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Producing Bark-based Polyols through Liquefaction: Effect of Liquefaction Temperature

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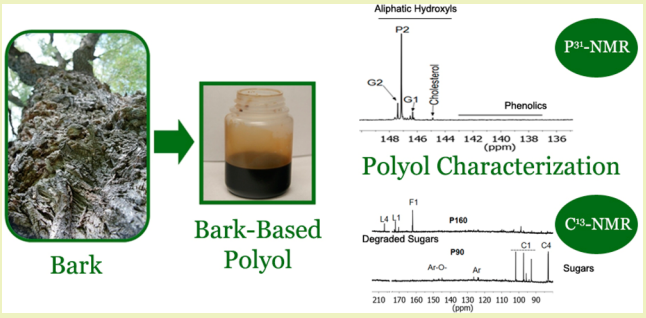
ABSTRACT: Bark-based polyols were synthesized through a solvent liquefaction in a polyethylene glycol (PEG)/glycerol cosolvent. Liquefaction reactions were carried out at temperatures of 90, 130, and 160 °C. The bark-based polyols were analyzed for their yield, composition, and structural characteristics using the standard titration method for hydroxyl value, combined with gel permeation chromatography (GPC), Fourier transform infrared (FTIR), and liquid state phosphorus (^{31}P), carbon (^{13}C), and proton (^{1}H) NMR analyses. As the liquefaction temperature increased, viscosity of the polyols became higher with a corresponding broadening of the molecular weight (MW) distributions that also shifted toward higher MW. The liquefaction of biomass induced a high degree of modification to the bark components. These polyols had similar hydroxyl values but differed greatly in molecular structures. The polyol obtained through liquefaction at 90 °C had more secondary alcohols and contained sugars. Meanwhile, sugars were degraded into levulinate and formic esters in the polyols obtained at 130 and 160 °C. None of the polyols had condensed tannins, neither in their polymeric or monomeric state. Instead, aromatic ethers were seen in the carbon NMR spectra and various carboxyl functionalities were observed from the FTIR analysis. These results demonstrated the influence of the liquefaction temperature on the liquefaction behaviors of the bark biopolymers and provided an insight into the physical and structural properties of these bark-based polyols.



KEYWORDS: *Bark, Extraction, Liquefaction, Polyol, Polyurethane*

INTRODUCTION

Bark has been attracting great interest as a renewable raw material for the production of precursor chemicals for the synthesis of phenol-formaldehyde adhesives[1] and polyurethanes foams (PUFs).[2−5] PUFs are made through an addition reaction of an isocyanate with a polyether or a polyester polyol, all of which are conventionally derived from petroleum-based resources. Recently, significant efforts have been made to derive polyols from renewable resources through methods such as the chemical modification of plant oils and the thermo-mechanical mixing or alkoxylation of ground biomass particles. In addition, it was reported that a liquefaction of lignocellulosic biomass through glycolysis with an acid catalyst could also digest the biomass into a low viscosity liquid polyol. This approach has been applied to ground particles of wood,[6] paper,[7] starch,[8] straw,[9] bamboo,[10] sugar cane,[11] and bark.[4,5,12] Bark is an appealing, yet underutilized source of biomass materials suitable for industrial applications. It accounts for 10−15% of the weight of a pine tree.[13] Currently, bark is a mill residue that is usually burnt in a boiler for heat recovery. However, it is a rich source of polyphenolic compounds like condensed tannins at up to 30% of the bark's weight.[14]

Condensed tannins are polymeric in nature and range from a single monomer to twenty units for bark-based tannins.[15] Their potential utility in making a polyol stems from their high level of hydroxyl functionality enabling their reactivity with isocyanate; their ease of extraction compared to recalcitrant biopolymers like lignin and cellulose; and their aromaticity that can potentially impart thermal stability to their resultant PUFs.[16,17]

