °C to 200 °C, then cooled again to −20 °C and scanned once again. PU films were first scanned from +20 °C to 170 °C, then cooled to −50 °C and scanned again. In all cases, glass transition temperature (Tg) was measured from the second scan. The measurements were done at a heating rate of 10 °C min$^{-1}$. According to DIN 53765, Tg was defined as a temperature where half of the change in heat capacity (0.5 ΔCp) takes place (Affolte et al., 2001).

### 2.12. Thermal gravimetric analysis (TGA)

TGA of LPU was realized in nitrogen and air atmosphere (flow rate 50 mL min$^{-1}$) using a Metler Toledo Star TOA/SDTA 851$^e$ device at a heating rate of 10 °C min$^{-1}$. A sample weight of 8 mg was used. Temperature range was 20–1000 °C. The first derivative of the thermogravimetric curve (DTG) was used for discussion.

### 2.13. Analytical pyrolysis (Py-GC/MS)

The analysis was performed using a Frontier Lab Micro Double-shot Pyrolyser Py-2020iD (pyrolysis temperature 500 °C, heating rate 600 °C s$^{-1}$) directly coupled with the Shimadzu GC/MS – QP 2010 apparatus with a capillary column RTX-1701. The regimes of analysis are described in detail elsewhere (Arshanitsa et al., 2013).

## 3. Results and discussion

### 3.1. Characteristics of lignin fractions

As shown in Table 1, the Tg of non-fractionated Biolignin$^{TM}$ is 177 °C. This suggests that the main chain molecular motion of the lignin used in this study is markedly restricted. Comparing with the other wheat straw lignin produced by the ethanol based organosolv process; it is considered that a high-condensed structure is fabricated by the acid based organosolv process (Huiggen et al., 2014).

The total yield of the fractions separated from lignin by sequential extraction was 40.1%. The fraction dissolved in the mixture of solvents was the most representative, namely, 18.2% (Table 1).

The FTIR spectra of the fraction soluble in dichloromethane differed significantly from those of other fractions and non-fractionated lignin by the highest absorbance in the region of

**Table 1**
Molecular weights, functional groups' content and Tg of lignin and its fractions.

| Index | Lignin and its fractions | | | |
|---|---|---|---|---|
| | Lignin | DCM-F | MET-F | MET/DCM-F |
| Yield[a] (%) | – | 7.4 ± 0.2 | 14.5 ± 0.7 | 18.2 ± 0.9 |
| Mw (g mol$^{-1}$) | 11100 | 1970 | 2200 | 5300 |
| Mn (g mol$^{-1}$) | 1050 | 334 | 540 | 1100 |
| Mw Mn$^{-1}$ | 10.6 | 5.9 | 4.1 | 4.8 |
| $OCH_3$ content (mmol g$^{-1}$) | 3.12 ± 0.03 | 2.96 ± 0.03 | 3.55 ± 0.06 | 3.67 ± 0.03 |
| OH acetylated content (mmol g$^{-1}$) | 4.53 ± 0.15 | 3.24 ± 0.06 | 5.30 ± 0.10 | 5.00 ± 0.10 |
| OH aliphatic content (mmol g$^{-1}$) | 3.76 ± 0.28 | 1.65 ± 0.19 | 4.47 ± 0.30 | 4.35 ± 0.23 |
| OH phenolic content (mmol g$^{-1}$) | 1.47 ± 0.08 | 2.12 ± 0.10 | 2.06 ± 0.10 | 1.60 ± 0.08 |
| COOH content (mmol g$^{-1}$) | 0.71 ± 0.05 | 0.53 ± 0.03 | 1.18 ± 0.10 | 0.88 ± 0.05 |
| Total OH groups' content (mmol g$^{-1}$) | 5.94 ± 0.25 | 4.30 ± 0.12 | 7.71 ± 0.30 | 6.83 ± 0.20 |
| $OH_{aliph.}/OH_{total}$ | 0.63 | 0.38 | 0.58 | 0.64 |
| Average OH functionality | 6.2 | 1.4 | 4.2 | 7.5 |
| Tg (°C) | 177 | 14 | 121 | 160 |

[a] On the oven dry ash-free matter of non-extracted lignin.

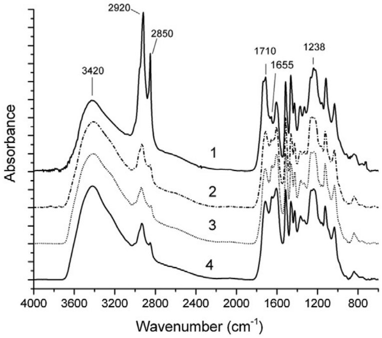

**Fig. 2.** Normalized (1515 cm$^{-1}$) FTIR spectra of lignin (4) and its fractions soluble in dichloromethane (1), methanol (2) and a mixture of both solvents (3).

**Table 2**
Relative content of liphophilic, carbohydrate and lignin derived compounds in pyrolysis products of lignin and its fractions according to Py-GC/MS data.

| Compounds | Content (%) | | | |
|---|---|---|---|---|
| | Lignin | DCM-F | MET-F | MET/DCM-F |
| Liphophilics | 4.5 | 28.1 | 8.7 | 1.7 |
| Carbohydrates | 31.8 | 21.1 | 34.2 | 31.3 |
| Lignin | 63.7 | 50.8 | 57.1 | 67.0 |

2850–2920 cm$^{-1}$ (C—H bonds in aliphatic structures), 1720 cm$^{-1}$ and 1238 cm$^{-1}$ (carboxylic and ester bonds) (Fig. 2). It is explained by the presence of high amounts of lipophilic extractives (waxes and paraffins) therein, intrinsic to wheat straw. The results obtained by the Py-GC/MS method confirmed the FTIR data (Table 2).

The difference in the spectra of the fractions soluble in the mixture of solvents and pure methanol was less significant. The higher content of conjugated C═O (bands at 1655 cm$^{-1}$) and the lower content of C—H bonds (bands at 2850–2920 cm$^{-1}$) in MET/DCM-F are explained by the highest content of the lignin constituent and the removal of extractives in the latter by two previous extraction steps (Table 2).

Lignin was the predominant component of all samples under study, although a noticeable amount of compounds originated from carbohydrates as well as lipophilic extractives was also present in pyrolysates (Table 2). Therefore, the term "lignin-enriched by-products" would be stricter. However, for the purpose of abridging, the term "lignin" was used in this paper. The presence of carbohydrates moieties covalently bonded to the lignin (Monteil-Rivera et al., 2013) can be considered as a favorable factor for valorization of non-modified technical lignins as polyols due to the high reactivity of aliphatic OH groups towards isocyanate (Saunders and Frisch, 1962). The action of lipophilic extractives as a hydrophobic plasticizer of the PU network can be proposed.

Both the total content of OH groups and their allocation between aliphatic and acidic (phenolic plus carboxylic) groups are the main parameters, characterizing the lignin fractions as a macromonomer aimed at LPU synthesis. The lowest total content of OH groups, namely, 4.30 mmol g$^{-1}$ was determined in DCM-F vs 5.94, 7.71 and 6.83 mmol g$^{-1}$ in lignin, MET-F and MET/DCM-F, respectively (Table 1).

The relative portion of the aliphatic OH groups most reactive towards isocyanates for lignin fractions obtained was increased for the following row of solvents used: DCM < MET < MET/DCM. The ratio of the sum of the portions of phenol and benzene derivatives to the sum of guaiacol and syringol derivatives in pyrolysis products of lignin fractions indicates that the degree of lignin condensation is increased in the same row (Arshanitsa et al., 2013).

Both factors, namely, the increasing of the molecular weights and degree of condensation of lignin constituents, led to the increase of the Tg of fractions from 14 °C for DCM-F to 160 °C for MET/DCM-F (Table 1). The average OH functionality of polyol is defined as a number of OH groups per one molecule (Ionescu, 2005). These values were equal to 1.4, 4.2 and 7.5 for DCM-F, MET-F and MET/DCM-F, respectively (Table 1). Therefore, the different crosslinking effect can be expected from the incorporation of the same amounts of different lignin fractions at an equal NCO/OH ratio into the PU matrix.

### 3.2. Reactivity of lignin fractions with isocyanate

The conversion of NCO groups into urethane ones as a result of the MDI reaction with OH groups of separated lignin fractions was established by kinetic investigations.

A simplification, assuming equal reactivity for all hydroxyl groups present in the reaction mixture, was considered for all fractions. This approach is widely used for monitoring the formation of PU systems, containing complex renewable polyols enriched with OH groups of different origin (Cateto et al., 2008; Cordeiro et al., 1997; Evtiougina et al., 2001; Pavier and Gandini, 2000). The linearity of the second order plot was observed up to about 51–55% of the NCO group conversion (Table 3, Fig. 3). The positive deviation from the second order plots achieved at higher conversions was pro-

**Table 3**
Kinetic data of lignin fractions' interaction with MDI in dioxane media.

| Fraction | $k \times 10^4$ ($L\,mol^{-1}\,s^{-1}$) | NCO groups' conversion (%)[a] | Insoluble fraction (%)[b] |
|---|---|---|---|
| DCM-F | 2.27 ± 0.15 | 54.5 ± 5.2 | 62.0 ± 5.0 |
| MET-F | 4.73 ± 0.43 | 53.1 ± 3.5 | 86.0 ± 3.2 |
| MET/DCM-F | 3.87 ± 0.36 | 50.9 ± 2.2 | 96.7 ± 3.5 |

[a] Conversion limit when the linearity of second order plots was observed ($R^2 = 0.991$-$0.995$).

[b] Content of the dichloromethane insoluble fraction in reaction products at complete NCO groups' conversion.

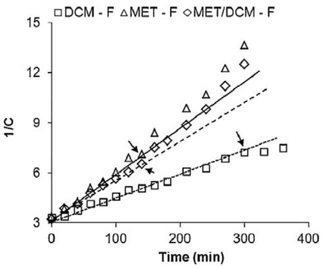

**Fig. 3.** Second-order plots for the reaction of lignin fractions with MDI in dioxane solution (the points at which the deviation from the second order begins are marked by an arrow).

nounced for comparatively high reactive MET-F and MET/DCM-F and can be explained by the autocatalytic effect induced by urethane bonds formation (Cordeiro et al., 1997; Saunders and Frisch, 1962).

The reactivity of the investigated lignin fractions with MDI in dioxane solution was increased in the following order: DCM-F < MET/DCM-F < MET-F (Table 3). The highest reactivity of the MET-F fraction could be explained by the higher portion of aliphatic OH groups contained therein (Table 1) and their steric availability due to the not-too-high degree of lignin condensity (Arshanitsa et al., 2013).

When the complete NCO conversion was achieved, the products of MET-F and MET/DCM-F condensation with MDI in dioxane solution were uniform gels. In the same conditions for DCM-F, high viscous but non-gelated products were observed. Correspondingly, the content of the cross-linked fraction, insoluble in dichloromethane, removed from the polycondensation products of this fraction with MDI, was the least (Table 3). The yields of the fractions, non-soluble in dichloromethane, were conditioned by the 3D PU network formation as a result of lignin interactions with bifunctional isocyanates. This effect was the most pronounced for the highest functional MET/DCM–F.

### 3.3. Composition of LPU and their swelling behavior

In order to suit the requirements of the constant NCO/OH ratio in preparing LPU, the increase of the OH groups' content in the lignin fraction resulted in a decrease of the PEG (soft segment) content in the LPU composition at the same lignin content (Table 4). Both structural parameters, namely, the variation of the soft segments' content in the PU matrix and its crosslink density, defined as the amount of covalent bonds (in moles) per units' volume of the polymer, have a significant effect on the mechanical and thermal properties of lignin based PU elastomers (Yoshida et al., 1990; Thring et al., 2004; Rials and Glasser, 1984; Vanderlaan and Thring, 1998; Ni and Thring, 2003; Saraf and Glasser, 1984).

The most pronounced effect of crosslinking was established for the LPU prepared on the basis of DCM/MET-F, and the least – for DCM-F (Fig. 4a). The results obtained were in good agreement with the values of the average functionality of lignin fractions (Table 1). The effect of DCM-F and MET/DCM-F on the weight gain and the yields of the sol fractions of LPU at swelling had a reverse corre-

**Table 4**
Compositions for LPU films' casting.

| Lignin (%) | DCM-F | | MET-F | | MET/DCM-F | |
|---|---|---|---|---|---|---|
| | PEG (%) | PMDI (%) | PEG (%) | PMDI (%) | PEG (%) | PMDI (%) |
| 0 | 57.9 | 42.1 | 57.9 | 42.1 | 57.9 | 42.1 |
| 5 | 53.1 | 41.9 | 51.8 | 42.2 | 52.1 | 42.9 |
| 10 | 48.7 | 41.3 | 45.8 | 44.9 | 46.3 | 43.7 |
| 20 | 39.5 | 40.5 | 33.3 | 46.7 | 34.7 | 45.3 |
| 30 | 30.1 | 39.9 | 21.1 | 48.9 | 23.6 | 46.7 |
| 40 | 21.0 | 39.0 | 9.4 | 50.6 | 12.0 | 48.0 |

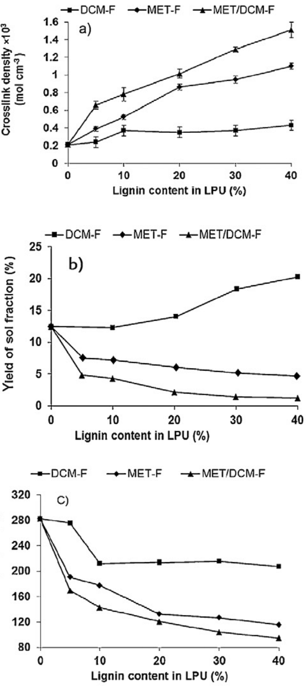

**Fig. 4.** Crosslink density (a), the yield of sol fraction (b) and mass gain (c) of LPU films determined by the swelling test as a function of lignin fractions' content.

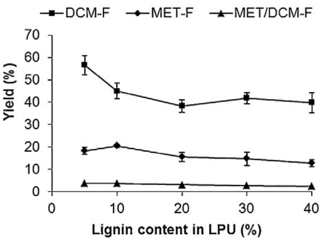

**Fig. 5.** Yield of the lignin portions removed from LPU films during swelling tests vs the lignin fractions content therein.

lation with crosslink density (Fig. 4a–c). However, for DCM-F, the relationships between the crosslink density and weight fraction of sol were unexpected. The small increase of crosslink density relative to lignin free PU films was accompanied by the increase of the sol fractions' yield from 12.5 to 20% as a result of the incorporation of 40% DCM-F into the LPU films (Fig. 4b). The contradictory results of the abnormally high sol fraction content at almost constant crosslink densities of PU films, containing ALCELL lignin and polycaprolactone 400, has been also reported (Cateto et al., 2011). On the contrary, a significant increase in the crosslink density of PU films as a result of the use of liquefied wood for PU formulation at the constant sol fraction yield has been observed (Kurimoto et al., 2001). The results obtained in the presented work could be explained by the polydispersity and inhomogeneity of the component composition of DCM-F. In particular, this low molecular fraction was characterized by the lowest average functionality, the highest $Mn/M_W$ ratio and the highest content of non-lignin admixtures (the main part of them were identified as lipophilic derivatives) (Table 2). It could be assumed that only part of this fraction contained more than 2 OH groups per one macromolecule capable of acting as a crosslinker. The crosslinking effect of DCM-F was testified by decreasing of swelling for DCM-F-containing LPU in comparison with the case of lignin free PU films (Fig. 4c). However, the other parts of lignin macromolecules, due to their low functionality (less than two) or the absence of OH groups (paraffins), did not form the 3D PU network and were extracted from LPU by DMFA during swelling tests. The direct measurements of the lignin fractions released from LPU in the swelling test using UV spectroscopy confirmed the validity of the above-mentioned explanation. In the cases of LPU films, containing DCM-F, MET-F and MET/DCM-F, the portion of lignin incorporated into the 3D network PU and therefore undissolved in DMFA consisted of about 60%, 82% and 97% of the total lignin amount introduced in LPU, respectively (Fig. 5). In the same row, the growth of average molecular weights and average functionality and the decrease of the non-lignin admixtures' content (i.e., the growth of the composition uniformity) were observed (Tables 1 and 2).

### 3.4. *Effect of lignin fractions on the Tg of LPU films*

The Tg of polymers depends on the segmental mobility of the main polymeric chains and therefore is a sensitive physicochemical parameter, reflecting the structural and composition changes of the amorphous polymeric matrix (Affolte et al., 2001). Besides, this physicochemical parameter correlates with the heat resistance of polymers—important characteristics of polymeric materials for their practical application.

A linear direct correlation of the Tg of LPU with the lignin fractions' content therein was observed (Fig. 6a). At an equal content of lignin, the Tg of LPU was increased in the row: DCM-F, MET-F, MET/DCM-F. It was established that the incorporation of fractionated lignin into the compositions of LPU enhanced the crosslink density of the obtained films (Fig. 4a) and decreased the content of PEG 400 (soft segments) therein (Table 4). For all series of the fabricated LPU films, the same correlation between the crosslinks density and PEG 400 content in LPU was not observed (Fig. 7). Each series was characterized by a specific dependence of crosslink density on the PEG content. Taking into account the constant NCO/OH ratio accepted as the necessary condition for films' preparation, it was shown that, at a given soft segment concentration, the crosslink density of LPU, containing different lignin fractions, was increased with increasing functionality of lignin fractions. Therefore, the separation of the varied contemporary soft segment content and crosslink density contributions into the process of LPU glass transition was a rather complicated task. A correlation analysis of the influence of the most important structural LPU parameters – soft segment content and crosslink density – on the Tg of LPU films was done (Fig. 6b,c). A rather good linear reverse correlation ($R^2 > 0.99$) between the Tg and the PEG 400 content in LPU was observed for

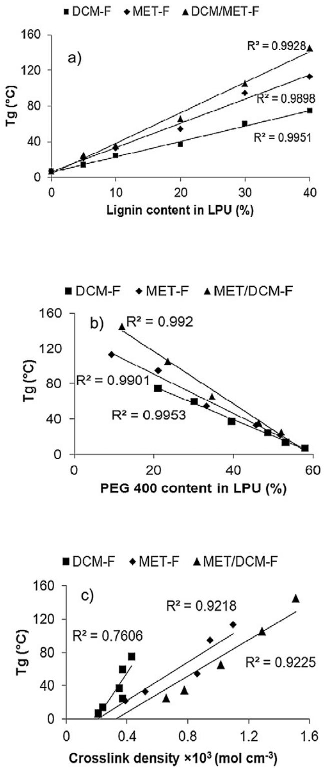

**Fig. 6.** Tg of LPU films as a function of lignin fractions (a), soft segment contents (b) and crosslink density of LPU(c).

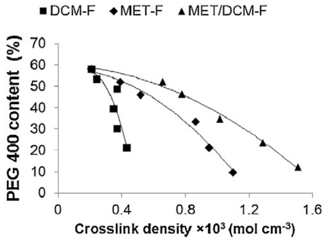

**Fig. 7.** Crosslink density of LPU films as a function of the soft segment content therein.

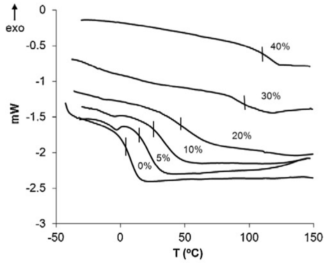

**Fig. 8.** DSC curves of LPU films differing by the content of MET-F (lignin content is shown by the upper curve) therein.

each series of samples. It was shown that at a given PEG content, the highest Tg was determined for the sample with the highest crosslink density (Fig. 6b). Both the decrease of the PEG content and the increase of the crosslink density enhanced the Tg of the investigated LPU. However, the relationship between the crosslink density of LPU and their Tg was less pronounced (Fig. 6c). This data suggests that the content of soft segments is the major factor influencing the heat mobility of polymeric chains in the LPU systems under study. The effect of crosslink density seems to be of less importance. An especially weak correlation was observed for LPU, containing low molecular DCM-F. It means the greatest contribution of the soft segment content to the heat mobility of polymeric chains for this sample in comparison with the contribution of crosslink density that varied in a narrow range of 0.21–0.43 × $10^{-4}$ mol $cm^{-3}$.

A single glass transition region for LPU in the whole investigated range of lignin concentration was observed. As an example, the DSC curves of LPU, containing MET-F, are presented (Fig. 8).

As mentioned above, the Tg of LPU films, containing each lignin fraction, steadily increased with decreasing soft segments' (PEG 400) content therein (Fig. 7). Both these results indicate that soft (PEG) and hard segments (PMDI + lignin) in the three component LPU system exist without phase separation. It has been proposed by Yoshida et al. (1990) that the incorporation of lignins in the PU matrix restricts the mobility of polymer chains due to the crosslink effect and therefore reduces the aggregation of hard segments into domains, preventing phase separation. A small typical melting region at about 0 °C was observed on DSC curves at the 5% concentration of high functional lignin fractions (MET-F and MET/DCM-F) in LPU films. Obviously, the part of linear PU chains in these conditions became strongly ordered, resulting in the formation of a crystal region that melted at about 0 °C. The enhancement of the lignin fractions' content led to the disappearance of this endothermic peak (Fig. 8).

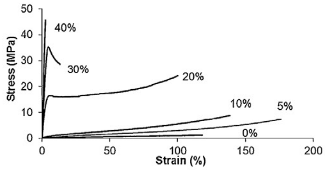

**Fig. 9.** Tensile stress-strain curves of LPU films, containing MET-F (lignin content is shown by the upper curves).

### 3.5. Tensile test of LPU films

The Tg magnitudes of lignin free PU and LPU films, containing 5% of MET-F, MET/DCM-F and 5–10% of DCM-F were below or near the tensile testing temperature of 22 °C (Fig. 6a). This means that these samples were in a rubbery state whereas the others were in a glassy state at testing. Therefore, the behavior of LPU in conditions of tensile stress detection differed significantly depending on the lignin fractions' content therein. The stress-strain curves of LPU films containing MET-F are presented as an example (Fig. 9). For lignin free PU films and those containing low amounts (5–10%) of lignin, the deformation curves of samples are typical for rubbery polymers. The further increase of lignin content up to 20–30% leads to the appearance of the forced rubberlike elasticity, which is characteristic of polymeric glasses and is followed by a decrease in ultimate strain. At the lignin content of 40% in LPU films, the fragile destruction prevailed and rigid but very fragile materials were obtained in all cases.

The lignin fractions used promoted the increase of the tensile strength and Young's modulus of LPU films in the following row: DCM-F < MET-F < MET/DCM-F, which coincided with increasing of the average functionality of lignin fractions (Fig. 10a,b). These parameters were enhanced steadily in the whole range of the lignin content in LPU using low and average functional lignin fractions (DCM-F and MET-F). In the case of the MET/DCM-F with the highest functionality, the strength and modulus of LPU were steadily enhanced with increasing lignin content therein up to 30% and 20%, respectively. At a higher content of lignin, these parameters remained constant. As shown earlier, the MET/DCM-F gave the highest crosslink density of LPU (Fig. 4a). A similar insensitivity of the tensile properties of high cross-linked epoxides and lignin-derived PU towards the increase of crosslink density has been previously reported by Saraf and Glasser (1984) and Yoshida et al. (1990). In the authors' opinion, the deformation of glassy highly cross-linked polymers proceeds due to stretching of covalent bonds and van der Waal's bonds, and the degree of crosslinking may have relatively little influence on the tensile properties. Another explanation could be connected with the accumulation of micro defects in the structure of high cross-linked LPU due to the strongly restricted segmental motion at curing.

At contents of MET/DCM-F, DCM-F and MET-F of 5%, 10% and 5–10%, respectively, in PU compositions, all the tested tensile parameters of lignin derived LPU, namely, strength, modulus and elongation at break exceeded the parameters of the reference lignin free PU (Fig. 10a–c). All series of LPU samples displayed a maximum in ultimate strain as a function of lignin content (Fig. 10c). The ultimate strain plotted against the temperature difference between the test temperature (T) and Tg showed that the maximum in all cases appeared at around T − Tg = 0 (Fig. 11). According to Reiman et al. (1990), the observed maximum relates to the transition of

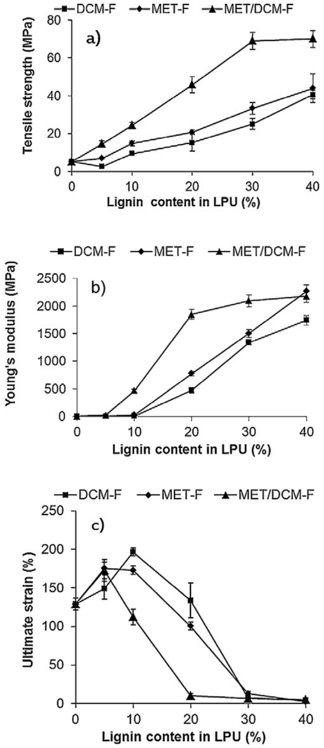

**Fig. 10.** Tensile strength (a), Young's modulus (b) and ultimate stress (c) of LPU films as a function of the lignin fractions content therein.

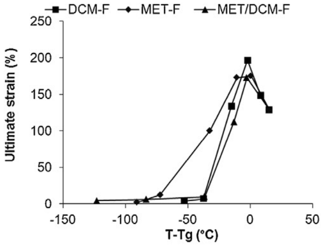

**Fig. 11.** Ultimate strain of LPU films as a function of the difference between the test temperature and Tg.

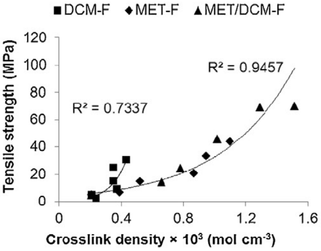

**Fig. 12.** Dependence of the tensile strength of LPU films on their crosslink density.

LPU from a rubbery state to a glassy one. The further increase of the lignin fractions' content led to a drastic depression of LPU strains. This depression was more pronounced for LPU, containing lignins with a higher functionality. At the given lignin content (till 30%), the flexibility (higher ultimate strain) of LPU increased in the row MET/DCM-F < MET-F < DCM-F, e.g., with decreasing molecular weights and functionalities of lignin fractions. At a high ($\geq$30%) lignin fractions content, rigid LPU films with a low ultimate strain were obtained in all series of experiments.

The tensile strength values plotted against the crosslink density values of LPU showed that this relationship for LPU, containing lignin fractions with the highest and medium functionality, was similar: the tensile strength grew exponentially ($R^2 = 0.946$) with increasing crosslink density independently of the lignin type. A weak correlation ($R^2 = 0.734$) was observed for low functional lignin, DCM-F (Fig. 12). This indicated that the influence of the crosslink density of LPU, containing MET-F and MET/DCM-F, on the tensile properties of films was more significant unlike the case of LPU, containing DCM-F, in which the decrease of the soft segment content had the major effect on the increase of the tensile strength of LPU films.

### 3.6. TGA test of LPU films

The thermal decomposition of PU is an important characteristic determining the technological prospects of their application. In its turn, the TGA analysis in inert and oxidizing atmospheres is a valuable analytical tool for gaining new fundamental knowledge regarding the mechanism of thermal degradation of polymers and their relationships with the polymer structure (Chattophadhyay and Webster, 2009).

The DTG curves obtained (Fig. 13) show the three distinguished stages of the thermal degradation of reference lignin free PU films in an air atmosphere. The regions with peak degradation rates at around 300 and 360 °C involve the scission of PU macromolecules into gaseous products (primary and secondary amines, olefins, carbon dioxide, vinyl and alkyl ethers, etc.) as a results of both thermal and radical processes (Chattophadhyay and Webster, 2009; Lattimer and Williams, 2002). The third high temperature region (peak rate at 531 °C) is connected mainly with the charcoal oxidation in heterogenic conditions (charcoal combustion).

The significant shifting of peaks' degradation rates, connected with PU chains' destruction in high temperature regions, was observed at minor (5%) incorporation of lignin fractions into PU compositions (Fig. 13). Moreover, in this case, some increase in the starting temperature of volatilization ($T_{start}$), the temperature when a half weight of the samples was lost ($T_{50\%}$), and the yield of the char residue was observed (Table 5) that can be explained by the antioxidant action of the lignin fractions used for LPU formulation. The radical scavenging activity of the lignin fractions under investigation has been revealed by the authors earlier, in tests with stable radicals: 2,2_-azino-bis(3-ethylbenzthiazoline-6-sulphonic radical ($ABTS^{\bullet}+$), 2,2-diphenyl-1-picrylhydrazyl radical ($DPPH^{\bullet}$) and superoxide anion-radical ($O2^{\bullet}-$). The radical scav-

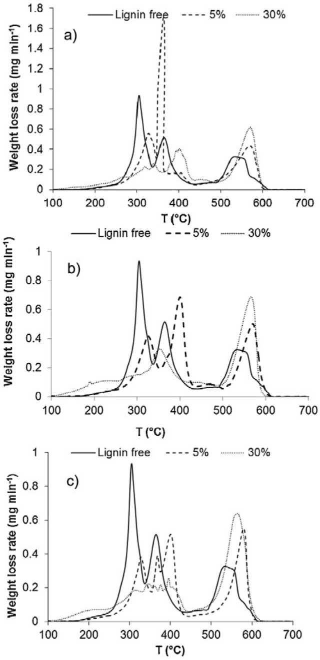

**Fig. 13.** DTG curves (in air) for lignin free PU and LPU, containing 5 and 30% of lignin fractions: DCM-F (a), MET-F (b) and MET/DCM-F (c).

**Table 5**
Effect of lignin fractions on the thermodegradation parameters of LPU films in the air.

| Fraction | Content in LPU (%) | $T_{start}$, (°C[a]) | $T_{50\%}$, (°C[b]) | Char residue at 500 °C |
|---|---|---|---|---|
| – | 0 | 274 | 365 | 27.0 |
| DCM-F | 5 | 281 | 367 | 33.7 |
| | 30 | 238 | 427 | 42.2 |
| MET-F | 5 | 279 | 403 | 32.4 |
| | 30 | 205 | 442 | 44.5 |
| MET/DCM-F | 5 | 286 | 402 | 35.7 |
| | 30 | 225 | 499 | 50.0 |

[a] The temperature when 5% of weight loss was achieved.
[b] The temperature when 50% of weight loss was achieved.

enging activity against stable radicals was increased in the row DCM-F < MET-F < MET/DCM-F with increasing condensation degree of lignin macromolecules and their aromaticity (Arshanitsa et al., 2013).

The increase of the lignin fractions' content up to 30% led to the further lowering of the LPU degradation rate in the air in a range of 250–450 °C and an increase of char residue yields (Fig. 14, Table 5). Besides, at a high content of the lignin fraction (30%), a decrease in the starting temperature of degradation ($T_{start}$) was observed, in comparison with the case of lignin free PU (Table 5). It could be connected with the formation of some amounts of thermolabile arylisocyanate-aryl alcohol urethane bonds, the thermo degradation of which started at around 120 °C (Chattophadhyay and Webster, 2009; Garcia et al., 2015). In total, the active degradation process of LPU, containing 30% of lignin fractions, started at a higher temperature and proceeded with a significantly lower rate in comparison with the degradation of lignin free PU. The temperature at which 50% of weight loss was achieved in LPU, containing 30% of lignin fractions, exceeds that for the lignin free PU by 60–130 °C (Table 5).

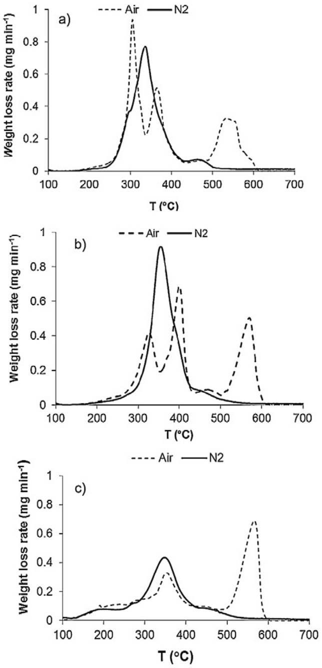

**Fig. 14.** DTG curves (in air and nitrogen) for lignin free PU (a) and LPU, containing 5% (b) and 30% (c) of MET-F.

The degradation rate of the PU material in the air is accelerated significantly due to the overlapping of both thermal stress and the processes of radical destruction of polyurethane chains (Chattophadhyay and Webster, 2009; Hirose et al., 1998; Jiao et al., 2013). The TGA analysis confirmed this conclusion for lignin free PU films. However, in the case of LPU films, the retardation of thermo degradation processes in the air, in comparison with that in nitrogen, was observed. The DTG curves of lignin free PU and MET-F-containing LPU are presented as an example (Fig. 14). This retardation effect can be explained by the simultaneous impact of different factors, including the radical scavenging activity of lignin fractions, their crosslinking action and the increasing of the thermostable aromatic constituents' content in LPU. We assume that, at a minor content of lignin fractions (5%), their antioxidative action is the prevailing factor, but at a high portion of lignin, the contribution of two other factors into the growth of the thermo-oxidative stability of lignopolyurethanes is enhanced.

As shown, all lignin fractions act as effective promoters of char formation at the thermo-oxidative degradation of the LPU under study (Fig. 13, Table 5). In the presence of char, the heat transfer from the flame to the condensed phase and emission of gases, hazardous for human health, are decreased (Jiao et al., 2013). Therefore, the incorporation of lignin fractions in combination with traditional flame retardants into PU systems could be a valuable pathway for increasing the thermostabilty and fire retardancy of PU materials. The residual lignin (60% from the initial), insoluble in organic solvents under study, can be oxypropylated, and the obtained propylene oxide – lignin copolymer can be also used as a macromonomer for PU synthesis (Arshanitsa et al., 2015).

## 4. Conclusions

Organosolv wheat straw lignin, Biolignin$^{TM}$, represents the group of technical lignins, the solubility of which in conventional organic solvents is limited. Therefore, they cannot be used as received for PU synthesis as a macromonomer. The obtained results have shown that the fractionation by organic solvents of different polarity could be considered as an approach for successful application of a significant part (up to 40%) of lignin types such as lignopolyol, able to substitute the different portions of fossil derived polyols, with simultaneous improvement of PU material operation characteristics.

The separated lignin fractions, reactive towards isocyanate, act as a crosslinking agent being incorporated in the model three components (lignin – polyethelene glycol – polymeric methyl diisocyanate) PU system, enhancing the glass transition temperature, tensile strength and Young's modulus of PU films. This activity directly correlates with the average functionality of the used lignin. Depending on the lignin fraction type and its content in the composition, the lignin derived PU films exhibit the tensile properties of elastomers with a rubberlike state at room temperature or the tensile properties of glassy and rigid cross-linked polyurethanes.

The effects of fractions' applications were observed from their minor content in PU (5%), when they revealed the antioxidative activity. However, at a 30% content of fractions in the compositions used for polyurethane synthesis, the crosslinking effect and the increasing of the thermostable aromatic constituents' content in lignopolyurethanes were revealed, leading to the further enhancement of their thermooxidative stability and charcoal yield at combustion.

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## P-3

**Arshanitsa, A.**, Vevere, L., Telysheva, G., Dizhbite T., Gosselink, R. J.A., Bikovens, O., Jablonski, A. Functionality and physicochemical characteristics of wheat straw lignin, Bi o lignin TM derivatives formed in the oxypropylation process. *Holzforschung* (**IF 1.875**). 2015, vol. 69, no. 6, pp. 785-793. Available from: doi: 10.1515/hf-2014-027 4

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The corresponding author ensures that the description of A. Arshanitsa contributions to the published work is accurate and agreed by all authors.
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# Functionality and physico-chemical characteristics of wheat straw lignin, Biolignin™, derivatives formed in the oxypropylation process

**Abstract:** The new organosolv process of wheat straw fractionation elaborated by Compagnie Industrielle de la matiere Vegetale (France) corresponds to the biorefinery approach, which allows separating cellulose, hemicelluloses, and lignin. The straw lignin (Biolignin™) is an attractive product, for which new applications are sought. In the present work, straw lignin (L) was converted into liquid lignopolyols via a batch reaction with propylene oxide (PO). The effects of the lignin content (L%) in the initial reaction mixture (L/(L+PO) on the oxypropylation process and the properties of whole lignopolyols and L/PO copolymers were studied. Almost complete disappearance of L-$OH_{phen}$ and L-COOH groups in copolymers was accompanied by an increase in the L-$OH_{aliph}$ groups' content therein. The polydispersity ($M_w/M_n$) of all copolymers obtained decreased essentially compared to the reference. The extent of PO grafting onto OH groups increased with decreasing lignin content in the initial reaction mixture. At a lignin content of 15–30% in the initial reaction mixture, the lignopolyols fulfil the requirements of polyol polyethers for rigid polyurethane foam production. The further increase in the lignin content leads to the appearance of the non-liquefied fraction and the undesirable increase in the viscosity of the liquefied part.

