

A Novel Latent Initiator for Cationic Polymerizations of Epoxides: Composite Catalysts Containing Aluminum Complexes Phase-Separated in Epoxides

S. MURAI, S. FUJIEDA, S. HAYASE

Corporate Research and Development Center, Toshiba Corporation, 1, Komukai-Toshiba-cho, Saiwai-ku, Kawasaki 212-8582 Japan

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ABSTRACT: A novel latent initiator for cationic polymerizations of epoxides heterogeneous aluminum complex/phenol initiator (HAP) is reported. Phase transitions are newly employed for realizing the latent property. The initiator consists of 4,4'-dihydroxydiphenylsulfone and aluminum tris(alkyl acetoacetate), with the alkyl group containing more than 18 carbons. The composite initiator is phase-separated and dispersed uniformly in epoxy resins at room temperature. When the mixture is heated to a temperature greater than 70°C, the composite initiator makes clear mixtures with epoxy resins because of the phase change in the aluminum complexes. Homogeneous epoxy resins containing these composite initiators are ready for various types of processing, including impregnation and injection. Gelation occurs rapidly at temperatures greater than 100°C. The phase change in the initiator makes it possible for the epoxy compounds to have a long storage stability at room temperature and a high curing speed at greater than 100°C. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1046–1053, 2002

Key words: latent catalysts; epoxy resins; aluminum complexes; storage stability; phase separation

INTRODUCTION

Epoxy resins have been used as insulation materials, coating materials, adhesives, and lamination materials.¹ Because initiators are generally incorporated into the epoxy resins, the viscosity of the epoxy resins increase, thus leading to a shortening of the storage life.

An increase in the curing rates has also been required for energy savings, but this contradicts the long storage stability of epoxy resin mixtures. Cationic polymerizations seem to be the most likely candidate for this purpose. Some sulfonium

salts are known to serve as latent initiators in cationic polymerizations triggered with heat or light. Triarylsulfonium salts are known to be initiators activated with lights, but they are not cured thermally.² Alkylsulfonium salts have been reported to decrease the initiation temperature for epoxy compounds, but the shelf life is not satisfactory.³ These sulfonium salts have excellent curing properties. However, the electrical properties of epoxy resins cured by these initiators are not satisfactory for the purpose of electrical insulators, especially at high temperatures over 100°C, because of the residual acid components leading to ionic impurities in the cured resin matrices.⁴ We have reported that epoxy resins cured by composite initiators containing either organic silanols and aluminum complexes

Correspondence to: S. Murai (shinji.murai@toshiba.co.jp).

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(AS initiators) or phenol compounds and aluminum complexes (AP initiators) have excellent electrical insulation properties both at room temperature and at elevated temperatures.^{4,5} The AP initiators have also been described in a patent.⁶ Although the storage stability of the AS initiator was improved by the use of alkoxy silanes instead of unprotected silanols, the latent property was not fully satisfactory.⁷

Our objective is to provide cationic initiators, based on AS or AP catalysts, that are excellent in their long-term storage stability and exhibit excellent curability. To realize latent catalysts, we need a mechanism to activate inert molecules. Chemical reactions have been commonly employed for the activation of inert initiators.^{3,5,8} We focused on another mechanism, activation caused by phase transitions. It is well known that phase transitions occur sharply on heating and are more sensitive to temperature than chemical reactions. In the course of our studies on AS composite catalysts, we have found that aluminum complexes bearing long alkyl chains of more than 18 carbons show phase transitions around 70°C and cause reversible phase separations in epoxy resins, depending on temperature. In this article, the mechanism of a novel latent catalyst and the relationship between the latent properties and catalyst structures are reported.

EXPERIMENTAL

General Procedures

Table I presents compound structures employed in this research. In this article, AP initiators that cause phase separations in epoxy resins at room temperature are named HAP (heterogeneous aluminum complex/phenol initiator). Aluminum tris(ethylacetoacetate) (Al-2) was commercially available and used after distillation. Ep1 (Celloxide 2021) was purchased from Daiseru Chemical Co. (Tokyo, Japan) and used without further purification. 4,4'-Dihydroxydiphenylsulfone (PhS) was commercially available and used after crystallization from toluene. The solvents were dried on CaH₂ and freshly distilled before use.

