

The Effect of Hydroxyl-Terminated Polybutadiene-Grafted Carbon Fiber on the Impact Performance of Carbon Fiber-Epoxy Resin Composites

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ABSTRACT: Carbon fiber (CF) containing 1.4 and 2.1 mmol/g of —COOH and —OH groups, respectively, was functionalized by using an excess of tolylene-2,4-diisocyanate. The NCO-modified CF was submitted to a graft reaction with hydroxyl-terminated polybutadiene (HTPB). The HTPB-grafted carbon fiber was employed as reinforcing agent for epoxy resin-based composites. The presence of the flexible HTPB at the interface between the fiber and the matrix resulted in a substantial improvement on impact strength. Additional improvement on toughness was achieved by using epoxy matrix containing dispersed phase of HTPB. The composite morphology was also studied by scanning electron microscopy. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1424–1431, 1999

Key words: carbon fiber; epoxy resin; polybutadiene-grafted carbon fiber

INTRODUCTION

Composite materials derived from epoxy resins and carbon fibers are being extensively employed in aircraft industries because of their strength, high modulus, and lightweight. The high performance of these materials depends essentially upon the degree of adhesion between fiber and matrix. An improvement on the interfacial adhesion is normally achieved with surface-treated fibers.^{1,2} The oxidative surface treatment produces mainly functional groups like carboxyl (COOH), carbonyl (CO), and hydroxyl (OH), which exhibit strong interactions with epoxy ma-

trices.^{3,4} In addition to chemical and physical bonding, the mechanical interlocking of the matrix into the irregularities present on the fiber surface also contributes for enhanced adhesion.^{5,6} This effect is also a function of the sizing resin and its deposition technique.⁷ The size or polymer coating constitutes the interfacial zone and permits a better contact between fiber and matrix. Some authors have also reported that the flexibility of the interface should improve the adhesion because the penetration of the matrix material across this phase is easier.⁸ The adhesion fiber matrix must be even higher if the polymer component of the interface is grafted onto the carbon fiber surface.^{9,10}

Considering the importance of the interface feature and the degree of adhesion on the development of high performance composite material, we decided to prepare carbon fibers grafted with hydroxyl-terminated polybutadiene (HTPB) and

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study the effect of these modified fibers on the impact resistance of carbon fiber–epoxy resin systems. For the graftization reaction, the carbon fiber was previously functionalized with isocyanate groups and then submitted to reaction with HTPB.

EXPERIMENTAL

Materials

Carbon fiber (CF) (Torayca T300) from Toray Industries, Inc., were extracted with chloroform in a Soxhlet apparatus for 6 h and dried under vacuum at 100°C before use. The phenolic hydroxyl and carboxyl groups at the CF surface were quantified by titration with aqueous solutions of sodium hydroxide and sodium bicarbonate, according to the literature.¹¹ The values found for the —COOH and —OH contents were 1.4 and 2.1 mmol/g, respectively.

The samples used for impact tests were prepared with a bisphenol-A-based epoxy resin (Araldit XGY 1109) and a polyamine-based hardener HY 943, both obtained from Ciba-Geigy. For the test using one fiber filament, a bisphenol-A-based epoxy resin (DER331) and a polyglycol diepoxide (DER731) from Dow Chemical Company were employed together with tetraethyl-enetetramine (TETA). HTPB, kindly supplied by Petroflex (Rio de Janeiro, Brazil), contains 0.9 mmol/g of hydroxyl groups. Its average number molecular weight is near 3000 g/mol. All resin components were dried under vacuum for 24 h. The HTPB sample was dried with molecular sieve.

Graftization of HTPB onto CF

The surface modification of CF was performed in two steps. The first one involves a reaction of CF with tolylene-2,4-diisocyanate (TDI). The functionalized CF with NCO groups was submitted to reaction with HTPB.

One gram of CF was introduced into a two-necked flask containing 150 mL of xylene and reacted with 1 mL of TDI and 1 mL of a 10% solution of tin octoate in xylene, as a catalyst. The flask was equipped with a reflux condenser and a nitrogen inlet. The mixture was heated at 120°C for different times under nitrogen. After reaction, the fiber was extracted with xylene under nitrogen atmosphere, to remove the unreacted TDI.

