

# Syntheses and Properties of Pentaerythritol-Containing Urethane Prepolymers and Crosslinked Films

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## Synopsis

Two series of polyhydroxyl urethane-prepolymers (Pre-PU) were synthesized from pentaerythritol (PETH), toluene diisocyanate (TDI), and polyglycols (PG). One is a single molecular type of PETH-(TDI-PG)<sub>n</sub>-TDI-PETH Pre-PU (S-Pre-PU). The other is a mixture of (PETH-TDI)<sub>n</sub>-PETH and S-Pre-PU. The Pre-PU mixed with an equivalent triisocyanate regenerator (Desmodur AP-Stable, a crosslinking agent) were baked to form the crosslinked PU films. The mechanical properties such as tensile strengths, elongation at break, and viscoelasticities of PG-modified crosslinked films were studied.

## INTRODUCTION

Pentaerythritol (PETH) is usually used to synthesize polyester coatings and polyurethane foams.<sup>1-4</sup> Few polyurethane coatings prepared from PETH have been reported. In this study, PETH, toluene diisocyanate (TDI), and polyglycols (PG) were used to produce polyhydroxyl urethane prepolymers (Pre-PU). The prepolymers were mixed with an equivalent amount of Desmodur AP-Stable, a crosslinking agent composed of trimethylol propane and phenol, in *m*-cresol to give a coating solution. The solution was coated and baked to give crosslinked polyurethane films. The mechanical-rheological properties such as tensile strengths, elongations at break, and viscoelasticities of PG-modified crosslinked films were studied. Polyethylene glycol ( $\bar{M}_n = 1000$ ) and two polypropylene glycols ( $\bar{M}_n = 1000$  and 2000) were used. The molar ratio of PG/TDI/PETH was varied and different polyglycols were used to give urethane prepolymers with different molecular weights. The synthetic urethane prepolymers are divided into two series. One is a single molecular type of PETH-(TDI-PG)<sub>n</sub>-TDI-PETH Pre-PU. The other is a mixture of (PETH-TDI)<sub>n</sub>-PETH and PETH-(TDI-PG)<sub>n</sub>-TDI-PETH.

## EXPERIMENTAL

### Materials

Trimethylol propane (TMP) (Hayashi Pure Chemicals EP, Japan) and phenol (Wako Pure Chemicals, Japan) were used in the preparation of Desmodur AP-Stable.

Reagents used in the synthesis of urethane prepolymers included pentaerythritol (PETH) (TCI EP, Japan), toluene diisocyanate (TDI) (San Ten Chemicals), and three different polyglycols of extra-pure grade: polypropylene glycol with  $\bar{M}_n = 1000$  [PPG(#1000)] (Hayashi), polypropylene glycol with  $\bar{M}_n = 2000$  [PPG(#2000)] (Wako), and polyethylene glycol with  $\bar{M}_n = 1000$  [PEG(#1000)] (TCI).

### Synthesis

Crosslinking agent (a triisocyanate regenerator): The synthetic method of the triisocyanate regenerator (Desmodur AP-Stable) was previously described.<sup>5</sup>

**Urethane Prepolymers.** Given quantities of TDI were added to a 100-mL 3-necked flask equipped with an electric stirrer, a reflux condenser, a dropping funnel, and inert nitrogen blanket. A calculated quantity of PG was added dropwise into the flask. The mixture was kept at room temperature for 30 min, and gradually heated to 50–60°C for 30 min, and then cooled to room temperature. To this mixture, a calculated quantity of PETH was added, the temperature was raised to 80°C for 0.5 h, to 100–120°C for 1 h, and to 140°C for another 1 h for completion. The resultant product was a hydroxyl-terminated urethane prepolymer.

### Film Casting

A 40% solid content solution was prepared by mixing hydroxyl-terminated urethane prepolymer and an equivalent amount of Desmodur AP-Stable in *m*-cresol. Thin 10-cm diameter circles were spread on aluminum foil. Upon baking at 200°C for 30 min, a crosslinked film was formed which adhered to the aluminum foil. To release the crosslinked polyurethane film, 6*N* HCl was used to dissolve the aluminum.

### Infrared Spectral Measurement

Infrared (IR) measurements of the crosslinked film, taken to observe the change of functional groups, were recorded on a Jasco IRA-2 IR spectrometer.