**Keywords:** copolymer, hydroxyl value (OHV), lignopolyols, oxypropylation, $^{31}$P-NMR spectroscopy, size-exclusion chromatography (SEC), straw lignin

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## Introduction

Bio-based plastics, which at least partly consist of renewable components, are among the fastest growing markets today. The average growth rates over the past years have constantly been double-digit (Storz and Vorlop 2013). Rigid polyurethane (PUR) foams are versatile polymeric materials used as thermal insulation of buildings, refrigerators, cold stores, pipes, refrigerated transport, and in various fields of the chemical and food industries (Ionescu 2005). The application of renewable resources is an important avenue in modern development of chemistry and technology of PUR foams (Lampinen 2011). Polyol polyethers production from renewable resources via oxypropylation (OP) is also a promising way to achieve this goal (Gandini and Belgacem 2008). The most abundant natural phenolic polymers are lignins, which are separated from plant biomass as by-products resulting from hydrolysis and pulping processes. As of 2010, the pulp and paper industry generated approximately 55 million t year$^{1}$ technical lignins, the bulk of which are being burned to generate energy for pulp mills (Li and Ragauskas 2012). The sustainable biorefinery concept is aimed at the optimization of biomass processing for profitable utilization of all products and byproducts. The aromatic nature of lignin containing phenolic and aliphatic hydroxyl groups ($OH_{phen}$ and $OH_{aliph}$) permits its utilization as the aromatic macromonomer moiety of the polyurethane matrix. On the other hand, there are limitations for utilization of technical lignins because of their low solubility and functional and molecular heterogeneity, as well as because of the steric hindrance of OH groups. The OP of lignin is an approach to overcome these disadvantages, while the resulting liquid high-functional lignopolyols are well suitable for PUR foam production. Several aspects of the OP of commercial technical lignins from softwood,

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hardwood, and grasses are described in the literature (Wu and Glasser 1984; Kelley et al. 1989; Oliveira and Glasser 1989; Gromova et al. 1993; Nadji et al. 2005; Gandini and Belgacem 2008; Cateto et al. 2009; Ahvazi et al. 2011; Li and Ragauskas 2012).

The production of bioethanol as an alternative to fossil gasoline can be performed by acid and enzymatic hydrolysis of various pretreated plant biomasses, and various processes are currently under development. This process leads to a new type of technical lignins, the properties of which are strongly dependent on the biomass origin and the pretreatment technology (Zhao et al. 2009; Gosselink et al. 2010). This is a challenge for the novel lignin-based polyols' synthesis for application in PUR foams.

In focus of the present study is a novel technical lignin from wheat straw, Biolignin™, which was obtained in biorefinery pilot plant [Compagnie Industrielle de la matiere Vegetale (CIMV) France] by the pretreatment of biomass with a mixture of acetic and formic acid (Delmas et al. 2011). The goal was to investigate the OP of the lignin, the composition of the obtained lignopolyols, and the structural and functional transformation of straw lignin as a result of copolymerization with PO in terms of the products' suitability for PUR foam production.

## Materials and methods

Straw lignin was supplied with a water content of about 48% by CIMV (France). The material was washed with deionized water to remove the residual free acids, then air dried up to the moisture content (MC) of 5% and ground in a laboratory-scale disintegrator DESI-11 (Desintegtrator Tootmise OU, Tallinn, Estonia). Before analysis, the lignin was ground in a Mixer Ball Mill MM200 (Retsch, GmbH, Haan, Germany) at frequencies of 30 $s^{-1}$ for 60 min and oven dried in vacuum at 50°C.

**Oxypropylation:** Six batches of lignopolyols (liquid products of lignin OP), differing by the lignin content in the initial reaction mixture from 15 to 40% (based on the dry mass of lignin, b.o.d.l.) were synthesized in a 1-l Parr reactor (Parr instrument company, Moline, IL, USA). In all cases, 140 g of PO (ACROS, Geel, Belgium), air dried lignin (5% MC), and KOH (Lachner, Neratovice, Czech Republic) (5% b.o.d.l.) were loaded into the reactor, which was sealed and heated under stirring to 160–176°C, when the signifying exothermic process started. The reactor pressure increased and then dropped to a value close to atmospheric pressure. After cooling, the KOH was neutralized by acetic acid; the product was dissolved in 200 ml of dichloromethane ($CH_2Cl_2$) (Evtiougina et al. 2002; Nadji et al. 2005) and filtered over a glass filter (pore size 40–100 μm). $CH_2Cl_2$ was distilled off from the soluble fraction in a rotavapor. The solid residue was washed with $CH_2Cl_2$ and dried in vacuum at 50°C. The non-liquefied fraction in the reaction products was weighted.

**Lignopolyols fractionation:** Oxypropylated straw lignin was isolated from lignopolyols by dissolving 5 g of a lignopolyol in 20 ml of MeOH, followed by a fivefold liquid-liquid extraction with 100 ml of hexane in a separating funnel to remove PO homopolymers (polypropylene glycols, PPG) soluble in non-polar solvents. Each extraction step was done by vigorous shaking by hand during 10 min. After 15-min storage, the MeOH layer was separated and was extracted again with a fresh portion of hexane. Finally, the copolymer fraction was precipitated in cool water (6°C), slightly acidized (pH=4.0) by 1 M HCl, filtered, washed with deionized water, and dried under vacuum at 50°C (Wu and Glasser 1984). The hexane layers of each extraction step were collected, and hexane was distilled off under vacuum. The contents of hexane-soluble homopolymer fractions and precipitated copolymer fractions were determined by weighing. For each lignopolyol, three parallel experiments were done.

**FTIR spectroscopy:** Spectrum One (Perkin Elmer, Beaconsfield, UK) instrument and KBr pellet technique were used (1% solid in KBr); resolution: 4 $cm^{-1}$; number of scans: 64.

**$^{31}$P NMR spectroscopy:** Thirty milligrams of a sample was dissolved in the solvent mixture consisting of *N,N*-dimethylformamide:pyridine:$CDCl_3$:2-chloro-4,4,5,5-tetramethyl-1,3,2,-dioxaphospholane=1:1:4:1v/v as described by Gosselink et al. (2010). The instrument used was the Bruker 400 MHz NMR spectrometer (Bruker UK Limited, Coventry, UK) with 30° pulse angle, inverse gated proton decoupling, a delay time of 5 s, and 256 scans (double experiments per sample). Signal assignment was according to Granata and Argyropoulos (1995).

**$^{1}$H-NMR spectroscopy in the liquid state:** Acetylated straw lignin and its oxypropylated derivatives in $CDCl_3$ were recorded on a BRUKER AVANCE 300 NMR spectrometer (Bruker UK Limited, Coventry, UK) at 298 K; 200–250 of 12 μs pulses were collected with a delay of 2 s at 90°. Signal assignment was according to Glasser et al. (1984).

**Size-exclusion chromatography (SEC):** The samples dissolved in hexafluoroisopropyl alcohol+0.02 M potassium trifluoroacetate were injected into two serially connected columns [PSS PFG linear M, 7 μm, 8 mm (ID)×300 mm (length) and a PSS PFG guard column, 8 mm (ID)×50 mm (length)] and eluted with the same solvent. Flow was 0.7 ml $min^{-1}$, at 40°C, with injection volume of 100 μl, by refractive index detection. Polymethylmethacrylate standards with $M_w$ ranging from 1.020 to 790.000 g $mol^{-1}$ served for calibration.

The TGA analysis was performed with vacuum oven-dried samples (8 mg) in $N_2$ atmosphere between 20 and 1000°C (10°C $min^{-1}$) in a Mettler Toledo Star System TGA/STDA $851^e$ (Mettler Toledo, Schwerzenbach, Switzerland). The first derivative of thermogravimetric curve (differential thermogravimetric, DTG) is the basis for discussion.

Glass transition temperatures (Tg) were determined by differential scanning calorimetry (DSC) using Mettler Toledo Star DSC 823e instrument (Mettler Toledo, Schwerzebach, Switzerland); 8 mg vacuum oven-dried samples, heating rate was 10°C $min^{-1}$ between -20°C and +180°C, with double experiments. The second scan was used for *Tg* calculation according to DIN standard 53765 (1994) (specific heat capacity, $\Delta Cp$, achieved a half of its change during the transition).

**Chemical analysis:** OMe group determination was performed in combination with GC separation of alkyl iodides concentrated in $CCl_4$ according to Baker (1996). The samples were treated in a sealed vial with HI for 20 min at 130°C. Ethyl iodide was added to the cooled vial with a syringe as internal standard (IS). The alkyl iodides were extracted with 10 ml of $CCl_4$ and dried over $Na_2SO_4$. The GC instrument was Agilent 6850 Series GC System (Agilent Technologies, CA, USA) with a FID detector equipped with a capillary column CP7946 (25 m×320 μm×1.2 μm film). Temperature program was 40°C for 5 min → 180°C (10 min), with injector at 200°C and detector at 250°C, and the carrier gas was He. The ratio of the peak area of methyl iodide to that of IS was calculated by the Agilent 6850 software; the system was calibrated with vanillin. The oxypropyl groups were determined via the content of isopropyl iodide deliberated from the copolymers. The hydroxyl values (OHV) of lignopolyols were determined via acetylation of samples with $Ac_2O$ followed by potentiometric titration of free acetic acid in excess with 0.1 N NaOH in water (Zakis 1994). The potassium acetate (KAc) content in lignopolyols (ethanol solution) was determined by potentiometric titration with 0.1 N HCl. The water content in lignopolyols was determined by the Karl Fisher (KF) titration method. The viscosity of lignopolyols was determined by means of rotation viscosimetry [HAAKE Viscotester 6L/R plus (Thermo Electron GmbH, Karlsruhe, Germany)] at 20°C.

## Results and discussion

### Oxypropylation and properties of lignopolyols

A typical pressure-temperature-time diagram of the lignin OP is presented in Figure 1. The maximum pressure ($P_{max}$) of PO decreased steadily from 30 to 21.7 bar with increasing lignin content in the reaction mixture from 15 up to 40% (Table 1), but the onset temperature ($T_{onset}$) for the rapid homopolymerization step differed less significantly. This can be explained by a partial consumption of PO at the low rate of the copolymerization reaction with acidic groups of lignin, which react with PO before the homopolymerization step in the presence of an alkali catalyst (Wu and Glasser 1984). The high rate of homopolymerization reactions takes place after the transformation of acidic lignin groups into aliphatic ones after finishing the low-rate copolymerization step. During the high-rate step, two processes proceed: formation of propylene glycol derivatives of different molecular weights and the propagation of the oxypropyl chains of the copolymer. These processes are competing because the rates of both of them are predetermined mainly by the nucleofilicity of oxyanions, originated from secondary hydroxyl groups. Between 20 and 35% lignin content, the process rates were approximately the same (Table 1), in the course of which a twofold decrease of maximal pressure in the reactor occurs ($\tau_{0.5}$). This can be explained by the increase of the catalyst content in the reaction mixture alongside the increase of the lignin content consumed for modification. Obviously, the retardation effect of lignin on PO homopolymerization was compensated by the catalytic effect of KOH. Between 15 and 40% lignin content, the above mentioned balance was broken because of the too low amount of the catalyst in the first case and the too high content of lignin in the second one. As a result, the delay of PO conversion was observed in both cases. The $T_{onset}$ was steadily decreased with increasing catalyst content in the initial reaction mixture. A direct correlation between $T_{max}$ and the composition of the initial mixture was not found, but the lowest rates of homopolymerization was combined with the lowest $T_{max}$.

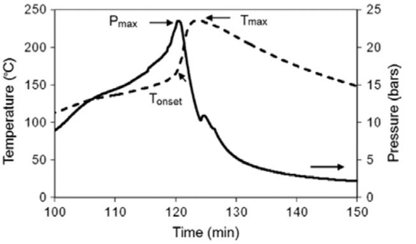

**Figure 1:** Typical pressure-temperature-time (P-T-t) diagram of straw lignin OP (L/(L+PO)=30%).

**Table 1:** Formulations related to the OP of straw lignin and operation conditions for this process.

| L/(L+PO) (%) | KOH (%) | $T_{onset}$ (°C) | $T_{max}$ (°C) | $P_{max}$ (bar) | $\tau_{0.5}$ (min) | Solid residue (%) |
|---|---|---|---|---|---|---|
| 15 | 0.7 | 176 | 225 | 30 | 4.7 | n.d. |
| 20 | 1.0 | 171 | 242 | 27.1 | 3.3 | n.d. |
| 25 | 1.2 | 168 | 235 | 25.9 | 3.4 | 0.2 |
| 30 | 1.5 | 166 | 236 | 24.5 | 3.2 | 0.1 |
| 35 | 1.7 | 166 | 235 | 23.1 | 3.4 | 1.3 |
| 40 | 1.9 | 160 | 227 | 21.7 | 7.1 | 7.5 |

n.d., not detected.

Higher lignin contents in the initial reaction mixture resulted in a steady increase of the OHV and viscosity of the lignopolyols (Table 2) in agreement with observation on Alcell lignin OP (Cateto et al. 2009). Based on the results listed in Tables 1 and 2, the conclusion is that at 15–30% lignin in the initial reaction mixture, the lignopolyols fulfil the requirements in terms of viscosity and OHV for PUR foam production (Nadji et al. 2005; Cateto et al. 2009). Higher lignin contents elevate the amount of non-liquefied solid fractions (up to 7.5%), and the viscosity of lignopolyols becomes higher than 100 Pa·s.

### Composition of lignopolyols

The L/PO copolymers were separated from the products of PO hopolymerization. As indicated in Table 2,

**Table 2:** Effect of the straw lignin content in the initial reaction mixture on the properties and composition of lignopolyols obtained.

| L/(L+PO) (%) | Viscosity at 20°C (Pa·s) | OHV (mg KOH g$^{-1}$) | KAc (%) | Composition (%) | | |
|---|---|---|---|---|---|---|
| | | | | Copolymer | PPG$^a$ | Total |
| 15 | 1.7 | 280.8 | 1.3 | 20.7±0.6 | 64.1±1.3 | 84.8 |
| 20 | 4.9 | 397.7 | 1.8 | 27.5±2.0 | 60.2±1.8 | 87.7 |
| 25 | 16.8 | 414.8 | 2.2 | 31.2±1.7 | 46.0±2.5 | 77.2 |
| 30 | 63.7 | 450.1 | 2.6 | 43.5±3.2 | 37.9±2.3 | 81.4 |
| 35 | 138.5 | 462.3 | 2.9 | 44.9±2.0 | 38.6±2.1 | 83.5 |
| 40 | >200.0 | 474.9 | 3.3 | 46.5±1.0 | 32.2±0.9 | 78.7 |

OHV, hydroxyl value; KAc, potassium acetate; L, lignin; PO, propylene oxide; PPG, polypropylene glycols. $^a$Hexane soluble.

increasing lignin contents go along with elevated amounts of the copolymer moieties, which caused higher viscosities, while the content of the homopolymer fraction soluble in hexane was reduced. The sum of the copolymer and PPG fractions was <100%. This is due to the limited solubility of homopolymers with low molecular weights in hexane compared to water. At molecular weights higher than 700 g mol$^{-1}$, the PPG becomes insoluble in water (Alexandridis and Hatton 1995). The part that is soluble in water is around 12.3–22% based on the total weight of lignopolyols. The contribution of water-soluble short-chain homopolymers to OHV is high. If the lignin content in the mixture is between 15 and 20%, the amount of water-soluble homopolymer will be 13.9 and 10.5%, respectively. Thus, the higher excess of PO in the reaction mixture promoted the formation of long-chain homopolymer and not only the copolymer/homopolymer ratio. This detail is important because the homopolymers act as a soft segment in the polyurethane matrix, which governs the balance between the rigidity and elasticity of the foam.

## Structure and functionality of the L/PO copolymers

The FTIR spectra confirms the OP (Figure 2) as the aliphatic groups CH, $CH_2$, and $CH_3$ (absorbance at 2975–2909 cm$^{-1}$, 1465 cm$^{-1}$) are elevated in the copolymer. The band at 1720 cm$^{-1}$ (unconjugated carbonyl moieties) is decreasing, and the band at 1125 cm$^{-1}$ is increasing due to the formation of ether bonds. As shown in Figure 3, the content of CH, $CH_2$, and $CH_3$ groups in copolymers estimated by the $S_2/S_1$ ratios was increased with increasing PO content in the initial reaction mixture. The same changes, but to a lesser extent, were observed in the FTIR spectra of solid fractions, separated from lignopolyols (data not presented). This testifies that solid fractions are also partly oxypropylated and therefore can act as a reactive filler of rigid PUR foams.

The data obtained by $^1$H NMR spectroscopy confirms the copolymerization of lignin with PO (Figure 4). The intensity of aliphatic proton signals (CH, $CH_2$, $CH_3$) are increasing while those of the OMe groups is decreasing

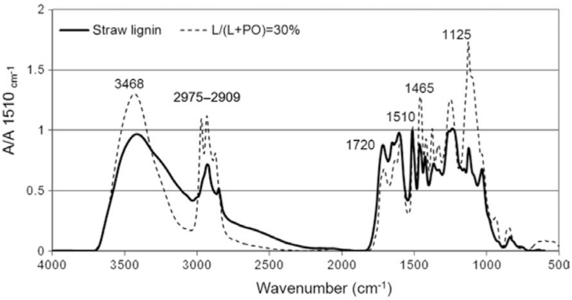

**Figure 2:** Normalized FTIR spectra of straw lignin and its oxypropylated derivative.

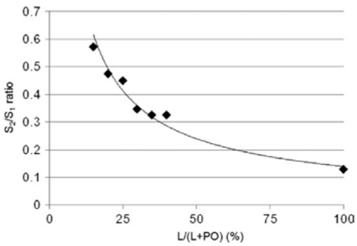

**Figure 3:** Ratios of the area enclosed by FTIR spectra in the range of 3035–2695 cm$^{-1}$($S_2$) to that enclosed in the range of 3705–3035 cm$^{-1}$($S_1$) for oxypropylated straw lignin derivatives vs. L/(L+PO) values.

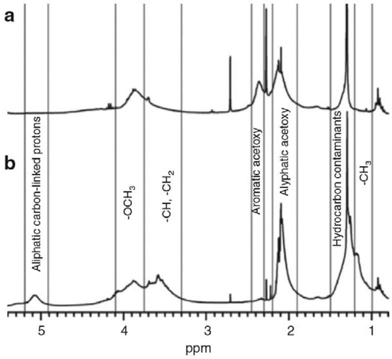

**Figure 4:** $^1$H NMR spectra of straw lignin (a) and its oxypropylated derivative (L/(L+PO)=30%) (b).

due to the dilution of aromatic constituents by PO grafting. The aromatic acetoxy signal disappears, and that of the aliphatic acetoxy signal is elevated.

The HI treatment led to the appearance of signals for isopropyl iodide (predominantly) and n-propyl iodide (traces) in products of the copolymers, while the lignin alone gives rise to only methyl iodide as a result of OMe group splitting (Figure 5). A series of successful experiments were also carried out with chloroform ($CHCl_3$) as $CCl_4$ is a dangerous chemical. In this experiment, the internal standards iso-propyl iodide and n-propyl iodide instead of ethyl iodide help to avoid overlapping of signals. The results are similar with both solvents.

The OP is initiated by hydroxyl-containing starters: the nucleophilic attack of the alcoholate group on the α-carbon of the oxirane ring ($S_N2$ normal attack), which is due to the low steric hindrance and the electron donor effect of the methyl group, which increasing the electron density at the β-carbon atom (Ionescu 2005). The OH groups in L/PO copolymers are presented mainly by secondary alcohol groups (Figure 6).

The apparently decreasing OMe content of the samples with increasing of PO grafting extent (Figure 7 and Table 3) is due to the dilution effect by the presence of more and more oxypropyl groups. Dimethoxylation of lignin does not occur during OP under the conditions of this study.

The $^{31}$P NMR spectra of lignin show that acidic OH groups with low reactivity ($OH_{phen}$+COOH) (Saunders and Frisch 1962) amounts to 60% of all OH groups present (Table 3). Lignin addition within the range of 15–40% led to the almost complete transformation of $OH_{phen}$ and COOH groups. For copolymers, the shear of aliphatic

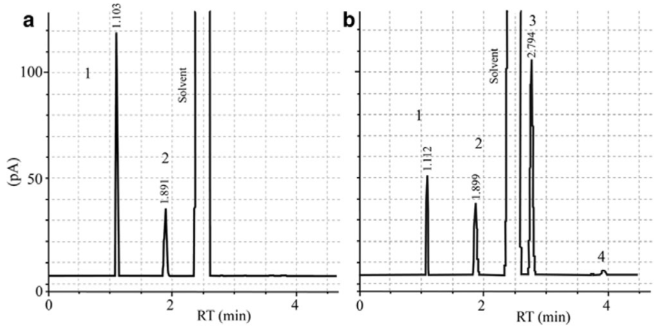

**Figure 5:** Gas chromatograms of $CCl_4$ extracts from straw lignin (a) and oxypropylated derivatives (b) obtained at L/(L+PO)=30% after their treatment by HI. (1) methyl iodide; (2) internal standard (ethyl iodide); (3) iso-propyl iodide; and (4) n-propyl iodide.

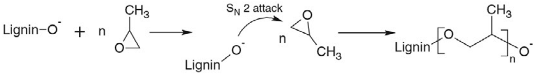

**Figure 6:** Scheme of the straw lignin-PO copolymers' formation according to the anionic $S_N2$ polymerization mechanism.

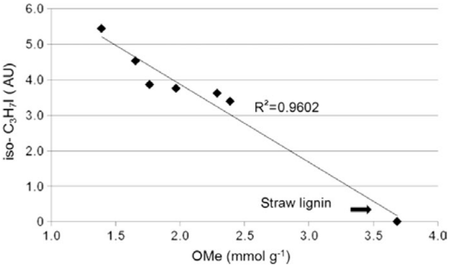

**Figure 7:** Correlation between the methoxyl groups' content in straw lignin, its oxypropylated derivatives, and the isopropyl iodide content in products of their treatment by HI.
AU (arbitrary units): a ratio of peak area of isopropyl iodide to that of the internal standard on chromatograms.

groups grew up to 92–95%. However, the total amounts of OH groups in copolymers diminished with decreasing L/(L+PO) ratios, due to PO grafting on lignin. The free $OH_{phen}$ groups for all copolymers are located mainly in 3,5- condensed structures, obviously because of their steric hindrance. The $OH_{phen}$ groups increment was low in case of lignin addition up to 40% (Table 3). The OP of wheat straw soda lignin under alkali conditions was reported to be more efficient even under mild conditions (water media, room temperature) (Ahvazi et al. 2011). Hence, the straw lignin seems to be less reactive toward PO in comparison with soda wheat straw lignins, but the reason for this is not yet clear (Arshanitsa et al. 2013).

Hindered phenols are known antioxidants for terminating free radical chain reactions, which are also applied in PUR foam production (Gray et al. 1996). Free $OH_{phen}$ groups in L/PO copolymers in amounts of 0.10–0.14 mmol $g^{-1}$ may be useful for influencing the PUR foam properties.

The data of mole mass distribution (MMD) in Table 3 indicate that the unreacted lignin has the broadest MMD. With advancing of OP, the polydispersity of copolymers decreased dramatically. Li and Ragauskas (2012) made similar observation with oxypropylated kraft lignin.

The results of DTG analysis confirmed the SEC data (Figure 8). The profile of the copolymer thermodegradation rate is narrower, but the peak degradation rate is higher compared with that of the lignin alone. The thermodegradation process of L begins at 190°C. The $T_{max}$ value inside the Parr reactor as the OP is initiated varies between 225 and 242°C (Table 1). In this temperature range, two opposite processes occur (Cui et al. 2013): the crosslinking process that proceeds via radical coupling leading to the growth of molecular mass, and thermal splitting resulting in macromolecule degradation. Radical coupling prevails under temperatures close to the *Tg* of lignin, while degradation reactions are dominant at higher temperatures (Brebu and Vasile 2010). These processes influence the MMD profiles. Moreover, molecular hydrodynamic volumes also influence the MMD (Gosselink et al. 2010).

**Table 3:** Content of functional groups and molecular mass distribution of straw lignin and its oxypropylated derivatives.

| | Data related to OH and OMe groups (mmol $g^{-1}$) | | | | | | Mol mass (g $mol^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|
| L/(L+PO) (%) | $OH_{aliph}$ | $OH_{phen}$ total | COOH | Σ | $OH_{aliph}$/OH Σ ratio | OMe | $M_n$ | $M_w$ | $M_w/M_n$ ratio |
| 100[a] | 1.39 | 1.62 | 0.50 | 3.51 | 0.40 | 3.69±0.10 | 2200 | 54 000 | 24.5 |
| 15 | 2.26 | 0.10 | 0.03 | 2.39 | 0.95 | 1.39±0.03 | 8200 | 30 000 | 3.7 |
| 20 | 2.53 | 0.10 | 0.04 | 2.67 | 0.95 | 1.66±0.01 | 4900 | 16 300 | 3.3 |
| 25 | 2.56 | 0.12 | 0.05 | 2.73 | 0.94 | 1.77±0.01 | 4100 | 16 900 | 4.1 |
| 30 | 2.59 | 0.14 | 0.05 | 2.78 | 0.93 | 1.97±0.01 | 4200 | 21 500 | 5.1 |
| 35 | 2.59 | 0.14 | 0.07 | 2.80 | 0.93 | 2.29±0.06 | 3600 | 19 700 | 5.5 |
| 40 | 2.65 | 0.17 | 0.06 | 2.88 | 0.92 | 2.39±0.06 | 3800 | 25 700 | 6.8 |

[a]Straw lignin.

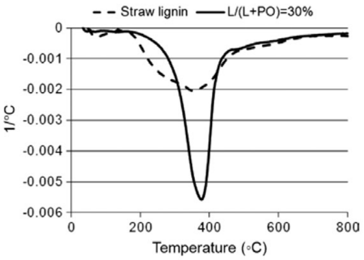

**Figure 8:** DTG curve of straw lignin and its oxypropylated derivative.

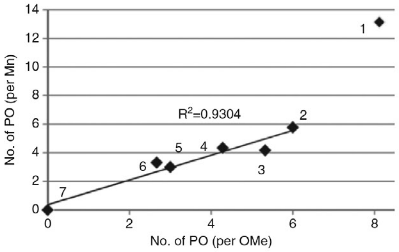

**Figure 9:** Average numbers of PO units grafted onto each OH function of straw lignin, calculated on the basis of the $M_n$ values of oxypropylated lignin derivatives vs. those calculated on the basis of methoxyl groups' content. Straw lignin content in the reaction mixture: (1) 15%; (2) 20%; (3) 25%; (4) 30%; (5) 35%; (6) 40%; and (7) 100%.

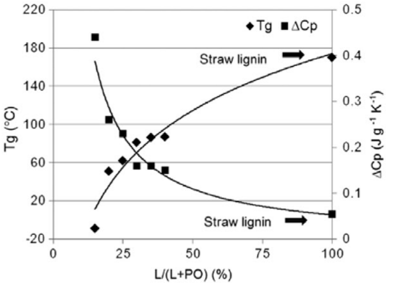

**Figure 10:** *Tg* and the corresponding $\Delta Cp$ for straw lignin and its oxypropylated derivatives vs. L/(L+PO) values.

The average numbers of PO units grafted onto each OH group of L, calculated on the basis of $M_n$ and OMe content, increases with decreasing L/(L+PO) values (Figure 9). Results calculated by both methods were similar for copolymers obtained at 20–40% of L. However, significant difference was observed for 15% of L content, which can be explained by overestimation of the molecular weight of copolymer due to higher hydrodynamic volumes of its macromolecule (Cateto et al. 2009).

Steady reduction of L/PO copolymers' *Tg* and increase of their $\Delta Cp$ with decreasing L content in the reaction mixture were observed (Figure 10). This can be explained by the increase of free molecular motion in copolymers relative to the straw lignin (Yoshida et al. 1987; Oliveira and Glasser 1989; Cui et al. 2013). According to DSC data, the extent of modification increased with decreasing L content in the reaction mixture. The batch OP successfully neutralized the lignins' molecular heterogeneity and diversity of its hydroxyl functionalities, and thus the control over the gelation of polyurethane networks was improved (Kelley et al. 1989). The PUR foams with $L_{\text{wheat straw}}$ based lignopolyols exhibit various beneficial properties compared to the foams obtained with commercial polyethers only (Arshanitsa et al. 2014).

## Reproducibility of the oxypropylation process

In the present work, 25 parallel syntheses were realized at 30% lignin content in the reaction mixture. The corresponding data are compiled in Table 4. The descriptive statistical analysis shows a normal distribution of the measured parameters for repeated experiments.

**Table 4:** Descriptive statistics of parameters of straw lignin OP and characteristics of lignopolyols obtained ($n$=25).

| | Parameters of OP | | | | Lignopolyol characteristics | |
|---|---|---|---|---|---|---|
| Statistical parameters | $T_{onset}$ (°C) | $T_{max}$ (°C) | $P_{max}$ (bar) | OHV (mg KOH $g^{-1}$) | Viscosity at 20°C (Pa·s) | Water cont. K.F. (%) |
| Mean | 164 | 241 | 24.7 | 447.3 | 57.5 | 0.05 |
| Median | 164 | 241 | 24.6 | 450.1 | 56.2 | 0.50 |
| Minimum | 161 | 235 | 24.0 | 409.2 | 50.1 | 0.03 |
| Maximum | 167 | 248 | 26.0 | 471.6 | 70.2 | 0.14 |
| Standard error | 0.35 | 0.64 | 0.10 | 2.80 | 1.11 | 0.02 |
| Standard deviation | 1.7 | 3.2 | 0.47 | 14.0 | 5.6 | 0.02 |
| [a]Coef. VA (%) | 1.0 | 1.3 | 1.9 | 3.1 | 9.7 | 40.0 |

[a]Variation coefficient.

Moreover, a high repeatability of OP parameters and the properties of the lignopolyols can be seen. The reproducibility of OHV values was higher than that of viscosity. The magnitude of the coefficient of variation did not exceeded 10%. The greatest data scattering was observed for the water content in lignopolyols. However, variations of these parameters do not influence the process of the further application of lignopolyols for PUR foam production. All 25 batches of lignopolyols (L/(L+PO)=30%) synthesized in this work were combined and successfully processed into PUR foam under the conditions of a commercial-scale equipment working with high-pressure spraying.

## Conclusions

A new type of wheat straw lignin, Biolignin™, was converted into liquid lignopolyol polyethers via bulk OP. The obtained lignopolyols consisted of two main constituents: the product of the interaction of the straw lignin with propylene oxide and derivatives of propylene glycol of different molecular weights. The grafting of oxypropyl chains onto the hydroxyl functions of the straw lignin was proven, and the structure and functionalities of the obtained oxypropylated products were characterized by a set of different independent chemical and physicochemical methods. The oxypropylated derivatives have a lower polydispersity and a higher segmental mobility, and the OH functionalities were converted to secondary aliphatic groups. The application of 30% lignin in the initiating mixture seems to be appropriate. The OP process and the properties of the obtained lignopolyols were highly reproducible.

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# Characteristics of wheat straw lignins from ethanol-based organosolv treatment

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ABSTRACT

Non-purified lignins resulting from ethanol-based organosolv fractionation of wheat straw were characterized for the presence of impurities (carbohydrates and ash), functional groups (hydroxyl, carboxyl and methoxyl), phenyl-propanoid structural moieties, molar mass distribution and thermal behavior. In accordance with its herbaceous nature, the syringyl/guaiacyl-ratio of the wheat straw lignins was substantially lower than of Alcell lignin. In addition, the content of *p*-hydroxyphenyl and carboxyl groups is substantially higher for the wheat straw lignins. The non-purified organosolv lignins had a high purity with 0.4–5.2% carbohydrate impurities, both originating from lignin to carbohydrate complexes and residual organosolv liquor. The use of $H_2SO_4$ in the organosolv process improved the lignin yield, but at low acid doses increased the carbohydrate impurities. For applications where a low amount of carbohydrates is important, lignin from a high-temperature autocatalytic organosolv process was found to be preferred. The highest content of total hydroxyl groups was determined when lignins were produced using 30 mM $H_2SO_4$ as catalyst or 50% w/w aqueous ethanol as solvent for the organosolv process. Aliphatic hydroxyl groups, the most predominant type of hydroxyl groups present originating for a substantial part from residual carbohydrates, were found to decrease with reaction time and ethanol proportion of the organosolv solvent. The correlations between organosolv process conditions and lignin characteristics determined can facilitate the use of organosolv lignins in value-added applications such as in polymers and resins and as a feedstock for bio-based aromatics.

## 1. Introduction

Lignin is the most abundant aromatic biopolymer in nature consisting of phenylpropane units that originate from three aromatic alcohol precursors (monolignols); i.e., *p*-coumaryl, coniferyl and sinapyl alcohol (Fengel and Wegener, 2003; Ghaffar and Fan, 2013). The cross-linked phenolic substructures that originate from these monolignols are defined as *p*-hydroxyphenyl (H, from coumaryl alcohol), guaiacyl (G, from coniferyl alcohol) and syringyl (S, from sinapyl alcohol) structural moieties (Fengel and Wegener, 2003; Buranov and Mazza, 2008). Cereal straw lignin is a GSH-type lignin containing all three monolignols (Dence and Lin, 1992). The composition of degradation products of lignins from wheat straw by thioacidolysis shows that the proportion of H, G, and S is 5, 49, 46% (Buranov and Mazza, 2008). During the biological lignification process, the monolignols form a complex network closely associated with hemicelluloses. Hydroxycinnamic acids (ferulic and *p*-coumaric) act as cross-linking agent between lignin and carbohydrates forming so-called lignin–hydroxycinnamate–carbohydrate complexes (Sun, 2010). The major inter-unit linkages within lignin are of an ether type with around 50% β-*O*-4 ether linkages (Ghaffar and Fan, 2013).

Lignin's aromatic nature makes it a potential renewable source of (aromatic) chemicals and performance products (Hu, 2002; Lora and Glasser, 2002; Bozell et al., 2007; Stewart, 2008; Zakzeski et al., 2010). Potential applications of lignins from various sources include the production of chemicals such as phenol(ics) and BTX (benzene, toluene and xylene) (Zakzeski et al., 2010). The use of lignin in various material applications has been studied such as phenolic resins (Da Silva et al., 2013; Lora and Glasser, 2002; Stewart, 2008), polyurethanes (Lora and Glasser, 2002; Pan and Saddler, 2013), epoxy resins (Lora and Glasser, 2002; Stewart, 2008), and carbon fibers (Hu, 2002; Pan, 2013). Finally, the use of lignin as antioxidant has been reported (Dizhbite et al., 2004; Pan et al., 2006; El Hage et al., 2012). In spite of the various potential applications, the current industrial use of lignin is still limited due to

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limited industrial supply and challenging lignin properties such as its complex and non-uniform chemical structure (Vishtal and Kraslawski, 2011). However, the expected substantial increase in available technical lignins from pulp and paper processes, lignocellulosic biofuels production and biorefineries as well as lignin's unique chemical structure warrant additional research to develop (new) outlets (Vishtal and Kraslawski, 2011).

The desired lignin characteristics depend on the application. Monteil-Rivera et al. (2013) provide an interesting discussion on the required lignin properties for various applications. For example, molar mass (polydispersity) and (total) OH content are physicochemical lignin characteristics that are important for the use of lignins in lignin-polymer blends. For many applications, lignins having a high purity, i.e. low in ash, residual carbohydrates etc. are preferred. Isolation of lignin from lignocellulosic biomass e.g. by using organic solvents (organosolv) enables production of such high-purity lignins (Pan, 2013).

Organosolv fractionation is considered to be a promising biorefinery approach given the coproduction of cellulose products (e.g., fibers or enzymatically digestibly cellulose), high-purity lignin and hemicellulose-derived products such as xylose, furfural and acetic acid (Zhao et al., 2009; Pan, 2013). Coproduction of these materials seems critical to improve the cost-effectiveness of biorefinery schemes for second generation biofuels such as bioethanol. Organosolv processes currently operated at pilot-scale include the ethanol-based process of Lignol in Burnaby, BC, Canada (former Alcell® process) (Arato et al., 2005) and the acetic and formic acid-based process from CIMV in Pomacle, Champagnes-Ardennes, France (Delmas et al., 2011).

Characterization of lignins produced including dependency on the organosolv process conditions is a prerequisite for the development of value-added lignin applications and, thereby, an economically viable organosolv biorefinery concept. In the literature, lignins extracted by ethanol-based organosolv processes have been widely studied for various types of biomass such as loblolly pine (Sannigraphi et al., 2010), switchgrass (Hu et al., 2012), flax (Buranov et al., 2010; Monteil-Rivera et al., 2013), fiber hemp (Zomers et al., 1995; Monteil-Rivera et al., 2013) and wheat straw (Monteil-Rivera et al., 2013). Characterization of organosolv lignins including correlation to organosolv process conditions have been reported for bagasse (Vallejos et al., 2011), hybrid poplar (Pan et al., 2006), olive tree pruning (Toledano et al., 2011) and Miscanthus (El Hage et al., 2010). However, in most studies washed or otherwise purified lignins have been used in order to remove non-bonded impurities and to be able to study the chemistry occurring during the organosolv process. Whether the lignin product will be washed or otherwise purified in an industrial organosolv process depends on the economic trade-off between potentially improved lignin application possibilities and additional costs for the purification step. In this study, we focused on non-purified organosolv wheat straw lignins.