The NCO content incorporated at the fiber surface was determined by reacting the modified fiber with di-n-butylamine. The excess of amine was then titrated with a 0.1M aqueous solution of HCl, using bromo-cresol green as indicator.

The NCO-functionalized fiber was then submitted to a reaction with 10 g of HTPB and 1 mL of the tin octoate solution, at 120°C for 6 h, under nitrogen atmosphere. After the reaction was completed, the fiber was extracted with acetone in a Soxhlet apparatus for 12 h, to remove the unreacted HTPB.

XPS Analysis

XPS spectra were taken on a Kratos Analytical Instruments XSAM-800 dual-chamber spectrometer equipped with a hemispherical electron energy analyzer and a quad-anode x-ray source. The analyzer was operated in a fixed retardation ratio mode. The energy scale of the instrument was calibrated by setting Cu2p = 932.7, CuLMN = 918.7, Ag3d = 368.3, Au4f = 84, Ni(E_{Fermi}) = 0 eV. The spectra were acquired using a MgK α excitation. The x-ray gun was operated under mild conditions (75 W, 15 kV, 5 mA). The pressure in the analysis chamber was maintained at 10⁻⁹ Torr. The samples were mounted onto a sample holder using a double-sided adhesive tape. Quantitative analysis of the sample surface was made based on the integral peak intensities as described elsewhere.¹²

Composite Preparation for Impact Test

To facilitate the preparation of composite specimens for impact test, the CF was wrapped on a glass cylinder of 100 mm length and 15 mm diameter. The cylinder surface (80 mm of the length) was completely full with CF. Each cylinder contained near 0.7g of CF. The wrapped CF was then submitted to the extraction and functionalization procedures as earlier described. Different formulations containing 0–20 phr of HTPB and 100 phr of XGY 1109 resin were made. These formulations were stirred for 5 min and submitted to vacuum to eliminate the adsorbed gases. Then, 23 phr of HY943 curing agent were added. The modified CF was removed from the glass cylinder by carefully cutting the fiber in a longitudinal way to the cylinder. The mold (120 × 80 × 5 mm) was full with the resin mixture intercalated with fiber layers. The fibers were in the center of the mold, in the width direction. Four

layers of CF were placed into the mold. Each layer corresponds to the CF contained in one cylinder. The system was cured at 120°C for 90 min. After curing, the specimens for Charpy impact test were taken from the plaque by cutting the cured material in the carbon fiber direction. The composite contained nearly 19 wt % of CF, as indicated by thermogravimetric analysis of samples collected from several regions.

The impact test was performed with the help of a Charpy Monsanto tensiometer by using notched specimens of 50 × 12 × 5 mm. The tests were carried out at room temperature.

Sample Preparation for the Test Using One Fiber Filament

For this test, blend containing 62 wt % of a DER 331 epoxy resin and 31 wt % of DER731 as flexibilizer was mixed with 7 wt % of TETA hardener to form an homogeneous mixture and degassed in a vacuum chamber. The epoxy mixture was then carefully cast into an American Society for Testing and Materials 638 dogbone mold containing a single fiber running along the center.¹³ The curing was performed at 80°C for 2 h. The bulk epoxy specimens were strained using an Instron testing machine at a strain rate of 0.05 mm · min⁻¹.

Microscopy Analysis

The fracture surface of the composites was investigated with a JEOL JSM-5300 scanning electron microscope, after coating with a thin layer of gold. The accelerating power was 20 kV.

Optical microscopy was made with the help of an Olympus BX50 microscopy.

RESULTS AND DISCUSSION

Modification of CF with HTPB

As described in the experimental part, the CF used in our studies contains 1.4 and 2.1 mmol/g of

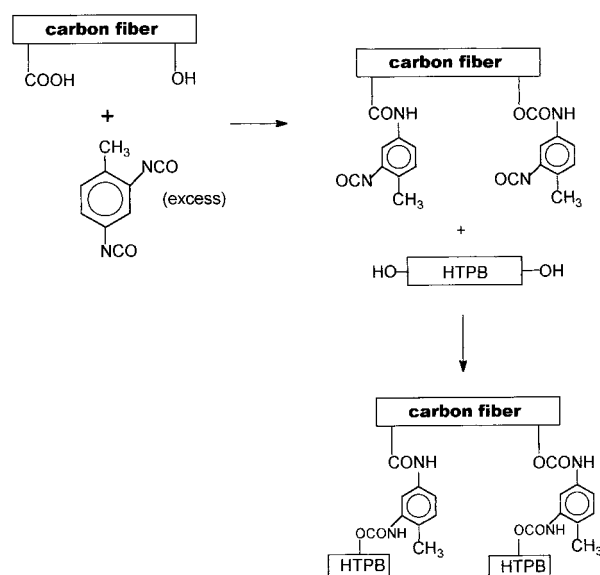


Figure 1 Probable reactions that occur during the functionalization of carbon fiber with HTPB.

