Carbon Black Containing IPNs Based on Unsaturated Polyester/Epoxy. I. Dynamic Mechanical Properties, Thermal Analysis, and Morphology

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ABSTRACT: A series of carbon black containing interpenetrating polymer networks (IPNs) based on unsaturated polyester/epoxy (weight ratios 10/90, 20/80, 30/70) were developed. Scanning electronic microscopy exhibits that the compatibility was decreased and the morphology seemed to become less rigid as the content of unsaturated polyester increased in IPNs. The results also indicate that flame retardants were uniformly distributed in the IPN matrices. It is found that the heat resistance, damping, and mechanical properties were all improved simultaneously by adding the plate-shaped carbon black flame retardants to the unsaturated polyester/epoxy IPNs. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1904–1910, 2002

Key words: carbon black; flame retardant; unsaturated polyester; epoxy; IPN; damping properties

INTRODUCTION

Interpenetrating polymer networks (IPNs) usually exhibit the properties of partial compatibility and broad distribution of the molecular relaxation. Because of that, a broader temperature range of thermal transition can be obtained. This characteristic is shown to be suitable for the application as damping materials.[1] Many researchers obtained excellent damping properties from IPNs such as polyurethane/polymethyl methacrylate (PU/PMMA),[2] epoxy/acrylics,[3] and PU/epoxy.[4,5] On the other hand, a series of unsaturated polyester/epoxy IPNs were developed in our lab.[6] It was found that they exhibited a broad temperature range of thermal transition.

Materials usually exhibit the best damping properties at temperatures close to glass transition temperature (T_g). Moreover, the relationship between temperature and frequency is given by Ferry.[7] It was further found the shift of frequency by one order would correspond to the temperature change at about 6–7°C.[8] To meet the requirement of practical damping applications, the materials should exhibit a large loss factor ($\tan \delta > 0.3$) over a wide temperature range.[9] Furthermore, the damping behavior of polymer composites results from the internal friction of molecules, interaction between molecular chain and filler, and the friction between fillers.[10] Chua[11] analyzed the damping properties of the polymer composite materials by dynamic mechanical analysis (DMA). This provides more accurate measurement of interfacial damping in polymer composite than any other mechanical tests. By this technique, the mechanical strength of the material from the storage modulus (E'), the damping properties from loss modulus (E''), and loss tangent ($\tan \delta$) can be obtained.

A variety of mechanisms such as condensed-phase retardation, gas-phase retardation, and dissipation of combustion heat was proposed to explain the potency of the flame retardants.[12,13] In this work, carbon black flame retardants were chosen to improve the flame resistance of the IPNs. The volume of the carbon black flame retardants would expand as they are heated over 220°C. Consequently, the expansion of carbon blacks can inhibit the diffusion of oxygen and heat into the IPNs.[14] Moreover, their porous structures are able to adsorb the volatile gas and liquid. These would effectively improve the flame resistance of the materials. However, some flame retardants may significantly decrease the mechanical properties of polymers.[15,16] It is important that the addition of flame retardants into the polymers would not affect the mechanical properties drastically. It is even more desirable if the mechanical properties can be improved by the addition of flame retardants. Saravanos et al.[17,18] demonstrated that the addition of beam-, plate-, or shell-shaped structures of flame retardants can enhance the damping properties of materials. In this study, plate-shaped carbon black flame retardants such as HM00-02 and RL00-02 from Inter. Carbide Tech. Corp. were added to a series of unsaturated

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TABLE I
Formulations of IPNs (wt %)

	Unsaturated polyester	Epoxy	Flame retardant
IPN1	10	90	0
IPN1R	10	90	30(R)[a]
IPN1H	10	90	30(H)[a]
IPN2	20	80	0
IPN2R	20	80	30(R)
IPN2H	20	80	30(H)
IPN3	30	70	0
IPN3R	30	70	30(R)
IPN3H	30	70	30(H)

[a] R: RL00–02; H: HM00–02.

polyester/epoxy IPNs with various compositions. By adding these plate-shaped carbon black flame retardants, one would expect to observe how the flame resistance, damping, and mechanical properties can be affected.

