Surface-pegylated chitin whiskers as an effective additive to enhance the mechanical properties of recycled ABS

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ABSTRACT: The recyclability of materials is a key issue related to the use of polymers in the automotive and electronic industries, among others. The multiple thermal and mechanical operations used in recycling can cause severe damage to the molecular architecture and microstructure of polymers that frequently leads to a reduction in their mechanical properties, which restricts their recyclability. In this work, nanocomponents (whiskers) derived from chitin were surface-modified by grafting different molar masses of methoxylated poly(ethylene glycol) (mPEG). The modified chitin whiskers were then incorporated into reprocessed ABS (acrylonitrile–butadiene–styrene) to yield nanocomposites with 0.5% (mass/mass) whiskers. The obtained whiskers and nanocomposites were investigated using techniques such as transmission electron microscopy, atomic force microscopy, scanning electron microscopy, infrared spectroscopy, and thermogravimetric analysis. The properties of the nanocomposites were also investigated using tensile tests and dynamic mechanical tests. The results show that the surface-modified chitin whiskers with high molar mass mPEG grafts increased the strength, elongation at break, and stiffness of the reprocessed ABS over virgin and reprocessed ABS and reprocessed ABS nanocomposites with unmodified whiskers. This indicates that the use of surface-modified chitin whiskers can be valuable in improving the mechanical properties of recycled polymers and, consequently, enhancing their recyclability. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42463.

INTRODUCTION

The recyclability of materials is a major environmental and commercial issue that impacts the design of components, devices, and products. This is particularly true for polymers used in the automotive and electronic industries, as recent legislation requires that the end-of-life of their products must include recycling and the reuse of materials and parts.[1] However, the thermal and mechanical cycles associated with the recycling of common thermoplastics usually lead to polymer degradation and the consequent reduction of mechanical properties, including brittleness.[2,3] To achieve the high levels of recyclability that are required and pursued, recycled polymers must have high mechanical properties.

In this work, the hypothesis that reprocessed ABS (acrylonitrile–butadiene–styrene) could have its mechanical properties enhanced by the use of nanotechnology was tested. ABS polymers are widely used in home and electronic appliances and in the automotive industry. ABS consists of an amorphous phase of poly(styrene-*co*-acrylonitrile) (SAN) and a second rubber-like phase of polybutadiene (PB) dispersed in the SAN. The properties of ABS originate from the properties of the two phases and vary depending on the amount of each phase present in the material. The main challenge in ABS recycling is the oxidative degradation of the rubber butadiene phase throughout the material's lifetime.[4–9] Many approaches have been tested and used to restrict the deterioration of mechanical properties of ABS due to recycling. The combination of recycled ABS with elastomers and chain extenders is one of the main approaches tested to limit the consequences of ABS degradation.[10–13]

Chitin is a biopolymer of high molecular mass that was first identified in 1884. It can be found in the exoskeletons and shells of arthropods and in the spines of cephalopods. Its rate of production in 2000 was close to that of cellulose. Therefore, it is considered to be the second-most important natural polymer and the second-most abundant in nature.[14–16] It occurs in nature as ordered crystalline microfibers that compose the exoskeletons of arthropods and also appears in the cell walls of fungi and yeasts where it acts as a reinforcing agent. Commercial sources include shrimp peels and crab shells. It is obtained in industrial processes *via* an acid treatment that dissolves calcium carbonate followed by protein extraction in an alkaline

medium. Nanocrystals (whiskers) derived from chitin can be obtained through the disintegration of the amorphous part of the structure of chitin to yield tough and elongated nanometric crystalline structures.[17,18] Nanocomponents derived from chitin have been tested as reinforcing agents for many polymers such as poly(vinyl alcohol),[19] polyurethanes,[20] cellulose,[21] gelatin,[22] polydioxanone,[23] among others. Incorporation of chitin whiskers into soft and hydrophilic polymers has usually led to improvements in strength of the resulting nanocomposites.[22] The presence of chitin whiskers in polymers was also shown to be able to control the swelling behavior of hydrogels, the crystallization of polymers and to enhance barrier properties among other properties.[22]

Nanocomponents, such as clay nanoparticles, carbon nanotubes, cellulose, and chitin nanowhiskers, have been tested and used as reinforcing agents in many polymer systems. They have proven to be highly effective in improving the strength and stiffness of polymers, but they usually also lead to reduction in strain at break that can be related to an increase in brittleness.[24]

In this study, the incorporation of surface-modified chitin nanocomponents (whiskers) was used to manipulate the properties of reprocessed ABS. The idea was to functionalize the surface of the whiskers with polymer chains that could interact with the reprocessed ABS. The level of interaction between the reprocessed ABS and the nanoparticles was tailored by grafting methoxylated poly(ethylene glycol) derivatives with different molar masses onto the surface of the chitin whiskers. The promotion of chain interpenetration, intermolecular bonding *via* van der Waals forces, formation of entanglements and chain slippage between polymer grafts and chains derived from the polymer matrix can yield interfaces with multiple functionalities that can result in materials with new or improved properties, such as a combination of high strength, toughness, and stiffness.

