

Development of an Epoxy System Characterized by Low Water Absorption and High Thermomechanical Performances

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ABSTRACT: Water absorption and thermomechanical properties of epoxy systems based on multifunctional dicyclopentadiene epoxy novolac resin Tactix556 cured with 4,4'-diaminodiphenylsulfone (4,4'-DDS) as curing agent has been studied. The base system was modified by the addition of a novel 40 : 60 PES : PEES (Polyethersulphone : Polyetherethersulphone) amine-ended copolymer to improve toughness properties. The effect of thermoplastic addition on water adsorption was studied by gravimetric experiments. The viscoelastic properties of the resulting blend were analyzed by means of dynamic mechanical thermal analysis. The formulated systems were compared with a system based on

tetraglycidyl-4,4'-diaminodiphenylmethane resin (MY721) cured with 4,4'-diaminodiphenylsulfone. The use of Tactix556 resin showed that water uptake values were minimized while retaining high glass transition temperatures, and toughness values were found in the same range of standard toughened matrices used for aerospace composites. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4880–4887, 2006

Key words: epoxy; thermoplastic; toughness; water absorption

INTRODUCTION

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

A challenging problem for epoxy resin is the water uptake values, which set a limit on utilization in the aerospace market. In fact, water absorption decreases the thermomechanical properties of composite materials. Moreover, it has to be considered that as an aeroplane flights at different altitudes, its materials are subject to high hygrothermal stress. That is why water absorption values have become a very important parameter for the choice of appropriate material as matrix. It is well-known that cyanate ester¹ resin shows a lower value of water absorption, but the high costs limit extensive use in aerospace construction.

Analysis² of the water absorption characteristics of epoxy resins showed the existence of water in two

different environments: molecules bound to specific sites as "bound water" and clustered in microvoids as "free water." The amount of bound water is mainly dependent on the polarity of molecules while the amount of free water is determined by network structure. Therefore, improvements in water performance could be made by an appropriate choice of the molecular structure of epoxy resin.

Another challenging problem for thermosets to be used as matrices for advanced FRP is the resistance to crack propagation. The modification of epoxy resins with reactive liquid and solid elastomers such as carboxyl-terminated butadiene acrylonitrile rubbers (CTBN) or crosslinked rubber particles showed an increase in the fracture toughness of brittle epoxy.^{3–7} However, the modification by addition of low glass transition temperature (T_g) materials, such as rubbers, results in a significant decrease of modulus and glass transition temperature of the cured resin. Recent studies have confirmed a decay in the water resistance of epoxy systems modified by the addition of liquid reactive rubbers.⁸

To overcome these problems, many attempts have been made to modify epoxy resin with high performance engineering thermoplastics that are characterized by high T_g and high toughness, such as polysulfone,^{9,10} poly(ethersulfone) (PES),^{11–13} poly(etherimide),^{14,15} and polyimide.¹⁶

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Recently, we reported on the synthesis and the use of novel copolyethersulphones as reactive toughening agents for epoxy resins.^{17–23} The previous studies were focused on the understanding of the behavior of epoxy/thermoplastic blends, varying the curing agent,²⁰ the epoxy resin,^{21,22} and the modifier concentration.²³ All the systems analyzed were based on the addition of a 40 : 60 PES : PEES amino-terminated polymer. Those studies demonstrated²⁰ that varying the curing agent is possible to change the morphology from particulate to homogeneous morphology. The change from particulate to homogenous morphology leads to the decrease of toughness. Moreover, we showed that the addition of reactive copolymer left the cure reaction rate unaltered.

In another study,²³ we analyzed the effect of modifier concentration and we obtained morphologies ranking from particulate to phase inverted. The amount of thermoplastic added to the blend influenced the thermomechanical properties and the water absorption behavior. In particular, the highest percentage of copolymer (30 wt %) gave the highest toughness but also the higher value of water up take. Some difference was found on the water uptake behavior in another paper²¹ but, in this case, the blends were characterized by a homogenous morphology.

