

Study of siloxane-modified epoxy resin using thermally stimulated current

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Summary

The low temperature relaxation of epoxy resin modified with siloxane oligomers was investigated by using thermally stimulated current (TSC) and relaxation map analysis (RMA). The β -relaxation of epoxy resin and the glass transition temperature of siloxane oligomer were folded and shifted to higher temperature as the concentration of trifluoropropyl (TFP) in siloxane oligomer increased. In the systems containing over 50% of TFP a new relaxation peak due to the dipole orientation was observed at around -45°C . As the concentration of TFP increased the compensation temperature (T_c) and the degree-of-disorder (DOD) were increased while the compensation time, τ_c was decreased.

Introduction

The addition of siloxane oligomer into epoxy resins has been available for the relaxation of internal stress in epoxy molding compound (EMC) used for the encapsulation of semiconductor (1-5). The addition of these siloxane oligomers which have basically high thermal stability, oxidation stability and low T_g increases the durability, low temperature stability, and impact properties of the high strength resins such as epoxy and polyimide resins (5).

The low temperature relaxation of cured epoxy resins has been studied by many workers (6-8) with dynamic mechanical analyzer (DMA) and dielectric technique as an important factor indicating the material characteristics such as the impact strength at ambient and the physical properties at subambient atmosphere. Recently the thermally stimulated current (TSC) which has high sensitivity even at low frequency (10^{-2} – 10^{-4} Hz) has been used for the study of low temperature relaxation of epoxy resins (9-14).

In this study the modification method of epoxy resins with siloxane oligomer and the changes in low temperature relaxation, as a function of the type of siloxane oligomer, have been studied by using TSC and RMA. The TSC study of Bucci (15) was based on the single Debye relaxation theory. According to the theory the sample polarizing at the temperature, T , has a value of polarization, P_0 , after infinite time and the value of polarization without field can be written in a following equation;

$$P(t) = P_0 \exp(-t / \tau(T)) \quad (1)$$

The corresponding depolarization current, $J(t)$, is expressed as follows;

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$$J(t) = -dP(t) / dt \quad (2)$$

Equation (2) can be rearranged as follows;

$$J(t) = P(t) / \tau(T) \quad (3)$$

where $\tau(T)$ is the relaxation time. If we arrange $\tau(T)$ according to the Arrhenius equation, It becomes;

$$\tau(T) = \tau_0 \exp(E/kT) \quad (4)$$

where τ_0 is the pre-exponential factor, E is the apparent activation energy, and k is a Boltzman constant. If $\log \tau_0$ has a linear relationship with E, the mechanical retardation and dielectric relaxation time around T_g can be expressed as follows;

$$\tau_0 = \tau_c \exp(-E/kT_c) \quad (5)$$

From equations (4) and (5)

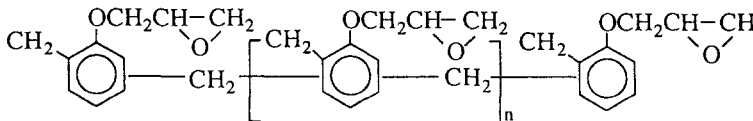
$$\tau(T) = \tau_c \exp \frac{E}{k} \left(\frac{1}{T} - \frac{1}{T_c} \right) \quad (6)$$

where τ_c and T_c are the compensation time and temperature respectively, as phenomenological parameters.

Experimental

o-Cresol novolac type (EOCN) epoxy resin, ESCN-195XL (Sumitomo Chemicals), and phenol novolac type (PN) curing agent, PN-1 (Nippon Kayaku Co), which have chemical structures shown in Fig. 1, are used in this study. In addition, 1,8-diazabicyclo (5,4,0) undec-7-ene (DBU, San Apro Co) as a catalyst, and dimethyl siloxane homoooligomer and dimethyl-methyltrifluoropropyl siloxane cooligomer (containing 30, 50 and 70% of trifluoropropyl), which were synthesized in this laboratory as stress relaxation agents are used. The siloxane cooligomers with the molecular weight of 2800g/mole were obtained by equilibration reaction among octamethylcyclotetrasiloxane (Toshiba Corp), trifluoropropylmethylcyclotrisiloxane (Chisso Co) cyclomer and 1,3-bis(aminopropyl)tetramethyl-

