

Composite Materials Based on Modified Epoxy Resin and Carbon Fiber

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Copolímero em bloco de resina epoxídica modificada com polibutadieno líquido, funcionalizado com grupos carboxila foi preparado e o material reticulado correspondente foi comparado com resina epoxídica pura ou sua mistura física com polibutadieno líquido hidroxilado. A resina modificada com polibutadieno líquido carboxilado apresentou resistência ao impacto superior e melhor desempenho mecânico em termos de propriedades de tensão e de flexão. Essa melhora foi atribuída à presença de partículas de borracha homogeneamente dispersas dentro da matriz epoxídica. Esse sistema modificado também resultou em melhora das propriedades mecânicas dos compósitos correspondentes com fibra de carbono. As propriedades superiores foram atribuídas a uma melhor interação fibra-matriz, evidenciada por microscopia eletrônica de varredura.

Epoxy resin networks have been modified with block copolymer of polybutadiene and bisphenol A diglycidyl ether (DGEBA)-based on epoxy resin. The epoxy resin modified with carboxyl-terminated polybutadiene presented improved impact resistance and outstanding mechanical performance in terms of flexural and tensile properties because of the presence of rubber particles homogeneously dispersed inside the epoxy matrix. This modified system also resulted in an improvement of mechanical properties of the corresponding carbon fiber based composites. The outstanding properties were attributed to a better interaction fiber-matrix, as indicated by SEM micrographs.

Keywords: carbon fiber, epoxy resin, polybutadiene, impact modifier, composites

Introduction

Composite materials derived from epoxy resin and carbon fiber are being extensively employed in aircraft industries because of their strength, high modulus and light weight. The use of epoxy resins (ER) as a matrix is very popular because of their good engineering properties which include high stiffness and strength, creep resistance, chemical resistance and good adhesion to many substrates.¹ However, the major drawback of these resins is their brittleness in the cured state. It is well known that a small amount of reactive liquid rubber can greatly improve the fracture toughness of ERs by forming discrete rubbery particles chemically bonded to the matrix.^{2,3} The use of low molecular weight rubber material is recommended to avoid an excessive increase of viscosity so that the processability of the system is not impaired.⁴ The most popular rubbery modifying agent

is carboxyl-terminated butadiene-acrylonitrile random copolymer (CTBN) because of its miscibility with the epoxy-hardener mixture during the initial polymerization period and also because the carboxyl functional groups in CTBN can react with the epoxide groups, thus achieving a high level of interfacial adhesion.^{5,6} The enhancement in toughness is achieved because the elastomeric phase precipitates at some stage of the curing process as particles of very small size.^{7,8}

Hydroxyl-terminated polybutadiene (HTPB) is also a good candidate to improve the toughness of epoxy resin and also its flexibility. In order to impart some compatibility between HTPB rubber particles and epoxy matrix and to provide a better interfacial adhesion, it is important that both components are chemically joined resulting in a block copolymer. This can be achieved by first end-capping the polybutadiene with the epoxy molecules before the curing process, using a procedure similar to that one adopted in CTBN-modified epoxy resin.

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Recently, we have modified epoxy resin with hydroxyl-terminated polybutadiene and studied the mechanical properties of the corresponding cured resins.⁹⁻¹¹ An improvement of compatibility between ER and polybutadiene has been achieved by the use of polybutadiene functionalized with carboxyl groups (CTPB), followed by the reaction with an excess of epoxy resin, according to the scheme presented in Figure 1. An increase on tensile properties of the corresponding cured resin was achieved with the addition of as low as 10 phr (part *per* hundred part of rubber) of carboxyl-modified HTPPB.¹¹

The aim of the present work is to examine the effect of the polybutadiene-modified epoxy resin on the mechanical and morphological properties of composites with carbon fiber. For this study, composites constituted by epoxy matrix modified with HTPPB and the carboxyl-modified HTPPB (CTPB) were developed in order to compare the mechanical performance of different samples.

