





## DISSOLUTION BEHAVIOUR OF BLACK ALDER BARK EXTRACTIVES IN POLYURETHANE SYNTHESIS MEDIA: A COMPREHENSIVE STUDY

\*Maris Lauberts , Matiss Pals , Jevgenija Ponomarenko , Alexandr Arshanitsa 

Latvian State Institute of wood chemistry, Latvia

\*Corresponding author's e-mail: maris.lauberts@kki.lv

### Abstract

Two approaches to incorporating black alder (BA) bark extractives-derived polyol into a polyurethane (PU) network were studied. In the first case, fractionation of bark extractives with tetrahydrofuran (THF), focusing on isolating the biomass fraction available for obtaining PU elastomers by casting methods using cyclic ethers as a solvent, was employed. Another approach aimed to obtain liquid bio-polyols that could be suitable for producing rigid PU foams. For this purpose, oven-dried crude BA bark water extracts were liquefied with polyethylene glycol (PEG 400) at temperatures of 130-170°C. The effect of adding sulfuric acid as a catalyst on biomass processing was studied. Wet chemistry, GC, FTIR spectroscopy, analytical pyrolysis (Py-GC/MS/FID) and rheological methods were employed to characterize the obtained polyols and insoluble fractions, enabling an assessment of biomass transformation during processing. The resulting THF-soluble fraction comprised 62% of the BA bark extract, mainly consisting of the xyloside form of the diarylheptanoid compound oregonin, along with oligomeric flavonoids and carbohydrates. The THF-insoluble fraction was most enriched with carbohydrate compounds. Moreover, it was observed that the PEG 400-insoluble fractions were predominantly composed of carbohydrate components. The results indicated that the use of sulfuric acid as a catalyst (1-1.5% of solvent) promotes the complete liquefaction of extractives, enabling biomass content in polyols of up to 15-25%. Surpassing the extract content in the starting suspension up to 30% resulted in incomplete liquefaction of biomass. These findings offer valuable insights into tailoring BA bark extractives as building blocks suitable for obtaining PU materials.

**Keywords:** bark, extraction, fractionation, liquefaction, polyurethane, plant polyphenolic.

### Introduction

In modern human society, plastics are indispensable materials with a global annual production of about 391 MT in 2021, expected to triple by 2060 (European Commission, n.d.) More than 97% of plastics are derived from fossil resources, not available for biodegradation, and therefore make a significant impact on the emergence of environmental and economic problems (Chem4Us, n.d.). Alternative feedstocks must be biobased and therefore renewable monomers, thus reducing the industry's dependency on fossil-based materials and possessing the circular life cycle of plastic materials. This task is highly urgent in the PU materials industry, which comprises the most versatile class of polymers with a continuously increasing global market (Ma *et al.*, 2022).

Today substituting fossil-based polyols with renewable alternatives in isocyanate-based PU is recognized as the most viable pathway for the development of bio-based PU plastics (Rubens *et al.*, 2022). The lignocellulosic biomass composed in major from plant polyphenolics and carbohydrates which are reached in phenolic and aliphatic OH respectively are recognized as one of the readily available natural resources for biobased polyol obtaining (Phung Hai *et al.*, 2021). Lignin and tree bark biomass the multi-tonnage underexploited wastes of pulping and timber industry correspondingly were lignocellulosic components most studied as a precursor of bio-polyol available for PU obtaining (Dizhbite *et al.*, 2012; D'Souza *et al.*, 2014; Mahmood *et al.*, 2016). The transition of lignocellulosic materials from a solid to a liquid state via their chemical modification or dissolution in inert (aprotic) solvents or polyols used in PU synthesis serves as the basis for developing approaches to their use as macromonomers in PU

systems (Belgacem & Gandini, 2008).

The widely used chemical modification through oxypropylation transforms solid biomass into liquid polyols with uniform OH functionality and allows obtaining rigid PU foam with properties comparable to those of commercial materials (Li & Ragauskas, 2012; D'Souza *et al.*, 2014). But, the high temperature (200-250°C) and pressure (20-30 bar) increase the risk of fire and explosion, and low scalability does not allow characterizing this processing as sustainable.

