

Epoxy Formulation Including an Acrylic Triblock Copolymer Adapted for Use in Filament Winding

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Commercial triblock copolymers with a poly(butyl acrylate) (PBUA) central block joined to two poly(methyl methacrylate) (PMMA) end blocks (denoted as MAM) or to two random copolymers end blocks based on MMA and *N,N'*-dimethylacrylamide (DMA) (denoted as MAM-N), can be employed as toughening agents for thermoset composites. However, their use in epoxy formulations for filament winding, requiring low viscosities during the fiber-impregnation step associated with an adequate glass transition temperature of the cured product is not trivial. In this study, we show that a blend of diglycidylether of bisphenol A (DGEBA), 4,4'-diamino-3,3'-dimethyldicyclohexylmethane (3DCM) and benzylamine (BA), with 20% of amine hydrogens provided by BA, and containing 5 wt% MAM, can be used for these purposes. The addition of MAM increased the critical stress intensity factor from 0.63 MPa.m^{1/2} to 1.0 MPa.m^{1/2}, the glass transition temperature from 138°C to 145°C, and the glassy modulus at 25°C from 2.95 GPa to 3.15 GPa. MAM was a better choice for the envisaged applications than MAM-N because it led to solutions of lower viscosity. The higher viscosity produced by MAM-N was explained by specific interactions between the epoxy-amine solvent and DMA units present in its terminal blocks. POLYM. ENG. SCI., 00:000–000, 2016. © 2016 Society of Plastics Engineers

INTRODUCTION

Cross-linked epoxies exhibit outstanding properties that have placed them as the standard option for a variety of applications such as adhesives, coatings, and composites for structural applications [1]. Some processes used for the manufacture of composites require formulations with a low initial viscosity, an appropriate pot-life and a relatively high glass transition temperature (T_g) after full cure. This is the case of formulations used in filament winding processes. A variety of epoxy formulations is available for these purposes from different suppliers. However, when toughening of the epoxy matrix is required, development of an appropriate formulation is not a simple task due to viscosity limitations. A variety of toughening agents can be added to the initial formulation such as rubbers (CTBN, ATBN, etc.) [2–7], thermoplastic polymers [8], core-shell particles [9–11], or a large variety of block copolymers [12–19].

In this study, we selected a couple of acrylic triblock copolymers (Nanostrength[®], Arkema, France), as toughening agents of an epoxy formulation adapted for filament winding. These triblock copolymers have a poly(butyl acrylate) (PBUA) central block joined to two poly(methyl methacrylate) (PMMA) end

blocks (denoted as MAM) or to two random copolymers end blocks based on MMA and *N,N'*-dimethylacrylamide (DMA) (denoted as MAM-N). The rubbery central block (PBUA) is initially immiscible or becomes immiscible during polymerization [20]. As long as the terminal blocks remain miscible in the epoxy matrix during reaction, micellar morphologies are generated with a PBUA core and a miscible shell. The random copolymer containing DMA provides a better miscibility of the shell with several epoxy formulations [21, 22]. Addition of small amounts of these block copolymers produces a significant increase of the fracture resistance of neat epoxy formulations and their composites [21, 23–30].

After selecting the toughening agent, the epoxy formulation must be adapted to achieve low values of viscosity and reactivity at the temperature employed for the fiber-impregnation step, and required values of thermal and mechanical properties of the cured products. Several hardeners are proposed in the literature [21, 23–30] and in Arkema brochures for use in combination with typical epoxy monomers based on diglycidylether of bisphenol A (DGEBA) and Nanostrength[®] copolymers. However, the resulting formulations do not meet requirements for use in filament winding or do not give desired properties of final materials (in particular, we focused on formulations leading to a cured product with a glass transition temperature, T_g , located above 130°C). Therefore, the aim of this study was to develop an epoxy formulation toughened by Nanostrength[®] copolymers, suitable for filament winding, and leading to a T_g of the cured polymer network equal to or higher than 130°C.

EXPERIMENTAL

Materials

The epoxy monomer was DER 383 (Dow), based on diglycidylether of bisphenol A (DGEBA), with an epoxy equivalent weight of 183.8 g/eq and a viscosity of 12500 mPa.s at 25°C. The curing agent was 4,4'-diamino-3,3'-dimethyldicyclohexylmethane (3DCM, Ancamine 2049 from Air Products), with an equivalent weight of 62.8 g/eq. The reactive diluent was benzylamine (BA 99% from Riedel-de Haen), with an equivalent weight of 53.6 g/eq. The triblock copolymers, Nanostrength[®] MAM and MAM-N, were kindly supplied by Arkema (France). Both have a poly(butylacrylate) (PBUA) central block; MAM has two terminal poly(methyl methacrylate) (PMMA) blocks and MAM-N has two terminal blocks based on random copolymers of methylmethacrylate (MMA) and *N,N'*-dimethylacrylamide (DMA). Characterization of these block copolymers is reported in the Results and Discussion section. Chemical structures of the different compounds are shown in Fig. 1.

