Polyols Based on Poly(ethylene terephthalate) and Tall Oil: Perspectives for Synthesis and Production of Rigid Polyurethane Foams

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ABSTRACT: This study presents the synthesis of novel polyols made from tall oil (TO) and poly(ethylene terephthalate) (PET) with different TO/PET molar ratios. Rigid polyurethane foams based on these synthesized polyols were obtained and characterized to evaluate polyols' suitability for the development of light materials with insulating properties. The effect of TO/PET molar ratios on the physical, morphological and mechanical properties of the obtained foams, as well as their thermal insulation characteristics, were evaluated. Increasing amounts of PET in polyurethane foams resulted in higher compression strength and closed cell content, while water absorption was not affected. Results indicated that certain TO/PET polyols can be successfully used for preparing rigid polyurethane foams.

KEYWORDS: Rigid polyurethane foams, PET glycolysis, tall oil, renewable materials

1 INTRODUCTION

The production of polyols derived from natural sources and recycling materials is of great interest for the manufacturing of polyurethanes (PURs). Nowadays, global PUR production uses polyols and isocyanates based on hydrocarbons, whose availability remains uncertain in the near term, both for environmental and economic reasons [1, 2].

Tall oil (TO) and poly(ethylene terephthalate) (PET) scraps have great potential as raw materials for the production of polyols through chemical synthesis. The joint application of these natural and recycling materials may contribute to the reduction of the environmental impact.

Vegetable oils are very good feedstocks for synthesis of biobased materials because of their wide availability, low cost and large variety of potentially reactive groups in their structure [3, 4]. Specifically, the synthesis of polyols from different vegetable oils has attracted considerable attention since the late nineties. Many studies have been carried out about the synthesis of biobased polyols from vegetable oils with applications in rigid PUR foams [5–13] and reinforced PUR composites [14–21]. One of the disadvantages of vegetable oils is that most of them are first generation biobased raw materials, so they are also used in food production. Therefore, polyol synthesis from TO, which is a second generation biobased raw material, is an excellent option [22]. However, only a few works about the utilization of TO for biobased PURs are readily available in the literature [23–26]. TO is a byproduct of the Kraft pulping process of pine wood. The crude oil, an oily dark liquid, is formed by the acidification of a black liquor soap skimming with sulfuric acid. Unlike vegetable oils consisting of triacylglycerols, TO contains higher amounts of unsaturated free fatty acids (36–48 wt%), mainly oleic acid (C18-1) and linoleic acid (C18-2), and resin acids or rosin (26–42 wt%) which are cyclic terpenes [27]. In this case, a TO-based polyol can be obtained by reaction of carboxyl groups present in fatty acids with triethanolamine (TEA) or diethanolamine via an esterification or amidization pathway [28]. Also, the esterification of TO with aromatic polyester polyols is found in the patent literature. In addition, these polyols were found to be compatible with trichlorofluoromethane blowing agent [29].

PET is one of the most well-known thermoplastic materials because of its use in textile fibers and soft-drink bottles, which are its main applications. However, due to its increasing consumption and non-biodegradability, the higher amounts of waste PET produced result in disposal problems. Consequently, since the late 80s there has been a great interest in recycling this material through eco-friendly technologies. Chemical recycling offers the possibility to recover useful monomers or oligomers for further synthesis of new materials. In this sense, different chemical recycling methods, such as aminolysis, glycolysis, hydrolysis and alcoholysis, have been developed. Depolymerization of PET by glycolysis is carried out using mainly metal acetate as a catalyst and different glycols like ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol, 1,4-butanediol, propylene glycol, among others. Bis(2-hydroxyethylene) terephthalamide is the product formed via PET glycolysis using the excess EG as reactant [30–33]. This monomer can be used for rigid PUR formulation to improve the mechanical properties of the foams. However, PET glycolyzed products often are incompatible with some blowing agents commonly used in PURs.

