

# Structured Thermoplastic/Thermoset Blends Using Block Copolymers

Thomas Fine,<sup>1,2</sup> Jean-Pierre Pascault<sup>1</sup>

**Summary:** Thermoplastic/thermoset blends have been compatibilized by block copolymers. The thermoplastic is poly(phenylene ether) and the thermoset precursors are a liquid epoxy, diglycidyl ether of bisphenol A (DGEBA) and an aromatic diamine (4,4' methylene bis [3 chloro 2,6 diethylaniline], MCDEA). The triblock poly(styrene-*b*-butadiene-*b*-methyl methacrylate), SBM has been chosen because (i) PS blocks interact very favourably with PPE (ii) PMMA blocks remain miscible with the thermoset during the whole curing process, and (iii) PB mid blocks are expected to cover the interface. Morphologies of blends were observed by Transmission Electron Microscopy and phase composition evaluated by Dynamic Mechanical Thermal Analysis. It was observed that the strong repulsion between PPE and PMMA blocks governs the organization of the blend before and during the curing process. During polymerization a purification of the matrix is induced. As expected, a large proportion of block copolymer is at the interface between the matrix and nodules. It was demonstrated that the number of SBM micelles and their degree of dispersion is the main parameter controlling the mechanical properties.

**Keywords:** blends; compatibilization; poly(phenylene ether); polyepoxide; triblock copolymers

## Introduction

As a result of the high interfacial tension between the components, most immiscible blends of two Linear/Thermoplastic Polymers (TP) form coarse mixtures with large domain sizes and sharp interfaces. Their morphology strongly depends on their processing history and they exhibit inferior mechanical properties compare to their components taken separately. Compatibilization and the resulting enhancement of mechanical properties of such immiscible blends can be achieved by adding appropriate block copolymers (BCP) to the mixture. BCPs act as interfacial agents, reducing the interfacial tension and inhibiting also the coalescence of the dispersed

phase. This is well-known and well-described in the literature.<sup>[1]</sup> To our knowledge, in comparison to this considerable literature existing on blends based on two thermoplastics, few works have been done on compatibilized blends based on one TP and one Thermoset (TS).<sup>[2,3]</sup>

These blends are materials resulting from the mixing of the TP with the TS precursors and the subsequent reaction of the precursors.<sup>[4]</sup> In the typical case, the system goes from a homogeneous mixture to a phase-separated blend as the growth in molar mass of the TS component changes the equilibrium state. One important factor controlling the phase separation process and the generated morphology is the initial composition of the blend, in terms of the mass fraction of TP,  $\phi_{TP}^0$  compared to the critical composition  $\phi_{TP, crit}$ . If  $\phi_{TP}^0$  is lower than  $\phi_{TP, crit}$ , the final morphology will consist in a dispersion of TP-rich particles in a TS-rich continuous matrix. For off critical

<sup>1</sup> INSA de Lyon, IMP/LMM; CNRS, UMR 5627, Ingénierie des Matériaux Polymères, Villeurbanne, F-69621, France

<sup>2</sup> CERDATO, ARKEMA, 27470 Serquigny, France

compositions, TS-particles are segregated in a TP-rich continuous phase. But when the TP concentration is close to the critical point (in the range of 15–20 wt% of thermoplastic<sup>[4]</sup>), various morphologies can be observed: bicontinuous structure, double phase morphology, and ribbonlike structures. Besides the initial blend composition, the intrinsic miscibility of the TS precursors and TP polymers involved and the competition between reaction kinetics and phase separation rate may influence the phase separation process.<sup>[5–10]</sup>

In some works an intractable TP, poly(phenylene ether) (PPE) was selected as the thermoplastic phase and an amine cured polyepoxide as the thermoset phase. The initial miscibility conditions, kinetics aspects including gelation and vitrification, the reaction-induced phase separation process, and final morphologies of this system have been already described.<sup>[11–14]</sup> When 4,4' methylene bis [3 chloro 2,6 diethylaniline], MCDEA was used as hardener, was demonstrated the strong effect that the presence of a symmetrical poly(styrene-*b*-methyl methacrylate) diblock copolymer can have on the reaction-induced morphology of a PPE/Epoxy-Diamine blend<sup>[2]</sup> was demonstrated. It was shown that the choice of an appropriate diblock copolymer can deeply affect the blend morphology by zeroing the interfacial tension of an initially spherical interface. The diblock copolymer used was, chosen because (i) PS blocks interact very favourably and thus exhibit a negative interaction parameter with PPE,  $\chi_{PS/PPE} = -0.1$ <sup>[15]</sup> and (ii) PMMA blocks were shown to remain miscible with the chosen polyepoxide system during the whole curing process whatever the concentration and the temperature<sup>[16]</sup> are. PMMA is also highly immiscible with PPE,  $\chi_{PMMA/PPE} = +0.5$ .<sup>[17]</sup>

In the present work, the choice of the block copolymer is guided by the pioneering work of Stadler,<sup>[18]</sup> which shows the potentiality of using an ABC triblock copolymer, containing an elastomeric mid block, as a compatibilizer in immiscible blends of two thermoplastic polymers. In

our case, the triblock is a Poly(styrene-*b*-butadiene-*b*-methyl methacrylate), SBM and it has been used for compatibilization and mechanical properties enhancement of PPE/DGEBA-MCDEA blends. Epoxy thermosets blended with SBM triblock copolymers have been investigated before and after the epoxy-amine reaction by Ritzenthaler et al.<sup>[19]</sup> In contrast to classical linear homopolymers, macroscopic phase separation can be avoided with block copolymers. When MCDEA was used as hardener, it was shown that before reaction, the three blocks self-organize on a nanometer scale, the PS spheres being surrounded by PB nodules while the PMMA blocks are solubilised with the epoxy precursors, forming a swollen corona. After reaction, the domain sizes were unaffected throughout the network formation and transparent nanostructured thermosets were obtained. The final structure is composed of undiluted PS and PB blocks forming a “spheres on spheres” morphology, and most of the PMMA chains remaining embedded in the epoxy network. What is happening when SBM is added as a compatibilizer between the PPE-rich phase and the epoxy-rich one is the subject of this paper.

