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# Study of polyester-modified epoxy resin using thermally stimulated current

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## Summary

In order to characterize the low temperature relaxation of epoxy resin modified with aromatic polyester, thermally stimulated current (TSC) and relaxation map analysis (RMA) were investigated. Two relaxation peaks at around -85 and 70 °C were observed as the indication of β-relaxation of epoxy resin and $T_g$. of polyester, respectively. The unknown peak of ESE-102 at around 20 °C was observed due to dipole orientation. The RMA data was showed that compensation temperature ($T_c$) and degree-of-disorder (DOD) were increased with increasing the concentration and the molecular weight of polyester, whereas the compensation time ($\tau_c$) was decreased. It can be concluded that the cooperative molecular motion in cured epoxy resin was more active as the concentration and the molecular weight of polyester increase.

## Introduction

Cured epoxy resins are one of the most important thermosetting polymers and have wide use as structural adhesives and matrix resin for fiber composites, but they are brittle and have poor resistance to crack propagation. To enhance the fracture toughness and impact resistance of epoxy network the rubbers such as carboxyl-terminated butadiene acrylonitile copolymers (CTBN) and amine-terminated butadiene acrylonitrile copolymers (ATBN) or engineering thermoplastics have been widely used as epoxy modifiers (1-5). Engineering thermoplastics are interesting materials as modifiers for epoxy resins from the view point of the maintenance of mechanical and thermal properties for matrix resins. The material characteristics of the cured epoxy resins have been studied by many workers (6-8).

The low temperature relaxation of cured epoxy resins has been studied with dynamic mechanical analysis and dielectric technique. Recently the thermally stimulated current which has high sensitivity even a low frequency ($10^{-2}$~$10^{-4}$ Hz) has been used for the study of low temperature relaxation of epoxy resin (9-13). In previous papers (9-11), the low temperature relaxation of siloxane- and rubber-modified epoxy resins has been

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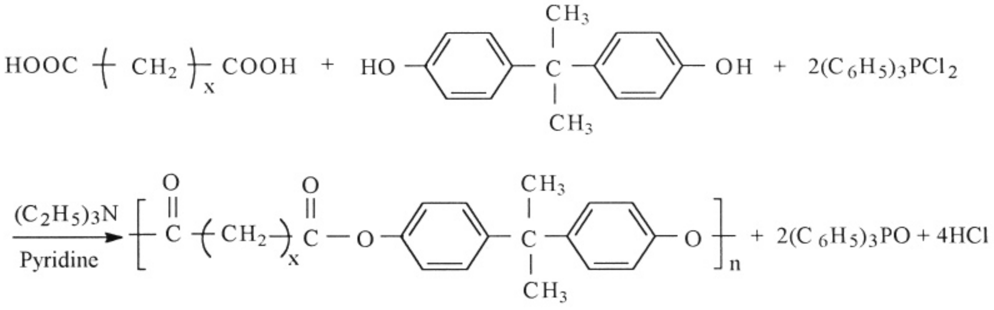
studied by using TSC and RMA. In this study, the low temperature relaxation of polyester-modified epoxy resin was investigated by TSC and RMA. TSC and RMA studies were based on the single Debye relaxation theory by Bucci (12) and Arrehenius equation (15-16).

## Experimental

Diglycidyl ether of bisphenol A (DEGBA) type epoxy resin, EPON-828 (Kumho Shell Chemical Co.) and aromatic amine curing agent, 4,4'-diaminodiphenylmethane (DDM, Tokyo Kasei Organic Chemicals), which have chemical structures shown in previous paper (11), were used in this study. The epoxy modifiers were prepared by direct polycondensation from bisphenol A and aliphatic dicarboxylic acids (adipic acid, suberic acid, sebacic acid, dodecanedioic acid). Triphenylphosphine and hexachloroethane were used as condensing agents. In chiorobenzene, the polyesters were obtained by using acid acceptors such as triethylamine and pyridine. The details of the synthetic procedures followed the Kitayama experimental method (17). The synthetic route of the polyesters was presented in Fig. 1.



where x = 4 : adipic acid (poly-bisphenol A-adipic acid: PBAD)
x = 6 : suberic acid (poly-bisphenol A-suberic acid: PBSU)
x = 8 : sebacic acid (poly-bisphenol A-sebacic acid: PBSE)
x = 10 : dodecanedioic acid (poly-bisphenol A-dodecanedioic acid: PBDO)

Fig. 1: Synthetic route to aromatic polyesters.

