Development of Water-Blown Bio-Based Thermoplastic Polyurethane Foams Using Bio-Derived Chain Extender

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ABSTRACT: Water-blown bio-based thermoplastic polyurethane (TPU) formulations were developed to fulfill the requirements of the reactive rotational molding/foaming process. They were prepared using synthetic and bio-based chain extenders. Foams were prepared by stirring polyether polyol (macrodiol), chain extender (diol), surfactant (silicone oil), chemical blowing agent (distilled water), catalyst, and diisocyanate. The concentration of chain extender, blowing agent, and surfactant were varied and their effects on foaming kinetics, physical, mechanical, and morphological properties of foams were investigated. Density, compressive strength, and modulus of foams decrease with increasing blowing agent concentration and increase with increasing chain extender concentration, but are not significantly affected by changes in surfactant concentration. The foam glass-transition temperatures increase with increasing blowing agent and chain extender concentrations. The foam cell size slightly increases with increasing blowing agent content and decreases upon surfactant addition (without any dependence on concentration), whereas chain extender concentration has no effect on cell size. Bio-based 1,3-propanediol can be used successfully for the preparation TPU foams without sacrificing any properties. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012
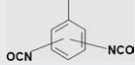
INTRODUCTION

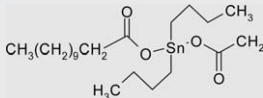Polyurethanes (PUs) are one of the most important classes of polymers due to their versatility in wide range of applications such as thermosets, thermoplastic elastomers, adhesives, coatings, flexible, and rigid foams.[1] Their properties can be tailored by altering their reactants composition such as isocyanates, polyols, and chain extenders. This explains the evergrowing demand for polyurethanes in automotive products, electronics, glazing, footwear, and in industrial machinery.[2–4] Like almost all commonly used polymers, PUs depends on petroleum oil as the feedstock for their major components: hydroxyl-containing polyols and isocyanates. Their extensive use has induced environmental issues as a result of accumulation of polymeric waste and recycling difficulty in their thermosetting form. Also, the accelerated depletion and more recently the increase in the prices of petroleum resources risk to seriously affect the raw materials cost for the polymer processing industry.[5] Many recent efforts have focused on replacing all or parts of the conventional petroleum-based polyols with renewable equivalent compounds[6] such as vegetable oils,[7–9] cardanol,[10–12] lignin,[13,14] chitosan,[15,16] biopitch.[17]

PU foams form the major contribution to polyurethane applications. These foams play an important role in several industrial products like footwear, insulation, furniture, car seating, packaging, etc. In recent days, the use of polyurethane foams is speedily increasing due to their light weight, superior insulating abilities, good energy absorbing performance, and comfort.[18] Segmented PUs are traditionally synthesized by the reaction of diisocyanates with polyols and chain extenders which are derived from petroleum resources.[19] However, research efforts are also being focused on developing PU foams from renewable resources.[18–21] Polyurethanes from vegetable oils have similar or better chemical and physical properties than PU based on petroleum resources like high tensile strength, high tear strength, enhanced hydrolytic tendencies, and thermal stability.[19–23]

PU foams can be prepared using physical and/or chemical blowing agents. Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) are widely used as physical blowing agents. The use of CFCs was however recently prohibited due to environmental issues such as ozone depletion and global warming, and the HCFCs were accepted only as interim blowing agents.

Table I. Characteristics of the Materials Used in the Study

	Chemicals	Structure	M^a (g mol^{-1})	Physical state $T_{ambiant}$	T_m ^{b} (°C)	Density (g/cm^3)	Fn^c
Isocyanate	TDI		174	Clear liquid	20	1.21	2
Macrodiol	PEG 400		400	Viscous liquid	4–8	1,1–1,2	2
Chain extender	PDO		76	Clear liquid	−30	1,05	2
Chain extender	Bio PDO		76	Clear liquid	−30	1,05	2
Catalyst	DBDTL		632	Liquid	10	1,050	–
Surfactant	Silicone oil 550	–	–	Liquid	–	1,07	–

^{a}M, molecular weight, ^{b}T_m, melting temperature, ^{c}Fn, functionality.

Substitutes for CFCs and HCFCs, such as hydrofluorocarbon and cyclopentane, were therefore developed and their applications for cellular materials have been studied. Distilled water is one of the widely used chemical blowing agents in the production of PU foams. It reacts with diisocyanate and generates carbon dioxide (CO_2) and polyurea. The formed CO_2 causes foaming and the formation of cellular structure.[24,25]

The literature reports different works on the preparation of segmented PU foams and analysis of their properties.[26–28] This article aims at developing water-blown segmented PU foams based on renewable resource in order to later adapt them for reactive rotational molding (RRM). The criteria to choose the formulations for RRM are therefore (i) one-step bulk polymerization where all the raw materials are premixed without solvent and placed in the mould, (ii) reaction carried out at ambient or slightly higher temperature so that heating and cooling cycle times are reduced, (iii) product should be formed in short time (∼ 10–15 min), and finally (iv) the product obtained should be thermoplastic to allow easy recycling. In this context, a series of foams were prepared by replacing the synthetic 1,3-propanediol (PDO) by bio-based PDO derived from corn syrup. The effects of change in macrodiol/chain extender ratio, as well as in concentrations of blowing agent and surfactant were studied and compared. Several experimental techniques were employed to characterize the foams including differential scanning calorimetry (DSC), Fourier transform infrared (FTIR), Scanning Electronic Microscopy (SEM), and Thermo Gravimetric Analysis (TGA).

EXPERIMENTAL

Materials
The raw materials used in this study were obtained from commercial sources. All raw materials such as polyol, chain extender, and isocyanate chosen bear functionality 2 in order to avoid any crosslinking reactions and to obtain foam in segmented thermoplastic form. Polyethylene glycol (PEG), toluene diisocyanate (TDI) and 1,3-propanediol (PDO) used in the preparation of water-blown polyurethane foams were purchased from Sigma Aldrich, France. Dibutyl tin dilaurate (DBTDL) catalyst was purchased from Fluka, France. Silicone oil 550 purchased from OSI, France, was used as a surfactant and distilled water as a blowing agent. Bio-based Susterra® 1,3-propanediol derived from corn oil was kindly provided by Dupont Tate & Lyle BioProducts, USA. The characteristics of all raw materials used in the study are presented in Table I.