EXPERIMENTAL

Materials

The unsaturated polyester (2504APT-S, Eternal Chemical Co., Kaoshiung, Taiwan) and epoxy (Epikote 815, Shell Co.) were cured by MEKPO (Union Chemical Works Ltd., Hsinchu, Taiwan) (1 phr on unsaturated polyester) and amine curing agent (No. 951, Golden-Gate Chemical Co., Taipei, Taiwan, 12 phr on epoxy), respectively. Activated carbon black flame retardants (HM00-02 and RL00-02, Inter. Carbide Tech. Co., Taoyuan, Taiwan) were added to the IPNs with 30 phr on total resin content, respectively. The detailed formulation of IPNs is shown in Table I.

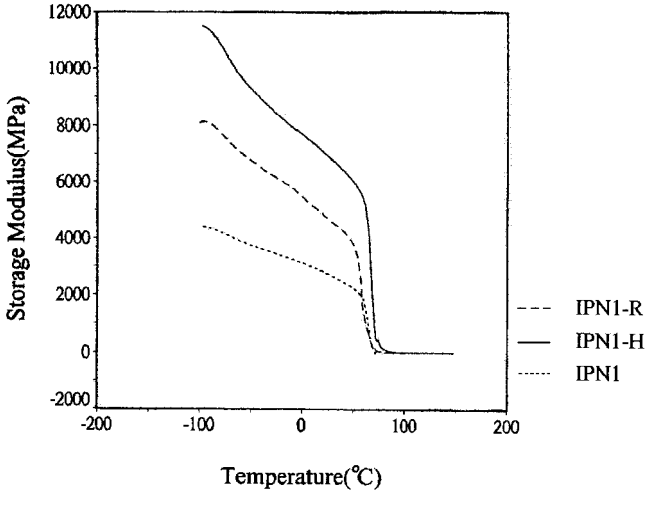

Figure 1 Temperature dependence of the storage moduli (E') for the unsaturated polyester/epoxy (10/90) IPNs (1 Hz).

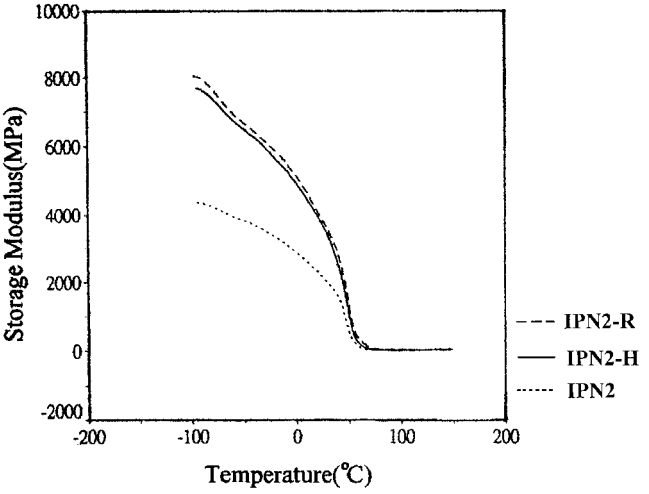

Figure 2 Temperature dependence of the storage moduli (E') for the unsaturated polyester/epoxy (20/80) IPNs (1 Hz).

Instruments

Mechanical properties of IPNs were investigated by using a DuPont V2.5HTA DMA at frequencies of 1, 3, and 10 Hz (heating rate of 3°C/min). The specimen size is 0.5 × 0.5 × 0.3 cm. The thermal degradation behavior was investigated by using a Perkin–Elmer, TGA7 thermal gravimetry analysis (TGA) at a heating rate of 20°C/min. The flammability test is measured by using an oxygen index meter (Polymer Laboratories, FTAII) by a modified method as reported by literature.[19,20] Scanning electronic microscopy (SEM) was used to analyze the morphology of the fracture surface of samples.

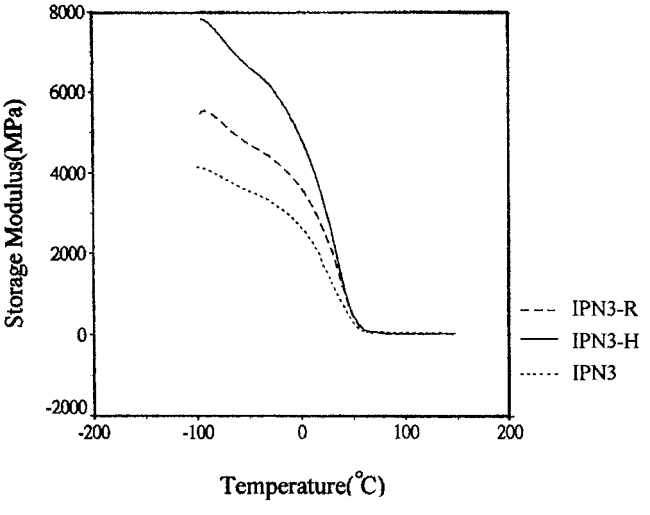

Figure 3 Temperature dependence of the storage moduli (E') for the unsaturated polyester/epoxy (30/70) IPNs (1 Hz).

