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Study of siloxane-modified epoxy resin using thermally stimulated current(II)

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Summary

Thermally stimulated current (TSC) and relaxation map analysis (RMA) was used to characterize the low temperature relaxation of epoxy resin modified with siloxane oligomers. In aminopropyl-terminated siloxane oligomer (ATSO) the β-relaxation of epoxy resin and the glass transition temperature of siloxane oligomer were folded regardless of the concentration of diphenyl. The β-relaxation of epoxy resin and the glass transition temperature of oxiranylmethoxy-terminated siloxane oligomer (OTSO) were folded and shifted to higher temperature as the concentration of diphenyl in siloxane oligomer increased. In the systems containing of diphenyl in siloxane oligomer a new relaxation peak due to the space charge was observed in the range of -80°C to -50°C and -30°C to 5°C . As the concentration of diphenyl increased the compensation temperature (T_c) and the degree-of-disorder (DOD) were increased while the compensation time, τ_c was decreased.

Introduction

In epoxy molding compound (EMC) used for the encapsulation of semiconductor, the integrated circuits (IC) devices are stressed because of the thermal mismatch of silicon chips and cured epoxy resins. This internal stress causes package cracks, deformation of aluminum patterns on IC devices, and passivation film cracks. It is, therefore, necessary to reduce the thermal expansion coefficient and the elastic modulus of epoxy molding compound to reduce internal stress. The addition of siloxane oligomer into epoxy resins has been available for the reduce of internal stress. For this epoxy resin, modified siloxane oligomer or rubber is used. The material characteristics of the cured epoxy resins have been studied by many workers (1-5).

The low temperature relaxation of cured epoxy resins has been studied with dynamic mechanical analysis. Recently, the thermally stimulated current which has high sensitivity even at low frequency has been used for the study of low temperature relaxation of epoxy resins (6-10). In a previous paper (11), the low temperature relaxation of siloxane-modified epoxy resin that contains trifluropropyl (TFP) polar group has been studied by using TSC and RMA (11). In this paper, siloxane oligomer which contains aromatic diphenyl group was used instead of TFP polar group, and the low temperature relaxation of siloxane-modified epoxy resin has been studied by using TSC and RMA.

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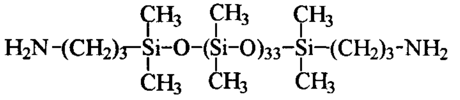
Experimental

o-Cresol novolac type (EOCN) epoxy resin, EOCN-103S (Nippon Kayaku Co.), and phenol novolac type (PN) curing agent, PN-1 (Nippon Kayaku Co.), which have chemical structures shown in previous paper (11), were used. In addition, 1,8-diazabicyclo(5,4,0)undec-7-ene (DBU, San Apro Co.) as a catalyst, and aminopropyl-terminated dimethyl siloxane homooligomer, aminopropyl-terminated dimethyl-diphenyl siloxane cooligomer (diphenyl content = 20, 40, 60%), oxiranylmethoxypropyl-terminated dimethyl siloxane homooligomer, and oxiranylmethoxypropyl-terminated dimethyl-diphenyl siloxane cooligomer (diphenyl = 20, 40, 60%), which were synthesized in this laboratory as stress relaxation agents were used. The siloxane oligomers with molecular weight of 2800g/mole were obtained by equilibration reaction among octamethylcyclotetrasiloxane (Toshiba Corp.) cyclomer, octaphenylcyclotetrasiloxane (Aldrich Chem. Co.) cyclomer, 1,3-bis(aminopropyl)tetramethyldisiloxane (Chisso Co.) end blocker, and 1,3-bis(oxiranylmethoxy)propyltetramethyldisiloxane (Chisso Co.) end blocker in the aid of base catalyst. The equilibration reaction was carried out at 80~100°C for 40~50hrs, and the temperature was increased to 150°C to decompose the catalyst. The molecular weight of siloxane oligomers were determined by end group analysis and gel permeation chromatography. Each composition of siloxane cooligomers was determined by ^1H NMR. The chemical structures of synthesized siloxane oligomers are presented in Figs. 1 and 2.