The objective of this paper is to characterize non-purified lignins resulting from an earlier study in which we reported on ethanol-based organosolv pretreatment of wheat straw for enzymatic cellulose hydrolysis (Wildschut et al., 2013). Wheat straw is an attractive low-cost feedstock for the production of bio-based chemicals because of its annual renewability and abundance, being an agricultural residue from the production of cereals (Buranov and Mazza, 2008; Sun, 2010). In this study, selected wheat straw lignins will be analyzed for their composition (carbohydrate and ash impurities), physical properties as molar mass distribution (SEC), thermal degradation (TGA) and glass-transition temperature (DSC), as well as hydroxyl, carboxyl and methoxyl functional groups (both by wet chemical methods and $^{31}$P-NMR). The influence of the organosolv process conditions on the lignin characteristics will be assessed. Alcell® lignin, an ethanol organosolv hardwood lignin, will be used as a reference lignin.

## 2. Materials and methods

### 2.1. Lignin samples

Lignin samples from an earlier study (Wildschut et al., 2013), in which lignin was isolated from wheat straw using an ethanol-based organosolv process, were selected for characterization such that the influence of the main process parameters of the organosolv process on the lignin characteristics could be assessed. In addition, the optimum process conditions for enzymatic cellulose digestibility and lignin yield were included (Wildschut et al., 2013). Table 1 gives an overview of selected lignin samples including the organosolv process conditions used. In addition to the wheat straw organosolv lignins, Alcell® (here and further Alcell) lignin was included in all lignin characterizations as a reference material. Alcell ethanol–water organosolv lignin from mixed hardwoods was obtained from Repap Technologies, Canada.

The methods used for the organosolv delignification experiments as well as the analysis method used to determine the lignin content of the resulting wheat straw pulp and thereby the delignification degree have been reported earlier (Wildschut et al., 2013). The summative composition of the wheat straw was (% w/w, dry basis): glucan, 35.4; xylan, 19.8; arabinan, 2.1; galactan, 1.4; lignin, 17.6; ash, 3.5; extractives, 10.2 (Wildschut et al., 2013). The elemental composition was (%): C 47.3, H 6.4, N 0.7, and O 44.6 (Wildschut et al., 2013). The liquids resulting from the organosolv process, i.e. the "organosolv liquor" and the solution resulting from pulp washing, were combined and added to chilled water to separate the dissolved lignin by precipitation (4 °C, 3:1 w/w dilution ratio $H_2O$: organosolv liquor). Precipitated lignin particles were sedimented by centrifugation, the liquor was decanted and the lignin was dried. No further purification steps, such as washing, were applied on the lignin. For more details on the lignin isolation procedure, we refer to Huijgen et al. (2010). Analysis of the sugar content of the combined liquors was performed by High Performance Anion Exchange Chromatography with Pulsed Amperometric Detection (HPAEC-PAD) after post-hydrolysis of oligomeric sugars present, as described earlier (Huijgen et al., 2012).

### 2.2. Lignin composition

The dry matter content (DM) was measured using a halogen moisture analyzer (Mettler Toledo HR83, Columbus, OH). The ash content was determined in duplicate using thermogravimetric analysis under air (Mettler Toledo TGA 850, Columbus, OH). 10 mg of sample was heated with 10 °C/min to 900 °C, including an isothermal interval at 105 °C to determine the dry weight of the sample.

The residual carbohydrate content of the lignin samples was determined using an analytical procedure for summative composition analysis of lignocellulosic biomass, which has been reported in earlier work (Huijgen et al., 2011, 2012) and is based on the standard Laboratory Analytical Procedures (LAP) of NREL (Golden, CO) (National Renewable Energy Laboratory (NREL), 2009). The lignin samples were finely crushed to powder and hydrolyzed in two steps: (1) 12 M (72% w/w) $H_2SO_4$ (30 °C, 1 h) and (2) 1.2 M $H_2SO_4$ (100 °C, 3 h). The acid-insoluble lignin (AIL) content was defined as the amount of ash-free Klason lignin (i.e., the solid residue corrected for its ash content according to NREL/TP-510-42618 (National Renewable Energy Laboratory (NREL), 2009)). The hydrolysate was analyzed for acid-soluble lignin (ASL, UV-absorption at 205 nm) as well as monomeric sugars

**Table 1**
Characteristics of the organosolv process used for the production of the lignin samples (Wildschut et al., 2013).

| Sample | Key feature sample/process parameter changed | Organosolv process conditions[a] | | | | | Results organosolv process | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $T$ (°C) | $t$ (min) | $[H_2SO_4]$ (mmol/L) | Content EtOH in aqueous ethanol (wt%) | Pulp yield (% dw) | Residual lignin in pulp (%)[b] | Yield isolated lignin (%)[b] | Mass balance lignin[c] (%)[b] |
| 1 | Starting point of study | 190 | 60 | 0 | 60 | 67.7 | 62.3 | 46.3 | 108.6 |
| 2 | Temperature | 200 | 60 | 0 | 60 | 63.2 | 50.9 | 58.9 | 109.8 |
| 3 | Temperature | 210 | 60 | 0 | 60 | 53.5 | 39.9 | 73.2 | 113.0 |
| 4 | Ethanol content organosolv solvent | 190 | 60 | 0 | 50 | 64.3 | 61.2 | 55.8 | 117.0 |
| 5 | Ethanol content organosolv solvent | 190 | 60 | 0 | 80 | 79.3 | 79.2 | 28.9 | 108.1 |
| 6 | Time of treatment | 190 | 90 | 0 | 60 | 65.6 | 53.5 | 54.4 | 108.0 |
| 7 | Time of treatment | 190 | 120 | 0 | 60 | 64.0 | 51.2 | 60.0 | 111.2 |
| 8 | Catalyst dose | 190 | 60 | 15 | 60 | 62.6 | 47.2 | 60.2 | 107.4 |
| 9 | Catalyst dose | 190 | 60 | 30 | 60 | 43.0 | 24.2 | 85.4 | 109.5 |
| 10 | Optimum conditions for enzymatic hydrolysis | 210 | 90 | 0 | 50 | 48.6 | 40.9 | 83.1 | 124.0 |
| 11 | Optimum conditions for lignin yield | 210 | 90 | 15 | 60 | 48.1 | 31.1 | 97.6 | 128.7 |

[a] Liquor-to-solid ratio of 10 l/kg.
[b] Based on lignin content feedstock (AIL + ASL).
[c] Sum of residual lignin in pulp and isolated lignin yield.

(after neutralization of the hydrolysate using $BaCO_3$). Analysis of monomeric sugars was performed using HPAEC-PAD, using a method that has been reported before (Huijgen et al., 2012). No correction factors for possible sugar degradation during hydrolysis were applied.

### 2.3. *Physical properties*

#### 2.3.1. *Molar mass distribution*

Molar mass distribution of lignin was determined in duplicate using alkaline size exclusion chromatography (SEC) according to Gosselink et al. (2010). 0.5 M NaOH was used to dissolve the lignin samples and as eluent (Gosselink et al., 2004, 2010). The following modifications were made to the published protocol: a column temperature of 40 °C, a flow rate of 1 ml/min and a home-packed column with Toyopearl HW-55 F of 7.8 mm ID × 3/8″ OD × 300 mm L were used.

#### 2.3.2. *Thermal degradation*

The thermal degradation behavior of the lignin samples was studied by thermogravimetric analysis (TGA) analysis using a Mettler Toledo Star system (TGA/SDTA851) and an inert nitrogen atmosphere. Regime: temperature range 20–1000 °C, heating rate 10 °C/min, sample weight ~8.000 mg. Analysis was performed in duplicate.

#### 2.3.3. *Glass transition temperature*

The glass transition temperature was measured using Differential Scanning Calorimetry (DSC). 8–10 mg of sample was analyzed with a Mettler Toledo DSC 823. The temperature program consisted of three stages: heating from 20 to 140 °C (rate 20 °C/min), holding time 5 min, quenching from 140 °C to −50 °C (rate 20 °C/min), holding time 5 min, and finally heating from −50 to 200 °C (rate 10 °C/min). The final heating run was used for analysis.

### 2.4. *Functional groups*

The presence of functional groups was determined both by wet chemical methods (Section 2.4.1) and by $^{31}$P-NMR (Section 2.4.2).

#### 2.4.1. *Wet chemical analysis*

The content of methoxyl and (carboxylic, aliphatic and phenolic) hydroxyl groups was determined using wet chemical methods described by Zakis (1994). For each analysis, 3–5 repeated measurements were performed. All samples were vacuum dried at 50 °C during 48 h before analysis.

In short, the content of methoxyl groups was determined using 57% HI for splitting of $CH_3I$ followed by three subsequent quantitative reactions yielding free $I_2$ and titrating $I_2$ with thiosulfate (Zeisel–Vieböck–Schwappach method) (Zakis, 1994).

Lignin hydroxyl groups (OH total) consisting of phenolic OH, aliphatic OH and carboxylic OH. Firstly, carboxyl groups were determined using a calcium acetate-based chemisorption method. Secondly, the sum of phenolic hydroxyl and carboxyl groups (i.e., acid hydroxyl groups) was determined using $BaCl_2$-based chemisorption. The phenolic hydroxyl content was calculated from the difference between both chemisorption methods. Subsequently, the lignin samples were acetylated during 24 h at 50 °C using acetic anhydride and pyridine as catalyst (Verley's method, see Zakis (1994)). The excess of acetic anhydride was decomposed by water into free acetic acid, which was titrated with 0.1 N KOH. Lignin sample size was chosen such that the volume of KOH solution used for the titration was less than 80% of the quantity required for titration of the blank sample. Difference between amount of acetic acid determined for the lignin and blank samples was used for calculation of the 'OH acet.' groups content. Finally, aliphatic OH

**Table 2**
Composition of lignin samples.

| Sample | DM[a] (%) | Carbohydrates (% dw)[b] | | | | | | Ash (% dw) | Lignin (% dw) | | Sum (% dw) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Arabinan | Xylan | Galactan | Glucan | Sum | Ratio C5:C6 | | AIL[c] | ASL[d] | |
| 1 | 97.0 | 0.4 ± 0.0 | 1.7 ± 0.1 | 0.3 ± 0.0 | 1.2 ± 0.6 | *3.6* | *1.4* | 1.5 ± 0.0[e] | 88.2 ± 0.3 | 2.7 ± 0.0 | 96.0 ± 1.0 |
| 2 | 97.8 | 0.1 ± 0.0 | 0.9 ± 0.0 | 0.1 ± 0.0 | 0.4 ± 0.0 | *1.6* | *1.8* | 0.9 ± 0.1[e] | 94.1 ± 0.3 | 1.4 ± 0.0 | 98.0 ± 0.4 |
| 3 | 97.3 | 0.1 ± 0.0 | 0.5 ± 0.0 | 0.1 ± 0.0 | 0.3 ± 0.0 | *1.0* | *1.6* | 1.0 ± 0.1[e] | 94.9 ± 0.2 | 1.8 ± 0.0 | 98.6 ± 0.3 |
| 4 | 96.4 | 0.5 ± 0.0 | 3.3 ± 0.0 | 0.4 ± 0.0 | 0.7 ± 0.0 | *4.9* | *3.4* | 1.7 ± 0.0[e] | 86.5 ± 0.2 | 1.9 ± 0.0 | 95.0 ± 0.3 |
| 5 | ND[f,g] | 0.1[h] | 0.1[h] | 0.1[h] | 0.5[h] | *0.8* | *0.4* | ND[f] | 95.0[h] | 1.1[h] | 96.9 |
| 6 | 97.1 | 0.3 ± 0.0 | 1.3 ± 0.0 | 0.2 ± 0.0 | 0.5 ± 0.0 | *2.3* | *2.2* | 1.4 ± 0.0[e] | 91.9 ± 0.4 | 1.4 ± 0.0 | 97.1 ± 0.4 |
| 7 | 97.4 | 0.1 ± 0.0 | 0.7 ± 0.0 | 0.1 ± 0.0 | 0.4 ± 0.0 | *1.3* | *1.6* | ND[f] | 96.3 ± 0.4 | 1.2 ± 0.0 | 98.8 ± 0.4 |
| 8 | 96.9 | 0.5 ± 0.0 | 3.7 ± 0.0 | 0.3 ± 0.0 | 0.7 ± 0.0 | *5.2* | *4.3* | ND[f] | 88.6 ± 0.3 | 1.4 ± 0.0 | 95.3 ± 0.2 |
| 9 | 96.8 | 0.5 ± 0.0 | 1.0 ± 0.1 | 0.1 ± 0.0 | 0.4 ± 0.0 | *2.0* | *3.1* | 0.1 ± 0.0[e] | 92.7 ± 0.3 | 1.1 ± 0.0 | 95.9 ± 0.4 |
| 10 | 97.3 | <0.02 | 0.1 ± 0.0 | 0.0 ± 0.0 | 0.2 ± 0.0 | *0.4* | *0.6* | 0.7 ± 0.1[e] | 95.9[g] | 2.0 ± 0.1 | 99.0 ± 0.2 |
| 11 | 95.8 | 0.0 ± 0.0 | 0.4 ± 0.0 | 0.0 ± 0.0 | 0.3 ± 0.0 | *0.8* | *1.3* | 1.1 ± 0.0[e] | 96.2 ± 0.5 | 1.5 ± 0.0 | 99.7 ± 0.5 |
| Alcell (De Wild et al., 2012) | 96.9 | <0.05 | 0.1 ± 0.0 | <0.05 | 0.1 ± 0.0 | *0.1*[i] | *1.9* | 0.0 ± 0.0[j] | 93.8 ± 0.3 | 1.9 ± 0.0 | 95.8 ± 0.2 |

[a] Dry matter content.
[b] Mannan and rhamnan below detection limit in all cases.
[c] Acid-insoluble lignin: ash-corrected gravimetric residue $H_2SO_4$ hydrolysis; includes 'pseudo-lignin'. No correction for N-content (protein derivatives) was made (National Renewable Energy Laboratory (NREL), 2009).
[d] Acid-soluble lignin: determined by UV absorption using a standard absorption coefficient of 110 L/g cm (Huijgen et al., 2012).
[e] Determined by TGA.
[f] Not determined.
[g] Estimated dry matter content of 97.0% used in calculations.
[h] Single measurement.
[i] A round robin within the 'Eurolignin' network using a similar approach resulted in 0.3 dw% total carbohydrate impurities (Baumberger et al., 2007).
[j] Determined in duplicate by combustion at 550 °C according to NREL/TP-510-42622 (National Renewable Energy Laboratory (NREL), 2009).

was calculated as: 'OH acet.' + carboxylic OH—phenolic OH (Zakis, 1994).

### 2.4.2. $^{31}$P-NMR

The use of $^{31}$P-NMR for lignin characterization has been reviewed extensively by Pu et al. (2011). Lignin samples were analyzed in duplicate using $^{31}$P-NMR according to Gosselink et al. (2010). In a 1 ml vial, 30 mg of lignin was mixed with 100 μl DMF/pyridine (1:1 v/v) and 100 μl internal standard solution containing 15 mg/ml cyclohexanol (internal standard) and 2.5 mg/ml chromium(III) acetylacetonate in pyridine. This suspension was stirred overnight at room temperature. Derivatization (100 μl) reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane) was mixed with 400 μl of deuterated chloroform ($CDCl_3$) prior to addition to the lignin suspension. After mixing, the mixture was analyzed by NMR (Bruker 400 MHz), with 30° pulse angle, inverse gated proton decoupling, a delay time of 5 s and 256 scans. Signal assignment was performed as described by Granata and Argyropoulos (1995). The results are expressed on a dry lignin weight basis. The moisture content of the lignins samples was determined by drying at 105 °C overnight till constant weight.

## 3. Results and discussion

### 3.1. Delignification and lignin yield

The organosolv process conditions have a clear influence on the lignin yield (Table 1) (Wildschut et al., 2013). The yield of precipitated lignin increases with reaction temperature, time and sulfuric acid dose, while it decreases as a function of the EtOH proportion of the solvent (in the range of 50–80% w/w EtOH). The maximum lignin yield is 97.6% w/w based on the lignin content of the feedstock (experiment 11). The sum of the lignin yield and the residual lignin in the pulp is in all cases >100% (Table 1), which indicates the formation of 'pseudo-lignin' (as well as possibly 'furan derived humins'). 'Pseudo-lignin' is a product of lignin condensation with extractives, proteins and hemicellulose derived products such as furfural that cannot be distinguished from native lignin by the analytical hydrolysis protocol used (Section 2.2). Formation of 'pseudo-lignin' during alcohol-based organosolv process has been reported previously in literature (Zhao et al., 2009; Huijgen et al., 2011). Also for other lignocellulose processes, the incorporation of carbohydrates degradation products in the lignin matrix has been discussed in literature, e.g. for wheat straw soda lignin (Bikova et al., 2006) and softwood acid-catalyzed hydrolysis (Dizhbite et al., 2011). The highest sum of the lignin yield and residual lignin in the pulp (>120%) was found for experiments 10 and 11, the optima for enzymatic cellulose hydrolysis and lignin yield, respectively. In these experiments, the highest reaction temperature (210 °C) was combined with a prolonged reaction time as well as a low ethanol–water ratio or added $H_2SO_4$. A high temperature at acidic conditions promotes the dehydration of hemicellulose sugars to furfural and thereby the formation of a lignin–furfural condensation product.

### 3.2. Composition lignin

The amount of carbohydrate impurities varies between 0.4 and 5.2% w/w depending on the organosolv process conditions (Table 2). The non-purified wheat straw lignins show a higher amount of carbohydrate impurities than the washed Alcell reference lignin (0.1–0.3% w/w, see Table 2) (Arato et al., 2005). Carbohydrates present in lignins might originate from polysaccharides covalently bonded to the lignin in the wheat straw. In literature, covalent bonds between lignin and hemicellulose have been widely discussed (Fengel and Wegener, 2003; Monteil-Rivera et al., 2013; Sun, 2010). However, since in this study the wheat straw lignins were not washed or otherwise purified, carbohydrate impurities might also (partly) originate from residual organosolv liquor adhering to the precipitated and sedimented lignin particles. Fig. 1 shows the correlation between the carbohydrate impurities present in the lignins and the concentration of sugars in the corresponding organosolv liquor. Interestingly, for galactose, xylose and arabinose the amount of a particular carbohydrate present in the lignin seems to depend on the concentration of that carbohydrate in the liquor (with the noticeable exception of lignins 2, 7 and 9). For glucose, results are less conclusive. However, it seems that for most lignins the carbohydrate impurities originate for some part from hydrolyzed (oligomeric) sugars in residual organosolv liquor. Thus, it seems that the lignin purity might be further increased

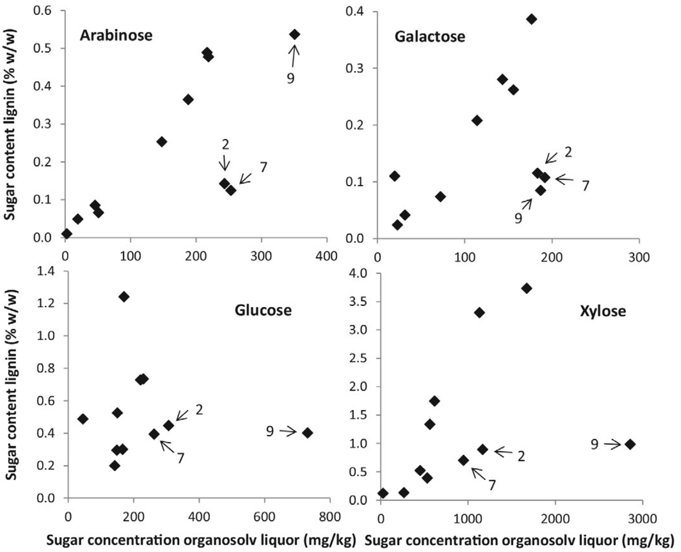

**Fig. 1.** Content of carbohydrate impurities in lignin compared to the concentration of sugars in organosolv liquor determined after post-hydrolysis.

by extensive washing procedures. Lignins 2, 7 and 9 deviate from this correlation for all sugars (Fig. 1). Lignin 9 is the only lignin produced at acidic conditions due to the use of 30 mM $H_2SO_4$ as catalyst (organosolv liquor pH 3.3, in all other cases pH >4 (Wildschut et al., 2013)). Lignins 2 and 7 were produced at a later date than the other lignins. In the meantime, the protocol used for lignin isolation had been improved resulting in less adhering moisture to the sedimented lignin precipitate and, thereby, lower amounts of residual carbohydrates.

The total carbohydrate content decreases upon higher organosolv temperatures, ethanol proportion and reaction time. The high amount of carbohydrate impurities (4.9% w/w) of lignin 4, in which 50% w/w aqueous ethanol is used as solvent, is probably due to increased hemicellulose hydrolysis resulting in higher concentrations of sugars in the organosolv liquor (Fig. 1). The use of sulfuric acid as a catalyst first increases the amount of carbohydrate impurities from 3.6% w/w without $H_2SO_4$ to 5.2% w/w using 15 mM $H_2SO_4$. However, at the highest dose of 30 mM $H_2SO_4$ (experiment 9), the amount of sugars has been decreased to 2.0% w/w. It seems that $H_2SO_4$ acts as catalyst for two competitive processes: hydrolysis of polysaccharides (leading to higher amount of carbohydrates in the residual organosolv liquor) and lignin condensation reactions (formation of inter- and intra-molecular bonds including those with residual or cleaved carbohydrates and their acid-catalyzed degradation products). In addition, ethoxylation of sugars occurs at the higher catalyst dose possibly changing the interaction of carbohydrates with lignin.

Interestingly, the process conditions, except the organosolv temperature, also affect the ratio between C5 and C6 sugars present in the lignin, varying from 0.6 to 5.1 (Table 2). The largest effect is observed for the $H_2SO_4$ dose. Addition of 15 mM $H_2SO_4$ increases the C5:C6 ratio from 1.4 (experiment 1) to 4.3 (experiment 8), substantiating the hypothesis that the carbohydrate impurities originate from the adhering liquor rather than lignin–carbohydrate complexes. A higher $H_2SO_4$ dose increases hydrolysis of the hemicellulose during the organosolv process, leading to particularly more C5 sugars in the liquor. Experiments 10 and 11 (i.e., optimum conditions for enzymatic digestibility and lignin yield, respectively) show the lowest ratio of C5:C6 sugars. At these severe conditions, most sugars formed upon hydrolysis degrade to furfural leading to a high amount of pseudo-lignin and low amount of carbohydrate impurities.

The ash content of the wheat straw lignins (Table 2) is generally substantially higher than that of Alcell hardwood lignin as well as of previously reported wheat straw organosolv lignins (De Wild et al., 2012) (except lignin 9). The lower ash content of hardwood Alcell lignin is due to the different type of biomass from which it originates. The reason for the higher ash contents compared to those of earlier wheat straw lignins is unknown, but might be attributed to differences in biomass used (e.g. different growing conditions, type of soil, time of storage of straw in open air (leaching of ash by rain fall)). It could also be that drying of adhering organosolv liquor plays a role, although lignin 2 (produced with the improved lignin production protocol, see above) did not show a substantially lower ash content. Finally, the pH used for organosolv pulping seems to affect the ash content since lignin 9 (30 mM $H_2SO_4$ case) shows a remarkably lower ash content.

### *3.3. Physical properties*

#### *3.3.1. Molar mass distribution*

Organosolv lignins generally have a low molar mass and polydispersity compared to other types of lignin (Gosselink et al., 2010). For lignins, size exclusion chromatography (SEC) mainly gives relative molar mass values, since the absolute molar mass of lignins determined by SEC is known to be dependent on the set-up used

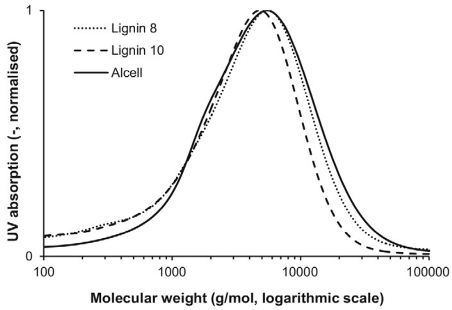

**Fig. 2.** Molar mass distribution of lignins 8 (lowest Mw of wheat straw lignins), 10 (highest Mw), and Alcell lignin.

(Gosselink et al., 2004), including way of packing of the columns, as well as on the calibration and calculation methods applied. Therefore, in this paper SEC results are used only relatively without discussing the absolute mass-average molar mass (Mw) and polydispersity (PD) determined.

Fig. 2 shows, as example, the molar mass distribution of lignins 8, 10 and Alcell. Lignins 8 and 10 were found to have the lowest and highest mass-average molar mass of the wheat straw lignins studied. No significant effect of the organosolv process conditions within the ranges studied was found on the molar mass distribution of the wheat straw-derived lignins. The average molar mass of all wheat straw lignins was lower than that of the reference Alcell lignin.

### *3.3.2. Thermal degradation*

Thermogravimetric analysis was used to study the pyrolytic thermal stability of the wheat straw and Alcell lignins. Fig. 3 shows the thermogravimetric (TGA) weight loss curves and their first derivatives (DTG) for lignins 5, 6, 9 and Alcell as example. The volatiles content and residual char were determined from the TGA weight loss curve. The peak in the DTG curve corresponds to the temperature at which the lignins exhibit the maximum rate of degradation. The determined inflection points of maximum rate of degradation are for lignin 5: 360 °C, lignin 6: 354 °C, lignin 9: 359 °C and Alcell lignin: 374 °C, which are typical values for technical lignins such as Kraft, steam explosion and organosolv lignins (Gaur and Reed, 1998; De Wild et al., 2012; Monteil-Rivera et al., 2013). In general, lignins such as ball milled wood lignin that are generally considered to resemble the native form of lignin in the plant more than technical lignins show a lower temperature at which the thermal degradation is at its maximum (typical values around 316–330 °C (Gaur and Reed, 1998)). In these lignins, the easily degradable β-*O*-4 intramolecular ether linkages are more abundant compared to technical lignins. The DTG curves show a low-temperature shoulder in between 200 and 300 °C, which indicates the possible existence of a thermally less stable domain within the lignin polymer. Finally, a number of samples showed (limited) weight loss between 150 and 200 °C, which might be attributed to coprecipitated or condensed proteins and hemicellulose degradation products (Toledano et al., 2011).

The residual weight at 900 °C of lignin 5 is with 29.5% w/w substantially lower than that of the other wheat straw lignins and Alcell (35.2–40.1% w/w). The latter does not seem to be related with the relatively low content of residual carbohydrates in lignin 5 (Table 2), but rather with the low total amount of OH groups in this sample (Section 3.4). It is known that thermal treatment of lignin is accompanied by condensation processes with participation of OH groups of lignin. These processes proceed in the temperature range of 150–270 °C and finally led to the formation of unsaturated C=C and C—C bonds. As a result, the yield of residual char at high-temperature treatment is enhanced. Obviously, because the total OH groups in lignin 5 is lowest from all samples under study (see Section 3.4) the processes of condensation take place in less extent in comparison with other lignins and therefore the yield of char is reduced correspondingly.

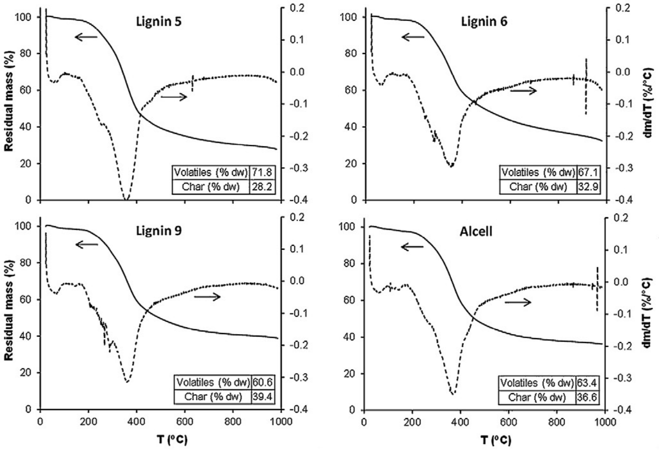

**Fig. 3.** Thermogravimetric TG (A) and differential thermogravimetric curves DTG (B) of lignins 5, 6, 9, and Alcell lignin.

**Table 3**
Glass transition temperatures of lignin samples.

| Sample | Tg (°C) |
|---|---|
| 1 | 110 |
| 2 | 110 |
| 3 | 97 |
| 4 | 110 (59)[a] |
| 5 | 133 (14)[a] |
| 6 | 112 (8)[a] |
| 7 | 110 |
| 8 | 119 |
| 9 | 116 |
| 10 | 87 |
| 11 | 103 |
| Alcell | 100 |

[a] Number between brackets: additional low-temperature inflection point of DSC curve.

### 3.3.3. Glass transition temperature

Table 3 shows the determined glass-transition points (Tg) using differential scanning calorimetry (DSC). Typical DSC graphs of organosolv lignins are given in Fig. 4, showing lignin 1 (reference point), lignin 8 (highest in carbohydrate residues), lignin 10 (lowest in carbohydrate residues) and Alcell lignin.

Determined glass transition temperatures were between 87 (lignin 10) and 133 °C (lignin 5). For Alcell, a Tg of 100 °C was determined. Approximately the same value of Tg (97 °C) of Alcell lignin was reported by Lora and Glasser (2002). A high process temperature seems to reduce the Tg since the three experiments at 210 °C showed the three lowest glass transition points, although no difference between lignins 1 and 2 (190 and 200 °C) was observed. Interestingly, a correlation could be made between the average molar mass (Mw) and the Tg showing that a lower Mw results in a lower Tg, except for lignin 5 (Fig. 5). Lignin 5 (80% w/w EtOH) showed a substantially higher Tg than all other lignins, but the organosolv conditions at which this lignin was produced allowed isolation of only 28.9% of the initial lignin present in wheat straw (Table 1). If we leave lignin 5 out of consideration, lignins 10 and 8 resulted in the lowest and highest Tg and Mw, respectively (Fig. 5). These lignins also showed the lowest and highest amount of carbohydrate residues, respectively, although no correlation between the amount of carbohydrate residues and Tg could be determined based on all wheat straw lignins.

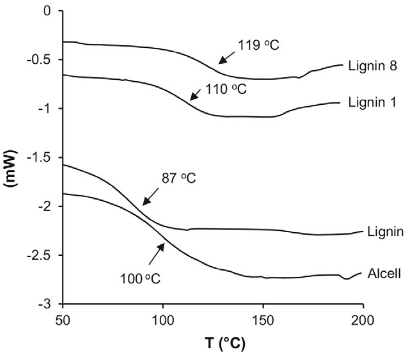

**Fig. 4.** DSC curves of lignin 1, lignin 8 (highest in residual carbohydrates), lignin 10 (lowest in residual carbohydrates), and Alcell lignin.

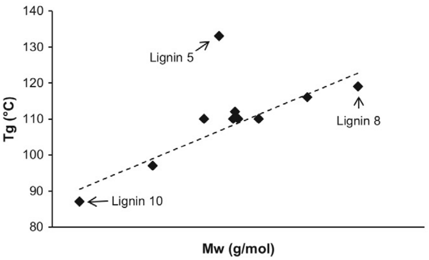

**Fig. 5.** Comparison of glass-transition temperature (Tg, Table 3) with mass-average molar mass (Mw).

The Tg of lignin as amorphous polymer reflects the segmental mobility of lignin polymeric chains at heat treatment and depends on a lot of factors including molar mass distribution (see Section 3.1.1), crosslinking degree, hydrogen bonding and presence of low molecular admixtures that act as a plasticizer increasing the free volume of polymer (Ghaffar and Fan, 2013). It is difficult to quantitatively estimate the input of each factor. Therefore, direct correlation between organosolv process conditions and Tg of lignin obtained was not observed. However, we can conclude that the Tg of most wheat straw lignins under study is in the range of 97–119 °C and do not differ significantly from reference Alcell lignin (Table 3). The ethanol-based organosolv process seems to produce lignin with a comparatively low-crosslinked structure independently of raw material origin (hardwood and wheat straw) and process conditions.

Data analysis for lignins 4–6 showed a second inflection point in the DSC curve at a low temperature (<60 °C). For all other lignins, no low-temperature inflection point was found. The presence of this second inflection point seems to indicate that these samples are not fully homogenous because of phase separation. Presence of the second phase immiscible with the main lignin phase might be explained by extractives incorporated from native wheat straw.

## 3.4. Functional groups

Analysis of functional groups using wet chemical methods (Table 4) and $^{31}$P-NMR (Table 5) resulted in substantial discrepancies between results. First, the influence of the organosolv process conditions on the content of functional groups as determined by wet chemical methods (Section 3.4.1) and $^{31}$P-NMR (Section 3.4.2) will be discussed separately. Subsequently, the differences between the analyses will be discussed in Section 3.4.3.

### 3.4.1. Wet chemistry

Wheat straw lignins contain lower amount of methoxyl groups (3.3–4.7 mmol/g) than Alcell lignin (5.6 mmol/g) as determined by wet chemistry (Table 4). Wheat straw lignins most rich in methoxyl groups are those resulting from a $H_2SO_4$-catalysed process (experiments 8 and 9). However, it should be noted that the method used to determine methoxyl groups cannot distinguish between methoxyl and ethoxyl groups (Zakis, 1994; Monteil-Rivera et al., 2013). A part of the methoxyl groups determined will therefore in fact probably be ethoxyl groups resulting from etherification of aliphatic OHs or esterification of carboxyl groups during the organosolv process.

In contrast to the methoxyl groups, the total amount of hydroxyl groups is in most cases higher for the wheat straw lignins (6.7–8.6 mmol/g) than for Alcell lignin (6.6 mmol/g) (Table 4). Only lignin 10 has a slightly lower amount of hydroxyl groups

**Table 4**
Functional groups by wet chemistry.

| Sample | Content of functional groups (mmol/g dw)[a] | | | | |
|---|---|---|---|---|---|
| | Hydroxyl | | | | Methoxyl |
| | $OH_{COOH}$ | $OH_{phenolic}$ | $OH_{aliphatic}$ | $OH_{total}$ | $OCH_3$ |
| 1 | 1.12 | 0.97 | 5.94 | 8.03 | 3.95 |
| 2 | 0.88 | 0.78 | 5.46 | 7.12 | 3.96 |
| 3 | 0.76 | 0.85 | 5.48 | 7.09 | 3.76 |
| 4 | 1.14 | 0.82 | 6.61 | 8.57 | 3.91 |
| 5 | 0.86 | 0.94 | 5.09 | 6.89 | 3.29 |
| 6 | 0.96 | 0.46 | 5.80 | 7.22 | 3.70 |
| 7 | 0.62 | 0.81 | 5.27 | 6.70 | 3.85 |
| 8 | 1.01 | 1.06 | 5.52 | 7.59 | 4.16 |
| 9 | 1.39 | 0.70 | 6.32 | 8.41 | 4.68 |
| 10 | 0.49 | 1.36 | 4.52 | 6.37 | 3.87 |
| 11 | 0.72 | 0.63 | 5.33 | 6.68 | 3.63 |
| Alcell | 0.94 | 2.47 | 3.24 | 6.65 | 5.58 |

[a] Standard deviation for $OH_{acet}$, $OH_{phen+COOH}$ ($BaCl_2$ method), and $OH_{COOH}$ (CaAC method) is ≤10%. Standard deviation for $OCH_3$ is 3–6%. Standard deviation for phenolic, aliphatic and total OH cannot be indicated because those data were calculated (see Section 2.4.1).

(6.4 mmol/g). In general, lignins produced at the highest organosolv temperature (experiments 3, 10 and 11) and the longest reaction time (experiment 7) tend to have the lowest amount of hydroxyl groups. The same holds for the lignin produced using 80% w/w aqueous ethanol, which might be due to etherification of the hydroxyl groups although lignin 5 shows the lowest amount of alkoxy groups present (Table 4). The highest content of total hydroxyl groups is found for lignins 4 and 9, i.e. lignins produced using 30 mM $H_2SO_4$ or 50% w/w aqueous ethanol. Aliphatic hydroxyl groups are the most predominant type of hydroxyl group present. The amount of aliphatic hydroxyl groups was found to decrease with reaction time and ethanol proportion of the organosolv solvent. Aliphatic hydroxyl groups are strongly related to the presence of carbohydrate impurities containing aliphatic hydroxyl groups.

