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Fluoroelastomer-Modified Thermoset Resins

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Toughening of epoxy and polyimide matrices with fluorocarbon elastomers was investigated. The introduction of polar groups into the fluorocarbon backbone gave rise to compatible blends of elastomer and partially cured epoxy matrix. During postcure, however, the elastomer phase separated out. Through a careful control of postcure conditions, production of "tailor-made" morphology and, consequently, physical–mechanical properties may be possible. In epoxy blends, a bimodal distribution of the elastomer particle size and a concomitant fourfold increase in the critical strain energy release rate were found. Blends containing the polyimide matrix were incompatible at all stages of cure. The effect of addition of elastomer on thermal stability of the blend was more pronounced with the polyimide than the epoxy matrix.

THE MODIFICATION OF THERMOSET RESINS by incorporation of elastomers continues to be an active area of research. The inherent brittleness of thermosets restricts the range of their use, particularly as the matrix material in composites. Hence, considerable research has been conducted on the toughening of thermosets. Advances in studies of the most common toughening route (i.e., the addition of elastomers) previously were compiled (*1*) and are further discussed in this book.

In general, toughened thermosets are characterized by an increase in impact strength and, unfortunately, a simultaneous decrease in the glass transition temperature (T_g) and modulus. Various elastomers have been used to toughen thermosets. For instance, modification of epoxy resins with carboxyl-terminated copolymers of butadiene and acrylonitrite (CTBN) significantly improved the toughness (*2*, *3*). Many factors affect the nature of the elastomer phase, such as its chemical composition and concentration, the type of curing agent, and the kinetics of cure. Some workers have concluded that

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the improved toughness was related to the size and distribution of rubber domains (*4*, *5*), whereas others have expressed the view that the resin–rubber compatibility determined the toughness (*6*). In spite of the reported results, however, the fundamental relationships between processing (cure), morphology, and properties of elastomer-modified thermosets remain incompletely understood.

We have undertaken an innovative approach in controlling the formation of rubbery phase. A fluorocarbon elastomer, initially incompatible with resin, was chosen as toughening agent. Our first hypothesis was that a chemical modification of the elastomer (e.g., introduction of polar groups) would result in compatibility with partially cured resin network through various intermolecular interactions. The latter, however, would be disrupted at high temperature (postcure) leading to the separation of the rubbery phase. A careful control of postcure conditions (time and temperature) would then allow one to control the morphology of the blends; the morphology, in turn, determines their physical–mechanical properties.

We have recently embarked on a research program of investigating the synthesis–morphology–property relationship in elastomer-modified thermosets. The objectives of this part of that program were to investigate the mechanism of formation of rubbery phase in epoxy and polyimide matrices during cure and to correlate the morphology of cured systems to their physical–thermomechanical properties.

Experimental

Epoxy Systems. In the first set of experiments, a diglycidyl ether of bisphenol A (DGEBA) liquid epoxy resin (Epon 828, Shell Chemical Corporation) was cured with 4,4′-sulfonylbisbenzamine [4,4′-diaminodiphenyl sulfone (DDS)]. Both compounds were used without further purification.

Polyimide Systems. For the second set of experiments, a polyimide resin was synthesized according to Scheme 1.

The phosphine oxide component (**I**), used as the starting material in the synthesis of polyimide resin, was made from triphenylphosphine oxide by nitration and a subsequent reduction of nitro groups to amino groups. The product was characterized by IR spectroscopy and had a melting point of 260 ± 2 °C. The imide monomer (**II**) was also identified by IR spectroscopy, and the characteristic absorption bands resulting from the presence of imide rings were recorded at 1710 and 1780 cm^{-1}, as seen in Figure 1.

Fluoroelastomer Modifier. A fluorocarbon elastomer (Viton GF, Du Pont) was used as a modifier. Because of its incompatibility with Epon 828, Viton GF was further modified, first by the introduction of double bonds into the main chain and then by the addition of various polar groups on the double bond. The entire sequence of chemical reactions used to modify Viton GF is shown in Scheme 2. The modified Viton GF used in this study in blends with epoxy matrix is shown by Structure C in Scheme 2 and is hereafter referred to as the polar Viton GF. Both double-bond containing Viton GF and polar Viton GF were used in blends with polyimide matrix.

Preparation of Polyblends. The polyblends were prepared by the solution cast method described in Table I.

