# Study of the Curing Process Giving the Rigid Polyurethane Foam by Dynamic Viscoelastic Method

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## Synopsis

Dynamic viscoelastic properties of the rigid polyurethane foam, which is used in Japan as a thermal insulator for refrigerators were studied during the curing process using the RDS-7700 Dynamic Spectrometer. The curing process, in which large volume expansion and heat evolution occurred, was easily analyzed by this method. The apparent storage modulus ($G'_{app}$), the apparent loss modulus ($G''_{app}$), and the apparent loss tangent (tan $\delta_{app}$) were measured as a function of cure time. The effects of the curing temperature and the amine catalyst on the curing process were investigated. It was found that the curing process proceeded through three stages: logarithm of $G''_{app}$ (log $G''_{app}$) increased with increasing cure time in the first stage, log $G''_{app}$ increased with increasing logarithm of cure time in the second, and the change of $G''_{app}$ cannot be expressed simply in the final. Curing behavior can be estimated from changes of rheological parameters during the curing. The fluidity of reaction mixture can be also predicted from the peak time of tan $\delta_{app}$.

## INTRODUCTION

Polyurethane foam has been used as a thermal insulator in many products because of its low thermal conductivity and low density. However, the curing behavior during reaction processing resulting in polyurethane foam has not been studied in detail yet, this is because the curing reaction proceeds very rapidly and the volume of the reaction mixture is largely expanded with foaming. Perferable curing conditions, which influence productivity and workability in the process, are usually estimated by a conventional gel time method, the rise rate method,[1,2] and also the processing in practical mold.

Recently, studies on the curing process for polyurethane have been done for the reaction injection molding (RIM) of nonfoaming polyurethane by thermal[3-5] and rheological[6-9] methods, but none for polyurethane foam. The present paper is concerned with a method which is used to clarify the curing behavior and estimate the productivity and workability during the reactive processing which produces polyurethane foam.

Generally, the curing process for polyurethane foam is characterized as follows. (1) The reaction mixture changes from the liquid state to the solid state. (2) The curing reaction is completed in a few minutes. (3) The volume of the reaction mixture is expanded greatly with foaming.

Thus, the method must satisfy the following criteria. (a) To be used in the wide range from the liquid to the solid states. (b) To be able to determine the rapid curing rate. (c) To be a simple measurement. (d) To be capable of

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TABLE I
Formulation of Rigid Polyurethane Foam

| | Parts by weight |
|---|---|
| A components | |
| aromatic amine-based polyol | 70 parts |
| ("Excenol 454AR® ", OHV 450, Asahi Glass Co., Ltd.) | |
| sugar-based polyol | 20 parts |
| ("SBU polyol 0478® ", OHV 530, Sumitomo Bayer Urethane Co., Ltd.) | |
| glycerin-based polyol | 10 parts |
| ("MN 700® ", OHV 235, Mitsui-Toatsu Chemicals Inc.) | |
| water | 1.5 parts |
| Freon-ll | 40 parts |
| ("FR-ll® ", Asahi Glass Co., Ltd.) | |
| silicone surfactant | 1.5 parts |
| ("L-5340® ", Nippon Unicar Co., Ltd.) | |
| catalyst[a] | $5.6 \times 10^{-5}$ mol/g[b] |
| B components | |
| TDI prepolymer[c]/crude MDI[d] | 143 parts |
| ("TR-50BX® ", NCO 30.5% by weight, Mitsui-Toatsu Chemicals Inc.) | |

[a]catalyst:
$N,N,N',N'$-tetramethylhexamethylenediamine (TMHDA)
("Kao Lizer No. 1® ", Kao Corp.)
$N,N,N',N'',N''$-pentamethyldiethylenetriamine (PMDETA)
("Kao Lizer No. 3® ", Kao Corp.)
1,4-diazabicyclo(2,2,2)octane (DABCO)
("Dabco® ", Sankyo Air Products Co., Ltd.).
[b] $5.6 \times 10^{-5}$ mol of catalyst was added to 1 g of A components excepting Freon-11.
[c] Tolylene diisocyanate.
[d] 4,4'-Diphenylmethanediisocyanate.

obtaining information about productivity and workability. We applied a viscoelastic method for this object by considering the above requirements.