## Experimental

### Materials

Because it is a good solvent for many linear polymers, the thermoset precursor is a liquid epoxy, diglycidyl ether of bisphenol A with a low degree of polymerization, (DGEBA  $n = 0.15$ , Araldite LY556 from Huntsman). As already mentioned, the hardener is the 4,4' methylene bis [3 chloro 2,6 diethylaniline], MCDEA from Lonza. The diamine was used at the stoichiometric ratio of epoxy to amino-hydrogen groups equal to 1. The PPE is supplied by General Electric (blendex 820).

Three different poly(styrene-*b*-butadiene-*b*-methyl methacrylate) triblock copolymers from ARKEMA have been used.  $S_{20-26}B_{26}M_{54}$ -SB29-S14 represents a copolymer as received and composed of  $S_{20-26}B_{26}M_{54}$

pure triblock copolymer and 29 wt. % of SB diblock copolymer and 14 wt. % of PS. The numbers 20, 26, and 54 represent the weight percentage of the respective PS, PB, and PMMA blocks; 26 is the molar mass of the PS block in  $\text{kg mol}^{-1}$ . The presence of SB diblock and PS “impurities” is due to the process used for the triblock copolymer synthesis,<sup>[19]</sup> 29 and 14 represents the wt. % of impurities. The others as received triblock copolymers used during this study are:  $\text{S}_{13}^{16}\text{B}_{15}\text{M}_{72}$  SB17-S3 and  $\text{S}_{23}^{36}\text{B}_{27}\text{M}_{50}$  SB50-S5.

The purification of SBM copolymers can be achieved by precipitating initial SBM in cyclohexane<sup>[19]</sup> and purified triblocks have also been used.

For the formulation composition, per means per cent resin, and resin means the blend, PPE = epoxide, DGEBA-MCDEA.

### Blends Protocol

Depending on the problematic and the studied composition, several techniques have been employed. To follow the structuration of the system, two techniques have been used depending on the total amount of PPE. When the content of PPE is around 10 wt. %, a test tube heated by an oil bath is used. The PPE is first dissolved in the DGEBA at 180 °C using a mechanical stirrer. Once the solution is homogeneous, the SBM is added. Finally, after the complete dissolution of the triblock, the MCDEA is introduced. For PPE contents higher than 20 wt. %, an internal mixer is used. Because the addition of PPE in the liquid DGEBA is not easy in such equipment, a master batch of DGEBA/PPE 50/50 has been prepared by extrusion.<sup>[20]</sup> The pellets are then added to the internal mixer and an addition of DGEBA is done in order

to get the right ratio. The SBM and MCDEA are added in the same order than previously.

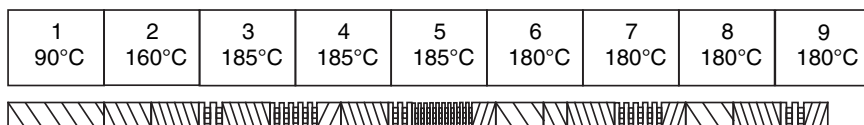
In order to measure the mechanical properties of the samples, cured plates have been prepared. In this case, a twin screw co-rotative extruder has been used. The DGEBA/PPE pellets and a dry blend of MCDEA/SBM are added in the main hopper. The DGEBA is injected just after the melting zone. The screw and temperature profiles are described in Fig. 1. The blends are then immediately placed into a preheated mould (160 °C) and then polymerized directly under press. This technique has been used to avoid any cooling down of the blends between the twin screw-extruder and the polymerization in the mould. The blends are polymerized at 160 °C and post cured at 220 °C. The times for curing, from 4 h to 8 h at 160 °C and at 220 °C depend on the blends compositions.

### Experimental Techniques

**Dynamic Mechanical Thermal Analysis (DMTA)**  
DMTA was carried out on cured blends with a Rheometrics solid analyzer (RSA II) to obtain tensile dynamic mechanical spectra (storage modulus  $E'$ , loss modulus  $E''$ , and loss factor  $\tan \delta$ ) between 20 and 250 °C at a frequency of 1 Hz in the linear viscoelastic domain. The samples used were parallelepipedic bars ( $1 \times 2.5 \times 34 \text{ mm}^3$ ).

### Transmission Electron Microscopy (TEM)

Ultrathin sections were prepared with an ultramicrotome equipped with a diamond knife and stained during 2 h with osmium tetroxide ( $\text{OsO}_4$ ) vapors. Because of the applied staining conditions, PB appears black, PS or PPE are grey, and PMMA is slightly whiter than the epoxy-amine net-



**Figure 1.**

Scheme of the twin-screw profile used to prepare the blends.

work.<sup>[2,3,19–21]</sup> Sections were observed with a Philips CM120 transmission electron microscope at an accelerating voltage of 80 kV.

