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ULTRASONIC PROPERTIES IN BISPHENOL A-BASED THERMOSETS CURED WITH MNA AND ALIPHATIC DIAMINE

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Résumé.—L'influence des différents types de liaisons des époxydes de bisphénol A ont été étudiées sur leurs propriétés ultrasoniques. Ces liaisons engendrent une β relaxation et une diminution de l'élasticité des résines à l'état congelées.

Abstract.— In the bisphenol A-based epoxides, effects of crosslinking on the ultrasonic properties were studied. Crosslinking gives rise to the β relaxation and the decrease of elasticity and density in the glassy state resins.

1. INTRODUCTION

In spite of the outstanding characteristics and usefulness of epoxides in the glassy state, most studies have employed investigations of the rubbery state, owing to the ease of obtaining low frequency dynamic and thermal measurements(ref./1/2/). This is because such measurements are not appropriate for sensitive analysis of the high elasticity in the glassy state, in which network structures are frozen. There is, however, a strong necessity for non-destructive testing in thermosets and thermo-plastics, requiring the detailed analysis of the elasticity in the glassy state(ref./3/). In addition, some recent studies have discussed the contribution of sub relaxations, in the glassy state to the impact strength(ref./4/). So in this work, we have studied the effect of polymerization and crosslinking in glassy state resins, on the elasticity, with especial consideration to the results from the ultrasonic measurements in the MHz range.

2. MATERIALS AND TECHNIQUES

The networks in resin were formed by the condensation of the diglycidyl ether of bisphenol A-based epoxy resin (Epon 828, Shell Chemical Co.) with curing agents. The agents used in this study were Diaminobutane(BDA) and methyl nadic anhydride(MNA) catalyzed with imidazole.

The procedure for preparing the samples is given below. For the first preparation of resins, the amount of BDA used was 50–100%, where the stoichiometric amount of BDA to Epon 828 at 100% reflects a ratio of 1:1. The mixture was held in vacuum for degassing to eliminate void formation and cured overnight at 0–5°C. It was, then, held for 1hr at 60°C, 3hr at 100°C and 3hr at 150°C. For MNA, 88–100% of the stoichiometric amount was used with a little imidazole. The mixture was heated for 1hr at 100°C, 5hr at the range of 100 to 200°C. All samples were gradually cooled to room temperature.

A pulse technique was used for measuring ultrasonic properties. In this technique, the specimen and two transducers are immersed in water or silicone oil, which are controlled from 10 to 100°C to an accuracy of 0.5°C. Ultrasonic pulses are sent from one PZT transducer to the other and the longitudinal wave velocities could be found using the observed difference in time of flight with and without the sample. For longitudinal attenuation, wide band transducers whose nominal frequencies were 10MHz were also used in addition to the PZT transducers. The pulses received by the wide band transducers were digitized and analyzed in the frequency region using Fast Fourier Transform

with a personal computer. The averaged resulting spectra from specimens of different thickness yielded the attenuation as a function of frequency. Thermal expansion in specimen thickness was of course considered in these measurements and calculations.

The dynamic storage modulus and loss modulus were measured at low frequencies over the temperature range of -150 to 250°C by a dynamic viscoelastometer (VIBRON) built by ORIENTEC. The dielectric permittivity and linear thermal coefficient of resins were also measured respectively using an impedance gain phase analyzer, built by HP and a thermo-mechanical analysis system (TMA) built by RIGAKU.

3. RESULTS AND DISCUSSION

Figure 1 shows the typical plots of the dynamic storage modulus E' and loss modulus E'' against temperature measured at 110Hz . In general, E' decreases dramatically at the glass transition which reflects the changes of the state from glassy to rubbery. E'' also shows two peaks α, β which respectively results from main α and sub β relaxations.

Fig.1 Dynamic storage modulus E' and loss modulus E'' of resins measured at 110 Hz .

Table 1 T_{α} of cured resins at 110 Hz .

A) Resins cured with MNA.

B) Resins cured with BDA.

		Curing Temperature ($^{\circ}\text{C}$)						Curing Agent	T_{α} ($^{\circ}\text{C}$)
		100	120	140	160	180	200		
Curing	88%	122	150	170	182	175	173	50%	127
Agent	94%	124	150	169	180	183	184	60%	130
	100%	123	149	170	184	196	198	75%	133
								100%	138

As shown in Table 1, high curing temperature and stoichiometric amount of curing agents cause a rise in the α peak at 110Hz (T_{α}). This reflects the advance of crosslinking and the improvement of high temperature stability. In MNA cured resins, the temperatures of α peak at 110 Hz were almost always higher than those in BDA cured resins. These differences, caused by bonding conditions between resin and curing agents, also result in the strength of the low temperature loss peak β . For the β peak, the loss moduli E'' varies slowly over a wide temperature range with respect to the distribution of relaxation times in the glassy states. This peak has been reported to result from a particular mode of motion in side groups, owing to crosslinking (ref./5/). The key results here are the difference in the strength of β peak between BDA and MNA cured resins. As can be seen in