Experimental Design and Formulations
Several experiments were carried out to choose the best formulation and to optimize the procedure for the preparation of foams. With the optimized procedure, the effects of the following variables in the foam formulation on the properties of water-blown polyurethane foams were studied: (1) macrodiol/chain extender ratios: 90/10, 80/20, 70/30, and 60/40; (2) water concentrations: 0, 2, 2.5, and 3 parts per hundred diols (pphp); and (3) concentration of surfactant: 0, 2.5, 3, and 3.5 pphp. Other components in the foam formulations such as catalyst, and the molar ratio NCO/OH (NCO index - 1.05) were kept constant. The concentration of catalyst and NCO index in the foam formulation was determined first to ensure that all foam products could be prepared within the stipulated time (∼ 10 min). DBTDL is a very effective catalyst; therefore low concentration (0.02 pphp) was used. The amount of isocyanate added to each formulation was based on the total hydroxyl content of the diols and water. To ensure the repeatability, three replicate foams were produced for each formulation.

Non bio-based foam samples were designated as "TPU foam XYZ-a (s)" where "X" indicates the amount of polyol, "Y" the amount of chain extender, "Z" the concentration of catalyst, "a" the concentration of blowing agent, and "s" the concentration of surfactant, such that TPU foam 912-3 (3) has 90% of PEG, 10% PDO, 0.02 pphp catalyst, 3 pphp blowing agent and 3 pphp surfactant respectively. Bio-based TPU foams were prepared with same formulations and procedure by replacing synthetic 1,3-propanediol with renewable resourced Susterra® 1,3-

Table II. Formulations of Prepared TPU Foams

Sample code	Macrodiol	Chain extender	Blowing agent	Catalyst	Surfactant	Diisocyanate
TPU/Bio TPU foam	PEG (mL)	PDO/Bio PDO (mL)	Distilled water (mL)	DBTDL (μL)	Silicone oil (mL)	TDI[a] (mL)
912-2(3)	9	1	0.20	2	0.3	8.5
822-2(3)	8	2				10.5
732-2(3)	7	3				12.5
642-2(3)	6	4				14.5
912-2.5(3)	9	1	0.25			9.0
822-2.5(3)	8	2				11.0
732-2.5(3)	7	3				13.0
642-2.5(3)	6	4				15.0
912-3(3)	9	1	0.30			9.5
822-3(3)	8	2				11.5
732-3(3)	7	3				13.5
642-3(3)	6	4				15.5
822-3(0)	8	2			0	11.5
822-3(2.5)					0.25	
822-3(3.0)					0.30	
822-3(3.5)					0.35	

[a]Required isocyanate = NCO/OH Index × $(EW)_{iso}$ [pbw of polyol/$(EW)_{polyol}$ + pbw of diol/$(EW)_{diol}$ + pbw of H_2O/$(EW)_{H_2O}$], where NCO/OH index = NCO/OH molar ratio = 1.05, $(EW)_{iso}$ = equivalent weight of isocyanate, $(EW)_{polyol}$ = equivalent weight of polyol, $(EW)_{H_2O}$ = equivalent weight of H_2O, and pbw = weight fractions.

propanediol and designated as "Bio TPU foam XYZ-a (s)". All formulations adopted in this study for preparation of non bio-based and bio-based TPU foams are shown in Table II.

To investigate the effect of the surfactant concentration on the properties of foams, the amount of silicone oil was varied (0, 2.5, 3, and 3.5 pphp), while the amounts of PEG, PDO, distilled water, and DBTDL were fixed at 80, 20, 3, and 0.02 pphp, respectively (Table II).

Preparation of Polyurethane Foams

A standard laboratory mixing and pouring procedure for making foams was used.[29] Intensive mixing was generated by a magnetic stirrer. The required amounts of diols, catalyst, surfactant, and blowing agent were added by volume into a glass beaker and stirred on magnetic stirrer at high speed for 5 min under fuming hood. Then, required amount of diisocyanate was added and stirred for other 8–10 s at the same speed. The reaction mixture was then poured immediately into the silicone moulds ($100 \times 40 \times 40$ mm^3) and allowed to rise. The raised foams were removed from the mould after 10 min and kept for conditioning ($23 \pm 2°C$, $50 \pm 5\%$ relative humidity) for 1 week at least before further testing.

Characterization

Fourier Transform Infrared Spectroscopy. A Fourier-transform infrared spectroscopy (FTIR) analyzer (Nicolet 380 FTIR, Thermo Scientific, USA, with OMNIC software for data collection and analysis) equipped with attenuated total reflectance (ATR) attachment was used to record FTIR-ATR spectra. Samples were cut using a razor blade to $20 \times 20 \times 10$ mm^3 cubes from the center of the foam buns. The foam was pressed against the ATR crystal to ensure complete contact. A total of 64 scans

were taken on each sample over the wavelength range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1}. Three FTIR-ATR spectra were collected at different locations of the sample to verify sample uniformity. Three samples were tested for each foam formulation.

Adiabatic Temperature Rise. The foaming process was monitored by the evolution of reaction temperature as a function of time. Addition of TDI was considered as the zero time of the reaction. Temperature profiles during foaming were recorded using house made type J thermocouples.

Kinetics. The kinetic characteristics of the foaming reaction were noted by a cup test, in which the cream, gel, and rise times were noted for both nonbio-based and bio-based polyurethane foams. For this purpose, the PU foams were prepared by using the same volume ratio of reactants as in the case of molded foams, under exactly the same conditions. The viscosity of the adiabatic reacting mixture remains low, until close to the gel point, and rapidly tends to infinity.[30] This phenomenon is used to experimentally determine the gel point by moving a glass rod in the reacting liquid, until the movement is hindered by a sudden rise in viscosity.[31] The cream time is the time at which the reacting liquid gets saturated with the blowing gas and is marked by a creamy appearance of the liquid. The rise time is the time at which the rise of the foam stops, which corresponds to the macroscopic expansion of foam.

Density. Density of the samples was determined according to ASTM D 1622 standard. The foam samples were cut into cubes of 30 mm^3 using a bench saw. Samples were weighted carefully using an analytical balance and exact dimensions were measured
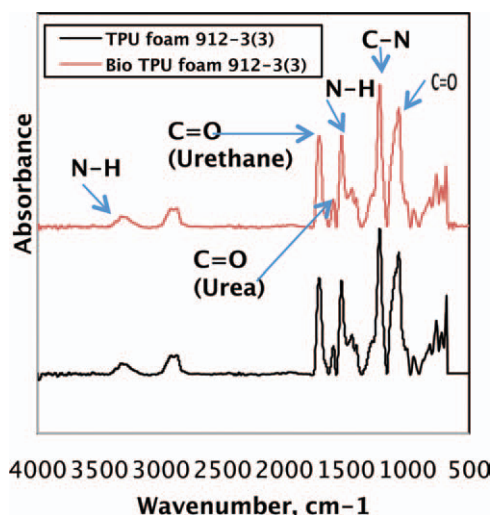
Figure 1. Typical FTIR-ATR spectrum of Bio TPU foam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

using digital vernier caliper. Each measurement is the average of at least six cubes.