In this work, alternative and more sustainable methods of lignocellulosic biomass liquefaction without deep chemical modification were applied. These include the fractionation of biomass by dissolving it in THF as an aprotic solvent utilized for obtaining PU elastomers through the casting method (Arshanitsa *et al.*, 2016; Arshanitsa *et al.* 2023a; Arshanitsa *et al.*, 2023b), and the liquefaction of biomass using a hydroxyl-rich solvent such as PEG 400, with a focus on the possible application of liquid products for rigid PU foam production (Gosz *et al.*, 2020). The ease of feedstock approach, low labor, and short time required for the isolation of extractives using a green solvent, high yield of extractives (~20% on DM of bark), the presence of phenolic and aliphatic OH groups capable of condensation with isocyanate, and the oligomeric form of constituents motivated the choice of BA bark extractives as an object of investigation. The properties of bark extractives-derived polyols and the chemical alterations in crude extractives after the isolation of a fraction suitable for obtaining PU were studied and discussed.

### Materials and Methods

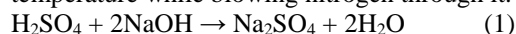
Bark removed by handle debarking of black alder (*Alnus glutinosa*) harvested in Talsu municipality of Latvia was used as a biomass feedstock. The extraction

of bark was performed by water at 90°C using microwave extractor of original construction followed by filtration and lyophilization as described (Arshanitsa *et al.*, 2022; Pals *et al.*, 2022). The THF was applied for fractionation of BA extractives at solid/liquid ratio 1:10 (w/v). The undissolved fraction was separated by filtration. The soluble fraction after distillation of THF was redissolved in water and lyophilized again.

OH, functionality crude and THF fractionated BA bark extractives was analyzed in duplicate by <sup>31</sup>P NMR using 600 MHz Bruker (Biospin Rheinstetten, Germany, BASIC PROBHD) spectrometer as described in (Arshanitsa *et al.*, 2023a).

The total phenolic (TPC) content in crude and fractionated BA bark extractives expressed as grams (g) of gallic equivalent (GAE) per gram of dry biomass was determined by wet chemistry methods (Singleton *et al.*, 1999).

The BA bark water extract was mixed with polyethylene glycol with Mn=400 g·mol<sup>-1</sup> under different conditions. These conditions included a temperature range of 130-170°C, a catalyst concentration ranging from 0% to 3% of H<sub>2</sub>SO<sub>4</sub> by weight of PEG 400, and a bark extract content ranging from 15 to 30% in the PEG 400-extract mixture. Consequently, the bark water extracts were fractionated into PEG 400-soluble polyol and PEG 400-insoluble fraction. The acid used as a catalyst was neutralized after solubility experiments through the reaction represented by equation (1), and the resulting water generated during the reaction was eliminated from the obtained biopolyol through continuous heating of the liquefied mixture at the designated temperature while blowing nitrogen through it.



The sum of monomeric sugar content including C6 (glucose, galactose, rhamnose) and C5 (xylose, arabinose) was determined by GC method after complete hydrolysis of biomass (Pals *et al.*, 2020).

Radical scavenging activity of crude and THF fractionated extracts was evaluated using the stable 2,2-diphenyl-1-picrylhydrazyl free radicals (DPPH<sup>•</sup>) test (Dizhbite *et al.*, 2004; Lauberts *et al.*, 2017).

The Py-GC/MS/FID analysis of crude BA extract, its PEG 400 insoluble fractions was performed at 500°C (heating rate 600°C·s<sup>-1</sup>) using a Frontier lab Micro Double Pyrolyzer Py-3030D directly coupled with Shimadzu GC/MS/FID-QP device (Arshanitsa *et al.*, 2021).

The Spectrum One spectrometer (Perkin Elmer) was used for study of FTIR spectra of biomass. The KBr technic was employed for preparing of samples. Each spectrum was scanned in duplicate.

The OHV of polyols containing liquified biomass were determined by acetylation method (Zakis, 1994) Viscosity of polyols was determined at 25°C using Modular Compact Rheometer. Each test was performed in triplicate, followed by the calculation of the average value and standard deviation (Std). Water content in polyols was determined by Karl Fischer titration.

## Results and Discussion

The yield of extractives isolated from BA was 18.4±2.0 % on DM of biomass. The yield of BA bark extractives fraction soluble in THF and therefore available to condensation with isocyanate as biopolyol for obtaining of PU elastomers by casting method consisted of 62±2% on DM of extractives.

The relative content of phenolic and carbohydrate constituents in raw extracts differs strongly from that of THF soluble and insoluble portions (Table 1).

