

Influence of Copolymer's End Groups and Molecular Weights on the Rheological and Thermomechanical Properties of Blends of Novel Thermoplastic Copolymers and Epoxy Resins

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Received 2 November 2004; accepted 10 June 2005

DOI 10.1002/app.23275

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this paper, we present a study on the properties of epoxy resins blended with copolyethersulfones. Several copolyethersulfones were synthesized by varying the molecular weights and the end groups. The obtained thermoplastics were then mixed with diglycidyl ether of biphenol A (DGBEA) (15% wt ratio), cured with methylene bis(2,6-diethylaniline) (MDEA), and the resulting blends characterized by the use of dynamic thermal mechanical analysis (DMTA), rheometry, and fracture mechanics tests. The morphology of the blends was studied by the use

of scanning electron microscopy (SEM). The different molecular weights of the copolymers had a significant effect on the rheological and thermomechanical properties of the resins, as well as the different end groups on the reaction rate and on the thermomechanical properties of the blends. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 250–257, 2006

Key words: epoxy resins; thermoplastics; polyethersulfones; rheology; phase separation; viscoelastic properties; toughness

INTRODUCTION

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

Recently, we reported a study on the use of a novel 40:60 PES:PEES amino-terminated polymer as reactive toughening agent for epoxy resins.^{13–17} Such work

was focused on the curing of the epoxy/thermoplastic blends by varying the curing agents,¹⁴ the epoxy resins,^{15,16} and the modifier concentrations.¹⁷ Those studies demonstrated¹⁴ that by varying the curing agent it is possible to change the morphology of the blends from particulate to homogeneous with the consequent decrease in toughness. Moreover, it was shown that the addition of the reactive copolymer did not change cure reaction rate.

In another study,¹⁷ we analyzed the effect of the modifier's concentration and, in this case, the morphologies ranked from particulate to phase inverted. The amount of the thermoplastic influenced the thermomechanical and the water absorption properties. In particular, by using the highest percentage of copolymer (30 wt %), we obtained both the highest toughness as well as an higher value of water up take.

Different studies have also been devoted to investigate the viscosity of polymer–polymer emulsion. Palierne, for example, focused his attention on linear rheology of viscoelastic emulsion of two immiscible thermoplastic blends by taking into account the interfacial tension and the relaxation times,¹⁸ and Graebling and Muller¹⁹ have used Palierne's model to determine the interfacial tension of the thermoplastic/thermoplastic blends in the melt phase. Ohta et al.²⁰ has carried out the computer simulation of the domains growth under steady shear flow, to predict the morphology evolutions, the change in viscosity, and

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Contract grant sponsor: Italian MURST.

the normal forces with the shear rate. Onuki²¹ showed the initial homogenous thermoplastics blends that phase separate during the quench.

The study of the viscosity evolution of the thermosets by adding the thermoplastics, and the characteristic phase separation, are not widely reported in literature as well as in the case of thermoplastic/thermoplastic blends. The first important work in this field, reported by Bonnet et al.²² described the viscosity evolution of an epoxy blended with polyetherimide (PEI), and they showed that by varying the PEI content, there is a change of the shape in the fluctuation associated to the phase separation phenomena. Recently, we found similar results¹⁴ on epoxy systems based on the addition of a reactive copolyethersulphone, and also we showed that the viscosity fluctuation shifts to lower times by increasing the temperature in accordance with the phase separation mechanism.

Kim and Char²³ also studied the effect of phase separation on the rheological properties during the isothermal curing of epoxy resins modified with a polyethersulphone, and they also proposed a suspension model to simulate the viscosity evolution.

Yu et al.²⁴ studied the effect on rheology and thermomechanical properties of the addition of an hydroxyl-terminated polyethersulphones to PEI/epoxy blends and showed that, by varying the amount of PES and its molecular weight, different patterns in the viscosity evolution occur.

The aim of this paper is to study the influence of the copolyethersulphones structural parameters, such as the molecular weight and end group type, on the properties of epoxy/copolyethersulphone blends. In particular, the rheological and thermomechanical properties, such as thermal transition and fracture mechanics, are reported.

