

# Hybrid composites based on polypropylene and carbon fiber and epoxy matrix

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## Abstract

Polypropylene fiber and mercapto-modified polypropylene blend fiber (PPEVASH) were combined with carbon fiber as reinforcing elements in so-called hybrid epoxy composites. The impact performance and dynamic mechanical properties of these materials were investigated. Hybrid composites containing PPEVASH blend fibers display higher impact strength than plain carbon fiber composites but the performance is lower than plain PPEVASH–epoxy composite. The increasing of damping resistance and glass transition temperature, measured in terms of maximum damping temperature, of the hybrid EP/PPEVASH/CF composite may be attributed to several factors and include the interfacial adhesion PPEVASH fiber–matrix and PPEVASH–carbon fiber layers and the increasing of the crosslinking degree of the matrix, promoted by the presence of mercapto groups at the modified PP fiber surface. The presence of mercapto groups in the modified PP fiber also contributes for an improvement of the thermal stability, measured by thermogravimetric analysis. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Composite materials; Hybrids; Polypropylene fibers

## 1. Introduction

Fiber-reinforced composites offer great potential for use in aircraft and automotive primary structures. They are generally manufactured by using fibers as reinforcement and polymeric resin as a matrix. One of the most popular composite systems involves the combination of carbon fiber and epoxy resin. Carbon fibers present several advantages such as high modulus, high strength and stiffness and good creep resistance. In addition, these fibers show good compatibility with epoxy matrix. The interfacial adhesion between these components is attributed to the presence of some polar groups (hydroxyl and carboxyl) at the fiber surface, which are able to interact with the active groups present in the epoxy matrix [1]. Unfortunately, these composites are rather susceptible to impact damage. One of various approaches employed to improve the mechanical performance of these systems consists of replacing some amount of the carbon fiber by more ductile fibers [2–5]. Composites containing a combination of different fibers are called hybrid composites. The presence of two reinforcing phases in a composite may result in deviations from property estimations based on the weighted contributions of

the constituents alone. Such deviations are known as hybrid effects and can be positive or negative from the properties predicted by the rule of mixtures [6]. Several studies in the literature have been directed to the carbon/high-performance polyethylene fiber system [6–10]. The combination of the intrinsic mechanical properties of both reinforcement materials gives rise to unique structural materials in terms of impact, strength and stiffness [7–9].

Polypropylene (PP) fibers may also be a good candidate for the preparation of carbon fiber-based hybrid composites because of its low cost, relatively high strength and low density [11]. However, its chemical inertness is disadvantageous for a good adhesion with epoxy matrix. To overcome this problem, we recently performed the surface modification of polypropylene fiber by melt spinning a mixture containing polypropylene and mercapto-modified ethylene–vinyl acetate copolymer (EVASH) in a proportion corresponding to 100:5 phr [12]. This polyblend fiber was employed in the preparation of epoxy-based composites, giving rise to outstanding impact property material as compared to pure polypropylene fiber-based composites [13]. These results were attributed to a better fiber–matrix interfacial adhesion promoted by the presence of mercapto groups at the PP fiber surface.

Since the hybridization of brittle carbon fibers with

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Table 1  
Impact strength of the epoxy resin-based composites

Code	Composite components					Impact strength (J/m)
	Epoxy resin (vol%)	Fiber (vol%)				
		CF	PP	PPEVASH	Total	
EP/CF	56	44	–	–	44	209 ± 32
EP/PP	55	–	45	–	45	259 ± 38
EP/PPEVASH	55	–	–	45	45	951 ± 148
EP/PP/CF	60	15	25	–	40	246 ± 18
EP/PPEVASH/CF	50	15	–	35	50	352 ± 78

ductile PE fibers has proven to be highly effective in improving the impact properties of the composite [6–8] and considering the high impact performance of the composite constituted by mercapto-modified PP fibers [13], the combination of these two fiber components is expected to improve the impact performance of carbon fiber-based composites.

This paper investigates the effect of the hybridization with PP or PPEVASH fibers on impact resistance and dynamic mechanical properties of carbon fiber–epoxy resin composites. The arrangement of fibers within the hybrid strongly affects the mechanical properties of the composite [3,8]. In this work, an arrangement like a sandwich construction with carbon fiber as a core layer was employed. This design was chosen because of the good impact performance achieved with this type of construction in the carbon/Kevlar hybrid composite [3].

