Toughness Properties of Lightly Crosslinked Epoxies Using Block Copolymers

Pierre Gerard,[1] *Nicolas Passade Boupat,*[1] *Thomas Fine,*[2] *Laurent Gervat,*[1] *Jean-Pierre Pascault*[3]

Summary: In this work is discussed an alternative approach to the toughening of epoxy networks by the addition of acrylic block copolymers, composed of rigid and rubbery blocks. Once the reaction is completed, the initial self-assembly of block copolymers in epoxy thermoset precursors produces rubbery domains: depending on the block copolymer structure and composition, these domains are of the micrometer or the nanometer size. Nanostructures are obtained when the rigid block is a random copolymer of methylmethacrylate and *N,N*-dimethylacrylamide. The rubbery domains prevent rapid crack propagation and the highest toughness is obtained with filament-like microparticles or wormlike micelles.

Keywords: CTBN; jeffamine; polyepoxide; toughness; triblock copolymers

Introduction

Applications of epoxy-based glassy polymers are often limited by an inherent brittle behavior of the matrix but the prevalence of epoxy polymers in composites and engineering adhesives means that it is important to know, to understand, and to be able to reinforce their performance in-use. The case of static/dynamic loading is of particular significance in many applications, especially in aerospace products. Their toughness is conventionally improved by additives. Several types of impact modifiers have been developed for this purpose. Among them, reactive liquid rubbers or high T_g thermoplastics are the most widespread and, to a lesser extent, core-shell particles. These blends are materials resulting from the mixing of the additive with the thermoset precursors and the subsequent reaction of the precursors. In the typical case, the system goes from a homogeneous mixture to a phase-separated blend as the growth in molar mass of the thermoset component changes the equilibrium state; this process is called reaction or polymerization-induced phase separation.[1] In the fully cured epoxy thermoset, micron size additive-rich domains can be observed, and most of the studies on such thermoset blends were focused on final morphologies or mechanical properties. Several authors[1–4] have shown that a careful control of the morphology of these systems was necessary to obtain a good balance of properties and an efficient toughening. The selection of the type of organic toughening agent is often influenced by the crosslink density of the epoxy polymer.[5] Thereby, soft rubbery polymers are often added as toughening agents for lightly crosslinked epoxies. The yield strengths for these materials are relative low, i.e. such materials display an inherent ability to shear yield. In these systems, the most efficient toughners are the ones containing a high level of rubber phase that can cavitate to initiate shear bands in the epoxy matrix at the crack tip. The most widely used are the liquid rubbers CTBN (Carboxyl Terminated Butadiene acryloNitrile

[1] GRL, ARKEMA, BP34, Lacq, F-64170, France
[2] CERDATO, ARKEMA, Serquigny, F-27470, France
[3] Ingénierie des Matériaux Polymères, IMP UMR CNRS 5223, LMM, INSA-LYON, Bât. J. Verne, 20 Av. A. Einstein, F-69621, France
E-mail: pascault@insa-lyon.fr.

random copolymers). The adhesion between the domains and the matrix is ensured by the carboxyl functionality.

An alternative approach to the toughening of epoxy network consists of micro-or nano-scale structuring of the epoxy network obtained by the self-assembly of amphiphilic block copolymers in the epoxy precursors and fixation of the resulting morphologies by the cross-linking reaction.[6] In particular, block copolymers composed of rigid and rubbery blocks can self-assemble into vesicles or micelles which can significantly increase the fracture resistance of cured epoxies with a minimum impact on glass transition temperature and modulus.[7–11] Block copolymers used for these purposes are composed of one block that is immiscible in the epoxy precursors and another one that is initially miscible and does not phase separate during the network formation at least up to very high conversions. In this way the self-assembled structure is fixed by the cross-linking reaction.[6,12,13] Another possibility of generating self-assembled structures is to start with a diblock copolymer with both blocks being initially miscible in the reactive solvent. Reaction-induced phase separation of one of the blocks may also lead to a structured epoxy network if the other block remains miscible in the growing thermoset up to high conversions.[14]

