PREPARATION AND CHARACTERIZATION OF BIODEGRADABLE RIGID POLYURETHANE FOAMS FROM THE LIQUEFIED EUCALYPTUS AND PINE WOODS

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ABSTRACT

In this study, eucalyptus (*Eucalyptus camaldulensis* L.) and pine (*Pinus sylvestris* L.) woods were liquefied using the the blended solvents mixture of polyethylene glycol PEG-400/glycerin in the presence of sulfuric acid as a catalyst at 140-160°C for 120 min. The insoluble parts in the liquefied eucalyptus and pine were found as 17.8 and 5.5 wt. %, respectively. The acid and hydroxyl numbers of the liquefied eucalyptus and pine were determined and compared with each other. Polyurethane-type rigid foams (RPUFs) were successfully prepared by a co-polymerization of the liquefied woods (LWs) and polymeric methylene diphenylene diisocyanate (PMDI). The compressive strength (120 to 250 kPa), the modulus of elasticity (1 to 6 MPa), the density (20 to 50 kg.m^{-3}) and thermal conductivity (0.0352 to 0.0374 W.mK^{-1}) of the RPUFs prepared from the LWs were found to be almost comparable to those of the synthetic foams. Furthermore, the biodegradability of the biomass-based foams was higher than that of the synthetic ones.

INTRODUCTION

Liquefaction of biomass using polyols is a common method in terms of utilization of wood residue for production of polyurethanes (PUs). PUs are one of the most multipurpose classes of three-dimensional polymers, because they can be used in assorted forms of materials, e.g., sheets, foams, elastomers, adhesives and paints. (Philips and Parker 1965, Ferrigno 1967, Mkrtchyan et al. 2008, Sivak et al. 2008, Campbell et al. 2009). PUs are one of the largest polymer product groups within the plastics world. In Europe, PU consumption is about 3 million tons per year in the early 21st century. It is composed of about 1.8 million tons flexible PU foams, 0.7 million tons rigid PU foams and 0.4 million tons PU elastomers and other products (Mounanga 2008).

Polyurethane-type rigid foams RPUFs have closed cell structure with low thermal conductivity, high compression strength, low density, high strength-to-weight ratio, and low moisture permeability (Lim et al. 2008a).

Lignocellulosic materials can be used as polyol for PUs preparation since they contain natural polymers (e.g., cellulose, lignin, hemicellulose, and tannins) with more than two hydroxyl groups per molecule. Therefore, many studies have been made to utilize the agricultural and or forestry wastes for synthesis for PUs for various purposes in recent years (Saraf and Glasser 1984, Saraf et al. 1985, Kennedy et al. 1993). All these wastes have potential use and will contribute in the properties of the end product due, especially, to their high content of cellulose. Lignocellulosic PUs can be produced from biomass in the forms of unmodified (Kurth and Becker 1953) or chemically modified (Yoshida et al. 1990, Reinmann et al. 1990, Shiraisi et al. 1996) fiber or powders and liquefied solution (Glaser and Sarkanen 1989, Yao et al. 1993, 1995, Jin-Jie and Sakai 1996a) at various NCO/OH ratio by using different types of isocyanate (aliphatic and aromatic), polyethylene glycol, or other types of soft segment in different molecular weight. The utilization of lignocellulosic materials into PUs system has been found to affect the properties of PUs produced, such as the stiffness of the chains, strength, crosslink density, and the thermal properties because of increasing the hard segment content resulted from saccharides and lignin (Kennedy et al. 1993, Yoshida et al. 1990, Yao et al. 1995, Cheradame et al. 1989, Minnen et al. 2007, König et al. 2008, Zatorski et al. 2008, Wang et al. 2008, Song et al. 2008).

In the production of PU-type foams (PUFs), biomass including wood, agricultural wastes and barks liquefied with polyhydric alcohols with appropriate molecular weight (PEG-400), polypropylene and ethylene glycol can be directly used as polyol to produce PUF without any additional reaction or treatment (Yao et al. 1993, 1995, Jin-Jie and Sakai 1996a, Cheradame et al. 1989, Jin-Jie and Sakai 1996b). It has been reported that the properties of biomass-based PUFs prepared from lignocellulosic wastes are comparable to those of commercial PUFs and much more biodegradable when compared with commercial ones.

