# Development of a Toughened DGEBS/DDS System Toward Improved Thermal and Mechanical Properties by the Addition of a Tetrafunctional Epoxy Resin and a Novel Thermoplastic

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**ABSTRACT:** It was the object of the present article to discuss the effect of the addition of a tetrafunctional resin, namely, tetraglycidyl-4,4'-diaminodiphenylmethane (TG-DDM), and of a novel 40:60 polyethersulfone:polyetherethersulfone (PES:PEES) copolymer on a blend constituted by a difunctional resin, diglycidyl ether of bisphenol S (DGEBS), and an aromatic ammine, 4,4'-diaminodiphenylsulfone (4,4'DDS). The formulated blends were fully characterized in terms of the morphology and the viscoelastic and mechanical properties. The modification by the tetrafunctional resin was proved to be a useful means to improve the glass transition temperature and, therefore, to widen the range of the working temperature. The addition of the novel copolymer resulted in a marked increase in toughness with-out negatively affecting the thermal and elastic properties of the blend. TEM analysis, despite the high amount of thermoplastic used, showed a homogeneous morphology that would lead to the conclusion of the existence of a full-IPN network. Moisture-uptake experiments were conducted both on the blend and on the resins on their own. It was shown that the combination of the difunctional resin with the tetrafunctional led to a decrease of the percent of the water absorbed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 268–273, 2003

**Key words:** thermoplastics; toughness; interpenetrating networks (IPN)

## INTRODUCTION

Epoxy resins are currently used as the matrix in advanced fiber-reinforced polymers (FRPs) because of their superior thermal, mechanical, and corrosion-resistance properties. The usage of epoxy resins as a matrix for FRPs has required, in the last decade, an enhancement of these characteristics, and for these purposes, modifications by rubbers and engineering thermoplastic have been investigated.

The modification of epoxy resins with reactive liquid elastomers such as carboxyl-terminated butadiene acrilonytrile rubbers (CTBNs) or crosslinked rubber particles has been shown to be successful to increase the fracture toughness of brittle epoxy.[1–5] However, modification by the addition of low $T_g$ materials as the rubbers results in a significant decrease in the modulus and the glass transition temperature of the cured resin. Recent studies confirmed a decay of the moisture resistance of epoxy systems modified by the addition of liquid reactive rubbers.[6]