COOH and OH groups, respectively. The functionalization of carbon black with isocyanate groups was reported in the literature.^{14,15} Those techniques were then adapted to the carbon fiber functionalization, by using excess of TDI as the functionalization agent. The NCO groups incorporated to the fiber react in a subsequent step with the OH groups of the HTPB chains, resulting in carbon fiber chemically modified with HTPB. The probable reactions involved in the graftization of carbon fiber with HTPB are illustrated in Figure 1. The extent of the fiber functionalization with NCO as a function of the reaction time is presented in Table I, where we can observe that a maximum was achieved after around 45 min of reaction. The maximum amount of NCO groups at the fiber surface was about 3.1 mmol/g. Since an excess of TDI was employed in this step, it is believed that all functional groups (1.4 mmol/g COOH and 2.1 mmol/g OH) at the fiber surface have been reacted with TDI. Thus, the amount of

Table I Amount of TDI Incorporated at the Carbon Fiber Surface as a Function of the Reaction Time

Reaction Time (min)	NCO Incorporated (mmol/g)	Functionalization Efficiency ^a (%)
20	1.5	42.8
30	2.8	80.0
45	3.1	89.0
60	3.1	89.0

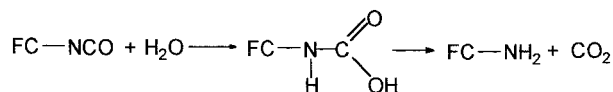
^a Functionalization efficiency calculated from the total amount of COOH and OH groups at the fiber surface.

Table II Surface Composition of Carbon Fiber Determined by XPS Spectroscopy

Elements	Commercial CF	CF Functionalized with NCO Groups
C1s (%)	76	73
O1s (%)	20	17
N1s (%)	3.5	6.7
N1s/C1s	0.046	0.092
O1s/C1s	0.26	0.23

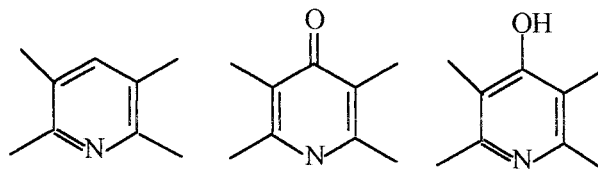
NCO lower than 3.5 mmol/g may be explained by some cross reactions between the second NCO groups with the COOH or OH groups of the fiber. Nevertheless, this side reaction is not so important, since 89% of functionalization efficiency were achieved, if one considers all COOH and OH present at the fiber surface.

The subsequent reaction of the carbon fiber (3.1 mmol of NCO/g) with HTPB resulted in a modified fiber composed of 20 wt % of HTPB, that is, 0.25 g of elastomer/g of the fiber. The HTPB sample employed in this work contains 0.9 mmol/g of hydroxyl groups. If all hydroxyl groups of the grafted HTPB reacted with the NCO groups of the fiber, one can consider a grafting efficiency as low as around 7%. This behavior may be attributed to side reactions between NCO groups and some impurities in the HTPB sample. It is important to point out that a commercial sample of HTPB has been employed. In spite of previous drying with molecular sieve, this sample may contain some impurities as alcohol and water, which react easily with the NCO groups. Water, for example, gives rise to amine groups along the fiber surface, according to the following reaction:



The chemical composition of the fiber surface was analyzed by the XPS technique. Table II presents the atomic concentration of carbon, oxygen, and nitrogen at the fiber surface. The presence of oxygen atoms in the commercial fiber is expected since this fiber is indicated for using in epoxy composites, and therefore has received an oxidative surface treatment where oxygenated groups as carboxyl, carbonyl, and phenolic hydroxyl groups are introduced at the surface. In addition to oxygen and carbon atoms, the presence of ni-

trogen can be attributed to the heterocyclic structures, as illustrated below¹⁶:



The functionalization with TDI resulted in an increase of the N/C ratio. The difference between the amount of nitrogen atoms in the NCO-modified and pure fiber is 3.2%, which corresponds to 1.14 mmol/g of NCO groups. This value is inferior to that found by titration experiments probably because XPS is a surface analytical method and the composition determined by this method does not correspond to the composition of the fiber as a whole.