Hartman[2] and Ge et al.[3] made bark-based PUFs by mechanically mixing bark or tannin extractives into polyols[3,18−20] and found the bark-based PUFs were able to biodegrade.[21] Even though liquefaction of bark was also used to produce PUFs, the prior work focused mostly on the foam properties with limited attempts to systematically investigate the impact of the liquefaction conditions on properties of the bark-based polyols.[4,22] In some studies, bark was liquefied at high temperatures using the bisulfite method to produce polyurethane foams and films.[5,12] At 250 °C, these polyols were shown to contain tannin degradation products featuring phenolic compounds with varying degree of acetyl, methyl, and hydroxyl functionalities.[23]

Yamada et al.[24,25] and Jasiukaityte et al.[26] studied the liquefaction of cellulose and wood and found that the liquefaction at higher temperatures, such as 150 °C, was too harsh and resulted in substantial degradation of cellulose to levulinate esters. At this temperature, lignin was modified by

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glycols undergoing condensation reactions with the phenolic hydroxyls to produce aliphatic hydroxyl groups.[27] However, their studies did not look into the liquefaction behavior of wood and cellulose at lower temperatures. Since properties of the polyurethane foams depend on the molecular structure and properties of the polyols, it is crucial to determine how the liquefaction conditions affect key characteristics of the bark polyols. Moreover, with the incorporation of the bark components in the polyol, the suitability of some standard characterization methods originally developed for conventional polyols would need to be examined before their usage for analyzing the bark-based polyols.

Therefore, in this study bark liquefaction reactions were carried out under mild, medium, and high temperatures to study the impact of the liquefaction temperature on bark-based polyols. The three temperature levels are 90, 130, and 160 °C. At the mildest liquefaction temperature of 90 °C with water as the cosolvent, the reaction was a hybridization of a solvent liquefaction with a hot-water extraction, with the latter being the method commonly used for condensed tannin extractions. The highest liquefaction temperature of 160 °C was chosen to produce a polyol containing highly degraded bark-biopolymers. The medium liquefaction temperature of 130 °C represented an intermediate condition where some levels of bark polymer degradation were expected.

EXPERIMENTAL SECTION

Materials. Polyethylene glycol with a molecular weight of 400 Da (PEG) was purchased from Fisher Scientific. Glycerol, sulphuric acid, xylene, NaOH, dioxane, toluene, THF, and pyridine were purchased from Caledon Laboratories. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, benzoyl chloride, chromium(III) acetylacetonate, cholesterol, DMSO-d_6, imidazole, and phthalic anhydride were purchased from Sigma Aldrich. $CDCl_3$ was purchased from Cambridge Isotope Laboratories Inc. All chemicals were used as received without further purification. Mountain Pine Beetle infested Lodgepole Pine bark was supplied by FPInnovations and was ground into a bark powder using a Wiley mill and then passed through a 70 mesh (0.211 mm).

Liquefaction. The experiments were carried out at three different temperatures (90, 130, and 160 °C). The corresponding bark-based polyols were labeled as P90, P130, and P160, respectively. Polyethylene glycol (PEG; 37.5, 30, and 38 g), glycerol (1.99, 1.59, and 2.02 g), sulfuric acid (1.99, 0.80, and 0.67 g), bark (37.5, 15, and 12.67 g), and a cosolvent (water 200 mL, xylene 30 mL, none) were added to a flask fitted with a condenser. The flask was then heated for 2 h at the respective temperature under a nitrogen environment. After which NaOH (0.814, 0.325, and 0.275 g) was added to neutralize the sulfuric acid. Next, the solution was diluted with a dioxane−water (8:2) solution (400 mL) and allowed to stir overnight. The solutions were then centrifuged at 1500 rpm for 15 min, filtered, and washed with dioxane−water (8:2). The solid residues were then dried at 60 °C in an oven to determine the amount of unliquefied bark residue.

$$\%\ \text{residue} = \text{weight of residue}/\text{weight of biomass} \times 100$$

Unliquefied Bark Residue Analysis. The extractives content of the residues were determined by the TAPPI standard method T-204 cm97: Solvent Extractives of Wood and Pulp; however benzene was substituted with toluene. The acid insoluble lignin content was determined by the TAPPI standard method, T-222 om-02: Acid-insoluble Lignin in Wood and Pulp. The acid soluble lignin content was found to be negligible and it has been reported to be less than 1% for softwood species.[28]