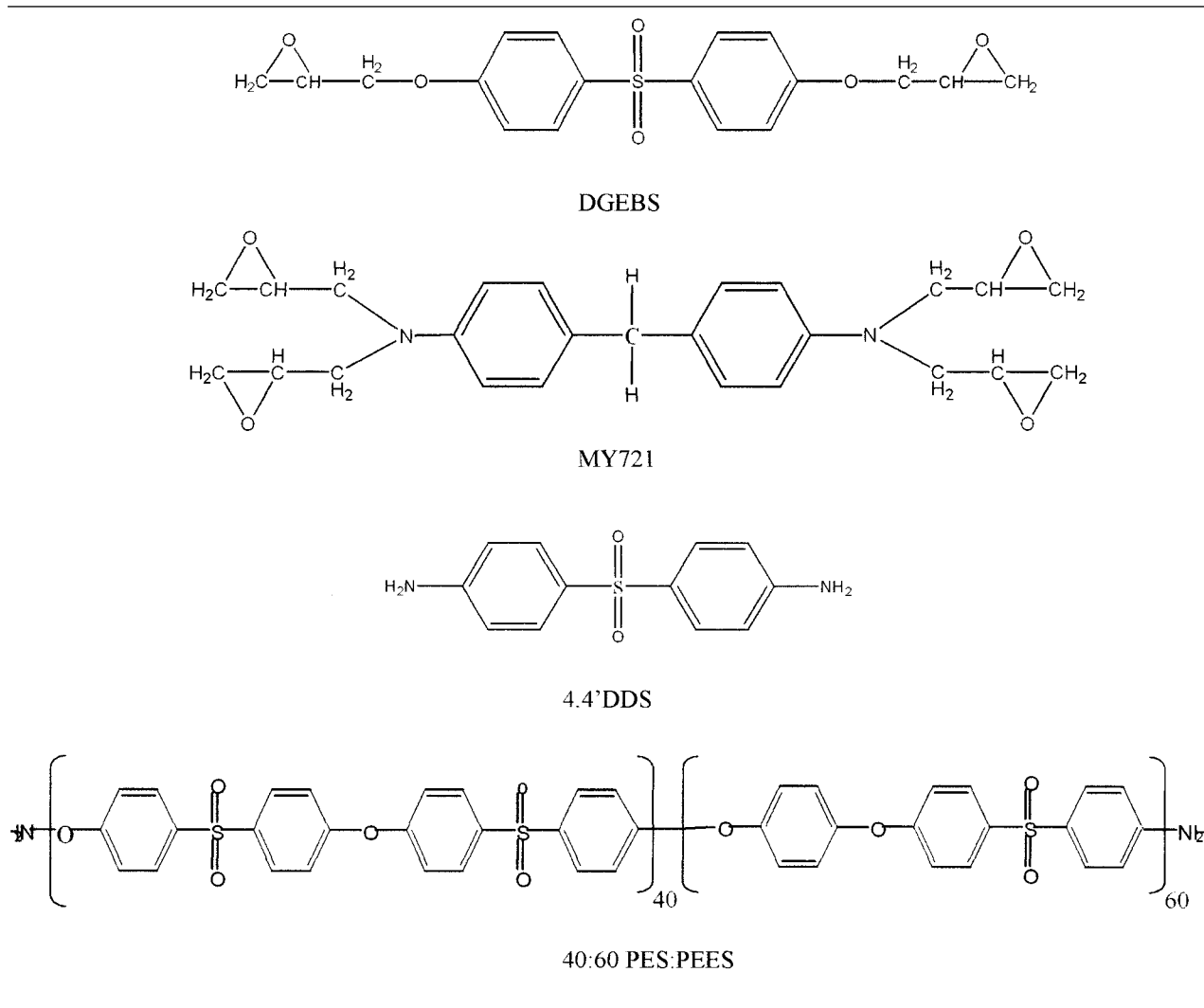To overcome these problems, many attempts have been made to modify epoxy resin with high-performance engineering thermoplastics that are characterized by a high $T_g$ and high toughness, such as polysulfone (PSF),[7,8] polyethersulfone (PES),[9–11] polyetherimide (PEI),[12,13] and polyimide (PI).[14] The addition of a high-performance engineering thermoplastic led, under appropriate conditions, to phase separation into different phases.

On the other hand, attempts have been made to dissolve the thermoplastics in the epoxy resins homogeneously.[15–17] This technique implies the formation of an interpenetrating polymer network (IPN) which blends two polymers by the entanglement of their networks without chemical bonding between them. The formation of the full-IPN structure makes it possible to homogeneously blend the epoxy matrix and the thermoplastic or to uniformly disperse the thermoplastic in the epoxy matrix at a microscopic level. The full-IPN network shows combined properties of the two polymers because of the composite structure at the molecular level.

We previously reported the synthesis and the toughening effect on thermosets of copolymers polyethersulfone:polyetherethersulfone (PES:PEES) with different reactive groups.[18–22] PES:PEES copolymers with an amine end group have been blended with different epoxy resins and their effects on the thermal–mechanical[23] and rheological properties[24] have been investigated.

**TABLE I**
**Structures of DGEBS, MY721, 4,4' DDS, and 40:60: PES:PEES**

DGEBS

MY721

4.4'DDS

40:60 PES:PEES

In previous studies, we analyzed the effect on the morphology and thermomechanical properties of an epoxy system, based on diglycidyl ether of bisphenol S (DGEBS) and 4,4'-diaminodiphenylsulfone (4,4'DDS) of the addition of a novel PES:PEES copolymer. The thermoplastic addition led to increases both in the $T_g$ and toughness of the blend without negatively affecting the modulus of the resin. Nevertheless, the higher value of $T_g$ reached was 150°C when a 30% by weight of a thermoplastic was employed.