EXPERIMENTAL

Materials
The following materials and reagents were obtained from Sigma Aldrich, USA: commercial chitin, 750, 2,000 and 5,000 g/mol methoxylated poly(ethylene glycol) (mPEG), succinic anhydride, 1-ethyl-3-(3-dimethylaminopropylcarbodiimide) hydrochloride (EDC) and pyridine. Potassium hydroxide (KOH), sodium chlorite (NaClO$_2$), sodium acetate (CH$_3$COONa), hydrochloric acid (HCl), diethyl ether, ethanol, tetrahydrofuran (THF), and acetone were obtained from Synth, Brazil. ABS (CYCOLAC MGABS02) was produced by SABIC.

Production of Chitin Whiskers
The extraction of chitin whiskers used in this study was based on the one proposed by Paillet and Dufresne.[18] It consists of two stages, the removal of the proteins from the raw chitin (deproteinization) and the breakage of the chitin into nanometer-scale pieces – whiskers.

In brief, the chitin whiskers were prepared by heating chitin for 6 h in a 5% KOH solution at 100°C. Then, the solution was kept under agitation overnight at room temperature and washed and vacuum filtered several times with distilled water. After that, the treated chitin was dispersed in a solution of 17 g of NaClO$_2$ in 1 L of a 0.6 mol/L buffer solution of CH$_3$COONa for 2 h at 80°C (this process was repeated three times). The purified chitin was then suspended again in a 5% KOH solution for 48 h to remove any protein residues still present in the material. After another cycle of washing and vacuum filtration, the deproteinized chitin was centrifuged at 3600 rpm for 15 min.

The next stage began with the hydrolysis of the deproteinized chitin in a 3-mol/L HCl solution at 100°C for 90 min. Thirty milliliters of solution was used per gram of sample. The purified chitin was diluted with distilled water and centrifuged at 3600 rpm for 15 min. This process was performed three times. The obtained material was then transferred to dialysis membranes and kept in distilled water for 2 h. Then, these membranes were placed in running water overnight to reach a pH of 4. The suspension was subjected to an ultrasonic bath and lyophilized, and the product was finally stored at a temperature near 0°C.

Functionalization of the Whiskers
To modify the ability of the chitin whiskers to interact with the ABS polymers, different molar mass methoxylated poly(ethylene glycol) chains were grafted onto the surface of the chitin whiskers. For pegylation (chemical functionalization with poly(ethylene glycol)) of the whiskers, methoxylated poly(ethylene glycol), or mPEG, was used because this polymer has one end group capped with a methyl group. The use of nonmethoxylated PEG, which has two functional en25 (with hydroxyl groups), may result in cross-linking.[25] The molar masses of the chosen mPEGs (Sigma Aldrich) were 750, 2000, and 5000 g/mol. To graft mPEG onto chitin whiskers, 10 mmol mPEG was initially reacted with succinic anhydride to add carboxylic acid end groups[26] in the presence of pyridine as a catalyst at 60°C for 24 h. The mixture was precipitated and washed twice with diethyl ether, followed by vacuum drying. This stage is referred to as product 1, functionalized mPEG. Succinic anhydride functionalizes mPEG, transforming it into mPEG-COOH, the carboxylic end group of which can be used to promote mPEG grafting onto chitin[27] (Figure 1).

In the following stage, referred to as product 2, chitin was dispersed into aqueous media. Chitin whiskers (0.96 g; 1.53 mmol) was added to deionized water (15 mL) and then agitated until a clear dispersion was obtained. Product 1 was dissolved in an aqueous solution of 0.588 g of EDC and HCl (3.06 mmol), mixed with product 2 and placed under agitation at room temperature for 24 h. Then, vacuum filtration was used to collect the modified whiskers. During vacuum filtration, acetone was used exhaustively to wash the collected whiskers to remove any unreacted species.

Figure 1 schematically illustrates how mPEG, after it has become reactive *via* the action of succinic anhydride, can link to both the OH groups of chitin and even NH$_2$ groups, in the case of a partially deacetylated chitin.

