

PROPERTIES OF POLYURETHANE ELASTOMERS PREPARED FROM 1,1'-ISO-PROPYLIDENE BIS- (p-PHENYLENE-OXY) DI-PROPANOL-2, A POLYETHER (OR POLYESTER), AND 4,4'-DIPHENYLMETHANE DIISOCYANATE (MDI) BY ONE-STEP REACTION METHOD*

ZHANG Jun (张 钧)

(*Tianjin College of Textile Engineering, Tianjin*)

Goodman, I., Fort, R.J. and Sheldon, R.P.

(*Postgraduate School of Studies in Polymer Science, University of Bradford, U.K.*)

ABSTRACT

Two new types of block polyurethane elastomers were prepared using two polyols polyethylene adipate and PTHF respectively, and diisocyanate MDI extended with Dianol-33 (a new extender), by one step reaction and casting method.

The properties of these polyurethane were studied by employing Instron infrared spectroscopy, DSC and wide angle X-ray diffraction etc.

INTRODUCTION

The properties and morphology of polyurethane block copolymers have been under extensive investigation over the past thirty years. Polyurethane casting elastomers have some superior properties such as high tensile strength and elongation, and excellent abrasion resistance, oil resistance and tear strength^[1-2]. Further-more, the most important feature of polyurethane elastomers is their castability which makes processing very simple. Due to the broad range of structural variations that are possible in these systems, their physical properties range from soft and flexible gum-like materials to rigid and tough semicrystalline thermoplastics.

1,1'-Isopropylidene bis-(p-phenylene-oxy) di-propanol-2 (Dianol-33) is a new kind of diol used as a polyurethane extender^[2]. When used in polyurethane elastomers it can improve the mechanical properties, such as tensile strength and resilience and also give better chemical resistance. Little work in this field has been published so far.

In the present work, polyurethane elastomers were prepared, by casting, by one-step reaction of Dianol-33 with polyethylene adipate (PEA, *MW* 2026) or polytetramethylene ether-glycol (or polytetrahydrofuran, PTHF, *MW* 650, 1000, 2000) and MDI.

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EXPERIMENTAL

1. Materials

(1) Polyethylene adipate (PEA) of molecular weight 2026, acid value 0.34, hydroxyl value 43.74, obtained from Imperial Chemical Company (ICI) was dried by applying a vacuum of 4.5 mmHg at 120°C for 2.5 h until no more gas bubbles were evolved.

(2) The polytetramethylene ether-glycols (or polytetrahydrofuran PTHF) used were obtained from the Quaker Oats Company (Polymeg, *MW* 2000, 1000) and the Du Pont Company (Teracol, *MW* 650).

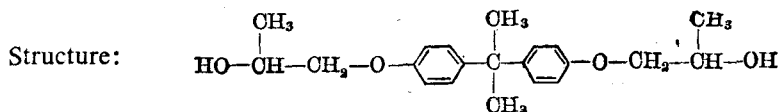
(3) Diisocyanate

4,4'-Diphenylmethane diisocyanate (MDI) obtained from ICI. The trade name of the MDI is Suprasec MPR. It is a white to pale-yellow solid at ambient temperature. It was melted (about 60°C) and then stored in the absence of moisture until use.

(4) Low molecular weight diol

Chemical name: 1,1'-isopropylidene bis-(p-phenylene-oxy)
di-propanol-2

Trade name: Dianol-33



Melting point: 70–80°C

Appearance: Colourless to slightly yellow solid

It was obtained from Akzo Chemie Netherlands.

2. Elastomer preparation

Required amounts of polydiol PEA (or PTHF) and low molecular weight diol Dianol-33 were weighed into a four-necked round-bottom flask, equipped with a mechanical stirrer, a thermometer, a nitrogen inlet and a vacuum outlet, and then heated in an oil bath to about 80–90°C. The molten mixture was degassed by stirring under vacuum, after about 30 minutes, the vacuum was broken and dry nitrogen was then let into the flask and molten MDI (5 mole % excess) was added. This operation of adding molten MDI must be carried out as fast as possible, because quick reaction occurs in some formulations. Vacuum was reapplied and stirring continued. After 0.5–2 minutes, the stirring was stopped, the vacuum broken and dry nitrogen was let into the flask and the reacting mixture was poured into a Teflon-coated mould (which had been heated to about 110°C) to give a sheet about 0.3 cm thick. This was cured in an oven at 90–130°C for 6–24 hours. The polyurethane elastomer was removed from the mould and allowed to "age" for at least one week at ambient temperature prior to testing. The resulting products were transparent and bubble-free elastomers. In order to compare the properties, conditions were varied (6, 12, and 24 hours; 90, 110 and 130°C).