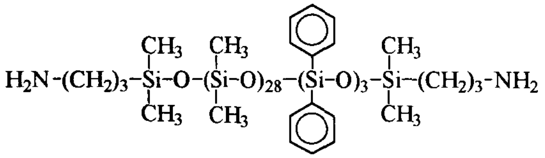
Aminopropyl-terminated dimethyl siloxane homooligomer



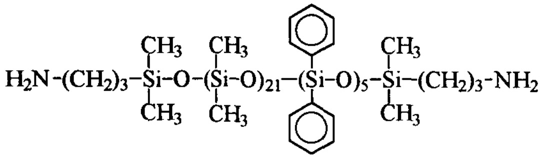
$$H_2N\text{-}(CH_2)_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}(\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O)_{33}\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}(CH_2)_3\text{-}NH_2$$

I

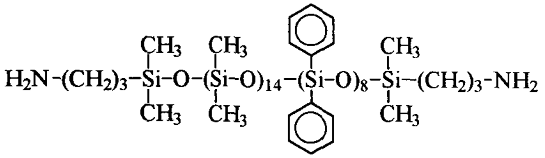
Aminopropyl-terminated dimethyl-diphenyl siloxane cooligomer



II(diphenyl=20%)

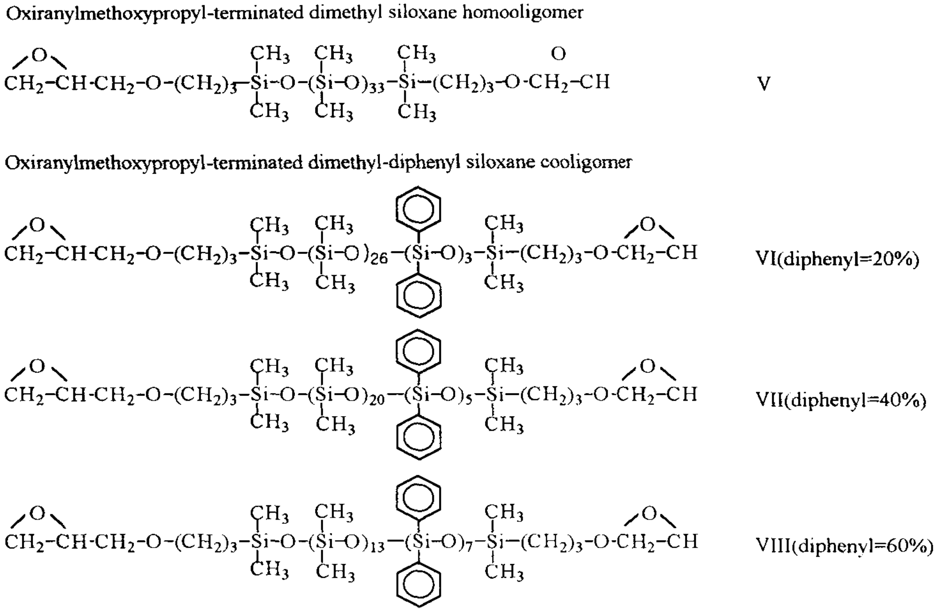


III(diphenyl=40%)



IV(diphenyl=60%)

Fig. 1: Chemical structures of aminopropyl-terminated siloxane oligomer (ATSO)



Oxiranylmethoxypropyl-terminated dimethyl siloxane homooligomer

V

Oxiranylmethoxypropyl-terminated dimethyl-diphenyl siloxane cooligomer

VI(diphenyl=20%)

VII(diphenyl=40%)

VIII(diphenyl=60%)

Fig. 2: Chemical structures of oxiranylmethoxypropyl-terminated siloxane oligomer (OTSO)

The prereactions between epoxy resin and siloxane oligomer are carried out in two different ways. One is to react aminopropyl-terminated siloxane oligomer (ATSO) and excess EOCN, and the other is to react oxiranylmethoxypropyl-terminated siloxane oligomer (OTSO) and excess PN at 110~140°C for 4~8hrs. EOCN and PN calculated by stoichiometry, and catalyst (DBU) were added into the prereacted siloxane-resin mixtures, and then the mixtures were fully mixed by using a Plasti-Corder (PL-V150, Brabender Co.) and used for casting various testing samples. The content of siloxane oligomer was maintained as 8.5% in all system. The resin formulations and the cure conditions used in this study are described in Table 1. TSC and RMA analysis were carried out by using TSC/RMA 91000 (Solomat Co.)