Production of ABS Nanocomposites with Chitin Whiskers
Studies of the incorporation of chitin whiskers and surface functionalized chitin whiskers at levels of 0.5% (mass/mass) in
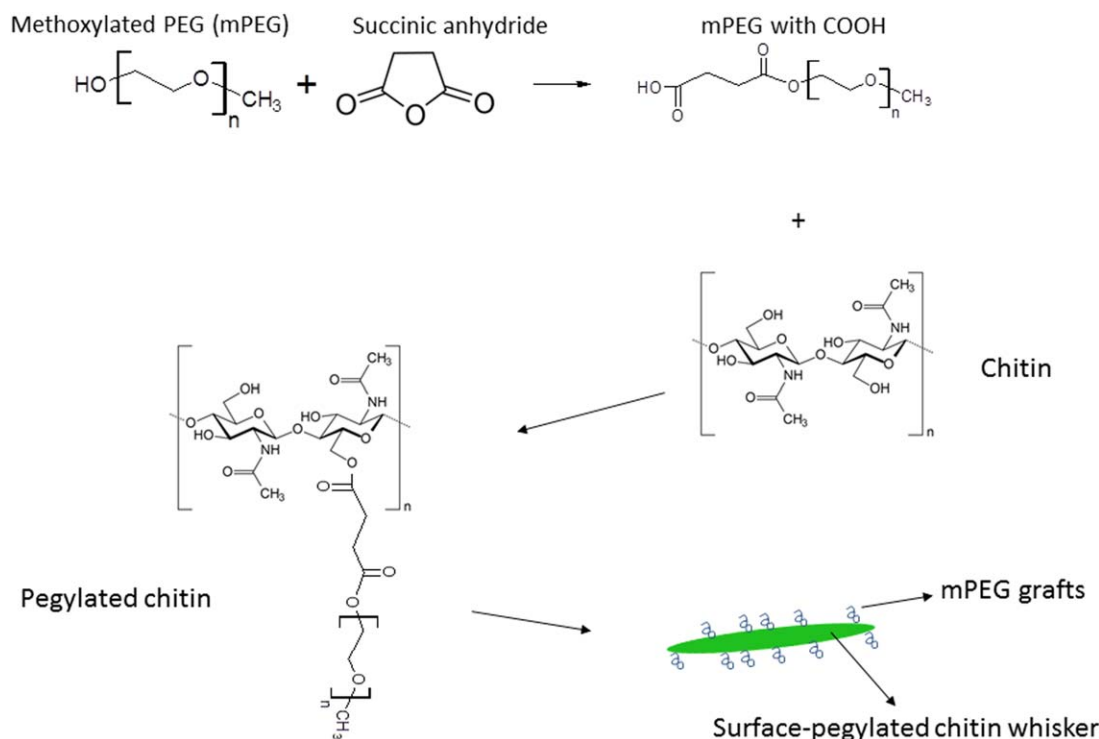
Figure 1. Functionalization of chitin by mPEG activated by succinic anhydride. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ABS and reprocessed ABS matrices were performed to evaluate the effects of such incorporation on the mechanical behavior of these materials. In addition, samples with no incorporated chitin whiskers were tested as a reference. To simulate the behavior of a reprocessed material under controlled conditions, ABS was subjected to six extrusion cycles in a single-screw extruder at 30 rpm and a temperature of 150°C.[1,28]

To avoid agglomeration of the whiskers during the production of the nanocomposites, a dissolution-precipitation technique was used to prepare the reprocessed ABS sample films containing pegylated chitin whiskers. In this technique, chitin whiskers were homogenously dispersed in a 5% (wt/wt) solution of reprocessed ABS in THF. THF can be considered to be a good solvent for ABS and PEG because the solubility parameters of THF, ABS, and PEG are 9.1, 9.2, and 9.1 cal$^{1/2}$ cm$^{-3/2}$, respectively.[29,30] Next, ethanol (a poor solvent for ABS) was rapidly added to the clear chitin dispersion, which immediately led to the precipitation of ABS. The almost instantaneous precipitation of ABS restricted the possibility of the agglomeration of the chitin whiskers. The precipitate was then collected and submitted to vacuum drying at 50°C for 6 h. One millimeter thick films were produced by hot pressing the precipitated mixture at 130°C and cutting it into specimens in accordance with standard ASTM D638 for tensile tests.

Characterization of the Prepared Whiskers and Nanocomposites

FTIR spectra of the chitin whiskers, pegylated whiskers, and nanocomposites were collected using a 6700 Thermo spectrometer using a zinc selenide ATR accessory with a 4 cm^{-1} resolution and 32 scans.

Thermogravimetric curves were obtained on a 7200 Seiko Exstar Thermal Analysis System by heating the samples at 10°C/min up to 600°C under N$_2$.

