A New Class of Epoxy Thermosets

Emmanuel Girard-Reydet,[1] *Jean-Pierre Pascault,*[1] *Anthony Bonnet,*[2] *François Court,**[2] *Ludwik Leibler*[3]

[1] Laboratoire des Matériaux Macromoléculaires – UMR CNRS 5627, Bât. J.Verne, INSA, 20 av. Albert Einstein, 69621 Villeurbanne Cedex, France
[2] CERDATO, ATOFINA, 27470 Serquigny, France
[3] Laboratoire Matière Molle et Chimie, UMR ESPCI-CNRS-ATOFINA, 10 rue Vauquelin, 75231 PARIS CEDEX 05, France

Summary: The reinforcing strategies of epoxy thermosets rely on the control of the phase separation between the additive and the growing thermoset. With standard additives, such as reactive liquid rubbers, the length scale of the resulting domains is the micrometer. Here, we present a route that enable a control of the morphology down to the nanometer scale. This strategy is based upon the self-assembly process of blends of epoxy and SBM triblock copolymers, namely Poly(Styrene-b-1,4 Butadiene-b-Methyl methacrylate). It relies on the respective affinities between the epoxy precursors and each of the three blocks. Liquid epoxy has a strong affinity for PMMA, whilst it is not miscible with polystyrene nor polybutadiene at standard processing temperatures. Thus, within the reactive system, microphase separation leads to a regular network of S-B domains. This nanostructure is governed by thermodynamics. The size and geometry of the dispersed domains are controlled by the concentration and the ratio between blocks lengths. The domain size is of the order of magnitude of the chain length, ranging typically from 10 to 30 nanometers. What controls the blend's morphology throughout the curing process of the thermoset was one topic on which we focused our interest. Nanostructured thermosets have been obtained. These supramolecular architectures yield significant toughness improvements while preserving the transparency of the material. The reinforcing mechanisms are not yet fully understood : it is intriguing to induce significant toughening with elastomer domains smaller than 30 nanometers in diameter. Besides being efficient epoxy tougheners, SBM can broaden the scope of applications of thermosets due to specific rheological behaviors. Thanks to the self assembly process taking place in the blend of the SBM block copolymers with the epoxy thermosets precursors, the reactive solvent can be turned into a reactive gel or solid (before curing). This physical gelation is induced by the microphase separation and is thus thermoreversible. At relatively moderate loadings of block copolymers the reactive blend behaves like a thermoplastic material, with adjustable modulus and tackiness. These results evidence that SBM block copolymers open a broad area for designing new class of thermoset materials.

Keywords: nanostructures, rheology, thermosets

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Introduction

Epoxy thermosets are used in many demanding applications in which stiff, high glass transition temperature, T_g, low creep and high heat resistant materials are required. On the other hand, compared to most materials, epoxies are very brittle, and toughening of such thermosets has been a major objective of polymer science for many years. Several types of impact modifiers have been developed for this purpose. Among them, reactive liquid rubbers, like CTBN (Carboxyl Terminated Butadiene acryloNitrile) are the most widespread and, to a lesser extent, high T_g thermoplastics and core-shell particles. Nevertheless, significant progress is still highly desirable in this field. Users are seeking additives that would toughen epoxy without adversely reducing their T_g or stiffness. Furthermore, in some cases, the tougheners commercially available are just not efficient. As far as processing is concerned, thermosets have peculiarities that have to be taken into account when designing a new reinforcing strategy. In most thermoplastics toughening is obtained by melt blending together the polymer and the impact modifier, the toughening of thermosets can only be achieved by the *in situ* strategy. The impact modifier is added to the epoxy precursors (epoxy oligomer and hardener) prior to curing, hence, process wise, the solubility of the additive in the precursors is required.

