

# Seawater Degradable Thermoplastic Polyurethanes

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Received 8 June 2009; accepted 23 August 2009

DOI 10.1002/app.31343

Published online 7 October 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Degradable thermoplastic polyurethane (TPU) elastomers incorporating poly(D,L-lactide-co-glycolide) (PLGA) were synthesized and characterized. The soft segments consisted of a mixture of poly(butylene adipate) (PBA) and PLGA with PBA/PLGA ratios of 100/0, 75/25, and 50/50 wt %. Two PLGA polyesters were used. BD-PLGA was initiated from butanediol; whereas BHMBA-PLGA was initiated from 2,2-bis-(hydroxymethyl)butanoic acid. The hard segments consisted of dicyclohexylmethane-4,4'-diisocyanate (H<sub>12</sub>MDI) and 1,4-butanediol (BD). The hard segment content, expressed as the weight ratio of BD to polyol used in the TPU formulation, was set either at 8 or 12% (31.2 or 38.1% hard segment by weight, respectively). In all cases initial [NCO]/[OH] ratio was 1.03. The tensile modulus of the TPUs ranged from 9 to 131 MPa and ultimate strains ranged from 100 to 750%. DMA was

used to probe the thermomechanical transitions of the TPUs and indicated useful application temperatures from well below zero up to 60–80°C depending on the formulation. Hydrolytic degradation of the TPUs was tested in seawater at 37°C. All of the PLGA-containing TPUs showed enhanced degradation compared to those with only PBA as the soft segment. The latter compositions remained essentially unchanged throughout the test while the PLGA-containing TPUs lost as much as 45% of their initial mass in 153 days. Molecular weights of TPUs containing degradable polyols were lower than those derived from 100% PBA polyol. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1873–1880, 2010

**Key words:** biodegradable; polyurethanes; seawater degradable; poly(D,L-lactide-co-glycolide)

## INTRODUCTION

Large volumes of plastic waste are generated aboard military, merchant, and pleasure vessels at sea, particularly film used for pallet stretch wrap and food packaging. This waste currently must be stored onboard the ships until port is made, and this represents a significant cost in labor and storage space. Biodegradable plastics that could be safely and ecologically disposed of at sea represent a strategic solution to this problem.

Biodegradable polymers were originally developed for surgical use within the human body and most of these materials consist of hydrolytically unstable polyesters with physical properties suitable for moderate-strength fibers and/or brittle plastics, depending upon their composition and degree of crystallinity.<sup>1</sup> Well-known examples are poly(L-lactic acid) (PLLA) and poly(glycolic acid), both of which are semicrystalline fiber-forming polyesters.

Hydrolytic degradation of these conventional biodegradable polymers in salt water is very slow,<sup>2</sup> but degradation can be accelerated through the use of copolymers and blends, which decreases crystallinity, and by the inclusion of hydrophilic groups such as carboxylic acid.<sup>3</sup>

In recent years, there has been a great deal of interest in the development of thermoplastic polyurethanes (TPUs) that are rendered degradable by the incorporation of hydrolytically unstable polyester chain segments.<sup>4–17</sup> TPUs are created through the reaction of a diisocyanate with a mixture of a chain-extending diol (and/or diamine) and a polymeric polyol. TPUs typically possess a phase separated morphology caused by thermodynamic incompatibility between the so-called hard segments (HS) and soft segments (SS). The HS are composed of alternating diisocyanate and chain extender residues, and the SS are the polyol residues.<sup>18</sup> The properties of TPUs are readily tunable to span a range of physical properties from elastomeric, to plastic, to high-strength fiber, by varying the amount and composition of each segment. Thus TPUs represent a convenient means of incorporating biodegradable polyester chain elements into a family of polymers whose properties can be readily tuned for a variety of applications, including soft plastic and

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Contract grant sponsor: Naval Research Laboratory/  
NAVSEA; contract grant number: N00173-06-2-C008.  
Contract grant sponsor: Robert M. Hearin Foundation.

elastomeric applications for which traditional biodegradable polymers are ill-suited.

Aliphatic isocyanates are preferred for degradable TPUs due to the toxicity of aromatic diamines, which are the presumed degradation products of an aromatic polyurethane.<sup>6</sup> Aliphatic isocyanates that have been used to create biodegradable polyurethanes include 1,4-butanediisocyanate,<sup>11,14,15</sup> 1,6-hexanediisocyanate,<sup>10,13</sup> and ethyl (or methyl) 2,6-diisocyanatohexanoate (L-lysine diisocyanate, ethyl ester) (LDI).<sup>5,6,9,10,12</sup> The latter is particularly desirable from a toxicity standpoint since its ultimate degradable product is expected to be the naturally-occurring amino acid, L-lysine. However, we have shown that LDI-based polyurethanes have an upper use temperature of only about 60°C,<sup>12</sup> which precludes its use in most nonbiomedical, consumer plastics applications. In this article we describe the synthesis, characterization, and degradation of TPU elastomers based on dicyclohexylmethane-4,4'-diisocyanate (H<sub>12</sub>MDI) and a mixed polyol system-consisting of poly(butylene adipate) (PBA) and poly(D,L-lactide-co-glycolide) (PLGA).

