



Original Article

Green composites of thermoplastic corn starch and recycled paper cellulose fibers

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Abstract

Ecological concerns have resulted in a renewed interest in environmental-friendly composites issues for sustainable development as a biodegradable renewable resource. In this work we used cellulose fibers from recycled newspaper as reinforcement for thermoplastic starch in order to improve its mechanical, thermal and water resistance properties. The composites were prepared from corn starch plasticized by glycerol (30% wt/wt of glycerol to starch) as matrix that was reinforced with micro-cellulose fibers, obtained from used newspaper, with fiber content ranging from 0 to 8% (wt/wt of fibers to matrix). Physical properties of composites were determined by mechanical tensile tests, differential scanning calorimetry, thermogravimetric analysis, water absorption measurement and scanning electron microscopy. The results showed that higher fibers content raised the tensile strength and elastic modulus up to 175% and 292%, respectively, when compared to the non-reinforced thermoplastic starch. The addition of the fibers improved the thermal resistance and decreased the water absorption up to 63%. Besides, scanning electron microscopy illustrated a good adhesion between matrix and fibers. These results indicated that thermoplastic starch reinforced with recycled newspaper cellulose fibers could be fruitfully used as commodity plastics being strong, cheap, abundant and recyclable.

Keywords: composites, thermoplastic starch, cellulose fibers, physical properties

1. Introduction

Ecological concerns and the approaching depletion of fossil fuels are urging the sustainable development of green

or environmental-friendly materials as biodegradable renewable resource. Green composites comprise biodegradable polymers as matrix and biodegradable fillers, e.g. cellulose fibers. When these integral parts are biodegradable the composites are anticipated to be biodegradable (Averous and Boquillon, 2004).

Starch is one of the most used materials for producing biodegradable plastics being naturally renewable, cheap and

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plentiful (Angellier *et al.*, 2006; Teixeira *et al.*, 2009). However, before being thermally processable as for thermoplastic polymers, starch must be converted to thermoplastic starch (TPS) by the addition of specific plasticizers combined with the application of heat and shear forces (Hulleman *et al.*, 1998; Curvelo *et al.*, 2001; Angellier *et al.*, 2006).

As plasticizers, water (Kalichevsky and Blanshard, 1993; Teixeira *et al.*, 2009) and/or polyol plasticizers such as glycerol (Ma *et al.*, 2005; Angellier *et al.*, 2006; Teixeira *et al.*, 2009) and sorbitol (Teixeira *et al.*, 2009) have been used. With regard to polyols, glycerol and sorbitol, glycerol appears to give the best results in decreasing the friction between starch molecules (Janssen and Moscicki, 2006). Besides, glycerol is a by-product generated in large amounts in the biofuel industry, and is becoming nowadays a waste product that must be disposed of with additional costs (Yazdani and Gonzalez, 2007).

In spite of the above clear advantages of the use of starch-based plastics for a sustainable development, the applications of TPS are still restricted by their too low mechanical properties and high moisture adsorption, that are considered as major drawbacks when compared to conventional plastics (Averous and Boquillon, 2004; Teixeira *et al.*, 2009).

As a method to improve its properties, composites of TPS with reinforcing fillers and fibers, and in particular with cellulose fibers, have been proposed (Curvelo *et al.*, 2001). TPS/cellulose fiber composites have been prepared by using fibers from different sources, such as flax and ramie fibers (Wollerdorfer and Bader, 1998), potato pulp fibers (Dufresne and Vignon, 1998; Dufresne *et al.*, 2000), bleached leafwood fibers (Averous *et al.*, 2001), bleached eucalyptus pulp fibers (Curvelo *et al.*, 2001), wood pulp fibers (Carvalho *et al.*, 2002), and cassava bagasse fibers (Teixeira *et al.*, 2009). Most of these authors have shown an improvement of the mechanical properties of the composites that was attributed to the chemical compatibility between the two polysaccharides, i.e. starch and the vegetal fibers (Wollerdorfer and Bader, 1998; Curvelo *et al.*, 2001; Averous and Boquillon, 2004). Consequently, water resistance of the composites substantially increased (Dufresne *et al.*, 2000; Ma *et al.*, 2005) as a direct consequence of the addition of the less hydrophilic fibrous filler (Averous and Boquillon, 2004; Ma *et al.*, 2005), but in our opinion also due perhaps to the constraint exerted by the fibers at the interface on the matrix swelling.

