

Dielectric Relaxation of Siloxane-Epoxy Copolymers

Chy Hyung Kim* and Jae Sup Shin†

Department of Chemistry, Chongju University, Chongju 360-764, Korea

†Department of Chemistry, Chungbuk National University, Chongju 361-763, Korea

Received May 28, 2001

The dielectric responses of 10 and 40 wt% siloxane-epoxy copolymers were investigated in temperature range near the glass transition of polydimethylsiloxane at which the dielectric transitions were also observed. On the other hand, the pure epoxy did not show any dielectric transition in measurement temperature range -90 to 150 °C. The experimental data showed that for the copolymer investigated, the temperature-frequency superposition principle could be applied to the dielectric response. From the Cole-Cole equation, the dielectric relaxation of the 10 wt% siloxane near the glass transition temperature resulted in a broad distribution with $\beta = 0.19$ and the relaxation time at -70 °C was 5.3×10^{-2} s. The glass transition temperature, 188 K, was estimated by using WLF relation, which was consistent with the data presented in experiment.

Keywords : Dielectric relaxation, Temperature-frequency superposition, Shifting factor, Cole-Cole, WLF relation.

Introduction

As one of the functional materials, epoxy polymers have been used extensively as adhesives and matrix resins for fiber reinforced composite materials because they have favourable properties such as high modulus, low creep, and reasonable performance at elevated temperature.¹⁻² However, such characteristics in an epoxy require high levels of crosslinking which usually results in brittle behaviour. It is well known that some brittle epoxy polymers can be toughened by the addition of a rubbery phase.³⁻⁸ For example, epoxy has been used as an encapsulation of the semiconductor chip. As the capacitance of the chip increases, the heat dissipation also increases and the crack of the epoxy is produced. Siloxane epoxy resin which has soft and hydrophobic properties can protect the crack. In addition, its mechanical flexibility and dielectric property can draw attention for the application of electromechanical polymer.

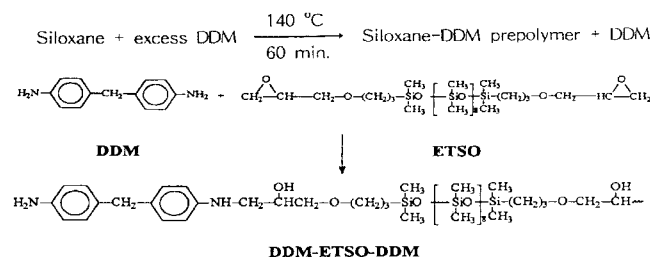
In this experiment copolymers of epoxy with siloxane were prepared by the reaction of diglycidyl ether bisphenol A with dimethylsiloxane prepolymer. And the dielectric properties of epoxy and its polydimethylsiloxane copolymers were studied. That is, the dielectric responses and relaxation mechanisms of the film-shaped epoxy, 10 and 40 weight% of two silicone copolymers were studied at several temperatures and frequencies. The dielectric study at low frequency range is particularly interesting because of the nature of polymer system which has long chain and high molecular weight. It is well known that most of the properties such as dielectric constant and elastic compliance in polymeric materials are dispersive even at low frequencies, reflecting relatively high activation energies for the motion of molecule unit and chain segments.⁹ The dispersion can be either non-cooperative or cooperative depending on the degree of correlation with other relaxations. We investigate the subglass transition temperature and the relaxation process by analyzing the dielectric

relaxation time with temperature to understand the possible dispersion mechanism. In addition, from the analysis of the epoxy and copolymer, we can get the idea about the nature or general features of dielectric responses in polymeric materials of this system.

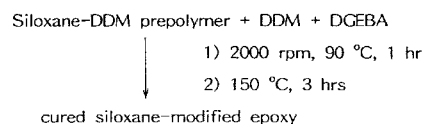
Experimental Section

Materials and Synthesis. The material used in our investigation consists of YD-128 which is a liquid diglycidyl ether of bisphenol-A (DGEBA) produced by Kukdo Chemical (epoxy equivalent : 185-190 g/mol, density : 1.16 g/cm³). Epoxy-terminated siloxane oligomer (ETSO) is TSL-9986 produced by Toshiba Silicon (epoxy equivalent : 447 g/mol, density : 0.99 g/cm³, MW : 950). The curing agent is an aromatic diamine, diamino diphenyl methane (DDM). The chemical structures of epoxy resin, ETSO, curing agents, and the synthetic procedure of epoxy-siloxane

1. Synthesis of siloxane-DDM prepolymer



2. Curing of siloxane-modified epoxy



Scheme 1

copolymer is illustrated in Scheme 1.

