

Emulsion of Polyurethane Having Thermosetting Properties. I. Preparation

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Synopsis

A method of preparation of an urethane emulsion which provides thermosetting film is described here. By reacting a urethane prepolymer containing terminal isocyanate groups with diethylenetriamine in the presence of ketones, poly(urethane-urea-amine) was prepared. In other organic solvents, however, gelation occurred immediately and preparation of polyurethane-urea-amine was not successful. The function of ketone was ascribed to the tentative formation of a Schiff base between the primary amino group of diethylenetriamine and ketone *in situ*, and the reaction of primary amine with isocyanate was partly masked to prevent gelation. Then the free amino group is generated when the polymer is treated with epichlorohydrin and the reaction occurs between them. After the solution was neutralized with an aqueous acid, the solvent was removed *in vacuo* to give a stable self-emulsifiable thermosetting urethane emulsion. Typical mechanical properties of film from this urethane emulsion are also given here.

INTRODUCTION

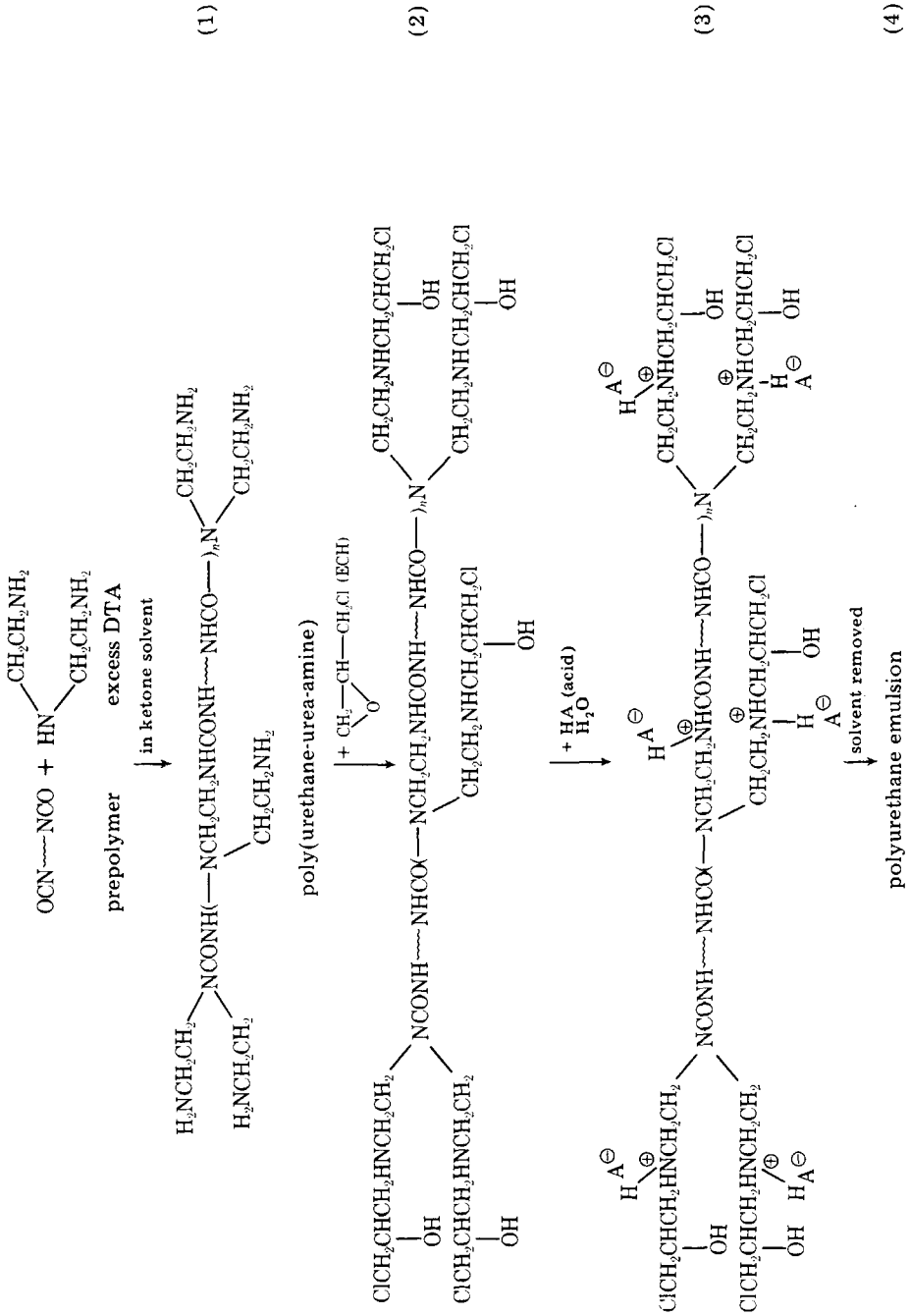
In a previous paper we reported the preparation of polytetramethylene glycol (PTMG) by using fuming sulfuric acid (SO₃ 15%–43%) as the catalyst.¹ This paper describes the preparation of polyurethane emulsion as one of the applications of PTMG.

