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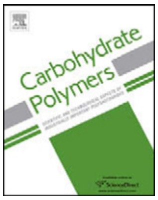

Starch/multi-walled carbon nanotubes composites with improved mechanical properties

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ABSTRACT

In this work, novel starch based nanocomposites containing very small quantities of multi-walled carbon nanotubes (MWCNTs) (0.027 wt% and 0.055 wt%) were developed. These materials exhibited highly improved tensile and impact properties as a consequence of wrapping the MWCNTs with a starch–iodine complex composed by the same starch of the matrix. Thus, good dispersion of the filler in the matrix and excellent adhesion between phases (as shown in FE-SEM micrographs) were achieved. Increments up to almost 70% in stiffness and 35% in ultimate tensile strength, keeping deformations higher than 80% without break were found. Therefore, tensile toughness also increased up to ~50%. Enhancements of up to ~100% in biaxial impact parameters (thickness related perforation energy and disc maximum strength values) were also observed. The significant improvements in all uniaxial tensile and biaxial impact properties obtained for such significantly low contents of filler, as a result of the type of functionalization used, have not been already reported in the literature and point out these biodegradable composites as a very appealing alternative to traditional materials for different applications.

1. Introduction

The development of nanocomposites based on traditional polymers has been an attractive topic of study for materials to be used in different applications beyond packaging, including military and energy, pharmaceuticals, medicine, and cosmetics. Many packaging industries are trying to implement new technologies in bags, plates, cups, bowls, and coatings (Avérous & Boquillon, 2004; Wang, Rakotonirainy, & Papua, 2003). Although toxicity of some nanofillers such as carbon nanotubes appears still controversial in the literature, nano packaging is being designed to enable materials to interact with food, emitting antimicrobials, antioxidants, nutraceuticals, etc; and to alter the properties and traits of food, including its nutrition, flavor, texture, heat tolerance and shelf life (Lyons, 2010). However, other applications rather than packaging seem to be more appropriate for these fillers. In particular, nowadays the Biomedical Industry has shown a great interest in the development of nanocomposites for their use as sensors or stimulators of bone cells (Harrison & Atala, 2007; Tsai, Chen, & Liaw, 2007; Wu & Liao, 2007).

A frequent problem of synthetic nanocomposites is their relatively high price as well as the possible environment pollution they can provoke. To solve these problems, nanostructured materials based on biodegradable, renewable and low cost polymers became of interest. Among these polymers, starch is viewed by companies as a good alternative in biodegradable formulations for packaging due to its great availability, high biodegradability and low cost (Shogren, Lawton, Doane, & Tiefenbacher, 1998; Sorrentino, Gorrasi, & Vittoria, 2007; Talja, Helén, Roos, & Jouppila, 2007). Starch films have a strong and flexible structure and transparency, derived from the linear structure of amylose (one of the components of starch), and they are resistant to fats and oils. Starch packagings are used in cushions and protections against shock and vibration during transportation (Villada, Acosta, & Velasco, 2007). In addition, they are odorless, tasteless, colorless, non-toxic and biologically absorbable (Wong, Camirand, & Pavlath, 1994). However, the use of starch based materials has been strongly limited

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because of their poor mechanical properties and high permeation compared to other non-natural polymers (Hansen & Plackett, 2008). The incorporation of micro and nano-sized fillers into starch has been the topic of many studies in order to overcome these disadvantages (Alemdar & Sain, 2008; Alvarez & Vazquez, 2006; Famá, Gerschenson, & Goyanes, 2009).