### Mechanical Property Testing

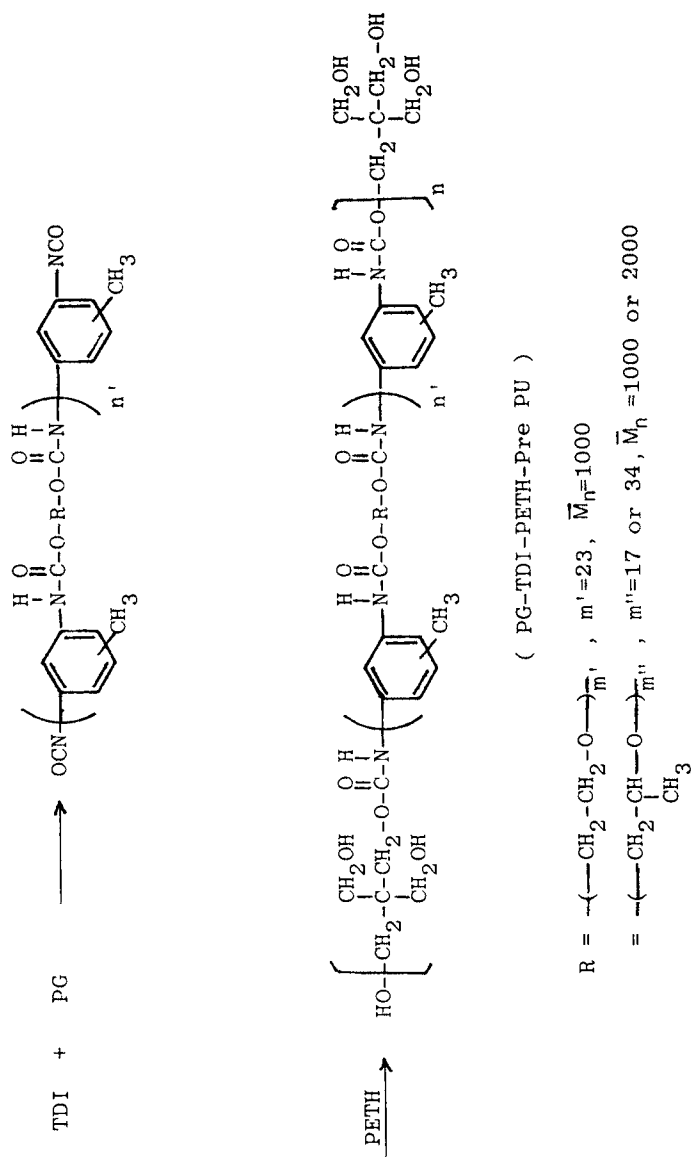
The crosslinked film was cut into dumbbell shapes with a length of 7 cm, a breadth within 1 cm at the neck, and a thickness of < 0.5 mm. An Instron Universal Tester was used to study the mechanical properties of the sample at room temperature at a drawing speed of 5 cm/min.

### Thermogravimetric Analysis

The thermogravimetric investigations were performed on the Du Pont 951 thermogravimetric analysis unit.

### Dynamic Viscoelasticity Test

The sample was cut into rectangular shapes 4.5 cm in length, a breadth within 5 mm, and a thickness < 0.3 mm. A Rheovibron DDV-II Dynamic Viscoelastometer was used to study the dynamic mechanical behavior of the sample in the temperature range of 25–230°C, at a frequency of 110 Hz.



Scheme 1.

## RESULTS AND DISCUSSION

## Urethane Prepolymers

Toluene diisocyanate (TDI) was reacted with polyglycol (PG) to give isocyanate-terminated polyurethane, then pentaerythritol (PETH) was added to produce hydroxyl-terminated urethane prepolymer, as shown in Scheme 1. Changing the molar ratio of PG/TDI/PETH and using different molecular weight PG can give different molecular weight urethane prepolymers.

The synthetic urethane prepolymers are divided into two series, A and B, as shown in Table I. Series A is a single molecular type of PETH-(TDI-PG)<sub>n</sub>-TDI-PETH Pre-PU. The molecular weight of Pre-PU increased with the increase of the molar ratio of PG/TDI. The crosslinking density of the crosslinked film decreased with increasing molecular weight of Pre-PU. Series B is Series A Pre-PU mixed with TDI/PETH-containing Pre-PU.

## Crosslinking Reaction of Urethane Prepolymers

The properties of crosslinked polyurethanes are dependent on the structure of *R* and the value of *n*: large *n* or *m* results in low crosslinking density, but