The predetermined amount of polyester was dissolved in epoxy resin without solvent by heating at 160 °C. Then the curing agent, DDM, was added to the mixtures which was kept at 120 °C. Thin films 0.05~0.2 mm thick were cast for the measurement of TSC. 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 60 °C with a polarization voltage of 1,800 V/mm using TSC/RMA 91000 (Solomat Co.). The heating rate was 7 °C/min. Dust and moistures in testing samples were removed under vacuum (at

$10^{-4}$ mbar for 24 hrs) prior to the test.

RMA measurements were carried out as follows. The sample was polarized at 1,800 V/mm for 2 min (the polarization time, tp) and cooled rapidly to the temperature which was 5 °C lower than the polarization temperature (Tp) and then the polarization voltage (Ep) was removed. The sample was hold at that temperature for another 2 min and rapidly cooled again to the temperature that was 30 °C lower than Tp by 20 °C/min and finally heated to a temperature that was higher than Tp at a heating rate of 7 °C/min.

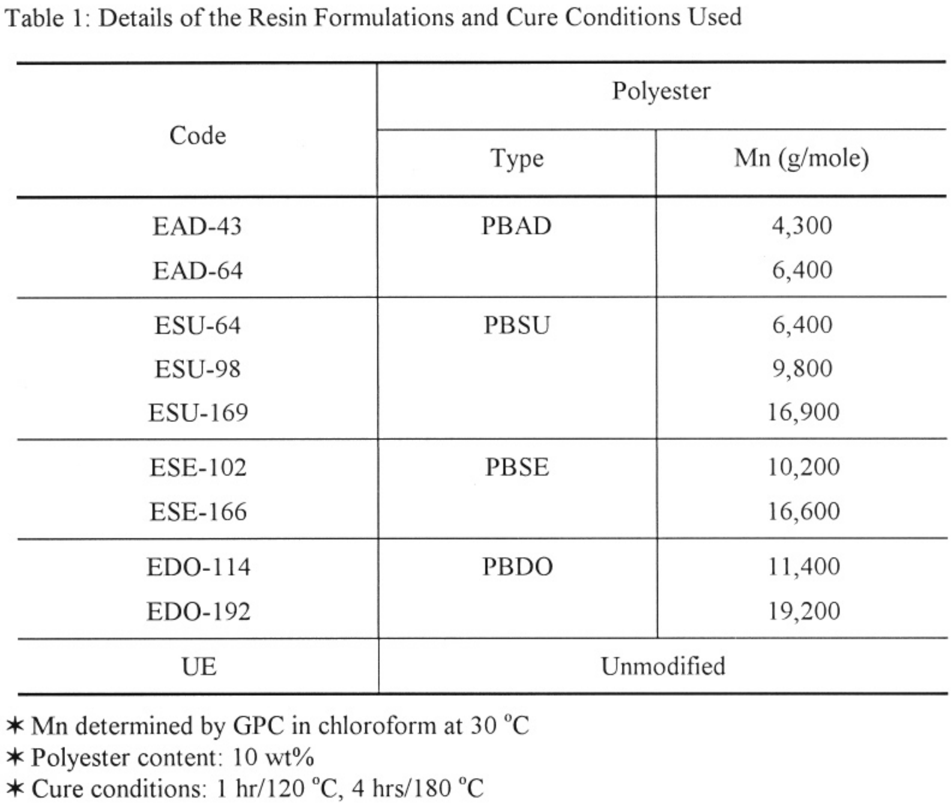


Table 1: Details of the Resin Formulations and Cure Conditions Used

| Code | Polyester | |
|---|---|---|
| | Type | Mn (g/mole) |
| EAD-43 | PBAD | 4,300 |
| EAD-64 | | 6,400 |
| ESU-64 | PBSU | 6,400 |
| ESU-98 | | 9,800 |
| ESU-169 | | 16,900 |
| ESE-102 | PBSE | 10,200 |
| ESE-166 | | 16,600 |
| EDO-114 | PBDO | 11,400 |
| EDO-192 | | 19,200 |
| UE | Unmodified | |

∗ Mn determined by GPC in chloroform at 30 °C
∗ Polyester content: 10 wt%
∗ Cure conditions: 1 hr/120 °C, 4 hrs/180 °C

## Result and Discussion

TSC spectra for the unmodified resin and polyester (PBSE) are shown in Fig. 2 and 3. In the spectrum of unmodified resin the β-relaxation peak resulted from the hydroxyether motion was observed at -85 °C, while an unknown peak at 15 °C was observed in the spectrum of PBSE with molecular weight 10,200 g/mole. The effect of the polyester concentration on the TSC spectra is shown in Fig. 4. Both the area and the height of TSC peak increase with increasing the concentration of polyester. $T_g$ of polyesters appeared at around 70 °C. TSC spectra as a function of the molecular weight of polyesters are shown in Fig. 5. Two relaxation peaks at around -85 and 75 °C can be seen in Fig. 5. The intensity and the area of TSC peak increased with increasing the molecular weight. It is believed to be due to the increase of the polar group content.