Scanning Electron Microscopy. The morphology of cell structure was observed under high vacuum with a Scanning Electron Microscope (SEM, S-4300SE/N, Hitachi, Japan) operating at 5 kV. Foam was frozen in liquid nitrogen and cut perpendicular to the foam rise direction with a razor blade and the fractured surface was coated with gold before observation. The cell window area which is the average diameter of cell, measured from 1 mm^2 area of SEM micrographs.

Thermal Analysis. Glass transition temperatures were determined by Differential Scanning Calorimetry (DSC 7, Perkin-Elmer Pyris, USA). Approximately 6 ± 0.1 mg of foam was loaded into an aluminum pan and sealed hermetically. The sample was first heated to 180°C at 10°C min^{-1} and equilibrated for 2 min, followed by cooling to 30°C at 10°C min^{-1} and hold for 2 min. Then, the sample was heated to 220°C at 10°C

min^{-1}. Glass transition temperatures were determined as the middle point of transition on the second heating cycles. All the DSC curves are normalized by sample mass in order to eliminate the error due to the mass of the sample.

Thermal stability was studied using a Thermo Gravimetric Analyser (TGA, Perkin-Elmer TGA-7, USA). The sample weighing about 7–8 mg was heated from 25 to 600°C under nitrogen at 20°C min^{-1}.

Mechanical Properties in Compression. Compressive strength and modulus were measured in the direction of free-rise during foaming using a standard tensile machine (Zwick 1474, Germany) at a crosshead speed of 3 mm min^{-1} according to ASTM D 1621. Compressive strength was determined following procedure A (absence of yield point; stress taken at 10% deformation). Foams were cut with a bench saw into cubes of 30 mm^3. The diameter and initial height of the samples were measured using vernier caliper. Compression properties reported are an average of six samples per foam.

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy

Figure 1 illustrates the typical FTIR-ATR spectrum of both Bio TPU and TPU foam. FTIR was used to probe the reaction completion and formation of polyurethanes. In both types of foams, nearly identical spectrum was obtained, which indicates the similar urethane formation. The wide absorption band at around 3330 cm^{-1} represents hydrogen bonded urethane N—H stretching vibration. The bands at 1530, 1220, and 1213 cm^{-1} can be attributed to N—H, C—N, and C—O of urethane linkages. The band at 1725 cm^{-1} represents the stretching vibration of hydrogen-bonded carbonyl groups between N—H and C—O of urethane linkages which indicates the formation of interurethane hydrogen bonding. The band at around 1698 cm^{-1} represents the stretching vibration of carbonyl groups of free urea.[32–34] Absence of isocyanate absorption band at around 2270 cm^{-1} indicates the complete conversion of isocyanate. The free urea band is less intense that the urethane band, indicating only some urea formation, as compared with the high number of urethane linkages.
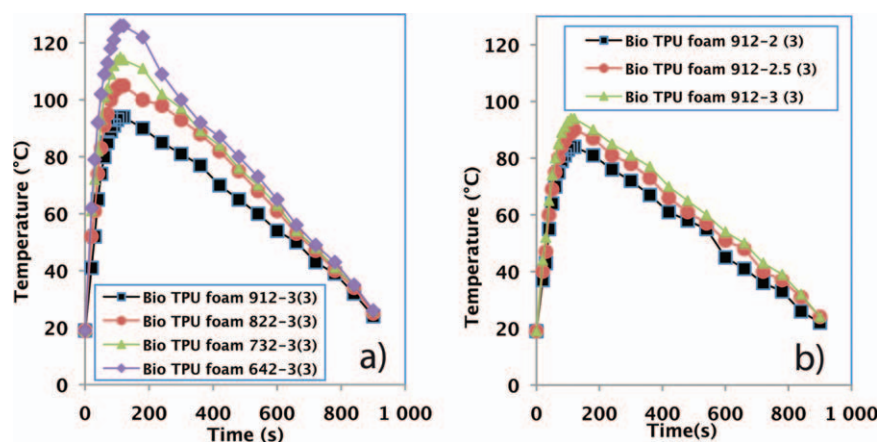

Figure 2. Adiabatic temperatures rise as a function of time at different: chain extender concentration (a) and water concentration (b) for Bio TPU foam samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
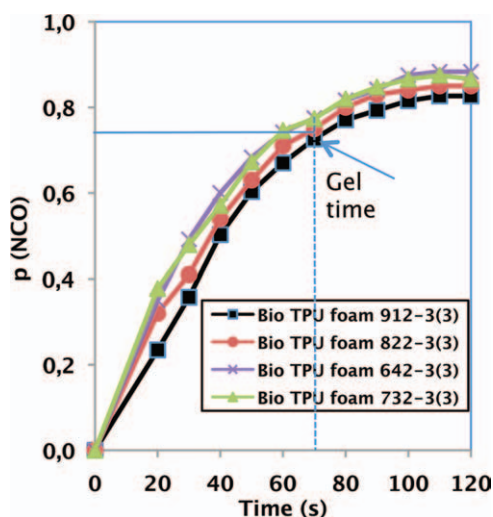
Figure 3. Calculated isocyanate conversions from the temperature rise during foaming. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Adiabatic Temperature Rise

Both gelling and blowing reactions are exothermic reactions during foaming. As foam takes on its shape, the cellular structures developed act as an insulation layer around the centre of a foam bun making it an adiabatic reactor. Figure 2 shows the adiabatic temperature rise profiles as a function of foaming process time for bio-based foams at different chain extender (CE) and blowing agent (BA) concentrations. Non bio-based foams show similar temperature profiles (not shown here). Exothermicity of the foaming process increases with increasing CE and BA concentrations.

High exothermicity as a result of increase in CE may be due to generation of substantial heat due to vigorous reaction between CE and diisocyanate. Both PDO and PEG have two OH groups in one molecule. Molecular weight of PDO is 76 and that of PEG used in this study is 400. It means that 100 g of PDO approximately contains 3.6 mol of OH groups, whereas PEG contains 0.5 mol. As mentioned above (section experimental design and formulations), the molar ratio of isocyanate groups to hydroxyl groups (NCO/OH) was kept constant at 1.05 for all formulations. Therefore, sample with high concentration of CE contains higher number of hydroxyl groups which causes more urethane linkages between OH groups and NCO groups. Increase in exothermicity as a result of increase in BA concentration may be explained by distilled water reaction with diisocyanate group, which generates carbon dioxide and polyurea with substantial amount of heat.

