

# Thermal Stability and Compatibility of Epoxy/Polycarbonate and Epoxy/Tetramethyl Polycarbonate Blends

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## SYNOPSIS

A series of the blends of tetrafunctional epoxy resins with polycarbonate (PC) or tetramethyl polycarbonate (TMPC) was prepared to investigate thermal stability and compatibility. The  $T_g$  behavior as a function of isothermal curing time was observed. The thermal stability of epoxy and epoxy/thermoplastics blends was estimated using thermogravimetric analysis (TGA). Fourier transform infrared (FTIR) investigation demonstrated the occurrence of thermal degradation and hydrolysis in epoxy and epoxy/PC blends during the curing process. The thermal degradation of cured epoxy was induced with etherification, a sort of side reaction, and resulted in the chain scission of networks leading to the decrease of  $T_g$ . The variance of thermal stability with a combination of two components in these blends resulted from the difference of the compatibility due to chemical structure similarity. The compatibility was corroborated with the morphology by scanning electron microscopy (SEM). © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Epoxy resins are one of the most important thermosetting polymers and possess such desirable properties as high tensile strength and modulus, good thermal and chemical resistance, and dimensional stability. Especially, there is an ever-increasing demand for high-performance composites, primarily for aerospace application. However, they have one major drawback: They are inherently brittle and have poor impact fracture strength.<sup>1</sup> The toughness of epoxy resins has been increased by blending them with reactive liquid rubbers or tough engineering plastics. Rubber toughening of epoxy, predominantly using amino- and carboxyl-terminated butadiene-acrylonitrile elastomers, increased the fracture toughness.<sup>2,3</sup> However, the improvements of these rubber-modified materials are invariably accompanied by a significant drop in the modulus and glass transition temperature ( $T_g$ ).<sup>4-6</sup> For this reason, an alternative approach has recently been devised to

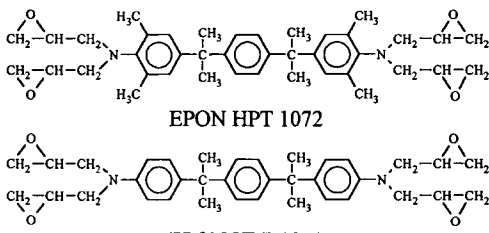
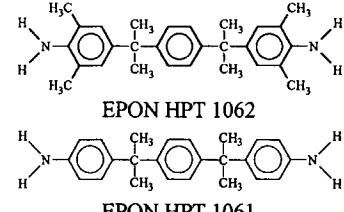
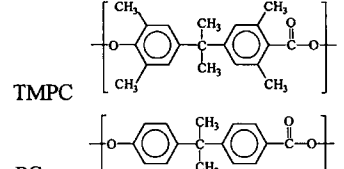
improve the toughness of highly crosslinked resins, based on the incorporation of tough, ductile, and thermally stable engineering plastics such as polyethersulfone and polyetherimide.<sup>7-11</sup>

Generally, all these materials are two-phase systems. In the case of these incompatible blend systems, phase separation takes place via the spinodal decomposition induced by the increase in the molecular weight of the epoxy as the cure reaction proceeds.<sup>12,13</sup> Many systematic studies on phase-separation phenomena in the binary mixtures have been done through light-scattering study and morphological analysis. Other studies on the toughening effect and mechanical properties have proceeded actively together. On the other hand, information on the compatible blend with molecular structure similarity between the thermosetting resins and the polymeric modifiers has rarely been reported.

This article concerns the blending of a tetrafunctional epoxy resin with structurally similar thermoplastics such as polycarbonate or tetramethyl polycarbonate. We observed the thermal degradation of epoxy resins and epoxy/thermoplastics blends that occurred during the curing reaction by FTIR spectroscopy and established the

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**Table I The Structures of Materials Used in This Study**

Description	Structure
Epoxy resin	 <p>EPON HPT 1072</p> <p>EPON HPT 1071</p>
Curing agents	 <p>EPON HPT 1062</p> <p>EPON HPT 1061</p>
Thermoplastics	 <p>TMPC</p> <p>PC</p>

chemical mechanisms. By investigation of the thermal stability, the effect of chemical structure similarity on the compatibility of the blends was observed. The compatibility was corroborated by a morphological investigation by scanning electron microscopy (SEM).

## EXPERIMENTAL

### Materials

The two epoxy resins used in this study were EPON HPT 1071 and 1072. Aromatic diamines, EPON HPT 1061 and 1062, were used as the curing agents. All materials were supplied by the Shell Chemical Co. The polycarbonate, LEXAN 121, was a com-

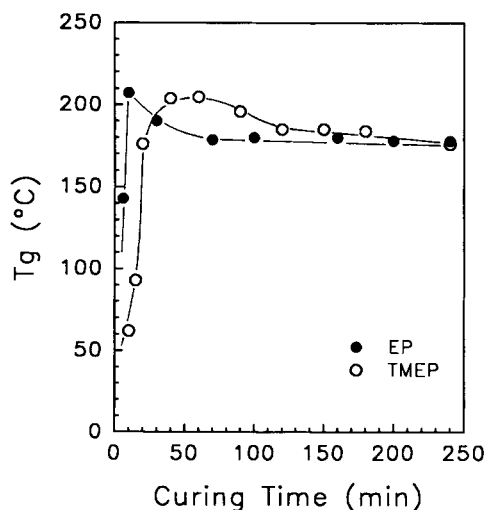
mercial product of General Electric with a molecular weight ( $M_w$ ) of 30,000. The tetramethyl polycarbonate (TMPC) was supplied by Bayer. These materials were used as supplied without further purification. Characteristics and structures of the chemicals used in this study are presented in Table I.