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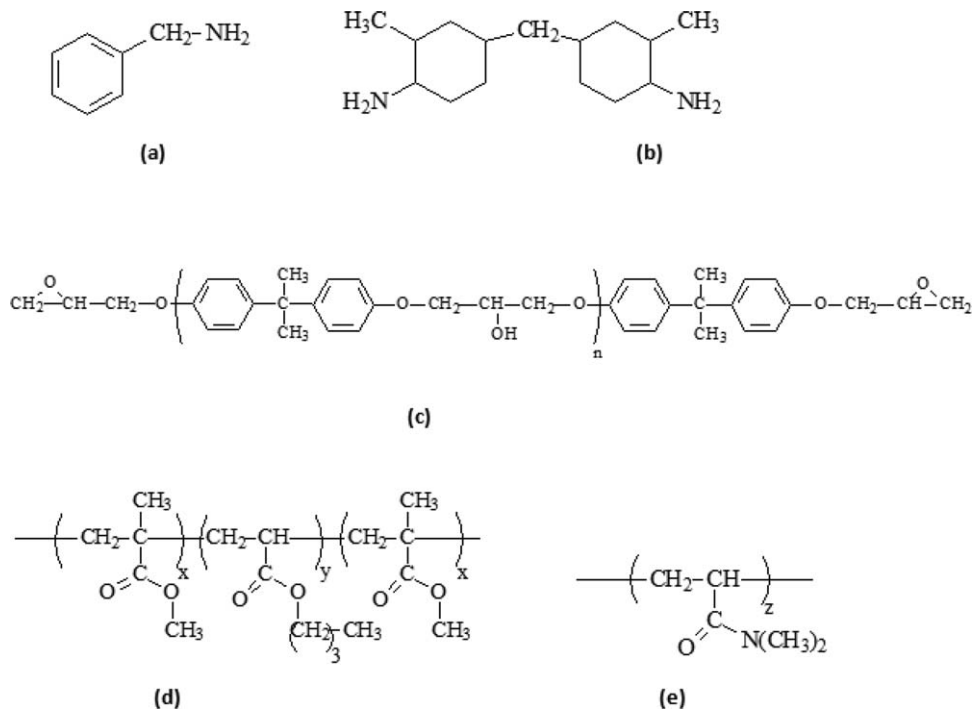


FIG. 1. Chemical structures of different compounds: (a) benzylamine (BA), (b) 4,4'-diamino-3,3'-dimethyldicyclohexylmethane (3DCM), (c) diglycidylether of bisphenol A (DGEBA), (d) PMMA-PBuA-PMMA (MAM), and (e) *N,N'*-dimethylacrylamide segment (DMA).

Sample Preparation

Neat epoxy formulations were prepared by mixing stoichiometric amounts of DGEBA with either 3DCM, BA, or 3DCM/BA blends. The composition of blends is indicated by the fraction of amine hydrogens supplied by BA. For example, the formulation DGEBA-3DCM/BA (20%) is based on 3DCM (2 moles), BA (1 mol), and DGEBA (5 moles). In this formulation, 20% of amine hydrogens (2/10) are supplied by BA.

Epoxy formulations containing 5 wt% BCP were prepared as follows. First, the appropriate amount of the block copolymer was completely dissolved in DGEBA at 160°C for 30 min with mechanical stirring. The solution was cooled to room temperature and the stoichiometric amount of either 3DCM, BA, or a 3DCM/BA blend was added.

Cured specimens were obtained by casting the formulation in an aluminum mold (20 × 15 × 0.5 cm), coated by a Teflon® film. Cure was performed in a programmable convection oven with the following thermal cycle: 60 min at 90°C, 90 min at 120°C and 60 min at 180°C. Formulations prepared without 3DCM were cured at 80°C for 2 h. Full conversion was attained with these thermal cycles.

Characterization Techniques

Glass transition temperatures (T_g) of cured samples were determined by differential scanning calorimetry (DSC, Shimadzu DSC-50). Measurements were carried out at a heating rate of 10°C/min and T_g values were taken at the midpoint of the heat flow transition.