In this paper, PEG-400/glycerin was chosen as liquefying agent since it is economical and environment friendly polyol and has also high liquefaction rate. In addition, eucalyptus and pine woods were preferred due to a fast-growing species and the common usage area, respectively. Thus, the aim of this paper was to study the liquefaction of eucalyptus and pine woods using PEG-400/glycerin blended solvents and to evaluate the effects of liquefaction temperature. Some mechanical, physical, thermal and biological properties of RPUFs successfully prepared by a co-polymerization of the LWs and PMDI were also studied.

MATERIAL AND METHODS

Material

Eucalyptus (*Eucalyptus camaldulensis* L.) and pine (*Pinus sylvestris* L.) woods were provided by a carpenter shop in the Southeastern Turkey, ground by a Wiley Laboratory Mill and passed through a 60 mesh screen for the liquefaction experiments. Also, polyethylene glycol (PEG-400), glycerin, sulfuric acid, 1,4-dioxan (as solvent), triethylene diamine (TEDA-D33LV, foaming catalyst), silicon-glycol copolymer (L3001, nonionic surfactants for rigid foams), and polymeric methylene diphenylene diisocyanate (PMDI-TED-31, crosslinking agent) were used without any further purification.

Liquefaction of the woods

The mixture of liquefaction solvents (PEG-400/glycerin (4/1, w/w) was placed in a 500 ml three-necked flask, and then oven-dried wood samples and sulfuric acid (3 wt.%) were added to the flask. Reaction system was heated at 140 to 160°C for 120 min under stirring. After a defined duration, the reactor was cooled to room temperature rapidly.

The reaction was concentrated by thin film evaporation at 60ºC to remove binary solvent (dioxane/water: 4/1) and then filtrated through a glass-fiber filter paper. The amounts of unliquefied biomass were determined. Dioxane-water mixture was added to liquefied sample to determine the percent of dissolved or soluble contents in dioxane.

Determination of percent dioxan-insoluble part

In order to determine the percent dioxan-insoluble part (i.e., unliquefied amount of eucalyptus and pine) mixtures obtained at the end of wood liquefaction were diluted with 1,4-dioxan and filtered as described above. Finally, percent dioxane-insoluble part (DIP) was calculated using the following equation:

$$DIP = \frac{W_R}{W_S} x 100 \qquad (\%)$$

(1)

where: W_R - the weight of residue (g), and
W_S - the weight of wood sample (g).

Determination of acid and hydroxyl values of LWs

A mixture of 8 g LW, 80 ml dioxane and 20 ml water was titrated with 1 M sodium hydroxide (NaOH) solution to the equivalence point. Acid number (AN) was calculated by the following equation:

$$AV = \frac{(C-B) \times N \times 56.1}{W} \qquad (mgKOH/g)$$

(2)

where: C - the titration volume (mL) of the sodium hydroxide solution at the equivalence point (mL),
B - the volume of the blank solution (mL),
N - the equivalent concentration of, KOH solution used, and
W - the weight of the biomass sample (g).

The measurement of hydroxyl number (HN) was conducted as follows: a mixture of 1 g LW sample and 25 mL of a phthalation reagent was heated at 110ºC for 20 min. After that, 50 mL of dioxane and 25 mL of distilled water were added and the mixture titrated wtih 1 M sodium

hydroxide solution to the equivalence point using pH meter. The phthalation reagent consisted of a mixture of 150 g phtlatic anhydride, 24.2 g imidazol and 1000 g dioxane. The hydroxyl number in mg KOH.g-1 of sample was calculated by the following equation:

$$HV = \frac{(B - A)xNx56.1}{W + AN} \qquad (mgKOH/g)$$ (3)

where: B - the volume of the blank solution,
A - the volume (mL) of the NaOH solution after the phthalation liquefied of reaction sample,
N - the normality of the NaOH solution,
W - the weight of liquefied of reaction, and
AN - the acid number.

Preparation of RPUFs

A definite amount of the concentrated LWs, the foaming catalyst, surfactant and blowing agent (water) and methyl ethylene glycol (MEG) were uniformly premixed in a paper cup. And then, a certain amount of PMDI (isocynate index of 130, 150, and 170 wt. %) was added to the premixed components and stirred at a speed of 8000 rpm for about 20 sec. The formulations of BRPUFs with the liquefied eucalyptus and pine polyol are listed in Tab. 1.