To improve the thermal properties of the blend, we mixed the tetrafunctional resin tetraglycidyl-4,4'-diaminodiphenylmethane (TGDMM) with a mixture composed of DGEBS/DDS and the 40:60 PES:PEES copolymer. The TGDMM is the most widely accepted base resin[26] employed in formulating epoxy systems to be used in aerospace applications where high hot/wet resistance is required. We have proved that by adding only a low percentage of TGDDM it is possible to attain the same performance as that of standard systems used in aerospace like the Cycom 977-2.

## EXPERIMENTAL

### Materials and preparation of samples

The epoxy resins used were DGEBS (Epiclon830S) supplied by Shell (Cedex, France), having an epoxy equivalent weight of 181.04, and a TGDDM sold by Ciba Ceigy (Basel, Switzerland) under the name of MY721, having an epoxy equivalent weight of 113. The curing agent used was 4,4'DDS supplied by Aldrich (United Kingdom). The toughening agent used was an amine-ended copolymer, 40:60 PES:PEES, prepared in our laboratories, with a molecular weight $M_n$ of 12,000. (See Table I). The curing agent was added in a 77% stoichiometry ratio. Cured samples were prepared by mixing the thermoplastic and the resins and stirring the resulting mixture for 2 h at 130°C. The curing agent was then added and the mixture stirred for 1 h at 80°C. The blended resin mixture was then poured into a preheated silicone rubber mold and degassed for 30 min at 145°C. The temperature was then increased at 2°C/min up to 180°C and held at this

**TABLE II**
**Formulations of the Systems**

| Component | Sample | | | | | |
|---|---|---|---|---|---|---|
| | 1A | 1B | 2A | 2B | 3A | 3B |
| Epiclon 830S | 79.11 | 55.38 | 53.96 | 37.77 | 0.00 | 0.00 |
| MY721 | 0.00 | 0.00 | 23.13 | 16.19 | 70.27 | 49.19 |
| 4,4' DDS | 20.89 | 14.62 | 22.91 | 16.04 | 29.73 | 20.81 |
| 40:60 PES:PEES | 0.00 | 30.00 | 0.00 | 30.00 | 0.00 | 30.00 |

value for 3 h. At the end of the cure cycle, the panels were left to cool slowly at room temperature. The formulations of the systems studied are listed in Table II.

### Experimental techniques

#### Morphological analysis

Ultrathin sections of the modified epoxy resins were cut and examined, using a transmission electron microscope (TEM; JEM-1200EX, JEOL, Co. Ltd.) to observe the microstructure. The specimens for the TEM observations were stained with ruthenium tetroxide (RuO4).

#### Mechanical analysis

Molded panels were used to produce samples for the following mechanical tests: A 3-point bend test was carried out at 5 mm min$^{-1}$ using a sample size of 50 $\times$ 10 $\times$ 3 mm to measure the flexural modulus. The yield strength ($\sigma y$) was measured in the tension mode using a sample size of 10 $\times$ 10 $\times$ 3 mm. The crack-opening stress intensity factor ($Kc$) and the energy of fracture ($Gc$) were measured at the speed of 1 mm/min using a sample size of 70 $\times$ 10 $\times$ 3 mm with a

single-edge notch. All measurements were made at 23°C.

#### DMTA analysis

DMTA tests were carried out for the cured samples by a dynamical mechanical thermal analyzer, MK IV by Rheometric Scientific, at a fixed frequency of 1 Hz with a 2°C/min heating rate using samples of sizes 4.5 $\times$ 10 $\times$ 3 mm. The dynamic modulus and tan $\delta$ were obtained by a dual-cantilever mode.

