

# Influence of a Selected Hardener on the Phase Separation in Epoxy/Thermoplastic Polymer Blends

I. Blanco,<sup>1</sup> G. Cicala,<sup>1</sup> O. Motta,<sup>2</sup> A. Recca<sup>1</sup>

<sup>1</sup>Department of Physical and Chemical Methodologies for Engineering, University of Catania, Viale Andrea Doria 6, 95125 Catania, Italy

<sup>2</sup>Department of Educational Science, University of Salerno, via Ponte Don Melillo, 84084 Fisciano (SA), Italy

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**ABSTRACT:** Low molecular weight thermoplastic PES : PEES (polyethersulfone : polyetherethersulfone) copolymer, bearing amine reactive end groups, was blended with a diglycidyl ether of bisphenol A (EPON828) epoxy resins. Two different curing agents, MDEA [methylene bis(2,6-diethylaniline)] and 3,3' DDS (3,3'-diamino diphenyl sulfone), were used separately to compare flow behavior, curing kinetics, and morphology of the final samples. Emphasis was placed on different phase behaviors of the cured systems, attributed to different solubilities of thermoplastic in the

thermoset system as well as to the reactivity of the two curing agents. The presence of PES : PEES was shown not to affect the reaction rate of epoxy blends with respect to the neat resin by the reactive nature of its end groups. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 361–371, 2004

**Key words:** epoxy resin; thermoplastics; interpenetrating networks (IPN); viscoelastic properties, differential scanning calorimetry (DSC)

## INTRODUCTION

Epoxy resins are extensively used as highly crosslinked materials in many applications where special performances, such as good mechanical, thermal, and electrical properties, are required. The incorporation of thermoplastic polymers into resins has been widely recognized as an alternative to rubber toughening to improve their inherent brittleness, without a significant decrease of desirable properties such as high glass transition, modulus, and chemical resistance.<sup>1–4</sup> Several studies have been carried out on epoxy blends containing thermoplastics such as poly(ether imide)s (PEIs),<sup>5,6</sup> polycarbonate,<sup>7–9</sup> poly(phenylene oxide),<sup>10</sup> and poly(ether sulfone).<sup>1,11</sup> The latter polymer was functionalized with different reactive groups to improve its interfacial adhesion between the two phases. In fact, such an adhesion is supposed to be of particular importance to achieve an effective toughening of epoxy.<sup>12,13</sup>

Addition of thermoplastics to thermosets leads to different phenomena. The initial mixture is generally homogeneous and phase separation could take place during the curing of the thermoset. This technique is called reaction-induced phase separation<sup>14</sup> and may

lead to several morphological types such as particulate, bicontinuous, and phase inverted. Nevertheless, the initial homogeneous mixture might not undergo phase separation under appropriate conditions during the curing of thermoset resin. In this way a homogeneous material is obtained. Examples of materials produced under these conditions are polycarbonate epoxy blends.<sup>7,15,16</sup>

This article regards a study of the effect of a curing agent on phase separation and rheological behavior of a thermoplastic-modified epoxy system.

Concerning the epoxy thermosets, the rheological changes occurring during the curing process can be measured by dynamic experiments detecting resin changes that range from a low-melting solid to a low-viscosity liquid and then through the gel point to a highly crosslinked, stiff solid. All these steps occur during the thermosetting process and are controlled by the transport phenomena and by reaction kinetics and structure formation of reactive materials. Therefore, morphological and calorimetric investigations of modified epoxy systems were performed to analyze the structure–property relationship and to gain an exact idea of the curing-related phenomena.

Correspondence to: A. Recca (preside@presidenza.ing.unict.it).

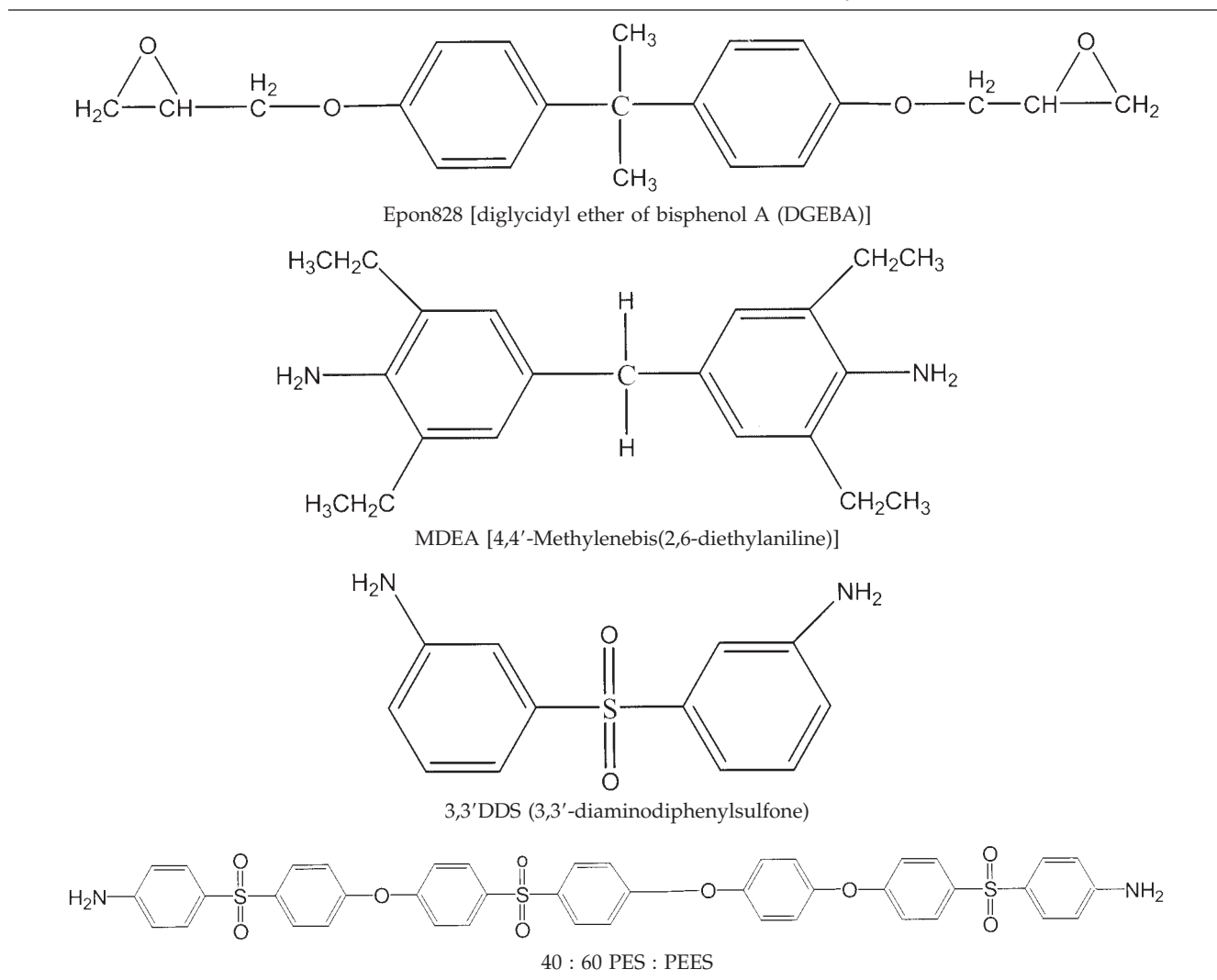
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## EXPERIMENTAL