### Toughness

The critical stress intensity factor,  $K_{Ic}$ , was obtained from three-point bending test performed on single edge notched specimens (SEN). The procedure proposed by Williams and Cawood<sup>[22]</sup> was strictly followed with a crosshead speed of 10 mm min<sup>-1</sup>.  $K_{Ic}$  was calculated as the mean value of 10 tests at least.

## Results and Discussion

### Blends with Low PPE Content. After Cure the Epoxy-Rich Phase is the Matrix

As said previously, PMMA homopolymer is initially miscible and remains completely miscible with DGEBA-MCDEA during the whole reaction process whatever the concentration and the temperature are.<sup>[16]</sup> On the opposite, PB is completely immiscible in the reactive solvent on the explored temperature range (up to 220 °C) and when a block copolymer with a PB block is introduced in DGEBA-MCDEA it leads to the formation of microsegregated domains.<sup>[3,23]</sup>

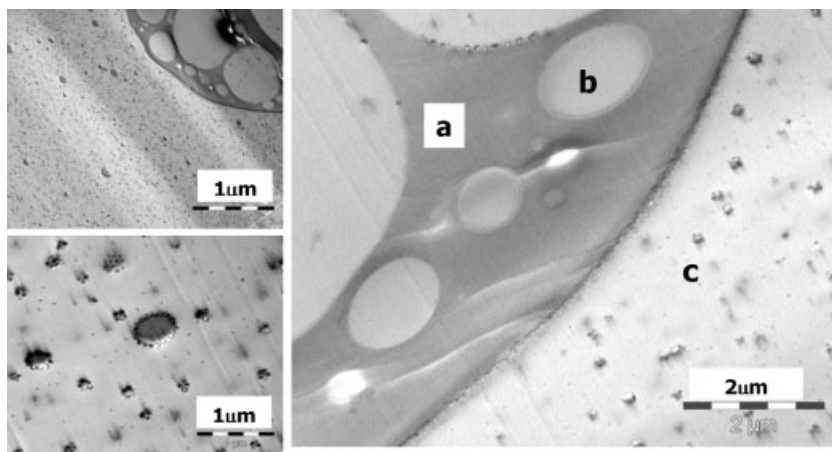
PPE/DGEBA-MCDEA and PS/DGEBA-MCDEA systems both are both exhibiting an upper critical solution temperature (UCST) behaviour (i.e., miscibility increases with temperature). Before reaction PPE and PS are fully miscible at  $T=160$  °C in the TS precursors, but a macrophase separation occurs very rapidly at the first step of the polymerization. PS is more miscible than PPE with the thermoset precursors, resulting in a higher extent of reaction at phase separation during an isothermal cure,  $x_{cp} \sim 0.2$  for PS and  $x_{cp} \sim 0.1$  for PPE (both were measured at 135 °C).<sup>[2–4]</sup>

DGEBA-MCDEA was first blended with a low PPE content, 10 wt. %, and with 5 pcr of a triblock SBM. At 160 °C and at  $t=0$  the blend is slightly opalescent. Knowing the high repulsion of PMMA and PPE, and because of the immiscibility of the

PB mid block, the triblock copolymers are supposed to be organised as micelles with a PMMA core swelled by epoxy precursors and dispersed into a homogeneous solution of DGEBA-MCDEA/PPE. During curing, the state of the solution will change rapidly: (i) first PPE will phase separate from the epoxy matrix; (ii) but as they hate to be near PPE, the PMMA blocks immediately prefer being in the epoxy-rich phase (iii) as at the same time, the growing thermoset is becoming a poor solvent for the PS blocks, a phase inversion of the SBM microsegregated domains with PS inside and PMMA outside is very likely to occur, (iv) finally the PS blocks become immiscible in the epoxy matrix and a driving force is expecting to lead them to the PPE-rich phase.

Figure 2 shows the final morphologies of the cured samples and confirms these assumptions. A two scale morphology with large (Fig. 2-a) and small (Fig. 2-c) particles in a continuous epoxy-rich matrix is clearly observed. Inside the epoxy matrix there are a lot of raspberry-like dispersed SBM-rich micelles with diameters  $\sim 20$  nm (Fig. 2-c). The dark PB domains can be easily seen at the surface of the micelles. Because the matrix is epoxy, it is confirmed that the PMMA blocks are trapped into the matrix and the PS blocks are forming the core (stained in grey). As the PB wt. % is quite similar then the PS wt. % a core shell structure was expected,<sup>[19]</sup> thus as raspberry-like particles are obtained, it is a clear evidence of the swelling of the PS blocks by some PPE molecules.

The large particles (Fig. 2-a) in the 1 to 10  $\mu$ m range are rich in PPE (stained grey); the interface of these large nodules with the matrix are stained in black due to the presence of SBM triblocks at this interface. As with the SM diblock,<sup>[2]</sup> the addition of SBM triblock to the PPE/DGEBA-MCDEA blend induces a change from a one-scale structure with spherical PPE-rich macro particles to a two scale structure with in addition SBM-rich micelles containing some PPE in the core. But contrary to the system compatibilized by a SM diblock copolymer, the interface doesn't show any



**Figure 2.**

TEM micrographs of fully cured DGEBA-MCDEA blends with 10 wt. % of PPE and modified by 5 pcr of purified SBM triblock,  $S_{20}^{26}B_{26}M_{54}$ . a) PPE-rich droplet  $\sim 10 \mu\text{m}$ , b) Epoxy-rich sub-structure, c) Epoxy-rich matrix with dispersed SBM micelles (OsO<sub>4</sub> staining).

strong instability and no complex “splat-like” PPE-rich macro domains. This is a clear evidence of the lowest emulsifying activity of the SBM triblock copolymer compared to the SM one. It can be assumed that it is more difficult for the SBM micelles than for the SM diblock molecules to diffuse through the PPE/epoxy interface and to drive the interfacial tension negative.