Tab. 1: Formulations for water–blown rigid polyurethane foams with the liquefied eucalyptus and pine polyols.

Ingredients	Parts by weight (wt. %)
Liquefaction eucalyptus and pine woods polyol	100
Triethylene diamine (foaming catalyst-D33LV)	3
Silicon glycol copolymer (surfactants-L3001)	2.5
Water	1
Methyl ethylene glicol (MEG)	10
Crosslinking agent (PMDI-TED-31)	130-170

Characterization methods of RPUFs

The prepared biomass-based foams were allowed to form at an ambient temperature and to be cured for two days before cutting them into specimens 50×5×50 mm (length×width×height) for measurements of the mechanical properties and densities. The mechanical properties (compressive strength and elastic modulus) of the prepared foam specimens were measured according to JIS K-7220 using a universal testing machine (Zwick).

The thermal conductivity of the foams was measured using a thermal conductivity meter (QTM-500) with the two plates on a guarded hot-plate apparatus according to the ASTM C1113-99 standard test method.

Thermogravimetric analysis (TG) was performed on a thermogravimetric analyzer (Shimadzu TGA-50) to measure the thermal degradation of the foams. Ten milligrams of the sample was heated from room temperature to 800°C with a heating rate of 10°C.min-1 under nitrogen (N2) atmosphere with a constant flow rate of 20 ml.min-1. Thermal decomposition of the samples was determined from the TG curves and its derivative curves.

The cell structure and surface morphology of the foams were determined using a scanning light microscope (Nikon scupse 80i LM).

In the biodegradation test, the oven-dried foam blocks (2×2×2 cm) were buried in culture soil (sand: 85.2, clay: 8.86 %, silt: 5.94, pH: 7.99, organic matter: 2.18 %, phosphorus: 2.96 kg.da^{-1}, potassium: 3.6 kg.da^{-1}, salinity: 0.011 %, lime: 14 %) and then incubated at 30ºC for 3, 6 and 9 months. Water content of the soil was maintained at 60 % by occasional addition of water. At the end of incubation period, impurities on the samples were completely removed and oven dried. Eventually, the percent weight loss (WL) was calculated using the following equation:

$$WL = \frac{W_d}{W_0} x100 \qquad (\%)$$

(4)

where: W_0 - the oven dry weight of the specimen (g) before soil burial test,
            W_d - the oven-dry weight of the sample after soil burial test (g).

In this study, the average results of at least three experiments are given within the experimental error of < ± 0.5 wt. %.

RESULTS AND DISCUSSION

Liquefaction of the biomass

Fig. 1 shows the percent residue content of eucalyptus and pine after liquefaction with the mixture of PEG-400/glycerin at different reaction temperatures. The percent residues of the eucalyptus and pine decrease from 58.4 to 17.8 wt. % and from 8.9 to 5.5 wt. %, respectively when reaction temperature increases from 140 to 160ºC. Moreover, the percent residue of the pine is considerably lower than that of the eucalyptus at all temperatures. This phenomenon can be clarified by differences in types and structures of lignin and hemicellulose of softwood and hardwood. It is known that while hardwood (e.g., eucalyptus) lignin consists of guaiacyl and syringyl units, softwood (e.g., pine) lignin composes of only syringyl units, which makes hardwood more susceptible to the destructive extraction in the liquefaction process compared to softwood (Sarkanen and Ludwig 1971, Alma and Basturk 2003).
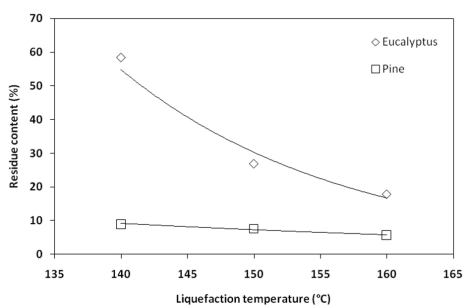

Fig. 1: Percent dioxin-insoluble part of eucalyptus and pine after liquefaction with the mixture of PEG-400 and glycerin as a function of temperatures (PEG 400-glycerin mixture: 4/1, liquid ratio: 3/1, acid concentration: 3 % and reaction time: 120 min).
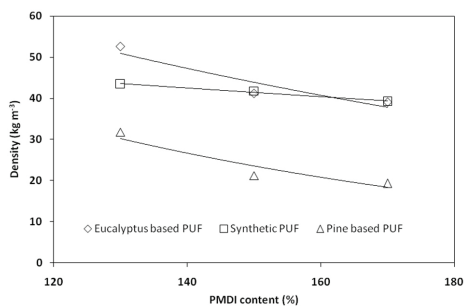
Fig. 2: Effect of the PMDI content on the density of eucalyptus-based PUF, pine-based PUF and synthetic PUF.