### 3.4.2. $^{31}$P-NMR

Table 5 shows the amount of hydroxyl groups as determined by $^{31}$P-NMR, consisting of aliphatic OH, condensed phenolic OH, S–OH, G–OH, H–OH and carboxyl groups. Presented values fit within a range of values reported earlier for $^{31}$P-NMR functional groups determination on various herbaceous crops, like Miscanthus (El Hage et al., 2010), switchgrass (Hu et al., 2012), triticale and wheat straw (Monteil-Rivera et al., 2013) (see also Pu et al., 2011). An example $^{31}$P-NMR spectrum of lignin 4 is given in Fig. 6. Lignin 4 has the highest content of total OH groups according to $^{31}$P-NMR (Table 5). Fig. 7 shows the correlation between aliphatic OH groups determined by $^{31}$P-NMR and residual carbohydrate content of the lignins (Table 2).

During the organosolv process, the amount of total —OH groups decreases to some extent as a function of the reaction time (experiments 1, 6 and 7). This decrease is mainly due to a reduction in the amount of aliphatic hydroxyl groups from 2.19 to 1.88 mmol/g (Table 5), which is strongly linked to the observed decrease in sugar residues (Fig. 7). On the other hand, the amount of condensed phenolic OH groups slightly increases from 0.65 to 0.78 mmol/g. An increase of the reaction temperature leads to a reduction of the amount of aliphatic hydroxyl groups due to lower amount of carbohydrate impurities (Fig. 7), whereas the amount of the other types of hydroxyl groups increases (Table 5, lignins 1–3). Overall, these effects lead to a maximum amount of total hydroxyl groups of 5.34 mmol/g for experiment 2 (200 °C), although differences are very small. The use of sulfuric acid as catalyst (lignins 1, 8 and 9) also leads to a maximum in the total hydroxyl content (5.41 mmol/g at 15 mM $H_2SO_4$, lignin 8). Lignin 8 contains the highest amount of aliphatic hydroxyl groups of all lignins studied (2.70 mmol/g). A further increase of the sulfuric acid dose (lignin 9) reduces the content of aliphatic hydroxyl and carboxyl groups, whereas all other types of hydroxyl groups increase.

**Table 5**
$^{31}$P-NMR results.

| Sample | DM (%) | Content of functional groups and phenyl-propanoid structural moieties (mmol/g dw)[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Aliphatic | Phenolic | | | | | Carboxyl | Sum |
| | | $OH_{aliphatic}$[b] | $OH_{phen\ cond}$[c] | S—OH | G—OH | H—OH | S/G-ratio | COOH | $OH_{total}$ |
| 1 | 93.5 | 2.19 | 0.65 | 0.50 | 0.92 | 0.34 | 0.55 | 0.57 | 5.17 |
| 2 | 88.8 | 2.02 | 0.85 | 0.48 | 1.00 | 0.40 | 0.48 | 0.58 | 5.34 |
| 3 | 93.6 | 1.61 | 0.87 | 0.53 | 1.06 | 0.40 | 0.50 | 0.60 | 5.08 |
| 4 | 91.7 | 2.61 | 0.79 | 0.44 | 0.96 | 0.39 | 0.46 | 0.60 | 5.79 |
| 5 | 92.7 | 1.87 | 0.54 | 0.28 | 0.67 | 0.32 | 0.41 | 0.50 | 4.19 |
| 6 | 93.8 | 2.04 | 0.69 | 0.50 | 0.92 | 0.34 | 0.55 | 0.56 | 5.06 |
| 7 | 94.1 | 1.88 | 0.78 | 0.46 | 0.95 | 0.36 | 0.49 | 0.53 | 4.97 |
| 8 | 91.6 | 2.70 | 0.66 | 0.39 | 0.83 | 0.41 | 0.47 | 0.43 | 5.41 |
| 9 | 86.2 | 1.75 | 0.92 | 0.56 | 1.06 | 0.47 | 0.53 | 0.38 | 5.15 |
| 10 | 92.8 | 1.39 | 0.98 | 0.55 | 1.13 | 0.45 | 0.49 | 0.64 | 5.15 |
| 11 | 86.4 | 1.49 | 1.06 | 0.56 | 1.17 | 0.52 | 0.48 | 0.62 | 5.42 |
| Alcell | 97.3 | 1.46 | 0.87 | 1.32 | 0.82 | 0.23 | 1.62 | 0.35 | 5.05 |

[a] Standard deviation typically <5% (some cases <10%).
[b] Aliphatic OH.
[c] Condensed phenolic OH (Granata and Argyropoulos, 1995).

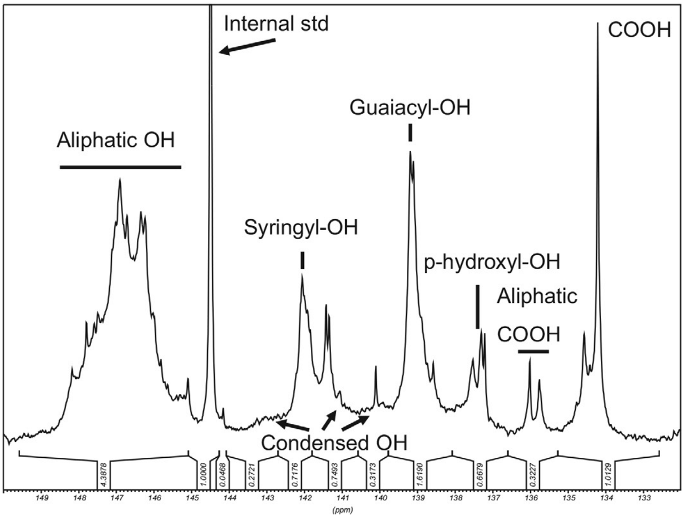

**Fig. 6.** $^{31}$P-NMR example spectrum of lignin 4 phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphopholane.

The most dominant effect on the presence of the functional groups is caused by the ethanol–water ratio of the solvent used (lignins 4, 1, 8). Lignin 4 (produced using 50% w/w aqueous ethanol) has the highest content of total hydroxyl groups, whereas lignin 5 (produced using 80% w/w ethanol) has the lowest content of total hydroxyl groups of all lignins studied (Table 5). Differences are probably due to the dependence of etherification of the hydroxyl groups on the ethanol–water ratio. The content of all types of hydroxyl groups analyzed reduces upon an increase of the ethanol–water ratio, except S–OH which shows an optimum at 60% w/w aqueous ethanol. The largest reduction occurs in the content of aliphatic hydroxyl groups; from 2.61 to 1.87 mmol/g at 50 and 80% w/w aqueous ethanol, respectively (Table 5). However, in contrast to the content of total hydroxyl groups, the content of aliphatic hydroxyl groups of lignins 4 and 5 is neither the highest nor the lowest of all lignins studied. For example, all experiments performed at 210 °C (lignins 3, 10 and 11) result in a lower amount of total aliphatic hydroxyl groups than the experiment using 80% w/w aqueous ethanol. The low amount of total hydroxyl groups for lignin 5 is because the content of "condensed phenolic OH" (Granata and Argyropoulos, 1995), S—OH, G—OH and H—OH are the lowest of all lignins studied.

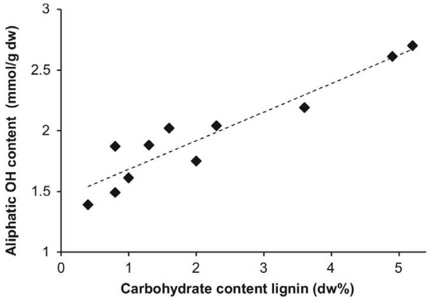

**Fig. 7.** Aliphatic OH content determined by $^{31}$P-NMR (Table 5) compared to the total carbohydrate content of studied wheat straw lignins (Table 2).

The wheat straw lignins have a similar content of total hydroxyl groups as Alcell lignin (Table 5), although particularly lignins 4, 8 and 11 (produced using either 50% w/w aqueous ethanol or 15 mM $H_2SO_4$ as catalyst) do contain up to 15% more OH groups than Alcell lignin. The type of hydroxyl groups present in wheat straw lignins is different than that of those present in hardwood-derived Alcell lignin due to the different botanical origin of the feedstock used. The content of S—OH is substantially higher in Alcell lignin (1.32 mmol/g) compared to wheat straw lignins (0.28–0.56 mmol/g) (Table 5). On the other hand, the content of H—OH and carboxyl groups is lower in Alcell lignin than in wheat straw lignins. As reported extensively in literature, in herbaceous plants, such as wheat straw, all three monolignols *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) occur in lignins in significant amounts, whereas hardwood lignins contain predominantly guaiacyl and syringyl units (Dence and Lin, 1992). The S/G-ratio for Alcell lignin is 1.62 compared to 0.41–0.55 for wheat straw-derived lignins.

### *3.4.3. Comparison functional groups analysis by wet chemistry and $^{31}$P NMR*

Comparison of functional groups analysis performed by wet chemistry (Section 3.4.1) and $^{31}$P-NMR (Section 3.4.2) shows substantial differences in results, a common phenomenon in functional group determination of (straw) lignins (Ghaffar and Fan, 2013).

Wet chemistry gives higher contents of aliphatic hydroxyl groups (2.0–3.6 times) and carboxyl groups (1.2–3.7 times, except lignin 10) than $^{31}$P-NMR. Remarkably, the hydroxyl content in Alcell determined by wet chemistry is also 2.5–2.9 times higher than by $^{31}$P-NMR for aliphatic, phenolic and carboxyl groups.

Differences between wet chemistry and $^{31}$P-NMR in the total content of hydroxyl groups are smaller than for the individual types of hydroxyl groups (wet chemistry:$^{31}$P-NMR = 1.2–1.6). Elucidation of the observed differences is beyond the scope of this paper. However, possible explanations include a potential difference in accessibility of the lignin functional groups. Different solvents are used in the analyses (acetic anhydride/pyridine in the case of lignin acetylation, alkaline water with added ethanol in the case of chemisorption, and DMF/pyridine/chloroform for $^{31}$P-NMR, see Section 2.4). In addition, methods developed for OH groups determination by chemical derivatization of lignin followed by NMR can be less accurate due to the broad signals related to different types of OH groups. In view of this, “wet acetylation” is considered a universal method both for individual compounds and multi-component systems of natural origin. Finally, the discrepancy between the wet chemistry and $^{31}$P NMR results could be related to the lower accuracy of the chemisorption methods used for acid hydroxyl groups determination.

It is important to note that despite differences in absolute values in contents of hydroxyl groups, the trends how these contents depend on the organosolv process conditions is in most cases the same. For example, a decrease of the amount of aliphatic hydroxyl groups upon the ethanol–water ratio as well as the reaction time has been found both by wet chemistry as well as by $^{31}$P-NMR. A noticeable exception is the influence of sulfuric acid on the content of aliphatic hydroxyl groups. According to the wet chemical method used, the aliphatic hydroxyl content is at minimum at 15 mM $H_2SO_4$ (lignin 8), whereas according to $^{31}$P-NMR a maximum occurs at this acid dose. These opposite results make it unclear how addition of sulfuric acid as catalyst influences the functional groups present, although the maximum in carbohydrate impurities found for lignin 8 supports a maximum in aliphatic hydroxyl content as found by $^{31}$P-NMR (see also Fig. 7).

### 3.5. *Lignin applications*

Organosolv processing aims to fractionate the lignocellulosic biomass as much as possible into its individual major fractions. As has been shown in this work, organosolv lignin has a high purity (low in residual carbohydrates and minerals). Consequently, the application spectrum of organosolv lignin is broader than that of the impure lignin residues derived from pretreatments such as steam explosion which are targeted toward the production of fermentable sugars.

Based on the identified dependencies of lignin characteristics on the organosolv process conditions, a first selection of conditions can be made for different potential applications of organosolv wheat straw lignin. For many applications of lignin such as feedstock for production of aromatic chemicals, lignins having a high purity, i.e. low in ash, residual carbohydrates etc. are preferred. The more pure the lignin is, the lower is the formation of other than aromatic chemicals in envisaged conversion processes. For a low amount of carbohydrates, lignin from a high-temperature autocatalytic organosolv process seems preferred (Section 3.2).

For the production of phenol-formaldehyde resins, a high content of non-sterically hindered aromatic hydroxyl groups is beneficial in combination with free aromatic ring sites on the ortho and/or para positions (Gosselink et al., 2010). Organosolv lignin with its relatively low molar mass, high purity and abundance of reactive groups is a preferred candidate for phenolic resins as was shown by Cetin and Ozmen (2003) who successfully replaced up to 30 wt% of phenol by organosolv lignin in a phenol-formaldehyde resin. Based on our study, lignin with maximum amount of hydroxyl groups can be produced by reducing the aqueous ethanol solvent to 50% w/w and using $H_2SO_4$ as catalyst. In addition, reduction of reaction temperature and time seems beneficial for high hydroxyl content.

According to $^{31}$P-NMR, lignin 8 contains the highest amount of aliphatic hydroxyl groups of all lignins studied. A high amount of aliphatic hydroxyl groups has been reported to be especially beneficial for application of lignin as polyol in polyurethanes (Monteil-Rivera et al., 2013). For example, encouraging attempts have been made to replace petrochemical polyols by organosolv lignin in the manufacture of rigid polyurethane foams. The foams contained up to 25–30 wt% of organosolv lignin (produced from hardwood) (Pan and Saddler, 2013).

Lignin 10, i.e. lignin produced at optimum conditions for subsequent enzymatic cellulose hydrolysis (Wildschut et al., 2013), shows the highest content of phenolic hydroxyl groups and the lowest for aliphatic hydroxyl groups (since it has the lowest amount of residual carbohydrates). El Hage et al. reported this particular combination of hydroxyl groups present to be beneficial for the antioxidant properties of Miscanthus organosolv lignins (El Hage et al., 2012). Pouteau et al. (2003) reported anti-oxidant trials for various lignins and concluded that especially a low molar mass, a low total OH content and a low polydispersity improve the antioxidant activity of the lignin–polypropylene blend.

Finally, the Tg values of the lignins studied are low compared to e.g. softwood Kraft lignins (Tg = 176 °C (Cui et al., 2013)), which gives favorable opportunities for chemical modification of wheat straw lignins in bulk and application of it as a renewable thermoplastic constituent for polymeric compositions.

## 4. Conclusions

Non-purified wheat straw lignins produced by ethanol-based organosolv fractionation under different process conditions were characterized for their yield, purity, residual carbohydrates, thermal behavior, functional groups, phenyl-propanoid structural moieties and molar mass distribution. In accordance with its herbaceous nature, the syringyl/guaiacyl-ratio of the wheat straw lignins was found to be substantially lower and the content of *p*-hydroxyphenyl and carboxyl groups to be substantially higher than of Alcell lignin.

The non-purified lignins were found to have a high purity with 5% carbohydrate impurities at most, both originating from lignin to carbohydrate complexes and from residual organosolv liquor. The use of $H_2SO_4$ in the organosolv process improved the lignin yield, but at low acid doses increased the amount of carbohydrate impurities (particularly, pentoses). For applications where a low amount of carbohydrates is important, lignin from a high-temperature autocatalytic organosolv process was found to be preferred.

The highest content of total hydroxyl groups is found when lignins were produced using 30 mM $H_2SO_4$ or 50% w/w aqueous ethanol as a solvent for organosolv process. Aliphatic hydroxyl groups, the most predominant type of hydroxyl groups present, were found to be strongly linked to the amount of residual carbohydrates and decrease with reaction time and ethanol proportion of the organosolv solvent, the latter probably due to reduced etherification of hydroxyl moieties.

In this study, correlations between organosolv process conditions and lignin characteristics have been determined. Understanding such correlations is of vital importance to facilitate the use of wheat straw organosolv lignins in value-added applications such as in polymers and resins and as a feedstock for bio-based aromatics.

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## P-5

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# Wheat straw lignin as filler for rigid polyurethane foams on the basis of tall oil amide[*)]

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**Abstract**: Rigid polyurethane (PUR) foams with the apparent density in the range of 45—60 kg/m$^3$ were produced from tall oil polyol (TOP) and organosolv wheat straw lignin as filler. PUR foams were filled with lignin in the amount of 0—6.3 wt %. Mechanical properties, dimensional stability, water absorption and thermal conductivity of prepared foams were investigated. The use of lignin increased the content of renewable materials in the end product, reaching together with TOP the value of 23.6 wt %. The viscosity of polyol system and foaming process parameters (cream time, gel time, tack-free time and full rise time) were determined. The viscosity of polyol system rose exponentially when concentration of lignin in the PUR foam was increased. The maximum value of compressive strength (0.35 MPa parallel to the foaming direction) was reached in the PUR sample where the concentration of lignin in foam was 1.2 wt %. It was concluded that wheat straw lignin can be used as a filler to obtain rigid PUR foams having the characteristics of thermal insulation material.

**Keywords**: rigid polyurethane foams, tall oil, polyol, lignin.

## Lignina ze słomy pszenicznej jako napełniacz stosowany do sztywnych pianek poliuretanowych na bazie amidów oleju talowego

**Streszczenie**: Stosując poliol z oleju talowego (TOP) oraz ligninę ze słomy pszenicznej jako napełniacz otrzymano sztywne pianki poliuretanowe (PUR) o gęstości pozornej 45—60 kg/m$^3$. Wyznaczono właściwości mechaniczne, stabilność wymiarową, chłonność wody oraz współczynnik przewodzenia ciepła przygotowanych materiałów w zależności od zawartości ligniny (0—6,3 % mas.). Wprowadzenie ligniny spowodowało zwiększenie udziału surowców odnawialnych w końcowym produkcie, które razem z TOP osiągają 23,6 % mas. W ramach pracy wyznaczono lepkość przedmieszki poliolowej oraz parametry technologiczne procesu spieniania (czas startu, czas żelowania, czas wzrostu, oraz czas suchego lica). Lepkość przedmieszki poliolowej wzrastała wykładniczo wraz ze zwiększaniem zawartości ligniny. Największą wytrzymałość na ściskanie (0,35 MPa w kierunku równoległym do wzrostu pianki) otrzymano w przypadku pianki PUR o zawartości ligniny 1,2 % mas. Stwierdzono, że lignina ze słomy pszenicznej może być użyta jako napełniacz w procesie otrzymywania sztywnych pianek PUR mających cechy materiałów termoizolacyjnych.

**Słowa kluczowe**: sztywne pianki poliuretanowe, olej talowy, poliol, lignina.

Nowadays it is important to find new ways to replace petro-chemical products with renewable raw materials because of environmental and economic concerns. Polyols used in polyurethane (PUR) production can be obtained from different natural oils and different natural fillers could be used to improve characteristics of PUR, reduce production costs and to enhance the renewable content in the material.

Lignin, a product of bio-refining, can be characterized as an amorphous heterogenic polymer with high amount of aromatic units in its structure. The common property of lignin is the content of three types of hydroxyl groups (aliphatic, phenolic, carboxylic), capable of chemical interaction with isocyanates, and/or physical interaction by hydrogen bonds with structural units of PUR [1]. Due to the hydroxyl functionality, lignin can be used as reactive filler in the production of PUR. The use of lignin can improve the mechanical characteristics and thermal stability of PUR in certain cases [2]. However the structural heterogeneity, functional composition and solubility of lignin vary depending on the methods of its isolation and the plant source. Correspondingly, the properties of PUR foams containing lignin depend on the lignin type (Kraft lignin, Klason lignin, organosolv etc.) used. Due to the

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development of new generation of biomass processing, the examination of novel lignin products for creation of lignin-containing PUR remains actual up to now.

A novel type of organosolv lignin marketed under the trade name biolignin$^{TM}$ extracted from wheat straw in organic acid media using biomass refinery technology developed by Compagnie Industrielle de la Matière végétale (CIMV, France) was used for preparation of lignin-containing PUR in this study [3]. The disadvantage of biolignin$^{TM}$, in its application as a macro monomer in PUR, is the weak solubility in polyols and in organic solvents.

The properties of PUR containing lignin depend on the method of lignin incorporation. The possible synthetic routes for lignin incorporation into PUR materials are following:

— as an additive filler in the form of powder,

— as a hydroxyl functional reactive filler in the form of powder [4—5],

— as a hydroxyl functional monomer in a liquid form obtained by chemical modification, for example by alkoxylation of lignin [2, 3—5].

The aim of this study was to test the possibility to use chemically non-modified biolignin$^{TM}$ as filler in rigid PUR foams and to evaluate the influence of lignin on the properties of PUR foams. The compositions of rigid PUR foams were based on tall oil polyol (TOP) to increase the content of renewable materials in the end product. The influence of lignin as filler on physical and mechanical properties, dimensional stability, water absorption properties and thermal conductivity were investigated and were evaluated according to European standard for thermal insulating products for buildings (EN 14315-1). It was assumed that lignin acts only as additive filler.

## EXPERIMENTAL

### Materials

Tall oil polyol (TOP, OH = 269 mg KOH/g; $H_2O$ = 0.2 wt %) was synthesized from tall oil and diethanolamine by amidization reaction. More detailed description of TOP synthesis is given in our previous work by Cabulis et al. [7]. Lupranol 3422 (OH = 490 mg KOH/g) from BASF is higher functional polyether polyol based on sorbitol and was used to increase the average functionality of polyol mixture. Glycerine (OH = 1824 mg KOH/g) from Sigma-Aldrich was used as an additional crosslinking agent.

The catalysts used were NIAX Catalyst E-A-1 from Momentive Performance Materials and 30 % solution of potassium acetate in diethylene glycol from Performance Chemicals Handels GmbH. NIAX Catalyst E-A-1 is an amine catalyst. Potassium acetate promotes reaction of isocyanate trimerization.

Surfactant NIAX Silicone L6915 from Momentive Performance Materials was used as an additive to provide closed foam structures.

Distilled water was used as a blowing agent.

Polymeric diphenylmethane diisocyanate — IsoPMDI 92140 (PMDI) from BASF was used as an isocyanate component ($w_{NCO}$ = 31.5 %).

Biolignin ($H_2O$ = 10 wt %) was ground with laboratory disintegrator DESI-11 (rotors rotation rate 10000 rpm). The ground lignin was dried for 24 h at 40 °C and $p$ = 30 mbar. After drying the moisture content of 2 wt % was reached.

### Sample preparation

The substrates for rigid PUR foams preparation is composed of PMDI and other ingredients, which was named polyol system. The composition of polyol systems used in this work are presented in Table 1. We developed two series of PUR compositions. Because lignin additive affects PUR foams apparent density, series 1 was prepared in order to investigate density and determine the amount of a foaming agent which will provide appropriate density of all foams. Therefore in series 1 only the amount of lignin differs, but in series 2 the samples with lignin contents of 7.5, 15 and 22.5 parts by weight (pbw) were repeated with adjusted amount of the blowing agent (series 2) to obtain samples with unified apparent density.

**Table 1. The composition of the mixtures, named polyol systems, that were added to PMDI in two series of prepared samples**

| Component | Content of component in polyol system, pbw | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | series 1 | | | | | | series 2 | | |
| | 1-1 | 1-2 | 1-3 | 1-4 | 1-5 | 1-6 | 2-1 | 2-2 | 2-3 |
| TOP | 75.0 | | | | | | 75.0 | | |
| Lupranol 3422 | 20.0 | | | | | | 20.0 | | |
| Glycerol | 5.0 | | | | | | 5.0 | | |
| Lignin | 0 | 1.88 | 3.75 | 7.5 | 15.0 | 22.5 | 7.5 | 15.0 | 22.5 |
| Water | 2.0 | | | | | | 2.5 | 3.5 | 3.5 |
| Catalyst EA-1 | 0.5 | | | | | | 0.5 | | |
| Potassium acetate | 0.5 | | | | | | 0.5 | | |
| L6915 | 1.5 | | | | | | 1.5 | | |

The amount of necessary PMDI was calculated according to equation:

$$m_{PMDI} = \frac{II}{w_{NCO}} \cdot \left( \sum \frac{OH_n \cdot m_n}{1336} + 4.67 \cdot m_{H_2O} \right) \quad (1)$$

II — isocyanate index (II = 155), $m_{PMDI}$ — mass of PMDI, $w_{NCO}$ — content of NCO groups of PMDI ($w_{NCO}$ = 31.5 %), $m_n$ — mass of each polyol, $OH_n$ — hydroxyl value of each polyol (in mg KOH/g), $m_{H_2O}$ — summary mass of water in polyol system.

In our experiments lignin was assumed to act as non-reactive filler. Therefore the hydroxyl group content of lignin was not taken into calculation of the necessary amount of PMDI needed.

Polyol systems were made as follows — polyol composition ingredients (TOP, cross linkage reagents, catalysts, surfactant, blowing agent) were mixed together in plastic cup for 3 minutes at the speed of 2000 rpm. Afterwards the necessary amount of the ground and dried lignin was added and mixed for 4 minutes at the speed of 2000 rpm. High speed mechanical stirrer IKA RW 20.n was used for mixing.

To prepare PUR samples the necessary amount of PMDI was added to polyol component and the whole system was mixed for 15 s at the speed of 2000 rpm. The parameters of foaming process (cream time, gel time, tack-free time and full rise time) were determined. Larger samples of PUR foams were prepared using 20 × 30 × 10 cm mold. The height of these foams was 8—10 cm. The obtained samples were conditioned for 24 h at the room temperature. PUR samples for testing were cut out afterwards.

### Methods of testing

Scanning electron microscope SEM Tescan TS 5136 MM was used to test the size of lignin particles. A&D moisture analyser MX-50 was used for in lignin determination of water content. Viscosity was tested for polyol systems kept for 5 days at two temperatures: room temperature and 50 °C. Temperature 50 °C was chosen to evaluate the influence of storage temperature to polyols viscosity. Higher temperature is not favorable for tall oil polyol storage. After conditioning the viscosity of polyol systems was tested with the rotation viscometer Haake Viscotester 6L/R Plus at 20 °C.

The tests of rigid PUR foam compression were performed on testing machine Zwick/Roell Z100 (LVS EN ISO 844:2009 standard, percent of compression 10 %). The measurements of closed cell content and apparent density were done according to the standards ISO 4590:2003 and ISO 845:2009, respectively. Water absorption was tested according to ISO 2896:2001 standard by immersing PUR samples in water for 7 days. The dimensional stability was established according to ISO 2796:1986 standard. The dimensional stability was determined for two sets of parameters: 28 days at 80 °C, ambient relative humidity (*RH*) and 28 days at 70 °C, *RH* = 97 %. The thermal conductivity in the range between 10 and 30 °C was tested with Linseis HFM (Heat Flow Meter) 200. Because the series 1 was made to determine necessary water amount needed in series 2 samples, only the apparent density was tested for series 1. All previously mentioned tests were carried out for samples with unified density.

## RESULTS AND DISCUSSION

### Characterization of lignin

Lignin disintegration was carried out to enlarge the active surface area and to reach uniform refinement of lignin. The size of lignin particles before and after grinding was determined using SEM images presented in Fig. 1. Before disintegration the size of lignin particles was higher than 50 μm but after disintegration it was between 1 and 20 μm. After drying the moisture content of 2 wt % was reached.

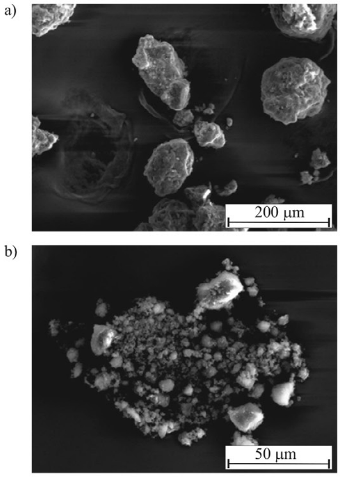

**Fig. 1. SEM images of lignin: a) before disintegration, b) after disintegration**

### Viscosity of polyol systems

The viscosity of polyol systems is an important parameter that determines the possibility and efficiency of mixing (which affects the quality and uniformity of foam). Viscosity is also an important parameter to deter-

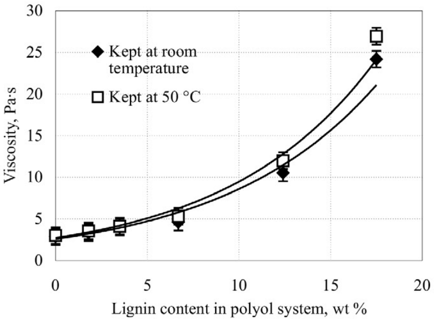

**Fig. 2. Viscosity at 20 °C of polyol systems with different lignin content**

mine the possibilities of polyol to be used in industrial production as well. The viscosity of polyols can be affected by its storage temperature. The viscosities of prepared polyol systems versus lignin contents are presented in Fig. 2. The viscosities of the mixture kept at the room temperature exponentially rises from 3.0 ± 0.1 to 24.2 ± 0.2 Pa · s when the concentration of lignin in polyol system increases from 0 to 17.5 wt %, respectively. The viscosity of mixtures kept at 50 °C was slightly higher than viscosity of samples kept at the room temperature. It could indicate the engorgement of lignin particles in polyol system as the result of physical and chemical interaction of polyols with functional groups of lignin located on the outer surface of lignin particles. The increase of viscosity during storage is caused by swelling of lignin particles in polyol.

## Rigid PUR samples characterization

Apparent density is an important property of rigid PUR foams because it strongly affects other properties of foams such as dimensional stability and compressive strength. Usually technical requirements for rigid PUR foams depend on apparent density. Figure 3 shows the effect of lignin concentration on apparent density of PUR foams prepared using both series of polyol systems. The density of series 1 samples increased from 45 to 60 kg/m$^3$. The quantity of blowing agent (water) was adjusted to obtain series 2 rigid PUR foams with density of 49.5 ± 1.8 kg/m$^3$. The changes of water content were taken into account when the necessary amount of PMDI was calculated. II was the same (II = 155) for all samples.

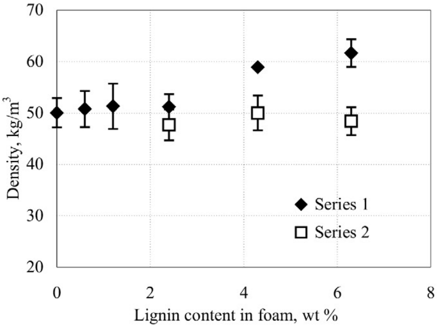

**Fig. 3. The apparent density of PUR foams with different lignin content: series 1 and series 2**

The closed cell content varied between 92 and 96 vol. %. Obtained rigid PUR foams were classified as CCC4 class for closed cell content (according to EN 14315-1).

Table 2 presents the foaming process parameters describing its kinetics.

**Table 2. Parameters of foaming process for samples with unified apparent density**

| Symbol of polyol system | Concentration of lignin in foam, wt % | Cream time, s | Gel time, s | Tack--free, s | Full rise, s |
|---|---|---|---|---|---|
| 1-1 | 0 | 19 | 55 | 86 | 135 |
| 1-2 | 0.6 | 20 | 59 | 93 | 150 |
| 1-3 | 1.2 | 20 | 65 | 98 | 148 |
| 2-1 | 2.4 | 23 | 73 | 115 | 150 |
| 2-2 | 4.3 | 23 | 110 | 185 | 215 |
| 2-3 | 6.3 | 37 | 170 | 315 | 328 |

The increase of lignin content slows down the foaming rise as evidenced by the rise of cream, string, tack-free and full rise time. It is a result of the acidity of lignin ($w_{COOH}$ = 1.71 ± 0.16 wt %) and increased viscosity (Fig. 2).

In Fig. 4 the compressive strength values of prepared samples are shown as a function of lignin concentration.

Compressive strength parallel to the foaming direction slightly increases in samples where the concentration of lignin in foam is up to 1.2 wt %. The maximum value of compressive strength (0.35 MPa parallel to foaming direction) is reached for PUR sample where the concentration of lignin in foam is 1.2 wt %. It complies with the CS(10\Y)300 level for compressive strength (according to EN 14315-1). The compressive strength decreases to 0.28 MPa when concentration of lignin is higher than 2.4 wt %. It complies with the level CS(10\Y)200 (according to EN 14315-1).

The thermal conductivities for samples with unified apparent density are listed in Table 3. The thermal con-

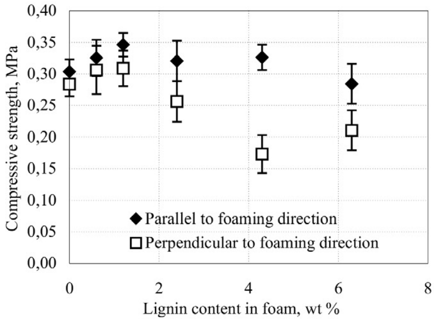

**Fig. 4. Compressive strength of PUR foams with different lignin content for samples with unified apparent density**

ductivity decreases from 0.0352 to 0.0298 W/m · K with increasing lignin content in PUR foam from 0 to 6.3 wt %.

**Table 3. Thermal conductivity for samples with unified apparent density**

| Symbol of polyol system | Lignin content in foam, wt % | Thermal conductivity, W/m · K |
|---|---|---|
| 1-1 | 0 | 0.0352 ± 0.0008 |
| 2-1 | 2.4 | 0.0324 ± 0.0011 |
| 2-3 | 6.3 | 0.0298 ± 0.0002 |

**Table 4. Water absorption and dimensional stability for samples with unified apparent density**

| Symbol of polyol system | Concentration of lignin in foam wt % | Water absorption vol. % | Dimensional stability | |
|---|---|---|---|---|
| | | | volume change (80 °C, ambient *RH*), % | volume change (70 °C, *RH* = 97 %), % |
| 1-1 | 0 | 1.86 ± 0.40 | 0.6 ± 0.4 | 1.0 ± 0.5 |
| 1-2 | 0.6 | 1.67 ± 0.18 | 0.1 ± 0.4 | -0.7 ± 0.5 |
| 1-3 | 1.2 | 2.24 ± 0.12 | -0.8 ± 0.4 | 0.1 ± 0.5 |
| 2-1 | 2.4 | 2.25 ± 0.27 | -0.4 ± 0.4 | 0.3 ± 0.5 |
| 2-2 | 4.3 | 1.87 ± 0.21 | -0.4 ± 0.4 | 0.0 ± 0.5 |
| 2-3 | 6.3 | 1.97 ± 0.15 | -0.6 ± 0.4 | 0.1 ± 0.5 |

For samples with unified apparent density the water adsorption and dimensional stability were determined and were collected in Table 4. Water absorption after 7 days is 2.1 ± 0.2 vol. % (Table 4). Absorption of water is not affected when lignin is added. Volume changes of PUR samples are no more than 1.5 % for all samples (Table 4). It complies with the level 3 for dimensional stability under the specified temperature and humidity conditions (according to EN 14315-1).

## CONCLUSIONS

It was concluded that it is possible to use chemically non-modified biolignin™ as filler in rigid PUR foams. The rigid PUR foam composition was developed where total concentration of lignin in PUR foam reached 6.3 wt %. The viscosity of the polyol component system too much when more than 6.3 wt % of lignin was added. Increasing viscosity decreased the efficiency of component mixing and slowed down the time of foam rise. Lignin did not impact water absorption and dimensional stability indicators in PUR materials. The maximum value of compressive strength (0.35 MPa parallel to the foaming direction) is reached in PUR foam sample where the content of lignin in foam is 1.2 wt %. Increasing concentration of lignin in rigid PUR foam improved thermal insulation properties (thermal conductivity decreased).These rigid PUR foam compositions can be used for further research as thermal insulation material using renewable raw materials. In this case flame retardants should be added. It was possible to obtain rigid PUR foams with the renewable raw materials in the amount of 23.6 wt % due to the use of TOP and lignin.

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# Fractionation of technical lignins as a tool for improvement of their antioxidant properties

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ABSTRACT

The modern biorefinery concept is aimed at the elaboration of sustainable processes with the most profitable utilization of all biomass products obtained at the technological cycle. Lignin separated as by-product in the lignocellulosic chemical processing is recognized as an important component of polymer systems. The presence of sterically hindered phenolic hydroxyl groups in the lignin macromolecule opens the possibility of its application as antioxidant for composites, e.g. polyurethanes (PU), which are considered as one of the most versatile polymeric materials. In the present work, the object of investigations was lignin obtained as a product, so-called BIOLIGNIN$^{TM}$, of wheat straw organosolv processing for pulp and fuel ethanol production (CIMV pilot plant, France). However, heterogeneity of the lignin obtained negatively influences its applicability that can be overcome by fractionation. Three soluble fractions were isolated from CIMV lignin by a sequential extraction with dichloromethane (A fraction), methanol (B fraction) and mixture of both the solvents (C fraction) and characterized in terms of their composition, functionality and structure using analytical pyrolysis (Py-GC/MS), $^{31}$P NMR and Size Exclusion Chromatography (SEC) methods. Antioxidant properties of BIOLIGNIN$^{TM}$ fractions were assessed in the tests with free radicals ABTS$^{\bullet+}$ and DPPH$^{\bullet}$. Application of Py-GC/MS for characterization of the fractions opened an opportunity to found some novel "structure–activity" correlations needed for understanding and tuning of antioxidant properties of lignins. The antioxidant activity of the fractions under investigation was tested by their influence on thermo-oxidative destruction of prepared model PU films. The data of TGA method (oxidative conditions) clearly testified the antioxidant effect of all three fractions with the most prominent activity for C fraction. The shifting of the exothermal maxima connected with oxidizing of volatile products of PU destruction to the higher temperature region by 20–30 K and 30–40 K was registered.