Urethane polymers have widely been used as foams, elastomers, coatings, and elastic fibers.² Recently, an aqueous emulsion of an urethane polymer which does not contain organic solvent has drawn much attention from an environmental standpoint.

For the preparation of polyurethane emulsions in water, the use of an emulsifying agent³ and a method in which a polyurethane containing tertiary amino groups is prepared and quaternized⁴ as well as a method in which anion groups are attached along the polyurethane chain have been employed. The former method, using emulsifiers, requires a considerable amount of emulsifier, and consequently the emulsifier exerts a bad effect on the properties of the film products after the emulsion is dried. Therefore, the use of products containing emulsifiers is quite limited.

In the methods in which tertiary amino groups in the polyurethane chain are quaternized and anion groups are attached along the polyurethane chain, the stability of the emulsion is poor when the molecular weight of the polyurethane is high. On the other hand, when the molecular weight of the polyurethane is reduced in order to obtain a stable emulsion thereof, the physical properties of films prepared from such emulsions become poor.

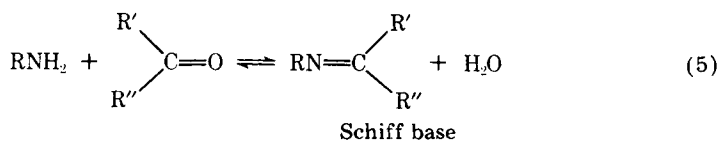
In the present paper, a new self-emulsifiable polyurethane is described which is prepared by the following two reactions: First, urethane prepolymer con-



taining terminal isocyanate groups is reacted with an excess amount of diethylenetriamine (DTA) in ketone solvent to prepare poly(urethane-urea-amine), eq. (1), and then the primary amino group present in the form of a Schiff base in poly(urethane-urea-amine) is regenerated and reacted with epichlorohydrin, eq. (2). After neutralizing the resulting product with aqueous acid, eq. (3), the ketone solvent is finally removed by distillation *in vacuo*. When the emulsion, eq. (4), prepared by the above method is subjected to heat treatment, the crosslinking reaction takes place between the chloromethyl groups and the amino groups, and the physical properties of the film are improved. Therefore, it is not necessary to use high molecular weight polymer in the original emulsion, and a stable polyurethane emulsion can be prepared.⁵

In eq. (1), the prepolymer containing terminal isocyanate groups which was prepared from excess tolylene diisocyanate (TDI) and polyether diol is reacted with an excess amount of DTA in ketone solvent to prepare poly(urethane-urea-amine). In general, the rate of the reaction of the isocyanate group with the amino group is very fast. Therefore, when the prepolymer was reacted with DTA in ethyl acetate, THF, DMF, and benzene, crosslinking occurred immediately, and consequently a homogeneous polymer solution could not be obtained by separating insoluble matter. However, when the prepolymer was added to a DTA solution in ketone solvent after the DTA solution had been maintained at room temperature over 1 hr, the polymer solution, eq. (1), was not crosslinked. But when the prepolymer was added to a DTA solution in ketone immediately after the DTA solution was prepared, crosslinking did occur.

The function of the ketone was ascribed to the tentative formation of a Schiff base, eq. (5), between part of the primary amino group of DTA and ketone to suppress crosslinking. Next, free amino groups are regenerated when the polymer is treated with epichlorohydrin, and reaction takes place between the primary amino groups and epichlorohydrin:



EXPERIMENTAL

Materials

Methyl ethyl ketone (MEK), acetone, ethyl acetate, tetrahydrofuran (THF), and dimethylformamide (DMF) were commercial reagents of extra-pure grade of JIS (Japan Industrial Standards). The water content in these solvents was less than 0.05%. *n*-Butylamine, *n*-dibutylamine, and diethylenetriamine (DTA) were commercial reagents of JIS extra-pure grade. Tolylene diisocyanate (TDI) was an 80/20 mixture of 2,4- and 2,6-tolylene diisocyanates (Sumidur 80, Sumitomo Bayer Urethane Co., Japan). Polytetramethylene glycol (PTMG) had an acid number of 0.01, a hydroxyl number of 54.8, and a maximum water content of 0.05% (Kao Soap Co.). Epichlorohydrin (ECH) and 70% glycolic acid (GA) were commercial reagents of JIS extra-pure grade.