EOCN



PN

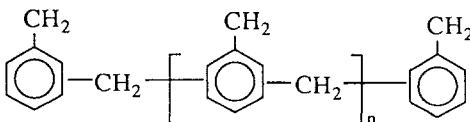
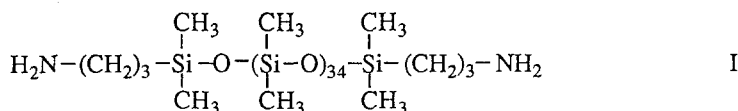


Fig. 1: Chemical structures of EOCN and PN.

disiloxane (Chisso Co) end blocker in the aid of base catalyst. The equilibration reaction was carried out at 80–100°C for 40–50hrs, and then the temperature was increased to 150°C to decompose the catalyst. The mixed cyclics remaining in the oligomers were removed by vacuum distillation at 150°C. The molecular weight of siloxane cooligomers were determined by end group analysis and gel permeation chromatography. Each composition of siloxane cooligomers was determined by ¹H NMR. The siloxane homooligomer was prepared by the same procedure without trifluoropropylmethylcyclotrisiloxane. The chemical structures of synthesized homo- and cooligomers are presented in Fig. 2.

Aminopropyl-terminated dimethyl siloxane homooligomer (DMS)



Aminopropyl-terminated dimethyl-methyltrifluoropropyl siloxane cooligomer (DMTS)

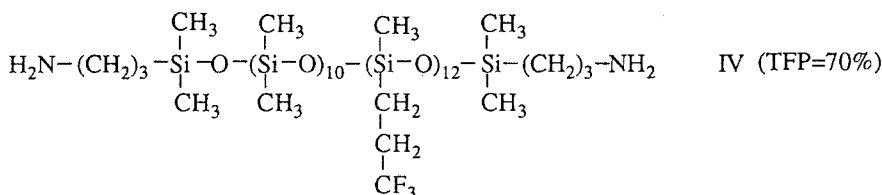
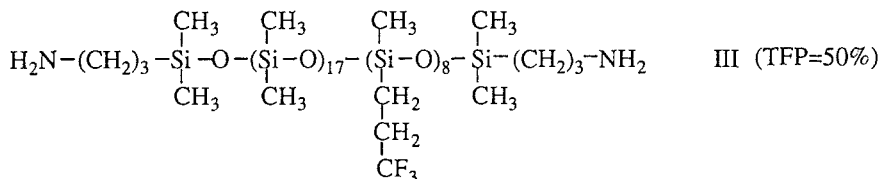
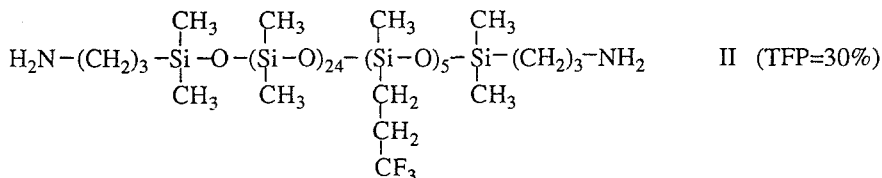


Fig. 2: Chemical structures of aminopropyl-terminated siloxane oligomers.

The prereaction between epoxy resin and siloxane oligomer are carried out in two different ways. One is to induce the reaction in melting state at 110–140°C for 4–8hrs and the other is to do in toluene solution state at 100–110°C for 10hrs. In latter case solvent was removed under the vacuum after the completion of the reaction between siloxane oligomer and excess epoxy resin (4). Curing agent (PN) and catalyst (DBU) were added into the prereacted siloxane-epoxy resin mixture, and then the mixture was fully mixed by using a Plasticorder (PL-V150, Brabender Co) and used for casting various testing samples. The content of siloxane oligomer was maintained as 11.5% in all systems.

The resin formulations and the cure conditions used in this study are described in Table 1. TSC measurements were carried out by polarizing the sample at 0°C with a polarization voltage of 1800 V/mm using TSC/RMA 91000 (Solomat Co). The heating rate was 5°C/min and the sample thickness was 0.05–0.2 mm. Dust and moistures in testing samples were removed under the vacuum (at 10⁻⁴ mbar for 24 hrs) prior to the test. RMA measurements were carried out as follows. The sample was polarized at 1800 V/mm

for 2 min and cooled rapidly to the temperature, 5°C lower than T_p and then the polarization voltage was removed. The sample was hold at that temperature for another 2 min and rapidly cooled again to the temperature, 30°C lower than T_p by 20°C/min and finally the relaxation spectrum was obtained by heating the sample up to the temperature, 30°C higher than T_p at a heating rate of 5°C/min (16-17).