The adiabatic temperature profile directly depends on the reaction kinetics, and in the case of PU foam formation, the change in temperature may be related to the consumption of diisocyanate.[24] Equation (1) shows the relationship between the isocyanate conversion and the temperature rise.

$$p(\text{NCO}) = \frac{r\Delta T_m}{\Delta T_{\text{rxn}}} \qquad (1)$$

$$\Delta T_{\text{rxn}} = \frac{Q}{C_p m_T} = \frac{\Delta H_{r,u} + \frac{m_w}{M_w} + \Delta H_{r,r} + \frac{m_{\text{OH}}}{M_{\text{OH}}} f_n}{C_p m_T} \qquad (2)$$

where p is the isocyanate conversion, r is the stoichiometric ratio of functional groups, which is 1.05 in this case, ΔT_m is the temperature rise during foaming measured via thermocouple, ΔT_{rxn} is the maximum temperature rise, Q is the total amount of heat generated during foaming; C_p is the specific heat capacity of foam, which is taken as 1.5 J/(g°K); m is the reactant mass; ΔH_r is the heat of reaction; M is the molecular weight of reactant; fn is the functionality of the polyol, subscripts u, r, w, T and OH represent urea, urethane, water, total, and polyol respectively. $\Delta H_{r,u}$ and $\Delta H_{r,r}$ were taken as -125.5 kJ mol^{-1} and -93.9 kJ mol^{-1} (See Refs. 33 and 35). Maximum isocyanate conversion is assumed to be at maximum temperature rise (T_{max}). Therefore, temperature profile till T_{max} is considered to calculate isocyanate conversion.

Figure 3 shows the isocyanate conversion versus time curves computed from the temperature rise profiles presented in Figure 2 for a series of four BioTPU formulations. The conversion profiles depend on the macrodiol/CE ratio until the gel point, and then they become very similar. Before gel time, the increase in CE concentration increases exothermicity which accelerates conversion, as explained above.

During the first 20 s of reaction, the consumption of diisocyanate occurs faster with increase in CE concentration. Further, the rate of consumption is slower at 40 s. The difference in diisocyanate consumption could be attributed to the difference in urethane formation rates. The fact that foams containing higher concentration of CE have higher isocyanate conversion rates during the first 20 s of foaming suggests that urethane formation was a significant factor in TDI consumption. However, the difference in isocyanate conversion between the foams is much less at 100 s. In general, the overall foaming kinetics is similar for all the PU foams.

Foaming Kinetics

The cream time, gel time, and rise time for the foaming process of both bio based and nonbio-based TPU foams were measured (Table III), and compared between bio based and nonbio-based TPU foams of same formulations. In Bio TPU foams, these times remain unaltered or, comparable with that of nonbio-based foams, differences between bio and nonbio formulations noted are not significant. The cream time is the same for all the foams, indicating that there is sufficient unbound water, so that the time to generate enough CO_2 to saturate the reacting mixture is not affected as the solubility of CO_2 in the reacting mixture is very low.[36] The results also indicate that the polymerization reaction is accelerated with increasing concentrations of CE and BA (lower gel time). The enhancement in the polyurethane reaction rate may be due to the presence of the reaction products of the blowing reaction such as polyurea, which can act as cocatalyst for the polyurethane reaction.[37] Foam rise time decreases with growing CE concentration which may be ascribed to the presence of a higher number of reactive primary hydroxyl groups. Furthermore, the foam blowing is faster with increase in BA concentration (lower rise time).

