Preformed Microspherical Inclusions for Rheological Control and Physical Property Modification of Epoxy Resins

M. Frigione,[1] E. Calò,[1] A. Maffezzoli,[1] D. Acierno,[2] C. Carfagna,[2] V. Ambrogi[2]

[1]Department of Innovation Engineering, University of Lecce, Lecce, Italy
[2]Department of Materials and Production Engineering, University of Naples, Naples, Italy

ABSTRACT: Epoxy microspheres, with average diameters in the order of 4–5 μm, were first produced as insoluble gel resulting from the reactions of a bisphenolic epoxy resin with an aromatic hardener in solution. They were then used as reactive flow modifiers and toughening agents for bisphenolic epoxy resins with same chemical composition. Thermal analysis, rheological measurements, and impact tests were performed to assess their ability to modify the viscosity of the uncured resin and to determine the effects on the cured resins with respect to the glass transition temperature and impact strength.

Two similar epoxy systems modified with the addition of different amounts of microspheres preserve the glass transition temperature of the cured unmodified epoxy. The addition of microspheres is responsible for secondary transition. The addition of a small fraction of microspheres does not affect the reactivity of the epoxy resin, while the inclusion of a higher content leads to a noticeable reduction in the gel time of the epoxy systems, indicating that microspheres are not inert fillers. Finally, a limited enhancement of the toughness of the epoxy resin was observed, as a consequence of strong interactions between the matrix and the microspheres. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 748–757, 2006

Key words: reactive microspheres; toughening agents; rheological analysis

INTRODUCTION

Epoxy resins find applications in several fields owing to outstanding properties, such as mechanical strength, resistance to chemicals, and capability to adhere to different materials, of the products obtained. A main deficiency of cured epoxy is its brittleness, which limits its use in several applications. The traditional method to enhance the toughness of epoxy resins is by the addition of liquid reactive modifiers, which are able to precipitate as rubbery particles during the crosslinking reactions.[1] Low molecular weight modifiers ($M_n = 2000–4000$) are usually used to limit the viscosity increase of the epoxy resin.[2] The same effects can be attained with the addition of some reactive thermoplastics, even if the processability of the system is reduced.[2]

The addition of fillers to epoxy resins is a feasible way to improve the mechanical properties and to reduce costs. The effect of the incorporation of fillers on the properties and characteristics of epoxy resins depends substantially on the type of filler and the amounts used. In particular, mineral fillers are likely to produce an increase in density and viscosity, which is likely to impair the processing characteristics.[3] On the other hand, if the target is the modification of viscosity of the resin during processing, a suspension of solid particles in the resin, as for some thermoplastic fillers, can be very useful in balancing the desired viscosity profile.

In the present work, crosslinked microspheres, obtained as insoluble products of the chemical reaction between a bisphenol epoxy resin and an aromatic amine hardener, are evaluated as reactive flow modifiers and toughening agents for bisphenol epoxy resins of similar composition. Over the last years, a growing interest in the production of polymeric particles has been registered, in particular as spacers, slip property improvers for plastic films, adhesives, paints, sealants, and binders dispersed in a solvent, as fillers in the composite materials, and in the field of microencapsulation.[4–10]

In this article, different tests were performed with the aim to assess the ability of the crosslinked microspheres to modify the viscosity of the uncured resin, to alter the reactivity of the epoxy, and to effectively toughen the cured epoxy, without any reduction in glass transition temperature. The effect of the microspheres content was evaluated using resins with different epoxy equivalent values.

EXPERIMENTAL

Materials

Two bisphenolic epoxy resins were employed in this study. The first was Epon 825 (supplied by Shell Company, Germany), having an epoxy equivalent of 175–180. The second was Der 332 (supplied by Dow Plastics), with an epoxy equivalent of 171–175, characterized by a negligible content of dimers with respect to the first resin.

The hardener, 2,4-diaminotoluene, DAT (supplied by Aldrich, Italy), is able to cure bisphenolic epoxy resins at relatively high temperatures. A stoichiometric amount of hardener was added to each resin, corresponding to the molar ratio resin/DAT = 2/1. The corresponding weight ratio for both epoxy resins was resin/DAT = 85/15 wt % (the resins possessing the same molecular weight).

The microspheres, evaluated as flow modifiers and toughening agents for the epoxy resins, were prepared as reported elsewhere.[11] They were based on Epon 825 crosslinked with DAT at a molar ratio of 2/1 in polypropyleneglycol solution. The amount of microspheres added to each mixture of epoxy/hardener was 5, 10, and 20 pphr (part per hundred resin).

For comparison purpose, a Der 332 mixture containing 20 pphr of microspheres was also prepared and analyzed. Similarly, a mixture of microspheres and DAT in the same weight ratio used for the systems with the two epoxy resins (corresponding to a mixture DAT/microspheres, 47/53 wt %) was produced. The described mixtures were obtained by mixing the ingredients and heating the mixture at 100°C for a few minutes until it became transparent.

Crosslinked Epon 825/DAT, Epon 825/DAT containing 20 pphr microspheres [corresponding to a mixture Epon 825/DAT/microspheres (72.6/12.9/14.5 wt %)], Der 332/DAT, and Der 332/DAT containing 20 pphr microspheres (corresponding to a mixture Der 332/DAT/microspheres 72.6/12.9/14.5 wt %) were produced by curing each selected formulation in an oven at 140°C for 1 h. The obtained systems were characterized by dynamic mechanical analysis and impact tests.

Spectroscopic and microscopic characterization of microspheres

Fourier transform infrared (FTIR) spectroscopy was performed on the microspheres to identify the main chemical bonds of the product. The IR analysis was repeated on a sample of microspheres postcured in an oven at 170°C for 1 h, to determine whether any further chemical reaction takes place from unreacted groups in the microspheres.

