Polyurethane Foams Derived from Liquefied Mountain Pine Beetle-Infested Barks

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ABSTRACT: In this study, lodgepole pine (*Pinus contorta* Dougl.) bark infested by the mountain pine beetles (*Dendroctonus ponderosae hopkins*) was liquefied using either polyethylene glycol (PEG) or polyethylene glycol/glycerol (PEG/G) as the solvent. It was found that the addition of glycerol to PEG reduced the residue ratio during bark liquefaction. The liquefied bark fraction obtained by using PEG/G had a slightly higher hydroxyl number than that obtained by using PEG. The residue from PEG/G liquefaction contained less lignin and more cellulose than the residue from PEG liquefaction. Various polyurethane foams containing liquefied bark fractions were made, and it was found that the weight ratios of liquefied bark to pMDI used in foam formulation and bark liquefaction solvents affected the density, gel content, thermal stability, mechanical properties, and the cell structure of the resulting foams. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2849–2858, 2012

Key words: mountain pine beetle; lodgepole pine; bark; liquefaction; polyurethane; foams; biopolymers

INTRODUCTION

Currently, polyurethane (PU) foams are widely used in many applications, ranging from construction, automotive, furniture, footwear, toy, to packaging areas. PU foams can be obtained by reacting polyols, such as polyhydric alcohols, with isocyanate through the formation of urethane linkages. By selecting proper components and adjusting polyol to isocyanate mixing ratio, both flexible and rigid PU foams can be obtained.

Commercially, polyols used for manufacturing PU foams are predominantly derived from petroleum-based resources. With the increasing concern on fossil fuel depletion and environmental footprint, there is a strong global interest to explore renewable resources as alternative feedstock for making PU foams. Currently, natural oil polyols made from vegetable oil, soybean oil, castor oil, and other natural oils are either commercially available or under intensive development.[1–4]

Meanwhile, there is a growing concern on the negative impact of industrial demand on food related biomass resources and food supply system globally. In comparison, bark is a non-food related biomass resource available in large quantities as waste residues from forest product mills. Bark contains all major wood polymers, i.e. cellulose, lignin, and hemicellulose, but it has higher amounts of extractives and polyphenols. The hydroxyl groups in both aromatics and polysaccharides in wood and bark can react with isocyanate groups to form urethane linkages.

Moreover, due to recent massive mountain pine beetle (*Dendroctonus ponderosae hopkins*) infestation outbreaks in the western provinces of Canada, large amounts of beetle-infested lodgepole pine (*Pinus contorta Dougl.*) wood and bark resources are available for utilization. Even though beetle infestation can affect bark composition, previous study has shown that beetle infestation had no impact on the properties of the liquefied bark-derived PF resin.[5] Using the liquefied beetle-infested bark for producing PU foams could potentially result in substantial environmental and economic benefits.

Literature has shown that bark, wood, starch, waste paper type of lignocellulosic materials could be liquefied in polyols with the addition of an acid catalyst.[6–13] According to these studies, the lignocellulosic-containing polyols possessed a large amount of phenolic and alcoholic hydroxyl groups with high reactivity. The functional groups in lignocellulosic-containing polyols are suitable for preparing PU foams, adhesives, and resin precursors. Studies have also shown that tannin and bark could act as effective crosslinking agents in making PU foams.[7,8] Both tannin and bark have shown to have sufficient hydroxyl groups for crosslinking. In addition, the

phenyl groups in tannins improved the chain rigidity and the ether bonds changed the chain configuration of the PU. It was reported that some PU foams containing liquefied waste paper were biodegradable.[6]

In this study, mountain pine beetle infested lodgepole pine bark was liquefied in polyhydric alcohols using sulfuric acid as the catalyst. The liquefied products were applied as polyols for making PU foams. The properties of the liquefied products and the resulting bark-containing PU foams were investigated.

EXPERIMENTAL

Materials

Mountain pine beetle (*Dendroctonus ponderosae hopkins*) infested lodgepole pine (*Pinus contorta Dougl.*) bark powder was sieved through a 35-mesh screen. Polyethylene glycol PEG400, average molecular weight: 400), polyethylene glycol (PEG400)/glycerol co-solvent (9 : 1 by weight, PEG/G), sulfuric acid (96%), and other chemicals were reagent grade, purchased from Caledon laboratory chemicals, Canada, without further purification. Polymeric methylene diphenyl diisocyanate (pMDI) resin was supplied by Huntsman Polyurethanes (Geismar, LA, USA).

Bark liquefaction and residue analysis

Before liquefaction, the bark powders were oven-dried at 105°C ± 2°C for 12 h. The weight ratio of bark powder to liquefaction solvent (PEG and PEG/G, respectively) was 1 : 3. 3% sulfuric acid (based on the liquefaction solvent weight) was used for bark liquefaction. The reaction was carried out in a 150°C oil bath for 90 min.

After liquefaction, the liquefied product was diluted with dioxane-water co-solvent (8/2, v/v) and was then filtered with Whattman millipores filters. The dioxane-water insoluble residues were dried in an oven at 105°C to constant weight, and the residue ratio was calculated based on the following equation.

$$R = \frac{W_r}{W_0} \times 100\%$$ (1)

where R is the residue ratio of the bark liquefaction reaction (%). W_r is the oven-dry weight of the residue after liquefaction. W_o is the original oven-dry weight of the bark before liquefaction.

