

Infrared Spectral Study on the Heat Curing Reaction of Glycerin-Terminated Urethane Prepolymers

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Synopsis

Glycerin, toluene diisocyanate (TDI), and polyglycol (PG) were reacted at various molar ratios to produce glycerin-terminated urethane prepolymers of different molecular weights. The prepolymers were mixed with equivalent phenol-blocked trimethylol propane-TDI-urethane triisocyanate in *m*-cresol to give a coating solution. The solution was coated and baked to give polyurethane crosslinked films. The changes of the functional groups during the crosslinking reaction and the mechanical properties of the polyurethane crosslinked films were studied. Experimental results show that the phenol-blocked urethane triisocyanate will deblock phenol to regenerate free isocyanate groups above 120°C and then react with the hydroxyl groups of urethane prepolymers. At 220°C, the rate of deblocking phenol to regenerate isocyanate groups is faster than that of the reaction of urethane prepolymers with isocyanate groups. The deblocking reaction is contemporaneous with the reaction of isocyanate groups with hydroxyl groups, so that the characteristic absorption peaks of isocyanate groups can be observed from IR spectra during the crosslinking reaction. The absorption peak of isocyanate groups gradually decreased with the crosslinking reaction, but the absorption peak increased after curing for about 50–60 min. This feature is caused by the reactivity of the secondary hydroxyl groups of glycerin which is slower than that of the primary hydroxyl groups of glycerin.

INTRODUCTION

There are two procedures for producing crosslinked polyurethane. One is to first synthesize prepolymers, which contain isocyanate groups in the terminal and/or side polymer chains. The prepolymers are then reacted with a chain extender or crosslinking agent to give crosslinked polyurethane. The second is to first synthesize prepolymers, which contain hydroxyl groups in the terminal and/or side polymer chains, followed by reaction with a crosslinking agent such as polyisocyanate or an isocyanate-regenerator to give crosslinked polyurethane. In the first procedure, polyol or polyamine, which can easily react with isocyanate groups, are used as the crosslinking agent. While in the second procedure, polyisocyanate or blocked isocyanate, which can easily react with hydroxyl groups, are used as crosslinking agents.

In polymeric synthesis, glycerin is generally used in producing alkyd polyester and is also used in the synthesis of polyurethane. Polyurethane is generally synthesized by reacting mixtures of glycerin and various polyols with polyisocyanate to give crosslinked polyurethane.¹⁻⁴ The three hydroxyl groups of glycerin have different reaction rates with isocyanate groups. Davis⁵ reported that the relative reactivity rate ratio of ethyl alcohol and isopropyl

alcohol with phenylisocyanate is about 3:1, but the reactivity of primary hydroxyl group of isobutyl alcohol is similar to the reactivity of the secondary hydroxyl group of isopropyl alcohol. The isocyanate group of TDI in the para-position is about eight times as reactive as the isocyanate group of TDI in the ortho-position at room temperature.⁶

The main purpose of this research is to study the reactivity of primary and secondary hydroxyl-containing glycerin-terminated polyurethane prepolymer with an isocyanate regenerator at elevated temperatures. Infrared spectroscopy was used to monitor the change of isocyanate groups to qualitatively study the formation of high molecular weight polyurethane.

EXPERIMENTAL

Materials and Apparatus

Monomers used in synthesizing urethane prepolymers and phenol-blocked triisocyanate, a crosslinking agent, were reagent-pure trimethylol propane (TMP) (Hayashi Pure Chemicals, Ltd., Japan), toluene diisocyanate (TDI) (San Ten Chemicals), and glycerin and phenol (WAKO Pure Chemicals, Ltd., Japan).

Polyglycols used in synthesizing urethane prepolymers were polypropylene glycol with $\bar{M}_n = 1000$ [PPG (#1000)] (Hayashi Pure Chemicals, Ltd., Japan), and polypropylene glycol with $\bar{M}_n = 2000$ [PPG (#2000)] (WAKO Chemicals, Ltd., Japan). Both of the polypropylene glycols were extra pure grades.

A IR spectrometer (JASCO IRA-2) and an Instron Universal Tester were employed.

Synthesis

Glycerin-Terminated Urethane Prepolymer. A given quantity of TDI was added to a 100 mL three-necked flask equipped with an electric stirrer, a reflux condenser, a dropping funnel, and an 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, then cooling to room temperature. Glycerin was then added before the temperature was raised to 40–50°C for 1 h, to 80°C for 30 min, to 100°C for 30 min, and to 120°C for 4 h for completion. The resultant product was hydroxy-terminated urethane prepolymers.

Phenol-Blocked Triisocyanate. A given quantity of TDI was added to a 100 mL three-necked flask equipped as above. The mixture of TMP and phenol in a beaker was heated to 55°C for dissolution and then cooled to room temperature. The mixture was added dropwise into the flask from the dropping funnel. The mixture was heated at room temperature for 30 min, and then the temperature was raised to 40–50°C for 1.5 h, to 80°C for 1 hr, to 110°C for 3.5 h, to 120°C for 6.5 h for completion. When the viscosity of the reactant increased, a suitable amount of anisole was added to the flask to reduce the viscosity of the reactant to enable smooth stirring. After the reaction was completed, a quantity of *m*-cresol was added to the flask. The product, phenol-blocked TMP-TDI-urethane triisocyanate, was a golden, viscous liquid at room temperature.

Film Casting

A 40% solid content solution was prepared by dissolving and mixing hydroxyl-terminated urethane prepolymer and an equivalent amount phenol-blocked triisocyanate in *m*-cresol. A thin 10-cm diameter circles were spread on aluminum foil. Upon baking at 220°C for given times, a crosslinked film was formed which adhered to the aluminum foil. The aluminum foil was dissolved in an HCl solution (6*N*) to release the crosslinked polyurethane film.

Infrared Spectral Measurement

The crosslinked films and urethane prepolymers or phenol-blocked triisocyanate in the synthetic reaction were spread on KBr pellets, and IR measurement was taken.