Acid and hydroxyl values of LWs

The acid and hydroxyl values of the LWs are summarized in Tab. 2. The acid number of the eucalyptus (25.23 mg KOH.g^{-1}) is clearly higher than that of the pine (22.70 mg KOH.g^{-1}). However, the hydroxyl number of the pine (304 mg KOH.g^{-1}) is higher than that of the eucalyptus (277 mg KOH.g^{-1}). The increase in acid number can be attributed either to the increase of acidic substances or to the oxidation of the carbonhydrates and lignin during the liquefaction. Besides, the increase in hydroxyl number can be probably attributed to the cleavage of ester or ether linkages between the lignin units (Pu and Shiraishi 1994, Chen and Lu 2009).

Tab. 2: The results of acid and hydroxyl values of the Lws.

Biomass[a]	Acid number (mg KOH.g^{-1})	Hydroxyl number (mg KOH.g^{-1})
Eucalyptus	25.23	277
Pine	22.70	304

[a] PEG 400-glycerin mixture: 4/1, liquid ratio: 3/1, acid concentration: 3 % and reaction time: 120 min.

Characterization of RPUFs

Fig. 2 shows the effect of the crosslinking agent (PMDI) content on the density of biomass-based PUFs and synthetic PUF. As PMDI content increases from 130 to 170 wt. %, the densities of the eucalyptus-based PUF, pine-based PUF and synthetic PUF are found in the ranges of 52.6-39.1, 31.8-19.3 and 43.4-39.2 kg.m^{-3}, respectively. As is known, the densities of the foams are required to be in the range 20 to 50 kg.m^{-3}. As can be observed in Fig. 2, it is important to notice that the density of the eucalyptus-based PUF is significantly higher than that of the pine based PUF. This phenomenon may be explained by differences in types and structures of lignin and hemicellulose of used biomass.

Fig. 3 illustrates the effect of the PMDI content on the compressive strength of eucalyptus-based PUF, pine-based PUF and synthetic PUF. The maximum compressive strengths of the eucalyptus-based PUF, pine-based PUF and synthetic PUF are found as 252, 152 and 233 kPa in the PMDI content of 150 wt. %., respectively. It is known the compressive strength of the PUFs is required to be in the range 120 to 250 kPa. The results show that the compressive strength of the eucalyptus-based PUF is considerably higher than that of the pine-based PUF and the synthetic PUF.
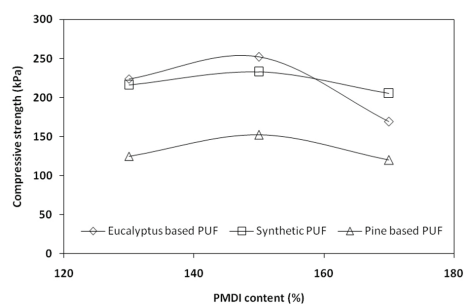

Fig. 3: Effect of the PMDI content on the compressive strength of eucalyptus–based PUF, pine–based PUF and synthetic PUF.
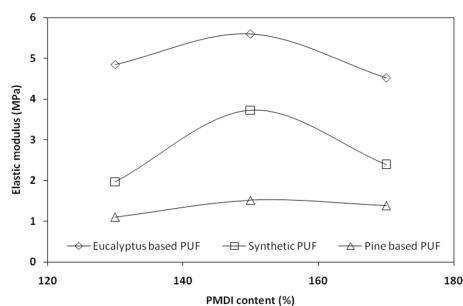
Fig. 4: Effect of the PMDI content on the modulus of elasticity of eucalyptus–based PUF, pine–based PUF and synthetic PUF.