### RESULTS AND DISCUSSION

Previously,[25] we characterized blends of DGEBS/DDS mixed with a 40:60 PES:PEES copolymer. We found that the addition of the copolymer to the epoxy resin led to an increase of the toughness and the glass transition temperature of the material. The maximum $T_g$ reached was, however, limited to 150°C, which is still an inadequate value for resins that have to be used as a matrix for aerospace composites. In fact, in such applications, an important requirement of the hot/wet resistance needs to be addressed.

To improve the thermal resistance, the base system, constituted of DGEBS/DDS, was blended with TG-DDM. TGDDM is widely recognized as the standard to formulate matrices characterized by a high $T_g$, but if it is used on its own, it is affected by brittleness.[26] Wright[26] outlined in his review that several attempts to toughen TGDDM with rubber or an engineering thermoplastic have ended with poor results, mainly because of the inherent high crosslink density.

In the present study, to improve the thermal performances, the base system was reformulated, including a 30% amount of TGDDM. The effect on the viscoelastic properties of this modification is summarized in
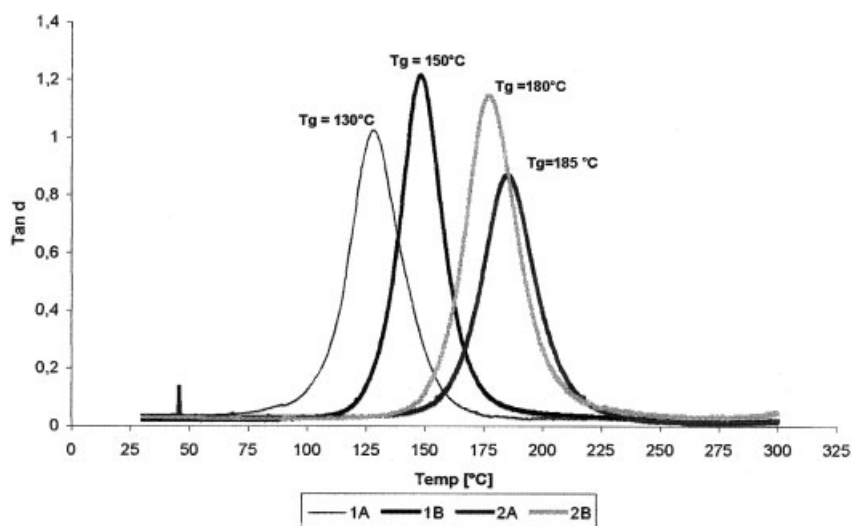


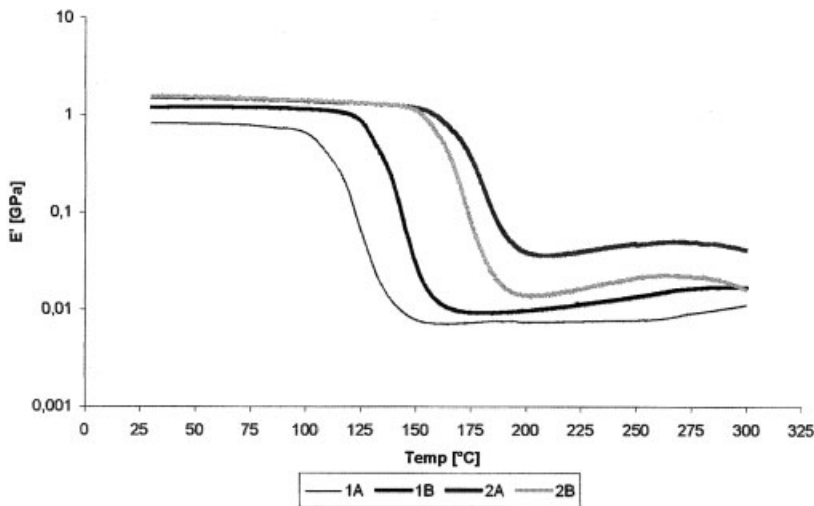**Figure 1** Tan $\delta$ behavior for the samples studied.