Carbon Fiber—Epoxy Composites

The results concerning the impact resistance of epoxy resin composites prepared with pure CF and HTPB-modified CF are presented in Table III. The epoxy/CF composite displays higher impact resistance than pure epoxy resin, as expected. When HTPB-modified CF was employed, a substantial improvement on impact properties was observed. In this case, HTPB grafted onto CF constitutes the polymer coating phase, well adhered at the fiber surface. The outstanding impact performance of this system may be associated with the elastomeric nature of the interface between epoxy resin and CF, which is able to dissipate the energy, increasing the toughness of the material.

The fracture SEM micrographs of both composites are illustrated in Figure 2. Both nonmodified and HTPB-grafted CF presented a considerable interfacial adhesion. The adhesion between non-

Table III Impact Strength of Epoxy Resin/Carbon Fiber Composites

Sample	Impact Strength (J/m)
Epoxy resin	7.0
Epoxy resin/CF composite ^a	24.0
Epoxy resin/HTPB-grafted CF ^a	43.4

^a CF or HTPB-grafted CF content in the composites approximately equal to 20 wt %.

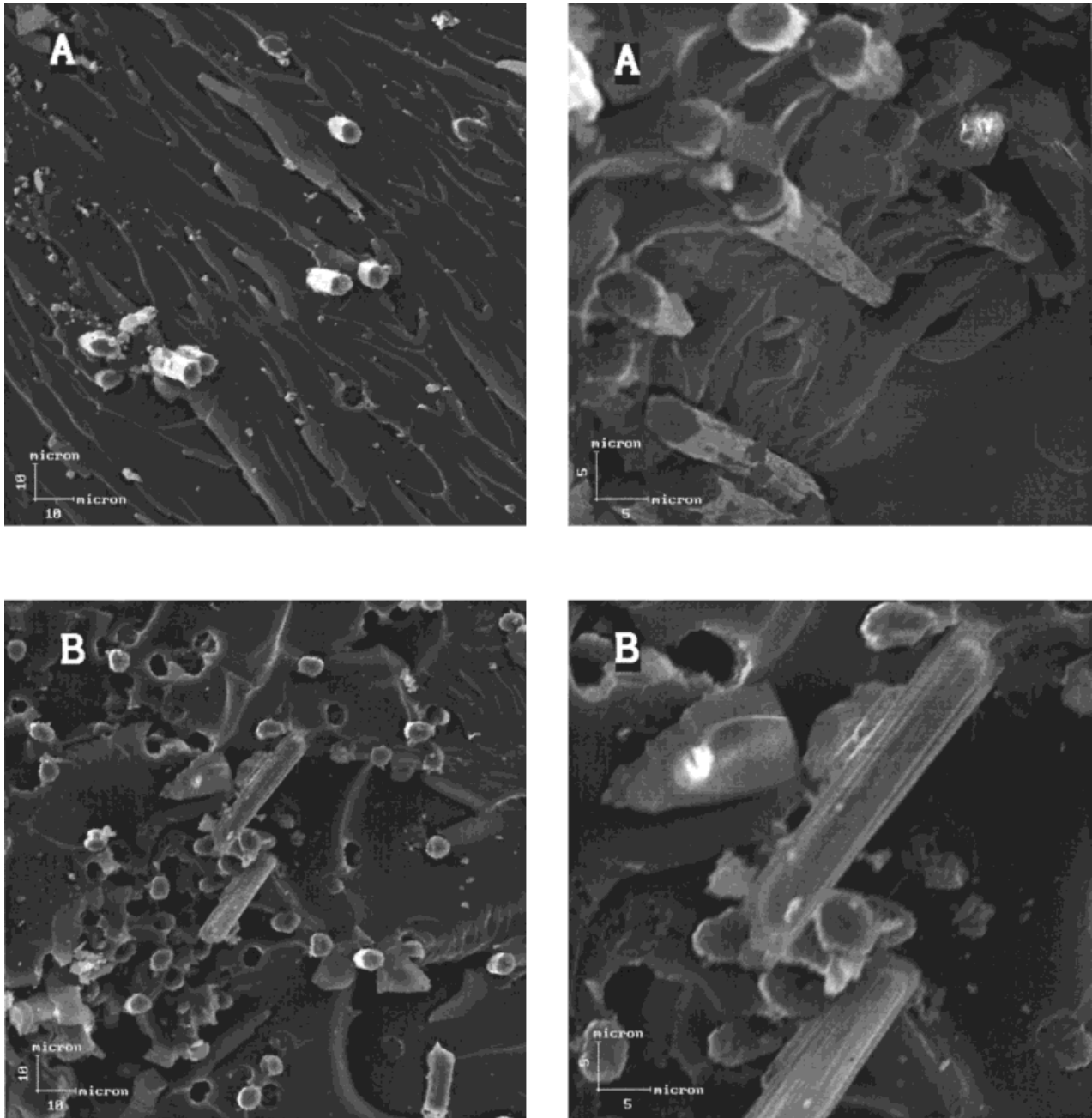


Figure 2 SEM micrographs of the fracture surface of epoxy resin/CF composites by using (A) HTPB-grafted CF and (B) nonmodified CF. (Micrographs at the right side correspond to the same sample at higher magnification.)