Hydroxyl Value and Acid Value Determination. The hydroxyl value (OHV) was determined by the standard esterification method using phthalic anhydride. Polyol (1g) and the pthalation reagent (25 mL) were heated at 100 °C for 15 min, cooled to room temperature, pyridine (50 mL) was added, followed by water (10 mL), and then titrated with 0.5 M NaOH to its equivalence point. The phthlation reagent was a solution of phthalic anhyrdride (41.43 g) and imidazole (6.43 g) in pyridine (250 mL). Where S and B_1 are the milliliters at the equivalence point of the sample and blank (no polyol), respectively; N is normality of NaOH; and W is the weight of the sample; OHV is the hydroxyl value in milligrams KOH per gram of sample.

$$\text{OHV}_{\text{PA}} = (B_1 - S)(56.1)(N)/W$$

The acid values (AV) were determined through 0.5 M NaOH titration of the polyol (4 g) in a 8:2 dioxane−water solution (50 mL) to the equivalence point. Where S and B_1 are the milliliters at the equivalence point of the sample and blank (no polyol; N is normality of NaOH; and W is the weight of the sample; AV is the amount of acid groups in units of milligrams KOH per gram of sample.

$$\text{AV} = (S - B_1)(56.1)(N)/W$$

Viscosity and Gel Pemeation Chromatography (GPC). A Brookfield Synchro-lectric viscometer was used and the value was reported as an average of three measurements. THF was used as an eluent on a GPC system consisting of a Waters 2695 Separations Module, Waters 2998 Photodiode Array, and Styragel HR4E and 5E columns in series. It was shown in the literature that benzoylation of the hydroxyl groups improved THF solubility of the polyols as well as the detector's ability to detect compounds previously invisible to the UV detector.[29] Therefore, samples in this study were prepared based on the procedure reported by Salanti et al.[29] Polyol (125 mg), pyridine (6.7 mL), and benzoyl chloride (77 μL) were stirred in a vial for 2 h, then diluted with a 1:3 water−ethanol solution (50 mL), and stirred for 5 min, followed by two liquid toluene (50 mL) extractions. The toluene was rotary evaporated, and the residue was dissolved in THF and passed through a filter prior to analysis. The amount of benzoyl chloride was in excess to the moles of OH groups (1.1:1), based upon an upper estimate of OHV equal to 280 mg KOH/g from the esterification titrations done in this work. A blank sample (a sample with no polyol) showed that excess benzoyl chloride would react with water and ethanol to produce side products of benzoic acid and ethyl benzoate, respectively. However, the low benzoyl chloride to OH groups ratio used to prepare the samples limited the concentration of the side products in the polyol samples.

Fourier Transform Infrared (FTIR). Analysis was performed on a Bruker Tensor 27 FTIR spectrometer using sodium chloride discs with the liquid polyol sample sandwiched in between.

NMR Spectroscopy. ^{31}P NMR analysis was done on a Varian Mercury 300 spectrometer using a 23 kHz spectral width with an acquisition time of 1.8 s, relaxation delay of 10 s, observation pulse of 30 μs, and 256 scans. Samples were prepared based on the phosphitylation method using 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP).[30,31] A stock solution of pyridine-deuterated chloroform (1:1.6, v/v) was prepared and used to prepare a relaxation solution using chromium(III) acetylacetonate (5 mg/mL), as well as a standard solution of cholesterol (5 mg/mL). All three were dried with molecular sieves. The samples were prepared by mixing the liquid polyol (15 mg), relaxation solution (0.1 mL), standard solution (0.1 mL), and stock solution (0.8 mL). Finally, TMDP (0.1 mL) is added, shaken vigorously, and then transferred to an NMR tube for analysis. All spectra used a line broadening of 1 Hz were calibrated to the water peak at 132.2 ppm and had a peak for excess TMDP to ensure that all reactive species had been completely phosphitylated. The OHV values were an average of three samples and were integrated relative to the cholesterol standard. The water content of the polyol required a blank sample to be run to negate the amount of water absorbed from the environment and solvents. Carbon and proton NMR were done on a Varian 600 spectrometer in DMSO-d_6 at a concentration of 100 mg/mL. ^{13}C NMR measurements had a 0.1s relaxation delay, pulse angle of 45°, acquisition time of 1.42 s, spectral width of 35 kHz, and 20 000 scans. ^{1}H NMR used a 1 s relaxation delay, pulse angle of 30°, acquisition time of 1.7 s, spectral width of 9600 Hz, and 64 scans. Both were calibrated using Tetramethylsilane (TMS).