In the present article, we discuss the use of a new epoxy novolac resin (Tactix556) based on dicyclopentadiene as basis for the formulation of a toughened system characterized by low water absorption value. The epoxy resin Tactix556, cured with 4,4' DDS, was modified by the addition of a novel copolymer thermoplastic 40 : 60 PES : PEES with reactive amine end, synthesized in our laboratories.^{17,24}

The water uptake behavior of the epoxy blends was characterized by gravimetric tests in deionized water. The measured values were compared with those of a system based on tetraglycidyl-4,4'-diaminodiphenylmethane resin (MY721) cured with 4,4'-diaminodiphenylsulfone, which is a much used system in aerospace applications.

The use of the 40 : 60 PES : PEES copolymer demonstrated how the toughness performance of the brittle Tactix556/4,4' DDS system increases and makes the systems comparable to the actual matrices for aerospace composites.

EXPERIMENTAL

Materials and preparation of samples

The epoxy resins used were a multifunctional dicyclopentadiene epoxy novolac resin (Tactix556) supplied by Dow, and a tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) sold by Ciba under the name MY721. The curing agent used was 4,4'-diaminodiphenylsulfone supplied by Aldrich. The toughening agent

used was an amine-ended copolymer 40 : 60 PES : PEES prepared in our laboratories,^{17,24} with a molecular weight M_n of 12,000. Table 1 shows the structures of the materials.

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. Then the curing agent was added and the mixture stirred for 1 h at 80°C. Next, the blended resin mixture was poured in a preheated silicone rubber mold and degassed for 30 min at 145°C. Then the temperature was increased at 2°C/min up to 180°C and hold at this value for 3 h. At the end of the curing cycle, the panels were left to cool down at room temperature.

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

Experimental techniques

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 using a sample size of $50 \times 10 \times 3 \text{ mm}^3$ to measure the flexural modulus. The yield strength (σ_y) was measured in tension mode, using a sample size of $10 \times 10 \times 3 \text{ mm}^3$. The crack opening stress intensity factor (K_c) and the energy of fracture (G_c) were measured at the speed of 1 mm/min using a sample size of $70 \times 10 \times 3 \text{ mm}^3$ with a single edge notch. All measurements were made at 23°C.

Dynamic mechanical thermal analysis (dmta) testing

DMTA tests were carried out for cured samples by a dynamical mechanical thermal analyzer, ARES by rheometric scientific, at a fixed frequency of 1 Hz at a 2°C/min heating rate, using samples of sizes $4.5 \times 10 \times 3 \text{ mm}^3$. Dynamic modulus and $\tan \delta$ were obtained in torsion mode.

