

Emulsion of Polyurethane Having Thermosetting Properties. II. Relation Between the Mechanical Properties of Film and the Polyurethane Structure

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Synopsis

A self-emulsifiable polyurethane emulsion having thermosetting property was prepared by the following procedure: the polyurethane-urea-amine was first prepared by the reaction of diethylene-triamine with a prepolymer containing terminal isocyanate groups in a ketone solvent, and then the primary amino group in the polyurethane-urea-amine was reacted with epichlorohydrin. The mixture was neutralized with an aqueous acid, and finally the ketone solvent was removed by distillation *in vacuo*. In the polyurethane, polytetramethylene glycol (PTMG) was the base polymer functioning as the soft segment. The present paper reports the effects of the following variables on the mechanical properties of the film prepared from the polyurethane emulsion, i.e., the \overline{M}_n of PTMG, the molar ratio of diethylene-triamine (DTA) to prepolymer containing terminal isocyanate groups, the structure of the isocyanate end group and the molar ratio of tolylene diisocyanate (TDI) with PTMG. The best elastomer property was realized when \overline{M}_n of PTMG was 2000, TDI/PTMG molar ratio was 2.0, and prepolymer/DTA molar ratio was 0.85.

INTRODUCTION

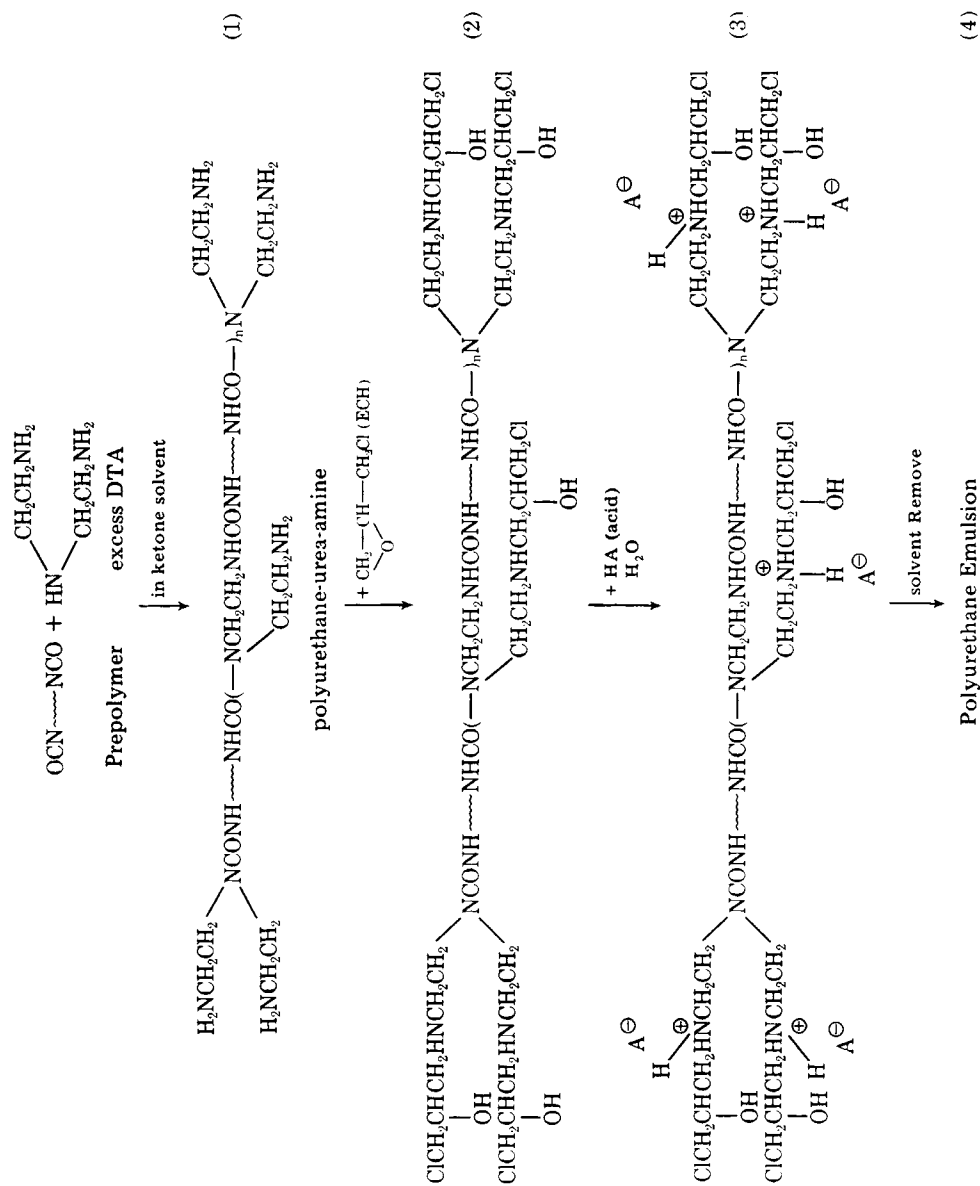
In a previous paper¹ we reported the preparation of polyurethane-urea-amine by reacting diethylenetriamine (DTA) with an urethane prepolymer containing terminal isocyanate groups in a ketone solvent. In this preparation, DTA was first reacted with ketone to form a Schiff base that in turn reacts with isocyanate, i.e., the reaction of amine with isocyanate was moderated. A thermosetting urethane emulsion could be prepared on the basis of polyurethane-urea-amine, i.e., a free amino group in the polyurethane-urea-amine was reacted with epichlorohydrin, the product was then neutralized with aqueous acid, and finally the solvent was removed by distillation *in vacuo* [eqs. (1)–(4)].