But as with SM diblocks, some epoxy-enriched substructures but without any SBM at the interface can be observed inside the PPE-rich large nodules (Fig. 2-b). The PPE-rich phase was known for macrophase-separating at low extents of reaction and was shown to be initially very impure, leading to the formation of internal TS-rich droplets. The fact that these internal droplets are not influenced by the triblock copolymer is a strong indication that during polymerization, the PPE-rich phase never contains SBM.

#### **Blends with High PPE Content. After Cure the PPE-Rich Phase is the Matrix**

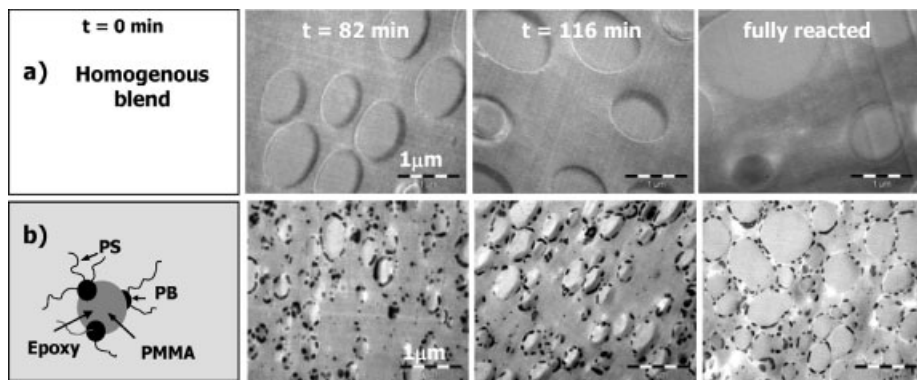
At  $T = 160^\circ\text{C}$  and before reaction ( $t = 0$ ) the blend containing 49 wt. % of PPE in the absence of block copolymer is completely transparent while the same blend contain-

ing this time 10 pcr of SBM is opaque. It confirms a two-phase system in this last case. As said for the previous blend with a low PPE content, the high repulsion between PPE molecules and PMMA blocks causes an immediate thermodynamic phase separation, even at high temperatures. However, because the PMMA and PPE contents are high, the triblocks are organised into large micelles with a swelled PMMA-rich core dispersed into a homogeneous solution of PPE/DGEBA-MCDEA (scheme in Fig. 3-b, at  $t = 0$ )

Figure 3 shows the evolution of the morphologies during the polymerization. For the initially homogeneous blend without SBM (Fig. 3a) a macrophase separation occurs rapidly during the reaction and after 82 min, epoxy nodules are formed with a diameter of the order of  $1 \mu\text{m}$ . Then the particle sizes increase as the polymerization goes on.

If this morphology is compared with the one of the system containing SBM (Fig. 3-b) with two phases at  $t = 0$ , at the same curing time the sizes of the epoxy-rich nodules are smaller,  $\sim 0.3\text{--}0.5 \mu\text{m}$ , and all the nodules are covered by black PB points. In spite of the presence of SBM at the interface, we can observe that the sizes





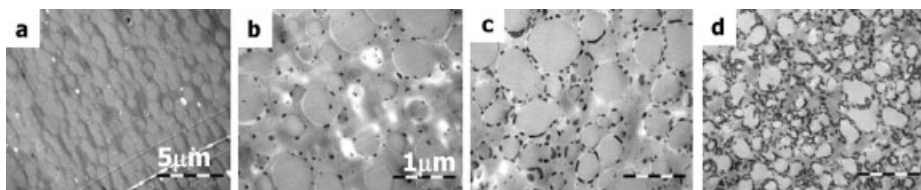
**Figure 3.**

TEM micrographs of DGEBA-MCDEA blends cured at  $T = 160^\circ\text{C}$  and observed at different reaction times with a) 49 wt. % of PPE and b) modified by 10 pcr of purified SBM triblock,  $\text{S}_{20}^{26}\text{B}_{26}\text{M}_{54}$  ( $\text{OsO}_4$  staining).

increase progressively during polymerisation. The polymerization induces a purification of the matrix: the TS monomers, dimers, etc. present in the PPE-rich phase are able to migrate to the epoxy-rich dispersed phase.

For a better understanding higher amounts of  $\text{S}_{20}^{26}\text{B}_{26}\text{M}_{54}$ -SB29-S14 were added and the morphologies of the fully cured samples are shown on Fig. 4.

Nearly all the SBM are situated at the interface. Starting with a low SBM content, 2 pcr, the distribution of the triblock around the nodules is not very homogeneous (Fig. 4b). When 10 pcr of SBM (Fig. 4c) are introduced the PB domains are stretched around the interface; but it is only when a high quantity, 50 pcr (Fig. 4d) is added that the interface seems to be completely covered. If the average size of the particles decreases when the SBM content increase, 620, 385, and 165 nm for 2, 10 and 50 pcr respectively, the size distributions still stay large.

