Preparation and characterization of composites from copolymer styrene-butadiene and chicken feathers

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Abstract

Over five million tons of chicken feathers (CF) are generated all over the world by the poultry industry, with an immense potential to exploit. Keratin is an abundant protein found in chicken feathers that offers excellent thermal properties and it is durable, insoluble in organic solvents and chemically unreactive. Elastomers are materials with a wide application range, for instance, adhesives, shoe soles, plastic modifiers, tire industry, sealants, among others. However, it is necessary to improve their properties and mechanical performance at elevated temperatures. A good path to do so is to combine the elastomer with CF to obtain materials with enhanced properties. In present work, a composite based on styrene-butadiene (SB) elastomer and CF was prepared by means of melt mixing. Composites were characterized by FTIR, DSC, DMA and X ray diffraction techniques. The results show that there is an increase in stiffness of SB/CF composites compared with pure elastomer.

Keywords: *chicken feather, melting mixing, thermal properties, elastomer.*

1. Introduction

CF are considered a waste byproduct from poultry industry, with around 5 million tons per year[1]. The main component of CF is keratin, a protein with good thermal and mechanical properties, which is also resistant to the action of organic solvents. Its thermal decomposition occurs between 50 and 200 °C[2]. The presence of disulfide crosslinks from cystine and the predominant non-hydrophilic amino acids in the chain sequence give CF keratin a hydrophobic character. In addition, CF keratin is a self-sustainable and continuously renewable material[2].

Recently, the increasing interest in the use of natural or renewable materials as polymer matrix reinforcement, has led to the search for options to obtain composite materials. There are lots of reports about natural fibers as flax, bamboo, hemp, jute, agave, among others, but just a few of them are related to resources from animal proteins, as keratin[3,4]. In the last decades, this fact has generated the investigation of keratin as raw material for synthetic polymer blends, particularly because of its unique properties such as lightweightness, natural abundance and environmental compatibility, combined to its high mechanical and thermal resistance[5,6]. The latter, could help to improve the performance of current synthetic polymers and to obtain materials with mechanical properties comparable to the conventional ones[7].

Styrene-butadiene copolymers (SB) have applications as shoe soles, impact modifiers, asphalt modifiers, adhesives and sealants[8]. SB copolymers are materials that flow easily at processing temperatures, however at higher temperatures their mechanical properties decrease. To enhance keratin fibers attributes, such as impact resistance, thermal oxidation, physicochemical and mechanical properties, their reinforcement has been considered by using an elastomeric SB copolymer, with styrene content ranging from 25% to 45%[9].

There are several studies on composite materials using styrene-butadiene rubber (SBR), nitrile-butadiene rubber (NBR) and keratin from chicken feathers that revealed the influence of different variables on the thermal and mechanical behavior and the various valid tools for observing these variations[2,3,10-14].

In present work, a composite based on SB copolymer and CF was prepared by melt mixing, studying 3 types of SB copolymers (varying styrene content), keeping constant chicken feather amount. Thermal properties were studied; infrared spectroscopy (FTIR) and X ray diffraction were also carried out to evaluate the possible interactions between polymer matrix and reinforcement.

2. Materials and Methods

2.1 Materials

CF were obtained from a local slaughterhouse in Altamira city, México; and three types of SB: SB1 45% styrene content, SB2 32% styrene content and SB3 25% styrene content, were provided by Dynasol Elastomers S.A. de C.V. CF were cleaned with several washes, first with distilled water, then

with acetone and finally with ethanol. Thereafter, feathers were dried at room temperature to be clean, sanitized and odor free. Then, the barbules were removed with cutters barrel and quill (the main component of CF is keratin), was finally grinded in both sides of the feather.

2.2 Composites preparation

Composites were prepared by melt mixing using a plasticorder/Brabender PL2000 torque rheometer, establishing the optimum conditions at 185 °C and 20 minutes of mixing, using roller blades with 100 rpm speed, keeping constant CF content in 5 phr. After the materials were compressed in a Dake press with 10 Tons for 20 min, using appropriate molds.