Among different block copolymers, this work will focus on the following acrylic block copolymers: Poly(styrene-*b*-butadiene-*b*-methylmethacrylate), SBM[10,15] prepared by anionic polymerization and Poly(methylmethacrylate-*b*-butylacrylate-*b*-methylmethacrylate), MAM synthesized by controlled free radical polymerization. In both cases, the nanostructuring block is the PMMA. It was recently demonstrated that random copolymers of methyl methacrylate (MMA) and *N*,*N*-dimethylacrylamide (DMA) containing different molar fractions of DMA, can be used for a better control of the solubility of the miscible block for the nanostructuration of epoxies of different polarities.[16] In this condition it is possible to significantly improve the intrinsic properties relative to these of the neat networks, without affecting at the same time preserving other key properties such as T_g, solvent resistance, stiffness, etc.

The aim of this work is to use these different acrylic block copolymers for the toughening of a lightly crosslinked epoxy often used as a structural adhesive. The nanostructuring block is expected to be the PMMA block or the random copolymer based on MMA and DMA. The results are compared to the ones obtained with a classical CTBN toughener.

Experimental Part

Materials

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). The hardener is the polypropylene oxide triamine, Jeffamine T403® from Huntsman. The triamine was used at the stoichiometric ratio of epoxy to amino-hydrogen groups equal to 1. In this condition the final glass transition temperature measured by DMTA at 1 Hz of the full cure network is $\sim 90\,^{\circ}C$.

Nanostrength® SBM, MAM and MAM-D are acrylic block copolymers produced by Arkema.

$S^{12}_{25}B_{25}M_{50}$-SB30-S1 represents an ABC type triblock copolymer as received and composed of $S^{12}_{25}B_{25}M_{50}$ pure triblock copolymer and 30 wt. % of SB diblock copolymer and 1 wt. % of PS. The numbers 25, 25, and 50 represent the weight percentage of the respective PS, PB, and PMMA blocks; 12 is the molar mass of the PS block in kg mol^{-1}. SB diblock and PS ''impurities'' are by-products of the triblock copolymer synthesis.[10,15]

MAM and MAM-D block copolymers were prepared by a Nitroxide Mediated Polymerization.[17] $M_xA^z_yM_x$-D_w represents an ABA type triblock copolymer where the A block consist of random copolymers of MMA and *N,N* dimethyl acrylamide, DMA. The numbers ''x'' and ''y'' represent the weight percentage of the respective A and

B blocks; ''z'' is the molar mass of the PBA block in kg mol^{-1}, ''w'' is the weight percentage of DMA vs MMA. Three products were evaluated in this study: $M_{25}A_{50}^{25}M_{25}$-D_0, $M_{28}A_{44}^{25}M_{28}$-D_{28}, $M_{18}A_{64}^{25}M_{18}$-D_{28}. The products will be called MAM, MAM-D1, MAM-D2. In MAM-D1, MAM-D2, the ''M'' hard blocks are composed by a random copolymer having 72% MMA and 28% DMA.

In the case of SBM, the anionic polymerization leads to a syndiotactic PMMA block, and in the case of MAM, the free-radical polymerization leads to an atactic PMMA block.

The CTBN used is Hycar CTBN-X8 from Noveon Speciality Chemical, with a content of acrylonitrile, AN units equal to 18 wt.% and an average molar mass, $M_n = 3600$ g.mol^{-1}

Sample Preparation

The liquid rubber or the block copolymer powder is added in the epoxy precursor at 50 °C (CTBN) or 160 °C (block copolymer) in a reactor. The blend is mixed up to dissolution of the additive in the epoxy, while it is degassed. When the blend is homogeneous, the temperature is fixed at 70 °C, and the hardener, Jeffamine T403, is introduced, and mixed as the blend is degassed for 5 min. under vacuum. The mixture is then poured in 6 mm thick moulds and cured for 120 min. at 120 °C.

