ELSEVIER

Polymer 40 (1999) 1677–1687

polymer

Use of block copolymers to control the morphologies and properties of thermoplastic/thermoset blends

E. Girard-Reydet, H. Sautereau, J. P. Pascault*

Laboratoire des Matériaux Macromoléculaires, UMR CNRS No. 5627, Institut National des Sciences Appliquées de Lyon, 20 Avenue A. Einstein, 69621 Villeurbanne Cedex, France

Received 20 May 1997; revised 11 March 1998; accepted 26 March 1998

Abstract

A new method for increasing fracture toughness of brittle thermoplastic-modified thermosets by using triblock copolymers has been successfully investigated. The selected systems were polyphenylene ether (PPE)- and polyetherimide (PEI)-modified epoxy networks. Our choice was restricted to available commercial copolymers possibly with some chemical modifications. PPE presents the substantial advantage of having a negative enthalpy of mixing with polystyrene. The maleic anhydride-modified poly(styrene-b-ethylene-co-butene-b-styrene) triblock copolymer, containing an immiscible elastomer central block, was then selected. The reactivity of succinic anhydride functions towards primary amines was used to graft on ethylene-co-butene blocks, chains which are miscible or able to react with the growing epoxy network. The two problems encountered with PEI is that PEI is not miscible with any other polymer and that a commercial triblock with a PEI block does not actually exist. The only copolymer commercially available is a poly(etherimide-b-dimethylsiloxane) segmented copolymer, with elastomer segments which are known to be strongly immiscible with any components. In order to obtain the characteristics of the required compatibilizer, the poly(caprolactone-b-dimethylsiloxane-b-caprolactone) triblock copolymer was associated since (a) the polydimethylsiloxane elastomer central block is chemically identical to the elastomer segment of the previous copolymer, and (b) the polycaprolactone blocks are totally miscible with epoxy. For both thermoplastic-modified epoxy networks, spectacular mechanical reinforcements were measured with only 10%b.w. thermoplastic as a result of interfacial activities of selected compatiblizing systems, with a relative enhancement of fracture toughness close to 50% with around 1% of copolymer. The positive effects on mechanical properties always result from the same causes: large decrease of the particle size (submicron size) and formation of a copolymer-rich interphase characterized by a micromechanical transition in mechanical spectroscopy. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Block copolymers; Thermoplastic; Thermoset

1. Introduction

The concept of thermoplastic-modified thermosets has become widely known in order to avoid the classical compromises between toughness and thermal stability associated with the rubber toughening of thermosets. One of the advantages of using the reaction-induced phase separation procedure is that by an adequate selection of cure cycles and initial formulations a variety of morphologies can be generated. Particulate, bicontinuous or inverted structures can then be achieved depending on both thermodynamic and kinetic factors, namely the modifier concentration and its molar mass, the curing temperature, the reaction rate, and the viscosity during phase separation. It has become evident [1–7], however, that fracture toughness is significantly improved by adding a nonreactive thermoplastic only when bicontinuous or inverted structures are generated. Alternatively, when phase separation produces thermoplastic-rich particles dispersed in a continuous thermoset-rich matrix, little or no improvement of fracture properties is obtained mainly due to the poor adhesion between the phases. Although a continuous thermoplastic-rich phase is easy to generate, the resulting drawback is the deterioration of solvent resistance and the creep properties of the material. To overcome the above mentioned limitations, the synthesis of tough, ductile, functionally terminated thermoplastics has been developed by several groups [8–14] with the intention of subsequently obtaining a chemical linkage between phases. Some enhancement of toughness was effectively reported by using functionalized thermoplastic modifiers. However, such syntheses are still limited and restricted to a number of thermoplastics. The reactivity of the modifier can also complicate the behaviour and the control of the phase separation process. Then, in view of

---

* Corresponding author.

0032-3861/99/$ - see front matter © 1999 Published by Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(98)00302-4

the growing demands for tough polymeric materials with high thermal and chemical stability, new means of increasing toughness in thermoset/thermoplastic blends while maintaining a continuous thermoset-rich phase are of interest.

In the field of thermoplastic immiscible blends, the emulsifying activity of diblock copolymers has been widely used [15–28] to solve the usual problem of strong immiscibility associated with high interfacial tension, poor adhesion and supposedly the reason for poor mechanical properties. An immiscible thermoplastic blend A/B can be compatibilized by adding a diblock copolymer, poly(A-b-B) whose segments are chemically identical to the dissimilar homopolymers, or poly(X-b-Y) in which each block is chemically different but thermodynamically miscible with one of the blend components. Theoretical models [29–32] have been developed to describe the molecular mechanisms of emulsification and compatibilization by block copolymers. The generated loss of conformational entropy is compensated by the gain in enthalpy due to the segregation of the blocks in the corresponding compatible homopolymer phases so that the overall interfacial free energy is lowered. The interfacial tension and, hence, the phase-separated domain sizes decrease. In any case the improvement of the mechanical phase adhesion requires a good thermodynamic and/or physical interpenetration of the block copolymer segments with respective homopolymers. To act as an efficient mechanical reinforcement of a blend A/B, a block copolymer poly(A-b-B) should then have a molar mass high enough to form entanglements with the two immiscible polymers [20–22,25,26]. The tendancy towards micelle formation of diblocks in one phase is concurrently favoured so that a compromise between molar mass and concentration has to be reached. This may be avoided by using a copolymer poly(X-b-Y) [23,24,27,28]. The negative enthalpic interactions between A/X and B/Y first enforce interpenetration. Secondly, the location of the copolymer at the interface is thermodynamically favoured in comparison to the formation of micelles in either of the two phases. Nevertheless, it has been observed [33] that the ultimate properties of a polyphenylene ether (PPE)/polystyrene-co-acrylonitrile (PSAN) blend effectively compatibilized by a poly(styrene-b-methyl methacrylate) could remain unsatisfactory. This was assigned to the inability of such diblock copolymers to avoid mechanical stresses at the phase boundary due to the difference between thermal expansion coefficients of the two homopolymers. Therefore, Auschra *et al*. [34] designed a poly(styrene-b-ethylene-co-butylene-b-methyl methacrylate) triblock copolymer, P(X-b-E-b-Y) with an immiscible central elastomer block, E. Due to the thermodynamic driving force, the PS and PMMA blocks efficiently intermix with the blend components and the triblock was actually located at the interface. Due to strong immiscibility of the elastomer central block with all other components, small ellipsoidal rubber domains were formed at the boundary between the phases [33]. Owing to this particular morphology, the triblock copolymer was found to significantly improve fracture toughness of the blend; the elastomeric microdomains were supposed to act as stress centres and help to initiate stable crazes.