AFM images were obtained using a XE-70 model from Park Systems in tapping mode. Drops of a whisker suspension of approximately 0.001% by mass in distilled and deionized water (previously subjected to an ultrasonic bath for 20 min) were
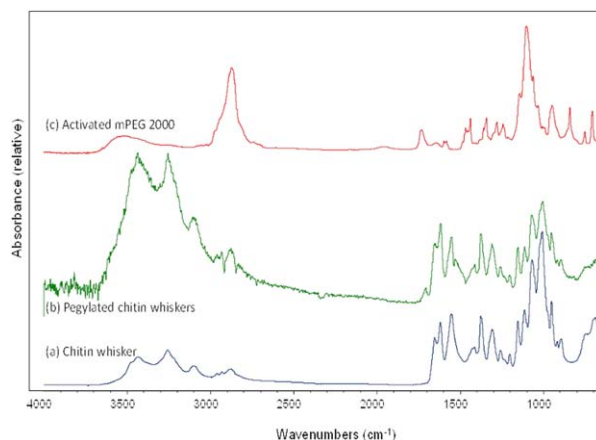

Figure 2. FTIR spectra taken from EDC-activated mPEG (A), pure whiskers (B), and whiskers functionalized with the mPEG (C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
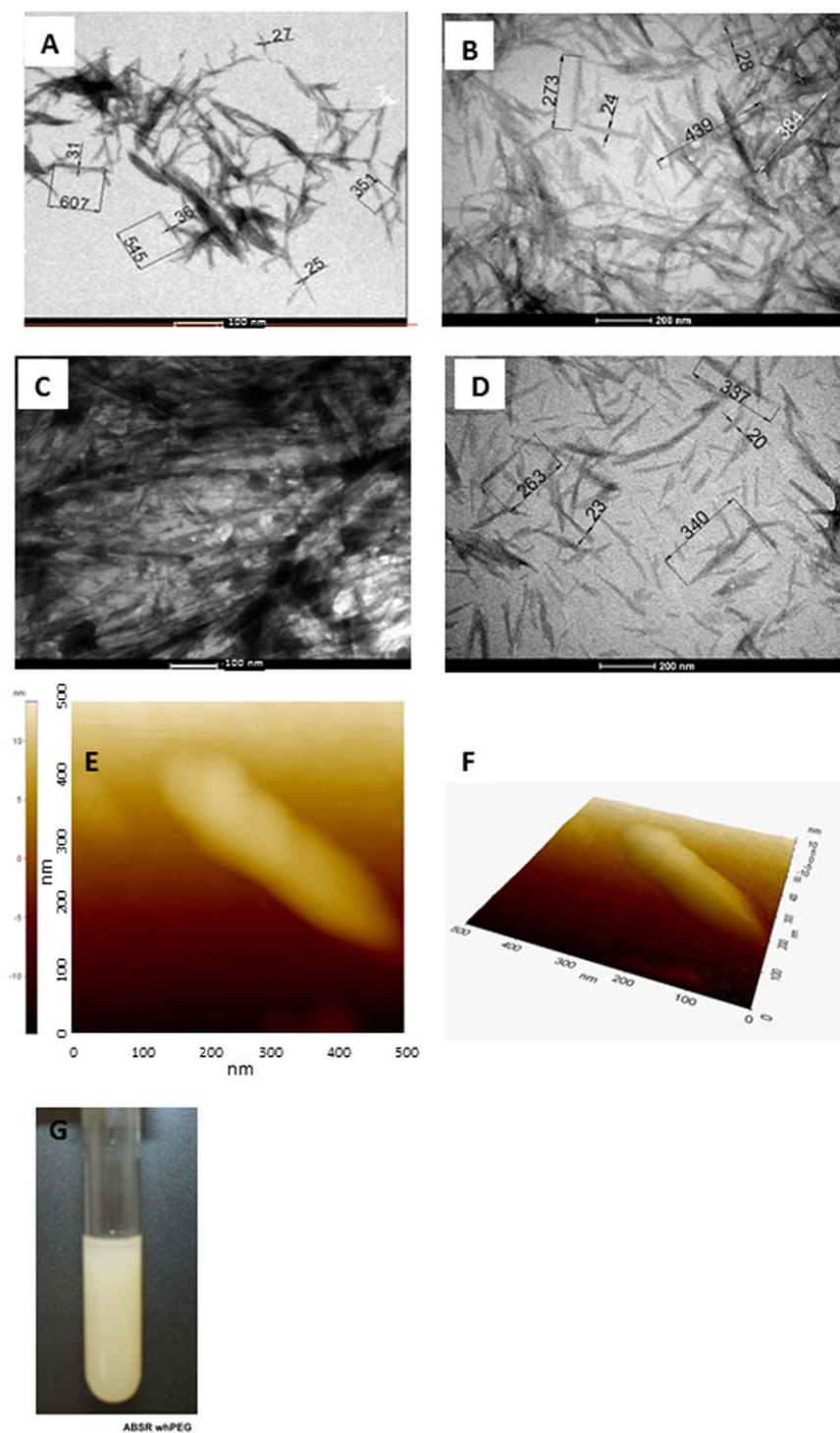
Figure 3. Transmission electron microscopy images of the nonfunctionalized whiskers (A) and the pegylated whiskers treated with 750 g/mol mPEG (B), 2000 g/mol mPEG (C), and 5000 g/mol mPEG (D). Atomic force microscopy (AFM) images of chitin whiskers functionalized with 2000 g/mol mPEG (E and F). A photograph that reveals the result of the Molau test performed in reprocessed ABS samples containing chitin whisker with 2000 g/mol mPEG grafts (G). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