### Sample Preparation

In all the systems under study, the stoichiometric ratio of epoxy to the amine curing agent was maintained to unity. Two different compounds of epoxy resin and the curing agent were prepared: One was EPON HPT 1071/1061 (named EP in this article), and the other, EPON HPT 1072/1062 (named TMEP here). They differ in the types of chemical structure: one with the tetramethyl group and the

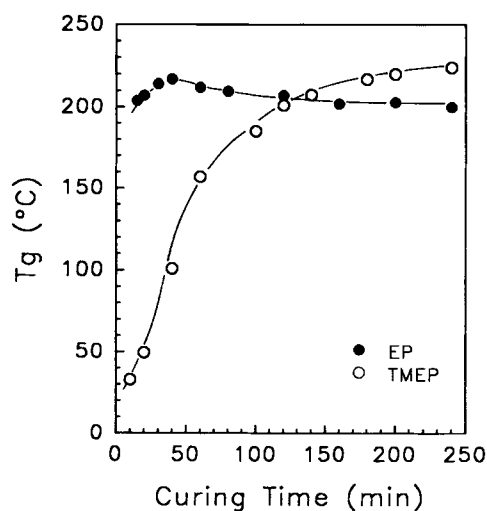
**Table II Blend Systems Prepared in This Study**

Epoxy	Curing Agent	Thermoplastic	Blend
EPON HPT 1071	EPON HPT 1061	PC	EP/PC
EPON HPT 1071	EPON HPT 1061	TMPC	EP/TMPC
EPON HPT 1072	EPON HPT 1062	PC	TMEP/PC
EPON HPT 1072	EPON HPT 1062	TMPC	TMEP/TMPC

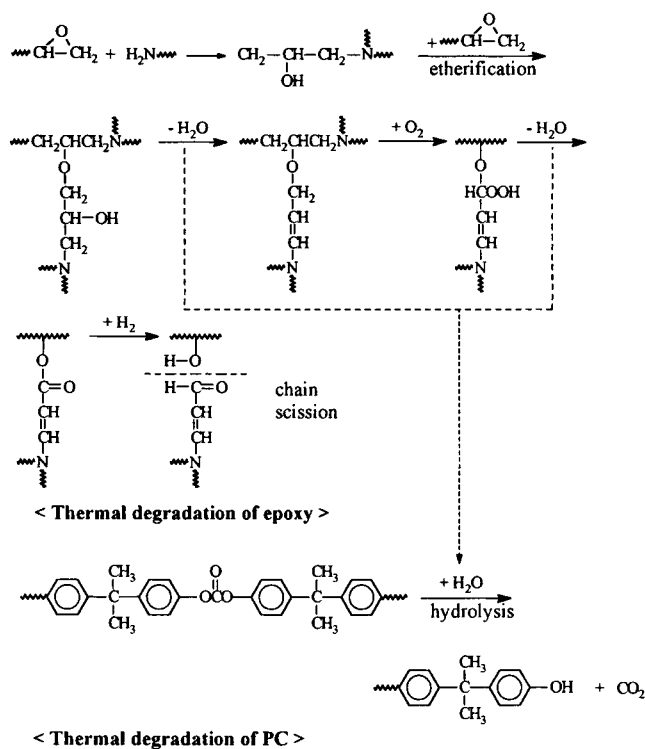


**Figure 1**  $T_g$  behavior of epoxy for isothermal curing at 230°C.

other without it. Four blend systems were prepared by changing the type of engineering plastics to control the molecular structure similarity and they are presented in Table II. The epoxy and thermoplastics were dissolved at 5 wt % of the total polymers in dichloromethane. The film was cast from the prepared solution mixture and dried under a vacuum for 72 h to remove the residual solvent. The film was inserted into a heating stage followed by an isothermal curing process at 200 and 230°C. The cured specimens thus obtained were investigated by DSC, TGA, FTIR, and SEM.



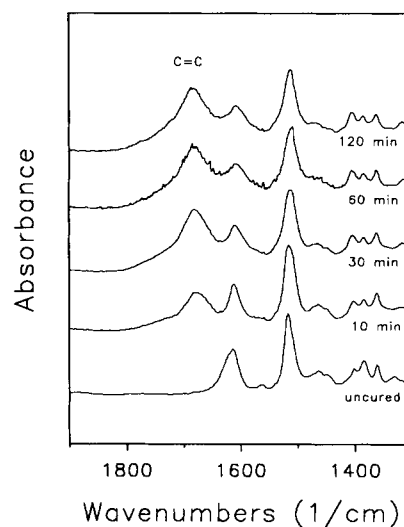
**Figure 2**  $T_g$  behavior of epoxy for isothermal curing at 200°C.



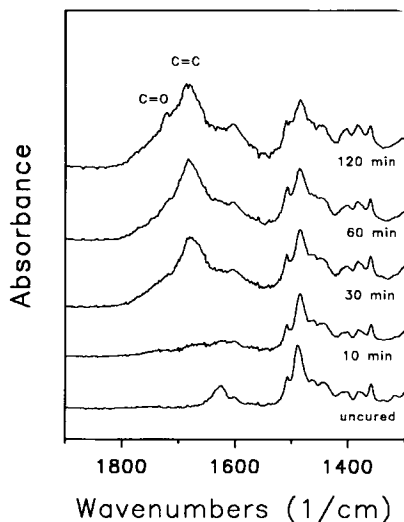
**Figure 3** Thermal degradation of epoxy/PC blend.

