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Synthesis and Characterization of Thermoplastic Polyurethaneureas based on Polyisobutylene and Poly(tetramethylene oxide) Segments

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New thermoplastic polyurethaneureas (TPUU) based on polyisobutylene (PIB) and poly(tetramethylene oxide) (PTMO) segments have been synthesized possessing tensile properties comparable to conventional PTMO based TPUs. PIB based TPUU containing 35 weight (wt)% hard segment was synthesized by chain extension of H_2N-Allyl-PIB-Allyl-NH_2 with 4,4′-methylene bis(phenylisocyanate) (MDI) and 1,4-butanediol (BDO) in toluene. The ultimate tensile strength (UTS) = 12 MPa and ultimate elongation = 70% were inferior to PTMO based polyurethane (UTS = 35 MPa, elongation at break = 600%). H_2N-Allyl-PIB-Allyl-NH_2 and HO-PTMO-OH in different proportions were chain extended in presence of MDI and BDO to obtain TPUUs containing 35 wt% hard segment. The polymers exhibited M_ns = 84000–138000 with polydispersity indices (PDIs) = 1.7–3.7. The UTS = 23–32 MPa and elongation at break = 250–675% was comparable to that of PTMO based polyurethane and significantly higher than the PIB based TPUU with the same Shore hardness. The Young's modulus of the polymers was strongly dependent and directly proportional to the PIB wt% in the SS of the TPUUs.

Keywords: Polyurea, elastomers, mechanical properties, biomaterials, polyisobutylene

1 Introduction

Segmented poly(ether urethanes) are one of the most important biomaterials owing to their design flexibility and ease of processing (1). Depending on the composition i.e., the volume fraction of the soft, elastomeric macrodiol, thermoplastic polyurethanes (TPUs) can be soft, rubbery or hard and rigid materials. They can be extruded, injection or compression molded or solution spun. Polyurethanes offer a broad range of physical- mechanical properties including high tensile and tear strength, chemical and abrasion resistance, good processibility, and protective barrier properties (2). However, these polymers are highly vulnerable to oxidative degradations (3).

Polyisobutylene (PIB) exhibits low glass transition temperature (T_g, $\sim -70°C$), high thermal, UV, oxidative and biostability and biocompatibility (4). Therefore efforts have been made to prepare PIB based polyurethanes and polyureas (5). Recently Kennedy and coworkers reported the synthesis of PIB polyureas using bis(4-isocyanatocyclohexyl) methane (HMDI) and α,ω-dialkylamines as chain extenders (6). However, the polymers exhibited low ultimate elongation (~100%) with adequate UTS (<20 MPa). Only the softest compositions with less than 10 wt% hard segments displayed adequate ultimate elongation (370–500%), however the UTS was very low (1.6–4 MPa). The poor mechanical properties may be attributed to the premature phase separation of hard (HS) and soft segment (SS) during synthesis resulting in a low molecular weight polymer (7). More recently, we have reported that the poor tensile properties of PIB based TPUs, which are also attributed to the low miscibility of the polar and apolar segments, can be significantly enhanced by substituting 10–30 wt% of PIB diol with PTMO diol (8). Kennedy and coworkers have also shown that, incorporation of 12 wt% of PTMO segment into PIB polyureas significantly improved the UTS to 29 MPa with 200% ultimate elongation (9). However, these polymers were processed by solution casting as polyureas generally exhibit melting temperatures above the decomposition temperature. We have recently reported the efficient synthesis of amino telechelic PIB with quantitative functionality (10). In this article, the synthesis and properties of PIB thermoplastic polyurethaneureas (TPUUs) are investigated relative to the PIB:PTMO soft segment composition.