Table 1:Details of the resin formulations and cure conditions used.

Siloxane oligomer type		Cured condition		Code	Phenyl content(%)
		Temp(°C)	Time(hrs)		
Unmodified		180	4	UE	-
ATSO	Homooligomer (I)	180	4	AS_0	-
	Cooligomer (II)	180	4	AS_1	20
	Cooligomer (III)	180	4	AS_2	40
	Cooligomer (IV)	180	4	AS_3	60
OTSO	Homooligomer (V)	180	4	ES_0	-
	Cooligomer (VI)	180	4	ES_1	20
	Cooligomer (VII)	180	4	ES_2	40
	Cooligomer (VIII)	180	4	ES_3	60

Results and Discussion

TSC spectra showing the changes in the interesting peaks, as a function of the type of siloxane oligomer (ATSO), are shown in Fig. 3. From this result, there is no consistent trend as the concentration of diphenyl, and one relaxation peak at around -110°C can be seen. In AS_0 containing siloxane homooligomer, the folded peak with the T_g of siloxane oligomer at -123.6°C and β-relaxation of epoxy resin at -110°C was observed. However, in the containing siloxane cooligomers (AS_1, AS_2, and AS_3) T_g peak of siloxane oligomer with the effect of diphenyl was not observed. It can be suggested that the reaction of the primary amine group of siloxane oligomer (ATSO) and epoxy group of EOCN is increased due to relatively higher concentration of hydroxy ether group (5).

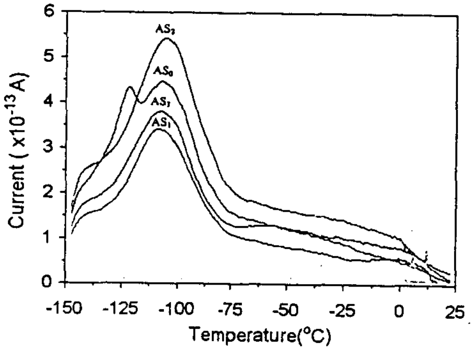


Fig. 3: TSC spectra of cured siloxane-modified epoxy resins showing the changes as a function of the type of siloxane oligomer (ATSO). Testing conditions are ; T_p = 0°C, E_p = 1800 V/mm and t_p = 5min.

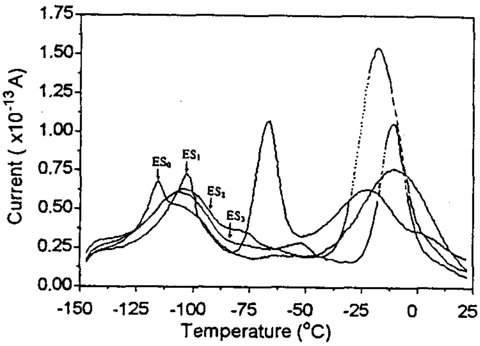


Fig. 4: TSC spectra of cured siloxane-modified epoxy resins showing the changes as a function of the type of siloxane oligomer (OTSO). Testing conditions are ; T_p = 0°C, E_p = 1800 V/mm and t_p= 5min.

