Longitudinal structural relaxation of a glass-forming epoxy oligomer

Mami Matsukawa, Hiroshi Yamura, Takahiko Otani* and Norikazu Ohtori**

* Department of Electronics, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan
**Graduate school of Sci. and Tech., Niigata University, Ikarashi ni-nocho, Niigata 940-2102, Japan

Abstract: The glass transition process of an epoxy oligomer (diglycidyl ether of bisphenol A) has been characterized by Brillouin scattering and ultrasonic pulse spectroscopy. Longitudinal wave velocities showed a large frequency dispersion at temperatures higher than Tg. Wave attenuation showed a peak of the main (α) relaxation. At the glass transition temperature (Tg), the velocity profiles showed a clear kink. The velocities still showed a clear frequency dispersion at temperatures lower than Tg. Concerning these results, the effect of other sub-relaxation is indicated.

INTRODUCTION

The curing process in thermosets is considered as an irreversible glass transition, in which the viscous polymer liquid changes into a brittle non-crystalline solid. In a series of papers, we have investigated the curing process of a common epoxy adhesive resins using a simple ultrasonic spectroscopy, and succeeded in the real-time monitoring of the process as changes of the ultrasonic wave velocity and attenuation. The glass transition during epoxy curing is formed by the polymerization, actually by the crosslinking between linear prepolymer. The linear prepolymer is usually an oligomer with a small distribution in molecular weight. It is viscous liquid at high temperatures. It however changes into a brittle solid at low temperatures, following the reversible glass transition process. In this study we have investigated the glass transition process of an epoxy linear prepolymer using the ultrasonic pulse spectroscopy and Brillouin scattering, focusing the structural relaxation observed during the transition.

CHANGES IN VELOCITY AND ATTENUATION DURING GLASS TRANSITION

The epoxy prepolymer used was a common DGEBA oligomer (diglycidyl ether of bisphenol A, Epon 828) supplied by Shell petroleum. Tg of the prepolymer was 248K from the Differential Scanning Calorimetry (DSC). During Brillouin and ultrasonic measurements, the temperature of the sample was controlled from 220K to 420K. Brillouin scattering measurement was used to obtain the hypersonic wave velocity and attenuation in the GHz range (3-8GHz), whereas the ultrasonic pulse spectroscopy was used for the measurements in the MHz range (2.25MHz).

FIGURE 1. The temperature dependences of (a) the velocity and (b) attenuation measured by Brillouin scattering and ultrasonic spectroscopy. Vo is the limiting low frequency velocity whereas V∞ is the limiting high frequency velocity.

1945
As can be seen in Fig.1, the longitudinal wave velocities increased with the decrease of temperature, showing the glass transition behavior. The velocity difference reached a maximum near room temperature and finally disappeared at about 420K. At Tg, both velocity profiles indicated a clear kink. On the other hand, the attenuations showed a peak in this transition region. The peak temperature became much higher in the data obtained from Brillouin scattering. From our former ultrasonic investigation of cured or polymerizing epoxy resins, the attenuation peak and velocity dispersion can be connected to the main relaxation in the glass transition region. This relaxation can be observed at higher temperatures at higher frequencies. This is in good accordance with the present attenuation data, if both peaks result from the identical main relaxation.

Assuming that the main relaxation in this prepolymer is a single relaxation, the limiting low frequency velocity Vo, the limiting high frequency velocity Vo and the relaxation frequency were calculated. Both velocities are shown in Fig.1. The temperature dependence of the relaxation frequency in Fig.2 (a) obeyed the linear behavior. This behavior of relaxation frequency is different from that of the main relaxation because the main relaxation frequency usually shows a non-linear change and an asymptotic relation to a fixed temperature at low frequencies. This frequency-temperature behavior of the main relaxation is expressed by a Vogel-Fulcher-Tammann (V.F.T.) equation. As can be seen in Fig.2 (a), the observed attenuation peaks followed this V.F.T. curve. This result implies that the relaxation could not be treated as a simple single relaxation.

The effect of other sub-relaxation should then be considered. In Fig.1, the observed velocity showed a clear dispersion at temperatures lower than Tg, where the effect of main relaxation could not be expected. The broad peak of the attenuation from Brillouin data also implies an overlap of relaxations in this frequency range. The Cole-Cole plots of the longitudinal moduli are illustrated in Fig.2(b). The plot from Brillouin data was more arc-skewed and indicated larger distribution of relaxation times. One can suppose that in the GHz range the main relaxation overlaps with other sub-relaxation, which is situated at much lower temperatures in the MHz range.

CONCLUSION

The glass transition process of an epoxy prepolymer was studied using two different techniques. From the investigation of the relaxation frequency, it seemed that at hypersonic frequencies the main relaxation overlaps with other sub relaxation in the glass transition region.

REFERENCES