Fig. 4 shows the influence of the PMDI content on the moduli of elasticity of the eucalyptus-based PUF, pine-based PUF and synthetic PUF. As can be observed in Fig. 4, the highest moduli of elasticity of the eucalyptus-based PUF, pine-based PUF and synthetic PUF are found to be 5.6, 1.5 and 3.7 MPa in the PMDI content of 150 wt. %., respectively. As

is known, the modulus of elasticity of the PUFs is required to be in the range 1 to 6 MPa. The modulus of elasticity of the PUF prepared from the liquefied eucalyptus is higher than that of the PUF from the liquefied pine and the synthetic PUF. This may be attributed that the cellulose content of eucalyptus wood is higher than that of pine wood. However, it is considered that the effect of strength/density ratio is important (Alma and Basturk 2003).

The influences of the different PMDI content on the thermal conductivity of eucalyptus-based PUF, pine-based PUF and synthetic PUF are presented in Tab. 3. The lowest thermal conductivities of the eucalyptus-based PUF, pine-based PUF and synthetic PUF are found to be 0.0368, 0.0352 and 0.0434 W.mK^{-1} in the PMDI content of 150 wt. %., respectively. It is known that the thermal conductivity of the PUFs is required to be 0.0350-0.0450 W.mK^{-1}. The reason of having lower thermal conductivity of the pine-based PUF may be attributed to polymer phase, solid structure, hydroxyl number, closed cell structure and density of the PUFs (Lim et al. 2008b, Tu et al. 2008).

Tab. 3: Effect of the PMDI content on the thermal conductivity of eucalyptus-based PUF, pine-based PUF and synthetic PUF.

	Thermal conductivity (W.mK^{-1})	
	PMDI (wt.%)	
	130	**150**
Eucalyptus-based PUF	0.0374	0.0368
Pine-based PUF	0.0364	0.0352
Synthetic PUF	0.0444	0.0434

Polyurethane foams are mainly used as heat insulating materials, and their thermal behaviors are very important. The thermogravimetric curves of the biodegradable foams, synthetic PUF with the (PMDI) of 150 wt. % and the biomass samples are shown in Fig. 5. As can be seen in Fig. 5, the eucalyptus wood is found to decompose at about 230°C and lost 86 wt. % of its initial weight at 500°C. The highest degradation temperature of the eucalyptus wood is found to be as 256°C. Furthermore, the pine wood is found to decompose at about 150°C and lost 89 wt. % of its initial weight at 500°C. On the other hand, the temperature at which the pine wood presented the highest decomposition rate is about 182°C. The TG results show that the decomposition temperatures of the eucalyptus and pine woods are different from each other. The eucalyptus-based PUF, pine-based PUF and synthetic PUF are found to decompose at about 200°C and lost 81, 82 and 70 wt. % of their initial weight at 500°C, respectively. The first step of the decomposition appears at about 215°C and can be attributed to the decomposition of pyranose rings and isocyanate, and the second step appears at 450 to 500°C and may be attributed to the decomposition of lignin and other more difficult to break parts. Furthermore, the temperature of the first and the second step of decomposition shift to the high temperature side with increasing the content of the LWs. The result indicate that the thermal stability is considerably improved by the hard segments, especially by the addition of the LWs, depending on the type of substituents on the isocyanate and polyol side (Chen and Lu 2009, Yan et al. 2008).
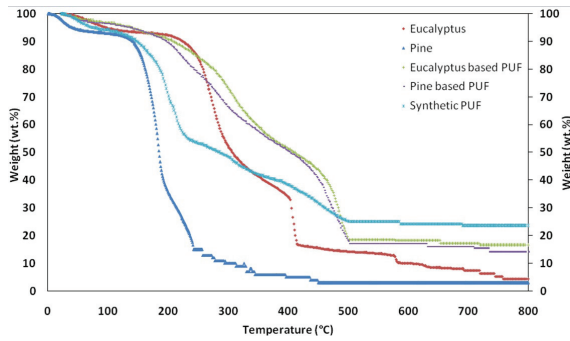
Fig. 5: TG curves of the raw materials, biomass–based PUFs and synthetic PUF.