### Preparation of materials and samples

The epoxy resin was a diglycidyl ether of bisphenol A (DGEBA, Epon828) supplied by Shell Chemical, Ak-

TABLE I  
Structures of the Materials Used in This Study



ron, OH), with an epoxy equivalent weight of 188.05. The curing agents were 3,3'-diaminodiphenylsulfone (3,3'DDS; Aldrich, Milwaukee WI) and 4,4'-methylenebis(2,6-diethylaniline) (MDEA; Lonza, Basel, Switzerland) and were added in a 77% stoichiometry ratio. The use of an excess of the epoxy species has found wide application for commercial formulations because it allows for a plasticization effect that improves the toughness of the resin. The thermoplastic polymer was an amine-ended copolymer, 40 : 60 polyethersulfone : polyetherethersulfone (PES : PEES), prepared in our laboratories<sup>17</sup> with a molecular weight of 9000  $M_n$ . The structures of the materials used are reported in Table I.

Cured samples were prepared by mixing the thermoplastic with these resins and stirring the resulting mixture for 2 h at 120°C, after which the curing agent was added to the mixture and stirred for 1 h at 80°C. The blended resin mixture was poured into a pre-

heated silicone rubber mold and degassed for 30 min at 145°C. The temperature was then increased at 2°C/min to 180°C and maintained at that temperature for 3 h. At the end of the curing cycle the panels were allowed to cool slowly at room temperature. Panels with dimensions 150 × 80 × 5 mm were obtained.

The formulations of the studied systems are shown in Table II.

### Testing techniques

#### Rheological characterization

Rheological characteristics of the matrix resin and thermoplastic-modified systems were determined on an Ares rheometer (Rheometric Scientific, Piscataway, NJ). Dynamic viscosity  $\eta^*$ , elastic modulus  $G'$ , and loss modulus  $G''$  were obtained by oscillatory shear measurements as a function of temperature and by a

TABLE II  
Formulation Used in This Study (in wt %)

Component/system	1a	2a	3a	1b	2b	3b
Epon828	75.90	64.51	53.13	79.77	67.81	55.84
MDEA	24.10	20.49	16.87	0.00	0.00	0.00
3,3'DDS	0.00	0.00	0.00	20.23	17.19	14.16
40 : 60 PES : PEES	0.00	15.00	30.00	0.00	15.00	30.00

series of isothermal experiments using parallel plates (40 mm diameter), separated by a 1.2-mm gap. The sample chamber was purged with nitrogen. Isothermal tests were performed by preheating the sample chamber to the fixed temperature, after which the sample was quickly inserted and the analysis started. The analysis was done with optimized instrumental parameters of 35% strain and angular frequency of 30 rad/s.

#### DSC measurements

Thermal properties of the samples were measured calorimetrically using a Mettler (Zurich, Switzerland) TC 11 differential scanning calorimeter operating under dry N<sub>2</sub> flux and calibrated using indium and zinc standards.

Samples were cured during a first temperature scan ranging from -50 to 300°C, at a heating rate of 10°C/min. That allowed an evaluation of thermal parameters such as glass transition of prepolymer ( $T_{g0}$ ), total enthalpy involved in the curing process ( $\Delta H_T$ ), and temperature at which the exotherm showed a maximum ( $T_{exo}$ ). Then a second scan was carried out to determine the glass-transition temperature of the cured materials ( $T_{gz}$ ). Moreover, samples were cured using different temperature scanning rates: 5, 10, 15, 20, 25, and 30°C/min to apply multiple scanning rate methods.

#### DMTA measurements

DMTA tests were carried out for cured samples with an Ares rheometer (Rheometric Scientific) at a fixed frequency of 10 rad/s and 0.1 strain, with a 2°C/min heating rate, using samples of sizes 12 × 40 × 3 mm. Storage modulus, loss modulus, and tan  $\delta$  were obtained by torsion mode.