The aim of this paper is to transfer the concept of compatibilization by P(X-b-E-b-Y) triblock with an elastomer central block to thermoset/thermoplastic blends generated via the reaction-induced phase separation procedure (exhibiting poor mechanical properties before phase inversion). Two thermoplastics were investigated: polyphenylene ether (PPE) and polyetherimide (PEI). Concerning PEI/thermoset blends, initial miscibility conditions and reaction-induced phase separation process have been already studied [35,36]. Kinetic studies, morphologies and mechanical properties were the subjects of previous work [7,37,38] as well. Our choice was to use low quantities of thermoplastics, 10%b.w. and available commercial copolymers, with or without chemical modification.

2. Experimental

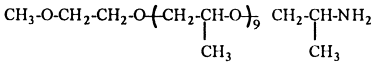
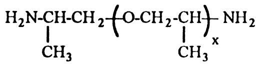
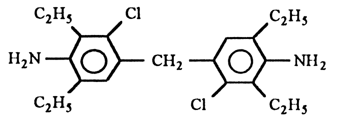
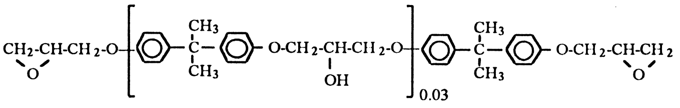
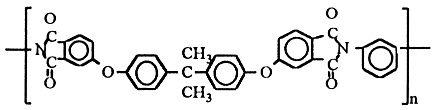
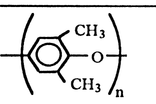
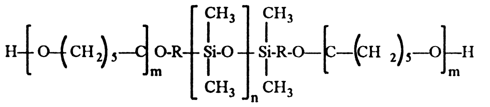
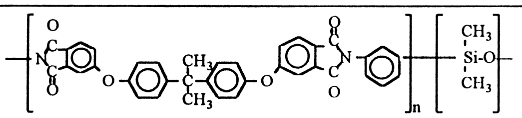
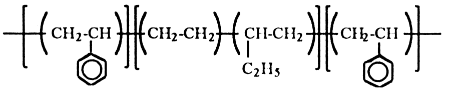
2.1. Materials

The epoxy system consisted of a diglycidyl ether of bisphenol A (DGEBA) with a low polydispersity index ($\bar{n} = 0.03$) cured with 4,4′-methylenebis[3-chloro,2,6-diethylaniline] (MCDEA). This system has been already described elsewhere [37,38]. Two thermoplastic modifiers were investigated: a polyphenylene ether, PPE 800, and a polyetherimide, PEI, Ultem 1000, both supplied by General Electric.

2.2. Choice of copolymers and strategy to obtain a triblock copolymer case of PPE

PPE presents the substantial advantage of having a negative enthalpy of mixing with polystyrene (PS) and it is well known that a variety of triblock copolymers containing PS blocks is commercially available. Among them, the maleic anhydride-modified poly(styrene-b-ethylene-co-butene-b-styrene) P(S-b-EB-b-S) triblock copolymer (see Table 1) does not possess directly all the characteristics of the previously defined P(X-b-E-b-Y) type triblock copolymer. Nevertheless, it contains an immiscible ethylene-co-butene, EB elastomer block, the reactivity of grafted succinic anhydride functions towards primary amines and may be used to graft onto EB blocks, chains which are miscible or able to react with the epoxy groups, as depicted in Fig. 1. Different graft reactions were then performed with MCDEA, polyoxypropylene (PPO) end-capped monoamine (M600) or diamine (D4000), described in Table 1, to investigate the influence of length and of reactivity of the grafted chains. Reactions were performed in bulk, under vacuum at the stoichiometric ratio of succinic anhydride to primary amine groups equal to 1 in the case of the monoamine M600 or with an excess of diamine in order to avoid

Table 1
Structure and characteristics of the different reactants used

Reactant	Formulæ	Supplier	$\overline{M_n}$ (g.mol^{-1})	$\overline{M_w}$ (g.mol^{-1})	Tg (°C)
α-amino polypropylene oxide Jeffamine M600	 $CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\left(CH_2\text{-}\underset{CH_3}{CH}\text{-}O\right)_9 CH_2\text{-}\underset{CH_3}{CH}\text{-}NH_2$	Hunstman	600	/	/
α-ω-aminopolypropylene oxide Jeffamine D4000	 $H_2N\text{-}\underset{CH_3}{CH}\text{-}CH_2\left(O\text{-}CH_2\text{-}\underset{CH_3}{CH}\right)_x NH_2$	Hunstman	4 000	/	/
4,4'-methylenebis[3-chloro 2,6-diethylaniline] (MCDEA)		Lonza	380	/	/
diglycidyl ether of bisphenol A (DGEBA) $\overline{n}$ = 0.03		Dow Chemical DER 332	348.5	/	/
polyetherimide (PEI)		General Electric Ref Ulthem 1000	26 000	50 000	210
polyphenylene ether (PPE)		General Electric PPE 800	12 500	23 000	210
poly(caprolactone-b-dimethyl-siloxane-b-caprolactone) (T)		Goldschmidt	8 500 n = 30 m = 27	/	/
poly(etherimide-b-dimethyl-siloxane)$_n$ (S)		General Electric Ref Siltem	29 000	52 000	/
poly(styrene-b-ethylene-co-butene-b-styrene) (K)		Shell (KFG)	$\overline{M_n}$ (EB)=37500 $\overline{M_n}$ (PS) blocks=7500	grafted MA 1.94 wt%	

gelation in the case of D4000. These reactions were studied by *FT*i.r. by following the disappearance of the absorption bands associated with anhydride C=O groups (1786 cm^{-1}, 1870 cm^{-1}) and the development of the absorption bands associated with imide groups (1713 cm^{-1}, 1773 cm^{-1}). Time/temperature conditions of 4 h at 150°C permitted getting complete reactions whatever the amine. For the sake of simplification, K-g-M600, for example, will denote the M600 grafted triblock copolymer.