Table 1

**The total polyphenolic (TPC) and monomeric sugar content (average ± Std of three parallel tests) in crude and THF fractionated BA bark extractives**

Index	Crude extract	THF-soluble fraction	THF-insoluble fraction
TPC, GAE, g·g <sup>-1</sup>	0.50±0.20	0.72±0.35	0.15±0.10
Sugar content, %	40.5±2.6	32.3±1.9	51.8±2.7

It was shown that due the moderate polarity (ε<sub>20°C</sub> = 7.43) THF promote the dissolution of plant polyphenolic versus that of more polar free carbohydrate. The content of polyphenolic in biomass was decreased in the raw: THF-soluble fraction ≥ crude extract ≥ THF-insoluble fraction. At that time the insoluble fraction is the most enriched with carbohydrates followed by crude extract and THF-soluble fraction (Table 1).

The presence of carbohydrates in THF-soluble fraction determined allowed proposition that they transfer to the THF-soluble fraction predominantly as phenyl glucosides. It was confirmed by HPLC data presented in our earlier manuscript (Arshanitsa *et al.*, 2023b). It

was shown that oregonin - xyloides form of diarylheptanoid is the dominant component of THF soluble fraction. NMR <sup>31</sup>P approved the mentioned results indicating the highest content of hydroxyl groups which by 90% presented by aliphatic ones in THF insoluble fraction. OH, functionality in THF-soluble fraction consists of almost equal proportion of alcohol and phenolic groups 'Figure 1a'.

Furthermore, the radical scavenging activity of the extract fractions, which is dependent on the phenolic compounds content, was evaluated using the stable 2,2-diphenyl-1-picrylhydrazyl free radicals (DPPH<sup>•</sup>) test and expressed as the IC<sub>50</sub> value (the concentration required to inhibit 50% of the initial free radicals).

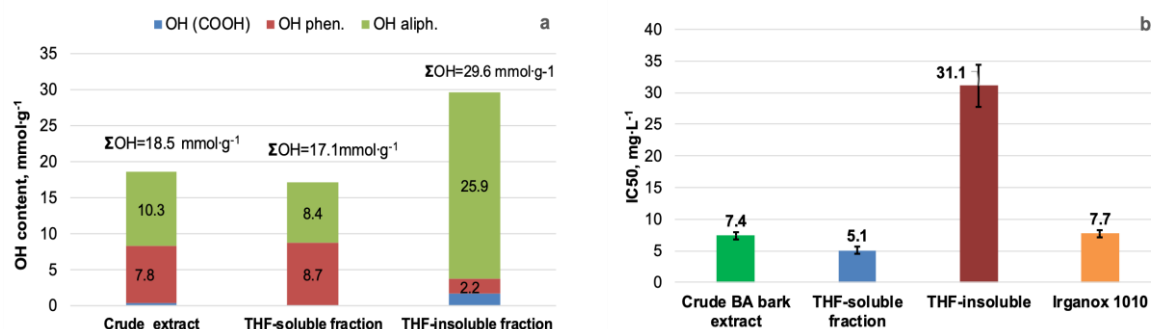


Figure 1. The content of OH groups total and differing by origination in crude and THF fractionated BA bark extracts according to <sup>31</sup>P NMR (a); the biomass concentration required to inhibit 50% of DPPH<sup>•</sup> radicals (b).

A lower IC<sub>50</sub> value indicates higher radical scavenging activity. The THF-soluble fraction exhibited the highest activity, surpassing both the crude BA bark extract and the synthetic antioxidant Irganox 1010 widely used in PU materials (Xiao *et al.*, 1994). Conversely, due to the increased content of free carbohydrates and decreased content of phenolic compounds, the THF-insoluble fraction displayed significantly reduced radical scavenging activity compared to the crude extract, see ‘Figure 1b’.

This fact allows us to consider the THF-soluble fraction of BA bark extractives as bio-polyols which could act in PU matrix simultaneously as macromonomers due to condensation of aliphatic and partly phenolic OH with isocyanate and as radical-scavenger due to the presence of remaining free phenolic groups. As a result, the substitution of PEG 400 up to 100% by THF-soluble fraction allows for a significant increase in the heat resistance, thermal stability in air, and mechanical properties at tensile of PU elastomers obtained by casting methods (Arshanitsa *et al.*, 2023b).