Storage and loss moduli as a function of temperature were measured by dynamic mechanical thermal analysis (DMTA,

Q800 TA Instrument), in the three-point bending mode, at 1 Hz and 5°C/min. Specimen's dimensions were 12.5 × 65 × 5 mm, with a 50 mm span.

The evolution of viscosity during the storage at 40°C was measured with a rheometer (Anton Paar, Physica MCR-301), provided with a CTD 600 thermal chamber. A parallel-plate configuration was used at a rotation speed of 1 rpm.

Molar mass distributions of the block copolymers were determined by size exclusion chromatography (SEC, Knauer K-501, RI detector Knauer K-2301), employing polystyrene standards. Chromatograms were obtained at 20°C with a Waters HR4E column, and THF as eluent at a rate of 1 mL min⁻¹.

The composition of block copolymers was determined by ¹H-NMR in deuterated chloroform with a Bruker Avance II 500 MHz NMR spectrometer. The molar fraction of methyl methacrylate (MMA) was obtained by integration of the peak located at 3.64 ppm corresponding to the chemical shift of the methyl protons of the ester group [31]. The molar fraction of butyl acrylate (BuA) was determined by integration of the peak located at 4.1 ppm assigned to the chemical shift of protons of the methylene of the butyl group next to the oxygen atom [31]. The molar fraction of *N,N'*-dimethylacrylamide (DMA) in MAM-N was determined by integration of peaks located at 3.02 ppm (cis methyl groups) and 3.05 ppm (trans methyl groups) [32].

Transmission electron microscopy (TEM) images were recorded using a JEOL 100CX device. Ultrathin sections (~60 nm in thickness) were obtained employing an LKB ultramicrotome. They were stained with RuO₄ vapor [33]. Scanning electron microscopy (SEM) images were obtained with a Jeol JSM-6460LV device after coating fracture surfaces with a fine gold layer.

TABLE 1. Glass transition temperatures of DGEBA-3DCM/BA epoxy networks as a function of the BA fraction.

% BA	0	20	40	100
T_g (°C)	181	138	96	56

The critical stress intensity factor, K_{IC} , of selected formulations was determined by three-point bending tests according to the standard ASTM D5045. Single-edge-notched beams (SENB), with dimensions $4.5 \times 9 \times 40$ mm, were tested using an Instron 3369 device with a crosshead speed of 0.2 mm/min. Reported values correspond to the average of six valid results for each formulation.

RESULTS AND DISCUSSION

Factors Taken into Account for Developing the Formulation

Let us first address the issue of the convenient morphologies for an effective toughening. The final morphology depends on the miscibility of terminal blocks (PMMA or PMMA-co-PDMA) during polymerization. If they keep their miscibility up to high conversions, micellar morphologies (spherical, wormlike, vesicles) are generated and the resulting materials remain transparent. If the miscibility is lost, a polymerization-induced phase separation takes place [7], generating a distribution of micrometer-size domains giving translucent or opaque cured materials. A few DGEBA hardeners enable to keep the miscibility of PMMA blocks up to high or complete conversion. Some of these hardeners are MCDEA: 4,4'-methylenebis(3-chloro 2,6-diethylaniline) [34], MDEA: 4,4'-methylenebis(2,6-diethylaniline) [35], and phenolic novolacs [33, 36]. Unfortunately, none of these hardeners is appropriate for the required application. The use of PMMA-co-PDMA as terminal blocks can produce miscibility with other hardeners due to the compatibilizing effect of DMA units [21, 22].

Micellar dispersions produce impressive increases in the fracture resistance. For example, Kishi et al. [33] used two MAM block copolymers to toughen a DGEBA-phenolic novolac matrix. For a 10 wt% MAM, the critical stress intensity factor (K_{IC}) increased from 0.64 MPa.m^{1/2} for the neat matrix to 1.87 MPa.m^{1/2} for a material with spherical micelles, and 2.49 MPa.m^{1/2} for a network with cylindrical micelles. However, other studies report similar toughening effects when the block copolymer is dispersed as micelles or is phase separated as larger particles. For example, Bashar et al. [28] used MAM and MAM-N block copolymers to toughen a commercial epoxy formulation. While MAM-N generated a dispersion of spherical micelles (transparent material), MAM produced a dispersion of spherical domains with sizes in the range of 200–400 nm (opaque material). However, they produced the same increase in K_{IC} (from 0.78 MPa.m^{1/2} for the neat matrix to 1.51 MPa.m^{1/2} for the opaque material containing 5 wt% MAM, and 1.48 MPa.m^{1/2} for the transparent material with 5 wt% MAM-N). Therefore, in our case the selection of the diamine was not determined by the morphologies generated. The focus was placed on a liquid diamine with a slow reactivity at the process temperature (i.e., in the pot used for the impregnation of fibers in filament winding), and leading to a high T_g of the cured material. This condition was necessary to support the decrease in T_g produced by the addition of the neces-

