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Novel bacterial cellulose–acrylic resin nanocomposites

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ABSTRACT

The preparation and characterization of new nanocomposite films based on two acrylic emulsions, composed of random copolymers of butyl acrylate and methyl methacrylate, and bacterial cellulose is reported. The new composite materials were obtained through a simple and green approach by casting water-based suspensions of the acrylic emulsions and bacterial cellulose nanofibrils. The excellent compatibility between these matrices and the natural reinforcing fibers, observed by scanning electron microscopy (SEM), was reflected in the enhanced thermal and mechanical properties of the ensuing composites. Thus, an increase of around 30 °C in the maximum degradation temperature was observed for a 10% content of bacterial cellulose. The new composites showed glass–rubber transition temperature profiles comparable to those of the pristine matrices, as shown by DMA, and increasing elastic moduli with increasing the bacterial cellulose content. The tensile tests revealed a substantial increase in Young's modulus and tensile strength and a corresponding decrease in elongation at break with increasing bacterial cellulose load.

1. Introduction

The use of natural (cellulose) fibers as reinforcing components in polymeric composite materials has been extensively explored during the last few years [1], mainly in response to the economic and environmental concerns associated with the extensive exploitation of petroleum–derived products. The main advantages of natural fibers, when compared with their synthetic or inorganic counterparts, are their biodegradability, high availability, diversity, abundance, renewability, low cost, low energy consumption, low density, high specific strength and modulus (with fibers possessing an adequate aspect ratio), high sound attenuation and comparatively easy processing ability, due to their flexibility and non-abrasive nature [2,3]. Additionally, cellulose-based composites are also very attractive materials because of their good mechanical properties, sustainability and environmental-friendly connotation, and have been used in a wide range of applications, such as in building, engineering, and automobile industries, as well as for the processing of furniture, packaging materials, recreation boats and toys, among others [4].

More recently, the use of micro and nano-cellulose fibers, obtained from a marine species (whiskers) [5] as well as by mechanical, enzymatic or chemical treatments of the vegetal fibers, for the development of high performance composite materials is attracting researchers from diverse fields [6,7], as the addition of very modest amounts of nanofibers leads to new composite materials with superior mechanical properties and new functionalities [8–10] when compared with their conventional cellulose fibers counterparts.

Bacterial cellulose (BC), produced by several microorganisms, particularly *Gluconacetobacter xylinus,* is becoming a promising biopolymer for several applications, including nanocomposite materials, due to its unique properties, such as high crystallinity, high mechanical strength, ultra-fine nanofibrillar network structure and high purity [11–13].

Several studies have been published dealing with the preparation and characterization of BC-based composites with different polymeric matrices, such as flexible polyurethane elastomers [14], cellulose acetate butyrate [15], acrylic thermosetting resins [16,17], phenolic resins [18], and poly(ethylene oxide) [19]. More recently, the preparation of BC-based biocomposites with plasticized starch [20,21] and polylactic acid [22] matrices has also been reported. However, most of these reported approaches were time consuming and involved the use of non environmental friendly organic solvents.

Following our interest on the development of new cellulose based-composite [21,23], we describe in the present work the preparation and characterization of new nanocomposite films based on two commercially available acrylic emulsions, composed of random thermoplastic copolymers of butyl acrylate and methyl methacrylate, designed for high performance coatings, and bacterial cellulose. The new composite materials, obtained through a simple and green approach by casting water-based suspensions of the acrylic emulsions and bacterial cellulose nanofibrils, showed an excellent com-

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patibility between the acrylic resins and bacterial cellulose and enhanced mechanical properties. The only other investigation which called upon the use of acrylic copolymer latexes and cellulose whiskers [24,25] differs from the present study in terms of both the fiber morphology and the nature of the copolymers.