### Thermal Analysis

The DSC thermograms were obtained using a DuPont 9900 differential scanning calorimeter on 5–7 mg samples at a heating rate of 10°C/min. The specimens were cured isothermally at 200 and 230°C under  $N_2$  gas for each given curing time.  $T_g$  was determined as the onset point in the DSC curve. For



**Figure 4** Change of FTIR spectra of EP as a function of time for isothermal curing at 230°C.

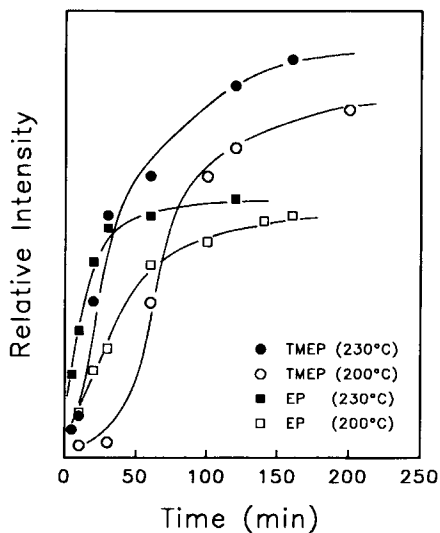


**Figure 5** Change of FTIR spectra of TMEP as a function of time for isothermal curing at 230°C.

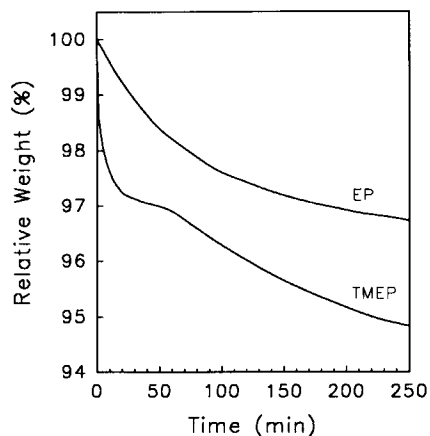
the thermogravimetric analysis, a Perkin-Elmer TGA 7 was used to measure the relative weight during the curing reaction under an isothermal condition. The measurements were performed on 10–12 mg samples at 230°C.

#### FTIR Spectroscopy

Infrared spectra were obtained at a resolution of 2 cm<sup>-1</sup> with a Mattson 5000 FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The wavenumber range scanned



**Figure 6** Normalized double-bond intensity, 1681 cm<sup>-1</sup> absorbance band as a function of time for isothermal curing at 230 and 200°C.

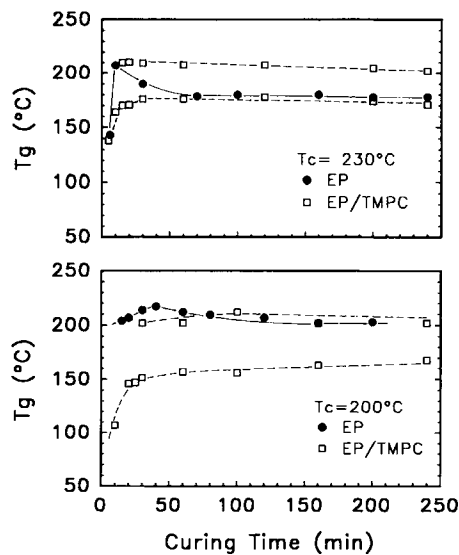


**Figure 7** TGA thermogram of epoxy for isothermal curing at 230°C. (A) EP; (B) TMEP.

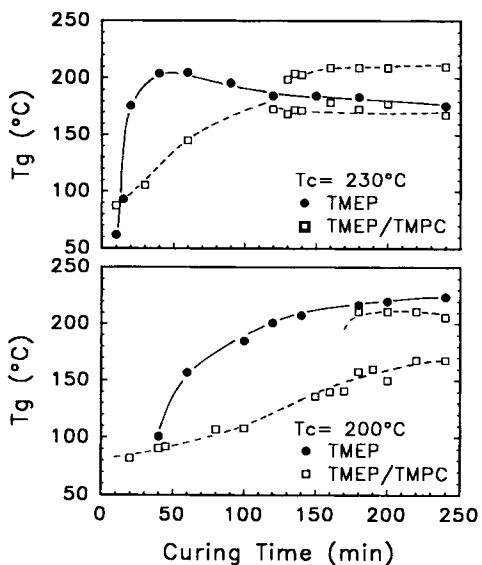
was 4000–400 cm<sup>-1</sup>. In the spectral analysis, the aromatic stretching absorbance band at 1510 cm<sup>-1</sup> was used as an internal standard band. The frequency scale was internally calibrated with a reference He—Ne laser to an accuracy of 0.02 cm<sup>-1</sup>. The measurements were carried out with thin films cast on KBr disks with an isothermal curing process. For investigation of thermal degradation, we used a heating stage under N<sub>2</sub> gas driven by a Hanyoung DX9 temperature controller to an accuracy of ±0.1°C.

#### Morphology

The epoxy/thermoplastic blend samples prepared by a solution-casting method were fractured in liquid



**Figure 8**  $T_g$  behavior of EP/TMPC (50/50) blend for isothermal curing at 200 and 230°C.



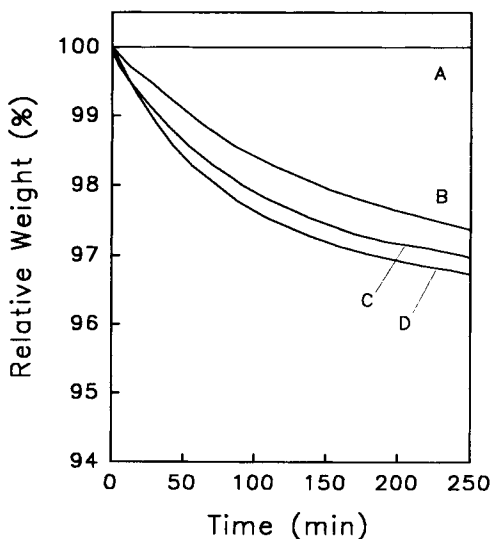
**Figure 9**  $T_g$  behavior of TMEP/TMPC (50/50) blend for isothermal curing at 200 and 230°C.

nitrogen and coated with gold. The fractured surfaces were observed by a JEOL JSM-840A scanning electron microscope (SEM).