Another approach was used to liquefy the BA bark extractives in PEG 400 with a focus on the application of liquid polyols for producing rigid PU foam. The crude BA bark extract was mixed with PEG 400 under different conditions. The effects of biomass in the starting suspension, conversion temperature, the addition of sulfuric acid as a catalyst, on the

liquefaction yield, viscosity, and hydroxyl value of polyols obtained were investigated. The yield of liquefaction was defined as the amount of biomass soluble in PEG 400 at given conditions and expressed as a percentage of the starting biomass weight in suspension. A yield of 100% means that the insoluble fraction was not detected in the final product using the analytical procedure described above, and therefore complete conversion/liquefaction of biomass was recognized in this case. During a 6-hour-long dissolution process, it proved challenging to fully dissolve the BA bark extract (at weight ratio of 20%) in PEG 400 to achieve complete liquefaction without the use of a H<sub>2</sub>SO<sub>4</sub> as catalyst, see ‘Figure 2a’. In this case the trend of increasing liquefaction yield was observed with increasing of processing temperature. But anyway about 15% of starting biomass was not converted in liquid polyol at 150-170°C. With the addition of 0.5% catalysts, the complete dissolution of the introduced extract in PEG400 was not achieved, resulting in an insoluble residue of approximately 16-20%. However, when the catalyst concentration was increased to 1%, a notable improvement in solubility was observed at these PEG 400-extract ratio. At a temperature of 130 °C, the insoluble portion decreased to only around 9%, while at 150°C and 170 °C, all of the introduced bark extract dissolved, enabling the attainment of a 20% concentration of biomass in liquid polyol, see ‘Figure 2a’.

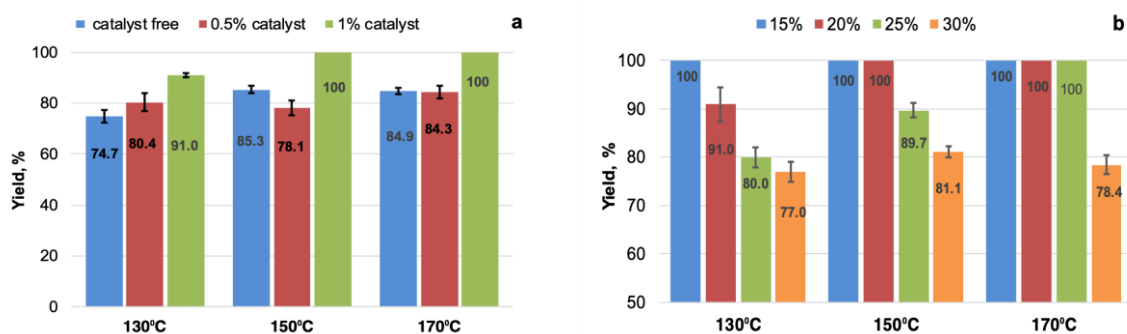


Figure 2. The effect of catalyst content on the liquefaction yield of BA bark extracts in PEG 400 during 6 hours processing at different temperatures with a fixed 20% of biomass content in starting suspension (a); the effect of biomass content in the starting suspension on its liquefaction yield at different temperatures during 6 hours processing with a fixed 1% content of catalyst (b). (The average values ±Std of three parallel tests are plotted on the graphs).

Further examination of BA bark extractives liquefaction in PEG 400 at variable biomass content in starting PEG 400 suspension in the range of 15-30% and fixed 1% of catalyst content indicated that for suspensions with 15% biomass content, complete conversion of extract at all tested temperatures was achieved, see 'Figure 2b'. However, at higher extract content of 20%, complete liquefaction was not achieved at 130°C but only at 150°C, and only at 170°C when the starting concentration of biomass was 25%. When the extract content was increased to 30%, complete dissolution was not possible at any of the temperatures utilized, leaving about 6-7% of solid in the final products, see 'Figure 2b'. Isolation of insoluble parts from the products of extractives liquefaction could allow the obtainment of liquid polyols containing about 25% of liquefied biomass, which is similar to that obtained by complete liquefaction of 25% biomass suspension performed at 170°C. This allows proposing that a 25% content of BA bark extractives in the starting suspension is the maximal for BA bark extractives complete liquefaction by PEG 400 under the conditions under study. Obviously, the further increasing of starting BA bark extractives content in suspension results in the decreasing of solvent-to-biomass ratio, thus promoting recondensation reactions of low molecular fragments obtained in the results of hydrolysis reactions of carbohydrates predominantly and increasing the non-liquefied portion of biomass (Jin *et al.*, 2011).

In all tests, PEG 400-insoluble fractions exhibited notable composition differences compared to the crude extract, see 'Figure 3a, b'.