## EXPERIMENTAL

### Materials

1,4-Butanediol (≥99%, BD), 2,2-bis(hydroxymethyl)butanoic acid (98%, BHMBA), dibutyl tin dilaurate (98%, DBTDL), tin(II) 2-ethylhexanoate (95%, SnOct), anhydrous dichloroethane (99.8%), 1-methylimidazole (≥99%, NMI), oxalyl chloride (98%), 4-(dimethylamino)pyridine (99%, DMAP), seawater (sterile, filtered), and anhydrous *N,N*-dimethylformamide (99.8%, DMF) were used as received from Sigma-Aldrich. D,L-lactide (≥99.5%) and glycolide (≥99.5%) were generously donated by Ortec, Inc., in Easley, SC, and were used as received. Dicyclohexylmethane-4,4'-diisocyanate (≥99.5%, H<sub>12</sub>MDI, Bayer Desmodur® W) was fractionally vacuum distilled and stored under nitrogen before use. Commercial poly(butylene adipate) (PBA, Bayer Desmophen® 2502) was used as received.

### Synthesis of degradable polyols

Poly(D,L-lactide-co-glycolide) (PLGA)

The following is a representative procedure for the synthesis of a 50/50 (mol/mol), 2,000 g/mol PLGA polyol carried out within a Vacuum Atmospheres Company Dri-Lab glove-box under an inert N<sub>2</sub> atmosphere. D,L-lactide, 52.896 g, and glycolide, 42.598 g, were charged to a 2-necked 250 mL round-bottom flask fitted with a mechanical stirrer. The reactor was submerged in a 150°C silicone oil bath, and the contents were stirred for 20 min to fully

melt the monomers. Then, 4.506 g of BD and 0.034 g of SnOct were added to the flask, and the mixture was allowed to react with stirring for 3 h. The product was then poured into a storage container and stored under vacuum.

### Synthesis of degradable TPUs

The following is a representative procedure for the synthesis of an H<sub>12</sub>MDI TPU carried out in a Vacuum Atmospheres Company Dri-Lab glove-box under an inert N<sub>2</sub> atmosphere. A 250 mL beaker was charged with 6.23 g of PBA, 6.23 g of PLGA and 100 mL of DMF. This mixture was set aside to allow the polyols to dissolve. A two-neck 250 mL round-bottom flask was charged with 100 mL of DMF, 6.162 g of H<sub>12</sub>MDI, 1.494 g of BD, and 0.032 g of DBTDL. The flask was then submerged into a 40°C silicone oil bath and fitted with a mechanical stirrer. The contents of the flask were allowed to react with stirring for 30 min after which the previously weighed polyol solution was added and the reaction was continued for an additional 22 h. Upon completion of the reaction, the DMF was removed by rotary evaporation. The resultant polymer was then dissolved in chloroform and poured into a 300 mL polytetrafluoroethylene (PTFE) dish. The dish was then placed in a room temperature vacuum oven to remove chloroform.

### Instrumentation

Relative molecular weights and polydispersity index (PDI) of polymers were determined using a calibration curve derived from PMMA standards in the range of 1300–910,500 g/mol and a GPC system consisting of a Waters Alliance 2695 Separations Module, a Waters 2410 refractive index detector, and two Polymer Laboratories HFIPgel columns connected in series. Freshly distilled 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were 5–30 mg/mL in freshly distilled HFIP, and the injection volume was 50 µL.

Solution <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were obtained on a Varian Mercury 300 MHz spectrometer using 5 mm o.d. tubes with sample concentrations of 10–20% (w/w) in deuterated chloroform (CDCl<sub>3</sub>) (Aldrich Chemical Co.) containing tetramethylsilane as an internal reference.

### Mechanical properties characterization

Films of each sample were made using a hot press at 140–150°C and a 10.2 cm × 10.2 cm × 1 mm mold covered with PTFE film using 5000 psi clamping

force. Mini-dog-bone specimens were then cut out of the films using a stamping tool.

Dynamic mechanical analysis (DMA) was utilized to determine the viscoelastic transition temperatures of the TPUs. A TA instruments DMA Q800 was operated in film tension geometry mode with sample thickness between 0.9 and 1.0 mm. Two films of each sample were tested at a frequency of 1 Hz and an oscillation amplitude of 5  $\mu\text{m}$  at a heating rate of 2°C/min from -80 to 150°C.

Mechanical tensile stress versus strain measurements were conducted using a Material Testing System Alliance RT/10 and analyzed using an MTS Testworks 4 software package. Mini-dog-bone specimens were clamped using AL 2000N pneumatic grips set at 60 psi. The tests were conducted using a 1 kN load cell and a strain rate of 10 mm/min. Three specimens were tested for each material.