In addition, it is well known that the size, shape, and interfacial adhesion between the polymer and the filler greatly influence mechanical properties of the final composite (Fu, Feng, Lauke, & Mai, 2008; Katz & Milewsky, 1978; Siqueira, Bras, & Dufresne, 2009). In general, smaller size fillers lead to materials with better mechanical properties, such as higher Young's modulus but with a detrimental effect in ductility (So, Cho, & Sahoo, 2007; Wisse, Govaert, Meijer, & Meijer, 2006). Especially attractive fillers, recently well studied due to their high aspect ratio, Young's modulus, tensile strength and electrical conductivity are carbon nanotubes. Because of these properties they seem to be the ideal reinforcement for different types of polymers (De Falco, Fascio et al., 2009; De Falco, Marzocca et al., 2009; Jia et al., 1999; Ruan, Gao, Yang, & Yu, 2003; Zilli et al., 2007). For example, Ruan et al. (2003) reported significant improvements in physical and thermal properties of ultra high molecular weight polyethylene (UHMWPE) with the addition of carbon nanotubes without compromising toughness. In particular, Ma, Chang, Yu, and Lu (2008) observed that the addition of functionalized MWCNTs to a starch matrix led to improvements in tensile strength and Young's modulus, but with reductions in the material toughness.

From the biomedical perspective it has been shown that nanotubes can stimulate bone formation, and at the same time, they are able to generate reinforcement (Harrison & Atala, 2007; Supronowicz et al., 2002). However, while promising to ameliorate some of the health and ecological problems, they also threaten to introduce new dangers to the environment and human health. Nowadays, there is little understanding of how they interact with humans and the environment. Some researchers found that the nanotubes work by severely damaging *Escherichia coli*'s cell walls, exhibiting powerful antimicrobial effects (Valdés, González, Calzón, & Díaz-García, 2009).

Despite the known potential of carbon nanotubes, there are many difficulties in transforming them into soluble materials that can be easily manipulated in aqueous solutions. In addition, the effectiveness of their utilization strongly depends on two factors: homogeneous dispersion of nanotubes throughout the polymer matrix without destroying the integrity of the tubes, and adequate interfacial adhesion between the phases. In many cases, the solubilization of carbon nanotubes can be achieved by their covalent sidewall functionalization, but this type of procedure usually destroys the extended networks on their surfaces, diminishing their mechanical and electronic properties. Star et al. (2003) showed that solubility in water of carbon nanotubes can be improved when they are wrapped by an aqueous solution of a starch–iodine complex. They suggested that iodine induces an initial preorganization of the amylose in starch into a helical conformation that makes its hydrophobic cavity accessible to a single carbon nanotube or bundles thereof.

The aim of this research was to develop novel starch based nanocomposites reinforced with a very low amount of MWCNTs previously wrapped with a starch–iodine complex, containing the same starch of the matrix, in order to obtain simultaneous improvements in stiffness, strength and toughness. In this way, replacing synthetic materials in different applications, without losing their attractive mechanical properties would be a goal. Under this framework, the effect of the addition of very small fractions of MWCNTs on the uniaxial tensile and on the biaxial impact behavior of the nanocomposites was investigated.

2. Experimental

2.1. Materials and nanocomposites preparation

Tapioca starch, provided by Industrias del Maíz S.A. (Argentina) and glycerol (Mallickrodt, Argentina) of analytical grade were used to prepare composites matrix. Multi-walled carbon nanotubes (MWCNTs), from Nanocyl (NC 3100), were used as reinforcement. Length and diameter of carbon nanotubes were approximately 1 μm and 15–20 nm, respectively.

MWCNTs were first subjected to a thermal treatment in air in a tubular oven. MWCNTs were heated at 35 °C/min till 400 °C and maintained at this temperature for 30 min to eliminate the amorphous carbon. Then they were allowed to cool down to room temperature inside the oven. Finally, treated MWCNTs were dried under vacuum at 120 °C for 3 h (De Falco, Marzocca et al., 2009).

MWCNTs were wrapped with an aqueous solution of starch–iodine complex prepared according to the method proposed by Star et al. (2003). The complex was performed at 0.5% of the same Tapioca starch of the matrix in distilled water with saturated iodine, stirred for 5 min at room temperature and stabilized during one night. The solubilized fraction of the complex was extracted avoiding any residual iodine. In this way, 93 g of the aqueous solution of the starch–iodine complex containing ~0.3 g of starch was obtained.

