

# Water-Blown Polyurethane/Polyisocyanurate Foams Made from Recycled Polyethylene Terephthalate and Liquefied Wood-Based Polyester Polyol

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**ABSTRACT:** Depolymerized polyethylene terephthalate and liquefied wood polyesters can be used as a polyol for the production of polyurethane/polyisocyanurate foams. In this research, liquefied wood was synthesized by using a combination of diethylene glycol and glycerol and due to the possibility of using glycerol that is a by-product in biodiesel production, our goal was to use as much glycerol in the liquefaction reagent as possible. We determined the properties of the polyols, properties of produced foams, and explained their correlation. Greater amount of glycerol in the liquefaction reagent resulted in higher OH number, molecular weight, functionality, and viscosity of the polyol, as well as in longer cream time and tack free time in foam preparation. Glass transition temperature, density, and water absorption of the foam increased with increasing amount of glycerol in liquefied wood. Compressive stress increased up to 30% of the glycerol in the reagent and then reduced, while thermal conductivity was not affected. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41522.

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## INTRODUCTION

Polyurethanes (PURs) are characterized by the urethane linkage formed by the reaction of organic isocyanate groups with hydroxyl groups, although other groups such as ether, ester, biuret, allophanate, amide, and others may be present in the polymer molecule. Isocyanate groups can also react with each other and one possibility is the reaction of cyclotrimerization resulting in the formation of isocyanurate linkages.<sup>1,2</sup> The introduction of isocyanurate structures in the polyurethane matrix improves the properties of PUR, especially thermal stability and fire behavior.<sup>3</sup> Foams represent one of the most important commercial products of PUR/polyisocyanurates (PIR) and rigid foams in particular are indispensable due to their excellent insulation, good adhesion, high strength-to-weight ratio, and durability.<sup>4,5</sup> PUR/PIR foams have been used as insulation in the appliance and construction industry, and in other fields such as furniture industry, packing, decoration, and transportation.<sup>6,7</sup> The raw materials for making PUR/PIR foams include polyisocyanates, polyols, blowing agents, catalysts, surfactants, and, optionally, flame retardants, antioxidants, fillers, colorants, and epoxides.<sup>1</sup>

PUR/PIRs have limited degradability when discarded after use and they can therefore cause different environmental problems.

Adding decomposable crosslinks such as lignocellulosic biomass or replacing petroleum-derived polyols with bio-based polyols could resolve the problem to some degree.<sup>7,8</sup> In the preparation of PUR/PIR foams, polyols have been substituted or modified with various natural substances and renewable raw materials. In addition, recycled materials such as depolymerized polyethylene terephthalate (PET) can also be used in the production of PUR/PIR foams.<sup>9,10</sup>

Nowadays, the exploitation of renewable resources is getting more and more important. Biomass-based materials and wood in particular are among the most abundant renewable resources and can play a major role in reducing the reliance on fossil fuels by its thermochemical conversion. One of the possible routes is the liquefaction of wood, where wood reacts with multifunctional alcohols to yield low molecular mass compounds with high reactivity. The final product can be used for the synthesis of various polymer materials, such as polyesters, PURs, and adhesives, or as a fuel.<sup>11–13</sup> In the liquefaction process, glycerol (a by-product from the production of biodiesel) can be used. Thus, 97% of the raw materials used in liquefied wood (LW) synthesis can originate from renewable resources. Like wood, PET is also used in a wide range of applications, but its most widespread and well-known use is in the manufacture of plastic beverage bottles.

The quantities of plastic bottles have reached extreme levels over the last few decades and as a result, the amount of PET waste has become a global problem. There are several methods of processing and recycling PET waste and, in addition to mechanical recycling, other options include chemical recycling, e.g. depolymerization by glycolysis, which is carried out in the presence of various glycols.<sup>14–16</sup> Both LW and depolymerized PET can provide OH groups and therefore have a potential for being used as a polyol in the PUR/PIR industry. The development of polymeric materials using renewable and/or recycled resources arises from the effort to develop alternative synthesis routes that are less hazardous to the environment. The goal is to reduce the demand for fossil fuels and to cut the production of carbon dioxide to reduce global warming.<sup>4</sup>