### Hydrolytic degradation analysis

Multiple disks (typically 10–15) of a given polyurethane were cut from the 1 mm thick melt-pressed film using a 19 mm diameter circular punch. Each disk was placed into a separate glass screw-cap jar (125 mL) filled with 100 mL of seawater. The jars and their contents were then placed into an incubator held at a constant temperature of 37°C. At a predetermined time interval (typically every two weeks), a single disc was removed from the seawater and placed into a preweighed polystyrene weighing dish. The disk was brought to constant mass in a vacuum oven, after which percent remaining mass ( $m_r$ ) was calculated using the following equation:

$$m_r = \left( \frac{m_{\text{dry}}}{m_0} \right) \times 100 \quad (1)$$

where  $m_{\text{dry}}$  is the mass of the sample after drying and  $m_0$  is the initial mass before immersion. At long degradation times, some disks became fragmented. In these cases, the pieces were captured on a tared,

fritted-glass filter and brought to constant weight. The degradation experiments were carried out for 20–22 weeks.

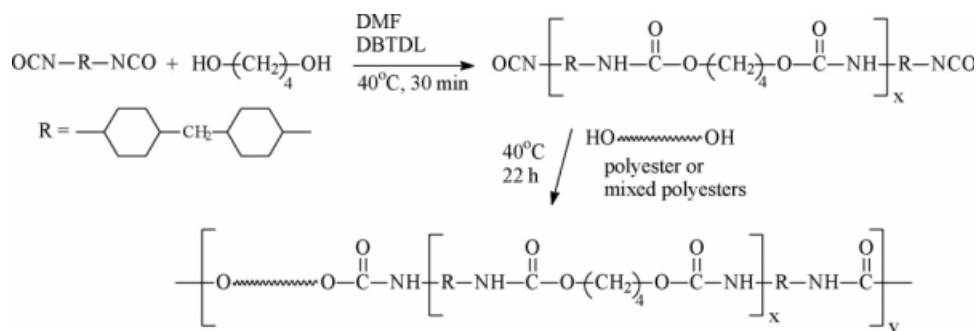
## RESULTS AND DISCUSSION

### Synthesis

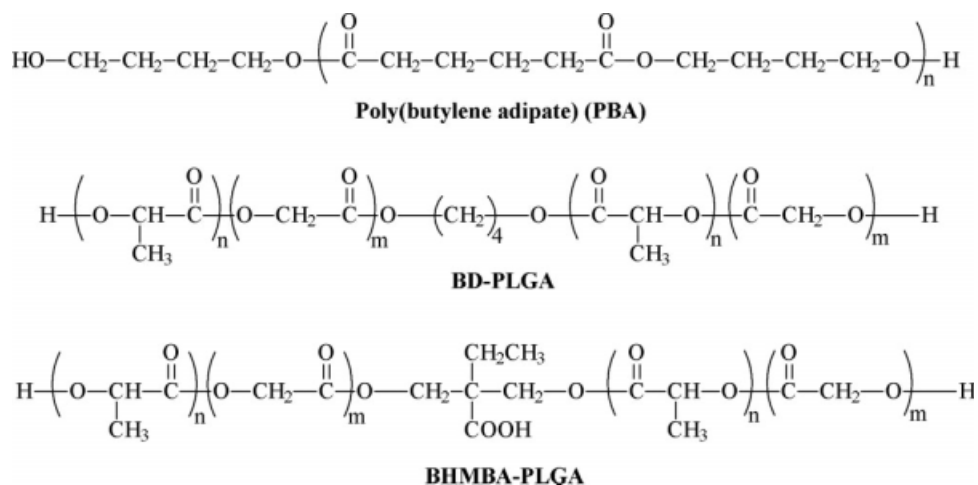
Scheme 1 outlines the synthesis of biodegradable TPUs. All possessed HSs derived from BD and the aliphatic diisocyanate, H<sub>12</sub>MDI. Since the parent diamine would be among the potential degradation products of a degradable polyurethane, the less toxic aliphatic diisocyanate was favored over an aromatic diisocyanate such as 4,4'-methylenebis(phenylisocyanate) (MDI). Polymerizations were carried out in DMF solution at 40°C using a two-stage process in which BD and H<sub>12</sub>MDI were pre-reacted before addition of the polyol.

Three different polyester polyols (Scheme 2) were used in the TPU syntheses, all with number average molecular weight of 2,000 g/mol. A commercial PBA, served as the base (nondegrading control) polyol. Degradable TPUs were created by substitution of a portion of the PBA with one of two 50/50 mol/mol, random copolyester, PLGA-based polyols: BD-PLGA and BHMBA-PLGA. Mixed polyols were used in this fashion to achieve a good balance of physical, thermal, and degradative properties. As shown in Scheme 2, BD-PLGA was initiated from DB; whereas BHMBA-PLGA was initiated from 2,2-bis(hydroxymethyl)butanoic acid, which places a pendant carboxylic acid group along the backbone of the polyol,<sup>3</sup> and is predicted to yield an increased rate of water uptake and increased overall rate of degradation of the polyol.