Hydroxyl number and acid number of the liquefied bark

Hydroxyl number and acid number of the liquefied bark were measured according to the reported method.[9] One gram of liquefied bark and 25 mL of phthalation reagent was heated for 20 min at 110°C. Afterwards, 50 mL of dioxane and 25 mL distilled water was added to the mixture. The mixture was titrated with a 1M NaOH solution to the equivalence point using a pH meter. The phthalation reagent was prepared by mixing 150 g phthalic anhydride, 24.2 g imidazol, and 1000 g dioxane. The hydroxyl number in mg KOH/g of sample was calculated as follows:

$$\text{Hydroxyl number} = \frac{(B - A)N \times 56.1}{W} + \text{acid number}$$
(2)

where A is the volume of the sodium hydroxide solution required for titration of the liquefied bark sample (mL); B is the volume of the blank solution (mL); N is the normality of the sodium hydroxide solution; and W is the weight of the liquefied bark.

A mixture of 8 g of liquefied bark, 80 mL dioxane, and 20 mL water was titrated with a 1M sodium hydroxide solution to the equivalence point. The acid number in mg KOH/g of sample was calculated by the following equation:

$$\text{Acid number} = \frac{(C - B)N \times 56.1}{W}$$ (3)

where C is the titration volume of the sodium hydroxide solution at the equivalence point (mL); B is the volume of the blank solution (mL); N is the normality of the sodium hydroxide solution; and W is the weight of the liquefied bark.

Chemical compositions of the liquefaction residues

The chemical compositions of the residues from bark liquefaction were analyzed based on the following standards. Extractive-free residues from bark liquefaction were prepared according to ASTM D1105-96. Holocellulose and α-cellulose contents were analyzed according to Zobel et al.'s method.[14] Acid-insoluble lignin content was analyzed according to ASTM D1106-96.

PUF synthesis and characterization

A calculated amount of liquefied bark and pMDI were first mixed thoroughly for 2 min, and then the catalyst (H$_2$O$_2$, 30%) was added and mixed for 1 min. No other additives were used for foam formulation. The mixtures were poured into a polystyrene cup and cured for 48 h. The weight ratios of the liquefied bark (denoted as LB), pMDI and catalyst are shown in Table I.

TABLE I
Weight Ratios in Foam Formulation

	LB	pMDI	Catalyst/LB		LB	pMDI	Catalyst/LB
PUF 1	1	1	0.2	PUF′ 1	1	1	0.2
PUF 2	1	1	0.4	PUF′ 2	1	1	0.4
PUF 3	1	1	0.6	PUF′ 3	1	1	0.6
PUF 4	1	0.75	0.2	PUF′ 4	1	0.75	0.2
PUF 5	1	1.5	0.2	PUF′ 5	1	1.5	0.2
PUF 6	1	2	0.2	PUF′ 6	1	2	0.2
PUF 7	1	0.5	0.2	PUF′ 7	1	0.5	0.2

PUF: foams made using PEG/G liquefied bark; PUF′: foams made using PEG liquefied bark; LB: liquefied bark.

The density of the foams was determined according to ASTM D1622-03. The weight of the specimens was measured using a balance, and the dimensions of the specimens were determined by using a vernier caliper. The density was calculated by dividing the weight of the sample by the volume of the sample. The average values based on a minimum of five replicates were reported.

Compression test was performed according to ASTM D1621-04. The test was carried out by using a dynamic mechanical analyzer (DMA Q800, TA instruments, USA) at 50°C. The specimens were cut into small cylinders with a dimension of 12.80 mm × 7.80 mm (diameter × thickness). The specimens were compressed between two stainless steel plates. The preload is set as 0.005 N, and the compressive force was increased at a rate of 3–18 N/min. The soaking time was 5 min. The compressive modulus was calculated as the slope of the initial linear region of the stress–strain curve. The results reported were an average of minimum five specimens.

The crosslink density of the foam made with different liquefied bark/pMDI weight ratios in this study was measured by determining the gel content according to previously reported method.[15] The sample was refluxed in dimethyl formamide (DMF) for 24 h, followed by drying to a constant weight at 60°C. The gel content was calculated by the following equation.

$$\text{Gel content} = \frac{W_{\text{after}}}{W_{\text{before}}} \times 100\%, \qquad (4)$$

where W_{after} is the weight of the dried sample after solvent treatment; W_{before} is the initial sample weight without solvent treatment.

Thermal stability of PUF

Thermal stability of the foams was measured using a thermal gravimetric analyzer (TGA-Q500, TA instruments, USA). Approximately 10 mg sample

was heated from room temperature to 700°C at the heating rate of 10°C/min under normal atmosphere.

FTIR study of the polyols and foams

The FTIR measurement was carried out using a FT-IR TENSOR 27 spectrometer with ATR attachment (Bruker Optics, USA) having a spectra range of 4000–400 cm^{-1}.