Our preliminary research (not published) investigating the use of LW or polyester from LW to produce PUR/PIR foams showed that the reaction times in foam preparation were very slow (cream time over a few minutes) while, conversely, the reaction times for PUR/PIR foams made from polyester from depolymerized PET were extremely fast (foaming started during mixing) and the foams were harder to the touch. Since too slow and too fast reaction times are not suitable for the production on the industrial level the goal of our research was to use a combination of polyester from LW and polyester from depolymerized PET in order to prepare polyol for PUR/PIR foam production and to determine the properties of the foams produced. We assumed that the composition of the LW would affect the foam properties so we varied the composition of the liquefaction reagent in the preparation of the LW. As a liquefaction reagent, we used a combination of diethylene glycol and glycerol. Our goal was to use as much of the glycerol as possible since glycerol that is a by-product from biodiesel production could be used. Polyesters were made due to the lower number of hydroxyl groups in comparison to LW and depolymerized PET, which means reduced isocyanate consumption. As a blowing agent, we used water, which is non-ozone depleting, non-toxic, and cheap.<sup>8,17–19</sup>

## EXPERIMENTAL

### Materials

Spruce wood (*Picea* spp.) and PET were obtained from commercial sources. The spruce sawdust was dried at 105°C for 24 h before use, while the PET was used as received. Glycerol (Merck), diethylene glycol (DEG) (Merck), *p*-toluenesulphonic acid monohydrate (Merck), polyethylene glycol 400 (PEG400) (Merck), adipic acid (Sigma-Aldrich), dibutyltin oxide (Sigma-Aldrich), imidazole (Merck), phthalic anhydride (Merck), sodium hydroxide (Merck), potassium hydroxide (Merck), phenolphthalein indicator (Merck), *N,N*-dimethylacetamide for HPLC (DMAc, Fluka), and lithium chloride (LiCl, Sigma-Aldrich) were of reagent grade and used without further purification. Additives for foam preparation were from Air Products. The isocyanate used was polymeric methylene diphenyl diisocyanate (pMDI, Suprasec® 5025 MDI, Huntsman).

### Liquefaction of Wood and Polyester Synthesis

Spruce wood sawdust was liquefied by using the mixture of glycerol and DEG as a liquefaction reagent and *p*-toluenesulphonic acid as a catalyst. Different combinations of glycerol

and DEG (glycerol/DEG) were used, namely 10/90, 30/70, 50/50, and 70/30. The weight ratio of wood sawdust to glycols was 1 : 3 and the amount of *p*-toluenesulphonic acid was 3% based on the weight of the glycols. The mixture of glycols and acid was charged into a three neck glass reactor equipped with a mechanical stirrer, thermocouple, condenser, and external heating. As the mixture in the reactor reached the temperature of 160°C, wood sawdust was added. Then the temperature was elevated to 170°C and maintained for 120 min to carry out the liquefaction reaction. After 120 min, adipic acid as an esterification reagent and dibutyltin oxide as a catalyst were added. The weight ratio of adipic acid to LW was 1 : 4 and the amount of dibutyltin oxide was 0.8% based on the weight of the adipic acid. The temperature was held at 170°C. Side products were continuously distilled from the reaction system using a nitrogen gas flow of 50 mL/min. The polycondensation/esterification reaction was carried out for 120 min.

### Depolymerization of Polyethylene Terephthalate and Polyester Synthesis

Polyester from recycled PET was prepared in two stages. In the first stage, depolymerization (glycolysis) of PET was carried out. A thermosetting glass reactor equipped with a mechanical stirrer, condenser, and thermocouple was charged with PEG400 and particles of PET at a weight ratio PEG400 : PET of 4.2 : 1. Dibutyltin oxide was used as the catalyst (0.3% based on the weight of PEG400). The reaction mixture was heated up to the temperature of 215°C and maintained for 150 min until the disappearance of PET particles. In the second stage, after the glycolysis, adipic acid and dibutyltin oxide were added to synthesize polyester via a polyesterification (polycondensation) reaction. The weight ratio of adipic acid to depolymerized PET was 1 : 8 and the amount of dibutyltin oxide was 0.75% based on the weight of the adipic acid. The temperature was held at 215°C and a nitrogen atmosphere inlet system was provided for the removal of reaction water. After the period of 90 min, the acid value fell into the range of 2–4 mgKOH/g and the polyesterification reaction was completed.