2.3 Composites characterization

Infrared spectroscopy technique was used to identify functional groups in the SB/CF materials. For that purpose, a Perkin Elmer Spectrum One model equipment was used, through the Attenuated Total Reflectance (ATR) technique with SeZn plates in a range of 4000-600 cm⁻¹, and 12 scans. Differential Scanning Calorimetry (DSC) was used to determine the thermal transitions of the composites; for that, a Perkin Elmer DSC8000 equipment was used. The employed method consists of an initial heating cycle from 30 °C to 230 °C at 10 °C/min, followed by a cooling cycle from 230 °C to -100 °C. The sample is kept for 5 min at this temperature before a second heating ramp from -100 to 230 °C takes place, with a heating rate of 5 °C /min. The sample amount was 10 ± 2 mg, and the tests were run under nitrogen purge (20 ml/min). Dynamic Mechanical Analysis was carried out in a DMA-Q800 TA-Instruments, with a double cantilever clamp and rectangular shaped samples with dimensions $30 \times 12 \times 3$ mm (length, width and thickness, respectively). Analysis were carried out in multifrequency mode with temperature range from -100 to 230 °C, with a heating rate of 5 °C min⁻¹, 1Hz frequency and 2μm amplitude. X-ray diffractometer Siemens D-500 was used to determine the presence of crystalline structures in composites (SB-CF). The equipment operates at 30 kV, 25 mA and angle scan range (2θ) from 4° to 40° at 0.05° min⁻¹. Samples were cut with dimensions of $30 \times 15 \times 1$mm. In order to observe the morphology of the obtained materials and the dispersion within the matrix, a scanning electron microscope JEOL model JSM-5800 was used, with an accelerating voltage of 10kV. For this purpose, a portion of previously compressed material, whose thickness is 0.01mm, was used.

3. Results and Discussion

3.1 Infrared spectroscopy

Figure 1 shows the IR spectra of SB3 and SB3/CF composite from 3850 cm⁻¹ to 600 cm⁻¹. It is emphasized that it is possible to identify some of the functional groups in the SB/ CF blends. SB3 signals are located at 3000 cm⁻¹ and 3100 cm⁻¹ associated to unsaturated carbons; meanwhile, at 2900 cm⁻¹ and 2850 cm⁻¹, the signals related to the stretching of methyl and methylene groups can be seen. Besides, the region of the aromatic ring is found from 2000 cm⁻¹ to 1850 cm⁻¹. CF signals are situated at 3300 cm⁻¹, corresponding to the range of amide bands and associated with ordered regions of NH group of amide A α-helix conformation, and at 2950 cm⁻¹, related to the asymmetric vibration of CH group of methyl.

It can be observed in Figure 2 that the main groups assigned to 1650 cm⁻¹ and 1550 cm⁻¹ from CF keratin are the amide I and amide II bands, respectively. The peaks at 1500, 1450 and 1250 cm⁻¹ are attributed to the bending plane of NH group that corresponds to β−sheet conformation, the bending of -CH3 group and CN group of amide III, respectively. Signals at 1150, 1100 and 1050 cm⁻¹ are assigned to C-C group vibrations; a peak around 700 cm⁻¹ its attributed to C-S group vibrations and finally, at 970 cm⁻¹, 910 cm⁻¹, 760 cm⁻¹ and 690 cm⁻¹, it is found the evidence of unsaturated aromatic carbon deformations[15-17].

3.2 Differential Scanning Calorimetry (DSC)

Table 1 shows the results obtained from DSC of SB1, SB2 and SB3 copolymers and SB1-CF, SB2-CF and SB3-CF composites. It is noted that CF has two transition temperatures (140 °C and 263 °C), corresponding to the
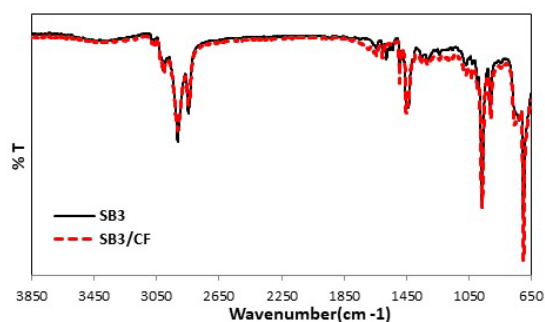

Figure 1. FTIR spectra of SB3 (Styrene-Butadiene with 25% styrene content) and SB3/CF (Chicken Feather) composite.
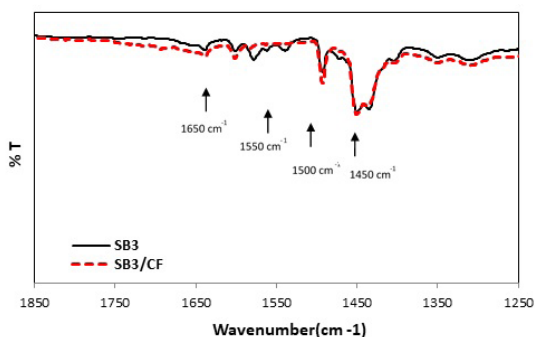

Figure 2. FTIR spectra of SB3 (Styrene-Butadiene with 25% styrene content) and SB3/CF (Chicken Feather) composite.

Table 1. Thermal transitions of copolymers and composites SBS/CF (Styrene-Butadiene-Styrene/Chicken Feather).