EXPERIMENTAL

Materials and preparation of samples

The epoxy resin used was a diglycidyl ether of biphenol A (Epon828) supplied by Shell (USA), with epoxy equivalent weight of 188.05, and the curing agent was 4,4'-methylene bis(2,6-diethylaniline) (MDEA) supplied by Lonza, (Switzerland), which was added in a 77% stoichiometry ratio. The use of an excess of the epoxy sample is widely used for commercial formulations, since it introduces a plasticization effect that improves the toughness of the resin. Random copolymers such as PES:PEES (Polyethersulphone:Polyethersulphone) (see Table I) were prepared in our laboratory varying the end groups and the molecular weights. The details on the synthesis are reported elsewhere.²⁵ The structures of the materials used are shown in Figure 1.

TABLE I
Physical and Chemical Properties of the Copolymers

Copolymer type	End group	M_n	Code
40:60 PES:PEES	Amine	5,000	C1
40:60 PES:PEES	Amine	9,000	C2
40:60 PES:PEES	Chlorine	10,000	C3
40:60 PES:PEES	Hydroxyl	12,000	C4

The resins were prepared by mixing the thermoplastic with the resin and stirring the resulting mixture for 2 h at 120°C, then the temperature was decreased to 80°C, the curing agent was added, and the resulting mixture stirred for 1 h at 80°C. The resin for rheological characterization was stored at -18°C until used for the tests. To prepare the cured panel for mechanical testing, the resin mixture was poured in a preheated silicone rubber mold and degassed for 30 min at 145°C. Then, the temperature was increased (2°C/min) up to 180°C and held for 3 h. At the end of the curing cycle, the panels were left to cool down slowly at room temperature. Panels with dimensions 150 mm × 80 mm × 5 mm were obtained.

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

Morphological analysis

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

Mechanical analysis

Three-point bending specimens 65 mm × 12 mm × 4 mm were used to perform fracture tests at low strain rate. The measurements were carried out at room temperature with an Instron apparatus Mod. 4301, using a crosshead speed of 1 mm/min. Before testing, the samples were sharply notched with the aid of a notch-vis apparatus by CEAST. The crack was then introduced in the sample by tapping a fresh razor blade. Fracture data were analyzed according to the concepts of linear elastic fracture mechanics (LEFM). A three-point bend test was carried out at 1 mm/min, on the Instron 4301, by using a sample size of 80 mm × 12 mm × 4 mm to measure the flexural modulus.

Dynamic mechanical thermal analysis

DMTA tests were carried out for cured samples by using a dynamical mechanical thermal analyzer,

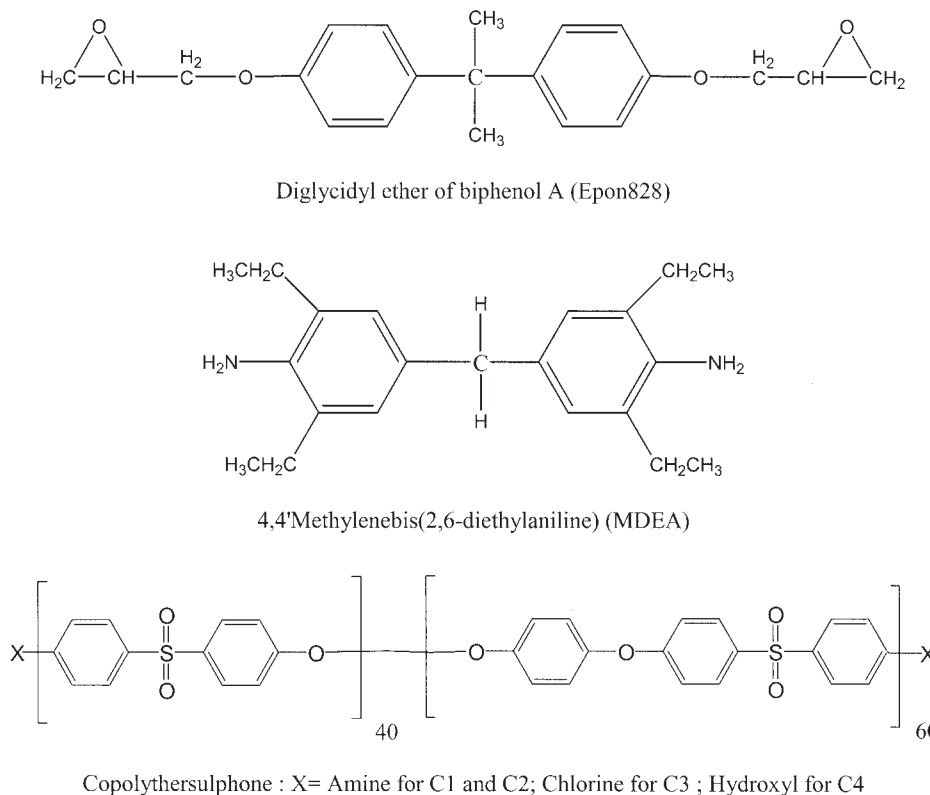


Figure 1 Chemical structures of the epoxies, curing agent, and modifiers.