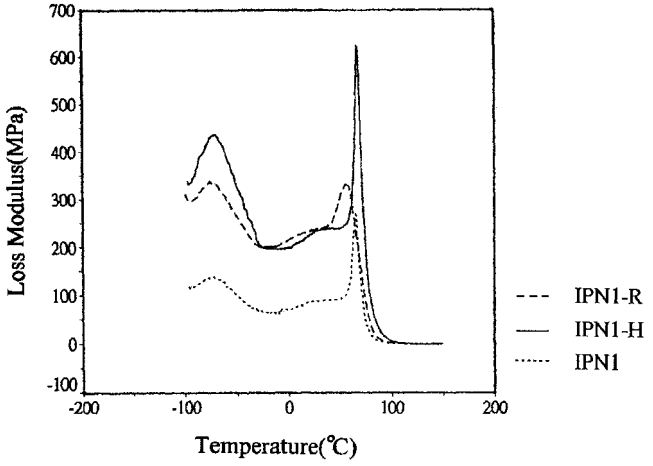

Figure 4 Temperature dependence of the loss moduli (E'') for the unsaturated polyester/epoxy (10/90) IPNs (1 Hz).

RESULTS AND DISCUSSION

Dynamic mechanical analysis

DMA measurements revealed that the transition temperature of the storage modulus (E') was broad, and the strength was decreased as increasing content of the unsaturated polyester in the IPNs (Figs. 1-3). The range of the transition temperature of IPN3 (Fig. 3) located at the lower temperatures was much broader than that of IPN1 (Fig. 1). Moreover, the storage moduli (E') of IPNs (IPN1, IPN2, IPN3) were increased as the carbon black flame retardants were added to the IPNs. These carbon black containing IPNs are IPN1R, IPN2R, IPN3R, IPN1H, IPN2H, and IPN3H (Figs. 1–3). The storage modulus of IPN1H was about three times as much as that of IPN1, and the storage moduli of IPN2H and IPN3H were about two times as much as those of IPN2 and IPN3, respectively. The storage moduli of IPN1R, IPN2R, and IPN3R were also about 1.5–2 times as much as those of IPN1, IPN2, and IPN3, respectively. This indicates that the mechanical properties of the IPNs were greatly enhanced as the carbon black flame retardants were added to the IPNs. It is important to note that the addition of HM00-02 exerted greater enhancement of mechanical properties than the addition of RL00-02.

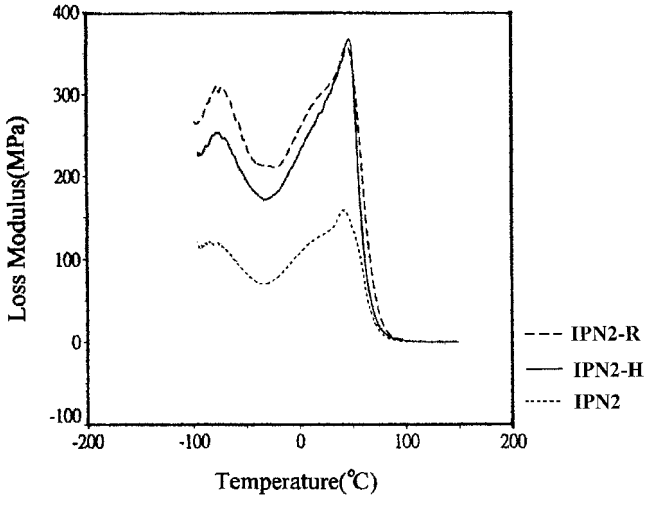

Figure 5 Temperature dependence of the loss moduli (E'') for the unsaturated polyester/epoxy (20/80) IPNs (1 Hz).