Only a few reported studies have dealt with the polyols from both recycled PET and natural vegetable oils. Badri *et al.* [34] investigated PET waste glycolysis with EG prior to blending with palm oil-based polyol. Beneš *et al.* [35] reported the chemical recycling of waste PET using castor oil as a reagent, where acyl-ester hydroxyl groups of castor oil ensure the depolymerization of PET. Cakić *et al.* [36] carried out PET glycolysis with poly(ethylene glycol) and produced saturated hydroxyl-functional polyester polyols with castor oil by transesterification process. More recently, Paberza *et al.* [37] proposed a synthesis method for preparation of polyols from rapeseed oil and PET in two steps: rapeseed oil transesterification with TEA and PET glycolysis with DEG. The resultant polyols showed excellent compatibility with blowing agents and high reactivity. They were successfully used for preparing PUR foams with high bio/recycled content and good thermal insulation properties.

The main purpose of this study is the obtainment of polyester polyols from TO and PET, and the evaluation of the possibility to use these polyols in rigid PUR foam production. At first, TO/TEA polyol was synthesized from TO and TEA by esterification, and then polyol synthesis from TO/TEA polyol, PET and DEG were carried out at different TO/PET molar ratios. The resultant polyols were characterized and used for preparation of rigid PUR foams. Afterwards, the properties of these foams were investigated and the impact of TO/PET molar ratios on the foams' characteristics was evaluated.

2 EXPERIMENTAL

2.1 Materials

TO/TEA polyol (OH value = 344 mg KOH/g; acid value = 5.06 mg KOH/g) was synthesized from distilled TO (resin acids = 20 wt%; from Forchem) by the esterification with TEA (min. 99.5%; from BASF). PET flakes (bulk density 0.25–0.4 g/cm^3; intrinsic viscosity 0.78–0.8 dl/g) from recycled bottles were supplied from PET Baltija. DEG (99%) from Sigma Aldrich was used as PET depolymerization agent. Zinc acetate dehydrate (≥98%) from BASF was employed as the transesterification catalyst in polyol synthesis.

Rigid PUR foams were prepared from synthesized TO/PET polyols, high functional polyether polyol based on sorbitol Lupranol 3422 (OH = 490 mg KOH/g) from BASF, reactive delayed action time amine-based foaming catalyst CAT NP-10 from Performance Chemicals Handels, surfactant NIAX Silicone L6915 from Momentive Performance Materials, flame retardant trichlopropylphospate from Lanxess and physical blowing agent Solkane 365/227 (pentafluorobutane/heptafluoropropane = 87/13) (Solkane) from Solvay. The isocyanate used was polymeric diphenylmethane diisocyanate (PMDI) (NCO group content = 31.5%) purchased from BASF. All reagents were used as received without purification.

2.2 Synthesis of TO/PET Polyols

At first, TO/TEA polyol was synthesized from distilled TO by the esterification with TEA (molar ratio TO/TEA = 1/1.33) in pilot-scale (50 L) stainless steel chemical reactor with stirrer and heating. The synthesis was conducted at 175 °C and duration was controlled from the change in the acid number of polyol (ISO 660:2009). A more detailed description of TO/TEA polyol synthesis is described in our previous work by Cabulis *et al.* [23]. The reaction scheme is shown in Figure 1.

