Polymer Bulletin 40, 599–605 (1998)

Polymer Bulletin

Study of rubber-modified epoxy resin using thermally stimulated current

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Received: 11 September 1997/Revised version: 25 November 1997/Accepted: 1 December 1997

Summary

In order to characterize the low temperature relaxation of epoxy resin modified with amine-terminated butadiene acrylonitrile copolymers (ATBN), thermally stimulated current (TSC) and relaxation map analysis (RMA) were investigated. Four relaxation peaks at around -140, -100, -60 and 0ºC were observed as the indication of γ, ß-relaxation of epoxy resin, T_g, new unknown peak of ATBN, respectively. The unknown peak at around 0ºC 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 content of acrylonitrile and ATBN, whereas the compensation time (τ_c) was decreased. It can be concluded that the cooperative molecular motion in cured epoxy resin was more active as the concentration of acrylonitrile and ATBN content increases.

Introduction

Epoxy resins are very important polymers that often exhibit high tensile strength and modulus, excellent chemical and corrosion resistance, and good dimensional stability. However, these highly cross-linked systems are usually brittle and consequently have limited utility in application requiring high impact and fracture strength. The rubbers or elastomeric modifiers into the epoxy resin have enhanced the fracture toughness and impact resistance of epoxy networks. For example, carboxyl-terminated butadiene acrylonitrile copolymers (CTBN) and amine-terminated butadiene acrylonitrile copolymers (ATBN) have been widely used as an epoxy modifiers (1-5).

Toughening of thermosets can be achieved by the incorporation of rubbers and leads to improvement in mechanical properties. This high impact strength has been attributed to the existence of low temperature molecular motions. The low temperature relaxation of cured epoxy resins has been intensively studied with dynamic mechanical analyzer and dielectric technique as an important factor indicating the material characteristics related with the impact strength at ambient and the physical properties at subambient atmosphere. Recently, the thermally stimulated current has been used for the

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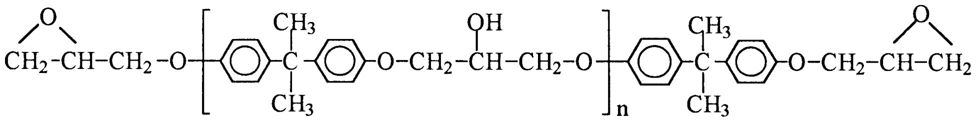
study of low temperature relaxation of epoxy resins (6-10). In previous papers (11, 12), the low temperature relaxation of siloxane-modified epoxy resin that contains trifluoropropyl and diphenyl polar group has been studied by using TSC and RMA. In this study, the low temperature relaxation of ATBN-modified epoxy resin was investigated by using TSC and RMA. TSC and RMA studies were based on the single Debye relaxation theory by Bucci (13) and Arrhenius equation (6-8).

Experimental

Diglycidyl ether of bisphenol A (DEGBA) type epoxy resin, EPON-828 (Shell Chemical Co.) and aromatic amine curing agent, 4,4'-diaminodiphenylmethane (DDM, Tokyo Kasei Organic Chemicals), which have chemical structures shown in Fig. 1, are used in this study. In addition, amine-terminated butadiene acrylonitrile copolymers (Hycar 1300x21, 1300x16, 1300x35, B.F. Goodrich Co.) are used as elastomeric modifiers.

DGEBA



DDM

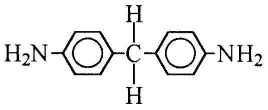


Fig. 1: Chemical structures of DGEBA and DDM

A mixture of ATBN and DDM as the curing agent was heated to dissolve at 120°C, and then EPON-828 as epoxy resin was added into the mixture. Thin films with 0.05 - 0.2mm thickness were casted from these mixtures 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 0°C with a polarization voltage of 1800 V/mm using TSC/RMA 91000 (Solomat Co.). The heating rate was 5°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 1800V/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/mm and finally higher than T_p at a heating rate of 5°C/min (8,9).

Table 1: Details of the resin formulations and cure condition used

Modifier		Cured condition		Code	Acrylonitrile content (%)	ATBN content of cured epoxy (%)
		Temp (°C)	Time (hrs)			
Unmodified		120/180	1/4	UE	-	-
ATBN	1300x21	120/180	1/4	NE$_{10}$	10	10
	1300x16	120/180	1/4	NE$_{18}$	18	10
	1300x35	120/180	1/4	NE$_{26}$	26	10
ATBN	1300x16	120/180	1/4	AE$_{5}$	18	5
	1300x16	120/180	1/4	AE$_{10}$	18	10
	1300x16	120/180	1/4	AE$_{15}$	18	15
	1300x16	120/180	1/4	AE$_{20}$	18	20
	1300x16	120/180	1/4	AE$_{25}$	18	25
	1300x16	120/180	1/4	AE$_{30}$	18	30

Results and discussion

TSC spectra showing the changes in the interesting peaks, as a function of the type of ATBN, are shown in Fig. 2. Four relaxation peaks at around -140, -100, -60 and 0°C can be observed from Fig. 2, γ-relaxation, ß-relaxation of epoxy resin, T_g peak, new unknown peak of ATBN, respectively (7,11).