Paper pulp cellulose fibers have also been used for the preparation of TPS composites (Averous and Boquillon, 2004) by using commercial cellulose fibers, but to our knowledge cellulose fibers extracted from used paper have not so far been employed. The global production of paper is expected to reach 400 million tons by the year 2010 with an increase by 77% from 1995 to 2020 (OECD, 2001), and generates a consequent increase of the amount of the used paper that imposes obvious recycling strategies.

In the present work, we have investigated the fabrication and the physical properties of TPS reinforced by cellu-

lose fibers extracted from used newspaper. TPS was obtained from corn starch by using glycerol as plasticizer and fibers were extracted from used newspaper by a deinking-washing process. Physical properties of composites were determined by mechanical tensile tests, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), water absorption measurements, and morphology assessment by scanning electron microscopy (SEM).

2. Materials and Methods

2.1 Cellulose fibers from used newspaper

Cellulose fibers were extracted from used newspaper with a deinking-washing process. The newspaper, collected from a waste container at the library of Faculty of Engineering, University of Trento, was firstly shredded to small pieces. Shredded paper (100 g) and equal amounts of deinking chemicals, i.e. sodium hydroxide (NaOH, 6 g) and sodium silicate (Na_2SiO_3 , 6 g), were filled with distilled water to a volume of 2 L and ground with a grinder to give a total of 5.6% consistency (percent solids in the pulp slurry) at 45°C under 800 rpm mechanical stirring for 20 min with the detected pH of 12. The pulp was then placed in a 16-mesh sieve, washed with running tap water (about 30 L) and subsequently with distilled water (1 L) until pH 7 was reached, and the remaining fibers were dispersed in distilled water to give about 1% consistency, and finally ultrasound stirred (Elma-S30H, Elmasonic) for 5 min. After washing with distilled water (2 L) followed by drying in oven at 100°C for 24 h and a last grinding (Kika-M20, Labortechnik), the final fibers were kept in desiccators. The average length (\pm SD) of the resulting fibers was 1.81 ± 0.48 mm with length/diameter ratio equal to 65 ± 17 , as evaluated by the ImageJ software on 20 fibers samples of SEM images (see Figure 1).

2.2 Matrix

Regular corn starch (Sigma-Aldrich) with 27% amylose content and glycerol (Sigma-Aldrich) with 99.5%

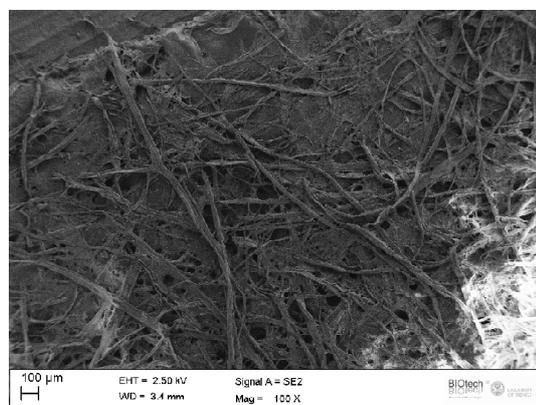


Figure 1. SEM micrograph of cellulose fibers from used newspaper

purity were used to prepare the TPS matrix. Starch, dried at 60°C for 24 h, and glycerol were manually pre-mixed in a polyethylene bag for 15 min until a powder was obtained. Preliminary experiments illustrated that the optimal glycerol content should be in the range of 20-35%; however, lower and higher glycerol content led to samples that were too brittle or to exudation phenomena of glycerol, respectively. For this reason samples used within this work contained 30% wt/wt of glycerol to starch.

2.3 Composites fabrication

TPS/cellulose fibers composites containing 0, 2, 4, 6 and 8% wt/wt of fibers to matrix were fabricated from the above prepared fibers and matrix as follows. First, the proper amounts of matrix and fibers were manually mixed for 15 min and successively melt compounded by using an internal mixer Rheomix 600p (Thermo Haake) at a temperature of 160°C and a rotor speed of 100 rpm for 6 min. The resulting combinations were hot pressed in a compression molding machine (Fred S. Carver Inc.) at 160°C to prepare 1 mm thick sheets with consecutive times-applied pressures of 10 min-no pressure, 10 min-0.74 MPa and 10 min-1.48 MPa. After molding, the sheets were cut into specimens for the following tests and were stored in desiccators at 23-25°C, 45-55% relative humidity (RH), till use. No glycerol loss or exudation was noticed during the hot pressing or the storage.