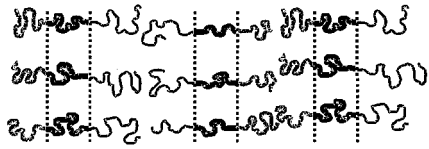
Thanks to their composition (butadiene + acrylonitrile) and low molar mass, CTBN are initially soluble in epoxy oligomers. When the material is being cured, the miscibility of CTBN with the growing network decreases which leads to phase separation.[1] In the fully cured epoxy thermoset, micron size rubber domains can be observed. The adhesion between the domains and the matrix is ensured by the carboxyl functionality. Several authors[1] 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 preformed core-shell particles used in epoxy range typically from 200 to 400 nm.[2] In both cases, the geometry of the dispersed rubbery phase is spherical or droplet like. Our motivation was to elaborate a new class of thermoset materials with completely unique morphologies, both, in terms of geometry and in terms of length scale. As far as the latter is concerned, a breakthrough would be to gain one order of magnitude, to control the formation of dispersed domains down to 10-20 nm., i.e. the order of magnitude of the chain length. The strategy is based upon the self-assembly process of blends of epoxy systems and linear A-B-C triblock copolymers, namely Poly(Styrene-b-Butadiene-b-Methylmethacrylate), SBM. Such a

strategy, first proposed by Leibler et al. [3,4] was shown to be successful in thermoplastics. It relies on the selective affinity of one of the block for the host matrix, PMMA and the epoxy precursors, in the present case. With this approach trully nanostructured thermosets have been obtained.[5-10] We will show that the final morphologies are governed *ab initio* by the SBM molecular characteristics. This illustrates both the versatility and the robustness of this route. Another aspect of robustness is the capacity to elaborate nanostructured materials with industrial samples. The toughness of SBM modified epoxy has been investigated and compared with standard macrophase separated systems. Another interesting aspect of SBM /epoxy is the blend behaviour before curing, its rheology will be the focus of this paper last section.

Experimental

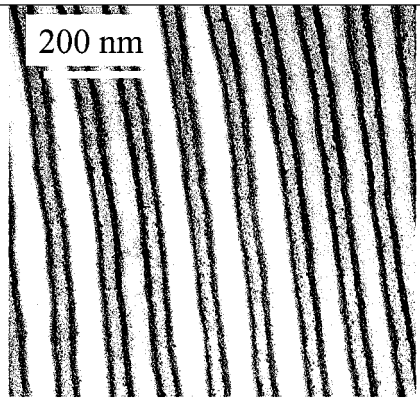
Techniques used in this paper, materials and samples preparation are given in reference.[10]

SBM Samples description. SBM are linear triblock copolymers. They are produced via anionic polymerization. Since its discovery in the sixties, living anionic polymerization has been used as the ideal synthetic route towards well defined block copolymers. For many years, anionic polymerization was limited to three monomers: styrene, butadiene and isoprene. In the eighties, it became possible to synthesize block copolymers with acrylates and methacrylates such as MMA.[11-14] Thanks to ATOFINA patented chemistry and process technology, the synthesis of SBM triblock copolymers can be performed at relatively elevated temperatures and in a non polar solvent, yielding a 1,4-microstructure of the polybutadiene block higher than 85% and a PMMA block with over 75% syndiotactic triads. The incompatibility between the three chemical species constituting SBM and the connectivity between the blocks lead to microphase separation as depicted in Figure 1. In the bulk, the resulting well ordered morphology can be evidenced by transmission electron microscopy as shown in Figure 2a. In this example, the SBM sample has a lamellar morphology. Depending on its composition, i.e. the percentage of styrene, butadiene and methylmethacrylate in the chain, a broad spectrum of morphologies and mechanical behaviors can be covered by SBM triblock copolymers. This variety of morphologies has been investigated in depth by R. Stadler and V. Abetz, who have established a SBM ternary phase diagram.[15-16] Figure 2, represent the morphologies of two SBM samples with different compositions, 30/30/40 and 20/25/55 respectively (expressed in terms of mas fraction of S , B and M).

