



Biodegradable starch based nanocomposites with low water vapor permeability and high storage modulus

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ABSTRACT

Nanocomposite materials based on a starch matrix reinforced with very small amounts of multi-walled carbon nanotubes (MWCNTs) (from 0.005 wt% to 0.055 wt%) were developed. The material's dynamic-mechanical and water vapor permeability properties were investigated. An increasing trend of storage modulus (E') and a decreasing trend of water vapor permeability (WVP) with filler content were observed at room temperature. For the composite with 0.055 wt% of filler, E' value was about 100% higher and WVP value was almost 43% lower than the corresponding matrix values. MWCNTs were wrapped in an aqueous solution of a starch-iodine complex before their incorporation into the matrix, obtaining exceptionally well-dispersed nanotubes and optimizing interfacial adhesion. This excellent filler dispersion leads to the development of an important contact surface area with the matrix material, producing remarkable changes in the starch-rich phase glass transition temperature even in composites with very low filler contents. This transition is shifted towards higher temperatures with increasing content of nanotubes. So at room temperature, some composites are in the rubber zone while others, in the transition zone. Therefore, this change in the material glass transition temperature can be taken as responsible for the important improvements obtained in the composites WVP and E' values for carbon nanotubes content as low as 0.05 wt%.

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1. Introduction

In recent years, current industries have shown an increasing interest in replacing non-degradable materials by renewable source-based environmental-friendly ones, without impairing their properties. In particular, the Biomedical Industry has been focused in the development of nanocomposites with appropriate characteristics for their use as sensors or stimulators of bone cells (Harrison & Atala, 2007; Tsai et al., 2007; Wu and Liao, 2007).

Starch appears as an excellent alternative to synthetic materials because it is abundant, renewable, low cost and biodegradable (Bertuzzi, Armada, & Gottifredi, 2007; Gonera & Cornillon, 2002; Talja, Helén, Roos, & Jouppila, 2007). Its properties allow starch to behave as an excellent polymer matrix for biodegradable

films-forming (Famá, Rojas, Goyanes, & Gerschenson, 2005; Famá, Flores, Gerschenson, & Goyanes, 2006; Famá et al., 2007, 2011; Flores, Famá, Rojas, Goyanes, & Gerschenson, 2007; García, Ribba, Dufresne, Aranguren, & Goyanes, 2009).

On the other hand, due to the extraordinary mechanical, electrical and thermal properties of carbon nanotubes (De Azeredo, 2009; Matayabas & Turner, 2000; Matayabas et al., 2000; Sung et al., 2005), considerable effort has been focused in their use as reinforcements or sensors (Harrison & Atala, 2007). The main advantage of nanotubes over nanoparticles is their high aspect ratio which allows achieving percolation with very low amounts of filler. This fact makes their main disadvantage: the price, not a drawback. From the biomedical point of view, it has been shown that nanotubes embedded in a biodegradable matrix can stimulate bone formation (Harrison & Atala, 2007) and also have the ability to generate a structural reinforcement. Besides biomedicine, the packaging industry is also a tempting industry for the use of composites based on starch and nanofillers. However, the use of carbon nanotubes as reinforcement could serve as secondary packaging application, not applicable directly to food.

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The addition of MWCNTs can modify the mechanical properties of the composite, depending on the adhesion between filler and matrix (Ajayan & Zhou, 2001; Suhr, Zhang, Ajayan, & Koratkar, 2006). Furthermore, the incorporation of carbon nanotubes to the polymer matrix also affects roughness and consequently, the material wear properties.

So far, no major effects have achieved with the addition of low contents of carbon nanotubes since they tend to aggregate, being very difficult to separate them and thus to have a high surface area with very low amounts of filler.

The effective utilization of composite materials strongly depends on the homogeneous dispersion of the filler throughout the polymer matrix and the adequate interfacial adhesion between phases (Zilli et al., 2007). A few years ago, Star, Steuerman, Heath, and Stoddart (2002) showed that an effective technique to disperse carbon nanotubes in an aqueous system was to wrap their surfaces by an aqueous solution of a starch–iodine complex. In this way, their desirable properties were preserved and their solubility was improved. This technique is ideal for introducing the filler in a starch-based matrix since; in addition to ensure a good dispersion, it is highly possible to obtain excellent interfacial adhesion because the same material is used as the matrix and for wrapping the nanotubes.