In the following the terms CS-NF0, and CS-NF2, 4, 6 and 8 are used to define the non-reinforced TPS, and TPS composites containing 2, 4, 6 and 8% wt/wt of fibers to matrix.

2.4 Mechanical tensile test

Mechanical tensile tests were carried out to measure ultimate tensile strength (UTS) and elastic modulus (E) according to ISO 527 standards (1993) by a tensile testing machine (Instron 4520), equipped with clamps of 100 N, operating with the crosshead speed of 5 mm/min. The tests were performed at room temperature on 5 dumbbell-shaped specimens with 30 mm gauge length.

2.4 Thermal analysis

Differential scanning calorimetry (DSC) was carried out by using a Mettler DSC 30 (Mettler Toledo) to determine thermal transitions. Samples weighing approximately 15-20 mg were placed in aluminum pans and the analyses were performed from -140 to 140°C under nitrogen flow of 100 mL/min at the heating rate of 5°C/min. DSC data were analyzed using STARe software v.6.10; in particular, glass transition temperatures were taken from the midpoint of the changes in heat capacity.

Thermogravimetric analysis (TGA) was performed by using a Mettler TG 50 (Mettler Toledo). Samples weighing approximately 20-25 mg were analyzed at a heating rate of

10°C/min from 40-800°C in an atmosphere of 100 mL/min flowing nitrogen.

2.5 Water absorption

Water sorption measurements were performed according to ISO 62 (1999) on three samples for each composition of size approximately 30x30x1 mm. Before immersion in distilled water, samples were dried at 50°C for 24 h, equilibrated at room temperature in desiccators, and weighed to determine the reference dry weight, W_D . They were then immersed in plates containing water, conditioned at 23-25°C and 45-55% RH for 24 h. After immersion in water, samples were removed from the water at selected times, gently and rapidly dried with tissue paper to remove the excess water, and subsequently weighed to define the wet weight, W_w . Percent of water absorption (%WA) was calculated as the following equation.

$$\%WA = (W_w - W_D) / W_D \times 100$$

2.6 Scanning electron microscopy

Scanning electron microscope (Supra 40, Zeiss) was used to determine the fiber dimensions as well as to visualize the fracture surface of the composites. For both, fibers and composites were gold-sputtered before imaging, and were observed at operating acceleration voltages of 2.5 kV and 15 kV for fibers and composites, respectively. For surface fracture imaging, composites were fractured in liquid nitrogen.

3. Results and Discussion

The TPS composites prepared in this study displayed homogeneous distribution of fibers.

3.1 Mechanical properties

The progression of the mechanical properties, i.e. UTS and E , as a function of cellulose fibers content, is shown in Figure 2 for the non-reinforced TPS and composites. Both of UTS and E of the composites increased almost linearly with the weight content of fibers, reaching for the 8% wt/wt composite (CS-NF8) values for UTS and E up to 175% and 292%, respectively, with respect to those of the non-reinforced TPS. The increase in mechanical properties is consistent with the intrinsic adhesion between fibers and matrix at the interface, favored by the chemical similarities between starch and cellulose fibers (Averous and Boquillon, 2004; Ma *et al.*, 2005).

3.2 Thermal properties

Glass transition of TPS is sometimes difficult to detect by DSC because of the small change of the heat capacity at the glass transition temperature (Averous and Boquillon,