Fig. 6 shows representative scan light microscope (SLM) images of the synthetic PUF and PUFs prepared from the LWs. It is possible to calculate the cell morphology of the biomass-based PUF if applicable (Hemasi et al. 2011). As can be seen in Fig. 6b, the inhomogeneous surface and irregular pore shape occurs increasing the content of liquefied pine in the polyol matrix. Some wrinkles showing the extent of homogeneity and microphase separation are shown on the images of the synthetic PUF (Fig. 6c).
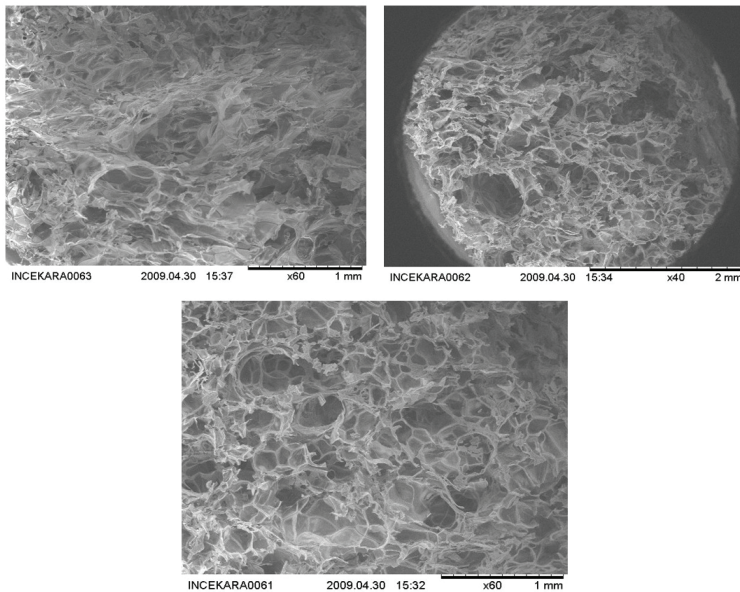

Fig. 6: SLM pictures of eucalyptus–based PUF a), pine–based PUF b) and synthetic PUF c).

The biodegradability of the biomass-based PUFs along with the synthetic PUF subjected to a 12-month soil burial biodegradation test are given in Fig. 7. The weight loss determined for the biomass-based PUFs prepared from the LWs are higher than that of the commercial PUF, revealing the biomass-based foams are much more biodegradable than commercial ones.
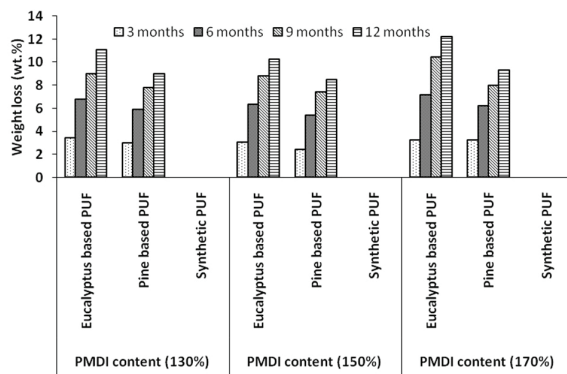
Fig. 7: Effect of the PMDI content on the biodegradability (weight loss) of eucalyptus–based PUF, pine–based PUF and synthetic PUF.

Furthermore, the maximum weight losses of the eucalyptus-based, pine-based and synthetic PUFs resulted from a 12-month soil burial biodegradation test are found to be about 12.2, 9.4 and 0.0 wt. % in the PMDI content of 170 wt. %, respectively. It is worthwhile to state that the percent weight loss of the liquefied eucalyptus-based foams due to the service test is greater than that of the liquefied pine-based ones. This may be due to higher hemicellulose content in eucalyptus when compared with pine (Chen and Lu 2009, Alma et al. 2002).

CONCLUSIONS

Eucalyptus and pine woods were liquefied using PEG-400/glycerin polyols in the presence of sulfuric acid as a catalyst. The insoluble wood content in LWs decreased with increasing reaction temperature. The acid number of the liquefied eucalyptus was found to be higher than that of the liquefied pine while the hydroxyl number of the liquefied eucalyptus was lower than that of the liquefied pine. The densities of the biomass-based PUFs were laid between that of the synthetic PUF, and the densities of the PUFs decreased with increasing PMDI content from 130 to 170 wt. %. The compressive strength, modulus of elasticity and thermal conductivity of the biomass-based PUFs prepared from the LWs were found to be almost comparable to those of the synthetic PUFs from commercial polyols. The biodegradability of the biomass-based foams was higher than that of commercial ones.

In conclusion, the results indicated that the biomass-based PUFs can be used as an insulating material and are also more an economical and environment friendly material when compared with synthetic foams.

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