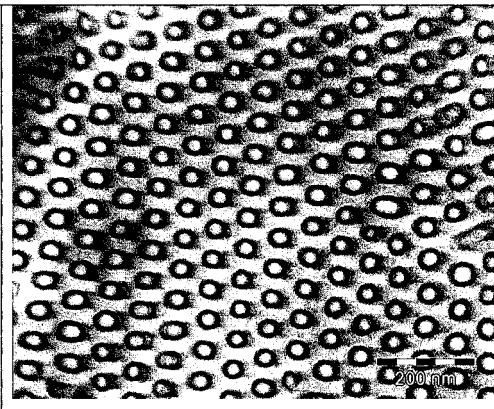


S-**B**-M M-B-S S-B-M

Fig. 1. Schematic representation of the chain organization of SBM triblock copolymers. Incompatibility between blocks leads to a self-organization process into a microphase separated morphology.



a- SBM-30/30/40 : alternating lamellar morphology



b- SBM-20/25/55 : PMMA matrix with hexagonally packed PS-PB core-shell cylinders.

Fig. 2. Transmission electron micrograph of pure SBM films solvent casted from chloroform. The polybutadiene blocks are selectively stained with osmium tetraoxide and appear black.

Synthesis of a Nanostructured Epoxy Thermoset

The molecular characteristics of the pure SBM sample used in this section are the following : the number average molar mass of the PS block is 27000 g/mol, the number average molar mass of the PB block is 11000 g/mol and the number average molar mass of the PMMA block is 84000 g/mol, i.e. the SBM composition is 22/9/69 expressed in weight fraction of S, B and M, respectively. This SBM sample is noted $S_{22}^{27}B_9M_{69}$. The epoxy precursors were diglycidyl ether of bisphenol A, DGEBA (LY556 from VANTICO) and 4,4'-Methylenebis-(3-chloro-2,6-diethylaniline), MCDEA as hardener, commercialized by LONZA.

Both, SBM and epoxy precursors (DGEBA + MCDEA) are soluble in chloroform. This solvent was used as a casting solvent to obtain a 1mm thick film of a 50/50 blend of SBM in the epoxy precursors. After full curing of the sample, for several hours under pressure at 190°C, a transparent film is obtained. This film was immersed for several days in toluene, the swelling observed remained smaller than 3% . Toluene is a good solvent of SBM, the non-swelling of the sample is a signature that this 50/50 blend consists of a continuous thermoset phase. This result in itself is worth noticing as in most thermoplastic/thermoset blends phase inversion occurs when the weight fraction of the thermoplastic exceeds 20%.[1] The transmission electron microscopy of the cured sample is presented in Figure 3a. The PB domains are all spherical in shape, their diameter is close to 10 nm., with a very narrow size distribution, and they are extremely well distributed within the matrix. One can observe that PB domains seem to gather by groups of three or four around a central brighter sphere. This central sphere hardly presents any contrast with the matrix. As schematically represented in Figure 3b, this central sphere is proposed to consist of the PS blocks of the SBM chains while the PB blocks form spheres decorating the PS sphere, the PMMA block being trapped within the epoxy matrix. This description is consistent with the macroscopic non-swelling behavior of the sample. Our conclusion is supported by dynamic mechanical analysis[10] which reveals the presence of a mixed phase PMMA+cured epoxy and two pure phases: PB and PS. Furthermore, the fact that the PB domains fail to cover continuously the surface of the PS sphere is consistent with the composition of the SBM sample used (22/9/69). We would like to emphasize the fact, that a similar morphology has already been reported in the literature.[15-16] Stadler et al. have observed such a morphology in a pure SBM sample with a highly asymmetric composition, 15/5/80, they described it as the *Spheres on Spheres* morphology. Considering that the epoxy swells selectively the PMMA phase, a mass balance would lead to a composition of 11/5/84 for the blend investigated here. This composition falls into the stability range of the *Spheres on Spheres* morphology of pure SBM, which is consistent with the morphological observation. As an additional test, the epoxy reactive system was modified with 10% of SB diblocks. The SB used are the precursors of the SBM 22/9/69 collected during the SBM synthesis. After curing, the film was turbid and transmission electron microscopy revealed micron size, macrophase separated, domains of SB diblocks within the epoxy matrix.[10] The

adhesion being so poor between the nodules and the matrix, most of the domains were torn off during the ultra-microtoming procedure.