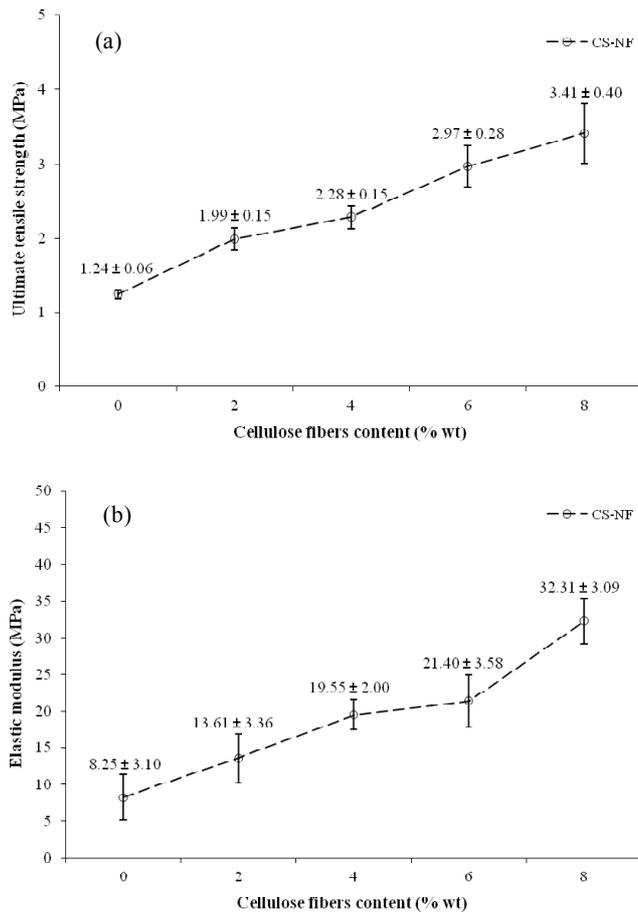


Figure 2. Effect of cellulose fibers content on the mechanical properties, (a) ultimate tensile strength and (b) elastic modulus, of non-reinforced TPS and composites

2004). Figure 3 shows the DSC thermal traces for the non-reinforced TPS and composites. Two transitions were detected in the non-reinforced TPS and composites, consistently with findings reported in the literature. The higher temperature (T_{11}) is clearly due to a starch-rich phase and hence referred to the TPS glass transition while the lower one (T_{12}) can be attributed to a starch-poor phase (Ma *et al.*, 2008; Forssell *et al.*, 1997). At higher fibers contents, both

transition temperature values increased as shown in Table 1, as a result of the interfacial interactions between polar components of fibers and matrix due to the formation of the hydrogen bonds (Averous and Boquillon, 2004).

The TGA results illustrating the thermal degradation of non-reinforced TPS and composites are reported in Figure 4 and Table 1. The behavior of TGA mass loss curves was similar in the non-reinforced TPS and composites and the weight loss gradually decreased with raising of the fibers contents. As shown in Table 1, the composite degradation temperatures of the maximum rate, obtained from derivative thermogravimetry (DTG) peaks, progressively increased with higher fiber content. The results are ascribed to the higher thermal stability of the fibers compared to starch, and specifically the good compatibility of both polysaccharides (Martins *et al.*, 2009). It seems that the degradation temperatures of composites varied between the values of matrix and of fibers with an additional effect (Averous and Boquillon, 2004).

The temperatures were close to 320°C; the weight losses at this temperature were determined and are summarized in Table 1. The percentage weight losses decreased with increasing fiber contents. As shown in Figure 4, the TGA mass loss curves expressed an initial mass drop from 50 to 100°C, corresponding to the loss of absorbed water (Teixeira *et al.*, 2009) that was lower in composites with

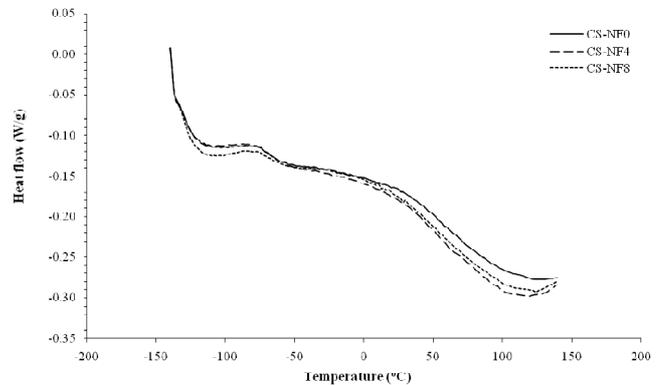


Figure 3. DSC scans for non-reinforced TPS and composites

Table 1. DSC and TGA results

Composites	DSC		TGA	
	T_{11} (°C)	T_{12} (°C)	Weight loss at 320°C (%)	Degradation temperature (max DTG peak) (°C)
CS-NF0	62.49	-69.26	61.35	314.74
CS-NF4	69.87	-65.66	58.23	316.73
CS-NF8	73.56	-61.13	54.55	320.70
NF	N/A	N/A	18.60	361.30