TABLE I  
Composition of Synthetic Urethane Prepolymers

| Pre-PU   | PG          | Molar ratio |     |      |        | Average hydroxyl equivalent weight <sup>a</sup> |
|----------|-------------|-------------|-----|------|--------|---|
|          |             | PG          | TDI | PETH | PG/TDI |   |
| A-P-I-1  | PPG (#1000) | 1           | 2   | 2    | 0.50   | 275   |
| A-P-I-2  |             | 2           | 3   | 2    | 0.67   | 466   |
| A-P-I-3  |             | 3           | 4   | 2    | 0.75   | 661   |
| A-P-I-4  |             | 4           | 5   | 2    | 0.80   | 857   |
| A-P-I-5  |             | 5           | 6   | 2    | 0.83   | 1053  |
| A-P-I-6  |             | 6           | 7   | 2    | 0.86   | 1248  |
| A-P-I-7  |             | 7           | 8   | 2    | 0.87   | 1444  |
| A-P-I-8  |             | 8           | 9   | 2    | 0.89   | 1640  |
| A-P-II-1 | PPG (#2000) | 1           | 2   | 2    | 0.50   | 437   |
| A-P-II-2 |             | 2           | 3   | 2    | 0.67   | 799   |
| A-P-II-3 |             | 3           | 4   | 2    | 0.75   | 1161  |
| A-P-II-4 |             | 4           | 5   | 2    | 0.80   | 1524  |
| A-P-II-5 |             | 5           | 6   | 2    | 0.83   | 1886  |
| A-E-I-3  | PEG (#1000) | 3           | 4   | 2    | 0.75   | 661   |
| A-E-I-4  |             | 4           | 5   | 2    | 0.80   | 857   |
| A-E-I-5  |             | 5           | 6   | 2    | 0.83   | 1053  |
| A-E-I-6  |             | 6           | 7   | 2    | 0.86   | 1248  |
| A-E-I-7  |             | 7           | 8   | 2    | 0.87   | 1444  |
| B-P-I-1  | PPG (#1000) | 1           | 10  | 10   | 0.10   | 186   |
| B-P-I-2  |             | 2           | 10  | 10   | 0.20   | 213   |
| B-P-I-3  |             | 3           | 10  | 10   | 0.30   | 235   |
| B-P-I-4  |             | 4           | 10  | 10   | 0.40   | 254   |
| B-P-I-5  |             | 5           | 10  | 10   | 0.50   | 270   |
| B-P-I-6  |             | 6.7         | 10  | 10   | 0.67   | 293   |
| B-P-I-7  |             | 7.5         | 10  | 10   | 0.75   | 303   |

<sup>a</sup>Average OH eqv. wt. =  $(n_1M_1 + n_2M_2 + n_3M_3)/2(n_1 - n_2 + 2n_3)$ , where  $n_1, n_2, n_3$  and  $M_1, M_2, M_3$ , are the molar ratio and the molecular weight of PG, TDI, and PETH, respectively.

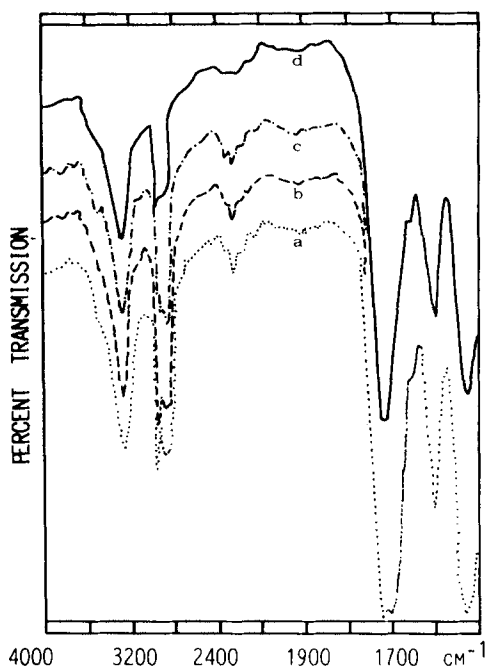


Fig. 1. Infrared spectra of the crosslinked film prepared from A-P-I-2 Pre-PU with equivalent AP-Stable baked at 220°C for different curing times: (a) 10 min; (b) 20 min; (c) 40 min; (d) 60 min.

small  $n$  and  $m$  give hard and brittle crosslinked films. Because  $R$  represents a soft segment, increasing  $n$  and  $m$  can vary the properties of crosslinked films from hard and strong to soft and elastic.

### IR Spectra of Crosslinking Reaction

Infrared spectra of the crosslinked films prepared from A-P-I-2 Pre-PU with equivalent AP-Stable baked at 220°C for different curing times are shown in Figure 1. From the change of isocyanate absorption at 2250  $\text{cm}^{-1}$ , it can be observed that when the crosslinking reaction of AP-Stable and urethane prepolymer took place, the AP-Stable deblocked phenol first and then reacted with hydroxyl groups of the urethane prepolymer. However, the rate of deblocking phenol to regenerate isocyanate groups is faster than that of the reaction of urethane prepolymer with isocyanate groups.

The ratio of the intensity of the absorption peaks of isocyanate groups and that of alkyl groups at 2900  $\text{cm}^{-1}$  is a function of curing time. As shown in Figure 2, the isocyanate group is regenerated first and then reacts with hydroxyl groups of urethane prepolymer to form urethane linkages. The absorption ratio of  $[\text{NCO}]/[\text{alkyl}]$  decreased linearly with curing time.