placed on a silicon wafer to allow AFM analysis. TEM images were obtained from a Tecnai G2-20 - SuperTwin FEI – 200 kV apparatus. A uranyl solution (2% in distilled and deionized water) was applied to enhance contrast.

The Molau Test was performed according to Sun et al.[31] to qualitatively check the interfacial interactions between chitin whiskers and ABS. Reprocessed ABS samples containing chitin whiskers with mPEG grafts were mixed with THF to yield a 5 wt %
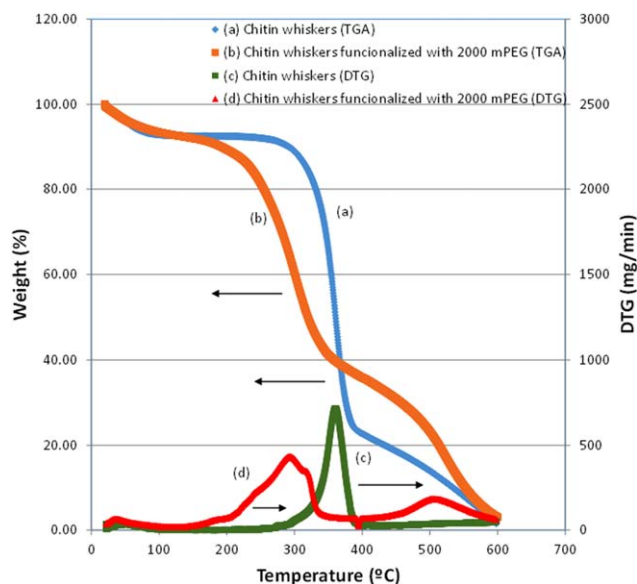
Figure 4. Thermogravimetric (TGA) and DTG (derivative TGA) analyses of chitin whiskers and chitin whiskers functionalized with 2000 g/mol mPEG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

uniform dispersion after agitation for 10 min. The dispersion was then kept still for 48 h to check the stability of the dispersion.

Mechanical tests were performed on a Universal Testing Machine (Instron-Emic - DL3000). The measurements were performed at room temperature at a speed of 10 mm/min with a 500-N load cell. The data were generated by the TESC 3.01 software package. Dynamic mechanical analyses were performed on a 6100 Seiko Exstar Dynamic Mechanical Spectroscopy analyzer in tensile mode. The frequency and heating rate used during the tests were 1 Hz and 1°C/min, respectively. A strain amplitude of 10 μm was used.

RESULTS AND DISCUSSION

Functionalization of Chitin Whiskers with mPEG (PEGylation)

The success of the pegylation of chitin whiskers was confirmed by the FTIR spectra presented in Figure 2. In this figure, the spectra of the obtained chitin whiskers (a), the activated (with succinic anhydride) 2000 g/mol mPEG (b), and the chitin whiskers functionalized with the 2000 g/mol mPEG are shown.

The comparison of curve (a) (pure whiskers) with curve (c) (pegylated whiskers) shows the addition of a new peak at 1735 cm^{-1} (carbonyl groups) and an increase in the intensity of the peaks at 1650 cm^{-1} (amide groups), 1100 cm^{-1} (C–O–C) and 2871 cm^{-1} (C-H bond), which suggests the grafting of mPEG.[26] Yoksan et al.[27] attributed the peak at 1735 cm^{-1} to carbonyl groups, the peak at 2875 cm^{-1} to CH groups and the peak at 1105 cm^{-1} to ether-type bonds (C–O–C). The carbonyl groups noted in both the activated mPEG and pegylated chitin are derived from the reaction between succinic anhydride and mPEG.

Helbert et al.[32] assumed that only 1/3 of the OH groups in the cellulose whiskers are located at the surfaces of the nanocrystals

and are accessible to react during the pegylation. In a review study, Casettari et al.[33] discussed the possibility of the pegylation of chitin and its derivatives for use in biomedical applications. The authors indicate several synthesis methods for pegylation to substitute the various functional groups in the chitin molecule, including in amine (NH$_2$) groups (in the case of partially deacetylated chitin), hydroxyl (OH) groups, and both groups at the same time.