Table 1 gives the information on these polyurethane elastomers.

Table 1 Polyurethane elastomer samples

Sample No.	Polyol/MDI/Dianol-33	Ratio (molar)	Hard segment (% wt)	Cure temperature (°C)	Cure time (h)
1	PEA 2525/MDI/Dianol-33	1/2/1	18	110	24
2	PEA 2525/MDI/Dianol-33	1/2.5/1.5	24	110	24
3	PEA 2525/MDI/Dianol-33	1/3/2	32	110	24
4	PEA 2525/MDI/Dianol-33	1/4/3	39	110	24
5	PEA 2525/MDI/Dianol-33	1/5/4	46	110	24
6	PTHF 650/MDI/Dianol-33	1/1.5/0.5	25	110	24
7	PTHF 650/MDI/Dianol-33	1/2/1	40	110	24
8	PTHF 1000/MDI/Dianol-33	1/2/1	32	110	24
9	PTHF 1000/MDI/Dianol-33	1/3/2	49	110	24
10	PTHF 2000/MDI/Dianol-33	1/2/1	21	110	24
11	PTHF 2000/MDI/Dianol-33	1/3/2	35	110	24
12	PTHF 2000/MDI/Dianol-33	1/4/3	44	110	24
13	PTHF 2000/MDI/Dianol-33	1/3/2	35	110	6
14	PTHF 2000/MDI/Dianol-33	1/3/2	35	110	12
15	PTHF 2000/MDI/Dianol-33	1/3/2	35	90	24
16	PTHF 2000/MDI/Dianol-33	1/3/2	35	130	24

3. Measurements

(1) Mechanical properties

Tensile strength measurements were made using a standard Instron machine (table model type 1026) with a crosshead speed of 50 mm per minute.

(2) Differential scanning calorimetry (DSC)

DSC experiments were performed with a Perkin-Elmer DSC-IB instrument scanning at a speed of 16°C/minute from -100 to 265°C. Samples were taken directly from the cast sheets. The samples weighed 20 ± 3 mg.

(3) Infrared spectrometry

IR spectra of the samples over 4000 to 400 cm^{-1} were obtained by using a Perkin-Elmer model 377 Grating Infrared Spectrophotometer. Samples of suitable thickness were prepared by solvent casting from tetrahydrofuran solutions.

(4) Wide angle X-ray diffraction

Wide angle X-ray diffraction patterns were recorded on flat photographic films using

X-ray diffraction generator type 1330 of Philips Scientific Equipment. $\text{CuK}\alpha$ radiation was used for 1.5 hours.

(5) Hardness

Hardness was measured by using an International Rubber Hardness Degrees, Wallace Hardness Meter.

RESULTS AND DISCUSSION

1. Mechanical properties

The properties of polyurethane elastomers based on PEA (or PTHF), diisocyanate (MDI) and Dianol-33 are shown in Table 2 and Figures 1—3. These illustrate that hardness, tensile stress at 300% elongation, and tensile strength at break of polyurethane elastomers are enhanced by an increase in the molar ratio of Dianol-33/PEA (or PTHF).

Elongation at break, tensile set at 300% elongation, and set after break decreased with increasing molar ratio of Dianol-33/PEA (or PTHF).

Table 2 shows that the value of hardness, tensile stress at 300% elongation, and tensile strength at break increased with increasing cure time (from 6—24 hours) at the same molar ratio of Dianol-33/PTHF. The tensile set at 300% elongation, set after break and elongation decreased with increasing cure time at the same molar ratio.