Preparation of Polyurethaneurea Emulsion

A typical method is as follows. In a 1-liter, four-necked flask provided with a stirrer, a thermometer, and a reflux condenser, 204.7 g (0.1 mole) PTMG (OHV 54.8) and 102.6 g MEK were added to 34.8 g (0.2 mole) TDI under nitrogen. The mixture was stirred at 80°C for 3 hr to obtain a urethane prepolymer having terminal isocyanate groups. The isocyanate groups content remaining in the resulting prepolymer was analyzed to be 2.45% (calcd value 2.46%).

Nonvolatile matter, i.e., solid polymer, was 70 wt-%. In another 2-liter separable four-necked flask, 268.2 g MEK and 4.73 g (0.046 mole) DTA were placed. And after the above mixture had been mixed at room temperature for 1 hr, 133.9 g (0.039 mole) of the above prepolymer solution was added dropwise to the DTA-MEK mixture under stirring over 2 hr at room temperature, and the mixture was heated at 50°C for 10 min (prepolymer/DTA molar ratio was 0.85/1). At the end of the addition the viscosity of the mixture was increased and was shown to be 300–400 cps. Nonvolatile matter was 24.2%. The IR absorption of the NCO group at 2270 cm^{-1} disappeared. The total amine value of poly(urethane-urea-amine) was 8.6, partial amine value was 0.26, and tertiary amine value was 0.26. The total amine value was calculated at 8.18 on the basis of the amounts of starting materials. Therefore, it was assumed that the reaction proceeded quantitatively according to eq. (1). Also, the observed amine values showed that the secondary amino group of DTA was reacted almost completely. The molecular weight based on the observed amine value was 14220, which is in good agreement with the calculated value of 14480 based on the molar ratio of isocyanate group and amine groups (all secondary amino groups and a small fraction of primary amino group).

Then, a mixture of 36.6 g water and 5.05 g (0.054 mole) ECH (equimolar amount to primary amino group) was added to 366.1 g of the above polyamine, and the mixture was heated at 50°C for 1 hr.

The pH value of the mixture was adjusted to 7.0 with 5.8 g 70% glycolic acid to which 300 g water was added. Finally, the solvent and the unreacted ECH were removed under 50 mm Hg pressure at a maximum of 50°C for 2.5 hr, and water was added to regulate a 30% solid concentration. Thus, 314 g of a stable, aqueous emulsion of 30% resin content was obtained. The chlorine content was 0.19%, which means that 31% of the charged ECH had reacted.

Analysis

Hydroxyl number and acid number were determined by the JIS methods. The total, partial, and tertiary amine values were by the A.O.C.S. TF1A-64 and TF2A-64. NCO value was determined by the ASTM D1638-59T method. Molecular weight of poly(urethane-urea-amine) was calculated on the basis of the observed amine value. Total chlorine content was determined by the Volhard method.

IR spectra were determined on a Hitachi Type 215. ^{13}C -NMR were determined at 15.03 MHz on JEOL JNM FX-60FT spectrophotometer. The ppm values were taken from the external TMS standard. Temperature was 25°C; repetition time, 3.0 sec; pulse width, 11 μsec (45°); data point, 8192; no. of pulses, 200; spectral width, 4000 Hz.

Preparation of Film

The emulsion was spread on a Teflon-coated plate to a thickness of approximate 1 mm of the dried film which was allowed to stand at room temperature for four days. After the film had been kept at 60% R.H. at 25°C for 24 hr, physical properties of the film were examined by the JIS K6301 (1962) method.

RESULTS AND DISCUSSION

Effect of Solvents on Preparation of Poly(urethane-urea-amine)

The prepolymer was added dropwise to a solution of DTA. A homogeneous polymer solution was obtained only in case of ketone solvent. Moreover, even in case of ketone solvent, if the prepolymer was added to the DTA solution immediately after DTA was dissolved in the ketone solvent, insoluble materials developed and a homogeneous polymer solution could not be obtained.

For these observations, some interaction between DTA and the ketone solvent was assumed. This problem was examined by means of IR and NMR spectroscopy first with a model reaction of *n*-butylamine and acetone. When equimolar amounts of *n*-butylamine with acetone were mixed at room temperature, absorption due to the ν C=N (1660 cm^{-1}) developed,⁶ and at the same time absorption due to ν C=O at 1710 cm^{-1} decreased with time. The absorption at around 1600 cm^{-1} due to δ_{NH_2} disappeared, too (Fig. 1).

When equimolar amounts of di-*n*-butylamine and acetone were mixed, no new IR absorption band was observed, and the IR spectrum itself did not change after 24 hr (Fig. 2).