**Figure 2** Elastic modulus behavior for the samples studied.

Figures 1 and 2. The addition of the tetrafunctional resin led to consistent increases of the glass transition temperature for the modified systems 2A and 2B compared to the unmodified systems 1A and 1B; in both cases, the increase is around 30–35°C. It is worthwhile to note that the addition of the copolymer in the reformulated system does not increase the $T_g$ of the resin, but, on the other hand, it slightly depresses the $Tg$. This effect can be attributed to the increase of the viscosity due to the presence of the thermoplastic. The increase in viscosity can slow the reaction rate and reduce the crosslink density.

If we observe the behavior of the elastic modulus $E'$ (Fig. 2) in the rubbery region, it is evident that sample 2A reaches higher values than does 2B. If we consider the relationship draw from the theory of the rubber elasticity, which links the molecular weight between the crosslink points ($Mc$) to the elastic modulus $E'$, we can conclude that the network formed by sample 2B is characterized by a lower crosslink density. An opposite trend is observed for the base system as shown in Figure 2. In fact, in this case, the elastic modulus in the rubbery region is higher for sample 1B.

Both the base system and the reformulated system do not show the presence of a double peak in the tan $\delta$ curve. This behavior can be attributed to the formation of a full-IPN network.

It is well known that the mixture of epoxy resins and PES shows a lower critical solution temperature (LCST) phase diagram, as reported schematically in Figure 3. Increase in the molecular weight of the epoxy species gives rise to a decrease of the cloud-point curve and, therefore, for a fixed fraction of PES to the demix of the thermoplastic phase. The morphology is frozen when the $T_g$ exceeds the curing temperature. Therefore, the final morphology is the result of the competition between the molecular weight increase of the epoxy, leading to phase separation, and the simultaneous crosslink which suppresses it. The TEM analysis (Fig. 4) shows no morphology for sample 2B. According to the mechanism exposed above, this would mean that the gelation of the resin occurred
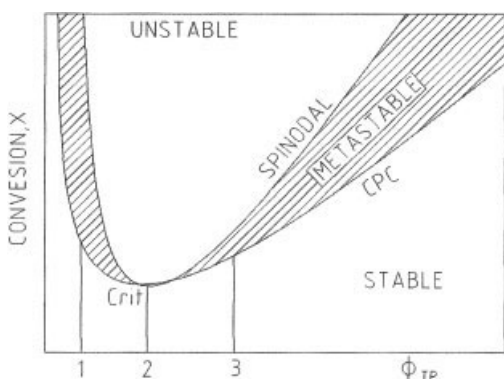


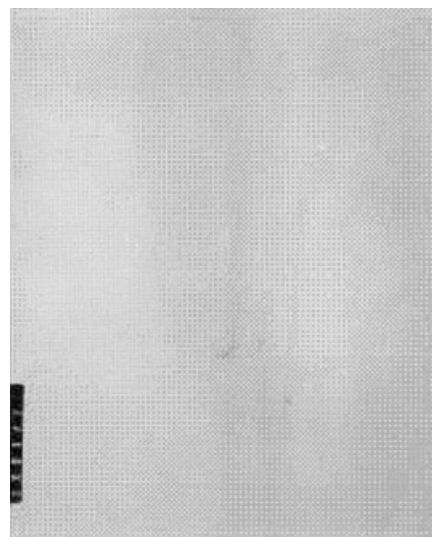**Figure 3** Schematic phase diagram for an epoxy/PES blend.
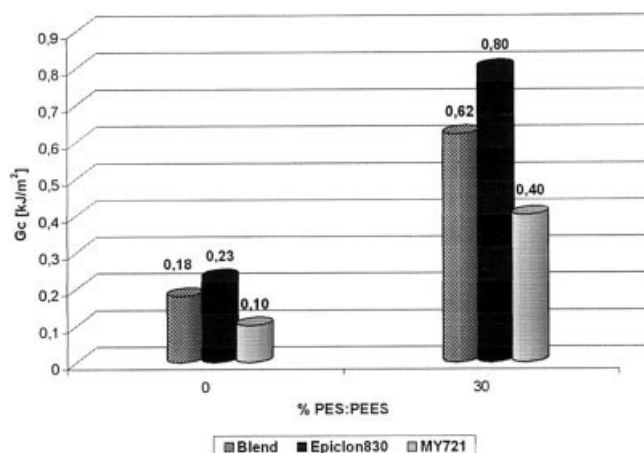


