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Fracture behavior of a commercial starch/polycaprolactone blend reinforced with different layered silicates

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ABSTRACT

In the present work, composites based on a commercial starch/PCL blend (MaterBi-Z) reinforced with three different nanoclays: natural montmorillonite (Cloisite Na^+ (MMT)) and two modified montmorillonites (Cloisite 30B (C30B) and Cloisite 10A (C10A)) were prepared in an intensive mixer. The aim of this investigation was to determine the effect of the different nanoclays on the quasi-static fracture behavior of MaterBi-Z nanocomposites. An improvement in the fracture behavior for the composite with low contents of C30B was obtained, probably due to the easy debonding of clay achieved from a relatively weak filler–matrix interaction. On the other hand, a strong interaction had a detrimental effect on the material fracture toughness for the MaterBi-Z/C10A composites as a result of the higher compatibility of this organo-modified clay with the hydrophobic matrix. Intermediate values of fracture toughness, determined using the J-integral approach (J_c), were found for the composites with MMT due to its intermediate interaction with the matrix. The different filler–matrix interactions observed were also confirmed from the application of Pukánszky and Maurer model. In addition, multifractal analysis was applied to describe the topography of fracture surfaces. Thus, the complex fracture process could be successfully described by both experimental and theoretical tools. The obtained results suggest that it is possible to tailor the mechanical properties of the studied composites taking into account their further application.

1. Introduction

Over the recent decades, biodegradable polymers have been extensively investigated for packaging and agricultural applications to reduce the environmental pollution caused by plastic wastes (Davis & Song, 2006; Scott, 2000; Siracusa, Rocculi, Romani, & Dalla Rosa, 2008). In order to compete with common synthetic plastics, biodegradable polymers must have low cost as well as comparable mechanical properties. Starch-based blends present an enormous potential to be widely used in the field of biomedical applications and environmentally friendly materials, as they are fully biodegradable, inexpensive (when compared to other biodegradable polymers) and available in large quantities (Chen & Evans, 2005; Sorrentino, Gorrasi, & Vittoria, 2007). Blends of gelatinized starch with biodegradable polymers such as polyhydroxybutyrate (PHB) or polycaprolactone (PCL) have been studied by many authors (Godbole, Gote, Latkar, & Chakrabarti, 2003; Corradini, Marconcini, Agnelli, & Mattoso, 2011; Reis et al., 2008; Rosa, Lopes, & Calil, 2005; Wu, 2003).

Particularly, blends of poly-ε-caprolactone (PCL) and starch were introduced into the market at the beginning of the 90s as packaging materials (Ishiaku, Pang, Lee, & Ishak, 2002; Siracusa et al., 2008). It has been shown that physical and mechanical properties of these blends are similar to those of some conventional plastics, but they have the advantage of being biodegradable in different environments (Corradini et al., 2011; Reis et al., 2008; Rosa et al., 2005).

In addition, it has been well established in the literature that the incorporation of inorganic fillers is also a possible way to improve mechanical properties of polymeric materials (Xu, Li, Heng, & Mai, 2006). Starch/PCL blends based composites have been extensively investigated (Chen & Evans, 2005; Vertuccio, Gorrasi, & Sorrentino, 2009; Zhang, Yu, Xie, Naito, & Kagawa, 2007). In previous works, the creep behavior, the tensile properties as well as the effect of water uptake on these properties for starch/PCL blends reinforced with different types of clays have been already analyzed (Pérez, Alvarez, Mondragón, & Vázquez, 2007; Pérez, Alvarez, & Vázquez,

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2008; Pérez, Alvarez, Mondragón, & Vázquez, 2008). Besides, the influence of the content and type of clay on the dynamic and isothermal crystallization behavior of these materials has been reported (Pérez & Alvarez, 2008; Pérez, Alvarez, Stefani, & Vázquez, 2006).

Although many works have been already published on biodegradable materials, as mentioned above, in order to extend the applications of this kind of polymers, its blends and composites, the tensile, fracture, impact and damage behavior should be analyzed. Elucidation of the different toughening mechanisms present in these materials should also be investigated. Most published works on biodegradable materials have not been specifically focused on the mechanical performance and hence, the fracture behavior of these materials is generally disregarded (Tuba, Oláh, & Nagy, 2011).

Furthermore, the analysis of fracture surfaces represents an important issue to identify the different toughening mechanisms and the effect of different parameters on the composites fracture behavior (Cotterell, Chia, & Hbaieb, 2007). For experimental studies, the fractal and multifractal theories have been successfully applied to describe morphology of fracture surfaces by variation of the characteristic parameters of the multifractal spectra (Liu et al., 2009; Pérez, Bernal, & Piacquadio, 2012; Tarafder, Das, Chattoraj, Nasipuri, & Tarafder, 2010; Venkatesh, Chen, & Bhole, 2008; Zhang, Bai, Li, Chen, & Shen, 2011).