A few papers about starch–carbon nanotubes composites have been reported in the literature (Cao, Chen, Chang, & Huneault, 2007; Ma, Jian, Chang, & Yu, 2008; Ma, Yu, & Wang, 2008; Zhanjun, Lei, Minnan, & Jiugao, 2011) but there, the nanotubes were non-covalent functionalized. Recently, Famá et al. (2011) have shown that the method proposed by Star et al. (2002) is very effective to disperse low contents of filler in the matrix, leading to simultaneous improvements in tensile strength, elongation at break and toughness. However, to our knowledge, there have not been already reported studies about the mechanical relaxations and the permeability of starch based composites reinforced with small amounts of carbon nanotubes.

The aim of this research was to determine the effect of the incorporation of very small fractions of MWCNTs (<0.06 wt%) previously wrapped using a iodine–starch complex, to a starch matrix on the material dynamic-mechanical and water vapor permeability properties.

2. Experimental

2.1. Nanocomposites preparation

Carbon nanotubes (Nanocyl, NC 3100) were subjected to a thermal treatment to eliminate the amorphous carbon (De Falco et al., 2009). Then, tubes surfaces were wrapped by a starch–iodine complex according with the procedure proposed by Star et al. (2002) as explained in details elsewhere (Famá et al., 2011). Four different amounts of wrapped carbon nanotubes (wMWCNTs), immersed in 93 g of the starch–iodine complex, were mixed with 4.5 g of tapioca starch (Industrias del Maíz S.A., Argentina) and 2.5 g of glycerol (Mallickrodt, Argentina) as plasticizer. The systems were heated at $\sim 3^\circ\text{C}/\text{min}$, till a temperature 5% higher than the temperature of gelatinization was reached, to ensure the gelatinization procedure was finished. The gels were degassed for 10 min, distributed in Petri dishes and dried at 50°C for 24 h. As a result, nanocomposites with only 0.005 wt%, 0.010 wt%, 0.027 wt% and 0.055 wt% (weight fractions percent, ϕ_f) of wMWCNTs were obtained with a thickness (e) of ~ 0.26 mm. Samples were conditioned over NaBr ($a_w \cong 0.575$ at 25°C) during four weeks prior to testing. After this time period samples weight had reached a constant value.

2.2. Scanning electron microscopy (SEM)

Cryogenic fracture surfaces were observed using field emission scanning electron microscopy (FE-SEM) at a magnification of $5000\times$ and $50,000\times$.

2.3. Water vapor permeability (WVP) determinations

Water vapor permeability was determined at room temperature in accordance with a modified ASTM E96-00 procedure. Circular acrylic cells containing the material were located in desiccators at relative humidity (RH) of $\sim 70\%$ and room temperature. Water vapor transport (WVT) was determined from the weight gain of the permeation, measuring over 24 h for 10 days. WVP were calculated as:

$$\text{WVP} = \frac{\text{WVT} \cdot e}{P_0 \text{RH}}$$

where e is the film thickness and P_0 the saturation vapor pressure of water at room temperature (Gennadios, Weller, & Gooding, 1994).

2.4. Dynamic-mechanical analysis

Dynamic mechanical tests were performed using a dynamic mechanical thermal analyzer (DMTA IV, Rheometric Scientific) in the rectangular tension mode at 1 Hz, in the range of temperature from -100°C to 75°C at a heating rate of $2^\circ\text{C}/\text{min}$, and using a set deformation of 0.04%, to ensure working in the linear viscoelastic range (Famá et al., 2005). Samples dimensions used were $15.0 \text{ mm} \times 5.0 \text{ mm} \times 0.26 \text{ mm}$ (length, width and thickness, respectively). Three replicates were tested for each system.

2.5. Moisture content determination

Moisture content of the different composites was determined using standard methods of analysis of the International Association of Official Analytical Chemistry (OMAAOAC, 1995). Samples (~ 0.5 g) were dried in a vacuum oven at 100°C , over calcium chloride, for 24 h until constant weight was reached. The reported results represent the average of four samples in each case.