A typical formulation at 10 wt. % loading of additive contains 160.02 g of DGEBA, LY556, 64.98 g of Jeffamine T403 and 25 g of additive.

Experimental Techniques

Dynamic Mechanical Thermal Analysis (DMTA)

DMTA was performed on a Rheometric Scientific Dynamic analyzer (RSA II). All the measurements were performed at frequency of 1 Hz and under a deformation of 0.1% at a heating rate of 2 °C/min. The samples used were parallelepipedic bars of dimension $1 \times 6 \times 34$ mm^3. The storage and loss moduli, E' and E'' were measured as well as the tangent of the phase angle tan $\delta = E''/E'$ in the three points bending. The measured temperature T_α corresponds to the maximum of tan δ.

Transmission Electron Microscopy (TEM)

TEM images were obtained with a Philips CM200 operated at 200 kV. The observations were generally made directly on sections from bulk moulded specimens after subsequent staining in aqueous RuO_4 or in a solution of phosphotungstic acid for MAM copolymers and in aqueous OsO_4 for SBM copolymer, and thin sections (about 100 nm in thickness).[17]

AFM

The AFM (Multimode Atomic Force Microscope, DI2000 from Digital Instruments Inc.) morphological investigations were operated in tapping mode (phase signals). Height and phase data were collected simultaneously.

SEM

Microdeformation mechanisms were investigated from *post mortem* fracture surface of the Edge Notched Bending specimens by use of scanning electron microscopy (SEM, LEO equipped with a field emission gun). SEM had the advantage over TEM of providing both local detail and a rapid overview of the damage zone in bulk specimens, and involved relatively straightforward specimen preparation, i.e. gold coating of a fractured surface.

Toughness

Fracture toughness parameters were calculated using single edge notched (SEN) specimens, following the ESIS protocol,[17] tested at room temperature and at different speeds with a MTS 831 servo-hydraulic tensile test machine adapted to maintain quasi-static conditions at the highest test speeds. A maximum stress intensity factor, K_{max} was derived from the maximum force of the resulting force-displacement curves and the strain energy release rate, G_I, from the area under the force-displacement curve at crack initiation. K_{max} is equivalent to the mode I critical stress intensity factor for crack initiation, K_{Ic} when strict conditions

for linear elastic fracture mechanics (LEFM) testing are met. This is not necessarily the case for low T_g, low cross-linked systems where the specimens were ductile. However, although K_{max} provides only a conservative estimate of K_{Ic} when LEFM are not met, it remains useful for comparing the crack initiation behavior of different materials under different conditions, given a fixed test geometry and test method. An approximate measure of the crack propagation energy, U_{prop} and hence an indication of the crack propagation mode, was provided by the area under the force-displacement curve for $F > F_{max}$.

Results and Discussion

As said in the introduction, block copolymers are expected to form ordered micro and nanostructures, such as vesicles, spherical micelles, or wormlike micelles depending on the block copolymer composition. These morphologies are expected to be retained with the full curing of the epoxy precursor. The domain sizes can be of the order of magnitude of the chain length, ranging typically from 10 to 200 nm. In our case, one experiment has been done first with 10 wt. % of a poly(methylmethacrylate) homopolymer, PMMA dissolved in the epoxy precursors. PMMA is miscible up to high conversions, but at the end of the reaction the sample is turbid which means that the PMMA is finally expulsed from the epoxy matrix. The same experiment but with a random copolymer containing 25 wt. % of DMA units, leads to a completely transparent network. These experiments mean that with block copolymers, in DGEBA-Jeffamine T403, only the random P(MMA-co-DMA) block is expected to stabilize a nanostructured morphology up to the end of the reaction.