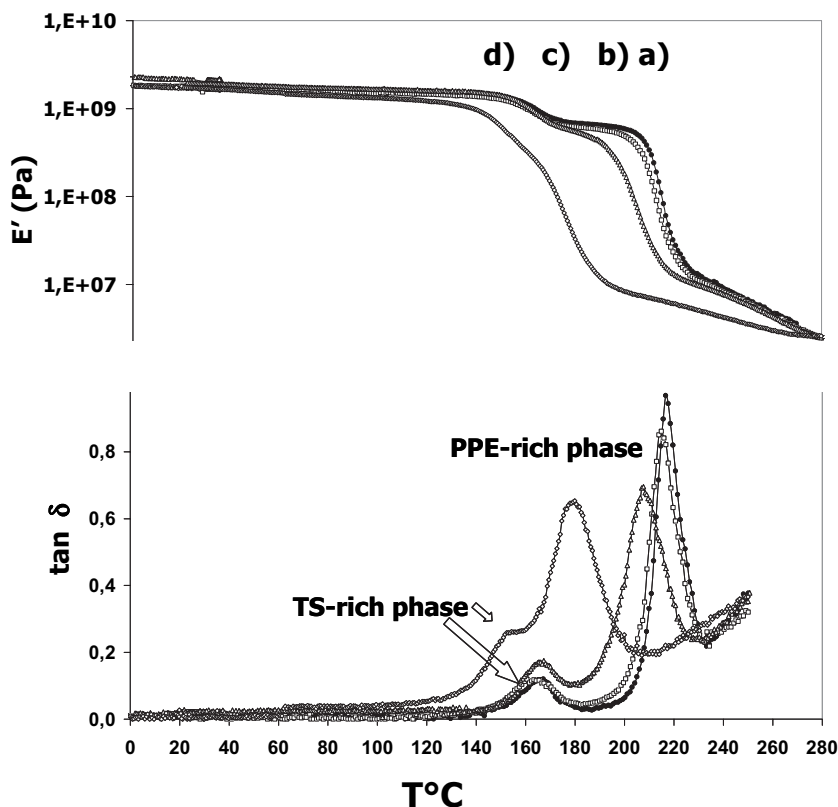


**Figure 4.**

TEM micrographs of fully cured DGEBA-MCDEA blends with 49 wt. % of PPE and modified by a) 2 pcr, b) 10 pcr, c) 50 pcr of as received SBM triblock,  $\text{S}_{20}^{26}\text{B}_{26}\text{M}_{54}$ -SB29-S14 ( $\text{OsO}_4$  staining).

Figure 5 shows the DMTA spectrum of the same samples from 20 to  $250^\circ\text{C}$ . For each blend, only two relaxations can be observed in this temperature range. Knowing the temperature of the  $\alpha$  relaxation of the neat DGEBA-MCDEA network ( $T_\alpha = 185^\circ\text{C}$ ) and of the PPE ( $T_\alpha = 220^\circ\text{C}$ ), the first relaxation at low temperature can be attributed to the epoxy-rich nodules and the second one at high temperature to the PPE continuous phase. In the absence of triblock, the measured  $T_\alpha$  for the thermoset nodules,  $167^\circ\text{C}$  is lower than the one of the neat epoxy network. This fact has already been observed<sup>[20]</sup> and might be due to the generation of free volume in the nodules, or to the consequence of a good adhesion between the phases.

In the presence of SBM, the two  $\alpha$  relaxations are observed at lower temperatures proportionally to the quantity of SBM. Assuming that the SBM is at the interface, the PS block ( $T_\alpha = 98^\circ\text{C}$ ) will plastify the PPE matrix when the syndio-



**Figure 5.**

DMTA spectra obtained at 1 Hz of fully cured DGEBA-MCDEA blends with 49 wt. % of PPE and modified by a) 2 pcr, b) 10 pcr, c) 50 pcr of as received SBM triblock,  $S_{20}^{26}B_{26}M_{54}$ -SB29-S14.

tactic PMMA block ( $T_{\alpha} = 135^{\circ}\text{C}$ ) will do the same in the epoxy-rich nodules. It is evident that the decrease in temperature, estimated using the Fox equation will be more important for the  $\alpha$  relaxation of the PPE matrix and it corresponds what we can observe.

#### Blends in the Range of Phase Inversion

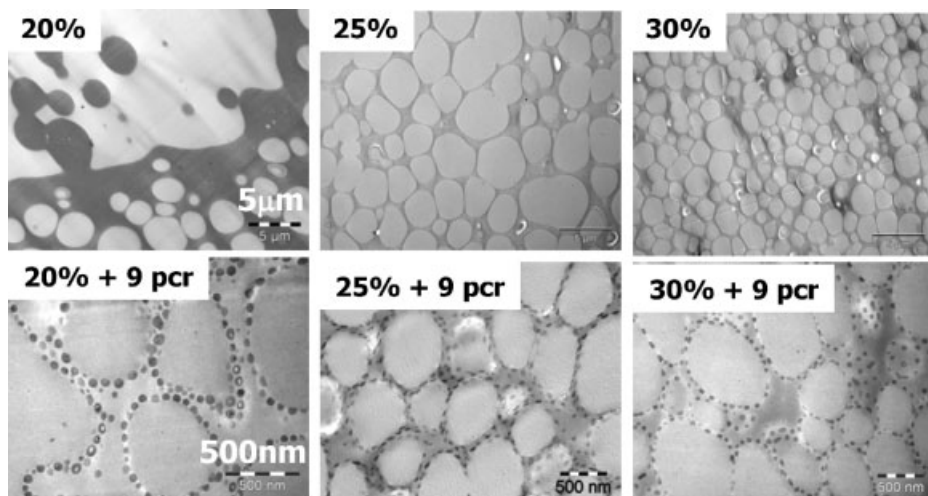
Until now, systems far from the phase inversion composition have been studied. For PPE/DGEBA-MCDEA blends without SBM, it is observed that the phase inversion occurs between 20 wt. % and 25 wt. % of PPE (Fig. 6).