Table 1: Details of the resin formulations and cure conditions used, and the measured conversion of cured samples.

Siloxane-modified epoxy resin		Cure condition		Conversion (%)	Code	TFP content (%)
Modification method	Siloxane type	Temp(°C)	Time(hrs)			
Melting state	Homooligomer (I)	Non-cure	—	0.0	MS0	—
	Homooligomer (I)	60	10	32.8	MS1	—
	Homooligomer (I)	90	1	51.4	MS2	—
	Homooligomer (I)	120	0.5	84.6	MS3	—
	Homooligomer (I)	150	0.5	98.0	MS4	—
	Homooligomer (I)	180	4	—	MS5	—
	Cooligomer (II)	180	4	—	MF3	30
	Cooligomer (IV)	180	4	—	MF7	70
Solution state	Cooligomer (II)	180	4	—	SF3	30
	Cooligomer (III)	180	4	—	SF5	50
	Cooligomer (IV)	180	4	—	SF7	70

Results and discussion

TSC spectra showing the degree of cure of the cured samples are shown in Fig. 3. Both of the area and height of TSC peak increase as the cure temperature increases, as can be seen from Fig. 3. This tendency observed is believed to be due to the increase of the

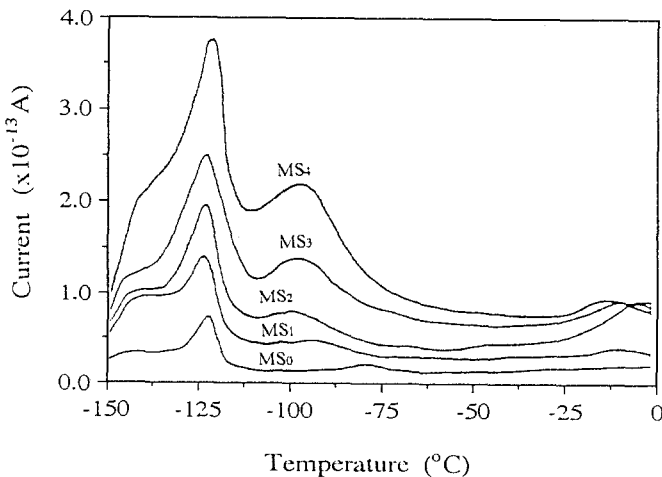


Fig. 3: TSC spectra of the siloxane-modified resins. Cure profiles for each samples are described in Table 1.

degree of cure (increases in chain segment), resulted from the increase of cure temperature. In all samples three relaxation peaks at around -140 , -125 and -100°C are observed. The second peak is related to the T_g of siloxane oligomer and the first and third peaks are to be due to the γ - and β -relaxations of epoxy resin respectively. In this study the relaxation peaks were identified by obtaining individual TSC spectrum (shown in Fig. 4) of unmodified resin and siloxane oligomer.

In the spectrum of unmodified resin [Fig. 4(a)] the β -relaxation peak resulted from hydroxyether motion at -107.3°C and γ -relaxation peak associated with diether linkage at -140°C were observed while the T_g peak at -115.5°C and the unknown peaks at -106.5 and -43.9°C were observed in the spectrum of siloxane homooligomer [Fig. 4(b)]. TSC spectra showing the changes in the interesting peaks, as a function of the type of siloxane oligomer, are shown in Fig. 5.