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RESULTS AND DISCUSSION

Yield and Composition of the Liquefied Bark. In this study a 20 wt % biomass fraction in the biobased polyols was set as the target for selecting liquefaction conditions at different temperatures to facilitate the comparison. As a result, the bark contents in the three polyols obtained at the selected temperatures were close to 20 wt % as shown in Table 1. Comparison of the compositional analysis of the unliquefied residues to the pristine bark provided some insight into the bark polyol composition indirectly.

Table 1. Comparison of Liquefaction Conditions and Yield

polyol type	liquefaction temperature (°C)	solvent/bark ratio[a]	bark content in polyol[b] (%)	unliquefied residue (%)
P90	90	1.05	17.6	77.5
P130	130	2.10	18.1	53.5
P160	160	3.16	20.1	20.4

[a]The cosolvent was not included in the weight ratio. [b]Values were calculated based on the residue yield and the amount of PEG and glycerol used.

From Figure 1, it can be seen that at 90 °C approximately half of the bark extractives as well as some accessible

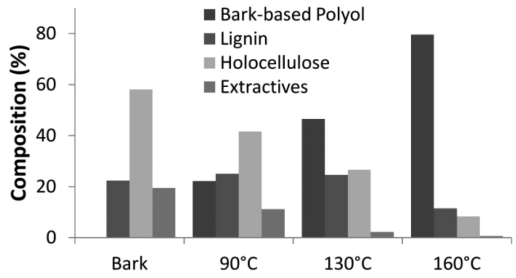

Figure 1. Effect of temperature on the residue composition and the yield. The first bar is the amount of bark that is successfully liquefied. The unliquefied bark residue values are broken down into their biopolymer fractions. This indirectly suggests which compounds were liquefied to produce the bark-based polyols.

polysaccharides, like hemicellulose and amorphous cellulose, were extracted from the bark. At 130 °C nearly all of the bark extractives and half of the holocellulose in bark were liquefied. At temperatures below 160 °C, lignin was not extracted from bark. The rise in lignin content from 22% in the original bark to around 25% in the unliquefied residues at 90 and 130 °C might be due to the production of tannin condensation polymers known as phlobaphenes. Interestingly, a small amount of extractives remained in the residues after liquefying at the highest temperature. This could be due to the limited diffusion through the bark cell walls during the liquefaction process. It should be noted that the residue amounts are relatively higher than those reported in the literature for other types of biomass. Phenolic compounds are known to easily recondense into insoluble large molecular weight lignin-based polymers, thereby increasing the amount of residues. Even though glycerol was found to retard the recondensation reactions,[32] a high glycerol content was not desirable since it could also lead to highly brittle foams.

Bark Polyol Characteristics. *Acid Value.* In Table 2, at the higher liquefaction temperatures the acid values decreased. Even under milder conditions of ethanol reflux tannins broke

Table 2. OHV Obtained via the PA and ^{31}P NMR Methods, AV, and Viscosities of the Three Polyols

	OHV (mg KOH/g)			
polyol type	PA	^{31}P	acid value (mg KOH/g)	viscosity (cP)
P90	265	228 ± 61	20.9	142.5
P130	275	235 ± 60	10.2	800
P160	231	331 ± 26	11.3	1650

down into phenolic acids.[33] Thus, P90 should have the highest acid content since it had the highest amount of bark extractives, especially since softwoods have high amounts of resins and fatty acids.[34]