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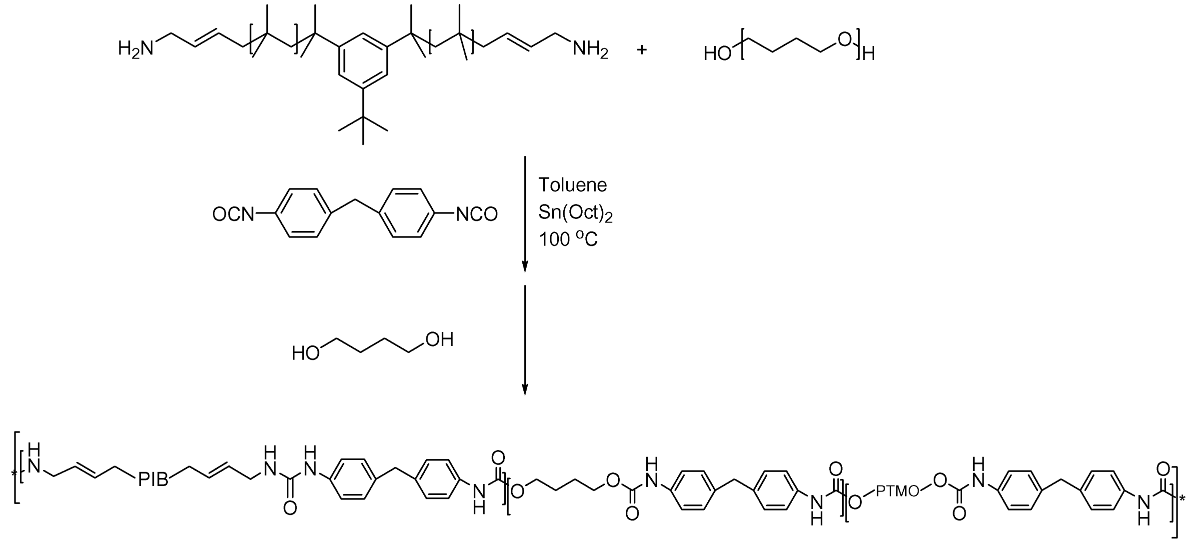
Table 1. Wt% of PIB and PTMO and GPC data of PIB-PTMO TPUU (Shore hardness ≈ 80A)

Code	H_2N-PIB-NH_2^a (wt% in SS)	HO-PTMO-OH[b] (wt% in SS)[c]	PTMO (wt% in TPUU)	M_n (GPC)	PDI (GPC)
PIB-80A	100	0	0	62000	3.5
PIB-PTMO-82-8	80	20	13	104000	1.8
PIB-PTMO-73-8	70	30	19	98700	2.5
PIB-PTMO-64-8	60	40	26	106500	2.8
PIB-PTMO-19-8	10	90	59	119000	1.6
Pellethane™ 2363-80A	0	100	—	142000	1.6

[a] H_2N-PIB-NH_2, $M_n = 2100$, [b] HO-PTMO-OH, $M_n = 1000$, [c] SS:HS = 65:35 wt%.



Scheme 1. Synthetic scheme for polyisobutylene (PIB) and poly(tetramethylene oxide) (PTMO) based thermoplastic polyurethaneurea (TPUU) using methylene bis(phenylisocyanate) (MDI) and 1,4-butanediol (BDO) as chain extender.