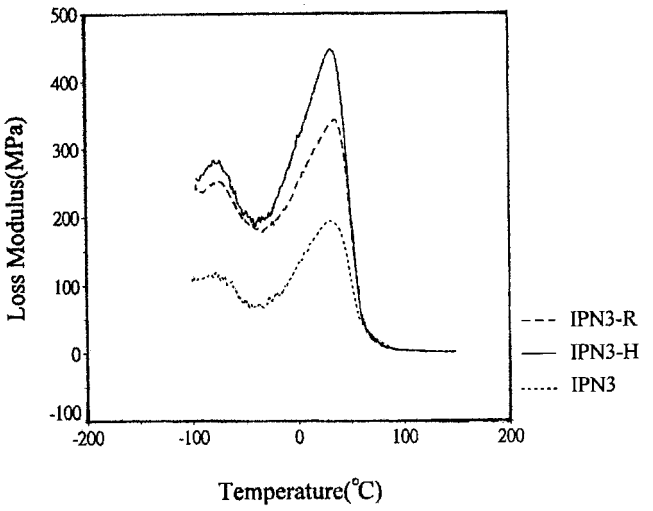

Figure 6 Temperature dependence of the loss moduli (E'') for the unsaturated polyester/epoxy (30/70) IPNs (1 Hz).

The loss moduli (E'') peak became broader as the content of unsaturated polyester increased in the IPNs (Figs. 4–6). The E'' temperature range of IPN3 (Fig. 6) located at the lower temperatures was much broader than that of IPN1 (Fig. 4). Moreover, the loss moduli (α-relaxation) of IPNs (IPN1, IPN2, IPN3) were increased as the activated carbon black flame retardants were added to the IPNs, respectively (Figs. 4–6). The loss moduli of IPN1H, IPN2H, and IPN3H were about 2.5 times as much as those of IPN1, IPN2, and IPN3, respectively, whereas the loss moduli of IPN1R,

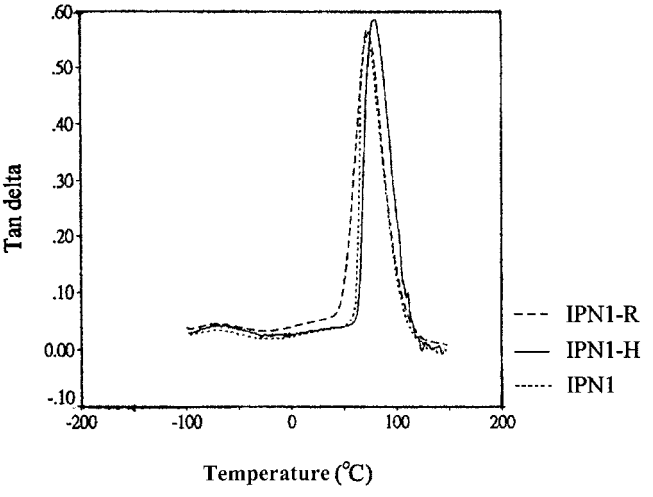

Figure 7 Temperature dependence of tan δ for the unsaturated polyester/epoxy (10/90) IPNs (1 Hz).

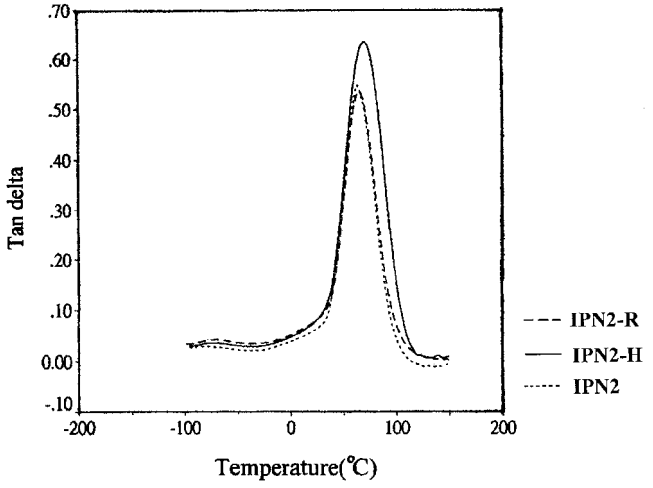

Figure 8 Temperature dependence of tan δ for the unsaturated polyester/epoxy (20/80) IPNs (1 Hz).