2.3. Choice of copolymers and strategy to obtain a triblock copolymer case of PEI

In the search for a P(X-b-E-b-Y) type triblock copolymer, the two problems encountered are that PEI, from our knowledge, is not miscible with any other copolymer and that there is no commercial triblock with a PEI block. The only copolymer commercially available is a poly(etherimide-b-dimethylsiloxane) (P(EI-b-DMS)) segmented

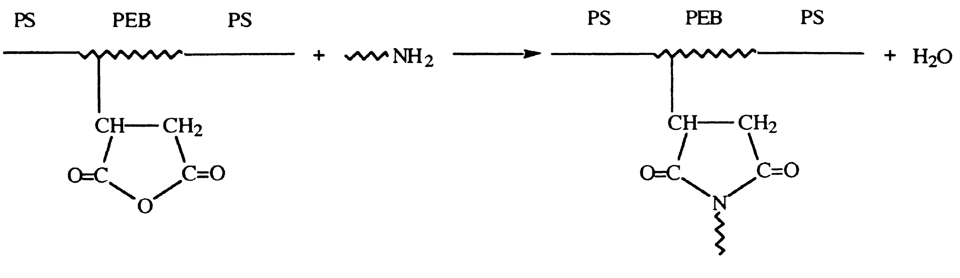


Fig. 1. Graft reaction scheme of end-capped amine chains on the maleic anhydride-modified poly(styrene-b-ethylene-co-butene-b-styrene) triblock copolymer

copolymer (S), described in Table 1. Nevertheless, this copolymer may be of interest since it contains, in addition to PEI segments, elastomer PDMS segments which are known to be strongly immiscible with any components. Concurrently, the α–ω hydroxypoly(caprolactone-b-dimethylsiloxane-b-caprolactone), P(CL-b-DMS-b-CL) triblock copolymer (T) presents characteristics which may be proved complementary: (a) the PDMS elastomer central block is chemically identical to the elastomer segment of copolymer S, and (b) the polycaprolactone blocks are totally miscible with epoxy. Therefore, one may expect to take advantage of a positive association of copolymers S and T to obtain the characteristics of the required compatibilizer.

2.4. Formulation

The thermoplastic and the corresponding copolymer(s) were first dissolved at 10%b.w. in toluene for PPE, or dichloromethane for PEI, and then mixed in the epoxy prepolymer by using a mechanical stirrer. Once the solvent has been removed under vacuum, MCDEA was added at 135°C at the stoichiometric ratio of epoxy to amino-hydrogen groups equal to 1. Note that in the case of K-g-diamine, excess amine functions remained free to react with the epoxy prepolymer so the amount of comonomer MCDEA was consequently adjusted to obtain the stoichiometry in the final blend.

The mixture was precured at a selected isothermal temperature, T_i, where it was initially macroscopically homogeneous (see results). The phase separation process occurs during this precure stage. To ensure that most of the structure developed isothermally, the precure times were chosen greater than the vitrification times of the epoxy system[35]. To obtain the final materials and to ensure complete cured networks without degradation, samples were post-cured 2 h at 185°C.

For the blend designation, 10PEI 0.5S–0.5T, for example, corresponds to the DGEBA-MCDEA system modified by 10 wt% PEI plus 0.5wt% S and 0.5wt% T.

2.5. Techniques

Cloud points were determined with a light transmission device[39], a technique which begins to detect particles when average diameters are of the order of 0.1 μm. The cloud point temperatures, T_{cp}, were determined, as were the onset temperatures, when a decrease in the transmitted light intensity was recorded.

Fourier Transform Infrared spectroscopic spectra were obtained with a Nicolet Magna-IR 550 spectrometer, with a resolution of 4 cm^{-1}.

Dynamic mechanical analyses were performed using a RSAII Rheometrics viscoelasticimeter equipped for rectangular samples in tensile testing. The storage modulus E′ and the loss factor tan δ were measured during temperature sweeps (3°C per step) at a constant frequency 1 Hz and a strain amplitude equal to 0.07%.

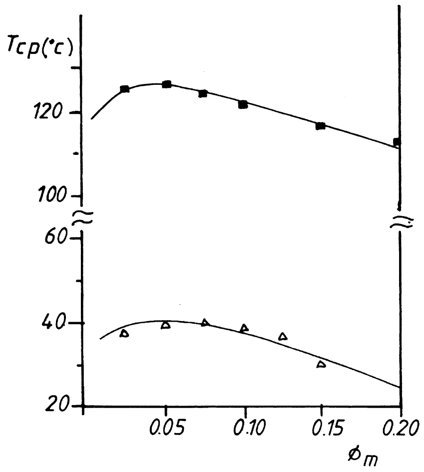


Fig. 2. Initial cloud point curves of (■) (DGEBA-MCDEA)$_o$-PPE; (△) (DGEBA-MCDEA)$_o$-PEI

The critical stress intensity factor, K_{Ic}, was obtained from three point bending tests performed on single edge notched specimens (SEN). An Adamel Lhomargy (DY25) testing machine was used. The procedure proposed by Williams and Cawood[40] was strictly followed with a cross-head speed of 10 mm min^{-1}. K_{IC} was calculated as the mean values of at least 10 tests.

The morphology of blends was studied by transmission electron microscopy (TEM) using a JEM-200CX. Ultrathin sections were performed at room temperature. A contrast existed between phases when a 80 kV accelerating voltage was used.

3. Results and discussion

3.1. Influence of the copolymer(s) on the initial miscibility of blends and phase separation

The cloud point curves (CPCs) of the initial (DGEBA-MCDEA)$_o$-PPE and (DGEBA-MCDEA)$_o$-PEI blends prior to any reaction are shown in Fig. 2. Both are typical of systems exhibiting upper critical solution temperature (UCST) behaviour. It is worth noting the narrow miscibility window available with PPE compared to the one available with PEI. A thermodynamic model [35] based on the Flory–Huggins–Staverman approach, taking thermoplastic polydispersity into account, was used to calculate the critical composition of the respective blends (before reaction). The resulting values, expressed as a thermoplastics mass fraction, were:

$$\Phi_{crit} = 11.4\% \text{ for (DGEBA-MCDEA)}_o - \text{PPE, and}$$
$$\Phi_{crit} = 10.7\% \text{ for (DGEBA-MCDEA)}_o - \text{PEI}$$

The addition of small amounts of copolymer(s) (typically the range of composition investigated in this work) was found not to affect these initial CPCs. Nevertheless, it has been observed experimentally that the elastomer blocks (PDMS or PEB) of selected copolymers S, T or K-g-amine were always immiscible whatever the temperature; but the light transmission technique is not sufficiently sensitive to such small domain sizes and concentrations. Therefore, the thermoplastic-modified systems containing copolymer(s) have to be considered as initially homogeneous only at the macroscopic scale.