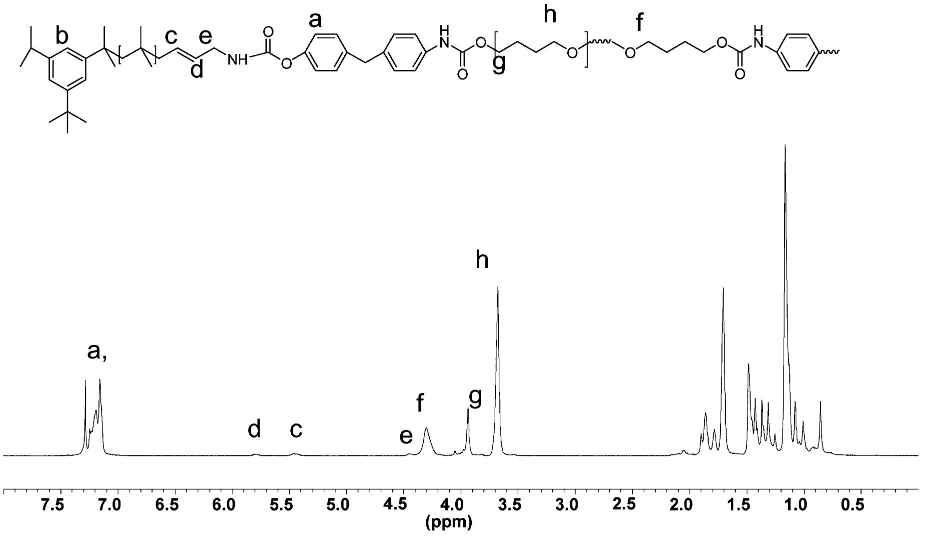


Figure 1. ^{1}H-NMR spectrum of PIB-PTMO-82-8 recorded in $CDCl_3$+TFA-D mixture.

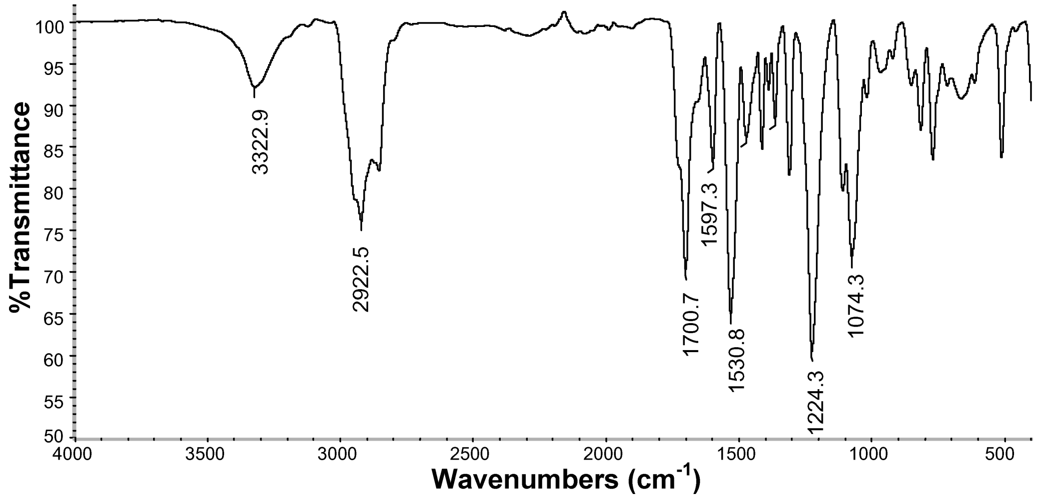


Figure 2. FT-RI trace of PIB-PTMO-82-8 thin film.

2 Experimental

2.1 Materials

Phthalimide, potassium derivative (Aldrich, 98%), 5-tert-butyl-isophthalic acid (Aldrich, 98%), methylmagnesium bromide (Aldrich, 3.0M solution in diethyl ether), diethyl ether (Aldrich, anhydrous, ≥99%), hydrochloric acid (Mallinckkrodt, 36.5–38%), Sn(Oct)$_2$ (stannous octoate, Polyscience), tetra-n-butylammonium bromide (TBAB, Alfa Aesar, 98+%), 4,4′-methylenebis(phenylisocyanate) (MDI, Aldrich, 98%), toluene (Aldrich, 99%), chloroform (Aldrich, ≥99.8%), Terathane® 1000 polyether glycol (Aldrich, $M_n = 1000$), 1,3-butadiene (BD, Aldrich, 99+%), LiBr (lithium bromide ReagentPlus, Aldrich, ≥99%), titanium tetrachloride (TiCl$_4$, Aldrich, 99.9%), and 2,6-di-*tert*-butylpyridine (DTBP, Aldrich, 97%) were used as received. Pellethane™ 2363–80A was received from Dow Chemical Co. Sodium azide, potassium hydroxide, hydrazine hydrate and potassium carbonate were purchased from Aldrich as reagent grade chemicals and were used without further purification. Tetrahydrofuran (THF) was dried by refluxing over sodium metal and benzophenone. Methanol was dried by refluxing over activated magnesium and iodine. Hexanes were refluxed in presence of concentrated sulfuric acid for 48 h. The organic layer was separated and washed with basic aqueous solution till neutral. The organic fraction was passed over sodium sulfate and distilled over calcium hydride prior to use. All the solvents were again distilled under nitrogen atmosphere prior to use.