Table I lists the various TPUs that were produced. The polyurethanes of Table I were synthesized at two different hard segment (HS) contents, designated 8 and 12%. As used herein, this parameter refers to the weight of chain extender (BD) times 100%, divided by the weight of polyol, used during TPU formation. In terms of actual weight



**Scheme 1** Synthesis of H<sub>12</sub>MDI-based TPUs.



**Scheme 2** Three polyester polyols used in TPU synthesis.

percentages, this translates into 31.2 and 38.1 wt % hard segment in the TPU, respectively. In all cases the initial [NCO]/[OH] ratio during the polymerization was 1.03. The sample designation used in Table I takes the form H-xxx/yy-I, where H is either 8 or 12% HS, xxx is the percentage of PBA polyol, yy is the percentage of PLGA polyol, and I, if applicable, indicates the initiator used to synthesize the PLGA, either BD or BHMBA.

### Characterization

$^{13}\text{C}$ -NMR was used to monitor the isocyanate-to-urethane conversion and to verify the incorporation of polyol components. Figure 1 shows a representative partial spectrum of A)  $\text{H}_{12}$ MDI and B) 12-50/50-BHMBA. The isocyanate peak of  $\text{H}_{12}$ MDI is visible at 122.3 ppm in spectrum A. The TPU spectrum (B) shows no isocyanate present as well as the formation of a urethane peak at 156.0 ppm. The carbonyl carbons of the two polyols are also present in spectrum B, butylene adipate at 173.2 ppm, and

the PLGA lactoyl units at 169.2 ppm and the glycol units at 166.5 ppm.

Molecular weight and PDI of the synthesized polymers, relative to PMMA standards, were evaluated using HFIP GPC, and the results are listed in Table I. HFIP was used as the mobile phase because the more common GPC solvents, such as THF, did not dissolve the polymers. Representative chromatograms are displayed in Figure 2. The chromatogram of the TPU synthesized with BA as the polyol is compared to the BA polyol to show the observed increase in molecular weight. The data in Table I show that the inclusion of PLGA causes a depression in molecular weight of the resulting TPU. This phenomenon was suspected to be caused by the presence of less reactive, secondary hydroxyl groups at the PLGA chain ends.

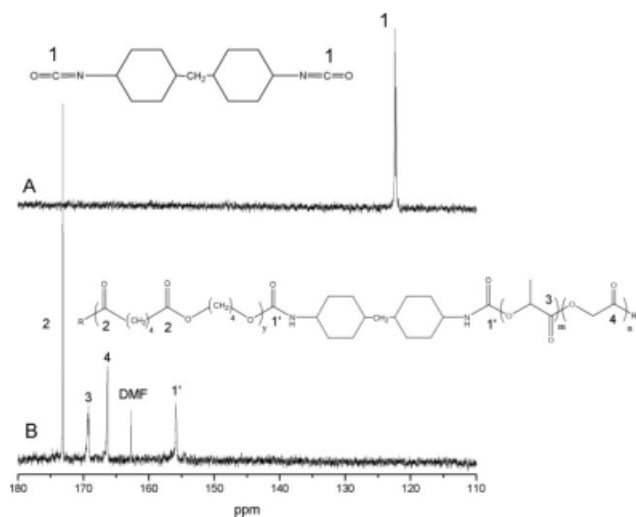
Dynamic mechanical analysis (DMA) was used to probe the thermomechanical properties of the TPUs, revealing thermal transitions and indicating useful temperature ranges. Figures 3 and 4 show storage modulus versus temperature (upper) and  $\tan \delta$

