ORIGINAL PAPER

Dynamic mechanical, thermal, and morphological study of ABS/textile fiber composites

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Abstract In this work, acrylonitrile–butadiene–styrene ABS terpolymer was mixed with acrylic fiber, cotton fiber, and waste textile fiber (WTF) (50/50 wt% cotton/acrylic fiber) with 10 and 30 wt% of fiber content in a batch mixer. The composites with 30 wt% of acrylic fiber showed the highest stabilized torque, while the compositions with 30 wt% of cotton were situated at the lowest values in torque rheometry. The fiber addition up to 30 wt% did not have effect on the degradation behavior of ABS matrix. The composites with 30% textile fiber showed a higher degradation step, which is related to fiber degradation. The fiber content resulted in a considerable increase in stiffness at all temperatures as can be observed on the dynamic mechanical thermal properties (DMTA). The reinforcing effect was higher in the region above the glass transition temperature, T_g, of the matrix, this is primarily due to the larger difference in mechanical properties between the filler and the matrix as it goes from the glassy to the rubbery state.

Keywords Composites · Fibers · Dynamic mechanical properties · ABS

Introduction

Natural fiber reinforced composites combine acceptable mechanical properties with low density. Such composites offer a number of well-known advantages which include low cost, availability of renewable natural resources, and biodegradability. However, the main disadvantage of composites made of polymer and natural fibers

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is the poor compatibility between the mainly hydrophobic polymer-matrix and the hydrophilic fibers [1].

Demand for natural fibers in plastic composites is forecast to grow 15–20% annually with a growth rate of 15–20% in automotive applications [2]. Polypropylene, polyethylene, and poly(vinyl chloride) are the most common thermoplastic materials that currently dominate as matrices for natural fibers composites while thermosets, such as phenolic resins and polyesters are also common matrices [2]. It is now possible to produce plastic composites using natural fibers for applications such as roofing, panelling, food grain silos, and low cost housing units. Natural fiber reinforced composites are now being seen as the most appropriate and cost effective building materials [3].

The reuse of fiber products shows the greatest advantages in terms of saving resources and energy for developing new materials. The production of synthetic fibers is more expensive compared to non-fibrous plastics. Commercial acrylic fibers used by the textile industry consist of not less than 85% acrylonitrile (AN), with the sum of additives and comonomers that cannot exceed 15%. [4]. Among synthetic fibers acrylic is after polyester and polyamide fibers in importance [4, 5]. The association of modacrylic fibers (synthetic polymeric product) with cotton fabrics (natural polymeric product) in a blend provides fire-proofing properties of interest [6].

Acrylonitrile–butadiene–styrene (ABS) terpolymer is a widely used engineering thermoplastic owing to its desirable properties which include good mechanical properties, chemical resistance, toughness, dimensional stability, good surface appearance, and easy processing characteristics [7–10]. ABS also exhibits certain limitations like low thermal stability, poor flame resistance, and low mechanical properties compared to other engineering plastics, these drawbacks can be overcome by addition of fibers [8, 9].

The aim of this work is to gain further understanding on the thermal, structural, and viscoelastic properties of composites made from ABS with cotton and acrylic fibers. The thermal behavior and structural transitions of composites have been investigated using thermogravimetric analysis (TGA), dynamic mechanical thermal analysis (DMTA), and scanning electron microscopy (SEM).

Experimental

Composites preparation

ABS (MAGNUM 9010, Dow Chemical, specific gravity 1.04 g/cm^3 and MFR 7 g/10 min at 230 °C/3.8 kg) and acrylic fibers (Radici Fibras Ind. Com. Ltda), cotton fiber (Paramount Textile Industry) and waste textile fiber (WTF) (50/50 wt% cotton/acrylic fiber, Stumpf Textile Industry) in 10 and 30 wt% of fiber content were mixed in a batch mixer with a capacity of 75 cm^3, coupled with a torque data acquisition system. The material was processed at 60 rpm and 170 °C for 500 s.