Remark: N/A = not available

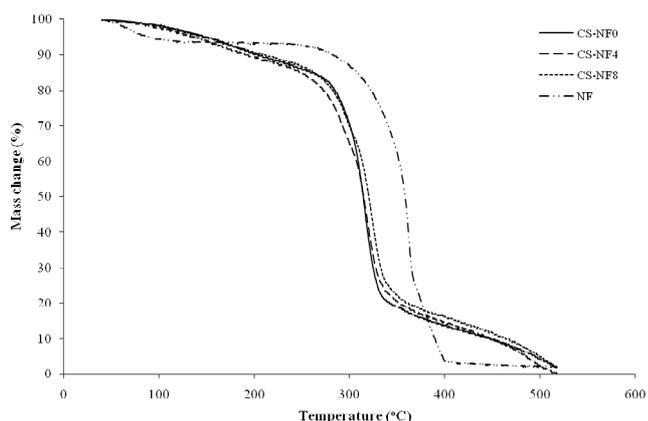


Figure 4. TGA scans for cellulose fibers, non-reinforced TPS and composites

respect to the pure matrix (Averous *et al.*, 2001). The less hydrophilic cellulose fibers lowered the polar character of the crystalline fibers used as filler (Averous and Boquillon, 2004; Averous *et al.*, 2001). Hence, the lowered water uptake induced by the cellulose fibers worked also to improve the thermal resistance of non-reinforced TPS.

3.3 Water resistance

Low water resistance is a drawback of TPS for many practical applications. Table 2 illustrates that the addition of cellulose fibers decreased the amount of absorbed water up to values of minus 63% for the 8% wt/wt composite when compared to the non-reinforced TPS. The results are described as a direct consequence of the addition of the less hydrophilic cellulose fibers when compared to starch (Averous and Boquillon, 2004; Ma *et al.*, 2005). The presence of cellulose fibers decreased the water absorption of TPS also because of the constraint exerted by the fibers at the interface on the matrix swelling.

3.4 Morphologies

SEM micrographs of the fracture surfaces of the non-reinforced TPS and composites are shown in Figure 5. Figure 5(a) shows the homogeneous pure matrix and Figures 5

Table 2. Water absorption measured according to ISO 62 for non-reinforced TPS and composites

Composites	Water absorption (%)
CS-NF0	243.07 ± 2.61
CS-NF2	213.46 ± 1.95
CS-NF4	201.98 ± 8.36
CS-NF6	191.32 ± 2.24
CS-NF8	180.37 ± 3.38

(b,c,d,e) indicate the good dispersion of fibers in the matrix.

Fibers appear to be embedded in the matrix, organized in bundles and well adhering to the matrix as shown in Figure 6. Besides, the absence of fiber pullout indicates their good interfacial adhesion (Curvelo *et al.*, 2001; Ma *et al.*, 2005).

4. Conclusion

This work showed an initial insight to develop green composites of TPS and recycled newspaper cellulose fibers. The introduction of the cellulose fibers effectively improved mechanical properties and thermal resistance, and decreased the water absorption. The composites containing 8% wt/wt of fibers to matrix presented the best improvement of mechanical properties and thermal resistance, and the highest decrease of percentage water absorption when compared to the others. When observed by SEM the composites showed good adhesion between TPS matrix and cellulose fibers. These composites could be used as commodity plastics like biodegradable artifacts, e.g. organic waste bags and seeding grow bags, being strong, cheap, abundant, and recyclable.