The TO/TEA polyol was further used to synthesize TO/PET polyols. These syntheses were carried out in a three-necked flask provided with a mechanical stirrer, a controlled argon atmosphere and a condenser. Syntheses were realized as follows: TO/TEA polyol was poured into the reaction flask and heated to 210 °C. The agitation was set at 300 rpm and zinc acetate (0.5 wt% of PET) was added. DEG was preheated at 70 °C and poured into the reaction mixture. Once the temperature was stabilized at 210 °C, PET flakes were added in two steps with an interval of 30 min. When complete miscibility of PET into the mixture was observed, the temperature of mixture was increased
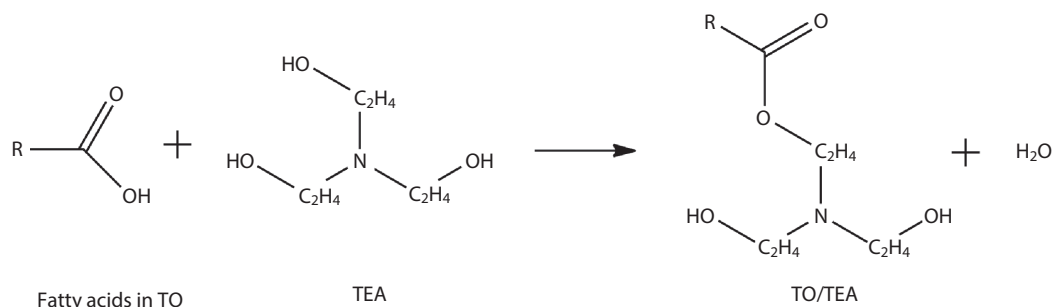
Figure 1 TO esterification with TEA; R – the fatty acid group [23, 24, 38].

Table 1 TO, PET and DEG molar ratios in synthesis of polyols.

Name of polyol	TO, mol	PET, mol	DEG, mol
TO/PET 1/1	1	1	2
TO/PET 1/2	1	2	4
TO/PET 1/4	1	4	8
TO/PET 1/6	1	6	12
TO/PET 1/8	1	8	16

and then held at 235 °C for 4 hours. After that, the flask was allowed to cool down.

Different TO/PET polyols were prepared using different TO/PET molar ratios, namely 1/1, 1/2, 1/4, 1/6 and 1/8, whose TO/PET/DEG molar ratios are shown in Table 1.

The reaction scheme of PET glycolysis with DEG is presented in Figure 2. This reaction consists of the transesterification of PET and the destruction of its polymer chain, resulting in the decrease of PET molecular weight [39].

In TO/PET polyol synthesis, transesterification between TO/TEA polyol and glycolyzed PET may take place. Two possible reactions of that are shown in Figure 3.

2.3 Characterization of Polyols

Hydroxyl (OH) value of the prepared TO/PET polyols was experimentally determined by acetylation method according to DIN 53240, and acid value (AV) was determined by the requirements of DIN 5340. The moisture content in polyol was tested using the Karl Fischer method according to DIN 51777.

Viscosity of polyols was determined according to DIN 53015 standard at 20 °C using a Falling Ball Viscometer KF 100 from Rheo Tec Messtechnik GmbH.

The FTIR-ATR spectra were made on a Thermo Fisher Nicolet iS50 FT-IR Spectrometer. The FTIR-ATR spectra of polyols were collected within the wave number ranging from 4000 cm^{-1} to 600 cm^{-1} at a resolution of 4 cm^{-1}.

Polyol compatibility with blowing agents was tested in plastic centrifuge tubes where 10 g of polyol was weighed and then 20% of blowing agent Solkane was added. Then the blends were centrifuged for 15 minutes at 55 rpm and kept at ambient conditions for 8 weeks for regular visual inspection.

The TO/PET polyols were also characterized by resulting content of renewable and recyclate, that was calculated as percentage by weight of TO and PET in polyol, respectively.

2.4 Preparation of Rigid PUR Foams

The foams were prepared at laboratory scale from a two-component (polyol and isocyanate) system by free-rising method in an open mold according to the formulations presented in Table 2.

The amount of necessary PMDI was calculated according to the isocyanate index 130 (the ratio of the equivalent amount of isocyanate used relative to the theoretical equivalent amount times 100). Rigid PUR foams were named the same as the TO/PET polyol in their formulation.

When PMDI was added to the polyol component, resulting mixture was stirred vigorously at 2000 rpm for 10 s and then instantaneously poured into an open mold of dimensions 30 × 30 × 10 cm. The process of rigid PUR foam formation was monitored by measuring foaming parameters: the duration of cream time, gel time, and tack-free time. All foam samples were allowed to cure at ambient conditions for 24 h prior to any further tests.