Table 2 Mechanical properties of polyurethane elastomers

Polyol/MDI/D 33	Ratio (molar)	Hard seg- ment (% wt)	Hard- ness	Tensile stress at 300% elon. (Kg/ cm ²)	Tensile strength at break (Kg/ cm ²)	Tensile set at 300%	Set after break (%)	Elon. (%)	Cure temp. (°C)	Cure time (hour)
PEA2526/MDI/D33	1/2/1	18	58	14.4	118.6	30	53.8	850	110	24
PEA2526/MDI/D33	1/2.5/1.5	24	68	28.2	305.2	1.5	3.1	600	110	24
PEA2526/MDI/D33	1/3/2	32	72	22.6	213.7	5.8	6.9	650	110	24
PEA2526/MDI/D33	1/4/2	39	88	96.1	362	0.8	0.8	450	110	24
PTHF2000/MDI/D33	1/2/1	21	50	4.1	19	61.5	211.5	1550	110	24
PTHF2000/MDI/D33	1/3/2	35	65	10.4	80.6	38.5	50	850	110	24
PTHF2000/MDI/D33	1/4/3	44	80	177.6	392.5	0.04	0.04	400	110	24
PTHF2000/MDI/D33	1/3/2	35	60	8.2	11.3	57.7	107.7	1000	110	6
PTHF2000/MDI/D33	1/3/2	35	65	12.7	28.9	38.5	84.6	850	110	12
PTHF2000/MDI/D33	1/3/2	35	74	14.6	82.8	38.5	57.5	920	90	24
PTHF2000/MDI/D33	1/3/2	35	65	12.6	68.7	26.9	38.5	750	130	24
PTHF1000/MDI/D33	1/2/1	32	70	38.9	225	11.5	7.7	430	110	24
PTHF650/MDI/D33	1/0.5/1.5	25	65	15.4	146	34.6	73.1	850	110	24

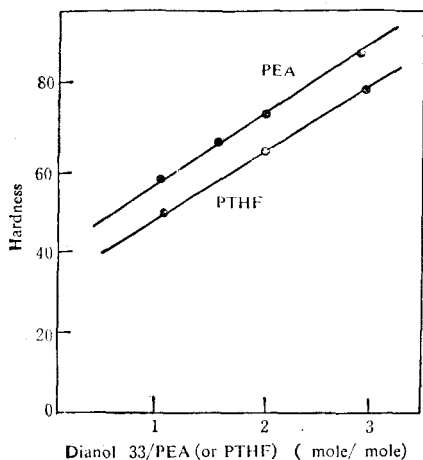


Fig. 1 Effect of ratio of diol to PEA or PTHF on hardness ($MW_{\text{PEA}} = 2026$, $MW_{\text{PTHF}} = 2000$)

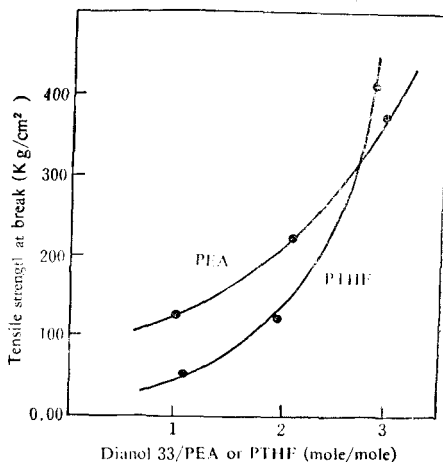


Fig. 2 Effect of ratio of diol to PEA or PTHF on tensile strength ($MW_{\text{PEA}} = 2026$, $MW_{\text{PTHF}} = 2000$)

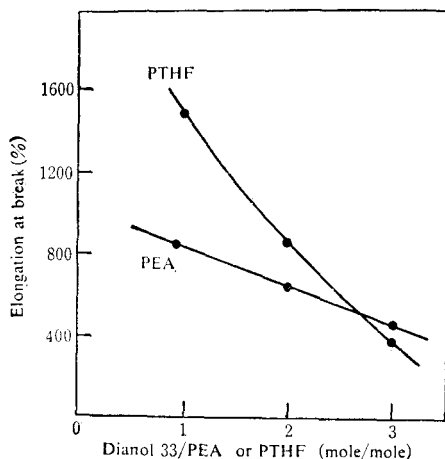


Fig. 3 Effect of ratio of diol to PEA or PTHF on elongation at break

Table also shows that hardness, tensile stress at 300% elongation, tensile strength at break, tensile set at 300% elongation, set after break, and elongation at break decreased with increasing temperature of cure (90, 110, 130°C) at the same molar ratio.

2. Thermal properties

The thermal properties of polyurethane elastomers can be readily characterized by differential scanning calorimetry (DSC) [3-10]. The DSC thermograms of some polyether and polyester urethanes are presented in Figures 4-7. The transition behaviour of all the polyurethane samples studied are collected in Table 3.

