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Organic rare-earth compounds as a new latent accelerator for curing of epoxy/anhydride system

Xinsheng Peng*, Yongxian Song, Rongxian Li, and Xiufeng Song

Laboratory of Polymer Physics, Changchun Institute of Applied Chemistry, Changchun 130022, People's Republic of China

SUMMARY

A series of organic rare-earth compounds has been found to be a latent accelerator for curing the epoxy resin/anhydride system. Incorporation of rare-earth ions into the epoxy resin caused an increase in the glass transition temperature (Tg) of the cured resin and the significant improvement in the dielectric and mechanical properties at high temperature which should be attributed to the higher Tg.

INTRODUCTION

The use of epoxy resins in the electrical and electronics industry as insulation materials has grown steadily over the years, and developments in formulations now enable them to be used for dipping, sealing, inpregnation, transfer moulding, bonding laminating, and surface coating etc. Many of these terms involve using anhydried curing agents which provide cured systems that have good mechanical and electrical properties and better high temperature stability than the amine-cured system[1,2]. Moreover, the resin-anhydride mixture has a low viscosity, long pot life, longer and higher temperature cure schedules. To overcome this drawback, it is necessary to add some form of accelerator to the formulation to speed the rate of cure. Consequently, several accelerators have appeared in the literature[3,4]. The ideal accelerator should be a "latent" one which is designed to be unreactive at room temperature but will give rapid cure process of resin with the application of heat. Recently we have developed a novel kind of latent accelerator, organic compound of rare-earth element[5-7]. The purpose of this work was to investigate the effect of various rare-earth metal(III) ions on both cure rate and properties of the resulting polymers after incorporating the rare-earth metal ions into the bulk of widely used epoxy resin.

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*Corresponding author

EXPERIMENTAL

Materials

The epoxy resin was a diglycidyl ether of bisphenol A (E-44, Shanghai Resin Factory), the anhydride curing agent was tung oil acid anhydride (TOA, Shanghai Resin Factory), and various rare-earth metal (RE) compounds in the form of tris(acetylacetonato) rare-earth metal [RE $(AA)_3$] or neodymium salts [trifluoroacetate, $Nd(FA)_3$; salicylate, $Nd(SA)_3$; naphthenate, $Nd(Naph)_3$] were prepared by the reaction of rare-earth trichloride with acetylacetone or corresponding acid respectively in aqueous solution. The E-44/TOA(1:1 wt.ratio) system served as the control and the rare-earth compounds were respectively added to the system at 1 phr, except varying concentration from 1 to 3 phr in study on the effect of $Nd(AA)_3$ content.

Samples preparation

The epoxy E-44 was heated to 120°C at which the solid rare-earth compound was then added and stirred until the compound dissolved and then the homogeneous material was fully mixed with TOA at room temperature. The mixed reactants of the E-44/TOA control or the RE ion-containing E-44/TOA (RE/E-44/TOA) systems were poured into an aluminum foil-lined casting mold and cured at 80°C for 2 hours and then at 120°C for 1 hour and postcured at 160°C for 5 hours. The specimens were prepared 30 mm diameter and 0.5 to 1 mm thick for dielectric measurements and 30×4×0.2 mm for dynamic mechanical tests.

Characterization

Gel times of the resins at different temperatures were determined on a SJH-751 torsional braid analysis (TBA) instrument by maxima in logarithmic decrement plots. Cure exotherms were obtained on a Perkin-Elmer Model 7 differential scanning calorimeter (DSC-7) at different heating rates of 2.5 to 15°C/min. Dielectric loss (Tan δ) of the cured specimens at different temperatures and a frequency of 60 Hz were determined on a TR-10C dielectric loss measuring set from Ando Electric Co. Dynamic mechanical properties were determined by dynamic mechanical analysis (DMA) at a heating rate of 2°C/min and a frequency of 3.5 Hz with Rheovibron DDV-II-EA dynamic viscoelastometer from Toyo Baldwin Co. Glass transition temperatures (Tg) of the cured epoxies were determined by both DMA and dielectric loss measuring. The polymer decomposition was monitored by a Perkin-Elmer TGS-2 thermogravimetric analyzer (TGA).

