잠재성 양이온 경화제로서 methylanilinium 염에 의해 개시된 에폭시 수지의 경화 동력학 및 열적 특성

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Cure Kinetics and Thermal Properties of Epoxy Resin Initiated by Methylanilinium Salts as a Latent Cationic Curing Agent

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KEY WORDS : epoxy resin, thermal latent initiator, cure behavior, thermal properties

ABSTRACT

The effect of novel *N*-crotyl-*N,N*-dimethyl-4-methylanilinium hexafluroantimonate (CMH) curing agent on cure behavior and thermal properties of DGEBA epoxy cationic system was investigated. From DSC measurements of DGEBA/CMH system, it was shown that this system exhibits an excellent thermal latent characteristic in a given temperature and reveals complex cure behavior as indicated by multiple exotherms. The conversion and conversion rate of DGEBA/CMH system increased with increasing the concentration of initiator, due to high activity of CMH. Viscoelastic properties during gel formation of DGEBA with CMH were investigated by rheological techniques under isothermal condition. The gel time obtained from the modulus crossover point, $t(G')=G''$, was affected by high curing temperature and concentration of CMH, resulting in high degree of network formation in cationic polymerization. The thermal stabilities were discussed in terms of the activation energy for decomposition and thermal factors determined from TGA measurements.

1. INTRODUCTION

Epoxy resins are used extensively as high performance polymers in composites, coating materials, and encapsulations in the electronic industry. The thermo-mechanical properties of epoxy resin can be achieved by traditional thermal cross-linking with multifunctional amines and anhydrides as hardeners.[1] In case of epoxy/amine system, there are, however, some problems such as toxicity of amine, the deterioration of electrical properties at high temperature, humidity, and inherently brittle behavior.

Recently cationic polymerization of epoxy has been studied intensively.[2-5] In the cationic mechanism, the epoxy groups are opened by active hydrogen that is replaceable by a metal to produce a new physico-chemical bond or a hydroxyl group. The most common agents for cationic curing of epoxy resins are Lewis acids generally used as complexes with Lewis bases with BF_3-monoethylanine which is one of the most commonly used in commercial applications.[6] This complex overcomes the disadvantages of excessively rapid gelation, high hygroscopicity, and light instability.[1] Particularly, the development of latent catalyst for cationic polymerization is desirable for enhancement of both pot-life and handling of thermosetting resins.[7] Usually, the latent initiator forms active species by external stimulation such as heat and photo-irradiation.

The purpose of this work is to synthesize new *N*-crotyl -*N,N*-dimethyl-4-methylanilinium hexafluroantimonate initiator and to obtain a detailed and precise information concerning the cure behavior and thermal properties with using DSC, rheometer, and TGA.

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2. EXPERIMENTAL

Materials and Sample Preparation

Epoxy resin used in this work was diglycidylether of bisphenol A (DGEBA, LY556 supplied by the Ciba-Geigy Co.) which has epoxy equivalent weight of 187 g/eq. and viscosity of 12,000 cps). *N*-crotyl-*N*,*N*-dimethyl-4-methylanilinium hexafluroantimonate as a cationic initiator was synthesized with aniline derivatives and allyl choloride.[8] The chemical structure of product were confirmed by the ^{1}H-NMR and FT-IR as follow;

^{1}H-NMR (δ, ppm) : 7.83 (2H, dd), 7.49 (2H, dd), 6.11 (1H, m), 5.41 (1H, m), 4.56 (2H, d), 3.27(6H, s), 2.42 (3H, s), 1.70 (3H, d).

FT-IR : 2944, 1680, 1504, 967, 851, 662 cm^{-1}.

The structures of DGEBA and CMH are shown in Fig. 1.

The 0.5 (0.22), 1 (0.44), and 2 wt% (0.44 mol%) of CMH dissolved in acetone was added the DGEBA resin. All formulations were stirred in at room temperature and degassed under a vacuum for 1 h to remove bubble and residual organic solvents. The bubble-free mixture was poured into a stainless mold and cured at 70℃ for 30 min, 150℃ for 3 h, and 200℃ for 1 h.