Figure 1, the β peak in BDA cured resins are much stronger than that in MNA cured resins, which indicates that different chemical reactions occur as curing proceeds. Contrasting the W.L.F. type main relaxation α , the β relaxation is referred to the Arrhenius type as thermo-plastics (ref./5//6/). Figure 2 shows the frequency temperature dependence of the β peak in BDA cured resins. The β peak changes linearly owing to the Arrhenius expression, which predicts the peak temperature in the MHz range, 70–80°C. Additional insight in BDA cured resins is provided by Figure 3 showing the values of longitudinal attenuation at 2MHz as a function of temperature. All the resins are in the glassy state over the observed temperature range. The attenuation in resins changes broadly and the peak temperatures are in good accordance with those predicted in Figure 2.

Fig.2 Temperature-Frequency correlation map of β relaxation.

Fig.4 Dependence of longitudinal attenuation on T_α .

Fig.5 Dependence of longitudinal velocity on T_α .

Fig.6 Dependence of room temperature density on T_α . (at 23°C)

Figure 3 also shows the increase of attenuation due to the amount of curing agents. This reflects that the β relaxation depends on the crosslinking process.

In the MNA cured resins, however, the β peak couldn't be found in the observed frequency and temperature range. The longitudinal attenuations at 23°C are presented graphically in Figure 4. The attenuation increased in those resins with high T_{α} , i.e. those which are cured at high temperature and with nearly stoichiometric amount of curing agents. Figure 5 also shows the longitudinal wave velocity at 2 MHz, on T_{α} . The wave velocities decreased as T_{α} increase. As mentioned above, T_{α} directly reflects the heat resistance ability and shows the development of curing and crosslinking within the resin. From these results, it is predictable that the elasticity in the glassy state resins decreases as the curing and crosslinking proceeds, which also implies an effect of crosslinking on the elasticity of glassy state resins. Of course, this effect seems to have no connection with β relaxation. These results, however, are quite opposite to the effect of crosslinking on the rubbery state resins, wherein the elasticity in the rubbery states resins have been reported to be proportional to the amount of crosslinks(ref./2/).

Table 2 Linear thermal coefficients of resins at $T_{\alpha}+10^{\circ}\text{C}$.
(Resins cured with MNA of 100%)

	Curing Temperature					
	100 °C	120 °C	140 °C	160 °C	180 °C	200 °C
Coefficients ($10^{-4}/\text{K}$)	1.90	1.79	1.76	1.74	1.71	1.69

Finally, room temperature measurements of resin density, plotted against T_{α} , are provided in Figure 6. In the first mixture of these resins, the ratio of Epon 828 and MNA were the same. The room temperature density of cured resins is, however, strongly dependent on T_{α} . In addition, Table 2 lists the linear thermal coefficients of resins measured at $T_{\alpha}+10^{\circ}\text{C}$. The coefficients vary inversely to the variation of curing temperature and the T_{α} of the resins. These results therefore show the hindering effect of crosslinking in the shrinkage process of resins from the rubbery state to the glassy state. This effect of crosslinking can also be connected to the changes of elasticity during the glass transition process.

4. CONCLUSION

In the bisphenol A-based epoxy resins, both the amount of curing agent and the curing temperature control the process of crosslinking, which can be shown as the increase of the temperature of the main α relaxation. The advancement of crosslinking affects the strength of the β relaxation in BDA cured resins. This relaxation also can be observed separated from the main relaxation in the MHz range. In addition, crosslinking seem to affect the shrinkage process of MNA cured resins, from the rubbery state to the glassy state. This is shown by the changes of the longitudinal wave velocity and attenuation in the glassy state resins.

REFERENCES

- /1/ T.Murayama, J.P.Bell, J.Polym.Sci. A2,3,p.437(1970)
- /2/ A.V.Tobolsky, J.Polym.Sci. C,9,p.157(1965)
- /3/ L.Piche, F.Massines, G.Iessard and A.Hamel, Proc.1987 Ultrasonics Symp.,IEEE cat#87CH24927, p.1125
- /4/ M.Ochi, S.Zhu and M.Shimbo, Polymer 27,p.1569(1986)
- /5/ M.B.M.Mangion and G.P.Johari, J.Polym.Sci. B,29,p.437(1991)
- /6/ G.E.Roberts and E.F.T.White,"Relaxation processes in amorphous polymers" in physics of glassy polymers,edited by R.N.Haward,(Applied science publishers, London,1973)