### Measurements of the Polyol Properties

The hydroxyl (OH) number of the polyols was determined using the ASTM Standard D4274-05 method in pressure bottles with imidazole and phthalic anhydride reagent.<sup>20</sup> The acid value of the polyols and of the product during the depolymerized PET polyesterification was determined by using the EN ISO 2114 Standard.<sup>21</sup> The viscosity of the polyols was measured by using a rheometer at  $25 \pm 2^\circ\text{C}$ . The values were recorded at the shear rate  $32.8 \text{ s}^{-1}$ .

The molecular weights of the polyols were measured by size exclusion chromatography (SEC). The Agilent Technologies system consisted of Agilent 1260 Infinity binary pump and Agilent 1260 Infinity refractive index detector. The columns used were precolumn + PLgel 5  $\mu\text{m}$  MIXED-D + TSKgel Alpha-2500 7  $\mu\text{m}$ . Polystyrene standards were used for the calibration curve. The polyol samples were dissolved in a 1% LiCl/DMAc solvent system and filtered through polytetrafluoroethylene filters (0.45  $\mu\text{m}$ ) prior to injection. The eluent (1% LiCl/DMAc) was pumped into the system at a flow rate of 0.5 mL/min.

**Table I.** Formulation for PET-PES + LW-PES Foams Preparation

PET-PES	15.00 g
LW-PES	15.00 g
GLYCEROL	2.40 g
H <sub>2</sub> O (distilled)	1.00 g
KOC (potassium octoate in DEG)	0.50 g
KAC (potassium acetate in DEG)	0.20 g
PC-5 (pentamethyldiethylenetriamine)	0.15 g
SI-3202 (silicone surfactant)	1.00 g

### Preparation of PUR/PIR Foams

Polyols for PUR/PIR foam preparation were polyester from depolymerized PET (PET-PES) and polyester from LW (LW-PES). One formulation of PET-PES and four formulations of LW-PES (with different compositions of liquefaction reagent) were used in this study. Polyols were prepared by using the formulation in Table I. The pMDI isocyanate had 31.2% NCO content, viscosity (25°C) of 190 cps, specific gravity (25°C) of 1.23, and functionality of 2.70. The NCO/OH index was 1.7.

The precise amounts of the components given in Table I were weighed into a paper cup and thoroughly premixed. Then the prescript amount of pMDI was added and mixed rapidly at a stirring speed of 1500 rpm for 10–15 s. Immediately after mixing, the mixture was poured into a plastic mold with a volume of 1.5 L and was allowed to rise freely under room conditions. Cream time and tack free time were determined. After 10 min, the foam was removed from the mold and allowed to cure at room temperature for two days before cutting it into test samples.

### Fourier Transmittance Infrared Measurements of PET-PES + LW-PES Polyols and PUR/PIR Foams

The polyols and foam samples prepared from the mixture of PET-PES and LW-PES were investigated using the Fourier transmittance infrared (FTIR) spectrum (Perkin Elmer Spectrum One) in the attenuated total reflectance (ATR) technique.

### Differential Scanning Calorimetry Analysis of PET-PES + LW-PES Based PUR/PIR Foams

For the determination of the glass transition temperature ( $T_g$ ), approximately 10 mg of each sample was scanned by the DSC 1 differential scanning calorimeter (Mettler Toledo) at a heating rate of 20 °C/min. The measurements were carried out in temperature range of –50 to 150°C under nitrogen gas flow of 20 mL/min.

### Properties of PET-PES + LW-PES Based PUR/PIR Foams

The foams were characterized according to the European standards by determining the density (EN 1602), compressive stress at 10% relative deformation (EN 826), thermal conductivity ( $T_{\text{average}} = 10^\circ\text{C}$ ,  $\Delta T = 20^\circ\text{C}$ ) (EN 12667), and long-term (28 days) water absorption by immersion (EN 12087).<sup>22–25</sup>

