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Chemistry and Mechanical Properties of Epoxy-Based Thermosets Reinforced by Reactive and Nonreactive SBMX Block Copolymers

Valéry Rebizant,[†] Anne-Sophie Venet,[‡] François Tournilhac,*[,†] Emmanuel Girard-Reydet,[‡] Christophe Navarro,[§] Jean-Pierre Pascault,[‡] and Ludwik Leibler[†]

Laboratoire Matière Molle et Chimie (ESPCI-CNRS UMR 167), Ecole Supérieure de Physique et Chimie Industrielles, 10 rue Vauquelin, 75231 Paris Cedex 05, France; Laboratoire des Matériaux Macromoléculaires (CNRS UMR 5627), Institut National des Sciences Appliquées, 20 avenue Albert Einstein, 69621 Villeurbanne Cedex, France; and ATOFINA, Groupement de Recherches de Lacq, B.P.34, 64170 Lacq, France

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ABSTRACT: Polystyrene-*block*-polybutadiene-*block*-poly[(methyl methacrylate)-*stat*-(methacrylic acid)] (SB(MA)) block copolymers incorporating acid-reactive functionalities in the last block have been synthesized and studied as modifiers for epoxy thermosets based on the diglycidyl ether of bisphenol A (DGEBA). Different techniques including differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), and transmission electron microscopy (TEM) have been used to demonstrate the effectiveness of the reaction-induced modification compared to that with the nonreactive or slowly reacting polystyrene-*block*-polybutadiene-*block*-poly[(methyl methacrylate)-*stat*-(*tert*-butyl methacrylate)] SB(MT) triblock copolymer. Morphological characteristics revealed by TEM indicate that SB(MT) and SB(MA) are both miscible with the epoxy prepolymer. The kinetics of grafting, network formation, and possibly phase separation were quantified from FT-IR, DSC, and cloud point investigations of DGEBA/DDS (4,4′-diaminodiphenyl sulfone) as an epoxy−thermoset model system in the presence of poly[(methyl methacrylate)-*stat*-(methacrylic acid)] (HT121) or the block copolymers. The cure of the thermoset/block copolymer system has been explored using six different curing processes: 2-phenylimidazole (2-PI), alone or in the presence of methyltetrahydrophthalic anhydride (MTHPA) as comonomer, accelerated dicyandiamide (DICY), and three different diamines as comonomers without accelerator: 4,4′-methylenebis(3-chloro-2,6-diethylaniline) (MCDEA), 4,4′-methylenedianiline (MDA), and DDS. The use of reactive block copolymers instead of nonreactive ones permits a better control of morphology. The materials' performances are analyzed in terms of transparency, glass transition temperature, T_g, and linear elastic mechanics at break (critical intensity factor, K_{IC}).

Introduction

Epoxy-based thermosets, thanks to their two components implementation, are choice elements for varying the characteristics of the end products following a quasi-infinite variety of recipes. To give only one example, the glass transition temperature of an epoxy−amine network can be finely adjusted between −15 and 220 °C as a function of the diamine used in the formulation. As a result, these materials are present in a broad range of applications such as adhesives, printed wiring boards, heavy duty and powder coatings, automotive and aircraft equipment, and so on.

Rubber-modified epoxies are widely described in the literature.[1] The aim of these systems is to reinforce (improve the properties of strength at break) brittle epoxide networks with a rubbery dispersed phase.[2−5] Among them, reactive liquid rubbers, like CTBN (carboxyl-terminated butadiene acrylonitrile), are probably the most popular. Substantial toughness improvements at low loadings while minimizing the effect on other important properties are a major issue. As the considered materials are heterogeneous, this may be achieved only through a careful control of phase separation and morphologies.

Hierarchic materials with a well-defined organization at different length scales are readily obtained from mixtures of block copolymers with homopolymers. This property is exploited in SBM (polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) triblock copolymers) reinforced materials in which the amount of the elastomeric inclusions can be limited to the strictly necessary quantity due to the spontaneous formation of core−shell inclusions. Ideal blending conditions are fulfilled when the homopolymer is compatible with one of the copolymer's blocks; this concept has been used by ATOFINA[6,7] for the reinforcement of PMMA-compatible thermoplastics. Thus, SBM-reinforced poly(vinylidene fluoride) (PVDF) and poly(vinyl chloride) (PVC) have improved mechanical properties: they keep high modulus and are super-tough.

Extending the same strategy to thermosets rises a particular difficulty: on curing, the chemical nature of the material is varying with time; as a result, a block copolymer selected for a given curable composition—for instance, a diblock with one of the blocks compatible with the reactive mixture—may become completely inappropriate once curing is completed. Ideally, the block copolymer entering in the composition has to be compatible with the matrix at any stage of the curing. Epoxy/block copolymer blends have been investigated;[8−14] there are several examples in which this condition has been fulfilled: Könczöl et al.[9] obtained submicronic dispersions of polycaprolactone-*block*-poly(dimethyl-

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[†] Ecole Supérieure de Physique et Chimie Industrielles.

[‡] Institut National des Sciences Appliquées.

[§] ATOFINA.

* To whom correspondence should be addressed. E-mail: francois.tournilhac@espci.fr.

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siloxane)-*block*-polycaprolactone copolymers into an epoxy–amine network. Highly ordered arrays of cylinders have been observed in the thermoset by using poly(ethylene oxide)-*block*-poly(ethylene-*alt*-propylene) copolymers[12–14] with short blocks. In both cases, nanostructured morphologies were obtained thanks to a careful selection of the block copolymer, one of the blocks [polycaprolactone (poly(ethylene oxide))] being initially miscible with the diglycidyl ether of bisphenol A (DGEBA) and probably also with the growing thermoset. More recently, Ritzenthaler et al. have extended the compatible block approach to ABC triblock copolymers, namely polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (SBM) block copolymers.[15–19] In this case, the miscibility of the PMMA block in DGEBA was adjusted by a very accurate choice of the diamine hardener. With respect to the reactive blends, the nature of the curing agent affects the structure of PMMA-modified epoxy networks.[15] The usual reaction-induced (macro)phase separation, RIPS, takes place whenever 4,4′-diaminodiphenyl sulfone (DDS) or 4,4′-methylenedianiline (MDA) is used as a hardener, leading to a material with a two-phase structure. On the other hand, the use of 4,4′-methylenebis(3-chloro-2,6-diethylaniline) (MCDEA) as curing agent does not entail any noticeable phase separation during curing. Going from homo-PMMA to triblock SBM, similar trends have been observed.[16–20] Transparent nanostructured thermosets were obtained solely when the PMMA remained soluble within the growing thermoset during the whole reaction, namely with MCDEA as hardener. When MDA or DDS was used, the phase separation of the PMMA block in the early stage of the process led to flocculated micrometer size elongated structures and opalescent materials.[18] Hence, these systems suffer from the lack of universality: the choice of a surface active agent such as a block copolymer compatible with a vast range of curable compositions is by itself difficult, but maintaining the miscibility in all such mixtures whenever they are reacted seems quasi-impossible.

To obtain an optimum adhesion between the epoxy matrix and the block copolymer, Bates et al.[21–24] used a different approach by incorporating functional groups into the block copolymer. The epoxy groups of glycidyl methacrylate in a poly(methyl acrylate-*stat*-glycidyl methacrylate)-*block*-polyisoprene copolymer were able to react with the amine end groups of the hardener (MDA), so that the block copolymer could cure within the epoxy network (DGEBA–MDA) without macrophase separation. More recently, the high-T_g (DGEBA–DDS) system was investigated in the presence of the reactive tetrablock copolymers, SBMG—polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate)-*block*-poly(glycidyl methacrylate).[25]

In this system, it was shown that oxirane functions of SBMG and DGEBA have approximately the same reactivity with respect to DDS. It was shown also that changing the number of reactive groups in SBMG enables to finely adjust the final morphology of the composite.

In all these works, glycidyl derivatives were considered,[21–25] as well as other oxiranes,[21] as the reactivity of such units can presumably enter in competition with the one of DGEBA. In this paper, we show that it is not necessary to imitate the reactive group of DGEBA and that it is possible to use a broader functional spectrum. Any functional group, preferably located on the nanostructuring block and able to react with either epoxy or amine groups (or even better with both of them), would suit.