2. Experimental section

2.1. Materials

Bacterial cellulose (BC) (a tridimensional network of nano and microfibrils with 10–100 nm width), in the shredded wet form (95% of humidity), was supplied by Forschungszentrum für Medizintechnik und Biotechnologie e.V. (Germany). Two commercially available acrylic copolymer emulsions, namely Primal AC-337 ER and Primal SF 016 (hereafter referred simply as AC and SF, respectively), with different proportions of butyl acrylate (BA) and methyl methacrylate moieties (MMA) were kindly provided by Rohm & Haas. The AC and SF emulsions had a solids content of 45.5% and 50.5% and the corresponding solid residues showed T_g values of 18–20 °C and 4–5 °C, respectively. The BA:MMA ratio was around 1:1 and 1:2, respectively for SF and AC resins as assessed by ^{1}H NMR spectroscopy. These resin emulsions are known to be free of environmentally harmful alkylphenol ethoxylate (APEO) surfactants, but the presence of other surfactants cannot be excluded.

2.2. Nanocomposites preparation

Different amounts of bacterial cellulose were added to the AC and SF emulsions, previously diluted fourfold with water, in order to obtain films with BC contents of 1%, 2.5%, 5% and 10% (dry weight BC in relation to the dry weight of the acrylic copolymer). Then, BC was dispersed in these emulsions and homogenized using an Ultra-Turrax stirrer for 40 min (500 rpm) and degassed to remove entrapped air. Both unfilled and nanocomposite films based on AC and SF acrylic copolymers and bacterial cellulose (BC–AC and BC–SF films) were then prepared by casting at 30 °C in a ventilated oven for 16 h, using a Petri dish coated with a fluorinated aluminum foil (10 cm diameter) as the mould. Finally, all the ensuing films were pressed at 4 MPa and 95 °C and 75 °C, respectively for AC and SF nanocomposites, during 10 min. The identification of all samples studied is summarised in Table 1.

2.3. Nanocomposite characterization

The composites were characterized using thermogravimetry (TGA), tensile tests, dynamical mechanical analysis (DMA) and scanning electron microscopy (SEM).

TGA essays were carried out with a Shimadzu TGA 50 analyzer equipped with a platinum cell. Samples (10–15 mg) were heated at a constant rate of 10 °C/min from room temperature to 800 °C, under a nitrogen flow of 20 mL/min. The thermal decomposition temperature was taken as the onset of significant (⩾0.5%) weight loss, after the initial moisture loss.

Table 1
Identification of the BC-based composites studied.

Sample	Acrylic resin	% of BC[a]
AC	AC	–
AC–BC1	AC	1
AC–BC2.5	AC	2.5
AC–BC5	AC	5
AC–BC10	AC	10
SF	SF	–
SF–BC1	SF	1
SF–BC2.5	SF	2.5
SF–BC5	SF	5
SF–BC10	SF	10

[a] In relation to the oven dry copolymers mass.

Mechanical testing was performed on a Shimadzu TA-Hdi Stable Micro Systems Texture Analyser using a load cell of 5 kgf operating at a deformation rate of 50 mm/s and 100 mm/s, respectively for BC–AC and BC–SF composites, and were performed under ambient conditions. Five specimens were tested for each composite. Tensile strength, tensile modulus, and elongation to break were calculated using the Instron Series IX software.

DMA measurements were carried on a Tritec 2000 DMA Triton equipment operating in the dual cantilever bending mode. Tests were performed at 1 Hz and the temperature was varied by 1 °C steps, from −10 to 60 °C and from −10 to 40 °C, respectively for BC–AC and SF–AC composites. The displacement amplitude was set to 20 μm. The test specimens had a typical size of 0.5 mm × 1 mm.

SEM micrographs of the composite fractured surfaces, produced after immersion in liquid nitrogen, were obtained with a HR-FESEM SU-70 Hitachi equipment operating at 15 kV. Air dried samples were deposited on an aluminum plate and coated with a carbon layer, approximately 15–50 nm thick, by evaporation of carbon rods (outgas time: 30 s, evaporating time: 1000 ms).

