

Polyurethanes Synthesized from Polyester Polyols Derived from PET Waste. II. Thermal Properties

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SYNOPSIS

Polyurethanes were synthesized from polyester polyols, derived from PET waste. The PET waste was first depolymerized by glycolysis. The glycolysed products were reacted with adipic acid to yield polyester polyols, and the polyester polyols were then reacted with either MDI or TDI to obtain polyurethanes. In this article, the thermal properties of the polyurethanes obtained are discussed in detail. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The PET is extensively used for making synthetic fibers, films, injection-molded articles, and blow-molded containers. Because the management of waste plastics is reaching a crisis worldwide, PET waste has become one of most valuable recyclable materials today.¹ The PET waste can be depolymerized by glycolysis to obtain oligomeric diol. The oligomers can be used to synthesize other polymers. The advantage of the utilization of PET waste is to generate value-added products, such as, unsaturated polyester^{2,3} and polyurethanes.⁴ Indeed, it is logical to apply reclaimed PET as a new feedstock for urethane polyols. In a previous article, we reported a number of polyurethanes synthesized from polyester polyols that were derived from PET waste.⁵ In this article, we discuss the thermal properties of the obtained polyurethanes.

Thermal properties, such as glass transition temperature (T_g), soft segment melting temperature (T_m), and decomposition temperature (T_d), of a number of polyurethanes are investigated. Glass transition temperature was determined by DSC, and other thermal properties were determined by TGA. Also measured were the mechanical properties, specifically the stress-strain curves and Young's mod-

ulus, which will be reported upon in our next publication.

EXPERIMENTAL

Preparation of Polyurethane

The recycled PET flakes, obtained from the Hosen Company, which is a local PET recycling plant in Taiwan, was glycolysed with an excess of ethylene glycol (EG), using 0.5 wt % zinc acetate, based on the amount of PET waste, as the catalyst, according to the procedure reported in our previous article.⁴ The glycolysed product has the components shown in Table I. The polyester polyols were prepared by reacting the glycolysed PET oligomers with adipic acid to obtain polyols with different molecular weights. Polyurethanes are then synthesized by reacting polyester polyols with either MDI or TDI. Table II shows the diisocyanates used in the synthesis of polyurethanes. The reactants of MDI or TDI with polyester polyol are then poured into a Teflon mold. The experimental details of the glycolysis, polyesterification of glycolysed PET, and synthesis of polyurethanes, were described in our previous article.⁴ A series of polyurethanes is synthesized with different $[NCO]/[OH]$ ratios, different molecular weights of polyol, and different sorts of isocyanate. The code of the formulations for the formation of polyurethane synthesized from polyols is summarized in Table III.

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Table I List of Components of Glycolized Product Used for Polyester Polyol Synthesis

Materials	Designation	Chemical Structure	Notes	Molecular Weight
Ethylene glycol	EG	HO-CH ₂ -CH ₂ -OH	Raw material	62
Bis(β -Hydroxyethyl Terephthalate)	BHET	HO-CH ₂ -CH ₂ -O-C(=O)-C ₆ H ₄ -C(=O)-O-CH ₂ -CH ₂ -OH	Monomer	254
Dimer	Dimer	HO-CH ₂ -CH ₂ -O-C(=O)-C ₆ H ₄ -C(=O)-O-C ₆ H ₄ -C(=O)-O-CH ₂ -CH ₂ -OH	Dimer	446

Thermal Measurement

For the measurement of thermal properties, differential scanning calorimetry (DSC) was used to detect glass transition temperature (T_g) of the resins. The specimen was placed in a cell. The sample cell was heated at a uniform rate (10°C/min) at the temperature range of -80 ~ 250°C and the nitrogen flow rate of 50 cc/min. Thermogravimetric analysis (TGA) was used to detect 50% weight loss as a function of temperature to obtain T_d . Using these data, the thermal stability of polymeric materials was studied. The sample cell was heated at a uniform rate (10°C/min) from 30°C to 750°C under the nitrogen flow rate of 70 cc/min.

RESULTS AND DISCUSSION

Softening Point

Figures 1 and 2 show typical DSCs of a series of MDI-based polyurethanes, having a molecular weight of 2096 and 991, respectively, with different $[NCO]/[OH]$ ratios. As pointed out by Masiulaniš,⁶ the thermal stability of polyurethane can be reflected in such reversible transitions as melting or softening points. T_m is a soft segment, associated melting temperature, attributed to the segmental arrangement of polyol units, which lies almost below 20°C on DSC. It is seen that in addition to T_g , this soft

segment melting temperature, T_m , has appeared. The appearance of T_m is more pronounced for higher molecular weight of polyol in both TDI- and MDI-based polyurethanes. It appears that the segment arrangement becomes more pronounced, due to the longer aromatic soft segment yielding a higher degree of ordering, allowing a more significant T_m endotherm. The lack of a significant T_m on DSC of the polyurethane, having a lower molecular weight of polyol and a higher $[NCO]/[OH]$ ratio, suggests that a segmental arrangement was absent or was at a minimum.