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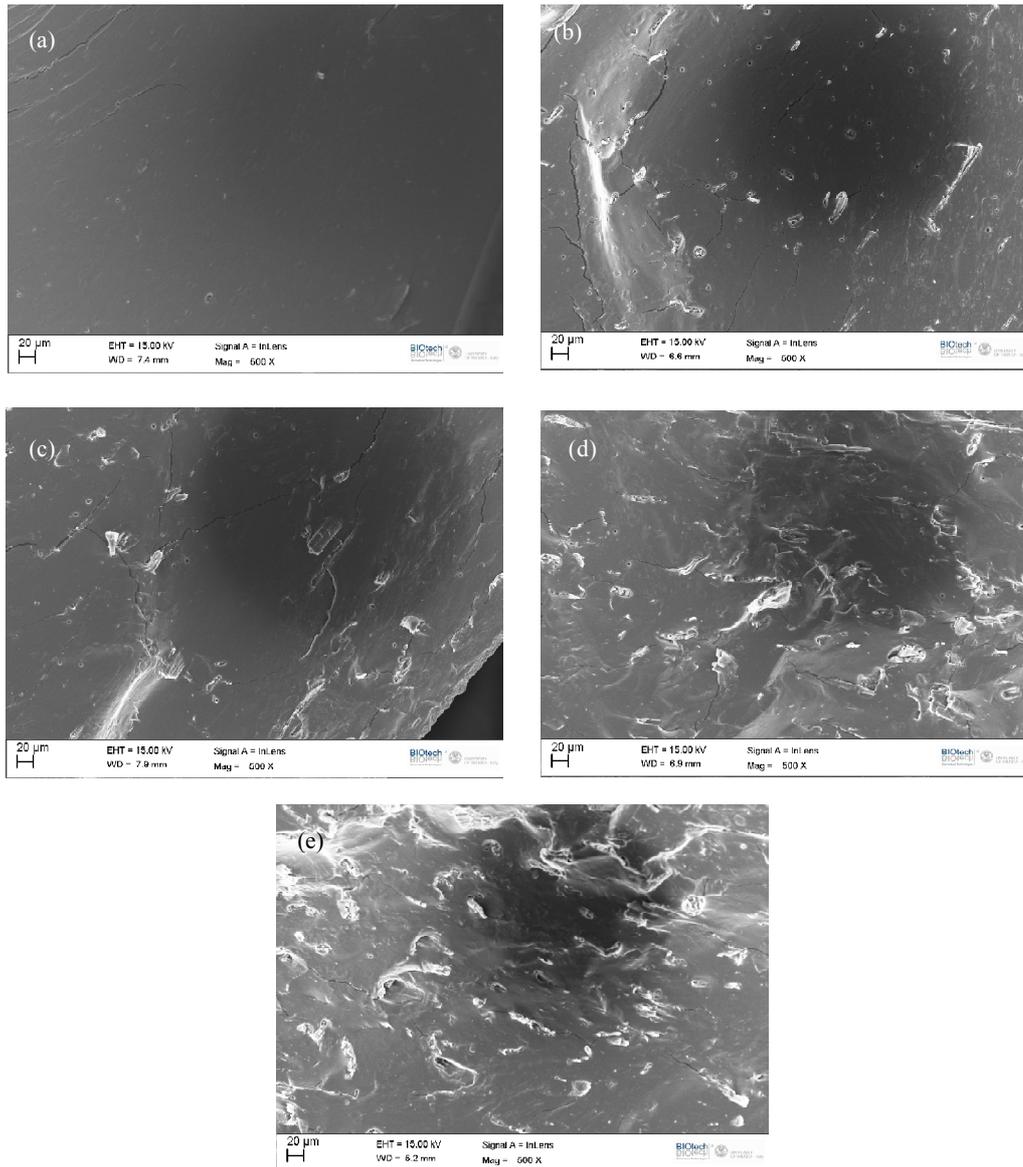


Figure 5. SEM micrographs of fragile fractured surface of (a) non-reinforced TPS and composites filled with different fibers contents, (b) 2%, (c) 4%, (d) 6% and (e) 8%

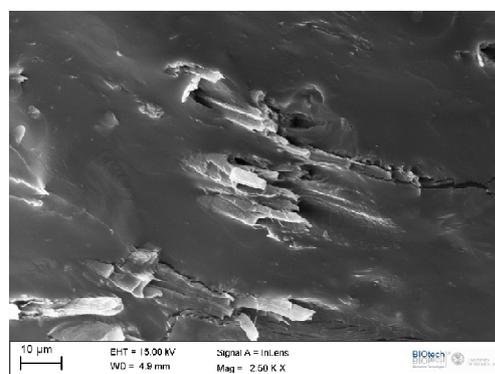


Figure 6. SEM micrograph of fragile fractured surface of TPS reinforced with 8% wt/wt of fibers to matrix

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