Before mixed with ABS, all the fibers were previously defibrillated in a high speed mill, resulting in fibers with approximated 30-mm length and 0.3-mm

diameter (L/D 100), for further melt processing into batch mixer. After processed in the batch mixer, the composites were grinded in a knife mill and dried in a vacuum oven for 24 h.

The composites were injection molded in a HIMACO LHS 150/80 injection molding machine in a temperature range from 210 to 240 °C with mold temperature of 45 °C.

Mechanical testing

Three-point bend flexural tests were performed using an Emic universal testing machine model DL3000. The width and thickness of the specimens were measured and recorded. Samples were tested at a crosshead speed of 1 mm/min. The tests were carried out in accordance with ASTM D 790. The flexural modulus and flexural strength were calculated from this test. At least five specimens were tested for each set of samples and the mean values were reported.

Thermal analysis—TGA

TGA analyses were performed in a Shimadzu TGA-50 from 50 to 750 °C in nitrogen atmosphere (50 mL min^{-1}) under a constant heating hate of 10 °C/min. The average sample weight used in TGA analysis was 10 mg.

Dynamic mechanical thermal analysis—DMTA

Dynamical experiments were carried out in DMA Q800, TA Instruments using single cantilever geometry. The experiment was conducted within the linear viscoelastic region using small amplitude (0.1%). The heating rate was fixed at 3 °C/min and the frequency was set to 1 Hz for all samples.

Morphological analysis—SEM

A Shimadzu Superscan SS-550 scanning electron microscope, 15 kV, with secondary electrons detector was used to observe the surface morphology of the composites, obtained from the cryogenic fracture. All samples were coated with a conductive layer of sputtered gold prior to the analysis.

Results and discussion

Processability study

When the polymer is introduced in the mixing chamber, the solid granules offer a certain resistance to the free rotation of the blades and therefore the torque increases [11]. When this resistance is overcome, the torque required to rotate the blades at the fixed speed decreases and reaches after a short time a steady state regime. When the heat transfer is sufficient to completely melt the core of the particles, the torque

decreases and reaches again a steady state condition. The observed torque in steady state condition is proportional to the viscosity of the composite in melt state, showing one value corresponding to the stabilized torque at the end of processing, as can be seen in Fig. 1. The processing was performed at 170 °C, because acrylic fiber and cotton fiber can suffer, chemical changes, such as cyclization, dehydrogenation, and chain scission [12, 13]. This chemical changes take place when these fibers are exposure to high temperatures in processing.

The results showed an increase of the stabilized torque with the fiber content, although the time to reach the stabilized torque was higher for the compositions with higher fiber content.

The compositions with 30 wt% of acrylic fiber showed the highest stabilized torque, while the compositions with 30 wt% of cotton were situated at the lowest values. The stabilized torque for WTF and cotton fiber presented a similar behavior when the same fiber content was used.

Mechanical testing

Figure 2 shows the flexural modulus for the all ABS/textile fibers composites. The addition of fibers resulted in an increasing of flexural modulus for all composites when compared to neat ABS.

The increase in flexural modulus and consequent reinforcement effect is probably a result of a good load transfer between the fibers and polymeric matrix. The reinforcement effect observed in the composites showed a linear relation with fiber content. As the fiber content increases higher Young's flexural modulus values are observed, resulting in a more rigid material. The highest flexural modulus was observed for the sample ABS/cotton fiber 70/30. Table 1 summarizes the flexural test results for all composites.
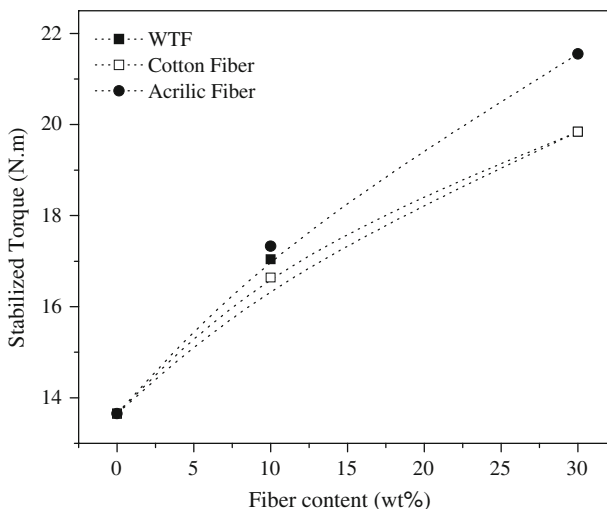