Material	Transition (°C)
Chicken feather (CF)	140/263
SB1 (45% styrene content)	-40
SB1/CF	-56
SB2 (32% styrene content)	-33
SB2/CF	-27
SB3 (25% styrene content)	-63
SB3/CF	-40

crystalline melting temperature of the CF Keratin, similar to previous reports [18]. Other references indicate that CF did not show any melting peak[19]. On the other hand, the Tg of the composites shows an interesting behavior, whose initial value with respect to the styrenic chains is -63 °C while the Tg of the SB3/CF composite is -40 °C. The increase of Tg (-23 °C) is possibly explained by an improvement in the rigidity at the molecular level due to the presence of CF, produced by the binding of the polypeptide chains of keratin with the styrenic chains of SB3. This behavior also occurs with the Tg of the SB2 copolymer and the SB2/CF composite but not in SB1 and SB1/CF, where the Tg is -40°C and -56 °C, respectively. A decrease in the Tg occurs due to the higher styrene content in SB1, so a better interaction between polystyrene block and keratin takes place and, as a result, chains are softened.

3.3 Dinamic Mechanical Analysis (DMA)

DMA is a useful technique to determine the viscoelastic properties of composite materials related to primary relaxations and other parameters. DMA was performed to evaluate the effect of the addition of CF to a SB elastomer matrix. Figures 3, 4 and 5 show the storage modulus E' and Tan δ versus temperature of SB copolymers and SB/CF composites.

Initial E' values of (-100 °C) of SB1, SB2 and SB3 are 2685, 993, and 2501 MPa, respectively. It is noted that in the SB2/CF compound the inclusion of keratin promotes an increase of the storage modulus to 1676 MPa with respect to the SB2 copolymer, improving the stiffness of the elastomeric matrix[3,20]. However, SB1/CF and SB3/CF compounds do not show similar behavior since E' decreases to 1157 and 2128 MPa respectively, being more noticeable the decrease of E' in the compound whose SB1 copolymer has 45% styrene. This behavior could be due to free movement of the polymer chains at high temperatures, in agreement with the results of DSC analysis.

Tan δ (Figure 3) is a useful tool to identify the interaction existing between the polymeric matrix and the keratin as reinforcement. A strong bond is reflected at low Tan δ values, although an elastomeric matrix, which has higher Tan δ values, was used. It is observed that Tg value in the SB/CF compounds is not significantly affected by the CF addition. This could be related to the result from Tan δ curve. Nevertheless, the SB3/CF composite at (-40 °C) has the highest Tg value compared to the SB1/CF and SB2/CF composites. This behavior has already been reported before, regarding the absence of significant changes in Tg value by effect of CF addition as reinforcement of a polymeric matrix[20].

3.4 Scanning Electron Microscopy (SEM)

Surface morphology of SB/CF composites was investigated by SEM. CF surface was previously reported as uniform with roughness at the micro level[21]. Reinforcing particles can be reduced in processing due to minor degradation according to the mixing temperature. Figure 6 shows the SEM images of the SB1/CF, SB2/CF and SB3/CF composites. It is possible identify CCF particles dispersed on the SB matrix, which reflect a proper interface. SB1/CF composites show bigger particles than the other composites, possibly because there was not a good dispersion of the keratin within the polymeric matrix. In spite of that, good physical interaction between reinforcing keratin and polymeric matrix exists due to the

great compatibility between both materials. It has been reported by Jiménez-Cervantes Amieva et al.[3] a similar behavior in recycled PP-Quill composites, attributed to the hydrophobic nature of keratin and to the fact that the polymer matrix has a proper interface.

3.5 X-Ray Diffraction (DRX)

X-ray diffraction is an important technique to determine the crystal structure in a material. XRD pattern of CF was formerly reported, showing broad peaks at 9 and 19° corresponding to the diffraction pattern of α−helix and β−sheet structure of CF [21]. However, for SB/CF composites the behavior was kind of different. Figure 7 shows the XRD patterns of SB/CF composites, the SB copolymers show
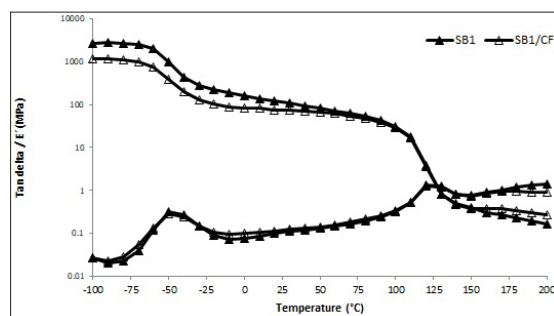