Composites were prepared incorporating 0.002 g and 0.004 g of carbon nanotubes in the solubilized aqueous starch–iodine complex. All the systems were sonicated in an ultrasonic bath for 1 h. Then, 4.5 g of Tapioca starch and 2.5 g of glycerol as plasticizer were added to each system. The mixture was heated at ≅3 °C/min, till complete gelatinization. The resulting gel was degassed with a vacuum pump during 10 min, and subsequently cast in glass Petri dishes and dried at 50 °C during 24 h. Samples were conditioned over NaBr ($a_w \cong 0.575$ at 25 °C) for 4 weeks before characterization.

Final weight fraction percentages (ϕ_f) of MWCNTs were 0.027 wt% and 0.055 wt%. They were calculated by only taking into account 4.8 g of starch (0.3 g of the starch derived from the starch–iodine complex plus 4.5 g of starch from the mixture) and 2.5 g of glycerol. In all studied samples, thickness (e) was 0.26 ± 0.01.

2.2. Scanning electron microscopy (SEM)

MWCNTs dispersed in alcohol and in the aqueous solution of the starch–iodine complex and the cryogenic fracture surfaces of the nanocomposites were observed using field emission scanning electron microscopy (FE-SEM) at different magnifications.

2.3. Mechanical characterization

Uniaxial tensile tests were carried out in an Instron dynamometer at 1.2 mm/min following ASTM D882-02 (2002) standard recommendations. Nominal stress (σ)–strain (ε) curves were obtained and Youngı̆s modulus (E), tensile strength (σ_u), strain at break (ε_b) and tensile toughness values were determined.

Biaxial impact tests were performed using a "falling weight" Fractovis of Ceast at 3 m/s. Thickness related perforation energy (U/e) values were obtained by numerical integration of the load–displacement curves. Disc maximum strength (σ_d) was evaluated as:

$$\sigma_d = 2.5\frac{P_{\max}}{e^2}$$

where P_{max} is the maximum load attained in the test and e is the sample thickness.

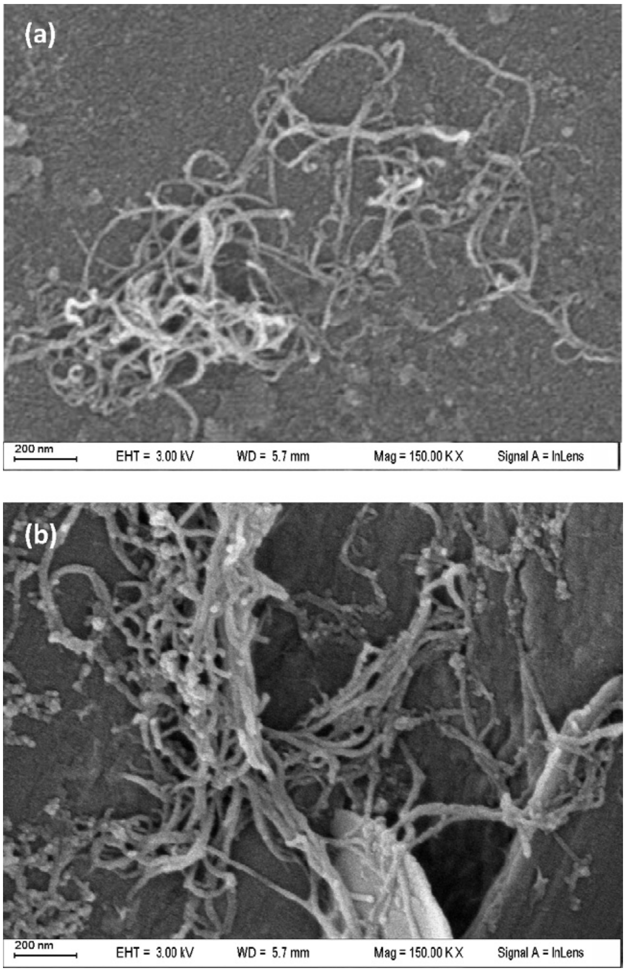

Fig. 1. SEM micrographs of MWCNTs. (a) Dispersed in alcohol, and (b) wrapped by the aqueous solution of starch–iodine complex.