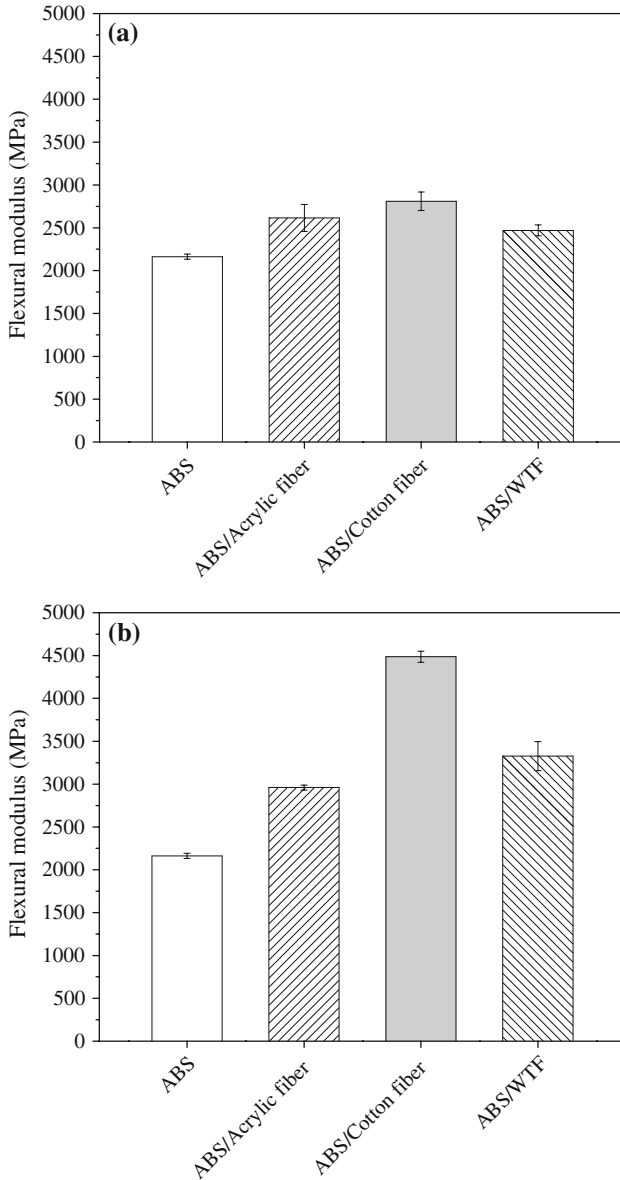**Fig. 1** Stabilized torque as a function of fiber content for all composites

Fig. 2 Flexural modulus of ABS/fibers composites **a** 90/10, **b** 70/30

It can be noted that in the composites with lower fiber content, there was a decrease in the flexural strength values. This phenomenon occur mainly because less fiber content makes the material more fragile, thus, in this case the fiber behaves like a defect in the polymer matrix making difficult the internal load transfer between the polymeric matrix and the fibers. Flexural yield strength depends very much on fiber

Table 1 Mechanical properties data of ABS/fibers composites

| Sample	Flexural yield strength (MPa)	Flexural modulus (MPa)
Pure ABS	46.17 ± 0.43	2,162 ± 30.90
ABS/acrylic fiber (90/10)	45.70 ± 0.45	2,616 ± 157.30
ABS/acrylic fiber (70/30)	51.98 ± 0.47	2,960 ± 29.39
ABS/cotton fiber (90/10)	39.37 ± 0.33	2,810 ± 108.60
ABS/cotton fiber (70/30)	51.56 ± 0.90	4,486 ± 64.54
ABS/WTF (90/10)	44.10 ± 0.20	2,469 ± 63.37
ABS/WTF (70/30)	45.94 ± 0.45	3,327 ± 169.5

alignment and the location of resin-rich areas. Lower fiber content regions can act as cracking propagation, resulting in lower flexural yield strength.