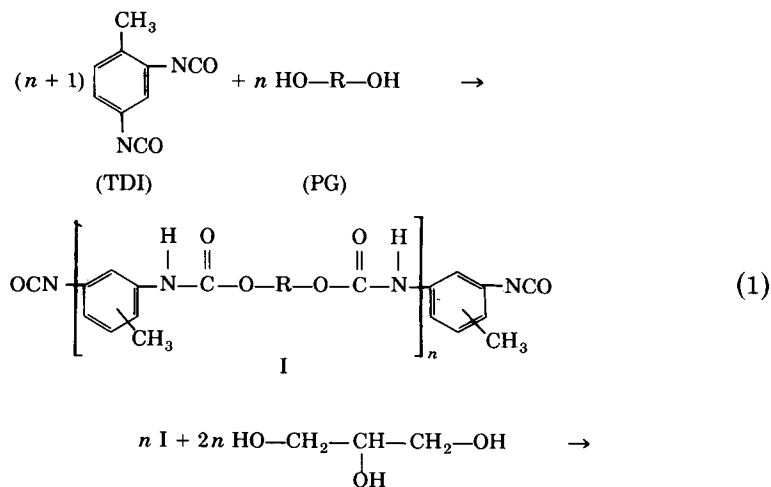
Mechanical Property Testing

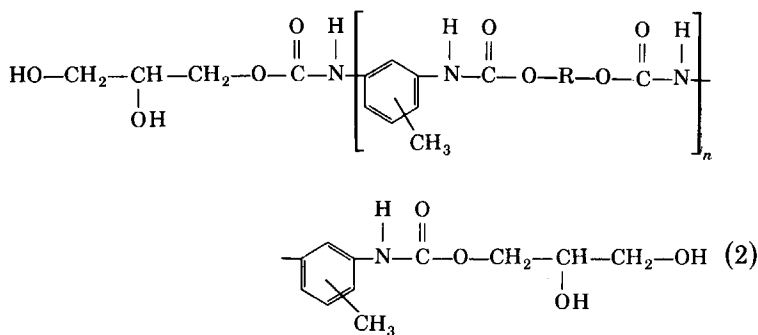
The crosslinked film was cut into dumbbell shapes with a length of 7 cm, a breadth within 1 cm at the neck, and a thickness of < 0.5 mm. An Instron Universal Tester was used to study the mechanical properties of the sample at room temperature at a drawing speed of 5 cm/min.

RESULTS AND DISCUSSION

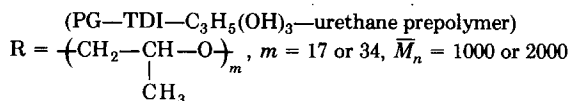
Glycerin-Terminated Urethane Prepolymers

TDI was reacted with PG to give isocyanate-terminated polyurethane, as shown in reaction (1). Glycerin was added to produce glycerin-terminated urethane prepolymer, as shown in reaction (2). Changing the molar ratio of PG/TDI/C₃H₅(OH)₃ also gave urethane prepolymers of different molecular weight. All the synthetic urethane prepolymers are listed in Table I.





II



During the synthesis of urethane prepolymers, IR spectra were taken to follow the change of absorption peaks. Figure 1(a) represents the IR spectrum of PPG(#2000)/TDI = 3/4-polyurethane; (b) represents the IR spectrum of the mixture after a calculated quantity of glycerin was added and the temperature was raised within 1 h to 100°C and held for 30 min; (c) and (d) represent spectra of the mixture which was heated at 120°C for 1.5 and 2 h, respectively. The figure shows that the absorption peak of the isocyanate group decreased in the course of reaction, but the absorption peak of carbonyl group increased. The disappearance of the absorption peak at 2250 cm⁻¹ represents the completion of the reaction. Generally, this urethane prepolymer system can be gradually heated to 120°C within 1.5 h and held at 120°C for another 2 h for completion.

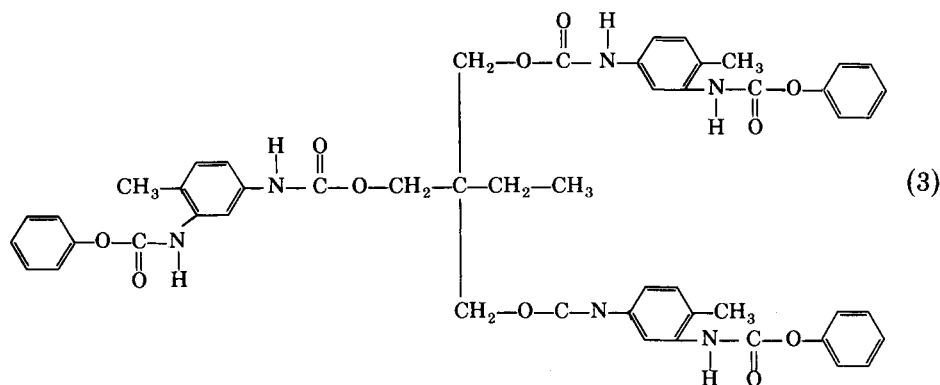
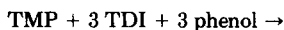
Phenol-Blocked TMP-TDI-Urethane Triisocyanate

Synthesis of phenol-blocked TMP-TDI-urethane triisocyanate is shown in reaction (3). TDI is reacted with TMP to give isocyanate-terminated urethane, which in turn is reacted with phenol to give phenol-blocked TMP-TDI-urethane triisocyanate.

TABLE I
Synthetic Urethane Prepolymers

PG	PG/TDI/C ₃ H ₅ (OH) ₃
PPG(#1000)	1:2:2
	2:3:2
	3:4:2
PPG(#1000)	1:2:2
	2:3:2
PPG(#1000)	0.2:1:1 ^a

^aThe urethane prepolymer contains hydroxyl groups in the middle of the polymer chain.



III
(phenol-blocked urethane triisocyanate)

In the synthesis, isocyanate groups of TDI will gradually disappear in the course of the reaction as shown in Figure 2. Generally, the reactivity of the hydroxyl groups of TMP is faster than that of the hydroxyl group of phenol at low temperature. Thus phenol and TMP can be added together to TDI and the reaction kept at low temperature at the beginning for a long period. The temperature was gradually raised, when the hydroxyl groups of TMP were used up. In this case the reaction was kept at room temperature for 30 min, and then the temperature was raised 15°C to 120°C and held at 120°C for 6.5 h, as show in Figure 2(d).