All mechanical tests were carried out at room temperature. A minimum of five tests were performed and the average values were reported.

3. Results and discussion

3.1. Dispersion of carbon nanotubes

Fig. 1a and b shows FE-SEM micrographs of the MWCNTs dispersed in alcohol and in the aqueous solution of the starch–iodine complex, respectively. It can be observed in this figure that most MWCNTs dispersed in the starch–iodine complex (Fig. 1b) are coarser than the original ones, indicating that they were properly wrapped by this complex. Some irregularities are also seen in the walls of these carbon nanotubes which could be attributed to the starch used to wrap them. These irregularities are expected to contribute to carbon nanotube–polymer adhesion by mechanical interlocking (Wong et al., 2003). In addition, Fig. 1b also shows the typical morphology of functionalized MWCNTs as a result of the glue of starch (Cao, Chen, Chang, & Huneault, 2007; Wong et al., 2003).

3.2. Fracture surface analysis

Fig. 2 presents cryogenic fracture surfaces of the investigated materials. A well-developed vein pattern can be observed in the nanocomposites (Fig. 2b and c), suggesting that the residual amorphous matrix controlled the material deformation behavior. In addition, the space between veins was found to decrease with filler content. This result is in agreement with reported observations of materials containing nanocrystals (Bian, He, & Chen, 2002) where the vein pattern becomes thinner and denser with increasing filler volume fraction.