The cloud point conversions, x_{cp}[35] (always located before the gel conversion, x_{gel} close to 0.6) were also found not to be modified by the presence of small amounts of copolymer(s). This means that the macroscopic phase separation between the growing epoxy-amine copolymer and the thermoplastic is induced at the same reaction extent with or without the copolymer.

3.2. Influence of the copolymer(s) on final morphologies

The amount of thermoplastic was fixed to 10%b.w. before the critical composition to ensure that phase separation generates a continuous epoxy-rich phase. For a branched

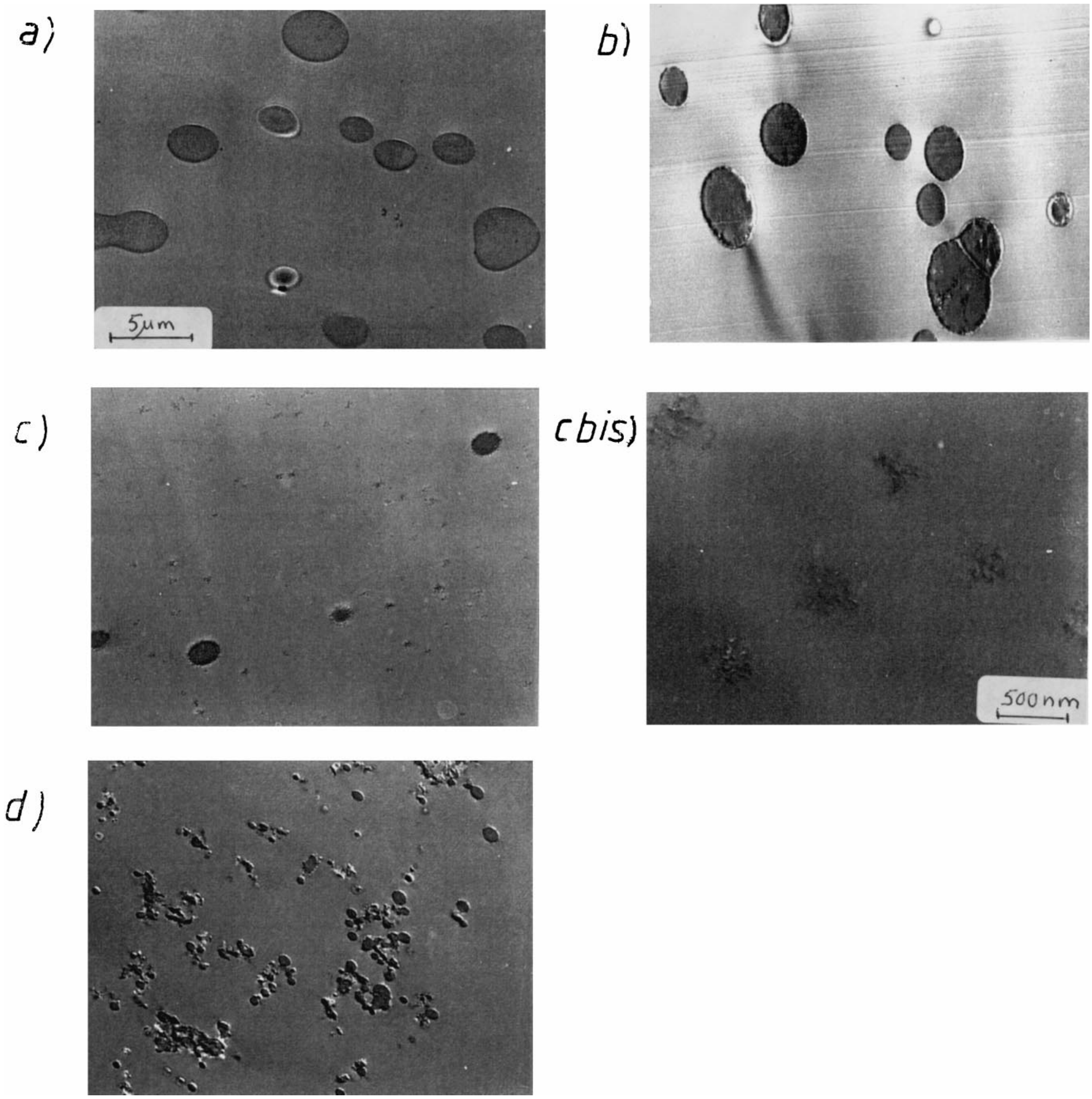


Fig. 3. Transmission electron micrograph of the 10PPE blends: (a) without copolymer; and containing (b) 1.5K-g-M600; (c) and c *bis* 1.5K-g-MCDEA; (d) 1.5K-g-D4000; $T_i = 160°C$ and 185°C (same scale, except c *bis*)

polymer which obeys classical statistics, like the growing DGEBA-MCDEA copolymer before gelation, the critical composition does not vary much with the extent of the reaction[41].

3.2.1. PPE-modified systems

The micrograph in Fig. 3*a* shows the domain structures of the 10PPE system without copolymers for a precure temperature $T_i = 160°C$ and a post-cure at 185°C. The bright parts correspond to the epoxy-rich phase (α phase) and the dark parts to the PPE-rich phase (β phase). As expected, the phase separation process resulted in the formation of rather large thermoplastic-rich (particles, with sizes around 2–5 μm, dispersed in a continuous matrix.

The morphologies of the 10PPE system containing 1.5K-g-M600, 1.5K-g-MCDEA and 1.5K-g-D4000 are given in Fig. 3*b,c,d,* respectively.

Fig. 3*b* first highlights that 1.5K-g-M600 did not affect the morphology of the 10PPE blend, meaning that K-g-M600 is not effective in promoting compatibility. Since PS blocks are longer than M600 grafts, one can expect a preferential segregation of K-g-M600 in the PPE-rich domains. This may be supported by contrast fluctuations in these last domains (see Fig. 3*b*).