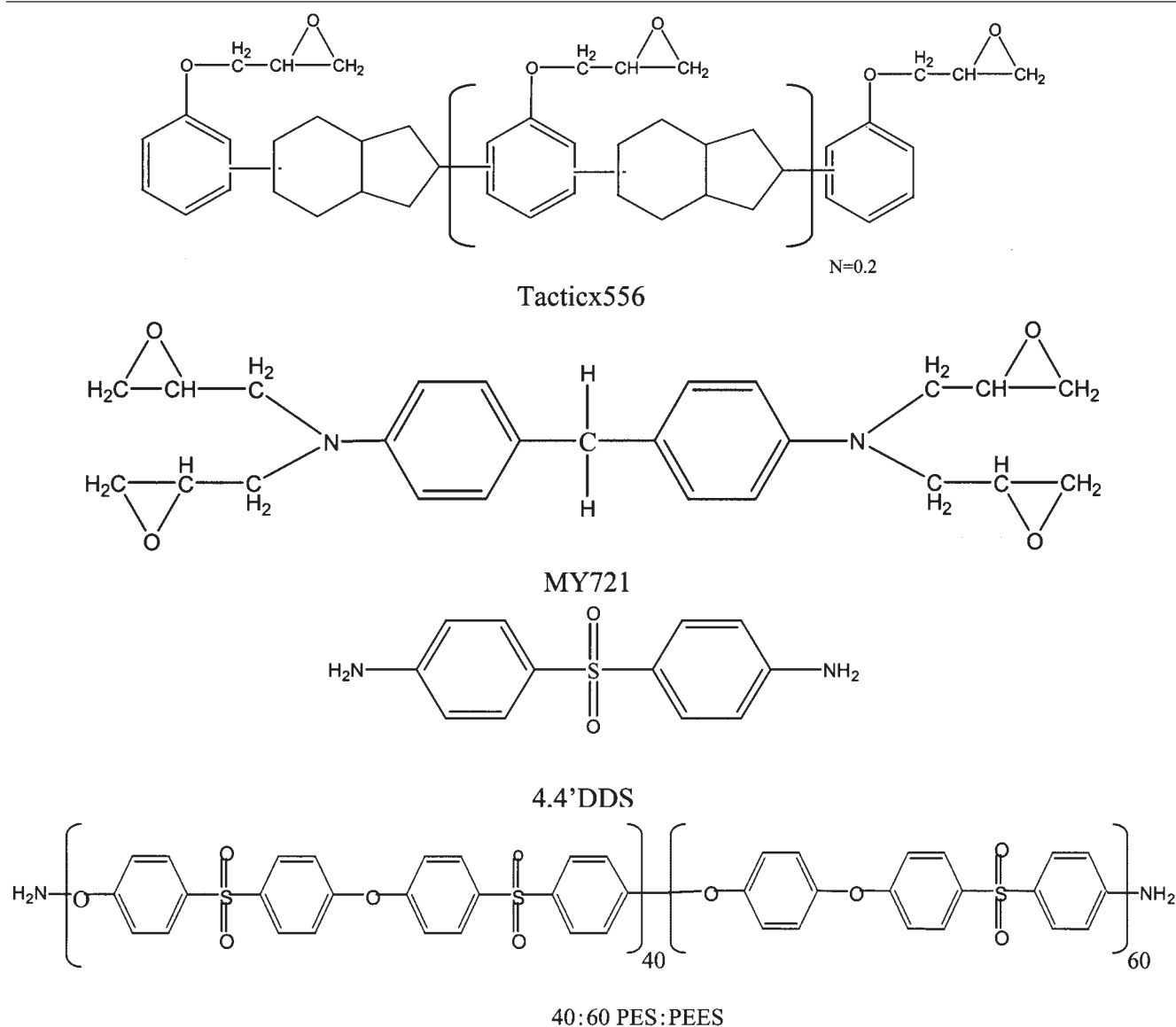
Morphological analysis

Ultra-thin section of 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 TEM observations were stained with ruthenium tetroxide (RuO_4).

Water uptake testing

Five square samples ($1.5 \times 1.5 \text{ cm}^2$) were cut from each cured panel and dried at 80°C in full vacuum until no residual water was found in the samples.

TABLE I
Structure of the Components Used



Then the dried samples were dipped in a jar full of deionized water and, after being wiped with a dry cloth, weighed on a balance to monitor the percentage of absorbed water. The average weight gain for these five samples was plotted against time to evaluate the behavior of the different systems.

RESULTS AND DISCUSSION

The importance of low water uptake values for thermoset to be used as matrix for aerospace composites has already been discussed. One of the much used epoxy resins for advanced application is tetraglycidyl-

TABLE II
Formulation of the System Analyzed

Component/Sample	1A (wt %)	1B (wt %)	1C (wt %)	2A (wt %)	2B (wt %)	2C (wt %)
Tactix556	82.48	74.23	57.74	0.00	0.00	0.00
MY721	0.00	0.00	0.00	70.27	63.25	49.19
4,4'DDS	17.52	15.77	12.26	29.73	26.75	20.81
PES180	0.00	10.00	30.00	0.00	10.00	30.00