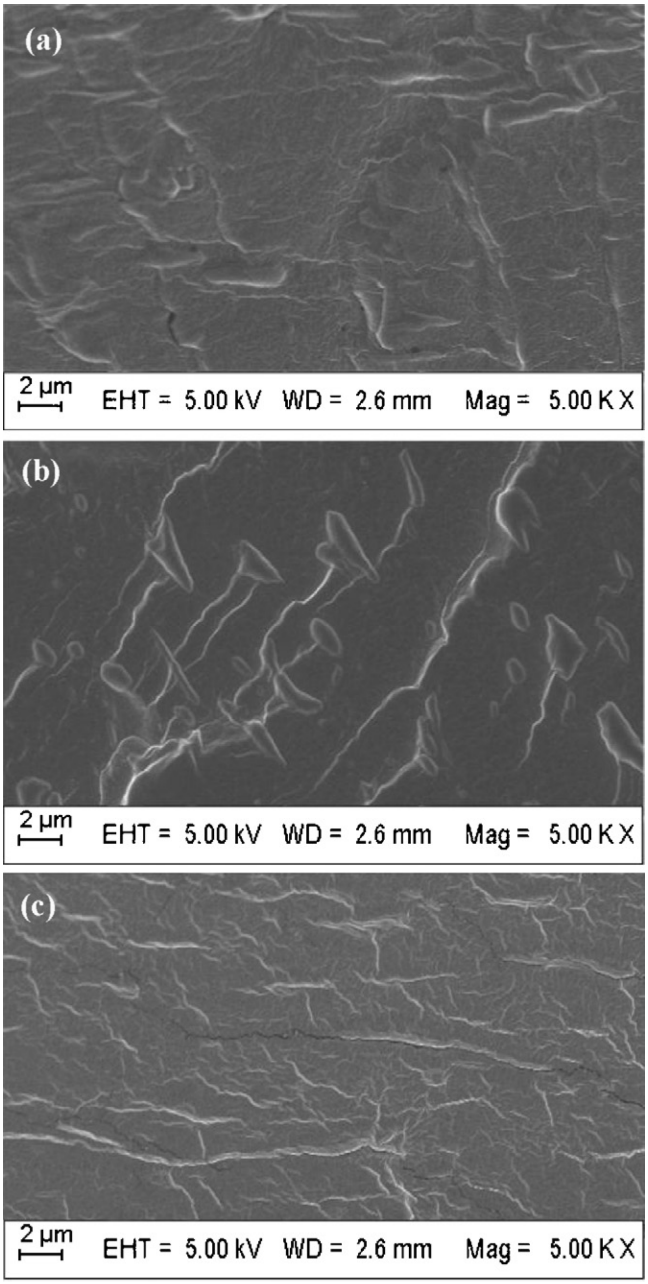

Fig. 2. SEM micrographs of cryogenic fracture surfaces for: (a) starch matrix, (b) composite with 0.027 wt% MWCNTs and (c) composite with 0.055 wt% MWCNTs.

In the composite with 0.055 wt% of MWCNTs some carbon nanotubes were found to be agglomerated (Fig. 3a). They were entangled together in the form of random arrays. MWCNTs were apparently clustered together forming clusters of micrometric dimensions. Failure around the MWCNTs agglomerate occurred within the starch matrix rather than between MWCNT and its starch coating, indicating strong MWCNT–starch adhesion. Closer examination of an individual MWCNT (Fig. 3b) revealed that it was uniformly covered by a thick layer of the starch material, especially at the matrix–tube interface. Therefore, carbon nanotubes were

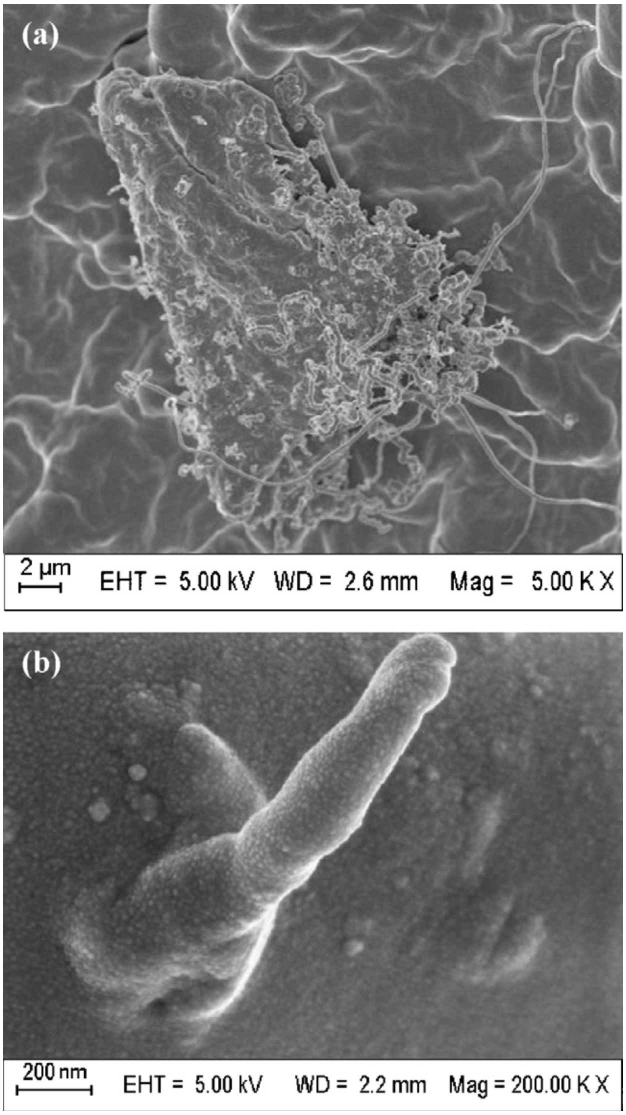

Fig. 3. SEM micrographs of the fracture surface of the composite with 0.055 wt% MWCNTs. (a) An agglomerate of MWCNTs (5 KX) and (b) a single carbon nanotube wrapped with the starch–iodine complex (200 KX).

properly wrapped with the starch–iodine complex used which was composed by the same starch of the matrix, and good adhesion between matrix and filler was achieved.