RESULTS AND DISCUSSION

The gel time data shown in Table 1 indicate the effectiveness of these rare-earth compounds as the accelerator for anhydride-cured epoxy resin system. From the data in Table 1, it is noted that fast gel times at 150°C (i.e., <50 minutes for most of them) can be observed with small amount i.e., 1 phr of the accelerators whereas the control showed lower rate of cure, the gel time being 196 minutes. The presence of rare-earth ions was found to dramatically accelerate the heat curing of the resin.

Table 1 Cure Behavior of RE Ion-Containing Epoxies

RE compounds	Gel time at 150°C(min)	E (kJ/mol)	$K_{150}\times10^3$ (min^{-1})	$K_{25}\times10^7$ (min^{-1})
control	196	63.8	2.80	14.00
La(AA)$_3$	26	82.5	14.30	7.62
Pr(AA)$_3$	26	79.7	10.00	9.78
Nd(AA)$_3$	30	81.0	12.20	7.70
Sm(AA)$_3$	28	93.1	7.36	1.11
Gd(AA)$_3$	46	91.4	7.73	1.43
Nd(FA)$_3$	28	79.7	9.19	6.86
Nd(SA)$_3$	80	90.2	13.10	2.80
Nd(Naph)$_3$	97	78.8	6.46	5.34

As shown in Table 1, it has also been found that the gelation reactivity of E-44/TOA system with different rare-earth acetylacetonates is nearly the same and reflects the similarity in chemical nature of 4f electron orbitals in all rare-earth elements; still, their activity as accelerators appears to be somewhat different and the order of them as follows: La≈Pr>Nd≈Sm>Gd. This may be attributed to the difference in the number of electrons that acuppy the 4f orbitals. The catalytic activity order above mentioned is just identical with the order of increase in the number of 4f orbital electrons. On the other hand, in the case of neodymium salts, it is obvious that the effect of the anion group of the salts on the time to gelation is even greater than that of the rare-earth element. Besides, the effect of concentration of the rare-earth compounds i.e., Nd(AA)$_3$, Nd(SA)$_3$ in the epoxy system has shown the decrease in the gelation time with increasing concentration(Figure 1).

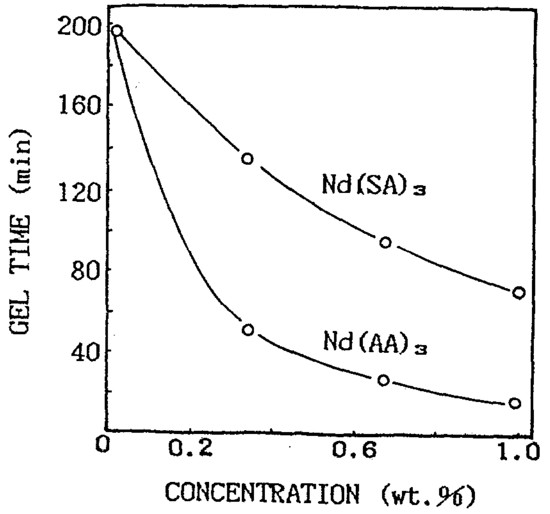

Fig.1. Dependence of gel time on concentration of accelerators.

For the cure reaction with and without the rare-earth compounds, the kinetic parameters: apparent activation energy E, preexponential A, rate constants at 150°C and 25°C respectively K_{150} and K_{25} were obtained from DSC data[6] and shown in Table 1. Appreciable latency is shown by these rare-earth compounds as demonstrated by these parameter data.

The addition of the rare-earth compounds gave rise to increase in the activation energy. That suggests the rate constants for RE ion-containing system are more sensitive to the temperature of cure. In other words, the acceleration effect of the rare-earth compounds only appears at elevated temperatures, but less or none so at lowered temperatures. Further it would be reasonably expected that the RE ion-containing epoxy resins will show more sluggish curing properties than the control resin does when the temperature of cure lowers to a critical point. This latency feature can be confirmed by K_{150}, K_{25} data and the gel time vs. storage time curves shown in Figure 2. From the data in Table 1, it can be seen that the rate constant at 150°C for RE ion-containing E-44/TOA systems is much higher than that for the control system, but there is the contrary at 25°C. Figure 2 shows the decrease in the gel time at 170°C with extending storage time at 40°C for Nd ion-containing system is more smooth than that for the control system. It is evident that the Nd(AA)$_3$/E-44/TOA system would be expected to display better storage stability at room temperature in comparison with the control system.