The morphology of the microsphere, studied by environmental scanning electron microscopy (ESEM)
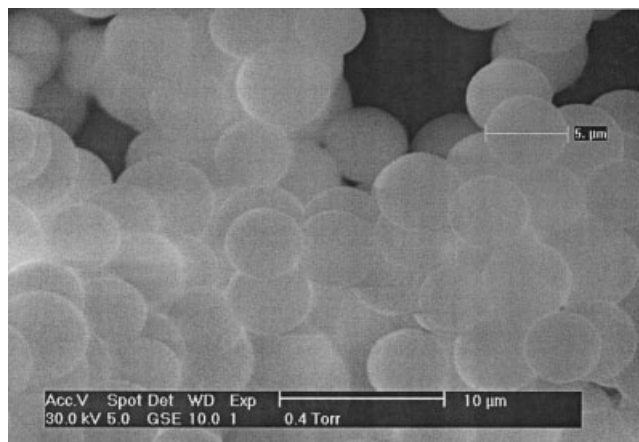

Figure 1 ESEM image of the microspheres as produced.

using an FEI, model XL30, is shown in Figure 1. This shows that the microspheres are very regular particles with average diameters in the region of 4–5 μm.

The same microscopic analysis was also performed on the fractured surface of cured samples of Der 332/DAT and Der 332/DAT/microspheres (72.6/12.9/14.5 wt %) after impact tests.

Thermal characterization

Differential scanning calorimetry (DSC) was employed to monitor the reactions and thermal transitions of the mixtures of epoxy resin and hardener, using a Thermoanalyzer DSC-7 (by PerkinElmer). Each dynamic scan was performed by heating a sample from 25 to 280°C, at 10°C/min under nitrogen atmosphere.

In the first dynamic scan were examined unreacted mixtures of each epoxy resin and the DAT hardener. The exothermic reaction was analyzed by determining the peak temperature and the heat of the crosslinking reactions. In the subsequent scan, the glass transition temperature (T_g) of each completely cured system was determined.

The microspheres were also analyzed by DSC to calculate, in a first scan, the residual heat of reaction, if present, and in a second scan, the T_g of the fully crosslinked system.

Mixtures based on each epoxy resin and DAT with 20 pphr microspheres were examined by DSC analysis, calculating from a first scan the heat of reaction and reaction peak temperature, and from a second scan, the T_g of the system. The results were then compared with those found for the corresponding systems not containing the microspheres.

DSC analysis was also performed on the mixtures based on DAT containing 53 wt % microspheres and Der 332 containing 20 pphr wt % microspheres, both prepared as described previously. These experiments
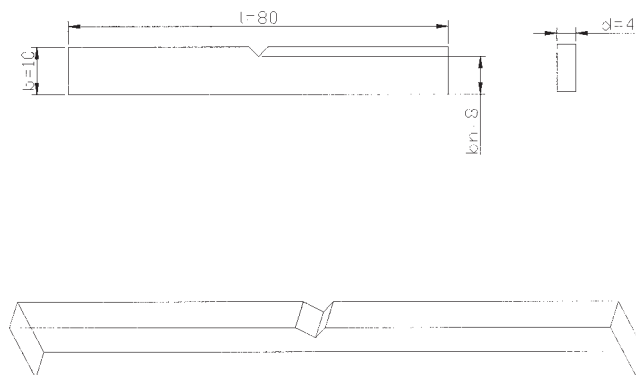
Figure 2 Sketch of the sample used in impact strength test.

were designed to examine the reactions of the microspheres with the hardener and with the epoxy, respectively.

Dynamic mechanical analysis

Dynamic mechanical tests in the torsion mode were performed on cured systems Epon 825/DAT, Epon 825/DAT/microspheres (72.6/12.9/14.5 wt %), Der 332/DAT, and Der 332/DAT/microspheres (72.6/12.9/14.5 wt %) using the torsional DMA accessory for rheometric ARES rheometer. Curing was carried out for 1 h at 140°C. The dimensions of the samples were $15.0 \times 10.0 \times 1.2 \text{ mm}^3$. A temperature ramp of 3°C/min and a strain of 0.2% were used. The T_g of each cured system was determined from the peak temperature of the loss modulus curve.

Rheological characterization

Several rheological tests were carried out using a strain-controlled rheometer Rheometric ARES. The influence of the presence of microspheres on the processing characteristics of the epoxy resin was investigated by means of rheological tests preformed on the control resin Der 332 and on mixtures of the resin with different amounts of microspheres, that is, 5, 10, and 20 pphr. The tests were carried out with cone and plate flow geometry (radius of the plate, 12.5 mm) in steady state mode. Each sample was tested at 25 and 40°C and repeated twice to assess the reproducibility of the results.

The crosslinking reactions of the systems containing the DAT hardener were monitored by performing dynamic rheological experiments at 140°C. The flow geometry used was by parallel plate (radius of the plate, 12.5 mm), with a frequency of 1 Hz and a 10% deformation. The gel point of each system was calculated as the time for the complex viscosity (η^*) to become equal to 10^4 Pa s.[12,13] The gel point calculated for the control system, that is, the one not containing the micro-

spheres, was compared with that calculated on the systems containing different amounts of microspheres. These results were analyzed in conjunction with the calorimetric data, to evaluate the effect of microspheres on the reactivity and on the gelation of the epoxy resin.

