Dissolution Behaviour of Bark Extractives in Polyurethane Synthesis Media: A Comprehensive Study

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Article

Dissolution Behaviour of Bark Extractives in Polyurethane Synthesis Media: A Comprehensive Study

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Abstract: The production of polyurethane films from bark-derived polyols requires the complete solubility of all components in the polyurethane synthesis media. In this study, a comprehensive investigation was conducted to achieve the copolymerization of black alder bark water extract-derived polyol with isocyanate for polyurethane film synthesis in THF solution. A fractionation approach using tetrahydrofuran (THF) as a solvent was employed to dissolve the extract, followed by filtration and removal of the solvent. The resulting THF-soluble fraction comprised 62±1% of the dry weight of the alder bark extract, mainly consisting of the xyloside form of the diarylheptanoid compound oregonin, along with oligomeric flavonoids and carbohydrates. The THF-insoluble fraction was the most enriched with carbohydrate compounds, followed by the crude extract and THF-soluble fraction. Another approach was aimed at obtaining bark extractives based liquid polyols suitable for producing rigid PU foams. For this purpose, oven-dried crude black alder bark water extract was liquefied with polyethylene glycol (PEG 400). The liquefaction of black alder bark and pine bark extractives was studied under different conditions, including varying temperature ranges (130-170^{0}C), catalyst concentrations (0-1,5%), and bark extract content in the mixture (15-30%). The results showed that the use of sulphuric acid as a catalyst (1-1.5%) significantly improved the solubility of both extractives, enabling the attainment of extract concentrations up to 25% at 170^{0}C. However, increasing the extract content beyond a certain threshold led to incomplete solubility. It was shown that the PEG-insoluble fractions consist mainly of carbohydrate components. To increase the content of biomass in liquid polyols, the effect of glycerol additions into the liquefaction agent is under study. The findings provide insights into tailoring bark-sourced polyols for polyurethane foam production through appropriate liquefaction conditions.

Keywords: extraction; bark extractives; biobased polyols; fractionation; analytical pyrolysis; polyurethane

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Generation of biopolyols for polyurethane film synthesis. To facilitate the copolymerization of bark-derived polyol with isocyanate and achieve the production of polyurethane films using casting method, complete solubility of all components in THF was imperative. Therefore, the most promising approach involved fractionating the black alder bark water extract, obtained through microwave-assisted dynamic heating at 90°C, by dissolving the extract in anhydrous THF. In this process, 20 grams of extract were weighed and placed in an Erlenmeyer flask, followed by the addition of 200 mL of THF. The solution was stirred for 24 hours and subsequently filtered. The resulting THF solution was separated, and the solvent was removed using a rotor evaporator. The obtained fraction was then redissolved in water and dried through lyophilization. The yield of the THF-soluble fraction was determined to be 62±1% based on the dry weight of the alder bark extract. Briefly, the composition of the fraction can be summarized as follows: it consists of 74% by weight of the xyloside form of the diarylheptanoid compound, oregonin, along with 26% oligomeric flavonoids and carbohydrates. The average molecular weight (M_n) of the fraction is 750 g·mol^{-1}, and it has an OH content of 15 mmol·g^{-1}. The hydroxyl groups are evenly distributed between aliphatic and phenolic groups.

To assess the chemical alterations in the crude alder bark extract subsequent to the isolation of a fraction suitable for polyurethane film synthesis, analytical pyrolysis (Py-GC-MS/FID) was employed in conjunction with other analytical techniques. This method enables the simultaneous analysis of diverse

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components present in the bark by subjecting the sample to thermal degradation, resulting in the production of a complex mixture of volatile products. By characterizing the pyrolysis products, valuable insights into the chemical structure and functional groups of the components can be obtained. Py-GC/MS/FID analysis was conducted at a pyrolysis temperature of 500°C with a heating rate of 600°C·s^{-1}. The analysis was performed using a Micro Double-shot Pyrolyzer Py-3030D (Frontier Laboratories. Ltd., Fukushima, Japan) directly coupled with the Shimadzu GC/MS/FID-QP ULTRA 2010 apparatus (Japan). The apparatus was equipped with a capillary column RTX-1701 (Restec, Metairie, Louisiana, USA) 60 m × 0.25 mm × 0.25 μm. The injector temperature was set at 250°C, and the ion source had an electron impact (EI) of 70 eV. The mass scan range of the MS was from m/z 15 to 350. The carrier gas used was helium at a flow rate of 1 mL min^{-1} with a split ratio of 1:30. For the analysis, the mass of the sample probe was in the range of 1.00-2.00 mg, with a residual moisture content of less than 1%. The oven program consisted of an initial isothermal hold at 60°C for 1 minute, followed by a temperature ramp of 6°C min^{-1} up to 270°C. The final temperature was held at 270°C for 10 minutes. Identification of individual compounds was performed based on GC/MS chromatography using the Library MS NIST 11 and NIST 11s. The relative area of each compound's peak (% from chromatogram) was calculated using Shimadzu software, which utilized GC/FID data.

The Py-GC/MS results indicate that the THF-soluble fraction produces significantly higher levels of aromatic volatiles, primarily derived from phenolic extractives, and lower levels of aliphatic volatiles, mainly derived from carbohydrates, during the pyrolysis process compared to the crude extract (Table 1, Figure 1).

Table 1. Pyrolysis products of black alder bark water extract and its fractions

Identified compound	MW	Retention time, min	Normalized peak area, % from chromatogram		
			Crude extract	THF-soluble fraction	THF-insoluble fraction
Carbohydrates derivatives					
Acetic acid	60	7.417	3.97	2.73	6.64
Formic acid, methyl ester	60	8.538	0.55	0.36	0.25
Propanoic acid	74	9.059	0.52	0.49	0.54
2-Propenoic acid	72	9.469			0.15
2-Propenoic acid, methyl ester	86	9.745	0.4	0.39	0.16
Acetic acid, methyl ester	74	10.025	0.74	0.55	0.85
Propanoic acid, 2-oxo-, methyl ester	102	11.004	1.42	1.02	1.43
Butanoic acid, 2-methyl-	102	12.348	0.37	0.46	0.19
Crotonic acid vinyl ester	112	13.56			0.07
Propanoic acid, 2-methylpropyl ester	130	14.755	0.36	0.14	0.48
Propanoic acid, 2,2-dimethyl-, methyl ester	116	15.363	0.07	0.09	
1,3-Propanediol, 2-ethyl-2-(hydroxymethyl)-	134	26.724	0.36	2.1	
Methylglyoxal	72	5.912	3.67	3.53	1.98
2,3-Butanedione	86	6.522	0.75	1.06	1.7
2-Butanone, 1-hydroxy-	88	6.675	0.46	0.51	