2.5 Characterization of Rigid PUR Foams

The closed cell content and apparent bulk density were tested according to the standards ISO 4590 and ISO 845, respectively. Compressive strength and modulus of elasticity were measured by the requirements of EN
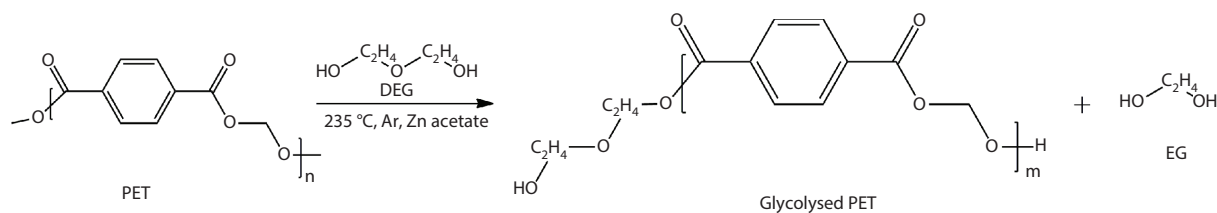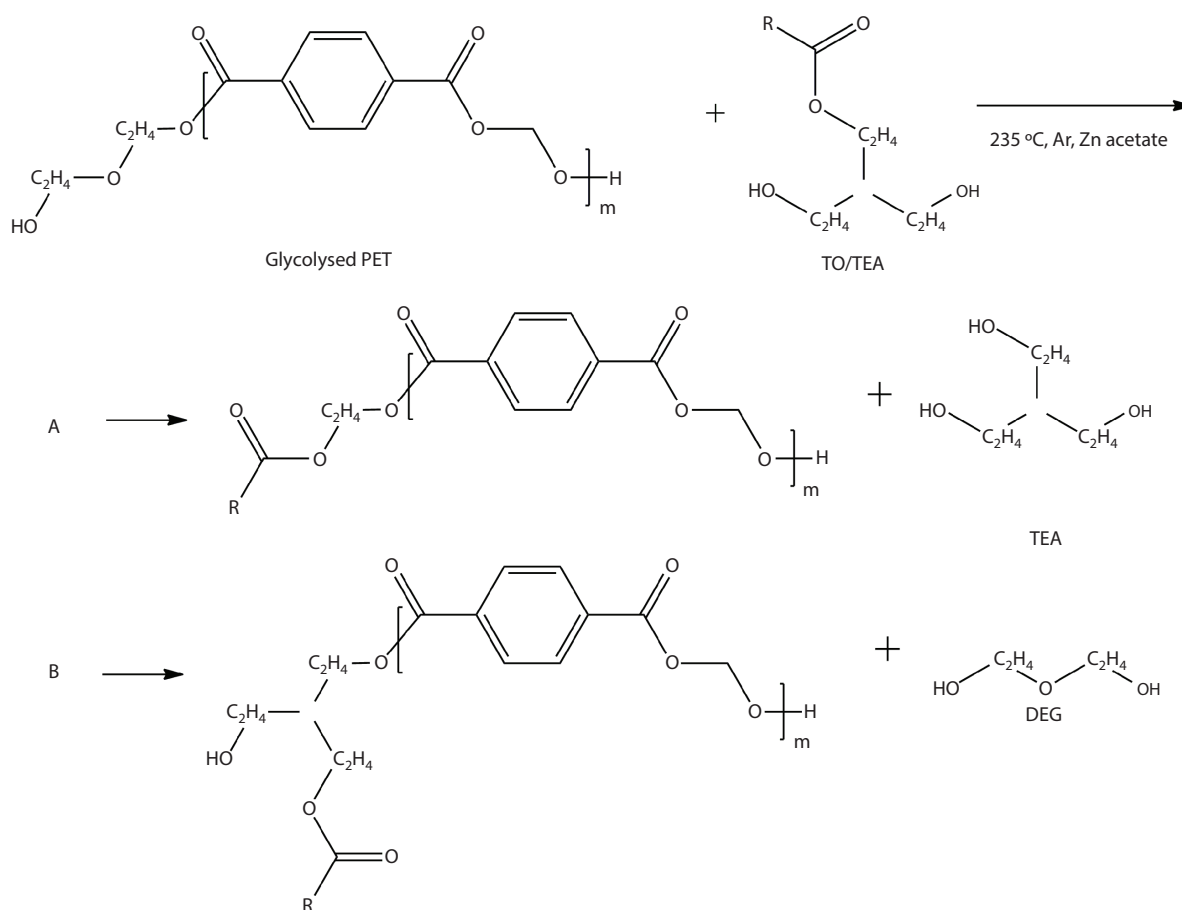
Figure 2 PET glycolysis with DEG [39, 44, 45].