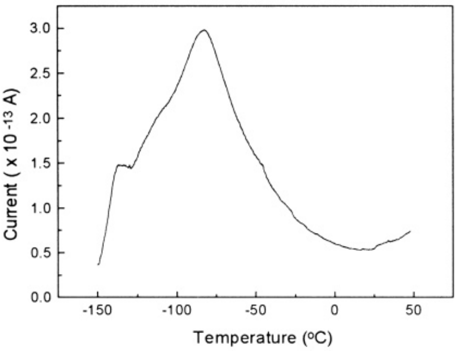


Fig. 2: TSC spectrum for unmodified resin: Testing conditions; $T_p$=60 °C, $E_p$=1,800 V/mm and $t_p$=5 min.

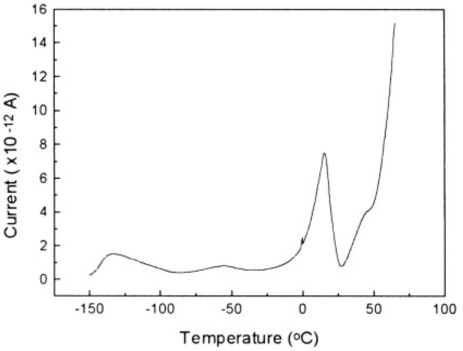


Fig. 3: TSC spectrum for PBSE with molecular weight 10,200 g/mole: Testing conditions; $T_p$=60 °C, $E_p$=1,800 V/mm and $t_p$=5 min

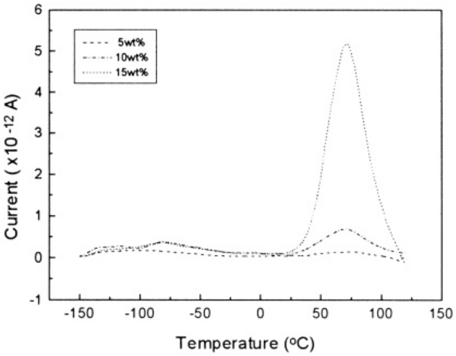


Fig. 4: TSC spectra of cured polyester-modified epoxy resins with different concentrations of polyester (ESU-64): Testing conditions; $T_p$=60 °C, $E_p$=1,800 V/mm and $t_p$=5 min.

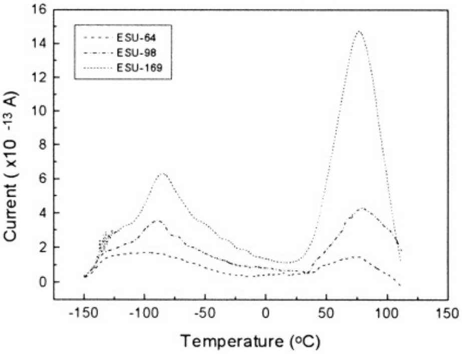


Fig. 5: TSC spectra of polyester-modified epoxy resins with different molecular weights of polyesters (PBSU): Testing conditions; $T_p$=60 °C, $E_p$=1,800 V/mm and $t_p$=5 min.

TSC spectra of the modified resin systems are shown as a function of the chain length units of polyesters in Fig. 6. The β-relaxation of epoxy resin was located at around -85 °C and the α-relaxation of polyester at around 70 °C. However, in ESE-102, a new peak was observed at around 20 °C due to the dipole orientation from the changes on peak intensity with the changes in polarization voltage (9-11).

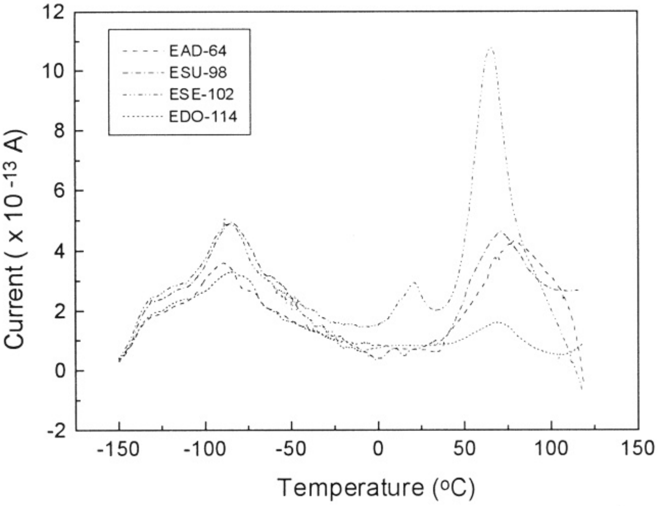


Fig. 6: TSC spectra of polyester-modified epoxy resins with different chain length units of polyesters: Testing condition; $T_p$=60 °C, $E_p$=1,800 V/mm and $t_p$=5 min.