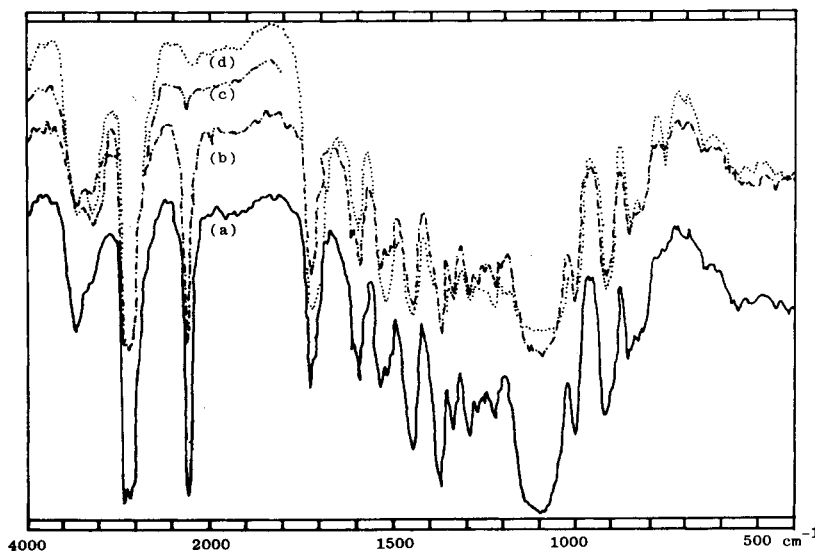


Fig. 1. IR spectra of (a) PPG(#2000)/TDI(3/4)-and (b, c, d) PPG(#2000)/TDI/C₃H₅(OH)₃(3/4/2)-urethane prepolymers at different reaction temperatures: (a) room temperature, 30 min; (b) 100°C, 30 min; (c) 120°C, 90 min; (d) 120°C, 120 min

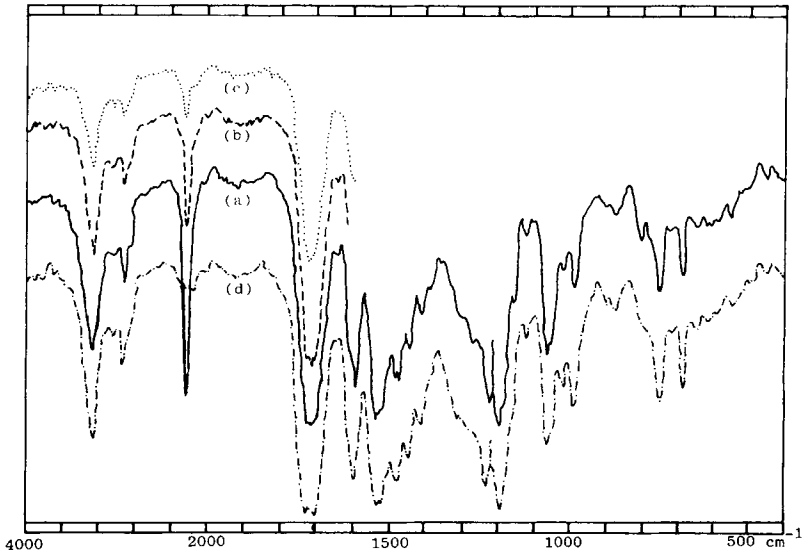


Fig. 2. IR spectra of the reaction mixture [PhOH/TMP/TDI (3/1/3)] during the synthesis of urethane triisocyanate at 120°C for different reaction times. (a) 1 h; (b) 2 h; (c) 5 h; (d) 6.5 h.

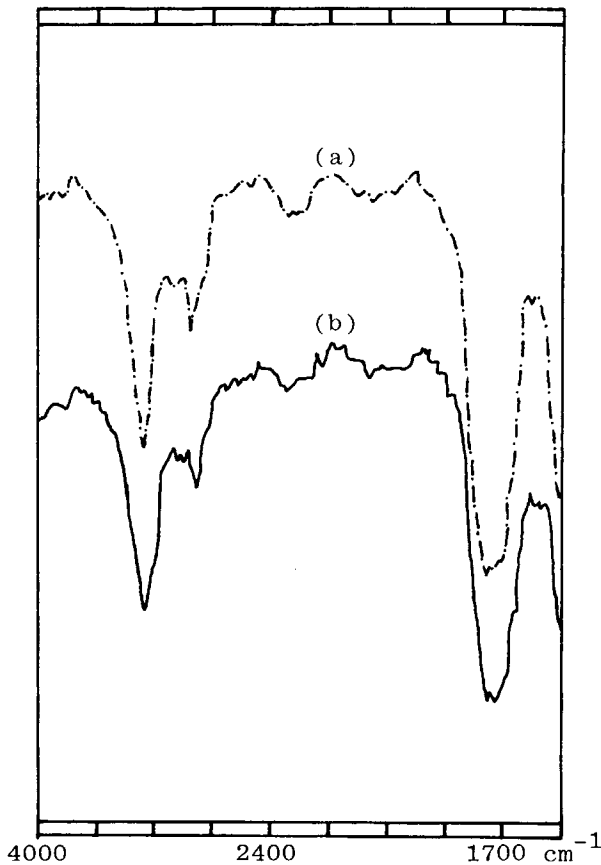
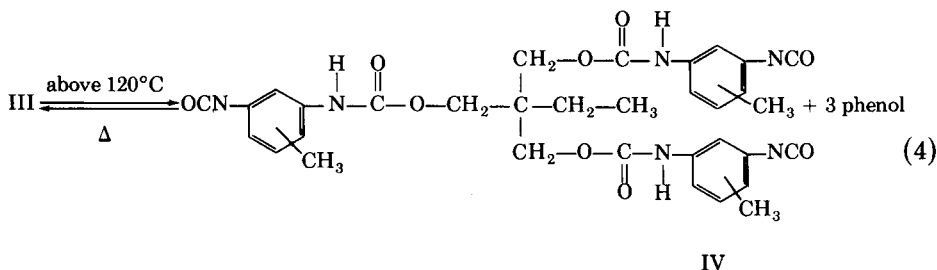


Fig. 3. IR spectra of phenol-blocked urethane triisocyanate [PhOH/TMP/TDI (3/1/3)] at 80°C for 1 h compared with those of unheated phenol-blocked urethane triisocyanate: (a) unheated; (b) heated.