IPN2R, and IPN3R were also about 1.5–2 times as much as those of IPN1, IPN2, and IPN3, respectively. Furthermore, the intensity of the α- and β-relaxation peaks were increased, and the loss moduli were more than 200 MPa over a broad temperature range from −100 to 60°C as the carbon black flame retardants were added to the IPNs. This indicates that the damping properties of IPNs were greatly enhanced after the addition of the carbon black flame retardants to the IPNs. Moreover, the HM00-02 containing IPNs exhibited a more pronounced enhancement on the damping properties than the RL00-02-containing IPNs.

The peak of loss tangent (tan δ) became broader and shifted to the lower temperatures as the content of unsaturated polyester increased in the IPNs (Figs. 7–9). The tan δ peaks of IPN1 (from 70 to 100°C) and IPN3 (from 40 to 90°C) were over 0.3. It is important to note that the carbon black containing IPNs exhibit

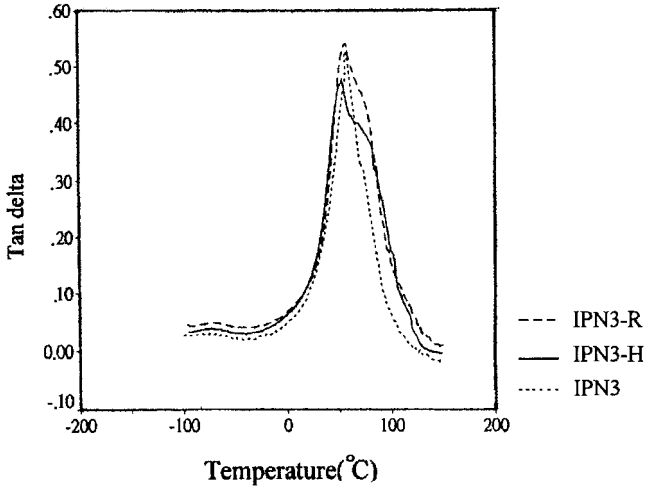

Figure 9 Temperature dependence of tan δ for the unsaturated polyester/epoxy (30/70) IPNs (1 Hz).

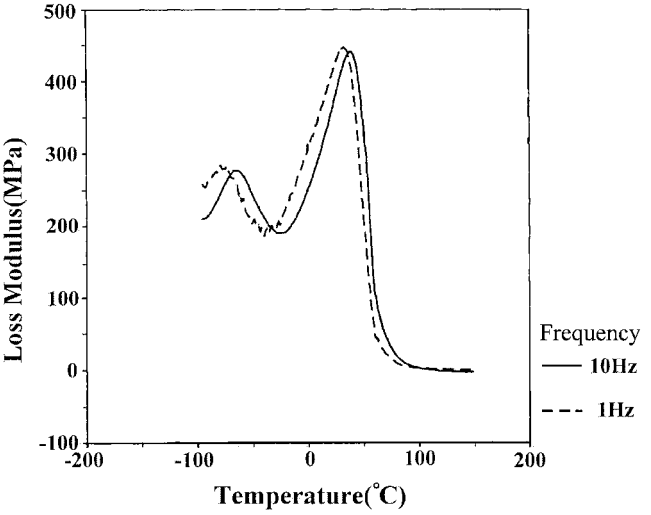

Figure 10 Temperature dependence of loss moduli (E'') for IPN3H at frequency 1 Hz and 10 Hz.

similar intensities of the tan δ peaks to those of the pristine IPNs. Moreover, the tan δ peaks became broader after addition of the carbon black flame retardants to the IPNs. The tan δ of IPN2H was over 0.3 with a temperature range from 50 to 100°C, whereas the loss tangents of IPN3H and IPN3R were over 0.3 with temperature ranges from 40 to 100°C. The broadening temperature range of tan δ peak would make materials more suitable for damping applications. The results also revealed that a shoulder (about 80°C) was found in Figure 9. This indicates that the homogeneity of IPN3 samples was poorer than the IPN1 and IPN2 samples. Moreover, the values of tan δ did not vary significantly with the addition of flame retardants. This is due to the fact that the E'' value was increased with increasing E' value as the flame retardant was added to the IPNs. The relationship between temperature and frequency is shown in Figure 10. The temperature of maximum loss modulus at a frequency of 10 Hz was