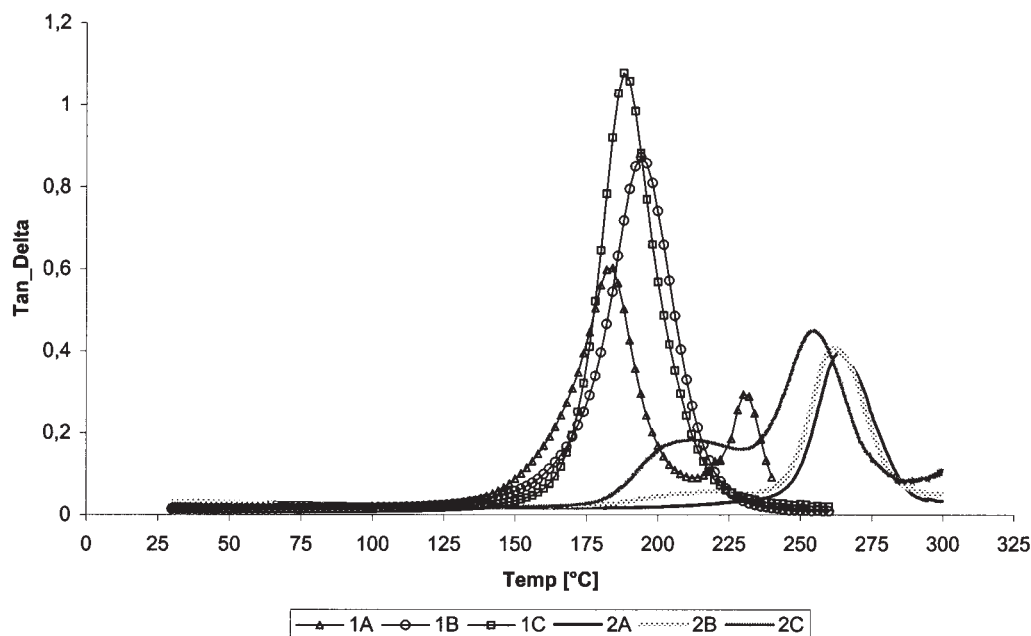


Figure 1 Tan δ behavior for the samples studied.

4,4'-diaminodiphenylmethane (MY721).²⁵ When this resin is cured with aromatic ammine, the resulting high glass transition temperature makes it highly suitable for advanced applications. As it is shown later, disadvantages of this resin are high values in water absorption and inherent brittleness due to high functionality. As an alternative to MY721, we considered the multifunctional dicyclopentadiene epoxy novolac resin Tactix556 and its structure is shown in Table 1. It is characterized by a multifunctional nature and by a low polarity backbone. These properties make this resin an ideal alternative to MY721 resin. Therefore, blends of Tactix556 and 4,4'-DDS with a 40 : 60 PES : PEES copolymer were compared with blends of MY721, 4,4'-DDS, and 40 : 60 PES : PEES.

To evaluate the viscoelastic behavior of the blends, DMTA testing were carried out and the results are shown in Figures 1 and 2. Figure 1 shows the tan δ course in dependence with the temperature. Sample 1A shows a double peak, and consequently, we draw the conclusion that Tactix556 is not a pure resin. In fact, the presence of a small peak at high temperatures could be attributed to different molecular species in the resin that results in a formation of two interconnected networks of different density. Samples 1B and 1C show a single peak in the temperature range of 185–200°C. The absence of a double peak for the samples with thermoplastic can be explained in terms of superposition of the peaks of the different components being blended. In fact, the copolymers 40 : 60 PES : PEES have a T_g (glass transition temperature) in the temperature range of 185–190°C. Figure 2 shows the behavior of the systems based on the MY721 resin.

Sample 2A shows a peak in correspondence with the glass transition temperature of 260.08°C. Systems 2B and 2C are characterized by the presence of a small shoulder in the temperature range of 190–200°C. In a previous²³ work, we reported about the occurrence of two clearly distinct peaks for blends thermoset/thermoplastic characterized by a coarse phase inversion. Samples 2B and 2C do not show (Fig. 3) any morphology and the panels appeared transparent. In literature,²⁶ such a behavior has already been reported for polyurethane–unsaturated polyester interpenetrating networks. The absence of two clearly separated transitions could be attributed to the formation of a full-IPN (full-Inter Penetrating Network) characterized by the semimiscibility between the two networks. As a further confirmation, we have to refer to a previous paper²⁷ that reports about the feasibility of the 40 : 60 PES : PEES copolymer amine, which is used as curing agent for MY721 resin. The work carried out demonstrated that reactive-ended copolymer could result in the formation of cured networks if having a reaction with the epoxy resin without a curing agent. Therefore, the formation of two interpenetrated networks is possible if used in blends of resin and curing agent.