Thanks to the affinity between the PMMA block of SBM triblocks and the epoxy system used in this study a nanostructured thermoset was obtained. The complex *Spheres on Spheres* morphology is the template of a morphology of a pure SBM, nevertheless it presents the characteristics of a thermoset material. Due to the length scale of the structure the resulting material is transparent.

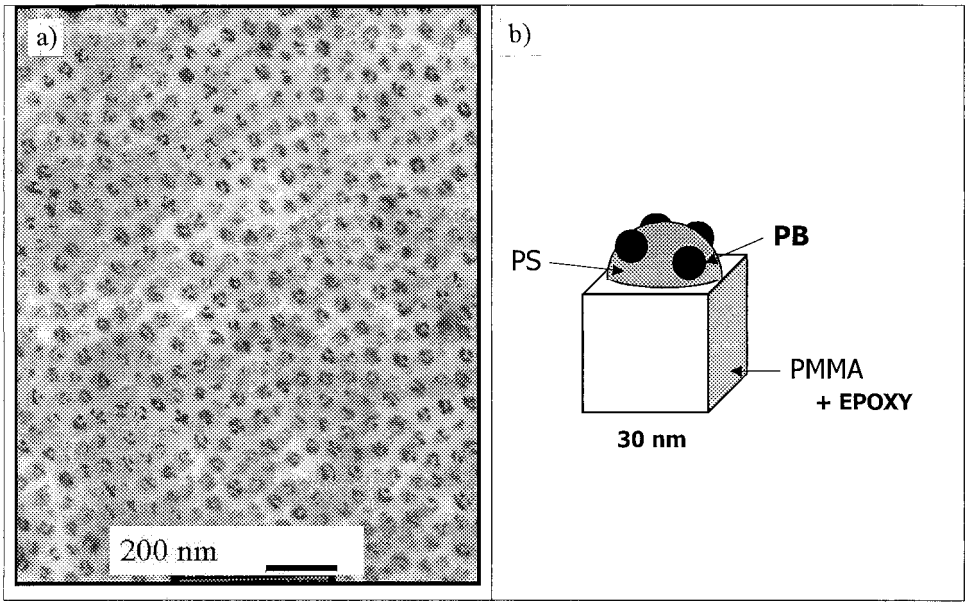


Fig. 3. a) Transmission electron micrograph of a blend Epoxy/SBM-50/50 after curing. Purified SBM composition is 22/9/69 in mass fraction of S, B and M respectively ($S_{22}^{27}B_9M_{69}$).The polybutadiene blocks are selectively stained with osmium tetraoxide and appear black. b) Schematic representation of the spheres on spheres morphology.

A Robust Route towards Nanostructured Materials

As mentioned, the synthesis technology used in this study enables the anionic polymerization of the methacrylic block at relatively elevated temperatures. This is a key to the industrial production

of SBM. Though, in the given conditions, some of the living SB precursors of the triblocks are „killed" during the polymerization of MMA. In other terms, the product obtained is not a pure SBM triblock but a blend of SBM triblocks and their SB diblock precursors. In this section two different SBM+SB mix were used. One of them is the blend of the SBM triblock and the SB diblock investigated in the previous section. The second system is also composed of an SBM triblock copolymer with a large PB block and a similar PMMA block. The numbers between brackets are the number average molar mass of the corresponding blocks:

SBM1 : $S_{22}^{27}B_9M_{69}$ (27000-11000-84000) + 21 % SB diblock (27000-11000)

SBM2 : $S_{12}^{14}B_{18}M_{70}$ (14000-27000-85000) + 10 % SB diblock (14000-27000)

Both products were added to the epoxy precursors to obtain epoxy/SBM-70/30 blends. TEM observations were conducted on the cured transparent samples, the results are presented in Figures 4a and 4b for SBM1 and SBM2, respectively. In both cases, a regular morphology, with dispersed domains smaller than 100 nanometers, is obtained. These results are to be compared with the experiment conducted on pure SB diblocks in the previous section. In the presence of SBM chains, the SB diblocks do not macrophase separate. Thus, nanostructured thermosets can be obtained from blends of SB and SBM, in other terms from unpurified industrially produced triblocks. A result which illustrates the robustness of this route toward nanostructured epoxy.