Synthesis of Aluminum Complexes

Various aluminum complexes were synthesized by the reaction of Al-2 with various long-chain alcohols. A representative method is as follows.

Table I Chemical Structures

	Al-2
	Al-16
	Al-18
	Al-22
	Ep1

Synthesis of Aluminum Tris(octadecyl acetoacetate) (Al-18)

Al-2 (98.4 g, 0.238 mol), octadecanol (202.3 g, 0.750 mol), and dry toluene (500 mL) were put in a four-necked, round-bottom flask equipped with a mechanical stirrer, a condenser, and a dry argon inlet. The mixture was heated to 120°C, and ethyl alcohol that formed with an ester-exchange reaction was removed continuously. Toluene was added to the reaction mixture to supply the amount of toluene removed with ethanol. The reaction was continued until the ethyl moiety of Al-2 disappeared. After the toluene was removed

under reduced pressure, the residue was recrystallized from hexane to give a white powder (213.2 g, 82.5%).

mp: 70.9°C. IR (KBr): 2920, 2854, 1609, 1539, 1520, 1470, 1410, 1319, 1292, 1176, 1000, 783, 719, 629, 501 cm^{-1} . $^1\text{H-NMR}$ (270 MHz, CDCl_3 , δ): 0.878 (t, $J = 6.20$ Hz, 18H), 1.15–1.40 (brs, 180H), 1.50–1.65 (m, 12H), 1.918 (s, 3H), 1.927 (s, 3H), 1.952 (s, 9H), 1.971 (s, 3H), 3.90–4.26 (m, 12H), 4.911 (s, 1H), 4.938 (s, 3H), 4.957 (s, 1H), 4.964 (s, 1H). ELEM. ANAL. Calcd. for $\text{C}_{66}\text{H}_{123}\text{O}_9\text{Al}$: C, 72.9%; H, 11.4%. Found: C, 72.9%; H, 11.0%.

Aluminum Tris(hexadecyl acetoacetate) (Al-16)

This complex was prepared in a manner analogous to that described previously. 1-Hexadecanol was employed instead of 1-octadecanol.

White powder. Yield: 82%. mp: 60.9°C. IR (KBr): 2920, 2854, 1607, 1547, 1520, 1470, 1412, 1319, 1292, 1178, 1067, 1000, 781, 629, 503 cm^{-1} . $^1\text{H-NMR}$ (270 MHz, CDCl_3 , δ): 0.880 (t, $J = 6.63$ Hz, 18H), 1.10–1.38 (brs, 156H), 1.50–1.65 (m, 12H), 1.925 (s, 3H), 1.932 (s, 3H), 1.954 (s, 9H), 1.974 (s, 3H), 3.98–4.10 (m, 12H), 4.909 (s, 1H), 4.936 (s, 3H), 4.952 (s, 1H), 4.961 (s, 1H). ELEM. ANAL. Calcd. for $\text{C}_{60}\text{H}_{111}\text{O}_9\text{Al}$: C, 71.8%; H, 11.1%. Found: C, 71.7%; H, 10.9%.

Aluminum Tris(docosyl acetoacetate) (Al-22)

This complex was prepared in a manner analogous to that described previously. Behenylalcohol was employed instead of 1-octadecanol.

White powder. Yield: 73%. mp: 80.9. IR (KBr): 2920, 2854, 1609, 1543, 1522, 1473, 1292, 1176, 1073, 1006, 785, 719 cm^{-1} . $^1\text{H-NMR}$ (270 MHz, CDCl_3 , mixture of trans and cis isomer, δ): 0.880 (t, $J = 6.63$ Hz, 18H), 1.17–1.38 (brs, 228H), 1.52–1.67 (m, 12H), 1.925 (s, 3H), 1.932 (s, 3H), 1.954 (s, 9H), 1.976 (s, 3H), 3.96–4.20 (m, 12H), 4.908 (s, 1H), 4.936 (s, 3H), 4.952 (s, 1H), 4.963 (s, 1H). ELEM. ANAL. Calcd. for $\text{C}_{78}\text{H}_{147}\text{O}_9\text{Al}$: C, 74.6%; H, 11.8%. Found: C, 74.6%; H, 11.4%.

