

# Viscoelastic Properties of Elastic Polyurethaneureas in the Curing Process

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## Synopsis

Dynamic viscoelastic properties of a system, NCO-terminated polyurethane-aniline-cresol-formaldehyde liquid resin were studied during the curing process using an R-17 Weissenberg Rheogoniometer. For gel time determinations a new method was developed, the gel time being then defined as the cure time when the relaxation time  $\tau = 3$  s at a frequency of 0.1 Hz was achieved. The dynamic storage modulus  $G'$ , the dynamic viscosity  $\eta'$  and the relaxation time  $\tau$  have been determined as functions of curing time. The effects of cure temperature and of curing agent concentration on  $G'$ ,  $\eta'$ , and  $\tau$  were studied. The influence of cure temperature on the gel time and on the visco-elastic properties determined at 18 ks (5 h) of curing was discussed. Based on the experimental results, it was concluded that curing at higher temperature led to the more crosslinked polymer. Activation energy values for the gel time were also determined and compared with the values for polyurethanes and polyurethaneureas reported elsewhere. A relationship between the relaxation time and the effect of frequency on modulus  $G'$  was presented, and it appeared to be independent of cure temperature, curing agent concentration, and curing time, being then presumably a useful method for comparative studies of viscoelastic behavior of different materials in curing process. This relationship was compared with the approximate relationship between  $\tan \delta$  and  $d \ln G' / d \ln \omega$  given by Staverman and Schwarzl. The agreement at shorter relaxation times and some discrepancy at longer times were obtained.

## INTRODUCTION

Viscoelastic properties are very sensitive to the molecular changes proceeding in curing process, what makes them a useful tool for studies on curing mechanism. Information about these properties can also help the process engineer to develop optimum curing conditions.

The viscoelastic properties of different types of polyurethanes or polyurethaneureas in the curing process have been studied in some papers.<sup>1-4</sup> The inflexion of storage modulus curve versus curing time, damping or  $\tan \delta$  maximum<sup>1-3</sup> and also the sharp increase of storage modulus at the beginning of curing and lack of  $\tan \delta$  or loss modulus maximum<sup>3,4</sup> have been found.

The polyurethaneurea system examined in our study is different from the systems investigated in the above-mentioned papers. As crosslinking agent for NCO-terminated PU prepolymer we applied aniline-cresol-formaldehyde resin having then  $\text{NH}_2$  and OH groups in the same compound while in other papers curing of PU resins with  $\text{NH}_2$ - or OH-terminated agents has been investigated separately.

The purpose of our study was to examine the effect of curing temperature and curing agent concentration on the viscoelastic properties during curing process of such complex system.

## EXPERIMENTAL

### Materials

#### *Component A*

NCO-terminated PU prepolymer synthesized from polyoxypropylene diol of  $\overline{M}_w \approx 2000$  and toluene diisocyanate and containing ca. 50% carbon fillers (free NCO content < 1%).

#### *Component B*

Liquid aniline-cresol-formaldehyde resin of the amine number equal to 320 (40% solution in dibutyl phthalate).

### Viscoelastic Measurements

Dynamic mechanical measurements were performed on a model R-17 Weissenberg Rheogoniometer. The parallel serrated plates system, diameter 2.5 cm, was used. The distance between the plates and, at the same time, the sample thickness was 0.1 cm. Since the gap between the plates was very small, we assumed that any temperature variation during cure, due to the exothermic reaction, had only a negligible effect on the results of measurements.

The measurements were performed during the curing process, under isothermal conditions. Curing temperatures and curing agent concentrations, at which the measurements were performed are presented in Table I.

Three frequencies were used: 0.1, 1, and 10 Hz. For temperatures 274.0, 283.9, and 284.2 K, the amplitude of  $1.94 \times 10^{-3}$  rad and, for higher temperatures, the amplitude of  $4.85 \times 10^{-3}$  rad were used. It was proved that these amplitudes were in the linear range.

The weighed amount of the curing agent (component B) was added to filled polyurethane prepolymer (component A) and the mixture (0.1 kg) was stirred for 120 s. Then the sample was taken out and transferred to the preheated plates of the Weissenberg Rheogoniometer. Recording was started after few hundred seconds (at "zero" time the end of stirring was taken) and continued for 18.0–21.6 ks (5–6 h).

Dynamic viscosity,  $\eta'$  and dynamic storage modulus  $G'$  were calculated using the Walter's formulae.<sup>5</sup> The relaxation time  $\tau = \eta'/G'$  was also calculated.