Viscosity and GPC. Increasing the liquefaction temperature also increased the viscosity of the polyols as shown in Table 2. Two important factors for a polyol to produce a rigid-PUF are its functionality and OHV. Although the hydroxyl content varied slightly among the samples, it is clear that the molecular structures of the three would be vastly different, especially in terms of molecular weight and functionality. This was verified by the GPC data shown in Figure 2. All of the polyols featured

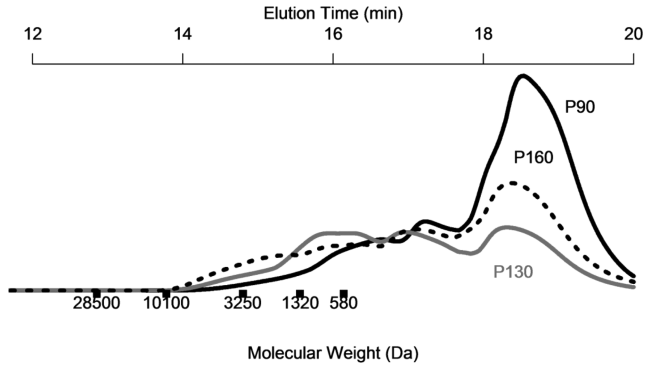

Figure 2. GPC profiles of P90, P130, P160 polyols. The spectra showed that a large fraction is low molecular weight. Also, the large molecular weight tail became more pronounced with the higher liquefaction temperature.

broad molecular weight distributions below 10 000 Da. P90 had a large fraction of low molecular weight (LMW) compounds below 580 Da that indicates the formation of degradation products, while a high molecular weight tail signified polymers formed from the condensation of phenolics.

The LMW compounds may also include partially benzoylated sugars and tannin degradation products as steric reasons would prevent complete derivatization. The low temperature used to produce P90 resulted in degradation exceeding the rate of recondensation. Similarly, P160 showed that the rate of degradation of sugars and lignin fragmentation exceeded the rate of recondensation; despite the large molecular weight fraction approaching 10 000. In contrast, P130 showed a balance, where the molecular weight profile featured a very broad plateau with shallow troughs. The great variation among these polyols demonstrated the need for a thorough characterization of the polyols as the molecular weight distributions were rarely obtained for liquefied biomass polyols previously, despite the molecular weight being a key characteristic for PUFs.

OHV and ^{31}P NMR Spectroscopy. In the literature, the characterization of liquefied biomass polyols has relied upon the standard esterification-phthalic anhydride method to determine the hydroxyl value.[35] This method was shown to

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be comparable to other methods for the determination of OHV,[36] although inaccuracies have been observed when solvents other than pyridine were used to analyze sterically hindered alcohols and phenolic alcohols.[37] Regardless, phenolics can escape the downstream reaction with an isocyanate,[38] and therefore, alternative methods are needed to characterize bark-based polyols to provide insight into the quantity of each type of hydroxyl groups present. A ^{31}P NMR method, based upon a hydroxyl group reacting with a phosphitylation reagent, is able to quantitatively determine the type of hydroxyl group and the water content.[39] The phosphitylation agent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) has been used quite extensively for analyzing lignin,[40] as well as carbohydrates,[41] but has not been applied previously to characterize liquefied biomass polyols.

The OHV values obtained by the phthalic anhydride method in Table 2 showed that all the three polyols were similar in their hydroxyl content and possessed a typical OHV used in formulations for making a rigid-PUF. The values obtained by the PA method were consistent to those derived from the phosphorus NMR method. However, the phosphorus NMR method provided more insight. The results from the ^{31}P NMR were summarized in Table 3, as well as a representative

Table 3. Quantitative ^{31}P NMR of the Liquefied Bark Polyols

	mg KOH/g		
region (ppm)	P90	P130	P160
aliphatic (148−146)	205 ± 67	261 ± 53	316 ± 12
phenolic (143−137)	0	0	0
water (132 + 16.2)	0	0	134 ± 17
water (wt %)[a]			2%

[a]The water content for P90 and P130 were negligible after blank correction.