These polyurethanes (for both PEA and PTHF urethane) generally exhibit four transi-

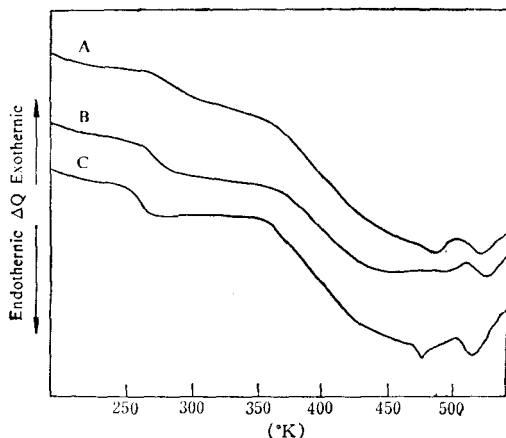


Fig. 4 DSC curves for urethane of PEA having molecular weight of 2026 (A, 1/4/3; B, 1/3/2; C, 1/2/1)

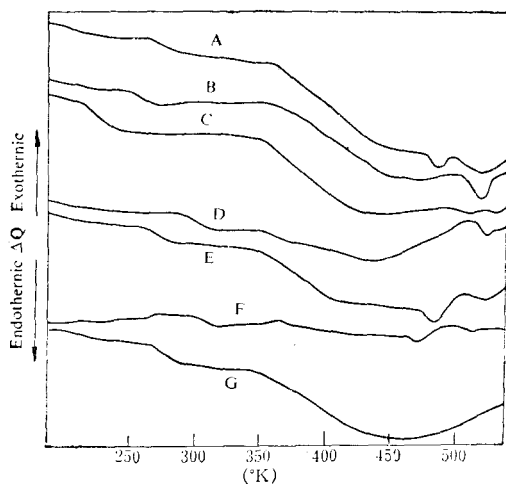


Fig. 5 DSC cures for urethane of PTHF having molecular weight (A 1/4/3, MW 2000; B 1/3/2, MW 2000; C 1/2/1, MW 2000; D 1/3/2, MW 1000; E 1/2/1, MW 1000; F 1/2/1, MW 650; G 1/1.5/0.5, MW 650)

tion regions as detected by DSC. The first transition is that of shift in base line in the region of -58 to 26°C which probably corresponds to the T_g of the soft segment. The second transition is that in the region of 70 to 92°C which probably corresponds to the disruption of short range order induced by room temperature annealing^[4]. The third transition is an endothermal peak (from 169 – 225°C) which is believed to represent the disordering of the better ordered hard segment domains^[4]. The region of 238 to 251°C is the fourth transition which corresponds to the melting temperature of the hard segment domains. It is also an endothermal peak.

It should be noted that these polyurethane soft segment T_g transitions are more sensitive to low molecular weight diol content, and they also show an increase of T_g with increasing hard segment concentration.

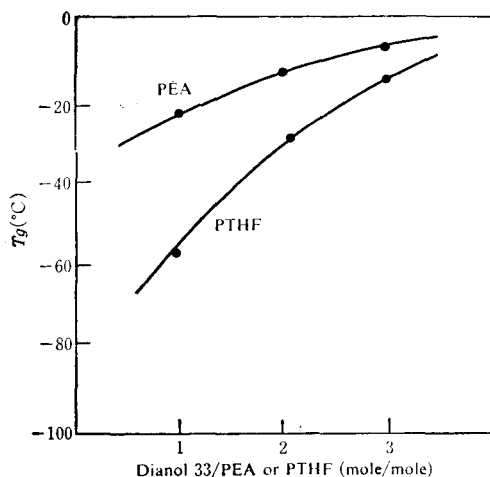


Fig. 6 Effect of ratio of diol to PEA or PTHF on T_g ($MW_{PEA} = 2026$, $MW_{PTHF} = 2000$)

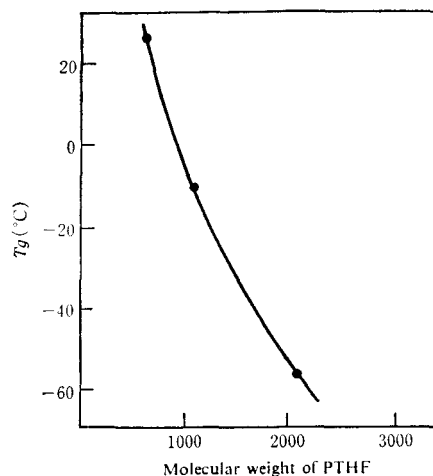


Fig. 7 Effect of molecular weight of PTHF on T_g (PTHF/MDI/Dianol-33 = 1/2/1 mole)