SEM of the foams

Scanning electronic microscopy (SEM, Hitachi S2500, Japan) was used to examine the cellular morphology of the foams. Samples were cut along the rising direction of the foam, and the fracture surface was sputter-coated with gold before scanning.

RESULTS AND DISCUSSION

Liquefied bark properties

The liquefaction residue ratio, hydroxyl number, and acid number of the polyols are given in Table II.

Polyethylene glycol (PEG) and glycerol were previously found to be the most effective liquefaction reagents. Past work on four softwood and three hardwood species has shown that wood liquefaction by using polyethylene glycol/glycerol (PEG/G) co-solvent can produce liquefied wood with a small

TABLE II
Residue Ratio, Hydroxyl Number, and Acid Number of Liquefied Bark

	Residue ratio (%)	Hydroxyl number (mg KOH/g)	Acid number (mg KOH/g)
LB/PEG	59.94 (3.25)	280.2	8.1
LB/PEG/G	21.52 (2.91)	289.8	8.4
PEG/G		418.0	0

LB/PEG: PEG liquefied bark; LB/PEG/G: PEG/G co-solvent liquefied bark; PEG/G: Polyethylene glycol (PEG #400) and glycerol co-solvent. Standard deviations are shown in brackets.

TABLE III
Chemical Components of the Liquefaction Residues

	Holocellulose (%)	Alpha-cellulose (%)	Lignin (%)
LBR/PEG/G	34.77 (2.50)	18.91 (4.35)	58.56 (2.46)
LBR/PEG	14.11 (2.69)	4.99 (1.53)	74.38 (1.98)

LBR/PEG: liquefaction residues from PEG liquefaction; LBR/PEG/G: liquefaction residues from PEG/G liquefaction; Average values were reported. Standard deviations are shown in brackets.

amount of residue and a hydroxyl number around 200-220 mg KOH/g. It was also found that the addition of glycerol to PEG can retard the recondensation reactions without reducing the hydroxyl number of the liquefied wood for all tested species.[9]

As shown in Table II, under the same reaction conditions, bark liquefied in PEG gave a higher residue ratio than bark liquefied in the PEG/G co-solvent. The addition of glycerol reduced the residue ratio, which was consistent with previous research.[9] The liquefied bark obtained from PEG/G liquefaction had a slightly higher hydroxyl number than that obtained from PEG liquefaction. Compared with the PEG/G liquefaction solvent itself, the hydroxyl number of the liquefied bark solution was lower. The reduction of the hydroxyl number was thought to be caused either by dehydration reactions between the liquefied products and polyhydric alcohols or by thermal oxidation reaction during the liquefaction.[6]

Residue analysis

The chemical compositions of residues after bark liquefaction are shown in Table III. The liquefaction residues from PEG liquefaction had a lower holocellulose, alpha-cellulose and higher lignin content than those from PEG/G liquefaction. During the liquefaction, condensation reactions may have occurred among various depolymerized and degraded compounds from cellulose and lignin to produce residues.[16] Compared with PEG alone, the addition of glycerol to PEG significantly reduced the residue ratio in bark liquefaction. These results showed that PEG can effectively liquefy the carbohydrates. The addition of glycerol as a co-solvent can enhance lignin degradation during the liquefaction; as a result, the lignin content in the residues was significantly decreased by using PEG/G as a liquefaction solvent.

Foam properties

Among all 14 types of foams, PUF1, PUF2, PUF3, PUF4, PUF'1, PUF'2, PUF'3, PUF'4, were flexible; while PUF5, PUF6, PUF'5, PUF'6 were more rigid.

PUF7 and PUF'7 did not foam very well probably due to the lack of pMDI for crosslinking and the recondensation of the degraded bark components.

Attempts were made to make foams using pMDI and PEG or PEG/G without bark components following the same preparation steps for foams containing liquefied bark. Unfortunately, the reactants cured too quickly by turning into rigid films with dark red color without foaming.

Figures 1–3 gave foam density, compressive modulus, and normalized compressive modulus by foam density, respectively. Higher pMDI usage made the resulting foams more rigid, while the foams made with a higher catalyst loading or a higher liquefied bark/pMDI weight ratio were more flexible. The foams made with higher level of catalyst loading exhibited higher density as shown in Figure 1. Under the same level of catalyst loading and bark liquefaction solvent, the foams made with a higher liquefied bark/pMDI weight ratio had a higher density than those made with a lower liquefied bark/ pMDI weight ratio. The compressive modulus of the foams varied with the weight ratio of liquefied bark to pMDI used in foam formulation and the type of bark liquefaction solvents (shown in Fig. 2). Since two liquefaction solvents gave different chemical compositions in the liquefied bark fractions, it was understandable that the properties of the resulting foams were affected.
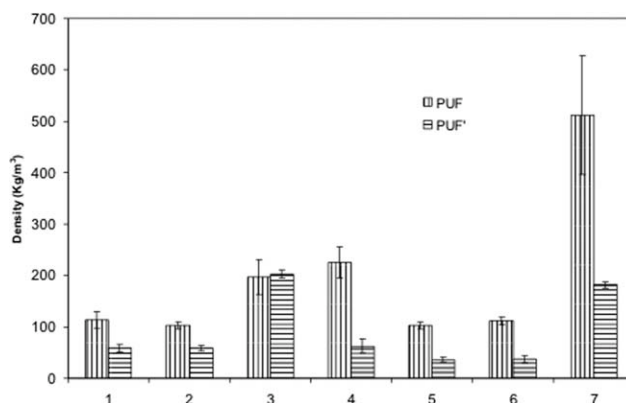