Deblocking of Phenol-Blocked Urethane Triisocyanate

A small amount of phenol-blocked urethane triisocyanate spread on KBr disc was heated to 80, 120, 150°C, and so on for different times. IR absorption of isocyanate group was observed at 2250 cm^{-1} , as shown in Figures 3 and 4. Because there is no isocyanate absorption peak observed in Figure 3, the phenol-blocked urethane triisocyanate is stable at 80°C and cannot deblock phenol to regenerate free isocyanate group.

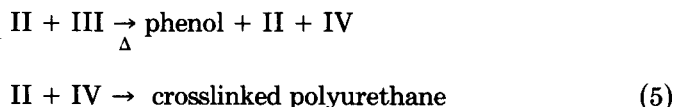
From Figure 4 it can be seen that the absorption peaks of isocyanate group at 2250 cm^{-1} increased with heating time and then decreased, implying that phenol-blocked urethane triisocyanate will deblock phenol to regenerate free isocyanate at above 120°C, as shown in reaction (4).



When the temperature is at 110–120°C, the reaction is reversible. Phenol coexists with the reactant, so that the reaction goes toward the left. In the curing reaction, phenol is evaporated and the reaction goes toward the right. After the isocyanate groups reach a maximum value, they react with other materials; for example, the moisture in air decreases the intensity of isocyanate absorption peaks. The absorption ratios of $[\text{NCO}]/[\text{alkyl}]$ were found to be a function of curing time, as shown in Figure 5, indicating that phenol-blocked urethane triisocyanate is easier to deblock phenol at 150°C than that at 120°C, and the quantity of the generated free isocyanate groups at 150°C is also larger than that at 120°C. Because of the decreasing tendency of the absorption ratio of $[\text{NCO}]/[\text{alkyl}]$, the regenerated free isocyanate group is found to react easily with the moisture in air at a high temperature.

IR Spectra of the Crosslinking Reaction

Solutions were prepared by dissolving and mixing different molecular weight urethane prepolymer and $\pm 10\%$ of equivalent amounts of phenol-blocked urethane triisocyanate baked at 220°C for different curing times. Reaction (5) is the crosslinking reaction that takes place



IR spectra of the crosslinked films prepared from PPG(#1000)/TDI/ $\text{C}_3\text{H}_5(\text{OH})_3$ (2/3/2) containing urethane prepolymer with equivalent phenol-blocked urethane triisocyanate baked at 220°C for different times are shown

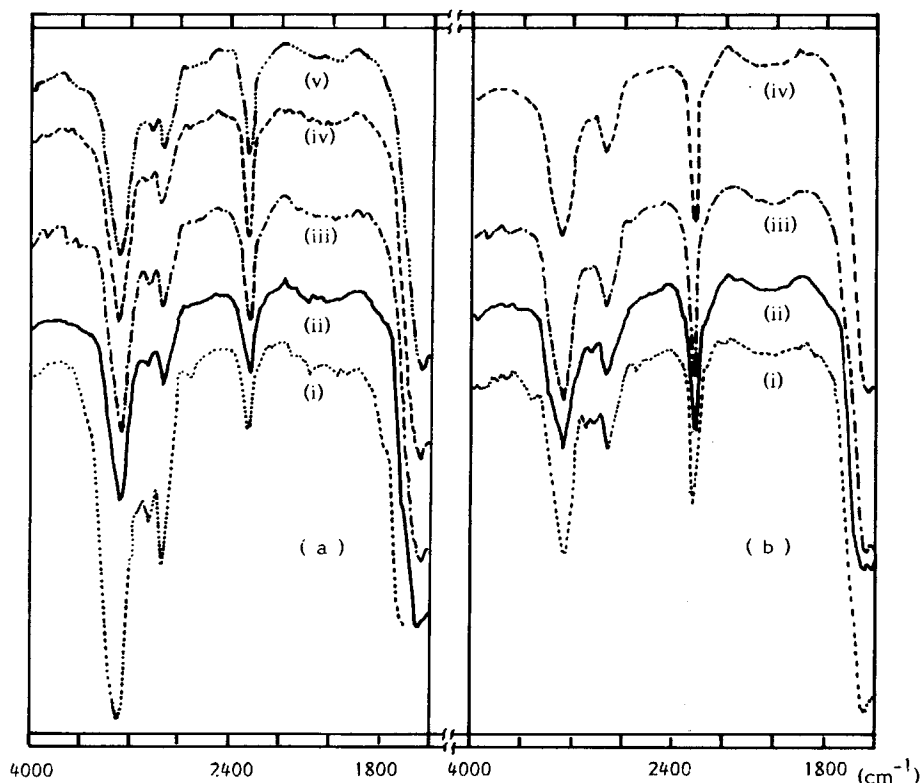


Fig. 4. IR spectra of phenol-blocked urethane triisocyanate [PhOH/TMP/TDI (3/1/3)] heated at (a) 120°C and (b) 150°C for different times: (a) 120°C : (i) 15 min; (ii) 25 min; (iii) 35 min; (iv) 45 min; (v) 80 min. (b) 150°C : (i) 5 min; (ii) 10 min; (iii) 20 min; (iv) 40 min.

in Figure 6. From the change of isocyanate absorption peaks at 2250 cm^{-1} , it can be observed that when the crosslinking reaction of phenol-blocked urethane triisocyanate and urethane prepolymer took place, the phenol-blocked urethane triisocyanate deblocked phenol first and then reacted with hydroxyl groups of the urethane prepolymer. However, the rate of deblocking phenol to regenerate isocyanate group is faster than that of the reaction of urethane prepolymer with isocyanate. The isocyanate absorption peaks are observable in the IR spectra.