After this first experiment, samples were prepared with different additives. Transparency observations are an easy way to compare the variations between the samples (Fig. 1). Compared to the neat epoxy (Fig. 1(a)), only the sample with 10 wt. % of MAM-D1 (Fig. 1(d)) is fully transparent, the sample with MAM-D2 (Fig. 1(e)) is rather translucent, and the others, SBM (Fig. 1(b)) and MAM (Fig. 1(c)) samples, are as opaque as the CTBN one (Fig. 1(f)), even if as explained later the morphologies that causes this opacity are completely different for the block copolymers and the CTBN. For the two samples with SBM and MAM block copolymers it confirms that the PMMA block is not able to stabilize the nanostructure up to the end of the reaction. For the two other block copolymers, the results are rather contrasted because only the sample MAM-D1 is fully transparent. The difference between MAM-D1 and MAM-D2 block copolymers is only the wt. % of the PBA mid-block, respectively 44 wt. % for MAM-D1, and 66 wt. % for MAM-D2. It confirms our previous results[16] by demonstrating that phase-separation is avoided if the molar fraction of DMA units in the random block is

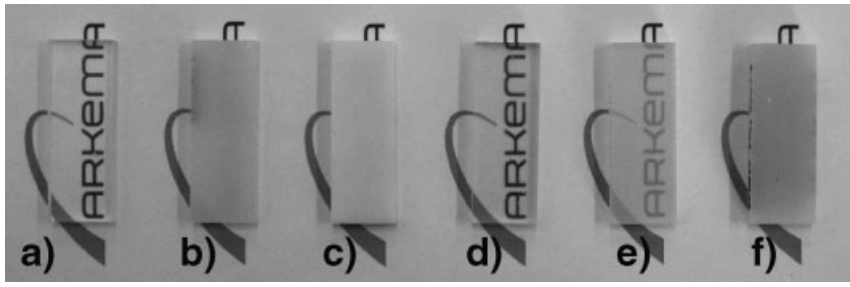

Figure 1.
Transparency test for different samples a) Neat epoxy DGEBA/T403; and with 10 wt % of additives: b) SBM, c) MAM d) MAM-D1, e) MAM-D2 and f) CTBN.

increased when the concentration of the PBA immiscible block is increased. This was qualitatively explained by the fact that the aggregation of the immiscible blocks confines the miscible blocks in the same region of space. This segregation produces a decrease in both the absolute value of the entropic contribution to the free energy and in the local concentration of solvent in contact with chains of the random copolymer. Both factors produce a decrease in the miscibility of the random copolymer when it becomes a block attached to the immiscible PBA block. Partial deswelling of the miscible block during reaction has been also monitored for other block copolymers dissolved in epoxy precursors by DMTA[10] or solid state NMR[19] methods.

These results are confirmed by the observation of TEM and AFM micrographs of fully cured DGEBA-T403 blends with 10 wt. % of different additives (Fig. 2 and 3). In the case of the CTBN sample and as expected from the literature, spherical nodules are randomly dispersed in the epoxy matrix (Fig. 2(a)). The chosen CTBN containing 18 wt. % of acrylonitrile units is one of the more initially miscible CTBN in the epoxies precursors, which means a reaction induce phase separation process at high conversion and explains why rather small rubber-rich nodules of a mean size of 0.5 μm are obtained in a high viscous medium.[1,2]

The morphologies of the samples with SBM and MAM (Fig. 2(b) and 2(c)) are quite similar, and are completely different from the morphology observed with CTBN as there is no isotropic sphere. A similar interconnected structure has been described in a thermoplastic-modified thermoset when the phase separation proceeds via spinodal demixion in a highly viscous medium.[20] In our case it can be assumed that when the PMMA block phase separates during curing at 120 °C, the PMMA block enters in its vitrification zone which means a very low mobility of the block copolymer and a partial suppression of the coarsening of the initial nanostructure. The result is that even with only 10 wt. % of block copo lymers, the demixing system is characterized