spectrum in Figure 3b. The spectra were similar in that the PEG (P_2) and the glycerol hydroxyl peaks (G_2; G_1) were the dominant features.[42] Furthermore, it was anticipated that with lignin and condensed tannin extractives that considerable amounts of phenolic groups would be observed in the spectra. However, quite surprisingly this was not the case. Instead aliphatic hydroxyls accounted for most of the hydroxyl groups. The loss of the phenolics may be due to their condensation with the PEG and the glycerol in solution, analogous to a chain-extension. Liquefaction converted the sterically hindered phenolics into an easily accessible primary alcohol. This conversion of a phenolic to an aliphatic alcohol is important for two reasons. Firstly, phenolics produce urethane linkages that are labile even under moderate temperature. Therefore, their chain extension to aliphatic alcohols is highly desirable for producing industrially relevant polyols. Secondly, variation in the hydroxyl type will alter reactivity and kinetics with isocyanate. When using TMDP, a primary alcohol is at a higher parts per million shift than a secondary alcohol. Although these regions are not strictly defined it would appear that the P90 aliphatic region had an additional primary alcohol and a greater diversity of secondary alcohols compared to both the polyols P130 and P160. Although specific assignments were not made, this pattern is consistent with the structure of a sugar, shown to be present in the P90 polyol from the carbon NMR results.

Carbon and Proton NMR. The carbon NMR spectra were dominated by the liquefaction solvent carbons as shown in

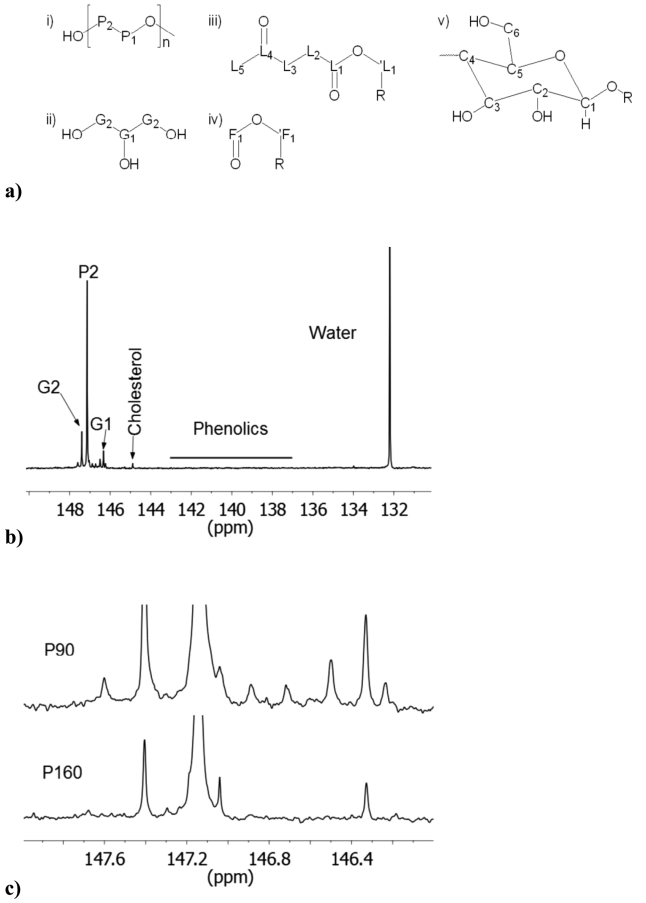

Figure 3. (a) Structure nomenclature for NMR assignments of (i) PEG, (ii) glycerol, (iii) levulinate ester, (iv) formic ester, (v) glucose; (b) ^{31}P NMR spectrum of P90 showed that only aliphatic hydroxyls and water are present, as the phenolic region had no visible peaks (also representative of P130 and P160); (c) ^{31}P NMR spectra of the aliphatic hydroxyl region showed the preservation of sugar hydroxyls in P90, in contrast to P160.