The FTIR spectra of the crude BA bark extract and its PEG 400-insoluble fractions obtained under different conditions provide confirmation of the solubility of aromatic constituents in PEG 400 and the concentration of carbohydrates in the insoluble fraction 'Figure 3a'. This is evident from the decreased absorption at approximately 1500-1600  $\text{cm}^{-1}$  and 1260-1320  $\text{cm}^{-1}$ , which are attributed to vibrations of aromatic rings. Additionally, the absorption bands in the range of 800-1200  $\text{cm}^{-1}$  associated with cellulose and hemicellulose are increased in the spectra of the PEG 400-insoluble fractions compared to the crude extract.

The Py-GC/MS/FID data also revealed a significant increase in the content of aliphatic volatiles predominantly derived from carbohydrates, and a drastic decrease in the content of aromatic pyrolysis products, mainly derived from phenolic extractives, in all PEG 400-insoluble fractions compared to crude extracts, see 'Figure 3b'. Based on these results, we can conclude that, unlike the PEG 400-insoluble carbohydrates, the phenolic extractives of BA bark can be easier incorporated into PEG 400-based mixed polyol due to their better solubility in glycols, as opposed to carbohydrates. The increasing of biomass content in starting suspension resulting in non-complete liquefaction, leads to a more effective concentration of soluble phenolic components in polyols compared to the case when complete liquefaction of BA bark extractive occurred. These findings coincide with the results presented in (Kurimoto *et al.*, 1999).

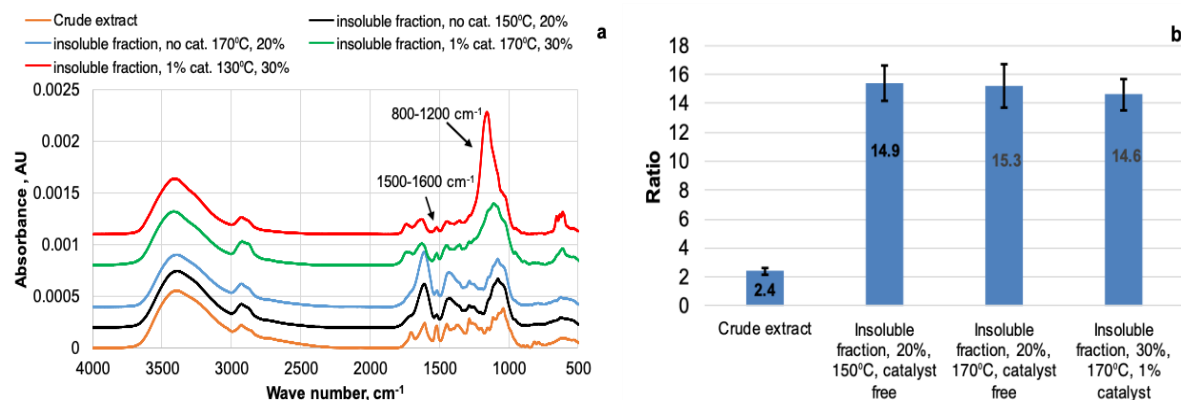


Figure 3. The different characteristics of crude extract versus fractions insoluble in PEG 400: FTIR spectra (a), and the ratio of sum peaks of aliphatic-derived compounds to that of aromatic-derived (average  $\pm$ Std of three tests) in pyrolysis products of biomass samples according to Py-GC/MS/FID data (b).

We therefore assume that the soluble portion of BA bark extractives in PEG 400-based polyol can act simultaneously as a crosslinking agent and technical antioxidant in PU foam, thereby enhancing the thermal oxidative characteristics of the material. This study is still under development. Such parameters as dynamic viscosity, hydroxyl value (OHV) and residual water content are the principal characteristics of polyols usable

for rigid PU foam obtaining. The polyols containing 15-25% of BA bark extractives completely liquified at 130°C-170°C were tested, see 'Figure 4a, b', (Table 2). As the concentration of the catalyst was in the range of 1-1.5%, the viscous stresses arising from polyol flow are linearly correlated with the deformation rate over time, allowing them to be characterized as Newtonian fluids, see 'Figure 4a'.