Figure 3 Possible reactions (A and B) between glycolyzed PET and TO/TEA polyol.

Table 2 Rigid PUR foam formulation.

Component	Application	Amount, pbw*
TO/PET polyol	Synthesized polyol	75
Lupranol 3422	High functional polyol	25
Trichlorpropylphosphate	Flame retardant	20
NIAX Silicone L6915	Surfactant	2
Potassium acetate	Catalyst	1.2
PC CAT NP-10	Catalyst	1.2
Solkane	Blowing agent	25
PMDI		Isocyanate index 130

*parts by weight

ISO 844 using a Zwick/Roell Z100 testing machine for cylinder specimens with diameter and height of ~20 mm. The thermal conductivity of the rigid PUR foams was measured periodically for 10 weeks after foam preparation. These tests were carried out based on ISO 8301 standard, using a Linseis Heat Flow Meter 200. Temperature range was +10...+30 °C and dimensions of samples were 20 × 20 × 3 cm. Water absorption was tested by immersing PUR samples in water for 7 days, according to ISO 2896 standard.

3 RESULTS AND DISCUSSION

3.1 Polyol Characterization

3.1.1 Chemical Structure of Polyols

The chemical structure of the synthesized TO/PET polyols was studied by FTIR measurements. Similarity of the chemical structure of TO/PET polyols was expected because reagents in synthesis are the same but molar ratio differs. The FTIR spectra are shown in Figure 4.
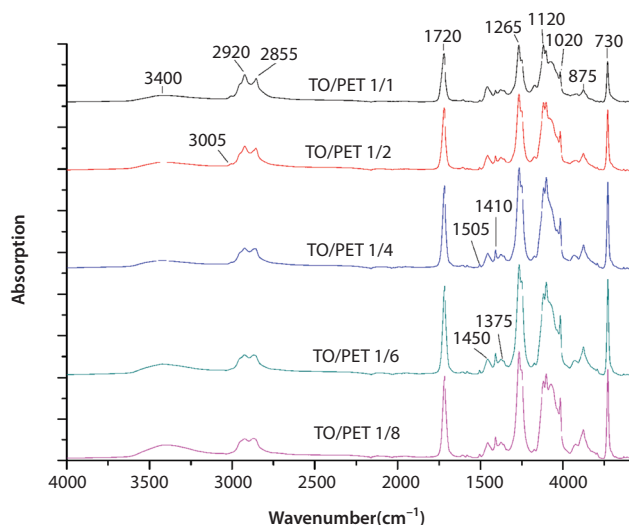

Figure 4 FTIR spectra of polyols.