#### Morphological analysis

Scanning electron micrographs were obtained using a Cambridge (UK) 90 SEM. Samples were prepared by polishing with alumina and then etched with a 3 : 2 mixture of sulfuric acid : distilled water. The acid mixture has the role of etching in the thermoplastic phase. Then the samples were washed with running

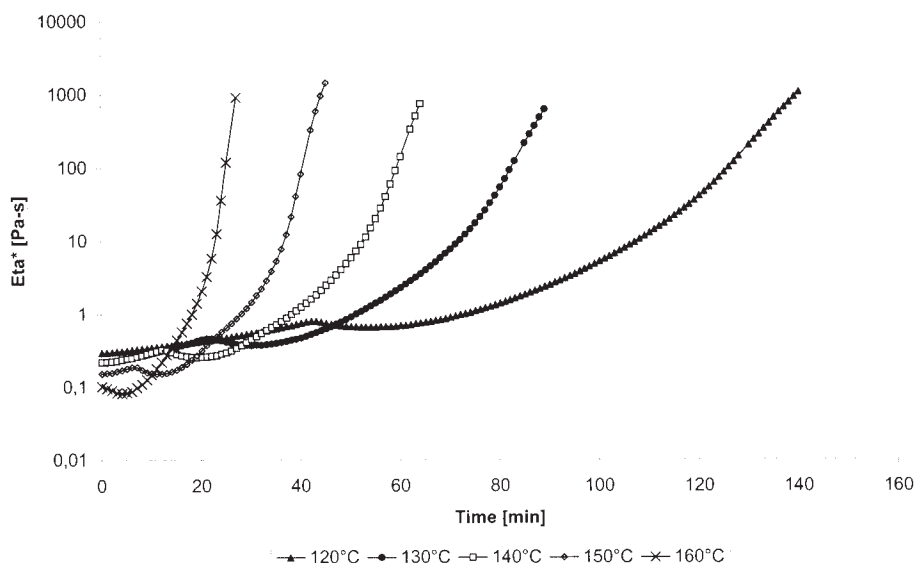
water and coated with gold before the SEM examination.

## RESULTS AND DISCUSSION

Studies on phase separation in thermoplastic-modified epoxy systems have been of interest for many investigations but the mechanism of phase separation has not yet been fully understood, given the system's great complexity. It is known that the mixture of epoxy resins and a thermoplastic polymer like PES shows a lower critical solution temperature (LCST)<sup>18</sup> phase diagram (as shown schematically in Fig. 1). An increase in molecular weight of epoxy species gives rise to a decrease of the cloud point curve and, therefore, for a fixed fraction of PES to the demixing of the thermoplastic phase. The increase of crosslinking density promotes an increase in the complex viscosity of the system that could freeze the morphology. Thus the final morphology of the systems is a result of the competition between molecular weight increase of epoxy, leading to phase separation, and simultaneous crosslinking that could suppress it. In fact, as noted by Pascault et al.,<sup>19</sup> most of the primary morphology development is arrested at gelation of the epoxy-rich phase. Beyond this conversion, deswelling of some of the thermoplastic remaining in solution may be ex-



Figure 1 Schematic phase diagram for epoxy/PES blend.



**Figure 2** Viscosity profile for Epon828/MDEA system with 15% 40 : 60 PES : PEES for isothermal test at 120, 130, 140, 150, and 160°C.

pected because of the contribution of elastic forces to the free energy of mixing. However, this effect is usually not significant in the overall phase-separation process, although phase separation inside the thermoplastic-rich phase may still continue beyond gelation of the epoxy-rich phase. This is attributed to lower conversion of the thermoset fraction segregated from the epoxy-rich phase. Usually, a postcure step at  $T > T_g$  (thermoplastic) is necessary to complete the reaction in the thermoplastic-rich phase and for the development of the final morphology of the thermoset-thermoplastic blend.

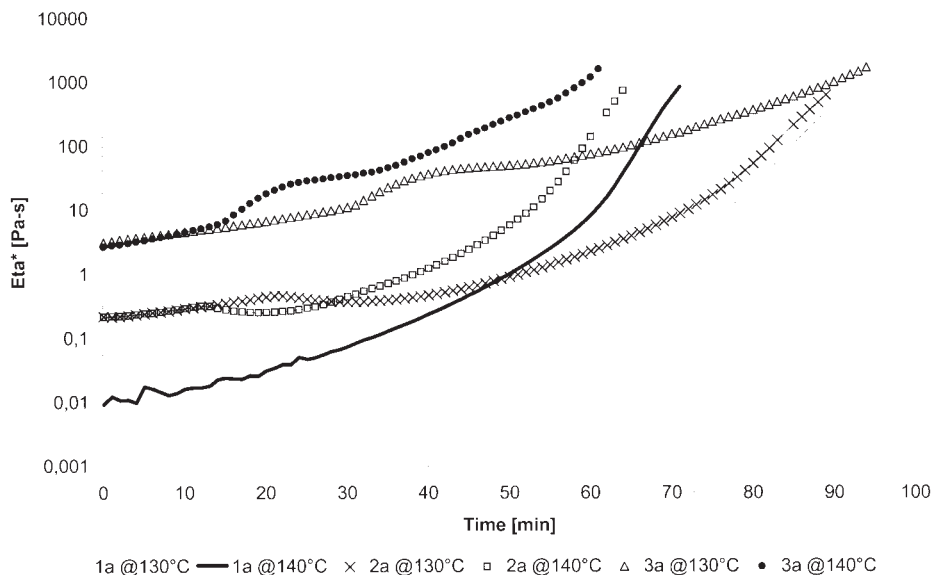
In our study we used a cure cycle at 180°C to prepare the samples for microscopic evaluation. This temperature is close enough to the thermoplastic  $T_g$  to allow complete development of the final morphology being the cure-cycle temperature close to postcure temperatures, as reported by Pascault et al.<sup>19</sup> In fact, as further confirmation, we can observe that the secondary phase separation, attributed to deswelling of the thermoplastic in solution, has been observed in the system studied by Girard-Reydet et al.,<sup>20</sup> but only on systems precured at low temperatures (80°C), and showed secondary phase separation just upon postcuring at high temperature (215°C).

In a meta-stable region, phase separation takes place by a nucleation-growth (NG) mechanism. If the blend reaches the unstable region, the phase separation occurs by spinodal demixing (SD). If the  $\phi_{TP}^0$  (thermoplastic volume fraction) is located in the off-critical region to the left of  $\phi_{TP,crit}^0$  the resulting morphology will consist of a dispersion of thermoplastic-rich particles in a thermoset-rich matrix. On the contrary, when  $\phi_{TP}^0$  is located in the off-critical region to the right of  $\phi_{TP,crit}^0$  a dispersion of thermoset-rich particles

in a thermoplastic-rich matrix is obtained. If the composition is close to the critical point  $\phi_{TP,crit}^0$  a variety of morphologies may be developed.

