

# Biodegradable Polyurethane Elastomers Prepared from Isocyanate-Terminated Poly(Ethylene Adipate), Castor Oil, and Glycerol

Naozumi Teramoto, Yuichi Saitoh, Atsuo Takahashi, Mitsuhiro Shibata

Department of Life and Environmental Sciences, Faculty of Engineering, Chiba Institute of Technology, Tsudanuma, Narashino, Chiba 275-0016, Japan

Received 25 June 2008; accepted 11 January 2009

DOI 10.1002/app.30019

Published online 2 November 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The curing reaction of tolylene-2,4-diisocyanate-terminated poly(ethylene adipate) (PEA-TDI) with a mixture of castor oil (CO) and glycerol (GO) with a NCO/OH ratio of 1.0 at 150°C gave crosslinked polyurethane (CO/GO-PU). All the polyurethanes were elastomeric materials at room temperature. The glass-transition temperature of the CO/GO-PU increased with decreasing CO/GO ratio. All the cured polyurethanes had a higher 5% weight loss temperature than PEA-TDI. The tensile strength and modulus of the polyurethanes increased with decreasing CO/GO ratio, and tensile residual strain after

300% elongation for all the CO/GO-PU was almost 0. All the polyurethanes had biodegradability, when measured by a biochemical oxygen demand method in an aqueous medium using activated sludge. The rate of the biodegradation of the polyurethanes increased with an increase of CO/GO ratio. The crosslinked CO-PU showed much higher biodegradability than the linear PEA-TDI. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3199–3204, 2010

**Key words:** biodegradable; cross-linking; polyesters; polyurethanes; castor oil

## INTRODUCTION

Bio-based polymer products derived from annually renewable agricultural and biomass feedstock have become increasingly important as sustainable and eco-efficient products that can replace the products based exclusively on petroleum feedstock.<sup>1,2</sup> Among the renewable natural resources, plant oils have been used for various applications such as coatings, inks, and agrochemicals.<sup>3–5</sup> Castor oil (CO) is a plant oil obtained from the seed of *Ricinus communis*.<sup>6</sup> It is a triglyceride in which approximately 90% of the fatty acid chains are ricinoleic acid with a hydroxyl group, as is shown in Figure 1. Compared to other seed oils that lack hydroxyl group, CO can be combined with various isocyanate compounds such as tolylene-2,4-diisocyanate,<sup>7,8</sup> diphenylmethane diisocyanate,<sup>9,10</sup> hexamethylene diisocyanate,<sup>11</sup> and isophorone diisocyanate,<sup>12</sup> etc. to give crosslinked polyurethane resins. However, disadvantages with the use of castor oil include low hydroxyl number leading to inherently soft materials and relatively low miscibility with highly polar isocyanate compounds. To improve these drawbacks, the addition of glycerol (GO) was investigated in this study. GO

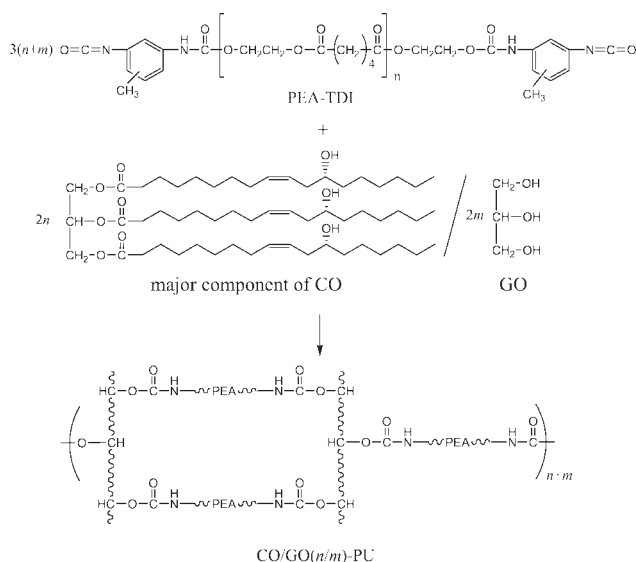
is an abundant bio-based triol with a relatively high hydroxyl number, which is a 10% byproduct of bio-diesel production via the transesterification of vegetable oils.<sup>13</sup> This study concerns the development of biodegradable elastomeric polyurethanes using a mixture of CO and GO. Regarding the improvement of mechanical properties and biodegradability of the CO-based polyurethanes, the addition of chitosan,<sup>14</sup> nitrocellulose,<sup>15</sup> nitrokonjac glucomannan,<sup>16</sup> soy dreg,<sup>17</sup> poly(ethylene glycol),<sup>18</sup> and polyricinoleate diol,<sup>19</sup> etc. had been recently reported. In this study, tolylene-2,4-diisocyanate-terminated poly(ethylene adipate) (PEA-TDI), which is a biodegradable polyester, was used as a diisocyanate compound combining with CO and GO.<sup>20</sup> Thermal, mechanical, and biodegradable properties of the crosslinked polyurethanes prepared by the reaction of PEA-TDI with CO and/or GO were investigated. Our attention was focused on the effect of the CO/GO ratio on the biodegradability of the polyurethanes based on PEA-TDI.

