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Effect of the orientation and rheological behaviour of biodegradable polymer nanocomposites

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ABSTRACT

The recent increasing interest towards biodegradable polymers has favoured the investigation on these systems, showing also their limits. On the other hand, the success achieved by nanocomposites has fostered the search for new systems where the polymer matrix is biodegradable. The final properties can depend on a number of factors, including the biodegradable polymer used as well as the nanosized filler, their mutual compatibility, the filler dispersion and the processing conditions. In this work, nanocomposites based on a starch-derived matrix and three different lamellar silicates were prepared, and the effects of the elongational flow on the dispersion, the improvement of intercalation/exfoliation and the possible aligning of the nanosilicate particles along the flow direction was investigated. Rheological, morphological and tensile tests showed that the properties were significantly different upon varying the compatibility between the polymer matrix and the nanofiller, as well as the draw ratio and therefore the orientation degree.

1. Introduction

Biodegradable polymers have been attracting an increasing interest over the last years, because of the rising concern over the environmental issues and the reduction of non-renewable, fossil-based resources. These have led both the academia and the industry to focus on the development of new, environmentally–friendly materials, that is obtained from alternative and renewable resources, with a reduced energy consumption and possibly no negative impacts on the environment [1]. On the other hand, it is reported that the majority of biodegradable polymers are more expensive that the traditional thermoplastic counterparts so far; furthermore, they show properties which are not sufficiently suitable to many practical applications [2], more specifically the unsatisfactory mechanical [3] and barrier [4] properties. It is therefore necessary to improve their properties in order to make them competitive with the thermoplastic polymers obtained via synthesis [5,6]. The outstanding success of nanocomposites has therefore fostered the search for new systems where the polymer matrix is biodegradable. Under this point of view, the degree of dispersion of the nanosized filler in the biodegradable matrix is of primary importance, since the achievement of a nanocomposite with significantly improved properties, in comparison to the neat polymer matrix, strongly depends on the achievement of intercalated and/or exfoliated structures. Literature reports several papers on the preparation and characterization of nanocomposites based on bio-polyesters, in particular poly(lactic acid) (PLA) [7–11] and polycaprolactone [12–13], and different types of lamellar silicates. Sinha Ray et al. [14] prepared PLA-organomodified montmorillonite nanocomposites by extrusion, finding that, upon using little amounts of compatibilizers, fully intercalated structures were obtained, allowing significant improvements

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of the properties both in the melt and solid state. Ogata et al. [15], prepared PLA-based nanocomposites via solvent intercalation, but the obtained filler dispersion was not optimal, resulting in the presence of micrometric-scale tactoids and only a small improvement of the main mechanical properties. Over the last years, much attention has been focused on starch-based biopolymers [6,16–20]. Starch is indeed an agro-sourced polymer which has attracted great interest because of some significant advantages such as low cost, wide availability and total compostability, without toxic residues. On the other hand, its mechanical and humidity absorption properties must be improved in order making this material competitive with traditional plastics [19,20]. Under this point of view, one of the most promising techniques is the development of starch-based nanocomposites [21]. The addition of nanosized fillers has shown to improve the main properties, such as mechanical properties [22], thermal stability [23] and resistance to humidity [24]. In general, this improvement can be attributed to the homogeneous filler dispersion inside the matrix and the good interfacial adhesion. This requires a good matrix/filler adhesion, which depends on the chemical nature of the used filler, but also the kind of starch and its possible chemical modifications, the presence of other polymers or plasticizers/additives [25], as well as processing conditions and thermal treatments that the polymer might have undergone [6,26–27]. To our best knowledge, although the Literature reports detailed studies and reviews on nanocomposites based on biodegradable polymers [28–30], there is no systematic study regarding the preparation of nanocomposites based on commercial starch-derived polymers and different nanosized clays. In this work, therefore, we have prepared nanocomposites based on a starch-derived matrix (MaterBi®) and three different lamellar silicates via melt mixing. In particular, the effects of the elongational flow on the dispersion, the improvement of the intercalation/exfoliation degree and the possible aligning of the nanosilicate particles along the flow direction was investigated. Rheological, morphological and tensile characterization showed also that the properties were remarkably different upon varying the compatibility between the polymer matrix and the nanofiller.

2. Experimental

2.1. Materials

The biodegradable polymer used in this work belongs to MaterBi® family produced by Novamont (Italy). In particular, a CF04P grade was used (measured melt flow rate = 7 g/10 min at 160 °C and 5 kg load). The composition of this biodegradable thermoplastic polymer is proprietary, however according to Cerruti et al. [31], it should be made with corn starch and a biodegradable copolyester. Three different nanosized fillers were used for the preparation of the nanocomposites. They were, respectively: a natural montmorillonite supplied by Southern Clay Products (USA) under the commercial name of "Nanofil 116"; a modified, organophilic montmorillonite (modified with 1.25 meq/g quaternary ammonium ions with two methyl and two alkyl groups) produced by Southern Clay Products (USA) and commercialized as "Cloisite 15A"; a modified, organophilic montmorillonite (modified with 0.9 meq/g quaternary ammonium ions with one methyl, one alkyl and two 2-hydroxyethyl groups) commercialized by Southern Clay Products (USA) as "Cloisite 30B".

2.2. Preparation and processing

The nanocomposites were prepared with a filler content of 5 wt% and directly compared to the neat MaterBi. All of the systems were processed in a Brabender (Germany) twin-screw counter-rotating extruder (D = 45 mm, L/D = 7) with a 90–120–150 °C thermal profile and a speed equal to 60 rpm.

2.3. Characterization

The obtained nanocomposites were subjected to several investigation methods. Rheological characterization in shear flow was performed by means of a TA Instruments (USA) ARES G2 rotational plate-plate rheometer and a CEAST (Italy) Rheologic 1000 capillary rheometer, operating at 150 °C. In the case of rotational rheometer tests, these were conducted on compression molded samples obtained with the aid of a Carver (USA) laboratory press set at 150 °C, compression time 3 min. The tests were conducted with a strain = 5%, determined after performing a standard procedure based on strain sweep tests in order to determine the limits of linear viscoelastic regime. Rheological characterization was also performed in non-isothermal elongational flow by using an IdeaInstr (Italy) SpinRheo apparatus. This equipment allows measuring the rheological properties in non-isothermal elongational flow on molten filaments coming out from any equipment producing them (such as extruders) and is equipped with a series of pulleys which grab the hot filament (cooling down gradually due to the contact with the air) and delivers it to a final pulley rotating at steady speed or steady acceleration. A dedicated load cell measures the force on the filament during the experiment and, at the breaking of the filament, the current force and speed are registered. The force in the molten filament at breaking corresponds to the "melt strength" (MS), while the ratio between the drawing speed at breaking (measured on the basis of the rotating speed of the pulley at the moment when the filament breaks) and the extrusion velocity (in runs in which the drawing velocity increases with a constant acceleration) corresponds to the breaking stretching ratio (BSR), which is basically the maximum elongation that the molten polymer can bear under those specific experimental conditions [32]. Furthermore, the apparatus allows preparing and collecting fibres at different draw ratios for the following characterizations. Mechanical characterization was performed on the extruded fibres by using an Instron (USA) 3365 universal machine. The test was performed at two different speeds: 1 mm/min for the first 2 mm of elongation, and then 100 mm/min up to fiber breakage. Morphological characterization included scanning electron microscopy (SEM) on nitrogen-fractured