Alternatively, for the two other investigated copolymers, a large decrease in particle size is observed, attesting that the copolymer is located in the interfacial zone so that the overall interfacial tension is decreased. These morphological observations first highlight that reactive triblock copolymers can be successful in promoting compatibility in thermoplastic/thermoset blends demixing during reaction. The most spectacular compatibilizing effect is obtained with MCDEA grafts. The micrograph in Fig. 3*c* exhibits mainly dispersed domains with sizes ranging from 200 to 500 nm. Moreover, at higher magnification (Fig. 3*c*), there is clearly no distinct interface between phases anymore. The diffuse boundary of the PPE-rich domains rather suggests the existence of an interphase. Compared to K-g-MCDEA, K-g-D4000 (Fig. 3*d*) leads to a lower compatibilizing effect: particles are globally much larger and the dispersion is not as good.

The length of the grafts does not emerge as the deciding factor in the interfacial activity of the copolymer. MCDEA grafts of lower molar mass lead to higher compatibilizing efficiency. Moreover, the macroscopic demixing of the thermoplastic/thermoset blend is induced at a low reaction extent (x_{cp} close to 0.1) and, at this stage, the conversion of the reactive diamine grafts remains certainly very low. Alternatively, the triblock copolymer was found to be efficient in compatibilizing the 10PPE blend only when it was grafted by a diamine, i.e. when it is capable of reacting *in situ* with the epoxy matrix. However, the fact that the reactivity of the grafts is a necessary requirement for interfacial activity must be considered with caution. Polyoxypropylene grafts, moreover initially miscible in the monomers, may form phase-segregated domains during epoxy-amine reactions, which, of course cannot occur with MCDEA grafts. In these conditions, the reactivity of PPO chains may be proved determinent since only their reaction with the growing thermoset allows the chemical stabilization of the copolymer at the matrix–particle interphase and prevents large coalescence of the dispersed domains.

3.2.2. PEI-modified systems

The respective effects of the addition of 1S, 1T and 0.5S–0.5T in the 10PEI system were studied for a same precure temperature $T_i = 135°C$ and a post-cure at 185°C. Fig. 4*a* constitutes the reference transmission electron micrograph showing the domain structures of the 10PEI system without copolymers. The bright parts correspond to the epoxy-rich phase (α phase) and the dark parts to the PEI-rich phase (β phase).

Fig. 4*b* shows that the addition of 1S did not affect the morphology of the 10PEI blend, meaning that S alone is not effective in promoting compatibility. The copolymer probably locates inside the β particles with a subsegregation of the PDMS segments. On the other hand, it can be seen in Fig. 4*c* that the addition of 1T alone strongly modified the morphology, leading to an undesirable inverted structure (continuous thermoplastic-rich phase). The occurrence of phase inversion is usually related to the ratio of viscosities of each phase and to interfacial tension; it can then just be stated that the introduction of 1T has affected one of these parameters or both, in such a way that phase inversion has occured. Even if this effect was not expected, it is not inconceivable either since the initial PEI concentration was close to Φ_{crit}.

The change in morphology resulting from the addition of both 0.5S and 0.5T is shown in Fig. 4*d*. A sharp decrease in dispersed phase size is seen to indicate a remarkable compatibilizing action of these two copolymers when they are associated. Most of the stucture consists now of β particles of submicron sizes. This large decrease of particle size attests that both copolymers are located in the interfacial zone. This was, however, confirmed by silicon microanalysis concurrently performed with TEM observations.

To investigate the influence of the copolymer concentrations, the morphologies of the 10PEI blends containing 0.7S–0.7T, 1S–0.5T, 1S–1T are given in Fig. 4*e,f,g,* respectively. In a similar way to 1T, the addition of 1S–1T leads to phase inversion. Alternatively, for the two other lower T concentrations, large compatibilizing effects are once again observed. A critical composition of triblock T close to 1wt% seems to exist after which phase inversion definitively occurs.

3.3. Influence of the copolymer(s) on the dynamic mechanical behaviour

Fig. 5 compares the dynamic mechanical data of the 10PPE, 10PPE 1.5K-g-M600, 10PPE 1.5K-g-D4000 and

