Reactive Microspheres as Active Fillers for Epoxy Resins

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ABSTRACT: Physical properties of epoxy resins filled with microparticles are presented and discussed. Microparticles were synthesized in the form of micron-sized, crosslinked spherical particles, with an excess of reactive amino groups on their outer surface, and subsequently blended with EPON828-3,3'DDS in different weight percents (10 and 20 wt %). Differential scanning calorimetry and scanning electronic microscopy were applied to investigate microsphere properties such as morphology, shape, size, and size distribution. Electron spectroscopy for chemical analysis was applied on particles to relate surface composition and reactivity of microspheres. Rheological, dynamic–mechanical, and mechanical properties of the cured blends were analyzed and related to the pure resin and to the same resin modified with PES180. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2031–2044, 2004

Key words: adhesion; crosslinking; curing of polymers; resins; thermosets

INTRODUCTION

It is well known that physical properties of thermosets can be improved by inclusion of a filler, as a second phase, to the resin batch. For example, toughness is noticeably increased by mixing reactive rubbers with epoxy resins. The same effect can be reached with the addition of some reactive thermoplastics.

In many cases, the target is viscosity modification during processing of thermosets. For this purpose, a suspension of solid particles, as well as of some thermoplastics, included in the resin can be very useful in balancing the proper viscosity profile during processing.

In this article, a novel approach to change the viscosity of epoxy resins is presented. The method is based on the inclusion of reactive microspheres previously prepared by reaction of the epoxy monomer with the curing agent.

Over the last several years, a growing interest in the production of polymer particles was recorded.[1–6] These materials are suitable as spacers, slip properties improvers for plastic film, paints, adhesives, sealant and binders if dispersed in a solvent, and fillers in the market of composite materials. Furthermore, polymer particles can be utilized in the field of microencapsulation, which includes a wide variety of possible applications among which that of drug release seems to be the most promising.[7] Because of the commercial and scientific interest in these particles, preparation of microspheres has been an active research field in recent years.

As far as epoxy resin particles preparation is concerned, several protocols were reported in scientific literature and patents.[3,8,9] In their work, Hibino and Kimura[8] proposed a novel synthetic approach for epoxy resin particles through nonaqueous dispersion polymerization by using polyethers as solvents. At the same time, Hseish and Woo[9] obtained crosslinked epoxy microparticles of spherical shape through a cure-induced phase inversion process in DGEBA/DDS/PMMA blends. They explained the morphology evolution of epoxy microsphere through a phase-inversion mechanism.

In this article, curing of epoxy resins in the form of micron-sized particles was carried out in polypropylene glycol (PPG). The starting solution was composed of the epoxy monomer and an amine-based curing agent dissolved in the solvent. The as-blended mixture was let react at constant temperature, without stirring, until the resin particle formation occurred. The mechanism was very complex because of the curing reaction between the epoxy monomer and the aromatic amine, which led to the crosslinked resin, followed by a phase-separation process, influenced by the miscibility of the reacting thermoset in the PPG.

Solute	Solvent	Concentration (wt %)[a]	Symbol	Reaction temperature (°C)	Reaction time (h)	T_g (°C)[b]
EPON825+DAT	PPG1000	9.0	**I**	130	15	150
		33.3	**II**	130	15	143
		47.4	**III**	130	15	153
	PPG4000	33.3	**IV**	130	15	150

[a] %wt is referred to as the weight ratio between EPON825+DAT (solute) and total weight (solute + solvent). The percentage values correspond to solute/solvent ratios of 10%, 50%, 90%, respectively;
[b] T_gs values were obtained from DSC second heating scans.

To relate experimental parameters, such as nature of solvent and composition of the solution, with the properties of microspheres, four systems were prepared, which differed in the epoxy + amine content, in the solvent, or in viscosity of the PPG. Electron spectroscopy for chemical analysis (ESCA) was applied on particles with the aim of relating the surface composition to the reactivity of microspheres.

One group of microspheres was selected as fillers for EPON828/3,3'DDS matrices. Two systems were analyzed; the first composed by 10 wt % and the second composed by 20 wt % of microspheres in the epoxy matrix. Rheological, dynamic–mechanical, and mechanical properties were studied in comparison with the neat resin and with EPON828/3,3'DDS/15 wt % PES180, where PES180 is a modifier.

EXPERIMENTAL

Materials

Epoxy resin microparticles

A commercial available Bisphenol-A-type resin (EPON825®, supplied by Shell Co.) and an aromatic amine, the 2,4-diaminotoluene (DAT; purchased from Aldrich Milan, Italy) were used for the preparation of particles. PPG with different molecular weights (PPG4000 with M_n = 40,000 and PPG1000 with M_n = 1000) were selected as solvents and purchased from Aldrich. All these products were used without further purification.

The different experimental conditions selected for the preparation of epoxy microspheres are reported in Table I. Glass transition temperatures (T_g's) of the obtained particles are also indicated.

In a typical procedure, EPON825 and DAT were dissolved in PPG. The mixture was allowed to heat at a constant temperature (see Table I) for 15 h without stirring, until a precipitate appeared. The solid residual product was washed with hot methanol, filtered, and vacuum dried at T = 60°C for 2 h.

Prior to being mixed, EPON825 and DAT were dissolved in PPG separately at T = 40°C and T = 80°C,

respectively, with the purpose of obtaining two homogeneous solutions of EPON825 in PPG and DAT in PPG to be mixed.

DAT was taken in a 35% molar excess with respect to the stoichiometric ratio (stoichiometric ratio between EPON825 and DAT is 2 : 1) to be sure that all the epoxy monomer introduced was reacted and to guarantee an excess of curing agent on the surface of the microspheres, as confirmed by ESCA, to react with the epoxy monomer of the matrix.

Materials used for rheological analysis

Rheological analyses were carried out on two systems composed by a Bisphenol-A-type resin (EPON828®, supplied by-Shell Co., EEW 185–192), 3,3'-diaminodiphenylsulphone (3,3'DDS; Aldrich, Milan, Italy), and two different weight percentages of epoxy microspheres, 10 and 20 wt %, respectively. In particular, the microspheres obtained from system **II** (see Table I) were used for these studies. The comparison of the two modified systems was made with the EPON828/3,3'DDS neat resin. We will refer to the three systems as 10% MICs, 20% MICs, and 0% MICs, respectively, later on.

In all the cases, the epoxy monomer, the curing agent, and the microspheres (when present) were mixed at the temperature of 110°C without solvent.

Mixtures of EPON828 and 3,3'DDS modified by addition of 15 wt % of a thermoplastic copolymer were used as comparison to the systems containing the microspheres.

The thermoplastic polymer was an amine-terminated copolymer 40 : 60 PES : PEES (polyethersulphone : polyetherethersulphone) prepared in our laboratories[10] with a molecular weight of 9000 M_n. Resin mixtures were prepared by mixing the thermoplastic with the EPON828 and stirring the resulting mixture for 1 h at 120°C; then, the curing agent was added to the mixture and stirred for 1 h at 80°C.

We will refer to the 40 : 60 PES : PEES copolymers as PES180 later on.

Materials used for DMTA and LEFM testing

Cured samples were prepared by mixing the microspheres with the EPON828 and stirring the resulting mixture for 30 min at 120°C; then, the curing agent was added to the mixture and stirred for 1 h at 80°C. The mixture was poured in a preheated steel mold and degassed for 30 min at 145°C. Then, the temperature was increased at 2°C/min up to 180°C and held at that value for 3 h. At the end of the curing cycle, the panels were left to cool down slowly at room temperature.