## RESULTS AND DISCUSSION

### Properties of PET-PES and LW-PES

The properties of PET-PES and LW-PES of different formulations are summarized in Table II. The results show that the properties of the LW-PES are very much affected by the com-

position of the liquefaction reagent. The OH number and viscosity of the polyol are important factors in the PUR/PIR foams production. The OH number is related to the isocyanate consumption, i.e. a higher number of OH groups means a greater amount of isocyanate needed for the reaction, while a low viscosity is needed for homogeneous and well mixed components in the polyol. With an increasing amount of glycerol in the liquefaction reagent, the OH number of the polyester increased from 381 mgKOH/g when the portion of the glycerol was 10% to 503 mgKOH/g when the portion of the glycerol was 70%. It is known that in the wood liquefaction process, a certain amount of the liquefaction reagent, e.g. glycols, remains unreacted<sup>26</sup> and that glycerol has a higher content of OH groups compared to DEG. Namely, the theoretically calculated OH number of the glycerol is 1827 mgKOH/g and is much higher than the calculated OH number of DEG (1057 mgKOH/g). A greater portion of glycerol in the liquefaction reagent means a greater amount of free glycerol in the final product and consequently gives the product a higher OH number. Compared to PET-PES, which had an OH number of 102 mgKOH/g, LW-PES of all formulations had at least three times as many hydroxyl groups. The acid value was not affected by the composition of the liquefaction reagent and was in the range 23.0–25.7 mgKOH/g for all formulations of LW-PES. Since a smaller amount of the catalyst was used in the production of PET-PES than in the production of LW-PES, the acid value of PET-PES was much lower, namely 2.8 mgKOH/g.

The molecular weight of the polyol increased with increasing the content of glycerol in the liquefaction reagent from 2850(±30) g/mol when 10% of the glycerol was in the reagent up to 4380(±60) g/mol when 50% of the glycerol was in the reagent. PET-PES had a molecular weight of 6020(±30) g/mol and was up to two times higher than that of LW-PES. From OH numbers and molecular weights, we calculated the functionality of the polyols using following equations:

$$\text{functionality} = \frac{\text{molecular weight}}{\text{equivalent weight}} \quad (1)$$

$$\text{equivalent weight} = \frac{56.1 \times 1000}{\text{OH number} + \text{acid value}} \quad (2)$$

Of all the polyols, PET-PES had the lowest functionality of 11.2, while different formulations of LW-PES had functionality greater than 20. Functionality increased from 20.5 when the portion of glycerol in the liquefaction reagent was 10% to 37.0 when the portion of glycerol was 70%.

The composition of the liquefaction reagent influenced the viscosity of the LW-PES. With the increase of glycerol in the liquefaction reagent, the viscosity of the LW-PES polyol increased drastically, especially when the portion of glycerol was 50% or more. The viscosity of the polyester made from LW where 70% glycerol was used in the liquefaction reagent was 50,000 mPa s and was much higher than the viscosity of the polyester made from LW where 10% glycerol was used in the liquefaction reagent (2080 mPa s). The viscosity of the PET polyester was 2320 mPa s, which is nearly in the range of LW-PES where 10% glycerol was used in the liquefaction reagent. The viscosity is in correlation with the functionality, namely a higher functionality

**Table II.** Properties of PET-PES and LW(Glycerol/DEG)-PES

Properties	PET-PES	LW(10/90)-PES	LW(30/70)-PES	LW(50/50)-PES	LW(70/30)-PES
OH number (mgKOH/g)	102	381	407	399	503
Acid value (mgKOH/g)	2.8	23.7	25.5	25.7	23.0
Molecular weight (g/mol)	6,020 ( $\pm 30$ )	2,850 ( $\pm 30$ )	3,400 ( $\pm 50$ )	4,380 ( $\pm 60$ )	3,940 ( $\pm 40$ )
Functionality (OH groups/mol)	11.2 ( $\pm 0.1$ )	20.5 ( $\pm 0.2$ )	26.2 ( $\pm 0.4$ )	33.2 ( $\pm 0.4$ )	37.0 ( $\pm 0.3$ )
Viscosity (mPa s)	2,320	2,080	7,190	43,800	50,000

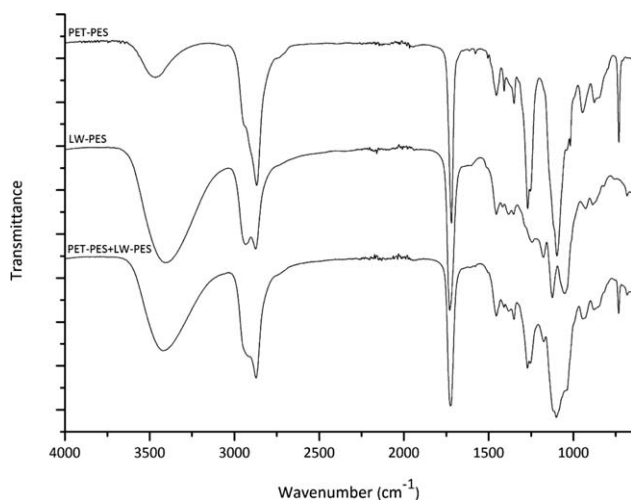
leads to a higher viscosity. A higher functionality means a greater amount of OH groups per molecule and a consequently larger amount of intermolecular bonding. The latter results in molecular mobility being reduced which increases the viscosity of the polyol.<sup>17</sup>