The chemical interaction between the ABS polar groups (nitrile groups) and the hydroxyl groups of the cotton fiber caused a better stress transfer from the matrix to the fibers, leading to a higher flexural modulus and higher flexural yield strength [1].

Thermogravimetric analysis results

Thermograms for ABS and its composites, with 10 and 30 wt% of textile fiber, respectively, acquired in nitrogen are shown in Figs. 3, 4.

Two main steps in the degradation pathway of ABS/textile fiber composites are observed. The first step, between 309 and 335 °C, can be attributed to the fiber degradation. The second degradation event occurs above 400 °C and it is related to the evolution of volatile products deriving from polybutadiene followed closely by the aromatics of the styrenic fraction that lead to the formation of a charred residue
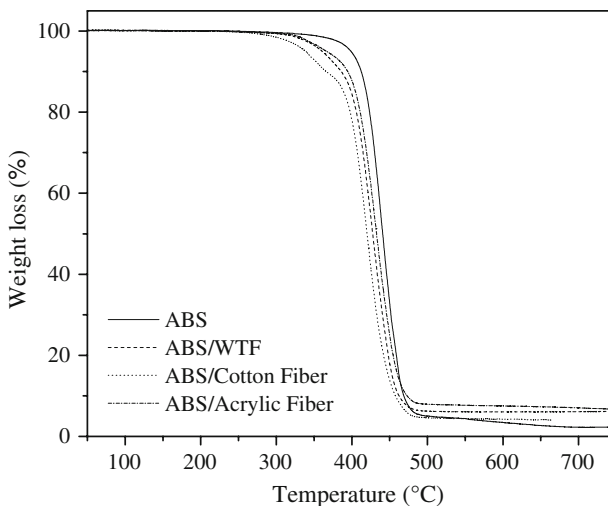
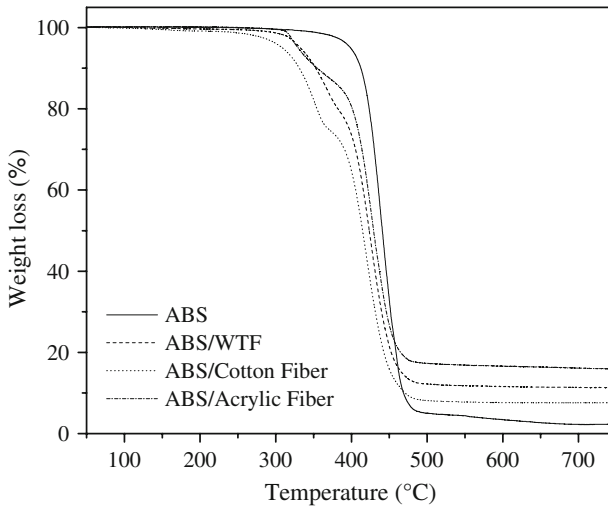**Fig. 3** TGA curves of ABS and its compositions with 10 wt% of WTF, cotton, and acrylic fibers

Fig. 4 TGA curves of ABS and its compositions with 30 wt% of WTF, cotton, and acrylic fibers

[13, 14]. Significant increase in the charred residue at 600 °C is observed for the composites studied when compared to the neat ABS.

The degradation of the composites with 10 and 30% of acrylic fiber occurs in two stages. Stage I occurs around 300 °C and stage II around 400 °C. The weight loss in stage I could be associated with nitrile oligomerization which produces volatile products (NH_3, HCN, CH_3CN, etc.) and subsequent chain scission [13, 14]. The second stage is related to ABS and acrylic fiber degradation. This curve showed the highest amount of char, compared with other fibers used in this study.

The degradation process of cotton fiber composites can be described as follows. The first weight loss centered on 300 °C corresponds to the thermal degradation of cotton [15]. The final weight loss above 400 °C is assumed to be due to oxidative degradation of the cellulosic char together with thermal degradation of ABS. The blending of cotton fiber and ABS may influences the weight loss stages to some extent.