ARES by TA instruments, at a fixed frequency of 10 rad/s with a 2°C/min heating rate, using samples of sizes 45 mm × 10 mm × 4 mm. Dynamic modulus and tan δ were obtained operating in torsion mode.

Rheological characterization

Rheological analysis were performed on a rotational rheometer (ARES by TA instruments) equipped with parallel plates of 40 mm diameter operating at a frequency of 30 rad/s. The unreacted samples were subjected to isothermal experiments.

RESULTS AND DISCUSSION

Complex viscosity (η^*) versus time is presented in Figure 2 for an isothermal test at 130°C for five blends: four systems contain the same amount (15% by weight) of thermoplastic modifier and one represent the nonmodified system. The test has been stopped

upon attainment of crossover between G' (storage modulus) and G'' (loss modulus). The copolymers analyzed had the same composition but different end groups and, in one case, different molecular weights. The end groups used had different reactivity ranking from the unreactive chlorine to the highly reactive amine. All the systems showed a fluctuation, similar to analogous systems previously studied,¹⁴ associated to the phase separation phenomena.

By comparison of the viscosity traces of the amine-ended copolymer (C2) with the chlorine ended (C3), we can observe that both show a decrease in viscosity when phase separation starts due to demix of high viscous thermoplastic from the initial dilute solution. However, the blend with C2 shows its fluctuation earlier than that of the blend with C3; furthermore, the viscosity of the former is slightly higher. This fact can be correlated with the presence of the reactive amine groups. In fact, as we reported previously,^{14,15,26} the amine-ended copolyethersulphones can act as curing agents for the epoxy resins. Therefore, some of the C2 macromolecules will be part of the building thermoset network and, clearly due to the high molecular weight of the copolymer, this affects its molecular weight and, in turn, its viscosity. It is known from the literature^{27,28} that phase separation in thermoset/thermoplastic blends is induced by the increase in molecular weight of the thermoset species; therefore, in our case, the use

TABLE II
Composition (wt %) of the Blends Studied

EPON 828	MDEA	Modifier
75.90	24.10	0.00
64.51	20.49	15.00

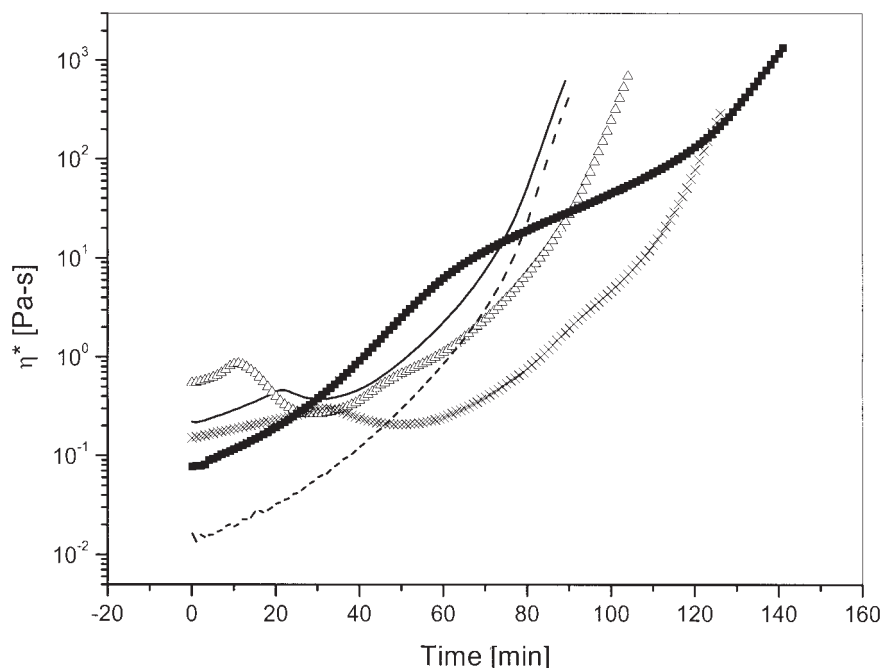


Figure 2 Rheological traces of isothermal experiment at 130°C: (---), 0% modifier; (■), 15% C1; (—), 15% C2; (X), 15% C3; (Δ), 15% C4.