## 2. Experimental

### 2.1. Materials and sample preparation

A common epoxy system, Ciba Geigy CY260/HY561 based on bisphenol A with a polyaminoamide curing agent, in a proportion of 100:26 phr, was used as the matrix material. Carbon fiber (CF), Torayca T300 was employed as received. Polypropylene (PPH206) was supplied by OPP Petroquímica S/A, RGS, Brasil. Mercapto-modified ethylene–vinyl acetate copolymer (EVASH) was prepared in our laboratory, by a transesterification reaction between mercaptoacetic acid and EVA copolymer containing 18 wt% of vinyl acetate (Petroquímica Triunfo, RGS, Brasil). The reaction was performed in toluene solution, giving rise to an EVASH copolymer with 24.9 mmol% of mercapto groups [14] PP fiber and PPEVASH (95:5 phr) blend fiber were prepared by melt spinning, according to a previous report [12].

Unidirectionally reinforced epoxy composites were manufactured by stacking the preimpregnated (prepregs) layers into an open mold, applying vacuum and curing at 120°C for 120 min at 350 kPa. The prepregs were prepared in the laboratory by first wrapping the fiber on a carton

cylinder of 80 mm of inner diameter and 200 mm length. The wound fibers were cut, fixed with a staple at one extremity and impregnated with the epoxy system. Details and scheme concerning the prepreg preparation procedure are described in a previous paper [13].

For the PP, PPEVASH or carbon fiber-based composites, six layers of the prepregs were employed. In the case of hybrids, a sandwich arrangement consisting of three layers of PP or PPEVASH prepregs, three layers of CF prepregs and three layers of PP or PPEVASH prepregs were employed. The thickness of the composites was around 5 mm, except for the plain CF composite where the thickness was kept around 3 mm.

### 2.2. Characterization of the composites

The amount of fiber in the composite as well the thermal stability of the materials were determined by thermogravimetric analysis, with the help of a Du Pont TA9900 TGA apparatus, mod. TGA-951. The analysis were performed in nitrogen at 10°C/min within the range of 25–800°C. The first step degradation was related to the epoxy resin, the second step corresponds to the PP or PPEVASH fiber and the residue corresponds to the carbon fiber.

Charpy impact tests of the composites were performed on an EMIC AIC-1 impact tester at a speed of 3.45 m s<sup>-1</sup>, using a pendulum with nominal energies of 2.7 and 5.4 J. The measurements were made according to the ASTM D256 method, by using rectangular unnotched specimens which were 60 mm long and 10 × 5 mm in cross-section. The samples were loaded interlaminarly, according to the literature [3]. The fibers were disposed transverse to the impact direction. The unnotched specimens were chosen because the volume fraction of the fibers in the composite is known to influence the mechanical properties of the material. Since the hybrid composites are constituted by fibers with different ductility and stiffness, the notch gives rise to different fiber compositions in that point which could affect the impact results.

Dynamic mechanical analysis (DMA) was performed on a Du Pont TA 9900, in a flexural mode, at a heating rate of 5°C/min within the range of 25–200°C.

The scanning electron microscopy (SEM) of the composite

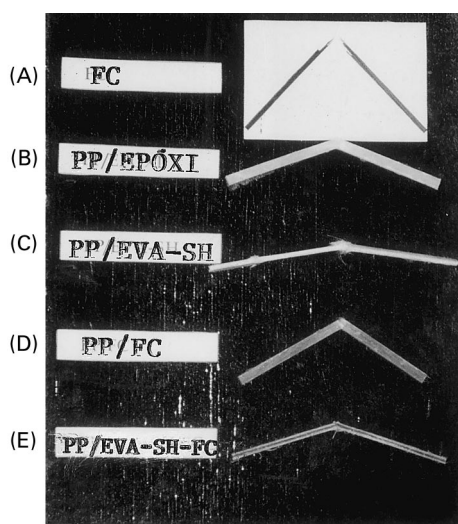


Fig. 1. Photographs of specimens after the impact test. Epoxy composites with: (A) CF; (B) PP fiber; (C) PPEVASH fiber; (D) PP/CF hybrid; and (E) PPEVASH/CF hybrid.

fracture surface was performed on a Zeiss-DSM 950. The surface was covered with a thin layer of gold.