Figure 2 shows the behavior of the elastic modulus against the temperature. This graph confirms all the observations made on the different systems analyzed in Figure 1.

The morphological analysis (Fig. 4) of the samples 1B and 1C revealed a homogeneous morphology, which lead to the conclusion that Tactix556/4,4'-DDS/PES180 blend resulted in the formation of a full-IPN network.

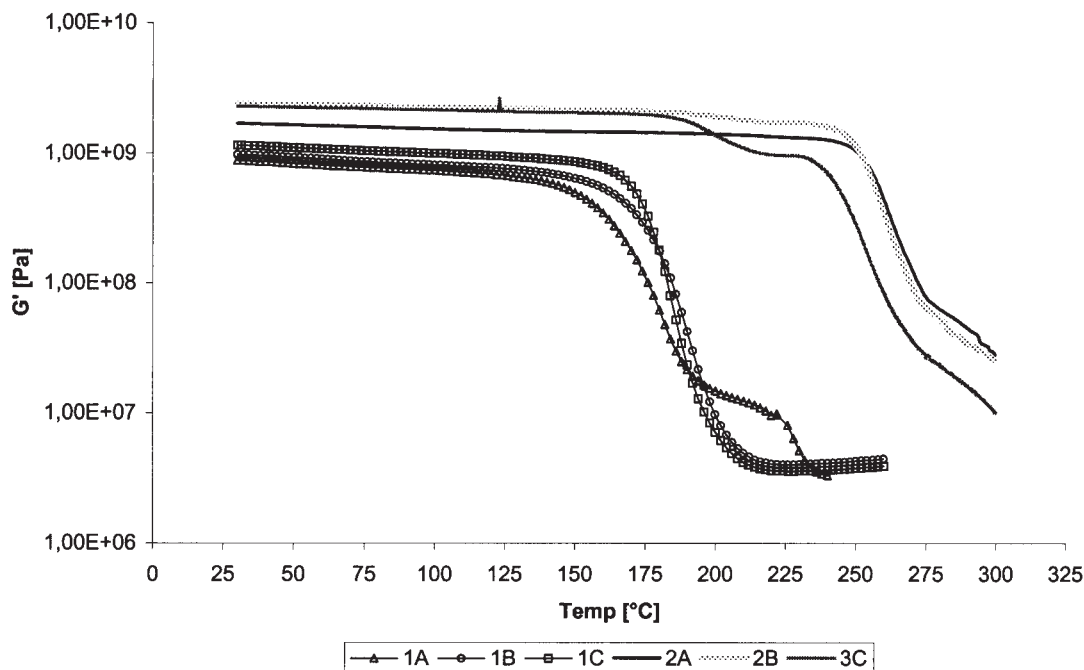


Figure 2 Elastic modulus behavior for the samples studied.

It is well-known that the mixture of epoxy resins and PES has a Lower Critical Solution Temperature (LCST) phase diagram, as shown schematically in Figure 5. An increase in molecular weight of the epoxy species results in the 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 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 that suppresses it. TEM analysis (Figs. 3 and

4) shows no morphology for all the epoxy samples blended with the PES : PEES copolymer. This would mean that, according to the mechanism mentioned earlier, the gelation of the resin occurred before any phase separation mechanism could have developed.