Impact tests

To evaluate the toughening effect resulting from the addition of the microspheres, a Charpy impact tester was used. The apparatus was equipped with a load cell for the determination of force and energy diagrams. Rectangular specimens (dimensions, $80 \times 10 \times 4 \text{ mm}^3$) of each formulation were obtained from samples cured in an oven at 140°C for 1 h. They were subsequently cut to produce a notch at the center of each specimen across the width, whose length was exactly measured with the aid of an optical microscope (see dimensions and shape in Fig. 2). The tests were performed following the appropriate standard, and the impact strength was calculated as the fracture energy divided by the cross section area ahead of the crack tip.[14]

After the impact test, the fractured surfaces of the samples of Der 332/DAT and Der 332/DAT/microspheres 72.6/12.9/14.5 wt % were observed under an ESEM.

RESULTS AND DISCUSSION

Control system Epon 825/DAT

In Figure 3 is shown the thermogram obtained from the dynamic scan performed on a sample of the uncured system Epon 825/DAT. The measured heat of reaction and peak temperature, calculated as the mean
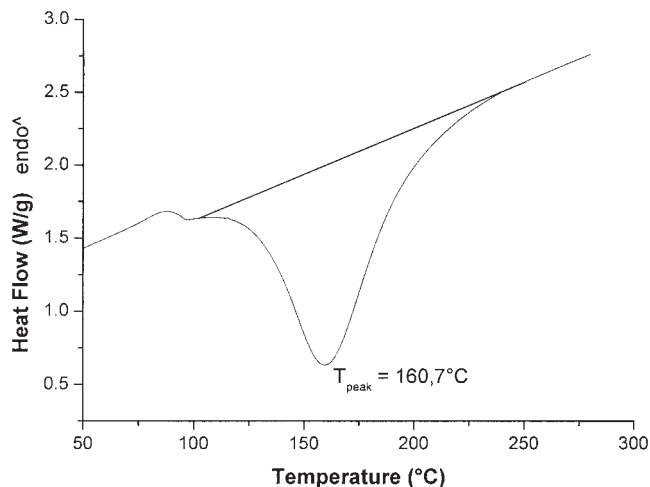

Figure 3 DSC thermogram of uncured system Epon 825/DAT.

TABLE I
Results from DSC Experiments Performed on Uncured Mixtures Realized

System	First dynamic scan		Second dynamic scan (T_g, °C)
	ΔH (J/g)	Peak temperature (°C)	
Epon 825/DAT	390.1	158.6	147.0
Microspheres (MS)	10.0	101.9	141.6
Der 332/DAT	475.0	158.6	168.0
Der 332/MS	11.3	152.4	—
DAT/MS	—	—	—
Epon825/DAT/20 pphr MS	395.0	161.1	148.0
Der 332/DAT/20 pphr MS	481.6	162.0	165.1

of three experiments, are 390 J/g and 158.6°C, respectively.

From the second heating scan performed on the same samples, an average T_g of 147°C was calculated for this system. All the results of calorimetric analysis are reported in Table I.

A T_g of about 140°C, corresponding to the peak temperature of G'', is shown in Figure 4. These results prove that the T_g of the system cured at 140°C is equal to the curing temperature used and is only slightly lower than the T_g calculated through the second thermal scan on the completely crosslinked system. The complete dynamic mechanical curves for Epon 825/DAT system are shown in Figure 4, and the results are reported in Table II.

Control system Der 332/DAT

The results of the thermal analysis performed on the system Der 332/DAT are reported in Table I. The heat of reaction and peak temperature, calculated on uncured system as the mean of three experiments, are 468 J/g and 159.0°C, respectively. An average T_g of
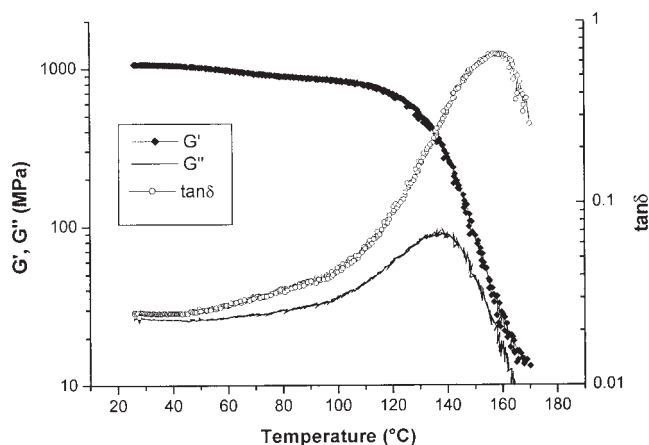
168°C was calculated for this system from the second heating scan performed on the same sample.

Dynamic mechanical tests were carried out on Der 332/DAT samples cured in an oven at 140°C for 1 h. From the G'' curve, a T_g in the region of 135°C was calculated. Again, the T_g of the system cured at 140°C is slightly lower than the T_g calculated on the completely crosslinked system and it is equal to the curing temperature used. The results are also reported in Table II.

Microspheres

The DSC scans performed on the microspheres were used to calculate the residual heat of reaction. The average value of the peak area calculated from all the experiments performed on the microspheres is 10 J/g, while the peak temperature is 102°C. After the second heating scan, the samples of microspheres showed an average T_g of 141.6°C. All the results of calorimetric analysis are reported in Table I. It is worth noting that the T_g of the fully cured microspheres is comparable to that found for the crosslinked Epon 825/DAT system, that is, 140°C. In other words, the geometrical features of the spherical particles were found to have no effect on the glass transition.

It is reminded that the microspheres were obtained by reacting, at 130°C, Epon 825 and DAT in polypropyleneglycol solvent for 15 h. DAT hardener was added in a 35% molar excess with respect to the stoichiometric ratio to ensure that all the epoxy monomer

Figure 4 Dynamic mechanical curves of cured system Epon 825/DAT.