In the course of our research in super-tough materials, the need arose of synthetic methods for producing high-T_g composites with a combination of functional properties such as high elastic modulus, improved transparency in a broad temperature range, and stability upon aging. The solubility of PMMA in thermoset precursors and during curing is a key point in the above-mentioned technologies,[6,15–25] but the effective dispersion of PMMA chains inside the cured thermoset may affect the end properties of the composite by averaging the glass transition temperature to a substantially lower value.

Newly synthesized block copolymers, containing the carboxylic reactive group COOH, are hereby investigated. Living anionic polymerization was selected for the ease of obtaining colorless compounds on the kilogram scale. This method permits to reach high degrees of polymerization in dienes, and particularly in butadiene with an excellent control of the PB microstructure at relatively high degrees of polymerization, and affords a high T_g value of the PMMA block due to a mainly syndiotactic character.

The blend properties were studied in terms of covalent bond formation, reaction rates, morphologies, and mechanical properties.

Experimental Section

Materials. Polystyrene-*block*-polybutadiene-*block*-poly[(methyl methacrylate)-*stat*-(*tert*-butyl methacrylate)] SB(MT) triblock copolymer was kindly supplied by ATOFINA. Hydrolysis of SB(MT) was carried out following the HCl/1,4-dioxane procedure,[26] giving rise to polystyrene-*block*-polybutadiene-*block*-poly[(methyl methacrylate)-*stat*-(methacrylic acid)] SB(MA) triblock copolymer. Alternatively, the ethylbenzene solutions stemming from the polymerization reactor were neutralized by the required quantity of *p*-toluenesulfonic acid (APTS, 20% w/w solution in *tert*-butanol) and hydrolyzed by an additional catalytic amount of APTS (typically 10% mol with respect to T).[27,28]

The composition, mass distribution, and microstructure of all synthesized materials have been determined by size exclusion chromatography, infrared, and NMR spectroscopies (Table 1). SB(MT)-77 and SB(MA)-77, containing about 30% SB diblock copolymer, have been purified by stirring at room temperature for 3 days in a cyclohexane/*n*-heptane 60/40 mixture whereby homo-PS and diblock impurities are selectively extracted,[29] affording diblock-free SB(MT)-78 and SB(MA)-78 specimens. For the sake of comparison, similarly synthesized homopolymers poly(*tert*-butyl methacrylate) (PtBMA), an industrial semiscale SBM terpolymer sample (SBM0.03, ATOFINA), and the commercially available poly[(methyl methacrylate)-*stat*-(methacrylic acid)] (P(MMA-*stat*-MAA); HT121, ATOFINA) containing 4.5% of methacrylic acid (MAA) have also been investigated.

Araldite LY556 resin was used as DGEBA epoxy prepolymer, with an average number of hydroxyl groups per molecule of $n = 0.15$. Polyadditions have been performed using 4,4′-diaminodiphenyl sulfone (DDS), 4,4′-methylenebis(3-chloro-2,6-diethylaniline) (MCDEA), and 4,4′-methylenedianiline (MDA) as hardeners. Unless otherwise mentioned, the diamine was used at the stoichiometric ratio of epoxy to N–H amino groups (Table 2).

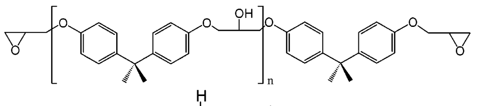
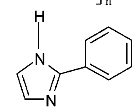
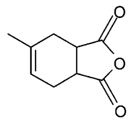
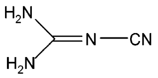
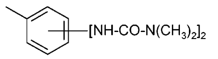
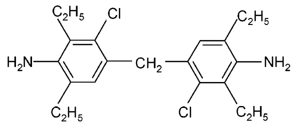
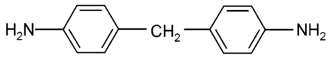
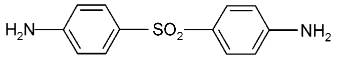
DGEBA was polymerized via an anionic process either alone (homopolymerization) or in the presence of an anhydride. In both cases, 5 wt % 2-phenylimidazole (2-PI) was used as anionic initiator. The anhydride cure was performed with methyltetrahydrophthalic anhydride (MTHPA) at a 0.85 anhydride-to-epoxide ratio.

Table 1. Characteristics of the Synthesized Block Copolymers

		PS precursor		block copolymer			microstructure	tacticity PMMA
sample	polymer[a]	M_n (kg/mol)	M_w/M_n	M_n (kg/mol)	M_w/M_n	% SB[b]	1,2-PB (%)[c]	*mm:mr:rr*
SBM-0.03	$S_{21}B_{21}M_{58}$	16	<1.5	86	<2.4	8	<15	
SB(MT)-214	$S_{31.5}B_{34}(M_{30}T_{4.5})$	28.2	1.18	103	1.48	30	11	72:22:6
SB(MA)-214	$S_{32}B_{34.5}(M_{30.5}A_3)$	28.2	1.18	96	1.40	30		
SB(MT)-77	$S_{33}B_{29}(M_{34.5}T_{3.5})$	23.3	1.21	77	1.58	30	10	74:21:5
SB(MA)-77	$S_{33.5}B_{29.5}(M_{35}A_2)$	23.3	1.21			30		
SB(MT)-78	$S_{24.5}B_{21.5}(M_{49}T_5)$	23.3	1.21	95		0	10	
SB(MA)-78	$S_{25}B_{22}(M_{50}A_3)$	23.3	1.21	93		0		

[a] Subscripts indicate the weight fraction of each block; parentheses indicate a statistical sequence. [b] Together with approximately 3 wt % S homopolymer. [c] Determined by ^{1}H NMR from the $PB_{vinyl}/(PB_{vinyl} + PB_{cis-trans})$ ratio.

Table 2. Characteristics of the Epoxy Prepolymer Comonomers and Initiator Used

Name	Designation	Chemical structure	M (g/mol)	Supplier
diglycidyl ether of bisphenol A	DGEBA (n = 0.15)		382.6	Huntsman
2-phenylimidazole	2-PI		144.18	Aldrich
methyl tetrahydrophtalic anhydride	MTHPA		165	Atofina
dicyandiamide	DICY		84.08	SKW Trostberg
[N,N''-(4-methyl-1,3-phenylene)bis(N',N'-dimethylurea)]	diuron		213.3	SKW Trostberg
4,4'-methylene bis(3-chloro-2,6-diethylaniline)	MCDEA		380	Lonza
4,4'-methylene-dianiline	MDA		198.27	Aldrich
4,4'-diaminodiphenyl sulfone	DDS		248.31	Fluka

Dicyandiamide (*N*-cyanoguanidine) (DICY) was also used as comonomer. With this reagent, cross-linking takes place through a rather complex mechanism involving both step and chain polymerization mechanisms.[30] DICY was used at a concentration of 6.5 wt %, a diuron, [*N,N''*-(4-methyl-1,3-phenylene)bis(*N',N'*-dimethylurea)], 0.4 wt %, was used as anionic initiator. It is in fact a blocked isocyanate, which at a certain temperature releases dimethylamine, able to form a tertiary amine by immediate reaction with DGEBA.[30]

Nuclear Magnetic Resonance Spectroscopy (NMR). ^{1}H NMR spectra were recorded on Bruker DPX300 [SB(MT)-214 and SB(MA)-214] and Bruker DRX500 [SB(MT)-77 and SB(MA)-77] spectrometers using tetramethylsilane (TMS) as an internal standard at room temperature. The copolymers were dissolved in $CDCl_3$ ($\delta = 7.25$ ppm).

The tactitiy of PMMA block was determined from the integral ratio of $C-CH_3$ signals. The peaks at 0.85, 1.02, and 1.20 ppm were recognized as syndiotactic (*rr*), atactic (*mr*), and isotactic contributions (*mm*), respectively.

The polystyrene content was calculated by integration of aromatic protons between 6.20 and 7.50 ppm. The poly(methyl methacrylate) content was calculated by integration of methoxy (OCH_3) protons at 3.60 ppm. Polybutadiene vinyl and cis−trans contributions were respectively calculated by integration of ethylenic protons at 4.90 ppm and between 5.20 and 5.50 ppm. The poly(*tert*-butyl methacrylate) content was calculated by difference with PMMA contribution on aliphatic protons between 0.6 and 2.4 ppm.