Preparation of Epoxy Compounds

Aluminum complexes were dissolved in Ep1 at 100°C and then cooled to room temperature slowly with stirring to give a mixture named EpAl. Ep1 containing Al-22 or Al-18 became turbid at room temperature, whereas Ep1 containing Al-2 or Al-16 was completely clear or partially turbid, respectively. The phase separations of these aluminum complexes were stable and did

Table II Epoxy Resin Compositions

	Ep1	Al-2	Al-18	Al-22	PhS	SI-100L
EpComp1	100	0.5			3	
EpComp2	100		0.5		3	
EpComp3	100			0.5	3	
EpComp4	100					0.9

SI-100L is commercially available from Sanshin Chemical Co. (Yamaguchi, Japan). Sulfonium hexafluoroantimonate salts were also used.

not aggregate. PhS was dissolved separately in Ep1 at 100°C and was cooled at room temperature to give a transparent mixture named EpPhS. EpAl and EpPhS were mixed at room temperature with mechanical stirring. The phase separation was still stable. Compositions are summarized in Table II.

Determination of the Amount of Aluminum Complexes Dissolved in Ep1

The amount of aluminum complexes dissolved in Ep1 was monitored with emission spectra from the aluminum complexes.

The aluminum complex (2 g) and 100 g of Ep1 were mixed and heated to 100°C. After the mixture became homogeneous, the mixture was cooled to room temperature during stirring. The turbid mixture was centrifuged to obtain a clear liquid and a solid part. A certain amount of the clear liquid was taken out and diluted to 20 mL with tetrahydrofuran (THF). The fluorescence spectra were monitored with a Hitachi model F-3000 (Tokyo, Japan). The excitation was carried out with 350-nm light, and the emission was monitored at a rectangular geometry. The emission wavelength from these aluminum complexes in THF and Ep1 was 391 nm. To obtain the height of the emission from the aluminum complexes, we subtracted total emissions from the mixture of THF, Ep1, and aluminum complexes from those of Ep1 and THF. The amount of dissolved aluminum complexes was determined with a calibration curve obtained by emissions from THF solutions containing a known amount of aluminum complexes.

General Analysis

$^1\text{H-NMR}$ spectra were recorded on a JEOL model GSX-270 spectrometer, and all NMR data were reported in parts per million (δ) downfield from

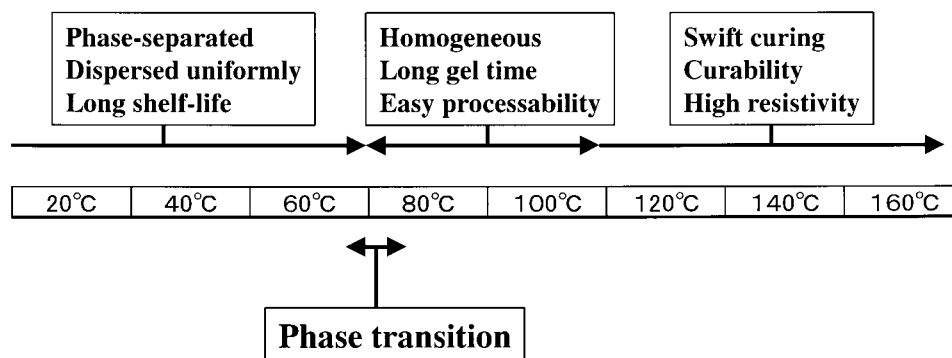


Figure 1 Concept for a novel latent initiator.

tetramethylsilane. IR spectra were obtained as KBr disks with a Hitachi FT/IR-7000 spectrometer. Thermal analyses were performed on a Seiko EXSTAR6000 thermal analyzer (Chiba, Japan) at a heating rate of 5°C/min for differential scanning calorimetry (DSC). The viscosity of each epoxy resin composition at a temperature of 25°C was measured with a Tokyo Keiki ELD viscometer (Tokyo, Japan). We evaluated the storage stability of the epoxy compounds by monitoring the increase in the viscosity of Ep1 stored at 30°C. The viscosity was measured at 25°C. The gelation time was evaluated by the measurement of the time when 0.5 g of the epoxy compounds on a thermostatic plate of a predetermined temperature gelled.