TABLE II
Results from DMA Experiments Performed on Systems Cured at 140°C for 1 h

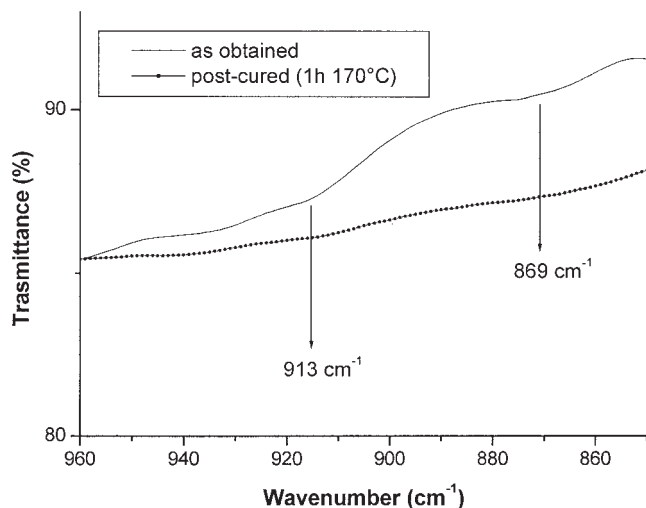| System	T_g (°C)
Epon 825/DAT	140
Der 332/DAT	135
Epon825/DAT/20 pphr MS	143
Der 332/DAT/20 pphr MS	152

Figure 5 FTIR spectra of pre- and postcured (at 170°C for 1 h) microspheres.

used was reacted and that an excess curing agent was still available to produce interfacial bonds with the epoxy resin of the matrix. The presence of unreacted amine groups on the surface of the microspheres was confirmed by Electron Spectroscopy (ESCA) measurements.[11] The small exothermic peak observed in calorimetric experiments is also attributed to the completion of the reaction of the remaining epoxy rings with the unreacted amine groups.

The FTIR spectra performed on a sample of microspheres, before and after post-curing, is reported in Figure 5. Small amounts of residual unreacted epoxy groups, associated to the absorbance peaks at 913 and 869 cm^{-1}, are noted for samples before the postcuring treatment, which are in accordance with the results obtained by DSC analysis. The same spectroscopic analysis performed on the postcured sample of the microspheres, also reported in the Figure 5, reveals the disappearance of the two peaks associated with epoxy groups and confirms that the reactions are complete by heating the sample at 170°C.

Systems Der 332/microspheres and DAT/microspheres

For comparison purposes, a mixture containing the Der 332 resin and the microspheres, at weight ratio 83/17, was heated in the DSC module. The results (Table I) showed an exothermic peak with an enthalpy value of about 11 J/g and a peak temperature of about 152°C. The enthalpy value normalized to the microspheres content is 64.7 J/g. This value is much higher than that calculated for the neat microspheres (ΔH = 10 J/g). This result indicates that the unreacted groups of the microspheres can react both with themselves and with the epoxide groups of the matrix resin

Der 332. This confirms that unreacted amine groups are present on the surface of the microspheres.

Similarly, a mixture DAT/microspheres (weight ratio, 47/53) was examined by DSC analysis. From this analysis it was not possible to identify any reaction taking place between any reactive groups in the microspheres and the amine hardener in the matrix. It is concluded, therefore, that although the microspheres still possess few unreacted epoxy sites, as observed through FTIR studies, the amounts present are too small to produce significant reaction with the amine hardener in the matrix.

System Epon 825/DAT/microspheres

The results of calorimetric experiments performed on the system Epon 825/DAT/microspheres (72.6/12.9/14.5 wt %) are reported in Table I. The total heat of reaction measured through DSC on this uncured modified system is 395 J/g, which when normalized to the resin/hardener content, equals to 462 J/g, that is, much higher than that measured on control system Epon 825/DAT (i.e. 390 J/g). It can be deduced that the overall crosslinking reactions involve the epoxy resin, the hardener in the matrix, and the unreacted sites of the microspheres. The peak temperature is 161°C for both control and modified systems, indicating negligible changes in the kinetics of crosslinking reactions. From the second dynamic scan, a T_g by about 148°C was calculated for the modified system.

The DMA curves of the same samples cured at 140°C for 1 h are shown in Figure 6. From the dynamic mechanical analysis, a T_g of about 143°C was confirmed for the fully cured Epon 825/DAT/microspheres (72.6/12.9/14.5 wt %). The first small peak for the G'' trace, observed in Figure 6 at about 62°C, is attributed to a secondary transition associated to the presence of the reactive microspheres. The T_g calcu-
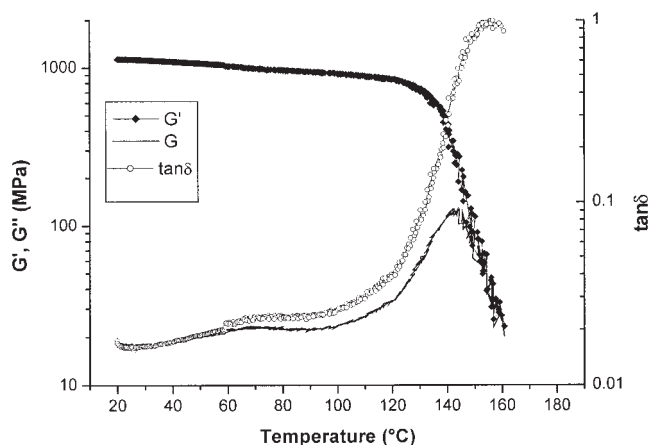