Let us now focus on the morphologies generated with SBM1 and SBM2. The dispersed domains in Figure 4a and 4b are nearly identical in size, though they have significantly different geometries. In the latter system, the B blocks, which appear dark, form a continuous corona on a central PS sphere (Figure 4b). In the former case, the outer limit of the PS sphere does not appear clearly as the contrast between the epoxy matrix and PS is very low. The presence of the central sphere is revealed by the respective positions of the darker and smaller B spheres that decorate its surface. This difference between the morphologies of the epoxy thermosets obtained from SBM1 and SBM2 is a direct consequence of the molecular characteristics of the SBM used and of the relative interaction parameters between the various chemical species. SBM2 has a PB block longer (larger molar mass) than its PS block, thus a negative curvature (convex) is expected for the S/B interface. The formation of a continuous B shell on the S sphere is energetically favored. The PB block of SBM1 is shorter than its PS block, the natural curvature of the S/B is thus positive (concave). A core-shell structure would impose a curvature that is not favored. The chains prefer

to self-assemble in a *Spheres on Spheres* type of morphology that respects the natural concave curvature.

The TEM pictures provide another interesting piece of information concerning the effect of the SB diblocks. Compared to the morphology obtained with the pure SBM1 triblock (Figure 3a) Figure 4a reveals that there are more PB spheres decorating the central PS sphere, that this sphere has "swollen" from 30 nm up to 100 nm. Nevertheless, the curvatures of the different interfaces, S/B and B/matrix, are globally maintained. This swelling is the consequence of the incorporation of the SB diblocks within the structure. This is also evidenced in Figure 4b: in the clear sphere formed by the PS blocks, a darker sphere can be observed like an inner core, this sphere is constituted of the B blocks of the residual SB diblocks. A schematic representation of the chains organization is presented in Figure 4c. It illustrates how the SBM triblocks act as stabilizers for the SB diblocks in the epoxy system preventing a macrophase separation.

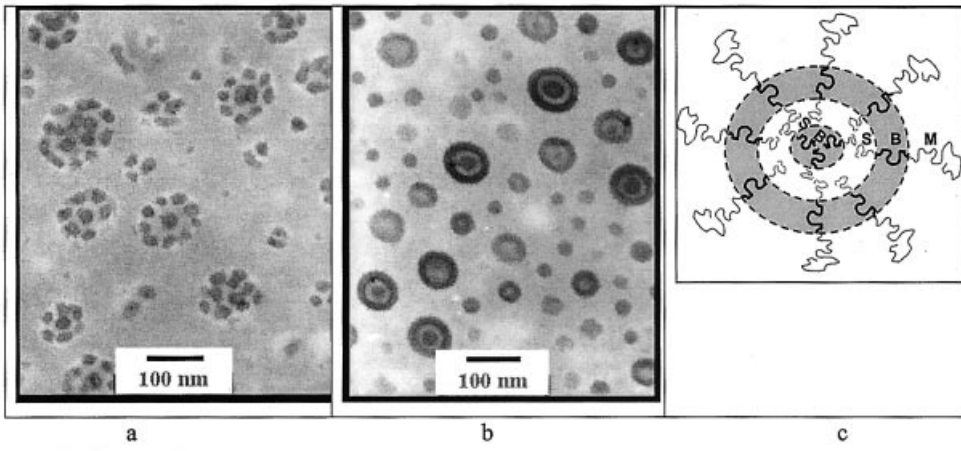


Fig. 4. a) Transmission electron micrograph of a blend epoxy/SBM1-70/30 after curing. b) Transmission electron micrograph of a blend epoxy/SBM2-70/30 after curing. c) Schematic representation of chains organization within the dispersed domains.

Such refined geometries of the nano-scaled domains are the consequence of the microphase separation of both, the PS and the PB blocks. It proves the versatility offered by ABC triblock over AB diblocks in controlling blends morphologies. It is worth recalling that another weakness of the diblock architecture is its abitility to incorporate defects. Nanostuctured thermosets can be

obtained from pure BM diblock copolymers, but not from „industrial" BM. The BM diblocks fail to stabilize their residual homopolybutadiene.[10] Macrophase separation is observed and it adversely affects the mechanical properties.