### 3. Results and discussion

#### 3.1. Impact strength and morphology of the epoxy composites

Table 1 presents the impact resistance of the epoxy-based composites studied in this work. Plain PP fiber–epoxy composite (EP/PP) displayed higher impact strength than the carbon fiber composite (EP/CF). Since PP fiber has no active sites at the surface, the better impact performance of this composite may be associated with the ductile characteristic of this fiber together with debonding phenomena. Similar results have been also reported in the literature for plain polyethylene (PE) fiber-based composites [6,10].

The hybridization between PP and CF fibers (EP/PP/CF) resulted in an improvement of this property when compared to plain carbon fiber composites. Considering the volume fraction of each fiber component in the hybrid, the impact strength predicted by the “rule of mixtures” should correspond to 215 J/m. Therefore, the experimental value found in the EP/PP/CF hybrid composite (246 J/m) suggests a positive hybrid effect. Peijs et al. also found a strong positive hybrid effect in composites prepared with PE fibers and carbon fibers [6]. They have attributed their results to an extensive debonding of PE fibers and longitudinal shear failures between PE and CF fiber components. These phenomena may also be happening in our system due to the high impact performance of PP fibers themselves.

Epoxy composites prepared with plain mercapto-modified polypropylene fiber (EP/PPEVASH) displayed a very high impact resistance ( $951 \pm 148$  J/m). As discussed in a

previous report, this behavior is a consequence of a better interfacial adhesion between fiber and matrix, promoted by the presence of the mercapto groups at the PP polyblend fiber surface, associated with the ductile characteristics of these fibers [13]. The hybrid composite containing these functionalized fibers exhibits outstanding impact properties as compared to the plain carbon fiber composite. However, from the rule of mixtures, this material presents a negative hybrid effect.

According to the appearance of the test specimens after impact, shown in Fig. 1, almost no PPEVASH fiber fracture occurred in the plain PPEVASH (Fig. 1C) and in the corresponding hybrid specimen (Fig. 1E). These features are in agreement with the values obtained from impact tests and other results reported in the literature [8].

Fig. 2 illustrates the SEM photographs of the fractured surface in the impacted tested composites containing plain carbon fiber and their hybrids. The fracture of carbon fiber takes place in a brittle way and agrees with the lower impact resistance of the corresponding composite (see Fig. 2a). Hybrids incorporating PP fibers fail in a more ductile way and present extensive PP fiber debonding, which agrees with the positive hybrid effect found in impact tests.

In the case of PPEVASH–CF hybrid composite, the fiber debonding is not so extensive and some interfacial adhesion can be observed. The presence of mercapto groups at the PPEVASH fiber surface promotes a good matrix–fiber interaction. It is believed that some interactions between PPEVASH and CF also take place through the polar groups at the surface of both fiber components. Such interactions may explain the lower level of fiber debonding when compared to nonfunctionalized PP fiber.

According to the microscopic results reported in the previous paper [13], the plain PPEVASH–epoxy composite does not present substantial fiber debonding. Therefore, its higher impact strength may be associated to the good matrix–fiber adhesion and the fiber ductility. In the case of the PPEVASH hybrid composite, the lower impact strength related to the plain PPEVASH composite is supposed to be originated from the interface between the PPEVASH fiber layer and the carbon fiber layer. The interactions at this interface and the brittle energy absorption in carbon fiber composite inhibit the elastic and plastic deformations of PPEVASH fiber layer close to the CF layer. This phenomenon is not enough to decrease the impact performance of this hybrid at a level corresponding to plain CF, plain PP or PP–CF hybrid composites but probably contributes to the negative hybrid effect in this system.

#### 3.2. Dynamic properties

DMA has been employed by several authors to estimate the interfacial adhesion in composites [15–22]. In this paper, the influence of the hybridization of the carbon fiber–epoxy composite on these properties was also investigated. Table 2 presents the results of the experiments