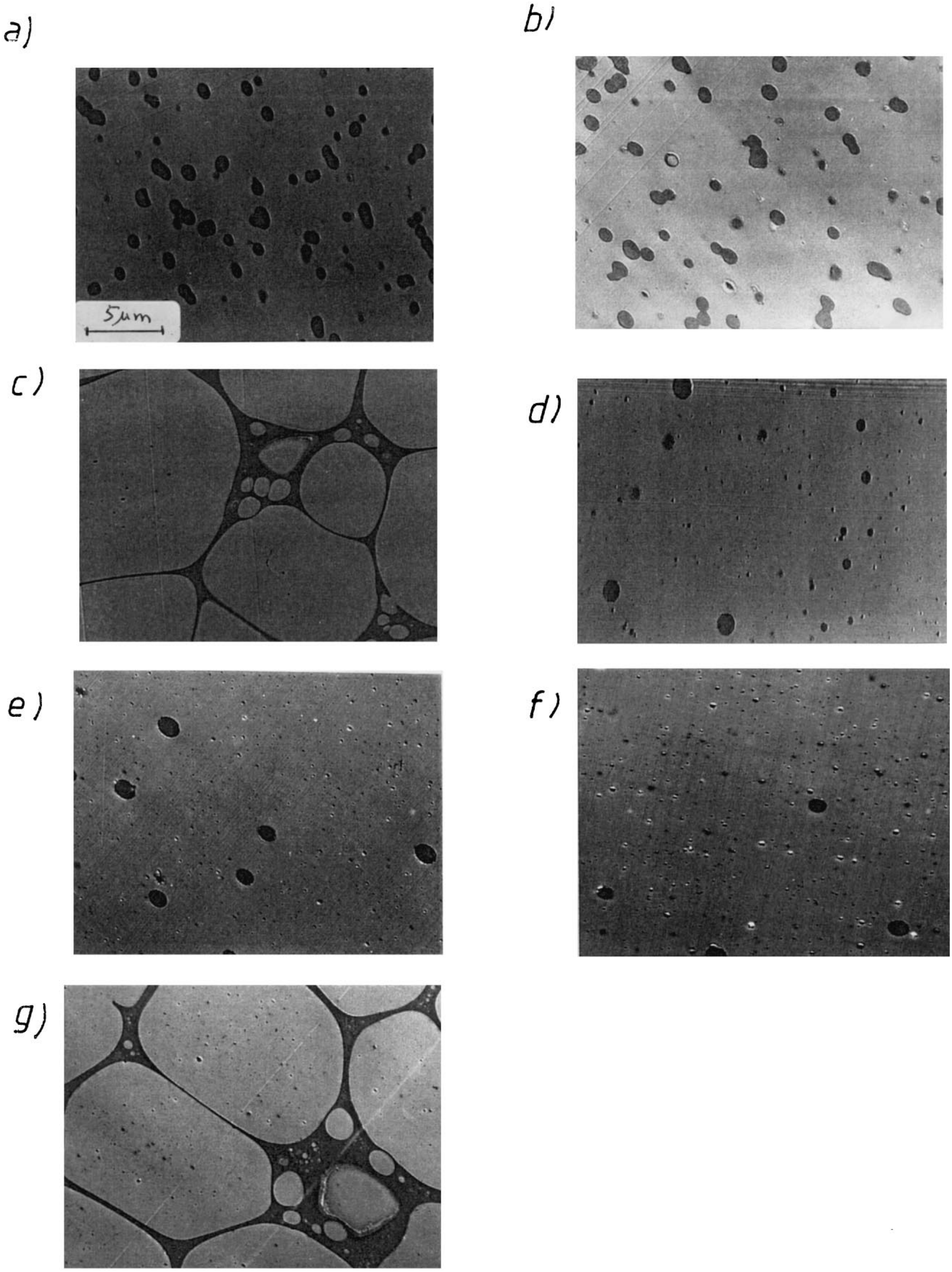


Fig. 4. Transmission electron micrograph of the 10PEI blends: (a) without copolymer; and containing (b) 1*S*; (c) 1T; (d) 0.5S–0.5T; (e) 0.7S–0.7T; f) 1S–0.5T; (g) 1S–1T; $T_i = 135°C$ and 185°C (same scale)

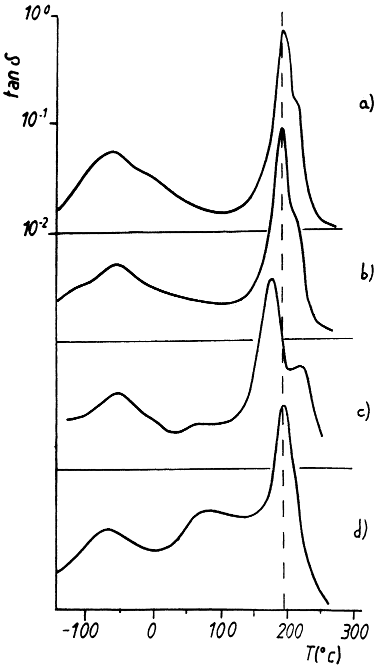


Fig. 5. Dynamic spectra: loss factor, tan δ *versus* temperature for (a) 10PPE; (b) 10PPE 1.5K-g-M600; (c) 10PPE 1.5K-g-D4000; (d) 10PPE 1.5K-g-MCDEA

10PPE 1.5K-g-MCDEA, for the same precure temperature $T_i = 160°C$ and post-cure at 180°C. The 10PPE tan δ curve exhibits three loss peaks: a low, broad peak at −68°C corresponding to the secondary relaxation of the α phase rich in epoxy and two distinct high temperature relaxation peaks respectively associated to the T_gs of the α phase and the β phase rich in PPE. As no major change of the tan δ curve is observed in the presence of 1.5K-g-M600, the addition of 1.5K-g-D4000 and, eespecially 1.5K-g-MCDEA, induce a very broad additional peak ranging from approximately 20°C to 150°C with a maximum around 70°C. The viscoelastic data of the pure copolymers are not needed to come to the conclusion that no single constituent in the blend has a distinct tan δ maximum in this temperature region. Otherwise, this transition would also appear on the viscoelastic behaviour of the 10PPE 1.5K-g-M600 system. The additional transition of the 10PPE 1.5K-g-diamine systems can therefore not be explained by a molecular transition in any of the original materials. In view of the respective effects of each copolymer on final morphologies, this relaxation is necessarily characteristic of the interfacial activity of K-g-diamine copolymers. Lastly, it can be observed that the T_g of the epoxy-rich α phase is shifted to a lower temperature in the presence of K-g-D4000. This decrease results from the involvement of more flexible D4000 chains, in excess with the grafted triblock (not involved in the graft reaction), in the epoxy network formation.

There is a striking similarity of the additional transition to that observed by Eklind *et al.*[42] on a polyphenylene ether/poly(methyl methacrylate) (PPE/PMMA) blend successfully compatibilized by a poly(styrene-graft-ethylene oxide), P(S-g-EO) copolymer. On the basis of an interlayer model for the ternary blend, which assumed that spherical PPE particles, covered by a shell of P(S-g-EO) (interphase), were formed in a PMMA matrix. The existence of this additional relaxation could theoretically be predicted in accordance with experiments[43,44]. In the model no adjustable parameter was necessary and only the original shear complex moduli, the volume fractions and the Poisson ratios of the constituents in the matrix interphase particle system were introduced. This transition was then found to result from the combined influence of the microstructure of the blend including an interphase and the relative temperature dependent moduli of the blend constituents. To distinguish it from ordinary molecular transitions, the authors have chosen to call this phenomenon a micromechanical transition.

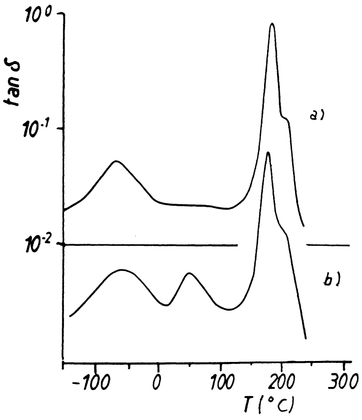


Fig. 6. Dynamic mechanical spectra: loss factor, tan δ *versus* temperature at 1 Hz for (a) 10PEI; (b) 10PEI 0.05S–0.5T

The existence of a micromechanical transition for the 10PPE 1.5K-g-diamine blend is therefore a strong indication that a copolymer-rich interphase with a certain volume and specific properties actually exists, agreeing well with TEM observations. Undoubtedly, the elastomer blocks are not able to form a continuous layer around the PPE-rich particles. This is, however, supported by jagged boundaries of the PPE-rich domains (Fig. 3*c*), which rather suggest the formation of isolated elastomer nanodomains. It seems then reasonable to assume that this copolymer-rich interphase corresponds to a more or less broad region made of elastomer nanodomains, PS blocks interpenetrated with PPE chains and amine grafts interpenetrated or linked with the epoxy network.