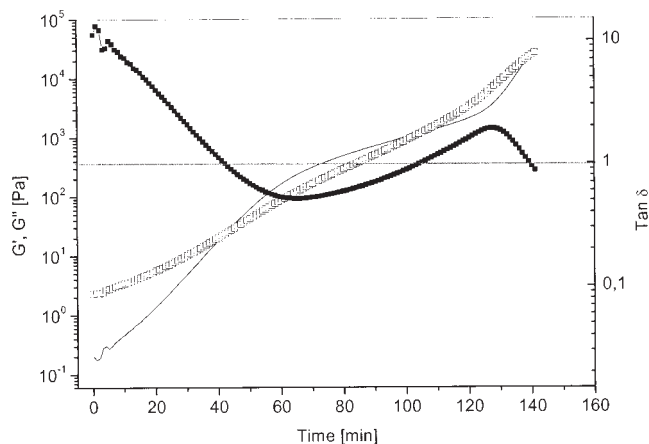
of the reactive groups induces earlier demixing of the thermoplastic from the solution. The presence of thermoplastic macromolecules chemically linked to the thermoset is further supported by the dynamic thermal mechanical analysis (DMTA) results.

In Figure 2 is reported the behavior of the blend when modified also with hydroxyl-ended copolymer (C4). In this case, when phase separation occurs, the viscosity evolution shows a slight increase of η^* rather than a decrease. Similar fluctuation has been observed for higher percentages of thermoplastic¹⁴ or an increase in the polymer molecular weight.²² This effect could be explained in terms of the possibility that the hydroxyl groups causes, through hydrogen bonding, the selfassociation of the thermoplastic macromolecules with the formation of high molar mass chains. Such an effect has been reported in the past by Chen et al.²⁹ when studying the miscibility of rubbers with different end groups with epoxy blends. The presence of higher molar mass chains would also explain the earlier starting of phase demixing for C4 blend compared with other systems and its higher viscosity.

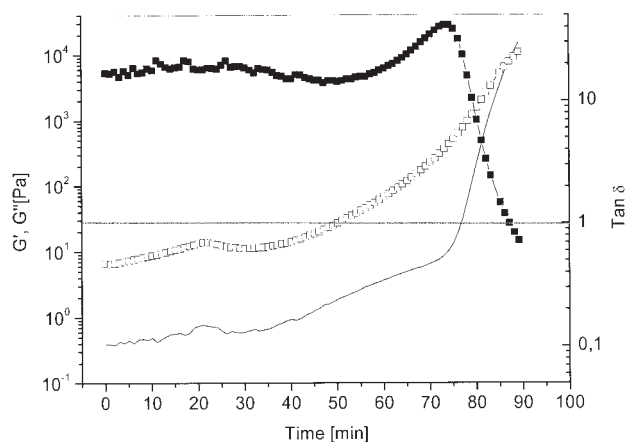
As mentioned earlier, the rheological test was stopped upon attainment of the crossover between G' and G'' . If we assume this point as the gel point, we can observe that by decreasing the end group reactivity there is an increase in the gel time. Similar trends have been reported in the literature^{30–32} for epoxy resins modified with nonfunctionalized thermoplastics, as a consequence of the decrease in the reactive groups because of the presence of the thermoplastic chains.

Figure 2 shows the comparison of the effect of the low molecular weight copolymer C1 and its higher molecular weight counterpart C2. The two copolymers have the same composition and end groups, but the difference in molecular weight causes a great change in the viscoelastic behavior of the blends; in fact, the fluctuation associated with the phase separation is shifted to higher times and the viscosity increase is faster, before the beginning of phase demix, in the case of use of C1 with respect to the C2 copolymer, and this is due to the lower molecular weight of the C1 copolymer. In fact, in a previous paper,¹⁷ we have shown that low molecular weight chains are preferable as crosslink agents because of their higher mobility deriving from their smaller dimensions. If we take into account the viscosity traces in the case of blends derived from the C1 copolymer, we can observe that when the phase separation takes place, at about 60–70 min, there is a decrease of the rate at which the viscosity increases. This behavior can be attributed to the combination of two causes: the decrease of viscosity caused by the demixing of the initial homogeneous solution of the copolymer and the depletion of the reactive chains of C1 that diffuses toward a thermoplastic rich region.