## MATERIALS AND METHODS

### Materials

Figure 1 shows the structure of the reagents used in this study. PEA-TDI ( $M_n$  2700, isocyanate content 3 wt %) was purchased from Sigma-Aldrich Japan (Shinagawa-ku, Japan). CO (LAV, hydroxyl value

Correspondence to: M. Shibata (shibata@sky.it-chiba.ac.jp).



**Figure 1** Synthetic scheme of polyurethane by the reaction of PEA-TDI with CO and/or GO.

161 mg-KOH/g, iodine value 86 g-I<sub>2</sub>/100 g) was supplied from Itoh Oil Chemicals (Yokkaichi, Chuo-ku, Japan). GO was purchased from Kanto Chemical (Tokyo, Japan).

### Curing reaction of PEA-TDI with CO and/or GO

In the reaction of PEA-TDI with CO and/or GO, the molar ratio of NCO/OH is adjusted to 1/1. The molar number of NCO was calculated from  $M_n$  2700 of PEA-TDI. When the telechelic terminal group of PEA-TDI is perfectly isocyanate as is shown in Figure 1, the isocyanate content becomes 3.11 wt %, which is in good agreement with the isocyanate content of 3 wt % shown in the reagent catalog. In the case of GO, the molecular weight calculated from the structure shown in Figure 1 was adopted. Although the theoretical hydroxyl value of CO based on the structure shown in Figure 1 was 180 mg-KOH/g, the observed value was 161 mg-KOH/g. For the calculation of feed amount, the observed value of CO was adopted. Table I summarizes the molar ratio of the functional groups of PEA-TDI, CO, and GO in the curing reaction and the density of the cured polyurethanes. The prescribed amounts of PEA-TDI, CO, and GO were mixed at 70°C for 10 min and then degassed *in vacuo*. The mixture was poured on a poly(tetrafluoroethylene) plate, again degassed *in vacuo*, and then cured at 150°C for 8 h. The relation of sample abbreviation and composition for the cured products of PEA-TDI, CO, and GO is summarized in Table I.

### Measurements

Fourier transform infrared (FTIR) spectra were recorded on a FTIR 8100 (Shimadzu, Kyoto, Japan) by