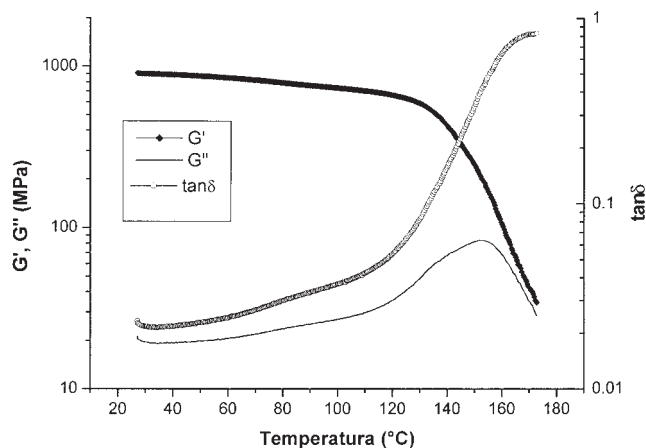**Figure 6** Dynamic mechanical curves of cured system Epon 825/DAT/20 pphr of microspheres.

Figure 7 Dynamic mechanical curves of cured system Der 332/DAT/20 pphr of microspheres.

lated from dynamic mechanical analysis on cured Epon 825/DAT/microspheres system is close to that measured on cured control system Epon 825/DAT (140°C). This result confirms that the modified system preserves the thermal properties of the parent control system.

From the calorimetric characterization, it can be concluded that the inclusion of even high percentages of microspheres does not affect the T_g of the cured unmodified epoxy system.

System Der 332/DAT/microspheres

The results of DSC analysis performed on the modified system Der 332/DAT/microspheres (72.6/12.9/14.5 wt %) are reported in Table I. In particular, the heat of reaction normalized to the resin/hardener content equals to 563 J/g. By comparing these results with those found for the control Der 332/DAT system (i.e., $\Delta H = 475$ J/g; $T_p = 159$°C), the reactivity of microspheres was confirmed, while the peak temperatures were found to be very similar. Again in this case, it is reasonable to suppose that the overall reaction involves the epoxy resin, the hardener, and the microspheres.

From the second DSC scans performed on the same samples, an average T_g by about 165°C was calculated, which is comparable to that measured on the control sample (i.e., 168°C).

A Der 332/DAT/microspheres sample, cured at 140°C for 1 h and then subjected to dynamic mechanical analysis, showed a T_g of about 152°C, as calculated from DMA curves (Fig. 7). This value is slightly lower than that calculated on samples crosslinked in the thermal dynamic scan (i.e., 165°C) and much higher than that measured for the control system, that is, the one not containing the microspheres. The same first small peak in the G'' trace (82°C), previously observed

for the system Epon 825/DAT/microspheres, was again attributed to a secondary transition associated to the presence of the microspheres.

From the dynamic mechanical characterization it be concluded that the presence of relatively high percentages of microspheres is able to increase the T_g of the cured unmodified epoxy system by upto 20°C. This is a very useful result, since traditional toughening agents for epoxies generally produce an appreciable decrease in their T_g.[15] A similar result was found for a bisphenolic epoxy system cured with diaminodiphenylsulphone (DDS) hardener to which 10 and 20 wt % of microspheres was added.[11] The effect of microspheres was attributed to an increase of crosslink density associated to the multifunctional nature of the microspheres. The increase in T_g in that case, however, was larger, since the unmodified epoxy systems possessed a much lower T_g than did the microspheres, around 120°C.

## Rheological characterization

The results of the rheological tests performed on the resin Der 332 and on its mixtures with 5, 10, or 20 pphr microspheres at 25 and 40°C are shown in Figures 8 and 9.

A first sweep experiment was always followed by a second experiment performed on the same sample and using the same conditions. From Figures 8(a) and 9(a), it can be observed that the viscosity at low shear rates of the uncured resin is significantly affected by the presence of even small quantities of microspheres, that is, the viscosity of the pure resin increases with the content of microspheres. This increase is much smaller at high shear rates. This observation suggested a possible effect of aggregation of the microspheres on the rheology of the mixture. For this reason, a second rheological experiment was performed on each sample under the same conditions. From these scans [Figs. 8(b) and 9(b)], the shear rate dependence of the systems containing the microspheres appeared Newtonian, as it is the case of the unmodified epoxy resin. The viscosity of the mixtures, however, is always higher than that of the pure resin mixture and it increases with the content of microspheres.

For a very dilute suspension of rigid spheres in a Newtonian fluid, the relationship between the viscosity of the fluid and that of the suspension was found to follow the Einstein's equation,[16] that is