Table III. Kinetics Characteristic Times of Prepared TPU Foams

| Sample code BioTPU foam	Kinetics time (s)			Sample code TPU foam	Kinetics time (s)		
	Cream	Gel	Rise		Cream	Gel	Rise
BioTPU 912-2(3)	15	45	69	TPU 912-2(3)	14	45	68
BioTPU 822-2(3)	14	45	68	TPU 822-2(3)	14	44	68
BioTPU 732-2(3)	14	44	66	TPU 732-2(3)	15	44	67
BioTPU 642-2(3)	13	42	65	TPU 642-2(3)	13	43	65
BioTPU 912-2.5(3)	14	42	67	TPU 912-2.5(3)	13	43	67
BioTPU 822-2.5(3)	13	42	66	TPU 822-2.5(3)	13	42	66
BioTPU 732-2.5(3)	15	41	64	TPU 732-2.5(3)	15	41	64
BioTPU 642-2.5(3)	14	40	63	TPU 642-2.5(3)	14	40	63
BioTPU 912-3(3)	15	40	64	TPU 912-3(3)	15	40	64
BioTPU 822-3(3)	14	38	63	TPU 822-3(3)	14	38	63
BioTPU 732-3(3)	15	38	61	TPU 732-3(3)	15	38	61
BioTPU 642-3(3)	13	37	60	TPU 642-3(3)	13	37	60
BioTPU 822-3(0)	11	36	61	TPU 822-3(0)	11	35	60
BioTPU 822-3(2.5)	14	38	63	TPU 822-3(2.5)	13	38	63
BioTPU 822-3(3.5)	14	38	64	TPU 822-3(3.5)	14	37	63
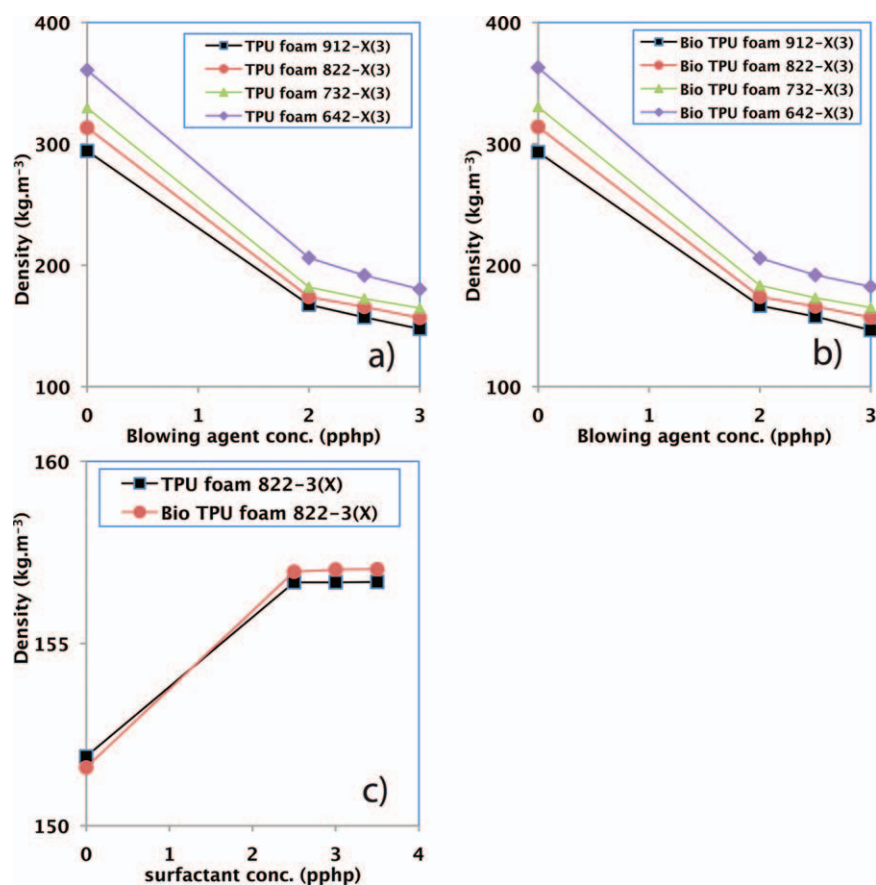
Figure 4. Effects of chain extender and water content on foam densities of TPU foams (a), BioTPU foams (b) and Effects of surfactant concentration on TPU and BioTPU foams (c). X is blowing agent concentration, 's' the surfactant concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
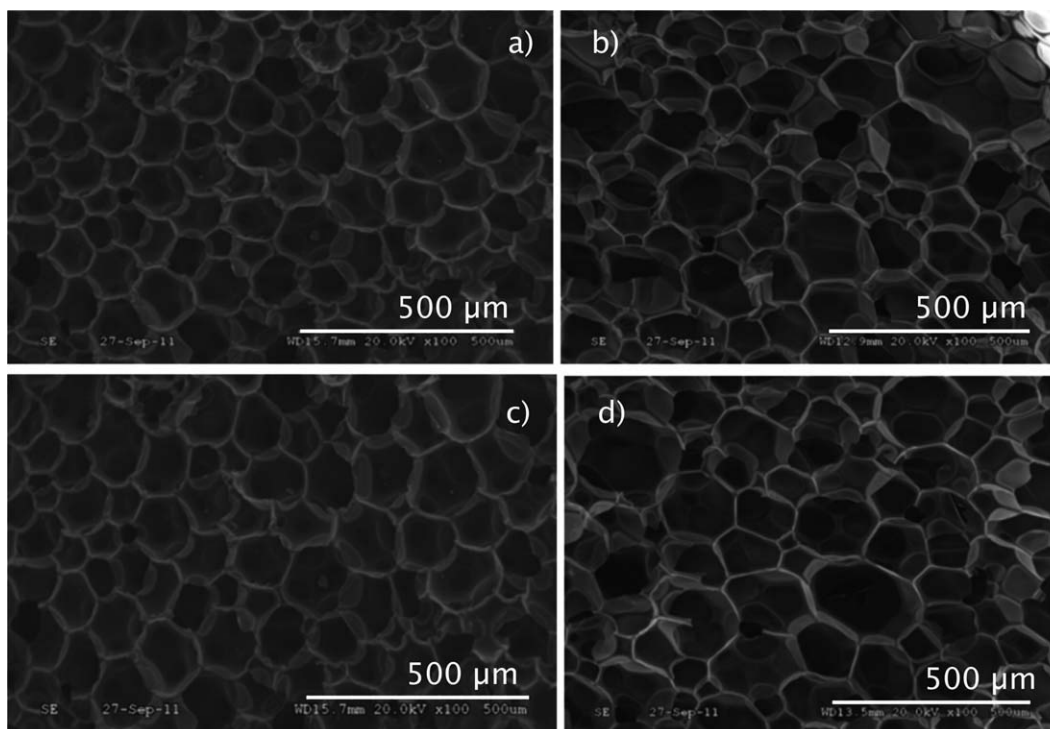
Figure 5. Scanning electron micrographs of the TPU foams: Bio TPU foam 822-2(3) (a), Bio TPU foam 822-3(3) (b), Bio TPU foam 642-2(3) (c), and Bio TPU foam 642-3(3) (d).

Density

The foam densities (Figure 4) increase with increasing CE concentration (from 146.6 to 182.4 kg m^{-3} when CE concentration increases from 10 to 40 pphp at 3 pphp BA). This increase may be explained by the existence of more urethane linkages as a result of higher concentration of hydroxyl groups of CE. When BA concentration increases from 0 to 3.0 pphp, the foam densities decrease from 293.2 to 146.6 kg m^{-3}, respectively, at 10 pphp CE content [Figure 4(a,b)]. High density at 0 pphp BA might be due to the presence of pores rather than cells. This pores formation is due to the presence of moisture in diols/diisocyanate. However, exothermicity of formulations without BA differs from BA containing formulations. Similar results were obtained by Thirumal et al.[38] Both nonbio-based and Bio TPU foams are characterized by similar behavior. Figure 4(c) shows

the effect of the surfactant concentrations (0 and from 2.5 to 3.5 pphp) at 3 pphp BA and 20 pphp CE respectively, on density of both bio-based and nonbio-based TPU foams. In the absence of surfactant, we have observed large and broken cells leading to decrease in foam density. The SEM morphology [Figure 6(a)] clearly shows the broken cells in the absence of surfactant leading to low density foam which is in contrast to the results obtained by Lim et al. who reported higher density in that case.[39] However, the reason for the differences between the results obtained in the present work and the work reported by Lim et al. in the absence of surfactant is still an open question and will be a subject for further studies. The foam density increases slightly from 151 to 156 kg m^{-3} upon surfactant addition (2.5 pphp) and does not vary significantly when surfactant concentration further increases.
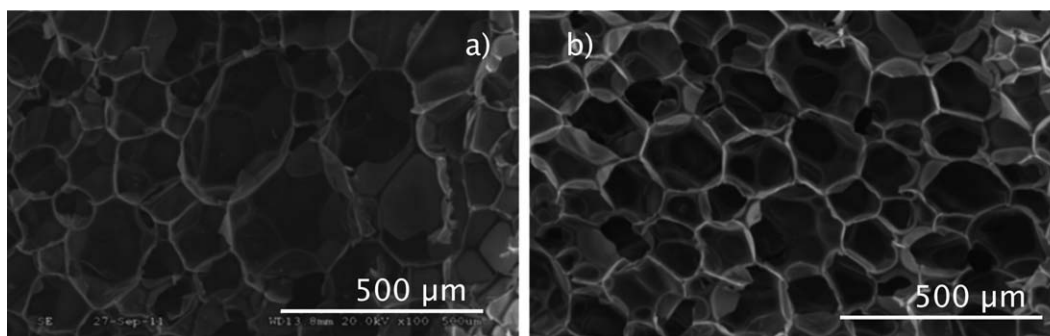