As the WTF is composed by acrylic and cotton 50/50 wt%, the degradation curves showed two steps, one referring to the cotton degradation occurring at 378 °C and another one at 317 °C, which correspond to acrylic degradation. When blending with ABS, the degradation temperature of the composites lied between 335 and 406 °C for composites with 10% of WTF, and 330 and 406 °C for composites with 30% of WTF.

As the acrylic content increases in the composites, the onset temperature becomes lower. However, the addition of cotton did not change the onset temperature of the composites. The second degradation event related to the ABS resin was more clearly showed in the composites with 30 wt% fiber content.

The fiber addition up to 30 wt% did not have significant effect on the degradation behavior of ABS matrix. All composites with 30% textile fiber showed a higher

degradation step related to the first degradation event, which is related to fiber degradation.

Dynamic mechanical results

The fiber or filler content effect on the dynamic properties resulted in a considerable increase in storage modulus at all temperatures; these effects are also seen in polymer nanocomposites [16, 17]. The reinforcing effect is higher in the region above the glass transition temperature of the matrix and this is primarily due to the larger difference in mechanical properties between the filler and the matrix as it goes from the glassy to the rubbery state. This fact can be observed in storage modulus for the composites studied as shown in Fig. 5a–c.

DMTA data can be used to estimate the heat distortion temperature (HDT) of a polymer [16]. In this work, the value of HDT was set at a stress of 1.8 MPa. This result of HDT was estimated using DMTA storage modulus data. Thus, it was possible to evaluate the fiber type and the fiber content effect on flexural stability of the composites in relation to neat ABS. Table 2 shows the HDT values estimated by DMA, storage modulus value (E') at −50, 25, 125 °C and glass transition (T_g) for all samples. The glass transition was defined as the maximum of the damping factor (tan δ).

The DMTA results had good correlation with the results obtained by applying the method described in ASTM D 648, as observed by Alcock et al. [18] using the dual cantilever geometry. This result is an estimative and thus cannot be taken as a model to describe a static HDT behavior.

As it can be observed in Table 2, there was an increase in storage modulus (E') values of the composites when compared with neat ABS. The increase in stiffness in all composites is caused, mainly to a physical interaction between the fibers and polymeric matrix, in this case ABS. In many scientific studies involving polymer/fiber composites [1–3, 19] the use of a compatibilizer agent is necessary in order to reduce the interfacial tension between the matrix and fiber, providing an increase in the mechanical properties in the final material. A good fiber/polymer adhesion results in good interfacial load transfer in the composite, thus improving the mechanical properties. The good interfacial load transfer can also be achieved by using as a polymeric matrix, copolymers having functional groups like hydroxyl, carbonyl, carboxyl, anhydride, and others that can interact with the functional groups of filler molecules by forming chemical bonds.

In our study, it was not used a compatibilizer agent because we initially believed that there could be a chemical interaction between the acrylic fiber and ABS matrix because of the presence of nitrile group, resulting in a decrease of the interfacial energy in the polymer/fiber system.

The reinforcement effect in polymer/fiber composites made of textile fibers formed by numerous filaments is not only just ruled by the fiber rigidity, but also for the fiber ability to store energy inside the filament bundle. The cotton fiber is less rigid than acrylic fiber; however, the addition of the acrylic fiber in ABS results in a minor reinforcement effect when compared to cotton fiber. Kim and co-workers [19] reported that fibers can entangle during melt processing, resulting in an increase in