Figure 2 shows complex viscosity versus time for isothermal investigation at different temperatures for the epoxy resin cured with MDEA and 15% of thermoplastic PES : PEES. It can be observed that, at different temperatures, the viscosity profile shows increased values that are caused by an increase of the molecular weight of the epoxy matrix. In addition, each curve shows a fluctuation that is presumably related to the separation of PES : PEES domains. Moreover it has to be noted that the fluctuation shifts at higher times when the test temperature decreases, a phenomenon that could be explained in terms of decreases of conversion rate as the test temperature is decreased. In fact a lower reaction temperature is also associated with a slower increase of molecular weight of the epoxy/amine species and therefore to a slower attainment of the conditions to favor the demixing of the phases, resulting in a delayed appearance of the fluctuation. In fact the main driving force of the demixing process is the decrease in the absolute value of the contribution to the free energy of mixing, attributed to the increase in the average molar size of the epoxy-amine oligomeric species. Kim and Char<sup>21</sup> demonstrated that the domain size of the separated PES phase has a marked effect on the viscosity of the mixture and the viscosity fluctuation is related to the increase of the domain size during phase separation.

Bonnet et al.<sup>22</sup> found similar results for blends of DGEBA cured with MCDEA (4,4'-methylenebis 3-chloro 2,6-diethylaniline) by varying the amount of PEI (polyetherimide). In particular according to these investigators, at low (10%) percentage by weight of modifier, the



**Figure 3** Viscosity profile for Epon828/MDEA systems with different amounts of 40 : 60 PES : PEES for isothermal test at 130 and 140°C.

complex viscosity shows a rapid decrease of viscosity that corresponds to the phase-separation process attributed to the demixing of highly viscous thermoplastic from the initial dilute solution. At high percentage by weight (33%) of modifier content a gradual increase in viscosity is shown as a consequence of the phase-separation process resulting from separation of low viscous epoxy/amine species from the predominant thermoplastic matrix. Recently Yu et al.<sup>23</sup> conducted a similar analysis on DGEBA/4,4'-DDS systems modified by the addition of PES-PEI blends; the experiments confirmed the results found by Bonnet et al. and showed that, by increasing the molecular weight of the PES component, the fluctuation associated with phase separation is smoothed and widened.

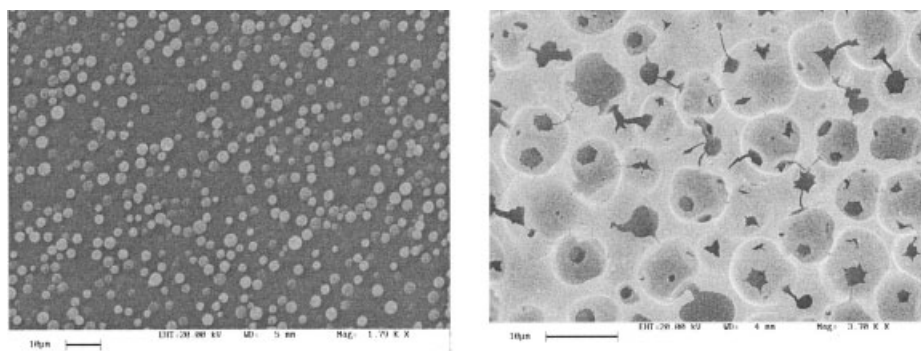
Figure 3 shows complex viscosity versus time for isothermal investigation at two different temperatures, 130 and 140°C, with different concentrations of thermoplastic PES : PEES.

A decrease in viscosity is shown for the system at 15% by weight of modifier, whereas at a high percentage, an increase in viscosity characterizes the phase-separation initiation.

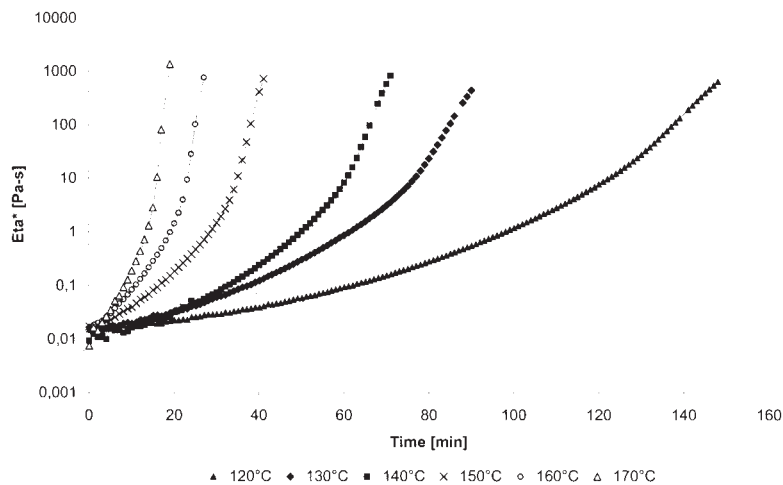
Microscopic observation by SEM on cured samples confirmed the presence of a phase separation in the samples cured with MDEA. In particular, the sample modified by the addition of 15% by weight of PES : PEES copolymer showed a particulate morphology [Fig. 4(a)], and the addition of 30% of copolymer led to a phase-inverted morphology [Fig. 4(b)].

Furthermore it has to be noted that both morphologies (Fig. 4) yield a regular two-phase structure that, as noted previously,<sup>18</sup> is associated with phase decomposition following a spinodal mechanism.

The viscosity profile (Fig. 5) of the epoxy system that was not modified with thermoplastic polymer shows, as expected, increasing values over the entire analyzed range caused by an increase in crosslinking



**Figure 4** SEM microphotographs of Epon828/MDEA system cured with different amounts of thermoplastic: (a) 15% 40 : 60 PES : PEES; (b) 30% 40 : 60 PES : PEES.