the KBr-pellet or attenuated total reflectance method. Solubility was tested after a mixture of sample (20 mg) and solvent (0.7 mL) was sonicated for 30 min. The differential scanning calorimetry (DSC) was performed on a Diamond DSC (Perkin-Elmer Japan, Yokohama, Japan) in a nitrogen atmosphere. The samples were cooled to −100°C and heated to 150°C at a rate of 20°C/min and held at 150°C for 1 min, again cooled to −100°C at a rate of −50°C/min, and then heated to 150°C at a rate of 20°C/min. The 5 and 20% weight loss temperature was measured on a Perkin-Elmer thermogravimetric analyzer (TGA 7) in a nitrogen atmosphere at a heating rate of 20°C/min. Dynamic mechanical analysis (DMA) of the rectangular plates (length, 40 mm; width, 2 mm; thickness 2 mm) was performed on a Rheograph Solid (Toyo Seiki, Tokyo, Japan) with a chuck distance of 20 mm, a frequency of 10 Hz, and a heating rate of 2°C/min. The maximum of loss modulus ( $E''$ ) was used to determine glass-transition temperature ( $T_g$ ). Tensile tests of the rectangular plates (length, 40 mm; width, 2 mm; thickness, 2 mm) were performed at 20°C by using a Shimadzu Autograph AG-I based on the standard method for testing the tensile properties of plastics (JIS K7113-1995). Span length was 20 mm and the testing speed was 10 mm/min. Five composite specimens were tested for each set of samples, and the mean values and the standard deviation ( $\sigma$ ) were calculated. Tensile residual strain was calculated from the length of the original sample and the sample after being kept for 1 min at 300% elongation using the Autograph AG-I. Biodegradability was determined according to JIS K6950-2000 (ISO 14851-1999) by measuring a biochemical oxygen demand (BOD) in the aerobic aqueous medium containing activated sludge. Phosphate buffer (pH 7.4, 200 mL) containing 0.25 mM CaCl<sub>2</sub>, 0.09 mM MgSO<sub>4</sub>, 0.09 mM NH<sub>4</sub>Cl, and 0.9  $\mu$ M FeCl<sub>3</sub> was mixed in a glass bottle. To the mixture, 4.35 mL of activated sludge containing 30 mg insoluble part, which was obtained from sewerage facilities of Chiba Institute of Technology, and 20 mg of the sample pulverized after immersion in liquid nitrogen was added. In the case of CO and GO, 20 mg

**TABLE I**  
Sample Abbreviation, Feed Ratio of Functional Groups, and Density for the Synthesized Polyurethanes

Sample abbreviation	Molar ratio of functional groups		Density of cured polyurethane (cm <sup>3</sup> /g)
	NCO/OH	[OH of CO]/[OH of GO]	
CO-PU	1/1	1/0	1.214
CO/GO(3/1)-PU	1/1	3/1	1.215
CO/GO(1/1)-PU	1/1	1/1	1.237
CO/GO(1/3)-PU	1/1	1/3	1.237
GO-PU	1/1	0/1	1.259

of liquid samples was added. The dispersion was steadily stirred with a magnetic stir bar. BOD was measured at 25°C by using BOD tester 200F (Taitec Corporation, Koshigaya, Japan). Carbon dioxide was absorbed into 50% sodium hydroxide aqueous concentrate in a cup equipped within the glass bottle. The volume of the consumed oxygen was directly measured with a scaled cylinder.

## RESULTS AND DISCUSSION

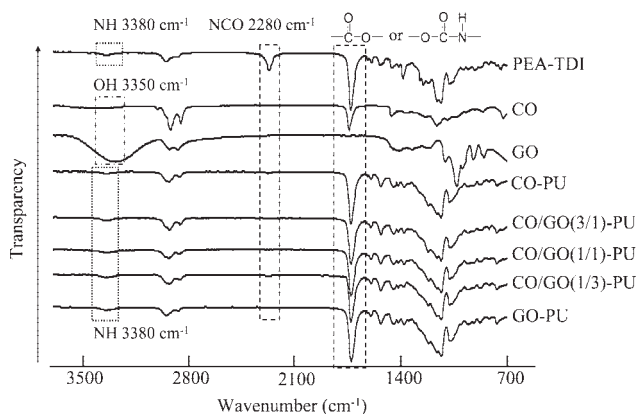
### Characterization of curing reaction of PEA-TDI with CO/GO

The mixture of PEA-TDI and CO took longer to get a homogenous liquid after stirring at 70°C than the mixture of PEA-TDI and GO. However, all the mixtures of PEA-TDI and CO/GO in this study finally became a homogeneous viscous liquid. FTIR spectra of the mixtures after curing at 150°C for 8 h are shown in Figure 2. The absorption peak, based on the isocyanate group, which was observed at 2280 cm<sup>-1</sup> for PEA-TDI, did not appear for the cured materials. The absorption peak for the C=O of the formed urethane overlapped with the peak of the C=O of the ester group of PEA-TDI and CO at 1710 cm<sup>-1</sup>. Also, the peak based on N—H stretching vibration of the urethane group was observed at 3380 cm<sup>-1</sup>. These results suggest that the urethane groups are formed by the reaction of PEA-TDI with CO and/or GO.