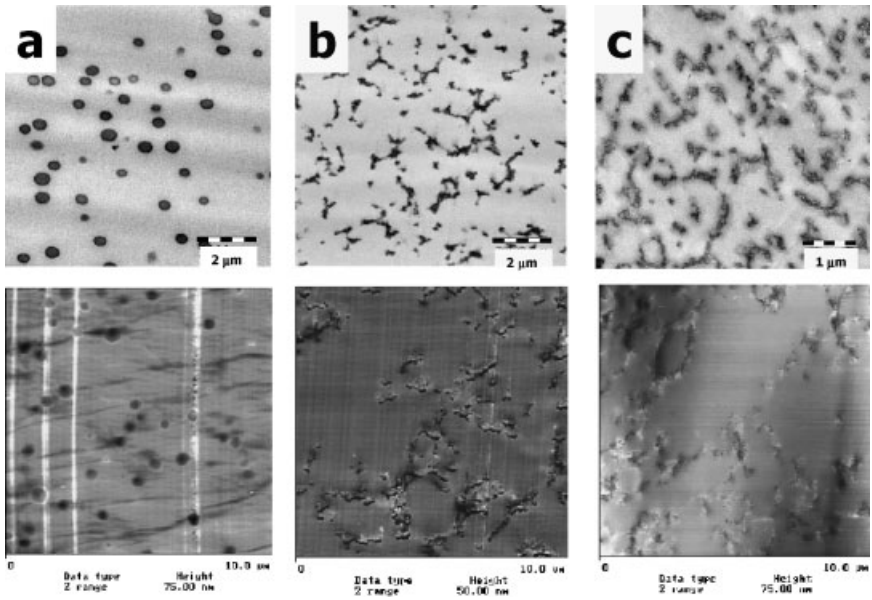

Figure 2.
TEM (OsO_4 or RuO_4 staining) and AFM micrographs (height images 10 μm × 10 μm area) of fully cured DGEBA-T403 networks modified with 10 wt % of additives: a) CTBN; b) SBM, c) MAM.