Adding 9 pcr of  $S_{20}^{26}B_{26}M_{54}$ -SB29-S14 in the system containing 20 wt. % of PPE induces a phase inversion and after curing a PPE matrix is obtained. In any cases, from

20 wt. % to 30 wt. % (and also 49 wt. %, Fig. 4), the  $S_{20}^{26}B_{26}M_{54}$ -SB29-S14 is always well-organised at the interface.

Another triblock copolymer,  $S_{13}^{16}B_{15}M_{72}$ -SB17-S3 was used. The main differences with the previous  $S_{20}^{26}B_{26}M_{54}$ -SB29-S14 are its longer PMMA block and its shorter PB block. As shown on the Figures 6 and 7, the SBM composition induces important changes in the final morphologies.

For the three different PPE contents, the SBM with the longer PMMA block is not only at the interface, but also in the epoxy-rich phase as illustrated by the raspberry-like structures. At 20 wt. % of PPE the matrix is still the epoxy-rich phase, and phase inversion occurs for higher PPE contents. These examples show that a



**Figure 6.**

TEM micrographs of fully cured DGEBA-MCDEA blends with different wt. % of PPE in the range of phase inversion and modified by 9 pcr of as received SBM triblock,  $S_{20}^{26}B_{26}M_{54}$ -SB29-S14 ( $OsO_4$  staining).

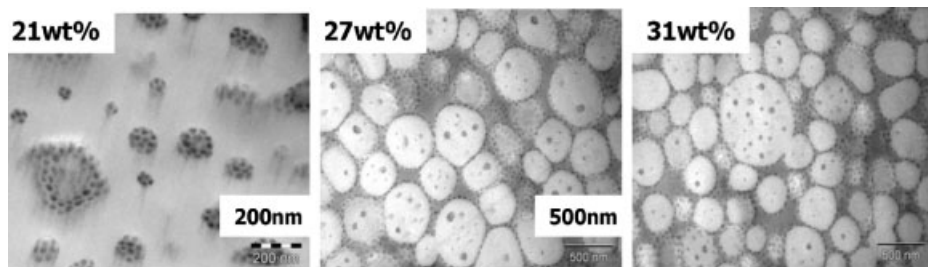
complex equilibrium takes place near the phase inversion.

### Blend Toughness

The aim of this work is to enhance the mechanical properties of PPE/DGEBA-MCDEA blends by the use of a compatibilizer. To evaluate this aspect, the critical stress intensity factors,  $K_{Ic}$  have been measured on different plates directly cured from the twin-screw extruder. The samples are not cooling down to room temperature to avoid any additional temperature-induced phase separation effects.

The  $K_{Ic}$  are plotted versus the PPE content in wt. % of and for different systems (Fig. 8). It is clear that the addition of a compatibilizer like SBM increases the blends resistance to the crack propagation. A significant increase is observed,  $K_{Ic} \sim 3$  for only 30 wt. % of PPE + 20 pcr SBM and is in the range of the value of the neat PPE for only 50 wt. % PPE with 50 pcr SBM.

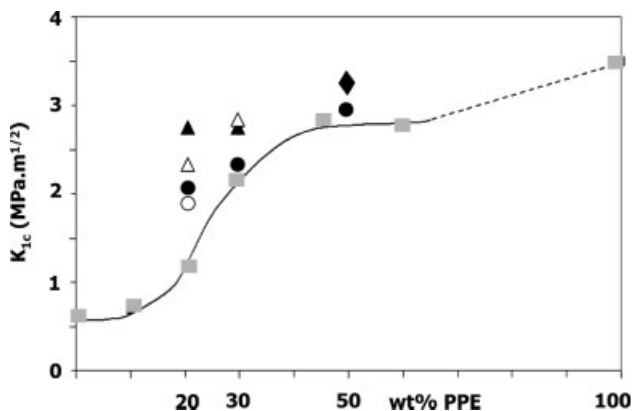
But it has also been observed that the reinforcing effect of the SBM decreases when the PPE content increases. For instance, with 10 pcr of  $S_{23}^{36}B_{27}M_{50}$ -SB50-S5, the  $K_{Ic}$  is multiplied by more than 2 for the system containing 20 wt. % of



**Figure 7.**

TEM micrographs of fully cured DGEBA-MCDEA blends with different wt. % of PPE, in the range of phase inversion and modified by 10 pcr of as received SBM triblock,  $S_{13}^{16}B_{15}M_{72}$ -SB17-S3 ( $OsO_4$  staining).





**Figure 8.**

Influence of as-received SBM concentrations and compositions on material toughness; (■) DGEBA-MCDEA/PPE blends without SBM, and with (○,●) 10, (△,▲) 20 and (◇,◆) 50 pcr of SBM; white symbol = S<sub>13</sub><sup>16</sup>B<sub>15</sub>M<sub>72</sub>-SB17-S3, black symbol = S<sub>23</sub><sup>36</sup>B<sub>27</sub>M<sub>50</sub>-SB50-S5.