Figure 1 Foam density, (PUF: foams made using PEG/G liquefied bark; PUF': foams made using PEG liquefied bark).
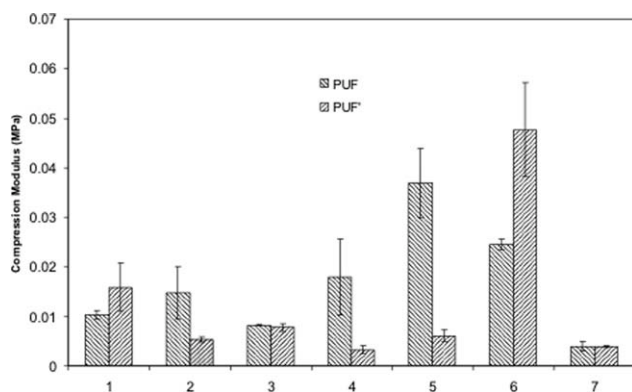
Figure 2 Foam compressive modulus, (PUF: foams made using PEG/G liquefied bark; PUF′: foams made using PEG liquefied bark).

Foam density was considered as an important structural parameter influencing the mechanical properties of the foams. Both the amount of the blowing agent and the volume fraction of the unexpanded resin can affect the foam density.[17] The unexpanded resins would lead to denser foams. However, our test results showed that there was no obvious relationship between foam density and compressive modulus for the bark-containing foams. Similar result was observed in previous research.[17]

Figure 3 gave the normalized compressive modulus obtained by dividing the compressive modulus by the foam density. By normalizing the compressive modulus by density, the improvement in the compressive modulus due to densification was removed. Instead, we are looking at the changes in the compressive modulus due to other structural and material factors. The foams made with lower liquefied bark/pMDI weight ratio (PUF6, PUF′6) had a higher normalized compressive modulus than those made with higher liquefied bark/pMDI weight ratio (PUF4, PUF′4, PUF1 and PUF1′). The foams made by using bark liquefied in PEG/G had differ-
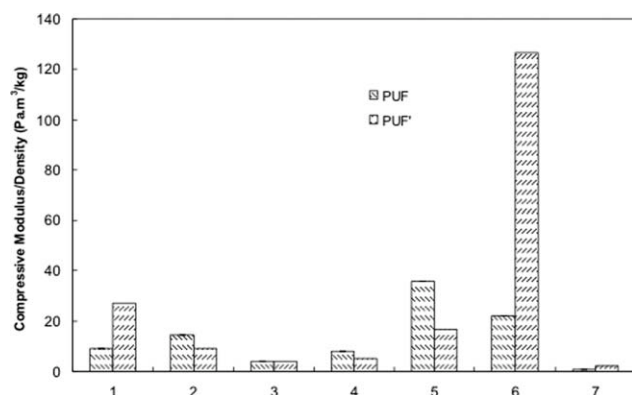
TABLE IV
Gel Content of the Selected Foams

Foams	Gel content (%)
PUF′ 6	37.09
PUF 6	27.86
PUF′ 5	22.41
PUF 5	30.32
PUF′ 4	13.93
PUF 4	18.81
PUF′ 1	23.60
PUF 1	17.92

PUF: foams made using PEG/G liquefied bark; PUF′: foams made using PEG liquefied bark.

ent normalized compressive modulus than those made by using bark liquefied in PEG when the weight ratio of liquefied bark/pMDI was the same.

The gel contents of the foams made with different liquefied bark/pMDI weight ratios are shown in Table IV. PUF1, PUF′1, PUF4, and PUF′4 were foams having higher liquefied bark/pMDI weight ratios; while PUF5, PUF′5, PUF6, and PUF′6 were foams with more pMDI usage. Gel content was an indicator for the crosslink density of the polymers.[15,18] The foams made with lower liquefied bark/pMDI weight ratios had higher gel content than those made with higher liquefied bark/pMDI weight ratios. Higher pMDI usage in foam formulation increased the crosslink density of the resulting foams.

Besides foam density, crosslink density was another important parameter affecting the mechanical properties of the resulting foams. There is a strong correlation between the gel content and normalized compressive modulus by foam density, indicating that the crosslink density significantly affected the mechanical properties of the resulting foams (shown in Fig. 4). It may help explain why
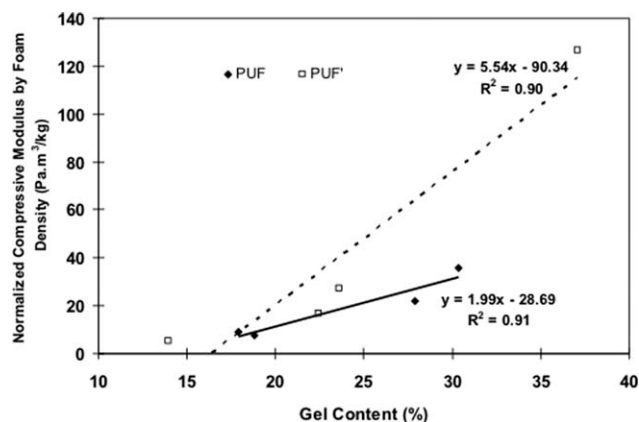

Figure 3 Compressive modulus to foam density ratio, (PUF: foams made using PEG/G liquefied bark; PUF′: foams made using PEG liquefied bark).