Size Exclusion Chromatography (SEC). Molecular weights (M_n) and molecular weight distributions (MWD, M_w/M_n) were measured by size exclusion chromatography (Waters 150 CV) equipped with a differential refractometer detector and a UV detector and 2 × PL GEL MIXED B 30 cm columns with tetrahydrofuran at 40 °C as an eluent at a flow rate of 1.0 mL/min and calibrated with PS as primary standards for samples at a concentration of 1 g/L with an injection volume of 100 μL.

Fourier Transform Infrared Spectroscopy (FT-IR). Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using a Perkin-Elmer 1600 series FTIR spectrometer (KBr windows, 4 scans, resolution 4 cm^{-1}) equipped with a SPECAC 5750 heating jacket. Because of the low amount of reactive units in the block copolymers, investigations have been carried out using the reactive polymer P(MMA-*stat*-MAA) as model compound. For all blends, the components were dissolved in THF prior to being cast onto KBr windows. The solvent was removed at room temperature and then 5 min under vacuum. Polyaddition was carried out at 135 °C in the thermal jacket. The advancement of the reaction in DGEBA/DDS was measured by recording the IR absorption (optical density) at 1630 cm^{-1} (δ_s DDS NH_2). The DDS absorption at 1145 cm^{-1} (ν_s SO_2) was taken as internal standard; degrees of conversion were calculated from the band intensity ratio 1630/1145. In the P(MMA-*stat*-MAA)/DGEBA system, the consumption of oxirane units was monitored by recording the intensity ratio of the 914 cm^{-1} (ν_{as} DGEBA epoxide) vs 1435 cm^{-1} (δ_{as} CH_3) absorption bands. After all experiments, the samples were overheated at 180 °C for 24 h to determine the reference absorption levels corresponding to 100% conversion.

Differential Scanning Calorimetry (DSC). Thermal analyses were performed at a heating rate of 10 °C/min under nitrogen with a TA Instruments Q1000 apparatus equipped with a quench cooling accessory or RCS thermocryostate and operating in the T4 mode. Samples of 5−10 mg, prepared from solvent-cast films, were embedded in nonhermetic aluminum pans. Transition temperatures and heats of reactions were measured from three different blends: DGEBA/DDS (epoxide/N−H = 1), DGEBA/SB(MA)-78 (epoxide/acid = 10), and DGEBA/PtBMA (epoxide/ester = 1).

Dynamic Mechanical Analysis (DMA). DMA was performed on a Rheometric Scientific solid analyzer RSA II. All the measurements were performed at a frequency of 1 Hz and under a deformation of 0.07%. Starting at −150 °C, data points were taken up to 250 °C at a heating rate of 2 °C/min. The samples used were parallelepipedic bars of dimension $1 \times 4 \times 34$ mm^3. The storage and loss moduli E' and E'' were measured as well as the tangent of the phase angle $\tan \delta = E''/E'$.

Transmission Electron Microscopy (TEM). Transparent 2 mm thick films of unblended block copolymers were slowly cast from $CHCl_3$ (SB(MT) case) or THF (SB(MA) case) at room temperature over a period of 2 days. The temperature was subsequently raised under vacuum up to 145 °C, by steps of 10 °C every 12 h.

Transparent films of 1 mm thickness were prepared by slow evaporation from a three-component solution (DGEBA/hardener/SBMX block copolymer) in THF. Solvent evaporation was achieved over 1 week at room temperature, followed by 24 h under vacuum. Curing was fixed to 5 h at 135 or 220 °C.

Ultrathin sections of the samples of about 60 nm thickness were obtained at −100 °C using a Reichert-Jung Ultracut E ultramicrotome equipped with a diamond knife and a liquid nitrogen cryostate.

Staining was performed by treating the ultrathin samples for 30 min with a 4% aqueous solution of osmium tetraoxide. Electron micrographs were taken from a LEO 902 transmission electron microscope equipped with a Megaview-2 SIS digital camera. The epoxy network forming the matrix appears as the light phase, while the dark phase is the polybutadiene of the block copolymer.

Cloud Point Measurement. Pieces of the transparent films whose preparation is described above under TEM were placed on the path of the light beam of a Leitz Orthoplan microscope equipped with a 12 V halogen lamp (color temperature about 3000 K) and a Mettler FP82 hot stage. The light intensity was measured using a Siemens BPW 34 photodiode under −9 V polarization. The reverse current flowing through a 3 kΩ serial resistance was recorded using a Keithley 197A multimeter in the 200 mV range. The data were collected as a function of time and at different temperatures (80, 135, 170, and 200 °C). The transmission Tr was determined by the relation $Tr(t) = (I(t) - I_D)/(I_0 - I_D)$, where I_0 is the intensity at $t = 0$ and I_D the dark current of the photodiode.

Mechanical Tests. The value of the critical stress intensity factor K_{IC} was determined with the help of the linear elastic mechanics at break.[31] This method consists of introducing a known defect at the origin of the break of the sample.

The trials performed at room temperature consist of a three-point flexural test on single edge notched parallelepipedic test bars. The notch is first achieved with a diamond saw before the sample is placed under compression in a vice. A razor blade is inserted into this first notch, and a slight knock on it leads to the propagation of the crack over a limited distance. A crack with a very small radius is thus obtained. The depth of the notch is then measured with a binocular magnifying glass.

The three-point flexural tests were performed on a MTS 2/m apparatus with a 50 daN force sensor and at a crosshead speed of 10 mm/min.

Results and Discussion

Synthesis and Self-Assembly of Unblended SB(MT) and SB(MA). The anionic copolymerization of methyl methacrylate and *tert*-butyl methacrylate has been investigated by Müller et al.[32] As *tert*-butyl esters are much more sensitive to hydrolysis than methyl ones, this reaction offers a simple way of obtaining functionalized PMMA blocks with a controlled number of reactive groups.

By sequential anionic polymerization in ethylbenzene,[33] we obtained SB(MT)-type block copolymers, where the (MT) block is a statistical copolymer of methyl methacrylate and *tert*-butyl methacrylate, with an amount of syndiotactic triads greater than 70%. The polymerization in an apolar solvent led to 1,4-polybutadiene as predominant microstructure. As polymerization was carried out at −40 °C, about 30% of chain termination led to the presence of SB diblock copolymer impurities in the SB(MT) triblock.