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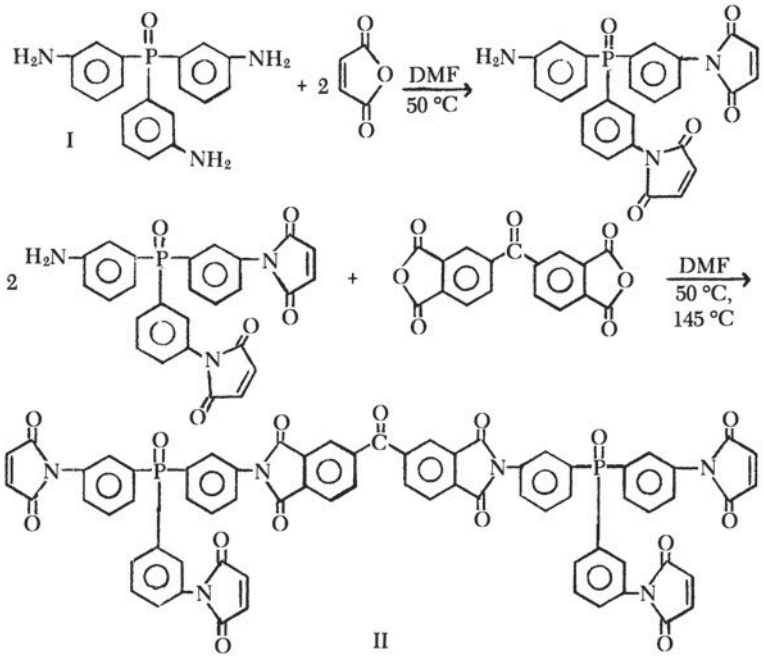

Scheme 1

Techniques. After processing, all samples were allowed to cool to 20 °C and were then kept in closed vials in a desiccator at 20 °C for 1 week before testing.

An IR spectrometer (Digilab–FTS–20B) was used for the analysis of chem-

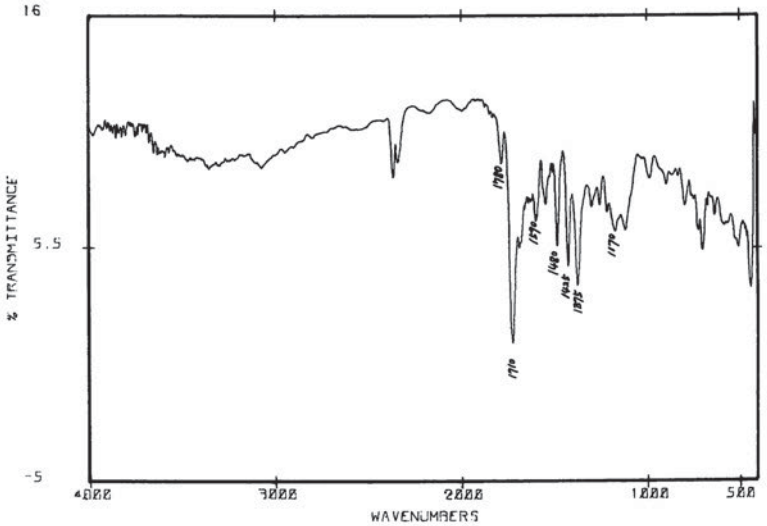

Figure 1. FTIR spectrum of trisimide monomer. Note the absorbance of imide rings at 1710 and 1780 cm^{-1}.

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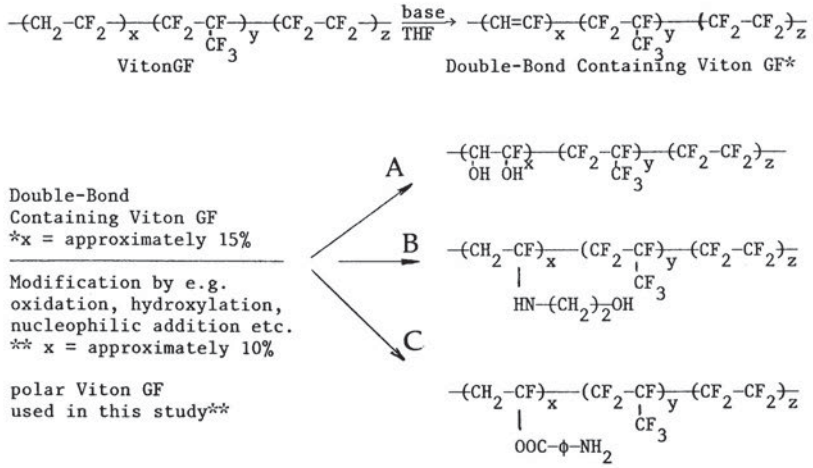

Scheme 2

ical composition. The specimens of modified Viton GF for Fourier transform IR (FTIR) analysis were first cast onto a glass plate at room temperature. Then, dried films (1 × 2 × 0.005 cm) were cut. Imide samples and various blends were prepared and analyzed in the form of KBr pellets.