The ratios of the intensity of the absorption peaks of isocyanate groups and that of alkyl groups at 2900 cm^{-1} are a function of the curing time, as shown in Figure 7. Figure 7(a) indicates that the isocyanate group is regenerated first and then reacts with the hydroxyl groups of the prepolymer to form urethane linkages. The reaction of deblocking phenol to regenerate the isocyanate groups were contemporaneous with the reaction of isocyanate groups and hydroxyl groups; the rate of deblocking phenol is faster than that of the reaction of urethane prepolymer with isocyanate. The absorption ratio of $[\text{NCO}]/[\text{alkyl}]$ increased initially, and then decreased gradually. In about 50–60 min, the ratio of $[\text{NCO}]/[\text{alkyl}]$ increased again. This feature may be caused by the fact that the reactivity of the secondary hydroxyl groups of glycerin is slower than that of the primary hydroxyl groups of glycerin. After

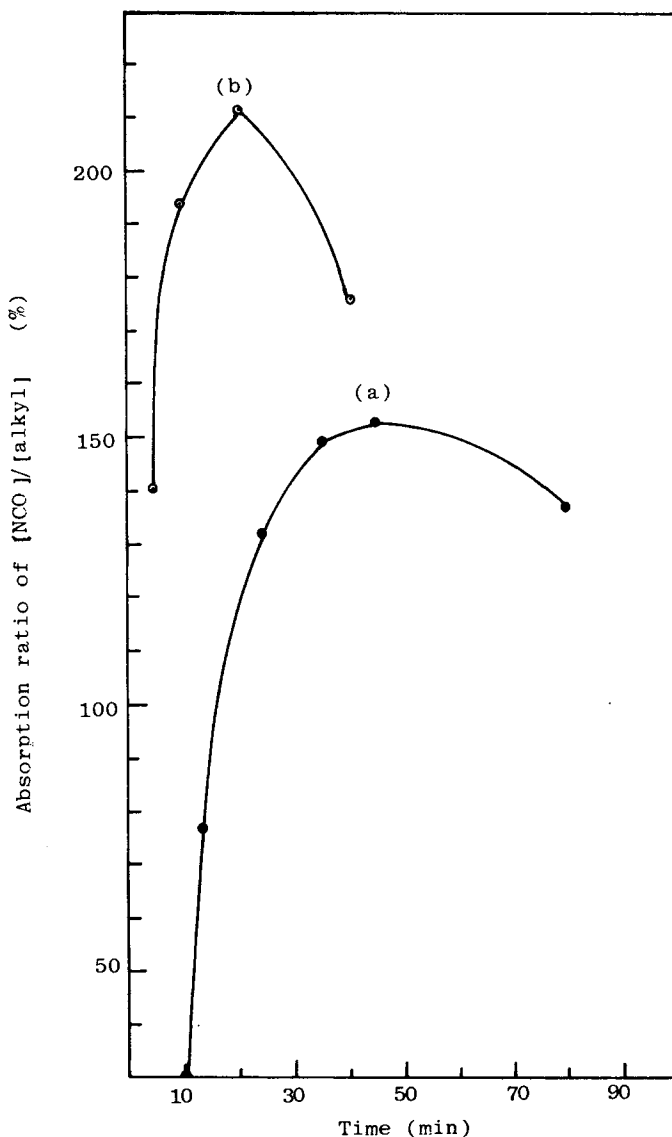


Fig. 5. Phenol-blocked urethane triisocyanate heated at (a) 120°C and (b) 150°C for different times. The IR absorption ratios of [NCO]/[alkyl] was a function of heating times.

50–60 min, the ratio of [NCO]/[alkyl] decreases rapidly because no new isocyanate groups were regenerated.

IR spectra of the crosslinked films prepared from PPG(#1000)/TDI/C₃H₅(OH)₃ (2/3/2) urethane prepolymer with 10% excess of equivalent phenol-blocked urethane triisocyanate baked at 220°C for different times are shown in Figure 8. It can be seen that the change of the characteristic absorption peaks were the same as those described in Figure 6, but by the end of this time study, isocyanate peaks increased. This feature is caused by the fact that the free isocyanate groups were increased after the hydroxyl groups

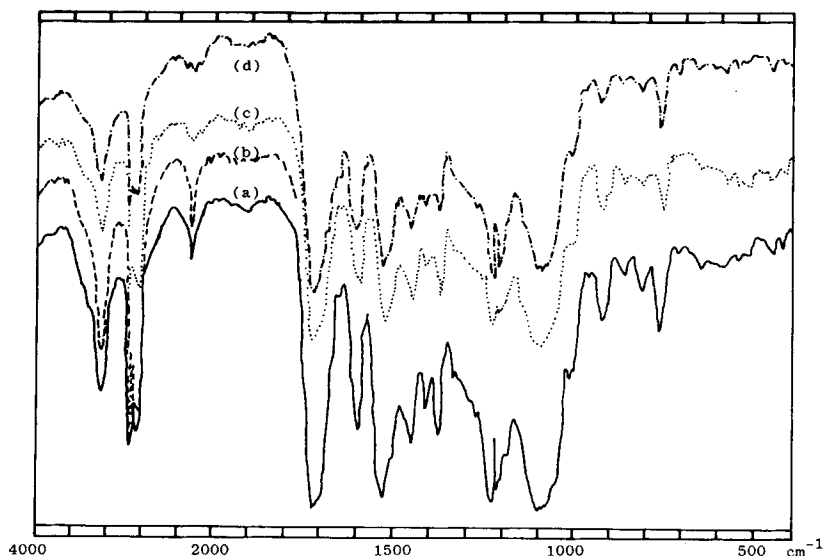


Fig. 6. IR spectra of the crosslinked films prepared from PPG(#1000)/TDI/C₃H₅(OH)₃ (2/3/2) urethane prepolymer with equivalent phenol-blocked urethane triisocyanate at 220°C for different curing times: (a) 10 min; (b) 20 min; (c) 100 min; (d) 120 min.

of urethane prepolymer were exhausted. The ratios of the intensity of the isocyanate and alkyl absorption peaks was a function of curing time, as shown in Figure 7(b). When the IR spectra of the crosslinked films prepared from PPG(#1000)/TDI/C₃H₅(OH)₃ urethane prepolymer with 10% less equivalent of phenol-blocked urethane triisocyanate were taken, the ratios of the intensity of the isocyanate and alkyl absorption peaks was also a function of curing time, as shown in Figure 7(c).