Figure 6. Scanning electron micrographs of the TPU foams without surfactant (a), with 2.5 pphp surfactant (b).
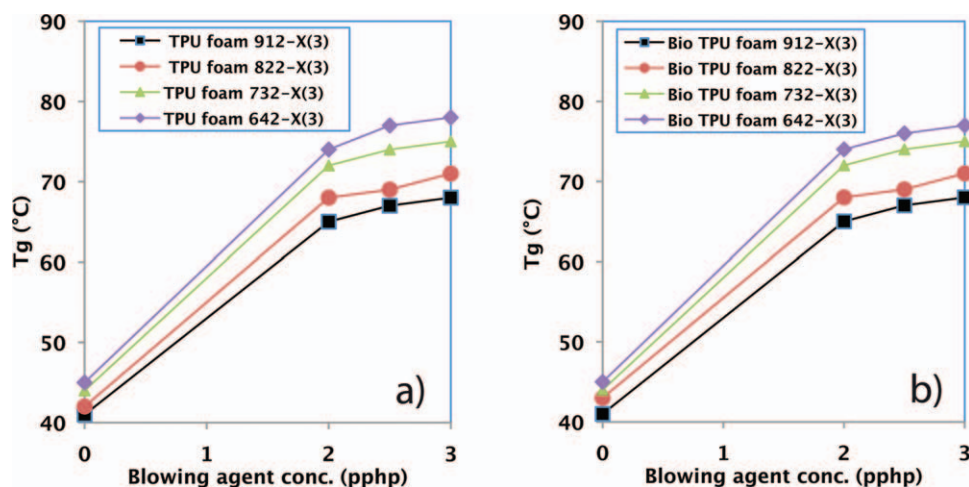
Figure 7. Glass transition temperatures at different chain extender and blowing agent concentrations of Bio TPU foam samples (a) non Bio TPU foam samples (b). X is blowing agent concentration, 's' the surfactant concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Cell Morphology and Size

Scanning electron micrographs of the foams cross sectional surfaces show that foam cell size increases with growing distilled water content. This is illustrated in Figure 5 on foam sample where water concentration varies from 2 to 3 pphp, respectively at 20 pphp CE [Figure 5(a,b)] or at 40 pphp CE [Figure 5(c,d)]. The cell size of Bio TPU foam 822-2 (3) is around 100 μm and increases to around 200 μm for Bio TPU foam 822-3(3). Distilled water, a chemical blowing agent, reacts with diisocyanate and generates carbon dioxide (blowing gas) accompanying the exothermic reaction heat. Because of the increase of the temperature of the reactant mixture, the concentration of blowing gas in the mixture exceeds its solubility limit and a nucleation of bubbles begins. During the rise time, the already formed bubbles grow and new bubbles nucleate.[37,40] The increase of distilled water generates more bubbles, and favors their coalescence. Therefore, the foam cell size increases with increasing distilled water concentration. The observed results are in accordance with the referred literature.[41]

The cell morphology analysis suggests that macrodiol/CE ratio (i.e., CE concentration) does not alter significantly the cellular structure of the foam. Thus any further observed changes in foam mechanical properties are unlikely to be due to cell size changes (see section Mechanical Properties).

In case of formulation without surfactant, foam cells are broken and arranged randomly, and also bigger [Figure 6(a)], whereas cell size decreases and foam cells are well organized in presence of surfactant [Figures 5 and 6(b)]. However, no change in cell size with further increase in surfactant concentration (up to 3.5 pphp) is noticeable [see Figures 5 and 6(b), where surfactant concentrations are 3 and 2.5, respectively]. The results with surfactant concentrations from 2.5 to 3.5 pphp are in accordance with those reported by Lim et al., who studied the effects of surfactant in PU foams by varying surfactant concentration from 0 to 5 pphp and found that cell size are almost similar at 2–3 pphp.[39]

Thermal Behavior

Glass Transition Temperature. The glass-transition temperatures (T_g) of thermoplastic foams increases from 65 to 68°C when BA concentration increases from 2 to 3 pphp at 10 pphp CE concentration (Figure 7), and from 65 to 77°C when CE concentration increases from 10 to 40 pphp at 2 pphp BA concentration. Reason might be the reaction of water with isocyanate group, which generates carbon dioxide and polyurea with the release of reaction heat. Polyurea is known to be more rigid than PU.[40] Therefore, when distilled water is used as a blowing agent, the mobility of the polymer chains would decreased and the T_g of the polymer would increase.[28] In addition, a urea group can react with TDI to generate biuret, which introduces additional
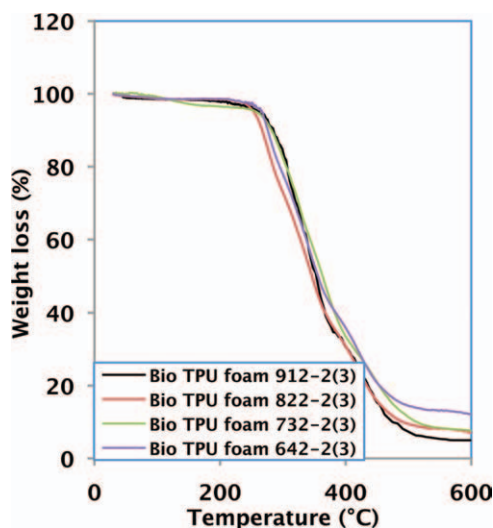