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Acetaldehyde, hydroxy-	60	7.141	2.5	5.92	1.15
Glycolaldehyde dimer	120	7.209	1.96		1.85
2,3-Pentanedione	100	7.706	0.24	0.25	0.37
2-Propanone, 1-hydroxy-	74	8.292	6.91	6.34	6.66
2-Butanone, 3-hydroxy-	88	8.897	0.17	0.18	0.2
2-Butanone, 1-hydroxy-, isomer	88	10.135	1.18	0.8	0.88
Propanal and Butanedial	58/86	11.158			0.24
3-Hexanone, 4-ethyl-	128	12.083	0.1	0.09	
2-Propanone, 1-(acetyloxy)-	116	12.569	1.28	1.17	0.98
2-Heptanone, 3-methyl-	128	12.958	0.13	0.11	0.2
2,5-Hexanedione	114	14.507	0.07	0.03	0.09
2-Butanone, 1-(acetyloxy)-	130	14.826	0.25	0.1	0.31
2-Propanone, 1,3-dihydroxy-	90	16.796	0.75	0.81	0.44
2,3-Pentanedione, 4-methyl-	114	18.221	0.22	0.13	
Pentanal and Pentanadial	86/100	20.855	0.27	0.18	0.45
2-Cyclopenten-1-one	82	11.606			0.51
2-Cyclopenten-1-one, 2-methyl-	96	12.95	0.17	0.09	0.22
4-Cyclopentene-1,3-dione	96	13.767	0.11	0.08	0.23
1,3-Cyclopentanedione	98	14.285	0.59	0.37	0.5
2-Cyclopenten-1-one, 3-methyl-	96	15.461	0.16	0.11	0.32
1,2-Cyclopentanedione, 3-methyl-	112	16.808	0.17	0.13	0.44
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	126	18.945			0.21
Furan, 2-methyl-	82	6.256	0.41	0.21	0.33
2(3H)-Furanone	84	10.499			0.08
3(2H)-Furanone	84	10.835	0.14	0.13	0.09
2(3H)-Furanone, 5-methyl-	98	11.152	0.4	0.47	0.23
Furfural	96	11.55	1.19	1.57	0.91
2-Furanmethanol	98	12.421	0.36	0.29	0.53
Acetylfuran	110	13.256	0.15	0.11	0.24
2-Furancarboxaldehyde, 5-methyl-	110	14.937	0.12	0.08	0.16
2(3H)-Furanone, dihydro-	86	15.604	0.26	0.2	0.42
2(5H)-Furanone	84	15.948	0.21	0.1	0.37
2(5H)-Furanone, 5-methyl-	98	16.15	0.08		0.1
2,5-Furandione, 3-methyl-	112	16.437	0.43		0.34
3(2H)-Furanone, 4-hydroxy-2,5-dimethyl-	128	18.039			0.34
Methyl 2-furoate	126	18.944	0.07	0.04	
5-(Hydroxymethyl)dihydro-2(3H)-furanone	116	20.161			
2(3H)-Furanone, 5-acetyldihydro-	128	22.117			0.22

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2,4(3H,5H)-Furandione, 3-methyl-	114	22.725	0.12	0.09	0.12
Benzofuran, 2,3-dihydro-	120	23.481	3.83	3.13	5.53
2-Furancarboxaldehyde, 5-(hydroxymethyl)-	126	24.698	0.61	0.2	0.33
5-Hydroxymethyldihydrofuran-2-one	116	25.188	0.22		0.3
4-Hydroxy-,5,6-dihydro-(2H)-pyran-2-one	114	16.244	0.11	0.4	0.04
4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	144	20.397			0.64
1,6-Anhydro- -D-glucopyranose	162	31.935	1.09	1.04	0.32
Non-methoxylated aromatic compounds					
Phenol	94	17.331	3.7	4.26	3.04
Phenol, 2-methyl-	108	18.503	0.41	0.46	0.38
Phenol, 3-and 4-methyl-	108	19.38	2.03	2.85	0.67
Phenol, 2-ethyl-	122	20.302	0.06	0.09	
Phenol, 3,4-dimethyl-	122	20.493	0.13	0.19	0.15
Phenol, 4-ethyl-	122	21.45	1.32	1.77	0.86
Phenol, 2,6-dimethyl-	122	22.093	0.09	0.15	
Phenol, 2-ethyl-5-methyl-	136	22.475			
Benzene, 4-ethyl-1,2-dimethoxy-	166	22.542	0.06	0.18	
Benzene, (ethenyloxy)-	120	23.131	0.07	0.08	
Benzene, 2,4-dimethyl-1-(1-methylethyl)-	148	25.205		0.13	
Phenol, 4-(2-propenyl)-	134	25.547			
Benzaldehyde, 3,4-dimethyl-	134	25.551	0.34	0.67	
Phenol, 2,4,6-tris(1-methylethyl)-	220	25.699		0.49	0.94
1,4-Benzenedicarboxaldehyde, 2-methyl-	148	25.805			
Benzenemethanol, .alpha.-ethynyl-	132	25.903	0.23	0.23	
Phenol, 2-(2-methyl-2-propenyl)-	148	26.384	0.31	0.55	
1,4-Benzenediol	110	27.074	1.24	0.66	2.49
1,4-Benzenediol, 2-methyl-	124	27.925			0.18
2-Propyn-1-ol, 3-(4-methylphenyl)-	146	28.327	0.45	0.7	
1,4-Benzenediol, 2-methoxy-	140	28.537	0.27	0.46	0.05
2-Butanone, 4-(4-hydroxyphenyl)-	164	31.533	1.07	1.97	0.15
Guaiacyl derivates					