3. Results and discussion

3.1. Thermal analysis

Thermogravimetric analysis of the composite materials was carried out to assess their thermal stability and degradation pro-

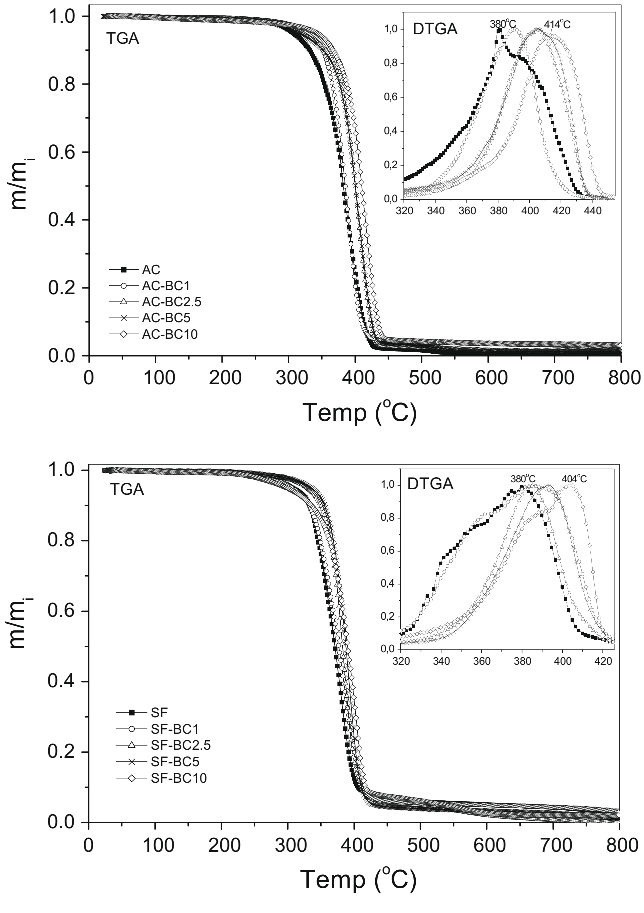

Fig. 1. Thermogravimetric curves for AC and SF copolymers and the corresponding BC-based composites.

files. The TGA tracing of both acrylic copolymers displayed a single weight loss step, with maximum decomposition rates at around 380 °C (Fig. 1). This behavior reflected the typical unzipping process of polymers being heated well above their monomer ceiling temperature.

BC also displays a single weight loss step with a maximum decomposition at 370 °C as reported elsewhere [26]. The thermal decomposition process of all BC–AC and BC–SF composites also presented one single weight loss step profile. However, the presence of low amounts (1–10%) of BC nanofibers in the AC and SF matrices, resulted in a considerable increase in the thermal stability of the composites, as observed by the increment in both initial and maximum degradation temperatures (Fig. 1). For example, the incorporation of 10% of BC resulted in an increase of the maximum degradation temperature of 34 and 24 °C, respectively for the AC and SF composites.

This increased thermal stability has already been observed with other cellulose substrates in polymeric matrices [27,28]. However, in those studies, regardless of the fact that higher reinforcing agent contents were normally used, particularly when vegetal cellulose fibers were used, the effects observed were much less pronounced than the values reported here. Indeed, such increments in the thermal stability promoted by the addition of cellulose fibers had never been reported previously to the best of our knowledge. This behavior possibly reflects the good dispersion and compatibility between the BC nanofibers and the acrylic polymers, as will be confirmed below by the mechanical tests and SEM imaging studies. The excellent interfacial adhesion between the BC nanofibers and the acrylic matrices is certainly due to the establishment of van der Waals interactions as well as hydrogen bonds between the hydroxyl groups of cellulose and the carboxyl groups of the acrylic polymer chains. Finally, it cannot be excluded that the presence of surfactant residues could have also contributed to this good interfacial compatibility between BC fibers and the two acrylic copolymers AC and SF.

3.2. Thermo-mechanical analysis

The dynamic mechanical experiments (DMA/DMTA) were performed for unfilled SF and AC films and for the corresponding composites with different BC contents (1%, 2.5%, 5% and 10%), in the temperature range −10 to 40 °C for the SF materials and −10 to 60 °C for the AC counterparts.

The curves of E'/Pa (storage tensile modulus) vs. temperature at 1 Hz are displayed in Fig. 2. Both unfilled AC and SF acrylic-based matrices display a typical behavior of amorphous polymers. In the glassy state the tensile storage modulus E' only slightly decreases with the temperature, and then drops considerably at around 20 and 40 °C, respectively for the SF and AC matrices. This relaxation phenomenon is associated with the glass-rubber transition of the copolymers.

