

Polyurethanes Synthesized from Polyester Polyols Derived from PET Waste.

III. Mechanical Properties

INTRODUCTION

Polyethylene Terephthalate (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 PET waste can be depolymerized by glycolysis to obtain oligomeric diols. The oligomers can then be used to synthesize other polymers. The advantages of the utilization of PET waste is to generate value-added products, such as unsaturated polyesters^{2,3} and polyurethanes.⁴ Indeed, it is logical to apply reclaimed PET as a new feedstock for urethane polyols. In a previous article,⁵ we reported thermal properties of polyurethanes synthesized from polyester polyols that were derived from PET waste. The term "urethane elastomer" is derived from the chemical entity that results from the reaction of an isocyanate with a hydroxy compound. It is the purpose of this work to outline some of the processes and properties of urethane elastomers synthesized from PET waste. Mechanical properties, such as tensile stress, tensile elongation, and Young's modulus of a number of polyurethanes synthesized, are measured and presented.

EXPERIMENT

Preparation of Polyurethane

The recycled PET flakes obtained from the Hosen Company, which is a local PET recycling plant in Taiwan, was glycolyzed 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 by Baliga and Wang.⁶ Polyester polyols were prepared by reacting the glycolyzed PET oligomers without further purification with adipic acid at fixed hydroxyl to carboxyl ratios of 1.2–1.5 at 170°C first for 3 h and then at 200°C for about 10 h to obtain polyols having the different molecular weights. Synthesis of polyurethanes were carried out by the one-step method by reacting polyester polyols with MDI. The polyester is first demoiatured by heating to 100–110°C for 3 h in a vacuum chamber. Then MDI is added to polyester polyol under stirring and immediately

cast into a Teflon mold having a cavity of dumb-bell-type pieces. The mixture is then heated at 100°C for 14 h to complete the reaction. The ratios of isocyanate to hydroxy groups were kept at 0.85–1.20 to obtain polyurethane type elastomers. The code of the formulations for polyurethanes synthesized from polyols having different molecular weights is summarized in Table I.

Mechanical Properties Measurement

Stress-strain curves were obtained by using an Instron tester with 500 mm/min extension ratio at the room temperature.

Table I Code of Polyurethanes Synthesized from Polyols Having Different Molecular Weights

Code	[NCO]/[OH] Ratio	Wt % Hard Segment (Calculated)	Molecular Weight
M991-85	0.85	17.7	991
M991-90	0.90	18.5	991
M991-95	0.95	19.3	991
M991-100	1.00	20.1	991
M991-110	1.10	21.7	991
M991-120	1.20	23.2	991
M1220-85	0.85	14.8	1220
M1220-90	0.90	15.6	1220
M1220-95	0.95	16.3	1220
M1220-100	1.00	17.0	1220
M1220-110	1.10	18.4	1220
M1220-120	1.20	19.7	1220
M1741-85	0.85	10.9	1741
M1741-90	0.90	11.4	1741
M1741-95	0.95	12.0	1741
M1741-100	1.00	12.6	1741
M1741-110	1.10	13.6	1741
M1741-120	1.20	14.7	1741
M2096-85	0.85	6.6	2096
M2096-90	0.90	7.0	2096
M2096-95	0.95	7.3	2096
M2096-100	1.00	7.7	2096
M2096-110	1.10	8.4	2096
M2096-120	1.20	9.1	2096