#### FTIR Spectra of the PET-PES + LW-PES Polyol and PUR/PIR Foam

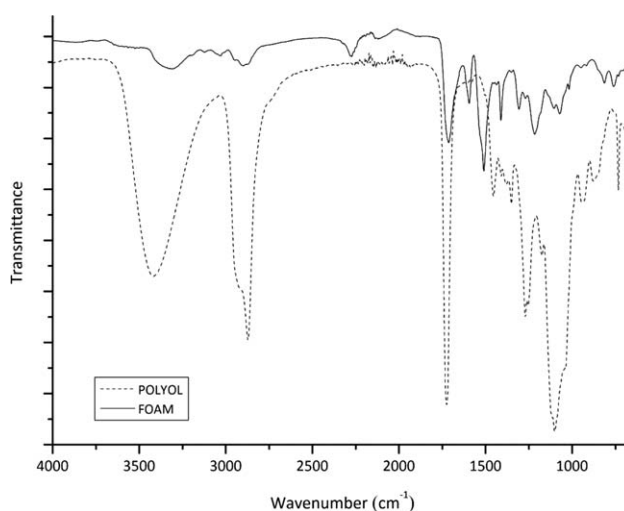
In Figure 1, infrared spectra of PET-PES, LW-PES, and mixture of PET-PES and LW-PES are presented. Mixture of PET-PES and LW-PES was used as a polyol in PUR/PIR foam production. The infrared spectra of the PET-PES + LW-PES polyol and PUR/PIR foam produced from the same polyol are shown in Figure 2. An example for a polyol and foam with PET-PES + LW-PES (glycerol/DEG = 50/50) is given.

Figure 2 clearly shows the difference between the polyol and the PUR/PIR foam, verifying that the reaction between PET-PES + LW-PES polyol and isocyanate (pMDI) took place and that polyurethane polymer structure exists. The absorption band at  $3419\text{ cm}^{-1}$  of the polyol indicates the presence of OH groups in large quantities, while this band was not found for foam suggesting that the OH groups of the polyol were completely consumed to form urethane linkages. Figure 1 clearly shows that greater amount of the OH groups in the polyol originates from LW-PES. Nonetheless, a  $3303\text{ cm}^{-1}$  absorption band characterizing urethane NH stretching is present in the spectrum of the foam. The spectrum of the foam shows the

presence of two characteristic bands that were not found in the spectrum of the polyol, the absorption band at  $2272\text{ cm}^{-1}$ , which indicates the presence of excess  $\text{—NCO}$  groups, and the absorption band at  $1215\text{ cm}^{-1}$ , which indicates the C—O bond in the urethane structure.<sup>6,27,28</sup> The absorption bands in the range of  $1350\text{—}1594\text{ cm}^{-1}$ , distinctive of the vibration of the aromatic ring, are much more intensive in the case of PUR/PIR foam. This is due to the presence of the aromatic ring in pMDI present in the foam structure. An absorption band at  $1509\text{ cm}^{-1}$ , which is absent in the spectrum of polyol, is characteristic of NH bond bending in urea formed during the reaction between NCO groups and water (blowing agent).<sup>28</sup> The isocyanurate structure is characterized by the absorption band at  $1411\text{ cm}^{-1}$  and is particularly intensive in the case of a foam. This proves that besides polyurethane, isocyanurate structures were also formed.<sup>19</sup> In the spectrum of the foam, absorption bands at  $1215\text{ cm}^{-1}$  and  $1071\text{ cm}^{-1}$  indicate the presence of C—O and COO bonds in urethane, respectively. The absorption bands at  $2872\text{—}3029\text{ cm}^{-1}$  (C—H bond),  $1713\text{ cm}^{-1}$  (C=O bond), and in the range  $1270\text{—}1100\text{ cm}^{-1}$  (C—O—C and C—OH bonds) are much less intensive or even absent in the spectrum of the foam. The reason for this might lie in the fact that in the polyol, the concentration of depolymerized woody components and depolymerized PET that contain such bonds (Figure 1) is higher than in the foam. Absorption band at  $1713\text{ cm}^{-1}$ , which indicates the presence of C=O stretching, can be attributed to the presence of C=O bond in urethane