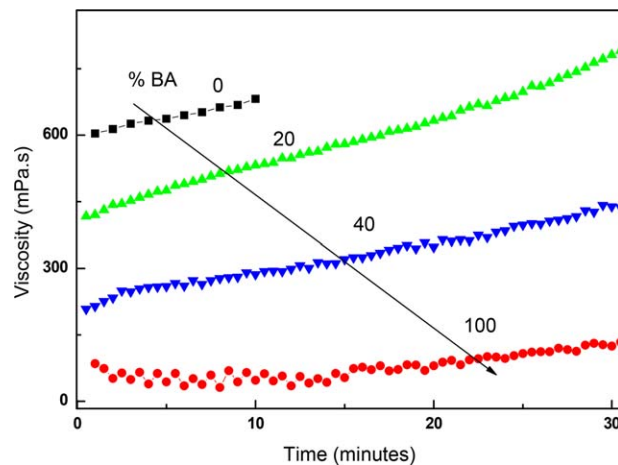


FIG. 2. Evolution of viscosities of selected DGEBA-3DCM/BA formulations with different fractions of amine hydrogens supplied by BA, at 40°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sary amount of a reactive diluent. The selected diamine was 4,4'-diamino-3,3'-dimethyldicyclohexylmethane (3DCM) with a viscosity of 142 mPa.s at 20°C. Previous studies report that PMMA is initially miscible in DGEBA-3DCM formulations, but becomes phase separated in the course of polymerization [37]. Therefore, in the case of MAM micrometer-size morphologies may be expected. The behavior of MAM-N in DGEBA-3DCM formulations was not previously reported.

A reactive diluent was necessary to adapt the initial viscosity to the required value (in the range of 500–1000 mPa.s). A variety of reactive diluents is available from commercial suppliers. Typical ones are based on 1,4-butanediol diglycidylether, 1,6-hexanediol diglycidyl ether, butylglycidyl ether, and several other alkylglycidyl ethers. Many other reactive diluents have been proposed in the academic and patent literature. In this study, we analyzed the possibility of using benzylamine (BA) as a reactive diluent to reduce the viscosity of toughened DGEBA-3DCM blends. BA has a very low viscosity (1.82 mPa.s at 20°C) and shows an ideal reaction with DGEBA (primary and secondary amine hydrogens react at the same rate) [38, 39]. The counterpart is that it reacts at a higher rate with DGEBA than 3DCM. A deleterious effect on the pot-life may be expected, partially compensated by the increase in the gel conversion produced by the introduction of a monoamine in the formulation. If the use of BA generates an important reduction of pot-life, it could be replaced by less reactive cycloaliphatic monoamines such as cyclohexylamine (viscosity equal to 1.944 mPa.s at 25°C).

Neat Epoxy Formulations

In this section we analyze the properties of formulations containing different amounts of the reactive diluent (BA) but

TABLE 2. Characteristic parameters of the triblock copolymers (BCP).

BCP	M_n (kg/mol)	M_w (kg/mol)	molar %:	MMA	BuA	DMA
MAM	46	66		59.8	40.2	—
MAM-N	47	71		46.8	46.0	7.2

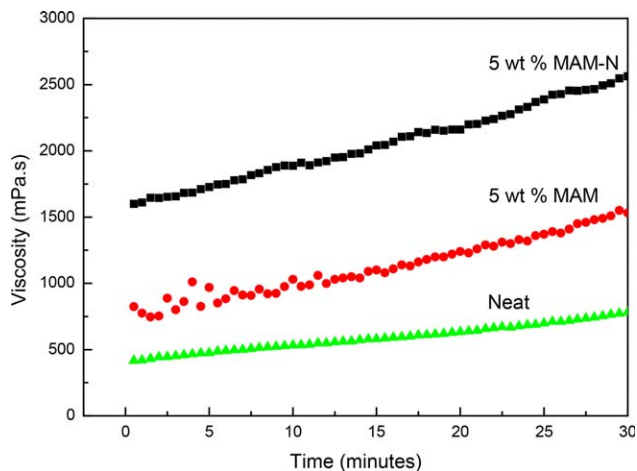


FIG. 3. Evolution of viscosities of DGEBA-3DCM/BA (20%) formulations at 40°C. Comparison between the neat formulation and those toughened with 5 wt% MAM or MAM-N. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

without toughening agent. DSC thermograms of cured materials showed a single glass transition temperature without any residual exotherm meaning that the reaction was completed with selected thermal cycles. Glass transition temperatures for samples containing different BA contents are presented in Table 1.