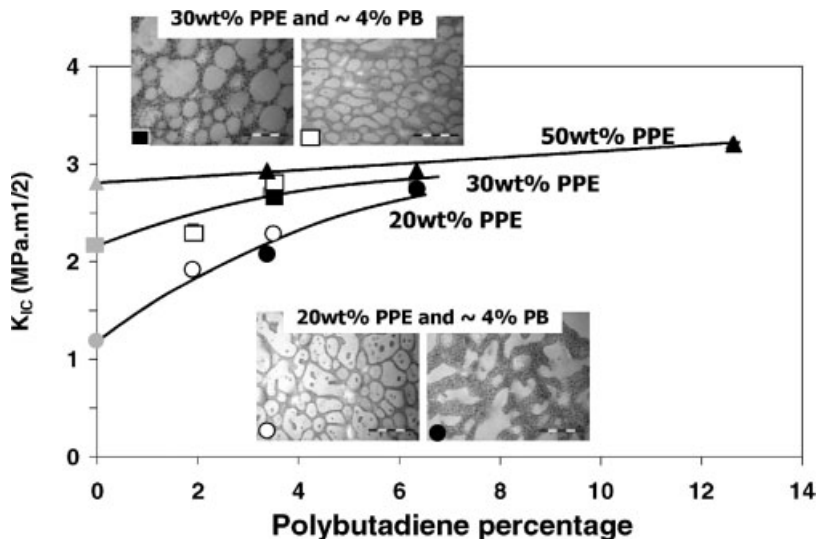
PPE, by 1.1 for 30 wt. % and only by 1.05 for 50 wt. %. It is clear that the better the performances of the initial blend are, the more difficult it is to improve them.

Looking at the composition of the triblock copolymer whatever the PPE content is, the S<sub>23</sub><sup>36</sup>B<sub>27</sub>M<sub>50</sub>-SB50-S5 triblock with the higher PB content gives always leads to a higher increase of  $K_{IC}$ . For instance for the blend with 20 wt. % PPE +

20 pcr of SBM, the  $K_{IC}$  is multiplied by 2.4 with S<sub>23</sub><sup>36</sup>B<sub>27</sub>M<sub>50</sub>-SB50-S5 and only by 2.0 when S<sub>13</sub><sup>16</sup>B<sub>15</sub>M<sub>72</sub>-SB17-S3 is used.

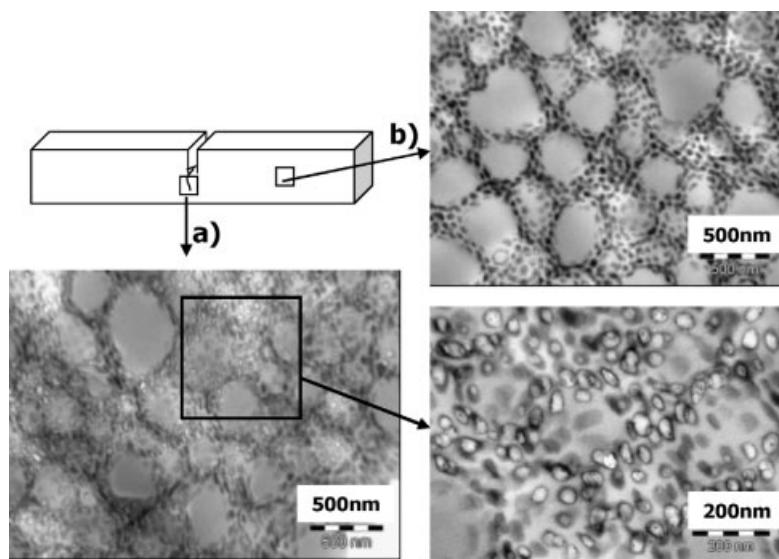
The same trends are observed but more clearly when the  $K_{IC}$  values are plotted versus the PB concentration in the blend (Fig. 9).

In this Fig. 9, the blend morphologies for the same PB content (~4%) and for 20 and 30 wt. % PPE are also compared. For a



**Figure 9.**

Influence of the polybutadiene content on material toughness for the same blends than Fig. 8; white symbol = S<sub>13</sub><sup>16</sup>B<sub>15</sub>M<sub>72</sub>-SB17-S3, black symbol = S<sub>23</sub><sup>36</sup>B<sub>27</sub>M<sub>50</sub>-SB50-S5.



**Figure 10.**

TEM micrographs of fully cured DGEBA-MCDEA blend with 30 wt. % PPE and 20 phr of  $S_{23}^{36}B_{27}M_{50}$ -SB50-S5 triblock; a) near and b) far from the crack propagation plane ( $OsO_4$  staining).

given wt. % of PPE content, the morphologies are quite different but the  $K_{Ic}$  are the same. The morphology at a large scale, sizes and size distributions of epoxy-rich nodules, is clearly not the main parameter controlling the mechanical properties. The TEM micrographs made on a mechanical-tested sample (Fig. 10) confirm this point.