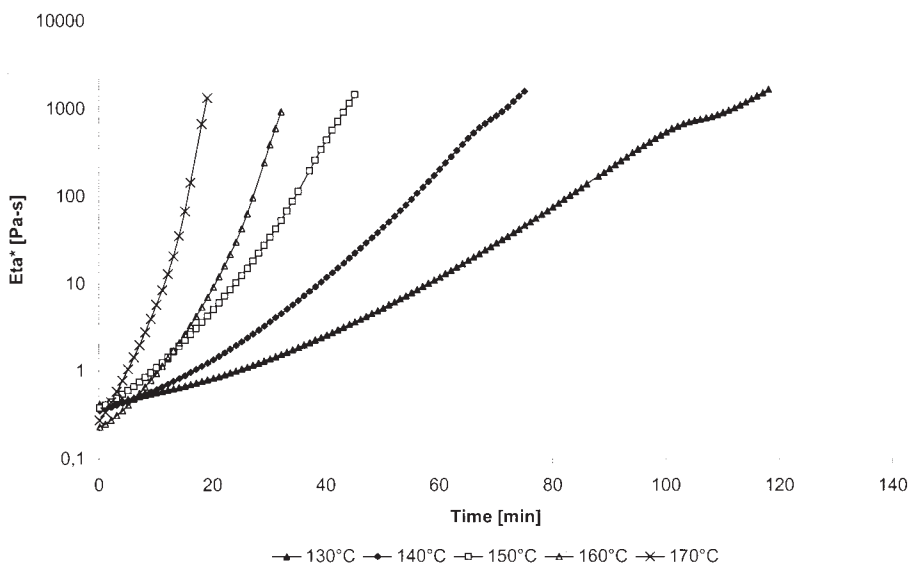
**Figure 5** Viscosity profile for Epon828/MDEA system with 0% 40 : 60 PES : PEES for isothermal test at 120, 130, 140, 150, and 160°C.

'density and an absence of fluctuation in the viscosity traces.

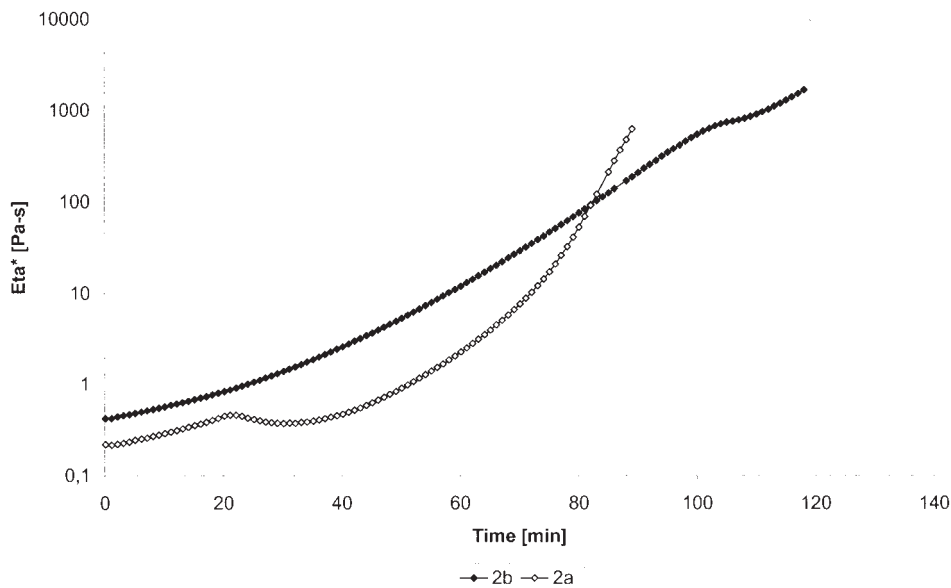
The behavior of the same epoxy resin cured with a different curing agent was also analyzed to compare the results and to understand better the phase-separation process. Systems that are cured with 3,3'DDS were prepared and analyzed under the same conditions. The results show that when 3,3'DDS was used as the curing agent no fluctuation was observed in the viscosity profile for the PES : PEES-containing system, as shown in Figure 6 for different temperatures. There were only increasing values of viscosity with the reaction time caused by an increase in molecular weight of the epoxy matrix. The lack of fluctuation can be attributed to the absence of phase separation. In this

case a homogeneous interpenetrating network (IPN) could be formed. Samples cured under the same conditions as samples with MDEA were analyzed by SEM and it was found that no morphology appeared, thus confirming the presence of a homogeneous IPN.

These different types of behavior could be related to the different solubilities of the thermoplastic in the thermoset system. Riccardi et al.<sup>24</sup> showed that, for a PEI/DGEBA system, a DDS-based system presents an increased solubility compared to that of a MDEA-based one. Conversion versus time traces (see Fig. 12 below) described in the following show that no meaningful difference exists in reactivity between the two systems. However, if we consider the rheological traces (Fig. 7) for the two systems we can observe that



**Figure 6** Viscosity profile for Epon828/3,3'DDS system with 15% 40 : 60 PES : PEES for isothermal test at 130, 140, 150, 160, and 170°C.