Experimental

Materials

The diglycidyl ether of bisphenol A (DGEBA)-based ER used in all experiments was DER 331, supplied by Dow Química S.A., with a number-average molecular weight (\bar{M}_n) of 380 g mol L⁻¹ and an epoxide equivalent of 192 g equiv⁻¹ as determined by acid titration. The cure agent was EPICURE 3140, a mixture of diethylenetriamine (DETA) and triethylenetetramine (TETA) with a number of amine groups corresponding to 378 g equiv⁻¹, supplied by Shell do Brasil. HTPPB (trade name: Liquiflex H, kindly supplied by Petroflex Ind. Com. S.A.) presents a \bar{M}_n of 3000 and a hydroxyl number of 0.8 g mequiv⁻¹. Maleic anhydride (Vetec Ltda) was distilled under vacuum before use. Triphenylphosphine (Merck) was used as received. All polymers were dried under vacuum for 24h at room temperature before use. The carbon fiber used in this work (AS2C) was supplied by Hexcel. The fibers were woven type with tows of around 3,000 g mol L⁻¹ individual fibers, disposed in 90 degrees from each other.

Preparation of epoxide end-capped HTPPB from carboxyl end-capped HTPPB

The epoxide end-capped HTPPB obtained from carboxyl end-capped HTPPB (CTPB) is denoted as CPBER. The synthesis of CTPB was performed by reacting HTPPB with maleic anhydride in a stoichiometric epoxy/anhydride molar ratio, as illustrated in Figure 1. The reaction was performed in bulk at 80 °C for 24 h with magnetic stirring,

under nitrogen atmosphere. The carboxyl content of CTPB was determined by titration with a NaOH methanolic solution of 0.10 mol L⁻¹, using phenolphthalein as an indicator. The block copolymers were obtained by reacting the epoxy resin with different amount of CTPB and 0.2% m/m of triphenylphosphine. The reagents were added into a three-necked reaction flask blanketed with nitrogen. The flask was placed in an oil bath at 80 °C and allowed to react under stirring conditions for 24 h.

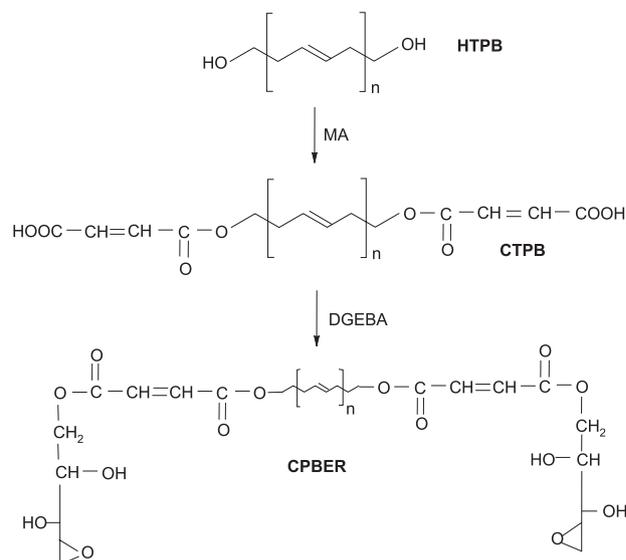


Figure 1. Synthetic steps involved in the preparation of polybutadiene-epoxy resin block copolymer.

Curing procedure

The ER was modified with different amounts of HTPPB or CPBER without the presence of solvent. All network polymers were prepared from mixtures of the ER and the hardener, EPICURE 3140 (see Table 1 for the formulations). ER/HTPB samples were prepared as follows: a proper amount of DER 331 was first degassed for 60 min in a vacuum oven at 80 °C. The rubber (HTPB) was also degassed separately under the same conditions. Both components were mixed and the curing agent was added. The mixtures were gently stirred for about 5 min to ensure proper dispersion of the hardener, degassed for 5 min and poured into appropriated molds for mechanical testing. The cure was performed at 100 °C for 120 min. This cure condition was chosen from DSC studies performed in the static mode at 100 °C, which revealed that almost all curing processes happened before 60 min.

The network polymers prepared from epoxy-polybutadiene block copolymers were obtained by mixing CPBER previously synthesized (containing pre-established proportion of epoxy-rubber) with the

EPICURE 3140. The CPBER sample was first degassed for 60 min in a vacuum oven at 80 °C. Then, the hardener was added and gently stirred for about 5 min. The resulting compositions were degassed for 5 min at 80 °C and poured into appropriated molds. The cure was performed at 100 °C for 120 min.