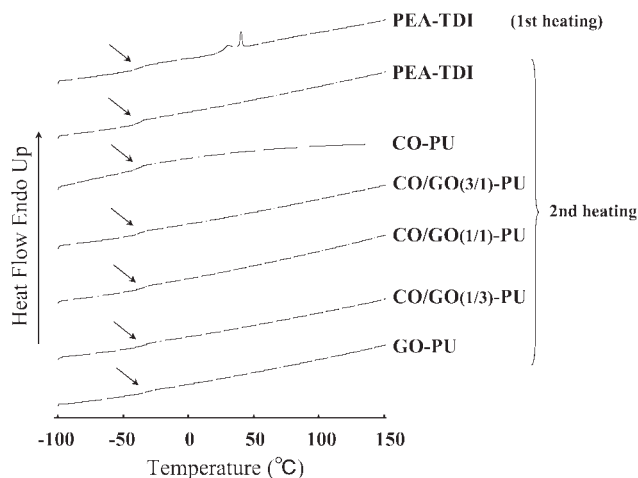
The raw materials, PEA-TDI, CO, and GO, were soluble in chloroform, tetrahydrofuran, acetone, and *N,N*-dimethylformamide. However, all the cured polyurethanes were insoluble in such solvents, indicating the crosslinking reaction certainly occurred.

### Thermal properties of CO/GO-polyurethane (PU)

Figure 3 shows the heating DSC thermograms of PEA-TDI and the cured polyurethanes. The PEA-TDI sample kept at room temperature showed double



**Figure 2** FTIR spectra of PEA-TDI, CO, GO, and the polyurethanes.



**Figure 3** DSC heating curves of PEA-TDI and the polyurethanes.

melting endothermic peaks at 31.0 and 40.5°C on the first heating thermogram. However, there was no endothermic peak on the second heating curve after cooling to -100°C at a rate of -50°C, suggesting that crystallization of PEA-TDI did not occur at the cooling stage from the melt. In the case of the cured polyurethane samples kept at room temperature, no melting peak was observed on the first and second heating thermograms, indicating that the crystallization of the poly(ethylene adipate) segments in the polyurethane molecules highly hindered the formation of the cross-linked structure. The glass-transition temperature ( $T_g$ ) determined from the second heating thermograms of the polyurethanes decreased with increasing CO/GO ratio (Table II). This result is in agreement with the fact that the distance between the two hydroxyl groups of CO with flexible ricinoleic acid triglyceride moiety is much longer than that of GO. As is shown in Table I, density of the polyurethanes also decreased with increased CO/GO ratio, indicating that an increase of CO/GO ratio causes a decrease of the cross-linking density.

Figure 4 shows DMA charts of the cured polyurethanes. The temperature where the storage modulus ( $E'$ ) starts to drop and the temperature of  $\tan \delta$  peak

**TABLE II**  
Thermal Decomposition Temperature and  $T_g$  of PEA-TDI and the Polyurethanes

Sample	$T_g$ (°C)		Thermal decomposition temperature (°C)	
	DSC	DMA	5 wt % loss	20 wt % loss
PEA-TDI	-38	—	314	408
CO-PU	-39	-29	333	388
CO/GO(3/1)-PU	-38	-28	331	381
CO/GO(1/1)-PU	-35	-26	328	384
CO/GO(1/3)-PU	-34	-22	322	378
GO-PU	-33	-22	319	377

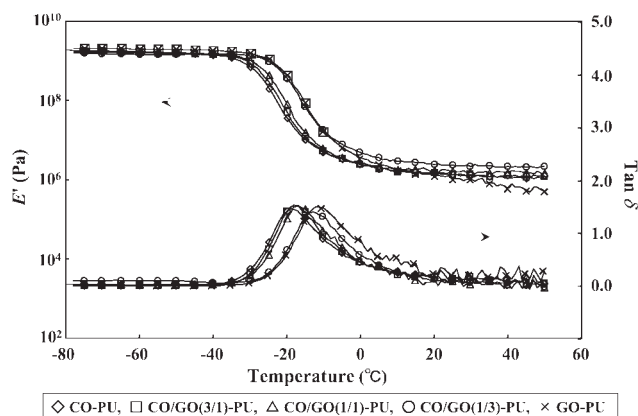


Figure 4 Dynamic viscoelastic curves of the polyurethanes.

decreased with increasing CO/GO ratio. Because the  $\tan \delta$  peak overestimates  $T_g$  especially at a relatively high frequency as is well known, the  $T_g$  determined from the maximum of loss modulus ( $E''$ ) measured by DMA is summarized in Table II. Although the  $T_g$  by  $E''$  is still a little higher than the  $T_g$  determined by DSC, their values are in good correlation.