Figure 3 presents images of the nonfunctionalized whiskers (A) and the pegylated whiskers treated with 750 g/mol mPEG (mPEG750, B), 2000 g/mol mPEG (mPEG2000, C), and 5000 g/mol mPEG (mPEG5000, D). Analysis of the images indicates that the pegylation technique did not cause significant alterations to the whiskers' morphology and that the functionalization process neither degraded nor caused a significant dimensional reduction in the whiskers. Figure 3(E,F) shows AFM images of the mPEG2000-functionalized whiskers. Measurements of the whiskers using TEM and AFM show that the lengths of both the nonfunctionalized and functionalized whiskers ranged from 263 to 439 nm.

The results of thermogravimetric analyses of nonfunctionalized whiskers and pegylated chitin whiskers (using the 2000 g/mol mPEG) are presented in Figure 4. The literature indicates that the thermal stability of cellulose whiskers may be increased[34] or may remain unaltered[35] by chemical modifications. Here, considerable thermal stability was observed for the neat chitin whiskers. The whiskers functionalized with mPEG2000 were less stable, experiencing mass losses between 200 and 320°C, whereas the pure whiskers exhibited significant mass loss between 270 and 370°C. The lower stability of the functionalized materials can be attributed to the presence of PEG, which intrinsically degrades at lower temperatures and leads to the formation of defects in the whiskers during functionalization, in turn causing them to be more prone to degradation. Mass losses at temperatures lower than 100°C are associated with the elimination of adsorbed moisture from the conservation of the materials.
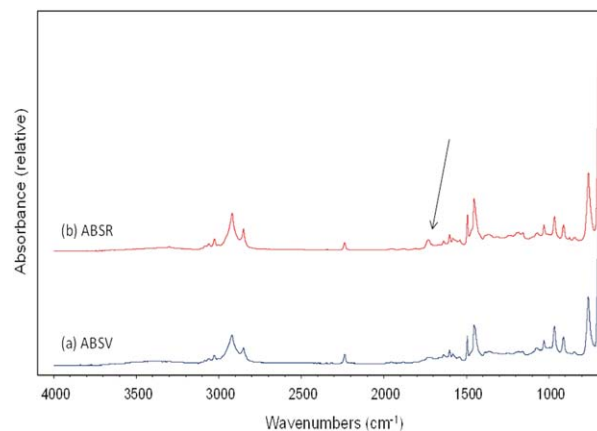

Figure 5. FTIR spectra of virgin (a) and reprocessed (b) ABS films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Mechanical Properties of the Virgin and Reprocessed ABS and ABS Nanocomposites Determined by Tensile Tests in Accordance with Standard ASTM D638 (The Average and Standard Deviation of the Measured Values are Reported)

Sample code	Sample description	Tensile strength MPa	Strain at break %
ABSV00 Hot Pressed[a]	Hot pressed virgin ABS pellets	28.6 ± 3	6.8 ± 1
ABSV00	Pure virgin ABS	31.6 ± 2	6.9 ± 2
ABSR00	Pure reprocessed ABS	31.3 ± 7	6.1 ± 2
ABSR0.5wh	Recycled ABS with 0.5% whiskers	20.9 ± 2	4.3 ± 1
ABSR0.5wh0750	Reprocessed ABS with 0.5% mPEG750-pegylated whiskers	28.2 ± 3	10.9 ± 4
ABSR0.5wh2000	Reprocessed ABS with 0.5% mPEG2000-pegylated whiskers	38.8 ± 2	10.1 ± 1
ABSR0.5wh5000	Reprocessed ABS with 0.5% mPEG5000-pegylated whiskers	41.7 ± 1	9.7 ± 1

[a] Virgin ABS pellets hot pressed at 130°C (i.e., sample that did not undergo the dissolution/precipitation process).

Production and Analysis of ABS Nanocomposites

FTIR was used to analyze the effect of the reprocessing (six extrusion cycles to simulate recycling conditions) of ABS on the chemical structure of the polymer. In Figure 5, typical absorption bands related to the components of ABS can be identified, such as the nitrile groups in acrylonitrile at 2246 cm^{-1}, the carbon double bonds in butadiene at 1637 cm^{-1}, and the out of plane bending of C–H groups in the aromatic rings of styrene at 698 and 762 cm^{-1}. The FTIR spectrum of reprocessed ABS also shows an absorption band near 1740 cm^{-1} that can be assigned to oxidized groups, such as carbonyl groups, that were inserted in the polymer backbone through thermal degradation. This finding indicates that the reprocessing caused thermo-oxidative degradation.[36]

The Molau test was performed to study the interfacial interactions between ABS and chitin whiskers and the results are shown in Figure 3(G). According to the test,[31] the formation of stable dispersions after mixing composites with good solvents indicates that there are high levels of interfacial interactions between the components of the composite. Otherwise, if precipitation or separation of the components can be well detected in the dispersions, it would indicate low levels of interfacial interactions between them. Figure 3(G) shows that the dispersion generated by mixing THF with reprocessed ABS nanocomposites containing chitin whiskers with 2000 g/mol mPEG whiskers was stable throughout the 48 h of observation. Therefore, the obtained results of the Molau test suggested that there are high levels of interfacial interactions between pegylated chitin whiskers and ABS.