Glass Transition Temperature

The glass transition temperature of various polyurethanes, as determined by DSC, are reported in Table IV. Table IV presents T_g s of polyurethane, correlated with the $[NCO]/[OH]$ ratio and molecular weight of polyols, having three different molecular weights. In general, it was observed that the glass transition temperature decreased with increasing molecular weight of polyol used.

It is shown in Table IV that the value of T_g decreased as the molecular weight of polyols increased. In contrast, the value of T_g increased as the $[NCO]/[OH]$ ratio increased.

In general, the value of T_g lies in the range of -21.7°C to 16.3°C, indicating the characteristics of elastomer at room temperature for both TDI- and MDI-based polyurethanes.

Table II List of Diisocyanates Used as Hard Segments in the Polyurethane Synthesis

Materials	Designation	Notes	Source
2,4-Toluene Diisocyanate	TDI	80% 2,4- and 20% 2,6-Isomeric mixture	E. Merk
Diphenylmethane Diisocyanate	MDI	Mixture of Di- and Triisocyanates Dark Brown Viscous Liquid	E. Merk

Table III Code of Polyurethanes Synthesized from Polyols

Code	[NCO]/[OH] Ratio	Wt % Hard Segment (Calculated)	Molecular Weight	MDI or TDI Used
M2096-85	0.85	9.2	2096	MDI
M2096-90	0.90	9.7	2096	MDI
M2096-95	0.95	10.2	2096	MDI
M2096-100	1.00	10.7	2096	MDI
M2096-110	1.10	11.6	2096	MDI
M2096-120	1.20	12.5	2096	MDI
T2096-85	0.85	6.6	2096	TDI
T2096-90	0.90	7.0	2096	TDI
T2096-95	0.95	7.3	2096	TDI
T2096-100	1.00	7.7	2096	TDI
T2096-110	1.10	8.4	2096	TDI
T2096-120	1.20	9.1	2096	TDI
M1741-85	0.85	10.9	1741	MDI
M1741-90	0.90	11.4	1741	MDI
M1741-95	0.95	12.0	1741	MDI
M1741-100	1.00	12.6	1741	MDI
M1741-110	1.10	13.6	1741	MDI
M1741-120	1.20	14.7	1741	MDI
T1741-85	0.85	7.8	1741	TDI
T1741-90	0.90	8.3	1741	TDI
T1741-95	0.95	8.7	1741	TDI
T1741-100	1.00	9.1	1741	TDI
T1741-110	1.10	9.9	1741	TDI
T1741-120	1.20	10.7	1741	TDI
M1220-85	0.85	14.8	1220	MDI
M1220-90	0.90	15.6	1220	MDI
M1220-95	0.95	16.3	1220	MDI
M1220-100	1.00	17.0	1220	MDI
M1220-110	1.10	18.4	1220	MDI
M1220-120	1.20	19.7	1220	MDI
T1220-85	0.85	10.8	1220	TDI
T1220-90	0.90	11.4	1220	TDI
T1220-95	0.95	11.9	1220	TDI
T1220-100	1.00	12.5	1220	TDI
T1220-110	1.10	13.6	1220	TDI
T1220-120	1.20	14.6	1220	TDI
M991-85	0.85	17.7	991	MDI
M991-90	0.90	18.5	991	MDI
M991-95	0.95	19.3	991	MDI
M991-100	1.00	20.1	991	MDI
M991-110	1.10	21.7	991	MDI
M991-120	1.20	23.2	991	MDI
T991-85	0.85	13.0	991	TDI
T991-90	0.90	13.6	991	TDI
T991-95	0.95	14.3	991	TDI
T991-100	1.00	14.9	991	TDI
T991-110	1.10	16.2	991	TDI
T991-120	1.20	17.4	991	TDI

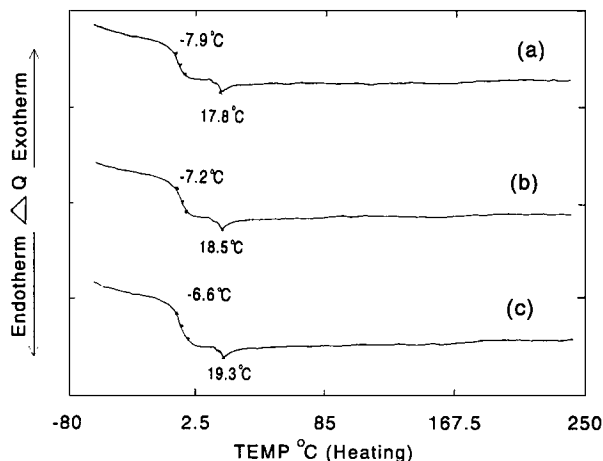


Figure 1 DSC curves of (a) M2096-100, (b) M2096-110, and (c) M2096-120.