Table 3 Thermal transitions by DSC

Polyol/MDI/Dianol-33	Ratio (mole)	Hard segment (% wt)	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_4 (°C)
PEA 2526/MDI/Dianol-33	1/2/1	18	-23	86	205	245
PEA 2526/MDI/Dianol-33	1/3/2	32	-12	92	220	250
PEA 2526/MDI/Dianol-33	1/4/3	39	-6	86	213	244
PTHF 650/MDI/Dianol-33	1/1.5/0.5	25	-4	70	195	—
PTHF 650/MDI/Dianol-33	1/2/1	40	26	92	198	240
PTHF 1000/MDI/Dianol-33	1/2/1	32	-11	71	209	250
PTHF 1000/MDI/Dianol-33	1/3/2	49	17	76	225	250
PTHF 2000/MDI/Dianol-33	1/2/1	21	-58	77	168	238
PTHF 2000/MDI/Dianol-33	1/3/2	35	-29	87	197	243
PTHF 2000/MDI/Dianol-33	1/4/3	44	-13	90	207	257

The most important point shown by Figure 6 is that the soft segment T_g of polyester urethane is higher than that of the polyether urethane of the same molecular weight (2000). This suggests that the polyether urethane elastomers have better microphase-separation than those based on polyester. The results are consistent with the conclusions of Clough and Schneider^[9,10].

Figure 7 shows that polyether urethane have a sharp decrease in soft segment T_g with increasing polyether molecular weight. This indicates that longer soft segments have better phase separation in these systems.

3. Infrared analysis

Polyether and polyester urethanes can be easily distinguished by infrared spectroscopy^[11-15]. Figures 8—9 show the IR spectra of polyether and polyester urethanes. These materials contain either PEA or PTHF as the soft segment and MDI-Dianol-33 urethane sequences as hard segment.

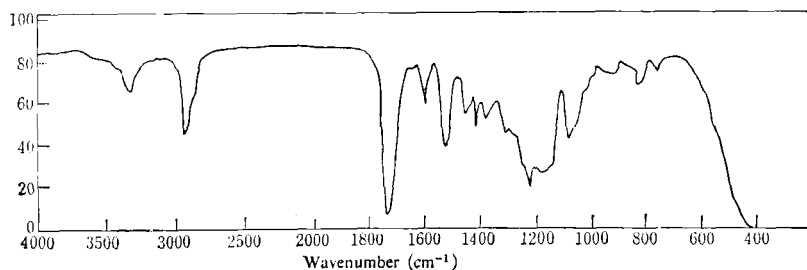


Fig. 8 IR spectra of PEA 2526/MDI/Dianol-33, 1/3/2

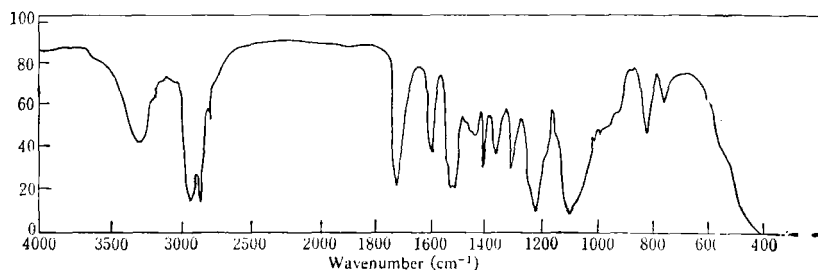


Fig. 9 IR spectra of PTHF 2000/MDI/Dianol-33, 1/3/2

The polyether urethanes can readily be identified by the strong absorption of the C—O—C linkage at 1105 cm^{-1} and a weak band at 990 cm^{-1} .

The polyester urethanes, on the other hand, show a relatively strong band due to the stretching vibration of the C—O—C of the adipate ester functional groups at 1175 cm^{-1} .

The urethane linkage is best characterized by the NH and C=O absorptions. The major NH absorption occurs at $3300\text{--}3330\text{ cm}^{-1}$ which is attributed to hydrogen bonded NH groups. In addition, the amide (NH, CH) absorptions at 1530 cm^{-1} , 1305 cm^{-1} , and 1200 cm^{-1} are also characteristic of urethane functionality. The urethane carbonyl absorption is at 1730 cm^{-1} . These are associated with hydrogen bonded and free urethane carbonyl groups but they cannot be clearly seen in this kind of polyether or polyester urethanes. This is due to the overlapping of the ester and urethane carbonyl absorptions.

Polyether carbonyls occur only in the aromatic urethane portion of the chain, but the polyester urethanes contain two different kind of groups, both of which may be free and hydrogen bonded components, i. e. they contain both ester and urethane carbonyl groups. Thus, there are four possible carbonyl peaks in the polyester spectra (free and bonded carbonyl absorption peaks for each of two types of ester and urethane carbonyl groups present).