Preparation of the composites

The reinforced epoxy composites were manufactured by stacking the pre-impregnated (prepregs) layers into an open mold and cured at 120 °C for 120 min. The prepregs were prepared in the laboratory by impregnating the carbon fiber in the form of a sheet, with the epoxy system. The prepared prepregs consisted of five layers of impregnated carbon fiber. The thickness of the composites was around 5 mm. The amount of carbon fiber in the prepreg after molding and curing was around 40-45% m/m, as determined by thermogravimetric analysis.

Characterization

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-7 equipment. The cure conditions were determined in a static mode at 100 °C and in dynamic mode at 10 °C min⁻¹ under nitrogen. The static mode has been employed to verify the necessary time to complete the curing process and the dynamic mode was employed to calculate the enthalpy related to the curing process.

The gel point was determined according to ASTM 2471, by putting about 100 mg of the sample in several tubes, which were placed into an oil bath at 100 °C. The tubes were withdrawn from the bath at different times and chilled in an ice bath to quench the reaction. The polymeric material was dissolved with tetrahydrofuran (THF). The gelation point was determined from the presence of insoluble fraction.

Scanning electron microscopy (SEM) was performed using a JEOL JSM-5610LV SEM with an electron voltage of 15 kV and secondary electron detector. The epoxy networks were handling fractured and the surface was first treated with chloroform to extract the rubber phase, then dried under vacuum and coated with thin layer of gold before analyzing. The SEM micrographs of the composites were taken from the surface after the impact test, which were also coated with a thin layer of gold before analyzing.

The size and size distribution of the dispersed particle were determined by means of semiautomatic image analysis. The SEM micrographs of the fractured samples

were first scanned and converted into digitized images, which were analyzed using an 'AnalySIS 3.0' program to obtain the average diameter values of the dispersed particles, d_n , and the particle size distribution.

Mechanical testing

Flexural tests of epoxy resin networks and the corresponding composites were performed using an Instron 4204 testing machine fitted with a three-point bending fixture at a crosshead speed of 1 mm min⁻¹, according to ASTM D-790. The dimensions of the specimens were 75 × 25 × 2 mm and the span-to-thickness ratio was set at L/D = 32 to 1 in all cases. The values were taken from an average of at least five specimens.

The tensile tests of the cured epoxy system without fiber were performed using an Instron 4204 testing machine at a crosshead speed of 1 mm min⁻¹, according to ASTM D-638. For the composites, the tensile tests were performed according to ASTM D-3039 method. The values were taken from an average of at least five specimens.

The impact strength of the notched specimens was determined by using a Charpy Monsanto Tensiometer, using rectangular specimens of 50 × 10 × 5 mm, according to ASTM D-256. The tests were carried out at room temperature and the values were taken from an average of at least ten specimens. Epoxy resin networks (without carbon fiber) were tested with the help of a 0.22 kg hammer and for the composites, a 0.9 kg hammer was employed.

Results and Discussion

Preparation and characterization of modified epoxy networks

The functionalization of HTPB with carboxyl groups (CTPB) is illustrated in Figure 1. The amount of COOH group in the CTPB sample was determined by titration and corresponded to 0.5 mmol g⁻¹. This value is lower than the initial concentration of maleic anhydride employed in the reaction (0.8 mmol g⁻¹) and may be due to the sublimation of substantial amount of the anhydride during the reaction at 80 °C, confirmed by the presence of white needles in the upper part of the wall of the reaction flask.

Before curing, a large excess of epoxy resin was pre-reacted at 80 °C with CTPB in the presence of triphenylphosphine as a catalyst for 24 h. The modified samples containing the CPBER block copolymer were liquid and no gelling was observed after pre-reaction.

The samples containing different amounts of the rubber component, were cured with EPICURE 3140 at 100 °C for 2 h. The cured samples (about 1 g) were milled and treated with hot toluene to extract the rubber component that was not chemically bonded to the epoxy matrix. The CPBER sample presented an amount of soluble, non reacted rubber corresponding to 10-15% of all rubber components in the mixture, indicating that almost all carboxyl-terminated rubber were chemically bonded to the epoxy matrix. It is important to emphasize that similar procedure carried out with epoxy resin containing non functionalized HTPB resulted in a complete extraction of the rubber phase.