**Figure 4** TEM micrograph of sample 2B.

**Figure 5** Variations of the energy of fracture ($Gc$) for the blends and the formulation with the single-epoxy resin.
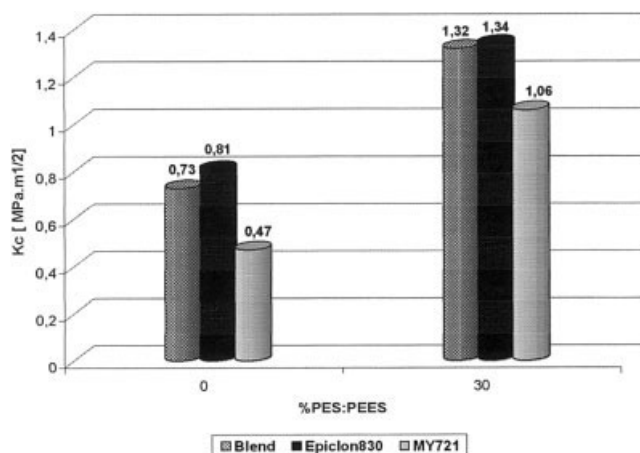


**Figure 6** Variations of the stress intensity factor ($Kc$) for the blends and the formulation with the single-epoxy resin.

before any phase-separation mechanism could have taken place. Mechanical tests were carried out on the cured samples to characterize the tensile and toughness properties of the resins with respect to the addition of different amounts of the thermoplastic.

It was reported in the literature[27] that in toughened epoxies characterized by a phase-separated morphology the progress of the crack is prevented by the dispersed particles of the thermoplastic component. The crack is split into some branches to avoid progressing through the dispersed particles. Accordingly, it may be concluded that the increase in the toughness of the particulate resins is due to the depression of the crack growth with the formation of the branches.

This toughening mechanism cannot be applied to homogeneous systems such as the mixtures of our study where the thermoplastic chains are interpenetrated within the resin matrix. When a homogeneous blend is obtained, the driven toughening mechanism is thought to be the shear deformation of the matrix.

The fracture resistance, expressed by means of energy to fracture $Gc$ and the stress intensity factor $Kc$, for the modified systems 2A and 2B, is reported in Figures 5 and 6. In the graphs, for comparison, the values obtained for the unmodified system 1A are also drawn. The Cycom 977-2 is a commercially epoxy-toughened resin, produced by Cytec Engineered Materials, used as a matrix in aerospace composites. Measurements of the toughness performed on neat resin plaques made of Cycom 977-2, cured with the same cure cycle of the samples of the present study, revealed values of $Gc$ of 0.60 kJ/m$^2$ and of $Kc$ of 1.30 MPam$^{0.5}$.

The addition of the PES:PEES copolymer greatly improves the fracture resistance of the brittle system 2A. The values of $Gc$ and $Kc$ obtained for sample 2B are in the same order as those for the system Cycom977-2 and, therefore, show the suitability of the reformulated system to be used as matrix for advanced fiber-reinforced composites.

Figure 7 shows variations of the elastic modulus $E$ for the samples studied. Therefore, the modification by the addition of the copolymer PES:PEES does not significantly affect the elastic modulus.