ETSO and excess DDM were placed and stirred in a 250 ml Erlenmeyer flask in an oil bath at 90 °C. The siloxane-DDM prepolymer was synthesized by heating the mixture under N₂ atmosphere at 140 °C for 1 hr. Siloxane-DDM prepolymer and DGEBA with DDM were placed and stirred at the rate of 2000 rpm at 90 °C for 5 min. The bubbles in the mixture were removed under vacuum for 30 min. The cured siloxane-modified epoxy was prepared by pouring the mixture to the mould which was preheated. The temperature of the mould was kept at 90 °C for 1 hr and then 150 °C for 3 hrs.

Dielectric property. The film-shaped epoxy polymer (0 wt%) and epoxy-siloxane copolymer (10 and 40 wt%) samples with a thickness ranging from 0.9 to 1.8 mm were used for dielectric measurements. As has been shown in an earlier investigation,¹⁰ the observed response for the sample of such thickness can be regarded as a bulk material with a uniform electric field distribution across the sample, approximately. Gold was vacuum deposited on both sides of the sample as the electrode. The dielectric properties were measured by a set-up of temperature controller (Lakeshore321) and a lock-in amplifier (SR850) which measures both the phase for loss tangent ($\tan \delta$), amplitude of the voltage, and current applied to the specimen, yielding the capacitance and the impedance of the sample over the temperature range -90 to 150 °C. Liquid nitrogen was used to keep the low temperature. The frequency was varied from 0.1 Hz to 3 kHz at each fixed temperature. The dielectric constant was estimated from the capacitance data using the equation,

$$k = Cd/(k_0A),$$

where k_0 is the permittivity of free space, 8.854×10^{-12} F/m, C is capacitance, d is thickness of the sample, and A is the area of gold plate.

Results and Discussion

The results in Figure 1(a) and (b) reveal that there are dielectric transitions at about -90 to -80 °C for 10 wt% and -80 to -50 °C for 40 wt% siloxane copolymers. The transition temperatures reflect the known glass transition temperature of polydimethylsiloxane.¹¹ On the other hand, the dielectric constant of pure epoxy increases continuously without any sudden change as temperature increases, indicating that there is only same type of thermal motion without any phase transition in measurement temperature range. The glass transition temperature of epoxy polymer is known as 170-180 °C. The dielectric property of the pure epoxy is higher than that of the other copolymers where the polysiloxane works as a soft segment and epoxy works as a hard one. The flexibility of the copolymer increases as temperature increases and thus the polarization induced by segment motion in copolymer appears more effectively at low frequency and high temperature range as can be seen in Figure 1(a). However, in Figure 1(b) the polarization and dissipation of soft segment are confined due to the slow response of