A micromechanical transition was also highlighted for the 10PEI 0.5S–0.5T (see Fig. 6*b*), 10PEI 0.7S–0.7T and 10PEI 1S–0.5T blends, as no change in the 10PEI tan δ curve was observed in the presence of 1S, 1T or 1S–1T. A copolymer-rich interphase is then formed each time S associated to T succeed in acting as interfacial agents. In these favourable cases, one may expect (a) the separation of PEI segments and PCL blocks in the α and β phases,

Table 2
Values of the critical stress intensity factor, K_{Ic} measured at 25°C and 10 mm/min for PPE and PEI-modified epoxies (for cure schedule see experimental part)

Reactive system	K_{Ic}(MPa.m$^{1/2}$)
neat DGEBA-MCDEA	0.60
M10PPE	0.68
M10PPE 1.5 K-g-M600	0.76
M10PPE 1.5 K-g-D4000	0.95
M10PPE 1.5 K-g-MCDEA	1.01
M10PEI	0.66
M10PEI 0.5S	0.77
M10PEI 1T	0.87
M10PEI 0.5S-0.5T	1.01
M10PEI 0.7S-0.7T	1.01
M10PEI 1S-0.5T	1.08
M10PEI 1S-1T	0.75

respectively, and (b) the presence of PDMS nanodomains in the boundary region due to the high surface energy between PDMS and other components.

3.4. Influence of the block copolymers on mechanical properties

The values of the critical stress intensity factor, K_{IC}, measured for the neat system and modified epoxy networks, are given in Table 2.

The fracture toughness of the 10PPE and 10PEI blends (without copolymer) were in the same range as the one with the unmodified epoxy network, highlighting the inability of such thermoplastics to improve the toughness of brittle epoxy network before phase inversion. The presence of voids on fracture surfaces corresponding to some extracted β particles clearly showed that brittle failure of the interface occurred without yielding in the rigid thermoplastic-rich particles. It should be pointed out that the determination of K_{IC} only considers the force leading to the initiation of the critical crack and does not take into account the propagation stage. It is indeed expected that such thermoplastic particles constitute obstacles to the propagation of the crack, contributing in a sense to the overall strengthening of the material as revealed by surface resilience measurements[7]. Anyway, the small effect on K_{IC} results from (a) the lack of interfacial adhesion, and (b) dramatic mechanical stresses at the phase boundary.

The copolymer K-g-M600, which was found to have no effect on the quality of the dispersion of the 10PPE blend, logically fails to increase its fracture toughness. Alternatively, spectacular mechanical reinforcements result from the interfacial activities of K-g-D4000 and K-g-MCDEA, with a relative enhancement of fracture toughness close to 50% with only 1.5% of the copolymer and without any decrease in thermal stability. Concerning PEI-modified systems, the achievement of a nanostructure (0.5–0.5T, 0.7S–0.7T and 1S–0.5T) similarly is associated with a large increase in fracture toughness. Note that even inverted structures (1S and 1S–1T) lead to lower reinforcements in spite of the continuity of the thermoplastic-rich phase. The resulting major conclusion is that the use of copolymers containing an elastomer block can actually be a suitable way of improving fracture toughness of brittle thermoplastic/thermoset blends while maintaining a continuous thermoset phase. Whatever the thermoplastic, these positive effects always result from the same causes: decrease of the particle size and thus of the interparticle distance and formation of a copolymer-rich interphase, characterized by a micromechanical transition in mechanical spectroscopy.

Several factors may be involved in this reinforcement: (a) creation of smaller scale microstructures, (b) increase in the interfacial adhesion, and (c) formation of an elastomer (soft)-rich interphase. Unfortunately, it remains very difficult to isolate each parameter and to quantify their respective implication. So we will only discuss here their order of importance. The decrease of particle size is undoubtely a first order parameter. Part of the toughness improvement was expected to result from the increase of interfacial adhesion. Brown *et al.*[45] have recently studied the effect of triblock copolymers with an elastomer midblock on the adhesion between immiscible polymers. By using an assymetric double cantilever beam test, the ability of copolymers to increase the interfacial adhesion can be isolated from the effect of emulsification by the measurement of fracture toughness of the interface. In spite of the large enhancement of ultimate properties, a poor adhesion was measured and directly linked to the location of the elastomer block in the interfacial region. The increase of interfacial adhesion is then probably a second order parameter in such systems. This seems, however, consistent with several drawbacks of the selected compatibilizing system in the case of PEI-modified systems: it is a blend of copolymers instead of a well-defined triblock and S is a segmented copolymer limiting the interpenetration of PEI segments in the PEI-rich phase. Lastly, the rubbery nanodomains in the interphasic region may first compensate for the mismatch of the thermal expansion coefficients of the glassy polymers, contributing to the strengthening of the blends. This is once again a second order effect in our blends since internal stresses due to different expansion coefficients were estimated not higher than 15 MPa. On the other hand, the ability of such a soft interphase to better distribute external stresses under loading is certainly a first order parameter.

4. Conclusions

In order to solve the usual problem of brittleness in thermoplastic-modified epoxy networks generated through the reaction-induced phase separation procedure, we have successfully developed the concept of compatibilization by P(X-b-E-b-Y) triblock with (a) X, chemically identical to or thermodynamically miscible with the thermoplastic, (b) Y, reactive or thermodynamically miscible with the epoxy system and (c) E, an immiscible central elastomer block. Our choice was restricted to commercially available copolymers. As we were never able to obtain such a triblock, we decided to:

1. chemically modify a commercial triblock for polyphenylene ether-modified systems; and
2. associate two commercial copolymers expected to be complementary for polyetherimide-modified systems.

Even if the elastomer blocks were always immiscible, the addition of small amounts of copolymers was found not to affect the initial cloud point curves of the blends before any reaction.

In spite of some restrictive conditions for each selected compatibilizing system, the introduction of copolymers could result in a large decrease in particle size (submicron size). Also, the observation of a micromechanical transition for efficiently compatibilized blends was a strong indication that a copolymer-rich interphase with a certain volume and specific properties did exist, in accordance with transmission electron microscopy observations. The elastomer blocks are expected to form isolated nanodomains in the interphase region, rather than a continuous layer around thermoplastic-rich particles.