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Guaiacol	124	17.949	1.5	2.16	0.93
p-Methylguaiacol	138	20.405	0.27	0.24	trace
p-Ethylguaiacol	152	22.323	0.19	0.26	0.09
p-Vinylguaiacol	150	23.67	0.73	0.8	0.36
Eugenol	164	23.979	0.7	0.9	0.13
trans-isoeugenol	164	26.5	0.14	0.16	0.08
Guaiacylacetone	180	29.777	0.18	0.15	0.13
Acetoguaiacon	166	30.791	0.12	0.09	0.13
Dihydroconifery alcohol	182	32.172	0.23	0.29	
Syringyl derivates					
Syringol	154	24.82	0.83	1.44	0.49
Syringol, 4-vinyl-	180	29.38	0.39	0.28	0.17
N-containing compounds					
1H-Pyrrole, 1-ethyl-	95	8.508			0.07
Formamide, N,N-dimethyl-	73	11.042			
Butanal, O-methyloxime($C_5H_{11}NO$) or Acetamide, N-methyl-	101/73	14.948		0.16	
Other compounds					
1,4-Dioxin, 2,3-dihydro-	86	8.099	0.33	0.32	0.18
2-Pentene, 4-methyl-	84	8.819			0.13
2-Cycloocten-1-one	124	12.083			0.14
2-Cyclohexen-1-one	96	14.061			0.08
Linalool oxide	170	15.87		0.08	
1,3-Dioxolane-2-methanol, 2,4-dimethyl-	132	19.55	0.19	0.09	
2-Naphthalenol	144	30.626	0.17	0.25	
1-Tridecanol	200	32.569	0.13	0.11	0.1
1-Naphthalenol, 2-methyl-	158	32.832		0.18	
2-Naphthyl methyl ketone	170	33.783	0.17	0.14	

On the contrary, the THF-insoluble fraction exhibits a significantly increased ratio of summary peak areas between aliphatic (carbohydrate-derived) and aromatic (phenolic extractives-derived) pyrolysis products (Figure 1).

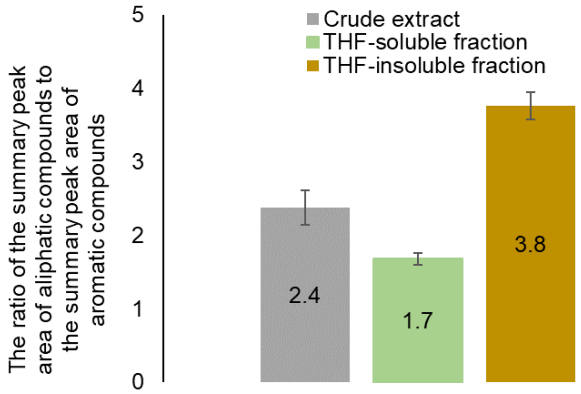

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Figure 1. The ratio of aliphatic to aromatic constituents as determined by analytical pyrolysis in the crude water extract and its fractions.

It can be hypothesized that carbohydrates transfer to the THF-soluble fraction only when bonded with other compounds, such as phenyl glucosides. To validate this hypothesis, Fourier transform infrared (FTIR) spectra were recorded in KBr pellets by Spectrum One apparatus (Perkin Elmer) by scanning from 500 to 4000 cm^{-1}, scan resolution and number of scans were 0.4 cm^{-1} and 64, respectively. The significantly increased ratio of the peak at 1035 cm^{-1}, attributed to the C-O-C vibrations of carbohydrates, to the peak at 1510 cm^{-1}, attributed to the aromatic ring vibrations, in the THF-insoluble fraction confirms that it contains a higher amount of carbohydrates compared to the crude extract. Conversely, the ratio of these peaks decreases in the THF-soluble fraction, indicating a reduced content of carbohydrates (Figure 2).

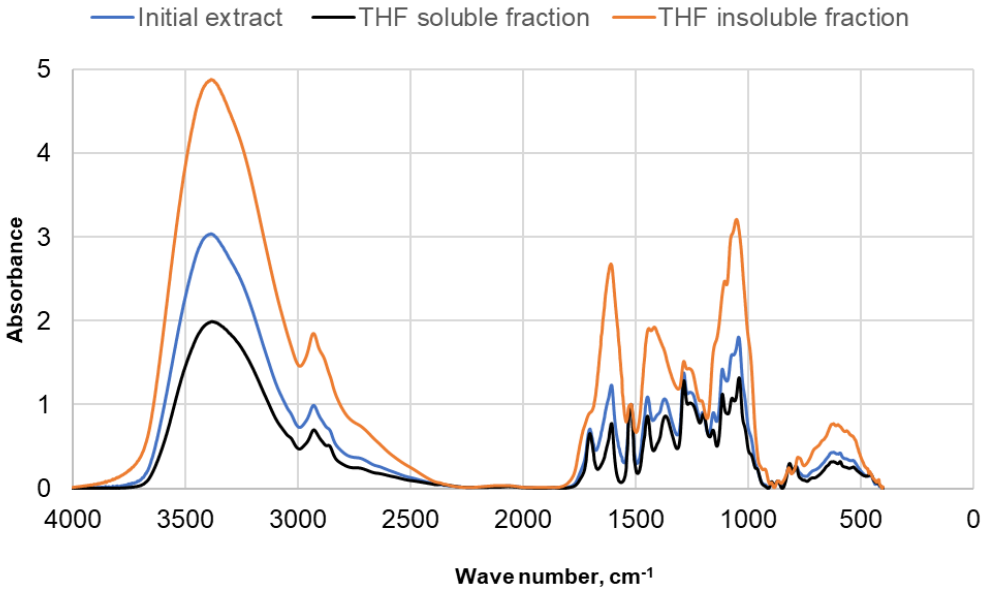

Figure 2. Normalized (1510 cm^{-1}) FTIR spectra of black alder bark water extract and its fractions.

Furthermore, the radical scavenging activity of the extract fractions, which is dependent on the phenolic compound content, was evaluated using the stable 2 2-diphenyl-1-picrylhydrazyl free radicals (DPPH•) test and expressed as the IC_{50} value (the concentration required to inhibit 50% of the initial free radicals). A lower IC_{50} value indicates higher radical scavenging activity. The THF-soluble fraction exhibited the highest activity, surpassing both the crude black alder bark extract and the widely used synthetic antioxidant Irganox 1010 in PU materials. Conversely, due to the increased content of free carbohydrates and decreased content of phenolic compounds and their derivatives, the THF-insoluble fraction displayed significantly reduced radical scavenging activity compared to the crude extract (Table 2).