RESULTS AND DISCUSSION

Concept for a Novel Latent Initiator

Figure 1 shows a schematic illustration of the concept for our novel latent initiators. Below 70°C, the initiators are phase-separated and dispersed uniformly in epoxy resins. Therefore, the composition has long-term storage stability. On heating, the initiators exhibit phase transfers and become soluble in Ep1. Between 70 and 100°C, the mixture of the epoxy resins and initiators (the Ep-Init mixture) becomes transparent and homogeneous, which makes it possible to impregnate the Ep-Init mixture into clothes or to inject them into fine pores. Some increases in the viscosity of the Ep-Init mixture are observed when the Ep mixture is kept at these temperatures, but they do not cause swift gelation. The initiator is phase-separated again on cooling to room temperature. Therefore, the Ep-Init mixture provides excellent

processability. This feature differentiates our latent initiators from other heterogeneous latent catalysts such as microcapsulated cure accelerators, which cause rapid gelation and never get back to the original feature.⁹ The Ep-Init mixture cures swiftly over 100°C.

Phase Transitions for Aluminum Complexes

Figure 2 shows DSC curves for Al-18. The DSC measurement is started at 110°C. On heating, Al-18 has two endothermic peaks at 38.5 and 70.9°C. Under optical polarization microscopic examination, Al-18 has birefringence at room temperature. When this is heated to 50.0°C at a rate of 5°C/min, it becomes a fluid liquid with birefringence that disappears at 70.0°C. Fan textures and spherulitic domains are observed, as shown in Figure 3. This suggests that a mesophase, in which alkyl groups are possibly aligned with one another to make ordered structures.⁹ The precise characterization of the mesophase is underway. Similar phase transitions and ordered structures have been reported for alkanoates of Li, Na, K, Rb, Cs, and Tl.⁹ As an example of metal complexes exhibiting mesophases, copper complexes have been reported. Binuclear copper(II) alkanoates such as cupric octadecanoate (C16Cu), docosanoate (C18Cu), and tetracosanoate (C22Cu) exhibit phase transitions from crystal to a columnar mesophase over a temperature range of 30–200°C, which has been relevant to magnetic susceptibilities.¹⁰

Table III summarizes phase transitions for Al-C16, Al-C18, Al-C22, and the corresponding *n*-alkyl alcohols. Phase-transition temperatures from a crystal to a mesophase (T_1) and a mesophase to an isotropic liquid (T_2) increase with an increase in the number of the alkyl carbons. These peaks are reversible for many runs. T_1 and

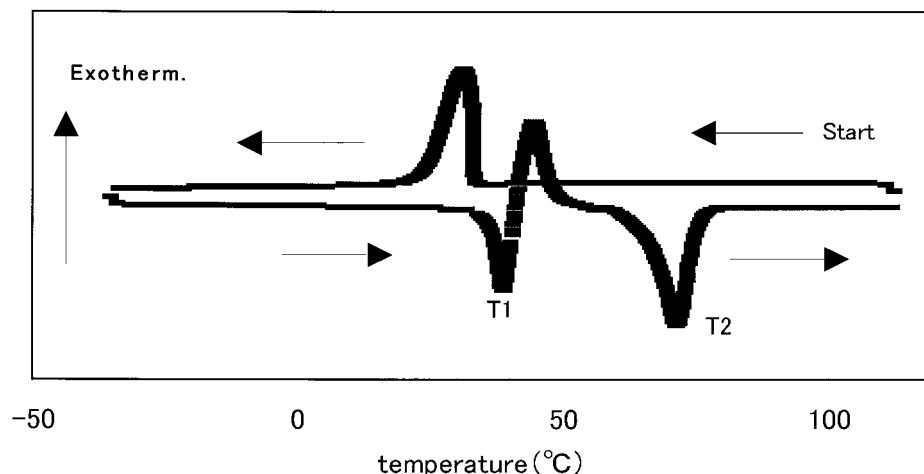


Figure 2 DSC curves for Al-C18. The data were taken after Al-C18 was heated to 100°C.

T_2 for Al-16, Al-18, and Al-22 are lower than those for copper compounds, and T_2 for copper compounds is not observed before decomposition, suggesting that these mesophases for the aluminum complexes are not as stable as those for the copper compounds.