3.3. *Quasi-static tensile behavior*

Fig. 4 shows typical nominal stress-strain curves obtained under quasistatic uniaxial tensile loading conditions for the matrix and the two nanocomposites investigated.

Features of stress–strain curve of starch did not change due to the addition of MWCNTs. All materials exhibited non-linear behavior until failure which occurs with a precipitous drop of load at the maximum stress with no necking before fracture. However, a significant improvement in Young's modulus (E) as well as an enhancement in tensile strength (σ_u) values were found from the incorporation of very small amounts of carbon nanotubes to the starch matrix (Table 1), keeping deformations higher than 80% without break. Stiffness increased almost 70% and ultimate tensile strength ~35% with only 0.055 wt% of MWCNTs. Moreover, all tensile parameters also increased with filler content. Consequently, improved tensile toughness was displayed by the nanocomposites and with filler loading.

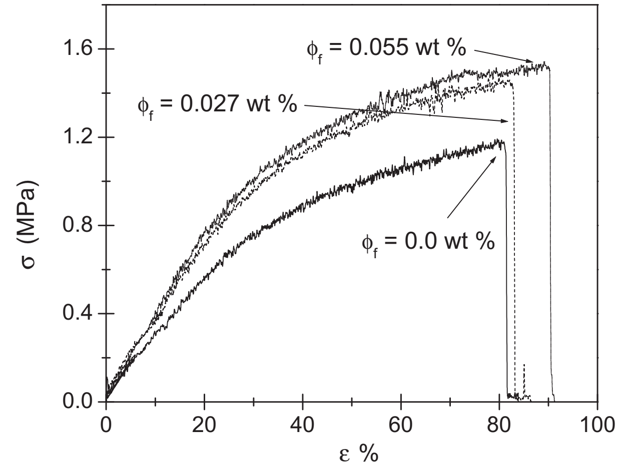

Fig. 4. Typical nominal stress–strain curves for the matrix and the nanocomposites.

It is important to remark that the above behavior is not very commonly found in the literature, especially with so small fractions of filler. Improvements in stiffness and yield strength (σ_y) have been reported for other matrices with addition of MWCNTs, but they were often accompanied by a reduction in σ_u and ε_b with a concomitant decrease in tensile toughness (Bhattacharyya, Peotschke, Abdel-Goad, & Fischer, 2004; Sierakowski, Souza, & Wypych, 2003). Only in a few cases, simultaneous improvements in Young's modulus, tensile strength and toughness were reported (Coleman et al., 2004; Ruan et al., 2003). But as far as authors know, even in the literature reporting improvements in mechanical properties for low filler loadings, filler volume fractions were not as low as those used in this work (Alvarez, Vazquez, & Bernal, 2005; Coleman et al., 2004; Ma et al., 2008; Wu, Zhang, Zhang, & Yu, 2009), and there is no report of starch with such improvements with very low contents of MWCNTs.The significant improvements in stiffness observed from the addition of the extremely low contents of carbon nanotubes used in this investigation, are the result of the high modulus of the filler as well as their homogeneous dispersion in the matrix. Furthermore, a shift in the glass transition temperature of the starch-rich phase to higher temperatures would have also contributed to the increase in stiffness mentioned above (Famá, Bernal, & Goyanes, 2009, 2010).

In addition, tensile strength and strain at break values also increased with filler loading, due to the MWCNTs were well dispersed in the starch matrix (as pointed out earlier) and the good interfacial adhesion achieved (as observed by FE-SEM). Thus, efficient load transfer from the matrix to the filler was attained and the high tensile strength and strain at break of the nanotubes was transferred to the composites. Therefore, the good interfacial adhesion

Table 1
Tensile parameters for the different materials investigated. Young's modulus (E), tensile strength (σ_u), strain at break (ε_b) and tensile toughness.