## 1. Introduction

The biorefinery concept is aimed at the elaboration of sustainable processes with the most profitable utilization of all biomass products obtained at the technological cycle. Lignins separated as by-products in lignocelluloses chemical and bio-chemical processing, despite their good recognized potentials for usage as an important component of polymer systems, is mainly (approximately up to 98%) burned for the improvement of energy balance of the main production processes and only a small portion (1–2%) is processed into value-added products [1,2].

In addition to traditional avenues for lignin application, e.g. binder, plasticizer, sorbent, filler of composite materials, polymeric carrier of biologically active agents, additive for animal food preparations [3,4], lignins are considered as prospective antioxidants. Hindered phenolic groups of lignin can act as stabilizers in reactions induced by oxygen and its reactive species and condition slowdown of ageing of composites and biological systems. The well documented antioxidant properties of lignins open variety of fields for their topical application in industry, healthcare and agriculture [5,6]. Lignin is characterized by higher thermal and biological stability than compounds with low molecular weight and could be applied in those fields in which the employment of a single molecule with antioxidant activity will be inefficient. However, the well-known polydispersity and chemical heterogeneity along MMD ask for the detailed characterization of the lignins composition and structure for determination of their applicability as antioxidants in targeted systems

The antioxidant efficiency of lignin is both related to its solubility in protecting material and structural characteristics [5]. Due to

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the molecular complexity of lignins, it is difficult to assign their antioxidant efficiency to specific structural elements, compared to the activities of synthetic antioxidants or naturally originated chemically defined polyphenols, e.g. tannins and flavonoids [7]. Researches carried out on the lignin model compounds indicate that free phenolic hydroxyl groups and ortho-methoxy substitution in aromatic ring are essential for antioxidant activity, but conjugated carbonyl group in the side chain has a negative effect on the antioxidant activity [8,9]. High molecular weight, polydispersity and heterogeneity in terms of functionality of lignin are factors that decrease radical scavenging activity [10,11]. Since lignins in situ are embedded in a complex network containing several types of polymers (polysaccharides, protein or other macromolecules – according to biological origins), isolated lignins contain admixtures, which may influence the efficiency of the lignins as antioxidants by changing the polarity (e.g. at the presence of polysaccharides that are more polar than lignins) and by decreasing the concentration of the reactive phenolic functions [5].

In the present work, the object of investigations was a novel type of technical lignins – BIOLIGNIN$^{TM}$, obtained as a product of a recently developed biomass refinery technology (CIMV, France) [12], which realizes efficient plant biomass fractionation with production of three main biomass components – cellulose, hemicelluloses and lignin that will themselves be marketable commodity chemicals and raw materials for further processing as well. Fractionation of technical lignins by extraction with organic solvents seems to be attractive opportunity for obtaining of more uniform by molecular mass distribution (MMD), component composition and, respectively, by properties, value added products [13,14].

The aim of the present work was the evaluation of suitability of fractionation of BIOLIGNIN$^{TM}$ as a tool for obtaining on its basis the products with good antioxidant properties for polymeric composite materials, specifically for polyurethanes (PU) on the basis of polyethers-polyols and aromatic isocyanates, e.g. elastomers. With this purpose, BIOLIGNIN$^{TM}$ was fractionated by sequential extraction using two organic solvents of different polarity and their mixture. Each soluble fraction obtained was characterized in terms of structure of lignin macromolecule and the presence of carbohydrate and other admixtures, using analytical pyrolysis, functionality, MMD, and radical scavenging activity. The characteristics obtained were compared with the data on effect of lignin addition in low quantity on the thermo-oxidative destruction of model PU elastomer used as indications of antioxidant efficiency of lignin fractions.

## 2. Experimental

### 2.1. Materials

BIOLIGNIN$^{TM}$ was extracted at pilot scale from wheat straw using a mixture of acetic acid/formic acid/water at the CIMV pilot plant (Pomacle, France). Purity of the lignin was about 95% [12].

Chemicals used for the analyses, including solvents, were of analytical grade (Sigma–Aldrich). All tests solutions were prepared freshly before use.

The parent BIOLIGNIN$^{TM}$ sample was dried in vacuum at 313 K (a vacuum drying oven VACIOTEM-T, Spain) to moisture content below 1%. The dried sample was grinded in a Retsch Mixer Mill MM200 (Retsch, Germany) at the frequency 30 s$^{-1}$ for 30 min and fraction with particle size $d$ < 0.5 mm was used for the further extraction with organic solvents and analyses.

### 2.2. Solvent fractionation

Lignin was fractionated in duplicate by successive extraction with dichloromethane, methanol and the mixture of methanol with dichloromethane (7/3, v/v). Lignin (225 g) was suspended in 1000 mL of the respective solvent and continuously stirred at room temperature for 2 h. The undissolved material was filtered off and resuspended for a second identical extraction. The fractions from both steps were combined. Collected dissolved material was filtered and vacuum dried. The yields of the fractions were shown in % on dry ash-free non-extracted lignin.

### 2.3. Chemical analysis

All analyses were done in triplicate. All results are expressed on a dry-weight and ash free basis. The dry weight was determined by separate oven drying of samples at 378 K for 18 h. Ash content was determined by the combustion of samples at 973 K for 3 h in a Carbolite furnace ELF 11/6B (UK).

The methoxyl group ($OCH_3$) content in lignin samples was determined according to the Viebock–Schwappach method in a Zeisel apparatus (domestic glassware). The procedure is described in detail in [15].

The contents of phenolic and aliphatic hydroxyl groups ($OH_{phen}$ and $OH_{aliph}$, respectively) and carboxylic groups ($OH_{COOH}$) were determined in the derivatizated lignin samples by $^{31}$P NMR with Bruker 400 MHz (30° pulse angle, inverse gated proton decoupling, a delay time of 5 s and 256 scans). The procedure is described in detail in [14]. Signal assignment was performed as described by [16].

The molar mass distribution (MMD) of the fractions obtained was analysed by alkaline SEC method in accordance with procedure described in [14]. Lignin samples of 1 mg mL$^{-1}$ dissolved in 0.5 M NaOH were injected into a manually packed column (4.6 cm × 30 cm) with ethylene glycolmethacrylate copolymer TSK gel Toyopearl HW-55F (thermostated at 298 K), eluted with the same solvent and detected at 280 nm. Standards for calibration of the molar mass distribution: sodium polystyrene sulfonates ($M_w$ range: 891–976,000 Da) and phenol.

### 2.4. Py-GC/MS

The Py-GC/MS analysis was performed using a Frontier Lab (Japan) Micro Double-shot Pyrolyser Py-2020iD (pyrolysis temperature 773 K, heating rate 600 K s$^{-1}$) directly coupled with the Shimadzu GC/MS – QP 2010 apparatus (Japan) with capillary column RTX-1701 (Restec, USA), 60 m × 0.25 mm × 0.25 μm film (the injector temperature 523 K, ion source 523 K with EI of 70 eV, the MS scan range $m/z$ 15–350, carrier gas helium at the flow rate of 1 mL min$^{-1}$ and the split ratio 1:30). The mass of a sample probe (residual moisture content < 1%) was 1.00–2.00 mg. The oven program was 1 min isothermal at 333 K, then 6 K min$^{-1}$ to 543 K, and finally held at 543 K for 10 min. The apparatus was modified by installation of the splitter of gas-carrier flow Vitreous Silica Outlet Splitter VSOS (SGE, Australia) in order to operate FID and MS detectors simultaneously. The mass spectrometer was operated in the electron impact mode using 70 eV electron energy. Fluoranthene is used as an inner standard for quantification of content of individual phenols. The identification of the individual compounds was performed on the basis of GC/MS chromatogram using Library MS NIST 147.LI13, whereas the relative area of the peak of individual compounds was calculated using the Shimadzu software on the basis of GC/FID data. The summed molar areas of the relevant peaks were normalized to 100% and the data for five repetitive pyrolysis experiments were averaged.

### 2.5. Assessment of radical scavenging activity

Testing radical scavenging activity was performed against stable radicals 2,2′-azino-bis(3-ethylbenzthiazoline-6-sulphonic cation radical ($\text{ABTS}^{\bullet+}$) and 2,2-diphenyl-1-picrylhydrazyl ($\text{DPPH}^{\bullet}$), and superoxide anion-radical ($\text{O}_2{}^{\bullet-}$).

In the $\text{DPPH}^{\bullet}$ radical scavenging assay the method described in [10] was adopted with minor modification. A sample solution in DMSO (0.03 mL) was mixed for 15 min with 3.0 mL of a $1 \times 10^{-4}\,\text{mol}\,\text{L}^{-1}$ $\text{DPPH}^{\bullet}$ methanol solution, and then the absorbance at 517 nm of the mixture was immediately measured using a Perkin Elmer Lambda 25 UV/VIS spectrometer.

$\text{ABTS}^{\bullet+}$ was produced by reacting 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) with potassium persulfate ($K_2S_2O_8$) [17]. A stock solution of ABTS (2 mM) was prepared by dissolving in 50 mM of phosphate buffered saline (PBS), consisting of 8.18 g NaCl, 0.27 g $KH_2PO_4$, 3.58 g $NaHPO_4 \times 11H_2O$ and 0.15 g KCl in 1 L of distilled water. The pH of the solution should be 7.4; otherwise it was adjusted with 0.1 M NaOH. The $\text{ABTS}^{\bullet+}$ solution was produced reacting 50 mL of stock solution with 200 μL of 70 mM $K_2S_2O_8$ water solution. The mixture was left to stand in the dark at room temperature for 15–16 h before use. For the evaluation of the antioxidant capability, the $\text{ABTS}^{\bullet+}$ solution was diluted with PBS to obtain the absorbance of 0.800 ± 0.030 at 734 nm. 0.03 mL of the sample solution in DMSO were mixed with 3 mL of the $\text{ABTS}^{\bullet+}$ solution in the 1 cm path length microcuvette. The absorbance at 734 nm was read at ambient temperature after 10 min. PBS solution was measured as a blank sample.

The characterization of the antioxidant activity against $\text{O}_2{}^{\bullet-}$ was carried out using the hypoxantine–xanthine oxidase system and $\text{O}_2{}^{\bullet-}$ was detected by the NBT (nitroblue tetrazolium) method [18], where the formazan formed upon NBT oxidation was controlled. The generation of $\text{O}_2{}^{\bullet-}$ was measured in a reaction mixture containing 250 μM hypoxanthine, 150 μM NBT, and 4 mU $\text{mL}^{-1}$ of xanthine oxidase in $NaHCO_3$–$Na_2CO_3$ buffer (pH 10.2). The reduction of the NBT concentration was measured by the change in absorbance at 560 nm for 12 min. Test solutions were prepared in DMSO and added to the reaction mixture to give a final concentration of 0.2% (v/v) DMSO. The solution without xanthine oxidase was used as a blank sample.

For all tests performed, the inhibition percentage (IP) of the radical species was calculated as follows:

$$\text{IP}\,(\%) = \frac{(A_\text{B} - A_\text{A})}{A_\text{B}} \times 100,$$

where $A_\text{B}$ is absorbance in blank probe (antioxidant was omitted) and $A_\text{A}$ is absorbance in the sample after 15, 10 and 12 min for $\text{DPPH}^{\bullet}$, $\text{ABTS}^{\bullet+}$ and $\text{O}_2{}^{\bullet-}$ assays, respectively. Using different concentrations of antioxidants, the dependence of the IP values on the antioxidant concentration was established and used for the calculation of $\text{IC}_{50}$ (the concentration of the tested sample required for a 50% inhibition of radical species). To calculate the $\text{IC}_{50}$ values, the linear regression analysis was made, using SPSS Statistics 17.0 (level of significance 0.05). According to the definition, higher antioxidant activity results in lower value of $\text{IC}_{50}$.

Trolox, 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (water soluble derivative of vitamin E) was tested as a reference antioxidant.

### *2.6. Obtaining model polyurethane (PU) elastomer films*

The model PU elastomers in the form of films were obtained in accordance with [19] using a system included PEG (polyethylene glycol) with $M_\text{n}$ of 400 g $\text{mol}^{-1}$, PMDI (commercial polymeric diphenylmethane diisocyanate Voratec SD 100) with the content of isocyanate groups (NCO) of 31% and DBTD (dibutyltin dilaurate) as a catalyst. The films were prepared by pre-polymerization of constituents followed by preparation of films by solution casting. PEG, PMDI and DBTD were dissolved each in extra dry THF (tetrahydrofuran), solutions obtained were combined and a system was pre-polymerized at 20 °C under argon atmosphere. The NCO/OH ratio in the composition was 1.05. In order to avoid bubbles appearance in PU films, the solutions were pre-treated in the ultra sound bath. The pre-polymerized mixture was then cast into the disk mold with flat bottom covered by polytetrafluorethylene (Teflon) for curing. After 24 h the cast films were peeled and dried for 7 days in desiccators above $P_2O_5$ at 20 °C following by thermal curing for 8 h at the temperature of 90 °C in air atmosphere. The films containing 5% of lignin fractions were prepared in the same manner, adding their solutions in extra dry THF on the pre-polymerization step.

The cross-link density of the PU elastomers obtained was measured as an effective number of cross-linked chains per volume unit of a polymer network, mol $\text{cm}^{-3}$ using Flory–Rehner method as described in [19]. Dimethyl formamide was used as a swelling agent.

### *2.7. The effect of lignin fractions on thermo-oxidative destruction of PU*

The thermo-oxidative destruction of the model PU elastomer films was studied in the temperature range 293–973 K by thermogravimetric analysis in air atmosphere (flow rate 50 mL $\text{min}^{-1}$) using the Metler Toledo Star System TGA/ADTA 851e device at a heating rate of 10 K $\text{min}^{-1}$. The sample size of 8–10 mg was used. The data for five parallel experiments were averaged.

## 3. Results and discussion

### *3.1. The fractionation of BIOLIGNIN$^\text{TM}$ and functionality of the fractions obtained*

The weak solubility of technical lignins in organic solvents usually used in PU chemistry (e.g. THF, glycol, dioxane) restricts their application in PU systems. The solvent fractionation is one of the pathways for obtaining more uniform completely soluble products for PU production.

Three soluble fractions were isolated from BIOLIGNIN$^\text{TM}$ by a sequential extraction with dichloromethane (A fraction), methanol (B fraction) and mixture of both the solvents (C fraction). The fractionation procedure in total solubilized about 40% of the lignin. Among soluble fractions, C fraction was dominating with the yield of (18.2 ± 0.4)% (from parent lignin), while A and B fractions were obtained with the yields of (7.4 ± 0.2) and (14.5 ± 0.3)%, respectively.

The results of SEC analysis (Table 1) showed that the fractionation yielded fractions of increasing molecular weight. The A and B fractions had rather close molecular weights, whereas both $M_\text{n}$ and $M_\text{w}$ of C fraction were substantially higher. All soluble fractions obtained had about twice lower polydispersity index ($M_\text{w}/M_\text{n}$) than that for parent BIOLIGNIN$^\text{TM}$.

The comparison of the results of functional analysis (Table 1) shows that the fraction obtained slightly differs by the content of phenolic hydroxyl groups, which have the important influence on the lignins antioxidant activity [10]. The difference in the content of metoxyl group, which is the diagnostic group for lignin, is more prominent. The $OCH_3$ group content is the highest in the fraction soluble in the $CH_3OH/CH_2Cl_2$ mixture (C fraction) and it was considerably higher than that in the parent lignin. For the same fraction the highest content of phenolic hydroxyl groups included in the so called condensed phenolic units, i.e. biphenyl- and diphenylmethane lignin substructures, was observed. This could indicate that the lignin yielded in C fraction has more condensed structure of lignin extracted by the mixture of solvents. The last assumption was confirmed by the data obtained using Py-GC/MS.

**Table 1**
Molar masses and functional groups contents of BIOLIGNIN™ and its fractions: A–F – $CH_2Cl_2$ soluble fraction; B–F – $CH_3OH$ soluble fraction; C–F – $CH_3OH/CH_2Cl_2$ soluble fraction.

| Index | Lignin sample | | | |
|---|---|---|---|---|
| | Unfractionated BIOLIGNIN™ | A–F | B–F | C–F |
| Average $M_n$, Da | 1051 ± 22 | 334 ± 2 | 541 ± 5 | 1094 ± 80 |
| Average $M_w$, Da | 11,143 ± 146 | 1973 ± 46 | 2201 ± 27 | 5295 ± 430 |
| $M_w/M_n$ | 10.6 ± 0.3 | 5.9 ± 0.1 | 4.1 ± 0.1 | 4.8 ± 0.1 |
| $OCH_3$ content, mmol $g^{-1}$ | 2.62 ± 0.03 | 2.67 ± 0.04 | 2.89 ± 0.02 | 3.22 ± 0.01 |
| $OH_{aliphatic}$ content, mmol $g^{-1}$ | 1.51 ± 0.01 | 0.94 ± 0.02 | 2.51 ± 0.08 | 1.68 ± 0.02 |
| $OH_{phenolic}$ content in condensed substructures,[a] mmol $g^{-1}$ | 0.50 ± 0.01 | 0.40 ± 0.01 | 0.43 ± 0.01 | 0.54 ± 0.01 |
| $OH_{phenolic}$ content in syringyl substructures, mmol $g^{-1}$ | 0.31 ± 0.01 | 0.45 ± 0.01 | 0.33 ± 0.01 | 0.36 ± 0.01 |
| $OH_{phenolic}$ content in guaiacyl substructures, mmol $g^{-1}$ | 0.54 ± 0.01 | 0.71 ± 0.01 | 0.67 ± 0.02 | 0.63 ± 0.01 |
| $OH_{phenolic}$ content in p-hydroxy-phenyl substructures, mmol $g^{-1}$ | 0.22 ± 0.01 | 0.12 ± 0.01 | 0.31 ± 0.01 | 0.27 ± 0.01 |
| Total $OH_{phenolic}$ content, mmol $g^{-1}$ | 1.58 ± 0.03 | 1.68 ± 0.04 | 1.74 ± 0.03 | 1.80 ± 0.01 |
| COOH, mmol $g^{-1}$ | 0.69 ± 0.02 | 0.67 ± 0.01 | 0.81 ± 0.02 | 0.48 ± 0.01 |
| Total OH groups content, mmol $g^{-1}$ | 3.77 ± 0.06 | 3.29 ± 0.08 | 5.10 ± 0.13 | 3.96 ± 0.01 |

[a] Biphenyl- and diphenylmethane substructures.

Evaluation of the phenolic hydroxyls composition of the fractions (Table 1) shows that the dichloromethane soluble fraction (A fraction) is characterized with the highest content of phenolic hydroxyl groups attached to syringyl and guaiacyl substructures. At the same time, this fraction is characterized by the much lower content of aliphatic hydroxyl groups as compared with parent BIOLIGNIN™ and other two fractions that could be connected with increased content of lipophilic admixtures in A fraction.

### 3.2. Characterization of BIOLIGNIN™ soluble fractions using Py-GC/MS

The distribution of lignin and carbohydrates related products detected by analytical pyrolysis for the parent BIOLIGNIN™ and its fractions is shown in Table 2. Lignin is the predominant component for parent BIOLIGNIN™ and its fractions, although noticeable amounts of compounds originated from carbohydrates as well as lipophilic admixtures are also present in the pyrolysates (Fig. 1). Application of the mixture of solvents allowed separating the C fraction with the highest molecular mass and the highest portion of the lignin derived compounds (Table 2, compounds 20–66) in the volatile pyrolysis products, which was higher than that for the parent BIOLIGNIN™. The latter is in conformity with the highest content of methoxyl groups detected for this fraction (Table 1). It could be explained by better affinity of hydrophilic/hydrophobic sites of lignin macromolecule to the combination of non-polar and polar solvents in the mixture used. At the same time, the lignin fraction soluble in $CH_2Cl_2$ (A fraction) differed from the parent lignin and other fractions by multi-times increased portion of aliphatic compounds (Fig. 1), which could originate from waxes and paraffins intrinsic to wheat straw. The volatile products from pyrolysis of B fraction are most enriched with the carbohydrates derived products. This is in good conformity with the results of $^{31}$P NMR showing the highest content of aliphatic hydroxyl groups in this fraction (Table 1).

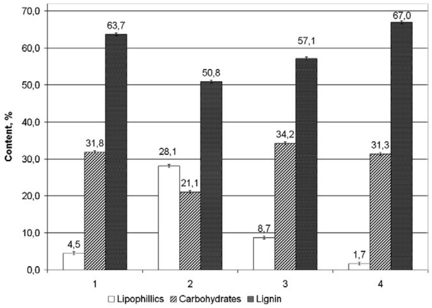

**Fig. 1.** Relative content (%) of lignin (L) derived compounds, carbohydrates (C) derived compounds and aliphatic compounds in the BIOLIGNIN™ and its fractions pyrolysis products. (A) Fraction – $CH_2Cl_2$ soluble fraction; (B) Fraction – $CH_3OH$ soluble fraction; (C) Fraction – $CH_3OH/CH_2Cl_2$ soluble fraction.

In order to determine the variations in the chemical structure of the lignin containing in the fractions differed by molecular mass, special attention was paid to lignin derived pyrolysis products. With this purpose, peak areas of lignin pyrolysis products were normalized to 100% and peak areas of lignin-derived phenols (individual phenols) were calculated as relative percentages (Table 3). The lignin component of the A fraction contains the highest amount of syringyl sub-structures (Table 3, compounds 14–25) in comparison with other soluble fractions and, simultaneously, the highest portion of the substructures with α-carbonyl groups (Table 3, compounds 9–13 and 21–25). The fraction soluble in $CH_3OH$ (B fraction) is characterized with the highest portion of lignin guaiacyl substructures (Table 3, compounds 1–13). Lignin components of both B and C fractions are characterized by higher aromaticity than parent lignin and lignin in the A fraction.

The highest ratio of the sum of portions of phenol and benzene derivatives to the sum of guaiacol and syringol derivatives in the pyrolysis products from the C fraction ($0.24 \pm 0.02$ against $0.15 \pm 0.02$; $0.10 \pm 0.01$ and $0.16 \pm 0.01$, respectively, for parent lignin, A fraction and B fraction) indicates the most high degree of condensation of the lignin contained in this fraction that coincided with its highest content of phenolic hydroxyl groups in condensed lignin units (Table 1). The significantly decreased portion of 4-vinyl-2-metoxyphenol (Table 3, compound 4) in the pyrolysis products from C fraction, as compared with other fractions and the parent lignin, also confirmed indirectly the increased degree of condensity of lignin contained in C fraction, because this compound is formed as the result of destruction of the aryl–alkyl ether bonds in lignin during analytical pyrolysis. Therefore, decreasing relative portion of 4-vinyl-2-metoxyphenol could reveal the lower relative portion of ether interunit bonds in lignin of the A fraction and, respectively, the higher portion of C—C bonds in its macromolecule.

### 3.3. Radical scavenging activity of BIOLIGNIN™ fractions

In the present study, the antioxidant properties of the soluble fractions of BIOLIGNIN™ were characterized using three

**Table 2**
Peak assignments and relative abundance (%) of lignin (L) and carbohydrates (C) derived pyrolysis products detected in parent BIOLIGNIN$^{\text{TM}}$ and its fractions: A–F – $CH_2Cl_2$ soluble fraction; B–F – $CH_3OH$ soluble fraction; C–F – $CH_3OH/CH_2Cl_2$ soluble fraction.

| Number | Compound | Origin | Compound proportion in the volatiles, % | | | |
|---|---|---|---|---|---|---|
| | | | BL[a] | A–F | B–F | C–F |
| 1 | Acetic acid | C | 9.13 ± 0.05 | 10.41 ± 0.05 | 7.71 ± 0.05 | 9.52 ± 0.05 |
| 2 | Octyl 2-methyl-2-propenoate | C | n.d[b] | 0.22 ± 0.01 | 0.07 ± 0.01 | n.d. |
| 3 | Prop-2-enal | C | Trace | Trace | Trace | Trace |
| 4 | Propanone | C | 0.53 ± 0.01 | 0.16 ± 0.01 | 0.51 ± 0.01 | 0.72 ± 0.03 |
| 5 | 2-Methylpropanal | C | 0.09 ± 0.02 | 0.02 ± 0.005 | 0.10 ± 0.01 | 0.10 ± 0.01 |
| 6 | Butane-2,3-dione | C | 0.18 ± 0.01 | 0.02 ± 0.005 | 0.17 ± 0.01 | 0.19 ± 0.01 |
| 7 | 3-Methylbutanal | C | 0.13 ± 0.01 | 0.03 ± 0.005 | 0.18 ± 0.01 | 0.14 ± 0.01 |
| 8 | 2-methylbutanal | C | 0.08 ± 0.01 | 0.04 ± 0.005 | 0.08 ± 0.005 | 0.09 ± 0.01 |
| 9 | Hexanal | C | Trace | 0.06 ± 0.005 | 0.05 ± 0.005 | Trace |
| 10 | 1-(Acetyloxy)-2-propanone | C | 0.07 ± 0.01 | Trace | 0.05 ± 0.005 | 0.07 ± 0.01 |
| 11 | Furan | C | 0.01 ± 0.005 | Trace | Trace | 0.06 ± 0.01 |
| 12 | 2-Methylfuran | C | 0.46 ± 0.03 | 0.32 ± 0.01 | 0.26 ± 0.01 | 0.47 ± 0.01 |
| 13 | Oxolane | C | n.d. | 0.21 ± 0.01 | n.d. | n.d. |
| 14 | 2,5-Dimethylfuran | C | 0.08 ± 0.01 | 0.05 ± 0.01 | 0.06 ± 0.005 | 0.11 ± 0.01 |
| 15 | 2-Ethyl-5-methylfuran | C | Trace | Trace | Trace | 0.04 ± 0.005 |
| 16 | Furan-2-carbaldehyde | C | 0.38 ± 0.02 | 0.15 ± 0.02 | 0.39 ± 0.01 | 0.33 ± 0.02 |
| 17 | 2,3-Dihydro-1-benzofuran | C, L | 3.68 ± 0.07 | 1.36 ± 0.02 | 5.76 ± 0.03 | 2.78 ± 0.05 |
| 18 | 5-Acetoxymethyl-2-furaldehyde | C | Trace | 0.14 ± 0.02 | Trace | Trace |
| 19 | 3,5-dihydroxy-6-methyl-2,3-dihydropyran-4-one | C | 0.07 ± 0.01 | Trace | 0.09 ± 0.005 | 0.09 ± 0.01 |
| 20 | Benzene | L | 0.04 ± 0.005 | Trace | 0.03 ± 0.005 | 0.03 ± 0.005 |
| 21 | Methylbenzene | L | 0.39 ± 0.01 | 0.30 ± 0.02 | 0.34 ± 0.02 | 0.31 ± 0.02 |
| 22 | 1,4-Dimethylbenzene | L | 0.08 ± 0.005 | 0.04 ± 0.005 | 0.09 ± 0.005 | 0.10 ± 0.01 |
| 23 | 1,2-Dimethylbenzene | L | 0.09 ± 0.005 | 0.12 ± 0.005 | 0.07 ± 0.005 | 0.08 ± 0.005 |
| 24 | 1,3- Dimethylbenzene, | L | Trace | 0.11 ± 0.005 | n.d. | n.d |
| 25 | Ethenylbenzene | L | 0.10 ± 0.005 | 0.05 ± 0.005 | 0.09 ± 0.005 | 0.06 ± 0.005 |
| 26 | 1,2,3-Trimethylbenzene | L | Trace | 0.07 ± 0.005 | 0.07 ± 0.005 | 0.08 ± 0.01 |
| 27 | 1,2,4-Trimethylbenzene | L | 0.05 ± 0.005 | 0.07 ± 0.005 | Trace | 0.04 ± 0.002 |
| 28 | 1-Methoxy-2-methylbenzene | L | 0.10 ± 0.01 | 0.01 ± 0.001 | 0.09 ± 0.005 | 0.09 ± 0.01 |
| 29 | Pentylbenzene | L | n.d | 0.04 ± 0.005 | n.d | n.d |
| 30 | Phenol | L | 0.85 ± 0.05 | 0.40 ± 0.02 | 1.15 ± 0.02 | 1.11 ± 0.03 |
| 31 | 2-Methylphenol | L | 0.23 ± 0.02 | 0.22 ± 0.01 | 0.27 ± 0.01 | 0.31 ± 0.01 |
| 32 | 2,3-Dimethylphenol | L | 0.03 ± 0.005 | Trace | 0.02 ± 0.005 | Trace |
| 33 | 4-Methylphenol | L | 1.07 ± 0.05 | 0.65 ± 0.02 | 1.05 ± 0.02 | 1.23 ± 0.02 |
| 34 | 2-methoxy-3-methylphenol | L | 0.04 ± 0.01 | 0.04 ± 0.005 | 0.06 ± 0.005 | 0.07 ± 0.005 |
| 35 | 3,4-Dimethylphenol | L | 0.21 ± 0.02 | 0.22 ± 0.01 | 0.18 ± 0.02 | 0.26 ± 0.02 |
| 36 | 1,2-Dimethoxy-3-methylbenzene | L | 0.08 ± 0.005 | 0.07 ± 0.005 | 0.05 ± 0.005 | 0.07 ± 0.005 |
| 37 | 4-Ethylphenol | L | 0.33 ± 0.02 | 0.22 ± 0.01 | 0.60 ± 0.005 | 0.68 ± 0.02 |
| 38 | 3′,5′-Dihydroxy-1-phenylethanone | L | 0.12 ± 0.01 | 0.16 ± 0.01 | 0.13 ± 0.01 | 0.16 ± 0.01 |
| 39 | 4-Ethyl-1,2-dimethoxybenzene | L | 0.09 ± 0.01 | 0.05 ± 0.005 | 0.04 ± 0.005 | 0.07 ± 0.005 |
| 40 | 3-methoxy-5-methylphenol | L | 0.19 ± 0.01 | 0.05 ± 0.005 | 0.14 ± 0.01 | 0.24 ± 0.01 |
| 41 | 4-Allylphenol | L | Trace | Trace | 0.08 ± 0.005 | 0.09 ± 0.005 |
| 42 | 2-Methoxyphenol | L | 3.06 ± 0.04 | 2.88 ± 0.05 | 3.56 ± 0.05 | 3.97 ± 0.05 |
| 43 | 2-Methoxy-4-methylphenol | L | 3.27 ± 0.05 | 2.96 ± 0.05 | 3.19 ± 0.01 | 3.87 ± 0.04 |
| 44 | 4-Ethyl-2-methoxyphenol | L | 1.14 ± 0.05 | 1.04 ± 0.01 | 1.47 ± 0.01 | 1.99 ± 0.04 |
| 45 | 4-Vinyl-2-metoxyphenol p-vinylguaiacol | L | 8.29 ± 0.05 | 7.57 ± 0.05 | 9.46 ± 0.05 | 5.25 ± 0.05 |
| 46 | 4-Allyl-2-methoxyphenol | L | 0.23 ± 0.01 | 0.24 ± 0.01 | 0.19 ± 0.01 | 0.23 ± 0.01 |
| 47 | 2-Methoxy-4-propylphenol | L | 0.15 ± 0.005 | 0.06 ± 0.005 | 0.15 ± 0.01 | 0.21 ± 0.01 |
| 48 | 2-Methoxy-4-[(Z)-prop-1-enyl]phenol | L | 0.22 ± 0.01 | 0.19 ± 0.01 | 0.21 ± 0.005 | 0.29 ± 0.01 |
| 49 | 2-Methoxy-4-[(E)-prop-1-enyl]phenol | L | 1.23 ± 0.02 | 0.77 ± 0.01 | 1.05 ± 0.02 | 1.18 ± 0.02 |
| 50 | 4-Hydroxy-3-methoxybenzaldehyde vanillin | L | 0.27 ± 0.01 | 1.56 ± 0.03 | 0.30 ± 0.01 | 0.20 ± 0.01 |
| 51 | 1-(4-Hydroxy-3-methoxyphenyl)ethanone acetoguaiacon | L | 0.19 ± 0.005 | 0.51 ± 0.01 | 0.18 ± 0.01 | 0.29 ± 0.02 |
| 52 | 1-(4-Hydroxy-3-methoxyphenyl)propan-2-one guacylacetone | L | 0.17 ± 0.005 | 0.09 ± 0.01 | 0.15 ± 0.01 | 0.19 ± 0.01 |
| 53 | 1-(4-Hydroxy-3-methoxyphenyl)propan-1-one propioguaiacone | L | 0.09 ± 0.005 | 0.07 ± 0.01 | 0.05 ± 0.005 | 0.07 ± 0.01 |
| 54 | 1-(4-Hydroxy-3-methoxyphenyl)propan-1-one-1-oxy propioguaiacone, alpha-oxy- | L | 0.37 ± 0.01 | 1.40 ± 0.01 | 0.31 ± 0.01 | 0.30 ± 0.01 |
| 55 | 2,6-Dimethoxyphenol syringol | L | 1.90 ± 0.03 | 2.43 ± 0.05 | 2.40 ± 0.05 | 2.38 ± 0.05 |
| 56 | 2,6-Dimethoxy-4-methylphenol syringol, 4-methyl- | L | 1.65 ± 0.05 | 2.00 ± 0.05 | 1.95 ± 0.03 | 2.25 ± 0.05 |
| 57 | 4-Ethyl-2,6-dimethoxyphenol syringol, 4-ethyl- | L | 0.28 ± 0.03 | 0.32 ± 0.01 | 0.31 ± 0.01 | 0.50 ± 0.01 |
| 58 | 4-Vinyl-2,6-dimethoxyphenol syringol, 4-vinyl- | L | 0.92 ± 0.02 | 0.91 ± 0.02 | 0.82 ± 0.01 | 0.74 ± 0.01 |
| 59 | 4-allyl-2,6-dimethoxy-phenol and 2,6-dimethoxy-4-propylphenol | L | 0.35 ± 0.005 | 0.26 ± 0.01 | 0.31 ± 0.01 | 0.37 ± 0.01 |
| 60 | 2,6-Dimethoxyphenol derivate | L | 0.07 ± 0.01 | 0.11 ± 0.01 | 0.06 ± 0.005 | 0.07 ± 0.005 |
| 61 | 2,6-Dimethoxy-4-[(E)-prop-1-enyl]phenol | L | 0.95 ± 0.01 | 0.67 ± 0.02 | 0.77 ± 0.03 | 0.91 ± 0.01 |
| 62 | 4-Hydroxy-3,5-dimethoxybenzaldehyde | L | 0.09 ± 0.01 | 1.50 ± 0.05 | 0.10 ± 0.01 | 0.14 ± 0.02 |
| 63 | 1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanone | L | 0.52 ± 0.02 | 0.46 ± 0.02 | 0.30 ± 0.01 | 0.63 ± 0.02 |
| 64 | 1-(4-Hydroxy-3,5-dimethoxyphenyl)propan-2-one | L | 0.08 ± 0.01 | 0.03 ± 0.005 | 0.11 ± 0.01 | 0.15 ± 0.01 |
| 65 | 1-(4-Hydroxy-3,5-dimethoxyphenyl)propan-1-one | L | 0.04 ± 0.005 | 0.05 ± 0.005 | 0.05 ± 0.006 | 0.06 ± 0.005 |
| 66 | 1-(4-Hydroxy-3,5-dimethoxyphenyl)propan-1-one-1-oxy | L | 0.18 ± 0.01 | 0.86 ± 0.01 | 0.21 ± 0.01 | 0.12 ± 0.005 |

[a] BIOLIGNIN$^{\text{TM}}$.
[b] n.d., not detected.