At room temperature (around 25 °C) the AC copolymer is in the glassy state, while the SF is in the rubbery state, i.e., they are below

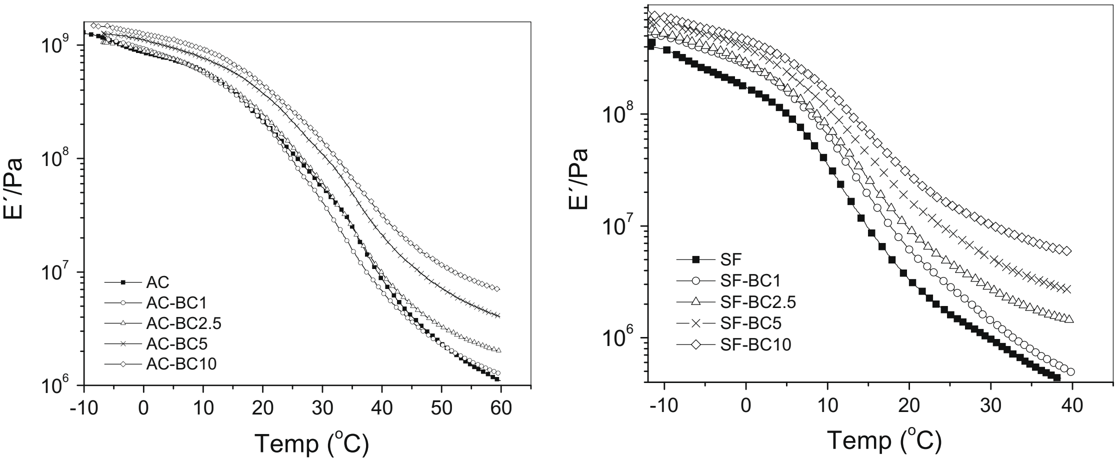

Fig. 2. Temperature dependence of the storage modulus of the AC and SF copolymers and the corresponding BC-based composites.

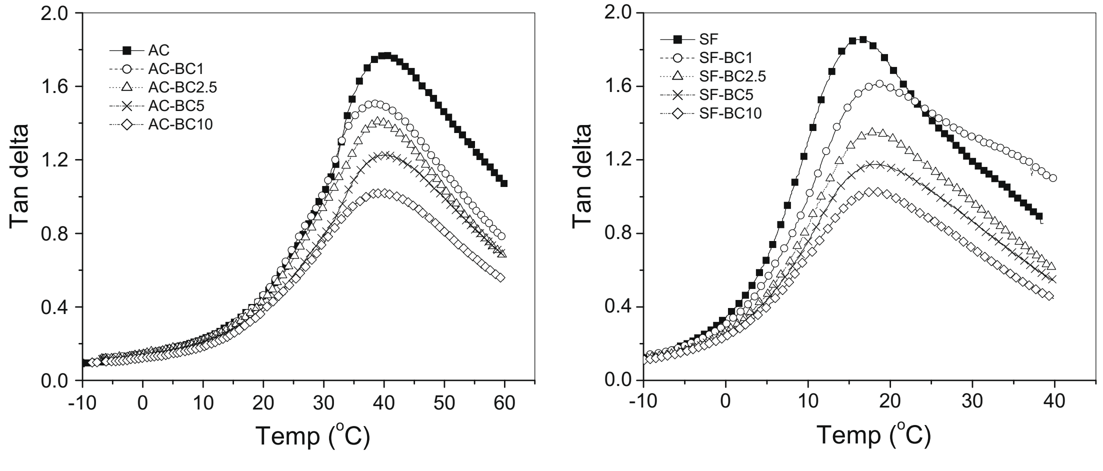

Fig. 3. Temperature dependence of tan δ of the AC and SF copolymers and the corresponding BC-based composites.

and above the corresponding T_g (around 40 °C and 20 °C), respectively. The higher the BA content in the copolymer, the lower its T_g, given its internal plasticizing role associated with its aliphatic side chain.

The addition of BC nanofibers increased the storage modulus, particularly the rubbery modulus, of both AC and SF matrices (Fig. 2) because the materials became more rigid. This effect increased with increasing BC content and was clearly attributed to the mechanical reinforcing brought about by the BC nanofibrils. The increments in the elastic modulus observed for both AC and SF nanocomposites with 10% of BC are quite similar to those reported for nanocomposites of tunicate whiskers and a copolymer of styrene and butyl acrylate [24,25]. However, in the present systems fiber–fiber percolation was not attained at 10% load, which differs from the much higher loads employed with whiskers, where a dramatic jump in modulus was observed between 20% and 30% fiber load [24,25].