modified CF and matrix is expected since the commercial CF used in this work contains polar groups, which are able to interact with the epoxy matrix. However, some roles are also observed as a consequence of the fiber pull-out during the fracture [see Fig. 2(B)]. The interfacial adhesion in HTPB-grafted CF/epoxy composite is more significant, as it can observe in Figure 2(A), taken

at higher magnification. These results are in agreement with those obtained from impact tests.

The interfacial adhesion between epoxy resin and CF was also observed from tensile test of specimens containing one fiber filament. A dog-bone-shaped specimen containing an embedded single fiber in the epoxy matrix was submitted to tensile test until fracture and analyzed by optical

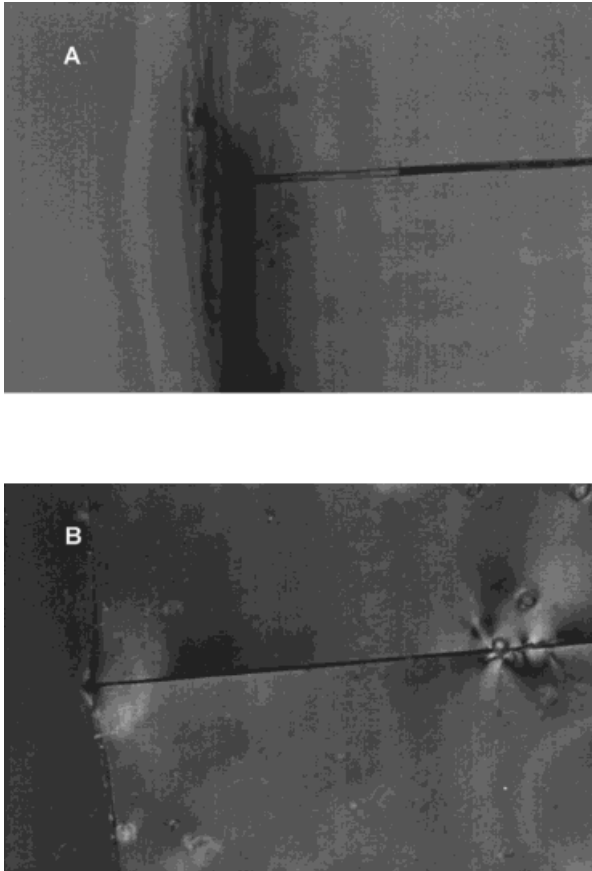


Figure 3 Optical microscopy of single-filament-composite. (A) Nonmodified CF and (B) HTPB-grafted CF.

microscopy. The photographs were taken in the fracture region. As illustrated in Figure 3(A), the nonmodified CF/epoxy resin system displayed a hole left by the pulled out fiber. The fiber fracture does not correspond to that of the epoxy matrix. On the other hand, the HTPB-grafted fiber broke together with the matrix. No fiber debonding in the fracture region was observed, indicating a great interfacial adhesion [see Fig. 3(B)].