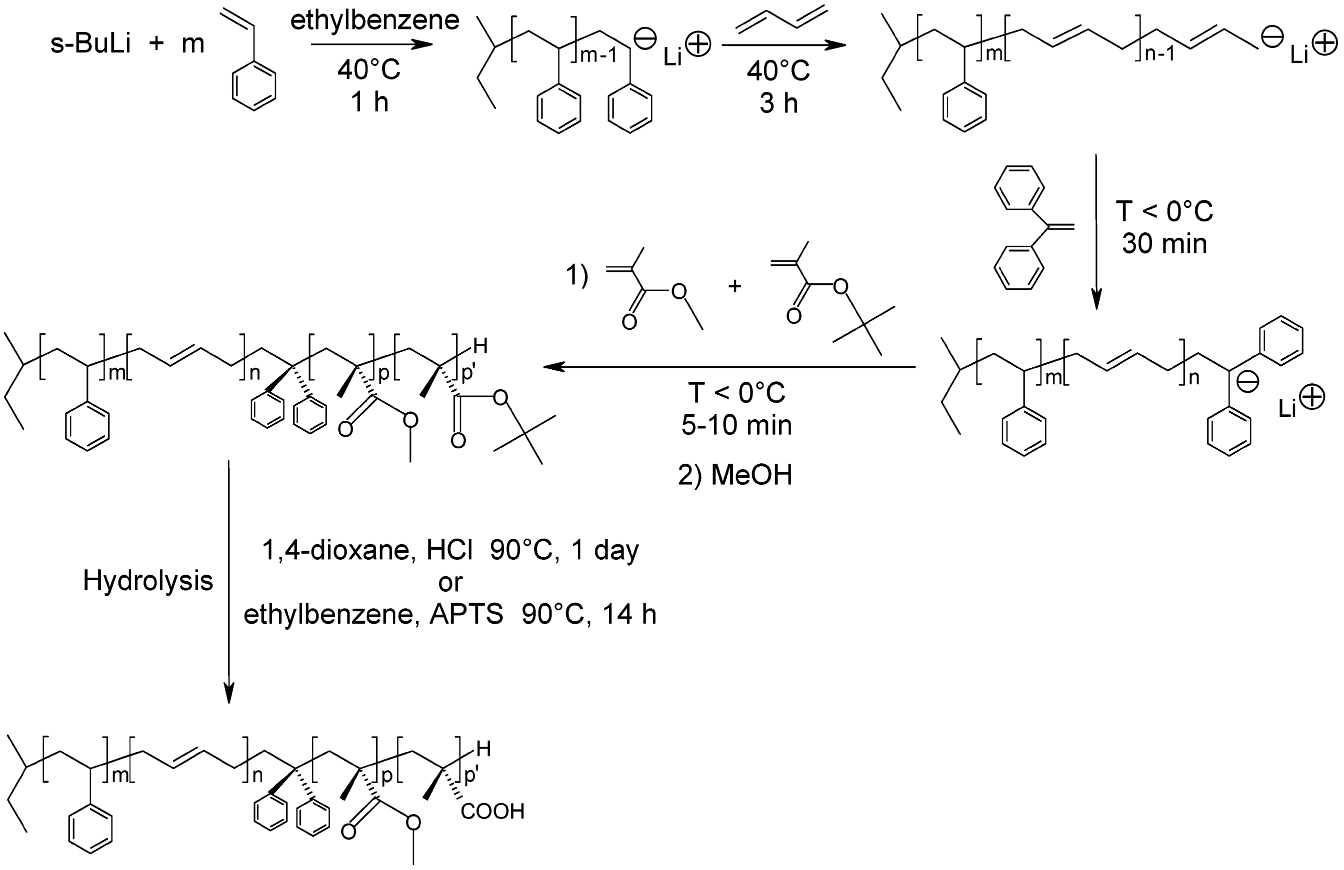
APTS in ethylbenzene[27,28] and aqueous hydrochloric acid in dioxane[26] proved to be equally efficient methods for the selective hydrolysis of *tert*-butyl ester groups leading to the corresponding SB(MA) block copolymer (Scheme 1).

Figure 1a displays a TEM micrograph of SB(MT)-78, with the unstained methacrylic block forming the matrix. In this matrix, four strongly stained cylindrical objects (PB) surrounding a PS core (stained gray) can be recognized (cylinders at cylinder c_ac morphology).[34] From our observations, this morphology is identical to the one observed in an SBM sample of similar composition ($S_{24}B_{19}M_{57}$); it is one of the characteristic structures encountered when the immiscible middle block is in the minority.[35,36] A TEM micrograph of the diblock free copolymer SB(MT)-78 is presented in Figure 1b. One can recognize dark lamellae of PB between fine lamellae of PS and broader ones of PMMA. The layers are strongly undulated and in some places a columnar organization seems to coexist with the lamellar morphology with dark PB cylinders intercalated between light PMMA layers.

It is worth to notice that these morphologies obtained from different solvents are not necessarily equilibrium states, which may also be the reason for the polymorphism in SB(MA) samples.

Morphologies of SB(MT)/Epoxy Blends. In a recent study of SBM block copolymer blends with epoxy−amine networks,[15−19] Ritzenthaler et al. showed that the PMMA block is fully miscible with several DGEBA/aromatic diamine mixtures before curing. Actually, it turns out that the PMMA block has a higher affinity for the DGEBA/MCDEA system than for the DGEBA/MDA or DGEBA/DDS ones. As a consequence, one can observe an important difference of structure in the DGEBA/diamine blends containing 30 wt % of SBM triblock copolymer.[17−19] In the case where the diamine is MCDEA, the system is nanostructured, while there is a flocculation of the triblock copolymer phase with MDA and with DDS. The triblock copolymer phase then forms a coarse filamentary structure in the epoxy−amine network matrix.

Scheme 1. Synthesis of SB(MT) and SB(MA) Block Copolymers by Anionic Polymerization



In our experiments using SB(MT) instead of SBM, the same behaviors were observed: In DGEBA/MCDEA/SB(MT), the TEM analysis of cured films confirms the presence of evenly dispersed PB inclusions of approximately 30 nm in size. Thus, in this case, the nanostructure of the initially miscible system is left untouched throughout the curing process. In contrast, MDA- and DDS-based systems are unstable and flocculate whenever the system is reacted. After cure, SB(MT)-rich domains are detected in the form of elongated structured aggregates of more than 200 nm length. As illustrated in Figure 2, the situation is the same in all other systems investigated. When 2-PI, MTHPA, or DICY is used as a hardener, flocculation occurs as soon as the reactive mixture is processed, giving rise to 100−500 nm large aggregates. In this respect, DGEBA/MCDEA appears as an exception for which the condition of full miscibility (interaction parameter between PMMA and epoxy close to zero or even more probably negative) is fulfilled.

Reactivity of SB(MT) and SB(MA) toward Curable Epoxy−DDS Compositions. In a recent system-

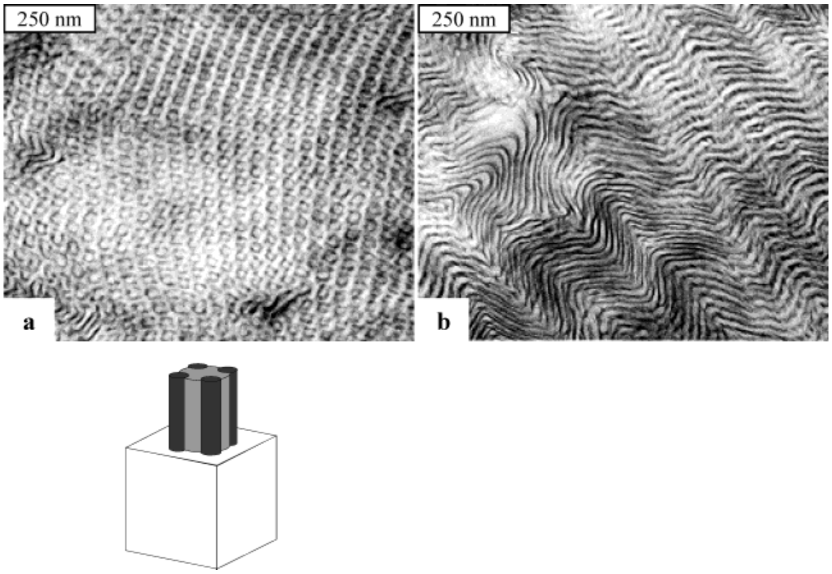


Figure 1. TEM micrographs of the block copolymers (a) SB(MT)-78 and (b) SB(MA)-78. Films prepared from a solution in $CHCl_3$ (a) or THF (b).