Fig. 3 shows the evolution of the damping factor tangent of the loss angle (Tan δ) as a function of temperature for the unfilled AC and SF matrices and the corresponding BC-based composites. Their plots displayed a maximum at around 20 and 40 °C, respectively for SF- and AC-based. The observed relaxation phenomenon is associated with the glass transition of the acrylic polymeric matrices, as previously discussed for the variation of the storage modulus E' (Fig. 2). The T_g values of both AC and SF matrices were hardly affected by the incorporation of BC nanofibrils, only a 2 °C increase for the SF-based composites, probably because of the favourable interactions between the components in the composite.

It was also observed (Fig. 3) that the magnitude of this relaxation process, which is related to the magnitude of the storage modulus drop, strongly decreased when increasing the BC content. This behavior is normally ascribed to the decrease of the matrices relative mass, responsible for the damping properties, i.e. a decrease in the number of mobile units that participate in this relaxation phenomenon. However, the relative damping is not only related to the filler volume fraction and could indeed be influenced here by interfacial events between the two components of the composite.

Tensile tests were also performed at room temperature for all composites. Fig. 4 shows the tensile mechanical properties, including Young's modulus (E), tensile strength and elongation at break, determined from the typical stress–strain curves (Fig. 5).

The Young's moduli of the unfilled SF and of the SF–BC nanocomposites were considerably lower than those of their corresponding AC-based materials because the SF copolymer was above its T_g, and, therefore, much more ductile. The Young's modulus of both AC–BC and SF–BC nanocomposites increased with the BC content, with the SF-based materials showing the most relevant increments (Fig. 4). At a BC content of 10%, the Young's modulus was three and two-fold higher than that of the unfilled matrices, respectively for SF and AC nanocomposites. These results are in good agreement with the DMA measurements.

The tensile strength also increased with increasing BC load and nearly doubled for a 10% content. Additionally, the presence of BC caused a considerable decrease in the elongation at break (Fig. 4), which, was more pronounced for SF composites (753% in SF down to 46% in SF–BC10), when compared with the AC counterparts (272% in AC down to 40% in AC–BC10). As already referred, this mechanical performance is obviously attributed to the reinforcement effect of the BC nanofibrils, which promoted an increment in the materials stiffness, compared with that of the unfilled matrices, and therefore a corresponding increase in their tensile modulus and strength and a decrease in the elongation at break.