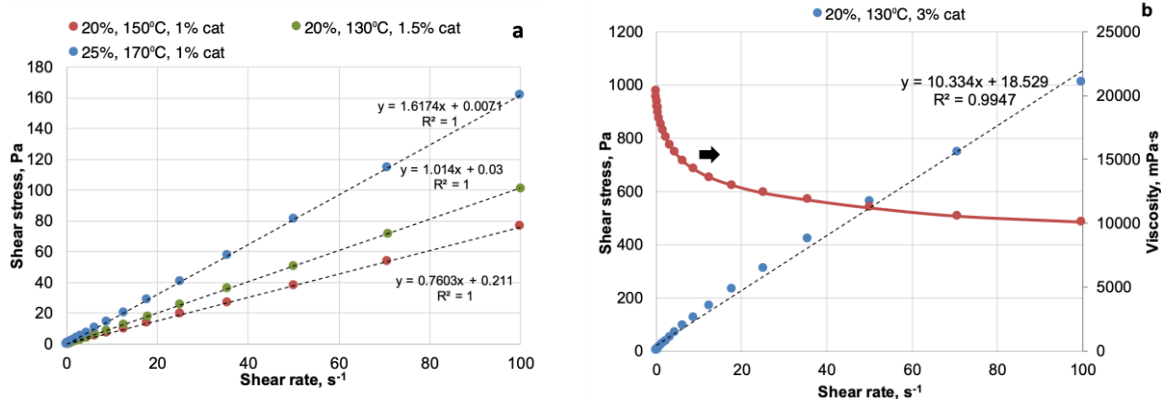


Figure 4. The Newtonian (a) and non-Newtonian (b) flow curves at 25°C for polyols vary based on the content of completely liquefied BA bark extractives, liquefaction temperature, and catalyst content.

Some increase in viscosity was observed with an increase in catalyst content up to 1.5% compared to that of 1% content (Table 2). The increase in catalyst content up to 3% results in a tenfold increase in polyol viscosity, which exhibits a trend of decreasing at deformation rate due to the degradation of their intrinsic structure, typical for pseudoplastic liquids (Table 2), 'Figure 3b'. Obviously, at high acid content, the shear of recondensation/repolymerization reactions inside the PEG 400-biomass system was

increased. Therefore, non-uniform products with higher viscosity were obtained.

For petroleum-derived polyols used for rigid PU foam preparation, the required values of OHV, viscosity, and water content have to be 300-800 mgKOH·g<sup>-1</sup>, below 300 Pa·s (at 25°C), and not more than 0.1%, respectively (Vieira *et al.*, 2011). The viscosity of all polyols containing completely liquefied biomass meets these requirements, being significantly lower than the critical value (Table 2).

Table 2

**The characteristics of polyols on the basis of BA bark extractives liquefied by PEG 400 under various regimes**

Liquefaction regime		Biomass content in polyol, %	Characteristics of polyol		
T, °C	Catalyst content, %		OHV, mg KOH·g <sup>-1</sup>	Viscosity at 25°C, mPa·s	Water content (K.F), %
130	1.0	15.0	192.7±29.0	630.0±35.0	0.35
150	1.0	20.0	363.3±13.5	804.0±60.0	0.49
170	1.0	25.0	318.5±10.0	1570.0±57.0	0.22
130	1.5	20.0	391.8±12.0	1100.0±50.	0.32
130	3.0	20.0	328.0±11.0	10700±720 (at 50 s <sup>-1</sup> )*	0.18

The OHV of polyols containing 20-25% biomass increases by 1.2-1.5 times that of PEG 400 (280.5 mg KOH·g<sup>-1</sup>) but is lower than that calculated using the additivity principle, which takes into account the content of each component and its OHV. This indicates the partial etherification of OH groups of biomass components by primary OH groups of PEG 400 in the presence of an acidic catalyst, resulting from alcoholysis reactions (Gosz *et al.*, 2020). The residual water content in polyols was in the range of 0.18-0.49%, which does not meet the requirements of commercial polyols. This can be explained by the technical difficulties of removing traces of water from a comparatively polar system. In this case, the correction of isocyanate content in the PU foam recipes should be done taking into account two-step interactions of water with the isocyanate.

The results presented above indicate that the liquefaction of BA bark extractives proceeds according to the basic principles of lignocellulosic biomass interaction with polyhydric alcohols in acidic conditions. Together with the use of BA bark extractives, it allows for obtaining lower viscous polyols with a higher content of completely liquefied biomass (up to 25%) compared to polyols obtained based on wood, bark, and lignin (Jin *et al.*, 2011; D'Souza *et al.*, 2014; Gosz *et al.*, 2020). Tests of the obtained polyols in rigid PU foam compositions are under development.