Dynamic mechanical measurements were performed in the Du Pont 981 model DMA connected to the 1090 thermal analyzer. Tests were run at a heating rate of 10 °C/min and at an oscillation amplitude of 0.2 mm peak-to-peak.

Linear elastic fracture mechanics (LEFM) analysis was applied to calculate

Table I. Various Polyblends and Their Preparation

Formulation	*Variable*	*Cure Schedule*
Epoxy		
Epon 828 + DDS (40 phr) + Viton GF	Viton GF (0–100 phr)	Components dissolved in acetone and mixed at room temperature for 10 min. Solvent removed by heating for 24 h at 40 °C and 12 h at 60 °C. Cured in silicon molds for 24 h at 125 °C and 5-h postcure at 200 °C.
Epon 828 + DDS (40 phr) + polar Viton GF	Polar Viton GF (0, 5, 10, and 15 phr)	Same as above
Polyimide		
Imide/double-bond containing Viton GF	Double-bond containing Viton GF (0–100 phr)	Components dissolved in DMF–acetone (1:1) and mixed at room temperature for 30 min. Solvent removed in a vacuum oven at 60 °C overnight. Cured at 300 °C for 30 min.
Imide/polar Viton GF	Polar Viton GF (0–100 phr)	Same as above

NOTE: phr = parts per hundred parts resin.

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the fracture energy of samples prepared in the form of adhesive joints. The use of height-tapered double cantilever beam (HTDCB) specimens for fracture energy measurements of similar systems has been described elsewhere (*7*). The preparation of aluminum beam surfaces has also been reported (*8*). The HTDCB samples were fractured in a tensile tester (Instron) at 20 °C/50% relative humidity (RH) and a crosshead speed of 0.05 in./min.

Thermogravimetric analysis (TGA) was performed in the Du Pont 951 model TGA connected to the 1090 thermal analyzer. Tests were run at a heating rate of 10 °C/min.

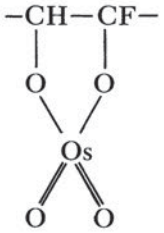
Differential scanning calorimetry (DSC) was performed in the Du Pont model DSC connected to the 1090 thermal analyzer. Tests were run at a heating rate of 10 °C/min.

Cast specimens were immersed in liquid nitrogen, removed, and immediately fractured in air. A scanning electron microscope (SEM) (AMR/1200) was used to study fracture surfaces. Prior to SEM, all samples were coated with a thin layer of gold. Transmission electron micrographs (TEM) (with a JEOL 300D model TEM) were obtained on thin sections prepared with an ultramicrotome (LKB 3800 III) equipped with a glass knife.

Results and Discussion

Modification of Viton GF. Viton GF was first modified by dehydrofluorination in order to produce the double-bond containing Viton GF. This reaction was carried out in the presence of dehydrofluorination catalysts [e.g., NH_4OH, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, and $(CH_2)_3N$].

Polar Viton GF (Scheme 2, Structure A) was obtained by reaction of osmium tetroxide (OsO_4) and double-bond containing Viton GF. Osmium tetroxide adds slowly and forms an osmic ester (*see* Structure 1). Upon subsequent hydroxylation, –OH groups are produced.



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Ethanolamine was added to the double-bond containing Viton GF in order to produce polar Viton GF (Scheme 2, Structure B). Similarly, *p*-aminobenzoic acid reacted with double-bond containing Viton GF to form the molecule shown in Scheme 2, Structure C. The Fourier transform IR (FTIR) spectra of double-bond containing Viton GF and polar Viton GF are shown in Figures 2 and 3, respec-

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tively. Note the appearance of characteristic C=C bond absorbance in Figure 2 at 1700 cm^{-1} and the amino group absorbances at 3350 and 3450 cm^{-1} in Figure 3.