Figure 3 reports the behaviors of G' , G'' , and $\tan \delta$ of the tests at 130°C for the blends containing C1 [Fig. 3(a)] and C2 [Fig. 3(b)]. It is interesting to observe that C1 shows a peculiar viscoelastic behavior characterized by the presence of three separate crossover points between G' and G'' . An explanation of such behavior



(a)



(b)

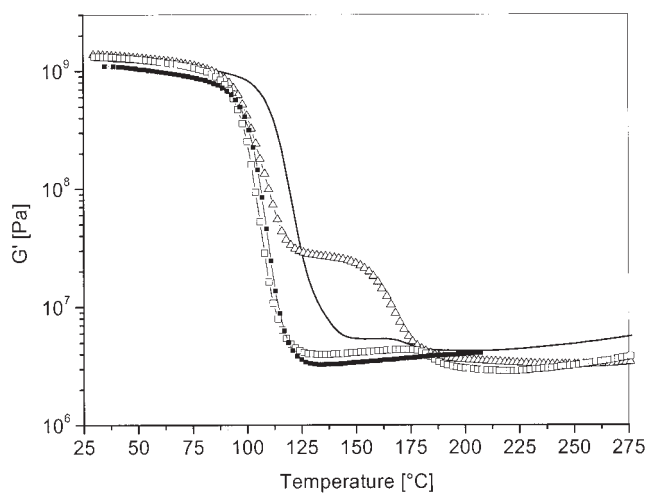
Figure 3 Viscoelastic properties [elastic modulus G' (—); viscous modulus G'' (□); $\tan \delta$ (■)] of isothermal tests at 130°C: (a) blend with 15% of C1; (b) blend with 15% of C2.

could be the creation of a bicontinuous structure, with a part rich of thermoplastic reacted with epoxy with a great enhance of the bulk elastic properties of the blends through the curing reaction.

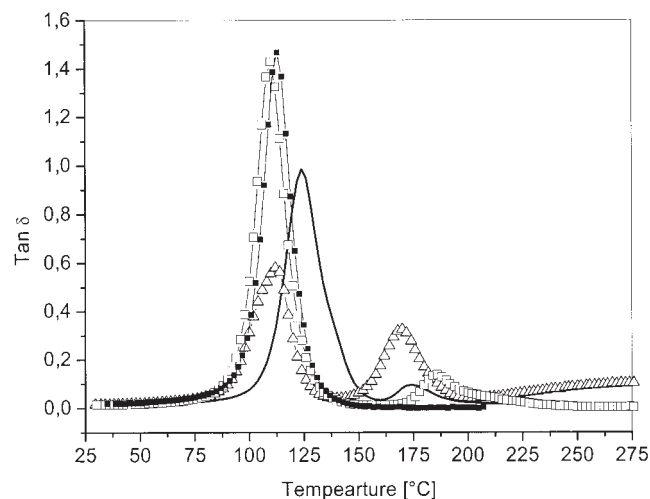
The DMTA analysis of the blends modified with different end group copolymers are shown in Figure 4. It is interesting to observe in Figure 4(a) the trend of the first decay of the elastic modulus by varying the end group. In fact, the unmodified system and the blend with the chlorine-ended copolymer (C3) have similar behavior, while the blend obtained from the amine ended (C2) and hydroxyl (C4) polymer relax at higher temperature. The difference can be explained with the different reactivity of the end groups with the epoxy group; the C2 polymer can chemically react with the epoxy forming epoxy/thermoplastic copolymer that then becomes part of the final crosslinked network as well as the C3 polymer can partially dis-

solve in the epoxy-rich matrix, but this chain do not actively contribute to the relaxation of the network.