Figure 3 show that the absorption at around 1660 cm^{-1} due to the ν C=N band was formed when equimolar amounts of DTA and MEK were mixed at room temperature. The ν C=N band was increased with the progress of time. At

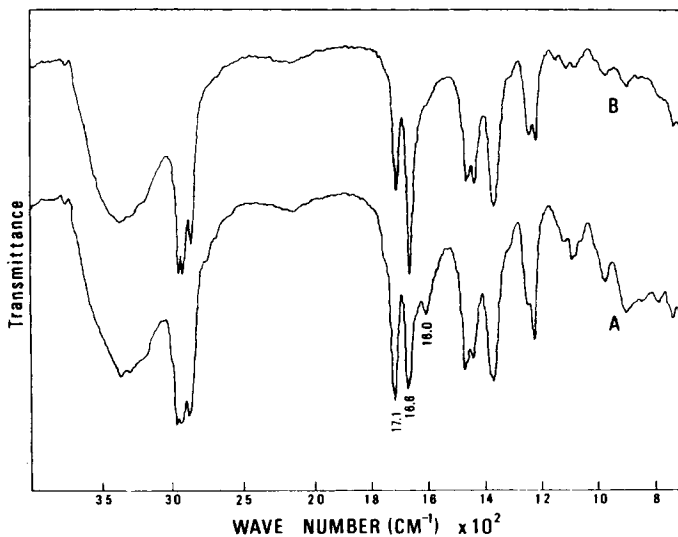


Fig. 1. IR spectrum of equimolar mixture of *n*-butylamine and acetone: A, immediately after mixing; B, after 24 hr.

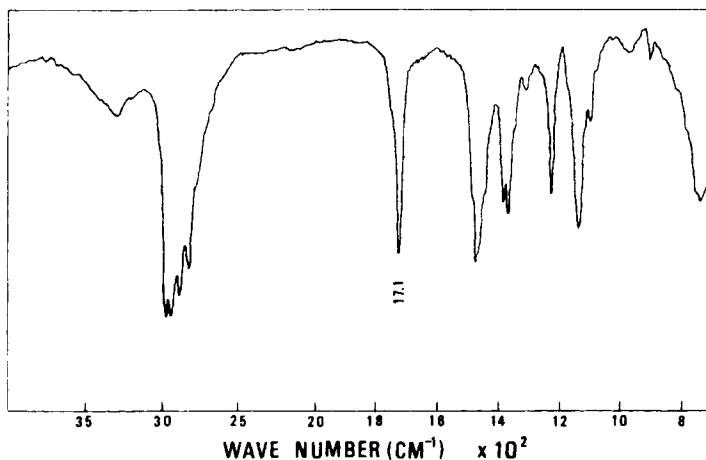


Fig. 2. IR spectrum of equimolar mixture of *n*-dibutylamine and acetone after 24 hr.

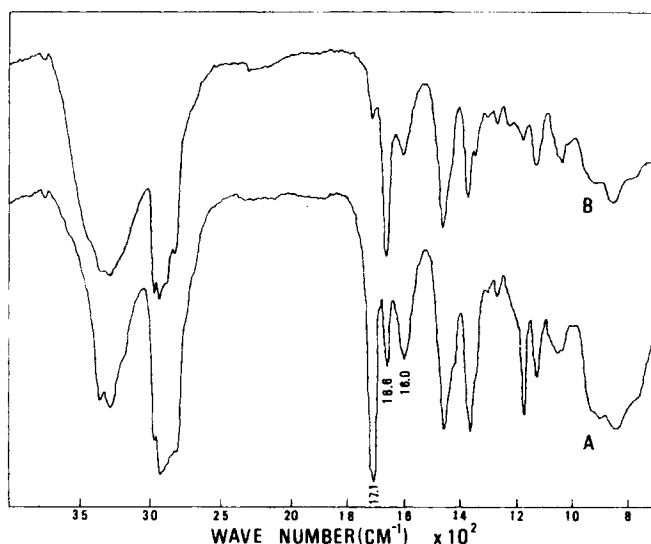


Fig. 3. IR spectrum of equimolar mixture of DTA and MEK: A, immediately after mixing; B, after 24 hr.

the same time, the absorption of ν C=O at 1710 cm^{-1} was decreased gradually and almost disappeared after 24 hr. The absorption at 1600 cm^{-1} due to the δ_{NH_2} was also decreased. Also, the absorptions at around $3100\text{--}3400\text{ cm}^{-1}$ became very broad. With acetone, the change of the IR spectrum was quite similar to that with MEK, but the development rate of the absorption of ν C=N was faster than that of MEK.

When an excess amount of acetone was mixed with DTA (acetone/DTA molar ratio 2.0 and 3.0), the change of the IR spectrum of the mixture was quite similar (Fig. 4).

From the above findings, it was concluded that a Schiff base was easily formed from the primary amino groups with ketone even at room temperature.

The amine-ketone reaction was also examined at room temperature by ^{13}C -FT-NMR spectroscopy.