Mechanical Tests

The results of tensile tests performed on ABS films (neat and reprocessed) and ABS films containing 0.5% pure chitin whiskers and mPEG-functionalized whiskers of three different molar masses (750, 2000, and 5000 g/mol) are shown in Table I. The samples were prepared by the precipitation technique described previously, even the samples without whiskers. The properties of pure and virgin ABS that did not undergo the dissolution-precipitation process (samples prepared by hot pressing ABS virgin pellets at 130°C) were also measured and the results are also reported in Table I. It was observed that the

mechanical properties of hot pressed ABS and ABS derived from the dissolution-precipitation technique were similar, suggesting that the dissolution-precipitation process did not alter the mechanical properties of the systems.

In the case of ABS, it was observed that the reprocessing did not significantly change the tensile strength, which had values of 31.6 MPa for the virgin material (ABSV00) and 31.3 MPa for the reprocessed ABS (ABSR00). Degradation and consequent modification of the butadiene phase caused a slight decrease in the deformation at break percentage, which changed from 6.9 to 6.1% after reprocessing. This decrease in the deformation at break was expected because butadiene, the ABS elastomeric component, is susceptible to thermal degradation. The modification of this phase resulted in the loss of elasticity in the polymer because the formation of ramifications and cross-links reduces the molecular mobility.[37]

The incorporation of 0.5% pure chitin whiskers and whiskers functionalized with low-molar-mass PEG (750 g/mol mPEG) into reprocessed ABS caused reductions in the tensile strength and strain at break. This type of behavior is typical of traditional composites containing fillers with poor adhesion toward the polymer. The lack of interfacial interactions between the polymer and reinforcing agent usually favors the nucleation and propagation of defects that end up reducing the overall properties of the polymer composites. Therefore, chitin whiskers with natural surfaces and chitin whiskers having low molar mass mPEG grafts were not able to interact with the ABS chains, leading to poor mechanical properties.

However, the addition of chitin whiskers that had been treated with mPEG2000 and mPEG5000 exhibited significant improvements in the tensile strength and deformation at break, with values better than those of reprocessed ABS and even of virgin ABS. In the cases of samples ABSR0.5wh2000 and ABSR0.5wh5000, which consisted of reprocessed ABS with the addition of 0.5% whiskers functionalized with 2,000 g/mol and 5,000 g/mol mPEG, respectively, the tensile strength increased from 31.6 to 38.8 MPa for mPEG2000 and to 41.7 MPa for mPEG5000, increases of 23 and 32%, respectively. The deformation at break increased from 6.12 to 10.09% (mPEG2000) and to 9.69% (mPEG5000), increases of 46.02 and 40.23%, respectively.
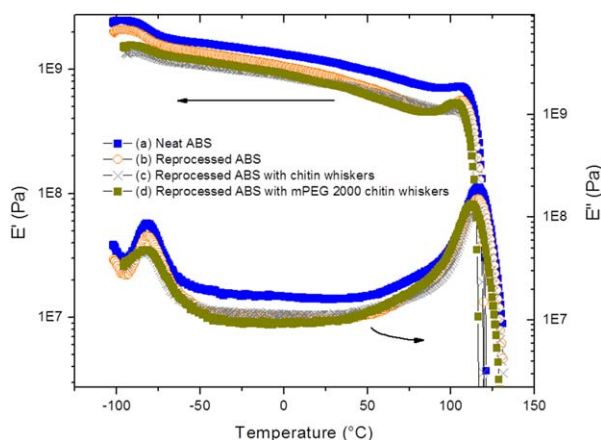
Figure 6. DMA taken from virgin ABS, reprocessed ABS films and reprocessed ABS nanocomposites containing chitin whiskers and pegylated chitin whiskers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The size of the PEG molecule was clearly an important factor in the observed improvement of properties. This behavior can be explained by the capabilities of the different PEGs to interpenetrate and entangle in the base polymer (SAN), thereby promoting better interaction. Because of its low molar mass, mPEG750 has less capacity to form entanglements with the ABS chains. The ability to interact with the polymer is higher for mPEG2000 and highest for mPEG5000. These last two can achieve a greater interpenetration into the polymer matrix, resulting in higher levels of intermolecular interactions and the formation of entanglements. Moreover, during the deformation of the nanocomposites, disentanglements of chains and chain slippage at the interface between the pegylated chitin whiskers and ABS matrix can absorb energy, leading to improvements in toughness and an increase in strain at break.
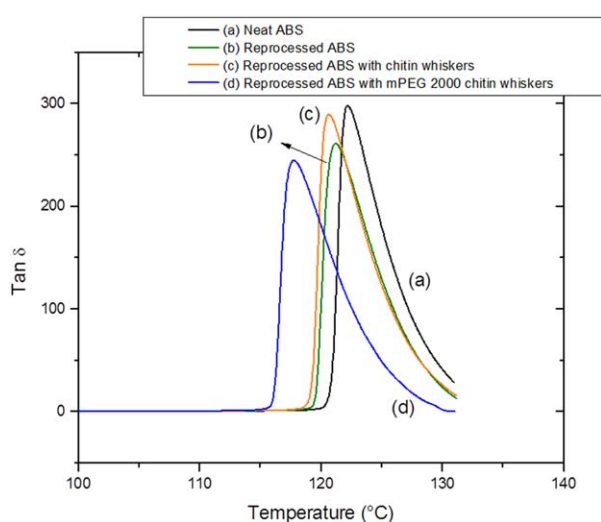