Instrumental

ESCA spectra were recorded by using a VG Instrument equipped with a X-ray source having a Mg anode (MgK$_{\alpha1,2}$ 1253.6 eV). In standard conditions, X-ray source worked at 100 W, 10 kV, and 10 mA. The instrument base pressure was 5×10^{-10} Pa and spectra were recorded at a pressure of 2×10^{-8} Pa. Pass energy was 100 eV for widescans, 50 eV for narrowscans, and 20 eV for O$_{1s}$ regions recorded for curve fitting. To get information on depth profiling, three spectra of each sample were recorded at different take-off angles of analyzed electrons (at 25°, 45°, and 90° with respect to sample surface, respectively). All data analyses (curve fitting, linear background subtraction, and area determination) were carried by using version 6 of VGX900× software of VG Instrument.

Rheological properties of the matrix resin and thermoplastic modified systems were recorded on an Ares rheometer (Rheometric Scientific). Dynamic-viscosity η^*, elastic modulus G', and loss modulus G'' were obtained by oscillatory shear measurements as a function of temperature and by a series of isothermal experiments employing parallel plates (40 mm diameter) separated by a 1.2-mm gap. Isothermal tests were performed by preheating the sample chamber to the fixed temperature; then, the sample was quickly inserted and the analysis was started. The analysis was done with optimized instrumental parameters of 35% strain and angular frequency of 30 rad/s.

Panels (80 × 16 mm) were produced for the linear elastic fracture mechanics (LEFM) and dynamical mechanical thermal analysis (DMTA). All the tests were conducted by using a sample size of 65 × 12.5 × 5 mm with a single-edge notch in a flexural mode at a constant speed of 1 mm/min. The precrack was applied by the razor tapping technique. The crack opening stress intensity factor, K_c, and the energy of fracture factor, G_c, were calculated according to the protocol [a] established by the European Structural Integrity Society (ESIS). All measurements were made at 23°C.

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 by using samples of sizes 12 × 40 × 3 mm. Storage modulus and tan δ were recorded by a torsion mode.

Differential scanning calorimetry (DSC) (TA Instruments model 2920) was used to evaluate the T_g's of microspheres. For each sample, a double heating scan from room temperature to 280°C at a rate of 10°C/min, under nitrogen atmosphere, was carried out.

Scanning electronic microscopy (SEM) was used to study morphology of particles and their sizes and to investigate the characteristics of fracture surfaces of composites, using a Hitachi microscope model S-2300. Prior to being observed, samples were metallized with a gold layer.

Morphological characterization was also carried out by using a transmission electron microscope (TEM; Zeiss model EM900) applying an acceleration voltage of 80 kV. The specimen support grids, lying on filter paper, were coated with carbon black. Five milligrams of the polymer was ultrasonically dispersed for 4 min in 10 ml isopropanol and 2 drops of the polymer suspensions were placed onto the coated grids; the solvent was then evaporated. The grids were prepared immediately before the observation to avoid the aggregation of polymer particles during storage.

RESULTS AND DISCUSSION

Reaction mechanism of microspheres formation

Formation of epoxy resin microparticles was achieved in a stationary reaction system, using a selected solvent. In a typical procedure, epoxy and curing agent (in a fixed molar ratio) were introduced in the dispersant and let react at a selected temperature, without stirring. As soon as the crosslinking reaction started, the material separated, as a result of its reduced solubility in the solvent, and was deposited as microsized particles.

In the early stage of the reaction, the system was found to be in the physical state of miscible liquid, which macroscopically corresponded to a situation of homogeneity and transparency of the solution. This state was held until a mechanism took place, which was able to force the energetic barrier (related in some way to the viscosity of the medium, the affinity with the solvent, the solvent/resin ratio, etc.) and induce phase separation. This mechanism was represented by the formation of the first nuclei of the cured resin, as a consequence of the crosslinking reaction between the epoxy monomer and the amine. In fact, as soon as the reaction between epoxy and amine occurred at a given time t, at random points the first nuclei were assumed to appear in the solution, similarly to the formation of the crystallization nuclei from a molten polymer. Because the overall system was in a metastable state, these bodies could dissolve into the solvent or separate from it as solid particles. As the curing reaction went on, the nuclei formed reached a critical degree of crosslinking (i.e., a critical dimension), so that it was
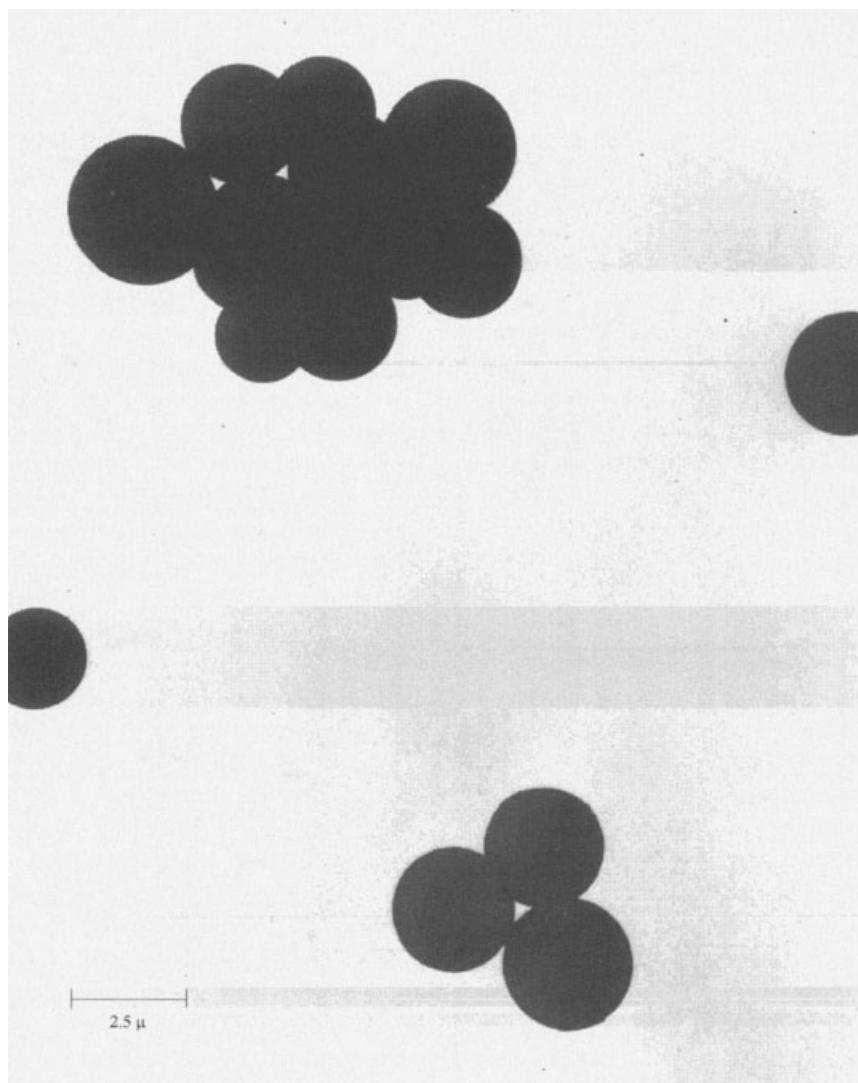
Figure 1 TEM image of microspheres obtained from system **II.**

not possible for the particles to dissolve in the solvent anymore. Hence, as a result of their growth, the particles separated from the solvent and were deposited by virtue of gravity.