This paper describes relationship between the mechanical properties of film and the polyurethane structure. Some literatures have discussed the structure-properties relationship with polyurethane.^{3–6} The material of this paper is characterized by a new method of preparation of the emulsion.²

EXPERIMENTAL

Materials

Methyl ethyl ketone (MEK), diethylenetriamine (DTA), epichlorohydrin (ECH), and 70% glycolic acid (GA) were commercial reagents of extra pure grade of JIS (Japan Industrial Standards).



The molecular weight of polytetramethylene glycol (PTMG) ranged from 1000 to 3600. Their acid numbers were less than 0.1, and the water contents were less than 0.05% (products of Kao Soap Co.).

Tolylene diisocyanate (TDI) was an 80/20 mixture of 2,4- and 2,6-isomers (Sumidur 80, Sumitomo Bayer Urethane Co., Japan). Other diisocyanates were commercial reagents, i.e., diphenylmethane-4,4'-diisocyanate (MDI) and hexamethylene diisocyanate (HMDI) (Japan Polyurethane Co.); 1,5-naphthylene diisocyanate (NDI) (Sumitomo Bayer Urethane Co., Japan); xylene diisocyanate (XDI, para/meta 30/70) (Takeda Chem. Ind. Ltd.).

Preparation of Polyurethane-Urea Emulsion

A typical method is as follows.

Preparation of Prepolymer. One-tenth mole (205.5 g) PTMG (\overline{M}_n 2055, calculated by observed OHV) reacts with 0.2 mole TDI in MEK solvent at 80°C for 3 hr at a concentration of nonvolatile matter (NV) of 70 wt %. Observed NCO value of the obtained prepolymer was 2.42% (calcd. value 2.44).

Preparation of Polyurethane-Urea-Amine. The molar ratio between the prepolymer containing terminal isocyanate groups and DTA was adjusted to 0.85. Thus, 4.60 g (0.045 mole) DTA and 263.9 g MEK were mixed and reacted with each other at room temperature for 1 hr, and 131.9 g (0.038 mole) of the prepolymer solution was added dropwise to the above DTA-MEK reaction mixture under stirring over 2 hr at room temperature, the total mixture being heated at 50°C for 10 min.