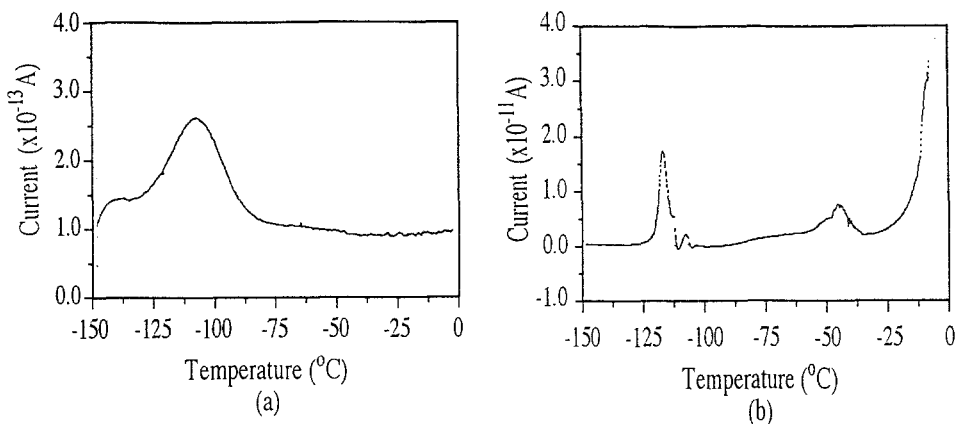


Fig. 4: TSC spectra for; (a) unmodified resin and (b) siloxane homooligomer (I). Testing conditions are; $T_p = 0^{\circ}\text{C}$, $E_p = 1800$ V/mm and $t_p = 5$ min.

Three relaxation peaks at around -110 , -45 and 8°C can be seen from the Fig. 5. In MSs containing siloxane homooligomer, as explained above, a weak peak at around 8°C was observed in addition to the peaks for the T_g of siloxane oligomer at -123.6°C and β -relaxation of epoxy resin at -100°C . However, in the system containing siloxane cooligomer (TFP = 30, 50, 70%) T_g peak of siloxane oligomer is shifted to higher temperature as the concentration of TFP increases, especially in the system containing 30% of TFP (MF3) the β -relaxation of epoxy resin and T_g peak of siloxane oligomer are folded. In addition, in the system containing 50 and 70% of TFP (MF5 and MF7) a new unknown peak is appeared at around -45°C and the peak intensity at 8°C becomes relatively greater. The changes in peak intensity are monitored as a function of polarization voltage in order to verify that the new peaks observed at around -75 -- -25°C in MF5 and MF7 are to be due to the dipole orientation (refer to Fig. 6). The changes in peak intensity have a linear relationship with the changes in polarization voltage. This implies that the new peak observed at around -75 -- -25°C is not to be due to the space charge but the dipole orientation (16, 17, 19, 20).

RMA measurements gave more detailed result. The results of compensation search for SF7 are shown in Fig. 7. It is noteworthy that the compensation lines extrapolate. This phenomenon is called compensation point which is related to the characteristics of the amorphous region of amorphous or semi-crystalline polymers. From this Arrhenius plot we can derive the activation enthalpy (ΔH) and entropy (ΔS). The degree-of-disorder

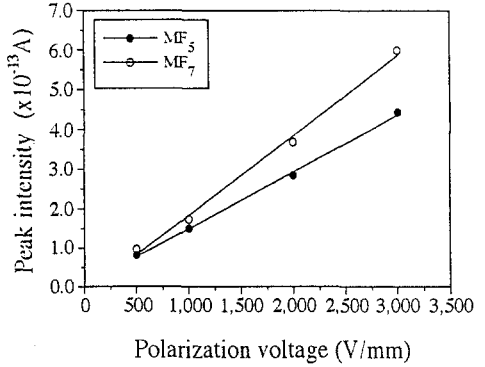
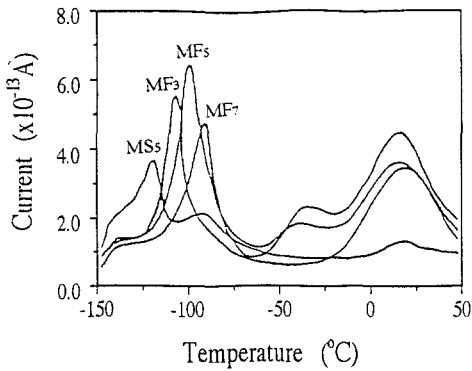


Fig. 5: TSC spectra of siloxane-modified epoxy resins showing the changes as a function of the type of siloxane oligomer. Testing conditions are; $T_p = 0^\circ\text{C}$, $E_p = 1800 \text{ V/mm}$ and $t_p = 5 \text{ min}$.

Fig. 6: TSC spectra of MF₅ (•) and MF₇ (○) showing the dependence of peak intensity on the polarization voltage. The spectra were obtained between -75°C and -25°C .

(DOD) is obtained by extrapolating the value of ΔS from $\Delta H = 0$. The value of DOD is shifted by 100 cal deg^{-1} in order to make it positive. Therefore, DOD is obtained from the coordinate $\log \tau_c$ and T_c of compensation point as follows;

$$\text{DOD} = 100 - 2[\ln(T_c \tau_c) + 23.76] \tag{7}$$

DOD value is also used to isolate the influences of compatibility and thermal stress of polymer blend (18).