All the samples of extracted spheres exhibited a distinctly single T_g, indicating that the spheres were likely to be formed by an homogeneous structure. T_g values are reported in Table I. Furthermore, the value of T_g was similar to that of the in bulk cured epoxy (T_g = 150°C). In addition, the microspheres were insoluble in all the common organic solvents, confirming the crosslinked nature of the materials.

To relate the nature of solvent and the monomer concentrations with particle morphology, four samples were prepared according to same procedure, at the same reaction temperature (T = 130°C). In particular, sample **IV** was prepared by using PPG4000 as solvent (see Table I), while samples **I, II,** and **III** were obtained from PPG1000 solutions, with different epoxy + amine to solvent weight ratio.

Figures 1 and 2 report the images obtained from TEM and SEM techniques, respectively, on sample **II** (see Table I). The particles are regular in shape and size, the latter ranging from 1 to 5 μm. The same was observed in the case of samples **I** and **III,** which also exhibit highly smooth and homogeneous surfaces, with regular dimensions.

On the contrary, sample **IV** appears irregular in its morphology and dimension (Fig. 3): this may be attributed to the high viscosity of PPG4000 in comparison with PPG1000. It seems that, due to the high viscosity of the solvent, the forming network segregates and grows at a lower rate, leading to bigger sized particles.

ESCA analysis

Microsphere action on crosslinking kinetics has to be related to their surface composition. Among surface characterization techniques, ESCA gives the opportu-
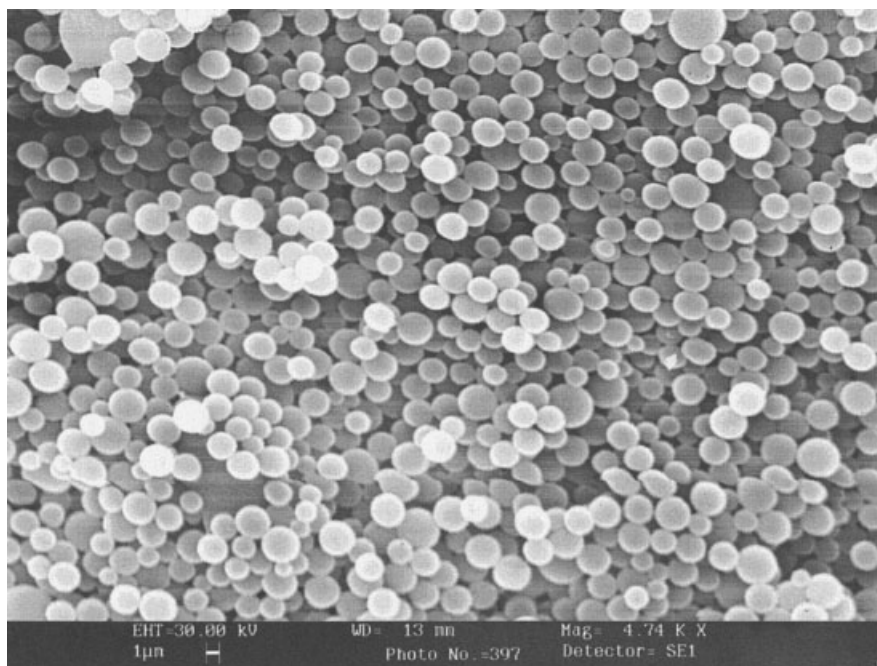
Figure 2 SEM image of microspheres obtained from system **II.**

nity to get semiquantitative information on the mean composition of the outermost layers ($\sim$ 100 Å). As is known from the photoelectronic peak areas (obtained multiplying the experimental values by the right sensitivity factors), it is possible to get data on the atomic abundance. Data obtained by this technique are reported in Table II.

In the interpretation of these data, it must be kept in mind that on the surface both DAT and PPG can be present at the same time. Actually, it is PPG presence that, determining a decreasing of the N_{1s}/C_{1s} ratio and the contemporaneous increasing of the O_{1s}/C_{1s}, makes necessary a further data elaboration before their correct interpretation. Aim of the elaboration is
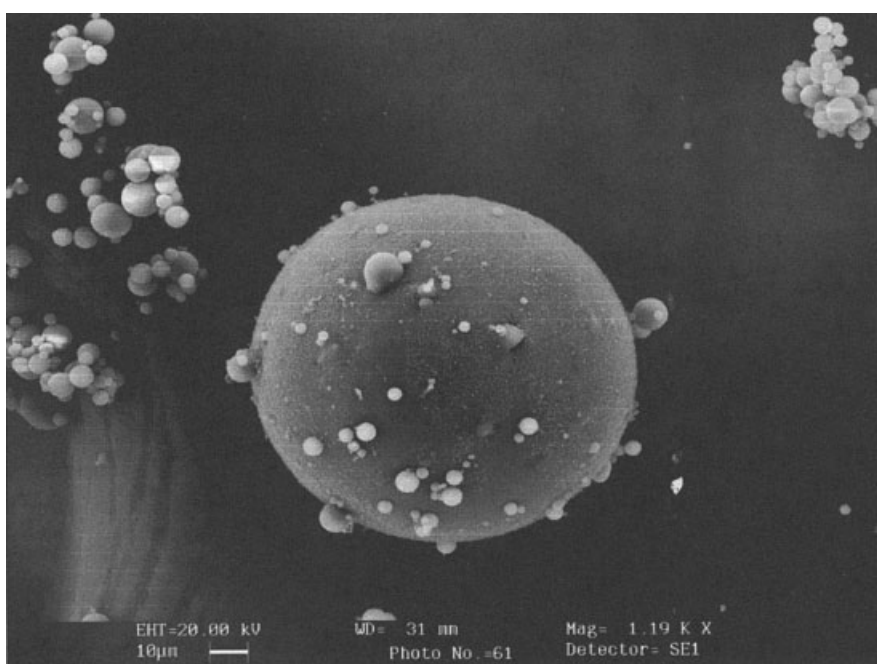

Figure 3 SEM image of microspheres obtained from system **IV.**

TABLE II
Atomic Ratios at Several Take-Off Angles
(t.o.a.) in Samples I–IV

Sample	O_{1s}/C_{1s}	N_{1s}/C_{1s}
I (t.o.a.25°)	0.163	0.0367
I (t.o.a.45°)	0.161	0.0329
I (t.o.a.90°)	0.160	0.0342
II (t.o.a.25°)	0.210	0.0343
II (t.o.a.45°)	0.220	0.0360
II (t.o.a.90°)	0.207	0.0353
III (t.o.a.25°)	0.205	0.0412
III (t.o.a.45°)	0.204	0.0373
III (t.o.a.90°)	0.199	0.0363
IV (t.o.a.25°)	0.204	0.0238
IV (t.o.a.45°)	0.202	0.0371
IV (t.o.a.90°)	0.206	0.0351

Figure 5 ESCA C_{1s} envelope of sample **IIbis.**

the individuation of the PPG amount eventually present on the microsphere surface and the calculation of new values of the atomic ratios reported in Table II obtained by subtracting the contributions deriving from PPG. To do this, we used another property of ESCA spectra. In fact, each photoelectronic peak is the result of the sum of all the contributions deriving from the presence, in the analyzed layer, of different oxidation states for the same atomic species (chemical shift). Then, it is possible, by a peak-fitting process, to fit into the photoelectronic peak all these contribution and in our case it can be worth analyzing the components of the C_{1s} peak.