The total amine value, partial amine value (secondary and tertiary amines), and tertiary amine value (due to impurities) were 8.7, 0.20, and 0.20, respectively (calcd. total amine value 8.18).

From the corrected total amine value corresponding to primary amino group, the molecular weight was calculated at 13660 (calcd. value on the stoichiometric reaction was 14,200).

Reaction with Epichlorohydrin. After adding 36 g water to 360 g of the above polyurethane-urea-amine, 5.05 g (0.054 mole) epichlorohydrin (equimolar amount to free amino groups in the polyurethane-urea-amine) was added, and the mixture was heated at 50°C for 1 hr.

Neutralization and Emulsification. The mixture obtained above was neutralized to pH 7 with 5.8 g 70% glycolic acid, and then 300 g water was added. Then, the solvent and the nonreacted ECH were removed under 50 mm Hg pressure at a maximum of 50°C for 2.5 hr; and finally, water was added to achieve a 30% concentration. Thus, 310 g of a stable, aqueous urethane emulsion was obtained. Total chlorine was 0.21%. It was shown that 34% of charged ECH was reacted.

Analysis

Hydroxyl number and acid number were determined by the JIS method. Total, partial, and tertiary amine values were determined by A.O.C. S TF 1A-64 and TF 2A-64, respectively.

The NCO value was determined by ASTM D 1638-59T. The molecular weight of polyurethane-urea-amine was calculated on the basis of the observed amine

value corresponding to primary amino groups. Total chlorine content was determined by the Volhard method.

Preparation of Film

The emulsion was spread over a Teflon-coated plate to an approximate 1-mm thickness of dried film and allowed to stand at room temperature for 4 days. Then the film was heat cured at 120°C for 20 min. After keeping the r.h. at 60% at 25°C for 24 hr, physical properties of film were determined by the JIS K 6301 (1962) method.

RESULTS AND DISCUSSION

Effect of \bar{M}_n of PTMG

The polymer composition (as molar ratio) for PTMG-TDI-DTA-ECH-GA (\bar{M}_n of PTMG, 1000–3600) is as follows:

TDI/PTMG	2.0
prepolymer/DTA	0.85
ECH/NH ₂	1.0

According to the above synthetic procedure, when the \bar{M}_n of PTMG is increased,

- (1) the molecular weight of prepolymer is increased,
- (2) the molecular weight of polyurethane-urea-amine is increased,
- (3) the number of crosslinking groups is decreased, and
- (4) the concentration of polar groups (urethane and urea) is decreased.

Figure 1 shows that as the \bar{M}_n of PTMG increased, the modulus and the tensile strength of film increased, as did the hardness of the film. As was described in part I of this series of papers, this film was swelled but insoluble in DMF.

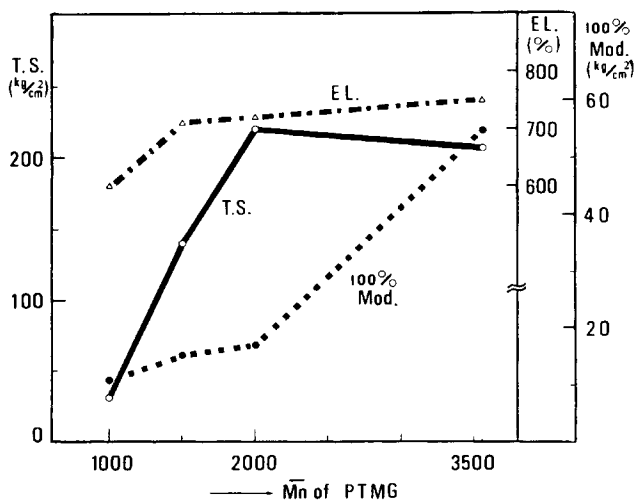


Fig. 1. Relation between \bar{M}_n of PTMG and film properties (EL., elongation; T.S., tensile strength; Mod., modulus).