The use of copolymers in thermoplastic/thermoset blends is an unusual line of research that may open up many perspectives. However, it would be necessary to study this in greater depth. From a fundamental point of view, the most important lack in information concerns the phase separation mechanism in the presence of these copolymers. A possible scenario may be that immiscible elastomer blocks act as nucleating agents in a heterogeneous nucleation and growth process. *In situ* small angle X-ray scattering measurements would be an appropriate way of investigation. The mechanisms of reinforcement would also require more thorough consideration. For this purpose it would be an advantage to be able to control the chemistry of the triblocks. In particular this would enable the influence of the block length on the adhesion and mechanical properties to be studied. From a practical point of view, it would be interesting to extend these results to industrial systems and to less brittle epoxy networks than these examined in this work. Moreover, industrial systems are generally used as matrices for composites, and therefore it is of major interest to know if the effects are still observed in the presence of fibres. In other research we are also trying to extend the results obtained to higher concentrations of thermoplastic.

Acknowledgements

The authors wish to thank the Direction de la Recherche et de la Technologie (DRET) de la Délégation Générale de l'Armement (DGA) for financial support, Vincent Vicard for mechanical measurements, and the Centre de Microscopie Electronique Appliquée à la Biologie, et à la Géologie (CMEABG) and especially Isabelle Bornard for preparing ultra thin sections.

References

[1] Raghava RS. J Polym Sci, Polym Chem 1987;25:1017.
[2] Murakami A, Saunders D, Ooishi K, Yoshiki T, Saitoo M, Watanabe O, Takezawa M. J Adhesion 1992;39:227.
[3] Mackinson AJ, Jenkins SD, Mc Grail PT, Pethrick RA. Macromolecules 1992;25:3492.
[4] Kinloch AJ, Yuen ML, Jenkins SD. J Mater Sci 1994;29:3781.
[5] Venderbosh RW, Meijer HEH, Lemstra P. J Polymer 1994;35:4349.
[6] Williams RJJ, Rozenberg BA, Pascault JP. Reaction-induced phase separation in modified thermosetting polymers. Adv Polym Sci 1996;128:95.
[7] Girard-Reydet E, Vicard V, Pascault JP, Sautereau H. J Appl Polym Sci 1997;65:2433.
[8] Hedrick JL, Yilgör I, Wilkes GL, Mc Grath JE. Polym Bull 1985;13:201.
[9] Hedrick JL, Yilgör I, Jurek M, Hedrick JC, Wilkes GL, McGrath JE. Polymer 1991;32:2020.
[10] Iijima T, Hiraaka H, Tomoi M. J Appl Polym Sci 1992;45:709.
[11] Srenivasan SA, Mc Grath JE. High Perf Polym 1993;5:259.
[12] Davies M, Hay JN, Woodfine B. High Perf Polym 1993;5:37.
[13] Min BG, Hodgkin JH, Stackurski ZH. J Appl Polym Sci 1993;50:1511.
[14] Norton LJ, Smigolova V, Pralle MU, Hubenko A, Dai KH, Kramer EJ, Hahn S, Berglund C, Dekoven B. Macromolecules 1995;28:1199.
[15] Gaillard P, Ossenbach M, Riess G. Makromol Chem, Rapid Comm 1980;1:771.
[16] Fayt R, Jérome R, Teyssier PJ. Polym Sci Phys 1981;19:1269.
[17] Fayt R, Jérome R, Teyssier PJ. Polym Sci Phys 1982;20:2209.
[18] Barlow JW, Paul DR. Polym Eng Sci 1984;24:525.
[19] Schwarz MC, Barlow JW, Paul DR. J Appl Polym Sci 1988;35:2053.
[20] Creton C, Kramer EJ, Hadziiaannou G. Macromolecules 1991;24:1846.
[21] Brown HR. Macromolecules 1991;24:2752.
[22] Thomas S, Prud'homme RE. Polymer 1992;33:4260.
[23] Auschra C, Stadler R, Voigt-Martin I. Polymer 1993;34:2081.
[24] Auschra C, Stadler R, Voigt-Martin I. Polymer 1993;34:2093.
[25] Adedji A, Jamieson AM. Polymer 1993;34:5038.
[26] Creton C, Brown HR, Deline VR. Macromolecules 1994;24:1774.
[27] Rieman RE, Braun H, Weese J, Schneider HA. New Polymeric Materials 1994;42:131.
[28] Braun H, Rudolf B, Cantow HJ. Polym Bull 1994;32:241.
[29] Noolandi J, Hong KM. Macromolecules 1982;15:482.
[30] Leibler L. Macromolecules 1982;15:1283.
[31] Noolandi J, Hong KM. Macromolecules 1984;17:1531.
[32] Leibler L. Makromol Chem, Makromol Symp 1988;16:1.
[33] Auschra C, Stadler R. Macromolecules 1993;26:6364.
[34] Auschra C, Stadler R. Polym Bull 1993;30:257.
[35] Riccardi CC, Borrajo J, Williams RJJ, Girard-Reydet E, Sautereau H, Pascault JP. J Polym Sci, Polym Phys 1996;34:349.
[36] Girard-Reydet E, Sautereau H, Pascault JP, Keates P, Navard P, Thollet G, Vigier G. Polymer 1998;39:2269.
[37] Girard-Reydet E, Riccardi CC, Sautereau H, Pascault JP. Macromolecules 1995;28:7608.
[38] Girard-Reydet E, Riccardi CC, Sautereau H, Pascault JP. Macromolecules 1995;28:7599.
[39] Verchère D, Sautereau H, Pascault JP, Moschiar SM, Riccardi CC, Williams RJJ. Polymer 1989;30:107.

[40] Williams JG, Cawood MJ. Polymer Testing 1990;9:15.
[41] Clarke N, Mc Leish TCB, Jenkins SD. Macromolecules 1995;28:4650.
[42] Eklind H, Schantz S, Maurer FHJ, Jannash P, Wesslen B. Macromolecules 1995;29:984.
[43] Eklind H, Maurer FH. J Polymer 1996;37:2641.
[44] Eklind H, Maurer FHJ. J Appl Polym Sci 1996;34:1569.
[45] Brown HR, Krappe U, Stadler R. Macromolecules 1996;29:6582.