Figure 4a: the ether carbons within the PEG (P_1), the PEG OH (60.1), and the primary and the secondary alcohols of the glycerol, respectively (G1, G_2). Upon comparison of the three polyols, P130 and P190 were similar, while P90 was quite distinctive. The liquefaction conditions of P90 produced the only polyol to show peaks in the aromatic region. The peaks in the 140−150 ppm region were consistent with a methoxy or an aromatic ether, such as a condensation product between a phenolic group and a PEG or glycerol molecule. Tannins degrade into a variety of structures under alcoholysis.[33] Here, large variation in the structure could have led to the aromatic carbon peaks to be too scattered and too weak to be significantly above the signal-to-noise threshold in the spectrum. This could also hold true for the aromatic peaks in the other polyols, where the large parts per million shifts for a diversity of substitutions might have resulted in peaks hidden by the noise.

Furthermore, only the liquefaction conditions used for P90 showed the presence of a sugar. Assignments of the sugar carbons can be difficult due to the multitude of peaks from the anomeric effect and whether or not C_1 and C_4 are involved in the glucosidic bonds. However, the peak assignments could be made for C_1, C_4, and C_6 as shown in Figure 4; as well as the peaks observed in the region typical of C_2, C_3, C_4, and C_5.

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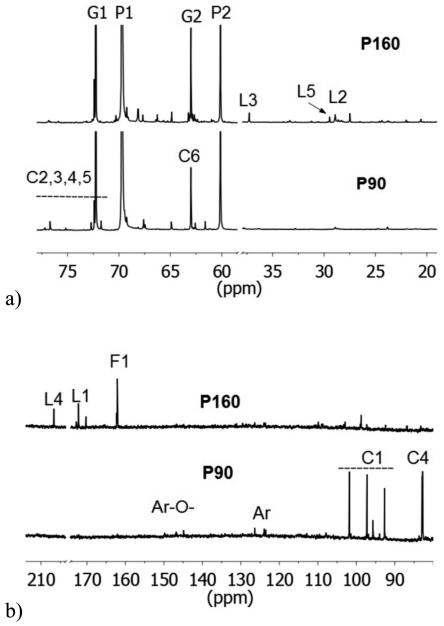

Figure 4. Carbon NMR spectra of P90 and P160. (a) Both have intense peaks corresponding to the carbons from the PEG and the glycerol. (b) P90 featured the peaks characteristic of a sugar and an aromatic compound, while P160 and P130 exhibited the peaks consistent with the presence of a formic ester and a levulinate ester.

Under the harsher conditions used to produce P130 and P160, the sugars had degraded into formate and levulinate esters. The characteristic carboxyl peaks of a levulinate ester (L_1,L_4) and a formic ester (F_1) can be seen in Figure 4b, as well as the methylene (L_2,L_3) and methyl (L_5) carbons. These results are further corroborated by the proton NMR spectra in Figure 5,

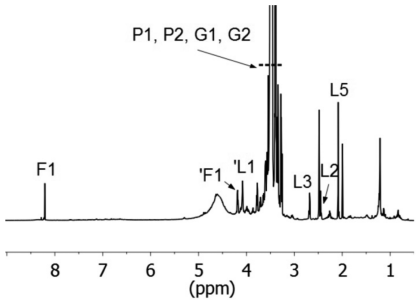

Figure 5. The proton NMR spectra of P160 and the peaks that correspond to a formic ester and a levulinate ester.

showing the presence of the levulinate ester methylene peaks L_2 and L_3; the methyl proton peak L_5; the aldehydic proton F_1 from a formate ester; and even the methylene protons (L_1 and F_1) from the alcohol side of the respective esters. A common feature of all the polyol spectra is the diversity of methyl and possibly methylene peaks in the 0.5−2.5 ppm region. Since these could not be attributed to the methine carbons of a sugar, nor a sugar degradation product, it was likely that these were the peaks for a tannin degradation product or another extractive compound, e.g. lignans, waxes, and terpenoids.

