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Communications to the Editor

Thermal Stability of Imidized Epoxy Blends Initiated by *N*-Benzylpyrazinium Hexafluoroantimonate Salt

Soo-Jin Park,*,† Hyun-Chel Kim, Hyung-Il Lee,‡ and Dong-Hack Suh‡

Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusong, Taejon 305-600, Korea, and Department of Industrial Chemistry, Hanyang University, 1 Haengdang, Seoul, 133-791, Korea

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Epoxy resins of bisphenol A (DGEBA) are extensively used as the structural adhesives in fiber composites for aircraft and also as the laminates in printed circuit boards or as the molding compounds for semiconductor encapsulations.[1,2] However, epoxy resins, initiated by a curing agent, often become brittle due to the inherent properties, resulting from the high degree of cross-linking during the process of self-polymerization. Hence, modification of epoxy resins has been the subject of intensive interesting research. For this reason, the blends of DGEBA and epoxy resins with high thermal properties have been interesting field due to the potential improvement in thermal properties of DGEBA.

In common epoxy/amine systems, there are some problems such as toxicity of amine, the deterioration of electrical properties at high temperature, humidity, and inherently brittle behaviors. In recent years, thus, the cationic polymerization of epoxide has been studied intensively.[3,4] The cationic epoxy formulations have long-term stability at room temperature in the absence of light and cure rapidly when exposed to high temperature. Particularly, the cationic epoxy system can improve the deterioration of electrical properties, which results from the hydrophilic character of the amine functional group in the epoxy/amine system.

In the cationic mechanism, the epoxy groups are opened by active proton (H^+) that is replaceable by a metal to produce a new physicochemical bond or a hydroxyl group. This catalyst is generally used as a complex, such as BF_3−ether, BF_3−amine, or SbF_6− epoxide. The complex overcomes the disadvantages of excessively rapid gelation, high hygroscopicity, and light instability. Particularly, the development of latent catalysts for cationic polymerization is desirable for the enhancement of both the pot life and handling of thermosetting resins.[5,6] Usually, the latent catalyst forms active species by external stimulation such as heat and photoirradiation.

The objective of this work is to study the effect of epoxy resin (EMPT) with high thermal properties on thermal stability of the DGEBA/EMPT system, initiated by cationic latent catalyst. The characterization of thermal stability for this system was monitored by thermogravimetric analysis (TGA).

The epoxy resin used in this study was the diglycidyl ether of bisphenol A (DGEBA, YD-128, supplied from Kukdo Chem. Co. of Korea). Another epoxy resin used was *m*-phenylenediaminebis(1,2,3,6-tetrahydro-3,4-epoxyphthalimide) (EMPT) which was synthesized using *m*-phenylenediaminebis(1,2,3,6-tetrahydro-3,4-epoxyphthalimide) (7.52 g, 0.02 mol) as a diimide in the Hanyang University lab.[7] The crude product was recrystallized in $CHCl_3$/ethyl alcohol (EA) (1/1) solution. Finally, the product was purified through column chromatography (70−230 mesh) using a $CHCl_3$/EA (1/4) solution as an eluent. The color of the product was white, and the yield was 4.0 g (49%). The purity and the chemical structures of the product were confirmed by infrared (FT-IR) spectroscopy, ^{1}H NMR, ^{13}C NMR, and elemental analysis as follows.

For FT-IR (KBr pellet): 3030 cm^{-1} (aromatic CH stretch), 1780 and 1710 cm^{-1} (imide C═O stretch), 1383 cm^{-1} (C−N stretch), 950−810 cm^{-1} (asymmetrical stretch or epoxide). For ^{1}H NMR ($CDCl_3$): δ 7.6−7.4 ppm

† Korea Research Institute of Chemical Technology.
‡ Hanyang University.
* Corresponding author. E-mail: psjin@pado.krict.re.kr.