Therefore it is reasonably assumed that crosslinking occurred while the film was heated. If the number of chemical crosslinks, as well as physical ones due to urethane groups, is considered, both of the above tendencies can be understood. It seems that the increase of \overline{M}_n of PTMG brings about the increase of the crystallinity of oxybutylene blocks, and hence the increases of modulus, tensile strength, and hardness.

Figures 2 and 3 show that a film made from PTMG having \overline{M}_n 3560 was plastic with a decreased elasticity. From the results of tension set and stress relaxation, it was shown that the most elastic film was obtained with PTMG of \overline{M}_n 2000.

Figure 4 shows that water resistance was improved as the \overline{M}_n of PTMG was increased. It is probably due to the decrease in the hydrophilic groups, such as

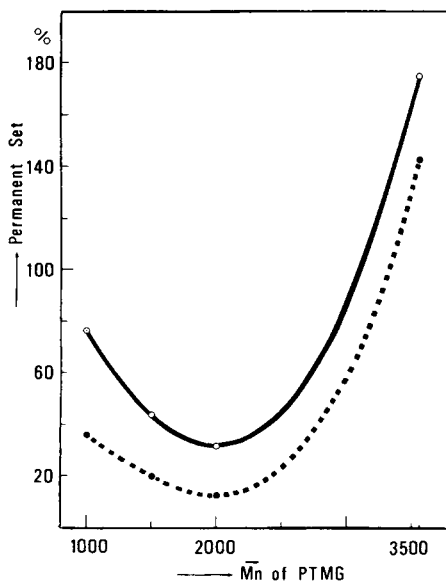


Fig. 2. Relation between \overline{M}_n of PTMG and tension set at 300% extension: -O-, after 1 min; ---●--- after 10 min.

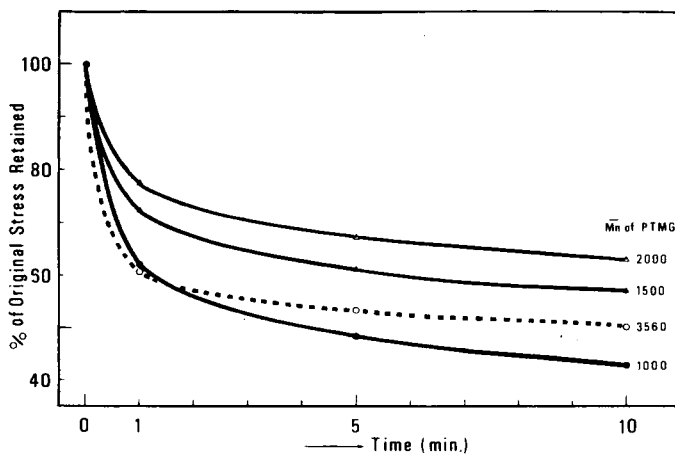


Fig. 3. Relation between \overline{M}_n of PTMG and stress relaxation during 10 min at 300% extension.

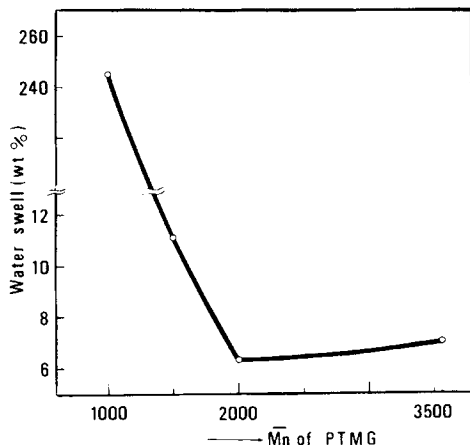


Fig. 4. Effect of \overline{M}_n of PTMG on water resistance: weight swell (%) at 50°C for 1 hr.

amine salts and urethane groups. However, it was not improved remarkably when \overline{M}_n of PTMG was higher than 2000.