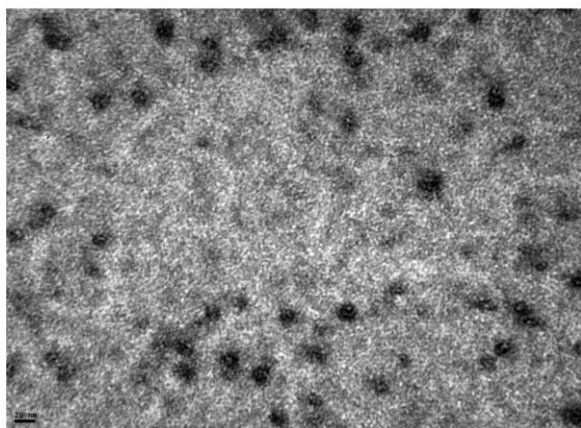
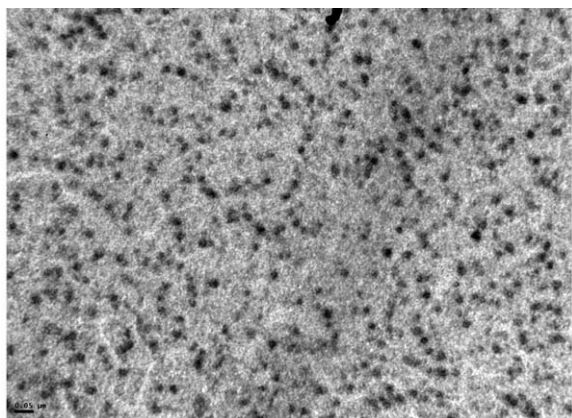


FIG. 4. TEM images of DGEBA-BA cured samples containing 5 wt% MAM-N. Bars indicate 50 nm in the upper image and 20 nm in the lower image.

Depending on the BA amount used as reactive diluent, glass transition temperatures of cured formulations spanned between 56 and 181°C. The maximum BA amount that can be added as reactive diluent depends on the envisaged application. For example, if a typical DGEBA-MTHPA (methyl tetrahydrophthalic anhydride) formulation used in filament winding processes is replaced by the DGEBA-3DCM/BA formulation, the maximum BA amount that can be added is close to 20% (in fraction of amine hydrogens as indicated in the Experimental Section). This gives glass transition temperatures slightly higher than those obtained using DGEBA-MTHPA formulations.

The evolution of viscosities of different DGEBA-3DCM/BA formulations, at 40°C, is shown in Fig. 2. The partial replacement of 3DCM by BA produced a significant decrease in the initial viscosity.

Toughened Epoxy Formulations

The commercial block copolymers were characterized by ¹H-NMR spectroscopy and size exclusion chromatography. Results are presented in Table 2.

Both copolymers have similar molar mass distributions and fractions of the central rubbery block. The main difference is that the end blocks of MAM-N contain 13.3% (7.2/54) molar fraction of DMA.

The influence of adding 5 wt% MAM or MAM-N on the evolution of the viscosity of DGEBA-3DCM/BA (20%) formulations, at 40°C, is shown in Fig. 3.

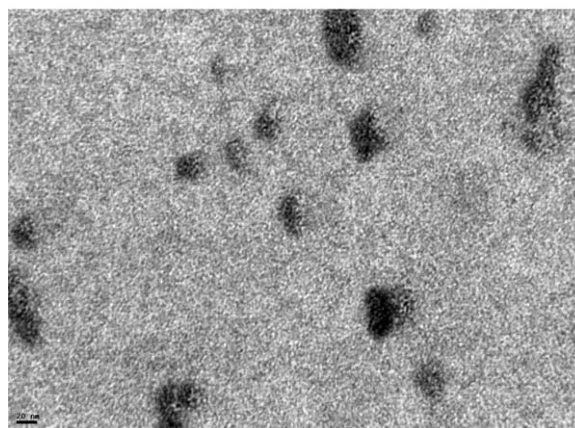
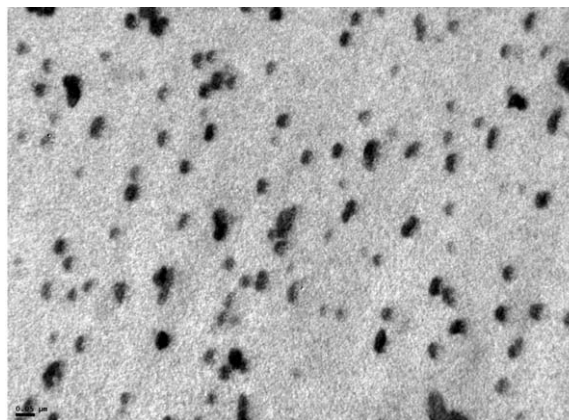


FIG. 5. TEM images of DGEBA-BA cured samples containing 5 wt% MAM. Bars indicate 50 nm in the upper image and 20 nm in the lower image.