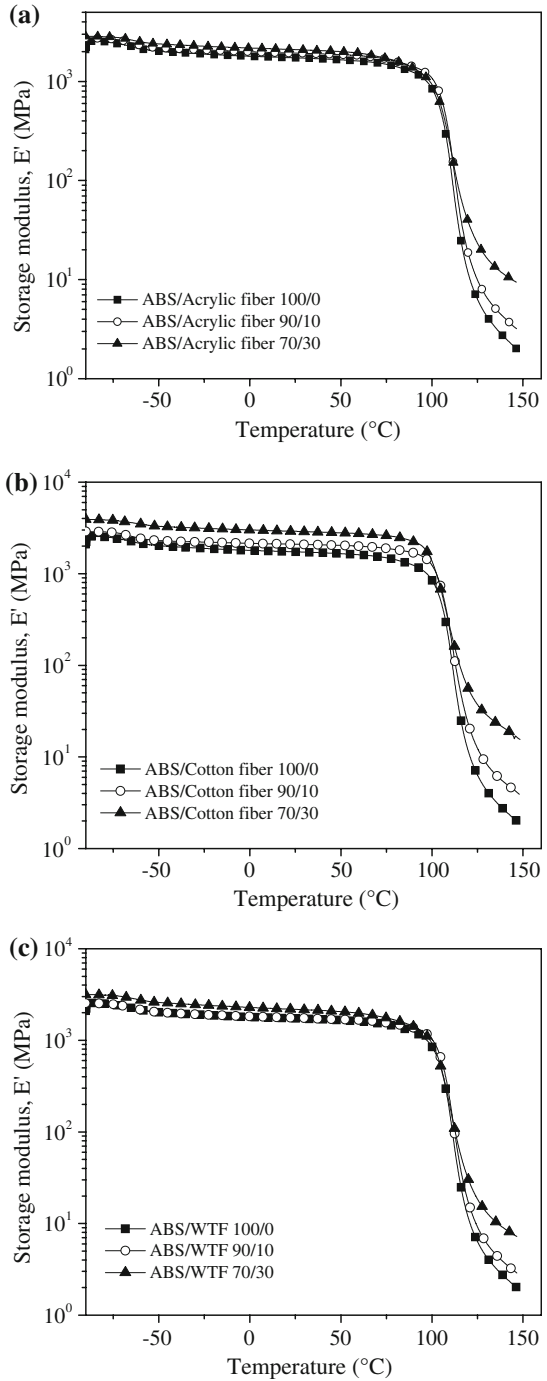**Fig. 5** Storage modulus vs. temperature for all ABS/fiber composites

Table 2 HDT, storage modulus, and T_g results for all samples

ABS/fiber	Type of fiber	HDT (°C)	E'; −50 °C (MPa)	E'; 25 °C (MPa)	E'; 125 °C (MPa)	T_g (°C)
100/0	–	100.8	2026.6	1735.3	6.2	115.5
90/10	Acrylic	103.9	2186.4	1932.5	9.9	115.5
70/30		102.1	2397.7	2099.1	23.2	114.1
90/10	Cotton	104.2	2305.0	2098.6	12.2	115.1
70/30		104.0	3300.9	2904.1	37.1	113.0
90/10	WTF	103.1	2029.3	1759.5	9.1	115.3
70/30		101.6	2595.1	2178.2	18.3	113.8

T_g defined as the maximum tan δ value

stiffness and consequently in mechanical properties. The results observed for DMTA corroborate with mechanical testing performed in this study.

On the other hand, in polymer/textile fiber composites, it is not present one interface only, but several interfaces among the threads that make up the fiber. Depending on how these threads are organized, or if there are voids among them, the composite can dissipate more energy per cycle of sinusoidal deformation, thus resulting in higher values for tan δ and consequently better reinforcement effect.

The presence of a higher viscous component in the composite can result in a minor reinforcement effect. This fact occurs because less stress is transferred among the interfaces, showing that even when fibers with higher elastic modulus are used, like acrylic fiber when compared to cotton fiber, there is no increase in dynamic-mechanical properties just because the fiber rigidity physical effect.

Figure 6 shows tan δ curves of ABS and its composites.

It can be clearly seen that the three characteristic transitions of ABS. The transition temperature observed at −65 °C is referred to the T_g of polybutadiene segments [20, 21]. A large secondary β relaxation from SAN phase can be seen between −40 and 95 °C. Finally, the T_g of SAN rigid phase is observed at 115 °C [20, 21].