This gives rise to a much broader carbonyl absorption region in polyester urethanes as compared to polyether urethanes.

4. Wide angle X-ray diffraction

X-ray diffraction was used to gain some understanding of the morphology of the polyurethanes^[16-22].

X-ray patterns of unstretched and of stretched PEA and PTHF urethanes are shown in Figures 10—11.

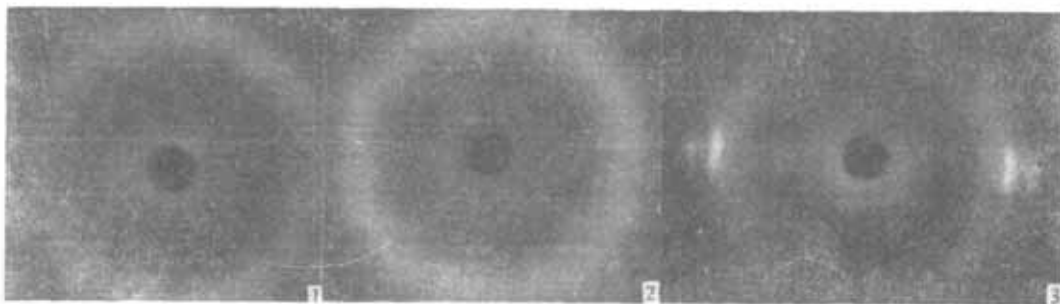


Fig. 10 X-ray patterns of PEA 2526 (1/3/2)
(1) Unstretched; (2) 200% extension; (3) 500% extension.

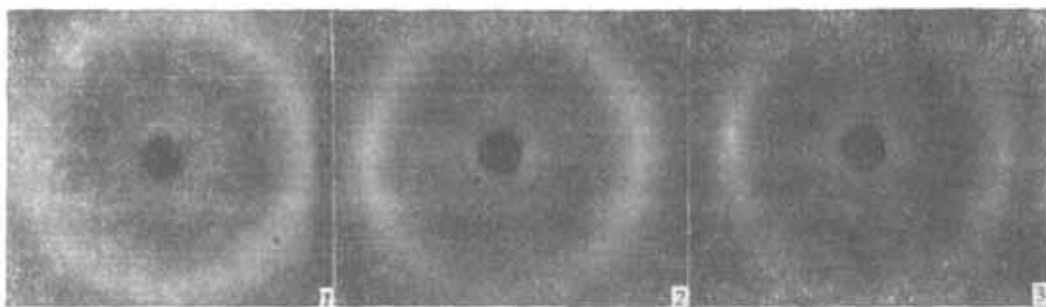


Fig. 11 X-ray patterns of PTHF 2000 (1/3/2)
(1) Unstretched; (2) 200% extension; (3) 400% extension

Obviously, both the PEA and PTHF urethanes unstretched samples of soft segment regions are amorphous. When they were stretched at room temperature, they showed evidence of stress-crystallization, the degree of which depends on the degree of stretching, i. e. the degree of stress-crystallization of the polyurethanes shows an increase with increasing in stretching.

CONCLUSIONS

New types of polyurethane were prepared by one-step reaction of a mixture of a diisocyanate (MDI), PEA (or PTHF), and low molecular weight diol Dianol-33 using casting method.

The tensile strengths of elastomers increase with increasing molar ratio of Dianol-33 to PEA (or PTHF). The elongation at break, tensile set at break, tensile set at 300% elongation, and set after break decrease with increasing molar ratio of Dianol-33 to PEA (or PTHF).

Hardness, tensile stress at 300% elongation, tensile strength at break, set after break, and elongation at break decreased with increasing temperature of cure (from 90 to 130°C).

In these polyurethanes the T_g of the soft segment is sensitive to diol content and shows an increase with increasing hard segment concentration.

Moreover, the T_g of the soft segment in the polyester urethanes is higher than that in the polyether urethanes. This suggests that the polyether urethanes have better micro-separation than the polyester based urethane elastomer.

The value of T_g of the soft segment of the polyether urethanes show a sharp decrease with increasing polyether molecular weight. This indicates that the longer soft segments have a better microphase-separation in this system.

Both the PEA and the PTHF urethane unstretched samples of soft segment regions are amorphous. They became stress-crystallized when stretched and the degree of stress-crystallization shows an increase with increasing degree of stretching.

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