A comparison of curves in Figure 7 reveals that the regenerated isocyanate groups of excess phenol-blocked urethane triisocyanate were larger. The ratio of [NCO]/[alkyl] absorption reached a maximum initially. The more regenerated isocyanate groups present, the greater the probability of collision between isocyanate and hydroxyl groups. All the hydroxyl groups of urethane prepolymer reacted at 80 min, so that the ratio of [NCO]/[alkyl] increased again. When urethane prepolymer mixed with equivalent or 10% excess equivalent phenol-blocked urethane triisocyanate, the primary hydroxyl groups reacts completely at 50 min. But urethane prepolymer mixed with 10% less equivalent phenol-blocked urethane triisocyanate, the primary hydroxyl groups reacts completely at 60 min. Because the fewer the regenerated isocyanate groups present, the less the probability of collision between isocyanate and hydroxyl groups.

The absorption ratios of [NCO]/[alkyl] in IR spectra of the crosslinked films prepared from the different molecular weight urethane prepolymers containing equivalent phenol-blocked urethane triisocyanate baked at 220°C for different curing times are shown in Figures 9 and 10. Figure 9 represents the series of PPG(#1000)-TDI-C₃H₅(OH)₃-containing urethane prepolymers. The amount of phenol-blocked urethane triisocyanate is dependent on

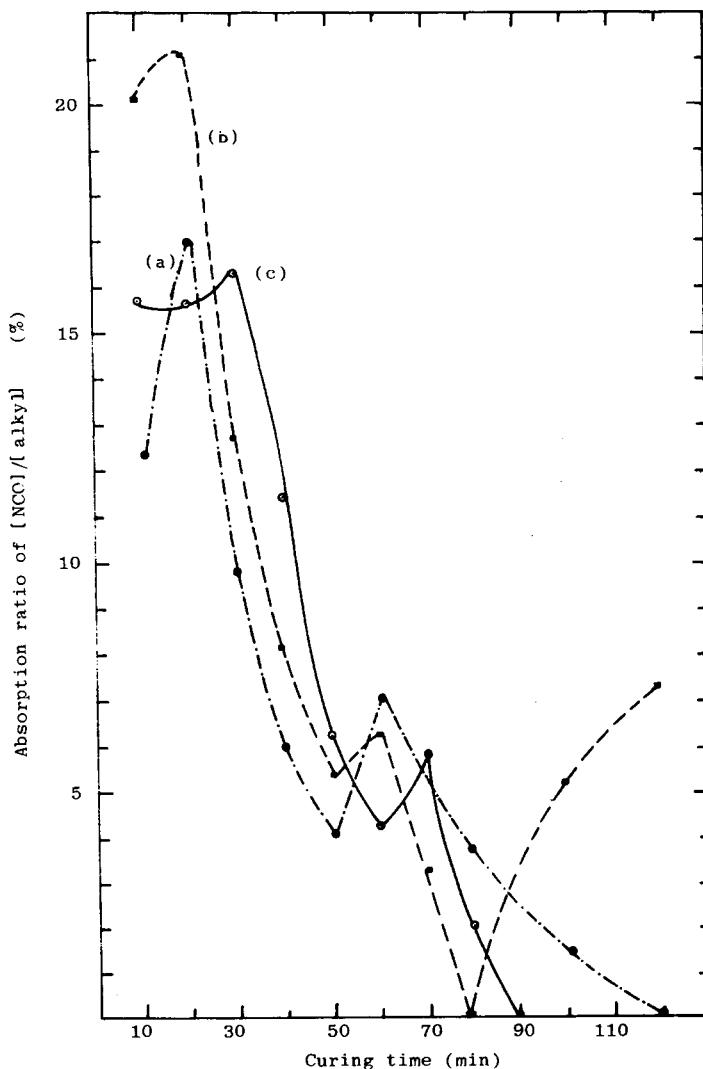


Fig. 7. IR absorption ratios of $[\text{NCO}]/[\text{alkyl}]$ as function of curing time. Sample: PPG(#1000)/TDI/ $\text{C}_3\text{H}_5(\text{OH})_3 = 2:3:2$ with (a) equivalent weight, (b) excess 10% equivalent weight, and (c) less 10% equivalent weight phenol-blocked urethane triisocyanate.

the chain length of urethane prepolymer. The longer the chain length is, the less phenol-blocked urethane triisocyanate is needed. The ratios of $[\text{NCO}]/[\text{alkyl}]$ in order of large are as follows: PPG(#1000)/TDI/ $\text{C}_3\text{H}_5(\text{OH})_3 = 1/2/2, 2/3/2,$ and $3/4/2$. When the crosslinked films were baked for 50–60 min, the increasing tendency of the ratios of $[\text{NCO}]/[\text{alkyl}]$ in order of large are as follows: PPG(#1000)/TDI/ $\text{C}_3\text{H}_5(\text{OH})_3 = 3/4/2, 2/3/2,$ and $1/2/2$. This was caused by the fact that the longer the chain length of prepolymer, the less active it was.

The change of the isocyanate groups during the crosslinking reaction of PPG(#2000)-containing prepolymer is shown in Figure 10. Each of the curves in the figure shows two peak maxima. One peak was caused by poor activity of

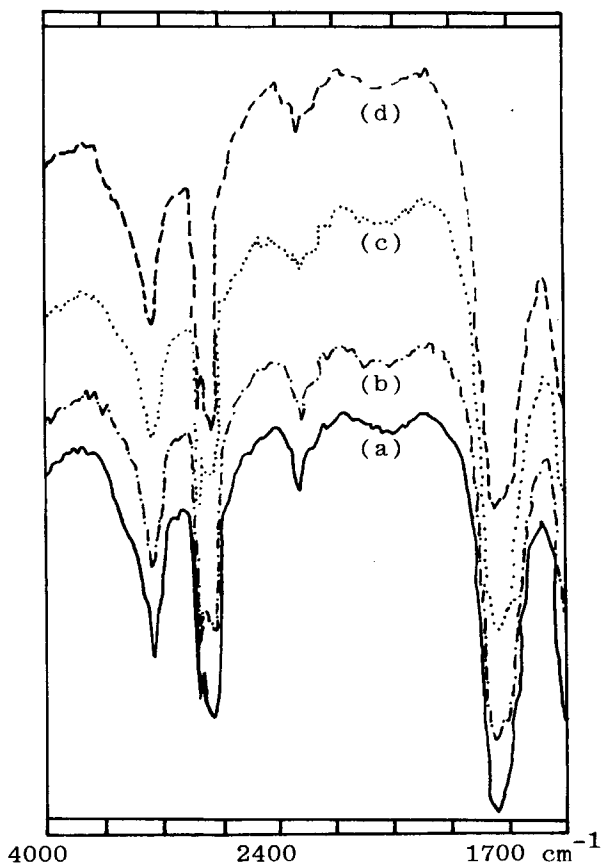


Fig. 8. IR spectra of the crosslinked films prepared from PPG(#1000)/TDI/ $C_3H_5(OH)_3$ (2/3/2) urethane prepolymer with 10% excess equivalent phenol-blocked urethane triisocyanate baked at $220^\circ C$ for different curing times: (a) 10 min; (b) 20 min; (c) 100 min; (d) 120 min.

the secondary hydroxyl groups of prepolymer, and the other was caused by the excessive long chain length of PPG, which results in the reduction of the probability of collision between the isocyanate and hydroxyl groups.