Below the T_g of polybutadiene segments, all composites showed minor values of tan δ when compared to neat ABS, this characteristics is due to fiber addition which makes the material store more energy in this thermodynamical transition. In the region between −40 and 95 °C is evident the additional mechanism of dissipation energy caused by the decrease in load transferred among the interfaces. It is clear that the addition of fiber contributed for the reinforcement effect in region above the maximum damping factor (tan δ) in the elastic plateau, as observed in storage modulus. This dynamical mechanical behavior was observed for all fibers used in this work.

Morphological analysis results

Scanning electronic microscopy was conducted in an attempt to interpret structure–property relationships. Figures 7, 8, 9 show the surface of the fiber–matrix interface of the composites studied.

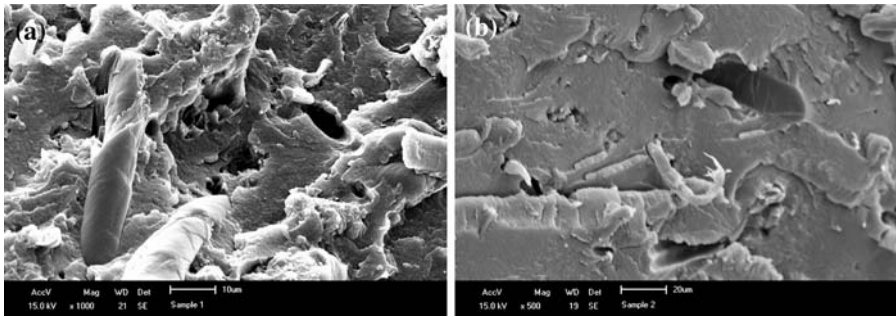**Fig. 6** Tan δ vs. temperature
for all ABS/fiber composites
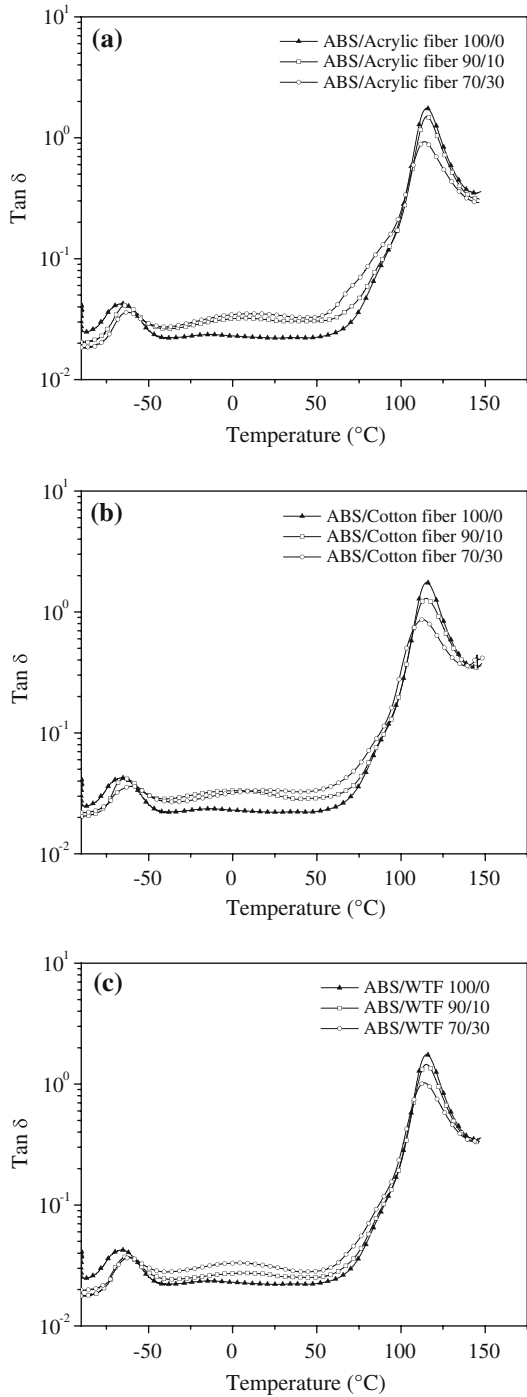
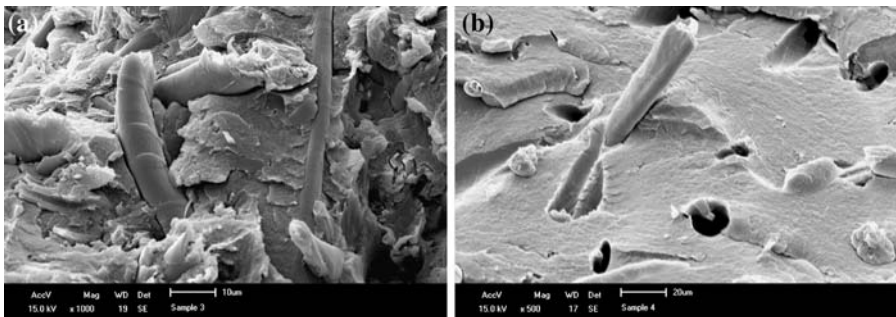**Fig. 7** SEM micrographs for ABS/WTF composites **a** 70/30, **b** 90/10