$$\eta = \eta_0(1 + 2.5\phi) \tag{1}$$

where η is the viscosity of each mixture, η_0 is the viscosity of the neat resin, and ϕ is the volume fraction of the filler. This relationship is valid for ϕ lower than 1%. For higher volume fractions, on the other hand,
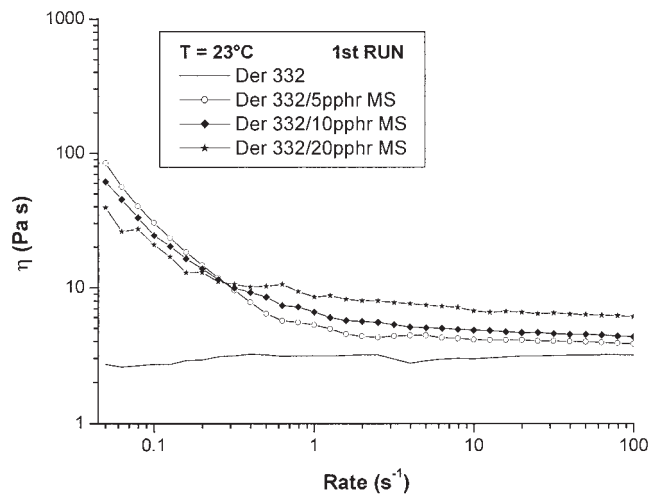
(a)
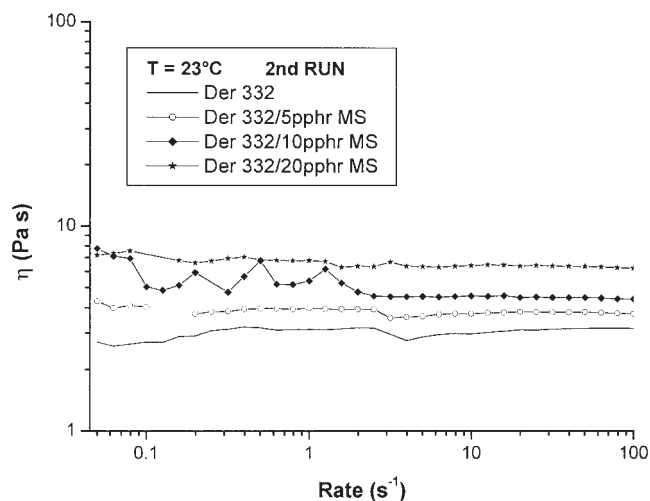
(b)

Figure 8 Rheological curves of the resin Der 332 and its mixtures with 5, 10, or 20 pphr of microspheres at 25°C: (a) first run and (b) second run.

another equation can be used, as first proposed by Batchelor[17]:

$$\eta = \eta_0(1 + 2.5\phi + 6.2\phi^2) \qquad (2)$$

To verify the validity of eq. (2) for the mixtures containing the microspheres, the volume fraction of the filler, that is, the microspheres, was calculated. To this end, the density of the microspheres was determined by porosimetry measurements, using mercury as fluid. A density by about 0.8 g/cm^3 was calculated for the microspheres. Since the density of the neat resin is 1.16 g/cm^3 and the measured density for the crosslinked unfilled resin is 1.26 g/cm^3, the presence of holes in the microsphere morphology can be deduced. The comparison between experimental values of viscosity of the control system and those of the

mixtures at 25°C as function of the volume fraction, for several values of shear rate, with the theoretical data expressed by eq. (2), is shown in Figure 10. It is worth noting that the deviations from the theoretical relationship are appreciable only at very high volume fraction values. This indicates that the microspheres act as inert fillers in the liquid resin.

The results of rheological analysis can be associated with the aggregation of the microspheres through weak chemical bonds, as confirmed by Figure 1. By applying high shear rates to the mixture of the resin and the microspheres, it is possible to disrupt these bonds between the microspheres, decreasing the viscosity of the whole system that assumes a Newtonian behavior. Therefore, the additional drag resistance observed in the first rheological experiment can be at-
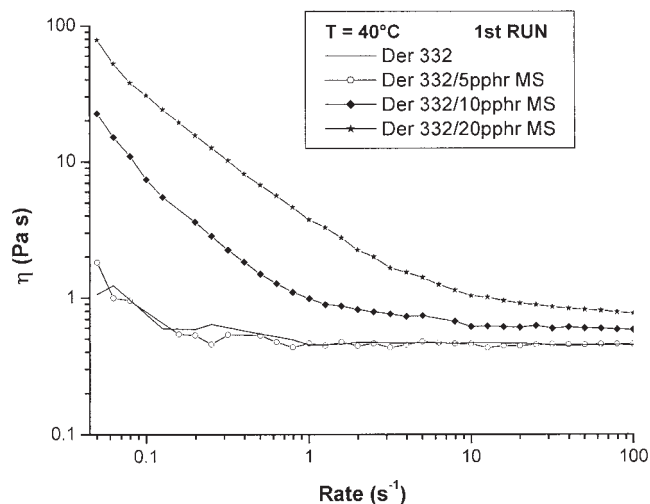
(a)
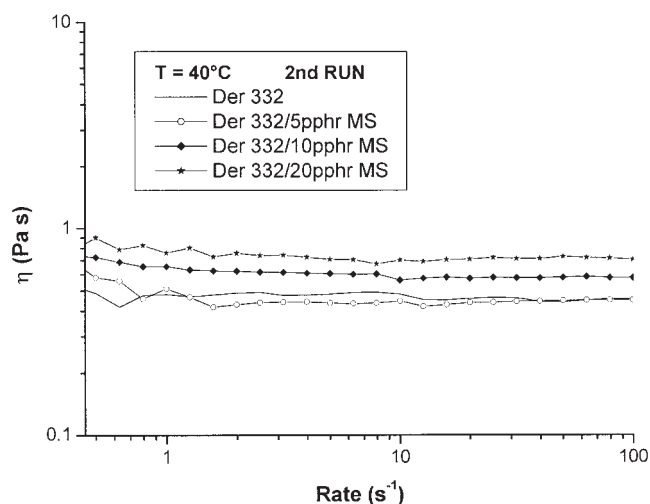
(b)

Figure 9 Rheological curves of the resin Der 332 and its mixtures with 5, 10, or 20 pphr of microspheres at 40°C: (a) first run and (b) second run.
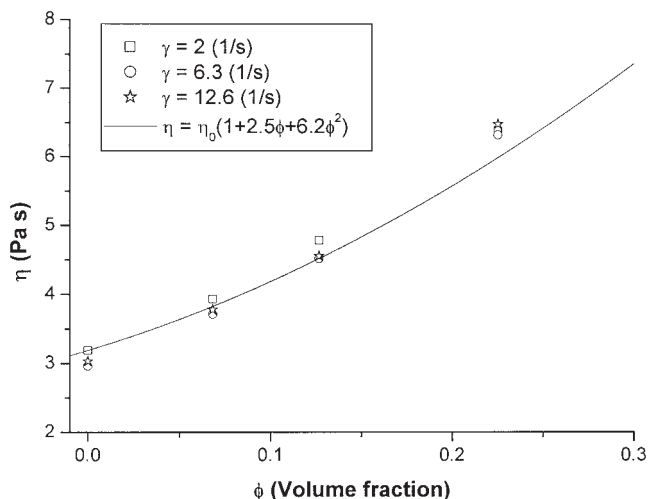
Figure 10 Comparison between experimental values of viscosity at 25°C of the control system Der 332/DAT and of the mixtures with 5, 10, or 20 pphr of microspheres as a function of the volume fraction, at several values of shear rate, with theoretical values from eq. (2).

tributed to the work employed to disaggregate the microsphere clusters.