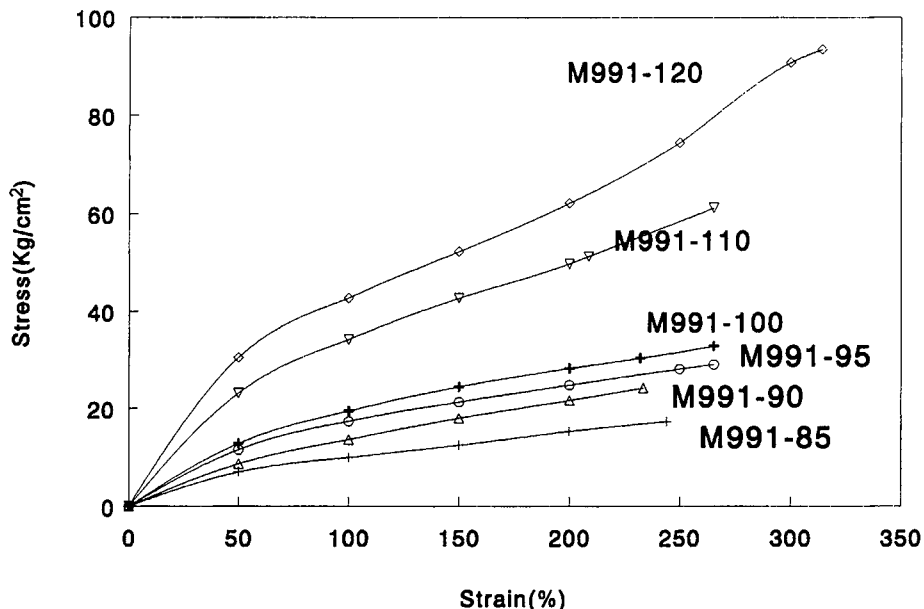


Figure 1 Stress-strain curves for polyurethanes synthesized from polyol having molecular weight of 991 at different weight percents of hard segment.

RESULTS AND DISCUSSION

Stress-strain curves of the test specimens of M991 and M1741 having the different molecular weights of 991 and 1741 are shown in Figures 1 and 2, respectively, by way of example. For Table II the mechanical properties of a

number of polyurethanes having four different molecular weights in different weight percents of hard segment are summarized. It is seen from Table II that the mechanical properties of polyurethane are dependent on molecular weights of the original polyols as well as weight percent of hard segment. In general, polyurethane having a lower molecular weight of original polyols indicates a higher

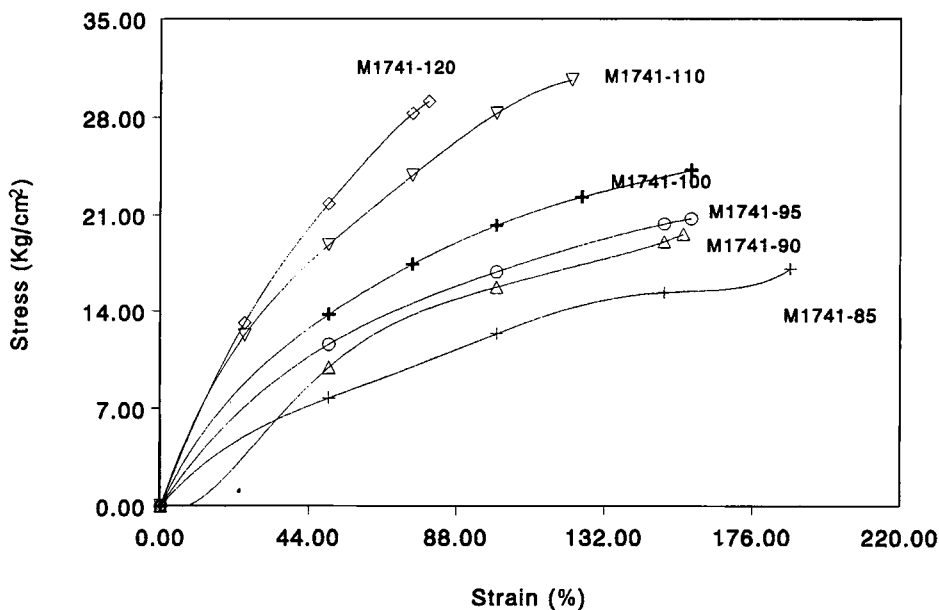


Figure 2 Stress-strain curves for polyurethanes synthesized from polyol having molecular weight of 1741 at different weight percents of hard segment.