In this paper, the dynamic viscoelastic method[8,10] was investigated for the curing process giving the rigid polyurethane foam, which is used especially as a thermal insulator for refrigerator. The amine catalyst used in this process was also discussed from the viewpoints of productivity and workability.

## EXPERIMENTAL

### Materials

A typical formulation for the rigid polyurethane foam shown in Table I was applied in the experiments. The foam density was 22–23 g/L.

### Measurement of Dynamic Viscoelastic Properties

Dynamic viscoelastic measurement was carried out using the RDS-7700 Dynamic Spectrometer (Rheometrics Inc.) at a frequency of 10 rad/s using 50 mmφ parallel plates with 3 mm gap and the amplitude of $1.2 \times 10^{-3}$ radians. The chamber temperature was thermostatted within $\pm 1$K during the measurements.

Changes of dynamic viscoelastic properties during the curing were measured as follows. A and B components kept at 292 K were mixed with high speed stirring (10,000 rpm) in a flask for 5 s and a portion of the mixture was transferred to the platen of the Rheometer. Then measurement was started.

A small portion of the sample overflowed from the platen due to foaming during the measurement, but the results were not affected by this as will be described later.

## Measurement of Temperature

The temperature change of reaction mixture was measured by inserting a copper-constantan thermocouple into the center of the reaction mixture.

## Measurement of Gel Time and Tack -Free Time

Gel time and tack-free time were determined on the same amount of sample used in viscoelastic measurement at 305 K. Gel time was determined by touching the foam surface with a metal needle for spinnability. Tack-free time was determined by touching the foam surface with a finger as a measure of tackiness.

## Measurements of Fluidity

Fluidity of the reaction mixture during curing was determined using a mold (see Fig 1). The reaction mixture (240 g) was poured into the mold which was kept at 314 K and cured. After curing, the foam was measured, and the length of the foam obtained was taken as a measure of fluidity.

## RESULTS AND DISCUSSION

When the rheological change is measured during curing for polyurethane foam, two factors, volume expansion and heat evolution, have to be taken into account. Though the volume expansion of reaction mixture was taking place, only a small portion of the reaction mixture was overflowed from the platen of the Rheometer until the apparent storage modulus ($G'_{app}$) and the apparent loss modulus ($G''_{app}$) reached about $10^3$ and $10^2$ Pa, respectively. Figure 2 shows the reproducibility of the data of the apparent storage modulus ($G'_{app}$) in repeated experiments with various degrees of overflowing, and they were in good agreement with each other. Further, $G'$ values of the polyurethane foam
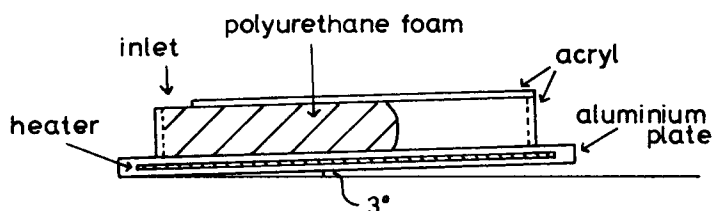


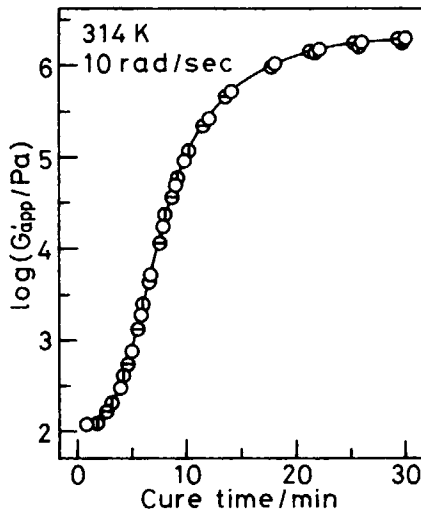Fig. 1.   Mold for the measurement of the fluidity. Length 2 m, width 0.12 m, height 0.03 m.