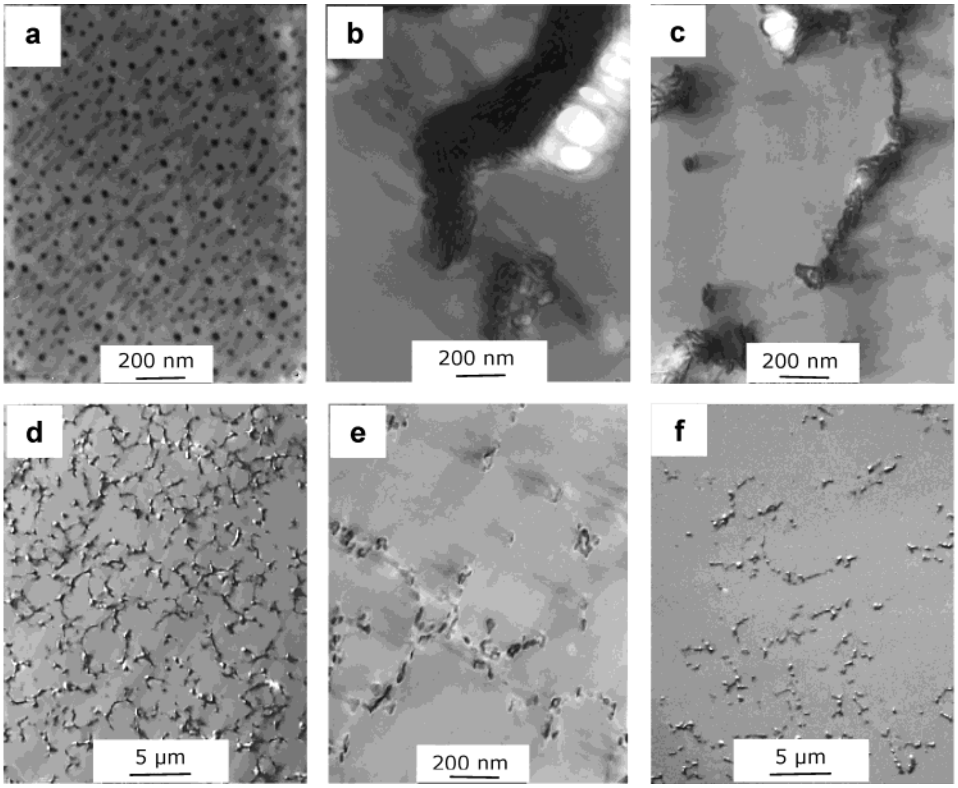


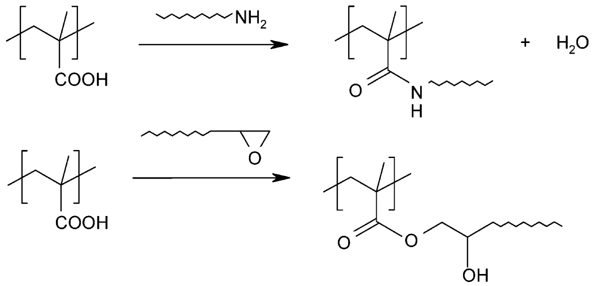
Figure 2. Typical morphologies of several epoxy thermosets, blended with the nonreactive or slowly reactive terpolymers SB(MT) or SBM. TEM micrographs of (a) DGEBA/MCDEA + 10% SB(MT)-77, (b) DGEBA/DDS + 10% SB(MT)-77, (c) DGEBA/MDA + 10% SB(MT)-77, (d) DGEBA/2-PI + 10% SB(MT)-77, (e) DGEBA/MTHPA + 10% SBM-0.03, (f) DGEBA/DICY + 3% SBM-0.03.

atic study, Orr et al.[37] have investigated the reaction kinetics of various functional mixtures able to promote the reactive blending process by condensation of different functional pairs. As far as epoxy or amine groups are concerned, the following series has been found by order of decreasing reactivity: amine + anhydride ≫ epoxy + acid > epoxy + amine > acid + amine.

By taking profit of the reactive blending approach, the situation depicted in Figure 2 may drastically change. Following this strategy, SBMG tetrablock copolymers bearing a reactive poly(glycidyl methacrylate) end-block have already been investigated.[25]

It was shown in that work that, starting from initially miscible compositions, the ability of forming a certain amount of covalent links between the initially miscible block of the block copolymer and the network in the early stage of its formation is enough for preserving the nanostructure until the end of the curing process. The same might be expected from SBMA tetrablock copolymers in which the end-block, A, would be a poly(methacrylic acid) fragment (PMAA). Moreover, when several carboxylic acid functions are close to each other as in PMAA, the formation of anhydride units on heating is likely, leading to an improved reactivity. However, the use of an A-block rises a particular difficulty: in contrast to poly(glycidyl methacrylate), homo-PMAA has a hydrophilic nature. Even at low molar masses, this polymer is completely insoluble in most organic liquids and in particular in DGEBA. Furthermore, PMAA is a high-T_g polymer (228 °C). Hence, a full A-block is likely to phase separate and therefore to slowly react if no precaution is taken to keep it mixed with DGEBA. The solubility of PMMA in DGEBA-type epoxy prepolymers is well-known; PMMA fitted with a certain number of COOH lateral groups may be still compatible and in the same time reactive with respect to epoxy−hardener mixtures. SB(MA) can therefore be proposed as a more appropriate candidate to evaluate the relevance of COOH units in the reactive-block approach. The COOH groups of SB(MA) are likely to react in two different ways in the presence of epoxy−diamine couples (Scheme 2): (1) by elimination of a water molecule and formation of amide bridges with the primary or secondary amine groups when present in the hardener; (2) by opening of the oxirane ring of DGEBA and formation of ester bridges. Similarly, SB(MT) may react through direct aminolysis or transesterification or more likely after thermal decomposition of the *tert*-butyl ester through isobutylene elimination, leading to the corresponding methacrylic acid, which may in turn react according to Scheme 2.

Scheme 2. Two Modes of Incorporation of SB(MA) in the Epoxy−Amine System



Before extending this method to a larger variety of useful compositions, we will focus in the next sections on one particular system, namely DGEBA/DDS, which is relevant in high-T_g applications and notoriously incompatible with SBM. Moreover, it has been already evaluated in the previous work based on SBMG.

Cure of (DGEBA/DDS)/SB(MT) Blends. The transparent noncured blends of DGEBA/DDS with 30 wt %

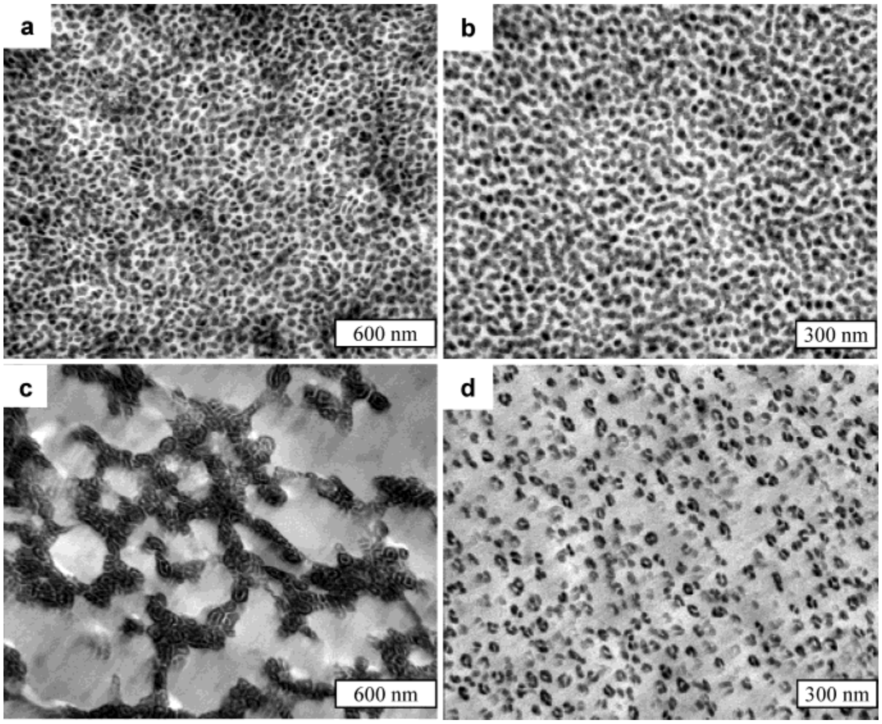


Figure 3. TEM micrographs of (DGEBA/DDS) blends with 30 wt % of (a) SB(MT)-77 before curing, (b) SB(MA)-78 before curing, (c) SB(MT)-77 after curing 5 h at 135 °C, and (d) SB(MA)-78 after curing 5 h at 135 °C.