Table II Mechanical Properties of Polyurethanes Synthesized from Polyols Having Different Molecular Weights and Different [NCO]/[OH] Ratios

Code	Tensile Stress (kg/cm ²)	Elongation (%)	Modulus (kg/cm ²)	T _g ^a (°C)
M991-85	18.2	247	18.8	3.6
M991-90	21.5	230	24.2	4.5
M991-95	28.4	262	32.3	6.0
M991-100	30.6	260	33.8	6.7
M991-110	50.3	265	57.3	11.7
M991-120	92.5	324	170.4	16.3
M1220-85	14.5	256	18.2	-0.5
M1220-90	16.0	285	23.4	1.1
M1220-95	28.7	211	45.6	2.3
M1220-100	30.2	273	36.7	4.6
M1220-110	45.2	245	66.7	5.8
M1220-120	58.5	300	70.0	7.8
M1741-85	15.5	186	16.6	-9.3
M1741-90	19.4	142	24.5	-8.6
M1741-95	20.2	149	26.3	-7.0
M1741-100	22.3	150	32.1	-6.8
M1741-110	30.0	120	45.6	-6.2
M1741-120	29.5	81	54.4	-5.8
M2096-85	11.0	165	11.3	-10.9
M2096-90	13.2	157	13.2	-9.6
M2096-95	14.8	213	18.8	-8.4
M2096-100	17.9	210	27.6	-7.9
M2096-110	19.5	240	26.4	-7.2
M2096-120	25.6	275	35.0	-6.6

^a Measured by DSC.⁵

tensile strength as well as Young's modulus at a same weight percent of hard segment. It is very interesting to find out that the elongation of polyurethane is increased as weight percent of hard segment is increased in the case of polyurethane having a lower molecular weight than the original polyols (see Table II and Fig. 1). On the contrary, the elongation of polyurethane is decreased as weight percent of hard segment is increased in the case of polyurethane having a higher molecular weight of original polyols (see Table II and Fig. 2). The chemistry of urethane reaction between polyol and diisocyanate might be very complex; the profound effects of the molecular weight of

original polyols and weight percent of hard segment, which is corresponding to [OH]/[CNO] ratio, are evident. It is found that the polyurethane having a lower molecular weight of original polyols (e.g., around 1000) in a higher weight percent hard segment (say 23.2) exhibits the most satisfactory elastomer characteristics, which can attain 90 kg/cm² in tensile stress with 320% in the elongation.

CONCLUSION

PET waste can be depolymerized by glycolyzing it with EG. Polyester polyol can then be obtained by reacting glycolyzed products with adipic acid. Polyurethanes were then synthesized by reacting these polyester polyols with an isocyanate. Polyurethanes reacted with MDI indicated satisfactory elastomer characteristics. It is found that polyurethane having molecular weight of original polyol of around 1000 in a higher weight percent of hard segment (say 23.2) exhibits a satisfactory elastomer characteristics, that can attain about 90 kg/cm² in tensile stress, with about 320% in the elongation, with the modulus of about 170 kg/cm².

References

1. G. R. Smoluk, *Mod. Plast.*, **65**(2), 87 (1988).
2. S. N. Tong, D. S. Chen, C. C. Chen, and L. Z. Chung, *Polymer*, **24**, 469 (1983).
3. U. R. Vaidya and V. M. Nadkarni, *J. Appl. Polym. Sci.*, **24**, 235 (1987).
4. U. R. Vaidya and V. M. Nadkarni, *J. Appl. Polym. Sci.*, **38**, 1179 (1989).
5. S. C. Lee, Y. W. Sze, and C. C. Lin, *J. Appl. Polym. Sci.*, **52**, 869 (1994).
6. S. Baliga and W. T. Wong, *J. Polym. Sci., Part A, Polym. Chem.*, **27**, 2071 (1989).

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Received July 13, 1994

Accepted August 8, 1994