Moisture sensitive reactions were carried out under a dry nitrogen atmosphere or in an Mbraun 150-M glove box (Innovative Technology Inc., Newburyport, Massachusetts).

2.2 Measurements

^{1}H-NMR spectroscopy for structural analysis was carried out on a Bruker 500 MHz spectrometer using mixture of CDCl$_3$ (Cambridge Isotope Laboratories, Inc.) and CF$_3$COOD as solvent. Molecular weights were measured with a Waters HPLC system equipped with a model 510 HPLC pump, model 410 differential refractometer, model 441 absorbance detector, on-line multi-angle laser light scattering (MALLS) detector (MiniDawn, Wyatt Technology Inc.), Model 712 sample processor, and five Ultrastyragel GPC coulmns connected in the following series: 500, 10^3, 10^4, 10^5, and 100Å. THF:TBAB (98:2, wt:wt) was used as a carrier solvent with a flow rate of 1mL/min. An AVATAR 370 FT-IR spectrometer was used to record the FT-IR spectra of the samples either in dry CCl$_4$ solutions or thin films on a NaCl pellet. Static tensile properties Young's modulus, UTS, and elongation were measured at room temperature (~25°C) and atmospheric conditions with a 50 N load cell on an Instron Model Tensile Tester 4400R at 50 mm/min extension rate. All tests were carried out according to ASTM D412. Samples were cut into dog-bone shape using an ASTM standard die. All samples were kept at room temperature and atmospheric conditions prior to testing. The polymers were compression molded at 160°C for 10 min using 17000–20000 lb in a Carver model C press equipped with thermostatic temperature control and a load capacity of 12 ton. The sample was weighed (approximately 1.5 g) and placed within a thin rectangular aluminum mold between a teflon coated aluminum foil. The aluminum foil containing the sample was then placed between the heated platens. The lower platen was raised and a load of about 20,000 lbs was applied. The load was released immediately and reapplied to enable venting of trapped air. After 8 min, the load was released and the sample was removed and kept immediately in a desiccator and allowed to cool to room temperature. The film formed was then removed carefully from the aluminum foil. The DSC analysis of the block copolymers were carried out in a Q100 TA instrument. The samples were heated and cooled under nitrogen atmosphere. The sample size was

Table 2. Solubility data of PIB-PTMO TPUU (Shore hardness ≈ 80A)

Polymer	*Chloroform/TFA 80/20*	*Xylene/DMF 80/20*	*THF (TBAB)*	*Chloroform*	*DMF*
xPIB-PTMO-19-8	++	−	++	−	−
PIB-PTMO-64-8	++	+−	++	−	−
PIB-PTMO-73-8	++	+−	++	−	−
PIB-PTMO-82-8	+−	+−	++	−	−

++ soluble, +− sparingly soluble, − insoluble.

maintained between 4–8 mg. The heating rate of 10°C/min was used unless otherwise noted. The data were recorded in "exo up" mode.

2.3 Synthesis of PIB-PTMO TPUU (Shore hardness ≈ 80A)

PIB-PTMO-82-8 was synthesized as follows. H_2N-Allyl-PIB-Allyl-NH_2 ($M_n = 2100$, 5.0 g, 2.38 mmol) and PTMO diol ($M_n = 1000$, 1.3 g, 1.3 mmol) were dried from a toluene solution by azeotropic distillation of toluene (10 mL). The mixture was kept at 45°C for 3 h under vacuum. To it, 25 mL of dry toluene was added followed by $Sn(Oct)_2$ (42 mg, 0.104 mmol) in toluene. The mixture was heated at 80°C under a slow stream of dry nitrogen gas. To it, MDI (2.6 g, 10.4 mmol) was added and the mixture was stirred vigorously for 30 min. To it, BDO (605 mg, 6.72 mmol) was added and the mixture was stirred for 4 h at 100°C. The mixture was cooled to room temperature, poured in a teflon mold and the solvent was evaporated at room temperature in air for 48 h. Finally, the polymer was dried under vacuum at 50°C for 12 h. ^{1}H-NMR ($CDCl_3$, ppm, δ): 7.2 (s, Ar), 7.14 (s, Ar), 5.9 (p, $-CH{=}CH-CH_2OCONH-$), 5.6 (p, $-CH{=}CH-CH_2OCONH-$), 4.4 (s, p, $-CH{=}CH-CH_2NHCONH-$), 4.3 (s, $-HN-COO-CH_2-$), 3.95 (s, $-C_6H_4-CH_2-C_6H_4-$), 2.0 (d, 2H, $C(CH_3)_2CH_2CH{=}$), 1.5–14 (br, $-CH_2C(CH_3)_2-$), 1.2–1.1 (br, $-CH_2C(CH_3)_2-$).