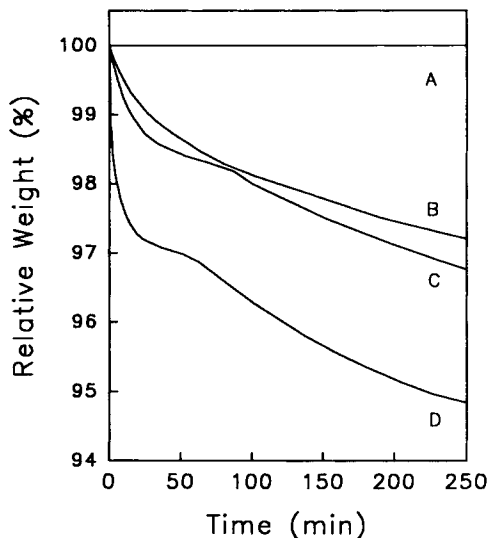
**RESULTS AND DISCUSSION**

**Thermal Degradation of Epoxy During Curing Process**

Figures 1 and 2 show the glass transition temperatures as a function of curing time for the samples

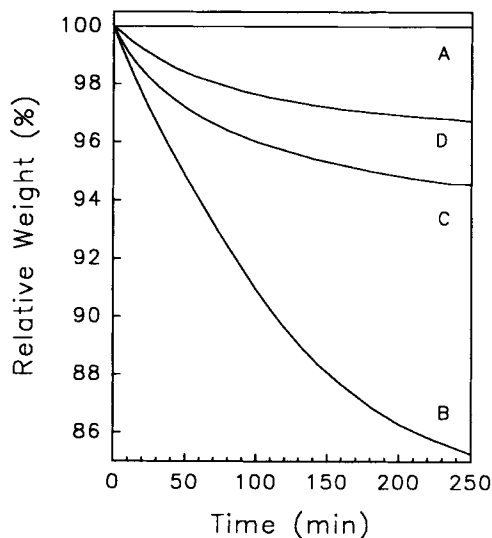


**Figure 10** TGA thermogram of EP/TMPC blend for isothermal curing at 230°C: (A) TMPC; (B) EP/TMPC (50/50); (C) EP/TMPC (75/25); (D) EP.

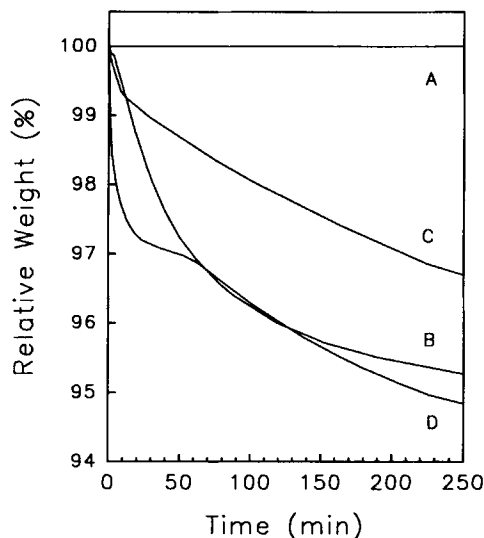


**Figure 11** TGA thermogram of TMEP/TMPC blend for isothermal curing at 230°C: (A) TMPC; (B) TMEP/TMPC (50/50); (C) TMEP/TMPC (75/25); (D) TMEP.

cured isothermally at 230 and 200°C, respectively. As the curing reaction proceeds,  $T_g$  increases due to increase of molecular weight in both EP and TMEP systems. After reaching the maximum  $T_g$ , their values decrease since the thermal degradation took place especially at high temperature, 230°C. The thermal degradation occurring during curing leads to a decrease in  $T_g$ . Therefore, increasing and decreasing behaviors in  $T_g$  due to the curing reaction and thermal degradation can actually be overlapped in some range of curing time. The measured  $T_g$  re-



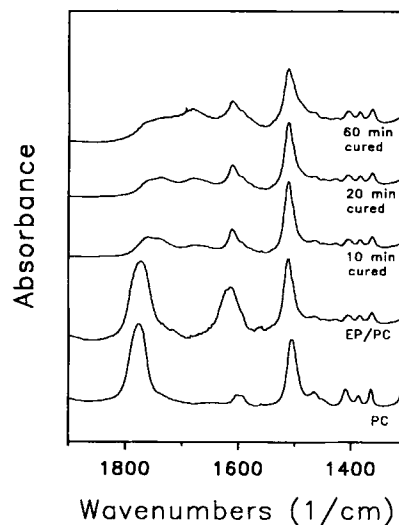
**Figure 12** TGA thermogram of EP/PC blend for isothermal curing at 230°C: (A) PC; (B) EP/PC (50/50); (C) EP/PC (75/25); (D) EP.



**Figure 13** TGA thermogram of TMEP/PC blend for isothermal curing at 230°C: (A) PC; (B) TMEP/PC (50/50); (C) TMEP/PC (75/25); (D) TMEP.

sulted from dominance in the competitive behaviors depending on the curing rate. In the case of EP, the curing reaction proceeded faster and the thermal degradation began earlier than those of TMEP; hence, decreasing behavior in  $T_g$  was conspicuous. In the case of TMEP cured at 200°C whose curing reaction was slowest, the  $T_g$  increased continuously with curing time, meaning that there is no significant thermal degradation at this condition.