Fig. 2. Logarithm of apparent storage modulus $G'_{app}$ vs. cure time plots (cured at 314 K, catalyst TMHDA). Reproducibility of the dynamic viscoelastic measurements in repeated experiments with various degrees of overflowing. (○) small; (◑) medium; (⊖) large.

sheet, which was cured in the mold at room temperature as an alternative measurement gave similar results.

Temperature change of the reaction mixture during curing was measured at various cure temperatures. Figure 3 shows an example of the temperature change of the reaction mixture during curing with catalyst DABCO. Temperature changes were observed in cure times up to 6 min, but the change was small (within one degree) in curings at 305–324 K. Therefore, we took the curings at 305–324 K as an isothermal curing reaction and those at 334 and 344 K were studied to learn the effect of temperature on curing.

Apparent storage modulus, apparent loss modulus, and apparent loss tangent (tan $\delta_{app}$) as functions of cure time were obtained. As examples, the plots
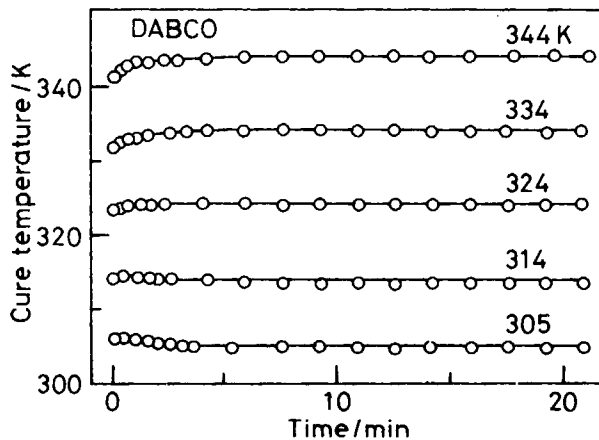