These phase transitions are also observed for Al-C18 and Al-C22 dispersed in Ep1. Al-C16 is partially soluble in Ep1, and the phase transition is not observed clearly with DSC measurements. T_1 and T_2 for Al-18 dispersed in Ep1 decrease by several degrees compared with those for neat Al-C18, suggesting that Ep1 is partially incorporated into aligned alkyl groups and disturbs their alignments. Decreases in the value of the melting

enthalpy (ΔH) also suggest the disordering of these alkyl chains. In Ep1, the dispersed aluminum complexes become homogeneous at T_2 , the temperature at which a phase transition occurs from a mesophase to an isotropic liquid. This implies that the temperature from heterogeneous mixtures to homogeneous mixtures is associated with the phase-transition temperature of the aluminum complexes.

The amount of aluminum complexes dissolved homogeneously in Ep1 has been determined with the method described in the Experimental section. At room temperature, the amounts of Al-C16, Al-C18, and Al-22 contained in Ep1 are 70, 1.6, and 1.4 wt %, respectively. These data show that the solubility of the aluminum complexes in the epoxy resin is controllable with long-chain

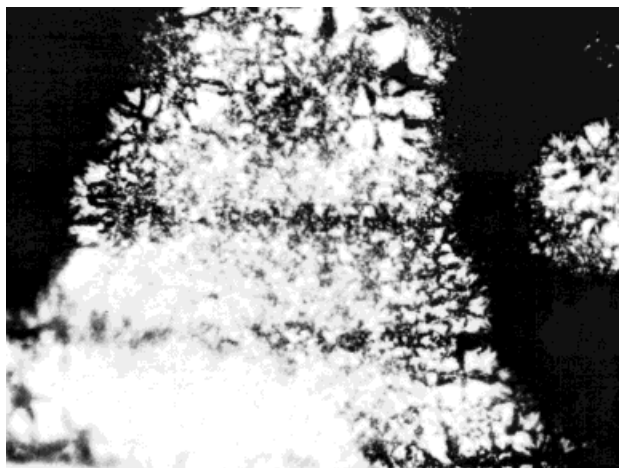


Figure 3 Birefringence observed with cross-polarized microscopy for Al-18 cooled from 76 to 50°C (original magnification, 200 \times).

Table III Phase-Transition Temperatures and ΔH for Aluminum Compounds

	T_1 (°C)	ΔH_1 (kJ/mol)	T_2 (°C)	ΔH_2 (kJ/mol)
Al-16	27.7	88.5	60.9	96.6
Al-18	38.5	40.4	70.9	135.9
Al-22	56.3	73.0	80.9	80.9
Al-18/Ep1	33.7	55.8	64.3	154
Al-22/Ep1	51.8	82.4	75.5	196.4
C16OH			53.3	65.7
C18OH			61.1	76.7
C22OH			74.5	94.7
C16Cu	116			
C18Cu	116			
C22Cu	119			

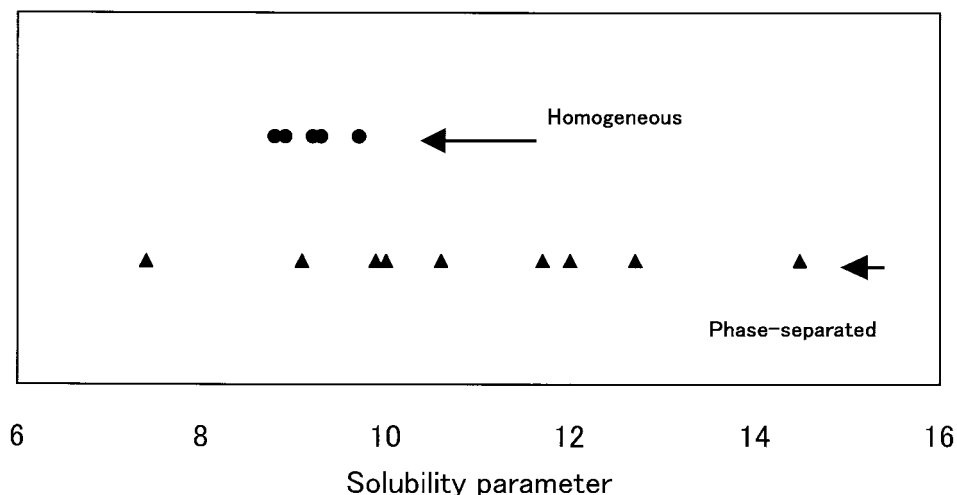


Figure 4 Relationship between the solubility parameter and solubility of Al-18 in Ep1: (●) Al-18 was soluble in the solvent at room temperature and (▲) Al-18 was phase-separated and dispersed uniformly in the solvent at room temperature.

substituents on the ligands of aluminum complexes. The solubility of aluminum complexes bearing alkyl groups of more than 18 carbon atoms is so low that almost all aluminum complexes are phase-separated and dispersed in Ep1 at room temperature.