The absorption ratios of isocyanate to alkyl groups of the crosslinked films prepared from the mixture of PPG(#1000)/TDI/ $C_3H_5(OH)_3$ (0.2/1/1)-containing urethane prepolymer and containing an equivalent phenol-blocked urethane triisocyanate baked at $220^\circ C$ for different curing times are shown in Figure 11. From the change of the absorption peaks of the isocyanate groups, it can be observed that the isocyanate absorption peaks decreased gradually with reaction time. Although the reactivity of the secondary hydroxyl groups of prepolymer is weaker than that of the primary hydroxyl groups of prepolymer, there are many hydroxyl groups in the prepolymer chain which give higher activity to the urethane prepolymer. The IR absorption of isocyanate groups are gradually reduced to zero.

Mechanical Properties of the Crosslinked Films

The mechanical properties of the crosslinked films are listed in Table II. The experimental results show that the tensile strength and elongation at

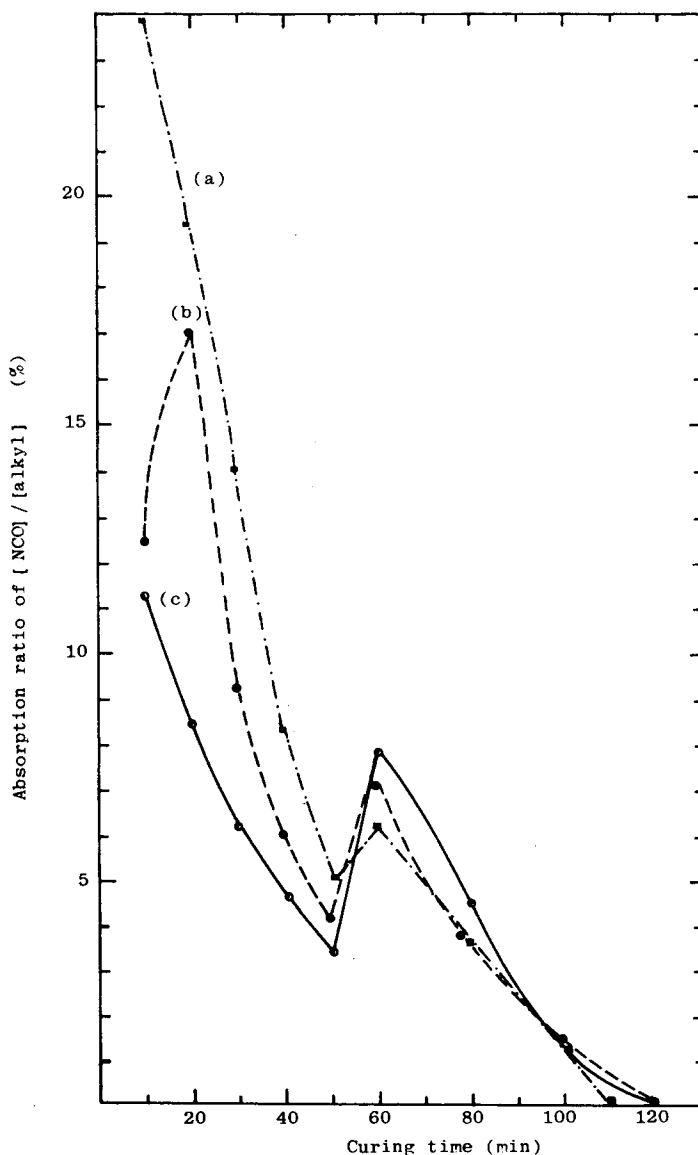


Fig. 9. IR absorption ratios of [NCO]/[alkyl] as function of curing time. Sample: PPG(#1000)/TDI/ $C_3H_5(OH)_3$ = (a) 1:2:2, (b) 2:3:2, and (c) 3:4:2.

break of the crosslinked films prepared from PPG(#1000)-containing urethane prepolymers are better than those of PPG(#2000)-containing urethane prepolymers. Meanwhile, the tensile strengths of the crosslinked films decreased with increase of the molar ratio of PG, but the elongation at break increased with increasing molar ratio of PG.

CONCLUSIONS

1. The crosslinking reaction rate of hydroxyl-terminated urethane prepolymer with isocyanate regenerator depends on the nature and mixing ratio of both reactants and baking temperature.

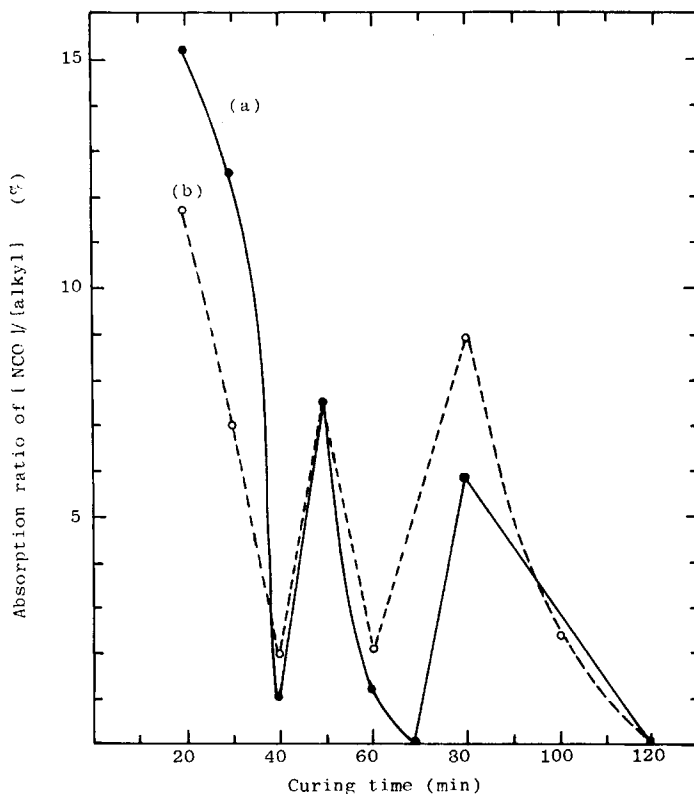


Fig. 10. IR absorption ratios of [NCO]/[alkyl] as function a of curing time. Sample: PPG(#2000)/TDI/ $C_3H_5(OH)_3$ = (a) 1:2:2 and (b) 2:3:2.