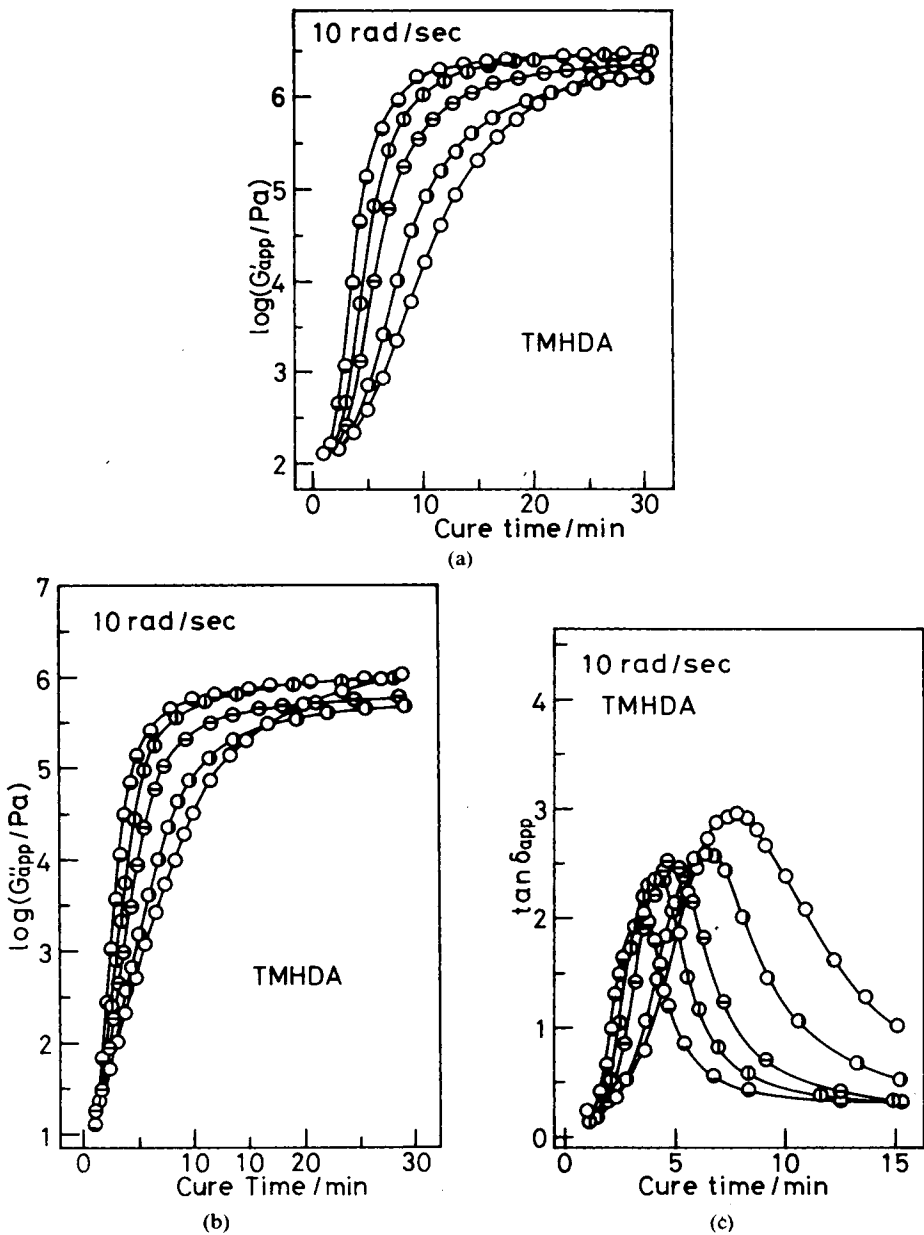Fig. 3. Temperature change of reaction mixture during the curing with catalyst DABCO.

Fig. 4. Rheological change during the curing with catalyst TMHDA. (a) Logarithm of apparent storage modulus (log $G'_{app}$) vs. cure time plots. (b) Logarithm of apparent loss modulus (log $G''_{app}$) vs. cure time plots. (c) Apparent loss tangent (tan $\delta_{app}$) vs. cure time plots. (○) 305 K; (◑) 314 K; (⊖) 324 K; (Φ) 334 K; (◉) 344 K.