Table 2. DPPH• scavenging activity of the black alder bark water extract and its fractions.

	IC_{50} $mg \cdot L^{-1}$
Crude black alder bark water extract	7.4
THF-soluble fraction	5.06
THF-insoluble fraction	31.07
Irganox1010	7.72

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Generation of bark-sourced polyols for polyurethane foam synthesis. Another approach was used to utilize the bark-derived polyols for the synthesis of polyurethane foam. The crude black alder bark water extract was mixed with polyethylene glycol (PEG 400) under different conditions. These conditions included a temperature range of 150-170°C, a catalyst concentration of 0-1% of H_2SO_4, and a bark extract content range of 20-30% in the PEG 400-extract mixture. Consequently, the crude black alder bark water extract was fractionated into PEG-soluble polyol and PEG-insoluble fraction. The acid used as a catalyst was neutralized 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 moisture content of the samples was monitored using the Karl Fischer method.

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O \quad (1)$$

During a 6-hour-long dissolution process, it proved challenging to fully dissolve the black alder bark extract in PEG400 to achieve a 20% content without the use of a catalyst. Even with the addition of 0.5% catalysts, the complete dissolution of the introduced extract in PEG400 (at a weight ratio of 20%) 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-extract ratios. At a temperature of 130 °C, the insoluble portion decreased to only around 9%, while at 150 and 170 °C, all of the introduced bark extract dissolved, enabling the attainment of a 20% concentration in PEG400 (refer to Figure 3).

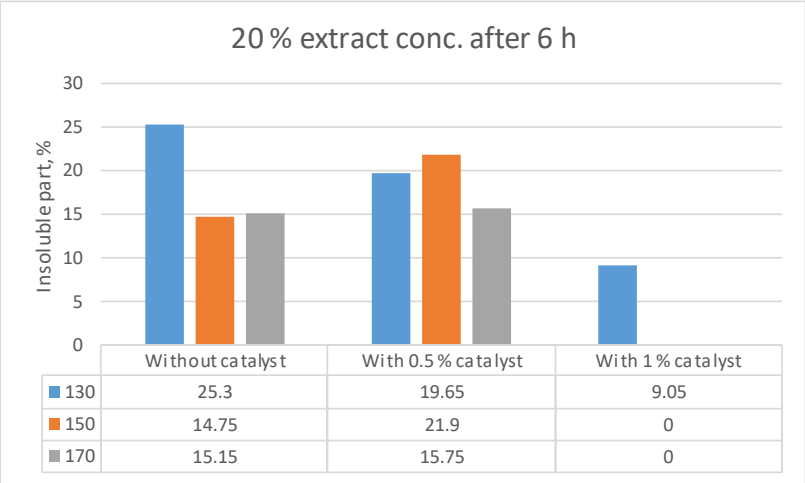

Figure 3. Solubility of Black Alder Bark Extracts in PEG400 as a Function of Temperature and Catalyst Concentration after 6 Hours of Dissolution Process.

Further examination of the extract to PEG400 ratio, using a 1% catalyst concentration, revealed that a ratio of 15:85 successfully enabled the dissolution of the extract at all tested temperatures (refer to Figure 4). However, at a higher extract content of a 20:80 ratio, complete dissolution was not achieved at 130 °C, but at 150 and 170 °C, complete dissolution was observed. Furthermore, when the extract content was increased to 30%, complete dissolution was not possible at any of the temperatures utilized (see Figure 4).

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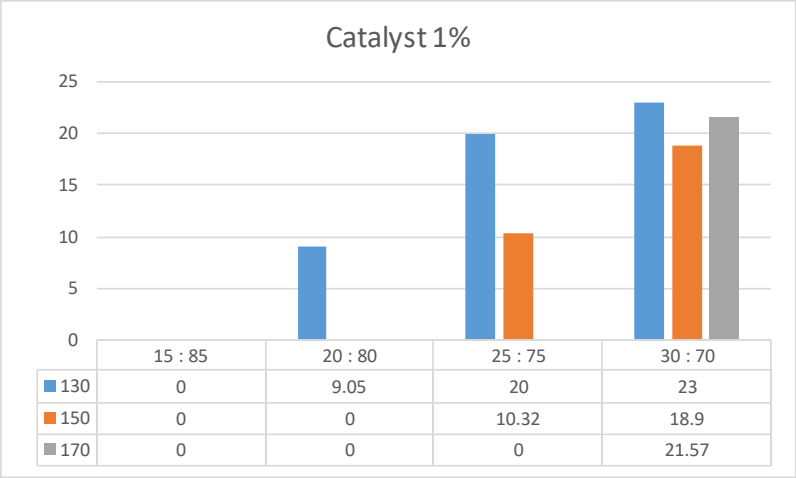

Figure 4. Dependence of Black Alder Bark Extract Dissolution on the Extract to PEG400 Ratio at a 1% Catalyst Concentration.

The dissolution of pine bark extracts in PEG400 followed the same procedure as for the black alder bark extract. However, unlike the black alder extract without catalyst (refer to Figure 3), the pine bark extract introduced in PEG400 at a weight ratio of 20:80 without catalyst exhibited significantly poorer dissolution results at all temperatures (see Figure 5). With the addition of a 0.5% catalyst, the insoluble portion of the introduced pine bark water extract varied between 21-37%, decreasing as the dissolution temperature increased. In contrast, the use of 1% catalysts led to complete solubility of the introduced pine bark extract, allowing for the achievement of a 20% extract concentration in PEG400 at all liquefaction temperatures.