2. In curing, the change of isocyanate absorption in IR spectra can be used to qualitatively study regeneration of the isocyanate group and the reaction rate of isocyanate and hydroxyl groups of urethane prepolymers.

3. Experimental results show that the curing reaction rate of glycerin-terminated PG/TDI/glycerin urethane prepolymer and PhOH-TMP-TDI isocyanate regenerator baked at 220°C are as follows:

(a) The reaction rate of the primary hydroxyl group of glycerin with isocyanate is faster than that of secondary hydroxyl group of glycerin with isocyanate.

(b) At 220°C , initially the isocyanate increased rapidly and then decreased gradually with curing reaction. When all primary hydroxyl groups were used up, isocyanate increased again. This feature was caused by the fact that the reactivity of the secondary hydroxyl groups is slower than that of the primary hydroxyl groups.

(c) For the same urethane prepolymer, the reaction rate is dependent on the quantity of isocyanate regenerator. Increasing the isocyanate regenerator will increase the reaction rate, but the reaction rate will slow down.

(d) When different molecular weight urethane prepolymer reacted with equivalent isocyanate regenerator, the lower the urethane prepolymer molecular weight, the greater the hydroxyl density and the faster the reaction is.

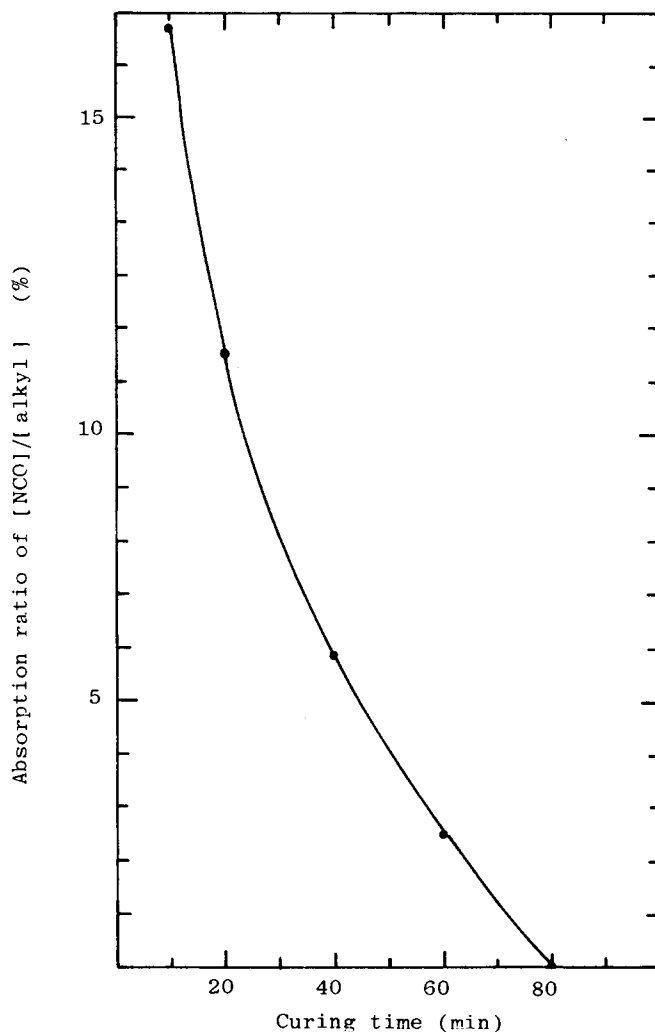


Fig. 11. IR absorption ratios of [NCO]/[alkyl] as a function of curing time. Sample: PPG(#1000)/TDI/ $C_3H_5(OH)_3$ = 0.2:1:1 with equivalent phenol-blocked urethane triisocyanate.

TABLE II
Mechanical Properties of the Crosslinked Films

PG	PG/TDI/ $C_3H_5(OH)_3$	Tensile strength (kg/cm^2)	Elongation at break (%)
PPG(#1000)	1:2:2	150	47
	2:3:2	94	95
	3:4:2	11	238
PPG(#2000)	1:2:2	2	19
	2:3:2	1	29
PPG(#1000)	0.2:1:1	530	5

Experimental results show that the change of $[\text{NCO}]/[\text{alkyl}]$ corresponds to a change of reaction rate.

(e) Experimental results show that when the molecular weight of glycerin-terminated urethane prepolymers is changed by varying the ratio of PPG to TDI or the molecular weight of PPG, the IR spectra changes of $[\text{NCO}]/[\text{alkyl}]$ are not the same during the curing reaction. For example, the ratio changes of the IR spectra for urethane prepolymers containing PPG(#2000) show one more peak than those of urethane prepolymer containing PPG(#1000). This might be due to the possibility that PPG of longer molecular chain would decrease the reaction rate between the secondary hydroxyl group and unreacted isocyanate groups.

(f) In the case of decreasing the quantity of PPG to reduce the molecular weight of urethane prepolymer, there is no $[\text{NCO}]/[\text{alkyl}]$ peak that appears in the curing reaction, because the hydroxyl density of the reactant affects the reaction rate.

4. The mechanical properties of crosslinked films prepared from glycerin-terminated PPG-TDI-glycerin urethane prepolymer with PhOH-TMP-TDI isocyanate regenerator are excellent. The properties of crosslinked films are dependent on the crosslinking density, so that changing the crosslinked density can give strong and tough elastic crosslinked films.

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