obtained for the cure with catalyst TMHDA are shown in Figure 4. The values of $G'_{app}$ and $G''_{app}$ increased with increasing cure time and then reached constant values. The values of tan $\delta_{app}$ increased with increasing cure time, but then decreased after its maximum point. These are observed in all examined curing processes. Plots of logarithm of $G''_{app}$ (log $G''_{app}$) versus cure time ($t$) and the plots of log $G''_{app}$ versus logarithm of cure time (log $t$) are
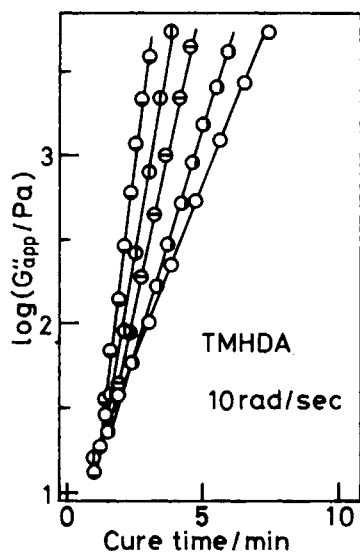
Fig. 5. Logarithm of apparent loss modulus log $G''_{app}$ vs. cure time plots (catalyst TMHDA). (O) 305 K; (◑) 314 K; (⊖) 324 K; (Φ) 334 K; (◕) 344 K.
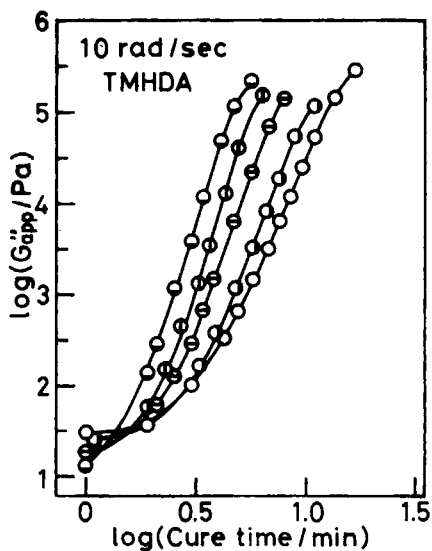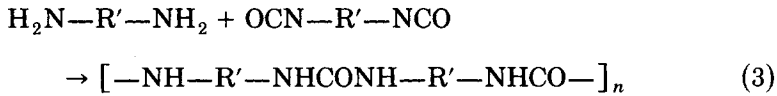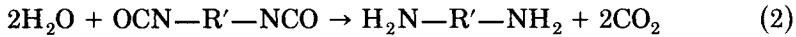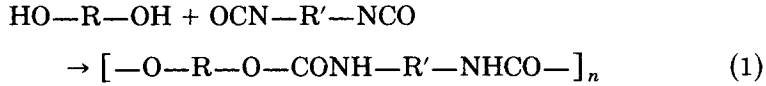


Fig. 6. Logarithm of apparent loss modulus log $G''_{app}$ vs. logarithm of cure time plots (catalyst TMHDA). (O) 305 K; (◑) 314 K; (⊖) 324 K; (Φ) 334 K; (◕) 344 K.

shown in Figures 5 and 6, respectively. As shown in these figures, in the curing examined, log $G''_{app}$ increased with increasing cure time in the range of $G''_{app} \leqq 10^3$ Pa and increased with increasing logarithm of cure time in the range ($10^3 < G''_{app} \leqq 10^5$ Pa). This showed that the curing process giving the rigid polyurethane foam proceeded through three stages: the first stage ($G''_{app} \leqq 10^3$ at 10 rad/s) in which log $G''_{app}$ increased linearly with $t$, the second stage
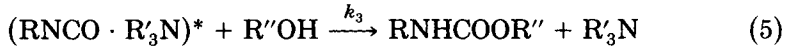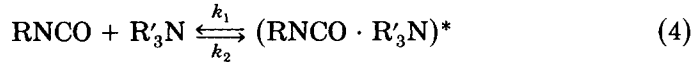
$(10^3 < G''_{app} \leqq 10^5$ Pa) in which $\log G''_{app}$ increased linearly with $\log t$, and the final stage in which the change of $G''_{app}$ could not be expressed simply $(G''_{app} > 10^5$ Pa). This may be considered as follows.

Generally, the following reactions occur in the polyurethane curing.

$$HO—R—OH + OCN—R'—NCO$$

$$\rightarrow [—O—R—O—CONH—R'—NHCO—]_n \qquad (1)$$

$$2H_2O + OCN—R'—NCO \rightarrow H_2N—R'—NH_2 + 2CO_2 \qquad (2)$$

$$H_2N—R'—NH_2 + OCN—R'—NCO$$

$$\rightarrow [—NH—R'—NHCONH—R'—NHCO—]_n \qquad (3)$$

Since the reaction rate of Eq. (3) is faster than that of Eq. (2),[11] Eqs. (1) and (2) are dominant in polyurethane curing.