Figure 8. TGA curves of Bio TPU foams for different chain extender concentrations: Definition of initial temperature of thermal decomposition (Tdi), thermal decomposition temperature (Td), and weight residues (WR at 500°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
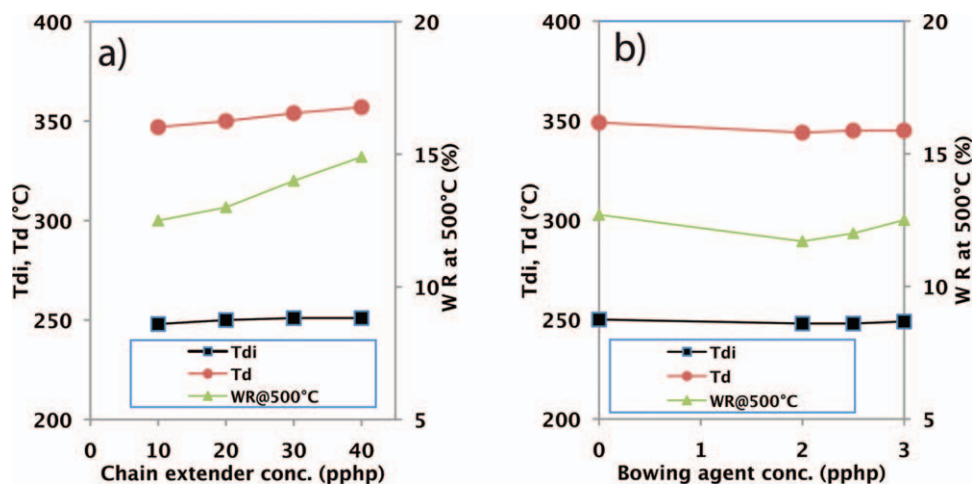
Figure 9. Initial temperature of thermal decomposition (Tdi), thermal decomposition temperature (Td) and weight residues (WR at 500°C) of Bio TPU foams: (a) chain extender concentration, (b) blowing agent concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

networks to the foam samples.[38] It is known that an increase in CE concentration increases the hard segment content of the foams. The hard segment is organized with urethane and a urea group, and the soft segment is organized with a polyol group. The urethane and urea group are more rigid than the polyol group. Thus, increase in T_g values may be due to the increase in the hard segment content of the foams.[41] In addition, differential scanning calorimetry (DSC) revealed a melting (endothermic) peak (ex. 177°C for Bio TPU foam 912–3(3), not presented here), which is a characteristics of thermoplastic polyurethanes.
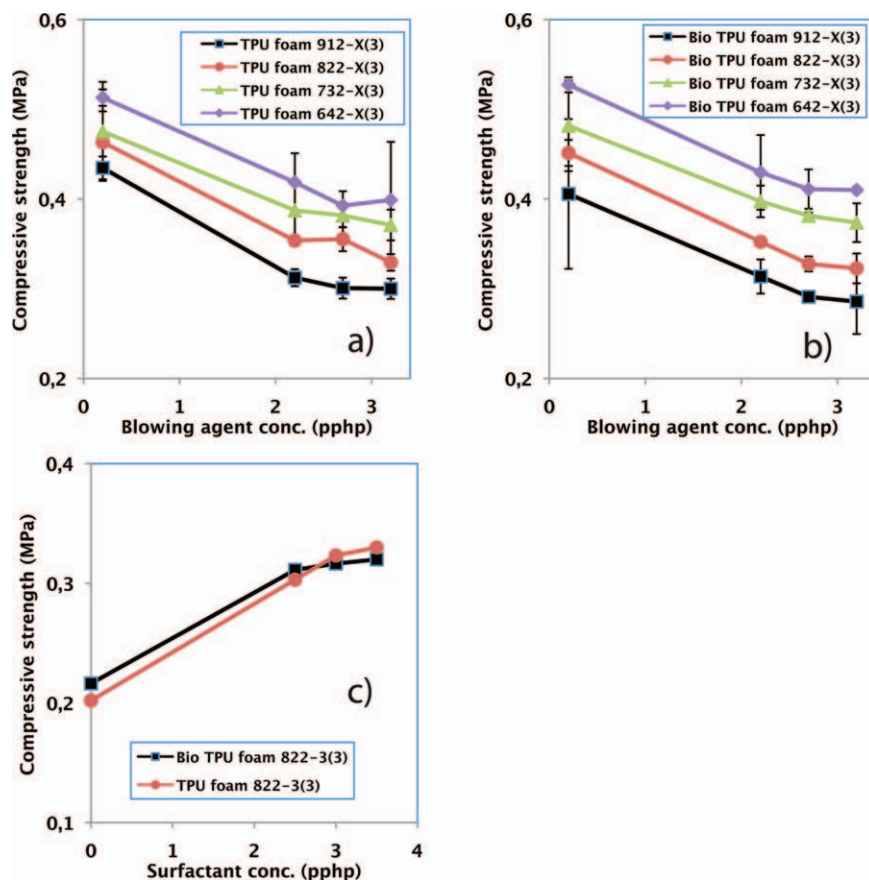

Figure 10. Compressive strength vs. chain extender and blowing agent concentrations of (a) TPU foams, (b) Bio TPU foams, and (c) surfactant concentrations of both non-Bio and Bio TPU foams. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 11. Compressive modulus vs. chain extender and blowing agent concentrations of (a) TPU foams, (b) Bio TPU foams, and (c) surfactant concentrations of both non-Bio and Bio TPU foams. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
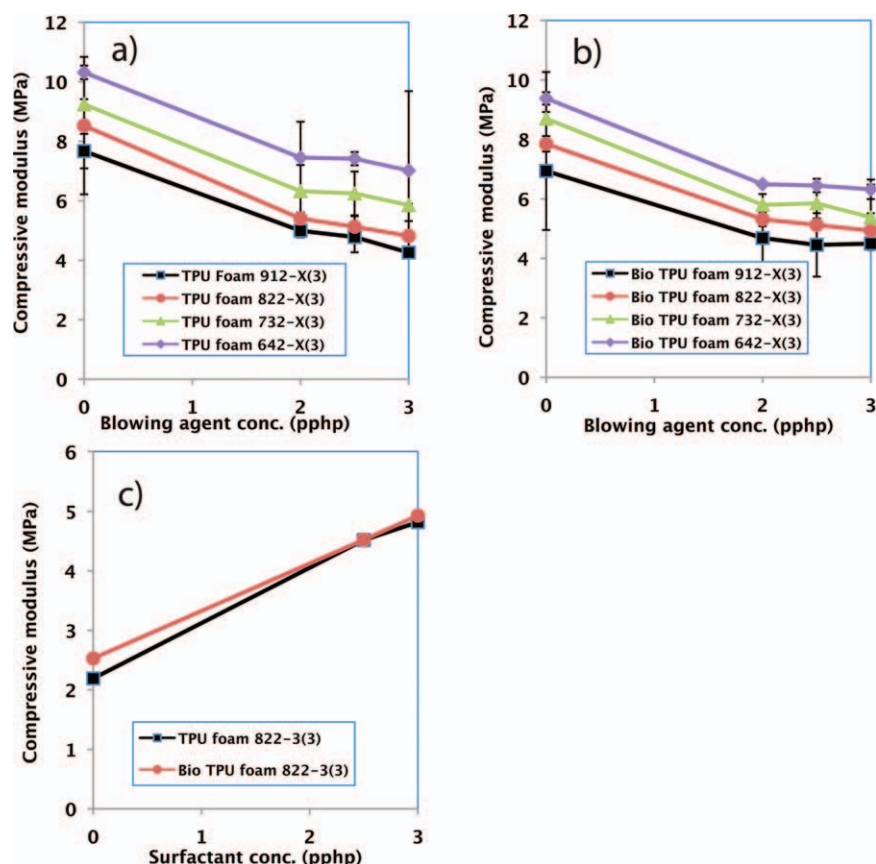
Thermal Degradation and Stability. Thermal stability of both bio-based and nonbio-based TPU foams was analyzed by thermo gravimetric analysis (TGA). Figure 8 shows typical TGA curves of PU foams. Each curve expresses the change in the percentage of weight residue (WR), $(mT/m_i) \times 100$, where mT is the sample weight at temperature T and m_i at initial temperature. The initial temperature of the thermal decomposition (T_{di}) was determined as the temperature at which samples show a 1% weight loss. Thermal decomposition temperature (T_d) was determined as the temperature of the cross point of extrapolated baseline and tangent line in a TGA curve. T_{di}, T_d, and WR at 500°C were plotted against the CE and BA concentrations [Figure 9(a,b)]. For all foams, T_{di} values are almost similar at around 250°C whereas T_d increases with increase in CE and BA concentrations, for both nonbio-based and Bio TPU foams. Hirose et al. have shown that urethane bonds dissociate to form hydroxyl and isocyanate groups at around 250°C.[42] Also, Kurimoto et al. reported that the degradation of PEG starts at around 250°C.[43] Accordingly, it is considered that the dissociation of urethane bonding starts at T_{di} for all PU foams studied here, irrespective of CE or BA concentration. WR at 500°C increases with growing CE and BA concentrations. This might be ascribed to the fact that increase in hydroxyl groups of CE increases the number of urethane linkages. Moreover, NCO groups are quite reactive, which may create additional bonding to the urethane linkage.