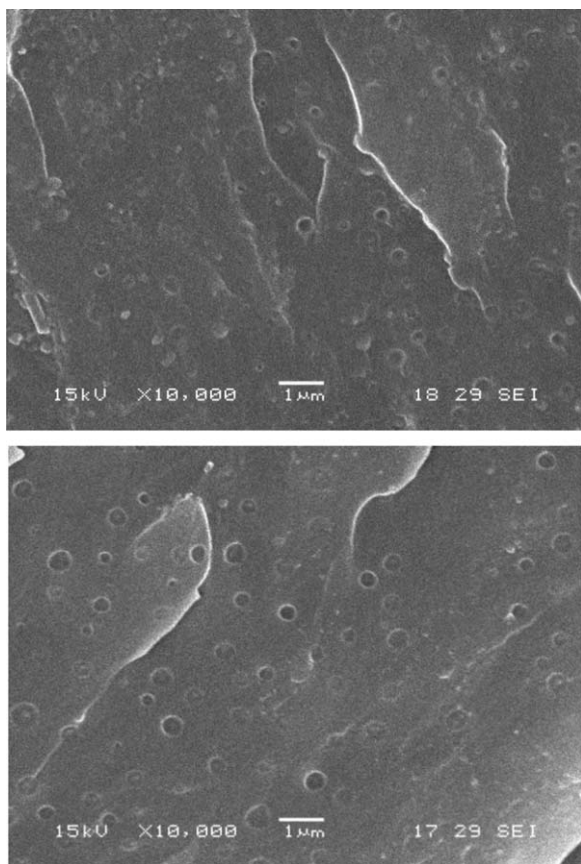


FIG. 6. SEM images of DGEBA-3DCM cured samples containing 5 wt% MAM-N (upper image) and 5 wt% MAM (lower image).

Due to the strong interactions between DMA units and the epoxy-amine solvent [22], the initial viscosity of the formulation containing 5 wt% MAM-N was much higher than the one with 5 wt% MAM. This is a significant result when low viscosities are required for processing purposes. In particular, the use of 20% BA as reactive diluent for formulations containing 5 wt% MAM can bring viscosity and pot-life to required values for filament winding, resin transfer molding, or several types of infusion processes. A fine-tuning may be achieved by slight variations of the DGEBA molar mass, the pot temperature, the BA amount or by replacing BA by cyclohexylamine.

In order to analyze the compatibility of both amines (BA or 3DCM) with the toughening agents (MAM or MAM-N), blends of DGEBA-BA, and DGEBA-3DCM containing 5 wt% of a block copolymer were prepared and cured as described in the Experimental section.

Cured DGEBA-BA samples modified by both block copolymers were transparent. Figures 4 and 5 show TEM images of cured materials, containing respectively, 5 wt% MAM-N and 5 wt% MAM.

The DGEBA-BA combination enabled to keep the solubility of PMMA and PMMA-*co*-PDMA up to high conversions leading to dispersions of spherical micelles. Therefore, BA does not only act as a reactive diluent but also as an excellent compatibilizer of the acrylic triblock copolymers with the epoxy formulation. As PBuA blocks are not miscible in DGEBA-based formulations (either initially or during polymerization) [20], these blocks must constitute the cores of micelles and PMMA

(in the case of MAM) or PMMA-*co*-PDMA (in the case of MAM-N) should form part of the shell of micelles swollen by the epoxy matrix. Sizes were in the range of 10–20 nm in the case of MAM-N and 20–40 nm in the case of MAM, indicating the better compatibility produced by the presence of PDMA.

In turn, cured DGEBA-3DCM samples containing the block copolymers were opaque. Therefore, when employing 3DCM a microphase separation took place during polymerization. This was expected for the case of MAM because it has been reported that a PMMA homopolymer undergoes reaction-induced phase separation in a DGEBA-3DCM solvent [37]. Partial replacement of MMA by DMA did not produce any significant compatibilization because the use of MAM-N instead of MAM led also to opaque materials. Figure 6 shows SEM images of DGEBA-3DCM cured samples with 5 wt% MAM-N or 5 wt% MAM.