For simplicity, consider the following steps (similar to Michaelis Menten kinetics):[12]

$$RNCO + R'_3N \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (RNCO \cdot R'_3N)^* \qquad (4)$$

$$(RNCO \cdot R'_3N)^* + R''OH \xrightarrow{k_3} RNHCOOR'' + R'_3N \qquad (5)$$

In Eq. (4), isocyanate groups and catalysts (tertiary amines), form active species $(RNCO \cdot R'_3N)^*$. These species react with polyol groups to form urethane products and tertiary amines. The rate of reaction $r$ is solved to

$$r = -\frac{d[RNCO]}{dt} = \frac{d[RNHCOOR'']}{dt} = \frac{k_1 k_2 [RNCO][R'_3N][R''OH]}{k_2 + k_3[R''OH]} \qquad (6)$$

by conventional method. Further, if $k_2 \ll k_1$, $k_3$, the rate of reaction is expressed as

$$r = \frac{k_1 k_2}{k_3}[RNCO][R'_3N] = K[RNCO][R'_3N] \qquad (7)$$

$$K = const.$$

By using the initial concentration ($C_o$: the number of moles of monomers per unit volume) and the conversion $p$ at time $t$, Eq. (7) is expressed as

$$r = -\frac{d[C_o(1-p)]}{dt} = KC_o^2(1-p)^2 \qquad (7')$$

On the other hand, the number average molecular weight ($Mn$) is expressed as Eq. (8).

$$M_n = \frac{C_o}{C} \qquad (8)$$

where $C$ represents the total number of moles existing in the unit volume before and after polymerization, respectively. The conversion $p$ is

$$p = \frac{C_o - C}{C_o} \tag{9}$$

Substituting Eq. (9) into Eq. (8) gives

$$M_n = \frac{1}{1 - p} \tag{10}$$

Equation (11) is obtained with Eqs. (7) and (10).

$$M_n = C_o Kt + 1 \tag{11}$$

It is known that the following relation is held[13]

$$\eta = AMw^\alpha (\alpha = 1 \sim 3.4) \tag{12}$$

here   $\eta$: zero sheer viscosity
    $Mw$:  weight average molecular weight
      $A$:  constant

If $\eta$ and $M_w$ are proportional to $G''_{app}$ and $M_n$, respectively. Eq. (13) is obtained from Eqs. (11) and (12).

$$\log G''_{app} \propto \log t \tag{13}$$

Equation (13) suggests that the logarithm of $G''_{app}$ changes linearly with the logarithm of cure time ($t$). As shown in Figure 6, $\log G''_{app}$ changed linearly with $\log t$ in the second stage. This may indicate that the curing reaction proceeds in proportion to the concentrations of catalyst and isocyanate group in the second stage. On the other hand, in the initial stage, $[RNCO] \gg [R'_3N]$ is held. Equation (7) can be expressed as follows

$$r = K'[R'_3N]$$
$$K' = K[RNCO] = \text{const.} \tag{14}$$

From Eq. (14), Eq. (15) is obtained in a similar manner as above.

$$\log G''_{app} \propto t \tag{15}$$

Equation (15) indicates that the logarithm of $G''_{app}$ increases with increasing cure time as shown in Figure 5. The curing reaction seemed to proceed in proportion to the concentration of catalyst in the initial stage. This implies that the effects of volume expansion may be ignored in this study. In the final stage, with decreased concentration of monomers, the frequency of collision begins governing the reaction rate. In other words, the diffusion rate of the

reacting polymer molecules became the rate determining process and the curing reaction deviated from Eq. (7) in the final stage. These may be considered as follows. The curing reaction proceeded in proportion to the concentration of catalyst in the initial stage, to the concentrations of catalyst and isocyanate groups in the second, and the final stage, in which the diffusion rate of reacting polymer molecules governed the reaction.