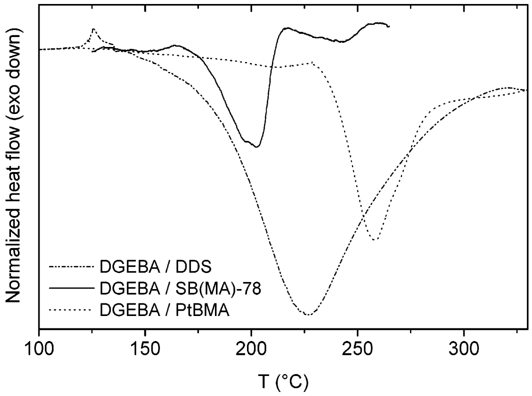


Figure 4. DSC heating traces for cure of DGEBA/DDS, DGEBA/SB(MA)-78, and DGEBA/PtBMA blends. Normalized data: the exotherms recorded in the 150−275 °C region have been normalized by taking into account only the fraction of potentially reactive functional groups in a one-to-one ratio.

of SB(MX) block copolymer (X = T or A) all exhibit nearly the same morphology (Figure 3a,b). The fine dispersion of block copolymer nodules exhibits a raspberry-like morphology[38] with dark spheres of polybutadiene on light spheres of polystyrene in the epoxy−amine matrix. The objects are remarkably uniform with an average size of 70 nm, hence confirming the miscibility of the PMMA block with the DGEBA/DDS precursor.

Condensations or isobutylene elimination involving *tert*-butyl methacrylate units have been hypothesized. Up to 230 °C, no significant heat is detected in the DSC trace of the DGEBA/PtBMA blend (Figure 4). The large exotherm recorded in the 230−290 °C range likely corresponds to the thermal elimination, giving rise to PMAA. As this step may be regarded as rate determining and since no reaction is perceptible on the heating traces of DDS/PtBMA and DDS/SB(MT) blends, SB(MT) grafting, if any, will probably occur after completion of DGEBA/DDS addition.

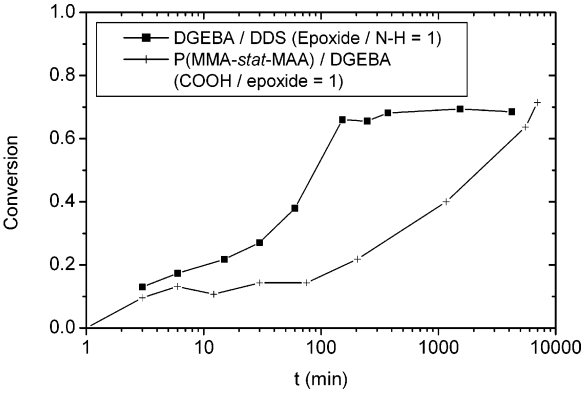


Figure 5. Kinetic studies of the DGEBA + DDS and P(MMA-*stat*-MAA) + DGEBA reactions by infrared spectroscopy at 135 °C.

The advancement of this reaction may be measured by several means; in our experiments, the decay of the δ_s NH_2 absorption relevant to DDS (1630 cm^{-1}) was used to generate the plot of Figure 5.

The light transmission of (DGEBA/DDS)/SB(MT) films as a function of time and curing temperature (cloud point curves) is presented in Figure 6. In all cases (from 80 to 200 °C), the abrupt drop of light transmission indicates a macrophase separation. The glass transition temperature of cured films detected by DMA (not shown here) is the one of the neat DGEBA/DDS matrix.

From comparison of infrared data of DGEBA/DDS and cloud point measurements at 135 °C, it is clear that the phase separation occurs well before gelation (~60% conversion).[29] The reaction kinetics of the DGEBA/DDS system is well documented. By using tabulated values of rate constants and numerical resolution of the differential equations, it is possible to evaluate the degree of conversion as a function of time and temperature.[39] This approach is also valid in blends, provided that

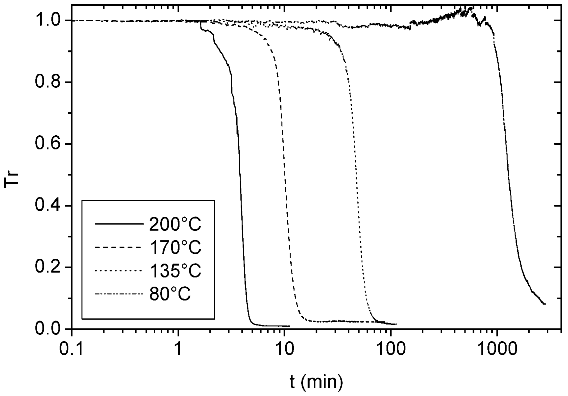


Figure 6. Cloud point curves of a (DGEBA/DDS)/SB(MT)-214 70/30 blend at different curing temperatures.

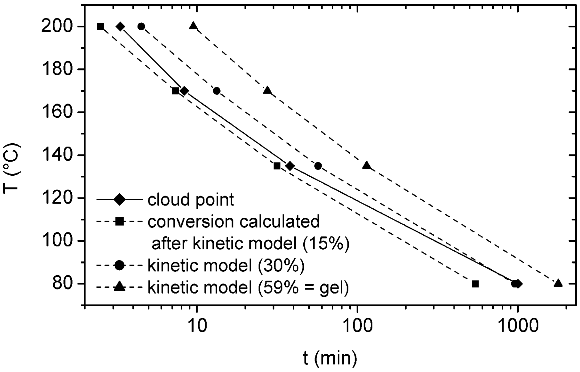


Figure 7. Comparison between the experimental values of cloud point and the conversions calculated after the kinetic model.

dilution effects are taken into account.[15,40] In the particular case of the epoxy/SB(MT) system, it was considered that only the initially miscible (MT) block decreases the effective concentrations of reactive groups. On the basis of this kinetic analysis, the conversion reached at the cloud point ranges from 17 to 32% in the whole 80−200 °C range (Figure 7). This confirms that the epoxy−amine system reacts and expulses the initially miscible block of the block copolymer before it can be grafted, whatever the curing temperature is.

The TEM micrographs of DGEBA/DDS blends with 30 wt % of SB(MT) block copolymers after curing (Figure 3c) display the phase separation between the epoxy−amine network and the block copolymer, which is flocculated and forms a locally structured phase.

Cure of (DGEBA/DDS)/SB(MA) Blends. As mentioned, the methacrylic acid units in the SB(MA) block copolymer do not constitute a block but are randomly dispersed along the PMMA block. A random copolymer poly[(methyl methacrylate)-*stat*-(methacrylic acid)], P(MMA-*stat*-MAA), was selected as a model compound in order to evaluate the reaction kinetics. In Figure 5, the degree of conversion deduced from infrared absorption data is plotted as a function of time. At first sight, the reaction of P(MMA-*stat*-MAA)/DGEBA seems much slower than the one of DDS/DGEBA, and thus the situation is much less favorable than the one encountered with DGEBA/DDS/SBMG in which the epoxide groups of SBMG and DGEBA were found to react at the same rate.[25]

The DSC heating traces of DGEBA/SB(MA) and DDS/SB(MA) blends compared with that of a DGEBA/DDS blend (Figure 4) show that the reaction exotherm occurs slightly earlier for the epoxide + acid reaction in DGEBA/SB(MA) than for the epoxide + amine reaction in DGEBA/DDS (maxima exotherms at 202 and 227 °C, respectively). The DDS/SB(MA) system showed no peak in 10 °C/min experiments, but only a smooth exothermic drift in the 130−320 °C range. Thus, the amine + acid reaction in this mixture proves to be the slowest one.

The TEM micrographs of DGEBA/DDS blends with 30 wt % of SB(MA) block copolymers after curing (Figure 3d) show a nanostructured morphology of raspberry-shaped block copolymer nodules in the epoxy−amine matrix. The diameter of these nodules is of 70 nm in average, like in the initial noncured blend.

A calculation by additivity shows that the deviation induced on the total solubility parameter by the presence of 10 wt % MAA units in the PMMA block is of the order of 2%. This effect alone cannot explain the difference of behavior observed between SBM and SB(MA). Much more probably, the compatibilizing effect of SB(MA) is related to the formation of chemical links. From cloud point experiments performed in DGEBA/DDS/SB(MT), we know that the phase separation is triggered at low conversion rates (below 30%), i.e., in the first 40 min of curing at 135 °C. In DGEBA/P(MMA-*stat*-MAA), even a minor conversion in the early reaction stage (1−3 min) promotes the formation of a sufficient amount of surface active grafted chains able to limit the interfacial tension and to maintain phase stability throughout the hardening. On the other hand, 10 wt % MAA on a 45 kg/mol molar mass PMMA chain represent around 50 reactive units per chain, allowing an effective grafting at relatively low epoxy conversions. It must be stressed that reaching an average number of one grafting per P(MMA-*stat*-MAA) chain does not require more than 2% conversion. In the case of SB(MA), the retention of the nanostructured morphology can thus be explained by the formation of covalent bonds according to the IR data collected from the model compound.