Spherical domains present in DGEBA-3DCM samples had dimensions that are an order of magnitude higher than those observed in a DGEBA-BA matrix. Sizes are comprised in the 300–500 nm range for MAM-N and in the 400–600 nm range for MAM. Again, MAM-N leads to a dispersion of slightly smaller domains.

The effect of adding 5 wt% of MAM or MAM-N on morphologies generated, and thermal, mechanical, and fracture properties, was investigated for DGEBA-3DCM/BA (20%). This formulation was selected because it gave a convenient

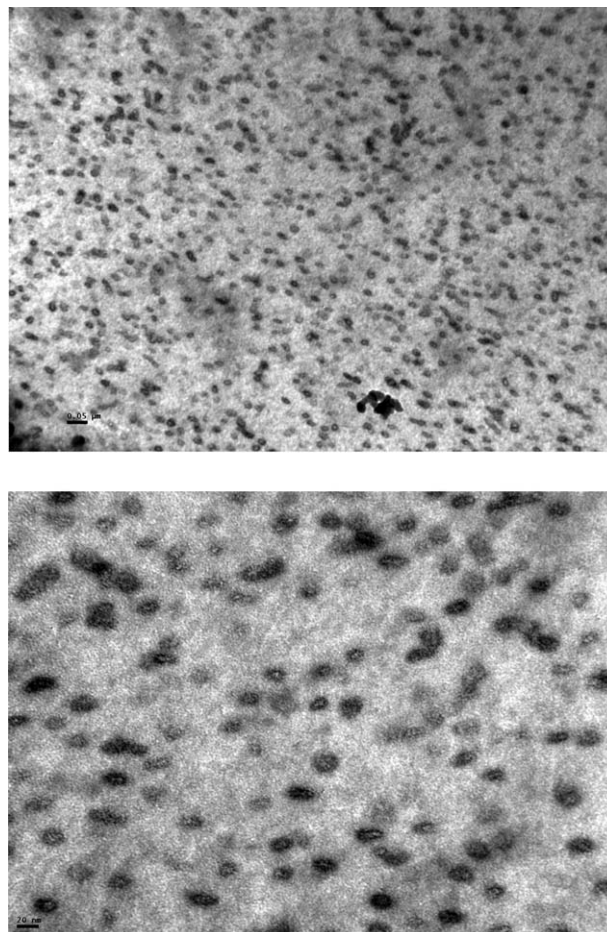


FIG. 7. TEM images of a DGEBA-3DCM/BA (20%) cured formulation containing 5 wt% MAM-N. Bars indicate 50 nm in the upper image and 20 nm in the lower image.

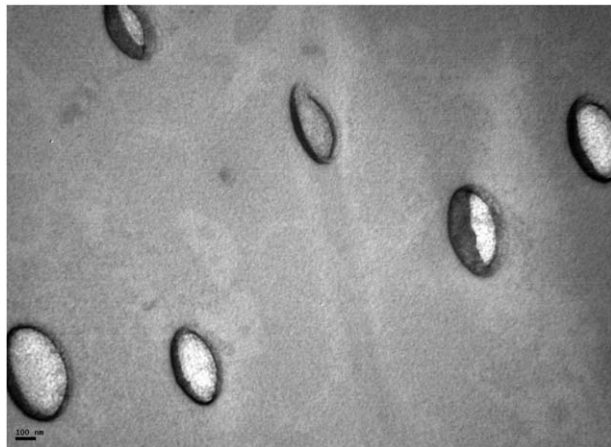
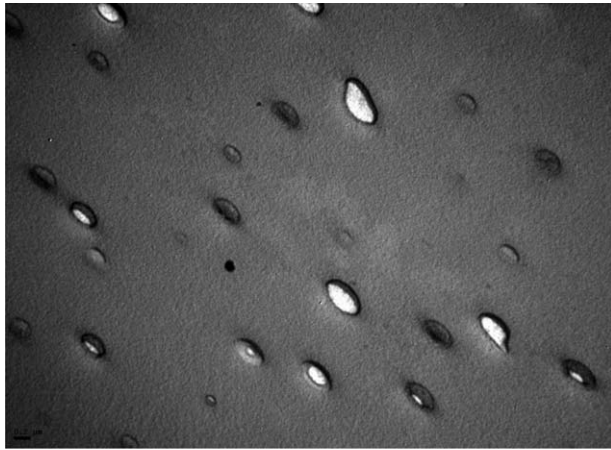


FIG. 8. TEM images of a DGEBA-3DCM/BA (20%) cured formulation containing 5 wt% MAM. Bars indicate 200 nm in the upper image and 100 nm in the lower image.

compromise among glass transition temperature, viscosity, and pot-life, as discussed previously.