Evaluation of the cure parameters

The effect of the carboxyl end-capped HTPB on the cure parameters of the epoxy matrix is compared to that of non-modified HTPB in Table 1. The ΔH values related to the cure process were determined from the area of the exotherm peak obtained from DSC analysis, taken in the dynamic mode. This peak appeared during the first heating run but was completely absent during the second heating cycle. The presence of HTPB or the block copolymer (CPBER) did not affect significantly the ΔH values, indicating no influence on the crosslink degree of the epoxy matrix.

The necessary time to produce the minimum amount of insoluble material (gel time) was the same when pure ER or HTPB-modified ER was submitted to the reaction with the hardener. However, when carboxyl end-capped HTPB was mixed with ER, a decrease of gel time was observed, indicating that the systems containing the block copolymers crosslink faster than those consisted of pure ER or HTPB-modified ER.

Mechanical properties

The impact strength, flexural and tensile properties of the cured ER samples containing different amount

Table 1. Formulations and curing parameters of pure ER and those rubber-modified Epoxy systems

ER (g)	hardener (g)	HTPB (g)	CPBER ^a (g)	ΔH^b (J g ⁻¹)	gel time (s)
100	25.4	0	0	290	225
95	24.1	5	0	280	225
90	22.8	10	0	280	225
95	21.7	0	5	280	190
90	20.6	0	10	280	190

^aCPBER is the block copolymer obtained by end-capping the carboxyl-modified HTPB with the ER; ^b ΔH obtained from DSC measurements taken in the dynamic mode.

of the rubber agent are summarized in Table 2. The modification of epoxy resin with rubber resulted in an improvement of the impact resistance. The best performance was normally achieved with 10 phr of rubber. Above this optimum rubber content, a fall in the impact strength was observed. Similar behavior has been also reported in other rubber-modified epoxy systems and attributed to the agglomeration of rubber particles with the increase of the rubber concentration.^{12,13} The presence of agglomerates acts as defects and initiates catastrophic failure.

Concerning the different epoxy-rubber systems, the addition of CPBER block copolymer containing around 10-15% of rubber resulted in the best impact resistance. The flexural properties were not affected by the addition of 5-10% of rubber in the form of CPBER block copolymer, when compared to the net epoxy network. Also, the best tensile strength has been achieved with this system.

Morphology

The SEM micrographs of the toughened epoxy networks containing 10 m/m of HTPB of CPBER are shown in Figure 2 and the corresponding particle size distribution curves are shown in Figure 3. The micrographs of ER modified with HTPB displayed distinct separated particles of rubber, indicating a heterogeneous system.

Table 2. Mechanical properties of rubber-modified epoxy networks

ER (%)	HTPB (%)	CPBER ^a (%)	impact strength (J m ⁻²)	flexural yield stress (MPa)	flexural modulus (MPa)	tensile yield stress (MPa)
100	0	0	9.7 ± 0.4	83.8 ± 0.3	2536	54.3 ± 5.4
95	5	0	11.4 ± 0.4	72.0 ± 0.1	2385	50.2 ± 4.2
90	10	0	14.2 ± 0.4	62.2 ± 0.1	1912	50.4 ± 2.3
85	15	0	11.2 ± 0.4	60.0 ± 0.2	1860	46.0 ± 5.0
95	0	5	11.5 ± 0.3	92.0 ± 0.2	2350	90.4 ± 1.7
90	0	10	16.1 ± 0.4	82.0 ± 0.1	2300	84.1 ± 0.7
85	0	15	13.7 ± 0.3	66.0 ± 0.2	2166	63.5 ± 3.0

^aCPBER is the block copolymer obtained by end-capping the carboxyl-modified HTPB with the ER.

The holes observed in the micrograph are related to the rubber particles that were withdrawn from the surface after the treatment with chloroform, indicating no chemical bond between the blend components. The particle size distribution was large, in the range of 0.1-75 μm , most of them situated in the range of 11-32 μm (Figure 3a).