**TABLE I**  
**Composition, Molecular Weights, Tensile Properties, and  $T_g$  from DMA for Degradable TPUs**

Entry	TPU	HFIP GPC			Modulus (MPa)	Energy to break (N*m)	Peak stress (MPa)	Ultimate strain (mm/mm)	$T_g$ (DMA) ( $^{\circ}\text{C}$ )
		$M_n$ (g/mol)	$M_w$ (g/mol)	PDI					
1	8-100/0	33,900	104,1005	3.07	$20 \pm 12$	$8.8 \pm 0.6$	$23 \pm 3$	$7.5 \pm 0.4$	-27
2	8-75/25-BHMBA	12,900	24,100	1.87	$15 \pm 1$	$3.3 \pm 0.1$	$10 \pm 0$	$5.5 \pm 0.1$	5
3	8-75/25-BD	18,400	36,400	1.98	$9 \pm 0$	$3.3 \pm 1.7$	$10 \pm 4$	$6.1 \pm 2.6$	-8
4	8-50/50-BHMBA	8,700	20,500	2.35	$131 \pm 4$	$0.5 \pm 0.1$	$7 \pm 0$	$1.1 \pm 0.2$	5
5	8-50/50-BD	16,200	36,000	2.22	$37 \pm 4$	$1.9 \pm 0.4$	$6 \pm 1$	$4.0 \pm 0.6$	-7
6	12-100/0	71,300	145,900	2.05	$13 \pm 2$	$6.9 \pm 2.3^a$	$20 \pm 3^a$	$6.1 \pm 0.9^a$	-27
7	12-75/25-BHMBA	12,300	29,600	2.42	$30 \pm 5$	$4.8 \pm 2$	$19 \pm 4$	$5.2 \pm 1.3$	-
8	12-75/25-BD	11,900	42,600	3.58	$27 \pm 1$	$6.5 \pm 0.8$	$22 \pm 2$	$6.0 \pm 0.4$	-
9	12-50/50-BHMBA	8,100	17,300	2.12	$94 \pm 9$	$2.9 \pm 0.1$	$12 \pm 0.3$	$3.4 \pm 0.1$	-
10	12-50/50-BD	11,500	35,400	3.09	$49 \pm 3$	$2.8 \pm 0.0$	$13 \pm 0$	$3.4 \pm 0.1$	-

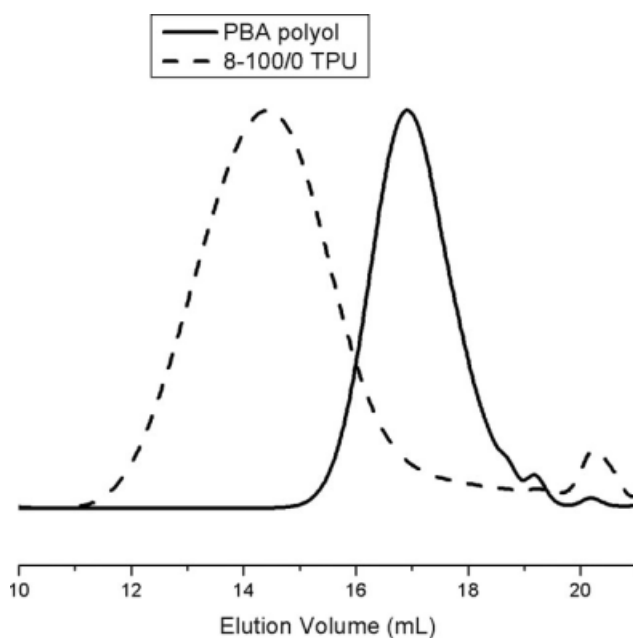
<sup>a</sup> Sample pulled out of grips before failure.





**Figure 1** Carbonyl region of  $^{13}\text{C}$ -NMR spectrum of (A)  $\text{H}_{12}\text{MDI}$  and (B) 12-50/50-BHMBA TPU (Entry 9, Table I).

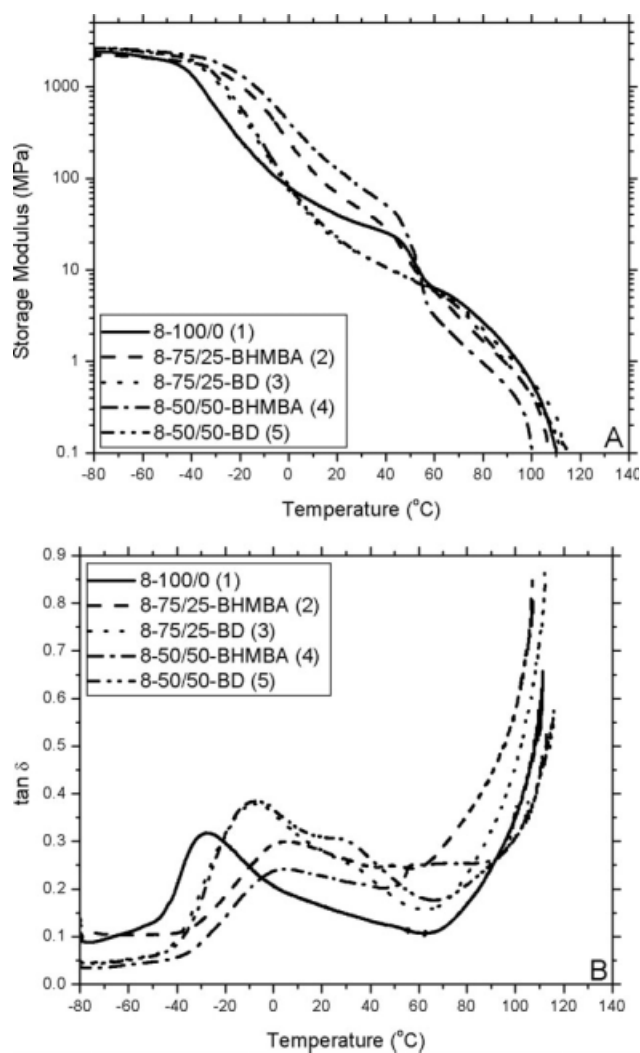
versus temperature plots (lower) for the 8% and 12% HS TPUs, respectively. In general, the  $\alpha$ -relaxation process, indicated by the low temperature peak in the  $\tan \delta$  plots and representing the glass transition of the soft segment domains, was very broad, suggesting only fair phase separation between soft and hard domains. For all of the 8% HS TPUs and the 12-100/0 control TPU (Entries 1-6 in Table I), this peak was sufficiently defined to allow assignment of a glass transition temperature ( $T_g$ ) based on the position of the peak maximum. These  $T_g$  values are included in Table I, and it is clear that the inclusion of PLGA raises the  $T_g$  significantly above the value