### Mechanical Properties of the Crosslinked Films

The mechanical properties of crosslinked PU films are listed in Table II. The tensile strengths of crosslinked films decreased with an increase of the PG molar ratio, but the elongations at break increased with increasing molar ratio

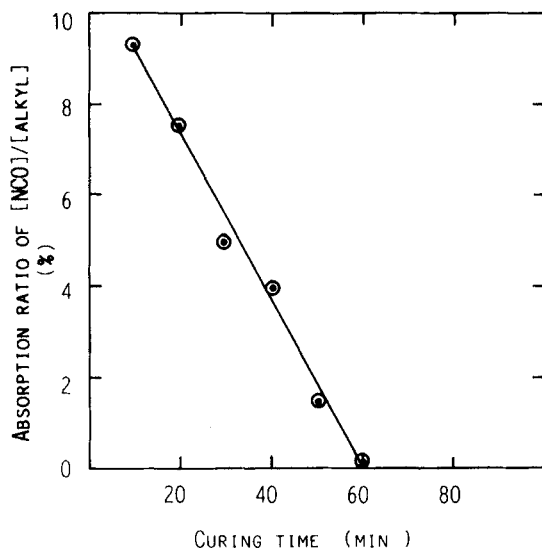


Fig. 2. IR absorption ratios of [NCO]/[alkyl] as a function of curing time.

TABLE II  
Mechanical Properties of Crosslinked Films

| Crosslinked films | Tensile strength (kg/cm <sup>2</sup> ) | Elongation at break (%) | Comments       |
|-------------------|--|-------------------------|----------------|
| A-P-I-1           | 249                                    | 9                       | hard & tough   |
| A-P-I-2           | 132                                    | 23                      | soft           |
| A-P-I-3           | 92                                     | 51                      | soft           |
| A-P-I-4           | 61                                     | 72                      | soft           |
| A-P-I-5           | 56                                     | 77                      | soft           |
| A-P-I-6           | —                                      | —                       | a              |
| A-P-I-7           | —                                      | —                       | a              |
| A-P-I-8           | —                                      | —                       | a              |
| A-P-II-1          | 114                                    | 12                      | hard & tough   |
| A-P-II-2          | 7                                      | 16                      | weak           |
| A-P-II-3          | 6                                      | 48                      | weak           |
| A-P-II-4          | 3                                      | 31                      | weak           |
| A-P-II-5          | —                                      | —                       | viscous        |
| A-E-I-3           | 14                                     | 57                      | weak & elastic |
| A-E-I-4           | 12                                     | 79                      | weak & elastic |
| A-E-I-5           | 5                                      | 76                      | weak & elastic |
| B-P-I-1           | 660                                    | 2                       | hard           |
| B-P-I-2           | 550                                    | 3                       | hard           |
| B-P-I-3           | 495                                    | 5                       | hard           |
| B-P-I-4           | 333                                    | 7                       | hard           |
| B-P-I-5           | 249                                    | 9                       | hard           |
| B-P-I-6           | 225                                    | 12                      | hard           |
| B-P-I-7           | 211                                    | 14                      | hard           |

a: These urethane prepolymers are insoluble in solvent.

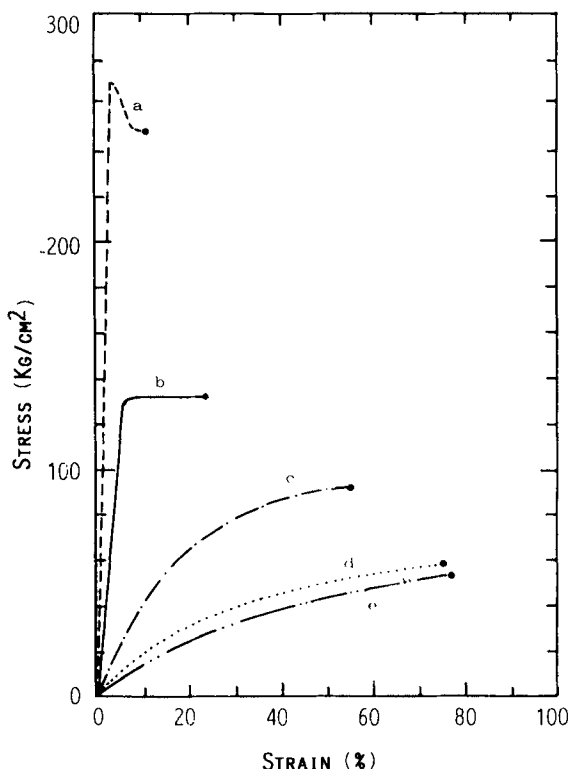


Fig. 3. Stress-strain curves of the crosslinked films prepared from A-P-I Pre-PU. Pre-PU: (a) A-P-I-1; (b) A-P-I-2; (c) A-P-I-3; (d) A-P-I-4; (e) A-P-I-5.