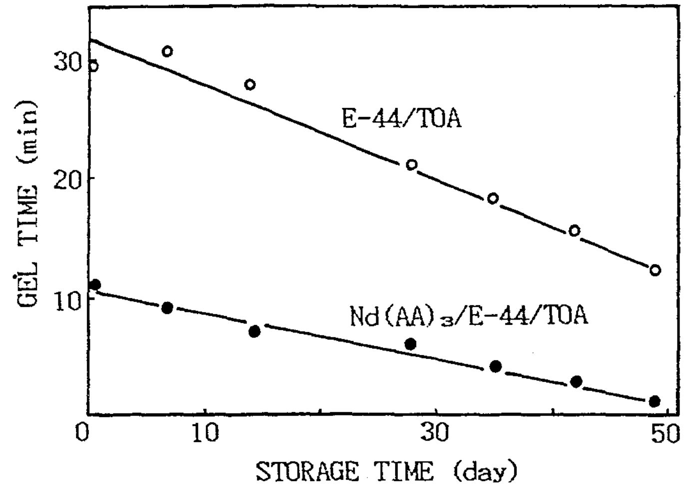

Fig.2. Gel time at 170°C vs. storage time at 40°C.

In regard to physical properties, the data of Tg, dielectric loss Tan δ, dynamic modulus E′ of the cured RE/E-44/TOA system and control are listed in Table 2 and the curves shown in Figure 3,4. The addition of RE ions to the epoxy resin caused a increase in the Tg value of the cured resins by 8 to 32 degrees (by DMA) and 7 to 26 degrees (by dielectric loss) depending on the RE compound species as a accelerator. The higher effective accelerator gave the more increase in the Tg value.

Table 2 Physical Properties of Cured RE Ion-containing Epoxies

RE compounds	Tg(°C)		Tan δ (%)			$E' \times 10^{-7}$ (dyne/cm^2)		
	By DMA	By Dielec.	37°C	130°C	155°C	25°C	130°C	155°C
control	58	58	2.03	5.75	34.42	660	5.5	6.5
La(AA)$_3$	90	84	0.47	1.55	9.65	831	12.5	13.2
Nd(AA)$_3$	86	83	0.46	0.73	3.00	636	14.9	15.6
Gd(AA)$_3$	86	70	1.00	3.50	22.53	716	15.1	15.8
Nd(SA)$_3$	78	72	0.72	6.50	9.50	789	11.0	12.1
Nd(Naph)$_3$	66	65	1.51	2.14	8.64	737	11.1	12.2

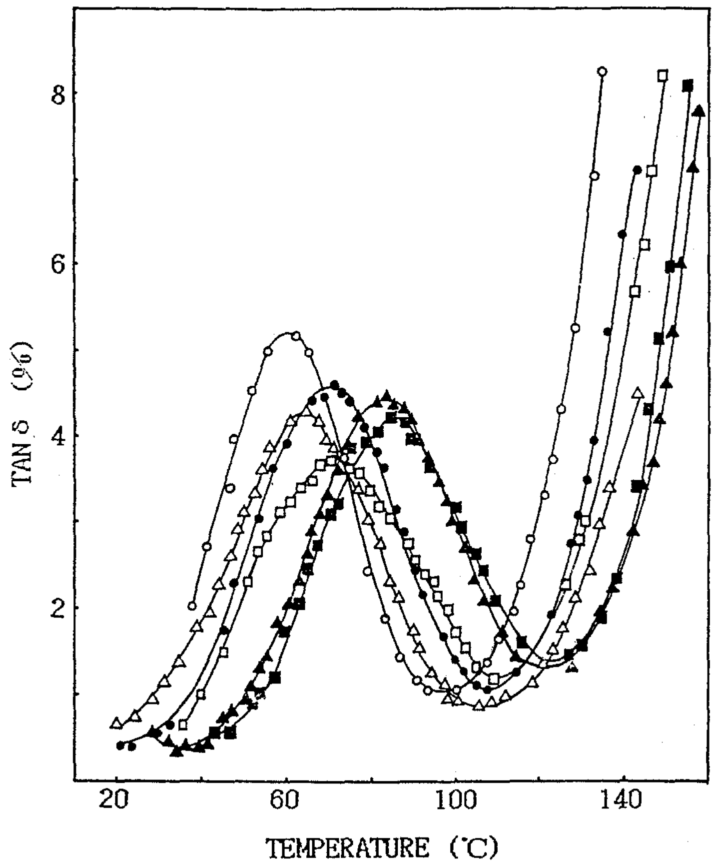

Fig.3. Dielectric loss spectra(60 Hz)
(○)Control; (△)Nd(Naph)$_3$; (●)Gd(AA)$_3$;
(□)Nd(SA)$_3$; (▲)Nd(AA)$_3$; (■)La(AA)$_3$.