3. Results and discussion

Fig. 1a and b shows typical images of the composite with 0.005 wt% of pristine carbon nanotubes and with the same content of carbon nanotubes previously wrapped by the starch–iodine complex, respectively. In the composite with pristine nanotubes (Fig. 1a), large agglomerates are observed, even for the very low filler contents used in this work. When carbon nanotubes were previously wrapped with the system composed by the same polymer of the matrix (the iodine–starch complex) (Fig. 1b), on the other hand, they are homogeneously dispersed and agglomerations are not present.

FE-SEM cryogenic fracture surfaces of the matrix and the composite with the highest filler content investigated (0.055 wt% of wMWCNTs) are shown in Fig. 2, as an example. As it has been previously reported for this material (Famá et al., 2011) and for other nanocomposites (Bian, He, & Chen, 2002; Famá et al., 2011; Zilli et al., 2005), a typical uniform vein pattern of well-dispersed nanofillers in the matrix can be observed in Fig. 2b. In addition, the space between veins was found to decrease as carbon nanotubes content increased and excellent adhesion between the wMWCNTs and the polymer matrix was achieved (Famá et al., 2011).

Fig. 3 shows the dependence of loss tangent values ($\tan \delta$) with temperature for the different composites investigated. $\tan \delta$ curves reveal two thermal transitions corresponding to the two phases of

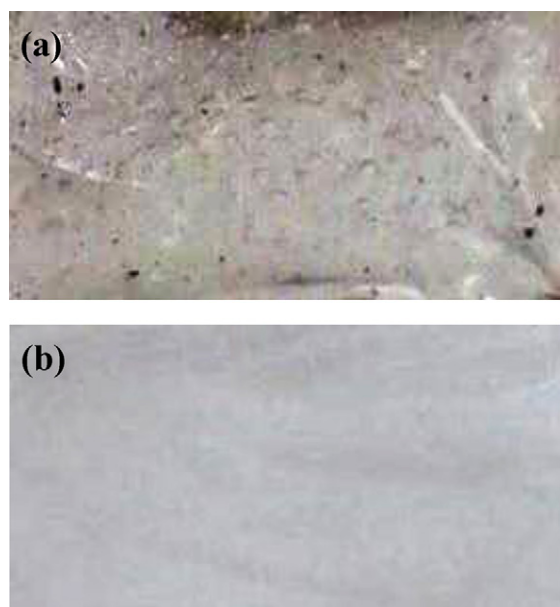


Fig. 1. Typical macroscopic images of the composites with 0.005 wt% of filler: pristine nanotubes (a) and carbon nanotubes previously wrapped by a starch–iodine complex (b).