The ESCA spectra of sample **II** (Fig 4) showed three photoelectronic peaks centred at about 285.1 eV (C_{1s} photoelectrons), 532.7 eV (O_{1s} photoelectrons), and 399.1 eV (N_{1s} photoelectrons), respectively. To get information on the peak positions, we prepared a sample (**IIbis**) of crosslinked EPON825 with DAT in the absence of PPG by using the same conditions of temperature and stoichiometry of sample **II**. The resulting spectra showed C_{1s}, O_{1s}, and N_{1s} envelopes centered at 285.0, 533.0, and 399.5 eV, respectively (Fig. 5).
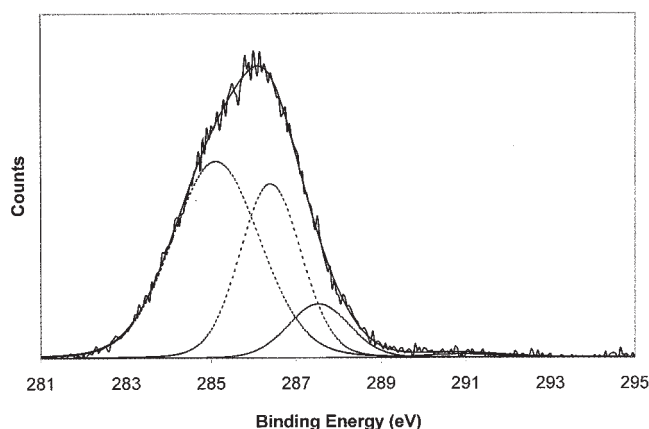

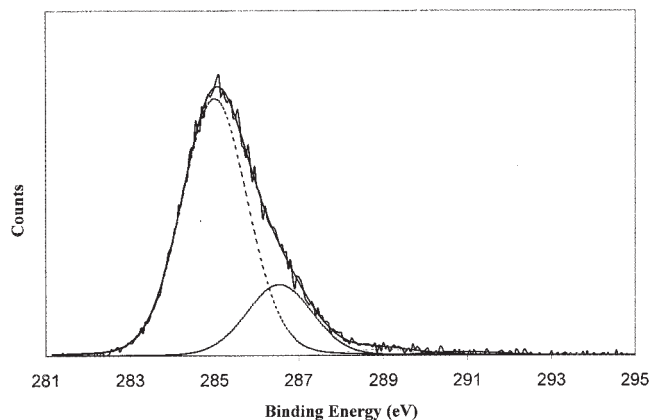**Figure 4** ESCA C_{1s} envelope of sample **II.**

Comparing the different shape of the C_{1s} envelope of samples **II** and **IIbis** (Figs. 4 and 5), we concluded that on microsphere surface there is a high concentration of PPG.

The peak fitting elaboration of C_{1s} envelope was carried out by taking into account the component position reported in literature for the carbon atoms of PPG[11] and EPON825[12] and DAT[11] centered at 285.0 eV for hydrocarbons, at about 286.4 eV for carbons single bonded to oxygen and at about 287.1 eV for carbon present in the oxirane ring, respectively. The results obtained in the case of the sample **II** spectrum recorded at a take-off angle of 25° (Fig. 4) show a relative abundance of these three peaks of 54.7, 33.8, and 10.5%, respectively. These values are in good agreement with a composition of the outermost layers of 38.2 wt % of PPG, 49.8 wt % of EPON825, and 12.0 wt % of DAT (molar ratio = 9:2:1.35). Such a composition would give a O_{1s}/C_{1s} area ratio of 0.217 and a N_{1s}/C_{1s} area ratio of 0.0344 very close to the experimental values. Through the same elaboration, it has been possible to calculate the amounts of PPG present in all the samples (Table III). A first analysis of the data reported in Table III shows that, in each sample, the abundance of the components varies as a function of the take-off angle. Remembering that the higher the take-off angle is, the deeper the analyzed layer, it is clear that at the surface of all samples there is a concentration gradient and that the PPG concentration is higher in the outermost layers. Moreover, analyzing the four sets of output for the different microspheres, it can be concluded that the gradient of concentration of PPG is present independently from solute concentration as well as molecular weight of solvent.

Having evaluated by this method the amount of PPG present at the sample surface, the following step was the elimination of the PPG contribution from the C_{1s} and O_{1s} area values, knowing that in EPON825 there is a proportion of 21 carbon atoms for every 4 oxygen atoms, whereas in the PPG repeating unit, the

TABLE III
Weight % of PPG Present on the Analyzed Layer and
N_{1s}/C_{1s} Atomic Ratios Corrected from PPG
Contribution for Samples I–IV

Sample	Wt % of PPG	Recalculated N_{1s}/C_{1s}
I (t.o.a.25°)	28	0.0488
I (t.o.a.45°)	25	0.0422
I (t.o.a.90°)	22	0.0424
II (t.o.a.25°)	38	0.0522
II (t.o.a.45°)	20	0.0432
II (t.o.a.90°)	17	0.0357
III (t.o.a.25°)	33	0.0584
III (t.o.a.45°)	21	0.0457
III (t.o.a.90°)	22	0.0450
IV (t.o.a.25°)	28	0.0317
IV (t.o.a.45°)	22	0.0460
IV (t.o.a.90°)	19	0.0421

atomic ratio carbon/oxygen is 3 to 1. In the same way, the contribution deriving from DAT was calculated considering that each nitrogen atom present at the surface theoretically carries with itself 3.5 carbon atoms. These calculations allowed us to remove the contribution because of PPG from the C_{1s} area values and to recalculate the N_{1s}/C_{1s} area ratio reported in Table III.

A first analysis of these results shows the presence of a DAT concentration gradient with an increase of the curing agent moving toward the surface. Moreover, knowing that the presence of a stoichiometric amount of DAT with respect to EPON825 would cor-

respond to a N_{1s}/C_{1s} ratio of 0.0408, the results clearly show that in the outermost layers there is an excess of DAT in each of the four samples. The amount of this excess, valuable from the value of the N_{1s}/C_{1s} ratio at a take angle of 25°, in the case of sample **II** reaches the 35 wt %.

Rheological analysis results

Figure 6 reports the three curves of viscosity versus temperature obtained for the 0% MICs, 10% MICs, and 20% MICs systems, respectively, at a heating rate of 2°C/min. The temperature value for the minimum viscosity decreases with increasing the percentage of microspheres in the sample, thus indicating that an increase of the microsphere percentage is responsible for a higher reactivity of the system. This effect may be related to the presence of reactive amino groups on the microsphere surface, as determined by ESCA. Furthermore, the figure shows that viscosity increases over the entire temperature range with the amount of microspheres. This result is promising for the reduction of the bleeding phenomena and thus makes the microspheres particularly attractive as rheology control modifiers for fiber-reinforced composites and adhesives.