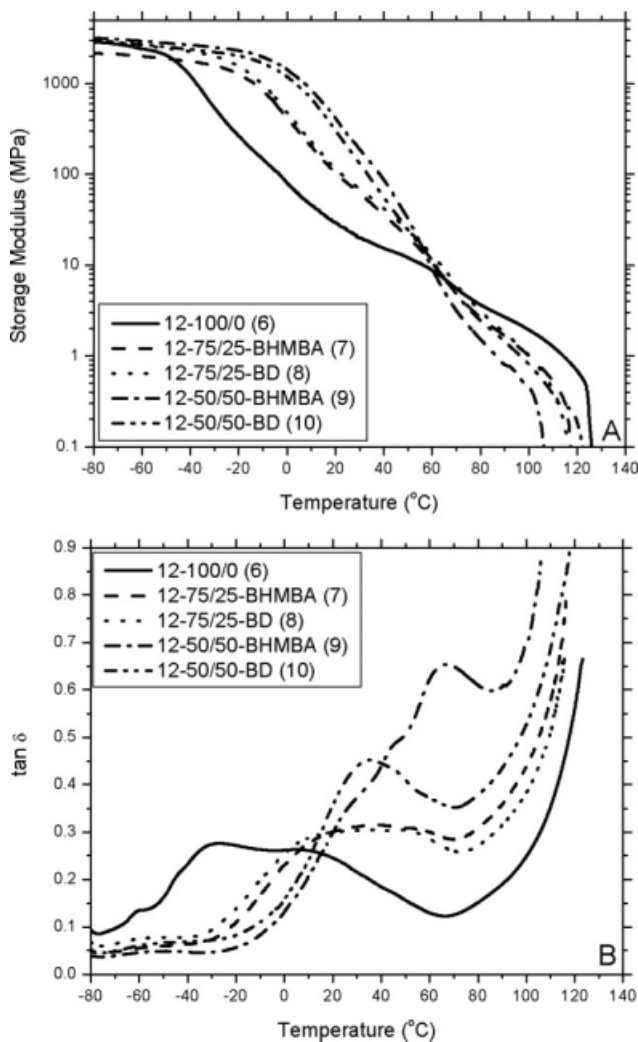
**Figure 2** HFIP GPC chromatograms of PBA polyol and 8-100/0 TPU (Entry 1, Table I).

of about  $-27^\circ\text{C}$  displayed by the 100% PBA control polymers. Most of the TPUs displayed one or more secondary relaxations in the  $\tan \delta$  plots. Well-defined examples may be observed at  $29^\circ\text{C}$  for sample 8-50/50-BD (Entry 5, Table I) and  $4^\circ\text{C}$  for 12-100/0 (Entry 6, Table I). These secondary relaxations were sufficiently prominent in the 12% HS TPUs containing PLGA (Entries 7-10 in Table I) that the peak maximum of the  $\alpha$  relaxation process could not be defined.

Dynamic properties of the 8% HS TPUs showed a strong dependence on the type of PLGA (i.e., whether initiated from BHMBA or BD), but were seemingly independent of the level of PLGA incorporation. The  $T_g$ , as indicated by the peak position of the  $\tan \delta$  plot, and the storage modulus of the 50/50 and 75/25 PBA/BD-PLGA were similar even though the level of incorporation of PLGA was



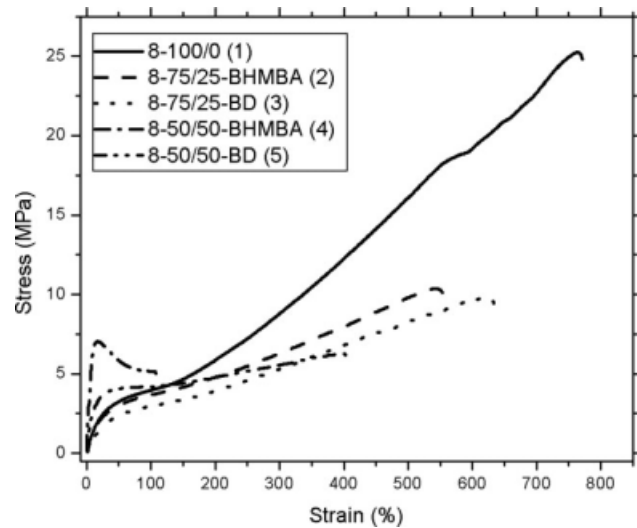
**Figure 3** Storage modulus versus temperature (A) and  $\tan \delta$  versus temperature (B) for the various 8% HS TPUs. The number in parenthesis corresponds to the entry number of Table I.