Figure 4 Relationship between normalized compressive modulus by foam density and gel content of PU foams containing liquefied bark, (PUF: foams made using PEG/G liquefied bark; PUF′: foams made using PEG liquefied bark).
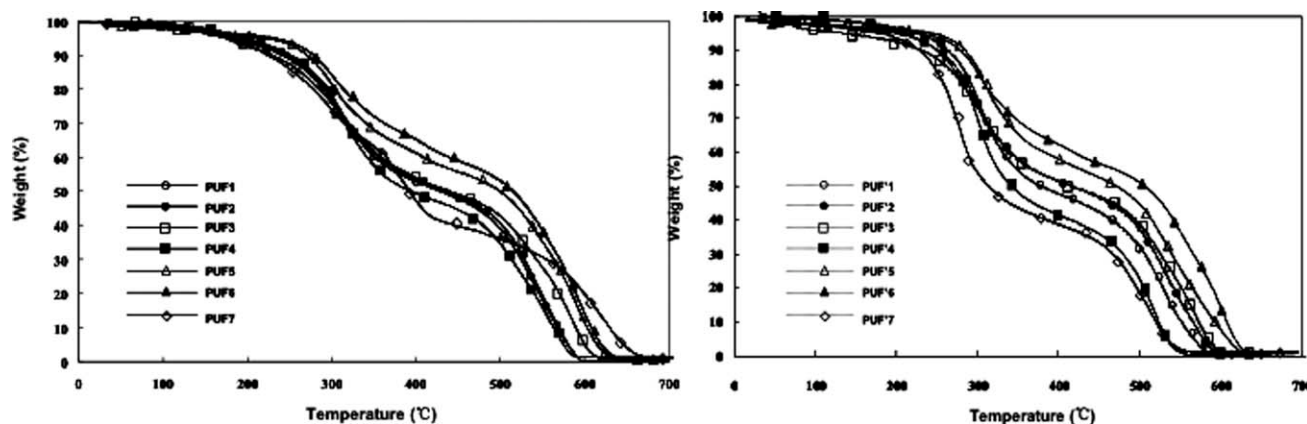
Figure 5 Thermal degradation curves of bark-containing foams, (PUF: foams made using PEG/G liquefied bark; PUF′: foams made using PEG liquefied bark).

PUF′6 had the highest normalized compressive modulus by foam density among all the foams (shown in Fig. 3). The crosslink density of the foams was also affected by the weight ratio of liquefied bark to pMDI used for foam formulation as well as the bark liquefaction solvents.

Thermal stability of the bark-containing foams

Thermal degradation of polyurethanes was usually described as a complicated process involving the dissociation of the initial polyol and isocyanate components. Thermal decomposition can lead to the formation of amines, small transition components, and carbon dioxide.[2,3,19]

The thermal degradation curves of the bark-containing foams are shown in Figure 5. There were two distinctive regions of major weight loss for these liquefied bark-containing PU foams. These results were different from those reported for PU foams made from liquefied waste paper which had only one region of major weight loss.[6] All liquefied bark-containing foam samples had a similar shape in their weight loss curves. The initial region of the significant weight loss took place at around 250°C, which could be attributed to the degradation of the relatively thermally unstable urethane bonds. The second region of the significant weight loss was around 400°C. The weight loss at the higher temperatures might be caused by the degraded bark and polyol components. The liquefied bark/pMDI weight ratio also affected the thermal stability of the resulting PU foams. The foams made with lower liquefied bark/ pMDI weight ratio had higher thermal stability than those made with higher liquefied bark/pMDI weight ratio.

The relationship between the initial degradation temperature and gel content of PU foams containing liquefied bark was shown in Figure 6. There was significant correlation between the gel content and initial degradation temperature of the foams. Higher usage of the pMDI increased the gel content of the resulting foams. Higher gel content indicated higher crosslink density, and higher crosslink density could contribute to higher initial degradation temperature and higher thermal stability of the foams. After 600°C, the weight loss was almost complete for all the samples.