TABLE I  
Cure Temperatures and Curing Agent Concentrations

Curing agent concentration (wt %)		Cure temperature (K)			
2.15			313.7	322.2	330.4
2.72		296.7	310.9		
3.28	284.2	292.2	312.3		
3.84	274.0	283.9	294.2	309.9	

### Gel Time Determination

The gel point was defined as the cure time when the relaxation time  $\tau = 3$  s at the frequency of 0.1 Hz was achieved. The relaxation time of 3 s was chosen on the basis of tests carried out using two different concentrations of curing agent: 2.72 and 3.28 wt %, at 296.7 and 292.2 K, respectively. A small portion of reacting mixture was observed simultaneously with the measurements performed on the Weissenberg Rheogoniometer. The thickness of the observed material was similar to the thickness of the sample in the apparatus (about 0.1 cm). The following cure times were noted at the point when the material was already elastic, but it could still flow: 4.8 ks for 2.72 wt % and 1.98 ks for 3.28 wt % of curing agent. At these cure times the relaxation time  $\tau$  values (at frequency 0.1 Hz) were 2.35 and 3.8 s, respectively, the mean value being about 3 s. It was found experimentally that the gel time, defined in such a way, is the upper limit of cure time at which the material can be still poured out. This particular method was especially developed in our laboratory since the relaxation time maximum and the inflexion of the modulus curve were not observed for the investigated system and therefore the gel time could not be determined by applying methods described in many other papers.<sup>1,6-20</sup>

### RESULTS AND DISCUSSION

Dynamic viscosity  $\eta'$ , dynamic storage modulus  $G'$ , and relaxation time  $\tau$  as functions of cure time were obtained. As examples, the plots obtained for 2.72 wt % of curing agent and for three different frequencies at 296.7 K are shown in Figures 1-3.

Increase of  $\eta'$  and  $G'$  and decrease of  $\tau$  during the curing process was found for all examined cure temperatures and curing agent concentrations. These changes are much faster in the first period of curing than in the second one.

#### The Viscoelastic Properties at 18 ks (5 h) of Curing

The experimental results (see Figs. 1-3) showed that after 18 ks (5 h) of curing the changes of viscoelastic properties became already slow.

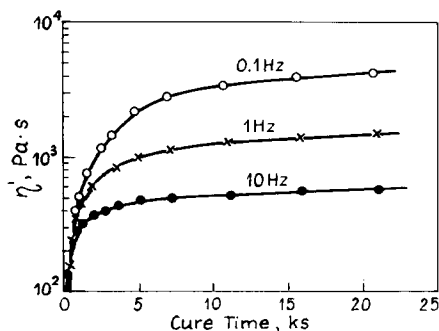


Fig. 1. Dynamic viscosity  $\eta'$  vs. cure time (2.72 wt % of curing agent, 296.7 K, frequencies: 0.1, 1, and 10 Hz).

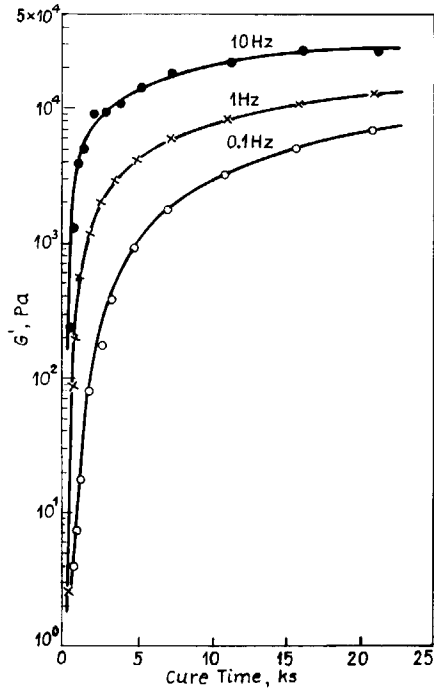


Fig. 2. Dynamic storage modulus  $G'$  vs. cure time (2.72 wt % of curing agent, 296.7 K, frequencies: 0.1, 1, and 10 Hz).

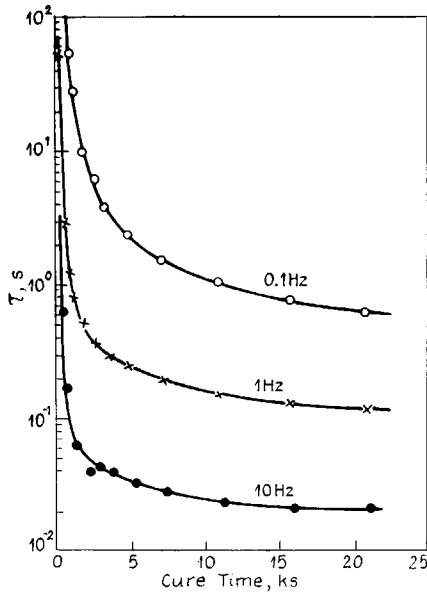


Fig. 3. Relaxation time  $\tau$  vs. cure time (2.72 wt % of curing agent, 296.7 K, frequencies: 0.1, 1, and 10 Hz).