The broad band at 3400 cm^{-1} is due to the stretching vibration of –OH groups. Absorption intensity of this band correlates with OH values of polyols (Table 3). In the range of 3000–2850 cm^{-1}, two bands can be observed due to the symmetric and asymmetric stretching of –CH$_2$– groups mainly from TO fatty acids. Small peak at 3005 cm^{-1} corresponds to cis-double bond stretching from oleic and linoleic acid in TO, therefore this peak increases for polyols with higher TO content. All FTIR spectra of polyols present a sharp band at 1720 cm^{-1}, which corresponds to the carbonyl bonds in ester group. For polyols with higher PET content the intensity of this peak, and also that of the ester bond peaks in the 1120–1020 cm^{-1} region, are higher because additional ester and ether bonds are introduced with depolymerized PET. The stretching vibration bands of aromatic ArCO–O ester group occur at 1265 and 1120 cm^{-1}. Aromatic structure introduced with PET is shown in FTIR spectra by stretching vibrations of aromatic C–H at 875 and 730 cm^{-1}, and small absorption bands of aromatic -C=C- stretching vibrations at 1505 and 1410 cm^{-1}. Small peak at 892 cm^{-1} (overlapped with peak at 875 cm^{-1}) corresponds to the -OC$_2$H$_4$ moieties of DEG backbone, and small peak at 920 cm^{-1} is due to the vibrations of C–O in DEG. These two peaks form the basis of the DEG detection according to the investigation of Ahmed *et al.* [40]. A peak around 1450 cm^{-1} indicates the presence of methylene groups, while an additional peak at about 1375 cm^{-1} is caused by a methyl group.

3.1.2 Chemical and Physical Characteristics of Polyols

Synthesized TO/PET polyols were homogenous, transparent, yellowish brown liquids. General characteristics such an OH value, AV, water content and viscosity are shown in Table 3.

With increasing TO/PET molar ratio, OH value of polyols increases from 193 to 384 mg KOH/g due to excess of DEG. The AV for polyols with TO/PET molar ratio from 1/4 to 1/8 is ~1 mg KOH/g higher

Table 3 Chemical and physical characteristics of TO/PET polyols.

Polyol	OH value, mg KOH/g	AV, mg KOH/g	Water content, %	Viscosity @ 20 °C, mPa·s	Compatibility with Solkane (+/–)	Crystallization time, months
TO/PET 1/1	193	6.2	0.23	1170	+	not observed
TO/PET 1/2	246	5.5	0.11	1500	+	not observed
TO/PET 1/4	306	3.6	0.08	1850	+	not observed
TO/PET 1/6	292	3.4	0.07	2300	+	2
TO/PET 1/8	384	3.7	0.22	2750	+	2

compared with similar synthesized polyols from rapeseed oil and PET [37] because tall oil contains 20 wt% resin acids which increase the AV of resulting polyols. The AV for TO/PET polyols with higher TO content is even higher—5.5 and 6.2 mg KOH/g. Acid value higher than 5 mg KOH/g can make polyol systems with an amine type catalyst for PUR more unstable because acid groups can react with amine groups of the catalyst. Viscosity of polyols increases two times (from 1170 to 2750 mPa·s) by increasing TO/PET molar ratio from 1/1 to 1/8. For all polyols the viscosity as well as water content is in an acceptable range for obtaining PUR foam.

An investigation by Paberza *et al.* showed that commercially available aromatic polyester polyol from PET was incompatible with Solkane [37]. Good compatibility between polyol and physical blowing agent is important because homogeneity of polyol system affects characteristics of rigid PUR foams. Polyol systems for commercial appliance have to be homogenous and without phase separation during storage [41]. Therefore all synthesized polyols were visually observed. After 2 months, crystallization of TO/PET 1/6 and TO/PET 1/8 began. All other polyols did not crystallize during the observation time (4 months). In addition, all polyols were compatible with the blowing agent Solkane—the mixtures after the centrifugation were homogenous and remained stable during visual observation time (1 month).

3.1.3 Content of Renewable and Recyclate

The TO/PET polyols were synthesized from renewable resource, tall oil, and recycled part – PET. Resulting content of renewable and recyclate is presented in Figure 5.

Figure 5 shows that by increasing TO/PET molar ratio, the renewable content in polyols decreases from 34 wt% to 8 wt% but content of recyclate material increases from 20 to 40 wt%. Total renewable and recyclate amount in synthesized TO/PET polyols reached ~50 wt%.

3.2 TO/PET Polyols as Raw Material for Rigid PUR Foam Preparation

3.2.1 Rigid PUR Foam Characteristics

Perspectives for the use of synthesized TO/PET polyols in rigid PUR foam were evaluated by obtaining PUR foams and characterizing them in terms of thermal conductivity, water absorption and compression strength.