Effect of Molecular Weight of Polyurethane-Urea-Amine

The molar ratio between DTA and prepolymer containing terminal isocyanate groups from the PTMG (\overline{M}_n 2000)-TDI system was varied, and its effect on physical properties of film was examined.

The polymer composition (as molar ratio) for PTMG(\overline{M}_n 2000)-TDI-DTA-ECH-GA was as follows:

TDI/PTMG	2.0
prepolymer/DTA	0.8-0.95
ECH/NH ₂	1.0

Figure 5 shows the effects of prepolymer/DTA molar ratio on tensile strength and elongation with heat-cured and air-dried films. Here the air-dried film was assumed to be not chemically crosslinked, because it was dissolved in DMF.

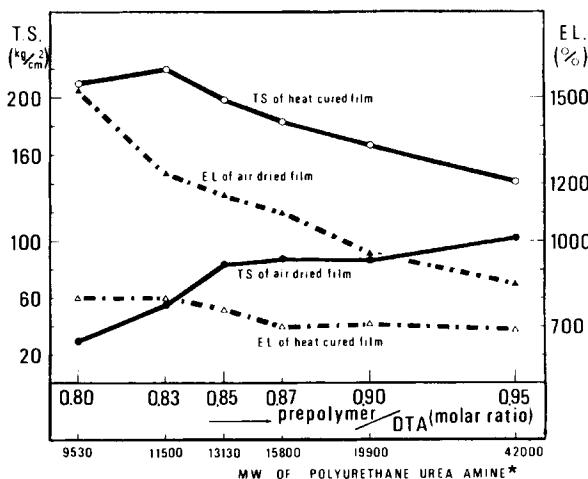


Fig. 5. Effect of prepolymer/DTA molar ratio on tensile strength and elongation. (The asterisk refers to the calcd. value on the basis of the observed amine value.)

As the molar ratio of prepolymer/DTA became close to 1, the molecular weight of polyurethane-urea-amine was increased. Therefore the tensile strength of the air-dried film increased as the molecular weight of polyurethane-urea-amine increased, but the tensile strength of the heat-cured film showed a maximum value at a molar ratio of 0.83. These results suggest that the balance between the molecular weight of polyurethane-urea-amine and the chemical crosslinkage is important and that tensile strength was maximum at the prepolymer/DTA molar ratio of 0.83. The elongation decreased as the molecular weight of polyurethane-urea-amine increased.

Figures 6 and 7 show that as the molecular weight of polyurethane-urea-amine increased, the tension set of the heat-cured film became smaller and the film became more rubbery.

At prepolymer/DTA molar ratios above 0.87 (molecular weight of polyurethane-urea-amine higher than 16,000), the tension set changed very little. The stress relaxation became smaller as the molecular weight of polyurethane-urea-amine was increased.

Figure 8 shows that water swell (%) became smaller as the molecular weight of polyurethane-urea-amine increased. Therefore the film was better for rubber as judged by the increase in the molecular weight of polyurethane-urea-amine.

Effect of the Structure of Isocyanates

The polymer composition (molar ratio) of PTMG(\overline{M}_n 2000)-Di-NCO-DTA-ECH-GA was	
Di-NCO/PTMG	2.0
prepolymer/DTA	0.85
ECH/NH ₂	1.0

Table I shows that the difference in the hardness of the film depending on the isocyanate structure was small. However, the film made from aliphatic isocyanate was rather soft and was easier to flow than one from aromatic isocyanate. It seems that those properties depended on the cohesive force of the aromatic ring.