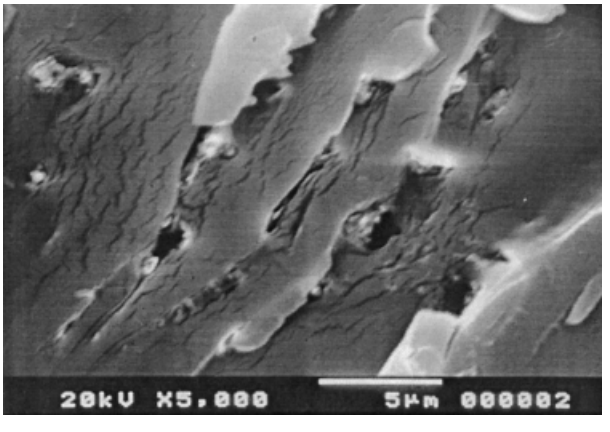

Figure 11 SEM photograph of IPN1.

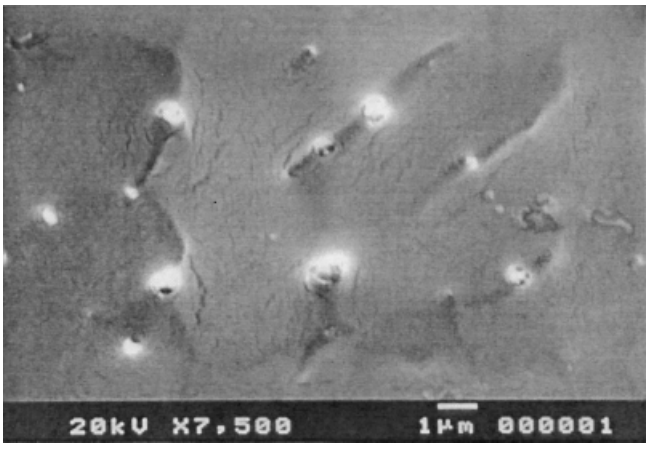

Figure 12 SEM photograph of IPN2.

about 7°C higher than that at 1 Hz. This is consistent with the results reported previously.[7,8]

Scanning electronic microscopy analysis

The results of SEM revealed that no sign of phase separation was observed for IPN1 and IPN2 samples (Figs. 11 and 12). Moreover, phase separation was vaguely observed from the morphology of IPN3 (Fig. 13). This implies that IPN3 was less homogeneous than IPN1 and IPN2. This is consistent with the results of tan δ analysis. For the carbon black containing IPNs, the cross-section area of RL00-02 containing IPN (IPN1R, Fig. 14) was edgier and less homogeneous than the IPNs with HM00-02 (IPN1H, Fig. 15). From DMA measurements, the loss modulus of IPN1R was smaller than that of IPN1H. This indicates that IPN1R was more brittle than IPN1H. Moreover, the storage modulus of IPN1H was also larger than that of IPN1R. These results along with the SEM analysis imply that better homogeneity was obtained for the IPN1H sample. Consequently, the IPN1H sample exhibited better dynamic mechanical properties.

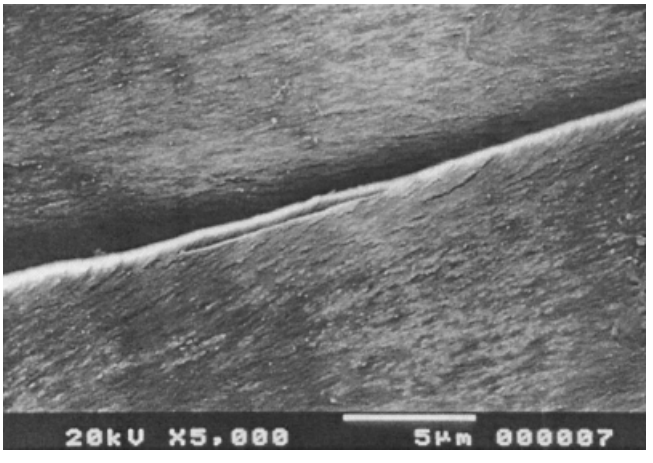

Figure 13 SEM photograph of IPN3.