**Conclusions**

- Two approaches aimed at introducing BA bark water extractives as building blocks in PU networks available for obtaining PU thermosetting

- films and rigid PU foam, respectively, were discussed. The fractions of BA bark water extractives insoluble in the THF medium used for PU elastomer synthesis exhibit an enrichment of carbohydrates compared to the crude extract. This suggests that introducing individual carbohydrate bark components into the PU elastomer structure is challenging and requires extensive modification.
2. Aromatic bark extractives, including those containing sugar units such as phenyl glucosides, can be utilized as biopolyols obtained under mild conditions. Liquid polyols of low viscosity containing up to 25% of BA bark extractives, completely liquefied by PEG 400 and therefore containing phenolic and aliphatic subunits, were obtained.
  3. The relative content of polyphenolic and carbohydrate components of extracts in polyol can be controlled due to their rather differing solubility in PEG 400. Tests of the polyols obtained, including their antioxidative effect in the recipe of rigid PU foam, are under development.

#### Acknowledgements

The financial support from the Latvian Budget - the State Research Programme No. lzp-2021/1-0207 'Complex application of products obtained by water extraction from tree bark for the formation of a three-dimensional polyurethane matrix with increased thermo-oxidative stability and availability to microbial mediated degradation' is gratefully acknowledged.

#### References

- Arshanitsa, A., Andersone, A., & Telysheva, G. (2021). Non-isothermal thermal analysis of different originated lignocellulosic biomass, non-treated and torrefied by microwave treatment. *Engineering for Rural Development*. DOI: 10.22616/ERDev.2021.20.TF090.
- Arshanitsa, A., Krumina, L., Telysheva, G., & Dizhbite, T. (2016). Exploring the application potential of incompletely soluble organosolv lignin as a macromonomer for polyurethane synthesis. *Industrial Crops and Products*, 92, 1–12. DOI: 10.1016/j.indcrop.2016.07.050.
- Arshanitsa, A., Ponomarenko, J., Lauberte, L., Jurkjane, V., Pals, M., Akishin, Y., Lauberts, M., Jashina, L., Bikovens, O., & Telysheva, G. (2022). Advantages of MW-assisted water extraction, combined with steam explosion, of black alder bark in terms of isolating valuable compounds and energy efficiency. *Industrial Crops and Products*, 181, 114832. DOI: 10.1016/j.indcrop.2022.114832.
- Arshanitsa, A., Ponomarenko, J., Pals, M., & Jashina, L. (2023a). Controlling the reactivity of hydrophilic bark extractives as biopolyols in urethane-formation reactions using various catalysts. *Industrial Crops and Products*, 204, 117385. DOI: 10.1016/j.indcrop.2023.117385.
- Arshanitsa, A., Ponomarenko, J., Pals, M., Jashina, L., & Lauberts, M. (2023b). Impact of Bark-Sourced Building Blocks as Substitutes for Fossil-Derived Polyols on the Structural, Thermal, and Mechanical Properties of Polyurethane Networks. *Polymers*, 15(17), 3503. DOI: 10.3390/polym15173503.
- Belgacem, M. & Gandini, A. (2008). *Monomers, Polymers and Composites from Renewable Resources*. Elsevier. DOI: 10.1016/B978-0-08-045316-3.X0001-4.
- Chem4Us. (n.d.). *Plastics and bioplastics: a 200-year history of research and development*. Retrieved February 28, 2024, from <http://www.chem4us.be/plastics-and-bioplastics-a-200-year-history-of-research-and-development/>.
- Dizhbite, T., Ponomarenko, J., Andersone, A., Dobeles, G., Lauberts, M., Krasilnikova, J., Mironova-Ulmane, N., & Telysheva, G. (2012). Role of paramagnetic polyconjugated clusters in lignin antioxidant activity (*in vitro*). *IOP Conference Series: Materials Science and Engineering*, 38, 012033. DOI: 10.1088/1757-899X/38/1/012033.
- Dizhbite, T., Telysheva, G., Jurkjane, V., & Viesturs, U. (2004). Characterization of the radical scavenging activity of lignins--natural antioxidants. *Bioresource Technology*, 95(3), 309–317. DOI: 10.1016/j.biortech.2004.02.024.
- D'Souza, J., Camargo, R., & Yan, N. (2014). Polyurethane foams made from liquefied bark-based polyols. *Journal of Applied Polymer Science*, 131(16). DOI: 10.1002/app.40599.
- European Commission. (n.d.). *Plastics strategy*. Retrieved February 28, 2024, from [https://environment.ec.europa.eu/strategy/plastics-strategy\\_en](https://environment.ec.europa.eu/strategy/plastics-strategy_en).
- Gosz, K., Kowalkowska-Zedler, D., Haponiuk, J., & Piszczyk, Ł. (2020). Liquefaction of alder wood as the source of renewable and sustainable polyols for preparation of polyurethane resins. *Wood Science and Technology*, 54(1), 103–121. DOI: 10.1007/s00226-019-01152-6.
- Jin, Y., Ruan, X., Cheng, X., & Lü, Q. (2011). Liquefaction of lignin by polyethyleneglycol and glycerol. *Bioresource Technology*, 102(3), 3581–3583. DOI: 10.1016/j.biortech.2010.10.050.
- Kurimoto, Y., Doi, S., & Tamura, Y. (1999). Species Effects on Wood-Liquefaction in Polyhydric Alcohols. *Holzforschung*, 53(6), 617–622. DOI: 10.1515/HF.1999.102.
- Lauberts, M., Telysheva, G., Venskutonis, P. R., Lauberte, L., Dizhbite, T., Kazernavičiūte, R., & Pukalskas, A. (2017). Diarylheptanoid-rich extract of grey and black alder barks: an effective dietary antioxidant in mayonnaise. *Chemical Papers*. DOI: 10.1007/s11696-016-0017-3.