Compatibility of Blends. In the next set of experiments, a series of blends of the epoxy formulation and Viton GF were prepared. All blends were incompatible as judged by the appearance of two separate endothermic events in DSC thermograms (Figure 4). (In blends containing 20% or less of either phase, the glass transition endotherm of that phase was very subtle.) The lower endotherm at −7 °C is representative of the T_g of Viton GF, and the endotherm at approximately 193 °C corresponds to the T_g of the epoxy resin. This finding was not surprising because of the low likelihood of compatibility of fluorocarbon polymers with epoxy resins. The calculation of solubility parameters by the group contribution method yielded values of 23 and 12.3 $(J/cm^3)^{1/2}$ for Epon 828 and Viton GF, respectively. We then postulated that the introduction of polar groups into the main chain of Viton GF would enhance its compatibility with the epoxy resin. Our hypothesis was corroborated by the calculation of solubility parameters of Viton GF containing a hydroxyl group (21.1) and a *p*-aminobenzoic acid group (18.0). Both numbers were much closer to the solubility parameter for Epon 828. We then prepared and investigated a series of blends of epoxy formulation with different amounts of polar Viton GF (5,10, and 15 phr). Blends that were not exposed to the final postcure of 5 h at 200 °C showed an increase in T_g upon the addition of polar Viton GF (Table II). The T_g was taken as the peak value in the loss modulus trace in the dynamic mechanical spectrum. This peak value is also clearly seen in the dynamic mechanical spectra of these blends shown in Figure 5. Hereafter, the glass transition of all samples is defined by the location of the α peak in the loss modulus curve. The single value of glass transition, observed in dynamic mechanical spectra, indicates that the precured blends of Epon 828 and polar Viton GF are compatible. Analogous results were obtained from DSC measurements and are shown in Figure 6. In general, however, the sensitivity of DSC results was inferior to that of dynamic mechanical measurements; hence, the latter were preferred. The observed compatibility is, we believe, a direct consequence of the modification of Viton GF. The apparent increase in T_g as a function of the concentration of polar Viton GF clearly suggests the existence of interactions between the resin network and polar Viton GF. The most pronounced effect upon T_g is obtained by the addition of up to 5% polar Viton GF. The low-temperature β transition (T_β), which is believed to be caused by various relaxations within the epoxy network, is also affected by the presence

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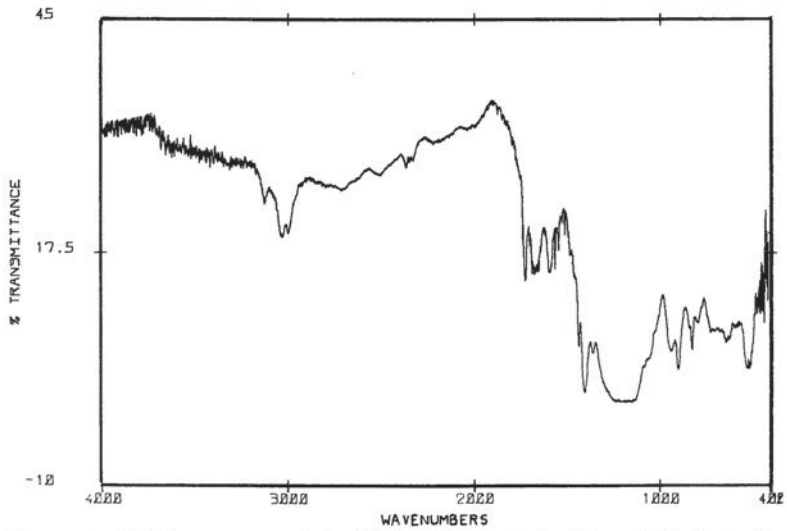

Figure 2. FTIR spectrum of double-bond containing Viton GF. Note the absorbance of C=C bond at 1700 cm^{-1}.

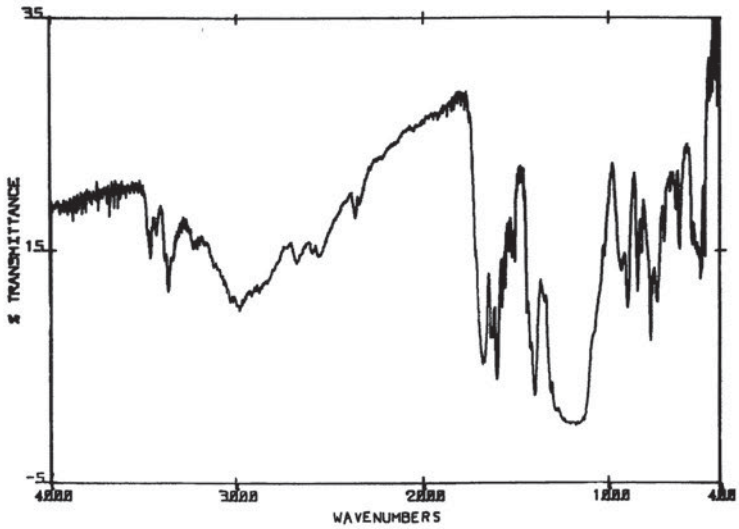

Figure 3. FTIR spectrum of polar Viton GF. Note the disappearance of C=C bond and appearance of NH_2 groups at 3350 and 3450 cm^{-1}.