Toughened Nanostructured Epoxy Thermosets

The properties of various nanostructured thermosets, including those described in the previous section, have been evaluated and compared to the reference unmodified epoxy system and to epoxy toughened with standard additives, such as liquid rubbers (Carboxy Terminated Butadiene-co-acryloNitrile rubbers). The results obtained on fully cured samples are reported in Table 1.

Table 1. Properties of modified epoxies.

Sample DGEBA/MCDEA +...	K_{Ic}^{*} ($MPa.m^{1/2}$)	T_g (°C)	Transparency	Morphology
Neat	0.65 ± 0.02	187	yes	x
30% SBM1	1.53 ± 0.12	171	yes	Figure 4.a
30% SBM2	1.27 ± 0.11	177	yes	Figure 4.b
15% CTBN8 (18% AN)	1.15 ± 0.10	161	no	x
15% CTBN13 (27% AN)	1.23 ± 0.11	149	no	x
10% SBM2	1.05 ± 0.10	184	yes	Figure 5

K_{Ic}^{*} : 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 [17] was strictly followed with a crosshead speed of 10 $mm.min^{-1}$. K_{Ic} was calculated as the mean value of 10 tests at least.
Materials: DGEBA (LY556) with hardener MCDEA; CTBN8 and CTBN13 from BFGoodrich ; SBM1 and SBM2 from ATOFINA as described in the previous section.

All the samples listed in Table 1 were immersed in toluene for a week. Toluene is a good solvent for SBM and CTBN. None of the samples underwent a swelling larger than 3%, which assesses that these materials consist of an epoxy matrix and a discrete, non-continuous, thermoplastic phase. With liquid rubbers phase inversion occurs at loadings close to 25%, whereas with the SBM used in this study no phase inversion was observed below 50% of SBM. This is a consequence of the material structure and thus a specificity of SBM triblocks compared to the other additives used to modify epoxy thermosets. The results in Table 1 show that both, SBM and

CTBN are efficient tougheners of the epoxy thermoset. The best increase of fracture toughness (K_{Ic}) was observed on the first two samples containing 30% SBM. At this stage, we have no explanation for the fact that the "raspberry" morphology (Figure 4a) seem to induce a better toughening than the "core-shell" or "onion" type morphology (Figure 4b). Substantial toughness improvements while minimizing the effect on other important properties is a key issue. Epoxy thermosets are used for their high heat resistance and low creep behavior, thus reducing the T_g of the epoxy matrix is detrimental to the material overall performance. It is observed that SBM induces a limited reduction of T_g while the addition of CTBN reduces T_g significantly. From Table 1, it can be assessed that the compromise of properties is clearly in favor of SBM over CTBN. Furthermore, it was observed that the fully cured thermoset keeps its optical clarity, which can be of interest in some applications. At this point, we would like to focus on the last sample tested. At 10% SBM the material remains as transparent as the non-toughened epoxy. The transmission electron micrograph (Figure 5) is consistent with the macroscopic observation.

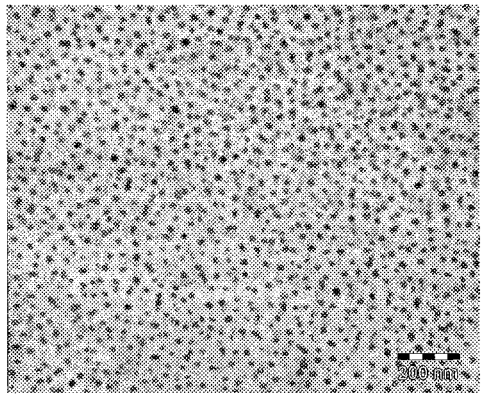


Fig. 5. Transmission electron microsgraph of a blend Epoxy/SBM1-90/10 after curing. The B block has been selectively stained with Osmium tetraoxide and appears dark.