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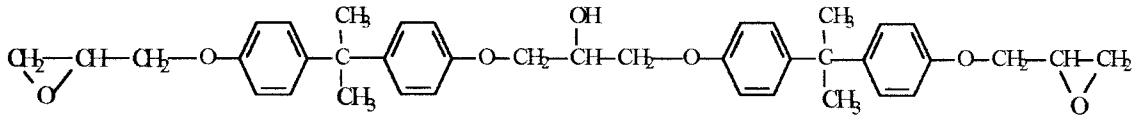
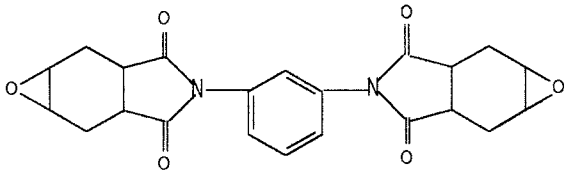
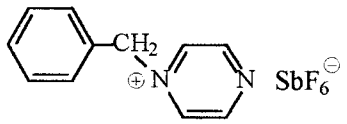


DGEBA



EMPT



BPH

Figure 1. Chemical structures of DGEBA, EMPT, and BPH.

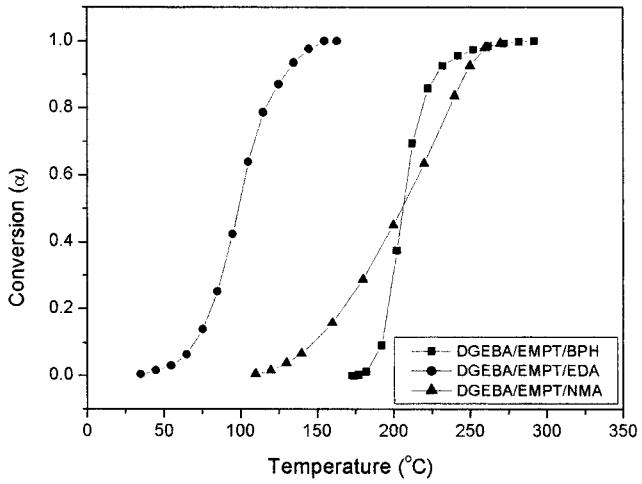


Figure 2. Conversion of DGEBA/EMPT with different curing agents, i.e., BPH, EDA, and NMA, as a function of curing temperature.

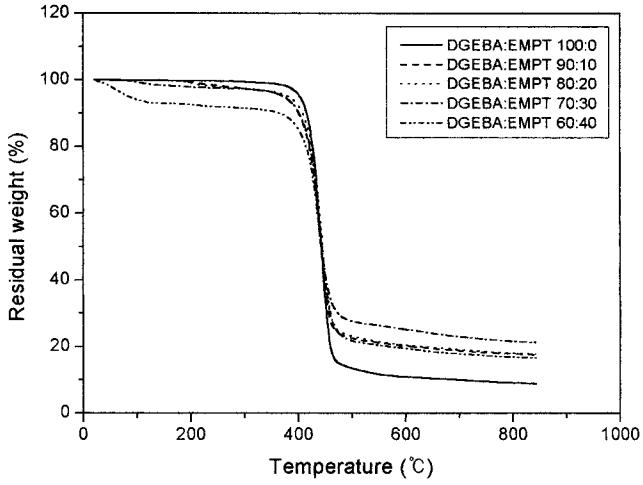


Figure 3. TGA thermograms of DGEBA/EMPT blend systems.

(aromatic 4H), δ 3.3 ppm (epoxide 4H), δ 3.0 ppm (aliphatic CH 4H), δ 2.8 and 2.4 ppm (aliphatic CH_2 8H). For ^{13}C NMR ($CDCl_3$): δ 50.68 ppm (epoxide), δ 179.12 ppm (carbonyl), δ 133.10, 129.38, 126.28, 124.58 ppm (aromatic), δ 35.58, 22.67 ppm (aliphatic). For elemental analysis: Calculated for $C_{22}H_{20}N_2O_6$: C, 64.7%; H, 4.9%; N, 6.9%; O, 23.5%. Found: C, 65.0%; H, 5.0%; N, 8.8%. For mass: 408 g/mol. For mp (DSC, 10 °C/min): 260−263 °C. The cationic latent catalyst (*N*-benzylpyrazinium hexafluoroantimonate, BPH) was synthesized throughout the recent work.[6,8] Figure 1 shows the structures of DGEBA, EMPT, and BPH.