Epoxy matrix modified with CPBER block copolymer also presented two-phase morphology in SEM micrograph (Figure 2b), but the size of the domain was considerably smaller than that observed for epoxy-HTPB system. The rubber particle size distribution was more uniform, with particle size diameters in the range between 0.5 to 3 μm (Figure 3b). This range was similar to those found by Chen and Jan¹⁴ in epoxy systems modified with epoxide end-capped CTBN. In addition, one can observe the presence of several rubber particles that were not extracted with chloroform, indicating strong interfacial adhesion. This morphological situation is believed to be responsible for the highest impact performance.

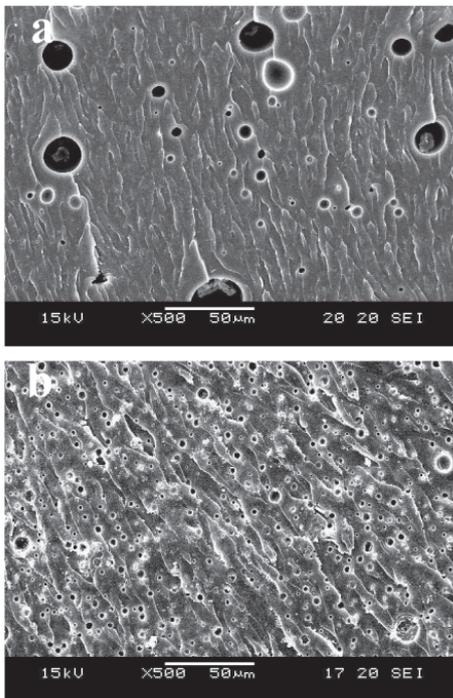


Figure 2. SEM micrography of toughened epoxy resin networks extracted with chloroform, containing 10% m/m of (a) HTPB and (b) CTPB.

Preparation and characterization of the composites with carbon fiber

Mechanical properties. Table 3 presents the mechanical properties of the carbon fiber-composites composed by modified epoxy matrix. For this study, we have used two different types of rubber-modified epoxy networks as the matrix. The presence of 10% of polybutadiene

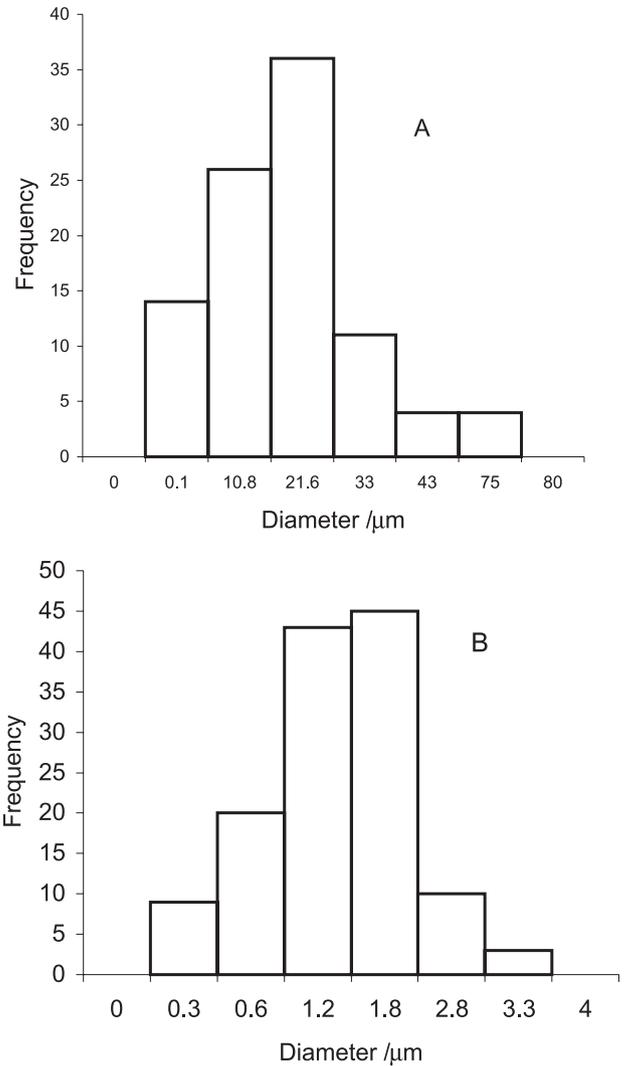


Figure 3. Particle size distribution for epoxy resin networks toughened with 10% of (A) HTPB and (B) CTPB.