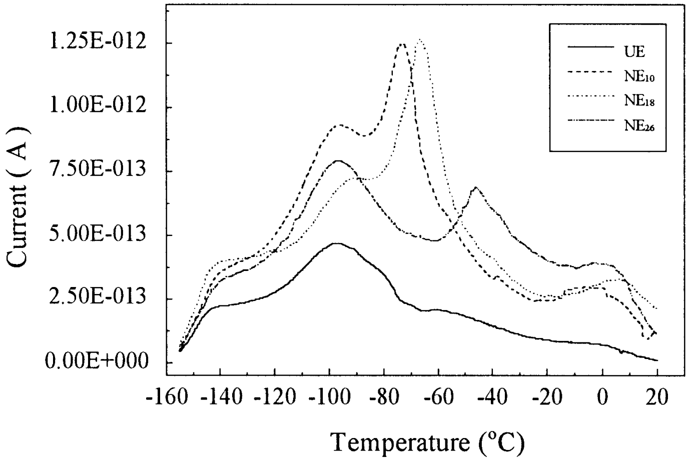


Fig. 2: TSC spectra of cured ATBN-modified epoxy resins showing the changes as a function of the type of ATBN. Testing conditions are; $T_p = 0°C$ $E_p = 1800$ V/mm and $t_p = 5$ min.

In cured epoxy resin system containing acrylonitrile group, both of the area and height of TSC peak were observed greater than those of the unmodified epoxy resin. T_g peak of ATBN is shifted to higher temperature as the concentration of acrylonitrile group increases. Especially the ß-relaxation of epoxy resin and T_g peak of ATBN are folded partially in the systems containing 10 and 18% acrylonitrile group (NE_{10} and NE_{18}), whereas T_g peak of ATBN is shown separately in the system containing 26% acrylonitrile group (NE_{26}).

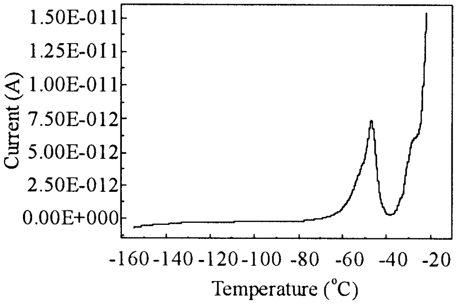


Fig. 3: TSC spectrum for ATBN (Hycar 1300x16). Testing conditions are; T_p = 0°C, E_p = 1800 V/mm and t_p = 5 min.

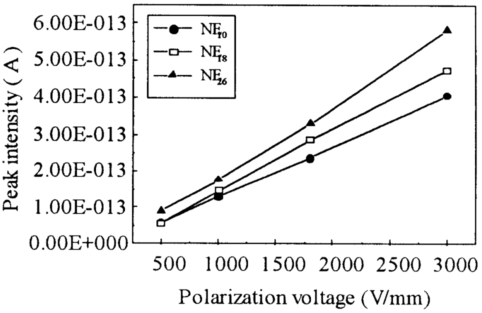


Fig. 4: TSC spectra of NE_{10}, NE_{18} and NE_{26} showing the dependence of peak intensity on the polarization voltage. The spectra were obtained between -10°C and 10°C.

The TSC spectrum of ATBN (Hycar 1300x16) shows the Tg peak at -46.5°C in Fig. 3. But T_g peak of ATBN (NE_{18}) in Fig. 2 is shifted to lower temperature at -62°C. This is believed to be due to the influence of ß-relaxation of epoxy resin. And in NE_{10}, NE_{18} and NE_{26} new peaks are appeared at around 0°C. Therefore, the changes in peak intensity are monitored as a function of polarization voltage in order to verify that the new peak of NE_{10}, NE_{18} and NE_{26} are to be due to the dipole orientation (Fig. 4). The changes on peak intensity have a linear relationship with the changes in polarization voltage. This means that the new peaks are not to be due to the space charge but dipole orientation (8,9,11).

TSC spectra of cured epoxy resins showing the changes as a function of the type of ATBN content are shown in Fig. 5. It is observed the weak γ-relaxation and ß-relaxation of epoxy resin at around -140 and -100°C, and relaxation peak is produced by ATBN at around -60 and 0°C. In addition, both of the area and height of TSC peak increase as the ATBN content increases. This tendency is believed to be due to the increase of the acrylonitrile content which has polar group.