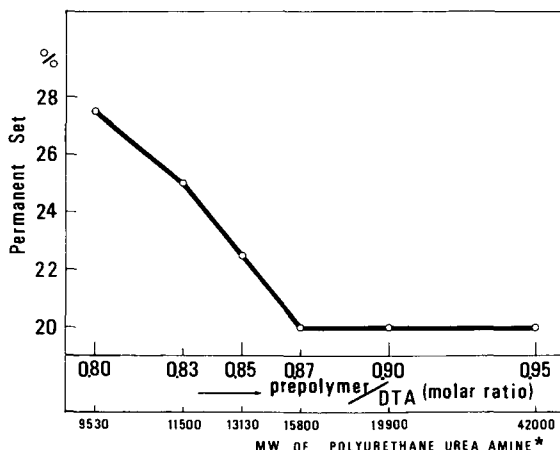


Fig. 6. Relation between prepolymer/DTA molar ratio and tension set after 10 min at 300% extension. (The meaning of the asterisk same as in Fig. 5.)

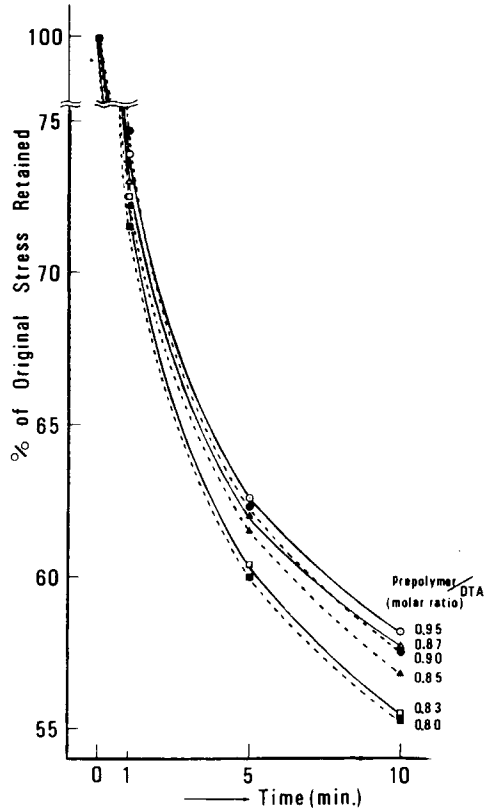


Fig. 7. Relation between prepolymer/DTA molar ratio and stress relaxation during 10 min at 300% extension: \circ , 0.95; Δ , 0.87; \bullet , 0.90; \blacktriangle , 0.85; \square , 0.83; \blacksquare , 0.80.

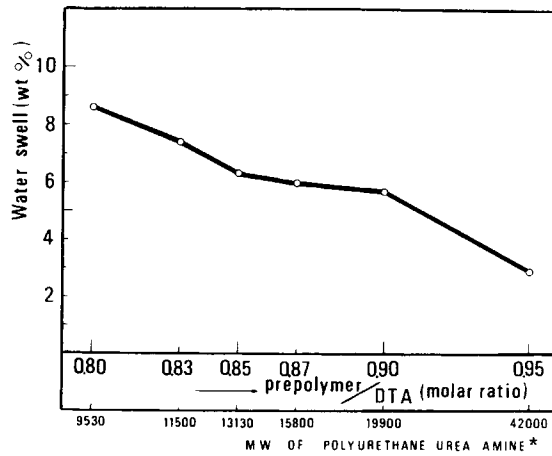
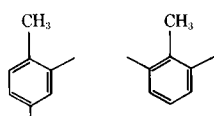
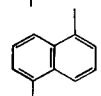
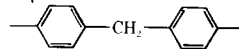
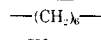
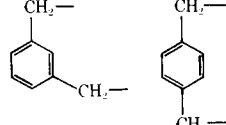


Fig. 8. Effect of prepolymer/DTA molar ratio on water resistance: weight swell (%) at 50°C for 1 hr. (The meaning of the asterisk same as in Fig. 5.)