functionalized with hydroxyl groups (HTPB) or carboxyl groups (CTPB) did not exert any influence on the impact resistance of the epoxy resin. However, a substantial improvement on this property was observed by increasing the proportion to 20%. The best result was achieved with CTPB because of the higher interaction between the rubber phase and the epoxy. In terms of tensile strength, the composite prepared with epoxy network modified with carboxyl terminated polybutadiene gave rise to a higher resistant material. These results are consequence of the presence of the rubber dispersed phase well adhered to the epoxy matrix. When this modified matrix is used in the composite, additional adhesion between the polar groups of the fiber surface and the modified epoxy matrix is achieved, contributing for the improvement of impact resistance and also tensile strength.

Morphology of the composites. The fracture surface of the samples after the impact testing was analyzed by scanning electron micrograph. The micrographs of the composites are compared in Figure 4. All composites displayed good adhesion between fiber and matrix. However, that consisted of epoxy network modified with

carboxyl terminated polybutadiene (Figure 4c) displayed a more effective interaction since all fibers have broken together with the matrix. There is no significant pull-out process of the fiber during impact test. This morphology may be responsible for the highest tensile strength of this composite.

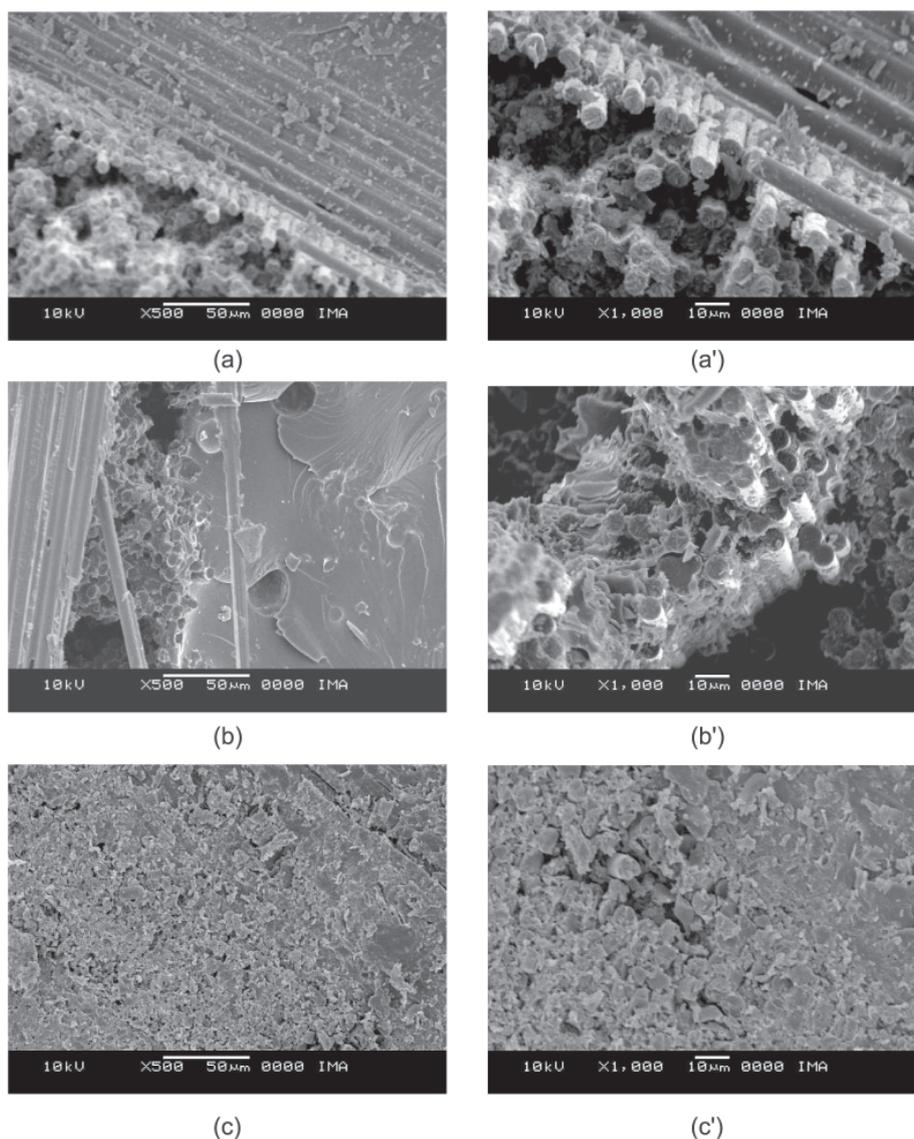


Figure 4. SEM micrography of carbon fiber-based composites as a function of the epoxy matrix. (a) epoxy; (b) epoxy modified with HTPB; (c) epoxy modified with CTPB; (The micrographs on the right are related to those taken at higher magnification).

Table 3. Mechanical properties of carbon fiber based composites containing rubber-modified epoxy matrix

ER (%)	HTPB (%)	CPBER ^a (%)	impact strength (J m ⁻²)	Young modulus (GPa)	Elongation at break (%)	tensile yield stress (MPa)
100	0	0	20 ± 3	9.5 ± 1.0	3.15	300 ± 304
90	10	0	19 ± 3	7.5 ± 1.0	2.80	203 ± 35
80	20	0	32 ± 7	-	-	-
70	30	0	28 ± 8	-	-	-
90	0	10	17 ± 5	15.5 ± 2.0	2.85	425 ± 50
80	0	20	40 ± 9	-	-	-