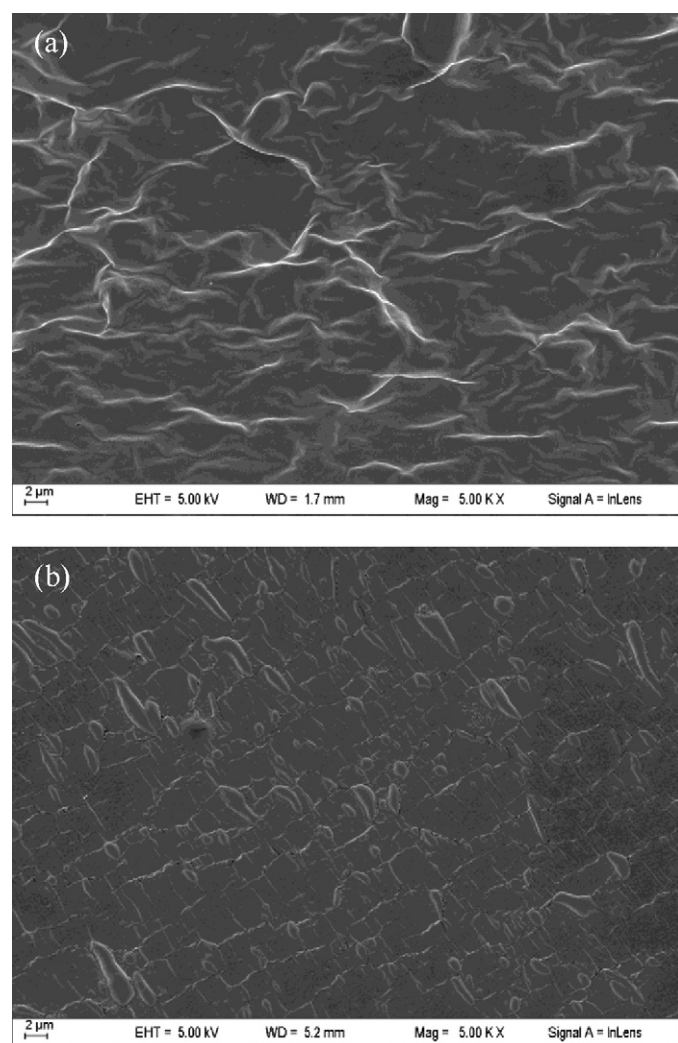


Fig. 2. FE-SEM micrographs of the cryogenic fracture surface of the matrix (a) and the nanocomposites with 0.027 wt% (b) and 0.055 wt% (c) of wMWCNTs (5000 \times).

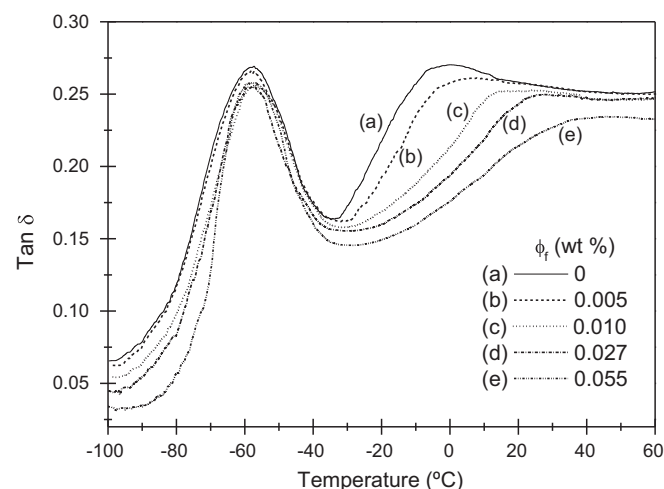


Fig. 3. Loss tangent, $\tan \delta$, as a function of temperature for the different nanocomposites investigated.

the glycerol–plasticized starch: the glycerol-rich phase at around -60°C and the starch-rich phase between 0°C and 20°C . These values agree well with those previously reported in the literature (Averous & Bouquillon, 2004; Cao et al., 2007; Famá et al., 2005, 2006; Famá, Gerschenson, & Goyanes, 2009; García et al., 2009; Ma, Yu, et al., 2008; Teixeira et al., 2009). The lower temperature peak did not change with filler addition suggesting that carbon nanotubes did not modify the distribution of the glycerol in the matrix. Nevertheless, the width of this peak decreased with the incorporation of a small amount of wMWCNTs, indicating that some restriction in the number of relaxation mechanisms existed in our composites. On the other hand, the upper transition peak broadened and was shifted to higher temperatures (the wrapped filler would have been interacting with the starch but not with glycerol). Besides, the peak intensity diminished with the increase in wMWCNTs content. The observed behavior can be attributed to the higher surface area promoted by the incorporation of the nanotubes and the very good adhesion between the matrix and the wrapped filler. During the glass transition temperature, the long-range polymer chain acquires mobility and therefore dissipates a great amount of energy through viscous movement. This is shown by the loss tangent peak in a dynamic-mechanical test. Hence, a depression in loss tangent values indicates the reduction of the number of mobile chains during the glass transition (Rao & Pochan, 2007). In our case, intermolecular interactions between starch and wMWCNTs, reduce the molecular mobility of the starch in contact with the carbon nanotubes surface (Ma, Jian, et al., 2008; Ma, Yu, et al., 2008) and therefore, decreased $\tan \delta$ values and increased relaxation peak temperature values were observed. It is also interesting to note, that even such a low content of filler as 0.055 wt% of well-dispersed nanotubes (approximately $1\ \mu\text{m}$ in length and $35\ \text{nm}$ in diameter) generates a surface area of about $90\ \text{m}^2/\text{g}$. The observed changes in the relaxation temperature peak from $\sim 0^\circ\text{C}$ for the matrix to $\sim 40^\circ\text{C}$ for the composite with the highest nanotubes content had important implications in the materials behavior at room temperature. While at 20°C , the matrix and some composites were in the rubbery state, other composites were around their glassy–rubbery transition zone.