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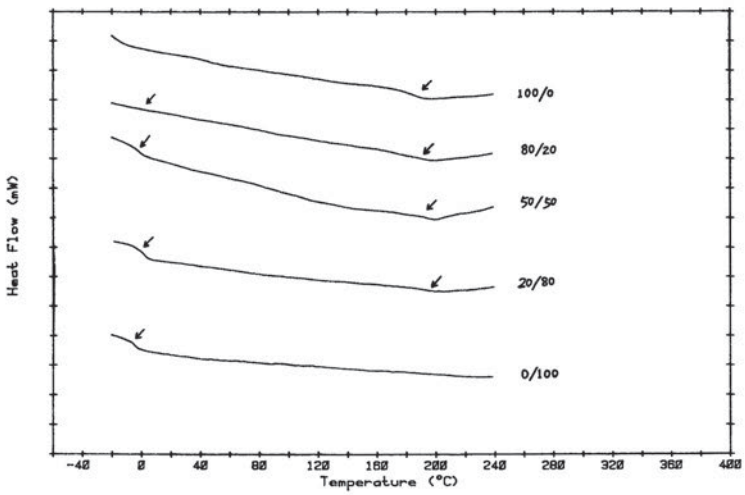

Figure 4. DSC thermograms of a series of Epon 828–Viton GF blends. The curves were shifted along the y axis for clarity.

of polar Viton GF. A small increase in T_β also suggests overall stiffening of the network.

Continuing with our hypothesis, we tested the permanence of the interactions between the epoxy network and the polar Viton GF. Next in our experimental procedure, the samples were subjected to the 5-h postcure at 200 °C (Formulation 2, Table I). As a result of this exposure to high temperature, the intermolecular interactions between the epoxy network and the elastomer were lost, and the rubbery phase separated. Simultaneously, the T_g of all blends increased, as shown in Figure 7. Analogous results were obtained from DSC measurements.

This increase in T_g results from additional cross-linking reactions within the epoxy network. However, with an increased concentration of polar Viton GF in cured blends, T_g decreased. Not all of the elastomer molecules are located within the discrete inclusions (*see* Figures 9 and 10). Instead, some remain scattered throughout the epoxy network and exert an apparent plasticizing effect. The changes

Table II. Glass Transition Temperatures of a Series of Epoxy–Polar Viton GF Blends Before and After Postcure

Concentration of Polar Viton GF (%)	T_g [a] (°C)	T_g [b] (°C)
0	120	193
5	160	191
10	163	189
15	164	176

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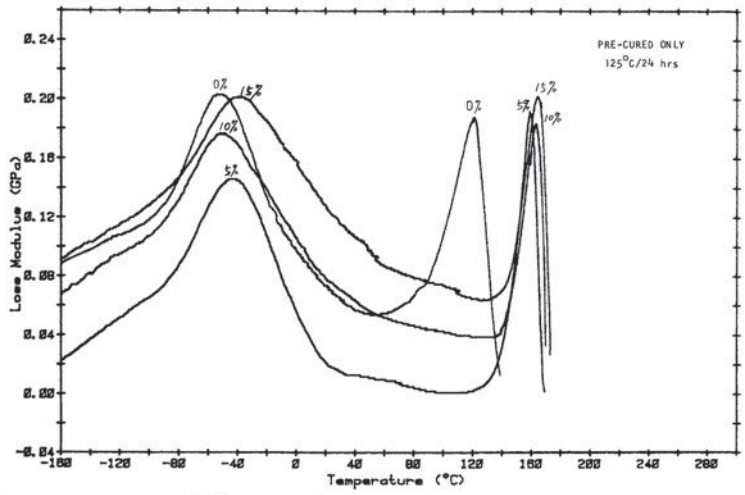

Figure 5. Loss modulus as a function of temperature with concentration of polar Viton GF as a parameter for precured epoxy blends.

in T_g of various blends after the initial cure and the postcure are summarized in Table II.

The analogous approach has been undertaken for blends of polyimides with double-bond containing Viton GF and polar Viton GF. Thus far, however, we have not been able to produce initially compatible blends. For instance, blends of polyimide double-bond containing Viton GF are incompatible, as seen in Figure 8. The T_g of each component in the blend shows no change as a function of com-

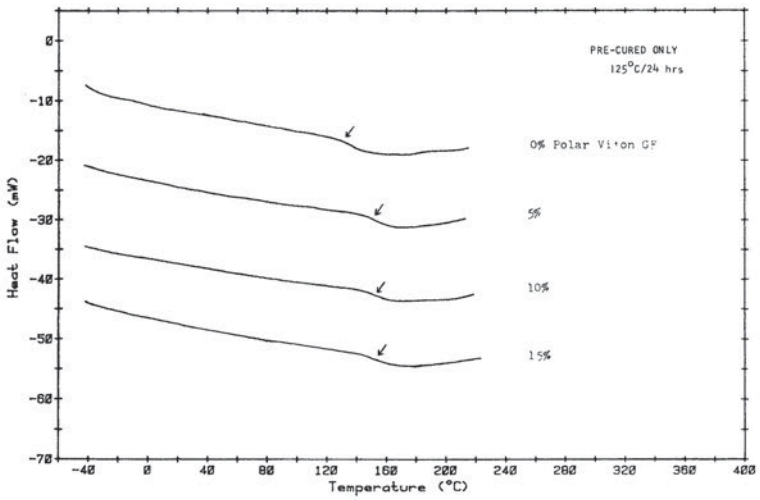

Figure 6. DSC thermograms of a series of precured Epon 828–polar Viton GF blends. The curves were shifted along the y axis for clarity.