The latent thermal properties of BPH for the epoxy blend system were characterized by measurement of conversion as a function of temperature. The relationship between temperature and conversion of epoxide with various curing agents for DGEBA/EMPT (60:40 wt %) is shown Figure 2. Ethylenediamine (EDA) shows activity under temperature less than 50 °C, and the activity of EDA increases with increasing experimental temperature. Meanwhile, BPH and nadic methyl anhydride (NMA) initiate the curing reaction at temperatures greater than 170 and 120 °C, respectively. However, BPH shows a significant increase in activity as the temperature increases, while the latency of NMA shows much lower activity than that of BPH in a range of experimental temperatures. As a result, the DGEBA/EMPT/BPH system has thermally stable latent properties at a given temperature conditions without any coinitiator.

For the thermal stability of the cured specimens, one of the basic requirements in the multicomponent epoxy system is to have a homogeneous mixture prior to the curing process. TGA thermograms of DGEBA prepared from blending by different contents of EMPT blends were superimposed in Figure 3. It is thus found that the decomposed residual weight of DGEBA/EMPT blends is somewhat increased as the EMPT content increases.

Meanwhile, it is generally accepted that reliable degradation temperature and kinetic parameters, such as the initial decomposed temperature (IDT), the temperature of maximum rate of weight loss (T_{max}), the integral procedural decomposition temperature (IPDT), and the activation energy for thermal decomposition (E_t), can be used to assess the thermal stability of the blend system. Among them, IPDT proposed early by Doyle[9] can be discussed in a quantitative thermal analysis containing the residual carbon yields of the resulting materials at high temperatures, whether TGA degradation is executed in a single process or multiprocess.

From the TGA results for determining the thermal stability factor of the blend system based on the Doyle's proposition, the IPDT is calculated using eq 1 as follows:[10]

$$\text{IPDT (°C)} = A^*K^*(T_f - T_i) + T_i \qquad (1)$$

Table 1. IDT and Thermal Stability Parameters for the DGEBA/EMPT Blend System

DGEBA/EMPT (wt %)	IDT (°C)	*A**	*K**	*A***K**	IPDT (°C)
100/0	403	0.5586	1.1865	0.7864	667
90/10	372	0.5832	1.4281	0.8329	708
80/20	381	0.5886	1.4301	0.8418	715
70/30	373	0.6121	1.5277	0.9352	789
60/40	84	0.5607	1.4195	0.7959	675

where A^* is the area ratio of total experimental curve divided by total TGA thermogram, K^* the coefficient of A^*, T_i the initial experimental temperature (30 °C), and T_f the final experimental temperature (850 °C).

The results of IDT and IPDT parameters (A^* and K^*) of thermal stability are listed in Table 1. As a result, the IDT is somewhat decreased from 403 to 372 °C between neat DGEBA and 30 wt % EMPT in the DGEBA blend system. This is attributed to the free gasification of low weight molecules of the blends as the temperature increases. Meanwhile, a significant decrease of IDT is shown in the case of the 40 wt % EMPT in DGEBA. This is a consequence of the weakening of cross-link density in the DGEBA/EMPT blend system, resulting from the presence of unreactive moieties in EMPT,[7] as seen in Figure 3. Especially, the IPDT evolution of the DGEBA/EMPT blend system is studied, as shown in Table 1. This result clearly indicates that the IPDT is systematically increased with increasing the EMPT content, up to 30 wt %. However, a marginal decrease is observed in the 40 wt % EMPT to DGEBA, as mentioned in the IDT results. It is then found that the addition of 30 wt % EMPT in DGEBA can lead to a more highly IPN structure in the DGEBA/EMPT/BPH blend system.

In summary, *N*-benzylpyrazinium hexafluoroantimonate (BPH) used as an initiator has good thermal latent properties in the DGEBA/EMPT blend system. The integral procedural decomposition temperature (IPDT) is increased with increasing the EMPT to neat epoxy resin up to 30 wt % of EMPT. However, the presence of 40 wt % EMPT in this blend system leads to the decrease of IPDT to be studied. This probably resulted from the lack of bulk side groups, including a long repeat unit and stable aromatic ring of DGEBA.

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