The water uptake behavior of the different samples is shown in Figure 6. The graph presents the average values for five samples of each formulation, and clearly shows that Tactix556 based resin has lower uptake values compared to MY721 based formulations. This behavior could be explained by the molecular structure of the two resins (Table 1). Tactix556 is characterized by a low

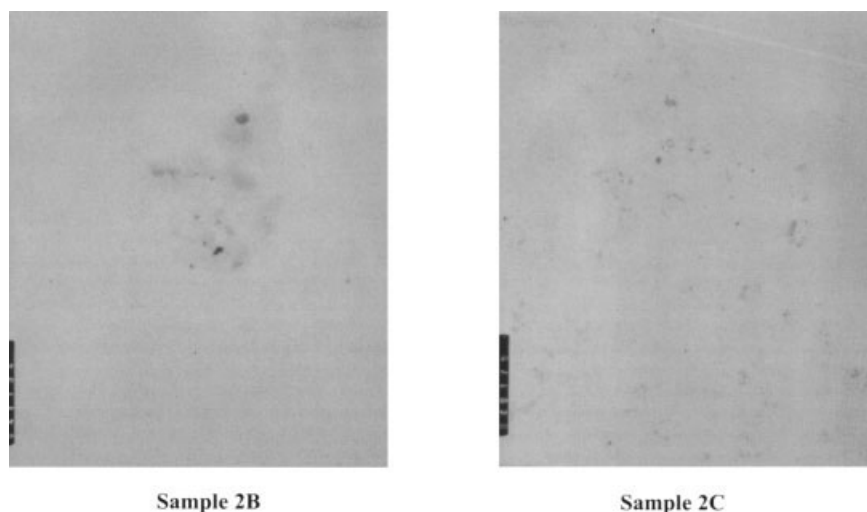


Figure 3 TEM pictures of samples 2B and 2C.

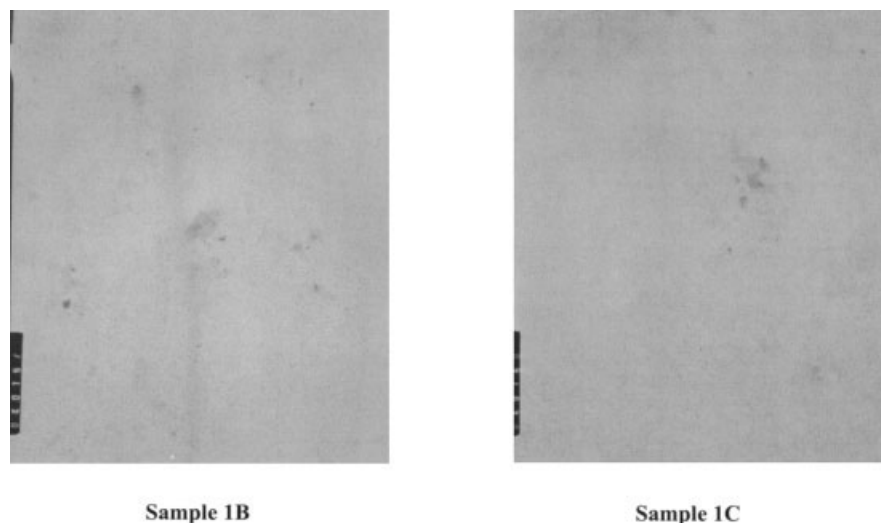


Figure 4 TEM pictures of samples 1B and 1C.

polar chain, while the MY721 has a chain with high polar N atoms in it. Therefore, it can be concluded that the amount of free water is lower in the Tactix556 based blend than in the MY721 formulation. But no clear trend is observed by varying the amount of thermoplastic in Tactix556 and MY721. In a previous work,²³ we reported about a negative trend when the amount of thermoplastic polymer within a blend of epoxy resin is increased, but it has to be noted that those blends were characterized by a coarse phase separation. It requires further studies to explain the effect of thermoplastic addition on the water absorption behavior of full-IPN network.

Figure 7 summarizes the findings of mechanical tests carried out on cured panels. The Figure 7(a,b) shows toughness measurements in terms of energy of fracture (G_c) and intensity factor (K_{Ic}). Both the curves show an increase of toughness depending on an increase of the amount of thermoplastic.