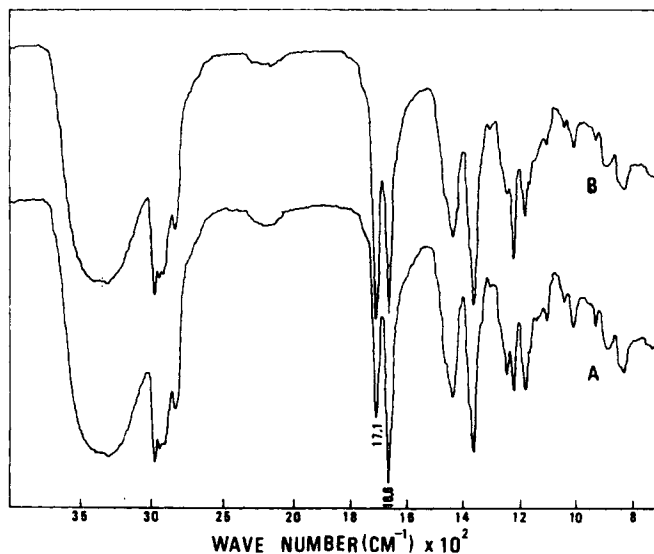


Fig. 4. IR spectrum of mixture of DTA and acetone: A, 1:2 molar ratio after 24 hr; B, 1:3 molar ratio after 24 hr.

In the ^{13}C -FT-NMR spectrum of a mixture of *n*-butylamine and acetone (Fig. 5), the peak of the $>\text{C}=\text{O}$ (205.1 ppm) disappeared gradually after mixing and the peak of $>\text{C}=\text{N}$ (165.7 ppm) appeared.⁷ In the mixture of di-*n*-butylamine and acetone, however, no significant change was observed in the peak of $>\text{C}=\text{O}$, and the peak of $>\text{C}=\text{N}$ did not appear. In case of a mixture of DTA and acetone, similar results were obtained, i.e., the peak of $>\text{C}=\text{O}$ (205.4 ppm) disappeared after 24 hr and the peak of $>\text{C}=\text{N}$ (167.8 ppm) appeared and developed with the time of reaction.

The results of IR and ^{13}C -NMR spectroscopic analyses showed that a Schiff base was produced from DTA and ketone at room temperature, which was

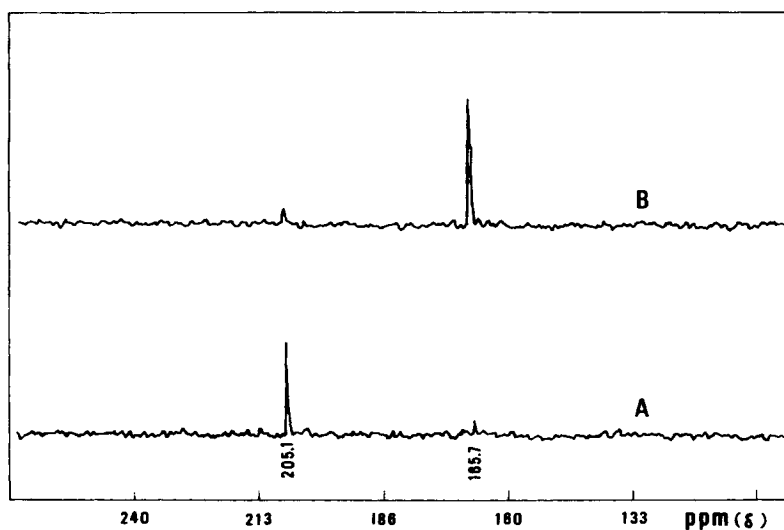
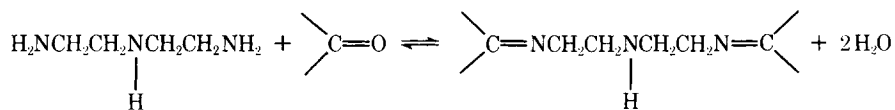


Fig. 5. ^{13}C -NMR spectrum of equimolar mixture of *n*-butylamine and acetone: A, immediately after mixing; B, after 24 hr.

present in equilibrium with DTA and ketone:



For the reaction of the isocyanate group of prepolymer and DTA in ketone solvent, it was assumed that the secondary amino group first reacted with isocyanate and that part of the primary amino groups reacted with isocyanate. As previously shown, the observed secondary amine value of poly(urethane-urea-amine) was zero. The IR spectra of the prepolymer containing terminal isocyanate group and the poly(urethane-urea-amine) are shown in Figures 6 and 7. After the prepolymer reacted with DTA, the absorption of NCO (2270 cm^{-1}) was no longer observed, whereas the absorption of NH_2 (δ_{NH_2} at 1600 cm^{-1}) was still recognized.