The thermomechanical behavior of cured films (not shown here) confirms this analysis. Up to a temperature of about 130 °C, the storage modulus E' values of DGEBA/DDS, DGEBA/DDS/SB(MT), and DGEBA/DDS/SB(MA) (10 wt % loadings) almost coincide. Actually, near the ambiant, both PS and PMMA are in the glassy state, softening mainly originates from elastomeric PB inclusions. But in the samples considered, the 10 wt % loading of SB(MT)-77 or SB(MA)-77 triblock copolymers do not represent more than a 3% PB volume fraction (Table 1).

At high temperatures, E' values of DGEBA/DDS/SB(MT) are again very close to those of the unblended matrix. In particular, the glass transition of the epoxy−amine system is observed at the same temperature (T_g = 213 °C), confirming that the block copolymer and thermoset do form separated subphases. In DGEBA/DDS/SB(MA), T_g is still recorded at about 210 °C, but a pretransitional decay is observed prior to the glass transition, meaning that a certain amount of the thermoset is plastified by the P(MMA-*stat*-MAA) chains of SB(MA), which is another confirmation of the compatibilizing effect through chemical grafting.

The comparison between SB(MT) and SB(MA) reactivities is also evident from the optical aspect of cured films (Figure 8): nanostructured SB(MA) samples appear opalescent with a hazy blue coloration (yellow in transmission), which is characteristic of Rayleigh-type scattering, while the phase-separated SB(MT) ones are

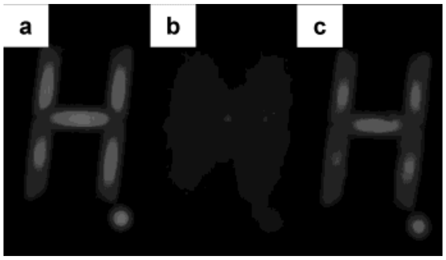


Figure 8. Optical aspect of the samples after curing 5 h at 135 °C. The light-emitting object (a LED display) is seen directly (a) and through 200 μm thick screens of (DGEBA/DDS) blends with 30 wt % of SB(MT)-77 (b) and SB(MA)-78 (c).

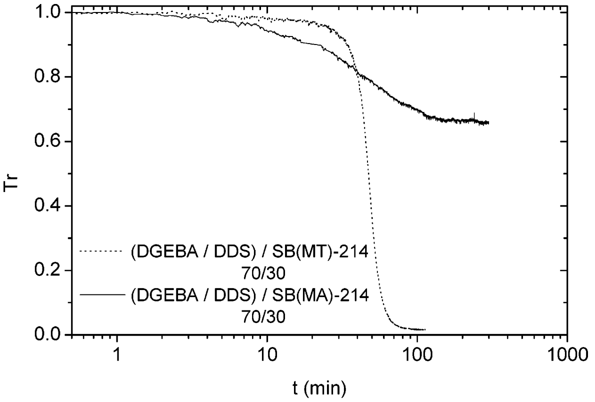


Figure 9. Cloud point curves of (DGEBA/DDS) blends with 30 wt % of SB(MT)-214 and SB(MA)-214 at 135 °C.

opaque (white in reflection), which is more characteristic of a Mie-type scattering by particles larger than 200 nm. The study of the light transmission of (DGEBA/DDS)/SB(MX) (X = T or A) films as a function of time at 135 °C (Figure 9) confirms the visual observation: in contrast to the blend with SB(MT) which appears as opaque (optical density higher than 1.8 for 1 mm thick film), only a fraction of the light is scattered for the blends with SB(MA), this being linked to the fact that the samples become opalescent. The overall optical density for a 1 mm film is not larger than 0.18 (66% transmission). This result may be compared to available data. In DGEBA/DDS/SBMG, a light transmisson of 85−90% is reported[25] for the same film thickness (optical density of about 0.05).

Extension of the Reactive Nanostructuring Block Approach to Other DGEBA/Hardener Systems. Considering the main curing processes used in epoxy technology, the above methodology was applied to a number of hardeners which are known to polymerize with DGEBA either by polyaddition or by anionic chain polymerization. As with DDS, the ring cleavage by the two aromatic diamines MDA and MCDEA results in the formation of C−N bonds, whereas the homopolymerization of DGEBA or its copolymerization with an anhydride like MTHPA, initiated by 2-PI, reminds of the chain homopolymerization of ethylene oxide. It is generally admitted that DICY[29] is able to react by both means, leading to the formation of C−O and C−N bonds.

Table 3. Morphologies and Glass Transition Temperatures of the Different Blends Studied after Curing

	SB(MT)		SB(MA)		
hardener	type	size (nm)	type	size (nm)	T_g (°C)
MCDEA	micelles	30	micelles	30	187
DDS	filaments	>1000	raspberry aggregates	70	211
MDA	filaments	>1000	micelles	30−70	187
2-PI	filaments	>1000	micelles	30	144
MTHPA/2-PI	filaments	>200	micelles	30	124
DICY/diuron	filaments	>1000	vesicles	300	141

When operating with 10% (3% with DICY) of block copolymer in these different systems, four different morphologies can be recognized (Table 3). With MCDEA, which was previously investigated in nonreactive SBM composites, fine dispersion of spherical micelles was observed in both SB(MT) and SB(MA) blends (Figures 2a and 10a), confirming the total miscibility of this reactive mixture with the methacrylic block throughout the curing process. This finding is not really surprising with SB(MA), as reactive groups can only enhance a situation which is already close to the optimum. In contrast, with SB(MT), the presence of 10% comonomers might be enough to bring the system out of its miscibility window. By group contribution additivity, we estimated that the Hansen parameters are not affected by more than 0.2−0.6 MPa$^{1/2}$. Evidently, this alteration was not able to upset the thermodynamics of the system as shown in Figure 10a. It is then very unlikely that such a subtle change will be efficient for driving another system toward miscibility. Actually, with SB(MT), all other investigated systems display a coarse filamentary structure made up of swarms of raspberry objects (Figure 2b,d−f), as observed above with DDS (Figure 2c). Most likely these swarms are the results of flocculation of initially well-dispersed nodules before cure. With all hardeners, the use of SB(MA) is effective in reducing the size of inclusions. MCDEA is an exception because with or without reaction with the triblock, the nanostructure is always stabilized. The results obtained with the other systems is an indirect proof of the reaction between the acid groups of methacrylic acid and the epoxide and amine groups of the epoxy−hardener systems. With MDA, 2-PI, and MTHPA, the morphologies after cure are very similar to those of MCDEA compounds. A scarce tendency to flocculate is still detectable with DDS. At 10% SB(MA) concentration, large areas up to 1 μm in size are inclusion free (Figure 10c). This effect, probably present also in 70/30 compositions, may be masked due to the large volume fraction of inclusions (Figure 3d). Finally, a particular morphology was observed with DICY as the hardener (Figure 10f). In this case, the epoxy/block copolymer system self-assembles in the form of vesicles of a few hundreds of nanometers diameter rather than in raspberry-type objects. The interfacial region, in which a strong dark/light contrast can be detected, is probably made up of several segregated sublayers. Inside the vesicles, but also to a less extend outside, highly stained dots reveal the presence of PB-containing micelles. In ultrathin cuts, the presence of voids at the copolymer/thermoset interface (which is sometimes evident especially with large inclusions, e.g., Figures 2b,c and 10f) shows the imperfect adhesion between the subphases.

The incidence of the nanostructure and the possible presence of such defects on the mechanical properties will be examined in the following section.