Measurements

Latent properties of DGEBA/CMH system were performed by the measurements of conversion as a function of temperature using dynamic differential scanning calorimetry (DSC6, PerkinElmer DSC6). Cure behavior of the DGEBA/CMH system was investigated using DSC and rheometer. DSC experiments were carried out using isothermal and dynamic method, which was calibrated using indium and zinc. The samples were placed in aluminum sample pans and experiments were performed under a flow of dry nitrogen gas. Temperature scan were performed at 5℃/min heating rate from room temperature to 300℃, while isothermal experiments were done at 130℃.

The rheological measurements at isothermal conditions were monitored using Physica (RheoLab. MC100) with parallel plate geometry. The 500 mm disposal plates were preheated in the rheometer environmental chamber for approximately 10 min at setting temperature before tests. Experiments were performed at 5 Hz frequency, gab size between the plates of 0.5 mm, and 140, 150 and 160℃ curing conditions.

The thermogravimetric analysis (TGA) were performed in nitrogen using a TGA 951 DuPont analyzer at a heating rate of 10℃/min to investigate the thermal stability of cured resin.

3. RESULTS AND DISCUSSION

Thermal Behavior

The initiator that shows no activity under normal condition but shows activity by external stimulation, such as, heating and photoirradiation is called latent initiator.[9] The conversion for DGEBA/CMH system is shown in Fig. 2. The CMH initiates the polymerization at temperature more than 140℃. As a result, CMH have thermally stable latent initiator in a given temperature condition without any co-initiator.

Fig. 3 shows the dynamic DSC curves for the cure of DGEBA initiated by CMH. The main exotherms show three distinct peaks and move to lower temperature with increasing concentration of CMH. The main exotherm should be due to cationic initiation and polymerization of epoxy by the salts. The initiation species for methylanilinium salts are postulated to be the cation formed by dissociation of the C-N bond. Initiation proceeds to give a $H^{+}SbF_6^{-}$ and cyclic tertiary oxonium ions. Propagation would then continue through subsequent attack of epoxy groups. Propagation in cationic polymerization of epoxy can proceed by the activated chain-end (ACE) or activated monomer (AM) mechanism.[10] The appearance of three peaks for the main exotherm indicates complex behavior with the possibility of multiple cure reactions occurring simultaneously or sequentially.

Fig. 4 shows the conversion vs. time curves at 130℃ isothermal temperature. The α increases with increasing the concentration of CMH due to high activity of methylanilinium salts.

Rheological Properties

The cure of a thermosetting resin involves transformation of low molecular weight monomers or oligomers from the liquid to solid state as a result of the formation of a polymer network by chemical reaction of the reactive groups of the system.[11] Two stages, which are divided by a gel point, are usually distinguished in this process. An infinite network on polymer chains appears and develops only after the gel point.

In order to analyze the influence of temperature on the gel time, storage modulus (G') and loss modulus (G'') at isothermal conditions was monitored by using the parallel plate geometry. Typical G', G'' and loss tangent ($tan\delta$) profiles are reported in Fig. 5. The storage modulus (G') indicates the elastic character of the materials, and the loss modulus (G'') is related to the viscous response of the materials. The gel time is determined according to the time at intersect of storage and loss moduli, i.e., $G'=G''$ or $tan\delta=G''/G'=1$.[12] As an experimental result, the two moduli increase sharply at gel time and then gradually level off as the cure approaches completion.

Table I shows the gel time results at isothermal temperatures (140, 150 and 160℃) for DGEBA/CMH system. The gel time decreases with increasing the cure temperature because the high temperature leads to increase of the molecular mobility. Therefore, the curing reaction occurs more rapidly. The gel time of this system also shows the maximum value in 2 wt% CMH, and systematically decreases as CMH content decreases, due to reduction of active sites.

The chemical conversion obtained from gel time is considered a constant for a given system.[11] Considering that kinetic constant of the reaction is related to the temperature by an Arrhenius relationship, as follow;

$$\ln t_{gel} = \frac{E_c}{R} \cdot \frac{1}{T} + C \qquad (1)$$

where, t_{gel} is the gel time; E_a, the activation energy; R, the gas constant; and T, cure temperature.