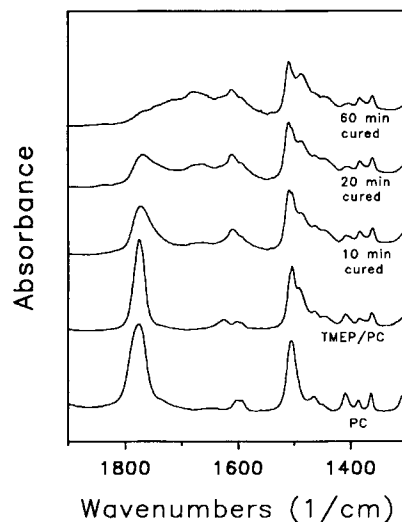
Thermal degradation was induced by the etherification, a sort of side reaction, and subsequently proceeded via dehydration and thermal oxidation and finally resulted in the scission of network chains. The degradation scheme based on the proposal by Neiman and co-workers<sup>14,15</sup> is shown in Figure 3. In the degradation process, the remarkable structural change is the production of double-bond (C=C) linkage and the carbonyl group (C=O) by dehydration. The FTIR spectra obtained as a function of curing time for the samples cured isothermally at 230°C verify these changes and are shown in Figures 4 and 5. Figure 4 gives the FTIR spectra of EP in the range 1300–1900  $\text{cm}^{-1}$ . Absorption due to the C=C double-bond stretching band is observed at about 1680  $\text{cm}^{-1}$  and the intensity increases gradually with curing. In Figure 5, the FTIR spectra of TMEP shows, in addition to a double-bond band, a small shoulder peak at 1732  $\text{cm}^{-1}$  which is responsible for the carbonyl stretching vibration. In comparison with EP, these peaks indicate that dehydration is relatively conspicuous for TMEP except for the initial stage of curing. Consequently, the de-



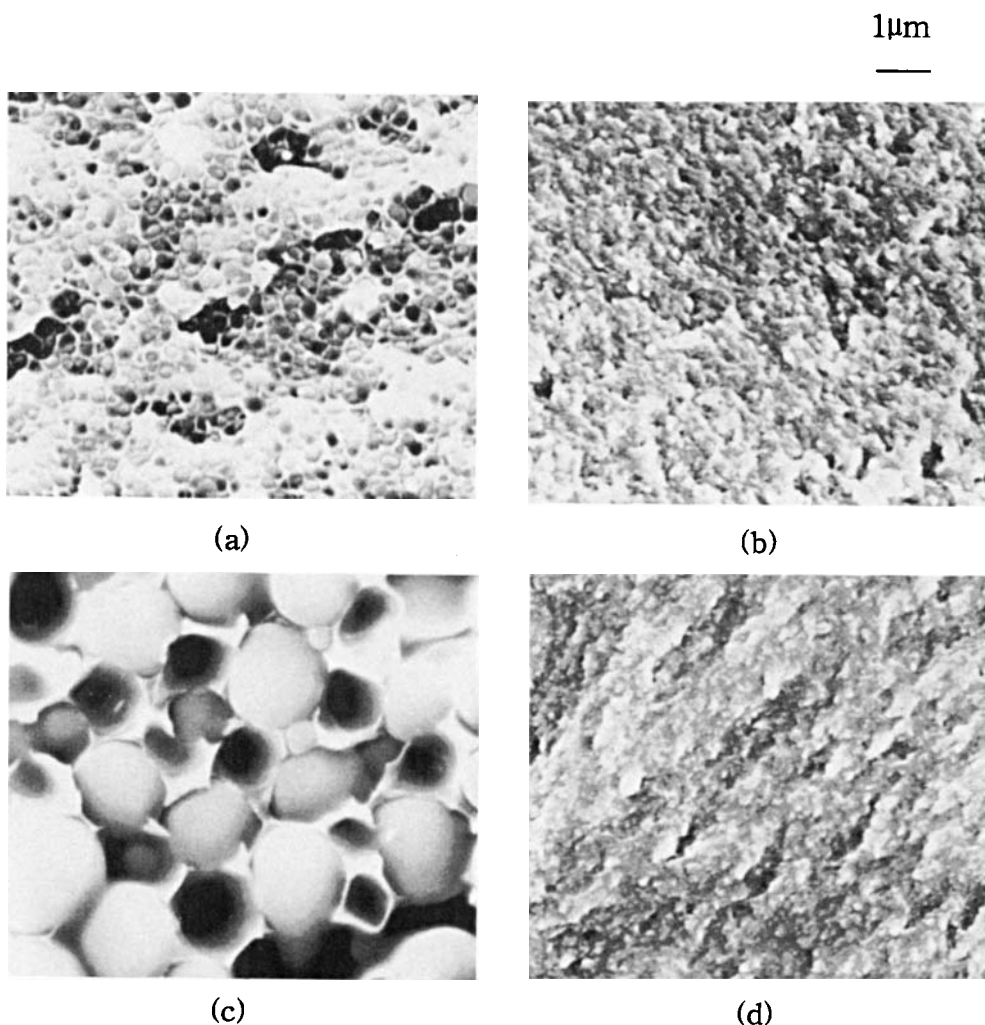
**Figure 14** Change of FTIR spectra of EP/PC (50/50) blend as a function of time for isothermal curing at 230°C.

gree of thermal degradation of TMEP is higher than that of EP. Experimental results at 200°C show the same trend with the data at 230°C. Figure 6 presents the intensity of the double-bond stretching absorbance band at 1680  $\text{cm}^{-1}$  normalized to the intensity of the internal standard band as a function of curing time for each temperature. The aromatic ring stretching absorbance band at 1510  $\text{cm}^{-1}$  was used as an internal standard band. Figure 6 agrees well with the above explanation.

TGA thermograms obtained from the samples cured isothermally at 230°C are shown in Figure 7.