If the morphology far from the crack propagation plane is observed (Fig. 10-b), SBM particles are located around the epoxy nodules and no modification has been induced by the mechanical test. On the opposite, near the crack propagation plane (Fig. 10-a) the morphology is completely different. The sizes of the SBM particles have increased and their inside has whitened. These observations are the result of a cavitation process inside the particles. It is interesting to remark that in a complex system such as the PPE/DGEBA-MCDEA system, the triblock SBM acts in the same way than in DGEBA-MCDEA thermoset alone.<sup>[19]</sup>

From all these observations it can be concluded that the wt. % PB and the degree of dispersion of SBM micelles inside the PPE matrix is the main parameter affecting

the mechanical enhancement, the epoxy nodules present at a larger scale are just a way of obtaining a good dispersion of the SBM micelles with their PB core.

## Conclusion

Blends of an intractable thermoplastic, PPE and an epoxy thermoset, DGEBA-MCDEA have been compatibilized by SBM triblock copolymers. The strong repulsion between the thermoplastic PPE and the PMMA blocks governs the organization of the blend before reaction. As a consequence, the block copolymer is always at the interface between the two phases during the curing process. But in some cases SBM can be also found inside the epoxy nodules depending on the length and % of the blocks. The polymerization only induces a purification of the matrix. The block copolymers can have some effects on the reaction-induced morphology of the blend, the stronger effect being observed in the region of phase inversion. The crack propagation resistance can be greatly enhanced by the presence of the triblock

copolymer, and it was demonstrated that the number of SBM micelles and their degree of dispersion inside the PPE matrix is the main parameter.

These blends based on PPE are easy to transform (in the range of 180 °C, Fig. 1) and they have also good fire resistance properties and a low dielectric constant.

**Acknowledgements:** The financial support of Arkema is gratefully acknowledged.

- [1] S. D. Hudson and A. M. Jamieson, in “*Polymer Blends, Volume 1: Formulation*”, D. R. Paul and C. B. Bucknall Editors, Wiley, 2000, 461–499.
- [2] E. Girard-Reydet, J. P. Pascault, H. R. Brown, *Macromolecules*, **2001**, 34, 5349.
- [3] L. Meynie, A. Habrard, F. Fenouillot, J. P. Pascault, *Macromol. Mater. Eng.*, 2005, 290, 906.
- [4] J. P. Pascault and R. J. J. Williams, in “*Polymer Blends, Volume 1: Formulation*”, D. R. Paul and C. B. Bucknall Editors, Wiley, 2000, in 379–415.
- [5] T. Ohnaga, W. Chen, T. Inoue, *Polymer* **1994**, 35, 3774.
- [6] N. Clarke, T. C. B. McLeish, S. D. Jenkins, *Macromolecules* **1995**, 28, 4650.
- [7] C. C. Riccardi, J. Borrajo, R. J. J. Williams, E. Girard-Reydet, H. Sautereau, J. P. Pascault, *J. Polym. Sci., Polym. Phys.* **1996**, 34, 349.
- [8] S. Elliniadis, J. S. Higgins, N. Clarke, T. C. B. McLeish, R. A. Choudhery, S. D. Jenkins, *Polymer* **1997**, 38, 4855.
- [9] G. E. Elicabe, H. A. Larrondo, R. J. J. Williams, *Macromolecules* **1997**, 30, 6550.
- [10] E. Girard-Reydet, H. Sautereau, J. P. Pascault, P. Keates, P. Navard, G. Thollet, G. Vigier, *Polymer* **1998**, 39, 2269.
- [11] B. J. P. Jansen, S. Rastogi, H. E. H. Meijer, P. Lemstra, *Macromolecules* **1999**, 32, 6290.
- [12] B. J. P. Jansen, H. E. H. Meijer, P. Lemstra, *Polymer* **1999**, 40, 2917.
- [13] S. Poncet, G. Boiteux, J. P. Pascault, H. Sautereau, G. Seytre, J. Rogozinski, D. Kranbuehl, *Polymer* **1999**, 40, 6811.
- [14] S. G. Prolongo, J. C. Cabanelas, T. Fine, J. P. Pascault, *J. Appl. Polym. Sci.*, **2004**, 93, 2678.
- [15] R. P. Kambour, J. T. Bendler, R. D. Boop, *Macromolecules*, **1983**, 16, 753.
- [16] S. Ritzenthaler, E. Girard-Reydet, J. P. Pascault, *Polymer*, **2000**, 41, 6375.
- [17] J. Kressler, H. W. Kammer, U. Morgenstern, B. Litauszki, W. Berger, *Makromolecular Chemie*, **1990**, 191, 243.
- [18] C. Auschra, R. Stadler, *Macromolecules*, **1993**, 26, 6364.
- [19] [19a] S. Ritzenthaler, F. Court, L. David, E. Girard-Reydet, L. Leibler, and J.P. Pascault, *Macromolecules*, **2002**, 35, 6245; [19b] S. Ritzenthaler, F. Court, E. Girard-Reydet, L. Leibler, J.P. Pascault, *Macromolecules*, **2003**, 36, 118; [19c] E. Girard-Reydet, J.P. Pascault, A. Bonnet, F. Court, L. Leibler, *Macromol. Symposia*, **2003**, 198, 309.
- [20] A. Bonnet, J. P. Pascault, H. Sautereau, M. Taha, Y. Camberlin, *Macromolecules* **1999**, 32, 8517.
- [21] L. Sawyer, D. T. Grubb, *Polymer Microscopy*, Chapman and Hall: London, 1997; pp 93–109.
- [22] J. G. Williams, M. J. Cawood, *Polym. Test.*, **1990**, 9, 15.
- [23] T. Fine, F. Lortie, L. David, J. P. Pascault, *Polymer*, **2005**, 46, 6605.