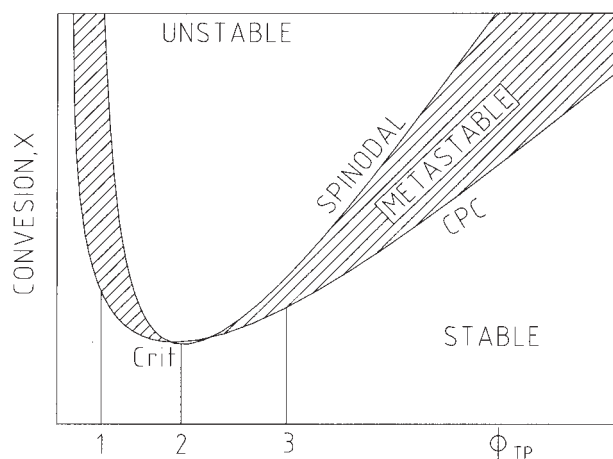


Figure 5. Conversion versus thermoplastic % diagram for epoxy/PES blends.

It has been reported in literature²⁸ that in toughened epoxies characterized by a phase separated morphology, the progress of crack is prevented by dispersed particles of thermoplastic component. The crack is split into some branches to avoid progressing through dispersed particles. Accordingly, it may be concluded that the increase in the toughness of the particulate resins is due to the depression of crack growth with the formation of the branches.

This toughening mechanism cannot be applied to homogeneous systems as the mixtures of our study in which the thermoplastic is finely dispersed within the resin matrix. When a homogeneous blend is obtained the toughening mechanism is thought to be a pure deformation of the matrix.

The comparison of the G_c values for the two resins Tactix556 and MY721 shows that the copolymers PES : PEES are more efficient in toughening the multifunctional dicyclopentadiene epoxy novolac resin than the tetraglycidyl-4,4'-diaminodiphenylmethane. Such a behavior could be explained in terms of crosslink density. In fact, Wright²⁵ already noted that the higher is the crosslink density of a resin, the less is the toughening effect of modifier such as thermoplastic or rubber, which is due to higher stiffness of the network that counteracts the deformation of the matrix and it leads to a lower shear yielding of the matrix. Therefore, the MY721 resin, which is characterized by a higher crosslink density, presents a stiffer network than Tactix556 and, as a consequence, is less sensitive to toughening actions due to thermoplastic addition.

Figure 7 shows the behavior of the elastic modulus [Fig. 7(c)] and of the yield strength in tension σ_y [Fig. 7(d)] for blends containing various amounts of the copolymer PES : PEES. The elastic modulus and the σ_y

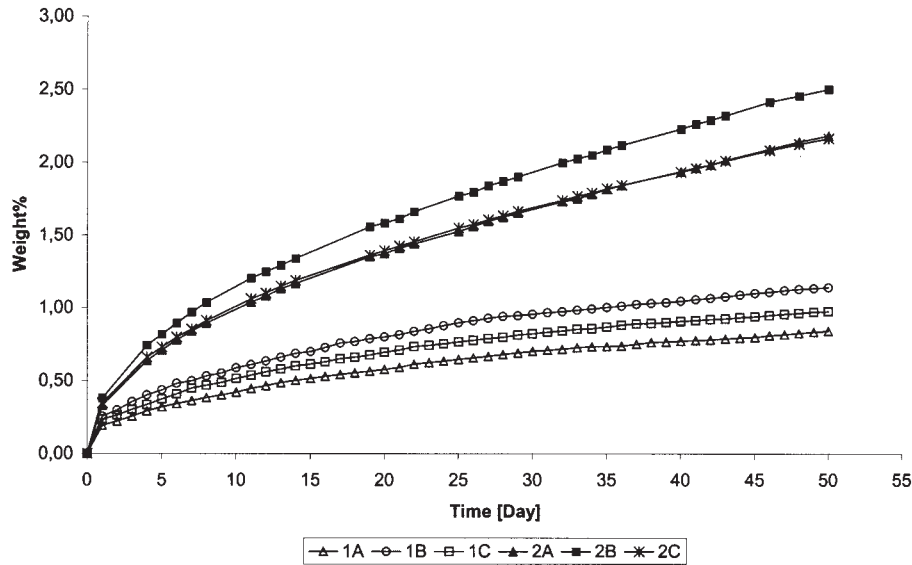


Figure 6 Water uptake behavior for the samples studied.

do not present significant changes when thermoplastic is added. In our previous studies,¹⁹ we noticed a small decrease in elastic modulus with an increase in the amount of the modifier, which was in accordance with the results from other investigators^{12,29}, but in such

cases, we should say that the systems were characterized by phase separated morphology.