ϕ_f (wt%)	E (MPa)	σ_u (MPa) [±0.1]	ε_b (%)	Toughness × 10^{-5} (J/m^3)
0	2.5 ± 0.2	1.1	80 ± 1	6.4 ± 0.5
0.027	3.6 ± 0.4	1.4	82 ± 2	8.4 ± 0.8
0.055	4.2 ± 0.5	1.5	90 ± 2	9.9 ± 0.9

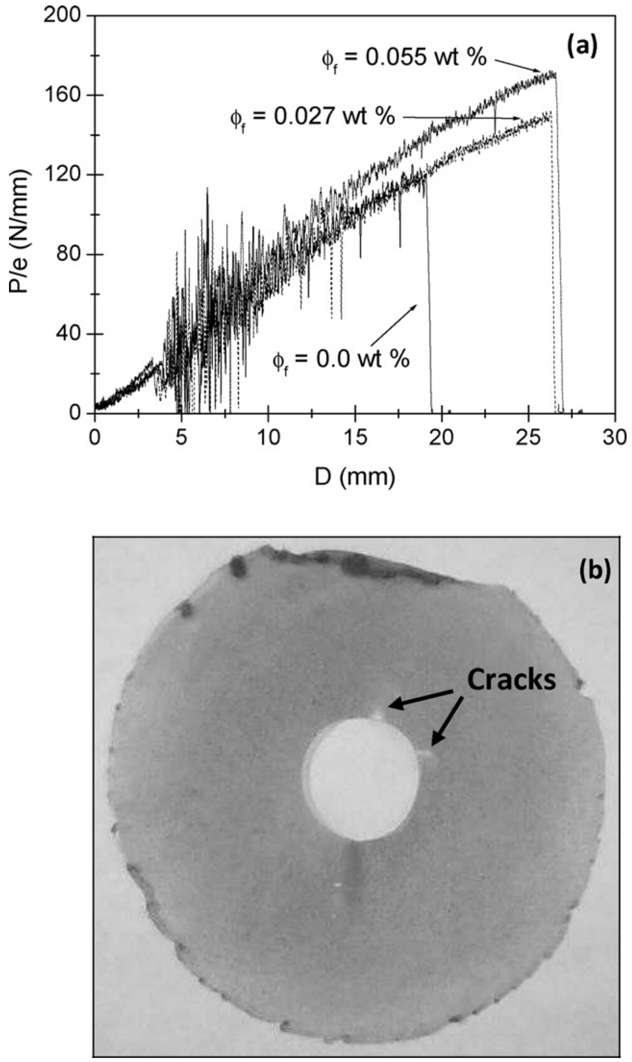

Fig. 5. (a) Thickness related load *versus* displacement curves obtained under biaxial impact conditions. (b) Typical macrophotograph of an impacted disc of the composite with 0.055 wt% MWCNTs.

obtained avoided the formation of holes and kept high deformations. As a result, the toughness defined as the work done to break a sample which is determined by integrating the stress–strain curve also increased with filler loading.

3.4. Biaxial impact behavior

Thickness related force *versus* displacement traces obtained under biaxial impact conditions are shown in Fig. 5a, while a typical macrophotograph of the impacted area of a composite sample with 0.055 wt% carbon nanotubes is presented in Fig. 5b, as an example.

As under quasistatic loading conditions, features of impact load–displacement curves did not change with the addition of MWCNTs. All the samples exhibited semi-brittle fracture behavior as judged from the non-linear load-deflection records which dropped to zero immediately upon reaching maximum load (Fig. 5a). Some radial cracks responsible for the final failure of specimens (Fig. 5b) were observed around the hole area of impacted samples. These cracks and the small deformed area around the hole also confirmed the semi-brittle fracture behavior reflected by load–displacement records.

Thickness related perforation energy (U/e), disc maximum strength (σ_d) and maximum displacement (d_{max}) values significantly increased with filler content (Table 2), showing improvements of up to ~100% in both U/e and σ_d. These results demonstrate that the addition of even a very small fraction of carbon nanotubes to the biodegradable matrix is also an efficient way to improve the material impact fracture behavior.