Figure 7 compares the EPON828/3,3'DDS/20% MIC with the EPON828/3,3'DDS/15% PES180 system. The viscosity increase is of the same order of magnitude in both cases. Moreover, even if the copolymer is aminoterminated, as reported by literature,
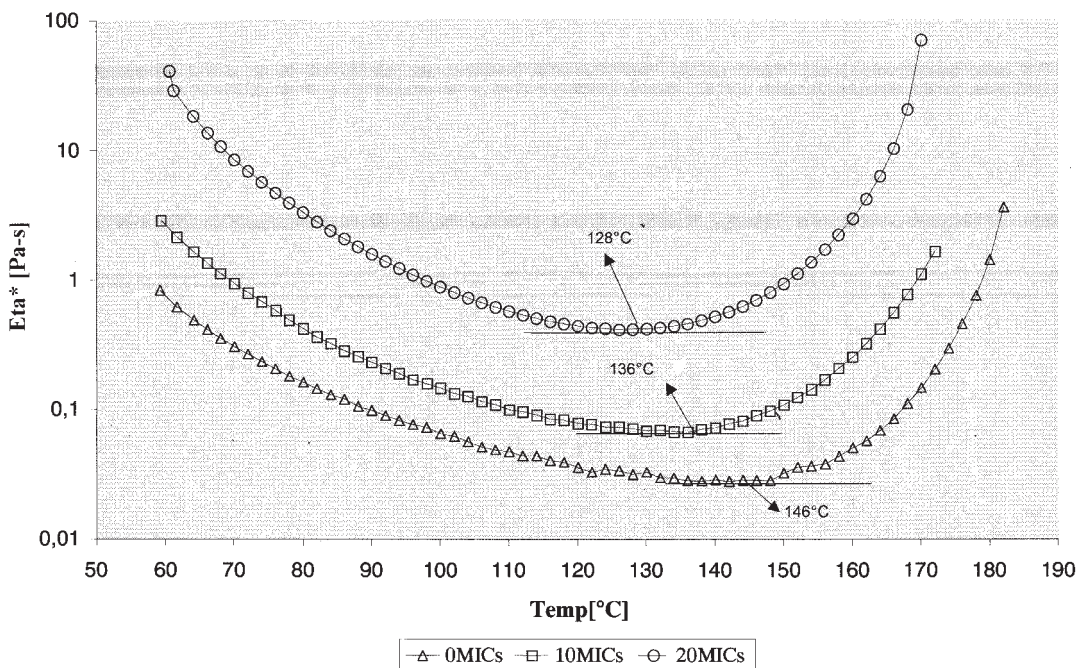

Figure 6 Viscosity versus temperature curves for the 0% MICs, 10% MICs, 20% MICs systems.
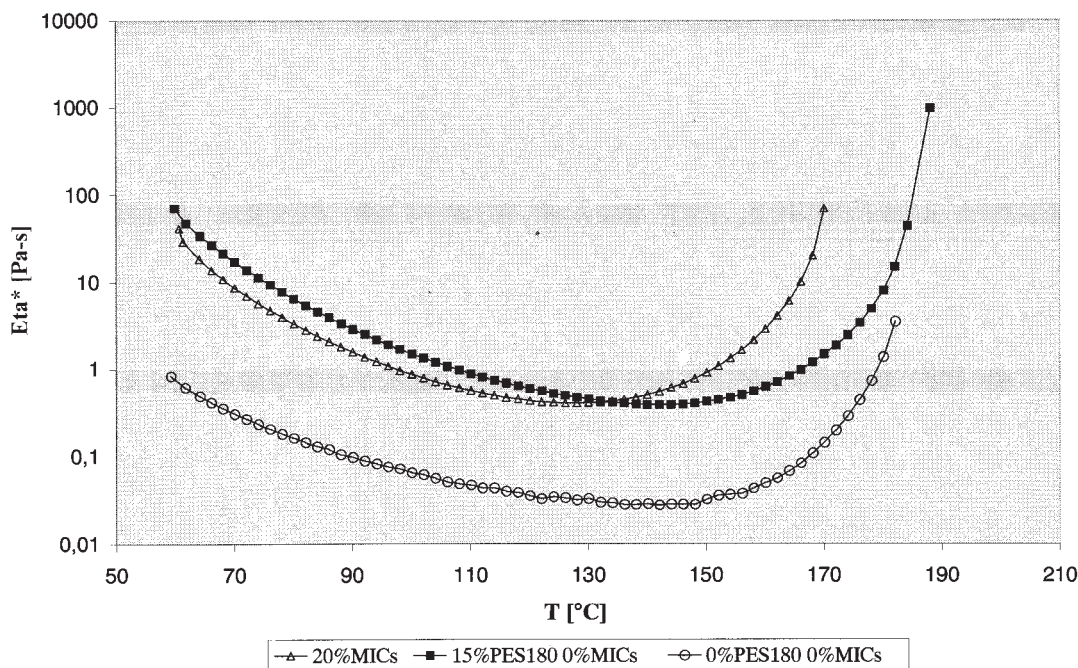
Figure 7 Viscosity versus temperature curves for the 20% MICs, 15% PES180 0% MICs, 0% PES180 0% MICs systems.

the influence on the reactivity is higher in the case of microspheres compared with the thermoplastic. This makes microspheres useful modifiers for medium temperature cycles.

Figures 8, 9, and 10 report the isothermal test performed on 0% MICs, 10% MICs, and 20% MICs systems, respectively. These tests were carried out in order to relate the amount of microparticles to the curing reaction, as well as to build up a model to use as a useful tool for predicting the gel times, as the point where the dynamic storage G' and loss G'' moduli crossover (i.e., tan $\delta = 1$), according to the criterion proposed by Tung and Dynes,[13] at different temperatures. This model turns out to be very useful for the
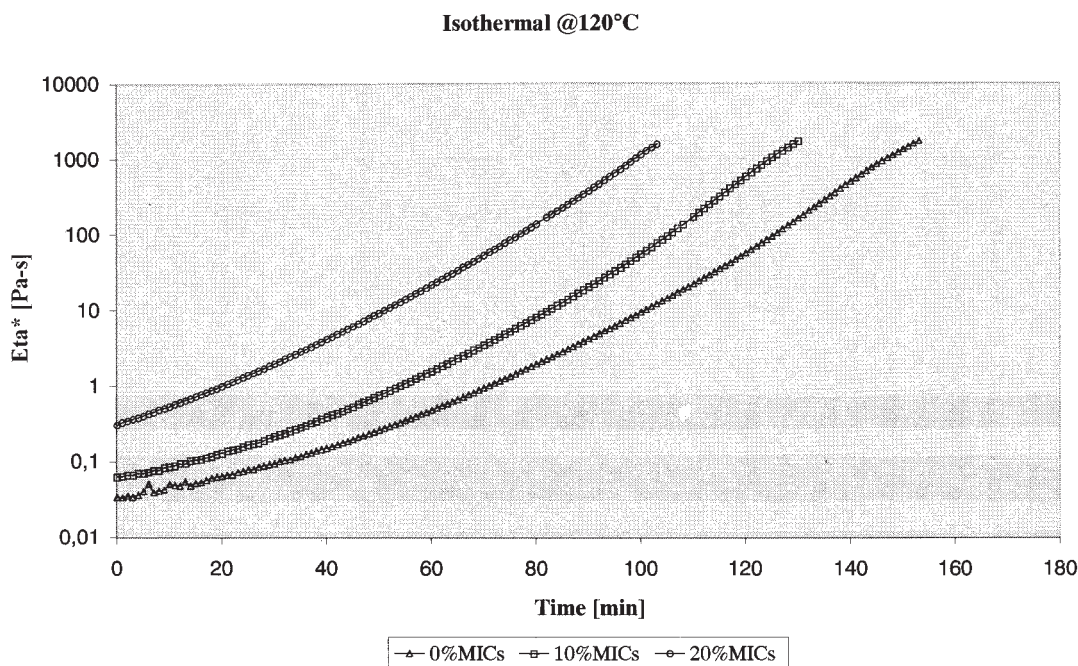
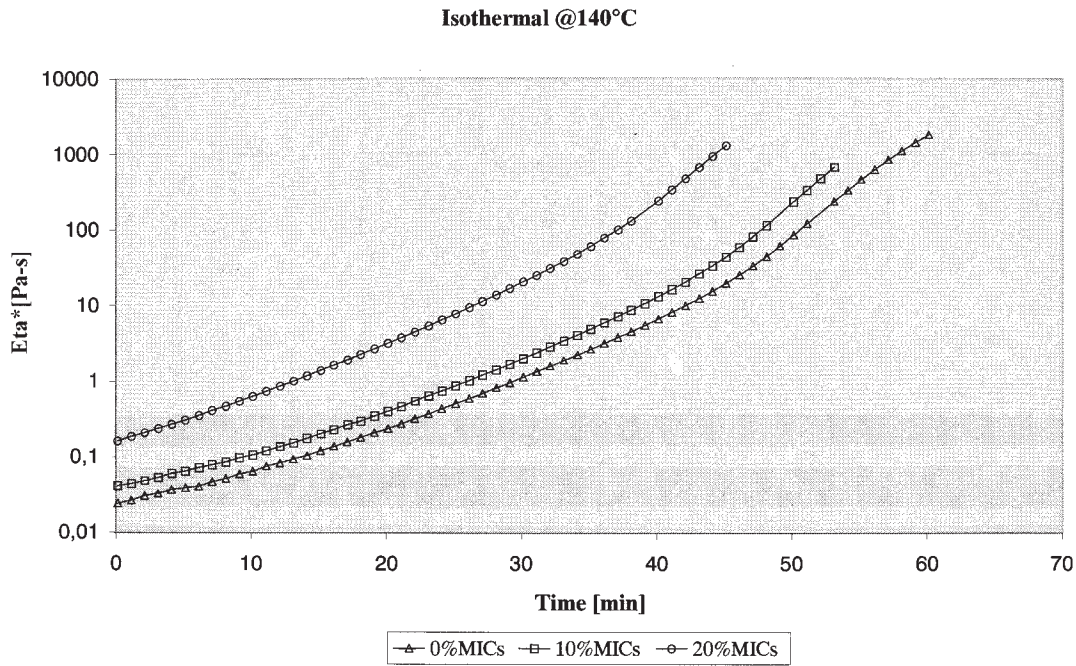**Figure 8** Viscosity versus time curves for the 0% MICs, 10% MICs, 20% MICs systems ($T = 120°C$).