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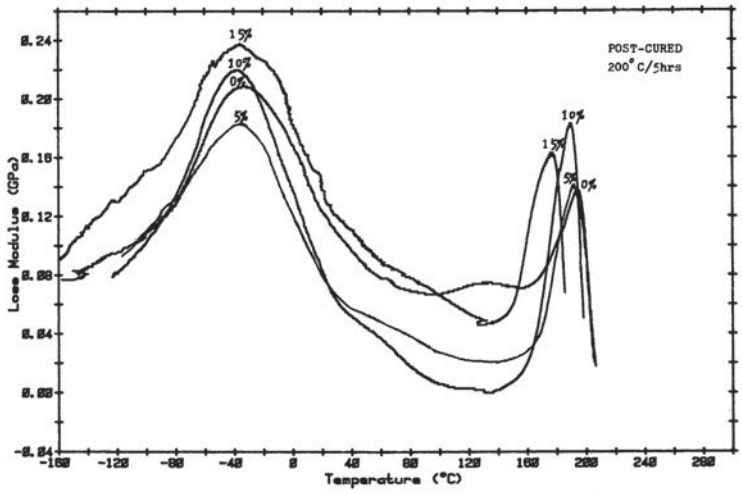

Figure 7. Loss modulus as a function of temperature with concentration of polar Viton GF as a parameter for cured epoxy blends.

position. Analogous results were observed with blends containing polar Viton GF.

Morphology of Blends. SEM and TEM were used to investigate the size and distribution of the rubbery phase in the epoxy matrix. The fracture surfaces of precured blends were featureless, an observation indicating that those blends were compatible. On the other hand, in the postcured blends of epoxy resin and 15% polar Viton GF, a bimodal distribution of rubber particle sizes was found. The diameter of smaller rubber particles ranged from 0.15 to 0.35

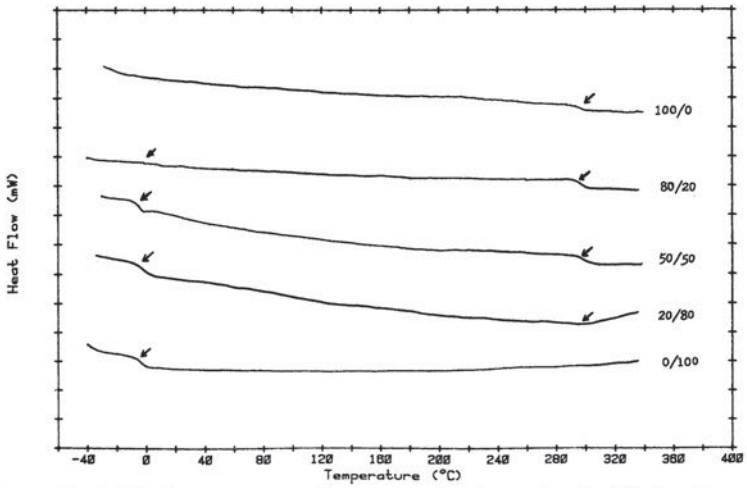

Figure 8. DSC thermograms of a series of polyimide–double-bond containing Viton GF blends.

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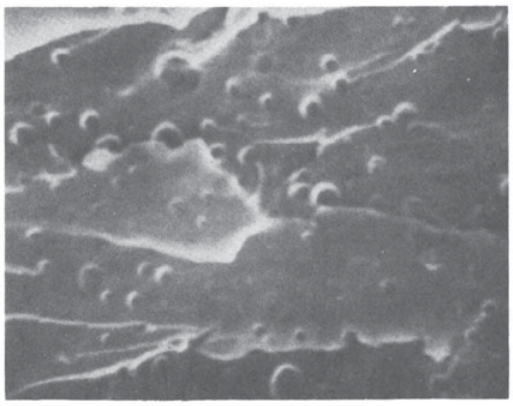

Figure 9. SEM of a fracture surface of an Epon 828–15% polar Viton GF blend. Magnification, 6,800 ×.