Figure 5 shows the TGA curves of PEA-TDI and the cured materials. Apparently, PEA-TDI had a two-step thermo-degradation curve. The first step is due to the decomposition of the urethane group, and the second step is related to the polyester chain

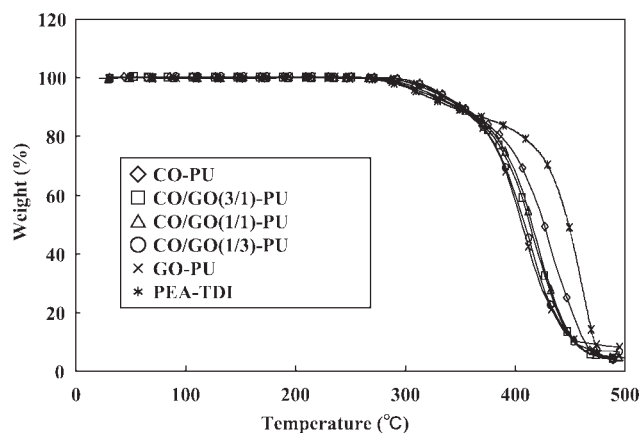


Figure 5 TGA curves of PEA-TDI and the polyurethanes.

degradation. In the case of the cured polyurethane, it seems that the second-step degradation shifted to a lower temperature region. As is shown in Table II, 20% weight loss temperature of the polyurethanes was lower than that of PEA-TDI. It is thought that the products formed by the decomposition of the crosslinked urethane bond promote the decomposition of the polyester chain. Regarding the first-step thermal degradation, all the cured polyurethanes had a higher degradation temperature than PEA-TDI, as is obvious from the comparison of the 5% weight loss temperature (Table II). The 5% weight