The water-pickup behavior of the formulated systems was studied by gravimetric experiments on predried specimens $30 \times 30 \times 3$ mm fully immersed in deionized water at 60°C. The graphs of the water uptake are shown in Figure 8. From this graph, it is possible to conclude that the tetrafunctional resin is characterized by an higher percent of water uptake. This behavior can be attributed to the high functionality of the resin that led to an higher percent of the OH group in the network, which, because of its polarity, can cause an higher absorption of water.

It is worthy to note that to blend TGDDM with DGEBS has a beneficial effect also on the water-uptake behavior according to the graph shown in Figure 8. A better understanding of the water-absorption phenomena would, however, require the analysis of the nature of the water within the network. The existence of water in an epoxy resin network in two different
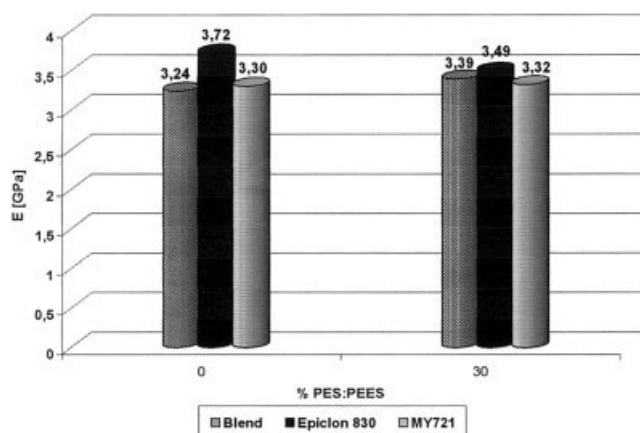


**Figure 7** Variations of the elastic modulus ($E$) for the blends and the formulation with the single-epoxy resin.
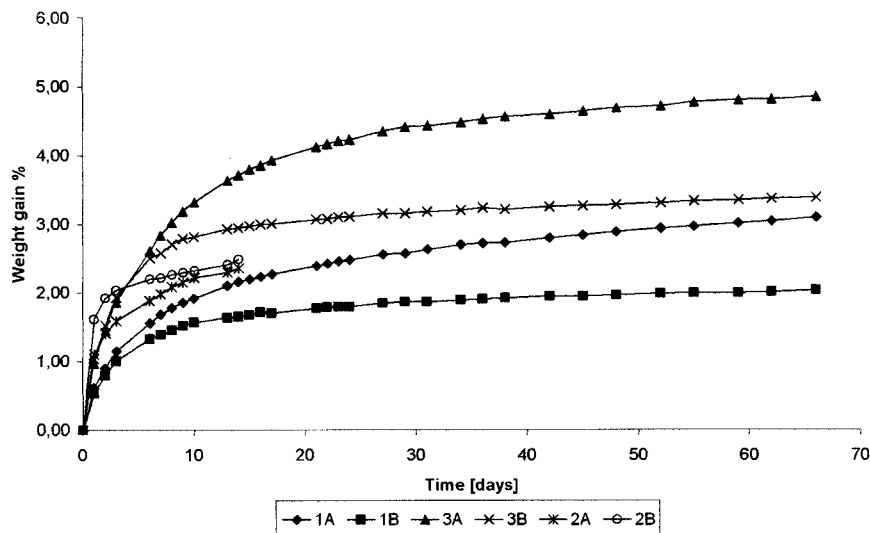
**Figure 8** Water-uptake behavior at 60°C for the sample studied.

environments is known[28]: molecules bound to specific sites as "bound water" and clustered in microvoids as "free water." To ascertain the proper nature of the water, dielectric measurements would enable us to characterize the nature of the water absorbed and could give a useful indication on the effect of blending a resin with different functionality and the addition of a thermoplastic.

## CONCLUSIONS

In this study, a complex mixture of epoxy resin and a novel PES:PEES copolymer was fully characterized by varying the thermoplastic content. Fracture toughness measurements confirmed the remarkable effect of an amine-ended copolymer to increase the impact resistance of inherently brittle epoxy resin. No decrease in the elastic modulus or strength yield in tension were found. TEM and viscoelastic analyses showed the presence of a single-phase morphology that can be attributed to the formation of a full-IPN network.