**Figure 1.** FTIR spectra of PET-PES, LW-PES, and mixture of PET-PES and LW-PES.



**Figure 2.** FTIR spectra of PET-PES + LW-PES polyol and PUR/PIR foam.

**Table III.** Properties of PUR/PIR Foams Depending on the Formulation of LW-PES

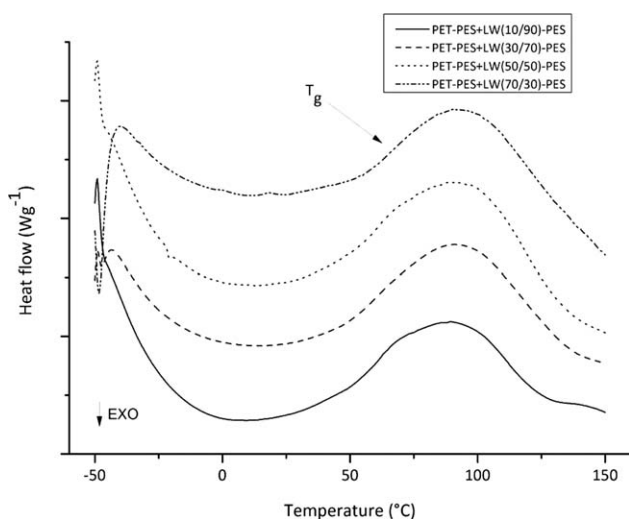
Properties	PET-PES+ LW(10/90)-PES	PET-PES+ LW(30/70)-PES	PET-PES+ LW(50/50)-PES	PET-PES+ LW(70/30)-PES
Cream time (s)	20	25	25	45
Tack free time (s)	40	50	60	90
$T_g$ (°C)	58.9	60.0	60.7	66.1
$\rho$ (kg/m <sup>3</sup> )	40.9	43.8	44.4	49.3
$\sigma_{10}$ (kPa)	323	401	344	317
$\lambda$ (W/mK)	0.0294	0.0294	0.0293	0.0289
WL(T) (vol %)	2.8	3.2	3.5	3.7

linkages and C=O of an ester group formed as a result of polyesterification reaction of LW and depolymerized PET.<sup>10</sup>

#### Properties of PET-PES + LW-PES Based PUR/PIR Foam

In Table III, the properties of PUR/PIR foams produced from the PET-PES + LW-PES based polyol are summarized: cream time, tack free time, glass transition temperature ( $T_g$ ), density ( $\rho$ ), thermal conductivity ( $\lambda$ ), compressive stress at 10% relative deformation ( $\sigma_{10}$ ), and long-term water absorption (WL(T)). DSC measurements of PUR/PIR foams produced with different polyols are shown in Figure 3.

The results showed that the cream time and tack free time increased with increasing the content of glycerol in the wood liquefaction reagent. The increase was most evident when the content of the glycerol increased over 50%. A large amount of intermolecular bonding is formed with the increase of functionality. As more OH groups occur per molecule, molecular mobility and foaming efficiency are reduced, resulting in longer reaction times.<sup>17</sup> With the composition of the liquefaction reagent, the cream time and tack free time in the PUR/PIR foam preparation can be tailored so that they satisfy the industrial production requirements.