**Table 3**
The distribution of lignin-derived methoxylated phenols in pyrolysates of BIOLIGNIN$^{TM}$ and its fractions normalized to 100% of lignin derived products.

| No. | Compound | Compound proportion in the lignin-derived volatiles, % | | | |
|---|---|---|---|---|---|
| | | BIOLIGNIN$^{TM}$ | A–F | B–F | C–F |
| 1 | 2-Methoxyphenol | 10.31 ± 0.01 | 9.08 ± 0.08 | 11.11 ± 0.08 | 12.69 ± 0.06 |
| 2 | 2-Methoxy-4-methylphenol | 10.97 ± 0.05 | 9.33 ± 0.06 | 9.90 ± 0.07 | 12.31 ± 0.11 |
| 3 | 4-Ethyl-2-methoxyphenol | 3.83 ± 0.08 | 3.27 ± 0.02 | 4.56 ± 0.03 | 6.33 ± 0.02 |
| 4 | 4-Vinyl-2-metoxyphenol | 27.82 ± 0.07 | 23.85 ± 0.09 | 29.43 ± 0.04 | 16.73 ± 0.12 |
| 5 | 4-Allyl-2-methoxyphenol | 0.78 ± 0.05 | 0.75 ± 0.02 | 0.59 ± 0.01 | 0.73 ± 0.04 |
| 6 | 2-Methoxy-4-propylphenol | 0.50 ± 0.03 | 0.19 ± 0.01 | 0.47 ± 0.02 | 0.67 ± 0.03 |
| 7 | 2-Methoxy-4-[(*Z*)-prop-1-enyl]phenol | 0.74 ± 0.03 | 0.60 ± 0.04 | 0.65 ± 0.01 | 0.92 ± 0.02 |
| 8 | 2-Methoxy-4-[(*E*)-prop-1-enyl]phenol | 4.13 ± 0.04 | 2.42 ± 0.06 | 3.26 ± 0.08 | 3.75 ± 0.06 |
| 9 | 4-Hydroxy-3-methoxybenzaldehyde | 0.91 ± 0.05 | 4.90 ± 0.03 | 0.93 ± 0.04 | 0.64 ± 0.02 |
| 10 | 1-(4-Hydroxy-3-methoxyphenyl)ethanone | 0.64 ± 0.01 | 1.60 ± 0.07 | 0.56 ± 0.03 | 0.92 ± 0.02 |
| 11 | 1-(4-Hydroxy-3-methoxyphenyl)propan-2-one | 0.57 ± 0,02 | 0.28 ± 0.04 | 0.47 ± 0.01 | 0.60 ± 0.03 |
| 12 | 1-(4-Hydroxy-3-methoxyphenyl)propan-1-one | 0.30 ± 0.02 | 0.22 ± 0.04 | 0.16 ± 0.02 | 0.22 ± 0.02 |
| 13 | 1-(4-Hydroxy-3-methoxyphenyl)propan-1-one-1-oxy | 1.24 ± 0.03 | 4.43 ± 0.08 | 0.96 ± 0.05 | 0.95 ± 0.03 |
| 14 | 2,6-Dimethoxyphenol | 6.38 ± 0.09 | 7.70 ± 0.10 | 7.45 ± 0.05 | 7.57 ± 0.05 |
| 15 | 2,6-Dimethoxy-4-methylphenol | 5.54 ± 0.08 | 6.28 ± 0.08 | 6.05 ± 0.07 | 7.16 ± 0.05 |
| 16 | 4-Ethyl-2,6-dimethoxyphenol | 0.94 ± 0.02 | 1.01 ± 0.03 | 0.96 ± 0.02 | 1.59 ± 0.06 |
| 17 | 4-Vinyl-2,6-dimethoxyphenol | 3.09 ± 0.06 | 2.86 ± 0.08 | 2.55 ± 0.02 | 2.35 ± 0.05 |
| 18 | 4-Allyl-2,6-dimethoxy-phenol and 2,6-dimethoxy-4-propylphenol | 1.17 ± 0.01 | 0.82 ± 0.08 | 0.96 ± 0.01 | 1.18 ± 0.04 |
| 19 | 2,6-Dimethoxyphenol derivate | 0.23 ± 0.02 | 0.35 ± 0.02 | 0.19 ± 0.02 | 0.22 ± 0.02 |
| 20 | 6-Dimethoxy-4-[(E)-prop-1-enyl]phenol | 3.19 ± 0.07 | 2,10 ± 0.06 | 2.39 ± 0.05 | 2.89 ± 0.08 |
| 21 | 4-Hydroxy-3,5-dimethoxybenzaldehyde | 0.30 ± 0.02 | 4.74 ± 0.08 | 0.31 ± 0.03 | 0.45 ± 0.03 |
| 22 | 1-(4-Hydroxy-3,5-dimethoxyphenyl) ethanone | 1.75 ± 0.08 | 1.54 ± 0.06 | 0.93 ± 0.03 | 2.00 ± 0.04 |
| 23 | 1-(4-Hydroxy-3,5-dimethoxyphenyl)propan-2-one | 0.30 ± 0.02 | 0.10 ± 0.02 | 0.34 ± 0.03 | 0.48 ± 0.02 |
| 24 | 1-(4-Hydroxy-3,5-dimethoxyphenyl)propan-1-one | 0.12 ± 0.01 | 0.16 ± 0.04 | 0.16 ± 0.01 | 0.19 ± 0.02 |
| 25 | 1-(4-Hydroxy-3,5-dimethoxyphenyl)propan-1-one-1-oxy | 0.60 ± 0.06 | 2.70 ± 0.08 | 0.65 ± 0.03 | 0.38 ± 0.01 |

A–F – $CH_2Cl_2$ soluble fraction; B–F – $CH_3OH$ soluble fraction; C–F – $CH_3OH/CH_2Cl_2$ soluble fraction.

antioxidant capacity assays frequently used to estimate antioxidant capacity of polyphenols. The results of the $ABTS^{\bullet+}$, $DPPH^{\bullet}$ and $O_2^{\bullet-}$ tests are presented in Table 4 in terms of $IC_{50}$ (the concentration of the tested antioxidant sample required for a 50% inhibition of radical species). The lower is this value the higher is radical scavenging activity of the compounds tested.

Radical scavenging activity against stable free $ABTS^{\bullet+}$ radicals of BIOLIGNIN$^{TM}$ soluble fractions was rather close to that of antioxidant Trolox, which is often used as a standard (Table 4). In opposite, in the test with free radical $DPPH^{\bullet}$, the radical scavenging activity of all fractions under study was almost 10-fold lower than that for Trolox. The values of radical scavenging activity obtained using the both above mentioned test did not strongly differ for various fractions. Unlike this, in the test with reactive oxygen form, namely superoxide radical anion, the radical scavenging capacity of C fraction was threefold higher as compared with the value found for the A fraction (Table 4). In this test the radical scavenging capacity detected for the C fraction was not much lower than that for Trolox. Some discrepancy between the results of $ABTS^{\bullet+}$ and $O_2^{\bullet-}$ tests, from one side, and $DPPH^{\bullet}$ test from other side, could be connected with the difference in mechanisms of the lignin radical scavenging activity in the various assays [20]. For the $ABTS^{\bullet+}$ and $O_2^{\bullet-}$ tests scavenging activity occurs by electron transfer–proton transfer (ET–PT) mechanism, whereas for the $DPPH^{\bullet}$ test the combination of ET path with H atom transfer is considered. In the latter case, the reaction could be very slow and hindered by side reaction, in particular, for o-methoxyphenols [20].

**Table 4**
The results of the tests on radical scavenging activity of BIOLIGNIN$^{TM}$ soluble fractions presented in terms of $IC_{50}$ (the concentration of the tested sample required for a 50% inhibition of radical species).

| Sample | $IC_{50}$, mg/L, in the tests with: | | |
|---|---|---|---|
| | $ABTS^{\bullet+}$ | $DPPH^{\bullet}$ | $O_2^{\bullet-}$ |
| $CH_2Cl_2$ fraction | 10.7 ± 0.3 | 50.0 ± 1.4 | 125.6 ± 5.5 |
| $CH_3OH$ fraction | 7.1 ± 0.3 | 42.7 ± 0.8 | 60.6 ± 10.7 |
| $CH_3OH/CH_2Cl_2$ fraction | 9.1 ± 0.3 | 42.8 ± 1.0 | 43.9 ± 2.0 |
| Trolox | 4.0 ± 0.1 | 4.7 ± 0.1 | 17.7 ± 0.4 |

The $CH_2Cl_2$ soluble fraction (A fraction) showed the lowest activity in the all tests applied that can be explained by the relatively high content of lipophilic admixtures in this fraction (Fig. 2). Besides, this fraction is characterized by the presence of the highest portion of lignin-derived compounds with α-carbonyl groups in the volatile products of pyrolysis (Table 3). The negative effect of conjugated carbonyl groups on antioxidant activity was noted earlier for monomeric lignin-related phenols [10].

$CH_3OH/CH_2Cl_2$ soluble fraction (C fraction) showed the highest radical scavenging activity, especially against superoxide-anion radicals, which can be compared with of flavanoids and other natural antioxidants. $IC_{50}$ values of $CH_3OH$ soluble fraction in tests with three different radicals also are relatively low.

Consideration of the results of radical scavenging tests together with the data of analytical pyrolysis opened an opportunity to precise some "structure–activity" correlations needed for understanding and tuning of antioxidant properties of lignins. It was found that the $IC_{50}$ value in the test with the reactive oxygen species (superoxide radical anion) linearly decreased with the increasing condensation degree of lignin macromolecules and aromaticity (the Pearson correlation coefficients $r = 0.993$ at the critical coefficient value $r = 0.988$). Formation of phenylpropanoid aroxyl radicals is an essential step in the realization of antioxidant activity of lignin. The stability of the aroxyl radicals strongly depends on unpaired electron delocalization. The development of condensed lignin structure with increased aromaticity leads to the extension of electron delocalization thus decreasing dangerous prooxidant potential of polyphenols.

### *3.4. The antioxidant effect of BIOLIGNIN$^{TM}$ soluble fractions on PU thermo-oxidative destruction*

The antioxidant activity of the BIOLIGNIN$^{TM}$ soluble fractions was tested by their influence on thermo-oxidative destruction of model PU films in air atmosphere. The PU films obtained were

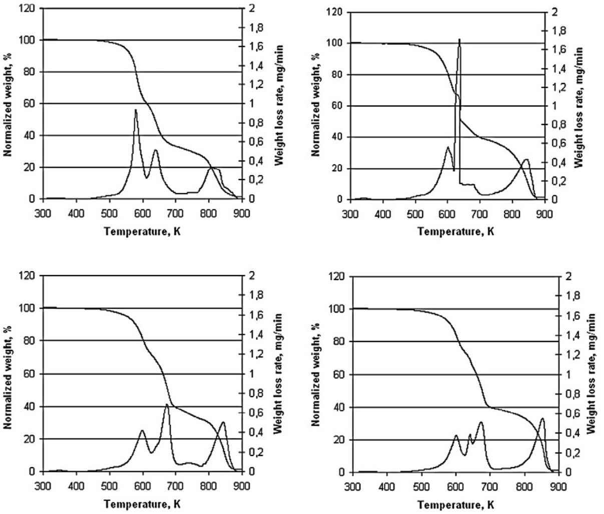

**Fig. 2.** Thermo-oxidative destruction results (TGA and DTG curves) for PU films: Control PU – lignin free PU film, (A) Fraction – PU film with addition of $CH_2Cl_2$ soluble fraction, (B) Fraction – PU film with addition of $CH_3OH$ soluble fraction, (C) Fraction – PU film with addition of $CH_3OH/CH_2Cl_2$ soluble fraction.

**Table 5**
Effect of BIOLIGNIN™ soluble fractions on characteristics of thermo-oxidative destruction of PU films. A-F – $CH_2Cl_2$ soluble fraction; B-F – $CH_3OH$ soluble fraction; C-F – $CH_3OH/CH_2Cl_2$ soluble fraction.

| Sample | $T_{start}$, K | DTG $T_{max}$, K | Maximal weight loss rate, mg min$^{-1}$ | $T_{50\%}$,[a] K | | DTA exo-peaks $T_{max}$, K | |
|---|---|---|---|---|---|---|---|
| Lignin free PU | 536 ± 2 | 577 ± 2 | 0.94 ± 0.05 | 633 ± 2 | 580 ± 2 | 639 ± 2 | 804 ± 3 |
| PU with A-F | 544 ± 2 | 616 ± 2 | 0.56 ± 0.02 | 638 ± 2 | 590 ± 2 | 639 ± 2 | 834 ± 3 |
| PU with B-F | 552 ± 2 | 624 ± 2 | 0.44 ± 0.03 | 675 ± 2 | 603 ± 2 | 675 ± 2 | 841 ± 3 |
| PU with C-F | 559 ± 2 | 675 ± 2 | 0.27 ± 0.02 | 675 ± 2 | 608 ± 2 | 675 ± 2 | 852 ± 3 |

[a] Temperature, when 50% weight loss of the sample is observed.

transparent, without solid inclusions and had the uniform thickness (~200 mkm).

The data of TGA (Fig. 2, Table 5) clearly testified the antioxidant effect of all three fractions, which is revealed in increasing temperatures of starting ($T_{start}$) and maximal development ($T_{max}$) of PU thermo-oxidative destruction as well as decreasing the process rate on the first stage of PU thermo-oxidative degradation. The data of DTA (Table 5) also confirmed the changes in thermo-oxidative behavior of model PU films: the exothermal maximum connected with oxidizing of PU destruction volatile products shifted to the high temperature region by 20-30 K (Table 5). It is considered in the literature [21] that for the polyether-based polyurethanes (used in the present study as model elastomers) this step involves the scission of the PU molecule into primary amine and proceeds by a radical chain process. The addition of antioxidants, in particular sterically hindered phenols, can stabilize PU against oxidation [22].

Lignins and lignocelluloses, mostly modified by oxialkylation, have long been a research subject in polyurethane chemistry as an aromatic polyol components [23,24]. It has been published that thermostability of PU synthesized using lignin-based polyols in enough quantities (10% and more) increases owing to significant changes in PU network structure, in particular an increase in PU cross-linked density up to 1.5–2.5 × $10^{-3}$ mol cm$^{-3}$ [25]. However, in the present study, the BIOLIGNIN™ fractions were added in small amounts (5%) that did not lead to increase in the cross-linked density of PU elastomers: it was changed from $(0.25 \pm 0.02) \times 10^{-3}$ mol cm$^{-3}$ (lignin-free elastomer) to $(0.26 \pm 0.02) \times 10^{-3}$ mol cm$^{-3}$ (A fraction was added), to $(0.35 \pm 0.02) \times 10^{-3}$ mol cm$^{-3}$ (B fraction was added) and $(0.6 \pm 0.05) \times 10^{-3}$ mol cm$^{-3}$ (C fraction was added). Therefore, the noticeable retardation effect of lignin fractions on PU thermo-oxidative degradation observed cannot be connected with the cross-linking action of lignin.

In correlation with the results of the test on radical scavenging activity towards superoxide radical anion, $CH_3OH$ and $CH_3OH/CH_2Cl_2$ soluble fractions decreased the PU thermo-oxidation rate stronger than that soluble in $CH_2Cl_2$. The action of lignin-based antioxidants manifested itself also in increasing the temperature of 50% mass loss by PU from 364 (control PU sample) up to 400 (PU with lignin fractions).

## 4. Conclusions

Fractionation of BIOLIGNIN™ with solvents of different polarity is a prospective tool for obtaining of more homogeneous lignin products, which reveal prominent antioxidant activity.

The results obtained clearly show that antioxidant activity of fractionated technical lignin is one more advantage for lignin application in PU production.

Application of Py-GC/MS opened an opportunity to found some novel "structure–activity" correlations needed for understanding and tuning of antioxidant properties of lignins.

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## P-7

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# Py-GC/MS for characterization of non-hydrolyzed residues from bioethanol production from softwood

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ABSTRACT

Analytical pyrolysis combined with gas chromatography/mass spectrometry (Py-GC/MS) was used to analyze chemical composition of non-hydrolyzed residues (LHRs) obtained by three methods of bioethanol production: softwood acid hydrolysis (AH), separate enzymatic hydrolysis and fermentation (SHF), and simultaneous saccharification and fermentation (SSF). Complementary techniques, such as EPR- and FTIR-spectroscopy, and routine chemical analysis procedures were used for this study as well. The Py-GC/MS analysis of the LHRs has shown a higher efficiency of carbohydrates hydrolysis upon SSF process in comparison with SHF and AH processes. Comparison of chemical analysis results and data obtained by Py-GC/MS of LHRs brought the direct evidence of incorporation of carbohydrates-derived fragments into the lignin matrix and formation of so-called pseudo-lignin upon different stages of softwood processing. Modifications of lignin component of LHRs on various stages of the process of bioethanol production, such as oxidation and condensation reactions, cleavage of ether bonds and destruction of side propane chain, were revealed using Py-GC/MS.

## 1. Introduction

At present bioethanol produced by hydrolysis of lignocellulosic materials is considered as a real alternative for gasoline for transport needs. The feedstocks for these processes include softwood, agricultural residues, municipal solid wastes and dedicated energy crops. The most abundant source of lignocellulose in the Northern hemisphere is softwood, which is considered as a raw material for fuel ethanol production in Sweden, Canada and USA [1].

Acid hydrolysis of lignocellulosic biomass has a long history and the technologies based on usage of diluted and concentrated acids have been developed [2]. At the present moment the enzymatic hydrolysis is considered to be the most promising technology for conversion of lignocellulosic biomass into sugars (from carbohydrates) and raw material (from lignin) for obtaining various value added products [3].

Any configuration of lignocellulose hydrolysis process, even the most efficient one, leads to 40–50% of raw material remaining as rich-in-lignin solid residue (LHR), which contains some amounts of non-hydrolyzed carbohydrates. The feasible use of this residue is the necessary condition for the cost-effective operation of bioethanol production. The composition of LHRs as well as structure and functionality of their lignin component vary significantly depending on bioethanol production process conditions. The profound knowledge of LHRs composition and structure is required to find methods for their conversion to value added products.

The aim of the present work was to study composition of LHRs, with emphasis on their lignin component chemical structure modification, obtained from various stages of the three methods of bioethanol production from softwood, namely AH, SHF, and SSF.

Py-GC/MS was applied for characterization of raw material and LHRs on the molecular level. EPR and FTIR spectroscopy as well as routine chemical analysis, were used as complementary techniques for this study.

Py-GC/MS is being successfully used for determination of the chemical composition of lignocelluloses and lignin for several decades [4–8]. An advantage of the Py-GC/MS method is that the products detected are being accurately identified. This allows to estimate the composition of analyzed lignin containing complex in whole by determination of Py-products referring to the structure forming units of wood components. Problems relating to lignin quantification based on traditional wet chemistry methods, such as kappa number or Klason procedure [9–11], can therefore be solved. Py-GC/MS has been used for characterization of lignins obtained by acid percolation hydrolysis of wood [12–14]. Lignin transformations during biodegradation of plant biomass have been thoroughly studied using Py-GC/MS method [15–18]. However, there is lack of literature sources devoted to detailed characteristics of lignin

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**Table 1**
The designation of LHRs under study.

| Sample designation | Type of treatment |
|---|---|
| Softwood | No treated |
| LHR pretreatment | Acid catalysed steam explosion pretreatment |
| LHR AH | Diluted acid hydrolysis of the pre-treated sample |
| LHR SHF | Enzymatic hydrolysis upon SHF[a] process of the pre-treated sample |
| LHR SSF | Enzymatic hydrolysis upon SSF[b] process of the pre-treated sample |

[a] Separate hydrolysis and fermentation.
[b] Simultaneous hydrolysis and fermentation.

component of non-hydrolyzed residues from bioethanol production *via* SHF or SSF processing of softwood.

## 2. Experimental

### 2.1. Materials

Four different non-hydrolyzed solid residues (LHRs), designations of which are presented in Table 1, were obtained after the key stages of the softwood processing for bioethanol production: acid catalysed steam explosion pretreatment and hydrolysis. Specimen of parent softwood (spruce chips) was used for the present investigation as well.

Softwood (moisture content of 12%) and LHRs (moisture content of 50–55%) were kindly supplied by Ornskoldsvik bioethanol production pilot plant (Sweden), where different techniques of the softwood hydrolysis are under development.

KBr of FTIR grade used for FTIR spectroscopy was from Sigma–Aldrich. Chemicals used for analyses, including solvents, were of analytical grade (Sigma–Aldrich). All tests solutions were prepared freshly before use.

### 2.2. Chemical analysis

Samples under investigation were dried in vacuum at 40 °C (a vacuum drying oven VACIOTEM-T, Spain) to moisture content below 1%. The dried samples were grinded in a Retsch Mixer Mill MM200 (Retsch, Germany) at the frequency 30 $s^{-1}$ for 30 min and fraction with particle size $d < 0.05$ mm was used for the analyses.

Klason lignin content was determined according to Tappi method T222, and carbohydrates in hydrolizates were analyzed as described in [19] using gas liquid chromatography (GC). GC analysis was performed on a Hewlett Packard 6890 instrument (USA) equipped with a BPX 70 column (12 m × 0.32 mm × 0.25 mm film thickness). The injector temperature was 230 °C, the detector temperature was 250 °C and the oven temperature was 215 °C. The carrier gas was He at a constant flow rate of 0.9 mL/min at the split ratio 1:100.

The methoxyl group ($OCH_3$) content in lignin samples was determined according to the Viebock–Schwappach method in a Zeisel apparatus (domestic glassware). The contents of phenolic hydroxyl ($OH_{phen}$) and carboxylic (COOH) groups were determined by acid–base conductometric titration performing the analysis with an automatic titration device ABU901 (Radiometer Analytical, France) coupling with Conductometer CDM 210 (MeterLab, France) and Titration manager TIM900 (Radiometer Analytical, France). The titration was carried out under nitrogen. The procedures are described in detail in [20].

All analyses were done in triplicate. All results are expressed on a dry-weight and ash free basis. The dry weight was determined by separate oven drying of samples at 105 °C for 18 h. Ash content was determined by the combustion of samples at 700 °C for 3 h in a Carbolite furnace ELF 11/6B (UK).

### 2.3. Py-GC/MS

The Py-GC/MS analysis was performed using a Frontier Lab (Japan) Micro Double-shot Pyrolyser Py-2020iD (pyrolysis temperature 500 °C, heating rate 600 °C/s) directly coupled with the Shimadzu GC/MS-QP 2010 apparatus (Japan) with capillary column RTX-1701 (Restec, USA), 60 m × 0.25 mm × 0.25 μm film (the injector temperature 250 °C, ion source 250 °C with EI of 70 eV, the MS scan range $m/z$ 15–350, carrier gas helium at the flow rate of 1 mL/min and the split ratio 1:30). The mass of a sample probe (residual moisture content <1%) was 1.00–2.00 mg. The oven program was 1 min isothermal at 60 °C, then 6 °C/min to 270 °C, and finally held at 270 °C for 10 min The apparatus was modified by installation of the splitter of gas-carrier flow Vitreous Silica Outlet Splitter VSOS (SGE, Australia) in order to operate FID and MS detectors simultaneously. The mass spectrometer was operated in the electron impact mode using 70 eV electron energy. Fluoranthene is used as an inner standard for quantification of content of individual phenols. The identification of the individual compounds was performed on the basis of GC/MS chromatogram using Library MS NIST 147.LI13, whereas the relative area of the peak of individual compounds was calculated using the Shimadzu software on the basis of GC/FID data. The summed molar areas of the relevant peaks were normalized to 100% and the data for five repetitive pyrolysis experiments were averaged.

### 2.4. EPR spectroscopy

The aromaticity of lignin in LHR samples was estimated using the value of the conjugation length of π-polyconjugation systems calculated from the EPR spectra as the number of CH fragments included in the region of unpaired electron delocalization [21]. For humic substances this parameter is correlated with aromaticity degree [22], which is obtained usually from $^{13}C$ NMR spectra [23]. EPR-spectra were recorded at room temperature with a Bruker EMX spectrometer (Germany) operating at 9.6 GHz and a 50 kHz magnetic field modulation. The central magnetic field was 345 mT, a resonance field corresponding to organic free radicals including lignin-related radicals. Spectra were recorded at a microwave power of 1 mW and modulation amplitude of 0.02 mT; the scan range was 10–20 mT. The spectra were obtained as the first derivative of absorption and the spin quantifications of the EPR signals were determined by double integration of the first derivative of the spectra relative to the spectrum of $DPPH^{\bullet}$ standard. Before EPR measurements the samples were annealed at 120 °C under high vacuum (ca. $1 \times 10^{-4}$ Torr) [24,25] to remove free radicals non-inherent to polyconjugated systems. The mass of a sample probe (residual moisture content <1%) was 10.0–20.0 mg.

### 2.5. FTIR spectroscopy

Fourier transform infrared (FTIR) spectra of the samples under investigation were recorded in KBr pellets by Spectrum One (Perkin Elmer, UK) FTIR spectrometer in the range of 4000–400 $cm^{-1}$ (resolution: 4 $cm^{-1}$, number of scans: 64).

The resulting spectra were normalized to the intensity of maximum at 1510 $cm^{-1}$, which is assigned to the aromatic skeletal vibrations in lignins [26].

## 3. Results and discussion

### 3.1. Chemical composition and functionality of LHRs

The bulk analytical characteristics of LHR and softwood samples are shown in Table 2. The Klason lignin content of LHR samples

**Table 2**
Chemical characteristics of LHR samples.

| Sample | Klason lignin content, % | $OCH_3$, mmol $g^{-1}$ | | $OH_{phen}$, mmol $g^{-1}$ | | COOH, mmol $g^{-1}$ dry sample | Carbohydrates, % dry weight |
|---|---|---|---|---|---|---|---|
| | | On dry sample | On Klason lignin | On dry sample | On Klason lignin | | |
| Softwood | 28.8 | 1.6 | 5.6 | n.d.[a] | n.d. | n.d. | 67.5 |
| LHR pre-treatment | 44.5 | 2.2 | 5.4 | 1.8 | 4.0 | 1.0 | 48.0 |
| LHR AH | 80.9 | 3.2 | 4.0 | 2.1 | 2.6 | 1.4 | 20.0 |
| LHR SHF | 74.6 | 3.7 | 5.0 | 2.3 | 3.1 | 0.7 | 24.2 |
| LHR SSF | 82.8 | 4.2 | 5.1 | 1.8 | 2.2 | 1.5 | 18.0 |

[a] Not determined.

varied between 45 and 83%. Comparison of the amounts of carbohydrate polymers in LHRs has shown that the SSF process was the most effective.

Taking into account the Klason lignin content, a reduction in methoxyl group content was observed for all LHRs, which is especially notable in the case of LHR AH. To some extent this could be connected with the formation of so called "pseudolignin" due to the grafting of intermediate products of destruction of carbohydrates on lignin macromolecules and formation of heteroaromatic cycles [27,28]. The presence of such heteroaromatic impurities was clearly shown using multi-wave UV–vis detection during size exclusion chromatography (SEC) analysis of softwood kraft lignin, wheat straw soda lignin and soluble fractions of lignin obtained by percolation hydrolysis [27,29,30]. Possibility of covalent bonding of lignin (with participation of α-C–OH, C=O and PhOH) and cellulose upon heating in the temperature range of 100–130 °C was confirmed by modeling of their solid phase interaction [31]. During hydrolysis the novel C–C bonds are formed in lignin on account of the splitting of mainly α-alkyl-aryl ether bonds with carbonium cations. As a result the structure of lignin becomes more condensed. The formation of condensed sub-structures combining 3–4 aromatic rings in the process of lignocellulose acid hydrolysis *via* secondary condensation reactions was suggested in the work [12]. The condensed lignin reacts with carbohydrate degradation products forming a lignin-like structures, which are insoluble in acid.

The comparison of the results of functional analysis of LHRs under study (Table 2) has shown that LHR AH and LHR SSF samples have the highest COOH group contents. It was assumed that the conditions of AH and SSF processes led to development of lignin oxidation. Decreasing content of $OH_{phen}$ groups under SSF hydrolysis conditions (Table 2) allowed suggesting occurrence of lignin condensation processes. The data obtained by Py-GC/MS as well as FTIR and EPR spectroscopy analyses of the samples under study confirmed these assumptions.

The results of FTIR spectroscopy are presented in Fig. 1 and Table 3. The main peaks used for analysis in this study were assigned in accordance with [26,32,33]: 1705 $cm^{-1}$ for unconjugated C=O and COOH stretching, 1500 $cm^{-1}$ for aromatic skeletal vibration in lignin, 1462 $cm^{-1}$ for aromatic C–H deformation, 1375 $cm^{-1}$ for C–H deformation in cellulose and hemicelluloses, 1158 $cm^{-1}$ for C–O–C vibration in cellulose and hemicelluloses, 1140 $cm^{-1}$ for aromatic C–H in plane deformation, typical for G-units, whereby $G_{condensed} > G_{etherified}$, 1035 $cm^{-1}$ – a complex band for aromatic CH deformation, C–O, C–C stretching and C–OH bending in carbohydrates and 898 $cm^{-1}$ for C–H deformation in cellulose.

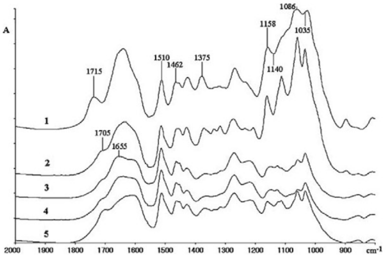

**Fig. 1.** FTIR spectra of parent softwood (1) and its processing solid residues (LHRs) obtained after pretreatment (2), SHF (3), SSF (4) and AH (5) processes.

The decrease in intensity of maxima at 1375 $cm^{-1}$ and 1158 $cm^{-1}$ in the FTIR spectra of the LHR AH, LHR SHF and LHR SSF (Table 3) in comparison with softwood sample revealed lowering of carbohydrate portion in samples upon wood processing. The decreasing intensity of the complex band with maximum at 1035 $cm^{-1}$ also could be assigned to removal of hydrolyzed carbohydrates. Among AH, SHF and SSF LHRs, the presence of carbohydrate originated admixtures and their influence on the spectral profile is a little more visible for the LHR AH (Fig. 1 and Table 3).

**Table 3**
Intensities of some lignin and carbohydrates related absorption bands in FTIR spectra of LHRs.

| Band wavenumber, $cm^{-1}$ | Band origin | Band intensity, normalized to $I_{1510}$ | | | | |
|---|---|---|---|---|---|---|
| | | Parent softwood | LHR pre-treatment | LHR AH | LHR SHF | LHR SSF |
| 1705 | C=O stretch in unconjugated carbonyl, carboxyl groups | n.r.[a] | 0.51 | 0.67 | 0.40 | 0.43 |
| 1655 | C=O stretch in conjugated carbonyl groups | n.r. | 0.88 | 0.80 | 0.84 | 0.88 |
| 1462 | C–H deformations | 1.1 | 0.95 | 0.83 | 0.75 | 0.73 |
| 1375 | Aliphatic C–H stretch in $CH_3$ | 1.09 | 0.95 | 0.69 | 0.49 | 0.49 |
| 1158 | C–O–C vibration in carbohydrates | 1.55 | 1.47 | 0.83 | 0.62 | 0.62 |
| 1140 | Aromatic C–H in-plane deformation | n.r. | n.r. | 0.78 | n.r. | 0.60 |
| 1086 | C–O deformation in secondary alcohols and aliphatic ethers | 2.50 | 2.80 | 1.00 | 0.80 | 0.60 |
| 1035 | C–O deformations in primary alcohols, aromatic C–H in-plane deformation | 2.54 | 1.09 | 1.04 | 0.89 | 0.74 |

[a] Not resolved.

**Table 4**
Parameters of LHRs structure aromaticity/condensity as inferred from EPR spectra.

| Sample | Conjugation length, CH number | Content of polyconjugated aromatic sub-structures per 100 lignin monomeric units |
|---|---|---|
| LHR pre-treatment | 12 | 1 |
| LHR AH | 17 | 10 |
| LHR SHF | 14 | 4 |
| LHR SSF | 14 | 5 |

The comparison of carbohydrate/lignin peak intensity ratios (normalized intensities of peaks assigned to carbohydrates) obtained for raw material and LHRs shows that the trends in the changes of lignin portion are in conformity to the results obtained by chemical analysis (Table 2). At the same time, a linear correlation between carbohydrate/lignin peak ratios and lignin content determined by the wet chemistry method, found in [32] for various lignocellulosic materials, was not established. This could be explained by overlapping of bands in IR spectra of LHRs and by overestimation of the lignin content by the Klason method as well.

Absorption maximum at 1715 cm$^{-1}$ in the parent wood FTIR spectrum, which corresponded to the acetyl ester groups, disappeared after the pretreatment stage (Fig. 1). For all LHRs under study, absorption maxima at 1705 cm$^{-1}$ originated from unconjugated carbonyl/carboxyl stretches with a shoulder at around 1660 cm$^{-1}$ (conjugated carbonyl stretching) were found (Table 3). The spectrum of LHR AH sample showed the highest absorption intensity at 1705 cm$^{-1}$ among all LHRs studied. These results indicate occurring of the lignin oxidation process under hydrolysis conditions, beginning with the pretreatment stage.

Some decrease in intensity of the maximum at 1462 cm$^{-1}$ in the spectra of LHRs in comparison with that for the parent sample (Table 3) indicates the condensation of lignin accompanied with substitution of protons at aromatic carbon atoms. Simultaneously the weak absorption maxima at 1140 cm$^{-1}$ (aromatic C-H in plane deformation, typical for G-units, whereby $G_{\text{condensed}} > G_{\text{etherified}}$ [26]) is observed in spectra of LHR AH and LHR SSF.

The EPR data (Table 4) show that in conditions of acid hydrolysis (AH process) the aromatization, estimated in terms of size and amount of polyconjugated aromatic sub-structures, is much more developed in comparison with the enzymatic hydrolysis processes.

### 3.2. Characterization of LHRs using Py-GC/MS

The distribution of lignin and carbohydrates related pyrolytic products for LHRs is shown in Table 5. The total content of volatile products resulted from carbohydrates pyrolysis decreased by 10% after softwood pretreatment and threefold and quadruple after enzymatic hydrolysis (SHF) and SSF process, respectively. After acid hydrolysis (LHR AH) the portion of carbohydrates related pyrolytic products decreased twofold in comparison with softwood raw material. The highest portion of lignin derived compounds in LHR SSF shows the efficiency of enzymatic hydrolysis process and *vise versa* the highest portion of the carbohydrates-derived pyrolytic products for LHR AH sample indicates development of side reactions leading to hindrance of hydrolysis. The latter could be connected with bonding of carbohydrate degradation products with lignin under acid hydrolysis conditions.

The relative content of $CO_2$ in volatile products of LHRs pyrolysis increased drastically in comparison with the parent softwood (Table 5). The relative abundance of $CO_2$ in volatiles released upon flash pyrolysis is supposed to be connected with the development of the process of oxidation of the primary carbon atoms of carbohydrates and lignin macromolecules upon a treatment. These Py-GC/MS data are in conformity with the results of FTIR spectroscopy showing that lignin oxidation process starts at the pretreatment step.

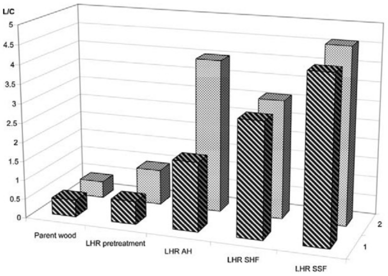

**Fig. 2.** Ratio of lignin and carbohydrates components contents in parent softwood and LHRs, calculated on the basis of Py-GC/FID (1) and chemical analysis (2) data.

The ratios of lignin content to carbohydrates content, calculated from the Py-GC/MS data (Table 5 and Fig. 2), are close to the results of chemical analysis of the parent wood and LHR samples obtained after both enzymatic processes (SHF and SSF), whereas approx. 50% discrepancies were found for LHR samples obtained after pretreatment step and AH process. The latter gives clear evidence of pseudo-lignin formation (incorporation of carbohydrates-derived fragments into lignin matrix). Comparison of relative contents of lignin- and carbohydrate-derived compounds (L and C, respectively) in volatile products of LHRs pyrolysis confirmed the highest efficiency of SSF process: for LHR SSF the C/L ratio was 0.2 against 2.2, 0.5 and 0.3, respectively for the parent wood, LHR AH and LHR SHF (Table 5).

Areas of pyrograms peaks, typical for carbohydrates and lignin degradation products, were summed up and normalized to 100% in order to characterize the changes in the composition of carbohydrate components of lignocellulosic complex and to determine the alteration in the chemical structure of the lignin component depending on the prehistory of LHR samples. Py-GC/MS analysis data show (Fig. 3) that aliphatic acids, esters, alcohols, aldehydes, ketones are prevalent carbohydrates derived products of the parent wood pyrolytic. At the same time, for LHR obtained after the

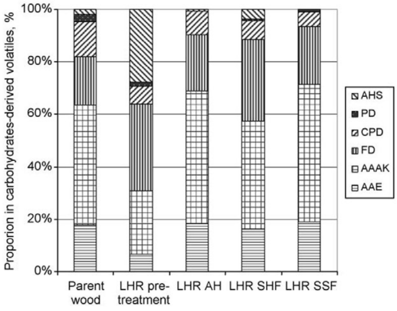

**Fig. 3.** Distribution (after normalization to 100%) of aliphatic acids and esters (AAE), aliphatic alcohols, aldehydes and ketones (AAAK), furan derivatives (FD), cyclopentane derivatives (CPD), pyran derivatives (PD) and anhydrosugars (AHS) in carbohydrates related volatile products from pyrolysis of parent softwood and LHRs.