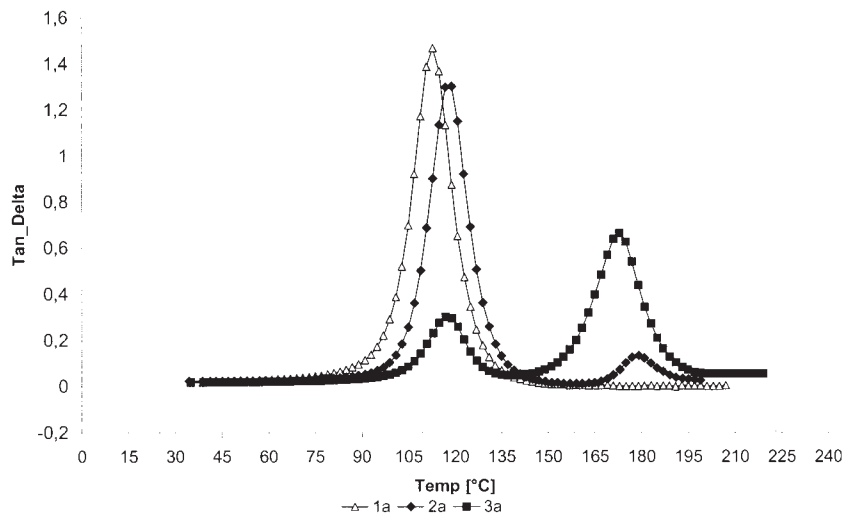


**Figure 7** Comparison of viscosity traces for systems **2a** and **2b** at test temperature of 130°C.

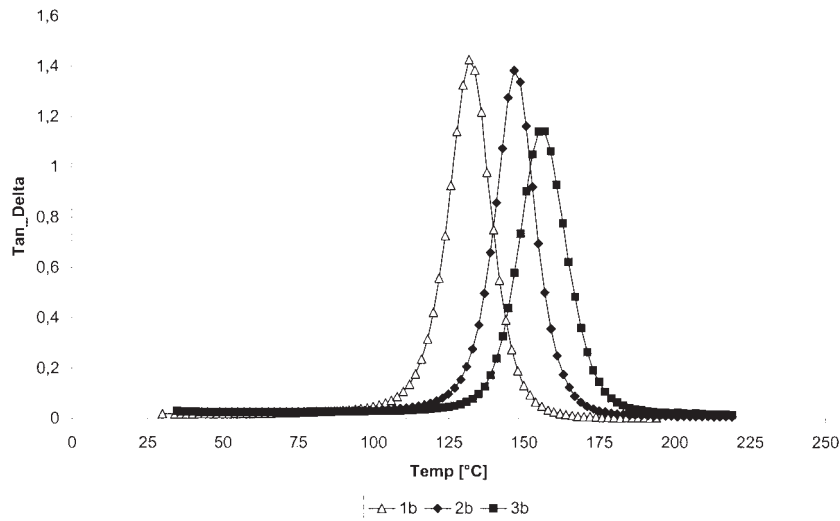
the 3,3'DDS-based system is characterized by higher viscosity compared to that of the MDEA system. Such a difference, coupled with the increased solubility of the PES : PEES in the DDS system, play against phase demixing. Similar results were found by Xie and Yang.<sup>25</sup> In their work these authors studied different blends with epoxy resin with similar chemical structure but higher prepolymer molecular weight; they showed that by increasing the viscosity of the blends the phase separation could be suppressed. If we compare (Fig. 7) the rheology traces for the Epon828/MDEA/15% PES : PEES and Epon828/DDS/15% PES : PEES systems at test temperature of 130°C we can observe a small fluctuation in the proximity of the gel point for the system cured with 3,3'DDS. That fluctu-

ation could be related to the beginning of the demixing process, although the higher viscosity<sup>20</sup> at that stage can suppress the phase-separation process leading to the formation of a homogeneous IPN network. The combination of different solubilities and viscosities seems to be the driving factor that controls the morphologies of the studied systems. For higher temperatures no fluctuation at all was observed for the Epon828/3,3'DDS/15% PES : PEES system.

DMTA analysis confirmed the presence of a phase-separated morphology for the systems cured with MDEA in the presence of the copolymer PES : PEES. In fact, two peaks that are related to the epoxy and thermoplastic phases appeared in the DMTA traces. The peak at higher temperature increased in area with



**Figure 8** Tan\_Delta curves for Epon828/MDEA system with different amounts of thermoplastic.

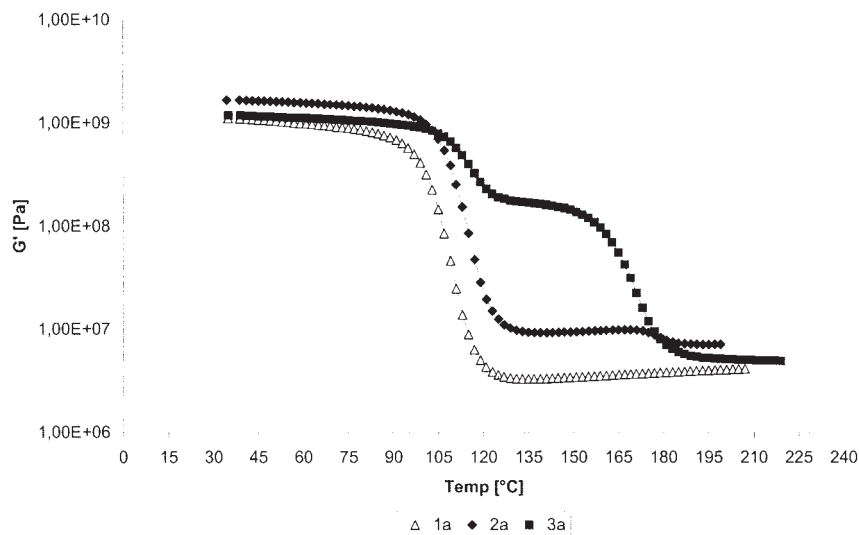


**Figure 9** Tan\_Delta curves for Epon828/3,3'DDS system with different amounts of thermoplastic.

the increasing amount of PES to the detriment of the one at lower temperature (epoxy phase). That is evidenced in Figure 8, where DMTA traces of epoxy resin with 0, 15, and 30% of thermoplastic were used. Moreover, it should be mentioned that the peak temperature, which can be associated with the  $T_g$  of the epoxy phase, increased slightly in the presence of PES : PEES, probably because high  $T_g$  PES : PEES was partially dissolved in the epoxy phase, although the amount of PES : PEES had little effect on the increase of  $T_g$ . That increase in  $T_g$  was also observed by DSC analysis. Moreover it must be noted that the peak associated with the thermoplastic phase shows small decreases at higher percentage of thermoplastic amount, an effect that can be attributed to the presence of epoxy/amine species being dissolved in the thermoplastic phase.