DAT hardener was added to the resin Der 332, as well as to its mixtures with 5, 10, or 20 pphr microspheres, and dynamic rheological experiments at 140°C were performed on the resulting systems. The curves of the complex viscosity calculated for each system are shown in Figure 11. The gel points, calculated for each system as the time for the complex viscosity to equal 10^4 Pa s, are listed in Table III.

From observations in Figure 11 and comparing the gel time data reported in Table III, it can be concluded
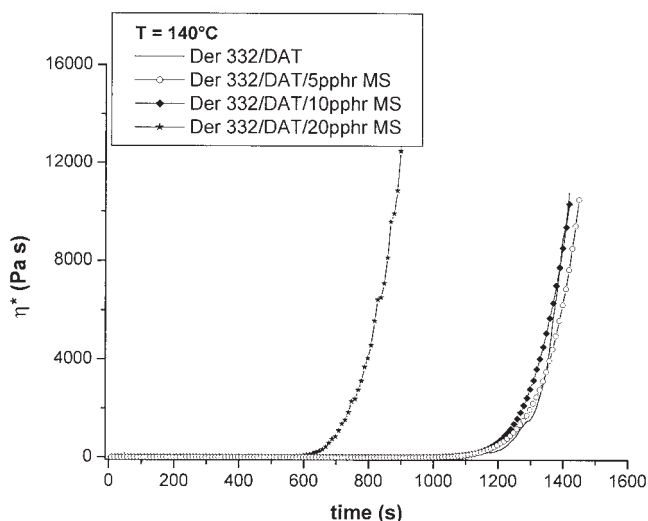

Figure 11 Rheological curves of the system Der 332/DAT and its mixtures with 5, 10, or 20 pphr of microspheres at 140°C.

TABLE III
Gel Time Values Calculated for Each Mixture at 140°C

System	Gel time (s)
Der 332/DAT	1418
Der 332/DAT/5 pphr MS	1448
Der 332/DAT/10 pphr MS	1419
Der 332/DAT/20 pphr MS	888

that the inclusion of 5 and 10 pphr microspheres does not affect the gel time of the resin. On the other hand, by adding a higher amount of microspheres, that is 20 pphr, a significant reduction of the gel time was observed. This confirms that microspheres display a significant reactivity toward the matrix. The growing branched molecules connected to the microsphere surface can lead to very fast gelation, since this microspheres represent sites characterized by a very high functionality.

The gel point calculated with Flory relationship depends on the stoichiometric ratio (r) and the functionality of amine ($f_a = 4$) and of epoxy ($f_e = 2$):

$$\alpha_g = \sqrt{\frac{r}{(f_a - 1)(f_e - 1)}} \tag{3}$$

This relationship for the neat resin ($r = 1$) leads to $\alpha_g = 0.58$. At concentrations above a critical value, eq. (3) can be rewritten as

$$\alpha_g = \sqrt{\frac{r}{(f_a - 1)(f_e - 1)(f_m - 1)}} \tag{4}$$

where f_m is the unknown functionality associated to the microspheres and r cannot be assumed equal to 1. In this equation three reactive species are considered. The value of f_m, the functionality associated to microspheres, is likely to be very high. Consequently, the term $f_m - 1$ in eq. (4) is very high, leading to a predicted much lower value of α_g. Since the reaction kinetic is unaffected by the presence of the microspheres, as obtained from calorimetric analysis, the gelification observed in Figure 11 for the resin loaded with 20% microspheres can be attributed to a lower α_g.

Impact test and morphological analysis

The results of the impact test performed on the cured systems Der 332/DAT and Der 332/DAT/microspheres (72.6/12.9/14.5 wt %) are reported in Table IV. The fractured surfaces of the same systems, from the impact tests, observed with ESEM technique, are shown in Figures 12(a) and 12(b). The Charpy impact strength of notched specimens (α_{CN}) was calculated as the specific fracture energy, that is

TABLE IV
Impact Test Results

System	Impact strength (kJ/m²)
Der 332/DAT	7.25 ± 0.56
Der 332/DAT/20 pphr MS	7.59 ± 0.83

$$\alpha_{CN} = \frac{W}{db_N} \tag{5}$$

where W is the impact energy effectively absorbed in breaking the specimen (i.e., the energy consumed to propel the sample was measured and subtracted from the total energy recorded), d is the thickness of the specimen, and b_N is the effective length of the width in correspondence of the notch. From the results shown in Table IV, it can be concluded that the inclusion of high amounts of microspheres is not able to produce any significant increase in impact strength, since the increase by about 5% is within the experimental error.[18]

The control sample, that is Der 332/DAT, after the impact test, shows the typical fracture of the brittle epoxy resins[Fig. 12(a)] characterized by distinct wave lines. Dispersed particles are discernible in the bulk of the sample Der 332/DAT/microspheres (72.6/12.9/14.5 wt %) [Fig. 12(b)]. However, these particles are not able to slow down appreciably the propagation of the fracture through the matrix resin, to act as crack stoppers, even though a good adhesion between them and the resin matrix can be observed. A morphology very similar to that observed for the control sample can also be, in fact, noted in the sample containing the microspheres. Moreover, the microspheres do not appear to be hollow, indicating that they could be filled by the matrix resin. The last observation can be supported by the calculation of the theoretical value of the density of the composite formed by crosslinked resin and the porous microspheres. This value is equal to 1.16 g/cm³, while the measured value of density for the system Der 332/DAT/microspheres (72.6/12.9/14.5 wt %) is about 1.20 g/cm³. This is higher than the theoretical value, but is still lower than that relative to the crosslinked unfilled resin, that is 1.26 g/cm³.