**Table 5**
Peak assignments and relative abundance (%) of lignin and carbohydrate derived pyrolysis products detected in parent wood and LHRs samples.

| Peak number | Compound | Origin | Compound proportion in the volatiles, % | | | | |
|---|---|---|---|---|---|---|---|
| | | | Softwood | LHR pre-treatment | LHR AH | LHR SHF | LHR SSF |
| 1 | $CO_2$ | C, L[a] | 4.9 | 14.5 | 14.6 | 20.8 | 21.3 |
| 2 | $H_2O$ | C, L | 5.2 | 2.6 | 3.8 | 4.3 | 4.5 |
| 3 | Methanol | C, L | 4.8 | 1.7 | 7.8 | 5.5 | 6.4 |
| 4 | Acetone | C | 2.2 | 6.5 | 5.8 | 3.8 | 3.5 |
| 5 | Methylglyoxal | C | 4.9 | n.d.[b] | n.d. | n.d. | n.d. |
| 6 | Furan,2-methyl | C | 0.9 | 1.0 | 0.5 | 0.5 | 0.5 |
| 7 | 2,3-Butanedione | C | 2.4 | 1.9 | 1.8 | 0.6 | 0.5 |
| 8 | 2-Butanone | C | 1.0 | Traces | Traces | Traces | Traces |
| 9 | Formic acid, methyl ester | C | 0.7 | 0.6 | n.d. | 0.9 | 0.7 |
| 10 | Hydroxyacetaldehyde | C | 2.4 | 0.4 | 2.0 | Traces | Traces |
| 11 | 2-Butenal | C | 1.7 | 0.1 | 0.1 | n.d. | n.d. |
| 12 | Acetic acid | C | 6.4 | 2.0 | 1.8 | 1.3 | 1.2 |
| 13 | Ethyl propenyl ether | C | 0.2 | n.d. | Traces | n.d. | n.d. |
| 14 | 2-Propanone | C | 6.7 | 0.7 | 2.1 | 2.0 | 1.5 |
| 15 | Propanoic acid | C | 0.1 | 0.3 | 0.3 | 0.3 | 0.3 |
| 16 | Propanoic acid, methyl ester | C | 0.1 | Traces | n.d. | n.d. | n.d. |
| 17 | Cyclopentanone | C | 0.1 | Traces | 0.1 | 0.2 | 0.1 |
| 18 | 2-Butanone,1-hydroxy | C | 0.1 | 0.2 | n.d. | 0.2 | 0.1 |
| 19 | 3-Hydroxypropanal | C | 1.7 | Traces | 0.3 | 0.6 | 0.3 |
| 20 | 2(5H)-Furanone | C | 2.1 | 0.3 | 0.6 | 0.4 | 0.2 |
| 21 | 5-(Hydroxymethyl)-2(5H)-furanone | C | 0.6 | 2.0 | n.d. | 0.3 | 0.2 |
| 22 | 2-Hydroxy,4-oxobutanal | C | 0.7 | n.d. | n.d. | n.d. | n.d. |
| 23 | 2-Hydroxy,3-oxobutanal | C | 1.9 | 0.2 | 0.4 | 0.5 | 0.2 |
| 24 | 2(3H)-Furanone,5-ethoxydihydro | C | 1.0 | 0.2 | 1.3 | n.d. | n.d. |
| 25 | Furfural (2-Furalaldehyde) | C | 1.9 | 6.2 | 1.3 | 2.7 | 0.9 |
| 26 | 2(3H)-Furanone,5-methyl | C | 0.2 | 0.5 | 0.2 | Traces | Traces |
| 27 | Furfuryl alcohol | C | Traces | Traces | 0.7 | 0.2 | 0.7 |
| 28 | Acetol acetate | C | 0.6 | Traces | Traces | 0.1 | 0.1 |
| 29 | 2-Cyclopentene-1-one,2-methyl | C | 0.2 | Traces | 0.2 | Traces | Traces |
| 30 | 2-Heptanone, 3-methyl | C | 0.4 | 0.3 | 0.1 | Traces | Traces |
| 31 | 2-Acethylfuran | C | 0.2 | 0.5 | 0.2 | 0.1 | 0.1 |
| 32 | 1,2-Cyclopentadione | C | 4.2 | 1,2 | 1.1 | 0.5 | 0.2 |
| 33 | Furfural,5-methyl | C | 0.2 | 1.2 | 0.3 | 0.8 | 0.6 |
| 34 | 2-Butanone, 1-hydroxy-acetate | C | 0.2 | 0.5 | n.d. | Traces | Traces |
| 35 | 2-Cyclopenten-1-one, 3-methyl | C | 0.2 | 0.2 | 0.2 | 0.1 | Traces |
| 36 | (3H)-Furan-2-one,dihydro | C | 0.3 | Traces | Traces | 0.1 | Traces |
| 37 | (5H)-Furan-2-one (gamma-Crotonolactone) | C | 2.1 | 0.3 | 0.6 | 0.4 | 0.2 |
| 38 | 2(5H)-Furanone, 5-methyl | C | 0.5 | 0.6 | 0.2 | 0.1 | 0.1 |
| 39 | 3-Hydroxy-5,6-dihydro-(4H)-pyran-4-one | C | 0.4 | 0.4 | Traces | n.d. | n.d. |
| 40 | 2-Cyclopenten-1-one, 2,3-dimethyl- | C | 0.1 | 0.1 | 0.2 | Traces | Traces |
| 41 | 1,2-Cyclopentanedione, 3-methyl- | C | 2.4 | 0.7 | 0.8 | 0.5 | 0.3 |
| 42 | 2-Cyclopenten-1-one,3-ethyl-2-hydroxy- | C | 0.4 | Traces | n.d. | n.d. | n.d. |
| 43 | Phenol | L | 0.3 | 1.0 | 1.6 | 1.4 | 1.7 |
| 44 | o-Guaiacol | L | 3.2 | 5.5 | 14.9 | 14.5 | 15.3 |
| 45 | o-Cresol (o-methylphenol) | L | 0.2 | 0.6 | 1.1 | 0.9 | 1.1 |
| 46 | Methyl 2-furoate | C | n.d. | 0.5 | n.d. | n.d. | n.d. |
| 47 | 3-Hydroxy-2-methyl-pyran-4-one | C | 0.3 | 0.2 | n.d. | n.d. | n.d. |
| 48 | Phenol,2,3/3,4-dimethyl- or phenol-2-ethyl | L | n.d. | n.d. | 0.2 | 0.2 | 0.2 |
| 49 | Guaiacol,6-methyl | L | 0.3 | 0.4 | 0.9 | 1.0 | 1.1 |
| 50 | p-Cresol | L | 0.2 | 0.4 | 0.6 | 1.2 | 0.9 |
| 51 | m-Cresol | L | 0.1 | 0.2 | 1.0 | 0.7 | 0.6 |
| 52 | 4-Methyl-5H-furan-2-one | C | 0.3 | Traces | n.d. | n.d. | n.d. |
| 53 | Guaiacol,5-methyl | L | n.d. | 0.3 | 0.4 | 0.3 | 0.4 |
| 54 | Guaiacol,4-methyl (p-Methylguaiacol) | L | 3.8 | 5.8 | 7.1 | 10.3 | 11.7 |
| 55 | Phenylpropiolaldehyde | L | n.d. | 0.6 | n.d. | n.d. | 0.2 |
| 56 | Phenol,2,3-dimethyl-or phenol-3-ethyl | L | 0.3 | 0.7 | 0.8 | 1.0 | 1.0 |
| 57 | Benzene, 1,2-dimetoxy-4-methyl | L | n.d. | n.d. | 2.8 | 0.6 | 0.6 |
| 58 | Benzene, 1,2-dimetoxy 3-methyl | L | n.d. | n.d. | n.d. | 0.2 | 0.2 |
| 59 | n-Pentanal (Valeraldehyde) Pentanedial | C | 1.0 | n.d. | n.d. | n.d. | n.d. |
| 60 | Levulinic acid | C | n.d. | n.d. | 2.6 | n.d. | n.d. |
| 61 | 3,5-Dihydroxy-2-methyl-(4H)-pyran-4-one | C | 0.1 | 0.1 | n.d. | n.d. | n.d. |
| 62 | Benzene, 1,4-dimetoxy-2-methyl | L | n.d. | n.d. | 0.1 | 0.1 | 0.1 |
| 63 | Phenol,2,5/,2,4-dimethyl- | L | n.d. | n.d. | 0.3 | Traces | Traces |
| 64 | Phenol, 4-allyl- | L | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 |
| 65 | 4-Hydroxy-2,4,5-trimethyl-2,5-cyclohexadiene-1-one | C | 0.1 | 0.5 | 0.5 | 0.7 | 0.8 |
| 66 | Guaiacol, 4-ethyl- | L | 0.1 | 0.5 | 0.5 | 0.7 | 0.8 |
| 67 | Phenol, 2-ethyl-5-methyl- | L | n.d. | n.d. | 0.2 | 0.2 | 0.2 |
| 68 | Hydroperoxide, 1-methylhexyl-( | C | 0.9 | 0.7 | n.d. | n.d. | n.d. |
| 69 | 2,4 (3H,5H)-Furandione, 3-methyl- | C | 1.0 | n.d. | n.d. | n.d. | n.d. |
| 70 | 2H-Pyran-3(4H)-one, dihydro- | C | 0.6 | 0.2 | Traces | 0.1 | 0.1 |
| 71 | Benzene, 1,2-dimethoxy-3-methyl- | L | n.d. | n.d. | n.d. | 0,2 | 0.2 |
| 72 | Ethanone,1-(2-hydroxy-4-methoxyphenyl)- | L | Traces | 0.5 | 0.3 | 0.6 | 0.6 |
| 73 | 1,4,3,6-Dianhydro-α-D-glucopyranose | C | 0.3 | 4.9 | 0.2 | Traces | Traces |

Table 5 (*Continued*)

| Peak number | Compound | Origin | Compound proportion in the volatiles, % | | | | |
|---|---|---|---|---|---|---|---|
| | | | Softwood | LHR pre-treatment | LHR AH | LHR SHF | LHR SSF |
| 74 | 1,4-Dimethoxy-2,3-dimethylbenzene (b.p.151) | L | n.d. | n.d. | n.d. | n.d. | 0.2 |
| 75 | Ethanone,1-(2-hydroxy-6-ethoxyphenyl)- | L | n.d. | n.d. | 0.2 | 0.2 | 0.2 |
| 76 | Guaiacol, 4-vinyl- | L | 3.6 | 1.8 | 3.5 | 3.0 | 3.2 |
| 77 | p-Eugenol | L | 1.4 | 0.5 | 1.0 | 1.2 | 1.3 |
| 78 | Phenol, 4-allyl- | L | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 |
| 79 | 5-Hydroxymethylfurfural (OMF) | C | 1.2 | 2.0 | 0.5 | 0.3 | Traces |
| 80 | 1,2-Dimetoxy-4-vinylbenzene | L | n.d. | n.d. | n.d. | 0.1 | 0.1 |
| 81 | 5-(Hydroxymethyl)dihydro-2(3H)-furanone | C | 0.1 | Traces | 0.1 | n.d. | n.d. |
| 82 | Isoeugenol (cis) | L | 1.0 | 0.2 | 0.5 | 0.6 | 0.6 |
| 83 | o-Eugenol | L | | 0.2 | | | |
| 84 | Phenol, 3-methoxy-5-methyl- | L | 0.1 | 0.7 | 0.2 | 0.2 | 0.2 |
| 85 | Phenol,2-methoxy-3-(2-propenyl)- | L | n.d. | n.d. | n.d. | 0.1 | 0.2 |
| 86 | Isoeugenol (trans) | L | 4.2 | 2.2 | 2.2 | 2.4 | 2.6 |
| 87 | Vanillin | L | 1.1 | 1.1 | 1.1 | 1.6 | 1.2 |
| 88 | Isovanillin | L | 0.1 | n.d. | n.d. | n.d. | 0.1 |
| 89 | Homovanillin | L | 0.6 | 0.7 | 0.2 | 0.2 | 0.2 |
| 90 | Vanillic acid, methyl ester | L | Traces | n.d. | 0.2 | 0.2 | 0.2 |
| 91 | Acetoguaiacone | L | 0.7 | 0.5 | 0.8 | 1.0 | 1.1 |
| 92 | Guaiacyl acetone | L | 0.5 | 0.7 | 1.0 | 1.0 | 1.2 |
| 93 | Homovanillic alcohol | L | n.d. | 0,1 | n.d. | n.d. | 0.6 |
| 94 | Propioguaiacone | L | 0.1 | 0.1 | 0.2 | 0.3 | 0.3 |
| 95 | Coniferyl alcohol | L | 0.4 | n.d. | n.d. | n.d. | n.d. |
| 96 | Ethanone,1-(3-hydroxy-4-methoxyphenyl)- | L | Traces | 0.5 | 0.3 | 0.6 | 0.6 |
| 97 | Dihydroconiferyl alcohol | L | 1.4 | n.d. | 0.6 | n.d. | n.d. |
| 98 | Levoglucosan | C | 0.8 | 7.2 | Traces | Traces | 0.5 |
| 99 | Homovanillic acid | L | n.d. | 1.0 | n.d. | 1.9 | 1.1 |
| 100 | Coniferylaldehyde | L | 0.7 | n.d. | 0.4 | n.d. | n.d. |
| 101 | 1,6-Anhydro-beta-D-glucofuranose | C | n.d. | 0.7 | n.d. | n.d. | n.d. |
| Carbohydrates originated products, total | | 57.0 | 45.6 | 25.6 | 16.7 | 12.4 | |
| Lignin originated products, total | | 25.3 | 27.3 | 47.1 | 50.3 | 43.6 | |

[a] C, carbohydrates originated product; L, lignin originated product.

[b] n.d., not detected.

pretreatment step the major part (more than 50%) of carbohydrates derived volatiles are presented by cyclic compounds: furan, pyran, cyclopentane derivatives and anhydrosugars. The drastic increase in relative contents of furfural, methylfurfural, hydroxymethylfurfural, levoglucosan and levoglucosenone in the volatile products of LHR pretreatment was observed (Table 5). These data show that the acid catalysed steam explosion pretreatment of softwood has not degraded polysaccharides (e.g. pentosans and cellulose) significantly. Comparison of the portions of furan and cyclopentane derivatives in the volatile pyrolytic products (Table 5) indicates more effective degradation of pentoses by enzymatic hydrolyses, in particular, by SSF process.

The destructive transformation of lignin macromolecule upon softwood hydrolysis is evident in comparison of Py-GC/MS data for LHRs with those for untreated softwood (Table 5). The increase in portion of guaiacyl derivatives with shortened side chains $\{Ph(C_1)+Ph(C_2)\}$ could be considered as a consequence of the cleavage of the native β-aryl-alkyl bonds in lignin [8], whereas an increase in the relative content of guaiacyl derivatives without side chains (Ph) points out that more severe lignin transformations take place. The ratio of $\{Ph+Ph(C_1)+Ph(C_2)\}$portion to the $Ph(C_3)$ compounds portion increases for all LHRs in comparison with the parent softwood (Fig. 4), confirming cleavage and degradation of lignin side chains [18].

The significant increase in the portion of phenyl derivatives and appearance of benzene derivatives (Table 5) indicates the condensation changes in the structure of lignin component upon all steps of softwood processing beginning with the pretreatment step. The highest development of condensation processes was observed for acid hydrolysis: LHR AH is characterized with the extremely high portion of benzene derivatives in pyrolytic volatile products (15 times higher than that for untreated softwood and 4–5 times higher in comparison with other LHRs investigated).

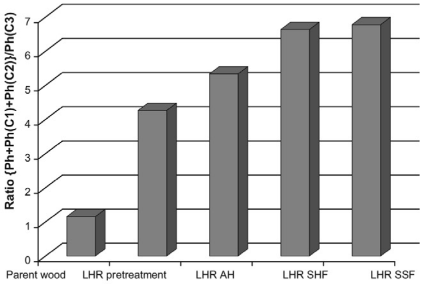

**Fig. 4.** Ratio of the portions of G-type phenols with shortened apliphatic chains $\{Ph+Ph(C_1)+Ph(C_2)\}$ and those with propanoid aliphatic chains $Ph(C_3)$ in the lignin-related volatile products from parent softwood and LHRs.

## 4. Conclusion remarks

Application of Py-GC/MS method for characterization of solid residues obtained from wood processing aimed at bioethanol production opens the opportunity for control of processing conditions and estimation of efficiency of different hydrolysis configurations. The highest efficiency in conversion of softwood carbohydrate components has been found for SSF process.

The development of condensation reactions, ether bonds cleavage, degradation of side propanoid chains and oxidation of LHRs lignin component has been revealed using Py-GC/MS together with complementary techniques and chemical analysis. The characterization of component composition of non-hydrolyzed residues by Py-GC/MS gave direct evidences of incorporation of part of carbohydrates as well as products of their degradation into lignin matrix.

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## P-8

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# Two approaches for introduction of wheat straw lignin into rigid polyurethane foams

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# Two Approaches for Introduction of Wheat Straw Lignin into Rigid Polyurethane Foams

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**Abstract**

In present work the BIOLIGNIN$^{TM}$ obtained in the result of wheat straw organosolv processing in CIMV pilot plant (France) was investigated as a component of rigid polyurethanes (PUR) foam systems. Different separate approaches of lignin introduction into PUR foam system were studied: as filler without chemical preprocessing and as liquid lignopolyol obtained by lignin oxypropylation in alkali conditions. The incorporation of increasing amount of lignin as filler into reference PUR foam systems on the basis of mixture of commercial polyethers Lupranol 3300 and Lupranol 3422 steadily decreased the compression characteristics of foams, their dimensional stability and hydrophobicity. The complete substitution of Lupranol 3300 by lignopolyol increases its cell structure uniformity and dimensional stability and does not reduce the physical-mechanical properties of foam. In both cases the incorporation of lignin into PUR foam leads to the decreasing of maximum values of thermodegradation rates. The lignin filler can be introduced into lignopolyol based PUR foam in higher quantity than in the reference Lupranol based PUR without reduction of compression characteristics of material. In this work the optimal lignin content in the end product - PUR foam as both polyol and filler is 16%.

**Keywords**: lignin, propylene oxide, lignopolyol, rigid polyurethane foam.

## INTRODUCTION

Rigid polyurethane foam is one of the most important materials used as thermal insulation of buildings, refrigerators, cold stores, pipes, refrigerated transport, and in chemical and food industries [1]. The world consumption of PUR foam systems in 2007 was 3720 million tones - 21% from global polyurethane market. PUR foam consumption is predicted to increase in the future steadily [2]. The application of renewable resources instead of petrochemical raw materials is one of the main directions in modern development of PUR foam chemistry and technology [3].

Lignin, the most abundant natural phenolic polymer, is separated from the plant biomass as by-products in results of hydrolysis and pulp making processes. Free phenolic and aliphatic hydroxyl groups allow lignin application in PUR foam compositions. Investigations aimed at incorporation of well known industrial wood lignins (kraft, lignosulfonates, hydrolysis and water-ethanol extracted lignin) into PUR foam system are known [4-6]. In this works lignins were introduced into polyol systems without any modification or were preliminary modified with propylene oxide (PO). Due to limited solubility in polyols the non-modified technical lignins acted in PUR foams mainly as active filler. In the result of oxypropylation liquid lignin containing polyols soluble in organic solvents were synthesized and then incorporated into PU polymeric matrix as a macromonomers. Beneficial effect of both approaches strongly depends on chemical and structural characteristics of lignin used. In the present work the object of investigation was a novel technical lignin – BIOLIGNIN$^{TM}$ obtained as product of wheat straw biorefinery based on biomass treatment with mixture of water solution of acetic and formic acids at CIMV pilot plant [7]. Its application in PUR foam systems as filler and liquid lignopolyol, obtained by oxypropylation of BIOLIGNIN$^{TM}$, is the aim of presented work.

## EXPERIMENTAL

*Materials*

BIOLIGNIN$^{TM}$ used for oxypropylation was washed for increasing pH up to 4.4 and air dried up to 5% of water content. BIOLIGNIN$^{TM}$ used as filler for PUR foam was ground in laboratory scale disintegrator DESI-11 and then oven dried for 24 hours at 105°C.

*Oxypropylation of lignin*

The reaction was carried out in 1 L. Parr reactor: 140.00 g of PO (Sigma-Aldrich), 63.15 g of washed and air dried lignin (water content 5%) and 3.00 g of KOH (Lachner) were loaded into reactor. Reactor was sealed and heated with stirring to 160-165°C when exothermic reaction has started. The pressure inside reactor increased to maximum and then dropped dramatically to value close to atmospheric. After reactor cooling the KOH was neutralized by acetic acid, product was dissolved in dichloromethane and filtered. Dichloromethane was distilled off in vacuum evaporator. Five repeated synthesis were made. All batches were combined together, characterized and used for PUR foam preparation.

*Chemical analysis*

The methoxyl groups ($-OCH_3$) content in lignin samples was determined according to the Viebock-Schwappach [8]. The combined content of both aliphatic and phenolic OH groups in lignin and hydroxyl value (OHV) of lignoplyols was determined using acetylation of samples by acetic anhydride and potentiometric titration of free acid by 0.1 N NaOH solutions in water [8].

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The contents of phenolic (-$OH_{ph.}$) and carboxylic groups (-$OH_{COOH}$) in BIOLIGNIN$^{TM}$ were determined by chemisorption method using barium chloride and calcium acetate [8]. The content of acid groups in lignopolyol was determined by acid-base conductometric titration [8]. The viscosity of lignopolyol was determined by rotation viscometer HAAKE Viscotester 6L/R plus at 20°C.

*PUR foam preparation and characterization*

All components of reference PUR foam system are shown in Table 1.

**TABLE 1** - The composition of reference PUR foam

| Constituent | Supplier | Content, pbw |
|---|---|---|
| Lupranol 3330 (OHV=400 mg KOH/g) | BASF | 70.0 |
| Lupranol 3422 (OHV=490 mg KOH/g) | | 30.0 |
| Water | | 0.5 |
| Catalyst Polycat 5 | Air Products | 0.5 |
| Potassium acetate | Performance Chemicals | 0.8 |
| TCPP (trichlorpropylphosphate) | Albemarle | 25.0 |
| Surfactant Niax Silicone L 6915 | Momentive | 1.5 |
| Blowing agent Solkane 365/227 (87:13) | Solvay | 20.0 |
| Isocyanate IsoPMDI 92140 (NCO=31.8%) | BASF | 130.7 |

Lupranol 3300 was gradually substituted by lignopolyol. The lignin filler was added into the polyol component of reference and lignopolyol containing systems. Correction of polymeric methylene diphenyl diisocyanate (PMDI) amount has been done for each composition taking into account NCO/OH=1.2. All foams were obtained by free rising method and tested. Measurements of compression strength, apparent density, closed cell content, dimensional stability, water absorption of foams were performed according DIN EN 826:1996, ISO 4590, DIN 53420, ISO 2796 and DIN 53428 respectively. Scanning electron microscope SEM TESCAN TS 5136 MM was used to study cell structure. The thermo gravimetric (TG) tests of foams were performed in nitrogen atmosphere in temperature range 10-1000°C using Metler Toledo Star System TGA/STDA 851$^{e}$. The glass transition temperature (Tg) of PUR foam was measured using Metler Toledo Star DSC 823$^{e}$ device. Samples were first heated to 170°C thereafter cooled to -20°C and then again heated to 170°C. Tg was determined from the second scan.

# RESULTS AND DISCUSSION

*Oxypropylation of lignin and characterization of lignopolyols*

BIOLIGNIN$^{TM}$ contains relatively high amount of hydroxyl groups able to copolymerize with PO in the condition of alkali catalysis (Table.2). Moreover 28.6% of total BIOLIGNIN$^{TM}$ OH groups are represented by acid hydroxyl groups ($OH_{ph}$ and $OH_{COOH}$), which could be more favorable for copolymerization with PO in alkaline conditions comparing to more neutral lignins [9].

**TABLE 2** - The functional composition of BIOLIGNIN$^{TM}$

| The content of functional groups, mmol/g | | | | |
|---|---|---|---|---|
| $OCH_3$ | $OH_{ph}$ | $OH_{COOH}$ | $OH_{aliph}$ | $OH_{total}$ |
| 3.1 | 1.1 | 1.3 | 6.0 | 8.4 |

At temperature ~160°C the activation barrier was reached and spontaneous exothermic process commenced.

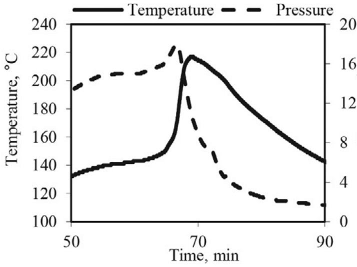

**FIGURE 1** - Pressure-time-temperature diagram of BIOLIGNIN$^{TM}$ oxypropylation in Parr reactor

Two major reactions take place: 1) copolymerization of PO with OH groups of lignin, leading to the disappearance of acidic OH groups and appearance of aliphatic OH groups distant from aromatic ring. 2) homopolymerization of PO leading to formation of polypropylene glycols. As the result liquid lignopolyols completely soluble in alcohols, cyclic ethers and dichloromethane were synthesized. Conductometric data testified the absence of free $OH_{ph}$ and COOH groups in lignopolyols.

**TABLE 3** - Characteristics of lignoplyols

| Batch | The lignopolyols characteristics | | |
|---|---|---|---|
| | OHV, mg KOH/g | Viscosity at 20°C, Pa*s | $H_2O$, % |
| 1 | 446.8 | 26.1 | 0.06 |
| 2 | 474.5 | 23.7 | 0.07 |
| 3 | 396.0 | 12.7 | 0.05 |
| 4 | 450.8 | 17.3 | 0.07 |
| 5 | 427.0 | 20.9 | 0.15 |
| (1-5) | 445.0 | 20.1 | 0.10 |

The results of repeated experiments testified that repeatability of OHV values was higher than that of lignopolyols viscosity values (Table 3). For all lignopolyols obtained the OHV and viscosity values correspond to the requirements for polyols usable in rigid foam formulation [1, 5].

*Characterization of PUR foam*

The kinetics of PUR foam formation is one of the factors influencing on the properties of materials.

**TABLE 4** – The change of gel time values of PUR foam compositions in dependence of lignopolyol content in them

| Substitution extent, % | Lignopolyol content, % | Lignin content, % | Gel time, s |
|---|---|---|---|
| 0 | 0 | 0 | 200 |
| 25 | 6.3 | 1.9 | 126 |
| 50 | 12.5 | 3.8 | 90 |
| 75 | 18.9 | 5.7 | 75 |
| 100 | 25.0 | 7.5 | 70 |

Lignopolyols are more reactive towards isocyanate comparing to the mix of both commercial polyethers used in reference sample. Almost threefold decrease of gel time was observed at complete substitution of Lupranol 3330 by lignopolyol (Table 4). The high reactivity of OH groups of lignopolyol and catalytic effect of potasium acetate (~2.5%) can explain the effect observed. The higher activity of PUR foam composition revealed itself in higher rate of heat release during foaming. As the result the apparent density of PUR foam decreased from 53 to 40 kg/m$^3$ at complete substitution of Lupranol 3300 by lignopolyol. Vice versa the retardation effect was observed at introduction of lignin as filler into PUR foam composition (Table 5).

**TABLE 5** - The gel time and density values of PUR foam compositions vs. lignin filler content

| Lignin content | | Gel time, s | Density, kg/m$^3$ |
|---|---|---|---|
| g /100 g of polyol | In PUR foam, % | | |
| 0 | 0 | 200 | 52.8 |
| 5 | 1.8 | 223 | 47.9 |
| 10 | 3.5 | 240 | 47.3 |
| 20 | 6.7 | 265 | 44.7 |
| 30 | 9.7 | 283 | 42.4 |
| 40 | 12.5 | 450 | 42.0 |
| 50 | 15.2 | 510 | 39.5 |

This fact can be explained by decrease of catalysts concentration in composition of PUR foam and by binding of basic amine catalyst with free acetic/formic acids present in lignin. The last assumption is confirmed by decrease of apparent density of lignin filled foam due to free carboxylic acids reaction with isocyanate and subsequent substituted amide and carbon dioxide formation, acting as a blowing agent [1].

Mechanical characteristics of PUR foam directly correlate with its density [1]. Therefore for comparison of characteristics of all PUR foams the compressive strength and Young's modulus values were normalized to density 44.5 kg/m$^3$.

Characteristics of PUR foams containing lignin filler and lignopolyol were evaluated taking into account total dry lignin content in material (lignopolyol contains 30% of lignin).

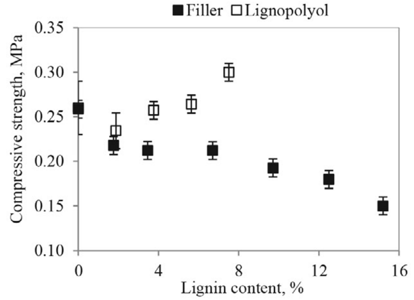

**FIGURE 2** - The compressive strength of PUR foams in direction to foam rising vs. lignin content

The steady decreasing of PUR foam compression strength with increasing of lignin filler content was observed while the increasing of lignopolyol content did not affect the strength of material (Fig. 2). Moreover at complete substitution of thee functional Lupranol 3330 by lignopolyol the increment of strength value was observed. The same type dependence was established for Young's modulus values.

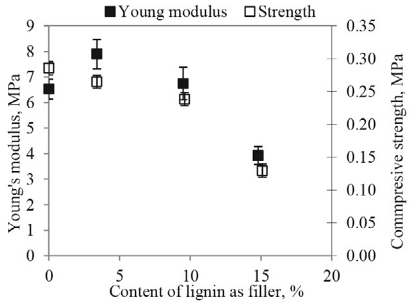

**FIGURE 3** - The effect of lignin filler content on compression characteristics in direction of foam rising of lignopolyol based PUR foams. (The characteristics of reference foam: Young modulus=6.87 MPa, strength =0.26 MPa).

It was found that up to 16% total lignin content does not reduce compressive characteristics of material. It was achieved at compete substitution of Lupranol 3330 by lignopolyol and simultaneous incorporation of 10% of lignin filler (Fig. 3).

These facts testify that not only two functional propylene glycols but also high functional modified lignin have been incorporated as reactive macromonomers into polyurethane (PU) matrix of lignopolyol containing foam. Moreover the compatibility of lignopolyol containing PU matrix with lignin filler was better in comparison with that of lignopolyol free PU matrix.

The data of TG analysis show that increasing of lignopolyol content in foam did not influence temperature values ($T_{max}$) at which maximum rates ($dm/dt_{max}$) of foam thermodegradation were achieved, though the magnitude of these rates were decreased dramatically (Table 6).

**TABLE 6** - The data of TG analysis for PUR foams

| Lignopolyol content, % | $T_{max}$, °C | $dm/dt_{max}$, mg/min | Charcoal yield at 1000 °C, % |
|---|---|---|---|
| 0 | 331 | 1.20 | 14.9 |
| 6.3 | 327 | 0.93 | 11.9 |
| 12.5 | 327 | 0.74 | 11.7 |
| 18.9 | 326 | 0.51 | 10.5 |
| 25.0 | 334 | 0.54 | 14.2 |

The yield of charcoal residue changed insignificantly. For lignopolyol free foams containing lignin filler the decreasing of thermodegradation rate was less pronounced, but the yield of charcoal was somewhat higher at the same content of lignin in foam.

The Tg values of reference PUR foam and foam with 6-25% of lignopolyol were in the range 110-119°C. This shows that lignopolyol can successfully substitute the three functional glycerol based commercial polyol in PUR foam systems without decreasing of heat resistance of material.

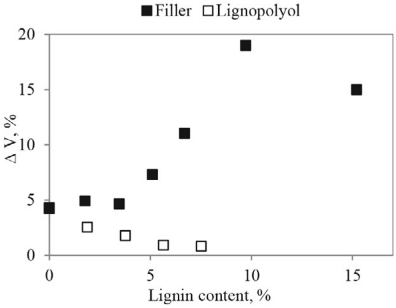

**FIGURE 4** - The increment of volume (ΔV) of PUR foam samples vs. lignin content after 28 days storage at 80°C in dry atmosphere

The lignopolyol containing PUR foams revealed much higher dimensional stability in comparison with reference samples and approximately the same hydrophobicity. Vice versa those characteristics declined significantly for lignopolyol free foams containing lignin filler (Fig. 4-5). This fact can be explained by lager cell structure of filled foams despite the same content of closed cells in all foams (92±3 %).

The ΔV and water absorption values for PUR foam containing 22% of lignopolyol and 9.5% of lignin filler were 0.6% and 3.1% respectively which is lower than data of lignopolyol containing foam without filler.

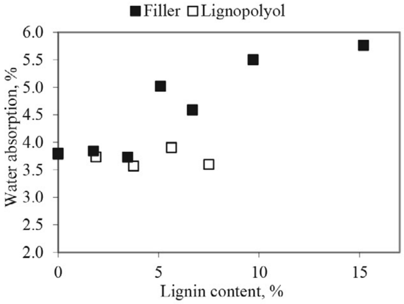

**FIGURE 5** - The water absorption values of PUR foams vs. lignin content after 7 days storage in fresh water

## CONCLUSIONS

The modification of BIOLIGNIN™ by propylene oxide allows production of highly reactive lignopolyols which can completely substitute commercial glycerol based polyether in PUR foam composition. This substitution improved dimensional stability and hydrophobicity of foam and did not affect on its compressive and heat resistance characteristics.

The introduction of BIOLIGNIN™ as filler into reference lignopolyol free composition leads to decreasing of the main characteristics of foams.

The best characteristics of material were achieved when BIOLIGNIN™ was simultaneously introduced into the foam compositions both as polyol and filler.

## ACKNOWLEDGEMENTS

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The corresponding author ensures that the description of A. Arshanitsa contributions to the published work is accurate and agreed by all authors.
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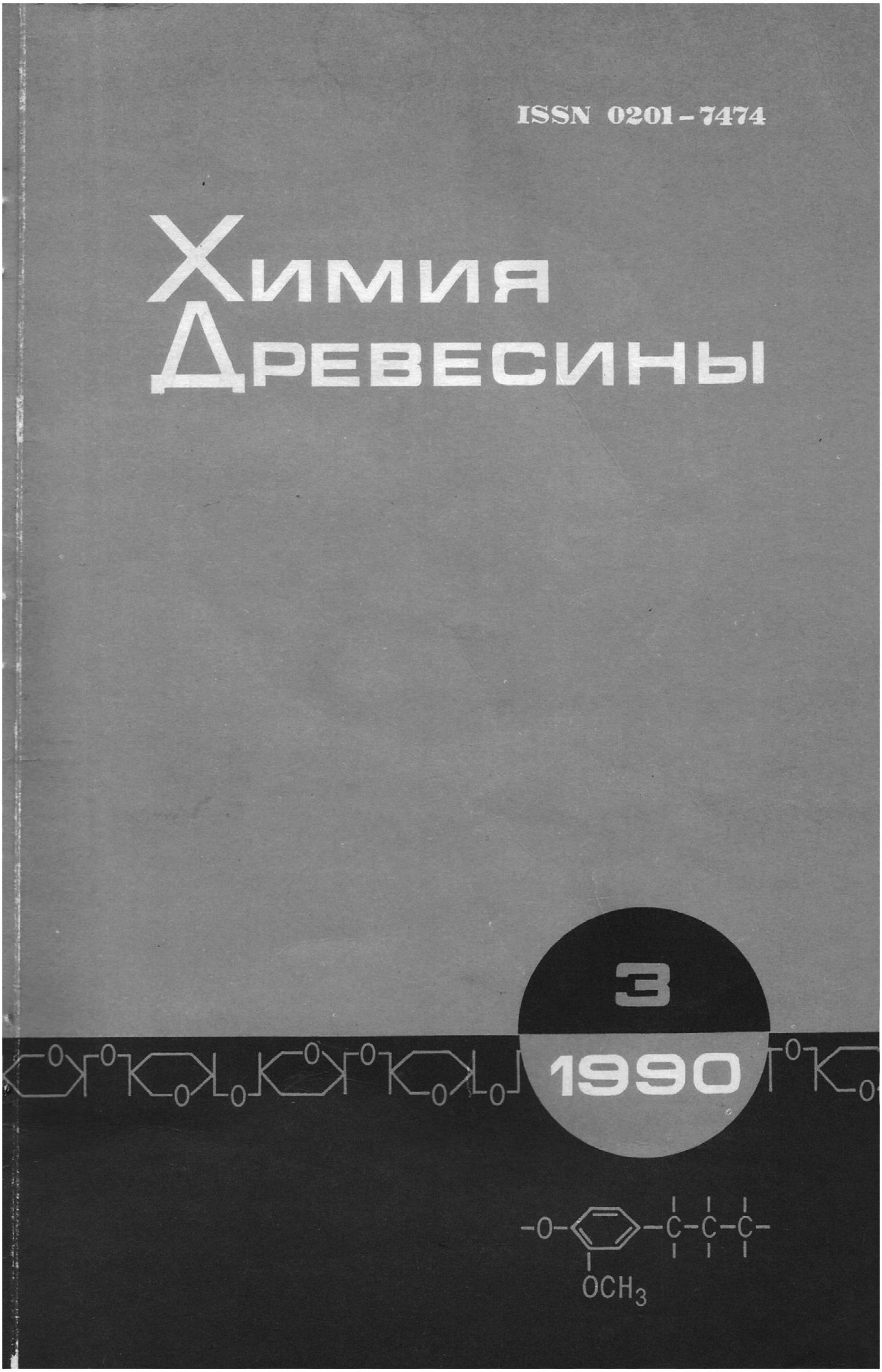

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# ВЛИЯНИЕ МЕХАНИЧЕСКОЙ ОБРАБОТКИ НА СВОЙСТВА ГИДРОЛИЗНОГО ЛИГНИНА КАК НАПОЛНИТЕЛЯ ЭЛАСТОМЕРОВ

При введении в действие всех мощностей гидролизного производства в стране ежегодно в отвалах, загрязняющих окружающую среду, будет скапливаться свыше 1 млн. т гидролизного лигнина [1]. Перспективным направлением утилизации гидролизного лигнина является использование его в качестве наполнителя эластомеров [2]. Однако необработанный лигнин вследствие низкой степени дисперсности не оказывает упрочняющего действия на полимеры, что вызывает необходимость его активации, например путем механической обработки. В настоящее время для механической активации различных материалов широко используется дезинтеграторная технология, при которой в процессе диспергирования изменяется химическая структура материала [3, 4].