Such an effect is usually shown in an epoxy rubber-toughened system when rubber remains dissolved in the epoxy phase. The DMTA traces of the resin cured with 3,3'DDS are shown in Figure 9. It should be noted that for all analyzed compositions a single peak in  $\tan \delta$  was observed, suggesting that there was a single phase but no phase separation. Figure 8 shows that the  $T_g$  of the system had increasing values with increasing PES : PEES content, which could be attributed to the formation of an IPN network characterized by permanent crosslink points caused by the reactive ends of the thermoplastic.

In Figure 10 the elastic modulus for the EPON/MDEA system containing 0, 15, and 30% of PES : PEES is shown. As can be noted the curves at 0 and 15% demonstrate similar behavior concerning the modulus



**Figure 10** Storage modulus ( $G'$ ) for Epon828/MDEA system with different amounts of thermoplastic.



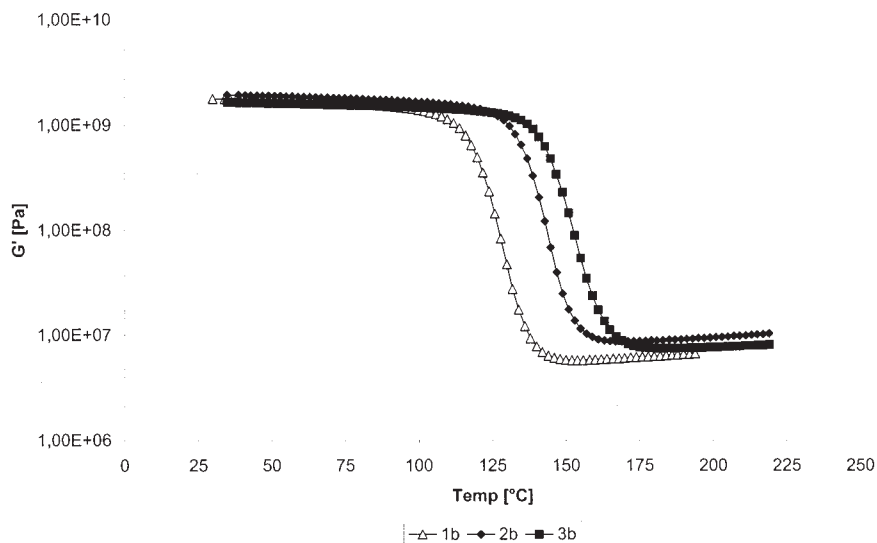


Figure 11 Storage modulus ( $G'$ ) for Epon828/3,3'DDS system with different amounts of thermoplastic.

decay, corresponding to the  $T_g$  of the epoxy phase. However, when a higher amount of PES : PEES is present (30%) a double-shaped curve is obtained and the second modulus decay, corresponding to the glass transition of the thermoplastic phase, is more pronounced than that for the system with 15% PES : PEES, in which only a small fluctuation was observed. Nevertheless, the curves (Fig. 11) of the systems cured with 3,3'DDS and 15 and 30% PES : PEES showed similar behavior compared to the system that did not contain the thermoplastic polymer (i.e., after the first decay there was no fluctuation). The only difference that could be noted was the temperature region at which the  $G'$  modulus decayed in correspondence with the glass transition of the system. That temperature region increased with an increase of thermoplastic content.

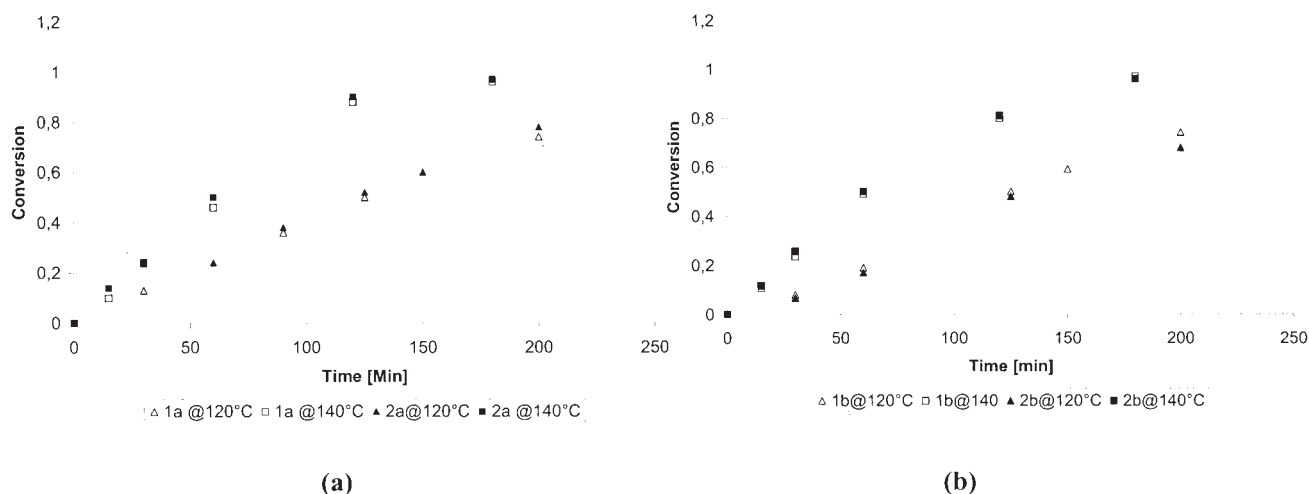
Differential scanning calorimetry was used to derive kinetic parameters of the reactions involved in the curing process, such as total enthalpy ( $\Delta H_T$ ) and temperature at which the exotherm is maximum ( $T_{exo}$ ), and to determine the evolution of curing during isothermal tests by measuring the residual heat ( $\Delta H_{resid}$ ) of the resin at different curing times. The technique is based on the assumption that the heat evolved during

the curing is proportional to the energy released as the epoxy groups react. The  $T_{g0}$  (glass-transition temperature of the prepolymer) and the magnitude of the curing exotherm were determined from the first temperature scan in the DSC at a heating rate of 10°C/min, whereas a second scan was used to evaluate the glass-transition temperature of the cured materials ( $T_{g\infty}$ ).