In equation (1), a linear relationship between $\ln t_{gel}$ and the reciprocal temperature for isothermal curing reaction can be considered. From the slope of this relationship, the cross-linking activation energy (E_a) can be obtained, as listed in Table I. These give the activation energies of 74.6, 75.7, and 76.8 kJ/mol for 0.5, 1, and 2 wt% CMH, respectively. Values are in the same range with those reported for other cationically cured epoxy system; e.g., the value of 74. 1 kJ/mol in case of DGEBA/*N*-benzylpyrazinium hexafluoroantimonate (BPH) reported in previous work[13] and values ranging from 79.5 kJ/mol reported by Pappas[14] for the curing of a difunctional glycidylether cured with various alkylsulfonium salts. The values of activation energies are approximately the same for all epoxy/CMH systems studied, which indicate that the overall mechanisms are nearly same.

Thermal Stability

The TGA thermograms of the DGEBA cured with CMH in a nitrogen atmosphere are illustrated in Fig. 6. The residual weight fraction increases with increasing the concentration of CMH, which resulted from more developed network formation. This degradation of epoxy is induced by the etherification, a sort of side reaction, and subsequently proceeded via dehydration and finally resulted in the scission of network chains. The thermal stability given by initial decomposition temperature (IDT), temperature of maximum rate of weight loss (T_{max}) and integral procedural decomposition temperature (IPDT)[15] increase with increasing concentration of CMH, as shown in Table III. An increase of thermal stability may occur when the system is fully cured as the increase of active sites in high concentration of CMH.

Table I. Gel Times and activation energies of DGEBA/CMH Curing Systems

wt% of CMH	Reaction temperature	Gel time (t_{gel})	E_a (kJ/mol)
0.5 wt%	140	1007	74.6
	150	807	
	160	359	
1 wt%	140	720	75.7
	150	359	
	160	267	
2 wt%	140	572	76.8
	150	265	
	160	210	

4. CONCLUSION

In this work, the cure and thermal behavior of DGEBA initiated by CMH as a cationic latent initiator was studied using DSC, rheometer, and TGA. This system shows more than two type of reaction, and CMH can be act as an excellent thermally latent initiator for DGEBA cure without any co-initiator. The gel times obtained from rheological technique increase with increasing concentration of CMH, and can be correlated with the results of thermal stability of cured sample, which could be resulted from more developed network formation.

REFERENCES

(1) C. A. May, "Epoxy Resin", Marcel Dekker, New York, 1988.

(2) S. D. Lee, T. Takata, T. Endo, *Macromolecules*, **29**, 3317 (1996).

(3) I. I. Abu-Abdoun and A. Ali, *Eur. Polym. J.*, **28**, 73 (1992).

(4) S. J. Park, M. S. Cho, and J. R. Lee, *Polymer(Korea)*, **23**, 413 (1999).

(5) S. J. Park, M. K. Seo, and J. R. Lee, *J. Polym. Sci., Polym. Chem.*, **38**, 2945 (2000).

(6) N. Bouillon, J. Pascault, and L. Tighzerr, *Makromol. Chem.*, **191**, 1403 (1990).

(7) J. Gu, S. C. Narang, and E. M. Pearce, *J. Appl. Polym. Sci.*, **30**, 2997 (1985).

(8) J. H. Shin, J. Park, Y. Lee, and C. Lee, *Bull. Korean Chem. Soc.*, **21**, 157 (2000).

(9) Y. C. Kim, S. J. Park, and J. R. Lee, *Polym. J.*, 29, 759 (1997).

(10) S. Penczek, P. Kubisa, and K. Matyjaszewski, *Adv. Polym. Sci.*, **37** (1980).

(11) P. G. Babayevsky and J. K. Gillham, *J. Appl. Polym. Sci.*, **17**, 2067 (1973).

(12) C. M. Tung and P. J. Dynes, *J. Appl. Polym. Sci.*, **27**, 569 (1982).

(13) S. J. Park, T. J. Kim, and J. R. Lee, *J Polym. Sci., Polym. Phys.*, **38**, 2114 (2000).

(14) S. P. Pappas and L. W. Hill, *J. Coat. Technol.*, **53**, 43 (1981).

(15) C. D. Doyle, *Anal. Chem.*, **33**, 77 (1961).