FTIR characterization of the polyols and bark-containing foams

The normalized FTIR spectra of the bark, liquefaction solvents (PEG and PEG/G), and liquefied bark obtained by using PEG and PEG/G solvents are shown in Figure 7. The assignment of the peaks was given in Table V. The intense and broad band at around 3400–3500 cm^{-1} indicated the presence of OH groups in large quantities in the bark, liquefaction solvent, and liquefied bark. The stronger peak at 2900 cm^{-1} from the CH_2 groups was observed in liquefied bark and liquefaction solvent. The intense
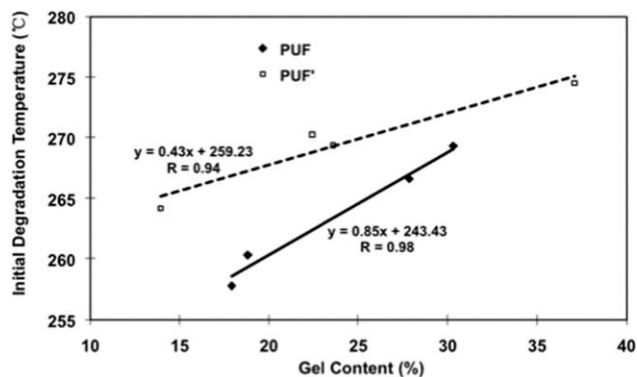

Figure 6 Relationship between initial thermal degradation temperature and gel content of PU foams containing liquefied bark, (PUF: foams made using PEG/G liquefied bark; PUF′: foams made using PEG liquefied bark).
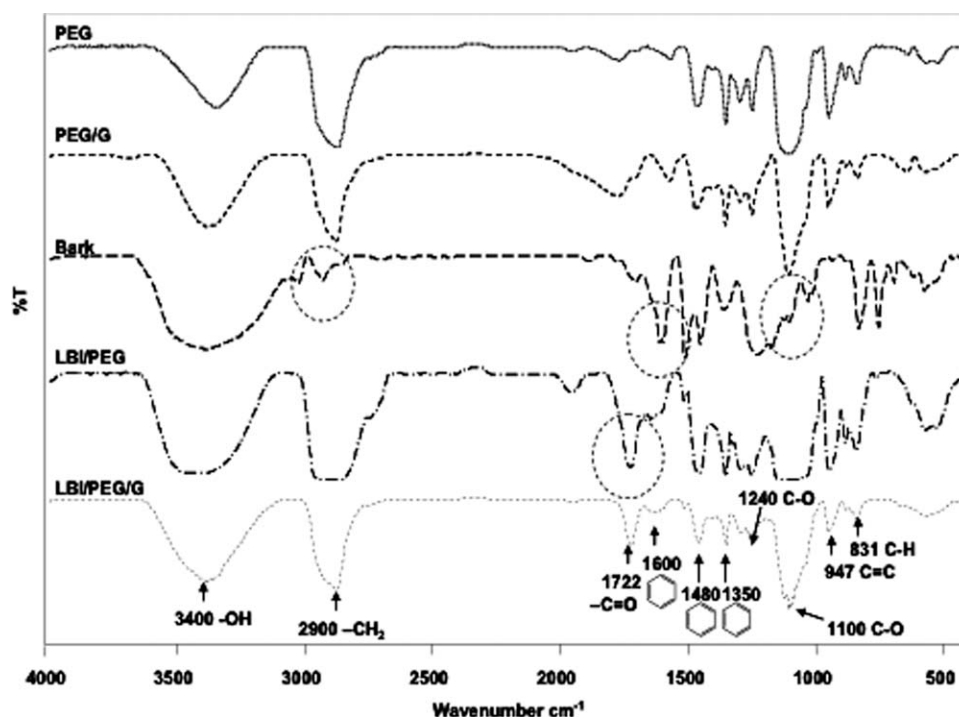
Figure 7 FTIR of the bark, liquefaction solvent and liquefied bark, (LB/PEG: PEG liquefied bark; LB/PEG/G: PEG/G co-solvent liquefied bark; PEG/G: Polyethylene glycol (PEG #400) and glyercol co-solvent; PEG: Polyethylene glycol (PEG #400)).

peak representing the C—O linkage of alcohol or ether typically for polyols was found at around 1100 cm^{-1} in liquefied bark and liquefaction solvent. The peaks around 1600, 1500, and 1350 cm^{-1} derived from aromatic skeletal vibration of lignin were observed in the liquefied bark and original bark. The intensity of the peak at 1600 cm^{-1} in the liquefied bark from PEG/G liquefaction was higher than that from PEG liquefaction, which further supported the

observation that the addition of glycerol promoted lignin degradation during bark liquefaction. Compared with liquefaction solvent and original bark, an intense peak at 1722 cm^{-1} attributed to the C=O stretching of esters and derivative of cellulose was observed in the liquefied bark. The esters were probably produced by the dehydration reaction between carboxyl groups of the bark components and the polyhydric alcohols under the acidic conditions. The