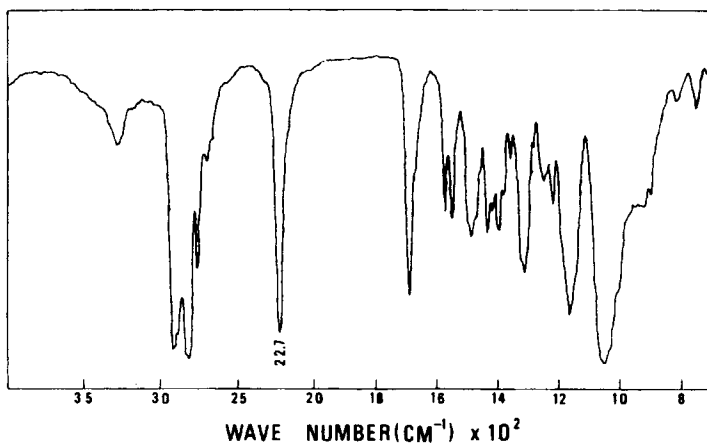


Fig. 6. IR spectrum of prepolymer containing terminal isocyanate groups.

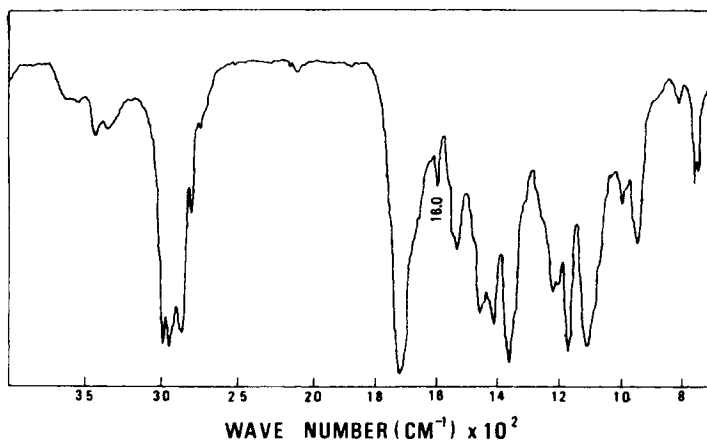


Fig. 7. IR spectrum of poly(urethane-urea-amine).

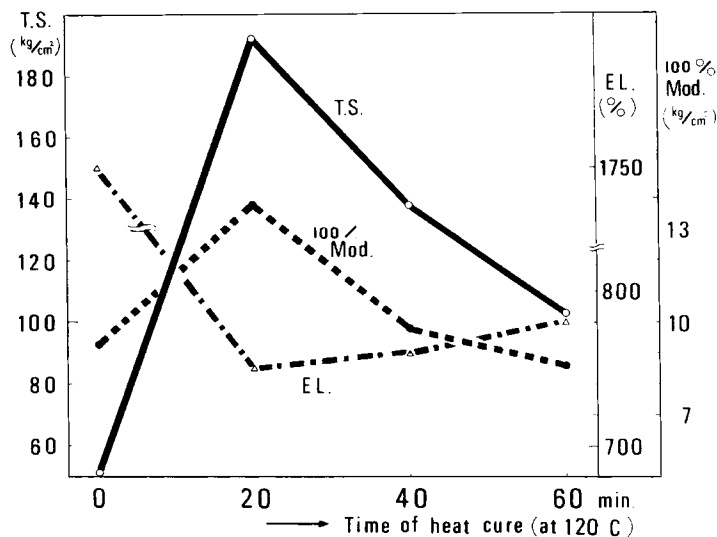


Fig. 8. Relation between time of heat cure (at 120°C) of film and physical properties (curing time 20–60 min) (T.S. = tensile strength; EL. = elongation; Mod. = modulus).

Physical Properties of Films

In Table 1, the physical properties of a film made from the aqueous emulsion are compared with those of a film made directly from the ketone solution. The compositions of the two polymers are the same. Both air-dried and heat-cured films made from the emulsion and from the ketone solution showed similar physical properties.

Figure 8 shows that the tensile strength (T.S.) of the films shows a maximum value for 20 min at 120°C and it then decreased with time.

Figure 9 shows that the tensile strength of the films shows a maximum value by heat cure at 120°C. The tensile strength of the films cured at 100°C is lower because of undercuring, whereas that of the films cured at 140°C is also lower, probably because of some thermal degradation.

Figure 10 shows that the tensile strength of the films was increased and the elongation (EL.) decreased upon heat cure. The heat-cured film shows good elasticity and softness as an urethane elastomer.

TABLE I
Physical Properties of Films Prepared from Aqueous Emulsion and Ketone Solution^a

	Film prepared from emulsion		Film prepared from solution	
	Air dried	Heat cured	Air dried	Heat cured
Modulus, kg/cm ²				
100%	12.3	14.7	12.1	14.9
200%	12.7	16.8	12.4	16.7
300%	12.5	18.7	12.3	18.0
400%	12.3	20.9	12.2	19.3
500%	12.1	25.2	12.0	23.3
Tensile strength, kg/cm ²	58	215	59	210
Elongation, %	>1180	740	>1300	860

^a Heat-curing conditions: 120°C for 20 min.