FTIR Analysis. The FTIR spectra of the polyols are shown in Figure 6, where the dominating feature in all three polyols was the broad hydroxyl peak at 3400 cm^{-1}, implying a significant amount of hydrogen bonding. The strong peak at

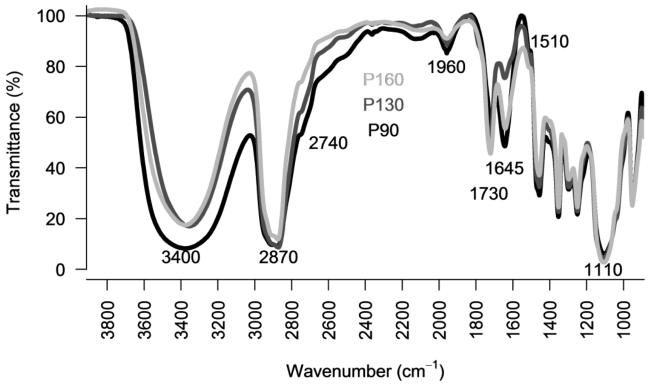

Figure 6. FTIR spectra of P90, P130, and P160 polyols.

2870 cm^{-1} corresponded to a C−H bond of an indiscernible origin. However, its shoulder that was more pronounced in P90 and P130 was indicative of the O═C—H stretch of an aldehyde. It was also observed that there was a peak at 1960 cm^{-1} that could be attributed to a carbon double bond originating from either fatty acids, triglycerides, terpenes, and stilbenes; all being typical bark extractive components. One significant difference among the polyols was the change in intensity of the peaks in the double bond region (2000−1500 cm^{-1}). The carbonyl peak at 1730 cm^{-1} is characteristic of aldehydes, ketones, esters, and carboxylic acids. This peak's intensity increased by increasing the liquefaction temperature. This result was consistent with the carbon NMR analysis that showed the presence of levulinate and formic esters in P130 and P160. The lowest peak intensity would be expected in P90 since sugars would not have been degraded under those reaction conditions. The lower frequency peak at 1643 cm^{-1} is indicative of a conjugated carbonyl.[43] These conjugated carbonyls are a common feature in oxidized flavanols produced from the degradation of tannins[33] and the oxidation products of lignin; the former being more likely in P90 with its greater concentration of extractives, while the latter is more likely to have occurred to the lignin found in P160. A more subtle feature was the very weak shoulder corresponding to the aromatic vibration peak at 1510 cm^{-1}. It was most prominent in the P160 polyol, likely due to the greater concentration of lignin fragments. A predominant peak was the ether bond at 1110 cm^{-1} stemming from the PEG solvent. Finally, as up-to 80% of the sample contained PEG and glycerol, the lower frequency range below 1500 cm^{-1} was dominated by C−H bending and CH_2 wagging.

CONCLUSIONS

Through liquefaction at three different temperatures and characterization of the resultant polyols, the effect of the liquefaction temperature on the structure and composition of the biobased polyols produced from the liquefied bark was studied. The GPC analysis showed the competition between the formation of LMW degradation products and high molecular weight recondensation polymers in the bark liquefaction reactions. Furthermore, at 130 and 160 °C, holocellulose was converted into levulinate and formic esters in the liquefied bark fraction; while at 90 °C sugars were still present. Lignin was only extracted at 160 °C and had undergone condensation reactions with the PEG and glycerol to yield the most viscous polyol. Even under the mildest conditions used for P90, neither the tannin polymer nor the

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tannin monomeric units were present in the polyol. Rather, structures with aldehydic/ketonic groups were evident from the FTIR results as well as aromatic ethers were found in the carbon NMR spectrum. This is consistent with the P NMR results that did not indicate the presence of phenolic groups. This is an important result since aliphatic polyols are favored by industry due to their better reactivity with isocyanate and produce more temperature stable urethane linkages, compared to phenolic-based polyols. These results help elucidate some of the complex changes to bark biopolymers and condensed tannins during a liquefaction reaction. Understanding the effect of the liquefaction conditions on the bark polyol's composition and molecular structures would be beneficial for utilization of these bark-derived biopolyols for making targeted polyurethane foam products.

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Notes

The authors declare no competing financial interest.

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