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Reinforcing capability of cellulose nanocrystals obtained from pine cones in a biodegradable poly(3-hydroxybutyrate)/poly(ε-caprolactone) (PHB/PCL) thermoplastic blend

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ABSTRACT

In this work, different loads (3, 5 and 7 wt%) of pine cone cellulose nanocrystals (CNCs) were added to films of poly(3-hydroxybutyrate)/poly(ε-caprolactone) (PHB/PCL) blends with a composition of 75 wt% PHB and 25 wt % PCL (PHB_{75}/PCL_{25}). The films were obtained after solvent casting followed by melt compounding in an extruder and finally subjected to a thermocompression process. The influence of different CNCs loadings on the mechanical, thermal, optical, wettability and disintegration in controlled compost properties of the PHB_{75}/PCL_{25} blend was discussed. Field emission scanning electron microscopy (FESEM) revealed the best dispersion of CNCs on the polymeric matrix was at a load of 3 wt%. Over this loading, CNCs aggregates were formed enhancing the films fragilization due to stress concentration phenomena. However, the addition of CNCs improved the optical properties of the PHB_{75}/PCL_{25} films by increasing their transparency and accelerated the film disintegration in controlled soil conditions. In general, the blend with 3 wt% CNCs offers the best balanced properties in terms of mechanical, thermal, optical and wettability.

1. Introduction

The recent increase in the social concern about environmental issues together with the increasing price of fossil fuels due to petroleum depletion [1], has given a rise in the development of new environmentally friendly materials as it is the case of biodegradable polymers. Biodegradable polymers challenges are related to their relatively poor mechanical and thermal properties compared to petroleum-based commodities and engineering plastics, restricting their wide use in industrial application [2]. The reinforcement of biodegradable polymers with nanoparticles has recently been proposed as a strategy to overcome some of the above-mentioned drawbacks. Specifically, bio-based nanoscale particles have been used to reinforce thermoplastic biodegradable polymers, such as poly(lactic acid) (PLA) [3–5], poly (hydroxybutyrate) (PHB) [6], poly(ε-caprolactone) (PCL) [7,8] and poly(butylene adipate-*co*-terephthalate) (PBAT) [9]. The improved thermo-mechanical performance of these nanoscale-reinforced polymer composites, together with their potential biodegradation, could lead these new materials to compete with many traditional petroleum-based polymers, such as polypropylene (PP), polyethylene or polyethylene terephthalate (PET) [10,11].

Cellulose nanocrystals (CNCs) from residual biomass (food, agriculture and forest) may be defined as one of the most promising reinforcing agents in terms of biodegradability, renewability, abundance in nature, variety and price [12,13]. These highly crystalline cellulose particles are obtained from lignocellulosic fibres generally through two main steps: first, an alkaline and bleaching treatment to isolate the cellulose fibres from the raw material and second, a hydrolytic treatment with acid which allows the selective removal of the amorphous cellulosic phase remaining the crystalline phase almost unaltered [14–16]. The physico-chemical properties of CNCs can vary widely, depending on the source of the cellulosic raw material and the conditions selected to perform the hydrolysis [17,18]. In previous studies, pine cones fibres were selected as raw materials to produce CNCs and

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the influence of the hydrolytic time on their properties and the processing yield was evaluated [D. García-García, R. Balart, J. Lopez-Martinez, M. Ek, R. Moriana, Optimizing the yield and physico-chemical properties of pine cone cellulose nanocrystals by different hydrolysis time, Cellulose, 2018]. Furthermore, the potential of using the pine cone CNCs as reinforcement in composites was discussed in terms of aspect ratio, crystallinity and thermal stability. It is known that the influence of the matrix-reinforcement interface and compatibility is of foremost importance for the resulting performance of the composite materials. Therefore, in this study, we propose to evaluate the reinforcing capability of the pine cone CNCs in a biodegradable thermoplastic blend composed of 75% poly(3-hydroxybutyrate) and 25% poly(ε-caprolactone) (PHB_{75}/PCL_{25}). The overall effect of CNCs as reinforcement in thermoplastic composites highly depends on the percentage of loading nanoparticles and the particle dispersion in the polymer matrix [19]. The main challenge to overcome to design CNCs based composites is related to the poor dispersion of these nanoparticles in hydrophobic polymers due to their high hydrophilic nature [20,21]. Chemical modification of the CNCs or the use of surfactants during the compounding step are the most used approaches to enhance the dispersion of CNCs on the polymeric matrix, avoiding the formation of aggregates [22,23]. However, Wang et al. [24] shown how the chemical modification of CNCs could disrupt their crystalline structure with the subsequent decrease in rigidity. Another important challenge in using CNCs in thermoplastic composites is their low thermal stability which could potentially be compromised during polymer processing, thus leading to partial CNCs degradation [25].