**Figure 3.** DSC measurements of PUR/PIR foams synthesized with different polyols.

As can be seen from the DSC measurements, the morphology transition of the PUR/PIR foam structure was affected by the composition of the liquefaction reagent. The glass transition temperature ( $T_g$ ) shifted to a higher temperature ranging from 58.9°C to 66.1°C, with an increase of glycerol in the liquefaction reagent from 10% to 70%. This could be due to the higher crosslink density of the foam when a greater amount of glycerol is present in LW-PES and consequently in the polyol.<sup>17</sup> In highly branched or crosslinked structures, the mobility of the molecules is reduced and more thermal energy is required to initiate chain movements. The thermal stability of the foam is thus improved.<sup>27</sup> Furthermore, testing physical and mechanical properties showed that the density of the foam increased from 40.9 kg/m<sup>3</sup> to 49.3 kg/m<sup>3</sup> when the amount of the glycerol in the liquefaction reagent increased from 10% to 70%. This suggests that more crosslinked structure is formed when there is a greater amount of the glycerol in the polyol. It is known that in the wood liquefaction process, a certain amount of the liquefaction reagent, e.g. glycols, remains unreacted<sup>26</sup> and can react with NCO group as well to form urethane linkages. The glycerol that is used in combination with DEG in the liquefaction reagent acts as a three-functional crosslinking agent with a low molecular weight and a high number of hydroxyl groups. This leads to more branched chains and therefore a more crosslinked structure. The increase in density is in correlation with the OH number and viscosity. Namely, a higher number of hydroxyl groups in the polyol increases the density of the foam.<sup>29</sup> Furthermore, the increase in the viscosity of the LW can also contribute to an increase in the crosslink density.<sup>30</sup> In our research, the OH number and viscosity of the LW-PES increased with the increase in the amount of glycerol in the synthesis of LW, consequently the density of the PET-PES + LW-PES based foams increased. There is an indirect relation between viscosity of the polyol and density of the foam. Viscosity of the polyol increases due to its higher OH number and functionality which causes greater degree of intermolecular bonding. Consequently, the viscosity of the polyol is increased because of molecular mobility being reduced. Greater degree of intermolecular bonding means that more crosslinked structure is formed resulting in greater density of the foam.

Compressive stress at 10% relative deformation of the PUR/PIR foams reached values of more than 320 kPa. It increased when the amount of glycerol in the liquefaction reagent increased

from 10% to 30%. After the 30% portion of glycerol, compressive stress at 10% relative deformation was reduced and at a glycerol content of 70% it reached approximately the same value as for foam based on a polyol with LW-PES where 10% of the glycerol was used in the liquefaction reagent. A possible reason lies in the fact that too high content of hard segments in the foaming mixture is formed when the content of glycerol in the LW-PES exceeds 30%.<sup>27</sup> The amount of glycerol in the LW synthesis did not affect the thermal conductivity of PUR/PIR foams. All the foams had thermal conductivity around 0.029 W/mK and could be used as an insulating material in various construction applications. With increasing amount of the glycerol in the LW synthesis, water absorption of the foams increased from 2.8% when 10% of the glycerol was used in the liquefaction reagent to 3.7% when 70% of the glycerol was used for wood liquefaction. One explanation for this could be that an increased glycerol content in the liquefaction reagent results in a higher yield of liquefaction. Namely, glycerol is more effective liquefaction reagent compared to DEG and less undissolved wood is present in the final product.<sup>31</sup> Greater yield of liquefaction means that more liquefaction products are formed during the process. Among those are hydrophilic substances such as hydroxymethylfurfural and levulinic acid.<sup>32</sup> With the greater amount of the glycerol in the liquefaction reagent, more hydrophilic substances are formed that contribute to the increased absorption of water in the foams produced.

## CONCLUSIONS

The combination of depolymerized PET and LW polyesters was used as a polyol in PUR/PIR foam production. LW was synthesized by using various combinations of diethylene glycol and glycerol. Due to the possible usage of glycerol as a by-product in biodiesel production, we used up to 70% of the glycerol in the liquefaction reagent and investigated its effect on the properties of the polyol and the PUR/PIR foams. The results showed that a greater amount of glycerol in the liquefaction reagent resulted in a higher OH number, molecular weight, functionality, and viscosity of the polyol. Cream time and tack free time in foam preparation increased with increasing the amount of glycerol. Furthermore, the glass transition temperature, density, and long-term water absorption of the PUR/PIR foam increased as the glycerol content increased. Compressive stress at 10% relative deformation increased up to 30% of the glycerol in the liquefaction reagent and then reduced. Thermal conductivity was not affected by the polyol formulation. PUR/PIR foam with good mechanical properties can be produced by using a polyol based on recycled PET and LW polyesters. With the formulation of LW, the properties of the polyol and PUR/PIR foams can be tailored to satisfy different industrial and application requirements. PET-PES lowers the OH number and the viscosity of the polyol, while LW-PES provides appropriate reaction times.

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