**Figure 15** Change of FTIR spectra of TMEP/PC (50/50) blend as a function of time for isothermal curing at 230°C.



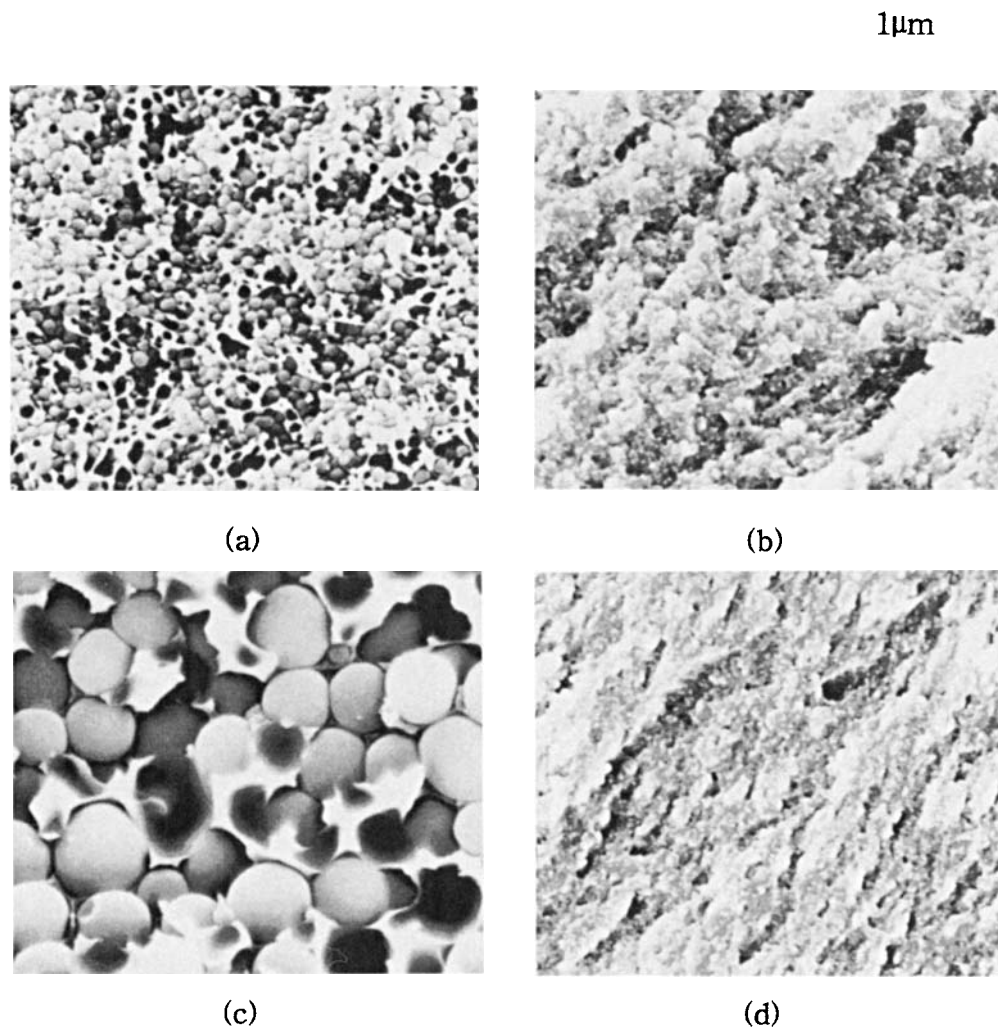
**Figure 16** Final morphology of EP/TMPC and TMEP/TMPC blends after curing at 230°C: (a) EP/TMPC (50/50); (b) TMEP/TMPC (50/50); (c) EP/TMPC (75/25); (d) TMEP/TMPC (75/25).

TMEP loses more weight than does EP. The weight loss is attributed mainly to the evaporation of dehydrated  $H_2O$  evolved in thermal degradation. TGA investigation of the thermal stability agrees well with the thermal degradation behavior observed by FTIR spectroscopy. The curing reaction of TMEP proceeds more slowly when compared to EP because of the decreased mobility due to the tetramethyl group. Accordingly, the concentration of the residual uncured epoxide group is higher for TMEP at the same curing time and the possibility of etherification which leads to the thermal degradation is greater for TMEP than those for EP.

#### Thermal Stability of Epoxy/TMPC Blends

One of the basic requirements in the multicomponent thermosetting system is to have a homogeneous

mixture prior to the curing process. For the epoxy/thermoplastic blend system used in this study, it was possible to prepare the homogeneous uncured mixtures with no apparent phase separation by the solution-casting method. Epoxy/TMPC blend samples of 50/50 and 75/25 in weight were prepared and  $T_g$  was measured as a function of curing time. In Figures 8 and 9, they exhibit a single  $T_g$  initially and subsequently split into two  $T_g$ 's, indicating that phase separation takes place due to the decrease in miscibility with increasing molecular weight of the epoxy. The higher the curing temperature and the composition of the epoxy, the earlier the phase separation starts. The onset time of the phase separation is shorter in EP/TMPC than in TMEP/TMPC since the curing rate of EP is much faster than that of TMEP. Among two  $T_g$ 's observed in Figures 8