The outstanding impact performance and interfacial adhesion of the HTPB-grafted carbon fiber/epoxy composite may be attributed to several factors. First of all, the elastomeric nature of the interface permits a better diffusion of the matrix across this interface, which contributes to an improvement of adhesion in this system. In addition, the chemical interaction between fiber and matrix promoted by the presence of functional groups in the modified fiber can enhance this adhesion. As previously discussed, the HTPB-grafted carbon fiber must contain amine groups originated from side reactions between

water as an impurity and NCO groups. Such amine groups can act also as curing agent of the epoxy matrix (together with the polyamine hardness), giving rise to an effective chemical bond between fiber matrix.

Carbon Fiber—Epoxy Composites Containing HTPB Dispersed in the Matrix

The fracture toughness of epoxy resins can be greatly improved with the addition of a small amount of rubber.^{17–19} This phenomenon is caused by the formation of homogeneously dispersed particles during curing cycle. The mechanical energy is uniformly distributed by the rubber particles, reducing the local stress concentration. Considering the potential toughening effect of rubbery phase, we decided to study the reinforcing behavior of nonmodified and HTPB-grafted CF in rubber-toughened epoxy matrix. For this purpose, the same HTPB sample used in the graft modification of CF was also employed as a rubber dispersed phase. The impact strength values of the composites containing different amount of dispersed HTPB are presented in Table IV. When HTPB was compounded with the epoxy resin without the presence of CF, the impact strength was not substantially affected probably because of the immiscibility between rubber and epoxy resin before cure and poor interfacial adhesion. The toughening effect of HTPB was higher in epoxy/CF composites. Indeed, the addition of 5 phr of rubber resulted in a great improvement of impact resistance of the composites constituted of both types of CF. Nevertheless, higher impact performance was obtained when HTPB-grafted CF was employed as reinforcing agent. In addition, the rubber content exerts a stronger influ-

Table IV Effect of the HTPB as a Rubber Dispersed Phase on the Impact Resistance of Epoxy Resin/Carbon Fiber Composites

HTPB phr	Impact Resistance (J/m)		
	Epoxy Resin	Epoxy Resin/CF	Epoxy Resin/HTPB-Grafted CF
0	7	24.0	43.4
5	6.7	45.4	75.2
10	12.5	50.7	147.5
20	8.5	65.7	No break ^a

^a The specimens could not be broken in the conditions of the Charpy tensiometer.

ence on this property when modified CF is present. The better results achieved with the epoxy/HTPB/HTPB-grafted CF system may be attributed to a stronger interfacial adhesion between the components.

The morphology of the impact fracture, taken from the scanning electron microscopy (SEM) analysis, is shown in Figure 4. The composite constituted by nonmodified fiber [Fig. 4(B)] presents some regions characterized by interfacial adhesion and some holes as a consequence of the pull-out phenomenon during the test. The interfacial adhesion of the modified carbon fiber with the epoxy matrix is more evident. Figure 4(C) shows that the fiber was broken during the impact test but still stayed strongly adhered into the matrix.

The presence of HTPB-grafted CF decreases the rubber domain size in the composite. This behavior may be explained by the higher curing velocity of the epoxy matrix in the presence of the HTPB-grafted carbon fiber, because of the probable presence of amine curing agent in this fiber. Increasing the curing process, decreases the probability of coalescence of rubber domains. Consequently, the dispersed particle sizes become smaller and more uniform, which may also be responsible for the higher impact strength.