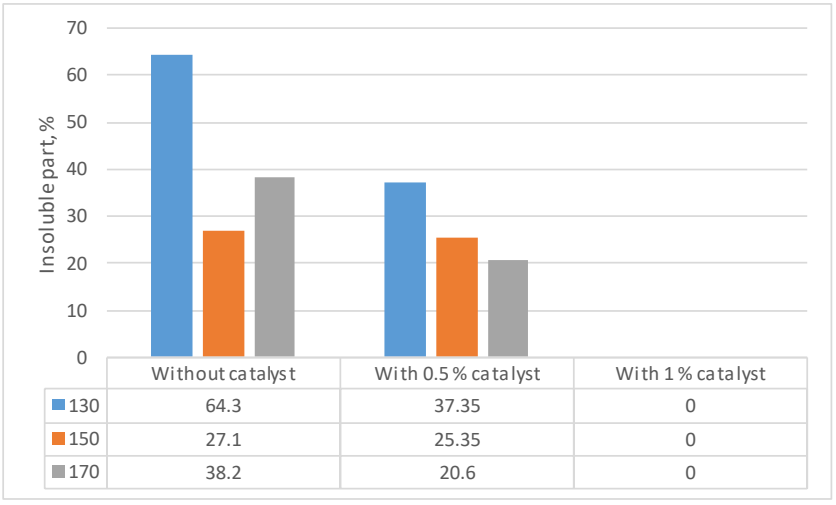

Figure 5. Solubility of Pine Extracts in PEG400 at a 20:80 Extract to PEG Ratio as a Function of Temperature and Catalyst Concentration after 6 Hours of Dissolution Process.

Increasing the pine bark water extract content in its mixture with PEG400 to 25% at a 1% catalyst concentration resulted in incomplete solubility of the pine bark extract at all tested temperatures. However, by increasing the catalyst concentration to 1.5% while maintaining the extract content in PEG400 at 25%, it can be observed that complete solubility (100%) can only be achieved at a temperature of 170 °C (refer to Figure 6).

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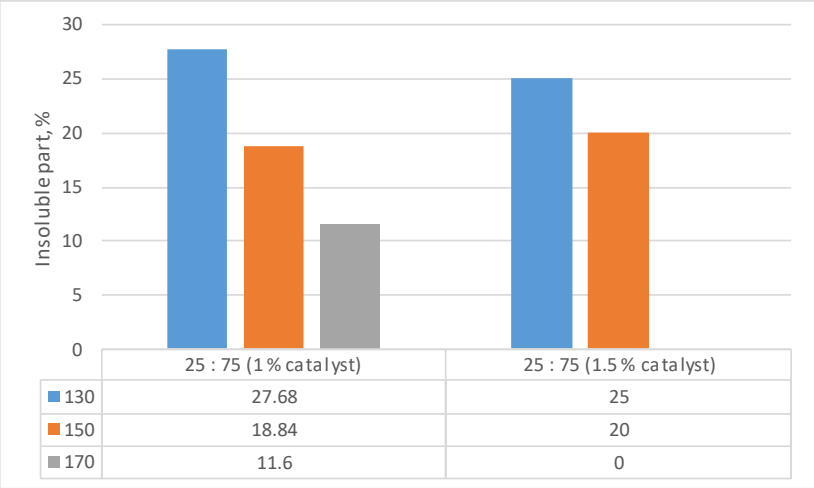

Figure 6. Dependence of Pine Bark Extract Dissolution on the Catalyst Content at a 25:75% Extract to PEG400 Ratio.

Depending on the liquefaction conditions, the bark extracts can be completely liquefied using PEG400 as a solvent, resulting in polyols suitable for the synthesis of polyurethane foams. Alternatively, they can be fractionated into a PEG-soluble polyol fraction and a PEG-insoluble fraction. The PEG-insoluble fractions exhibit notable differences compared to the crude extract, as indicated by the varying composition of volatile degradation products formed from biomass components during thermal decomposition using analytical pyrolysis (refer to Table 3). These composition differences can be attributed to the insolubility of carbohydrate components in the extract in polyethylene glycol, leading to an increased content of their derivatives in the PEG-insoluble fractions. The PEG-insoluble fractions of the black alder bark extract obtained without a catalyst at 150 and 170°C, using a 20:80 ratio of extract to PEG, exhibit similar compositions. However, the fraction that remains insoluble in PEG after treatment at 170°C with 1% H_2SO_4 as a dissolution catalyst and a 30:70 extract-PEG ratio shows significant differences from them (Table 3, Figure 7). It can be hypothesized that the use of a catalyst promotes the hydrolysis of glucoside bonds within the structure of the components of bark extracts, including phenyl glucosides, resulting in the formation of new PEG-soluble (aromatic) and insoluble (carbohydrate) products.

Table 3. Pyrolysis products of black alder bark water extract and its PEG 400-insoluble fractions obtained under different conditions.

Identified compound	MW	Retention time, min	Normalized peak area, % from chromatogram			
			Crude water extract of black alder bark	Fraction insoluble in PEG400, no cat., 6 h., 150°C, 20%	Fraction insoluble in PEG400, no cat., 6 h., 170°C, 20%	Fraction insoluble in PEG400, 1% cat., 6 h., 170°C, 30%
Carbon dioxide	44	5.035	11.72	21.13	21.89	10.82
Water	18	5.198	19.61	19.37	19.72	15.75
Carbohydrates derivatives						
Formic acid	46	6.637	1.2	0.35	0.36	0.42

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Acetic acid	60	7.091	3.18	5.09	4.62	1.98
(S)-2-Hydroxypropanoic acid	90	7.316	0.18	0.28	0.23	0.05
Acetic acid, hydroxy-, methyl ester	90	8.21		0.02	0.06	
Formic acid, methyl ester	60	8.322	0.45	0.22	0.17	0.2
Propanoic acid	74	8.627	0.46	0.64	0.58	0.41
2-Propenoic acid	72	8.985	0.16	0.19	0.33	0.21
Acetic acid, methyl ester	74	9.811	0.41	0.63	0.58	0.31
2-Propenoic acid, methyl ester	86	9.492	0.29	0.28	0.17	0.1
2-Propenoic acid, 2-methyl-	86	10.667		0.05	0.09	
Propanoic acid, 2-oxo-, methyl ester	102	10.802	0.93	0.96	0.8	0.64
2-Butenoic acid	86	11.822	0.07	0.06	0.05	
Crotonic acid vinyl ester	112	13.284	0.09	0.1	0.1	0.08
Propanoic acid, 2-methylpropyl ester	130	14.583	0.1	0.11	0.07	0.07
Propanoic acid, 2-hydroxy-, ethyl ester, (S)-	118	15.542	0.06			
2-Butene, 1,4-diethoxy-	144	23.224	0.42	1.71	1.22	0.78
1,2-Ethanediol	62	9.492	0.15	0.25	0.49	0.23
1-Butanol, 3-methyl-	88	14.506	0.09	0.18	0.2	0.14
2-Propanol, 1-ethoxy-	104	15.091		0.12	0.13	0.23
6-Heptene-2,4-diol	130	15.85		0.04	0.07	0.25
2-Heptanol, 5-methyl-	130	16.445				1.2
Glycerin (1,2,3-Propanetriol)	92	18.403	0.6	0.41	0.4	0.23
4-Heptanol, 2-methyl-	130	22.33		0.27	0.4	0.37
Methylglyoxal	72	5.698	2.84	3.57	3.3	2.41
2,3-Butanedione	86	6.321	0.51	0.89	0.92	0.45
2-Butanone, 1-hydroxy-	88	6.47	0.25	0.37	0.33	0.15
Acetaldehyde, hydroxy-	60	6.952	5.82	4.08	4.12	2.95
2,3-Pentanedione	100	7.526	0.19	0.38	0.33	0.31
2-Propanone, 1-hydroxy-	74	8.047	3.89	4.8	4.18	1.3