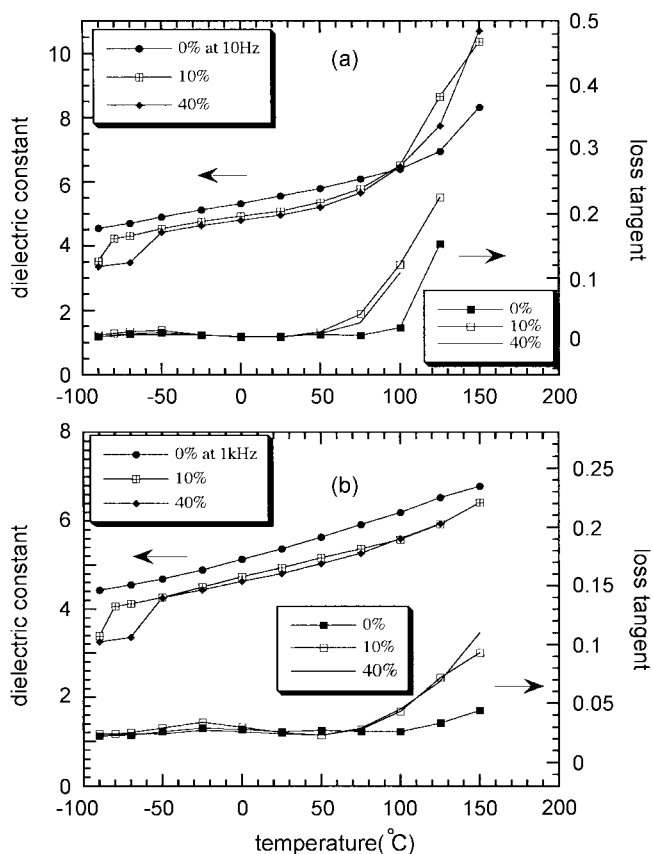


Figure 1. Dielectric constants and loss tangent of 0, 10, and 40 wt% siloxane-epoxy at (a) 10 Hz and (b) 1 kHz as a function of temperature.

molecular motion at 1 kHz, where some heavy polarizable motions are excluded. 10 and 40 wt% copolymers show almost the same dielectric property except a little difference in transition temperature.

The dielectric dispersion behavior of the 10 wt% siloxane-epoxy copolymer is characterized at several temperatures over the frequency range from 0.1 Hz to 3 kHz as presented in Figure 2(a) and (b). The relaxation of 10 wt% copolymer begins to appear at above -90 °C, which is different from the case of epoxy that has no abrupt dielectric gap with temperature increment. In the range of temperature from -80 to -50 °C, the relaxation process of 10 wt% copolymer can be observed easily from the dielectric loss tangent curve in Figure 2(b), which occurs as the peak when the change of the dielectric constant is large. The relaxation distribution is broad due to the large variation in the local environment and the length of chain segments involved in the motion. The dielectric behavior for the polymeric material can be described by Cole-Cole expression:⁹

$$k^* = k' - ik'' = k_\infty + \Delta k / \{1 + (i\omega t)^\beta\}$$

where k' and k'' are the real (relative dielectric constant) and imaginary part (relative dielectric absorption) of complex k^* , k_∞ is the relative dielectric constant at very high frequency, Δk is $k_0 - k_\infty$ where k_0 is the static relative dielectric constant, t is the effective relaxation time, β is the parameter in range

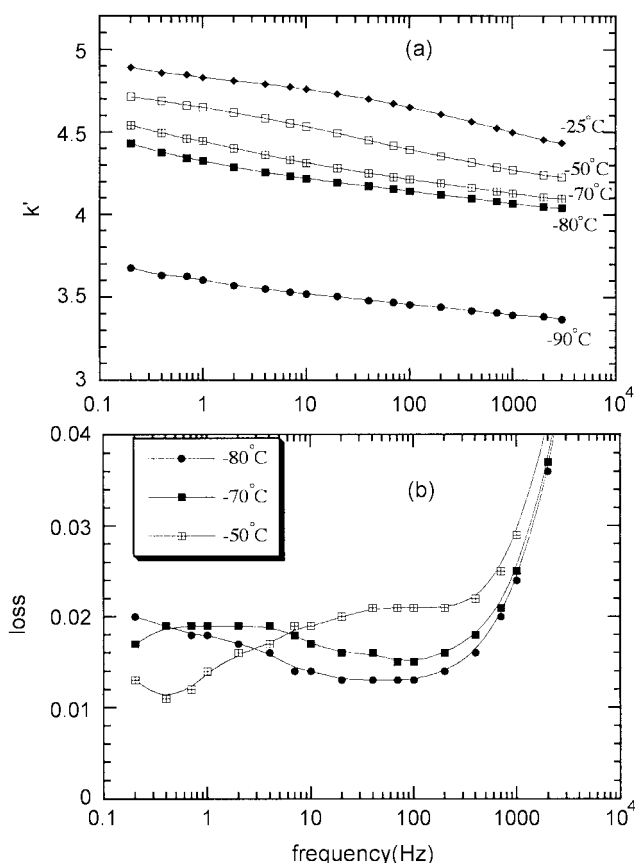


Figure 2. (a) Dielectric constant of 10 wt% siloxane-epoxy copolymer as a function of frequency at temperatures (from top to bottom): -25°C , -50°C , -70°C , -80°C , and -90°C . (b) Loss of same copolymer which shows clearly the relaxation processes.