TSC spectra showing the changes in the interesting peaks, as a function of the type of siloxane oligomer (OTSO), are shown in Fig. 4. Three relaxation peaks at around -110, -60, and -20°C can be seen from Fig. 4. In ES_0 containing siloxane homooligomer, a broad peak at around -13.2°C was observed in addition to the peaks for the T_g of siloxane oligomer at -117.1°C and β-relaxation of epoxy resin at -100°C. However, in the containing siloxane cooligomer (diphenyl = 20, 40, 60%) T_g peak of siloxane cooligomer is shifted to higher temperature as the concentration of diphenyl increase, especially in the system containing 20% diphenyl (ES_1) the β-relaxation of epoxy resin and T_g peak of siloxane oligomer are folded and a new unknown peak is appeared at around -69.4°C and -24.8°C.

In addition, in the systems containing 40 and 60% of diphenyl (ES_2 and ES_3) T_g peak of siloxane oligomer is shifed to higher temperature at around -78.2°C and -54.3°C than at around -110°C, and the new peaks are appeared at around -21.3°C and -13.7°C. Therefore, the changes in peak intensity are monitored as a function of polarization voltage in order to verify that the new peak of ES_0, ES_1, ES_2 and ES_3 are to be due to the dipole orientation (refer Figs. 5 and 6). In ES_1 of Fig. 5, a new peak of -69.4°C has not a linearity with the changes in polarization voltage. Similarly, the new peaks of -30~5°C (ES_0, ES_1, ES_2 and ES_3) have not a linearity in Fig. 6. This means that the new peaks are not to be due to the dipole orientation but space charge (8-13). RMA measurements gave more detailed result. The result of compensation search for ES_3 is shown in Fig.7.

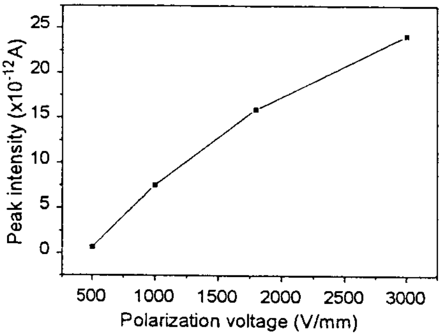


Fig. 5: Dependence of peak intensity on the polarization voltage for the TSC spectra of ES_1 obtained between -80°C and -50°C.

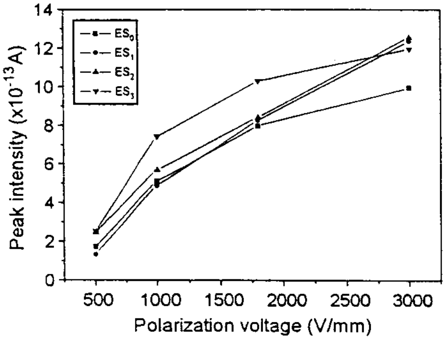


Fig. 6: Dependence of peak intensity on the polarization voltage for the TSC spectra of ES_0, ES_1, ES_2 and ES_3 obtained between -50°C and 5°C.

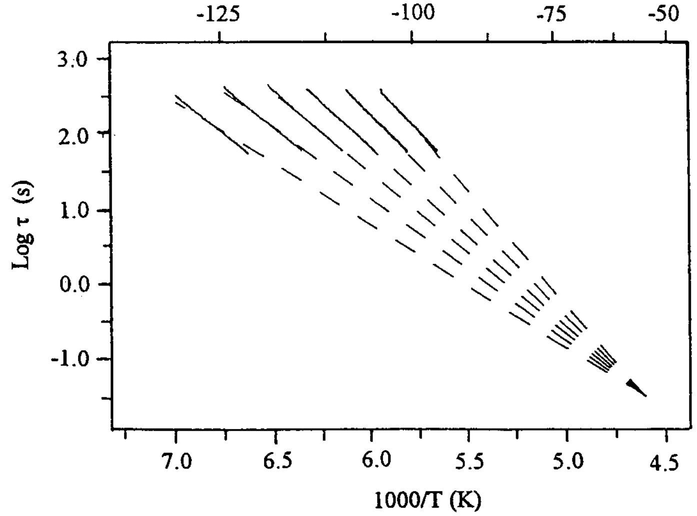


Fig. 7: Plot of the compensation search for RMA data of ES_3; T_p = -120~-95°C.