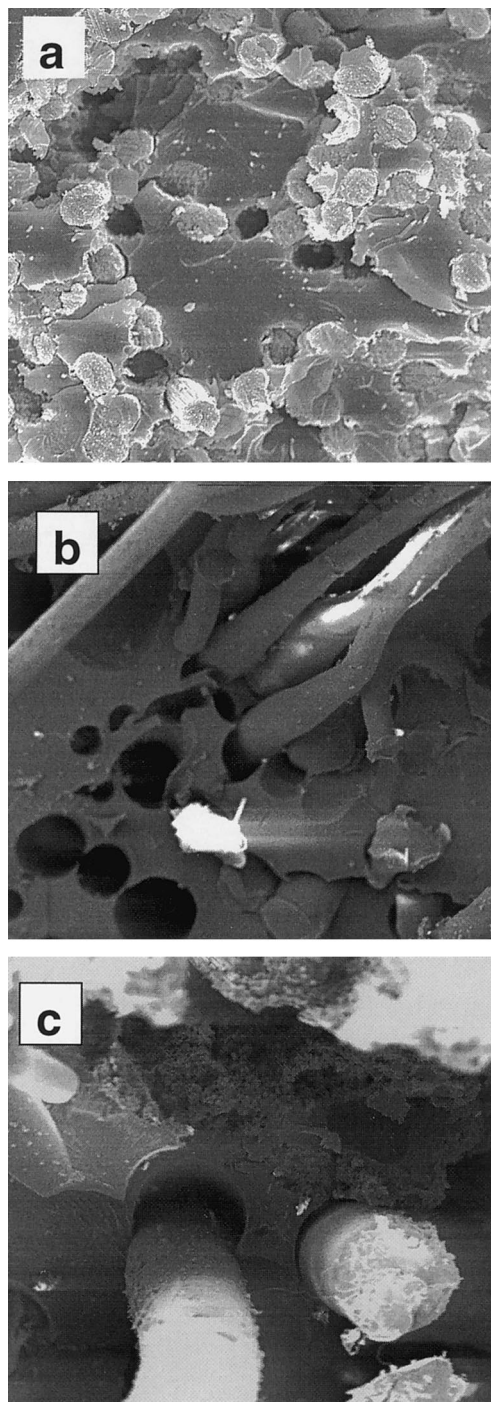


Fig. 2. SEM micrographs of the fracture surface of (a) plain EP/CF and the hybrids (b) EP/PP/CF and (c) EP/PPEVASH/CF composites.

recorded with the stress being applied in directions parallel with and transverse to the fiber orientation. The glass transition temperatures were taken from the maximum of the loss tangent ( $\tan \delta$ ) curves.

In all composites investigated, the flexural modulus (storage modulus,  $E'$ ) strongly decreases when the stress was applied transverse to the fiber orientation. This phenomenon was observed by other authors and explained

by the fact that, in the longitudinal direction, the stress is related to the deformation of the matrix–fiber as a whole [15]. Therefore, the modulus value is significantly affected by the fiber stiffness. As we can observe in Table 2, plain carbon fiber–epoxy composite (EP/CF) displays the highest flexural modulus in longitudinal direction due to the high CF stiffness. The presence of CF in the hybrid composites also contributes to an increasing of the modulus (taken in the longitudinal direction) although these values are very low when compared to plain CF composites. The soft characteristic of PP and PPEVASH fibers resulted in a substantial decreasing of the modulus of plain and hybrid composites.

The dynamic mechanical spectra of the hybrid composites are shown in Fig. 3. The epoxy-based composite constituted by PPEVASH/CF as fiber components displays a higher storage modulus than the hybrid PP/CF/epoxy composite. The onset of its decay is also shifted toward higher temperature. Further decay in the storage modulus of PPEVASH-based hybrid composites can be observed at around 200°C. The loss modulus ( $E''$ ) curve also presents a second peak. A similar shoulder at higher temperature was also reported by Kodama et al. for composites containing Kevlar fibers and polar matrices, which was attributed to specific interactions between fiber and matrix [16]. Concerning the PPEVASH/CF hybrid, the shoulder on the higher temperature side of  $E'$  and  $E''$  curves may be associated to the melting process of the functionalized fiber, which happens at 170°C by DSC techniques [12]. It is curious to observe that the  $E'$  and  $E''$  curves of the PP/CF hybrid do not present this second peak, although the crystallinity degree and melting temperature of the PP fiber are similar to those found in PPEVASH fibers. These results suggest that the melting process of the PPEVASH fibers is responsible for the second peak in the  $E'$  and  $E''$  curves. The higher modulus in this region when compared to PP/CF hybrids may be related to interactions between PPEVASH and CF layers due to the presence of polar groups in both reinforcing components. Such interactions decrease the flexibility of the PPEVASH fibers and inhibit their plastic and elastic deformations, thus increasing the modulus. In addition, the mobility of the epoxy matrix situated in between these layers is also decreased and may contribute to the increase of modulus in the higher temperature region.