The SBM domains are extremely evenly distributed and regular in size. As the diameter of the butadiene particles is 15 nm light cannot be scattered, hence the toughened material remains transparent. But, the most striking result is the toughening itself. It is indeed a major finding of this work that an epoxy thermoset can be toughened with such small particles. TEM investigations

were carried on a fractured specimen. In the area just beneath the crack propagation, cavitation of the nano-spheres was observed. Several authors have reported that elastomer particles cannot cavitate if their radius is smaller than a 100 to 200 nanometers.[18-20] These results are further detailed and discussed in a separate paper.[21]

Processing of Nanostructured Thermosets

In this section, we focus on the rheological behavior of SBM/epoxy formulations before curing. Thanks to their nano-scaled ordered structures, the epoxy thermosets investigated here are tough and transparent, this was the motivation of this work. However, ordered structures have a well-known drawback, they are difficult to process. Several studies on the rheological behavior of pure AB and ABA block copolymers have shown that microphase separation hinders flow. Below T_{ODT} (Order-Disorder Transition Temperature), i.e. when the material is in an ordered state, it remains highly elastic ; above T_{ODT} the material is disordered, it flows easily.[22] Block copolymers are known to have the ability to form micelles or ordered structures in selective solvent. Thus, SBM/epoxy blends are expected to present complex rheological behaviors, comparable to those of ordered block copolymers. For the sake of clarity, only the results obtained on non-reactive systems are presented here.

The blends of DGEBA liquid epoxy and SBM (without diamine hardener) are prepared by mechanical stirring in a glass reactor at a temperature of 160°C. After a couple of minutes, a complete incorporation of the triblock copolymer into the liquid DGEBA is obtained. At this temperature, the solution is fluid and transparent. Upon cooling the solution remains perfectly transparent. The influence of the SBM concentration on the viscoelastic properties of the solution was investigated using a plate/plate rheometer. The temperature range investigated goes from -20°C, the T_g of the liquid epoxy used, up to 200°C. The results obtained at three different SBM concentrations, 5%, 10% and 15%, are reported in Figure 6 and compared to the viscoelastic behavior of the pure liquid epoxy. The latter presents the simple rheological response of a low molar mass material. Above its T_g (-20°C) it flows easily, like a Newtonian fluid, the loss modulus, G'', is larger than the storage modulus, G'. The solution containing 5% of SBM shows a similar rheological behavior, it is just slightly more viscous than the pure epoxy solution. Complementary frequency sweeps measurements show that it also presents a Newtonian behavior at room

temperature, G' scales with ω^2 and G'' with ω. A major difference is observed when the SBM concentration is raised to 10%. The blend behaves like a gel, at room temperature and up to 135°C, its storage modulus is larger than its loss modulus. On complementary flow measurements (not presented) it is evidenced that its complex viscosity is highly shear rate dependent. On this temperature range, the 10% SBM blend is extremely viscous and does not present a Newtonian behavior.