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2-Butanone, 3-hydroxy-	88	8.687	0.09	0.17	0.06	
2-Butanone, 1-hydroxy-, isomer	88	9.904	0.61	0.62	0.61	0.25
Propanal and Butanedial	58/86	10.983	0.11	0.68	1.02	0.35
3-Hexanone, 4-ethyl-	128	11.867	0.06	0.1	0.09	0.07
2-Propanone, 1-(acetyloxy)-	116	12.38	0.65	1.06	0.71	0.33
2-Heptanone, 3-methyl-	128	12.753	0.13	0.15	0.16	0.09
3-Hexen-2-one, 5-methyl-	112	14.042	0.06	0.05	0.06	
2-Butanone, 1-(acetyloxy)-	130	14.662	0.17	0.19	0.12	0.22
2-Propanone, 1,3-dihydroxy-	90	15.099	0.27			
Glycolaldehyde dimer	120	16.293	0.91			
2-Butanone, 4-hydroxy-3-methyl-	102	18.517	0.55			0.23
2,3-Pentanedione, 4-methyl-	114	17.693		0.3	0.16	0.17
Propanal, 2,3-dihydroxy-	90	19.243	0.36	0.22	0.15	0.06
Pentanal and Pentanadial	86/100	20.559	0.22	0.76	0.96	0.09
3-Pentanone, 2-hydroxy-	102	28.236	0.57	0.59	0.61	
2-Cyclopenten-1-one	82	11.386	0.13	0.48	0.58	0.14
2-Cyclopenten-1-one, 2-methyl-	96	12.742	0.09	0.24	0.21	0.04
4-Cyclopentene-1,3-dione	96	13.508	0.14	0.17	0.12	0.12
1,2-Cyclopentanedione	98	13.916	0.63	0.82	0.96	0.56
2-Cyclopenten-1-one, 3-methyl-	96	15.203	0.2	0.27	0.27	0.1
1,2-Cyclopentanedione, 3-methyl-	112	16.47	0.3	0.85	0.79	
2-Cyclopenten-1-one, 2,3-dimethyl-	110	16.566	0.07	0.1	0.11	0.15
2-Cyclopenten-1-one, 3-ethyl-	110	18.042		0.05	0.06	
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	126	18.615		0.17	0.15	
Furan, 2-methyl-	82	6.059	0.39	0.4	0.49	0.36

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Furan, 2,5-dihydro-3-methyl-	84	10.101		0.05	0.07	
2(3H)-Furanone	84	10.284	0.05	0.05	0.07	0.04
3(2H)-Furanone	84	10.549	0.27	0.29	0.35	0.84
Furfural	96	11.321	1.53	1.06	0.54	2.36
Furan, 2-propyl-	110	11.565				0.04
2-Furanmethanol	98	12.107	0.51	0.55	0.44	0.21
Acetylfuran	110	13.027	0.11	0.16	0.12	0.14
2(3H)-Furanone, dihydro-4-hydroxy-	102	13.651	0.26	0.29	0.33	0.38
2-Furancarboxaldehyde, 5-methyl-	110	14.672	0.14	0.11	0.08	0.27
2(3H)-Furanone, dihydro-	86	15.387	0.21	0.26	0.22	0.07
2(5H)-Furanone	84	15.643	0.25	0.39	0.49	0.32
2,5-Furandione, 3-methyl-	112	16.174	0.29	2.09	2.8	1.92
2(5H)-Furanone, 3-methyl-	98	16.767		0.18	0.16	
3(2H)-Furanone, 4-hydroxy-2,5-dimethyl-	128	17.699				0.56
Methyl 2-furoate	126	18.6	0.13			0.11
3-Hydroxydihydro-2(3H)-furanone	102	18.943	0.28	0.45	0.3	0.14
4-Methyl-5H-furan-2-one	98	19.598		0.1	0.11	0.11
5-(Hydroxymethyl)dihydro-2(3H)-furanone	116	19.801	0.22			0.25
2,5-Furandione, dihydro-3-methyl-	114	19.909	0.05	0.1	0.16	
2(3H)-Furanone, 5-acetyldihydro-	128	21.943	0.04			
Furan, 4-methyl-2-propyl-	124	21.962		0.32	0.22	0.44
2,4(3H,5H)-Furandione, 3-methyl-	114	22.375			0.16	0.43
2(5H)-Furanone, 4-hydroxy-3,5-dimethyl-	128	22.44	0.25	0.14	0.11	
Benzofuran, 2,3-dihydro-	120	23.162	1.19	0.65	0.55	0.43
2-Furancarboxaldehyde, 5-(hydroxymethyl)-	126	24.383	0.91	0.77	0.05	1.94