The glass transition temperature and loss tangent ( $\tan \delta$ ) are influenced by the matrix–fiber interactions. Higher interactions result in a reduction of the mobility of the macromolecular chains located in the fiber surface environment and cause a shift of the glass transition point towards higher temperature ranges and a decreasing in damping [15–19]. Fig. 4 illustrates the dependence of loss tangent with the temperature for the hybrid composites with the fiber orientation in the longitudinal direction related to the applied stress.

The hybrid composite constituted by nonfunctionalized PP fibers presents a higher glass transition temperature and

Table 2  
Dynamic properties of the epoxy-based composites

Code	Flexural modulus (GPa)	$T_g$ (°C)	$\tan \delta$	$\tan \delta_c^0$	$\tan \delta_c^0 - \tan \delta$	$\varphi_f^a$
<i>Longitudinal direction</i>						
EP	3.01	82.2	1.34	–	–	–
EP/CF	38.3	105.2	0.48	0.75	0.27	0.44
EP/PP	2.98	103.3	0.34	0.74	0.40	0.45
EP/PPEVASH	2.30	131.0	0.26	0.74	0.48	0.45
EP/PP/CF	3.52	116.0	0.36	0.80	0.44	0.40
EP/PPEVASH/CF	4.93	136.0	0.24	0.67	0.43	0.50
<i>Transverse direction</i>						
EP/CF	5.02	93.7	0.67	0.75	0.08	0.44
EP/PP	2.11	103.9	0.55	0.74	0.19	0.45
EP/PPEVASH	0.52	126.0	0.34	0.74	0.40	0.45
EP/PP/CF	2.00	113.0	0.50	0.80	0.30	0.40
EP/PPEVASH/CF	1.07	128.0	0.36	0.67	0.31	0.50

<sup>a</sup> Volume fraction of fiber in the composite.

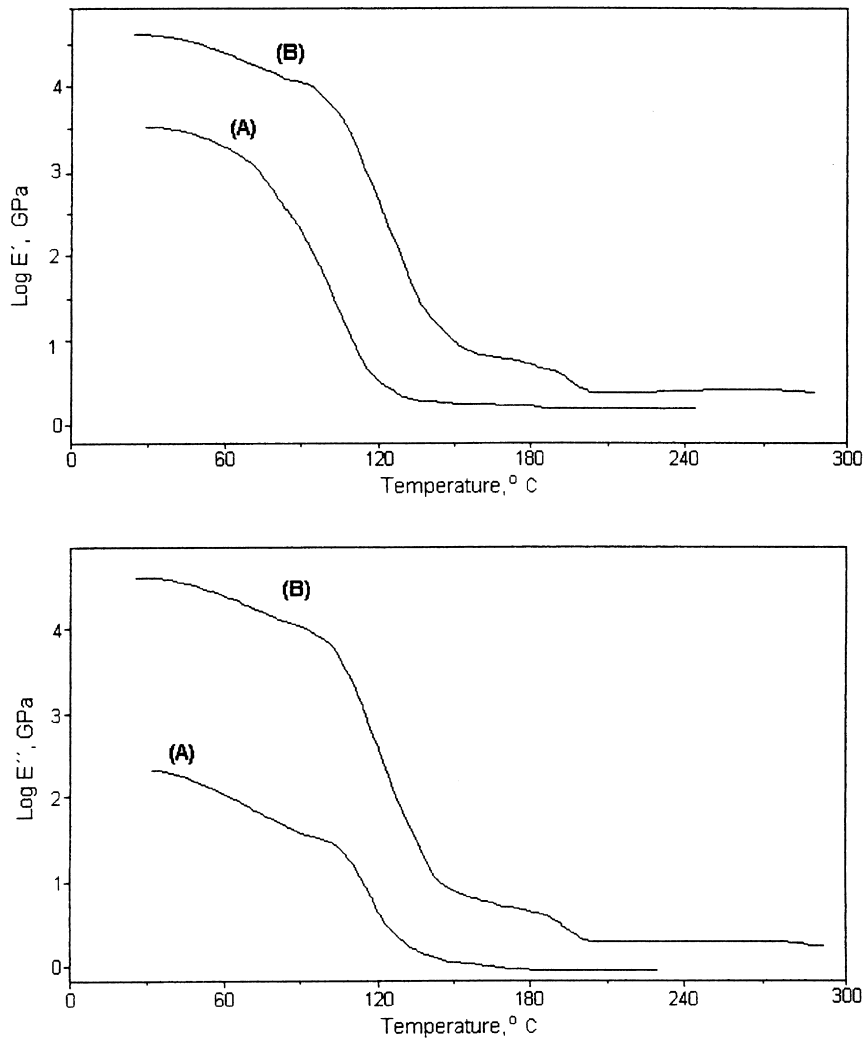


Fig. 3. Dynamic mechanical spectra of hybrid composites taken in a longitudinal way to the fiber direction. (A) PP hybrid and (B) PPEVASH hybrid composites.