**Figure 4** Storage modulus versus temperature (A) and  $\tan \delta$  versus temperature (B) for the various 12% HS TPUs. The number in parenthesis corresponds to the entry number of Table I.

different. The same trend was observed for the BHMBA-PLGA TPUs. For the 12% HS TPUs, exactly the opposite was observed. Although the peak maximum of the  $\alpha$  relaxation process could not be reliably distinguished, clearly its onset temperature (onset  $T_g$ ) was strongly correlated with the amount of PLGA incorporated. At 25% loading of PLGA, the onset occurred at about  $-30^\circ\text{C}$ ; whereas at the 50% loading the onset occurred nearer to  $-15^\circ\text{C}$ .

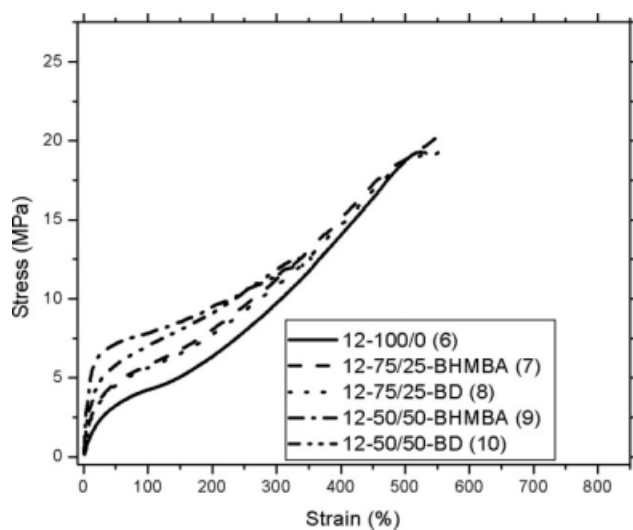
The overall effect of HS content was as expected; onset  $T_g$  for the 8% HS TPUs were lower than those of the 12% HS TPUs. Also, the 8% HS TPUs had lower modulus at high temperatures compared to the 12% HS TPUs. For instance, the temperature at which TPU modulus had decreased to 1 MPa was higher for the TPUs with 12% HS, where all but one sample reached this point at or above  $100^\circ\text{C}$ . In comparison, all of the 8% HS TPUs reached this modulus value at temperatures below  $100^\circ\text{C}$ . For all sam-



**Figure 5** Stress versus strain tensile test of 8% HS TPUs. The number in parenthesis corresponds to the entry number of Table I.

ples, the onset  $T_g$  was below zero. Thus the temperature range over which the various materials could be potentially used as an elastomer starts well below  $0^\circ\text{C}$  and goes up to about  $60\text{--}80^\circ\text{C}$ , depending on the formulation.

The various TPUs were subjected to mechanical testing. Figures 5 and 6 display representative stress versus strain plots of the 8% and 12% HS TPUs, respectively. Table I lists the modulus, energy to break, peak stress, and ultimate strain. Each value listed in the table is an average of three specimens per sample. In all cases except for 8-50/50-BHMBA (entry 4), the peak stress was also the ultimate stress. The two PBA control TPUs, 8-100/0 and 12-100/0, were both very tough, flexible materials with very high elongations and energy to break, in part due to the phase separated morphology typical of TPUs. Though it appears that sample 8-100/0 had a higher ultimate elongation and energy to break, it is important to note that sample 12-100/0 pulled out of the grips during the test for each of the three samples tested without breaking. Other than entry 4, there was not a drastic change in the physical properties with respect to PLGA type. As would be expected, with increasing PLGA content, the modulus of the resultant TPU increased while the ultimate elongation and energy to break decreased. All the 8% HS PLGA-containing TPUs showed reduced physical properties compared to the 100% PBA control. In the case of the 12% HS TPUs, the 25% PLGA-containing TPUs displayed physical properties that were surprisingly similar to the 100% BA control; although the control polymer did not break and thus its ultimate properties could not be measured. Again, at the 50% loading of PLGA there was a reduced ultimate elongation and energy to break with an