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5-Hydroxymethyldihydrofuran-2-one	116	24.79	0.19	0.34	0.34	0.08
2(3H)-Furanone, dihydro-4-hydroxy-	102	25.095		0.11	0.09	0.09
Benzofuran, 3-methyl-	132	25.618	0.12			
4-Hydroxy-,5,6-dihydro-(2H)-pyran-2-one	114	15.928	0.38	0.18	0.17	1.27
4H-Pyran-4-one, 3-hydroxy-2-methyl-	126	18.827		0.07	0.09	0.09
4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	144	20.022	0.23	0.11	0.08	0.15
4H-Pyran-4-one, 3,5-dihydroxy-2-methyl-	142	20.491	0.18			0.22
2H-Pyran-3(4H)-one, dihydro-	100	22.533		0.05	0.16	0.19
2-Hydroxymethyl-5-hydroxy-2,3-dihydro-(4H)-pyran-4-one	144	25.815			0.08	0.38
Isosorbide (D-Glucitol, 1,4;3,6-dianhydro-)	146	22.171			0.05	0.07
1,4;3,6-Dianhydro-.alpha.-d-glucopyranose	144	22.976	0.28			0.34
2-Deoxy-D-galactose	164	26.224	1.18	0.41	0.45	1.9
DL-Arabinose	150	27.836		0.11	0.16	
1,6-Anhydro- -D-glucopyranose; isomer	162	28.689	0.19	0.28	0.32	1.52
-D-Glucopyranoside, methyl-	194	30.048	0.13		0.11	0.68
-D-Glucopyranoside, methyl 3,6-anhydro-	176	31.054		0.49		
1,6-Anhydro- -D-glucopyranose	162	31.457	3.73	1.55	2.69	9.32
1,6-Anhydro- -D-glucofuranose	162	34.05	0.18			0.93
Phenyl and benzyl derivates						
Phenol	94	17.019	1.42	0.44	0.47	0.34
Phenol, 2-methyl-	108	18.221	0.2	0.17	0.15	0.05
Phenol, 3-and 4-methyl-	108	19.078	0.84	0.27	0.25	0.51
Phenol, 2,3-dimethyl-	122	20.217	0.11	0.05	0.07	0.02
Phenol, 2,6-dimethyl	122	21.098	0.07			0.07
Phenol, 4-ethyl-	122	21.161	0.29	0.06	0.1	0.3

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Phenol, 2,4-dimethyl-	122	21.807	0.06			
1,2-Benzenediol(Pyrocatechol)	110	24.314	7.16	0.55	0.56	1.4
1,2-Benzenediol, 3-methyl-(Pyrocatechol, 3-methyl-)	124	25.116	0.29			
Phenol, 4-(2-propenyl)-	134	25.256	0.1			0.07
1,2-Benzenediol, 4-methyl-(Homopyrocatechol)	124	25.974	2.51	0.08	0.12	0.44
1,4-Benzenediol (Hydroquinone)	110	26.606	0.45	0.64	0.54	0.2
1,4-Benzenediol, 2,3-dimethyl-	138	26.729	0.05			
Phenol, 2-ethoxy-4-methyl-	152	27.483	0.07	0.1	0.08	
1,2-Benzenediol, 4-ethyl-	138	27.771	1.2			0.08
1,2-Benzenediol, 3-methoxy-	140	28.164	0.51			0.11
Benzoic acid, 2,5-dimethyl-	150	30.749	0.27			
2-Butanone, 4-(4-hydroxyphenyl)-	164	31.257	0.49			0.32
Benzoic acid, 4-(1-methylethyl)-	164	32.131	0.65			
Guaiacyl derivates						
Guaiacol	124	17.708	1.41	0.51	0.49	0.1
p-Methylguaiacol	138	20.178	0.21	0.05	0.05	0.08
p-Ethylguaiacol	152	22.111	0.22			
p-Vinylguaiacol	150	23.436	0.54	0.22	0.24	0.17
Eugenol	164	23.77	0.11			
Vanillin	152	26.899	0.16			
-Hydroxypropiovanillone	196	30.538	0.06			
Dihydroconiferyl alcohol	182	31.837	0.44	0.17	0.15	0.12
Syringyl derivates						
Syringol	154	24.646	0.84	0.22	0.18	0.15
Syringol, 4-methyl-	168	26.502	0.08	0.05	0.07	0.07
Syringol, 4-ethyl-	182	28.01	0.08			
Syringol, 4-vinyl-	180	29.151	0.13			
Other compounds						

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1,4-Dioxin, 2,3-dihydro-	86	7.855	0.19	0.18	0.14	0.11
2-Naphthalenol	144	30.263	0.06			
2-Naphthyl methyl ketone	170	33.393	0.42	0.15		
Ethanol, 2-[2-(2-propenyloxy)ethoxy]-	146	22.919		0.55	0.72	
Triethylene glycol	150	23.002				1.65
Ethanol, 2-[2-(2-methoxyethoxy)ethoxy]-	164	27.619				0.1
Ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]-	178	28.603				0.23
1,3-Dioxan-5-ol (Glycerol formal)	104	28.851	0.56	0.34	0.29	
Ethanol, 2,2'-[oxybis(2,1-ethanediyloxy)]bis-	194	28.945		0.91	0.99	2.72
Ethanol, 2-(2-butoxyethoxy)-	162	31.358				1.34
Ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]-	178	33.844				0.32
Hexagol (3,6,9,12,15-Pentaoxaheptadecane-1,17-diol)	282	34.292		2.3	2.27	4.62
Heptaethylene glycol	326	39.649		4.64	4.46	9.17

The obtained data revealed a significant increase in the content of aliphatic volatiles, primarily derived from carbohydrates, and a drastic decrease in the content of aromatic pyrolysis products, mainly derived from phenolic extractives, in all PEG-insoluble fractions (Figure 7). Based on these findings, we can conclude that unlike the PEG-insoluble carbohydrates, the phenolic extractives of black alder bark can be incorporated into PEG-based mixed polyol compositions.

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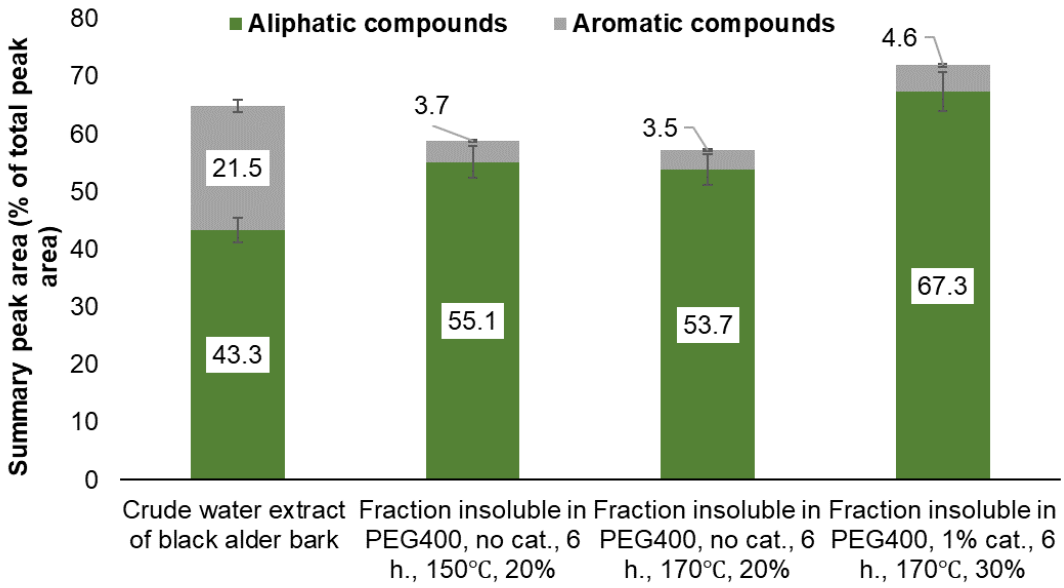