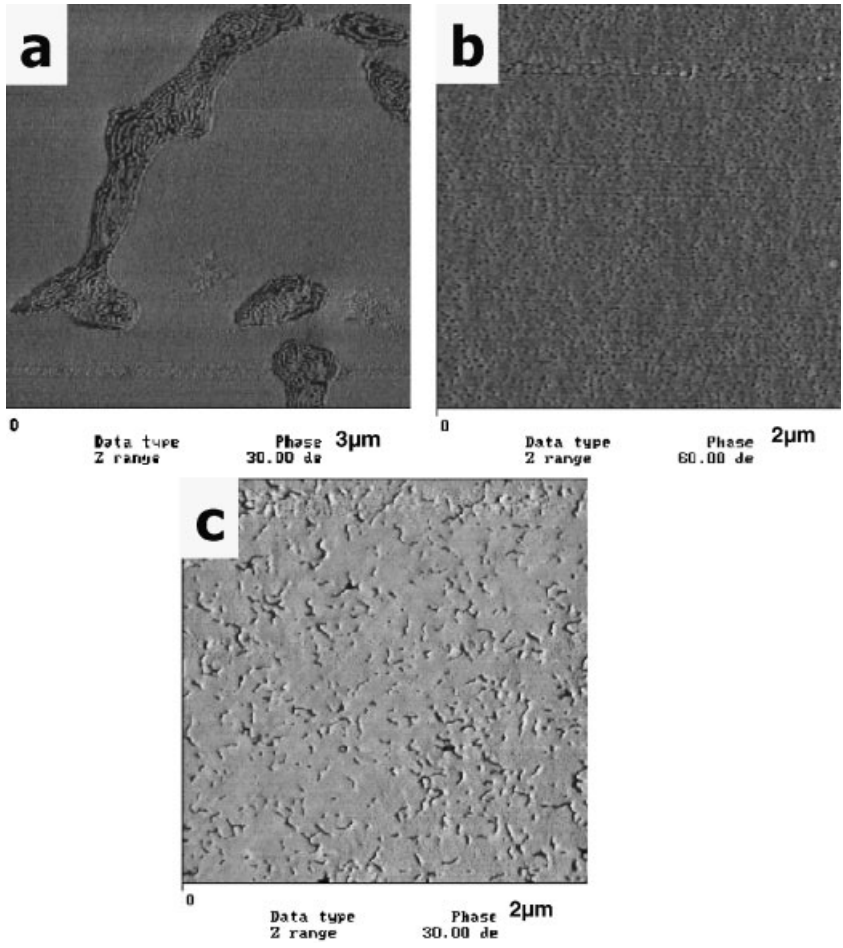

Figure 3.
Role of MAM copolymers composition on the morphologies of fully cured DGEBA- T403 networks modified with 10 wt % of additives. AFM micrographs: a) MAM; b) MAM-D1, c) MAM-D2.

by a filament-like structure with a high level of interconnectivity in both the minor and the major phases.

A comparison of the morphologies of three MMA block copolymers with different compositions of the nanostructuring block is given in Fig. 3. As expected from previous experiments with homoPMMA and previous results,[16] nanostructured epoxy networks are obtained only when DMA units are randomly introduced in the PMMA block (Fig. 3(b) and (c)). With the MAM-D1 block copolymer, spherical micelles well dispersed in the epoxy matrix are observed (Fig. 3(b)). Increasing the ratio of PBA vs. P(MMA-*co*-DMA) blocks, it is possible to obtain in the case of MAM-D2 (Fig. 3(c)), short wormlike micelles which are large enough to scatter light in spite of their small size, and thus the modified network is not perfectly transparent. These differences in morphologies can be explained by different levels of partial deswelling of the P(MMA-*co*-DMA): when the ratio of PBA vs. P(MMA-*co*-DMA) blocks is too high, the initial nanostructure has some difficulties to be stabilized leading to wormlike micelles (MAM-D2).

In the literature, a toughness improvement has been observed with ordered and

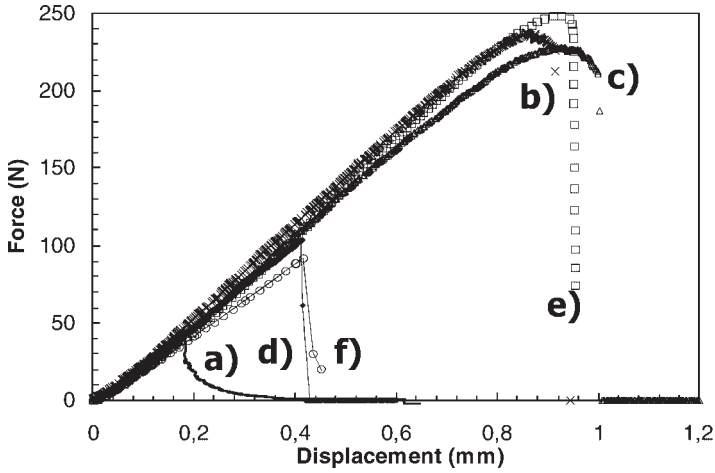

Figure 4.
Force-displacement curves made on Single Edge Notched specimens for a) — DGEBA/T403 network and with 10 wt. % of different additives, b) × SBM, c) △ MAM, d) ◆ MAM-D1, e) □ MAM-D2, and f) ○ CTBN.

nano domain size,[7–10] which means that it becomes possible to toughen ultra-thin films where the thickness of the epoxy layer is in the micron range. In the present case, it is interesting to compare the obtained results with five different micro and nanostructures. Typical force-displacement curves of acrylic-block-copolymers-toughened DGEBA/T403 epoxy networks, obtain during instrumented test are given in Fig. 4.

Fig. 4 compares the performances of CTBN with that of samples containing SBM, MAM, MAM-D1, MAM-D2 and as well as that of unmodified DGEBA/T403, illustrating the improved performance of the acrylic block copolymers for both K_{1c} and G_{1c}. Fracture mechanics analyses of the SEN tests and measurements of glass transition temperatures of the matrix are reported in Table 1 and comparison of the different values is given in Fig. 5.