The solubility of Al-18 in various solvents has been examined. Whether Al-18 is phase-separated at room temperature or not has been judged visually, and the data have been plotted against the solubility parameters for various solvents.¹¹ Figure 4 summarizes the results. Al-18 is phase-separated in various solvents with solubility parameters of more than 9.9 or less than 7.4. However, the aluminum complex is soluble in solvents with solubility parameters between 8.8 and 9.7. Solvents bearing carbonyl groups, such as ethyl acetate and methyl ethyl ketone, do not dissolve the aluminum complexes at room temperature, even though they have solubility parameters between 8.8 and 9.7. The solubility parameter for Ep1 has been reported to be 12, which is in the region of phase separation.¹¹

Catalyst Activity

Aluminum complexes have catalyst activity for ring-opening polymerizations of epoxides in the presence of a small amount of silanols or phenols.^{5,6} The catalyst activity greatly depends on the structures of the co-initiators.⁵ The relationship between the initiator activity and the structure of the initiators has been reported elsewhere

precisely.⁵ In this article, the representative properties of the novel latent initiator are reported with PhS as the co-initiator, which is one of the most active co-initiators among phenols and is easily purchased. We believe that the initiation mechanism for composite initiators containing aluminum complexes and phenols is the same as that for composite initiators containing aluminum complexes and silanols.⁵

Catalyst Activity at Temperature over 100°C

Table IV summarizes gelation times for EpComp3 containing Al-22 and EpComp1 containing Al-2, where both are homogeneous at temperatures above 100°C but the former is heterogeneous at room temperature and the latter is homogeneous at room temperature. The gel times at 150°C for EpComp2, EpComp3, and EpComp1 are considered to be in the same time regions, indicating that long alkyl groups do not retard the curing of epoxides because of their steric hindrance.

Table IV Gelation Times for Epoxy Resins Containing HAP

	Gel Time (s)		
	100°C	120°C	150°C
EpComp1	94	26	7
Epcomp2	90	30	9
Epcomp3	117	40	8

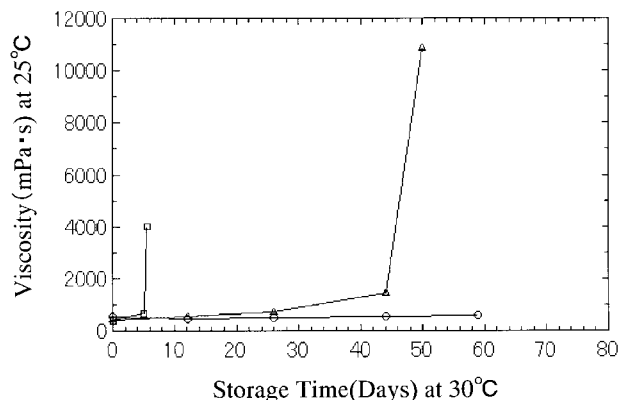


Figure 5 Shelf life for Ep1 containing various initiators: (□) EpComp1, (△) EpComp 2, and (○) EpComp3.

Shelf Life and Processability

Heterogeneous phenol compounds and aluminum complexes (HAP) initiators are phase-separated and dispersed uniformly in epoxy resins at room temperature, and epoxy compounds containing HPA initiators have excellent storage stability. Figure 5 shows the relationship between the viscosity and duration time when EpComp3, EpComp2, and EpComp1 are stored at 30°C. The viscosity for EpComp1 containing a homogeneous initiator (Al-2/PhS) increases steeply after 5 days. On the contrary, EpComp3 containing a heterogeneous initiator (Al-22/PS) is stable, and an increase in the viscosity is not observed for 59 days. EpComp2 is less stable than EpComp3. However, the viscosity is low for 44 days and then increases.