Figure 7. Relative contents of aliphatic and aromatic pyrolysis products in the crude black alder bark water extract and its PEG-400 insoluble fractions obtained under different conditions.

The FTIR spectra of the crude black alder bark extract and its PEG400-insoluble fractions obtained under different conditions provide confirmation of the solubility of aromatic constituents in polyethylene glycol and the concentration of carbohydrates in the insoluble fraction. This is evident from the decreased absorption at approximately 1500-1600 cm^{-1} and 1260-1320 cm^{-1}, which are attributed to vibrations of aromatic rings. Additionally, the absorption bands in the range of 800-1200 cm^{-1} associated with cellulose and hemicellulose are increased in the spectra of the polyethylene glycol-insoluble fractions compared to the crude extract. The use of a catalyst significantly increases the content of carbohydrates and decreases the content of aromatic compounds in the PEG400-insoluble fractions. This is because the catalyst promotes the hydrolysis of glucoside bonds, leading to the formation of insoluble carbohydrates derived from phenyl glucosides. Additionally, the released aromatic moieties of the latter are dissolved (see Figure 8).

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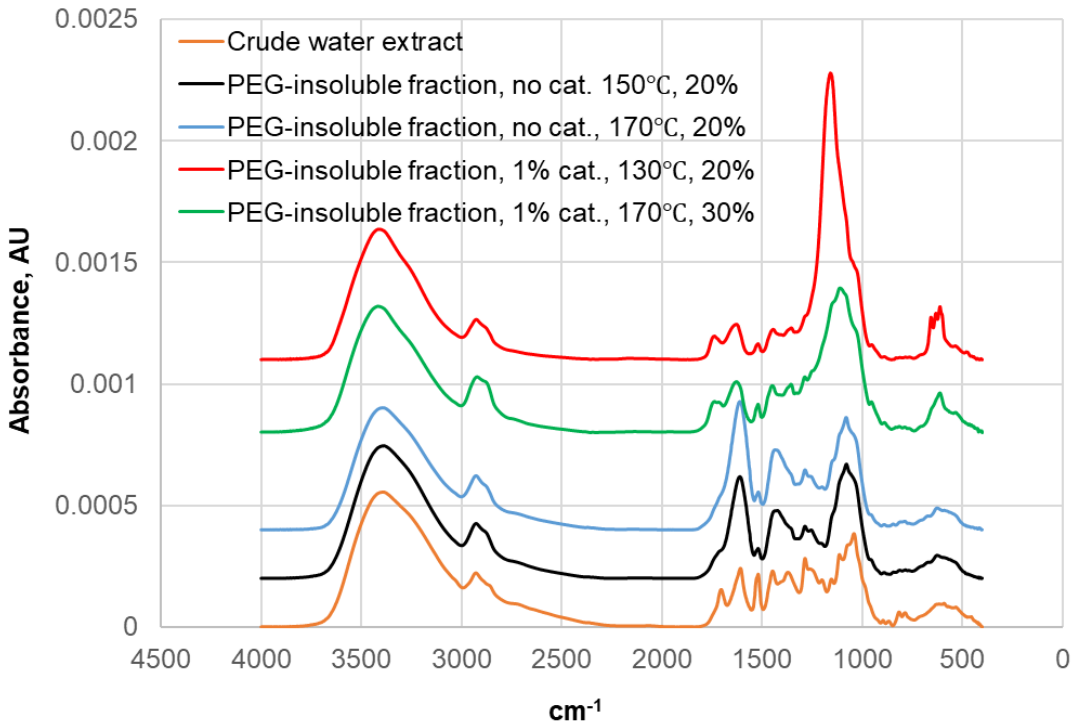

Figure 8. FTIR Spectra of crude black alder bark water extract and its PEG400-insoluble fractions obtained at different temperatures, catalyst content, and various extract content in mixture with PEG.

A higher extraction temperature can enhance the solubility of certain carbohydrates, as evidenced by the FTIR data. The PEG-insoluble fraction of the black alder bark water extract obtained using a 20:80 extract-to-PEG400 ratio at 130°C with 1% catalyst exhibits a significantly higher ratio of absorbance at 1100 cm^{-1} to 1515 cm^{-1}, indicating a notably higher content of carbohydrate constituents compared to the fraction obtained with 1% catalyst at 170°C (refer to Table 4).

Table 4. Proportion of aromatic moieties to carbohydrates moieties according to FTIR data in the crude black alder bark water extract and its PEG400-insoluble fractions depending on liquefaction conditions.

Liquefaction temperature (°C)	Extract-to-PEG400 ratio	Catalyst, %	Concentration of dissolved extract in PEG solution, %	Percentage of dissolved portion of the introduced extract	Ratio of absorbance at 1100 cm^{-1} to 1515 cm^{-1}
Crude black alder bar water extract					1.7
150	20:80	0	17.1	85.3	3.8
170	20:80	0	17.0	85.0	2.9
130	20:80	1	18.2	91.0	18.0
170	30:70	1	23.5	78.3	5.1

Summary

The fractions of alder bark water extracts that are insoluble in the medium used for polyurethane foam and film synthesis exhibit an enrichment of carbohydrates compared to the crude extract. This suggests that introducing individual carbohydrate bark components into the polyurethane structure is challenging and requires extensive modification. However, aromatic bark extractives, including those containing sugar units such as phenyl glucosides, can be utilized for polyurethane synthesis as biopolyols obtained under mild conditions.

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