In conclusion, the reactivity of the surface of the microspheres, giving rise to a strong interface bond, coupled with the ability of the epoxy resin to partly fill them, can be responsible for the poor ability of the microspheres to behave as toughening agents for the epoxy system.

CONCLUSIONS

Epoxy microspheres, previously synthesized, were investigated as possible reactive flow modifiers and toughening agents for bisphenolic epoxy resins. Different tests were performed with the aim to assess their ability to modify the viscosity of the uncured resin, to alter the reactivity of the epoxy, and to effectively toughen the cured epoxy.

The synthesized microspheres, which are the solid residue produced in the chemical reaction taking place between the bisphenolic epoxy resin Epon 825 and the hardener DAT, were characterized by unreacted groups, as found through calorimetric and spectroscopic studies. These groups readily react further, preferably with an epoxy resin, since the microspheres were synthesized with an excess of amine.

Both the epoxy systems studied, when modified with the addition of even high percentages of microspheres (i.e. 20 pphr), preserve the thermal properties, in particular the T_g, or the presence of microspheres is even able to appreciably increase the T_g of the cured unmodified epoxy. Moreover, the addition of microspheres is responsible for a secondary transition.
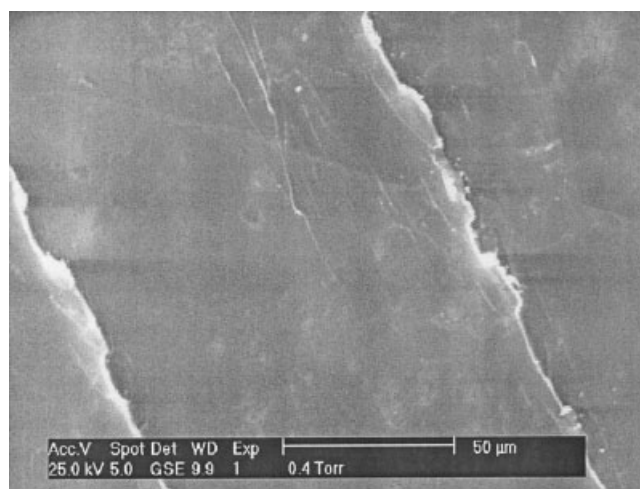
(a)
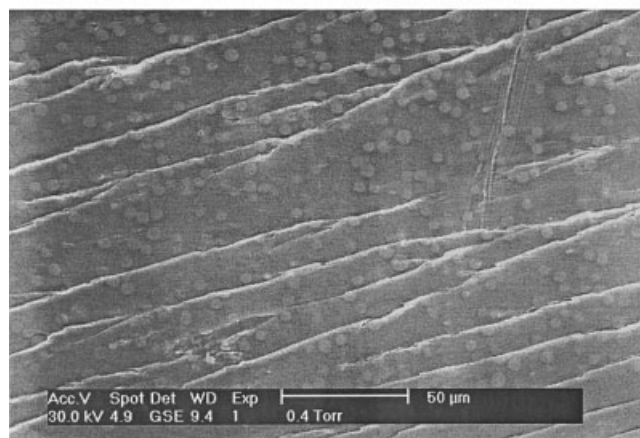
(b)

Figure 12 Sample surfaces fractured through impact tests: (a) Der 332/DAT and (b) Der 332/DAT/20 pphr of microspheres.

The addition of small percentages of microspheres (up to 10 pphr) does not affect the reactivity of the epoxy resin. On the other hand, the inclusion of a higher content of microspheres (i.e. 20 pphr) leads to a noticeable reduction in the gel time of the epoxy systems, indicating that microspheres are not inert fillers. In particular, the growing branched molecules connected to the microsphere surface can lead to very fast gelation, since these microspheres represent sites characterized by a very high functionality. Moreover, the addition of 20 pphr of microspheres produces an appreciable increase in the viscosity of the resin, which depends on the effectiveness of the mixing during the preparation of the system.

The expected enhancement of the toughness of the epoxy resin was not observed, as a consequence of the strong adhesion between the matrix and the microspheres. The poor ability of the microspheres to behave as effective toughening agent was also explained observing that the resin can possibly penetrate inside the particles. The morphological analysis of the fractured surface of the sample containing the microspheres confirmed the presence of dispersed particles not able to act as crack stoppers in the brittle epoxy matrix.

In conclusion, the microspheres, if present in sufficient quantity, can be regarded as reactive flow modifiers able to change the viscosity and to reduce the gel time of the epoxy resin when a curing agent is present. On the other hand, to increase the toughening ability of the microspheres, different stoichiometric ratios or epoxy monomer backbone can be employed, to tailor their crosslink density, leading to less rigid and, therefore, less brittle particles. Furthermore, the residual reactivity at the microsphere surface should be prevented so as to reduce their adhesion to the matrix.

Finally, the dispersed particles show a potential to hold additives that could be released to accelerate or retard gelation or to enhance the service-related properties and to be used in self-healing resins.

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