of PG. Because PG represents a noncrosslinkable soft segment, increasing the molar ratio of PG will decrease the crosslinking density and the tensile strengths of the crosslinked films. The increase of soft segment renders the crosslinked films easy to elongate, therefore, elongations at break increase with increase of PG. Tensile strengths of the crosslinked film prepared from A-P-I Pre-PU decreased gradually with the increase of PPG (#1000) (PPG-I). Tensile strengths of A-P-II-containing crosslinked films decreased rapidly with the increase of PPG (#2000) (PPG-II). The tensile strength of A-P-II-1 crosslinked film is about 114 kg/cm<sup>2</sup>, but crosslinked films prepared from the other A-P-II Pre-PU are very weak. This phenomenon is caused by the fact that if the soft segments of PPG-I are too long, a very low crosslinking density product is obtained. When PEG (#1000) (PEG-I) is used as the polyglycol, the crosslinked films are highly elastic but have poor tensile strength. A-P-I-6 to 8 Pre-PU are insoluble in *m*-cresol. A-E-I-6 and 7 Pre-PU cannot form crosslinked film. Tensile strengths of B-P-I-containing crosslinked films are strong, but their elongations at break are poor. All the crosslinked films prepared from B-P-I Pre-PU are hard and transient.

The stress-strain curves of A-P-I crosslinked films are shown in Figure 3. The crosslinked films prepared from A-P-I-1 Pre-PU are hard and tough. A-P-I-2 crosslinked films are soft and tough. The crosslinked films prepared from A-P-I-3 ~ 5 Pre-PU are soft and excellent elastomers.

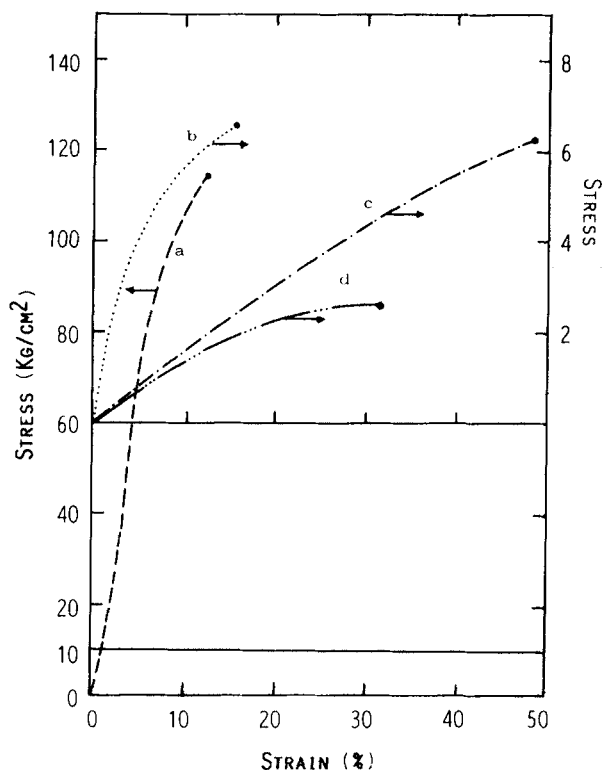


Fig. 4. Stress-strain curves of the crosslinked films prepared from A-P-II Pre-PU. Pre-PU: (a) A-P-II-1; (b) A-P-II-2; (c) A-P-II-3; (d) A-P-II-4.

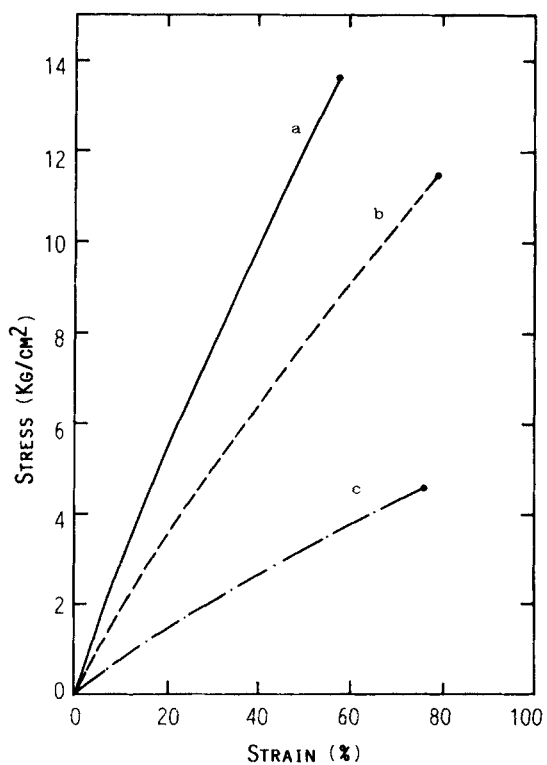


Fig. 5. Stress-strain curves of the crosslinked films prepared from A-E-I Pre-PU. Pre-PU: (a) A-E-I-3; (b) A-E-I-4; (c) A-E-I-5.