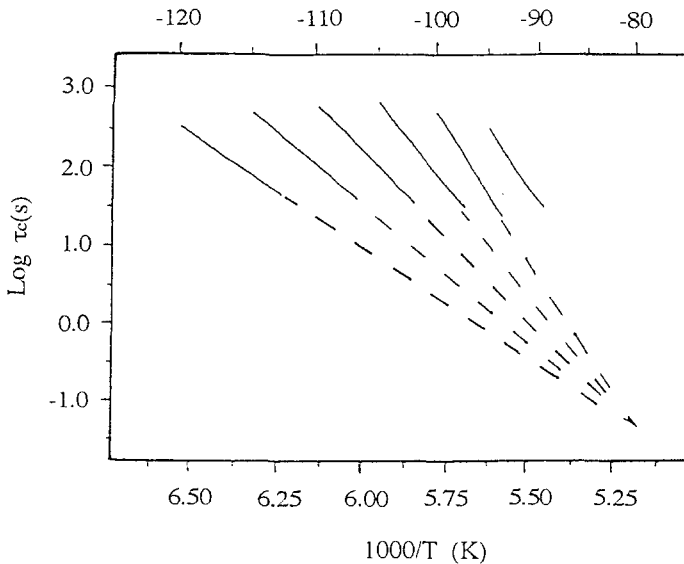


Fig. 7: Plot of the compensation search for RMA data of SF₇; $T_p = -120 \sim -95^\circ\text{C}$

The data of the critical temperature (T_c), relaxation time (τ_c) and DOD, obtained by the compensation search, are presented in Table 2.

Table 2: RMA data of the siloxane-modified epoxy resin systems.

Sample		T_c ($^{\circ}\text{C}$)	$\log \tau_c$ (sec)	DOD (cal/K)
Melting state	unmodified	-98.10	1.19	37.06
	MS ₅	-98.27	0.82	38.77
	MF ₃	-96.06	0.34	40.93
	MF ₅	-98.15	0.58	39.86
	MF ₇	-85.37	0.37	40.71
Solution state	SF ₃	-94.15	-0.58	45.15
	SF ₅	-50.49	-6.74	72.89
	SF ₇	-79.89	-1.37	48.61

The T_c values of the samples prepared in solution state are greater than those of the samples prepared in melting state. The values of the samples containing 70% of TFP (MF₇ and SF₇) are relatively greater and the sample containing 50% of TFP (SF₅) has the greatest value. The increase of T_c value, which is related here to the maximum number of the cooperative segmental motion, indicates the increase of the cooperative segmental motion. Consequently, the segmental motion is more active in the system containing TFP which has polar groups (16, 17, 21). On the other hand, the relaxation time ($\log \tau_c$) is much smaller in siloxane-modified resin systems than unmodified systems. It is smaller in the system containing TFP (MF₃, MF₅ and MF₇) and noticeably smaller in the system prepared in solution state (SF₃, SF₅ and SF₇) than melting state. The trends observed here is believed to be due to the cooperative effect of TFP having polar groups. The addition of TFP will increase the system compatibility and hence the small value of τ_c for the system prepared in solution state indicates the formation of homogeneous phase associated with the increase of system compatibility. The value of DOD is high in siloxane-modified system and noticeably higher in the system, prepared in solution state. This tendency is also considered to be due to the improvement of system compatibility. The high DOD will prevent the influence of thermal stress, and hence will satisfy the requirement of low-stress epoxy molding compound. Other noteworthy thing in table is that the data for SF₅ and MF₅ which showed reproducibility are out of the trend. These abnormal results are considered to be due to dipole orientation effect, but it is not clearly understood at this stage and further experimental works are going on in our laboratory.

From this study we could derive the following important results;

- (a) The peak area and intensity of TSC spectrum increase as the cure proceeds in the siloxane-modified resin systems.
- (b) The β -relaxation of epoxy and the α -relaxation of siloxane oligomer are folded and shifted to higher temperature with increasing the concentration of TFP.
- (c) A new peak observed in the systems containing 50 and 70% TFP is to be due to the dipole orientation of TFP.
- (d) As the concentration of TFP increases the critical temperature and DOD increase, and relaxation time decreases.

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