The aim of this investigation was to determine the effect of different types of nanoclay on the quasi-static fracture behavior of a commercial starch/PCL blend (MaterBi-Z). Some theoretical and experimental analyses were applied to study the fracture behavior observed for the different composites investigated.

2. Experimental

2.1. Materials

A commercial starch/PCL blend (called MaterBi-Z) kindly supplied by Novamont, Italy, was used as the matrix of the composites. It consists of 18 wt% starch, 75 wt% polycaprolactone (the main component) and 7 wt% additives.

Three different clays were used: one unmodified and two modified. The organoclays are prepared by modification of natural montmorillonite clays with different quaternary ammonium salts (Table 1), named Cloisite Na^+ (MMT), Cloisite 30B (C30B) and Cloisite 10A (C10A) purchased from Southern Clay Products Inc., USA. The reinforcements were employed as received. Their characteristics were first reported elsewhere (Pérez & Alvarez, 2008) Pristine montmorillonite (MMT) is hydrophilic while the modified clays (C30B and C10A) are more hydrophobic, being the second one (C10A) more hydrophobic than the first one (C30B).

2.2. Composites preparation

Composites with different clay contents (1, 2.5, 5 and 7.5 wt%) were prepared in an intensive Brabender type mixer with two counter-rotating roller rotors at 150 rpm and 100 °C for 10 min. After mixing, composite films with a nominal thickness of 0.4 mm were compression molded in a hydraulic press for 10 min at 100 °C under a pressure of 4.9 MPa.

2.3. Materials characterization

2.3.1. Fracture tests

Quasi-static fracture tests were carried out on deeply double edge-notched specimens (DENT), mode I (Fig. 1). The specimens were tested in a universal testing machine Interactive 10 K at 1 mm/min. Sample dimensions were: length (L) = 50 mm, width (W) = 20 mm and thickness (B) ≈ 0.4 mm. Distance between grips was 30 mm. Two properly aligned sharp notches of 5 mm were introduced by sliding a fresh razor blade into machined slots with the help of a specially designed device. The J-integral approach represents an extension of Linear Elastic Fracture Mechanics applied for not too ductile materials. In the last decades, the J-integral single-specimen formulation has been extensively applied in order to analyze ductile fracture of polymers (Bernal, Rink, & Frontini, 1999; Plati & Williams, 1975). In addition, the standard ASTM E 1820 allows to obtain a single point toughness value J_c to characterize quasi-brittle failure behavior (load–displacement curves with a sharp load drop at the point of fracture). J_c was calculated for the investigated composites based on the whole area under the load–displacement curve (U_{tot}) as follows:

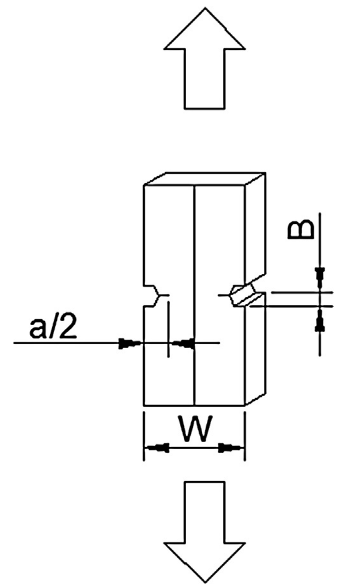

Fig. 1. Schematic showing a deeply double edge-notched specimen (DENT) considered for fracture tests.

$$J_c = \frac{\eta U_{tot}}{B(W-a)} \quad (1)$$

where U_{tot} is the overall fracture energy, B is the thickness, W is the width, a is the notch length and η is a geometrical factor defined by Grellmann and Reincke (2004):

$$\eta = -0.06 + 5.99\left(\frac{a}{W}\right) - 7.42\left(\frac{a}{W}\right)^2 + 3.29\left(\frac{a}{W}\right)^3 \quad (2)$$

All fracture tests were performed at room temperature. A minimum of five replicates were tested for each system and the average values with their deviations were reported.

2.4. Fracture surface analysis

Fracture surfaces of specimens broken in fracture tests were analyzed by scanning electron microscopy (SEM) after they had been coated with a thin layer of gold.

2.5. Multifractal analysis

Multifractal spectra were obtained by the box-counting method with the aim to analyze the fracture surfaces topography. First, SEM images were reduced to eliminate marks and then a global image for each material was obtained. The images were divided in many