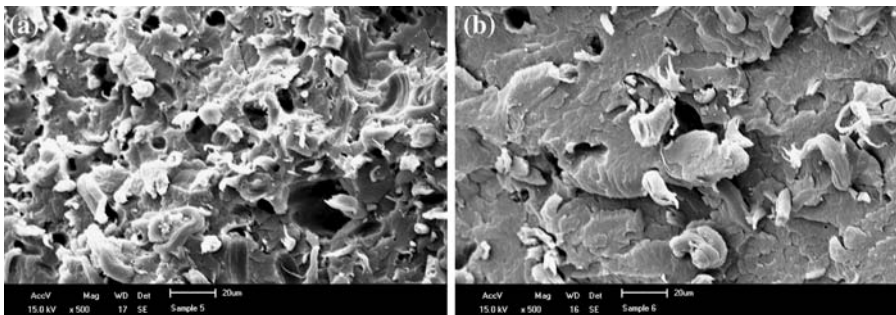**Fig. 8** SEM micrographs for ABS/cotton fiber composites **a** 70/30, **b** 90/10

Fig. 9 SEM micrographs for ABS/acrylic fiber composites **a** 70/30, **b** 90/10

Most of the fibers were pulled-out from the matrix during deformation; however, the matrix is still attached to the fibers. Failure occurs at the fiber matrix interface. The fiber surface appears clean and smooth.

The processing of the composites resulted in a dispersed morphology of the fibers. The good dispersion of fibers into the polymeric matrix ensures a reduction in the composites anisotropy, reflecting directly in the transfer load ability.

The micrographs evidence that there was no entanglement effect in the fiber, which makes stronger the assumption that the reinforcement effect would be closely related to the way that fiber threads are ordered, since the presence of voids in the inner fibers and, a poor interface among them could result in higher energy dissipation.

Conclusions

A series of ABS/textile fibers composites were prepared in a batch mixer using different fiber types and content.

The stabilized torque improved with fiber content, although the time to reach the stabilized torque was higher for the compositions with higher fiber content.

As the fiber content increases higher Young's flexural modulus values are observed, resulting in a more rigid material. The addition of fibers resulted in a more rigid materials.

The fiber addition of 10 wt% did not have significant effect on the degradation behavior of ABS. All composites with 30% textile fiber showed a higher degradation step related to the fiber degradation.

The presence of fiber resulted in a considerable increase in stiffness at all temperatures showed by DTMA. The reinforcing effect was higher in the region above the glass transition temperature. This was due to the difference in mechanical properties between the fiber and the matrix as it goes from the glassy to the rubbery state. The presence of interface in fiber filament bundle is the main cause of the additional mechanism of energy dissipation. The processing technique resulted in a dispersed morphology of the fibers.

The textile fiber is potential reinforcing filler in polymeric materials, and its use for this purpose tends to increase in the future.

The methodology developed in this study opens a new possibility for recycling of textile fibers residues.

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