We also propose as a means for prolonging the storage stability of epoxy resins the microcapsulation of a cure accelerator before it is dispersed in an epoxy resin. In this case, epoxy resin mixtures containing the microcapsulated cure accelerator are heated at a temperature higher than a predetermined temperature to melt the capsule, thus allowing the cure accelerator to elute into the epoxy resin to promote the curing reaction of the epoxy resins. Microcapsulated cure accelerators also exhibit excellent storage stability, but they may not sufficiently penetrate the interior of the small pores, for example, in the case of glass cloth.¹² In that case, the interior of the insulating layer may not be sufficiently cured because of an insufficiency of the cure accelerator at the occasion of heating. HPA initiators become homogeneous at 70°C, at which temperature curing does not occur swiftly. It takes about 2 h for EpComp3 to gel. That time is enough for the processing mentioned previously.

Properties of Cured Epoxy Resins

One of the properties featuring AS and AP catalysts is the provision of a resin composition capable of exhibiting excellent electric properties at temperatures greater than 100°C. The excellent insulating properties are taken over by HAP catalysts. Figure 6 shows the relationship between temperature and resistivity for EpComp1 and EpComp3. The curing is carried out at 150°C for 1 h. The resistivity for EpComp3 is almost the same as that for EpComp1. These resistivities are better than for those cured with sulfonium salts. The same results have been reported before and explained by the absence of ionic impurities in the cured epoxy resin matrices.^{4,5} Cured EpComp1, EpComp3, and EpComp4 have glass-transition temperatures of 117, 126, and 117°C, respectively. These results show that the curability of Ep1 cured with HAP initiators is as good as that with the sulfonium initiators. Gel times and properties for epoxy resins cured with HAP catalysts are the same as those cured with homogeneous AP catalysts reported before.^{4,5}

CONCLUSIONS

A novel initiator employing a phase-transition mechanism has been proven to exhibit latent properties sufficiently. HAP initiators are phase-separated and dispersed uniformly in epoxy resins at room temperature and give excellent stor-

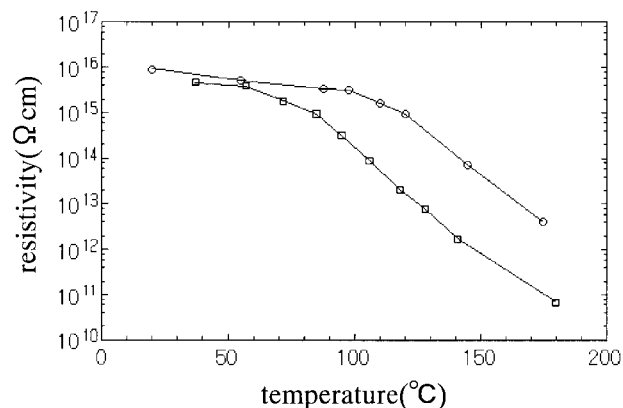


Figure 6 Relationship between temperature and resistivity: (○) resistivity for EpComp3 cured at 150°C for 1 h (with Al-18/PhS as the initiator; see Table II) and (□) resistivity for EpComp4 cured at 150°C for 1 h (with SI-100L as the initiator and sulfonium salts; see Table II).

age stability. On heating to 70°C, the phase of the HAP changes, and the phase-separated epoxy compositions become homogeneous. The catalyst activities at temperatures greater than 100°C are the same as those of homogeneous AP catalysts reported previously. The gel time at 70°C is 2 h, and the slow gel times enable the epoxy resin compositions to impregnate and fill small pores. We conclude that HPA initiators realize excellent long-term storage, swift curing, and sufficient curability and processability.