TABLE V
Assignment of Peaks in FTIR Spectra

| Liquefied bark		Polyurethane foams containing liquefied bark	
Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment
3400–3500	hydroxyl group, H-bonded OH stretch	3400–3500	OH stretch, H-bonded, N—H stretch (3350)
2900	CH$_2$ stretch	2889	CH$_2$ stretch
1722	C=O stretching of ester, cellulose derivatives	2272	—NCO asymmetric stretch
1600, 1500, 1350	Aromatic rings of lignin	1690, 1508, 1307	Amide I and II, NH associated with urethane linkages
1240	C—OH arrangement from alcoholic units	1595, 1411	C—C stretch in aromatic rings
1100	C—O—C from alcohols or ethers	1227, 1066	N—CO—O stretch, asymmetric
941	Aromatic double bonding	817	C—H out of plane bending in aromatic rings
831	Alkenes, C—H aromatic	763	O—C=O out of plane bending
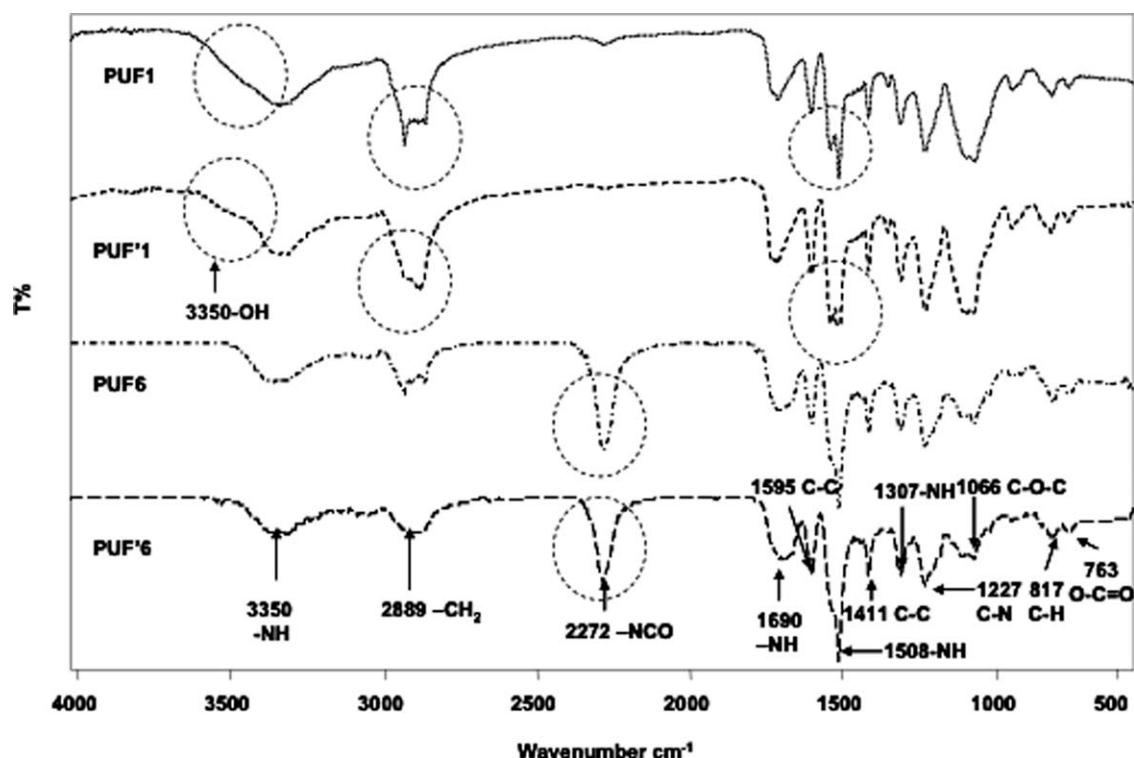
Figure 8 FTIR of foams made with different liquefied bark/pMDI weight ratio, (PUF: foams made using PEG/G liquefied bark; PUF′: foams made using PEG liquefied bark).

intensity of this peak was higher in the liquefied bark from PEG liquefaction than that from PEG/G liquefaction, which could further verified that PEG liquefied carbohydrates more effectively.

FTIR spectra of the foams made with different liquefied bark/pMDI weight ratios (PUF6 and PUF′6 had relatively lower liquefied bark/pMDI weight ratio; PUF1 and PUF′1 had relatively higher liquefied bark/pMDI weight ratio) are shown in Figure 8. The assignment of the peaks is present in Table V. According to the literature,[20,21] the peak at 2889 cm^{-1} was attributed to the CH$_2$ groups. The peaks at 3350 and 1690 cm^{-1} were assigned to N—H stretch and hydrogen-bonded carbonyl. The peaks at 1595 and 1411 cm^{-1} were associated with C—C stretch in benzene ring. The peaks at 1508 and 1307 cm^{-1} were attributed to the amide I and II and NH associated with the urethane linkages. The peaks of 1228 and 1069 cm^{-1} were assigned to C—N stretching and urethane C—O—C stretch. The peaks at 812 and 755 cm^{-1} were the C—H out-of-plane bending of benzene ring and O—C=O out of plane bending.

The strong peak at 2272 cm^{-1} from the —NCO group was observed in the foams made with lower liquefied bark/pMDI weight ratio, which indicated that there were still some non-reacted PMDI in those foams. For the foams made with higher liquefied bark/pMDI weight ratio, the intensity of the peak associated with the —NCO group decreased signifi-

cantly. The foams made with higher liquefied bark/pMDI weigh ratio (PUF1 and PUF′1) had a broader peak around 3500–3350 cm^{-1}, the small peak of OH group at 3500 cm^{-1} was still visible. While for the foams made with higher usage of pMDI (PUF6 and PUF′6), the OH peak disappeared, which meant that all the hydroxyl groups had reacted with pMDI. Only one peak at 3350 cm^{-1} from N—H stretch was observed. In addition, the peak at 1508 cm^{-1} from N—H groups representing urethane linkages in PUF6 and PUF′6 had higher intensity than those of PUF1 and PUF′1.