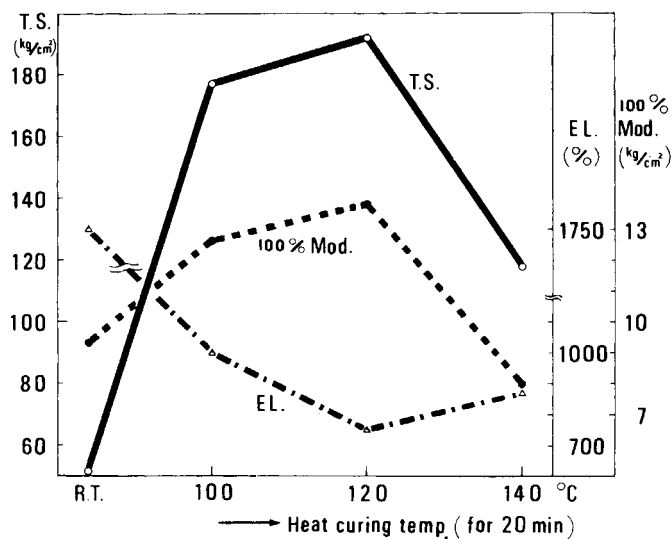


Fig. 9. Relation between heat-curing temperature and physical properties (curing time 20 min).

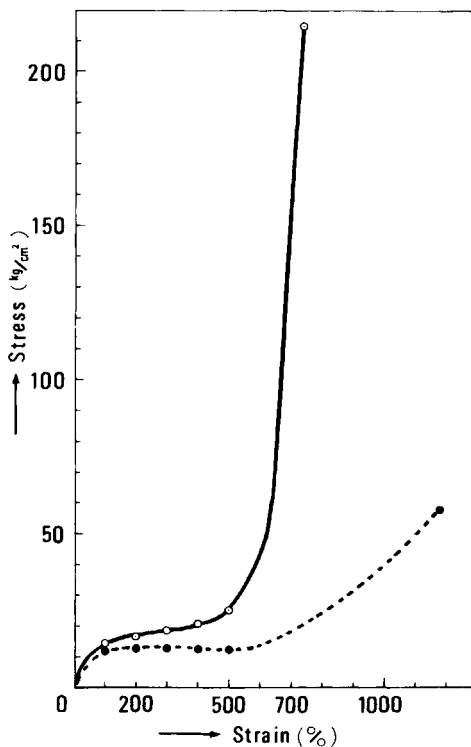


Fig. 10. Stress-strain curve at 25°C: (---) air-dried film; (—) heat-cured film at 120°C for 20 min.

Tear strength, abrasion resistance, and tension set are as follows. Heat-treated film (curing conditions 120°C, 20 min; measuring conditions 25°C, 60% R.H.): tear strength, 27 kg/cm; abrasion resistance (Taber abrader, load 1000 g, revolutions 1000), wheel CS-17, 9.4 mg, wheel H-18 95.6 mg; tension set 13% (after 10 min at 300% extension).

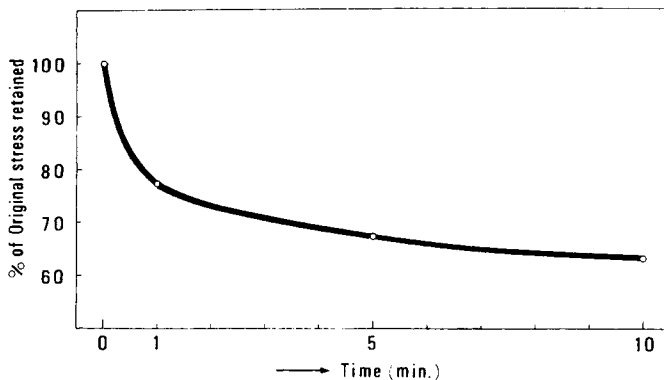


Fig. 11. Stress relaxation of heat-cured film (at 120°C for 20 min) during 10 min at 300% extension.

Figure 11 shows stress relaxation during 10 min at 300% extension.

Figure 12 shows that the 100% modulus at -30°C was approximately three times as high as that at 25°C , and the value at 70°C was 80%–90% of that at 25°C . The polyurethane film of the present study is characterized by a small temperature dependence.

Resistance to water and to DMF was as follows. Water swell (wt-%, 50°C , 1 hr, dipped): air-dried film, 32%; heat-cured film, 6% (120°C , 20 min). DMF swell (wt-%, 30°C , 48 hr, dipped): air-dried film, dissolved; heat-cured film, 380% (120°C , 20 min).