The dielectric loss (Tan δ) values of five different RE ion-containing cured epoxies were depressed by 39% to 87% at 130°C except Nd(SA)$_3$/E-44/TOA and by 35% to 91% at 150°C and the dynamic modulus (E′) values were increased by 1 to 1.7 times at 130°C and by 0.86 to 1.4 times at 150°C as compared with the control. The dramatic improvement in the dielectric and mechanical properties at high temperature should be attributed to the higher glass transition temperature. It appears that the introduction of RE makes the epoxy/TOA system have fuller cure and higher Tg owing to more complete crosslinking or more homogeneous network structure$^{4)}$.

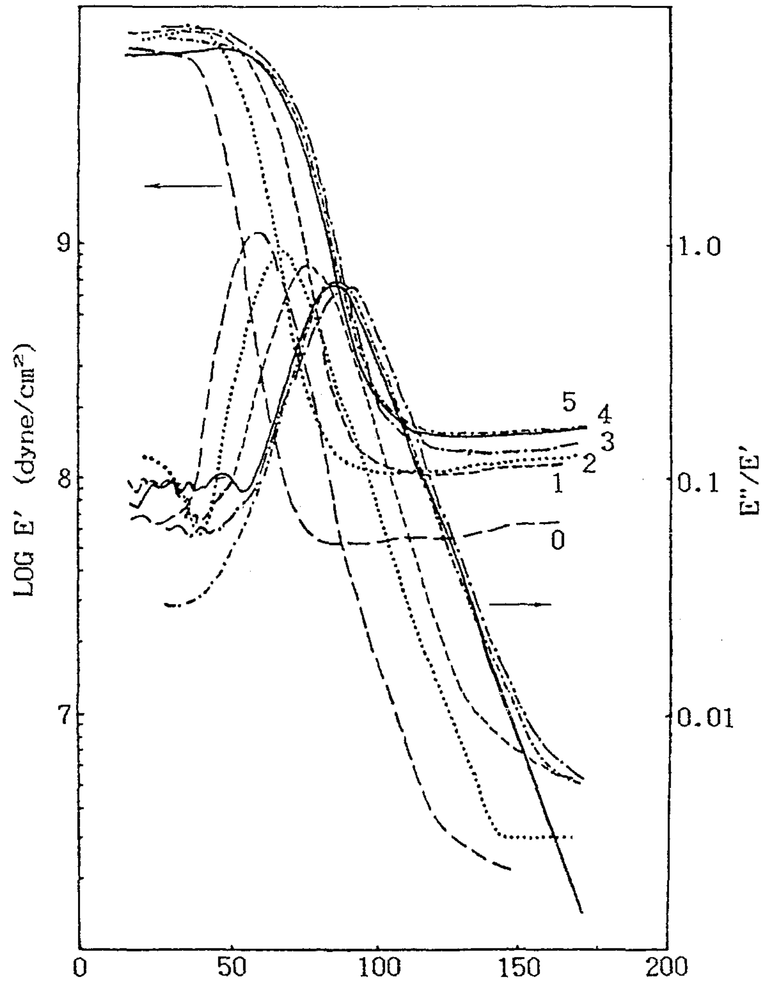

Fig.4. Dynamic mechanical spectra (3.5Hz)
0. Control; 1. Nd(SA)$_3$; 2. Nd(Naph)$_3$;
3. La(AA)$_3$; 4. Nd(AA)$_3$; 5. Gd(AA)$_3$.

The TGA thermograms for the cured Nd(AA)$_3$/E-44/TOA and the control system show that thermal stability of the cured Nd ion-containing epoxy is slightly higher than that of the control resin. The onset temperature of weight loss for the former is 2 degrees higher than that for the latter.

ACKNOWLEDGEMENT

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