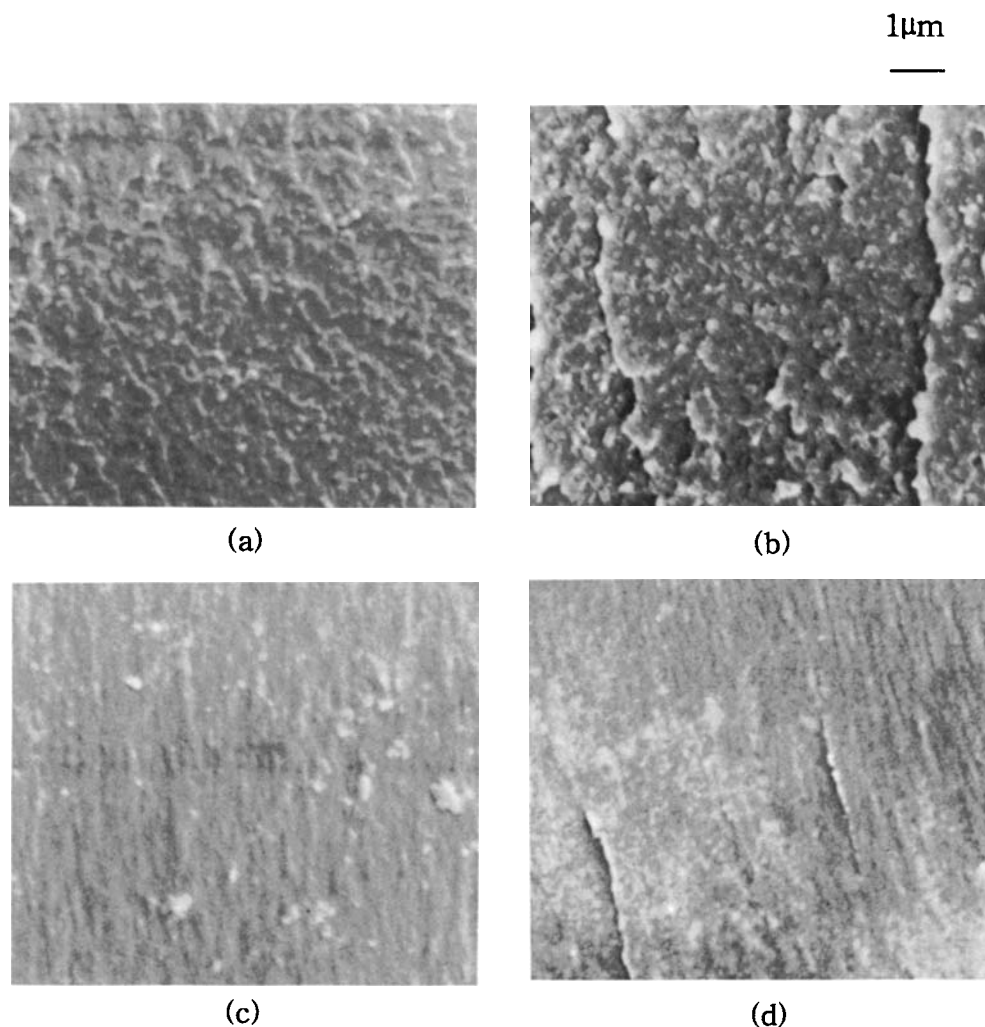
**Figure 17** Final morphology of EP/TMPC and TMEP/TMPC blends after curing at 200°C: (a) EP/TMPC (50/50); (b) TMEP/TMPC (50/50); (c) EP/TMPC (75/25); (d) TMEP/TMPC (75/25).

and 9, the upper one is believed to correspond to the  $T_g$  of the epoxy-rich phase, and the lower one, to the  $T_g$  of the TMPC-rich phase. This means that the following two things are worthy to note: First, in comparison with the  $T_g$  behavior of neat epoxy, there is no  $T_g$  decreasing phenomena observed in these blends. This indicates that the TMPC incorporated in the epoxy-rich phase improved the thermal stability of the epoxy. This interesting observation will be discussed later in more detail. Second, a large amount of epoxy is incorporated into the TMPC-rich phase. The  $T_g$  of neat TMPC was 195°C when determined by DSC. However, the maximum temperature of the lower  $T_g$  observed in Figures 8 and 9 is about 170°C. Therefore, a large amount of epoxy should remain incorporated in the TMPC-rich phase even after the separation takes place. The

epoxy remaining in the TMPC-rich phase acts as plasticizers and lowers the  $T_g$  of the TMPC-rich phase.

The improvement of the thermal stability of the epoxy when blended with TMPC can be corroborated by TGA. Figures 10 and 11 give TGA thermograms for the EP/TMPC and TMEP/TMPC blends, respectively. In Figure 10, the thermal stability of the EP/TMPC blend is close to that of pure EP. But Figure 11 shows that the thermal stability of the TMEP/TMPC blend is in the middle of the thermal stability of the two pure components, TMPC and TMEP. This means that the addition of TMPC to TMEP is more effective on the enhancement of the thermal stability than is the addition to EP. This may result from the compatibility difference due to the chemical structure similarity





**Figure 18** Final morphology of EP/PC and TMEP/PC blends after curing at 230°C: (a) EP/PC (50/50); (b) TMEP/PC (50/50); (c) EP/PC (75/25); (d) TMEP/PC (75/25).

(see the morphology presented in Figures 16 and 17). The TMEP/TMPC blend, where the chemical structures of both components are similar, has better compatibility so that more TMPC is incorporated into TMEP than into EP; thus, thermal degradation is prevented more effectively. It is presumed that the TMPC acts as the radical scavenger for the radicals produced from the TMEP degradation. On the other hand, less TMPC is incorporated into EP and the phase-separated epoxy-rich phase of the EP/TMPC blend undergoes almost the same thermal degradation as does neat epoxy. By the investigation of thermal stability, we could observe a difference in compatibility due to molecular structure similarity. Consequently, it is concluded that the compatibility of the TMEP/TMPC blend is better than that of the EP/TMPC blend.

### Thermal Stability of Epoxy/PC Blends

Investigation of the thermal stability of epoxy/PC blends was also carried out. Figures 12 and 13 show TGA thermograms of the EP/PC blend and TMEP/PC blend, respectively. In contrast with the investigation of the epoxy/TMPC blend, the greater the composition of PC, the worse the thermal stability of the epoxy/PC blend. In Figure 12, the degradation of EP/PC blends is more profound when compared to the two pure components. Also, this enhancement of thermal degradation is significant at high PC composition: EP/PC (50/50). But in Figure 13, the rate of degradation of the TMEP/PC blend is in between that of pure PC and that of pure TMEP. These abnormal behaviors may be induced by a unique duplicated thermal degradation. In the

epoxy/PC blend, the PC incorporated into the epoxy-rich phase is hydrolyzed by H<sub>2</sub>O dehydrated in the thermal degradation of epoxy and, thus, is decarbonated to produce a hydroxyl group and CO<sub>2</sub>. The degradation scheme is described in Figure 3. Therefore, the weight loss in the TGA thermograms is attributed not only to the evaporation of H<sub>2</sub>O produced from the thermal degradation of epoxy, but also to the loss of emitted CO<sub>2</sub> produced from hydrolysis of PC.