The T_g of T2096-85 is found to be the lowest, probably due to the higher molecular weight and the TDI's structure with a suitable degree of crosslinking, which offers higher flexibility to the UP network.

In general, polyurethane, based on MDI, has comparatively higher T_g than one based on TDI, with the same molecular weight of polyol and the same $[NCO]/[OH]$ ratio.

Thermogravimetry

Thermogravimetry has been used to study the degradation process in polymers. The determination in properties is a result of the cleavage of thermally weak bonds. The thermogravimetric analysis data

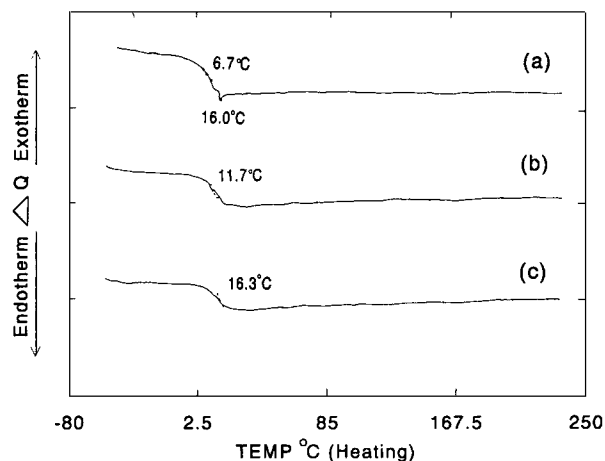


Figure 2 DSC curves of (a) M991-100, (b) M991-110, and (c) M991-120.

of some polyurethanes, based on TDI and MDI, are summarized in Table V.

It was observed that thermal stability is increased as molecular weight of polyol increased. Although the effect of this sort of isocyanate on stability is not significant, it appears that the polyurethanes, based on MDI, are better than those that are based on TDI. The thermal stabilities of TDI- and MDI-based polyurethanes should have been nearly equal, since both had thermally stable aromatic nuclei in their structure. However, the higher T_d value imparted by MDI can be explained by its higher functionality, which causes a higher degree of crosslinking. The T_g measurements show that the decomposition temperatures of the synthesized polyurethanes are relatively high, because the soft segmental polyols of these polyurethanes have aromatic nuclei in their structures.

Table IV T_g s of PU, Based on Polyols of $M_n = 2096, 1741, 1220, \text{ and } 991$

Code	T_g (°C)	Code	T_g (°C)	Code	T_g (°C)	Code	T_g (°C)
M2096-85	-10.9	M1741-85	-9.3	M1220-85	-0.5	M991-85	3.6
M2096-90	-9.6	M1741-90	-8.6	M1220-90	1.1	M991-90	4.5
M2096-95	-8.4	M1741-95	-7.0	M1220-95	2.3	M991-95	6.0
M2096-100	-7.9	M1741-100	-6.8	M1220-100	4.6	M991-100	6.7
M2096-110	-7.2	M1741-110	-6.2	M1220-110	5.8	M991-110	11.7
M2096-120	-6.6	M1741-120	-5.8	M1220-120	7.8	M991-120	16.3
T2096-85	-21.7	T1741-85	-20.0	T1220-85	-4.2	T991-85	-0.9
T2096-90	-19.8	T1741-90	-11.7	T1220-90	-2.2	T991-90	2.0
T2096-95	-12.0	T1741-95	-11.0	T1220-95	-1.9	T991-95	4.7
T2096-100	-11.1	T1741-100	-10.3	T1220-100	-0.6	T991-100	6.4
T2096-110	-10.9	T1741-110	-7.5	T1220-110	3.6	T991-110	7.1
T2096-120	-10.8	T1741-120	-7.1	T1220-120	5.7	T991-120	9.5

Table V T_d s of PU, Based on Polyols of $\bar{M}_n = 2096, 1741, 1220, \text{ and } 991$

Code	T_d (°C)	Code	T_d (°C)	Code	T_d (°C)	Code	T_d (°C)
M2096-100	365.9	M1741-100	363.2	M1220-100	358.7	M991-100	356.6
M2096-120	365.3	M1741-120	363.0	M1220-120	357.8	M991-120	356.7
T2096-100	362.7	T1741-100	361.0	T1220-100	358.8	T991-100	357.1
T2096-120	362.9	T1741-120	356.9	T1220-120	354.7	T991-120	352.1

CONCLUSION

PET waste can be depolymerized by glycolyzing it with EG. Polyester polyol can then be prepared by reacting glycolyzed products with adipic acid. Polyurethane has been synthesized by reacting these polyester polyols either with TDI or MDI. These polyurethanes have T_g s that range from -21.7°C to 16.3°C , indicating elastomeric characteristics at room temperature.

Polyurethanes, based on the polyols derived from PET waste, show a higher decomposition temperature in the range of 352.1°C to 365.9°C , indicating good thermal stability.

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