The process of rigid PUR foam formation was monitored by measuring foaming parameters, which are presented in Table 4. Results show a tendency for gel and tack-free time to decrease by using TO/PET polyol with higher PET content.

Rigid PUR foams from TO/PET 1/1 and TO/PET 2/2 polyols showed significant shrinkage, therefore were not used for further tests. Shrinkage of these rigid PUR foams could be explained by the low OH value of polyols. Formulations based on these polyols should be adjusted to get more stable rigid PUR foams. Rigid PUR foams from TO/PET 1/4, 1/6 and 1/8 polyols did not show shrinkage and were used for further tests. Table 3 also shows other foam characteristics such as apparent bulk density, closed cell content and water absorption. Density of obtained rigid PUR
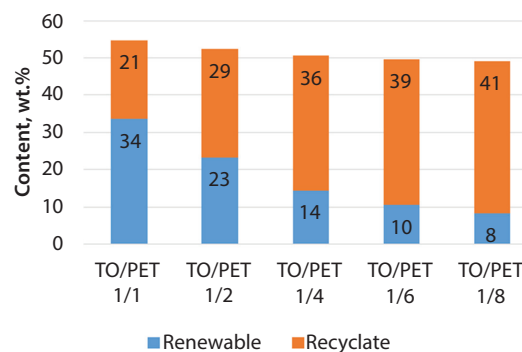
Figure 5 Content of renewable and recyclate in TO/PET polyols.

Table 4 Foaming parameters, density, closed cell content and water absorption of rigid PUR foams.

	TO/PET 1/1	TO/PET 1/2	TO/PET 1/4	TO/PET 1/6	TO/PET 1/8
Start time, s	20	20	17	20	22
Gel time, s	65	60	50	50	40
Tack-free time, s	90	80	65	70	57
Apparent bulk density, kg/m³	48	43	44	42	41
Closed cell content, vol%	–	–	92	96	97
Water absorption in 7 days, vol. %	–	–	12.36	12.32	12.39

foams was in the range of 41 to 48 kg/m^3, which is an appropriate value to use these foams as thermal insulation material. Closed cell content were in the range of 92 to 97 vol% and water absorption in 7 days was ~2.4 vol%.

3.2.2 Thermal Conductivity

Rigid PUR foams showed similar initial thermal conductivity (18.3–19.3 W/m·K) (Figure 6).

Thermal conductivity increases till 22.2–23.1 W/m·K in 10 weeks because of the air diffusion into foam. The lowest thermal conductivity during these 10 weeks of testing is shown by the rigid PUR foams obtained from TO/PET 1/6 polyol. Overall, thermal conductivity measurements indicate that these foams could be used as an insulating material in various construction applications.

3.2.3 Compressive Strength

As the mechanical properties of rigid PUR foams are significantly related to their apparent density, all compressive strength results were normalized with respect to a density of 45 kg/m^3 using the equation of Hawkins et al. [42] (Eq. 1):

$$\sigma_{norm} = \sigma_{exp}\left(\frac{45}{\rho}\right)^{2.1} \qquad (1)$$

where σ_{norm} is the normalized strength (MPa), σ_{exp} is the raw strength (MPa) determined from the stress–strain curve, and ρ is the apparent bulk density of sample (kg/m^3). Results of normalized elastic modulus and compressive strength of obtained rigid PUR foams are shown in Figure 7 and Figure 8, respectively.