As usually, the neat epoxy is very brittle with a $K_{1c} = 0.76$ MPa.m$^{1/2}$. With 10 wt. % of CTBN, unstable fracture is initiated in the linear portion of the force-displacement curve, corresponding to the lack of toughening effect and no stress-whitening at the crack tip. Under these conditions, the toug hness of the CTBN-modified system which showed a full brittle behavior is slightly increased with a $K_{1c} = 1.37$ MPa.m$^{1/2}$. In comparison, the toughness improvement of acrylic-block-copolymers-modified samples can be much more spectacular, ~3 MPa m$^{1/2}$, depending on the block copolymer composition, while other favourable properties such as T_g and modulus are at least maintained.

In the case of CTBN modified epoxies it is well known that there is always ~3–4% of the initial rubber which are still dissolved in the epoxy-rich matrix decreasing the T_g

Table 1.
Thermo-mechanical properties of a) DGEBA/T403 network and with 10 wt. % of different additives b) SBM, c) MAM, d) MAM-D1, e) MAM-D2, and f) CTBN.

Reference	T_α (°C)	K_{max} MPa.$\sqrt{m}$	G_{max} J/m^2	+% K_{max}	+% G_{max}	Plastic Deformation
Neat epoxy	92	0.76 (K_{1c})	183 (G_{1c})	0	0	No
+CTBN	86	1.37 (K_{1c})	875 (G_{1c})	81	377	NO
+SBM	97	2.96	4130	292	2150	YES
+MAM	96	2.97	4110	290	2140	YES
+MAM-D1	98	1.54	882	104	380	NO
+MAM-D2	98	2.29	2260	203	1130	PARTIAL

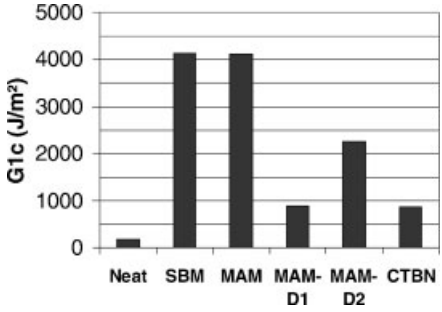

Figure 5.
Comparison of the G_{1C} values for the neat and modified epoxy networks.

(or T_α) and the modulus of the thermoset.[1,2] This plasticization of the matrix explains the T_α −6 °C decrease, observed in our case.

On the contrary, with acrylic block copolymers, even if part of the PMMA block is dissolved in the matrix, a slight increase of +4–6 °C of T_α is induced, since the neat epoxy has a T_g lower than the one of the PMMA block. But this T_α increase does not seem to be correlate with the partial deswelling of the PMMA or P(MMA-*co*-DMA) block as expected from the observed morphologies.

Coming back to the toughness results and as clearly demonstrated in the data (Table 1), acrylic block copolymers provide with excellent toughness improvement of the chosen epoxy network but depending on the block copolymer structure and composition different behaviours are observed. With 10 wt. % of SBM and MAM block copolymers, the crack became semi-stable and the size of the stress whitened zone around the crack tip increases and this was reflected by an impressive reinforcement of the matrix, presumably because of the full development of damage mechanisms associated with stress whitening (Fig. 6).

The stress intensity factor K_{max} of the SBM- or MAM-modified epoxies is ~3 MPa.m$^{1/2}$ and G_{max} is above than 4000 J/m^2. The whitened area of the fractured ligament (which corresponds to the stable crack growth area) covers most of the fracture surface, as illustrated in Fig. 6 and an energy of propagation can then be estimated. These two modified systems show a ductile / semi-brittle behavior. Widespread shear banding of the matrix, initiated by the cavitation of the rubbery phase of the particles is believed to be the predominant damage mechanism in these systems and the crack propagates in a stable/unstable manner (Fig. 7).

Crack deflection toughening contributes to the significantly higher levels of toughness. This behavior has to be related with the observed interconnected morphologies (Fig. 2(b) and (c)) and the large interfacial zone between the two phases.