Mechanical and Thermal Properties of Block Copolymer/Epoxy Network Blends. The mechanical properties of the different epoxy networks alone and blended with SB(MT) or SB(MA) block copolymers are

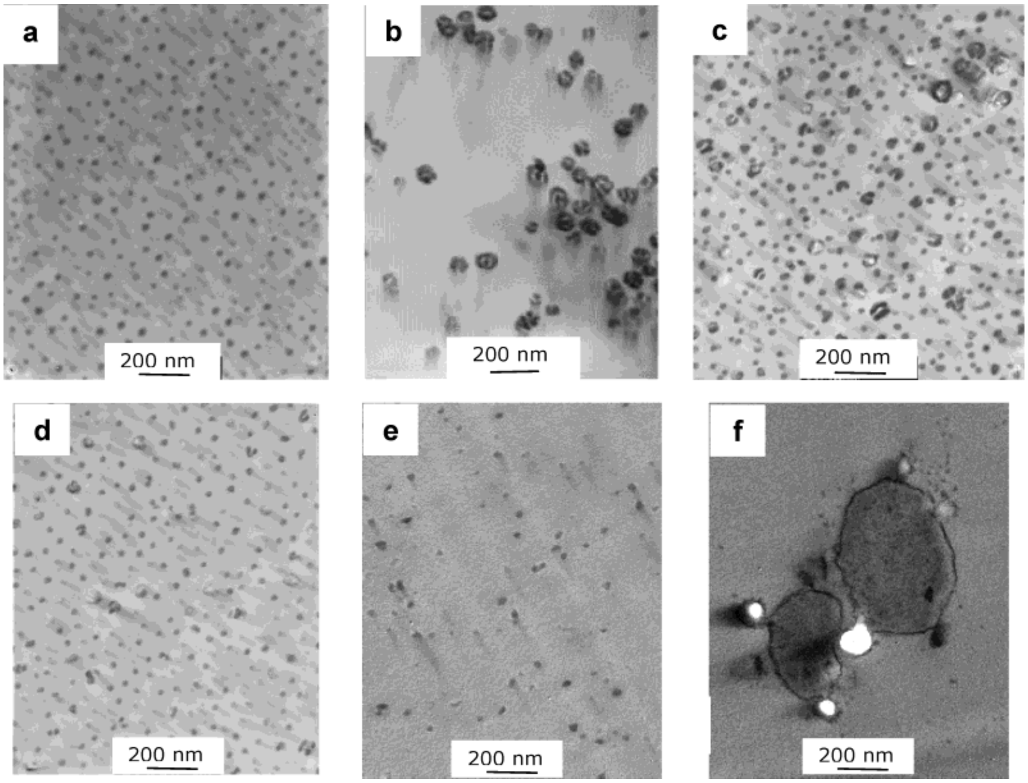


Figure 10. TEM micrographs of several epoxy thermosets, blended with the reactive terpolymer SB(MA). (a) DGEBA/MCDEA + 10% SB(MA)-77, (b) DGEBA/DDS + 10% SB(MA)-77, (c) DGEBA/MDA + 10% SB(MA)-77, (d) DGEBA/2-PI + 10% SB(MA)-77, (e) DGEBA/MTHPA + 10% SB(MA)-77, (f) DGEBA/DICY + 3% SB(MA)-77.

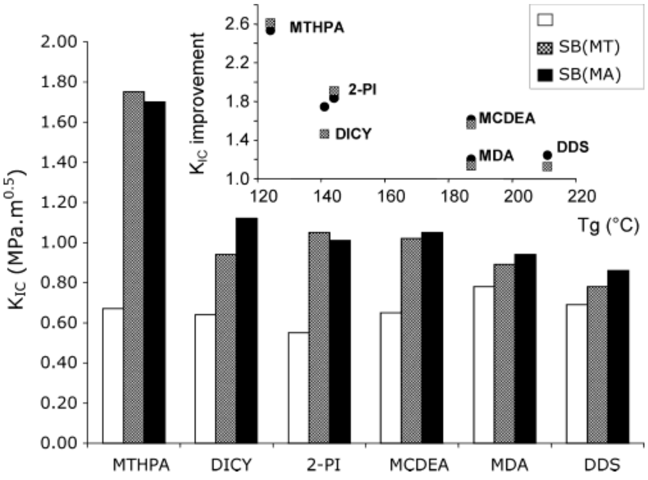


Figure 11. Value of the critical intensity factor, K_{IC}, as a function of the hardener type for different DGEBA/hardener networks alone and blended with 10% of SB(MT) or SB(MA) block copolymers.

presented in Figure 11. First of all, it must be noticed that both copolymers lead to reinforced materials, whatever the nature of the hardener and the curing process.

The effect of toughening by 10 wt % block copolymer was most evident in the epoxy−anhydride system (MTHPA) and to a lesser extent in anionically polymerized DGEBA (2-PI) that respectively show 2.6- and 1.8-fold improvements in K_{IC}. In these cases, the use of the reactive block copolymer SB(MA) instead of the nonreactive one is not beneficial. It may be considered that, in such hardening processes in which chain polymerization is involved, the COOH groups of SB(MA) may cause transfer reactions to occur.[41]

In epoxy/aromatic diamine networks, the value of K_{IC} is multiplied by a 1.15−1.6 factor in block copolymer blends. In this series, MCDEA appears as a privileged system. However, the level of toughening is approximately the same in both SB(MT) and SB(MA) adducts, which is not surprising having in mind that these composites display the same morphology and similar good adhesion between phases. Block copolymer toughening is also effective in DDS and MDA compounds, but in these cases, the improvement induced by a reactive one is more significant. This result is to be correlated with both the change of morphology induced by reactive blending with a reduction of size down to 30−70 nm and an increase of the adhesion between the two phases.

In the case of the DGEBA−DICY networks, the 1.5-fold increase of K_{IC} with only 3% of SB(MT) block copolymer is noteworthy, even though macrophase separation takes place during the reaction. In this matrix, the use of reactive copolymer is beneficial as in this case the total improvement is 1.7 when SB(MA) is employed instead of SB(MT). These data are even more surprising when considering that in this system the interfacial adhesion is less than perfect. The size reduction alone cannot explain such a large difference. In our opinion, this may be correlated with the appearance of the vesicular morphology. Such organization of the block copolymer in vesicular and other types of core−shell morphologies has been recently correlated with improved toughness in epoxy matrices.[22]

In all cases, the glass transition temperature of the blends were found to be very close to those of the neat matrices, with no shift larger than −4 °C. This feature has to be taken into consideration in the search of a performance compromise. Despite high levels of reinforcement, the conventional elastomeric additives induce a drop of the glass transition temperature. For instance, in the DGEBA/DICY system modified by 5% of reactive nitrile rubber (CTBN),[42] a 1.85-fold improvement is achieved with a −12 °C change of T_g. In the same matrix, the use of 3% SB(MA) induces a similar toughening, but without alteration of T_g.

Finally, it may be remarked from Figure 11 that, in agreement with the literature,[43,44] the lower T_g matrices lead to the highest reinforcement levels.

Conclusion

The present study demonstrates that the structuring power of SB(MT) and SB(MA) copolymers is retained in their blends with different types of epoxy-based reactive mixtures. Taking advantage of this property, we explored the implementation of block copolymer−epoxy composites with an organization at submicronic levels. By investigating DGEBA/DDS as a model system in the presence of P(MMA-*stat*-MAA) or the block copolymers, we were able to quantify the relative kinetics of grafting, hardening, and phase separation. In normal conditions of cure, the reactivity of SB(MT) is not sufficient for creating efficient links between the matrix and the block copolymer, and the final morphology of the composite cannot be controlled by this means. The situation is completely different once the methacrylic block is fitted with a certain number of randomly dispersed carboxylic acid groups as in SB(MA). In this case, the formation of ether links by addition of COOH onto the oxirane ring is quick enough to prevent phase separation to occur in the early stage of cure. In comparison with SBMG already investigated, SB(MA) seems to be very slowly reactive. Nevertheless, a large conversion index is not necessary to prevent the flocculation. Most probably, the formation of a certain amount of grafts in the early stage of the curing is sufficient to stabilize the interfaces and preserve the nanostructure until the gel point. The materials obtained by this means are nanostructured and present a slightly opalescent aspect similar to those obtained from SBMG[25] although slightly less transparent. But in contrast to glycidyl methacrylate compounds, SB(MA) can be easily synthesized by anionic polymerization in a micropilot reactor. In MCDEA cured compounds, already known to form nanostructured composites with SBM, the use of reactive groups does not afford further size reduction. Applying this methodology to a variety of other SBM incompatible systems permitted in all cases a better control of morphology. Hence, the use of reactive block copolymers is a more universal way of blending, which probably appears as the main income of this approach.

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