Isothermal @140°C

Figure 9 Viscosity versus time curves for the 0% MICs, 10% MICs, 20% MICs systems ($T = 140°C$).

selection of proper processing conditions. Rheological tests performed at different temperatures confirmed that with increasing the percentage of microspheres, viscosity and reactivity become higher. In fact, gel times decrease as the amount of microspheres is raised. An overall activation energy for polymerization can be calculated from gelation times, assuming that cure reactions may be described by equation containing one apparent activation energy,[14,15] as follows:

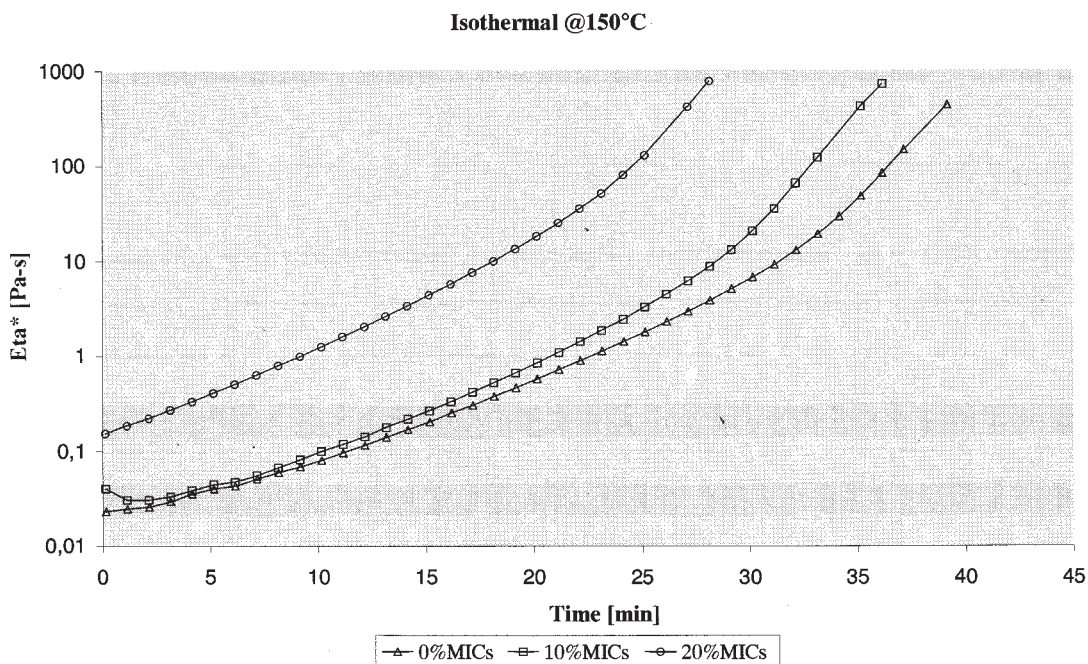$$\frac{dx}{dt} = A \exp\left(\frac{-Ea}{RT}\right)f(x) \qquad (1)$$

Isothermal @150°C

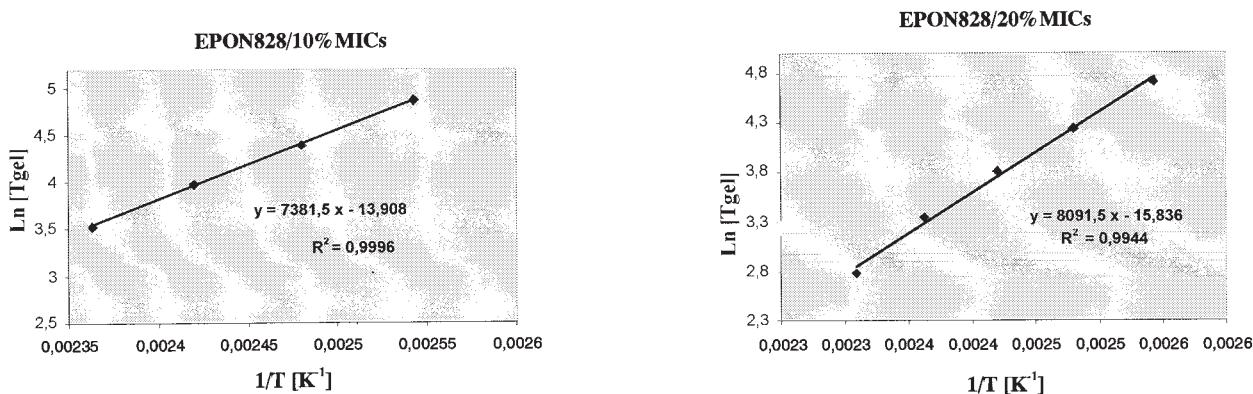**Figure 10** Viscosity versus time curves for the 0% MICs, 10% MICs, 20% MICs systems ($T = 150°C$).

Figure 11   In T_{gel} versus $1/T$ curves for the 10% MICs and 20% MICs systems.

where A is a constant, Ea is the apparent activation energy for the overall reaction, R is the gas constant, T is the absolute isothermal cure temperature, and $f(x)$ is a function of the reaction mechanism and the extent of reaction x. Integration of this equation from $x = 0$ to $x = x_{gel}$ by taking natural logarithms leads to

$$\ln \int_0^{x_{gel}} \frac{dx}{f(x)} = \ln\ A + \ln\ (T_{gel}) - \left(\frac{Ea}{RT}\right) \qquad (2)$$

Based on the Flory theory,[16] the extent of reaction at gelation is constant, so the above equation can be expressed as

$$\ln(T_{gel}) = C + \frac{Ea}{RT} \qquad (3)$$

where C is a constant. The model utilized to predict gel times at temperatures different from those used in the experiments is therefore based on a linear interpolation of eq. (3).