All the systems modified with copolyethersulphones show two peaks [Fig. 4(b)] in their $\tan \delta$ curves. This is a clear indication of the presence of phase separated morphology as further confirmed by SEM micrographs (Fig. 5). All the blends, except in case of the C4 system, showed a particulate morphology. The resin modified with the hydroxyl-ended polymer C4 showed an inhomogeneous morphology constituted by a dominant phase inverted structure [see Fig. 5(c)] and some regions with a particulate morphology [see Fig. 5(d)]. The characteristic morphology of C4 blends has a clear influence on its DMTA trace. In fact, the peak associated with the relaxation of the epoxy-rich phase is less intense than the corresponding peak of



(a)



(b)

Figure 4 Elastic modulus G' (a) and $\tan \delta$ (b) traces of cured blends modified with copolymers with different end groups: (■), 0% modifier; (—), 15% C2; (□), 15% C3; (Δ), 15% C4.

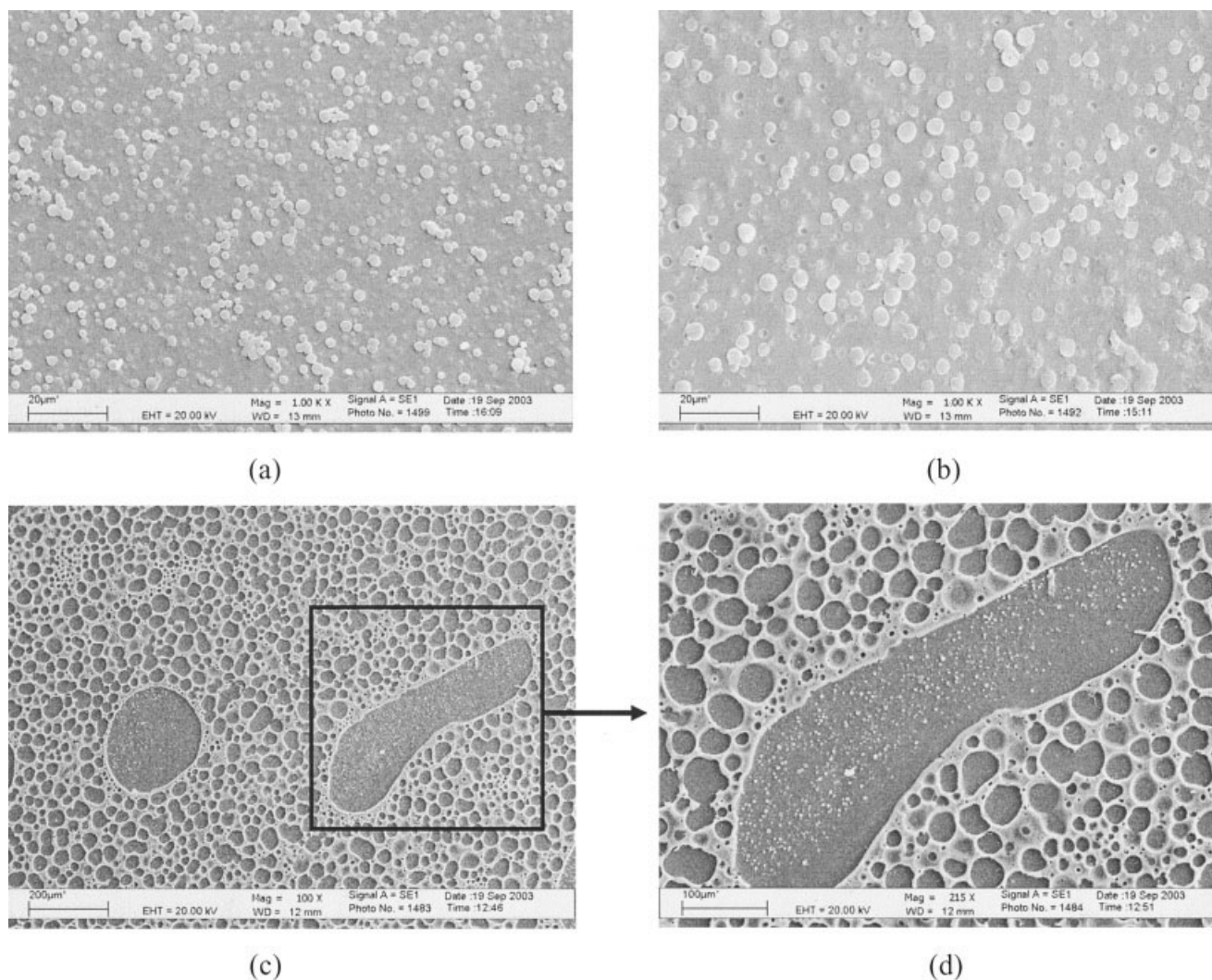


Figure 5 SEM micrographs of blends modified with copolymers with different end groups: (a) 15% C2; (b) 15% C3; (c) 15% C4; (d) 15% C4 [magnified particular of (c)].