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 systems.

Sample		T_c (°C)	τ_c (sec)	DOD (cal/K)
unmodified(UE)		-93.20	0.93	40.06
ATSO	AS_0	-59.69	-1.59	49.41
	AS_1	-55.25	-1.84	50.50
	AS_2	-44.90	-1.91	51.74
	AS_3	-40.25	-2.11	51.60
OTSO	ES_0	-76.79	-1.53	49.30
	ES_1	-66.66	-1.88	50.78
	ES_2	-47.72	-1.95	51.95
	ES_3	-47.49	-2.05	51.38

The T_c value of the unmodified epoxy resin is much smaller than those of the siloxane-modified epoxy resin systems. The increase of diphenyl group indicates the increase of the T_c values. In addition, in containing siloxane oligomer type (ATSO, OTSO) similar value is observed, it is much larger than TFP systems in a previous paper (11). The T_c value of AS_0 and AS_1 in containing ATSO is more large than ES_0 and ES_1 in containing OTSO. The T_c value is related to the maximum number of the cooperative segmental motion. The increase of T_c value indicates the increase of the cooperative segmental motion. Consequently, the increase of diphenyl group has more active segmental motion (8, 9, 14). On the other hand the relaxation time (log τ_c) is much smaller in siloxane-modified resin systems than unmodified systems. Although the value is much smaller value than TFP systems in a previous paper, it observed similar value in containing siloxane oligomer type (ATSO, OTSO). The trends observed in this study are believed to be due to the cooperative effect of diphenyl group. The value of DOD is increased with the increasing of diphenyl group.

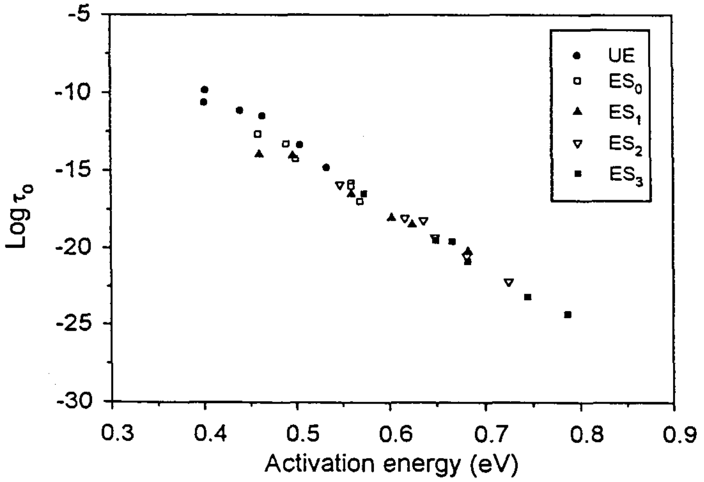


Fig. 8: Plot of the activation energy and log τ_0 for the peaks (-120~-95°C) of β-relaxation of epoxy resin and α-relaxation of siloxane oligomer.

The DOD will prevent the influence of thermal stress, and hence will satisfy the requirement of low stress epoxy molding compound (10). In Fig. 8, it can be shown that the activation energy has a linear relationship with relaxation time. From this result, it corroborated the existence of compensation law. The activation energy has to higher values as the increase of diphenyl concentration in the siloxane oligomer. The increase of diphenyl concentration in the epoxy resin system containing siloxane oligomer not only decreases relaxation time but also increases the activation energy. The high activation energy and low relaxation time may be explained only in terms of cooperative motion (8,9).

From this study, we could obtain the following results.

1) In the containing OTSO system, the β-relaxation of epoxy and the α-relaxation of siloxane oligomer are folded and shifted to higher temperature with increasing the concentration of diphenyl, however, in the containing ATSO system, only one relaxation peak at -110°C can be observed.

2) A new peak observed with the concentration of diphenyl is to be due to the space charge of diphenyl.

3) From RMA data, as the concentration of diphenyl increases the critical temperature and DOD is increased, and relaxation time is decreased.

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