The addition of the TGDDM to the base system constituted by DGBES/DDS and 40:60 PES:PEES led to considerable increases of the glass transition temperature of the resulting network without negatively affecting the fracture resistance. An improvement in terms of water uptake of the blend compared to the use of the TGDDM on its own was shown by gravimetric experiments.

## References

1. Rowe, E. H.; Selbert, A. R.; Drake, R. S. Mod Plast 1970, 47, 110.
2. Bascom, W. D.; Cottington, R. L.; Jones, R. L. J Appl Polym Sci 1975, 19, 2545.
3. Kinloch, A. J.; Shaw, S. J.; Huntson, D. L. Polymer 1983, 24, 1355.
4. Kinloch, A. J.; Huntson, D. L. J Mater Sci Lett 1987, 6, 137.
5. Yee, A. F.; Pearson, R. A. J Mater Sci 1986, 21, 2475.
6. McEwan, I.; Pethric, R. A.; Shaw, A. J. Polymer 1999, 40, 4213.
7. Hedrick, J. L.; Yilgor, I.; Wilkes, G. L.; McGrath, J. E. Polym Bull 1985, 13, 201.
8. Min, B.; Hodgkin, J. H.; Stachurski, Z. H. Polym Bull 1993, 50, 1511.
9. Kubotera, K.; Yee, A. F. ANTEC'92, 1992, 2610
10. Hedrick, J. L.; Yilgor, I.; Wilkes, G. L.; McGrath, J. E. Polymer 1991, 32, 2020.
11. Yoon, T. H.; Liptak, S. C.; Priddy, D.; McGrath, J. E. ANTEC'93 1993, 3011.
12. Yamanaka, K.; Inoue, T. Polymer 1989, 30, 662.
13. Bucknall, C. B.; Gilbert, A. H. Polymer 1989, 30, 213.
14. Hourston, D. J.; Lane, J. M. Polymer 1992, 33, 1379.
15. Nishi, S.; Sasaki, S.; Hasuda, Y. ACS Polym Prep 1987, 28, 175.
16. Teng, K.-C.; Chang, F.-C. Polymer 1996, 37, 2385.
17. Tanaka, N.; Iijima, T.; Fukuda, W.; Tomoi, M. Polym Int 1997, 42, 95.
18. Bottino, F.; Di Pasquale, G.; Pollicino, A.; Recca, A.; Stainland, A.; Wilde, C. J. Polymer 1992, 33, 1976.
19. Bottino, F.; Mamo, A.; Recca, A.; Brady, J.; Street, A. C.; McGrail, P. T. Polymer 1993, 34, 2901.
20. Recca, A.; Bottino, F.; Di Pasquale, G.; Pollicino, A.; McGrail, P. T.; Stainland, P. Polym Mater Encycl 1996, 728.
21. Abate, L.; Calanna, S.; Pollicino, A.; Recca, A. Macromol Chem Phys 1997, 198, 1437.
22. Recca, A.; Chisari, V.; Mamo, A.; Siracusa, V.; Carter, J. T.; McGrail, P. T. Polymer 2000, 41, 2001.
23. Di Pasquale, G.; Motta, O.; Recca, A.; Carter, J. T.; McGrail, P. T. Polymer 1997, 38, 4345.
24. Motta, O.; Mamo, A.; Recca, A.; Acierno, D. J Polym Eng 2000, 20, 151.
25. Blanco, I.; Cicala, G.; Lo Faro, C.; Recca, A. J Appl Polym Sci, in press.
26. Wright, W. W.; Epoxy Resins Systems for Aerospace Applications; Rapra Technology Ltd.: Shawbury, UK, 1989.
27. Mimura, K.; Fujyoka, H.; Ito, H. Polymer 2000, 41, 4451.
28. Grave, C.; McEwan, I.; Pethrick, R. A. J Polym Sci 1998, 69, 2369.