Figure 11 shows the interpolations obtained for the 10% MICs and 20% MICs systems. The calculation of parameters, intersection, and slope of eq. (3) enables us to draw out the gel_time versus temperature curves shown in Figure 12. Their trend represents a further confirmation of the higher reactivity related to the presence of microspheres.

DMTA analysis results

Figure 13 reports the storage modulus (G') behavior versus temperature for the systems with 0, 10, and 20 wt % of microspheres. The diagram shows a clear flex point associated with the glass transition temperature for all the systems. The T_g increases with the amount of the microspheres. This effect can be attributed to an increase of crosslink density associated with the multifunctional nature of the microspheres that, as it has
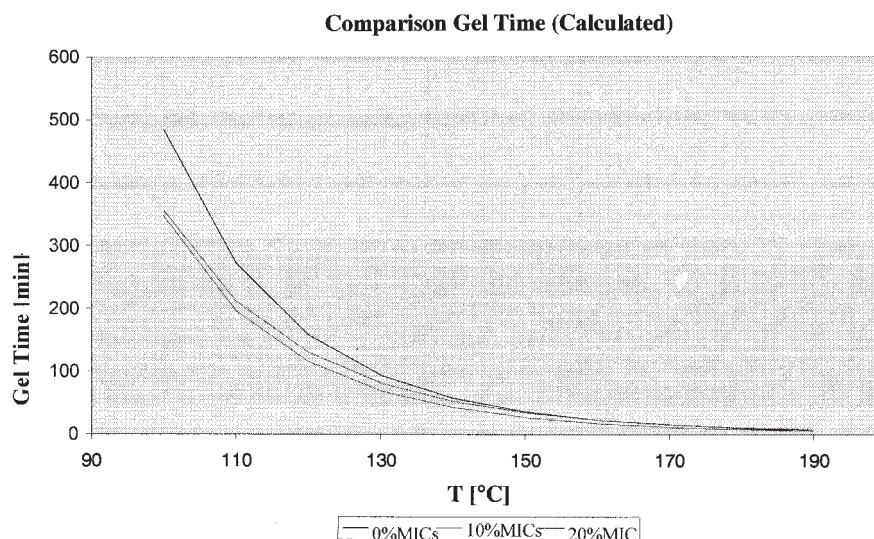

Figure 12   Gel time versus temperature curves for the 0% MICs, 10% MICs, 20 % MICs systems.
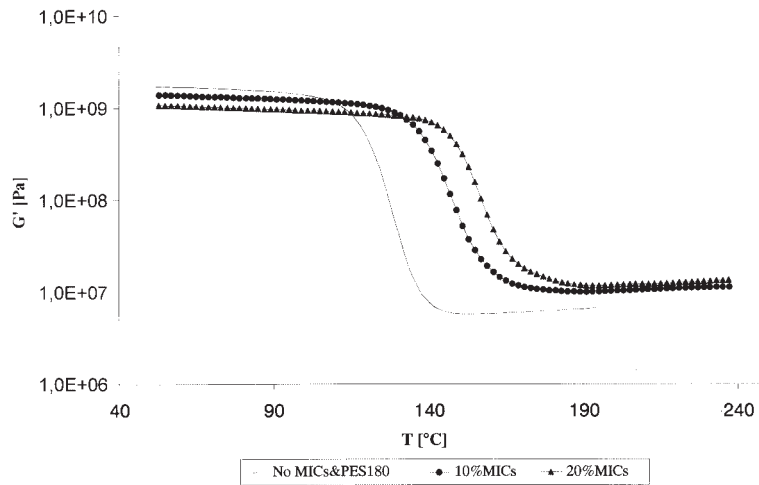
Figure 13 Storage modulus (G') versus temperature behavior for cured samples.

been showed previously by ESCA, are characterized by the presence of reactive amino groups on the surface.

The storage modulus G' (Fig. 13) in the rubbery region is shown to increase with increasing percentages of microspheres. Therefore, if we consider the relationship (4) drawn from the theory of the rubber elasticity, that links the molecular weight between the crosslink points (M_c) to the storage modulus G', we can conclude that the network formed by the addition of the microspheres results in higher crosslink densities

$$M_c = \frac{3\rho RT}{G}$$ (4)

where ρ is the density of the resin, R is the universal constant, T is the temperature, and G' is the storage modulus in the rubbery region.

Figure 14 reports the tan_delta (G''/G') curves for the systems modified by the addition of the microspheres and reports the behavior of the PES180 modified systems for comparison.

The increase of crosslink densities due to the addition of the microspheres causes a considerable increase of T_g. Figure 14 reports the curves for the systems modified by the addition of the thermoplastic copolymer PES180. The comparison shows that the 20% MICs blend has a T_g of the same order to the system 30% PES180. Therefore, it can be concluded that the reactive synthesized microspheres constitute a valid and economic alternative to the use of thermoplastics in those applications where the T_g increase is a primary issue.

LEFM analysis results

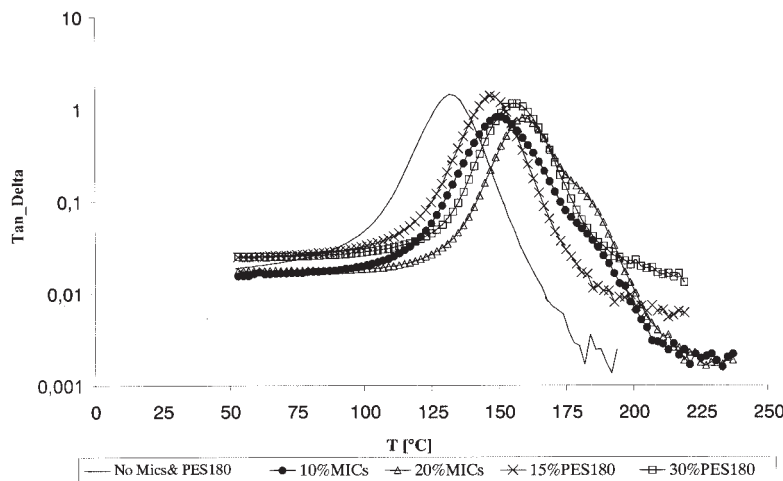Fracture mechanic tests were carried out in bending mode and quasistatic speed to characterize the micro-

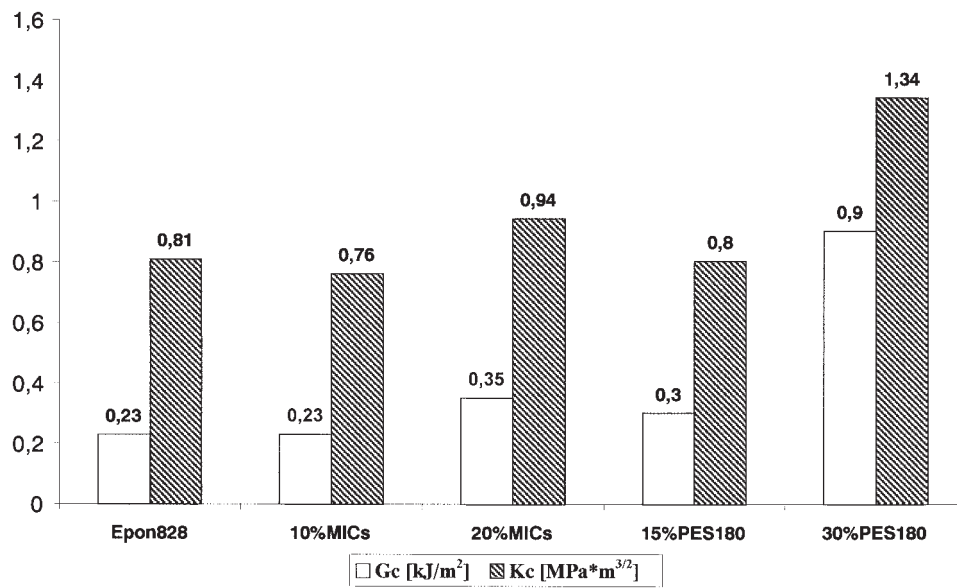**Figure 14** Tan_Delta versus temperature behavior for cured samples.