μm. The size and distribution of rubber particles were determined from the electron microscopy. Examples of an SEM and a TEM are shown in Figures 9 and 10, respectively. The transformation of compatible blends (before postcure; Figure 5) into incompatible ones (Figure 7) apparently occurs as a function of time and temperature of postcure. An important question is how those variables influence the size and distribution (morphology) of rubbery particles. Control of the morphology is of paramount significance, for it could allow the tailoring of blends with desired properties.

In the 15% polar Viton GF–epoxy blends, the rubbery phase comprises approximately 25% of the surface. The latter number was

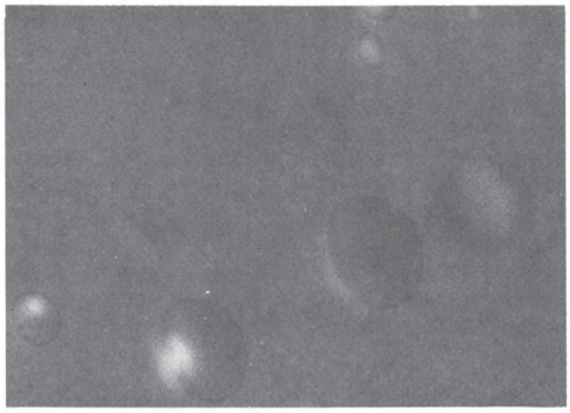

Figure 10. TEM of a thin section of an Epon 828–15% polar Viton GF blend. Magnification, 25,000 ×.

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obtained from electron micrographs of the fracture surface. An apparent "excess" of rubbery material indicates the existence of epoxy matrix within the rubbery inclusions. A two-phase-like appearance of the rubbery phase can be seen in Figure 10. The domain size did not increase in direct proportion with the increase in concentration of polar Viton GF. Apparently, molecules of elastomer exist within the epoxy network, particularly in the blend containing 15% of polar Viton GF. The presence of elastomer, in turn, explains the observed depression of the glass transition (Table II).

Fracture Energy Measurements. Changes in the toughness of a blend upon the addition of an elastomer can be measured by various tests of ultimate mechanical properties. In this study, the value of critical strain energy release rate in mode I ($\mathcal{G}_{Ic}$) was calculated. Samples were cured as outlined in Table I. The exact manner of the application of adhesive onto aluminum beams has been described elsewhere (*7*, *8*). An apparent fourfold increase in $\mathcal{G}_{Ic}$ was recorded as a result of the addition of 15% polar Viton GF to the epoxy network. The $\mathcal{G}_{Ic}$ values for the neat epoxy and the epoxy–15% polar Viton GF formulations were 273 and 1069 J/m^2, respectively. Only blends containing 15% polar Viton GF were tested because of the relatively large decrease in T_g in these blends (*see* Table II).

Thermal Stability of Blends. In addition to the effect of elastomers on physical–mechanical properties of modified thermosets, one is also concerned with the effect on thermal stability. A series of TGA thermograms, shown in Figure 11, indicates a small decrease in thermal stability of epoxy blends upon the addition of polar Viton GF. Thermal stability is reduced as the result of substitution of C–F

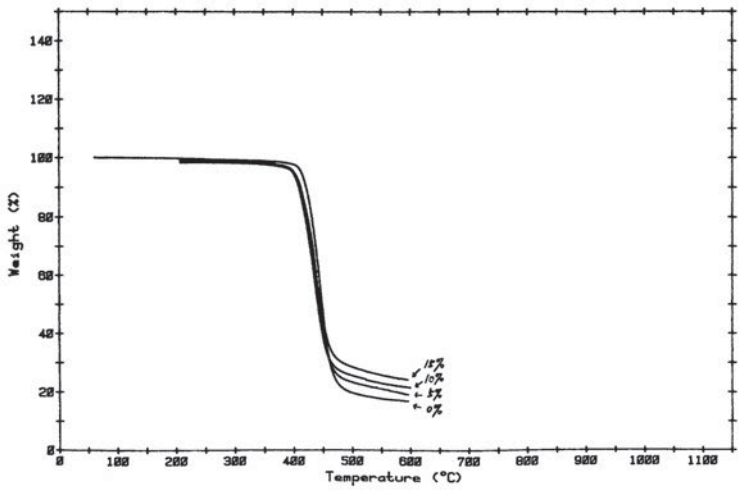

Figure 11. TGA thermograms for a series of Epon 828–polar Viton GF blends with the concentration of the polar Viton GF as a parameter.

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bonds with weaker C–N and/or C–O bonds. A decrease in decomposition temperature was also noted; the largest drop observed was between the neat resin and the formulation containing 5% of the modifier. On the other hand, the char yield increased in proportion with the amount of polar Viton GF in the blend (Figure 11).