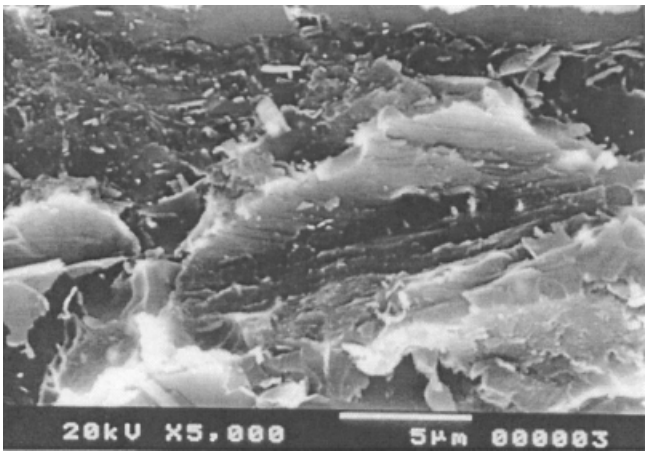

Figure 14 SEM photograph of IPN1R.

Thermal and flame-retardant properties

From TGA measurements, the respective char yields for IPN1, IPN2, and IPN3 were found to be <10% at 900°C (Figs. 16–18). On the other hand, the respective char yields for IPN1H, IPN2H, and IPN3H were about 20% at 900°C (Figs. 16–18). Moreover, the respective char yields for IPN1R, IPN2R, and IPN3R were about 30% at 900°C (Figs. 16–18). As reported previously,[21] the char yield is directly correlated to the potency of flame retardation. The abovementioned results indicate that the flame resistance of IPNs was increased as the carbon black flame retardants were added to the IPNs. Based on the above, RL00-02 is a better flame retardant than HM00-02. The decomposition temperatures (T_d's) of IPN1, IPN2, and IPN3 were very close to each other (about 370°C, Table II). However, T_d's were decreased as the flame retardant was added to the IPNs. T_d's were decreased to <355°C as the HM00-02 flame retardant was added to the IPN. Moreover, the T_d's were decreased to <330°C as the RL00-02 flame retardants were added to the IPNs (Table II). This indicates that T_d's were more pro-

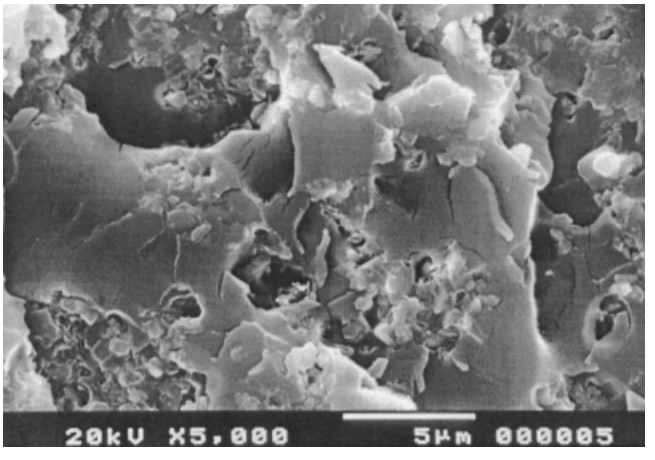

Figure 15 SEM photograph of IPN1H.

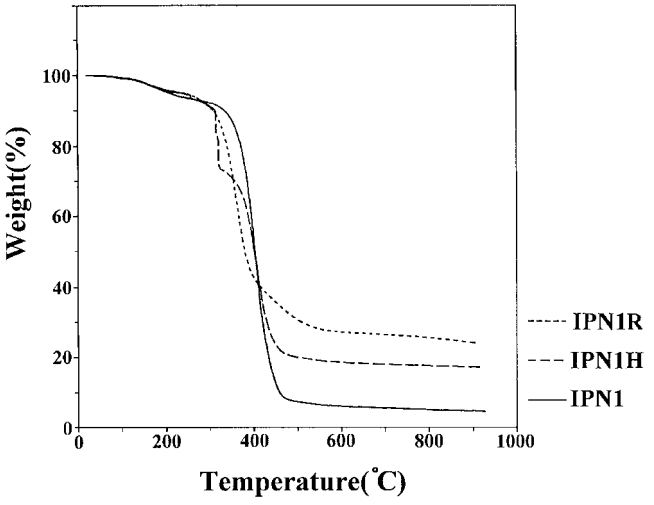

Figure 16 TGA thermograms of the unsaturated polyester/epoxy (10/90) IPNs.

nouncedly reduced when RL00-02 flame retardant was added to IPNs. It is noteworthy that the T_d's decreased with the addition of flame retardants. This phenomenon plays an important role in improving the flame retardance of the IPNs.[22] While in fire, the flame retardants first decompose and subsequently form a char-residue layer on the surface of materials. This char residue would help result in a higher char yield. This is confirmed by the char yield study mentioned earlier.