the other blends. Moreover, the peak is shifted to higher temperatures compared with the peak of the base system. The latter phenomenon is related to the presence of chemically linked thermoplastic chains within the epoxy-rich phase. The intensity of the peak can be associated to the presence of a dominant phase inverted structure rich in thermoplastic. We observed an analogous trend in a previous paper,¹⁷ when using 30 wt % of amine-ended copolyethersulphone, it was evident a phase inverted structure.

In Figure 6, we compare the DMTA traces of the blends obtained by using the two amine-ended copolymers with different molecular weights. The two blends show similar behavior [Fig. 6(a)] for the relaxation of the epoxy-rich phase with a consistent increase of relaxation temperature because of chemically linked thermoplastic chains. However, while the $\tan \delta$ trace of the C2 blend clearly shows two separate peaks, that one of the C1 blend shows only one clear

peak, thus leading to the conclusion that the system may have an homogenous morphology. Nonetheless, if we observe closely the $\tan \delta$ curves in the range between 145°C and 225°C [Fig. 6(b)], it is clear that the C1 blend has higher $\tan \delta$ values than that of the C2 blend and of the unmodified system. Therefore, we can conclude that the C2 blend has also a phase separated morphology but with smaller thermoplastic domains that are unable to give a clear separate peak in the $\tan \delta$ trace. Such conclusion is further confirmed by the SEM pictures shown in Figure 7.

Quasi-static tests in flexural mode on prenotched samples were conducted to determine the fracture resistance of the modified systems. The results, in terms of energy to fracture G_C and stress intensity factor K_{IC} are reported in Table III. The data show that the addition of the copolyethersulphones increases the toughness of the epoxy resin. However, a consistent difference in the toughness exists by varying the end

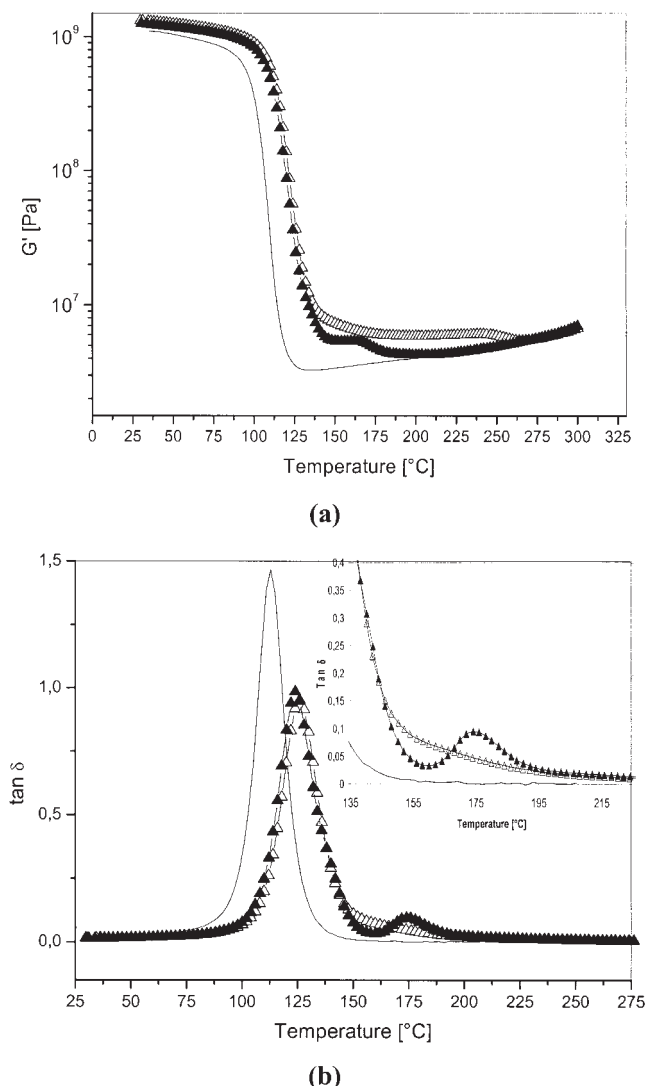


Figure 6 Elastic modulus G' (a) and $\tan \delta$ (b) traces of cured blends modified with amine ended copolymers with different molecular weights: (—), 0% modifier; (Δ), 15% C1; (\blacktriangle), 15% C2.