Figures 7 and 8 show TEM images of cured materials, containing respectively, 5 wt% MAM-N and 5 wt% MAM.

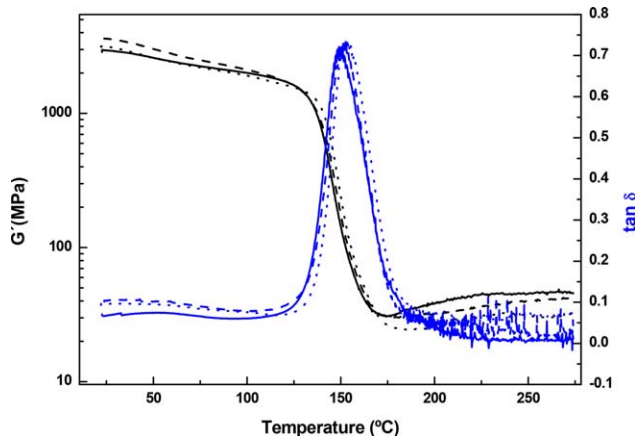


FIG. 9. Dynamic-mechanical spectra for the three cured samples based on DGEBA-3DCM/BA (20%): neat network (solid line) and networks toughened with 5 wt% MAM (dot line) or MAM-N (dashed line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 3. Thermal, mechanical and fracture properties of the neat DGEBA-3DCM/BA (20%) cured formulation and of those modified with 5 wt% MAM and 5 wt% MAM-N.

Sample	T_g (°C)	Max $\tan \delta$ (°C)	G' at 25°C (GPa)	K_{Ic} (MPa.m ^{1/2})
Neat	138	149.3	2.95	0.63 ± 0.06
With MAM	145	153.3	3.15	1.00 ± 0.07
With MAM-N	137	151.6	3.61	0.98 ± 0.13

The partial replacement of 3DCM by BA produced a significant increase in the compatibilization of the blend with MAM-N. This blend was transparent and showed a dispersion of spherical micelles with sizes in the range of 20 nm (Fig. 7). In the absence of BA, domains had sizes in the range of 300–500 nm (Fig. 6). The situation was quite different for the blend with MAM that was opaque. In this case, a microphase separation took place leading to domains with sizes comprised between 100 nm and 400 nm (Fig. 8), slightly smaller than those obtained with neat 3DCM (Fig. 6). Therefore, micellar dispersions were the result of two factors: the partial replacement of 3DCM by BA and the use of MAM-N.

Figure 9 shows the dynamic-mechanical characterization of the three cured samples. Thermal, mechanical, and fracture properties are summarized in Table 3.

Glass transition temperatures (DSC) and α -relaxations (DMTA) kept practically the same values as those of the neat epoxy network, meaning that the addition of the triblock copolymers did not produce any plasticization effect. Moreover, glassy moduli of the cured blends were higher than the one of the neat epoxy. The increase was higher for the blend with MAM-N, an effect ascribed to the strong interphase generated between dispersed domains and the epoxy matrix due to the interactions produced by DMA units and the epoxy-amine solvent [22], and the large increase of the interfacial area produced by the presence of a micellar dispersion.

In spite of the significant difference in the size of morphologies generated, both MAM and MAM-N produced similar increases in the fracture resistance of the epoxy networks. This means that micellar dispersions do not give necessarily better toughenability than micron-size dispersions. Bashar et al. reported similar findings for a different epoxy formulation [28].

CONCLUSIONS

Benzylamine (BA) is a useful reactive diluent and compatibilizer of blends of DGEBA-based formulations with acrylic triblock copolymers. The partial replacement of a cycloaliphatic diamine (3DCM) by BA combined with the use of MAM-N led to a micellar dispersion and transparency of the cured material. However, MAM-N led to initial solutions of higher viscosity than MAM, an effect associated with the strong interactions generated among DMA units and the epoxy-amine solvent [22]. Therefore, for requirements imposed by filament winding MAM was a better election than MAM-N. Even though MAM led to opaque cured materials due to the presence of micron-size dispersed domains, it produced the same increase in fracture toughness than the micellar dispersions of MAM. In particular, we showed that combining 3DCM and BA in a 2:1 molar ratio as a

hardener, with 5 wt% MAM, led to a basic formulation that can be adapted for filament winding applications. The addition of MAM increased the critical stress intensity factor from 0.63 MP a.m^{1/2} to 1.0 MPa.m^{1/2}, the glass transition temperature from 138°C to 145°C, and the glassy modulus at 25°C from 2.95 GPa to 3.15 GPa.

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