The following values were determined at 18 ks (5 h) of curing:  $G'$ , termed  $G'_{5h}$ ,  $\tau$ , termed  $\tau_{5h}$ , and  $\log G'_{10Hz} - \log G'_{0.1Hz}$ , termed  $\Delta \log G'_{5h}$ . The modulus  $G'_{5h}$  increased and the relaxation time  $\tau_{5h}$  decreased with the increase in cure temperature (Figs. 4 and 5).

When  $G'_{5h}$  and  $\tau_{5h}$  values obtained for three different frequencies were compared, distinctly smaller temperature effect on  $G'_{5h}$  and  $\tau_{5h}$  was observed for higher frequencies. Since the effect of frequency on viscoelastic properties diminishes as crosslinking proceeds,<sup>21,22</sup> it can be assumed that the observed phenomenon resulted presumably from higher degree of crosslinking attained by the material cured over the same time (18 ks) at higher temperature. This phenomenon can be even more clearly seen in Figure 6, where  $\Delta \log G'_{5h}$  (as defined above) is plotted vs. cure temperature.

### Gel Time

The temperature dependence of gel time at various curing agent concentrations (Fig. 7) showed that the effect of temperature was greater when the gel times were longer.

The Arrhenius relationship was used to plot gel time against temperature. From the Arrhenius plot showed in Figure 8 the "apparent" activation energy was determined. "Apparent" means that it depends on several individual reactions. Table II presents the values of activation energy for the various curing agent concentrations. These values of activation energy are similar to those obtained for polyurethanes by Lewis and Pietsch<sup>1</sup> ( $5.44 \times 10^7 - 6.28 \times 10^7$  J/kmol), but they are higher than reported for polyurethaneureas by the same authors ( $2.51 \times 10^7 - 5.02 \times 10^7$  J/kmol) or by Mizoguchi et al.<sup>2</sup> ( $2.03 \times 10^7 - 3.15 \times 10^7$  J/kmol). This difference can be explained by specific nature of amine curing agent used in our investigations. Assuming that its molecular weight was much greater than that of monomeric diamines applied by Mizoguchi, higher values of activation energy could be expected.

The relationship between  $\Delta \log G'_{5h}$  and gel time (obtained for samples containing various curing agent concentrations, for two different temperatures) (Fig. 9) showed that curing at higher temperature resulted in more crosslinked polymer at 18 ks curing time (lower  $\Delta \log G'_{5h}$  value), even if the materials cured at the same rate (defined by gel time) were compared.

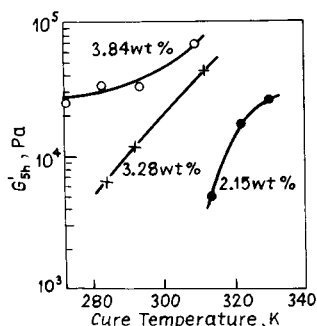


Fig. 4. Effect of cure temperature on storage modulus  $G'$  [frequency = 0.1 Hz, curing time = 18 ks (5 h), curing agent concentrations: 2.15, 3.28, and 3.84 wt %].

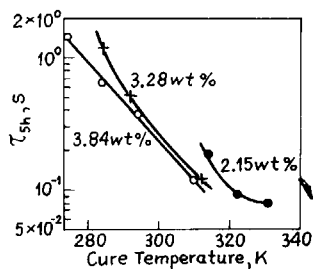


Fig. 5. Effect of cure temperature on relaxation time  $\tau$  [frequency = 0.1 Hz, curing time = 18 ks (5 h), curing agent concentrations: 2.15, 3.28, and 3.84 wt %].

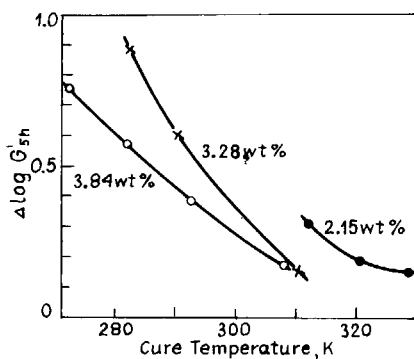


Fig. 6. Effect of cure temperature on  $\Delta \log G'_{5h}$  (2.15, 3.28, and 3.84 wt % of curing agent).

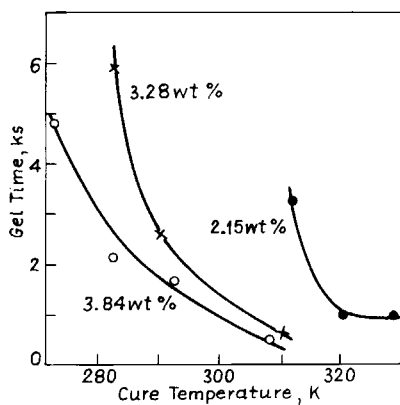


Fig. 7. Effect of cure temperature on gel time (2.15, 3.28, and 3.84 wt % of curing agent).