TABLE I
Effect of the Structure of the Isocyanates

Structure type	OCN-R-NCO	100% Modulus, kg/cm ²	500% Modulus × 100 / 100% Modulus
Aromatic	TDI 	16.8	191
	NDI 	17.7	172
Aliphatic	MDI 	17.8	146
	HMDI 	14.6	113
	XDI 	14.7	127

Effect of TDI/PTMG Molar Ratio

The polymer composition (molar ratio) of PTMG(\overline{M}_n 2000)-TDI-DTA-ECH-GA was

TDI/PTMG	1.5-3.0
prepolymer/DTA	0.85
ECH/NH ₂	1.0

According to the above synthetic procedure, when the TDI/PTMG molar ratio is increased (Fig. 9),

- (1) the content of the benzene ring is increased,
- (2) the molecular weight of polyurethane-urea-amine decreases as the average molecular weight of prepolymer decreases,
- (3) the urea group/urethane group ratio is increased, namely, the urea groups are increased, and
- (4) the fraction of free amino groups is increased.

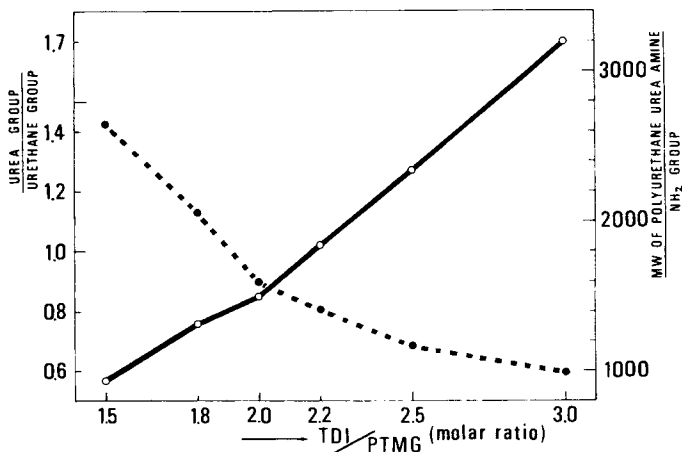


Fig. 9. Relation between TDI/PTMG molar ratio and polymer structure: O, urea group/urethane group ratio; ●, MW of polyurethane urea amine/NH₂ group.

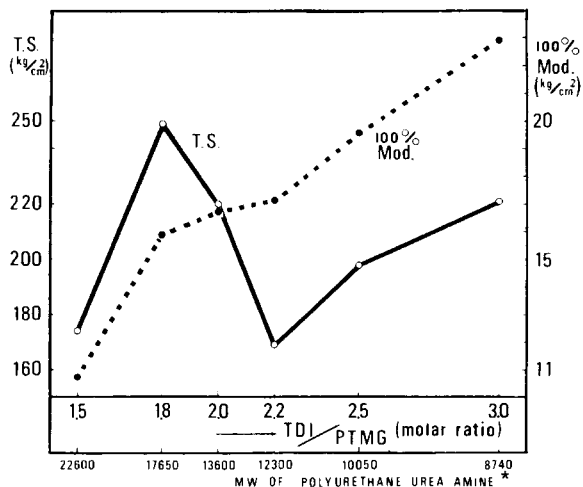


Fig. 10. Relation between TDI/PTMG molar ratio and physical properties. (Asterisk same as in Fig. 5.)

Figure 10 shows that the 100% modulus of the film increased as the TDI/PTMG molar ratio increased. It seems that the increase in the TDI/PTMG molecular ratio brings about an increase in the density of physical and chemical crosslinkage and also of the content of benzene ring. Therefore, the film became harder in response to increases in the TDI/PTMG molar ratio. No systematic variation of the tensile strength was observed.

Figures 11 and 12 show that from the results of tension set and stress relaxation, the most elastic film was obtained with a TDI/PTMG molar ratio of 2.0.

Figure 13 shows that the water swell of the film was 5%–6% at a TDI/PTMG molar ratio of 1.5–2.0. However, at a TDI/PTMG molar ratio of 2.2–3.0, water swell was 60%–126%. In the latter case, these emulsions showed a nearly clear aqueous state. This phenomenon resulted because the free amino groups (hydrophilic) and the urea groups of relative hydrophilic property were increased according to increase in TDI/PTMG molar ratio.