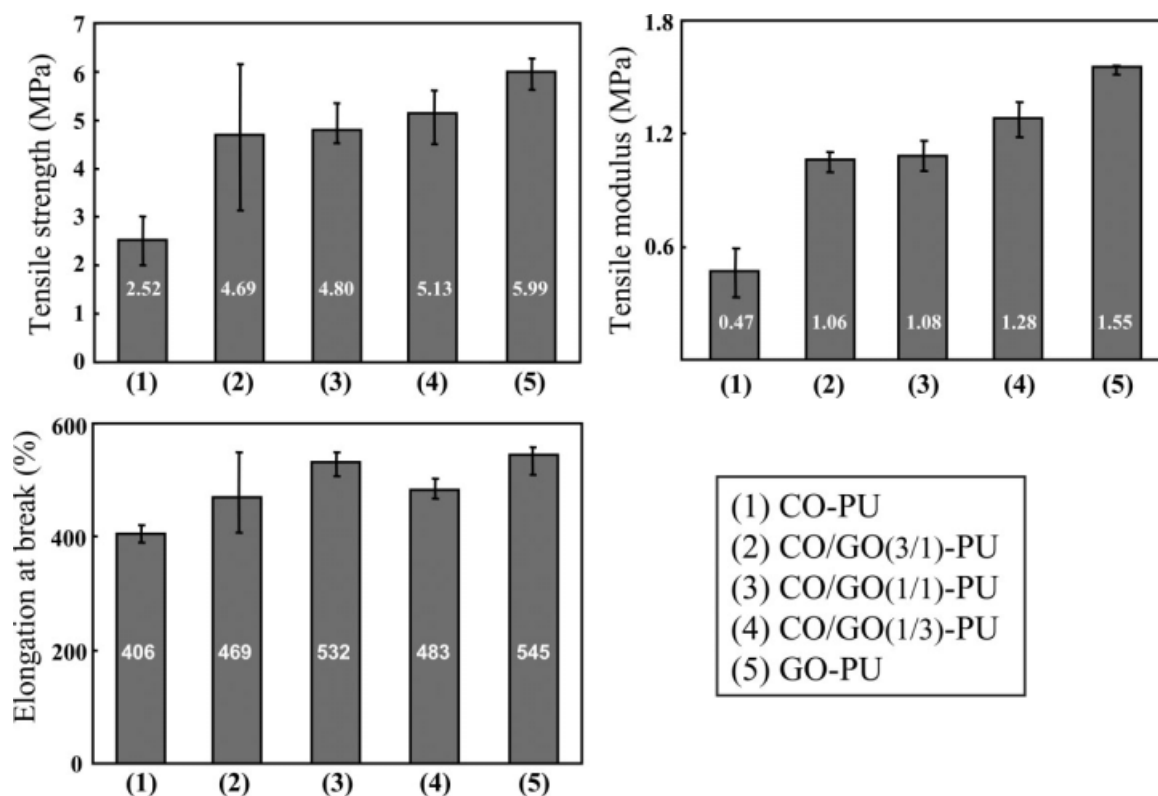


Figure 6 Tensile properties of the polyurethanes.



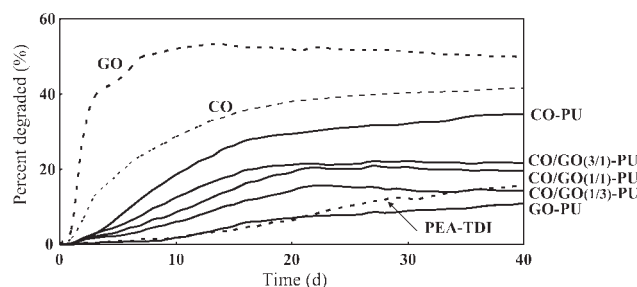
loss temperature of the cured polyurethanes slightly decreased with decreasing CO/GO ratio. The weight loss should be mainly attributed to the thermal degradation of urethane bond. Because the polyurethane with a lower CO/GO ratio has a higher concentration of urethane bond, the polyurethane showed a lower degradation temperature.

### Mechanical properties of CO/GO-PU

Figure 6 shows the tensile properties at 20°C for CO-PU, CO/GO-PU, and GO-PU. The GO-PU had the highest tensile strength and modulus among all the cured samples. The tensile properties of CO-PU and CO/GO(3/1)-PU samples had relatively large standard deviation as compared with the polyurethanes with a lower CO/GO ratio. There is a possibility that the CO-PU and CO/GO(3/1)-PU samples are not completely homogeneous. Certainly, CO had much lower solubility than GO toward PEA-TDI. The tensile strength and modulus decreased with an increase of CO/GO ratio, and CO-PU had the lowest strength and modulus. This result is attributed to the fact that CO-PU has a lower crosslinking density than GO-PU. The addition of GO is important to get homogeneity and rigidity of the polyurethane sample. All the cured materials had very high elongation at break of over 400%. Tensile residual strain after being kept for 1 min at 300% elongation for the cured polyurethanes was from 0.0 to 1.0%, suggesting all the cured polyurethanes are elastomeric materials.

### Biodegradability of CO/GO-PU

Figure 7 shows the biodegradability of PEA-TDI, GO, CO, and the cured polyurethanes measured by BOD in the aerobic aqueous medium containing activated sludge. Biodegradability of the crosslinked polyurethanes increased with an increase of CO/GO ratio. The biodegradability after 40 days of CO-PU, CO/GO(3/1)-PU, and CO/GO(1/1)-PU is 34.5, 20.0, and 18.5%, respectively, the values of which are higher than that of PEA-TDI (15.0%) and lower than those of GO (50.6%) and CO (41.4%). The incorporation of the CO unit in the crosslinked polyurethane structure was more effective than that of GO unit for biodegradation. Judging from the fact that GO has a higher biodegradability than CO, it is thought that the polyurethane with a looser crosslinked structure has a higher biodegradability. It is noteworthy that the loosely crosslinked CO-PU has much higher biodegradability than a linear PEA-TDI. Because CO-PU had a slightly lower  $T_g$  measured by DSC than PEA-TDI, it is thought that molecular motion of CO-PU is easier than that of PEA-TDI, and intermolecular distance of PEA segments for CO-PU is longer