Next, we considered the effects of catalysts on the curing rate and the fluidity of the reaction mixture, which were important factors in the molding of polyurethane foam. The temperature dependence of the time when each reaction reached some conversion was shown in Figure 7 for the first stage and Figure 8 for the final stage. The time $t_a$ when the value of $G''_{app}$ reached $10^3$ Pa was selected as a point for the first stage and the time $t_b$ when the value of $\tan \delta_{app}$ reach 1 after its maximum as the final stage. Here, $t_b$ was taken as representative of the final stage, because there existed a good correlation in $t_b$ versus the starting point of the final stage ($t_3$) (see Fig 9). In the amine catalysts used in this study, the curing rate decreased in the order of DABCO,
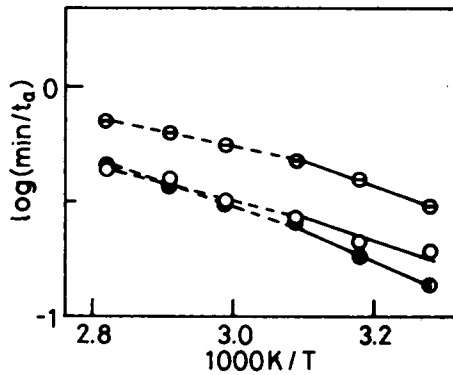


Fig. 7. The Arrhenius plots for the time $t_a$ when the value of apparent loss modulus reached $10^3$ Pa. (○) TMHDA; (◑) PMDETA; (⊖) DABCO.
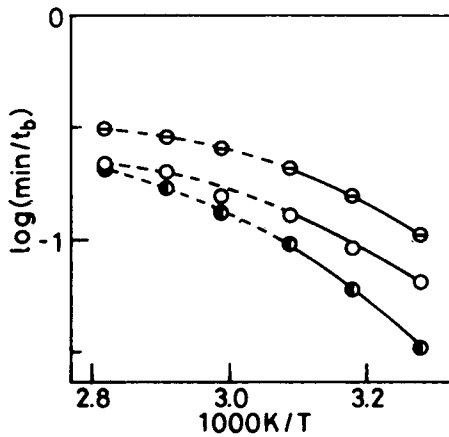


Fig. 8. The Arrhenius plots for the time $t_b$ when the value of apparent loss tangent reached 1 after its maximum point. (○) TMHDA; (◑) PMDETA; (⊖) DABCO.
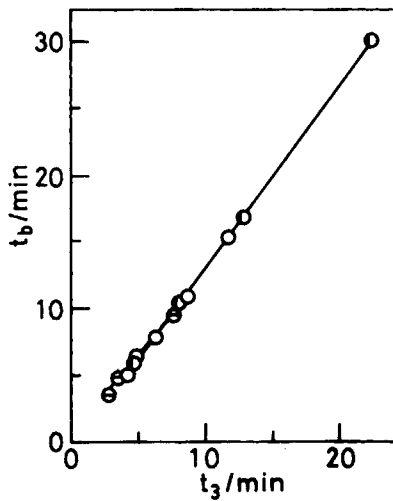
Fig. 9. Plots of the time $b_b$ when the value of apparent loss tangent reached 1 after its maximum point vs. the time $t_3$ when the curing transferred from the second stage to the final. (○) TMHDA; (◉) PMDETA; (⊖) DABCO.

TABLE II
Gel Time and Tack-Free Time on the Curing at 305 K

| Catalyst | Gel time s | Tack-free time s |
|----------|------------|------------------|
| TMHDA    | 158        | 193              |
| PMDETA   | 78         | 111              |
| DABCO    | 67         | 90               |

TMHDA, and PMDETA as seen in Figures 7 and 8. The gel time and the tack-free time, which have been used as measures of curing rate, are shown in Table II. The curing rate decreased in the order of DABCO, PMDETA, and TMHDA by the gel time method. This was different from the results obtained by the rheological method. It may be thought that the gel time and the tack-free time methods measure the curing rate on the foam surface layer, but the rheological method measures bulk properties. We think that the rate of cure ought to be measured by the change of bulk properties of the polyurethane foam.

In curing of polyurethane foam, higher cure rate and higher fluidity of the reactant are required. In other words, it is preferable that the cure rate be slow in the first (i.e., higher fluidity) and, on the contrary, that the cure rate increase in the second and final stages of curing. This is satisfied in the system of low cure rate at lower temperature and high cure rate at higher temperature. It means that the system having the large temperature dependence of the cure rate is appropriate. Temperature dependence of cure rate in the PMDETA cure was greater than that of others, and this was seem clearly in Figures 7 and 8.