Figure 15 Energy of fracture (G_c) and stress intensity factor (K_c) for samples modified with microspheres and thermoplastic copolymer PES180.

mechanical behavior of modified samples. Figure 15 reports the G_c and K_c values obtained. The G_c and K_c showed slightly increased at higher content of the microspheres. The fracture energy factor at 20% loading of microspheres has a value comparable to the systems modified by the addition of 15% of PES180. Due to the crosslinked nature of the microspheres, it can be attributed to a crack pinning mechanism, as reported for rigid particles,[17] but further studies are required to better understand the fracture mechanical behavior. However, the slight increase in fracture re-

sistance can be considered an advantageous feature for future application of the microspheres.

SEM analysis

SEM analysis provided useful information about microsphere segregation, degree of adhesion with the matrix, and fracture behavior.

Figure 16 shows the fracture surface of a sample fractured in N_2. By a careful observation of the resin surface, it can be seen that in some part of the sample
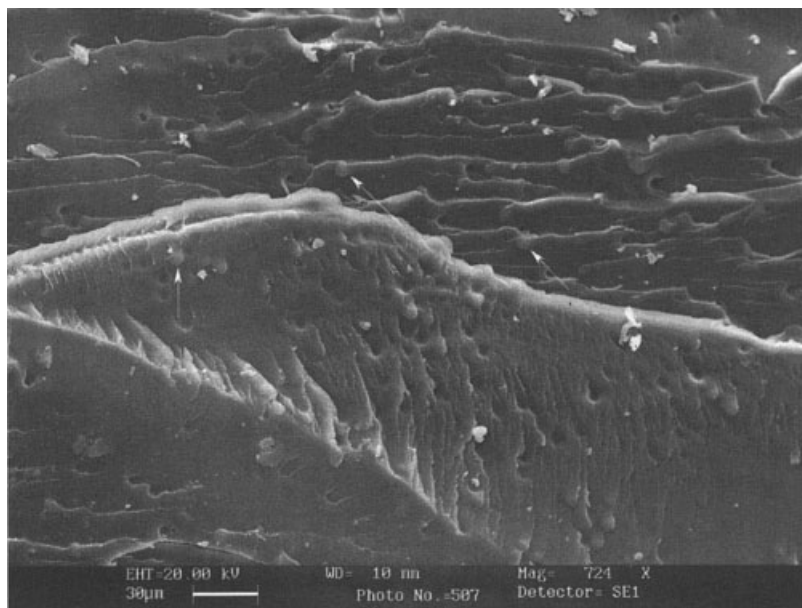

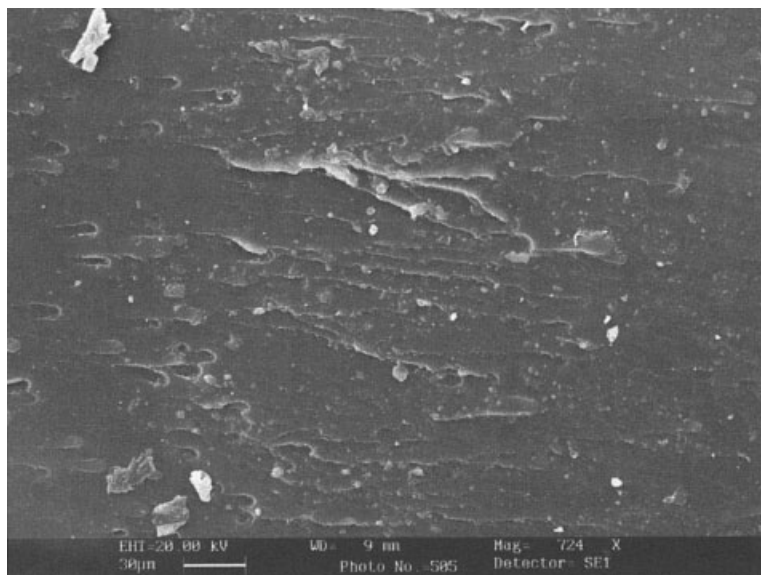**Figure 16** SEM image showing the morphology of 10% MICs sample fractured in N_2 (magnification, ×724K).

Figure 17 SEM image showing the morphology of 10% MICs sample after LEFM tests (magnification, ×724K).

the epoxy microspheres appear to be partially covered by the resin, indicating that the degree of adhesion between them is high. In other parts, spherical voids are well detectable, indicating that fracture carried out in liquid nitrogen removes microspheres from the matrix as a consequence of lack of adhesion at the interface.

For samples fractured after LEFM test at room temperature, no microspheres are detectable, indicating that, upon fracture, the matrix plastically deforms, covering the inclusions (Fig. 17).

CONCLUSION

In this article, the influence of microspheres based on epoxy resins on the viscosity, dynamic–mechanical properties, and fracture toughness of an epoxy systems was investigated. For this purpose, a three-step study was followed, consisting of the preparation of epoxy microparticles, the characterization of their morphology and reactivity of the outermost layer, and the rheological and mechanical characteristics of epoxy resin charged with different amounts of microparticles.

The preparation of microparticles was carried out in four different experimental conditions, in which the composition of the starting solutions (i.e., the epoxy + amine to solvent ratio) and the viscosity of solvent were changed. The temperature was kept constant in all cases. This was done with the aim of understanding whether the change in experimental parameters was responsible for different characteristics of the recovered microparticles.

Actually, from ESCA analysis, it was inferred that the PPG content was constant in the four samples (it only varied with the take-off angles), and that an excess of DAT (used as curing agent) was present on the microsphere surfaces. This explains the high reactivity of microspheres towards epoxy resins.

This reactivity was confirmed by the rheological results. Experiments performed on EPON828 resin charged with 10 and 20 wt % microspheres led to the conclusion that an increase of the microsphere percentage was responsible for a higher reactivity of the system, because the temperature value for the minimum viscosity decreased as the percentage of microspheres in the sample increased. This effect may be related to the presence of reactive amino groups on the microsphere surfaces.

The influence of microspheres on the reactivity is higher compared with the thermoplastic usually utilized in these cases and this makes microspheres useful modifiers for medium temperature cycles.

The addition of the microspheres has proved to be very effective in increasing the T_g of the blends without sacrificing the fracture resistance but slighting increasing the G_c and K_c values. Moreover, due to the presence of reactive amino groups, the adhesion between microspheres and matrix is improved, as inferred from SEM analysis.

Therefore, it can be concluded that the microspheres constituted a valid and economically advantageous alternative for high engineering thermoplastic in those applications where thermal resistance is a primary requisite and toughness is not a critical issue.

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