The addition of carbon nanotubes also modified storage modulus versus temperature curves (Fig. 4). As expected, at the lower transition range ($\sim -60^\circ\text{C}$) there were no significant changes in E' curves with filler content, whereas the upper transition exhibited a shift in E' curves to higher temperatures with the increase in carbon nanotubes content. In addition, an increment in E' values

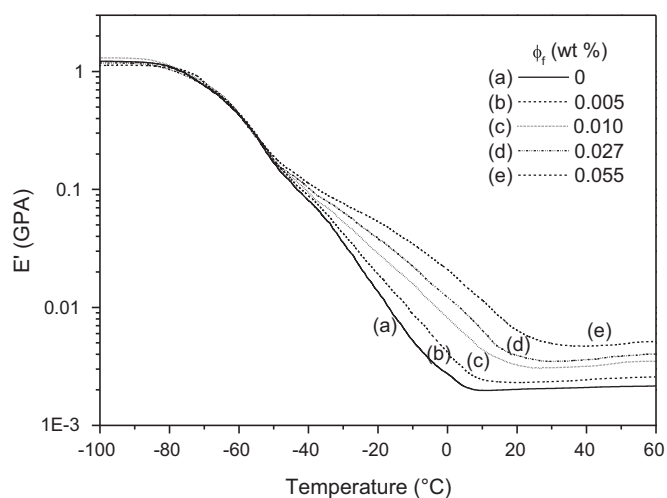


Fig. 4. Storage modulus, E' , as a function of temperature for the different nanocomposites investigated.

at room temperature for the composites was observed respect to the matrix, rising more than 100% in the case of the nanocomposite with the highest filler content investigated (Fig. 5). For carbon nanotube contents higher than 0.010 wt% (0.0074 vol%) a significant change in the material elastic behavior was observed. This change should be attributed to a change in the material state at room temperature, rather than to the existence of any percolation phenomenon. At room temperature, the matrix and some composites were in the rubbery state, whereas other composites were around the glassy–rubbery transition state, as pointed out above. For further increase in filler content the material was in an even more distant state than the rubbery state, thus leading to a further increase in E' value. Consequently, these results cannot be explained by any theoretical model for the elastic modulus of composite materials. The above change in the material state was also affected the material transport properties as it will be shown below.

The dependence of water vapor permeability values with filler content is shown in Fig. 6. The obtained value for the matrix is in the range of the values previously reported for starch–glycerol films (Famá et al., 2009; García et al., 2009) and it is in the same order of magnitude of the values reported by Ma, Jian, et al. (2008) for modified starch nanoparticles/plasticized-starch composites.

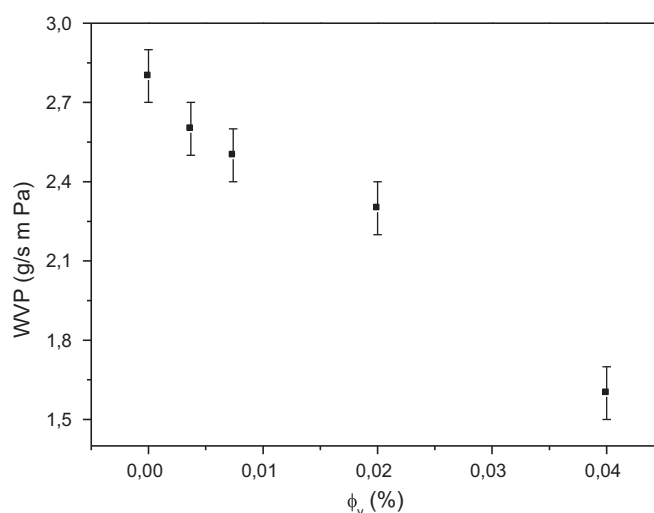


Fig. 6. Water vapor permeability, WVP, at room temperature, as a function of filler content.