3 Results and Discussion

3.1 Synthesis

The aminoallyl telechelic PIB ($M_n = 2100$) was prepared from chloroallyl telechelic PIB ($M_n = 2100$) by nucleophilic substitution with phthalimide potassium followed by hydrolysis with hydrazine hydrate under reflux conditions as reported before (10) H_2N-Allyl-PIB-Allyl-NH_2 and HO-PTMO-OH were chain extended with MDI and BDO to obtain a series of thermoplastic polyurethaneurea (TPUU) by adding BDO as the last reagent (Scheme 1). The 35:65 (wt:wt) hard: soft composition was maintained and the PIB:PTMO (wt:wt) ratio in the soft segment was varied. Toluene was used as the solvent for all chain extension reactions and the polymerization temperature was maintained at 100°C. The polymer compositions, molecular weights and PDIs are listed in Table 1.

In the ^{1}H-NMR spectra, a new resonance at 4.45 ppm for $-C\boldsymbol{H}_2NHCONH-$indicated successful polyurethaneurea synthesis (Fig. 1). The peak at 3.3 ppm accountable to aminomethylene proton disappeared indicating consumption of all amino chain-ends during synthesis. Peaks at 3.95, 4.3 and 3.7 ppm for $-C_6H_4-C\boldsymbol{H}_2-C_6H_4-$, $-NHCOO-C\boldsymbol{H}_2-C_3H_6OCO-$and $-COOC\mathit{H}_2-C_3H_6OCH_2-$were also observed indicating the incorporation of MDI, BDO and PTMO unit in the polymer backbone. In FT-IR spectrum of PIB-PTMO-82-8, the carbonyl stretching frequency of free −NHCONH-linkage was observed as a broad band around 1700 cm^{-1} (Fig. 2). Another peak at 1600 cm^{-1} was also observed for the strongly hydrogen-bonded carbonyl group of urea linkage. The shift in stretching frequencies of carbonyl group upon hydrogen bonding has been previously described

Table 3. DSC analysis of PIB-PTMO TPUUs (80A)

Polymer	T_{g1}(°C)	T_{g2}(°C)	T_{m1}(°C)	T_{m2}(°C)
PIB-80A	−51.6	58.2	—	187,214
PIB-PTMO-82-8	−52.3	61.8	—	181.9
PIB-PTMO-73-8	−53.2	63.5	134,164	182,210
PIB-PTMO-64-8	−46.1	56.0	—	181
PIB-PTMO-19-8	−41.3	58.3	148,159	—
Pellethane^{TM} 2363-80A	−43.5	—	137.7	—

Table 4. Static tensile properties of PIB-PTMO TPUUs (80A)

Code	*Shore A*	*UTS (MPa)*	*Young's Modulus (MPa)*	*Elongation at break (%)*
PIB-80A	82	12	54	70
PIB-PTMO-82-8	86	23	50	250
PIB-PTMO-73-8	85	26	30	310
PIB-PTMO-64-8	89	32	21	420
PIB-PTMO-19-8	86	29	5	675
Pellethane^{TM} 2363-80A	80	35	8	640