FTIR spectroscopic analysis was performed to verify the chemical change in this complex thermal degradation process. Figures 14 and 15 show the changes of the FTIR spectra for epoxy/PC (50/50) blends as a function of curing time at 230°C. The carbonyl stretching absorbance band at 1778 cm<sup>-1</sup> shown in the spectra of uncured EP/PC and TMEP/PC blends dwindles gradually as curing proceeds. Decarbonization resulted from the hydrolysis of PC. As already shown in Figures 6 and 7, TMEP is degraded more profoundly and produces more H<sub>2</sub>O than does EP. However, hydrolysis of PC in the EP/PC blend is more severe than that in TMEP/PC. This contradictory result can be explained when considering the difference of compatibility between EP/PC and TMEP/PC blends due to the chemical structure similarity. The EP/PC blend, where the chemical structures of two components are similar, has better compatibility than does the TMEP/PC blend so that more PC is incorporated into the epoxy-rich phase. For this reason, the amount of hydrolysis of PC is greater in the EP/PC blend. Thus, in spite of less production of H<sub>2</sub>O from the thermal degradation of epoxy, more profound weight loss is observed for the EP/PC blend.

Through the quantitative analysis of the hydrolysis, it is found in the epoxy/PC blend that the compatibility of the EP/PC blend is better than that of the TMEP/PC blend. Attempts to measure the *T<sub>g</sub>* of this blend as a function of curing time have failed since the transition curve was very broad and irregular, meaning that the various low molecular weight materials are produced from this extremely severe thermal degradation. This argument will be fortified by the morphological evidence presented in next section.

### Morphology of Epoxy/Thermoplastics Blends

All the epoxy/TMPC and epoxy/PC blends were examined by SEM. Scanning electron micrographs for the fractured surfaces of the epoxy/TMPC (50/50, 75/25) blends cured at 230 and 200°C are shown in Figures 16 and 17, respectively. The EP/TMPC

blend has a two-phase morphology which consists of spherical domains of the epoxy-rich phase dispersed regularly in a matrix of TMPC [Fig. 16(a) and (c) and Fig. 17(a) and (c)]. The phase separation took place via spinodal decomposition by the increase of the molecular weight of the epoxy. The domain size increases with increasing the composition of the epoxy and the curing temperature since the degree of curing is higher at the same curing time. The effect of the curing temperature and the composition of the epoxy on the morphology of this epoxy/thermoplastic blend has been reported elsewhere.<sup>16</sup> On the other hand, the morphology of TMEP/TMPC blends [Fig. 16(b) and (d) and Fig. 17(b) and (d)] shows the relatively fine heterogeneous morphology, although it is not regular and clear. This may be come from incomplete phase separation due to the better compatibility that resulted from the chemical structure similarity between the two components.

Figure 18 shows scanning electron micrographs of fractured surfaces of the epoxy/PC blend cured at 230°C. In the comparison to epoxy/TMPC blends, the more homogeneous morphology is observed. It is speculated that the various low molecular weight materials produced from the extremely severe thermal degradation are mingled randomly, thus making it very hard to observe the distinct two-phase morphology.

### CONCLUSIONS

From the experimental studies on the changes of thermal stability and chemical structure with curing, we found that the thermal degradation of epoxy occurred by etherification, a kind of side reaction during the curing process. The degree of thermal degradation of TMEP was higher than that of EP. It may be attributed to the difference in the curing rate due to different molecular mobility.

In epoxy/TMPC blends, the addition of TMPC enhanced the thermal stability of epoxy. The enhancement was more significant in the TMEP case than in EP, which is believed to have resulted from better compatibility of TMEP with TMPC. In epoxy/PC blends, it was found that at high temperature the added PC is hydrolyzed by the H<sub>2</sub>O dehydrated in the thermal degradation of epoxy. From the quantitative analysis of hydrolysis, it was found that the compatibility of the EP/PC blend is better than that of the TMEP/PC blend.

Thus, the estimated compatibility in all these blend systems was dependent on the chemical

structure similarity between consisting materials. It agrees well with SEM results. It is concluded from this study that there is a very strong relationship between compatibility and thermal stability.

## REFERENCES

1. A. J. Kinloch and R. J. Young, *Fracture Behavior of Polymers*, Applied Science, London, 1983.
2. A. F. Yee and R. A. Pearson, *J. Mater. Sci.*, **21**, 2475 (1986).
3. C. B. Bucknall and I. K. Partridge, *Polym. Eng. Sci.*, **26**, 54 (1986).
4. S. C. Kunz, J. A. Sayre, and R. A. Assink, *Polymer*, **23**, 1897 (1982).
5. P. J. Pearce, B. C. Ennis, and C. E. M. Morris, *Polym. Commun.*, **29**, 93 (1988).
6. A. C. Meeks, *Polymer*, **15**, 675 (1974).
7. C. B. Bucknall and I. K. Partridge, *Polymer*, **24**, 339 (1983).
8. C. B. Bucknall and A. H. Gilbert, *Polymer*, **30**, 213 (1989).
9. D. J. Hourston and J. M. Lane, *Polymer*, **33**, 1379 (1992).
10. J. A. Cecere and J. E. McGrath, *Polym. Prepr.*, **27**, 299 (1986).
11. R. S. Raghava, *J. Polym. Sci. Polym. Phys. Ed.*, **26**, 65 (1987).
12. K. Yamanaka, Y. Takagi, and T. Inoue, *Polymer*, **60**, 1839 (1989).
13. K. Yamanaka and T. Inoue, *Polymer*, **30**, 662 (1989).
14. M. B. Neiman, B. M. Kovarskaya, A. S. Strizhkova, I. I. Levanotoskaya, and M. S. Akutin, *Dokl. Akad. Sci. SSSR*, **135**, 1419 (1960).
15. L. H. Lee, *J. Polym. Sci.*, **3**, 895 (1965).
16. D. S. Lee, T. S. Yoon, and J. Kim, *Polymer (Korea)*, **18**, 754 (1994).

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