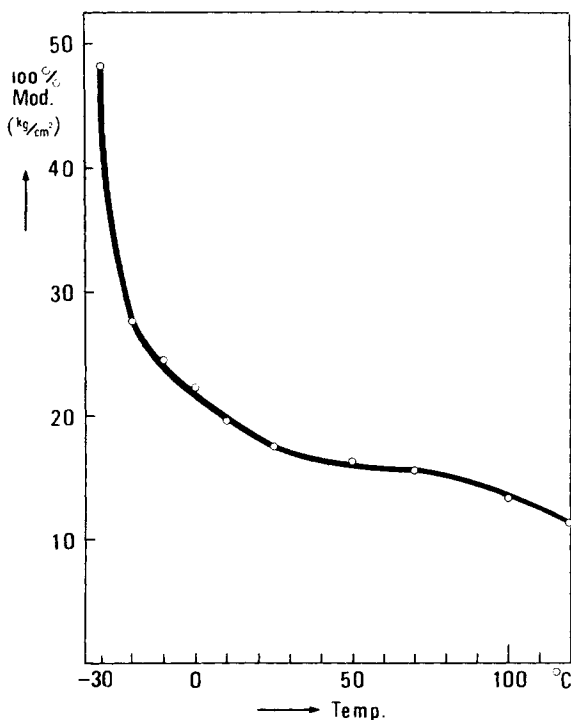


Fig. 12. Temperature dependence of 100% modulus of heat-cured film (at 120°C for 20 min).

The resistances toward water and DMF were increased as crosslinkage was developed by the heat treatment.

Table II shows that the physical properties of film made from the emulsion after six months of storage at room temperature showed no change.

Emulsion Properties

Some of the physical properties of the above-mentioned emulsion are as follows: pH, approx. 7; specific gravity (20°C), 1.03; total solids, 30%; particle size, 0.4 μ ; viscosity (25°C), 50 cps (Fig. 13).

Dilution Stability. This emulsion is very stable toward dilution, i.e., the emulsion was not destroyed when it was diluted from 25% (solids content by wt.) to 0.1%.

TABLE II
Physical Properties of Film Prepared from the Emulsion After Long Storage at Room Temperature^a

	Immediately after preparing	After one month	After six months
Modulus, kg/cm ²			
100%	16.8	18.5	18.4
200%	19.9	21.3	21.1
300%	22.4	23.6	23.1
400%	25.5	26.5	24.7
500%	32.2	32.4	27.9
Tensile strength, kg/cm ²	220	244	227
Elongation, %	720	740	830

^a Heat-curing conditions: 120°C for 20 min.

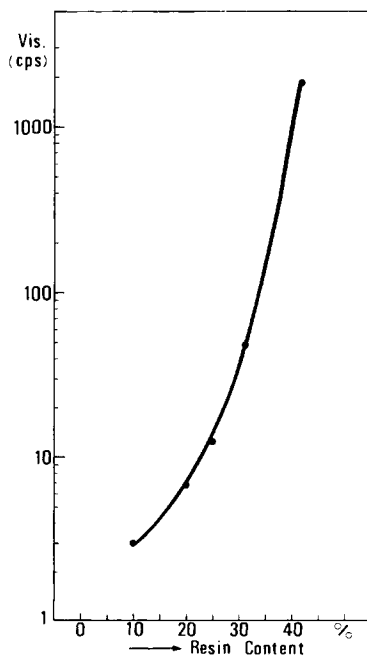


Fig. 13. Relation between resin content and viscosity of emulsion at 25°C.

Temperature Stability. The emulsion is very stable if it is heated at 60°C for five days.

Mechanical Stability. This emulsion is very stable if it is stirred vigorously in a homomixer for 15 min at a speed of 12,000 rpm, and the mechanical properties of the polyurethane film from the stirred emulsion were similar to those prepared from the original emulsion.

CONCLUSIONS

Poly(urethane-urea-amine) was prepared by reacting DTA with prepolymer containing terminal isocyanate groups in a ketone solvent. In the absence of ketone, gelation occurred immediately. In addition, the gelation occurred also when the prepolymer was added to DTA solution immediately after DTA was dissolved in a ketone solvent. From these findings it was concluded that Schiff base formation occurred between the primary amino group of DTA and ketone solvent to moderate the reaction of DTA with isocyanate by masking part of the primary amino groups. Then, the free amino groups in poly(urethane-urea-amine) were reacted with epichlorohydrin, and it was neutralized with an aqueous acid. Finally, the ketone solvent was removed by distillation *in vacuo*. Thus, a self-emulsifiable and thermosetting polyurethane emulsion was prepared. Typical physical properties of the film prepared from the emulsion were examined. The emulsion was found to be quite stable toward dilution, stirring, and heating (60°C). The film prepared from the emulsion showed the same mechanical properties as those of film prepared from the ketone solution.

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