$0 < \beta \leq 1$ to describe the distribution of relaxation time, and ω is the angular frequency. When $\beta = 1$, the equation gives semicircle in the plot of k'' vs. k' and is reduced to the non-cooperative single relaxation following the linear Arrhenius relation.¹² Based on the expression, the relaxation frequency of the dielectric absorption maximum, f_{max} , is expressed as

$$2\pi f_{\text{max}} t = 1$$

where the dispersion and absorption curves are symmetrical about the position $\omega t = 1$. Thus the f_{max} obtained experimentally can be used to determine relaxation time, t . From the Figure 2(b) it can be found that the dielectric relaxation shifts to higher frequency as temperature increases. Using the temperature-frequency superposition principal,¹³ one can construct the dielectric curves at several temperatures for the one curve at -70°C as illustrated in Figure 3(a) by shifting the frequency with a factor $a(t)$ which is the ratio of relaxation time (t_r) at a certain temperature to the relaxation time (t_r) at the reference temperature as

$$a(t) = t_r/t_r$$

In this case, we assume -70°C as the reference temperature. The shifting factors at other temperatures are represented in Figure 3(a). For the data in Figure 3(b), the fitting yields

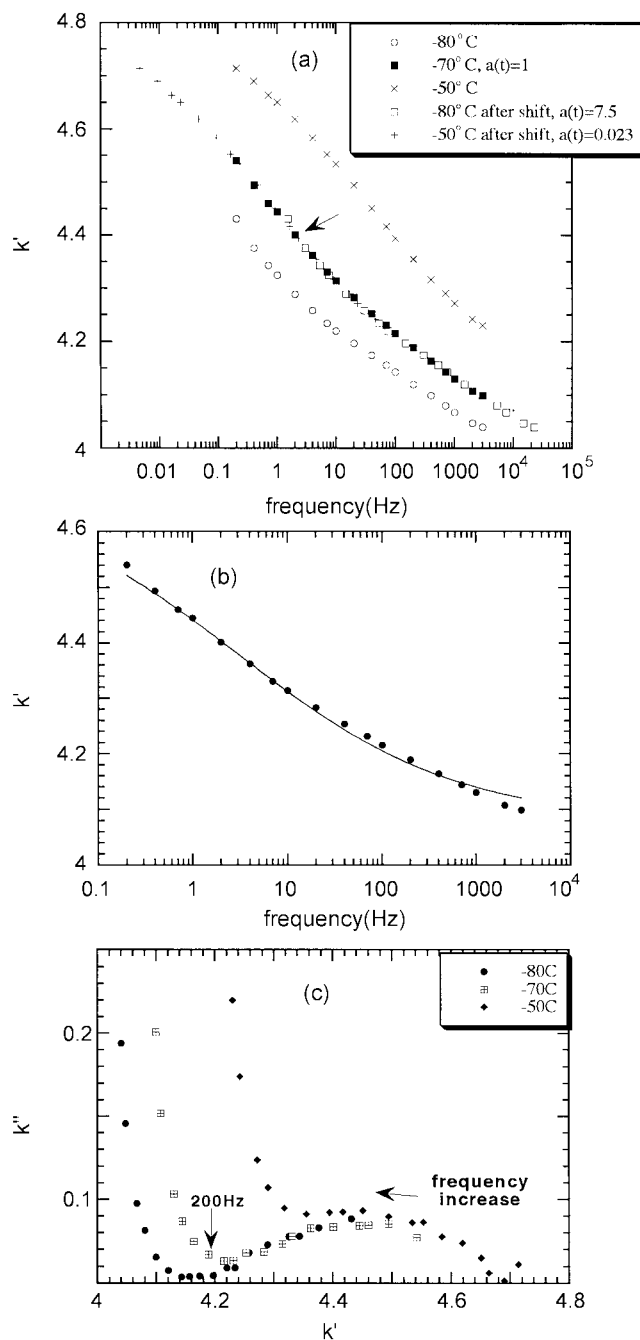


Figure 3. (a) Dielectric constant as a function of frequency at -50°C , -70°C , and -80°C (from top to bottom) with the same curves shifted to that at -70°C . The arrow indicates a relaxation point at -70°C . (b) The master curve for the dielectric constant at -70°C . (c) The Cole-Cole plots at -50°C , -70°C , and -80°C .