group and the molecular weight of the modifier. The smallest increase in toughness is registered for the blend with the copolymer owing the unreactive chlorine end group (C3). The blend based on C3 [see Fig. 5(b)] is characterized by a particulate morphology as other blends, but the lower toughness can be related to the weaker interface between the two phases due to the nonreactivity of the chlorine groups. A certain level of adhesion between the thermoplastic and the thermoset phase is required to reach the stress and strain transfers and to favor ductile stretching of the thermoplastic particles in the crack-bridging mechanism.³³

The blend based on the hydroxyl-ended polymer (C4) shows the highest toughness. This result can be related to the peculiar morphology due to the dominant phase inverted structure.

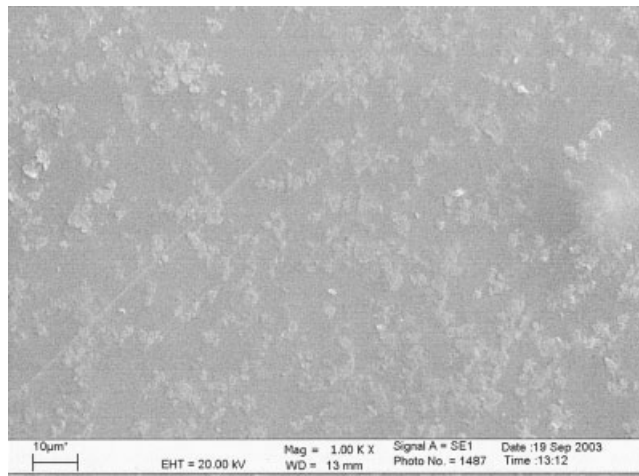


Figure 7 SEM micrograph of the blend modified with 15% (wt %) of C1.

Finally, if we compare the data of the C1 and C2 blends, we find that by increasing the molecular weight of the copolymer the toughness of the blend also increases. This trend can be related to the different morphology of the two systems. In fact, while the blend modified with C2 shows a regular dense distribution of round thermoplastic-rich particles, the blend containing C1 is characterized by less uniform and poorer distribution of smaller irregular thermoplastic particles.

CONCLUSIONS

The aim of this work was to characterize the rheological and thermomechanical behaviors of epoxy/copolyethersulphones blends by varying the copolymer end groups and molecular weights.

All the studied blends showed a fluctuation in the complex viscosity trace by curing at isothermal temperature in correspondence with the phase separation. End groups and molecular weights were shown to affect such fluctuation. The chlorine group shifted the phase separation to higher times compared with the amine group, while hydroxyl group, because of self-association effect, shifted to earlier times the phase separation.

TABLE III
Fracture Mechanics Results

Modifier	End group	M_n	G_c (kJ/m ²)	K_c (MPa m ^{3/2})
No modifier	Amine	—	0.23	0.92
C1	Amine	5,000	0.89	1.80
C2	Chlorine	9,000	1.15	2.07
C3	Hydroxyl	10,000	0.52	1.39
C4	End group	12,000	1.33	2.20

The behavior of amine-ended copolymer was strongly dependent on the formation of chemical crosslink points between the epoxy monomers and the copolymer chains. The evidence of such reaction was also found through the DMTA data of the blends. In fact, the amine-ended polymer significantly increased the relaxation temperature of the epoxy-rich phase.

All the blends showed phase separated morphologies, but while those obtained from the chlorine- and amine-ended polymers showed a particulate morphology, the blend obtained from the hydroxyl copolymer had a dominant phase inverted morphology with regions with a particulate morphology. In addition, a different end group influences not only the morphology but also the toughness of the blends. In fact, the blends obtained with the amine-ended copolymers showed higher toughness compared with the system modified with chlorine-ended polymer, even if they had similar morphology.

The authors are grateful to Prof. I. Fragalà and Prof. G. Malandrino for their invaluable help for the SEM analysis.

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