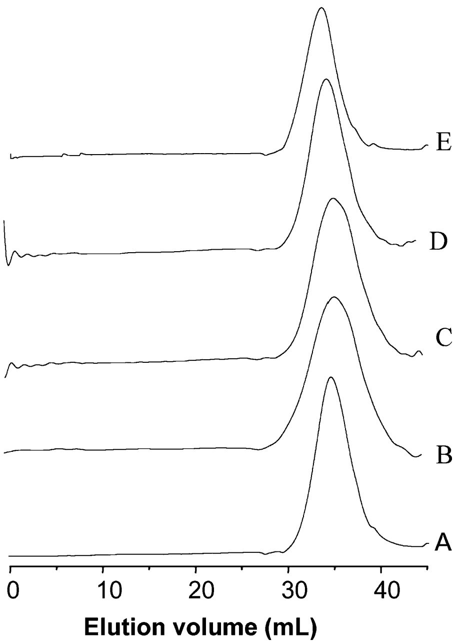


Figure 3. GPC-RI traces of (A) PIB-PTMO-82-8, (B) PIB-PTMO-73-8, (C) PIB-PTMO-64-8,(D) PIB-PTMO-19-8 and (E) Pellethane 2363-80 A recorded in THF:TBAB mixture

by Meijer and coworkers in PTMO polyetherurea based systems (11). The –NH stretching frequencies were observed around 3300 cm^{-1}. All TPUUs were soluble in TBAB/THF (2/98, wt/wt) solution and most of the TPUUs except PIB-PTMO-82-8 were soluble in warm TFA/CHCl$_3$ solution (Table 2). However, the time (48 h at 50°C) required for dissolution in THF/TBAB (98/2, wt/wt) was relatively longer compared to TPUs (6 h at 50°C) with similar Shore hardness (8).

The GPC-RI traces were monomodal in all cases with M_ns = 84000–138000 and PDIs = 1.7–3.7 (Fig. 3). The commercial PTMO based TPU (Pellethane^{TM} 2363-80A) also exhibited similar M_n (= 142000) and PDI (= 1.6).

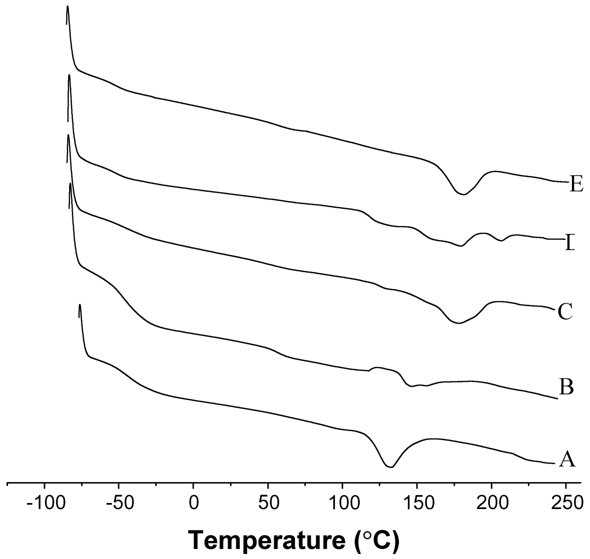


Figure 4. DSC first heating trace of (A) Pellethane 2363-80A, (B) PIB-PTMO-19-8, (C) PIB-PTMO-64-8, (D) PIB-PTMO-73-8 and (E) PIB-PTMO-82-8 recorded under N$_2$ atmosphere at 10°C/min heating rate.

3.2 DSC Analysis of PIB-PTMO TPUUs (Shore 80A)

The results of DSC analysis of the PIB-PTMO TPUUs with Shore 80A hardness are shown in Table 3 and Figure 4. All TPUUs exhibited two T_gs for the SS and HS. The TPUUs with higher PIB content exhibited the T_{g1} around −51°C, whereas for TPUUs having higher PTMO wt%, the T_{g1} was observed around −41°C. This suggested a partial phase mixing of SS and HS that is responsible for the increase in T_g of SS. In case of TPUUs with higher PTMO content, the extent of phase mixing was higher and hence a larger shift in T_{g1}. The T_g for the HS (T_{g2}) was observed in the range of 56-63°C. The TPUUs mostly exhibited T_{m1} (140–180°C, -MDI-BDO-MDI-) and T_{m2} (180–220°C, -MDI-BDO-MDI-BDO-MDI-). T_{m3} [220–250°C, (-MDI-BDO-)$_{3-4}$] was absent in all cases (Table 3). PIB-PTMO-82-8 and