As seen from these figures, elastic modulus and compressive strength of foams increase by using polyols with higher TO/PET molar ratio in rigid PUR foam formulation. The highest elastic modulus (~9 MPa) and compressive strength (0.37 MPa) are shown by the
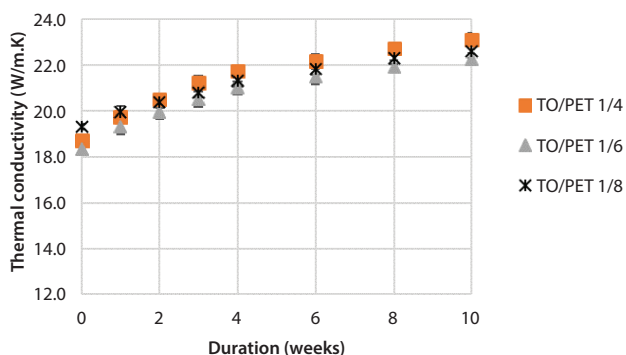
rigid PUR foams prepared from TO/PET 1/8 polyol. This is consistent with the investigations of Cabulis et al. and Van Haveren et al. [23, 43] in which the introduction of the aromatic structure into the PUR polymer matrix improves mechanical properties of foams. Overall, the compressive strength of TO/PET rigid PUR foams meets the requirements of the construction industry for thermal insulation materials.

4 CONCLUSIONS

The combination of TO/TEA polyol and PET, which is a novel approach in the existing literature, was used in polyol synthesis. The TO/PET polyols were synthesized by using different TO/PET molar ratios (from 1/1 to 1/8) while PET/DEG molar ratio remains the same (1/2 in all synthesis). PET increases the OH value whereas TO grants polyols with good compatibility with hydrofluorocarbon-type blowing agent as well as increases their stability against crystallization and lowers viscosity. Moreover, total renewable and recyclate content of ~50% in polyols was reached.

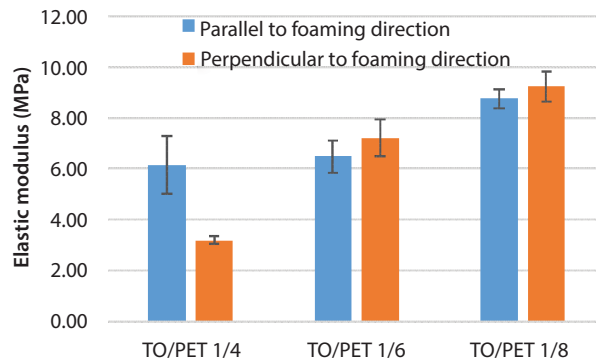Synthesized TO/PET polyols were used as the main polyol component to obtain rigid PUR foams.

Figure 7 Elastic modulus of rigid PUR foams.

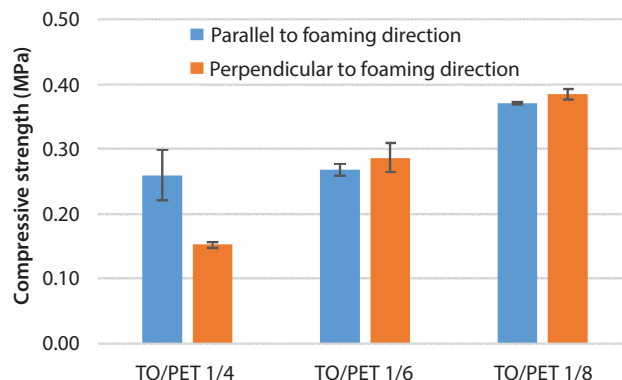**Figure 6** Thermal conductivity of rigid PUR foams.

Figure 8 Compressive strength of rigid PUR foams.

The effects of TO/PET molar ratio on the properties of resulting foams were investigated. The shrinkage of foams made from polyols TO/PET 1/1 and TO/PET 1/2 suggests that improved rigid PUR foam formulations have to be developed to get more dimensionally stable materials. On the other hand, TO/PET polyols with TO/PET molar ratios of 1/4 to 1/8 were found as suitable polyols for preparing rigid PUR foams. The lowest thermal conductivity was shown by rigid PUR foams made from TO/PET 1/6 polyol. Aromatic structure of PET improved the foams' mechanical properties and slightly increased closed cell content; however water absorption was not affected. Overall, results indicated that certain TO/PET polyols can be successfully used for preparing rigid PUR foams with characteristics suitable for thermal insulation materials.

ACKNOWLEDGMENT

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