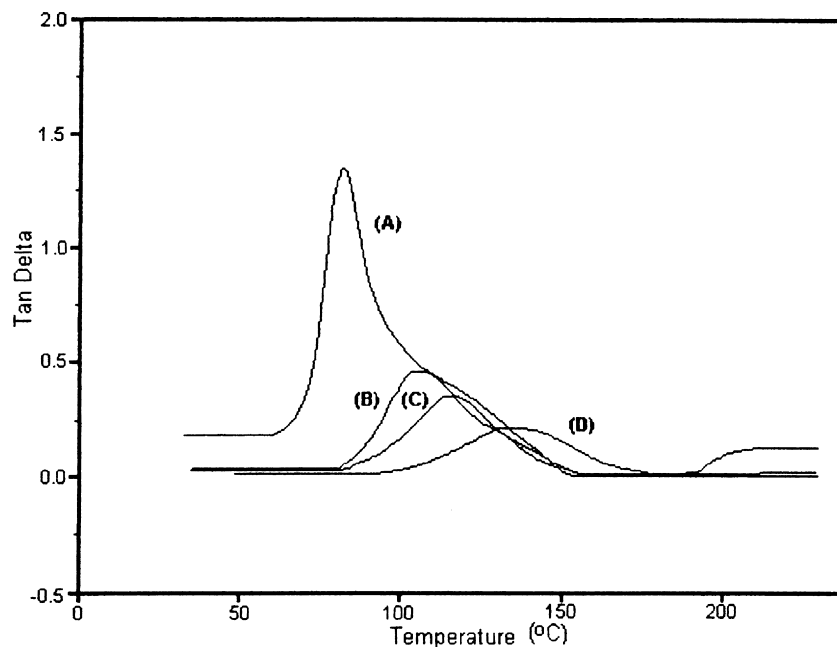


Fig. 4. Loss tangent,  $\tan \delta$ , as a function of temperature in (A) epoxy resin and the epoxy composites with (B) carbon fiber, (C) PP/CF and (D) PPEVASH/CF (stress applied in the longitudinal direction to the fiber orientation).

lower  $\tan \delta$ , as compared to the plain PP or CF composites. Since PP fibers are not able to promote specific interactions with the matrix or CF, the restraint of the molecular motions of the matrix may be due to the difference between the thermal expansion coefficients of the components.

The presence of mercapto-modified PP fiber (PPEVASH) in the hybrid composite promotes a substantial increasing of the glass transition temperature followed by a considerable decreasing of  $\tan \delta$  of the epoxy matrix. These phenomena also occur with the PPEVASH plain composite (see Table 2) and are observed when the stress is applied in both longitudinal or transverse directions. Several factors cause these results. First of all, the mercapto groups at the functionalized PP fibers interact with the polar groups of the epoxy matrix, promoting a good interfacial adhesion. These mercapto groups also act as a curing agent for epoxy resin and increase the crosslinking degree of the matrix. These phenomena affect the mobility of the chain segments of the matrix and consequently the dynamic mechanical properties.

In the case of the PPEVASH/CF hybrid, there must be additional interactions between the CF and PPEVASH fibers, reducing the flexibility of the fibers and mobility of the chain segments of the matrix located in between these fiber layers. Such interactions contribute to an additional shift of the  $T_g$  towards higher temperature and the presence of another damping peak around 200°C. This second damping peak can also be associated with the melting of the PPEVASH fiber, as discussed before.

The magnitude of  $\tan \delta$  in a composite is influenced by the volume fraction of the reinforcement and the interactions

between fiber and matrix. As suggested by Nielsen [23], the damping term of an ideal composite ( $\tan \delta_c^0$ ) can be estimated from the “rule of mixtures”, according to the following equation:

$$\tan \delta_c^0 = (1 - \varphi_f) \tan \delta_m$$

where  $\varphi_f$  is the volume fraction of the fiber and the subscripts c and m refer to the composite and matrix, respectively.