For the flame-retardant properties, limiting oxygen index (LOI) values of IPNs were decreased with increasing content of unsaturated polyester in the IPNs (Table II). Moreover, the flame-retardant properties of IPNs were obviously enhanced as the carbon black flame retardants were added to the IPNs. With the addition of RL00-02, the values of LOI for the IPNs were increased to values > 44, whereas the LOI values

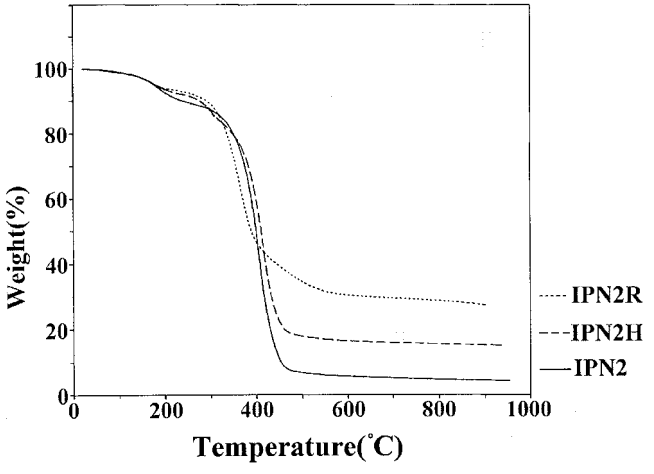

Figure 17 TGA thermograms of the unsaturated polyester/epoxy (20/80) IPNs.

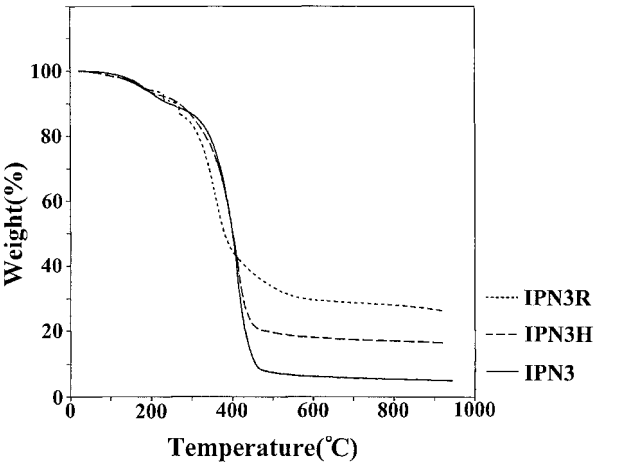

Figure 18 TGA thermograms of the unsaturated polyester/epoxy (30/70) IPNs.

were increased to nearly 40 for HM00-02-containing IPNs. These results revealed that RL00-02 is a better flame retardant than HM00-02. This is consistent with the analysis of the TGA.

CONCLUSION

A series of IPNs with excellent flame-retardant and damping properties were developed. DMA study indicates that IPNs became more flexible and exhibited a wider temperature range of thermal transition as the content of unsaturated polyester increased in the IPNs. Moreover, the HM00-02 flame retardant exhibited greater enhancement on the mechanical and damping properties for the IPNs than the RL00-02 flame retardant. However, the RL00-02 flame retardant exerted greater effect on improving heat resistance and flame retardance of IPNs than HM00-02 flame retardant. SEM study and DMA analysis (E'', tan δ) revealed that the IPNs became less homogeneous as the content of unsaturated polyester increased in the IPNs. Moreover, the SEM study also indicates that RL00-02-containing IPNs was less homogeneous than the HM00-02-containing IPNs. Based on DMA, TGA, and LOI analysis, the damping properties, mechanical

TABLE II
T_d's and LOI Data of IPNs

	T_d's (°C)	LOI
IPN1	372	27
IPN1R	325	52
IPN1H	346	39
IPN2	369	24
IPN2R	321	49
IPN2H	351	34
IPN3	367	22
IPN3R	305	44
IPN3H	354	29

properties, and flame resistance of IPNs were greatly enhanced as the carbon black flame retardants were added to the IPNs.

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