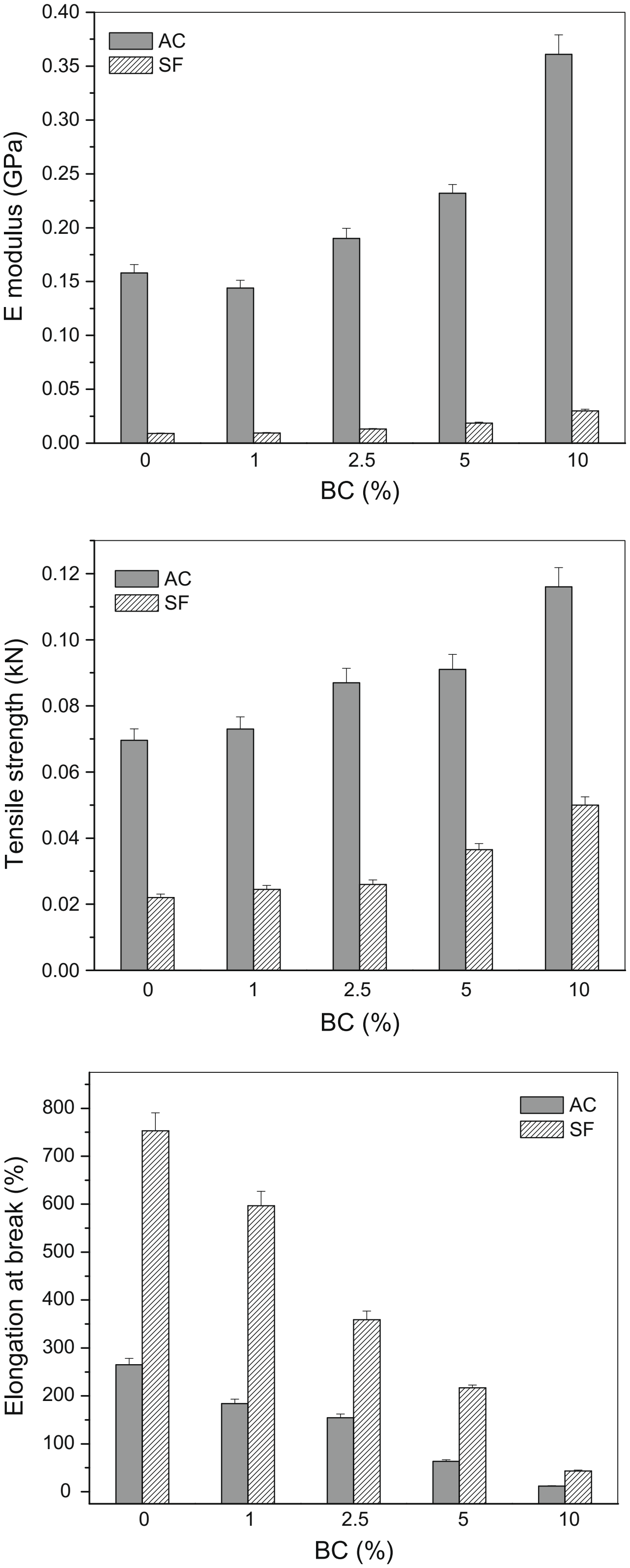

Fig. 4. Young's modulus, tensile strength and elongation to break of AC and SF copolymers and the corresponding BC-based nanocomposites.

3.3. SEM

The morphology of cellulose based-composites is a very important parameter because it is closely related with their mechanical performance. SEM micrographs of the fractured surface of the used BC and SF copolymers and of the corresponding AC–BC and SF–BC nanocomposites with 10% of BC are shown in Fig. 6. For each material, two different magnifications, 2000× and 10,000×, were used

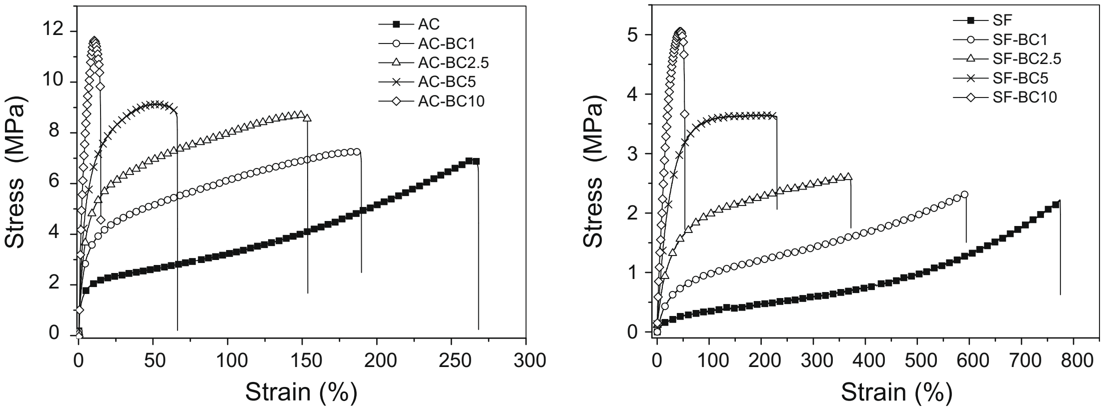

Fig. 5. Stress–strain curves of AC and SF copolymers and the corresponding BC-based nanocomposites.