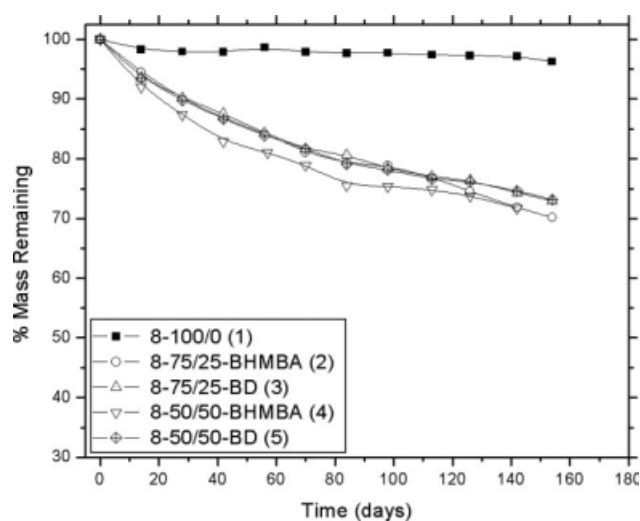


**Figure 6** Stress versus strain tensile test of 12% HS TPUs. The number in parenthesis corresponds to the entry number of Table I.

increased modulus. Perhaps the best formulation to balance physical properties and PLGA (hydrolytic degradability) content would be a 12-75/25-BD or 12-75/25-BHMBA.

Degradation of the TPUs in seawater was carried out at 37°C. This temperature was chosen to provide accelerated results, and so that the data could be compared to the large body of degradation data in the literature at this temperature. The degradation experiments probed only the hydrolytic degradation of the polymers; no biotic media were purposefully added to the degradation samples. Figures 7 and 8 illustrate the percent mass remaining versus immersion time at 37°C of the 8 and 12% HS TPUs, respectively. In all cases, the incorporation of PLGA into the TPU formulation enhanced hydrolytic degradation. The 8-100/0 and 12-100/0 control TPUs exhibited essentially no degradation throughout the test; however, there were very small, initial decreases in mass, likely due to the diffusion of residual DMF solvent out of the samples. Surprisingly, there was not a significant effect of the type of PLGA polyol on degradation. The BHMBA-initiated polyol may have provided a slight acceleration in degradation relative to BD-initiated polyols, particularly for the 12% HS TPUs, but the effect was minor.

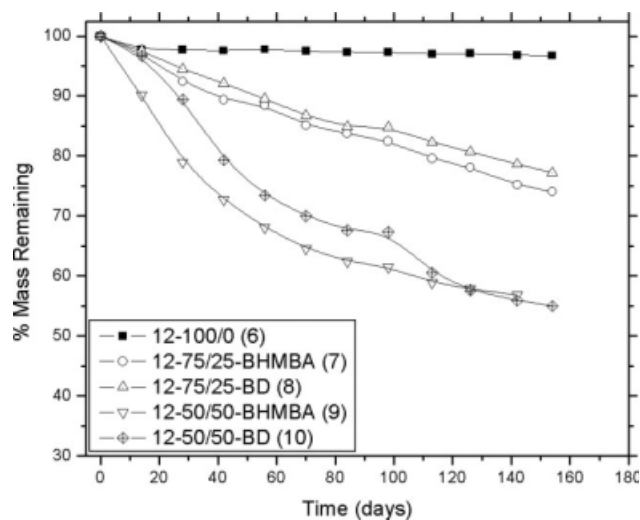
All of the 8% HS PLGA-containing TPUs had similar degradation profiles with about 27–30% mass lost after 153 days. The 12% HS PLGA-containing TPUs showed a marked dependence on the amount of PLGA in the TPU. The 12-75/25 TPUs degraded slower than the 8% HS PLGA-containing TPUs, but the 12-50/50 TPUs degraded more rapidly, with 55% mass remaining after 153 days.



**Figure 7** Remaining mass of 8% HS TPUs versus immersion time in seawater at 37°C. The number in parenthesis corresponds to the entry number of Table I.

## CONCLUSIONS

A series of degradable TPU elastomers based on H<sub>12</sub>MDI and mixed PBA/PLGA polyols was synthesized and shown to span a wide range of mechanical, thermal, and degradative properties. The PLGA-containing TPUs retained excellent physical properties and were able to undergo hydrolytic degradation in seawater. It was observed that a slight increase in the rate of degradation was achieved by incorporating carboxylic acid pendant groups on the polymer backbone, though not to the extent anticipated. The use of completely aliphatic reagents minimized the potential for toxic degradation byproducts. It was demonstrated that TPU properties can be tuned to some extent by



**Figure 8** Remaining mass of 12% HS TPUs versus immersion time in seawater at 37°C. The number in parenthesis corresponds to the entry number of Table I.

controlling the synthetic variables such as hard segment/soft segment ratio and polyol composition.

Molecular weights of the PLGA-containing TPUs were consistently lower than those containing only PBA polyol, thought to be caused by decreased kinetic reactivity of secondary hydroxyl endgroups of terminal lactoyl units on PLGA. However, other factors such as premature degradation of the degradable polyol, or compatibility or chain flexibility issues cannot be eliminated from consideration.

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