The values of  $\tan \delta_c$  of the composites were compared to the calculated  $\tan \delta_c^0$  in Table 2. No system listed in this table can be considered as an ideal composite since the  $\tan \delta_c^0$  values are always different from the experimental values. The plain PPEVASH fiber composite presents the highest deviation from the ideal composite in both longitudinal and transverse directions due to the strong interactions fiber–matrix and the higher crosslinking degree of the matrix promoted by the mercapto groups at the fiber surface, as discussed before.

Concerning the PPEVASH/CF hybrid composites, the deviation from an ideal composite ( $\tan \delta_c^0 - \tan \delta$ ) is lower than for plain PPEVASH composite. In the case of hybrids, the presence of different reinforcing fibers in the composite must be taken into account. The volume fraction of PPEVASH fibers (which contributes to the lowest  $\tan \delta$  value) in the hybrid is lower than in the plain PPEVASH composite (see Table 1). In addition, the second damping in this hybrid was not considered in these calculations. It is important to emphasize that Nielsen’s theory [23] was employed in composites constituted by one type of fiber.

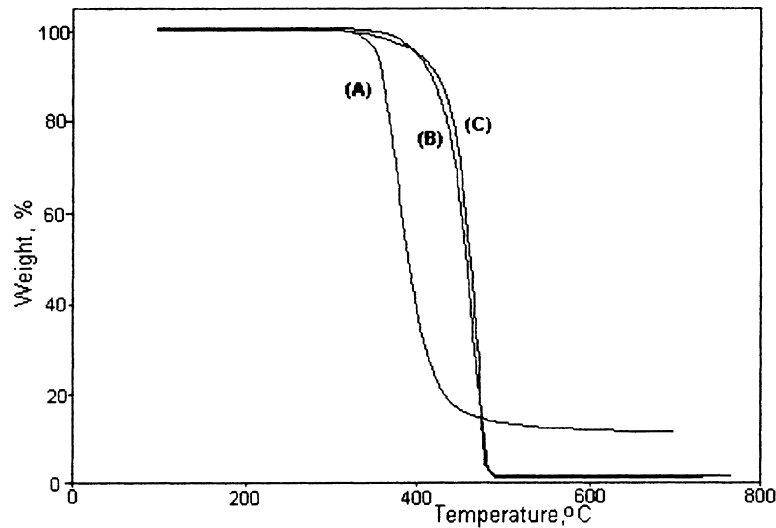


Fig. 5. Thermogravimetric analysis of: (A) epoxy resin; (B) PP fiber; and (C) PPEVASH fiber.

The application of the rule of mixtures in hybrid composites may not be efficient because of the different contributions of the fibers for damping.

### 3.3. Thermal stability

The thermal stability of the PP and PPEVASH fibers and the corresponding plain and hybrid composites has been studied by TGA analysis. Fig. 5 compares the thermal decomposition of the fibers with the epoxy resin. The fibers are thermally more stable than the epoxy resin. The presence of EVASH in the polyblend fiber resulted in a slight improvement of the thermal stability (see Fig. 5C). A similar behavior can be also observed in the plain PP or PPEVASH composites in Fig. 6. The effect of PPEVASH fiber on the thermal stability of the composite is more pronounced in the hybrid system. As we can observe in Fig. 7, the onset of the thermal decomposition in the

PPEVASH/CF hybrid composite coincides with the plain carbon fiber composite and is superior to that corresponding to the PP hybrid composite. The improvement of thermal stability of EVASH-based systems has been previously reported in other studies concerning natural rubber-based blends [24] and poly(methyl methacrylate)-based graft copolymers [25].

## 4. Conclusions

Polypropylene blend fiber modified with EVASH (PPEVASH) imparts good impact performance to epoxy resin-based composites. These fibers can also be employed in hybrids with carbon fiber to improve the impact resistance of these materials. Its outstanding impact performance may be attributed to the ductile characteristics of the PPEVASH fiber and the presence of mercapto groups at