**Figure 7** Biodegradability measured by BOD in the aerobic aqueous medium containing activated sludge for PEA-TDI, CO, GO, and the polyurethanes.

than that for PEA-TDI. As other factors, it is thought that CO-PU has much lower crystallinity than PEA-TDI and that CO-PU has no isocyanate group, although PEA-TDI is a diisocyanate compound. On the other hand, GO-PU had a lower biodegradability than PEA-TDI, in accordance with GO-PU, which has a higher  $T_g$  measured by DSC than PEA-TDI.

### CONCLUSION

Biodegradable polyurethane elastomers containing oligo(aliphatic ester) chain were prepared by the reaction of PEA-TDI and CO/GO with the NCO/OH ratio of 1. All the polyurethanes were elastomeric materials at room temperature, and tensile residual strain after 300% elongation for all the CO/GO-PU was almost 0. The glass-transition temperature, tensile strength, and tensile modulus of the polyurethanes increased with decreasing CO/GO ratio. All the cured polyurethanes had a higher 5% weight loss temperature than PEA-TDI. All the polyurethanes had biodegradability, when measured by a BOD method in an aqueous medium using activated sludge. The rate of the biodegradation of the polyurethanes increased with an increase of CO/GO ratio. The biodegradability of CO-PU was 34.5% after 40 d, which was much higher than that of PEA-TDI (15.0%).

### References

1. Kaplan, D. L. *Biopolymers from Renewable Resources*; Springer-Verlag: Berlin, 1998.
2. Mohanty, A. K.; Misra, M.; Hinrichsen, G. *Macromol Mater Eng* 2000, 276, 1.
3. Biermann, U.; Metzger, J. O.; Friedt, W.; Luehs, W.; Lang, S.; Machmueller, G.; Schneider, M. P.; Ruesch, G. K. M.; Schaefer, H. J. *Angew Chem Int Ed* 2000, 39, 2206.
4. Wool, R. P.; Sun, X. S. *Bio-based polymers and composites*; Academic Press: New York, 2005; pp 56–111.
5. Güner, F. S.; Yağcı, Y.; Erciyes, A. T. *Prog Polym Sci* 2006, 31, 633.
6. Ogunniyi, D. S. *Bioresour Technol* 2006, 97, 1086.
7. Quipeng, G.; Shixia, F.; Qingyu, Z. *Eur Polym J* 1990, 26, 1177.
8. Yeganeh, H.; Mehdizadeh, M. R. *Eur Polym J* 2004, 40, 1233.

9. Bai, S.; Khakhar, D. V.; Nadkarni, V. M. *Polymer* 1997, 38, 4319.
10. Araújo, R. C. S.; Pasa, V. M. D. *Prog Org Coat* 2004, 51, 6.
11. Jayabalan, M.; Lizymol, P. P. *Polym Degrad Stab* 1997, 58, 251.
12. Rodrigues, J. M. E.; Pereira, M. R.; Souza, A. G.; Carvalho, M. L.; Neto, A. A. D.; Dantas, T. N. C.; Fonseca, J. L. C. *Thermochim Acta* 2005, 427, 31.
13. Haas, M. J.; McAloon, A. J.; Yee, W. C.; Foglia, T. A. *Bioresour Technol* 2006, 97, 671.
14. Gong, P.; Zhang, L. *J Appl Polym Sci* 1998, 68, 1313.
15. Zhnag, L.; Zhou, Q. *J Polym Sci Part B* 1999, 37, 1623.
16. Gao, S.; Zhang, L. *J Appl Polym Sci* 2001, 81, 2076.
17. Chen, Y.; Zhang, L.; Deng, R.; Cui, Y. *Macromol Mater Engn* 2007, 292, 484.
18. Yeganeh, H.; Hojati-Talemi, P. *Polym Degrad Stab* 2007, 92, 480.
19. Xu, Y.; Petrovic, Z.; Das, S.; Wilkes, G. H. *Polymer* 2008, 49, 4248.
20. Filip, D.; Simionescu, C. I.; Macocinschi, D. J. *Serb Chem Soc* 2001, 66, 153.