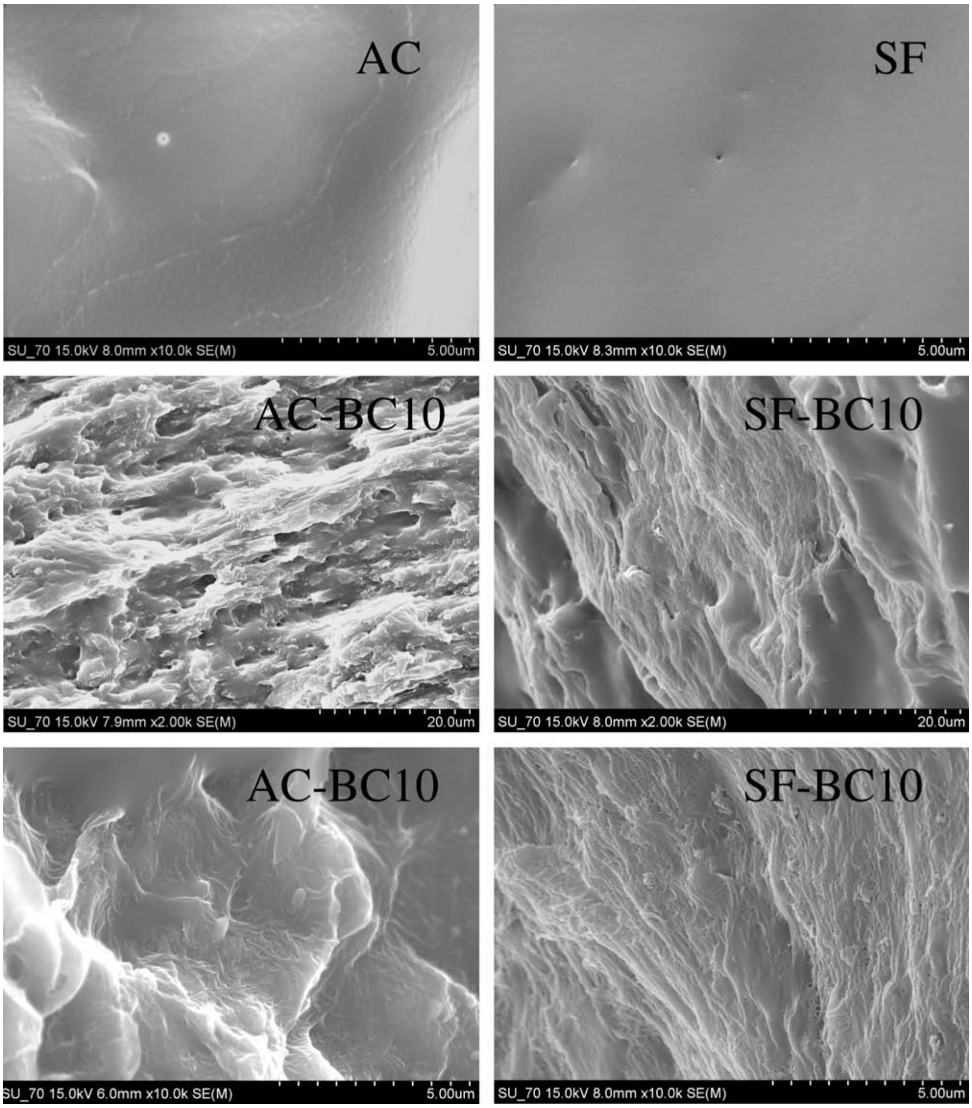

Fig. 6. SEM micrographs on the fractured surface of AC and SF copolymers and the corresponding BC-based composites with 10% of BC, at 2000× and 10,000× magnification.

to display both the nanofibers dispersion and the interfacial adhesion.

The SEM images of all AC–BC and SF–BC composites provided evidence of the strong interfacial adhesion between the two components, as shown by the complete impregnation of the BC nanofibrillar network into the polymeric matrices. This good dispersion of the BC network within the matrices without noticeable aggregates formation was also clearly displayed in Fig. 6.

These observations confirm the good compatibility between the BC and the acrylic matrices and explain the trends observed for the mechanical properties of these new materials (see Figs. 4 and 5).

4. Conclusions

This investigation showed that a simple casting method allowed composite materials to be prepared from BC and acrylic aqueous emulsions following a green procedure. Given the high compatibility between fibers and matrices, as shown by SEM, the ensuing composites displayed enhanced mechanical properties and thermal stability compared with those of the acrylic copolymers. The properties of these materials suggest that they could be successfully applied in such areas as packaging materials, particularly because bacterial cellulose is becoming a progressively more available raw material at reasonable price.

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