Figure 3. Storage moduli (E', MPa) and Tan δ as function of temperature for SB (Styrene-Butadiene) copolymer and SB1 (45% styrene content)/CF (Chicken Feather) composite.
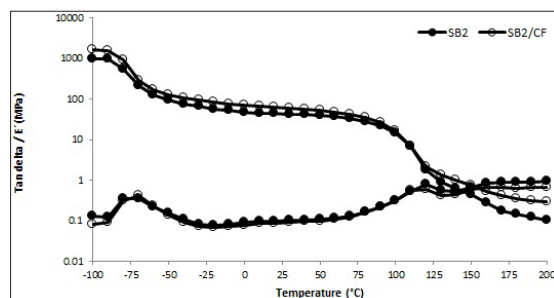

Figure 4. Storage moduli (E', MPa) and Tan δ as function of temperature for SB (Styrene-Butadiene) copolymer and SB2 (32% styrene content)/CF (Chicken Feather) composites.
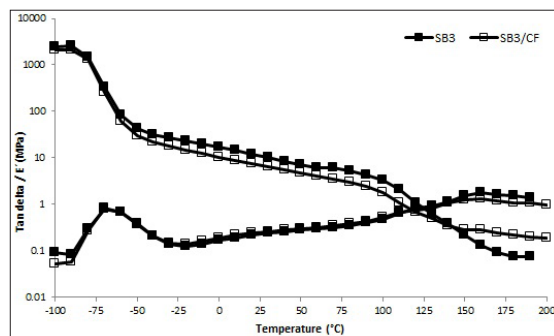

Figure 5. Storage moduli (E', MPa) and Tan δ as function of temperature for SB (Styrene-Butadiene) copolymer and SB3 (25% styrene content)/CF (Chicken Feather) composite.
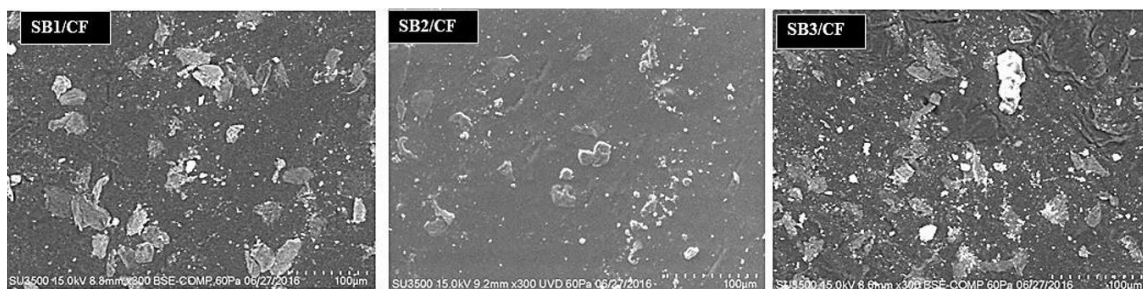
Figure 6. SEM micrographs for SB (Styrene-Butadiene)/CF (Chicken Feather) composites.
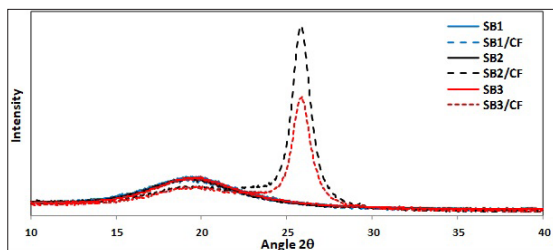

Figure 7. X-Ray Diffraction of SB (Styrene-Butadiene) copolymers and SB (Styrene-Butadiene)/CF (Chicken Feather) composites.

a broad peak around 19.7°, while in SB3/CF and SB2/CF peaks appear at 25.9° and 25.7°, respectively. That peak has not been reported before for CF composites, so its appearance suggest a new crystalline pattern. Keratin can exists in two different crystalline structures, α−helix and β−sheet. These kind of changes reported for CF materials are attributed to chemical treatment [22]. On the other hand, regarding the sample SB1 and SB1/CF composite, no changes were observed.

4. Conclusions

The results of infrared spectroscopy by ATR, although not conclusive, are useful to know more about the chemical interaction between the polymeric matrix and the keratin used as reinforcement. The Tg of composites increases with CF content and an improvement in the rigidity at the molecular level is produced by the binding of the polypeptide chains of keratin with the styrenic chains of SB3. This behavior also happens in SB2 and SB2/CF but not in SB1 and SB1/CF, where a diminution in the Tg occurs due to the higher styrene content in SB1, so a better physical interaction between polystyrene block and keratin takes place and, as a result, chains are softened.

In the SB2/CF composite, the inclusion of keratin promotes an increase in the storage modulus with respect to the SB2 copolymer, improving the stiffness of the elastomeric matrix. However, in the SB1/CF and SB3/CF compounds, E' decreases due to free movement of the polymer chain at high temperatures.

5. Acknowledgements

6. References

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