Mechanical Behavior in Compression

Figures 10 and 11 show the foams compressive strength and modulus as a function of CE and BA concentrations for non
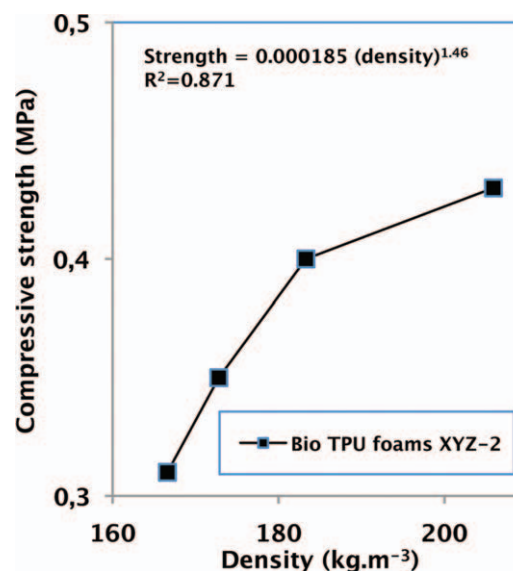

Figure 12. Compressive strength vs. density typical curve (Bio TPU foams XYZ-2(3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bio-based (a) and bio-based (b) TPU foams, and at different surfactant concentrations (c). When BA concentration increases at constant CE concentration, compressive strength and modulus of foam samples decrease. Reaction of BA with diisocyanate generates blowing gas (CO_2) accompanying exothermic reaction heat. Because of the increase of the temperature of the reactant mixture, the concentration of blowing gas in the mixture exceeds its solubility limit and a nucleation of bubbles begins. During the rise time, the already formed bubbles grow and new bubbles nucleate.[33,39] In consequence the increase in BA concentration induces the formation of numerous bubbles with larger size which leads to the reduction of the density, the compressive strength and modulus.

Besides, foam compressive strength and modulus increase with increasing CE concentration at constant BA concentration. This may due to the increase of hard segment content of the foam. As already mentioned above (section T_g), the hard segment is organized with urethane and a urea group, the soft segment is organized with a polyol group, and the urethane and urea group are more rigid than the polyol group. Upon surfactant addition, the compressive strength and modulus increases, and then remain similar with growing surfactant concentration.

It is generally known that the mechanical properties of a cellular material mainly depend on its density. Relationship between compressive strength and the density can be depicted by a simple power law [eq. (2)][24,37,40]

$$Strength = A(density)^B \qquad (3)$$

where A is a constant related to the temperature and physical properties of the resin and B is related to the deformation mechanics of cellular materials. Figure 12 shows that the compressive strength increases with increasing foam density. From Figure 12 using eq. (3), the value of "A" was deduced to be 0.000185 with coefficient of correlation found to be 0.871 and the density exponent value (B) was calculated to be 1.45. These values are quite similar to the values reported in the literature.[38,44] Thirumal et al.[38] reported the density exponent of 1.5 for compressive strength for the water blown polyurethane foams.

CONCLUSIONS

Development of bio-based thermoplastic polyurethane (TPU) foams was achieved by replacing the synthetic chain extender by its recently developed bio-based version. Foams were prepared by stirring polyether polyol (macrodiol), chain extender (diol), surfactant (silicone oil), blowing agent (distilled water), catalyst and diisocyanate. The concentration of chain extender, blowing agent, and surfactant were varied and their effects on foaming kinetics, physical, mechanical, and morphological properties of foams were investigated.

Foam density, compressive strength, and modulus decrease with increasing distilled water content and upon surfactant addition (independently of its concentration), and increase with growing chain extender concentration. The foam glass-transition temperature increases with increasing distilled water and chain extender concentrations. The foam cell size slightly increases with increasing distilled water content and decreases upon surfactant addition (without any dependence on concentration), whereas chain extender concentration has no effect on cell size. The improved compression strength and modulus with increasing chain extender concentration was ascribed to a combination of factors: high hard segment concentration, and improved hard domain ordering, and increase in glass-transition temperature.

All the properties of the developed foams were unaltered by the replacement of synthetic chain extender by bio-based one. Bio-based 1,3-propanediol can be used successfully for the preparation PU foams without sacrificing any properties. Also, the developed polyurethane foam formulations fulfill the requirements for reactive rotational molding, namely (i) reaction occurring at ambient temperature enabling reduced mould heating and cooling times, (ii) short product manufacturing time ($\sim$ 10–15 min), and (iii) and finally formation of a thermoplastic product. Further studies on the processing by reactive rotational molding of selected compositions of water-blown bio-based polyurethane foams are under progress in our laboratory.

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