CONCLUSION

The reaction between carbon fiber and TDI resulted in a NCO-modified fiber with a functionalization efficiency of 89% after ca. 45 min of reaction. The surface modification of these CF with HTPB increases the epoxy resin–CF interfacial adhesion. Consequently, an improvement in the impact strength was achieved. This adhesion may be attributed, among several factors, to the flexible nature of the grafted HTPB, which permits a better penetration of the epoxy matrix across the interfacial zone and to the presence of specific functional groups in the grafted carbon fiber, like amino groups, which react with the epoxy groups of the matrix, giving rise to an effective anchorage between the components. We believe this kind of interaction is more feasible than some interactions between hydroxyl groups in the HTPB grafted chains and the epoxy matrix. First of all, there are few OH groups available in the grafted chain because they were almost all consumed in the reaction with NCO groups. Second, this reaction was reported to be unlikely because gelation

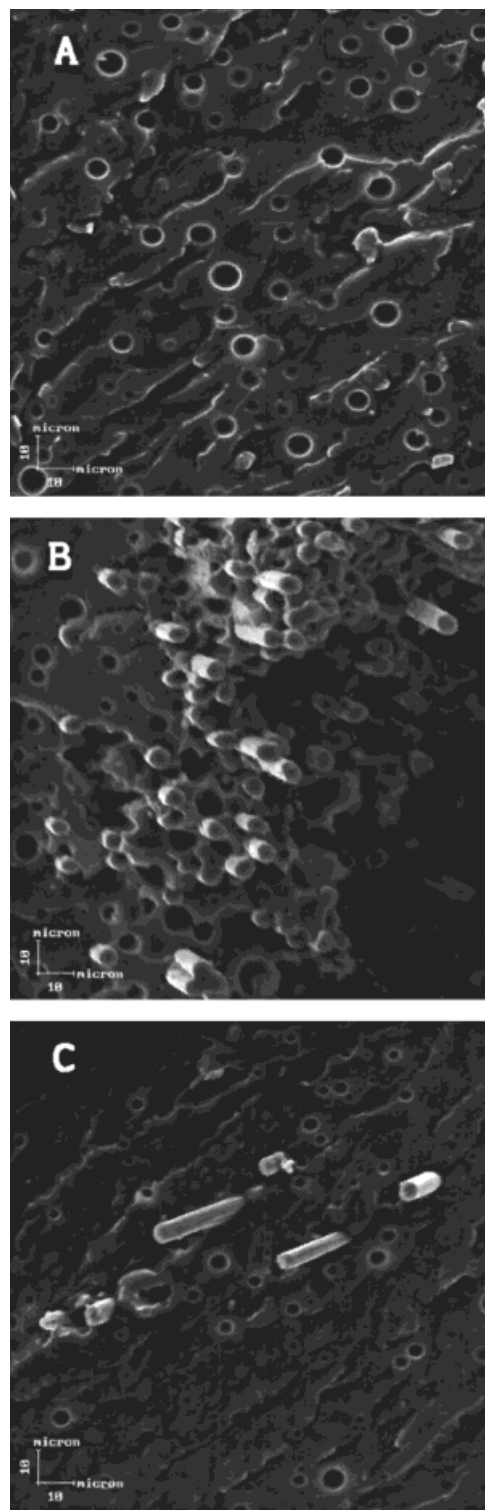


Figure 4 SEM micrographs of the fracture surface of epoxy resin/CF composites containing 5 phr of HTPB as the dispersed rubber phase. (A) Without CF, (B) with nonmodified CF, and (C) with HTPB-grafted CF.

of the matrix occurs before any substantial reaction of the OH groups in the rubber can take place.¹⁷

The addition of HTPB as a dispersed phase in nonreinforced epoxy matrix did not improve considerably the fracture properties because of the immiscibility between the rubber and the epoxy resin before cure. This characteristics resulted in a formation of larger rubber domains as indicated in SEM micrograph. When HTPB-grafted CF was compounded with the rubber-epoxy system, higher impact resistant materials were obtained. The outstanding fracture properties may be explained by the reinforcing character of the CF associated to the improved adhesion between the components. The modified CF also promotes a better dispersion of rubber particles, which also contributes to the toughness. It is reported that in rubber/epoxy blends, phase separation of the rubber is generally much faster than the curing process of the matrix.²⁰ Due to the probable presence of amino groups along the fiber surface, the matrix curing process is accelerated, thus diminishing the coalescence of the rubbery domains. The particle size becomes smaller with a more uniform size distribution. To conclude, a high fracture performance of epoxy-based composites can be achieved by employing CF coated with a flexible polymer layer chemically bonded to the fiber as reinforcing agent and a polymer matrix constituted by rubber particles dispersed in epoxy resin. In addition to the flexible interface, it is necessary that the fibers contain functional groups which is able to form chemical bond with the matrix.

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