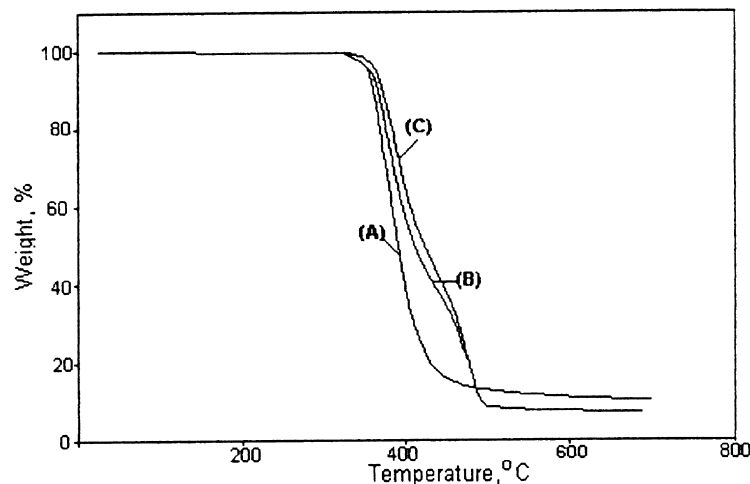


Fig. 6. Thermogravimetric analysis of (A) epoxy resin and the plain (B) EP/PP and (C) EP/PPEVASH composites.

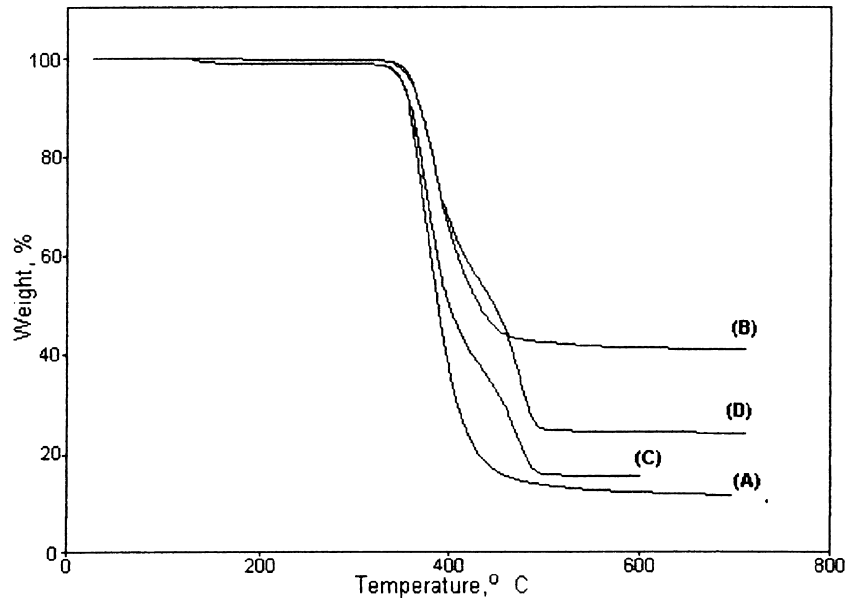


Fig. 7. Thermogravimetric analysis of (A) epoxy resin; (B) the plain EP/CF composite and the hybrids (C) EP/PP/CF and (d) EP/PPEVASH/CF composites.

the fiber surface which promotes a better interfacial adhesion between fiber and epoxy matrix. Since mercapto groups are good curing agents for epoxy resin, the interaction fiber–matrix may also promote a higher crosslinking degree of the matrix. The crosslinking normally results in a more brittle matrix, being also responsible for the shift of the glass transition temperature of the epoxy matrix towards higher values in both plain and hybrid composites. However, this phenomenon does not affect the impact performance of plain PPEVASH composites because of the ductile characteristic of the fiber. In addition, the adhesion of these fibers in a brittle matrix favors the stress transferring between the phases, and increases the ability of the system in absorbing the impact energy. The PPEVASH/CF hybrid composite displays lower impact resistance because of the brittle nature of the carbon fiber. The increasing of the crosslinking degree of the matrix promoted by the mercapto groups and the presence of the brittle CF contribute to a negative hybrid effect in the impact property of this composite. However, it is important to point out that the hybridization of CF-based composites with PP or PPEVASH substantially improves the impact performance of the material. The best results were achieved with the functionalized fiber.

In addition to the impact and damping properties, the presence of mercapto groups in the PPEVASH polyblend fiber results also in an increasing of thermal stability of the corresponding epoxy composites.

From all results presented in this work, we can conclude that the hybridization of CF-based composites with mercapto-modified PP fiber improves the impact resistance and increases the glass transition temperature without affecting the thermal stability. Considering the good properties of polypropylene as low density and low cost, the interesting features reached with the functionalization of PP fiber

may be very useful for the development of higher performance composites with a thermal stability comparable to the CF-based composites.

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