WVP values were found to decrease as the amount of carbon nanotubes increased, leading to a decrease of almost 43% for the composite with only 0.055 wt% (0.04 vol%) of wMWCNTs. The high efficiency of wrapped carbon nanotubes to reduce the material water vapor permeability cannot be explained in terms of the “tortuous path” (Pinnavaia & Beall, 2000). In addition, it is impossible to use any theoretical model to justify the obtained WVP decrease from the incorporation of such small fractions of carbon nanotubes. In agreement with the results of dynamic-mechanical analysis, improvements in WVP properties can be associated with changes of the starch-rich phase glass transition temperature. It is well known that above the T_g , the free volume increases orders of magnitude respect to its value below T_g . Since water diffusion occurs by jumping from free volume hole to free volume hole, it is expected that important improvements in composites WVP properties are obtained by simply generating changes in the free volume (Wicks, Jones, Pappas, & Wicks, 2007).

It should also be noted that no significant differences among the water content values for the different composites were observed (all values fall within the interval $36 \pm 1\%$). These values were determined after samples weight had been stabilized over NaBr ($a_w \cong 0.575$ at 25°C) during 4 weeks. Therefore, the samples were properly equilibrated before testing and the observed changes in the dynamic-mechanical and permeability properties cannot be attributed to any effect of the material water content.

4. Conclusions

In this research, it was shown that wrapping carbon nanotubes with a starch–iodine complex allows obtaining starch based nanocomposites with very small amounts of carbon nanotubes which exhibit important improvements in storage modulus and water vapor permeability properties respect to the starch matrix. The critical point in optimizing the benefits of nanotubes was achieved from its excellent dispersion after being wrapped with the same material used as the matrix, ensuring a high contact area with very high adhesion, with extremely low filler contents.

The addition of very small amounts of wMWCNTs to the starch matrix led to increased storage modulus values and decreased water vapor permeability, reaching an E' value about 100% higher and a WVP value almost 43% lower than that of the matrix in the composite with only 0.055 wt% of carbon nanotubes. These significant improvements in E' and WVP values could be explained in terms of the changes experienced by the material glass transition

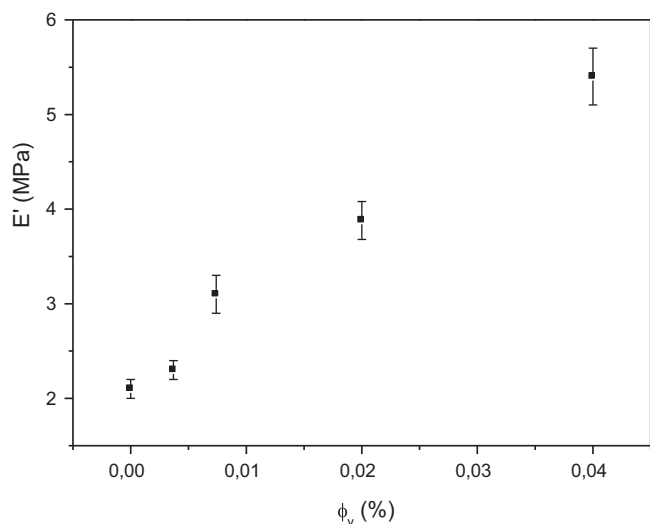


Fig. 5. Storage modulus values, E' , at room temperature, as a function of filler content.

temperature. The matrix material has its glassy–rubbery transition around 0 °C (below room temperature) whereas the T_g of the composite with 0.05 wt% of MWCNTs is around 40 °C. Then, at 20 °C the matrix is in the rubber state, while the composite with the highest filler content is in the transition state. The results of this study show that the addition of an extremely small amount of nanotubes can lead to major changes in the material behavior if the MWCNTs are well dispersed and the matrix material has its main relaxation near room temperature.

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