Modifications³⁰ of the system studied by McGrath, which aim at an improvement of the miscibility of its components, resulted in a single phase morphology,

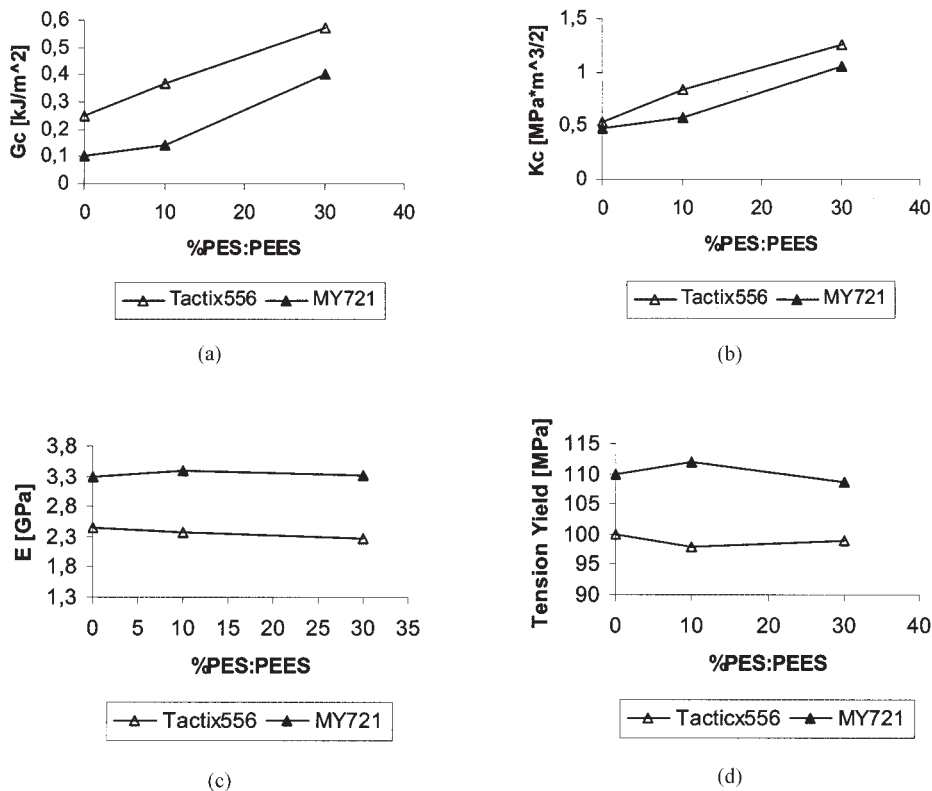


Figure 7 Mechanical testing resume: (a) G_c , energy for fractures; (b) K_c , stress intensity factor; (c) E , elastic modulus; and (d) σ_y , tension yield at various thermoplastic loadings.

with increases in the elastic modulus of the resulting mixtures. Consequently, we could say that the independence of the modulus and of σ_y from the thermoplastic addition can be attributed to the formation of an unique full-IPN network.

CONCLUSIONS

In this study, two epoxy systems based on a multifunctional dicyclopentadiene epoxy novolac resin and tetraglycidyl-4,4'-diaminodiphenylmethane cured by 4,4'-diaminodiphenylsulfone and novel PES : PEES copolymer were 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. There was not any decrease in elastic modulus and strength yield in tension.

TEM showed the presence of a single phase morphology, which can be attributed to the formation of a full-IPN network.

DMTA testing proved both the resins to be suitable as matrices for advanced fiber reinforced polymers, because the T_g values are higher than 180°C, which is the primarily required temperature for such applications.

Moreover, Tacticx556 appeared to be an optimum choice to minimize water absorption values because of its appropriate chemical structure.

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