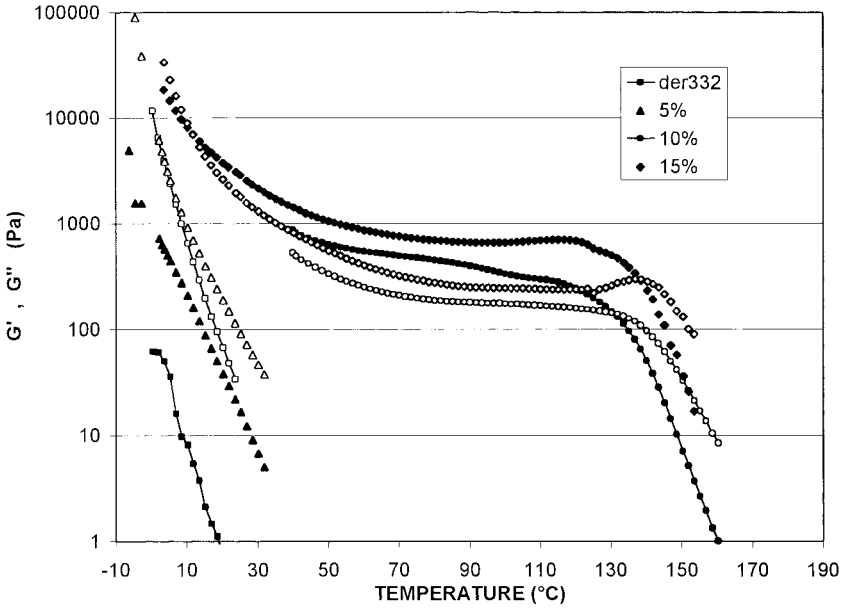


Fig. 6. Rheological behaviour of liquid epoxy modified with SBM. Elastic and shear moduli, G' and G'' respectively (G': filled symbols; G'': open symbols); squares: pure liquid DGEBA; triangles: DGEBA + 5% SBM; circles: DGEBA + 10% SBM; DGEBA + 15% SBM.

This gel-like behavior is thermoreversible. When the temperature is raised above 135°C, the material starts to flow, both G' and G'' drop sharply, G'' becomes larger than G' (Figure 6). In these conditions as evidenced by the flow measurement done at 150°C, the solution recovers a Newtonian behavior. Above 135°C, the scaling laws, G' α ω^2 and G'' α ω are obtained. The solution containing 15% SBM presents a similar viscoelastic signature : a sharp thermoreversible

sol-gel transition. The plateau level of the storage modulus is slightly raised and the crossover temperature is shifted 10°C higher.

Based on these experimental results and others obtained on various SBM/DGEBA blends, we propose that the physical sol-gel transition observed here is the consequence of a microphase separation transition, or Order-Disorder Transition. When the temperature is low DGEBA acts as a selective solvent for the PMMA block, thus a regular network of SB nanodomains is created within the material. When the temperature is raised, the segregation power decreases, the whole SBM chain becomes soluble in DGEBA, the structure is lost, the viscosity drops. For entropic reasons, it is expected that below a given concentration of SBM in DGEBA the system will remain disordered at any temperature. In the system investigated here, this critical concentration is located between 5% and 10% of SBM in DGEBA. The SBM loading is not the only parameter affecting the crossover temperature. It can be set at will by adjusting the molecular characteristics of the SBM chain. This specificity of SBM/DGEBA solutions can thus be turned into a real processing advantage and put to use in various applications.

Conclusions

Thanks to its PMMA block, SBM can be easily incorporated in epoxy precursors. SBM chains can be either dispersed at the molecular level, or form microphase separated structures. In the latter case, the liquid epoxy acts as a selective solvent of the SBM triblock copolymer, S and B blocks are not soluble and self assemble in regular domains. The transition from one state to the other depends on the segregation power, i.e. the temperature or the SBM concentration or the components molar masses. This transition was evidenced by its rheological signature, a thermoreversible sol-gel transition. The gel like behaviour is the consequence of the ordered structure present in the blend. The reactive liquid can thus be turned into a reactive gel or even a reactive solid at higher SBM loadings, in a switchable and controlable manner. We believe that important new applications for thermosets are expected from this unique behavior. It opens the possibility of handling and processing reactive systems like thermoplastic materials. Depending on the affinity between PMMA and the growing epoxy network,[10] the macrophase separation of the additive can be avoided and the initial morphology can be preserved througout the curing process. The choice of the SBM molecular characteristics and the blend composition enables one to

prepare nanostructured thermosets. A template of the morphology of a pure SBM has been obtained. Besides being versatile tools for finely tuning the thermoset morphology, we have shown that SBM is a robust route towards nanostructured epoxies. SBM act as a stabilizer, or surfactant, for the residual SB diblocks originating from the industrial synthesis. Controlling the morphology of epoxy thermosets was shown to have another advantage besides preserving transparency, significant toughnening has been obtained with SBM. The toughening mechanism deserves a carefull study as it is to our knowledge the first time that toughening of thermosets is reported with rubbery domains smaller than 20 nanometers. This is a major specificity of SBM over other styrenic block copolymers such as SB, SBS and SEBS that cannot be dissolved in DGEBA and are, thus, not used as modifiers for epoxy thermosets.

Acknowledgments

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