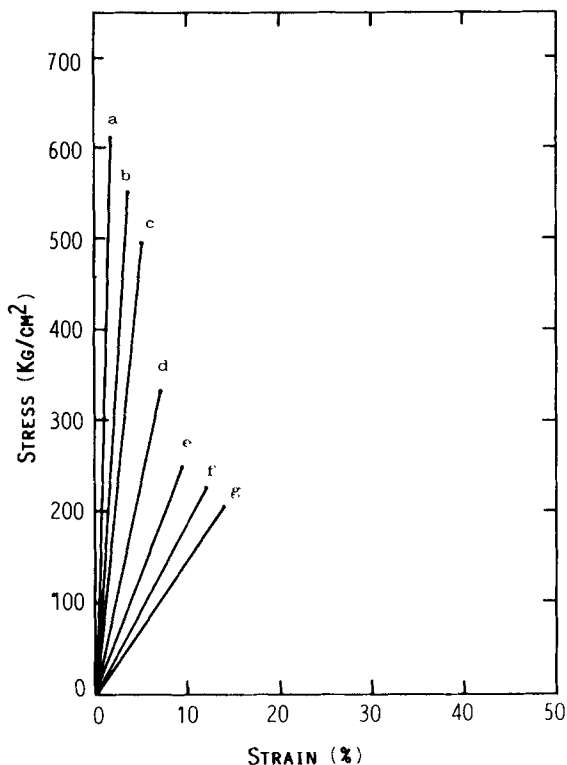


Fig. 6. Stress-strain curves of the crosslinked films prepared from B-P-I Pre-PU. Pre-PU: (a) B-P-I-1; (b) B-P-I-2; (c) B-P-I-3; (d) B-P-I-4; (e) B-P-I-5; (f) B-P-I-6; (g) B-P-I-7.

Substituting PPG-II for PPG-I, the stress-strain curves of the crosslinked films are shown in Figure 4. The crosslinked films prepared from A-P-II-1 Pre-PU are hard and tough. A-P-II-3 crosslinked films are good elastomers.

The stress-strain curves of the crosslinked films prepared from A-E-I Pre-PU are shown in Figure 5. Tensile strengths of crosslinked films decreased with the increase of PEG, but the elongations at break increased initially and then decreased with the increase of PEG. All the PEG-modified crosslinked films are soft and elastic.

The stress-strain curves of the crosslinked films prepared from B-P-I Pre-PU are shown in Figure 6. All the curves are linear, indicating that all these crosslinked films are strong and tough.

The relationship of tensile strength of the crosslinked films versus chain length of Pre-PU is shown in Figure 7. When the  $n'$  value in the range of 1-2, tensile strengths of PPG-II-modified crosslinked films decreased rapidly with  $n'$  while there is no change for  $n'$  values larger than 2. The tensile strength of PEG-modified crosslinked films also decrease with increasing  $n'$  values.

Figure 8 shows the relationship of elongation at break of the crosslinked films versus chain length of Pre-PU. The elongations at break of PPG-I-modified crosslinked films gradually increased with increasing the  $n'$  value. The elongations at break of PPG-II and PEG-modified crosslinked film increased first and then decreased with increasing  $n'$  values.

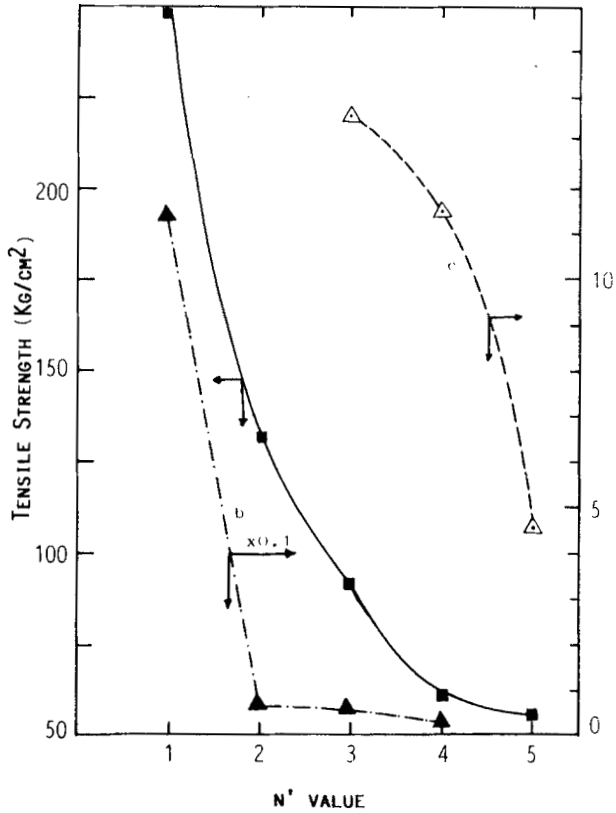


Fig. 7. The chain length of urethane prepolymer dependence of tensile strength for the crosslinked films prepared from Series A Pre-PU. PG: (a) PPG(#1000); (b) PPG(#2000); (c) PEG(#1000).