$\beta = 0.19$ indicating the existence of a broad distribution of the relaxation in the material and the relaxation time at -70°C is 5.3×10^{-2} s. The solid line in the Figure 3(b) is from the fitting and solid circles are the experimental data. The Cole-Cole plots of Figure 3(a) are shown in Figure 3(c). As the temperature increases from -80 to -50°C , the plot shifts to the right confirming again the phase transition of soft segment in this temperature range.

In addition, It was found that the shifting factor of the 10

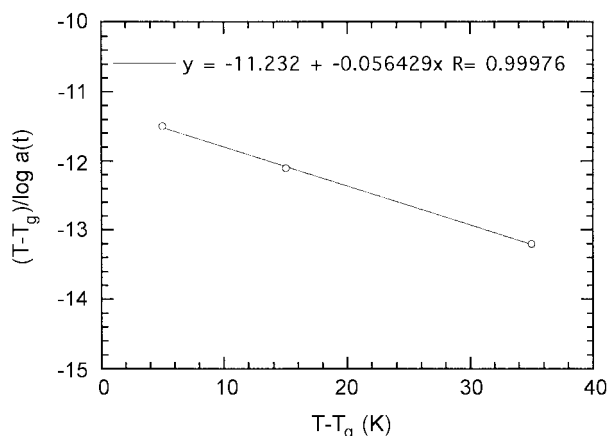


Figure 4. Temperature dependence of the relaxation process: WLF plot in 10 wt% siloxane-epoxy copolymer.

wt% copolymer follows the WLF (Williams-Landel-Ferry) relation⁹ at glass-rubber transition. A straight line in the plot $(T - T_g)/\{\log a(t)\}$ vs. $(T - T_g)$ where $a(t)$ equals to t/t_g can be observed in Figure 4. That is,

$$\log a(t) = -c_1(T - T_g)/(c_2 + T - T_g)$$

with $c_1 = 17.7$, $c_2 = 199.1$ K, and $T_g = 188$ K. The estimated glass transition temperature at 188 K ($= -85$ °C) is consistent with the experimental data (-90 to -80 °C) presented in Figure 1. It has been known that the parameters c_1 and c_2 have universal constants of 17.44 and 51.6, respectively, for amorphous polymers.⁹ The value of c_1 for the relaxation process of 10 wt% siloxane copolymer is in good agreement

with the known universal constant, which is relate to the attempt frequency of the motion of polar elements. However, c_2 value in this process is much higher than that of known one because the relaxation process is influenced by several factors such as presence of hard segment-epoxy domain, heating rate of the sample in measurement, and moisture⁹ although these variations do not seriously undermine the above relationship.

References

1. Kim, H.; Char, K. *Bull. Korean Chem. Soc.* **1999**, *20*, 1329.
2. Chae, K. H.; Song, H. B.; Sun, H. Y.; Chang, J. Y. *Bull. Korean Chem. Soc.* **2000**, *21*, 690
3. Bucknall, C. B.; Gilbert, A. H. *Polymer J.* **1989**, *30*, 213.
4. Nakamura, Y.; Tabata, H.; Suzuki, H.; Iko, K. *J. Appl. Polym. Sci.* **1986**, *32*, 4865.
5. Manzione, L. T.; Gillham, J. K. *J. Appl. Polym. Sci.* **1981**, *26*, 907.
6. Lin, S. T.; Huang, S. K. *J. Polym. Sci., Polym. Chem.* **1988**, *34*, 1907.
7. Hedrick, J. L.; Hofer, D. C.; Russell, T. P.; Haidar, B. *Polymer Bulletin* **1988**, *19*, 573.
8. Koh, J. S.; Kang, D. W. *Korea Polym. J.* **1996**, *4*, 39.
9. McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solid*; Dover: New York, 1967; p 102, p 116, p 129, p 130, p 171.
10. Wang, H. *Ph. D. Thesis*; The Pennsylvania State University: 1994.
11. Brandrup, J.; Immergut, E. H. *Polymer Handbook*; John Wiley & Sons: 1989; p VI/241.
12. Blythe, A. R. *Electric Properties of Polymers*; Cambridge University Press: 1977; p 46.
13. Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980; p 264.