Table II. Thermal Stabilities of DGEBA/CMH System

wt% of CMH	IDT (℃)	T_{max} (℃)	IPDT
0.5 wt%	342	446	506
1 wt%	372	448	565
2 wt%	373	450	594

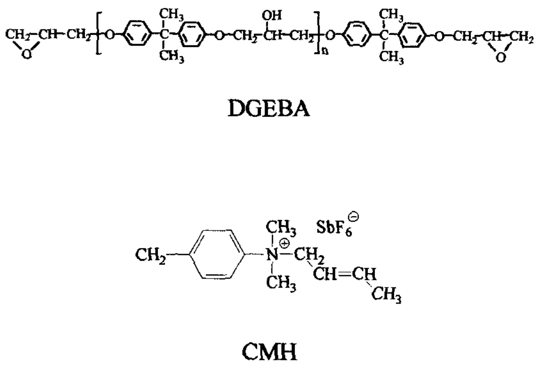

Fig. 1. Chemical structures of DGEBA and CMH.

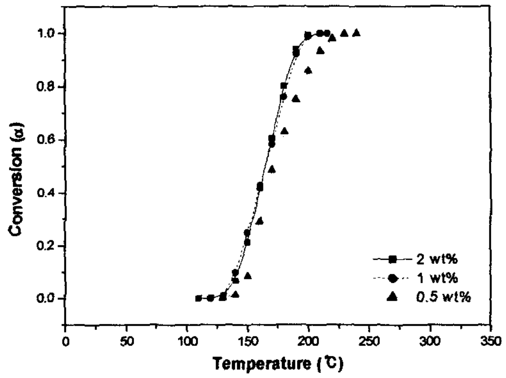

Fig. 2. Conversion of DGEBA initiated by CMH as a function of temperature.

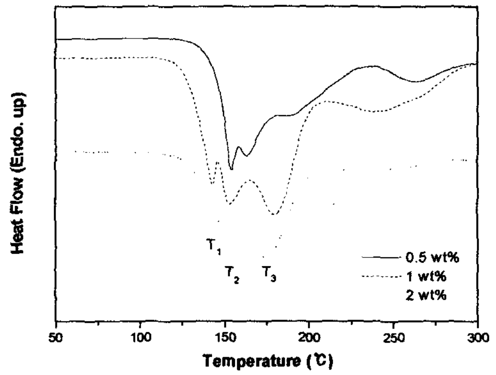

Fig. 3. Dynamic DSC thermograms of DGEBA/CMH system.

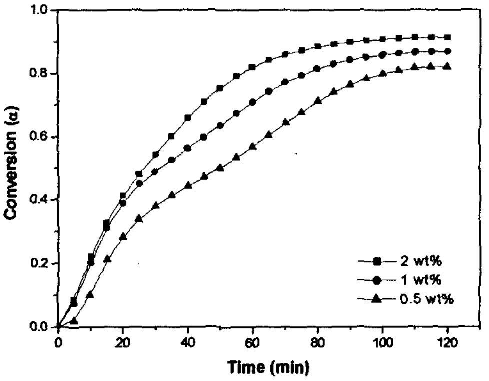

Fig. 4. Isothermal conversion of DGEBA initiated by CMH at 130℃.

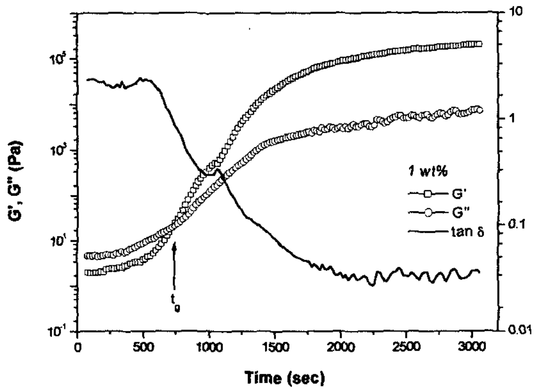

Fig. 5. Plots of G', G", and tanδ at 140℃ for DGEBA/CMH system.

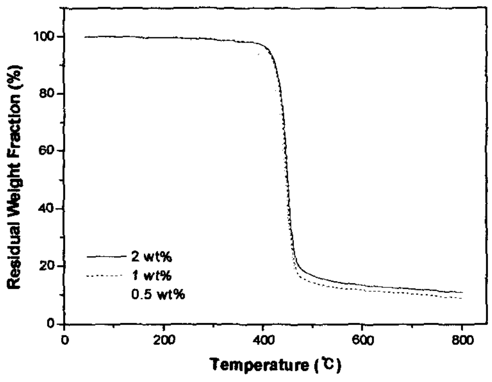

Fig. 6. TGA thermograms of DGEBA/CMH system.