With the two other block copolymers containing the P(MMA-*co*-DMA) nanostructuring block, the stress intensity factor increases as the structure goes from spherical (MAM-D1) to wormlike micelles (MAM-D2). The wormlike structure has been proposed as the morphology responsible for the significant toughness improvement by a crack deflection toughening mechanism.[21] With 10 wt % of MAM-D2, crack propagation became fully unstable beyond the maximum in the force displacement curve and no additional energy that the one included in the G_{1c} value is required to fracture the specimen. For this modified

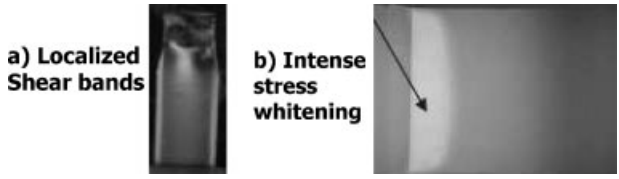

Figure 6.
Micrographs of a) DGEBA-T403 network and b) with 10 wt % SBM or MAM.

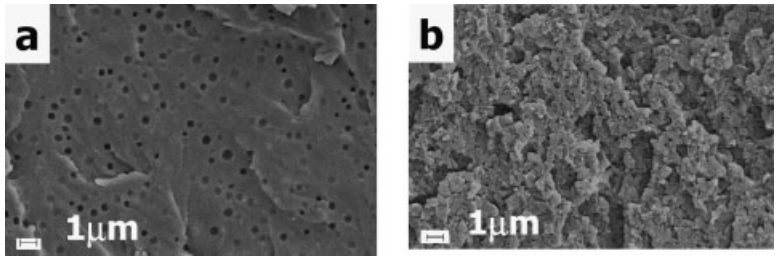

Figure 7.
SEM micrographs of DGEBA-T403 networks with 10 wt % of a) CTBN b) SBM or MAM.

system, the stress whitening zone is restricted to a process zone which is developed ahead of the pre-crack during the initiation process. The K_{1c} value is enhanced by 200% ($K_{1c} = 2.3$ MPa.m$^{1/2}$) and the material exhibits also a semi-brittle/brittle behavior.

The behaviour of the sample with the well-ordered spherical nanomicelles is quite different, and as for the CTBN microparticles, the unstable fracture is initiated in the linear portion of the force-displacement curve, and no stress-whitening at the crack tip is observed. This result was unexpected because it is quite different from previous results obtained with a similar morphology. For high T_g modified epoxies[10] it was proved that the PB-mid block of the added SBM triblock copolymer was able to cavitate, which is not the case with the PBA-mid block of this MAM-D1 block copolymer. But the comparison has also to take into account the fact that, in the case of SBM nanoparticles the PB elastomeric blocks were not the cores of nanoparticles but were just covering the PS cores, which is perhaps a better situation for promoting cavitations. It has also to be pointed out that the role of the interfacial zone on the toughness behaviour which is larger in the case of wormlike micelles or filament-like microstructures, is also unknown.

Conclusion

The initial self-assembly of acrylic block copolymers, SBM and MAM at a molecular scale in a DGEBA/Jeffamine epoxy-based glassy polymer (with a rather low T_g and a lightly crosslinked network) produces micro and nanostructured materials after reaction. The composition of the rigid nanostructuring block is important for controlling its expulsion or a partial deswelling during reaction. Depending on the P(MMA-*co*-DMA) block composition and on the ratio of the blocks, micro interconnected filament-like (no DMA) or wormlike and spherical micelles (both with 25% DMA but with higher or lower content of PBA) are obtained. The final structures enhance more or less the toughness properties while maintaining favorable properties, such as T_g and stiffness. It is possible to activate plasticity at the crack tip of the thermoset. But even if the toughening improvement is already very interesting, a nanostructuration (spherical micelles) does not lead to the most impressive toughening effect in this system as the highest toughness improvement is obtained in the case of filament-like interconnected microstructure brought by Nanostrength® acrylic block copolymers.[22]

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