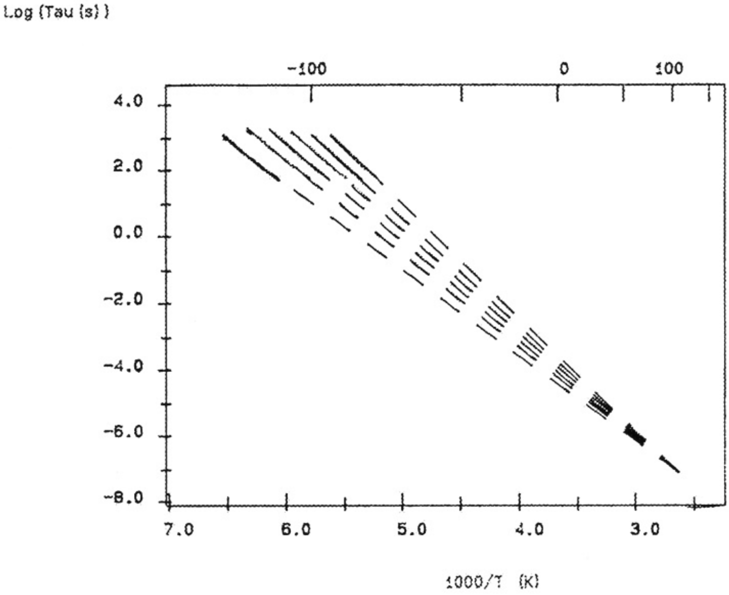


Fig. 7: Plot of the compensation search for RMA data of ESU-169: Testing condition; $T_p$=60 °C, $E_p$=1,800 V/mm and $t_p$=5 min.

RMA measurements yield more detailed result (9-13). The results of compensation search for ESU-169 are shown in Fig. 7.

The data of the critical temperature ($T_C$), the relaxation time ($\tau_C$) and DOD, obtained by the compensation search, are presented in Table 2.

Table 2: RMA Data of the Polyester-Modified Epoxy Resin Systems

| Sample | $T_C$ (°C) | Log $\tau_C$ (sec) | DOD (cal/K) |
|---|---|---|---|
| UE | 101.11 | -6.39 | 70.24 |
| EAD-43 | 108.88 | -6.78 | 72.00 |
| EAD-64 | 113.17 | -6.92 | 72.62 |
| ESU-64 | 108.51 | -6.84 | 72.29 |
| ESU-98 | 107.91 | -6.99 | 72.95 |
| ESU-169 | 112.77 | -7.03 | 73.11 |
| ESE-102 | 109.65 | -7.06 | 73.26 |
| ESE-166 | 113.98 | -7.06 | 73.18 |
| EDO-114 | 107.67 | -6.94 | 72.74 |
| EDO-192 | 109.60 | -7.00 | 73.01 |

The $T_C$ values of the polyester-modified epoxy resin systems were much larger than that of the unmodified epoxy resin. The increase in the molecular weight of polyester caused the increase in the Tc values. The critical temperature is related to the maximum number of cooperative movement; a high $T_C$ value means more cooperative segmental motion (12,13). On the other hand, the polyester modified resin system having a much lower relaxation time than unmodified resin system may be attributed to the more cooperative effect of the polar ester segments. In addition, the increase in the molecular weight indicated the decrease in the relaxation time. DOD was increased with the increasing the molecular weight of polyesters. Especially, in ESE systems DOD was larger than in other systems.

From this study, we could obtain the following results;

1) The TSC spectra of the modified resin systems showed two peaks. The higher temperature peaks were located near the $T_g$ of polyester. The lower temperature peaks corresponded to the β-relaxation of epoxy resin.
2) As the concentration and the molecular weight of polyester were increased, the peak intensities for β-relaxation of epoxy resin and the $T_g$ of polyester were increased.
3) As the concentration and the molecular weight increased, the critical temperature and DOD increased, while relaxation time decreased. We could conclude that the segmental motion was more active with increasing the molecular weight of the polyester.

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