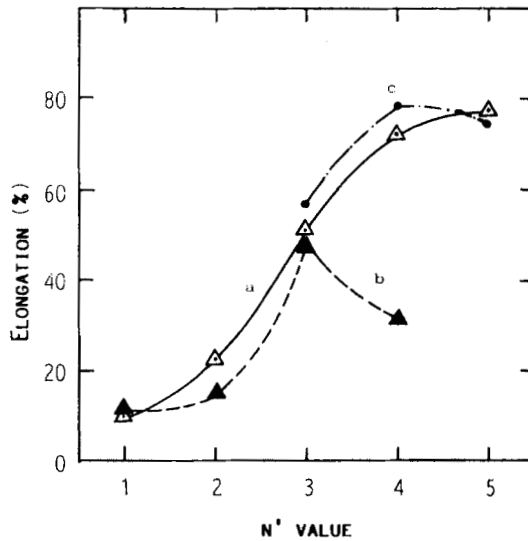


Fig. 8. The chain length of urethane prepolymer dependence of elongation at break for the crosslinked films prepared from Series A Pre-PU. PG: (a) PPG(#1000); (b) PPG(#2000); (c) PEG(#1000).

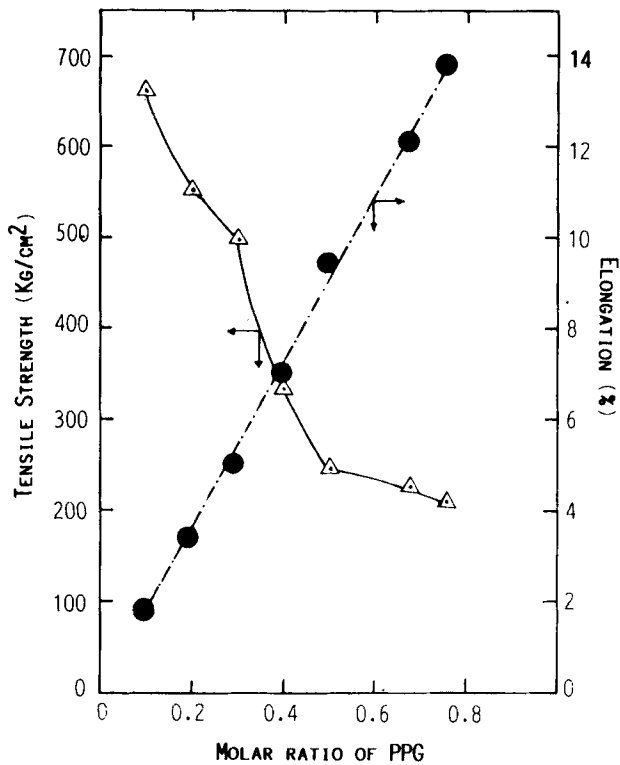


Fig. 9. PPG molar ratio dependence of tensile strength and elongation at break for the crosslinked films prepared from Series B Pre-PU.

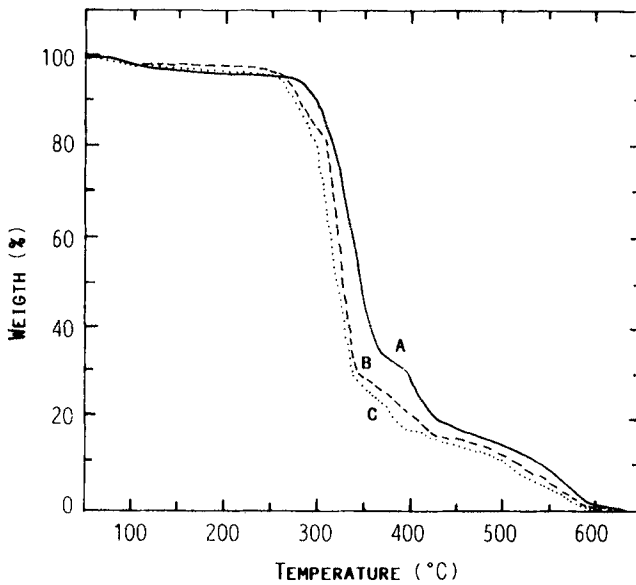


Fig. 10. TGA of the crosslinked films prepared from A-P-I Pre-PU. Sample: (a) A-P-I-1; (b) A-P-I-2; (c) A-P-I-3.