TABLE II  
Activation Energy Calculated for Gel Time

Curing agent concentration, (wt %)	Activation energy (J/kmol)
2.15	$8.70 \times 10^7$
2.72	$6.38 \times 10^7$
3.28	$6.17 \times 10^7$
3.84	$4.45 \times 10^7$

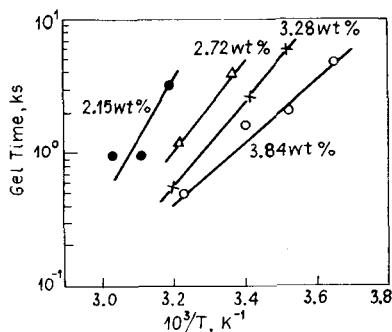


Fig. 8. The Arrhenius plot for gel time (2.15, 2.72, 3.28, and 3.84 wt % of curing agent).

This is further proof for the conclusion presented earlier in this paper based on the analysis of Figures 4–6. These results agree also with data reported in other papers where the formation of more crosslinked polymer at higher cure temperature has been suggested.<sup>23,24</sup>

#### Relationship between Relaxation Time ( $\tau$ ) and the Frequency Dependence of Storage Modulus ( $\Delta \log G'$ )

Figures 5 and 6 show that cure temperature dependences of  $\tau_{5h}$  and  $\Delta \log G'_{5h}$  are similar. Based on all  $\Delta \log G'_{5h}$  and  $\tau_{5h}$  data supplemented with our other experimental data obtained for various curing times, using three different curing agent concentrations and three different temperatures,  $\Delta \log G'$  was plotted vs.  $\tau$  (see Fig. 10), and it was found that such a relationship was independent on curing temperature, curing agent concentration, and curing time and was affected only by the frequency at which  $\tau$  values were determined.

Such an "independent"  $\Delta \log G' - \tau$  plot can presumably be useful for comparative studies of viscoelastic behavior of different materials in curing process. This  $\Delta \log G'$  on  $\tau$  dependence was compared with the approximate relationship between  $\tan \delta$  and  $d \ln G' / d \ln \omega$ , given by Staverman and

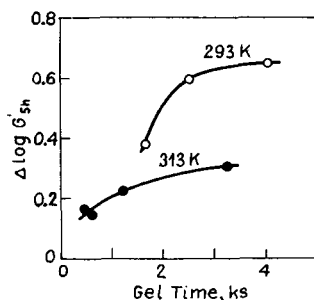


Fig. 9. Relationship between  $\Delta \log G'_{5h}$  and gel time. Approximate values of curing temperature (293 and 313 K) are given. For real values corresponding for each experimental point, see Table I and Figure 7.

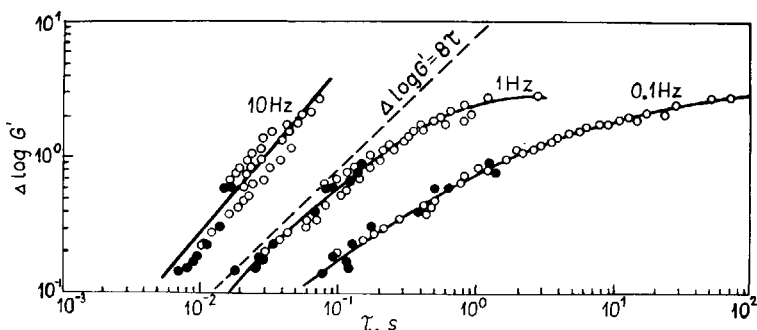


Fig. 10. Relationship between  $\Delta \log G'$  and relaxation time  $\tau$  (frequencies: 0.1, 1, and 10 Hz): (●) values obtained at 18 ks (5 h) of curing; (○) values obtained at other curing times.

Schwarzl<sup>25</sup>:

$$\tan \delta \approx \frac{\pi}{2} \frac{d \ln G'}{d \ln \omega} \quad (1)$$

where  $\omega$  = angular frequency (rad/s). This relationship gives

$$\Delta \log G' \approx 8\tau \quad (2)$$

for the frequency of 1 Hz, since

$$\tan \delta = \tau \cdot \omega \quad (3)$$

The  $\Delta \log G'$  on  $\tau$  dependence for the frequency of 1 Hz (in the middle of the range: 0.1–10 Hz) was compared in Figure 10 with the line  $\Delta \log G' = 8\tau$ . The course of the experimental curve is similar to this line at shorter relaxation times, the difference between them increasing with the increase of  $\tau$ .

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