Table 2
Parameters obtained under biaxial impact conditions: thickness related energy (U/e), disc strength (σ_d) and maximum displacement (d_d).

ϕ_f (wt%)	U/e (N)	σ_d (N/mm^2)	d_d (mm)
0	1212 ± 2	3225 ± 25	19.0 ± 0.5
0.027	2174 ± 3	6040 ± 33	26 ± 1
0.055	2578 ± 4	6324 ± 67	27 ± 1

It should also be noted that in agreement with tensile results, the improvements observed in impact properties are also due to an efficient load transfer from the matrix to the filler.

It is well established in the literature (Qian, Dickey, Andrews, & Rantell, 2000) that the mechanical effectiveness of reinforced materials depends on the efficiency of stress transfer from the external load to the reinforcing phase. This efficiency is determined by the available interfacial area between the filler and the matrix and also by the strength of the interface, increasing as the area-to-volume ratio of the filler and the interfacial adhesion increase. In this work, MWCNTs wrapped with the same starch of the matrix were used as the reinforcing phase. In this way, the following concomitant effects existed maximizing the stress transfer to the reinforcing phase and thus, leading to the important improvements in the mechanical properties observed.

(1) Carbon nanotubes have an extremely high area-to-volume ratio. This is about 1000 times that of spheres with similar radius (Crosby & Lee, 2007).
(2) The aspect ratio of the CNTs is high.
(3) Our surface-modified nanotubes are highly compatible with the starch matrix, as they were wrapped with a starch–iodine complex composed by the same starch of the matrix and thus, excellent adhesion between phases and good dispersion of the filler in the matrix were achieved. This was confirmed by SEM observations and is in agreement with Lee, Zhang, Emrick, and Crosby (2006) who reported that surface-modified nanoparticles were well distributed in a polystyrene matrix as a result of their high compatibility with the matrix.

In summary, the excellent filler–matrix adhesion of prepared composites induces a cohesive fracture of the matrix and the good dispersion of nanotubes gives place to a tortuous crack path, resulting in an increase of toughness with nanotubes content.

4. Conclusions

The strategy used to wrap the carbon nanotubes with a starch–iodine complex composed by the same starch of the matrix, was highly effective to obtain very well-dispersed nanotubes in the matrix and strong adhesion between the phases. Thus, stress transfer was maximized and important improvements in the mechanical properties were obtained.

Significant increases in the quasistatic tensile properties of starch were found from the incorporation of very small quantities of MWCNTs. Stiffness increased almost 70% and ultimate tensile strength ~35% with only 0.055 wt% of MWCNTs, keeping deformations higher than 80% without break. As a consequence, tensile toughness also increased (~50%).

Furthermore, noticeable enhancements in impact properties were achieved. All nanocomposites exhibited semi-brittle behavior in biaxial impact tests, with improvements of up to ~100% in both thickness related perforation energy and disc maximum strength values.

SEM observations indicate that carbon nanotubes were well dispersed in the starch matrix and good adhesion between matrix and filler was achieved. This is a consequence of the successful wrapping of the nanotubes with the complex composed by the same starch of the matrix. Thus, strong adhesion between matrix and filler was assured and also better dispersion of the MWCNTs was achieved by hindering Van der Waals attractions among them and therefore, avoiding CNTs agglomeration.

It is important to note that the inherent high stiffness and the high surface area of the MWCNTs, due to their nanometric dimensions, efficiently contributed to the enhancement of mechanical properties but they did not induce new failure mechanisms in the starch matrix.

Based on the results obtained in this investigation, it can be concluded that it is possible to develop novel nanocomposites from biodegradable, renewable and low cost source, reinforced with very small quantities of MWCNTs, with improved tensile and impact properties. Hence, these materials seem to be very promising to replace synthetic ones in many applications.

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