TGA thermograms of a series of blends of polyimide and double-bond containing Viton GF are shown in Figure 12. The onset of weight loss in the neat polyimide resin was observed at approximately 510 °C, and the maximum rate of decomposition was recorded at 610 °C. The char yield of 70% was obtained at 800 °C in nitrogen atmosphere. The double-bond containing Viton GF decomposes rapidly at temperatures above 400 °C. The thermal stability of various polyimide–double-bond containing Viton GF blends depends on the ratio of the two components in the blend, as seen in Figure 12. Similar results were observed in polyimide–polar Viton GF blends as shown in Figure 13.

Conclusions

Several fluoroelastomer-modified thermoset resins were prepared and investigated. The nonmodified elastomer was incompatible with the epoxy and the polyimide matrix. Modification via the introduction of polar groups resulted in a compatible blend of polar elastomer and partially cured epoxy resin. During the subsequent postcure, however, the elastomer phase separated. We believe that a careful control of postcure conditions could produce the desired blend morphology.

For the polyimide matrix, compatibility was not observed, regardless of the type of modification on the fluorocarbon elastomer.

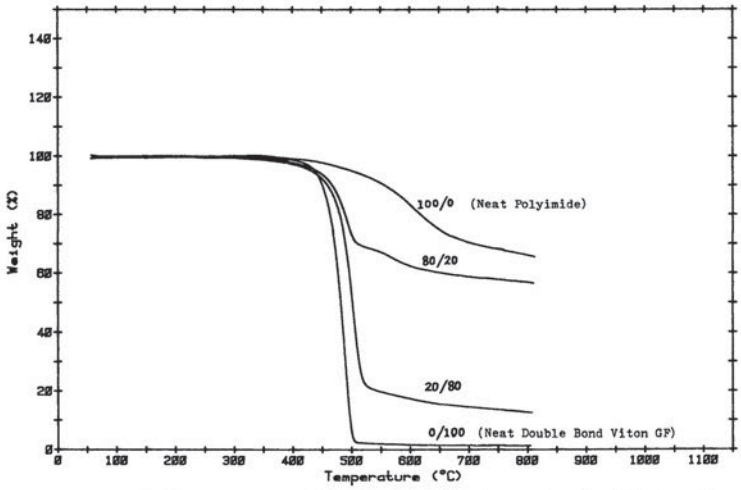

Figure 12. TGA thermograms for a series of polyimide–double-bond containing Viton GF blends with the concentration of the double-bond containing Viton GF as a parameter.

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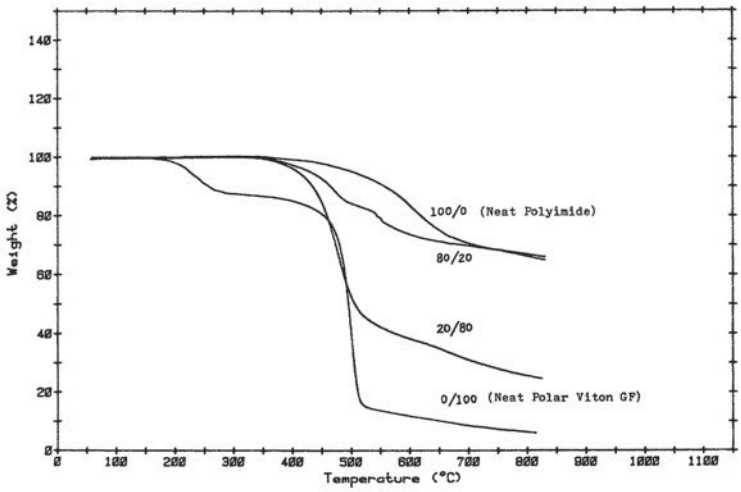

Figure 13. TGA thermograms for a series of polyimide–polar Viton GF blends with the concentration of the polar Viton GF as a parameter.

Blends containing 15% polar elastomer and epoxy matrix were characterized by the bimodal distribution of rubbery particles. Electron microscopy has shown that some epoxy resin exists within the elastomer inclusions. Interestingly, some elastomer molecules (particularly in blends containing 15% elastomer) remain within the epoxy network and cause an apparent decrease in T_g. Simultaneously, a fourfold increase in fracture energy was observed in comparison with the neat epoxy resin.

Finally, the polar fluorocarbon elastomer was found to be less thermally stable than the nonmodified one. The effect of addition of polar elastomer on the stability of blends was more pronounced with epoxies than polyimides.

Acknowledgment

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List of Symbols

E'' Loss modulus, Pa
$\mathcal{G}_{Ic}$ Critical strain energy release rate in mode I, J/m^2
T_g Glass transition temperature, °C

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