RMA measurements gave more detailed result (8-12, 14-16). The data of the critical temperature (T_c), relaxation time (τ_c) and DOD obtained by the compensation search, are presented in Table 2.

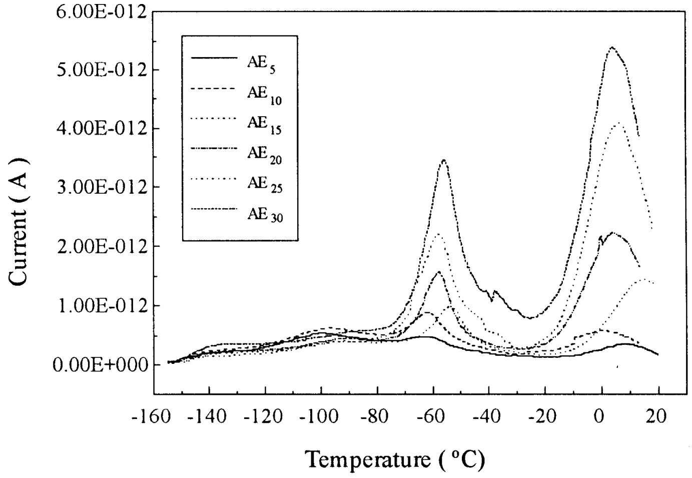


Fig. 5: TSC spectra of ATBN-modified epoxy resins showing the changes as a function of the type of ATBN content.

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

Sample	T_c (°C)	Log τ_c (sec)	DOD (cal/K)
UE	94.97	-5.50	66.20
NE$_{10}$	106.46	-6.00	68.45
NE$_{18}$	117.88	-6.21	69.33
NE$_{26}$	109.48	-6.19	69.28
AE$_5$	93.68	-5.75	67.38
AE$_{10}$	106.46	-6.00	68.45
AE$_{15}$	126.55	-6.09	68.75
AE$_{20}$	128.69	-6.38	70.06
AE$_{25}$	121.17	-6.58	71.03
AE$_{30}$	125.20	-6.63	71.25

The T_c value of the unmodified epoxy resin is much smaller than those of the ATBN-modified epoxy resin systems. The increase of acrylonitrile group (NE$_{10}$, NE$_{18}$, NE$_{26}$) and ATBN content (AE$_5$ - AE$_{30}$) indicate the increase of the T_c values. 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 as acrylonitrile group and ATBN content increase. On the other hand, the relaxation time is much smaller in ATBN-modified resin systems than unmodified systems. The increase of acrylonitrile group and ATBN content indicate the decrease of τ_c. The trend observed here is believed to be due to the cooperative effect of acrylonitrile group having polar group. The value of DOD is increased with the increasing of acrylonitrile group of ATBN content. T_c and DOD are much greater value, and τ_c is much smaller than that of siloxane oligomer systems in previous work (11, 12). It can be concluded that the crosslinking density was decreased due to difunctional epoxy resin compared with multifunctional epoxy resin in previous studies.

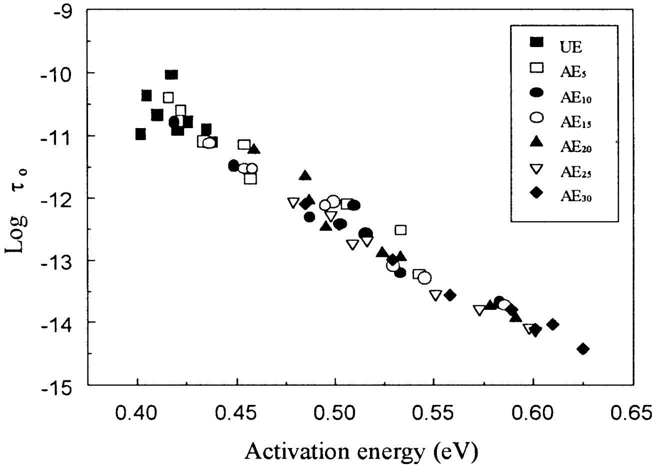


Fig. 6: Log τ_o vs activation energy diagram as a function of the type of ATBN content for the low temperature peaks (-120 ~ -85°C)

In Fig. 6, it can be shown that the activation energy has a linear relationship with relaxation time. From this result, it corroborated the existence has a linear relationship. As the ATBN content increase while the relaxation time decreases, and activation energy increases. 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) As the concentration of acrylonitrile group in ATBN increases, the ß-relaxation of epoxy and the T_g peak of ATBN are folded and shifted to higher temperature.
2) As the ATBN content increases, the area and height of TSC peak is increased.
3) A new peak observed with the concentration of acrylonitrile is to be due to the dipole orientation of ATBN.
4) From RMA data, the cooperative segment motion in ATBN-modified epoxy resin is more active with increasing the concentration of acrylonitrile and ATBN content.

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