В данной работе исследовано влияние дезинтеграторной обработки на процесс механоактивации гидролизного лигнина (ЛГ), изучены физико-механические свойства лигнонаполненных композитов на основе каучуков СКЭПТ-40 и СКФ-26.

В качестве объекта исследования использован ЛГ Кедайняйского биохимического завода (табл. 1). Дезинтеграторную обработку лигнина проводили в СКТБ «Дезинтегратор» (г. Таллинн), используя лабораторную установку Д-7119 с комплектом

Таблица 1

ФИЗИКО-МЕХАНИЧЕСКИЕ СВОЙСТВА ЛИГНИНА, ПОДВЕРГНУТОГО МЕХАНИЧЕСКОЙ ОБРАБОТКЕ*

| Параметры обработки | Влажность, % | Температура перехода, °С | Содержание ОН-групп, % |
|---|---|---|---|
| | Исходный лигнин** | | |
| — | 5,3 | 75 | 7,3 |
| | Обработка в дезинтеграторе | | |
| $n \cdot 10^3$ об/мин: | | | |
| 5,0 | 6,0 | 55 | 10,9 |
| 10,0 | 5,3 | 47 | 11,1 |
| 15,0 | 3,9 | 45 | 10,1 |
| 17,0 | 2,6 | 50 | 12,6 |
| 20,0 | 3,0 | 45 | 12,7 |
| | Обработка в шаровой мельнице | | |
| Продолжительность, ч: | | | |
| 1,0 | 3,6 | 60 | 7,6 |
| 3,5 | 4,2 | 55 | 8,2 |
| 9,0 | 3,9 | 55 | 9,2 |
| 24,0 | 4,1 | — | 9,3 |

* Зольность образцов ЛГ составляла 4,7 . . . 5,3%.
** Частицы диаметром менее 1,0 мм.

6-рядных роторов типа 6П при частоте вращения роторов $(2\ldots20)\cdot10^3$ об/мин. Расход материала составлял 2,5 кг/ч. Для иллюстрации особенностей диспергирования ЛГ путем дезинтеграторной обработки по сравнению с традиционными видами механической обработки исследованы свойства ЛГ, размолотого в шаровой мельнице. Продолжительность размола составляла 1,0 ... 24,0 ч. Анализ дисперсного состава лигнина выполнен комбинированным методом, совмещающим ситовый и седиментационный анализ. ЛГ фракционировали на комплекте сит с размером ячеек от 1,0 до 0,1 мм. Гранулометрический состав фракций с размером частиц менее 0,1 мм определяли на развертывающем фотоседиментографе «Analizette», результаты обрабатывались автоматически. В качестве рабочей жидкости был выбран бензол. При расчете гранулометрического состава плотность лигнина принимали равной 1,5 г/см³.

Удельную поверхность образцов ЛГ определяли двумя методами — методом тепловой десорбции аргона $S_{\text{Ar}}$ в токе гелия [5] и методом воздухопроницаемости $S_{\text{в}}$ [6]. Метод воздухопроницаемости позволяет оценить лишь площадь внешней поверхности частиц, методом тепловой десорбции определяли площадь их полной поверхности с учетом поверхности пор. Разность значений $S_{\text{Ar}}$ и $S_{\text{в}}$ характеризует степень развития пористой структуры ЛГ.

Для определения термомеханических характеристик ЛГ образцы, высушенные в вакууме при температуре кипения ацетона (56,2°C), помещали в термомеханическую установку [7] и охлаждали жидким азотом до −50°C. Затем образец нагружали ($p = 0{,}5$ МН/м²) и нагревали со скоростью 2°C/мин до 150°C. Температуру измеряли с точностью ±0,5°C, деформацию определяли с точностью ±2 мкм. Для предотвращения сорбции паров воды опыт проводили в атмосфере сухого газообразного аргона.

Общее содержание гидроксильных групп определяли методом ацетилирования [8].

Основными характеристиками наполнителей, определяющими их усиливающее действие на полимеры, являются дисперсность и пористость, которые обеспечивают развитую площадь контакта на границе раздела полимера с наполнителем [9, 10].

Как видно из рис. 1, при увеличении частоты вращения роторов дезинтегратора до 15 тыс. об/мин, что соответствует максимальной расчетной скорости удара 225 м/с, внешняя удельная поверхность частиц увеличивается более чем в два раза и при дальнейшем росте интенсивности обработки не меняется. Из данных фракционного анализа (рис.

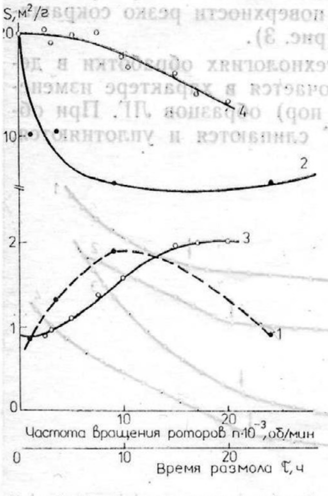

*Рис. 1.* Влияние механической обработки в шаровой мельнице (*1, 2*) и в дезинтеграторе (*3, 4*) на внешнюю $S_{\text{в}}$ (*1, 3*) и полную $S_{\text{Ar}}$ (*2, 4*) удельную поверхность гидролизного лигнина.

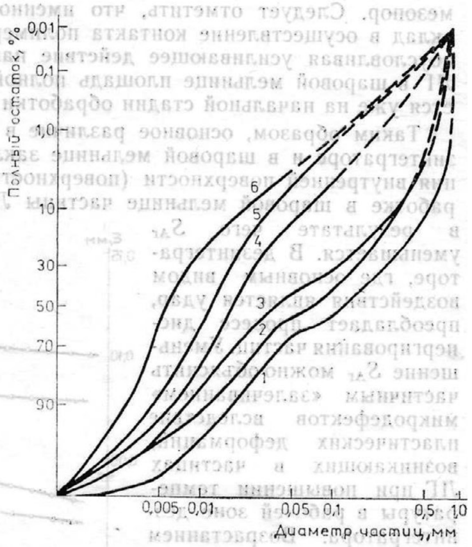

*Рис. 2.* Интегральные кривые седиментации в бензоле гидролизного лигнина, подвергнутого измельчению в дезинтеграторе при различной частоте вращения роторов: *1* — исходный ЛГ; *2* — 3000 об/мин; *3* — 5000 об/мин; *4* — 7500 об/мин; *5* — 10 000 об/мин; *6* — 20 000 об/мин.

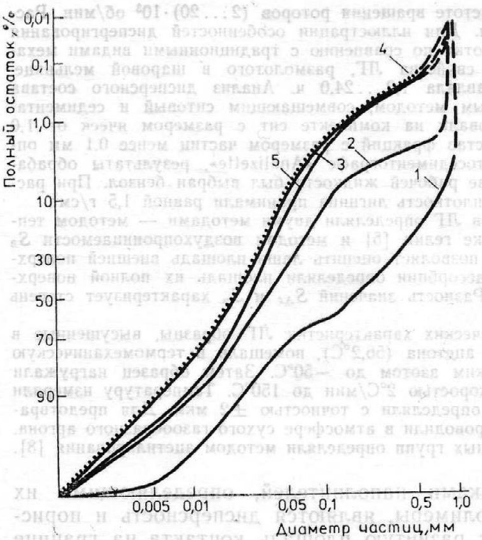

*Рис. 3.* Интегральные кривые седиментации в бензоле гидролизного лигнина, подвергнутого размолу в шаровой мельнице в течение различного времени: *1* — исходный ЛГ; *2* — 1,0 ч; *3* — 3,5 ч; *4* — 9,0 ч; *5* — 24,0 ч.

2) следует, что при этих условиях доля мелкодисперсной фракции (<0,01 мм) возрастает с 2,4 до 68...72%.

Размол ЛГ в шаровой мельнице в течение 9 ч также приводит к увеличению площади внешней поверхности до 2 м²/г (см. рис. 1), однако при более продолжительном размоле поверхность резко сокращается, что, по-видимому, связано с агрегацией частиц.

Полная удельная поверхность ЛГ $S_{Ar}$ после обработки в дезинтеграторе при частоте вращения роторов до 10 тыс. об/мин остается практически неизменной. Дальнейшее повышение интенсивности обработки приводит к монотонному уменьшению $S_{Ar}$. Существенные различия в значениях площади внешней и общей поверхностей частиц указывают на наличие в ЛГ достаточно развитого объема мезопор. Следует отметить, что именно мезопоры вносят основной вклад в осуществление контакта полимер—наполнитель в композитах, обусловливая усиливающее действие наполнителя [10]. При размоле ЛГ в шаровой мельнице площадь полной поверхности резко сокращается уже на начальной стадии обработки (рис. 3).

Таким образом, основное различие в технологиях обработки в дезинтеграторе и в шаровой мельнице заключается в характере изменения внутренней поверхности (поверхности пор) образцов ЛГ. При обработке в шаровой мельнице частицы ЛГ слипаются и уплотняются, в результате чего $S_{Ar}$ уменьшается. В дезинтеграторе, где основным видом воздействия является удар, преобладает процесс диспергирования частиц. Уменьшение $S_{Ar}$ можно объяснить частичным «залечиванием» микродефектов вследствие пластических деформаций, возникающих в частицах ЛГ при повышении температуры в рабочей зоне дезинтегратора. Возрастанием температуры по мере увеличения интенсивности обработки обусловлено и снижение влажности лигнина (см. табл. 1).

По результатам термомеханических исследований

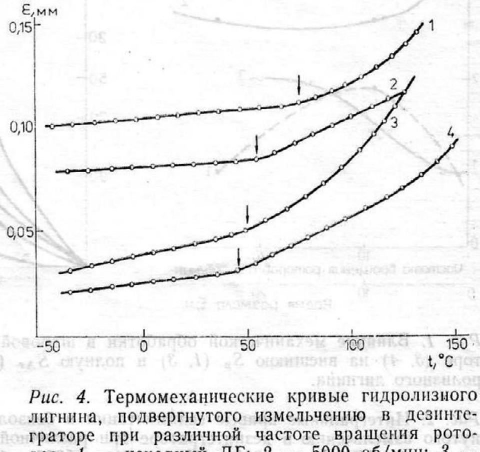

*Рис. 4.* Термомеханические кривые гидролизного лигнина, подвергнутого измельчению в дезинтеграторе при различной частоте вращения роторов: *1* — исходный ЛГ; *2* — 5000 об/мин; *3* — 17 000 об/мин; *4* — 20 000 об/мин.

Таблица 2

**ФИЗИКО-МЕХАНИЧЕСКИЕ СВОЙСТВА РЕЗИН, НАПОЛНЕННЫХ ГИДРОЛИЗНЫМ ЛИГНИНОМ, ОБРАБОТАННЫМ В ДЕЗИНТЕГРАТОРЕ**
(30 мас.ч./100 мас.ч. смеси)*

| Наполнитель | $n \cdot 10^3$ об/мин | Прочность при разрыве, МПа | Относительное удлинение, % |
|---|---|---|---|
| — | | 1,77 | 30 |
| Лигнин, размолотый в дезинтеграторе | 5,0 | 3,58 | 355 |
| | 10,0 | 3,61 | 445 |
| | 15,0 | 3,61 | 465 |
| | 17,0 | 3,81 | 410 |
| | 20,0 | 3,83 | 430 |
| Лигнин, размолотый в шаровой мельнице (9 ч) | — | 2,67 | 550 |

* Наполнение резин (композиция на основе СКФ-26 и СКЭПТ-40) осуществлено во Всесоюзном институте авиационных материалов.

образцов ЛГ, подвергнутых механической обработке, были установлены значения температурных переходов $T_п$. Для исходного ЛГ $T_п$ составляет 60...70°С, что связано с процессом расстекловывания лигнина [11]. Механическая обработка ЛГ как в дезинтеграторе, так и в шаровой мельнице приводит к снижению $T_п$ (рис. 4, табл. 1), что обусловлено разрушением сетки межмолекулярных связей.

Усиливающее действие наполнителей в полимерах определяется не только площадью поверхности контакта, но и энергией адгезионного взаимодействия, которая зависит от количества реакционноспособных групп на поверхности наполнителя.

Из данных химического анализа следует, что с ростом интенсивности механической обработки ЛГ как в дезинтеграторе, так и в шаровой мельнице содержание гидроксильных групп в лигнине увеличивается, причем в условиях дезинтеграторной обработки их концентрация достигает больших значений (см. табл. 1). ОН-группы могут образовываться в результате разрыва как простых эфирных связей в лигнине, так и лигноуглеводных связей. Можно полагать, что полярные ОН-группы, способные к неспецифическим взаимодействиям, могут обеспечить прочное адгезионное взаимодействие лигнина с эластомерами.

Как видно из табл. 2, прочность при разрыве резин, содержащих ЛГ, размолотый в дезинтеграторе, на 30...40% превышает прочность образцов, наполненных лигнином, размолотым в шаровой мельнице, при некотором снижении относительного удлинения. Различия физико-механических свойств наполненных композиций обусловлены как более развитой внутренней поверхностью ЛГ после дезинтеграторной обработки, так и возрастанием количества ОН-групп.

*Выводы.* При механической обработке ЛГ наряду с диспергированием частиц происходит разрушение межмолекулярных и внутримолекулярных связей, вследствие чего температурный переход ЛГ смещается в область более низких температур и содержание гидроксильных групп в нем возрастает; изменения наиболее выражены при обработке в дезинтеграторе.

2. При обработке гидролизного лигнина в дезинтеграторе формируется более развитая удельная поверхность, чем при обработке в шаровой мельнице, что объясняется сохранением его пористой структуры.

3. ЛГ, обработанный в дезинтеграторе, может быть использован как активный наполнитель эластомеров, более чем в два раза увеличивающий их прочность при разрыве.

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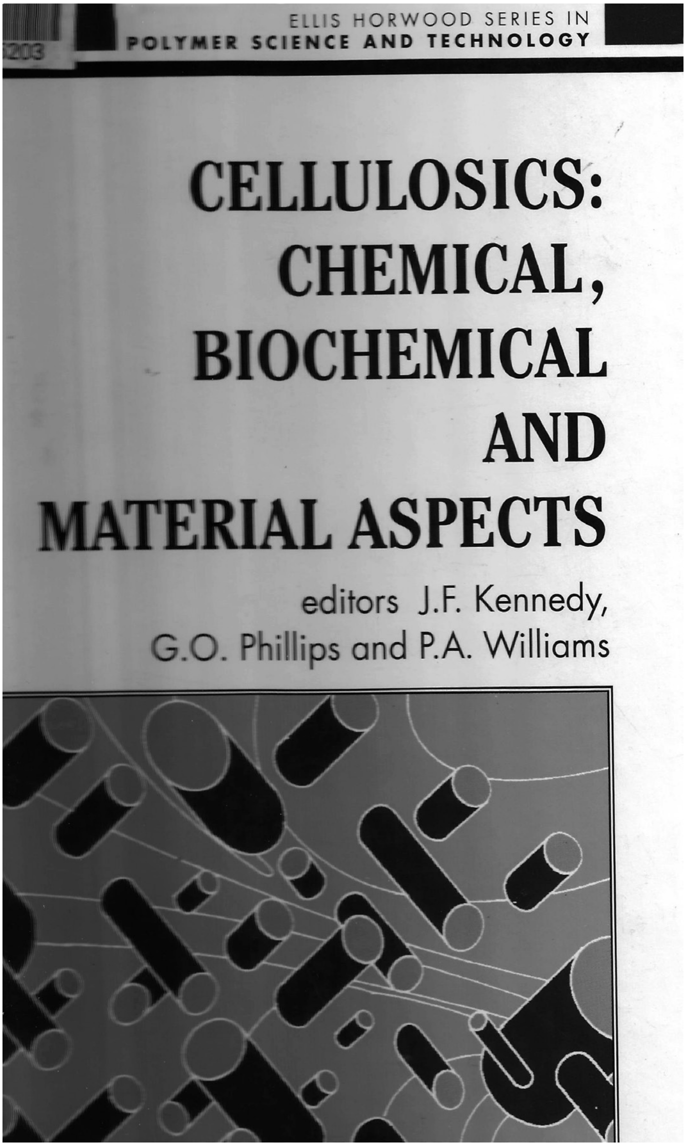
## P-10

Gromova, M. F., **Arshanitsa, A. S.**, Telysheva, G. M., Sevastjanova, A. D. Ligols – novel hydroxyl-containing multipurpose materials. **In book:** *"Cellulosics: Chemical, Biochemical and Materia! Aspects"*. London: Ellis Harwood Ltd., 1993, pp. 549-553.

Author contributions: 50 % (Methodology, Validation, Investigation).
The corresponding author ensures that the description of A. Arshanitsa contributions to the published work is accurate and agreed by all authors.
Corresponding author: M. Gromova.



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# Ligols – novel hydroxyl-containing multipurpose materials

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## ABSTRACT

Ligols - oligoethers based on technical lignosulphonates - were obtained by a hydroxypropylation method. High reaction ability of ligols in the reaction with isocyanates enable production of polyurethane materials with a wide application range, including rigid polyurethane foams and polyurethane binders. Ligols were successfully tested as additives to drilling fluids, surfactants and flotation reagents.

## INTRODUCTION

Hydroxypropylation of lignin-like model compounds, acid hydrolysis lignin and lignosulphonates (LS) under alkaline conditions in inert and hydroxyl containing solvents at different temperatures was studied in previous investigations, using propylene oxide [1,2].

It was observed that reaction mechanism involved first order kinetics with regard to propylene oxide (PO) concentrations and that the propoxylation rate constant, K, greatly depends on acidity of hydroxyl containing compound increasing with the growth of acidity. It was shown that synthesys parameters, such as reaction medium, temperature and pressure, KOH concentration and propylene oxide to lignin hydroxyl groups ratio had influence on the chemical structure of hydroxypropyl lignin derivatives. These results were in accord with the findings of Glasser et al. [3].

## EXPERIMENTAL

Commercial lignosulphonates were used throughout. LS had a methoxyl content 9.4...10.0%, a total OH content 9.6...10.3%, and elemental analysis values of 43.7...45.2% C, 4.7...5.6% H, 6.0...6.4% S, 4,6...5.3% Na, 0.4...0.5% Ca, 0.2 K% and 0.9...1.0% N. Ash and carbohydrate contents were 13.8...16.5% and 11.5...13.9%, respectively.

The reaction of PO and LS under alkaline conditions (KOH) in a medium of glycerol or propylene glycol was carried out in an industrial reactor with mechanical stirring at 110...150 C. After the reaction was completed, the reactor was cooled and KOH neutralized with acetic acid.

Depending on the properties of initial LS, solvent and temperature, the properties of ligols were as follows: hydroxyl number 300...660 mg KOH/g; density at 20 C 1.08...1.14 g/cub.cm; viscosity at 25 C 500...12000 MPa*s; solubility in water 100%.

## APPLICATION

High reaction ability of ligols in reaction with isocyanates was established (Figure 1). This property of ligols allows us to produce polyurethane materials, including rigid foams (Trade mark "Ligopor").

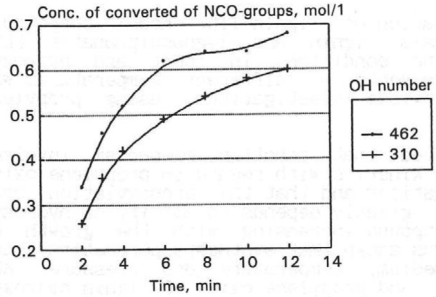

Figure 1. The reaction ability of ligols in the reaction with phenylisocyanate at 20 C.

Ligopors on the basis of ligols with definite characteristics (hydroxyl number 430...500 mg KOH/g and viscosity at 25 C 800...4100 mPa⋆s) were utilized in the production of furniture frames.

The characteristics of Ligopors:

| | |
|---|---|
| - density, kg/cub. m | 46...50 |
| - compression strength, MPa | 0.30...0.35 |
| - compression modulus, MPa | 5.0...6.0 |
| - tensile strength, MPa | 0.41...0.51 |
| - tensile modulus, MPa | 14.0...15.3 |
| - percentage elongation, % | 3.9...5.3 |
| - heat resistance, C | 148...152 |
| - closed cells, % | 90 |
| - water absorbtion per day, kg/sq. m | 0.2 |
| - natural color | light brown |

The replacement of phenol-formaldehyde resins in the binders for foundry moulds and cores by ligol-based binders increases the mechanical properties of the articles (Figure 2) and improves labour conditions due to elimination of evolving toxic monomers.

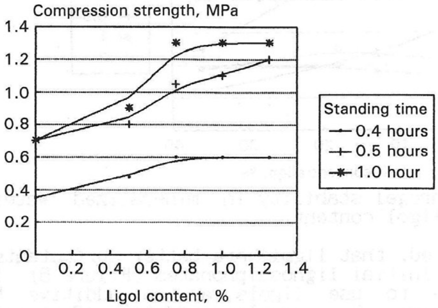

Figure 2. Compression strength of foundry moulds and cores depending on ligol content.

It was shown that ligols have various commercial applications. For example, application of ligols in methylcellulose-based drilling fluids enables regulation of the viscosity of the gel and the time of gel formation (Figure 3), to enhance the stability of drilling fluids in mineralized water (Figure 4) and to increase thermostability of drilling fluid.

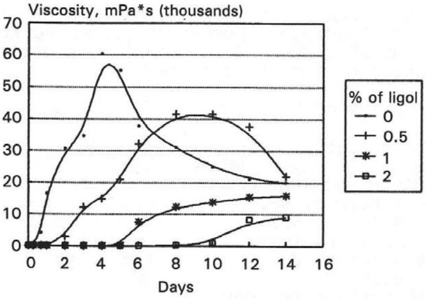

Figure 3. Viscosity changes of gel-forming systems, depending on ligol content.

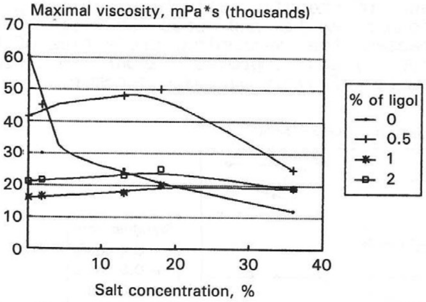

Figure 4. Hydrogel stability in mineralized water, depending on ligol content.

It was estimated, that ligols are better surfactants, compared with initial lignosulphonates (Figure 5). It makes possible to use ligols as an additive to flotation systems. For example, addition of ligols into flotation compositions increases the degree of extraction by 13% (relatively to phosphorous pentoxide) and by 5 up to 17,5% of KCl.

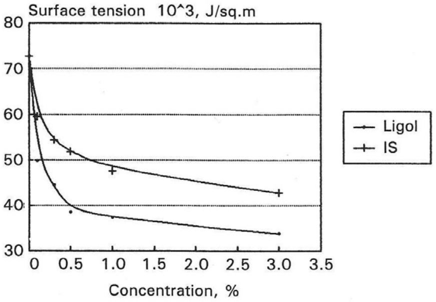

Figure 5. The surfactant properties of ligol and lignosulphonates in aqueous solutions.

## CONCLUSIONS

Ligols are suitable for polyurethane production as a replacement of traditional ether-polyols.

Ligols may be used as a component for drilling fluids and as industrial surfactants.

Ligols have been successfully tested as flotation reagents.

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## P-11

### European patent

LATVIAN STATE INSTITUTE OF WOOD CHEMISTRY. Method for production of heat-insulating materials [Verfahren zur Herstellung von Warmedammaterialien, Siltumizolācijas materiālu iegūšanas paņēmiens]. **A. Arshanitsa**, G. Telysheva, A. Paberza, U. Cabulis, L.Vevere, T. Dizhbite. Data of submission 2013-30-09. Pat. EP 2816052 A1, C 08G18/76, C 08G18/64, C 08L97/00, C 08H7/00, C 07G1/00. 2014-12-24. Available: https://www.google.com/patents/EP2816052A1?cl=en; https://register.epo.org/application?lng=de&tab=main&number=EP1318678; https://worldwide.espacenet.com.

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## (54) Method for production of heat-insulating materials

(57) The present invention relates to the method for production of heat-insulating material based on rigid polyurethane foam.

The method makes possible to expand the raw materials base for production of heat-insulating materials without using components obtained from petroleum and vegetable oils.

In the method for production of heat-insulating materials based on rigid polyurethane foam, by combination of isocyanate component with the polyol component, a complex formed by an industrial lignin non-soluble in organic solvents, which is oxypropylated, and then is combined with unmodified lignin in the course of the reaction in ratio from 7:1 to 2.3:1, is used as polyol component. Before being oxypropylated, unmodified lignin is previously oxidized by using POM/ $H_2O_2$ (polyoxometalates/ hydrogen peroxide) system.

The object of the present invention is achieved also by that unmodified lignin before combining with oxypropylated lignin is activated in an impact-type disintegrator increasing the total content of hydroxyl group and availability thereof to chemical interaction.

The object of the present invention is also achieved by that unmodified lignin before being combined with the main component of polyol system - oxypropylated lignin, is oxidized in POM/ $H_2O_2$ system.

Thus, lignin, which has not been utilized earlier for production of heat-insulating material based on rigid polyurethane foam, is used as one of the main raw materials, furthermore, the characteristics of the obtained material correspond to similar commercially available materials.

EP 2 816 052 A1

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## Description

### Technical Field

**[0001]** The present invention relates to a method for production of heat-insulating materials based on rigid polyurethane foams.

### Background Art

**[0002]** At present, methods for production of heat-insulating materials based on rigid polyurethane foams by combining the isocyanate component and the polyol component, obtained from the petrochemical raw material, are well known.

**[0003]** However, the components derived from petroleum, such as polyester and polyether polyols, have some disadvantages. The use of such polyester and polyether polyols contributes to the depletion of the petroleum reserves, which are non-renewable resources. The production of polyols is also an extremely energy-intensive process, because the production of polyol requires drilling for crude oil production, then oil extraction and transportation to an oil refinery plant for oil distillation and obtaining of purified hydrocarbons, which are then converted to alkoxides, and then to final polyol products. Due to the increasing public concern over the environmental impact of this industrial chain, the production of more environmentally safe products it required. To assist in diminishing the depletion of petroleum reserves, simultaneously satisfying the consumers' increasing demands, it would be profitable to replace fully or partially the petroleum derived polyester or polyether polyols, used in the production of polyurethane elastomers and foams, by multi-purpose, renewable, and environmentally friendly components (Sounders D., Frish C., polyurethane Chemistry, khimiya, Moscow, 1968).

**[0004]** The closest known method is the method for the production of heat-insulating materials based on rigid polyurethane foams by combining the isocyanate component and the polyol component obtained from vegetable raw materials, in particular, natural oils and hydroxylated and alkoxylated derivatives thereof. Castor oil, soya oil, Lesquerella oil and mixtures thereof (US application 2010060469, Bayer Material Science LLC) are used as oils.

**[0005]** However, utilized natural oils are foodstuffs, and application thereof for producing heat-insulating materials increases the cost of the final product. Besides, the resources of natural oils are also limited, and application thereof requires complicated prior processing steps for purification thereof.

**[0006]** Despite an introduction of new raw materials, at present most of polyols are produced from petroleum.

### Summary of invention

**[0007]** It is the object of the present invention to expand the raw material base for producing heat- insulating materials that allows avoiding the application of natural oils and utilization of products, which had not yet been used in the production of heat-insulating materials based on rigid polyurethane foams.

**[0008]** As the polyol component in the method for production of heat-insulating materials based on rigid polyurethane foams by combining the isocyanate component with the polyol component, there was used organic solvent insoluble technical lignin complex, which is oxypropylated and then in the course of reaction is combined with unmodified lignin in ratio from 7:1 to 2.3:1.

**[0009]** Before oxypropylation, unmodified lignin is subjected to oxidation by using the system POM/$H_2O_2$ (polyoxometalates / hydrogen peroxide).

**[0010]** The object of the present invention is achieved by the activation of unmodified lignin, before being combined with oxypropylated lignin, in an impact-type disintegrator, increasing the total content of hydroxyl groups and the availability thereof to chemical interaction.

**[0011]** The object of the present invention is achieved also by the oxidation of unmodified lignin, prior to combination with the main component of the polyol system - oxypropylated lignin, in POM/$H_2O_2$ system.

### Detailed Description of the Invention

**[0012]** The method according to the present invention is carried out in the following way.

**[0013]** Lignin, insoluble in organic solvents, is characterized by molecular heterogeneity, a high content of acid hydroxyl groups and, as a consequence, a low activity in reactions with isocyanates. Technical lignin, insoluble in organic solvents, is oxypropylated in a high pressure reactor in the presence of an alkaline catalyst; in this case, the process is carried out by simultaneous introduction of lignin, propylene oxide and KOH, where reagent ratio is 3:7:0.15. the reactor is equipped with an external thermal loop, with the aid of which a temperature in the reactor is reached up to 150-165°C, and propylene oxide vapor pressure of 22-25 bar is reached, when oxypropylation process in the reactor begins, accompanied by the temperature rise in the reactor up to 225-250°C and a vapor pressure drop due to the conversion of propylene oxide. The reaction is conducted in autothetrmal conditions; upon the completion of reaction and decrease of the temperature in the reactor up to a room temperature, the obtained product is treated with acetic acid to neutralize the catalyst, then the product is treated in a rotary vaporizer during 6-8 hours at a temperature of 80°C and at pressure decreased up to 0.3 bar. During oxypropylation process, propylene oxide not only reacts with the OH groups of lignin but is partially homopolymerized, resulting in production of propylene glycols of different molecular weight, which form copolymers upon the interaction with OH-acid groups of lignin. As a result, instead of OH-acid groups in lignin, new aliphatic OH groups are formed, the steric accessibility of which is much higher due to the remoteness from the aromatic ring. Besides, the introduction of flexible oxypropyl chains in the lignin structure ensures the solution of the oxypropylated lignin in propylene glycols being formed. Thereby, the enhancement of the reactivity of the product in reactions with isocyanate is reached due to the high reactivity of the polyol components that constitute the polyol - oxypropylated lignin and propylene glycols. In this case, the conditions of the reaction of compatibility of the polyol with unmodified lignin are improved, which is accompanied by the formation of a ligno-polyol system that is highly reactive in reactions with isocyanates, which ensure the chemical bonding of all components into a single three-dimensional polyurethane matrix.

**[0014]** Lignin oxypropylation products comprise a catalytically active additive of potassium acetate in quantities of up to 2-2. 5%, formed as the result of the neutralization of KOH with acetic acid, and which an important component in reactions of urethane formation and trimerisation of isocyanate groups that are the main ones in preparing rigid polyurethanes.

**[0015]** To increase the amount of functional groups in lignin, which are capable of the copolymerization reaction with propylenoxide, an air stream in the presence of the oxidation catalyst - polyoxometalates / hydrogen peroxide is passed through the water suspension of lignin. As a result of oxidation, the concentration of OH groups in lignin is increased by 15-30%. The oxypropylation of oxidized lignin is carried out according to a similar process with the same parameters as in the process of oxypropylation of lignin insoluble in organic solvents.

**[0016]** To increase the lignin component in the polyol system based on lignin, by combining the initial unmodified lignin with the polyol in the course of the reaction, lignin with a moisture content of 10% is treated in a disintegrator with impact-type rotors at the rotational speed up to 100 Hz. The mechanical activation of lignin increases the total specific surface of lignin particles, which makes it possible to increase contact surface of lignin particles with the polyol and enhances the combination reaction. Furthermore, the mechanical activation of lignin increases the total amount of hydroxyl groups in lignin up to 30% and simultaneously decreases the glass transition temperature of lignin, which is the evidence in favour of a partial depolymerization of lignin in the disintegration treatment process. The obtained product is dried in vacuum at a temperature of 80°C; then 10-30% of treated lignin is introduced into the polyol based on oxypropylated or preoxidated lignin at a temperature of 50°C, under intensive mixing.

**[0017]** An example of carrying out said method is given below.

**[0018]** To obtain the polyol component for rigid polyurethanes, the product of oxypropylation of unmodified or pre-oxidized lignin is reactively combined with dispersed and oxypropylated or pre-oxidized lignin without previous mechanical activation or the previously mechanically activated lignin in a disintegrator in ratio from 7:1 to 2.3:1. a crosslinking agent, a catalyst, and a mixture of surfactants and foaming agents are sequentially introduced to the obtained polyol systems under mixing. Then a polymer derivative of diphenylmethane diisocyanate is added to the obtained mixture, under mixing.

**[0019]** To determine the properties of the obtained material, the mixture is poured in an open-type mold, in which the formation and hardening of polyurethane occur. The obtained material contains 25-31 % of ligno-polyol complex.

**[0020]** Upon the expiration of 24 hours, specimens are cut out of the obtained blocks, and characteristic values for the material are determined and listed in the Table below.

**Table 1**

| | Polyurethane foam composition based on the lignin-containing polyol component | Polyurethane foam composition based on common polyester polyols Lupranol 3300 (70%) and Lupranol 3422 (30%) |
|---|---|---|
| Technical parameters of foaming | | |
| Start time | 22 s | 22 s |
| Gel time | 65-70 s | 200 s |
| Foam rise time | 110-133 s | 265 s |
| Properties of material | | |
| Apparent density, kg/m | 39-45 | 54 |
| compression strength parallel to the direction of foam rise, MPa | Not less than 0.25 | 0.29 |
| Glass transition temperature, °C | Not less than 120 | 110 |

(continued)

| | | |
|---|---|---|
| Properties of material | | |
| Young's modulus in compression parallel to the direction of foam rise, MPa | Not less than 7.1 | 6.8 |
| Water absorption within 28 days, Vol.% | Not more than 3.4 | 3.8 |
| Change in the specimen's volume upon exposure within 28 days at 80°C, % | Not more than 0.6 | 4.2 |
| Closed cell content, vol. % | Not less than 95 | 93.3 |
| Thermal conductivity coefficient, W/(m·K) | 0.0235-0.0265 | 0.0244 |

**[0021]** The decrease in the ratio of oxypropylated lignin to unmodified lignin in the ligno-polyol component below 2.3:1 considerably decreases the mechanical characteristics of the material and the characteristics of shape stability, and water absorption indices are increased 1.3-2-fold. Upon the increase of oxypropylated lignin - unmodified lignin ratio above 7:1 in the ligno-polyol component, the total content of the lignin component in the material relative to its optimum content is decreased, as a result of which shape stability of the material is decreased and water absorption indices are increased 1.5-fold.

**[0022]** Thus, the obtained heat-insulating material based on filled rigid polyurethane foams with the use of a lignin-containing polyol component has characteristics comparable with those of commercial polyurethane heat-insulating materials. In this case, the obtained material is more rigid, has greater load bearing capacity and is more thermally stable. The characteristics of the obtained material meet the requirements of the European Standard EN 14315-1 "Thermal insulating products for buildings - in-situ formed sprayed rigid polyurethane (PUR) and polyisocyanate (PIR) foam products".

**[0023]** The proposed method allows using new types of abundant raw materials that permits avoiding the use of both the products derived from petroleum and vegetable oils, including edible oils.

## Claims

1. A method for the production of heat-insulating materials based on filled rigid polyurethane foams by combining the isocyanate component with the polyol component, **characterized in that** a complex formed by the product obtained in the course of the reaction by combining oxypropylated modified lignin non-soluble in organic solvents, with industrial unmodified lignin in ratio from 7:1 to 2.3:1, is used as polyol component.

2. The method according to claim 1, **characterized in that** before being oxypropylated, the unmodified lignin is previously oxidized by using polyoxometalates / hydrogen peroxide system.

3. The method according to claims 1-2, **characterized in that** the unmodified lignin is previously activated in an impact-type disintegrator.

4. The method according to claims 1 - 3, **characterized in that** the unmodified lignin, before being combined with oxypropylated lignin, is oxidized in the polyoxometalates / hydrogen peroxide system.