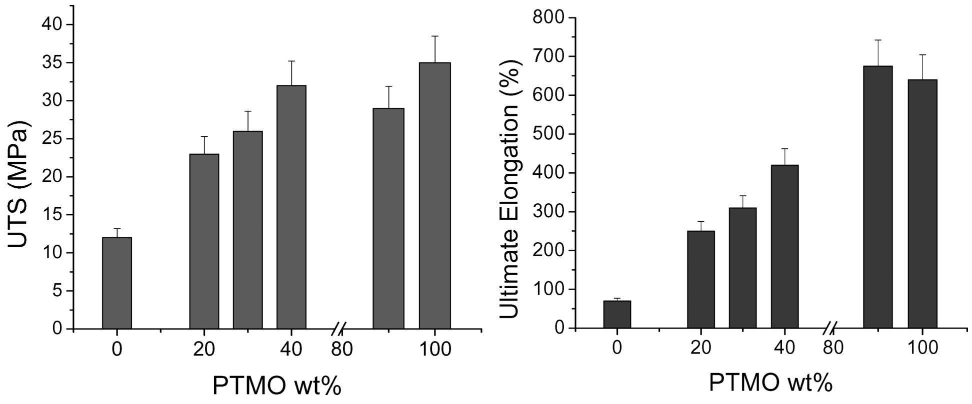


Figure 5. Correlation of UTS and % elongation with PTMO wt% in PIB-PTMO TPUU (Shore hardness ≈ 80A). The TPU with PIB/PTMO = 0/100 (wt%) is Pellethane^{TM} 2363-80A received from Dow Chemicals Co.

PIB-PTMO-64-8 exhibited a single T_m whereas PIB-PTMO-73-8 showed multiple T_ms. The T_m of the TPUUs with higher PIB wt% in the SS was observed at ~ 180°C, whereas the polymer with higher PTMO wt% in the SS (PIB-PTMO-19-8) exhibited T_m at 150°C. The lower T_m indicated the absence of higher order HS and a more uniform distribution of HS and SS in the polymer. However, PIB-TPUU exhibited two T_ms at 187 and 214°C, respectively.

3.3 Tensile Properties of PIB-PTMO TPUUs (80A)

The tensile properties of PIB-PTMO TPUU are described in Table 4. The Shore A hardness (85–89) of the TPUUs was higher compared to the PIB-PTMO TPUs with similar HS wt%, which may be due to the higher degree of hydrogen bonding in the urea linkages compared to urethanes (8). The UTS of the polymers (23-32 MPa) was significantly higher than that of the PIB-TPUU (12 MPa) and increased with the increase in PTMO wt% in SS of the polymers. The ultimate elongation at break also exhibited a similar trend and increased from 250 to 675% with the increase in PTMO wt% in SS, whereas the ultimate elongation of PIB-TPUU was only 70%. However, the Young's modulus of the TPUUs decreased with increase in PTMO wt% from 8 MPa for Pellethane^{TM} 2363-80A to 54 MPa for PIB-80A (Table 4). Figure 5 shows the effect of PTMO wt% on the UTS and ultimate elongation. Incorporating 20 wt% of PTMO in the SS doubled the UTS of the resulting polymer and also increased the ultimate elongation by ~100%. However, a minimum of 40 wt% of PTMO in the SS was essential to reach the plateau in the UTS.

4 Conclusions

Thermally processable TPUUs with mechanical properties comparable to conventional PTMO based polyurethanes can be synthesized by chain extension of PIB-diamine/PTMO-diol mixture. The DSC analysis shows phase separation of SS and HS by displaying two T_gs at ~ −50°C and 60°C. The ultimate tensile strength and elongation at break are comparable to Pellethane^{TM} 2363-80A and strongly depend on the PIB:PTMO ratio in the SS.

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