- Li, Y. & Ragauskas, A. J. (2012). Kraft Lignin-Based Rigid Polyurethane Foam. *Journal of Wood Chemistry and Technology*, 32(3), 210–224. DOI: 10.1080/02773813.2011.652795.
- Ma, Y., Xiao, Y., Zhao, Y., Bei, Y., Hu, L., Zhou, Y., & Jia, P. (2022). Biomass based polyols and biomass based polyurethane materials as a route towards sustainability. *Reactive and Functional Polymers*, 175, 105285. DOI: 10.1016/j.reactfunctpolym.2022.105285.
- Mahmood, N., Yuan, Z., Schmidt, J., & Xu, C. (Charles). (2016). Depolymerization of lignins and their applications for the preparation of polyols and rigid polyurethane foams: A review. *Renewable and Sustainable Energy Reviews*, 60, 317–329. DOI: 10.1016/j.rser.2016.01.037.
- Pals, M., Lauberte, L., Arshanitsa, A., Vevere, L., Jurkjane, V., & Telysheva, G. (2020). Organosolv delignification of residual plantation willow bark after extractive removal. *Research for Rural Development*, 35, 71–76. DOI: 10.22616/rrd.26.2020.011.
- Pals, M., Lauberte, L., Ponomarenko, J., Lauberts, M., & Arshanitsa, A. (2022). Microwave-Assisted Water Extraction of Aspen (*Populus tremula*) and Pine (*Pinus sylvestris* L.) Barks as a Tool for Their Valorization. *Plants*, 11(12), 1544. DOI: 10.3390/plants11121544.
- Phung Hai, T.A., Tessman, M., Neelakantan, N., Samoylov, A.A., Ito, Y., Rajput, B.S., Pourahmady, N., & Burkart, M.D. (2021). Renewable Polyurethanes from Sustainable Biological Precursors. *Biomacromolecules*, 22(5), 1770–1794. DOI: 10.1021/acs.biomac.0c01610.
- Rubens, M., Wesemael, M. Van, Feghali, E., Lufungula, L. L., Blockhuys, F., Vanbroekhoven, K., Eevers, W., & Vendamme, R. (2022). Exploring the reactivity of aliphatic and phenolic hydroxyl groups in lignin hydrogenolysis oil towards urethane bond formation. *Industrial Crops and Products*, 180, 114703. DOI: 10.1016/j.indcrop.2022.114703.
- Singleton, V. L., Orthofer, R., & Lamuela-Raventós, R. M. (1999). *Analysis of total phenols and other oxidation substrates and antioxidants by means of folin-ciocalteu reagent*, 152–178. DOI: 10.1016/S0076-6879.99.99017-1.
- Vieira, M. C., Carlos, R., Lelis, C., Couto, B., & Oliveira, G. D. L. (2011). Tannin Extraction from the Bark of *Pinus oocarpa* var . *oocarpa* with Sodium Carbonate and Sodium Bisulfite. 18(1), 1–8. DOI: 10.4322/floram.2011.017.
- Xiao, H. X., Yang, S., Kresta, J. E., Frisch, K. C., & Higley, D. P. (1994). Thermostability of Urethane Elastomers Based on p-Phenylene Diisocyanate. *Journal of Elastomers & Plastics*, 26(3), 237–251. DOI: 10.1177/009524439402600303.
- Zakis, G. F. (1994). *Functional analysis of lignins and their derivatives*. Atlanta (Ga.): TAPPI press.