Figure 7. Loss tangent vs. temperature for virgin ABS, reprocessed ABS films and reprocessed ABS nanocomposites containing chitin whiskers and pegylated chitin whiskers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Therefore, an optimal combination of chemical and macromolecular interactions (*via* interpenetration and entanglement formation) caused the unique effectiveness of the chitin whiskers in reinforcing the reprocessed ABS observed in this study. The addition of chitin whiskers modified with high-molar-mass methoxylated PEG resulted in simultaneous gains in mechanical properties (strength and deformation at break), something that is seldom observed during the preparation of traditional composites and nanocomposites.

Figure 6 shows the DMA results of the investigated ABS nanocomposites. The results indicate that the storage (E') and loss (E'') moduli tend to have lower values by both reprocessing and the addition of different types of chitin whiskers. This same type of reduction in moduli was also observed by others when degradation processes in ABS promoted by recycling and artificial weathering were studied.[8,10] Moreover, poor interfacial interactions (such as in ABS containing non-modified chitin whiskers) and interfaces having soft polymer grafts (such as in the case of ABS with 2000 g/mol mPEG grafts) are also responsible for reducing the elastic modulus of the nanocomposites. Figure 7 shows that the peak of the loss tangent, which corresponds to the SAN (styrene–acrylonitrile) component of ABS,[10] tended to shift toward lower temperatures when mPEG-modified chitin whiskers (with 2000 g/mol mPEG grafts) were added to the reprocessed ABS. This behavior indicates that the methoxylated PEG chains may interpenetrate regions of ABS that are rich in SAN, forming a miscible blend at the interface and reducing the T_g of the SAN phase.

In contrast, the glass transition temperature of the butadiene-rich phase, which is approximately $-80°C$ (loss modulus peak – Figure 6),[10] suffered no significant displacement. This finding suggests that there was a low degree of interaction between the whiskers and this phase.

CONCLUSIONS

In this work, the possibility of enhancing the mechanical properties of reprocessed ABS by incorporating surface-modified chitin whiskers into reprocessed ABS polymers was investigated. The feasibility of the chemical modification of the surfaces of chitin whiskers with methoxylated poly(ethylene glycol) (mPEG) of various molar masses (750, 2000, and 5000 g/mol) was demonstrated. The recycling of ABS was simulated by submitting ABS to multiple extrusion cycles. The results obtained after this simulation indicated slight losses in mechanical properties and oxidation of the ABS chains. The incorporation of a 0.5% concentration by mass of chitin whiskers modified with mPEG of higher molar masses (2000 and 5000 g/mol) resulted in significant increases in the strength and deformation at the break of reprocessed ABS compared with the same reprocessed polymer without whiskers or with nonmodified whiskers (even compared with the original ABS). The simultaneous increase in these properties, which is rare in traditional composites and nanocomposites, was correlated to the capability of the methoxylated chains of PEG to interpenetrate and entangle with SAN (styrene acrylonitrile phase of ABS) chains. The DMA results for the ABS system with chitin whiskers revealed a shift

in the glass transition temperature of the SAN phase toward lower temperatures for nanocomposites with whiskers that had been treated with methoxylated PEG. This displacement was attributed to the interpenetration of the PEG chains into the SAN matrix. The results of this work indicate that the incorporation of surface-modified chitin derived nanocomponents (whiskers) can increase the mechanical properties of reprocessed polymers (including toughness, ductility and strength), allowing them to be used as additives that can improve the recyclability of polymers.

ACKNOWLEDGMENTS

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