REFERENCES

1. (a) Lee, H.; Neville, K. *Handbook of Epoxy Resins*; McGraw-Hill: New York, 1967; (b) Kakiuchi, H. *Epokishi Jushi*; Shoko-do: Tokyo, Japan, 1977.
2. (a) Crivello, J. V.; Lam, J. H. W. *J Polym Sci Polym Chem Ed* 1979, 17, 977; (b) Crivello, J. V. *Annu Rev Mater Sci* 1983, 13, 173 and references therein.
3. (a) Nakano, S.; Endo, T. *Prog Org Coat* 1996, 28, 143; (b) Hamazu, F.; Akashi, S.; Koizumi, T.; Takata, T.; Endo, T. *J Polym Sci Part A: Polym Chem* 1991, 19, 1675; (c) Crivello, J. V.; Lockhart, T. P.; Lee, J. L. *J Polym Sci Polym Chem Ed* 1983, 21, 97; (d) Toneri, T.; Watanabe, K.; Sanda, F.; Endo, T. *Macromolecules* 1999, 32, 1293; (e) Pappas, S. P.; Hill, L. W. *J Coat Technol* 1981, 53, 43; (f) Barton, J. M.; Buist, G. J.; Hamerton, I.; Howlin, B. J.; Jones, J. R.; Liu, S. *J Mater Chem* 1994, 4, 379; (g) Ricciardi, F.; Romanchick, W. A.; Joullie, M. M. *J Polym Sci Polym Lett Ed* 1983, 21, 633.
4. Hayase, S.; Suzuki, S.; Wada, M.; Inoue, Y.; Mitsui, H. *J Appl Polym Sci* 1984, 29, 269.
5. (a) Hayase, S.; Onishi, Y.; Suzuki, S.; Wada, M.; Kurita, A. *J Polym Sci Part A: Polym Chem* 1987, 25, 753; (b) Hayase, S.; Onishi, Y.; Suzuki, S.; Wada, M. *Macromolecules* 1986, 19, 968; (c) Hayase, S.; Onishi, Y.; Suzuki, S.; Wada, M. *Nippon Kagakukai-shi* 1985, 328; (d) Hayase, S.; Onishi, Y.; Suzuki, S.; Wada, M. *Macromolecules* 1985, 18, 2778; (e) Hayase, S.; Onishi, Y.; Suzuki, S.; Wada, M. *J Polym Sci Polym Chem Ed* 1983, 21, 467; (f) Hayase, S.; Onishi, Y.; Yoshikiyo, K.; Suzuki, S.; Wada, M. *J Polym Sci Polym Chem Ed* 1982, 20, 3155; (g) Hayase, S.; Ito, T.; Suzuki, S.; Wada, M. *J Polym Sci Polym Chem Ed* 1981, 19, 2977; (h) Hayase, S.; Ito, T.; Suzuki, S.; Wada, M. *J Polym Sci Polym Chem Ed* 1981, 19, 2185.
6. Markovitz, M. U.S. Pat. 3,812,214 (1974).
7. Hayase, S.; Onishi, Y.; Suzuki, S.; Kurokawa, T. *Kobunshi Ronbunshu* 1984, 41, 581.
8. (a) Murai, S.; Nakano, Y.; Hayase, S. *Polym Prep Jpn* 1999, 48, 1059; (b) Murai, S.; Nakano, Y.; Hayase, S. *J Appl Polym Sci* 2001, 80, 181.
9. (a) Michels, J.; Ubbelohde, A. R. *J Chem Soc Perkin Trans 2* 1972, 1879; (b) Bonekamp, J.; Hegemann, B.; Jonas, J. *Mol Cryst Liq Cryst* 1982, 87, 13; (c) Busico, V.; Ferraro, A.; Vacatello, M. *Mol Cryst Liq Cryst* 1985, 128, 243; (d) Lindaue, J.; Hillmann, W.; Dorfler, H. D.; Sackmann, H. *Mol Cryst Liq Cryst* 1986, 133, 259.
10. (a) Abied, H.; Guillon, D.; Skoulios, A.; Giroud-Godquin, A. M.; Maldivi, P.; Marchon, J. C. *Colloid Polym Sci* 1988, 266, 579; (b) Abied, H.; Guillon, D.; Skoulios, A.; Weber, P.; Godquin, A. M. G.; Marchon, J. C. *Liq Cryst* 1987, 2, 269; (c) Giroud-Godquin, A. M.; Marchon, J. C.; Guillon, D.; Skoulios, A. *J Phys Lett* 1984, 45, L681; (d) Godquin, A. M. G.; Latour, J. M.; Marchon, J. C. *Inorg Chem* 1985, 24, 4452; (e) Strommen, D. P.; Godquin, A. M. D.; Maldivi, P.; Marchon, J. J. *Liq Cryst* 1987, 2, 689.
11. Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 2nd ed.; Wiley: New York, 1975; Chapter 4, p 337.