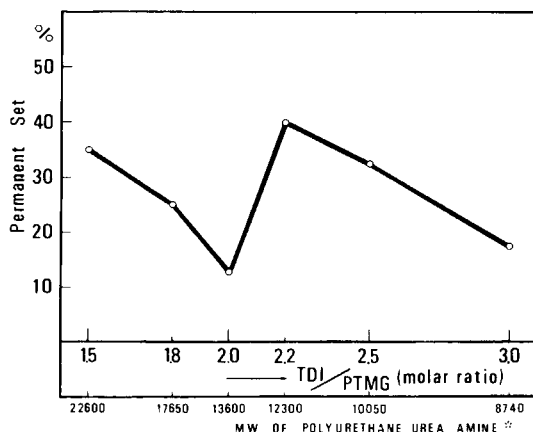


Fig. 11. Relation between TDI/PTMG molar ratio and tension set after 10 min at 300% extension. (Asterisk same as in Fig. 5.)

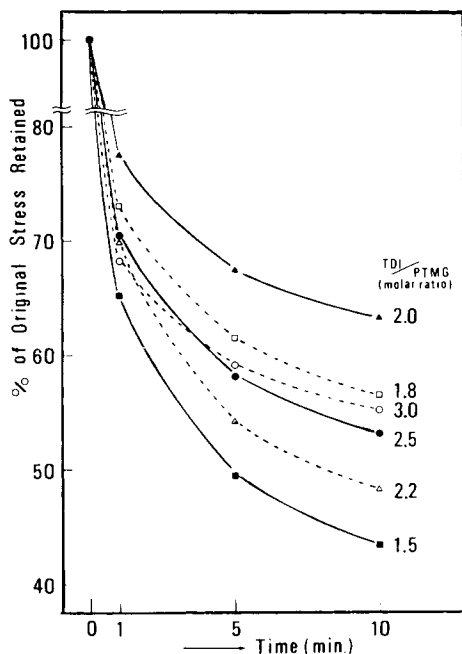


Fig. 12. Relation between TDI/PTMG molar ratio and stress relaxation during 10 min at 300% extension.

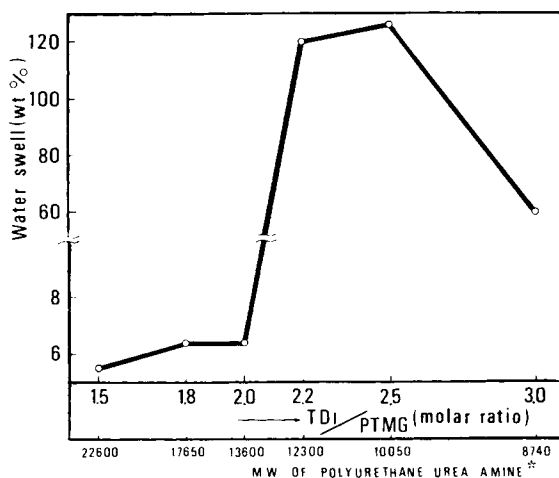


Fig. 13. Effect of TDI/PTMG molar ratio on water resistance: weight swell (%) at 50°C for 2 hr. (Asterisk same as in Fig. 5.)

CONCLUSIONS

In a self-emulsifiable polyurethane-urea-amine, PTMG was selected as the soft segment, and the effects of the \bar{M}_n of PTMG, prepolymer/DTA molar ratio, the kind of isocyanate, and the TDI/PTMG molar ratio on the mechanical properties of films from the polymer emulsion were examined.

The best elastomeric properties were obtained at PTMG \bar{M}_n 2000, prepolymer/DTA molar ratio 0.85, and NCO/PTMG molar ratio 2.0.

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