The calorimetric results are shown in Table III. It can be observed that the exothermic peak temperature does not change appreciably in the presence of the thermoplastic PES : PEES, indicating that the copolymer does not delay the curing reaction rate of the neat epoxy matrix, as it usually occurs in thermoplastic-modified systems.<sup>26,27</sup> However, a different behavior can be observed concerning the total heat of the reaction ( $\Delta H_T$ ) of both resin systems. The reported total heat of the reaction does not refer to the overall weight of the mixture, but only to the weight of the resin. Table III clearly demonstrates that the  $\Delta H_T$  of the epoxy resin cured with MDEA does not change with the presence of PES : PEES but is slightly influenced when 3,3'DDS is used as a curing agent. In addition, the table shows that the glass-transition temperatures of the prepolymer and the fully cured system are

TABLE III  
Thermal Properties of the Uncured Thermoplastic Modified and Unmodified EPON Resin with the Two-Curing Agent, Obtained at a Heating Rate of 10°C/min

	Epon-MDEA	Epon-MDEA 15% PES : PEES	Epon-3,3'DDS	Epon-3,3'DDS 15% PES : PEES
$T_{g0}$ , °C	-17.5	-9.7	-12.7	-3.6
$T_{g\infty}$ , °C	105	113	124	137
$\Delta H_T$ , J/g	245.8	248	296.8	260.7
$T_{exo}$ , °C	226.5	229	218.3	223.5



**Figure 12** Conversion curve for temperatures at 120 and 140°C representing: (a) conversion–time plot for systems **1a** and **2a**; (b) conversion–time plot for systems **1b** and **2b**.

higher for the 3,3'DDS-cured system compared to those for the MDEA system and that the presence of PES : PEES in both cases enhances both  $T_g$  values, as previously verified in the DMTA analysis. The effect of the curing agent on the glass-transition temperature could be explained by different chemical structures of the curing agents. In fact, 3,3'DDS is characterized by a higher polar and rigid group, the sulfone, in the center of its molecule, whereas the MDEA has  $\text{CH}_2\text{CH}_3$  groups on the benzene ring that do not favor molecular packing, leading to an increase of free volume and therefore to a decrease in  $T_g$ .

To study the reaction extent as a function of time and to determine the evolution of curing, we cured resin mixtures at  $T = 120, 140, 160,$  and  $180^\circ\text{C}$  and measured the residual heat ( $\Delta H_{\text{resid}}$ ) of the resins at different curing times. As expected, the reaction rate and final conversion increased with increasing curing temperature (as shown in Fig. 12). That increase proves that the reaction reached the point of vitrification at progressively higher conversion when higher reaction temperatures are applied.<sup>28</sup> However, it is worth noting that in all cases the addition of the PES : PEES copolymer to the epoxy does not decrease the reaction rate of the curing process. Different results have been found from various investigators dealing with thermoplastic-modified epoxy resins: that is, the presence of a thermoplastic polymer normally delays the curing reaction.<sup>28–30</sup> Nevertheless, in some cases<sup>31</sup> an increase in the reaction rate has been observed with increasing values of thermoplastic content.

These authors<sup>28–30</sup> explained the slower reaction rate of the thermoplastic-modified resin in terms of decreased density of the reactive groups. It should be mentioned that those articles refer only to the use of thermoplastic without reactive end groups. However, Su and Woo<sup>31</sup> explained the higher reaction rate in

terms of uneven segregation or distribution of DDS, in two phases and of a plasticization effect caused by PEI addition. Because of the reactive nature of the end groups and chemical structure of our copolymer, all those assumptions should not be applied in our case. In fact, the reactive nature of the end groups of the PES : PEES copolymer tends to counteract the effects of decreasing molecular mobility caused by increased viscosity resulting from the addition of the thermoplastic. Moreover, the backbone nature of this copolymer is characterized by an extreme solubility at an early stage of the reaction. We believe therefore that the balance between the reactive nature of the end groups, which favors the reaction of the epoxy, and the increased viscosity, which tends to slow down the reaction, results in a smaller difference both in terms of conversion and gelation time behavior of the modified systems.

## CONCLUSIONS

In this article the effect, in terms of morphology, viscoelasticity, rheometry, and curing kinetics behavior of a blend of DGEBA with a novel 40 : 60 PES : PEES copolymer, was studied by varying the amount of thermoplastic and type of curing agent.

The choice of curing agents, with different solubilities and viscosities of blends, demonstrated marked differences in the morphological and viscoelastic behavior of the epoxy system. The DGEBA/MDEA system showed a phase-separated morphology that can be seen in a double peak in the DMTA traces. The DGEBA/3,3'DDS was characterized by a homogeneous morphology so that an IPN network was formed. The difference in morphology was mainly attributed to different viscosity and solubility effects of the curing agents. The phase-separation effect was

detected in the isothermal rheological traces where a fluctuation for the DGEBA/MDEA system with 15% of PES : PEES appeared at an early stage of the curing reaction. For comparison, the same test was conducted for the DGEBA/3,3' DDS system with 15% of 40 : 60 PES : PEES and no fluctuation could be detected at an early stage of the reaction.

The DSC testing also underlined no significant change in the curing rate resulting from thermoplastic addition. This effect was related to the reactive nature of the copolymer end groups and to the high solubility in the epoxy system.

The basic study presented herein can help those interested in the development of novel epoxy resins. In particular the results shed more light on the effects of the choice of curing agent on the phase-separation behavior of thermoplastic/epoxy blends. The possibility of controlling morphology of the blends, as shown, has a profound effect on the viscoelastic behavior of the resin and therefore on its uses.

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