^aCPBER is the block copolymer obtained by end-capping the carboxyl-modified HTPB with the ER.

Conclusions

Epoxy networks have been modified with block copolymers prepared by pre-reacting functionalized polybutadiene with the epoxy resin. The block copolymer prepared from carboxyl end-capped HTPB resulted in faster gelation time as compared to the neat epoxy resin or that modified with HTPB.

Epoxy network modified with CPBER displays the best impact performance associated to improved flexural properties, because of the presence of rubber particles homogeneously dispersed inside the epoxy matrix. This modified system also resulted in an improvement of mechanical properties of the corresponding carbon fiber based composites. The outstanding properties were attributed to a better interaction fiber-matrix, as indicated by SEM micrographs.

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References

1. May, C. A.; Tanka, G. Y.; *Epoxy Resin Chemistry and Technology*, Marcel Decker: New York, 1973.
2. Riew, C. K.; Rowe, E. H.; Siebert, A. R.; *Adv. Chem. Ser.* **1976**, *154*, 326.
3. Frigione, M. E.; Mascia, L.; Acierno, D.; *Eur. Polym. J.* **1995**, *31*, 1021.
4. Kim, J. K.; Robertson, R. E.; *J. Mater. Sci.* **1992**, *27*, 161.
5. Sultan, J. N.; McGarry, F. J.; *Polym. Eng. Sci.* **1973**, *13*, 29.
6. Visconti, S.; Marchessault, R. H.; *Macromolecules* **1974**, *7*, 913.
7. Sasidharan, A. P.; Latha, P. B.; Ramaswamy, R.; *J. Appl. Polym. Sci.* **1990**, *41*, 151.
8. Verchere, D.; Pascault, J. P.; Sautereau, H.; Moschiar, S. M.; Riccardi, C. C.; Williams, R. J. J.; *J. Appl. Polym. Sci.* **1991**, *42*, 701.
9. Barcia, F. L.; Abrahão, M. A.; *J. Appl. Polym. Sci.* **2002**, *83*, 838.
10. Barcia, F. L.; Amaral, T. P.; Soares, B. G.; *Polymer* **2003**, *44*, 5811.
11. Soares, B. G.; Leyva, M. E.; Moreira, V. X.; Barcia, F. L.; Khastgir, D.; Simão, R. A.; *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 4053.
12. Ratna, D.; Banthia, A. K.; Deb, P. C.; *J. Appl. Polym. Sci.* **2001**, *80*, 1792.
13. Latha, P. B.; Adhinarayanan, K.; Ramaswamy, R.; *Int. J. Adhes. Adhes.* **1994**, *14*, 57.
14. Chen, T. K.; Jan, Y. H.; *Polym. Eng. Sci.* **1991**, *31*, 577.

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