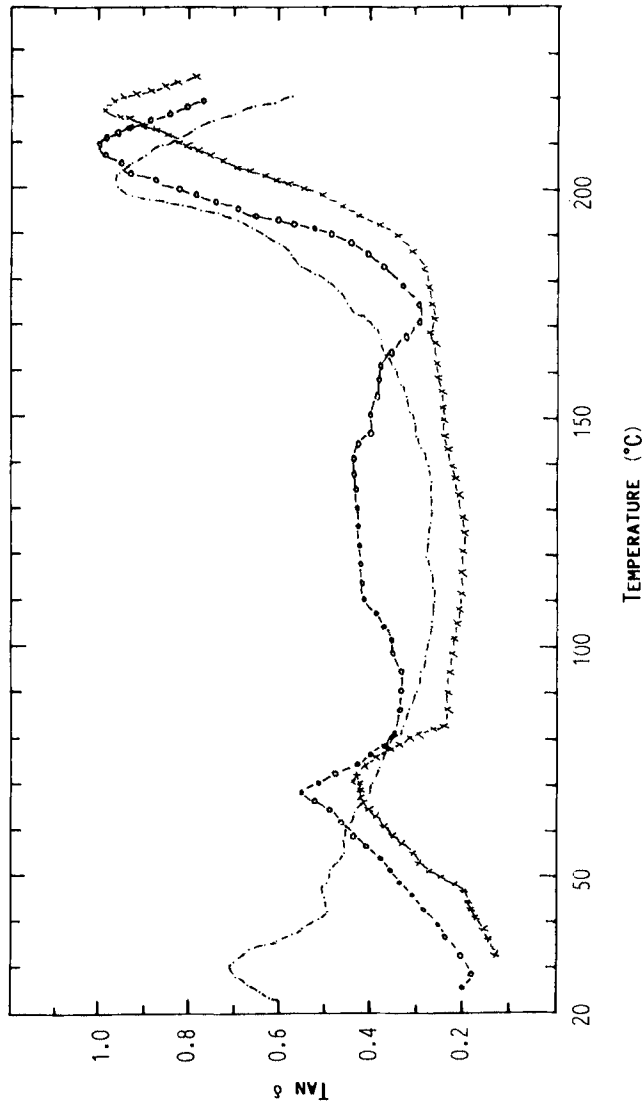


Fig. 11. The loss tangent of B-P-I-3 Pre-PU-containing crosslinked films as a function of temperature.

Figure 9 shows the relationship of tensile strengths and elongation at break of the crosslinked films prepared from B-P-I Pre-PU against the PPG-I/TDI molar ratio. When the molar ratio of PPG-I is between 0.1–0.3 and 0.5–0.7, the tensile strengths of the crosslinked films decreased gradually as the PPG-I molar ratio increased. When the molar ratio of PPG-I is in the range of 0.3–0.5, the tensile strengths decreased rapidly with increasing molar ratio. Elongations at break of crosslinked films nearly increased linearly with an increase of the molar ratio of PPG-I.

### TGA of Crosslinked Films

Thermogravimetric analysis (TGA) curves of the crosslinked film prepared from B-P-I-1 to -3 Pre-PU are shown in Figure 10. The initial pyrolysis temperature of crosslinked films is about 300°C and all the polymers decompose completely at about 630°C. Results show that the pyrolysis temperature shifts to low temperature as the molar ratio of PPG-I increases.

### Viscoelasticity of Crosslinked Films

The loss tangent of the crosslinked films as a function of temperature is shown in Figure 11. There are two glass transition temperatures ( $T_g$ ) of these three crosslinked films. The first is related to the transition of the hard segments and the second is related to the transition of the soft segments. The  $T_g$  shifts to low temperature as the molar ratio of PPG-I is increased. This is due to the softening of crosslinked films as the molar ratio of PPG-I is increased. Tan peaks of the hard segments of the crosslinked films appeared at 200, 208, and 218°C, respectively. Tan  $\delta$  peaks of soft segments of the crosslinked films appeared at 70, 65, and 30°C, respectively.

### CONCLUSIONS

1. Due to the poor solubility in organic solvents and high-density crosslinkability in the preparation of PU, PETH is seldom used in PU coatings. However, PETH-containing crosslinked PU films can be modified with suitable PG to give excellent tough materials.
2. The mechanical property of the crosslinked films prepared from PPG (#1000)-modified Pre-PU is better than those of the crosslinked films prepared from other PG-modified Pre-PU.
3. For single molecular type of PETH-(TDI-PG)<sub>n</sub>-TDI-PETH Pre-PU, the mechanical properties of the crosslinked films are dependent on the molecular weight of Pre-PU and the type of PG. The high molecular weight of Pre-PU gives low crosslinking density crosslinked films, which are soft and highly elastic. On the contrary, the low molecular weight of Pre-PU gives crosslinked films with high crosslinking density. These crosslinked films are strong and tough. The pyrolysis temperature of these crosslinked films is also high.
4. The viscoelasticity measurement of the crosslinked films prepared from heterogeneous Pre-PU, such as the mixture of PG/TDI/PETH and TDI/PETH Pre-PU, shows two transition temperature peaks, and these two transition temperatures shift with the change of the composition of Pre-PU.

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