TABLE III
Peak Time of Apparent Loss Tangent and the Fluidity
of the Reaction Mixture

| Catalyst | Peak time min | | Fluidity m |
|---|---|---|---|
| | 305 K | 344 K | |
| TMHDA | 7.6 | 3.6 | 1.39 |
| PMDETA | 10.4 | 4.0 | 1.42 |
| DABCO | 5.1 | 2.4 | 1.34 |

As previously described, the value of $\tan \delta_{app}$ increased with increasing cure time, but decreased after its maximum point. Because the value of $\tan \delta_{app}$ indicates the ratio of the loss component of the complex modulus to the storage component, the fluidity of reaction mixture decreases after $\tan \delta_{app}$ peak. Peak time of $\tan \delta_{app}$ and fluidity of reaction mixture are listed in Table III. The fluidity of the reaction mixture in curing was in accord with increasing the peak time. The catalyst used in this study decreased the fluidity in the order of PMDETA, TMHDA, and DABCO.

## CONCLUSIONS

It was found that the curing process giving rigid polyurethane foam was able to be analyzed by the dynamic viscoelastic method with ease and the following results were obtained.

The curing process of rigid polyurethane foam proceeded through three stages: the first stage in which the log $G''_{app}$ increased with increasing cure time ($G''_{app} \leq 10^3$ at 10 rad/s), the second stage in which the log $G''_{app}$ increased with increasing the logarithm of cure time ($10^3 < G''_{app} \leq 10^5$ Pa), and the final stage ($G''_{app} > 10^5$) in which the change of $G''_{app}$ could not be expressed simply.

The curing rate and the fluidity of rigid polyurethane foam in the curing, which were important factors in the processing of the polyurethane foam, were predicted by the rheological method. The curing rate and the temperature dependence of the curing were predicted by the change of the apparent rheological parameters during curing. The catalysts in this study increased the curing rate in the order of PMDETA, TMHDA, and DABCO, and the temperature dependence of the cure rate in the order of DABCO, TMHDA, and PMDETA.

The fluidity can be known from the peak time of $\tan \delta_{app}$. The catalyst in this study improved the fluidity in the order of DABCO, TMHDA, and PMDETA.

## References

1. H. P. Kato, *J. Cell. Plast.*, **5**, 25 (1969).
2. L. H. Hanusa and R. N. Hunt, *J. Cell Plast.*, **18**, 100 (1982).
3. S. D. Lipshitz and C. W. Macosco, *J. Appl. Polym. Sci.*, **21**, 2029 (1977).
4. E. Broyer, C. W. Macosco, F. E. Critchfield, and L. F. Lawler, *Polym. Eng. Sci.*, **18**, 382 (1978).

5. J. S. Osinski, *Polym. Eng. Sci.*, **23**, 756 (1983).

6. S. D. Lipshitz and C. W. Macosco, *Polym. Eng. Sci.*, **16**, 803 (1976).

7. E. B. Richiter and C. W. Macosco, *Polym. Eng. Sci.*, **20**, 921 (1980).

8. M. D. Hartley and H. L. Williams, *Polym. Eng. Sci.*, **21**, 135 (1981).

9. J. M. Castro, C. W. Macosco, and S. J. Perry, *Polym. Commun.*, **25**, 82 (1984).

10. A. Raszczuk, J. Kozakiewitz, and A. Orzechowski, *J. Appl. Polym. Sci.*, **31**, 135 (1986).

11. T. V. Davis and F. Ebersole, *J. Am. Chem. Soc.*, **56**, 885 (1934).

12. J. M. Baker and J. B. Holdsworth, *J. Chem. Soc.*, **713** (1947).

13. T. G. Fox and G. C. Berry, *Adv. Polym. Sci.*, **5**, 261 (1968).