SEM of the bark-containing foams

The SEM images of the foams are shown in Figure 9. The spherical cells and regular size distribution were clearly observed. All foams exhibited closed cell structures and the cells were evenly distributed. For foams made with higher liquefied bark/pMDI weight ratio (PUF1, PUF′1, PUF4, and PUF′4) broken cells were observed. PUF4 and PUF′4 seemed to have a larger and distorted cell structures when compared with PUF1 and PUF′1, which could be caused by the higher liquefied bark/PMDI ratio. More liquefied bark would cause the mixture less expandable and that gave rise to less uniform cell size. The mechanism of cell growth was dominated by the stiffness of the gas/polymer matrix, the rate
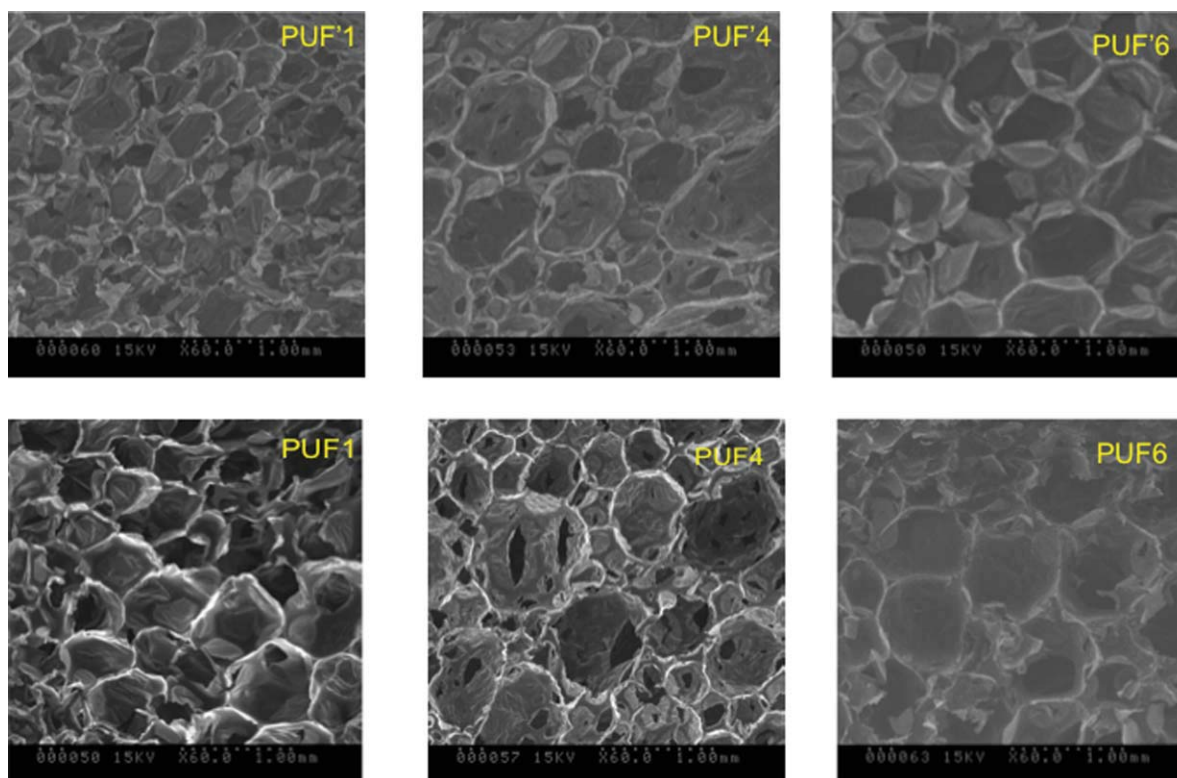
Figure 9 SEM of liquefied bark-containing foams, (PUF: foams made using PEG/G liquefied bark; PUF′: foams made using PEG liquefied bark). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of gas diffusion, and the amount of gas loss.[17] More liquefied bark used in foam preparation could also affect the matrix stiffness and gas loss. The relationship between the cell properties and mechanical properties of the bark-containing PUF foams is currently under investigation.

CONCLUSION

Lodgepole pine barks infested by mountain pine beetle were liquefied in PEG and PEG/G, respectively, with an acid catalyst. The liquefied bark fraction was further reacted with pMDI to produce bark-containing PU foams. The properties of the liquefied bark and bark-containing foams were investigated. The addition of glycerol to liquefaction solvent of PEG reduced the residue ratio of bark liquefaction. The lignin content of the residue from PEG/G liquefaction was lower than that from PEG liquefaction, while the cellulose content of the residue from PEG/G liquefaction was higher than that from PEG liquefaction. The different bark-containing PU foams had similar thermal weight loss curves. All the foams were completely degraded when temperature reached above 600°C. The density, mechanical properties, gel content, thermal stability, and cell structure of bark-containing PU foams were affected

by the liquefied bark/PMDI weight ratio and the bark liquefaction solvent.

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