PHB_{75}/PCL_{25} is a promising biodegradable blend of different thermoplastic polyesters that offers better thermal, impact resistance and elongation properties than the neat PHB, due to the high ductility (high elongation at break values together with low modulus which leads to a rubber-like behavior) that PCL can provide to this blend. However, PHB_{75}/PCL_{25} shows low miscibility resulting in a phase separation when melt-blended occurs [26], where finely dispersed PCL droplets positively contribute to improve toughness in a similar way as polybutadiene rubber has on toughened styrene-derived polymers such as poly(styrene-co-acrylonitrile) + polybutadiene rubber (ABS) [27]. Despite this, the lack of compatibility between the polymers affects the mechanical properties of the blend, because they are directly related to the ability of its components to transfer stresses [28]. In addition, it is expected that the higher difficulty of degradation of the PCL decreases the biodegradation rate of the blend with respect to the neat PHB [29]. Several studies have corroborated that cellulose nanoparticles could potentially act as compatibilizers between immiscible polymers through their preferential location among the polymeric interfaces, reducing interface tension which prevents from coalescence of the dispersed phase [30], all this, having a positive effect on the overall properties of composite blends. In this sense, Arrieta et al. [31,32] observed an improvement on interface adhesion between PLA and PHB extruded blends (75/25 wt%) by the addition of 5 wt% of CNCs. The incorporation of CNCs on this PLA/PHB blends enhanced the biodegradation rate, with respect to the unreinforced PLA/PHB blend. The present work aims to study the reinforcing capability of different pine cone CNC loads (3, 5 and 7 wt%), on the performance and disintegration rate of the biodegradable thermoplastic PHB_{75}/PCL_{25} blend. The influence of different CNCs loadings on the mechanical, thermal, morphological, optical and wettability of the PHB_{75}/PCL_{25} blend were studied. The effect of the CNCs on the disintegration rate of the PHB_{75}/PCL_{25} blend has also been compared with the disintegration of the neat PHB. The dispersion of the CNCs in the matrix have been performed by a combination of solvent casting procedure and subsequent manufacturing by extrusion and thermo-compression.

2. Experimental

2.1. Materials

Poly(3-hydroxybutyrate) (PHB) pellets (commercial grade P226) with an average molecular weight of 426 KDa, a density of 1.25 g cm^{-3} and a melt flow index of 10 g·10 min^{-1} (measured at 180 °C with a load of 5 kg) were supplied by Biomer (Krailling, Germany). Poly(ε-caprolactone) (PCL) in pellet form (commercial grade CAPA 6500) with an average molecular weight of 50 KDa was provided by Perstorp Holding AB (Malmö, Sweden). Chloroform ($CHCl_3$, ≥99%) was purchased from Sigma Aldrich (Sigma-Aldrich, Germany). Pine cones (*Pinus Pinea*) were collected from a local pine forest in Alicante (Spain).

2.2. Preparation and characteristic of pine cone cellulose nanocrystals

Pine cones were conditioned at 40 °C for 1 week and then were grinded in a Wiley mill from Thomas Scientific (New Jersey, USA) and subsequently sieved with a 20 μm mesh screen. Cellulose nanocrystals (CNCs) were isolated from pine cone following the procedure described by Moriana et al. [33]. In summary, grinded pine cone particles were subjected to an alkaline and bleaching treatment to remove the amorphous components, such as lignin and hemicellulose. Then, the bleached pine cones were hydrolysed with sulphuric acid (65 wt%) at 45 °C for 45 min. The obtained suspension was washed with Milli-Q water by using repetitive centrifugations with the following conditions: 10 min at 13.000 rpms and at a temperature of 4 °C. After this stage, the solution was dialyzed during 7 days with Milli-Q water with the aim of removing the free acid until the wash water reached a constant pH. The resulting CNCs shown a crystallinity index of 88.5%, an onset degradation temperature (T_0) of 150.3 °C, an average aspect ratio (L/D) of 113.4, an average diameter of 2.9 nm and a percentage cellulose of 97.8% [D. García-García, R. Balart, J. Lopez-Martinez, M. Ek, R. Moriana, Optimizing the yield and physico-chemical properties of pine cone cellulose nanocrystals by different hydrolysis time, Cellulose, 2018]. Moreover, an ion exchange resin Dowex Marathon MR-3 (hydrogen and hydroxide form) was added to the cellulose suspension for additional 48 h and the removed by filtration with the main aim of ensuring that all ionic moieties were removed except the H+ counter ions associated with the sulphate groups attached to the CNCs surfaces [11]. The resulting suspension was then sonicated using a Sonics Vibra-Cell VCX 750 sonicator from Sonics and Materials Inc. (Connecticut, USA) to promote CNCs dispersion and remove the remaining unhydrolyzed fibers by centrifugation. The final suspension containing CNCs was neutralized by adding NaOH (0.25 mol L^{-1}) until pH of 9 was reached. Finally, a freeze-drying process was carried out to obtain dry CNCs.

2.3. Processing of PHB_{75}/PCL_{25} films with pine cone CNCs

Films of PHB_{75}/PCL_{25} with different CNCs loading (3, 5 and 7 wt%) were prepared by combined melting processing technologies. Table 1 summarized the composition of all the developed materials. The films were obtained by solvent casting, granulated/pelletizated and subsequently subjected to extrusion and thermocompression process. The

Table 1
Composition and codes for poly(3-hydroxybutyrate)/poly(ε-caprolactone) (PHB/PCL) blend films with pine cone cellulose nanocrystals (CNCs).

Coding	PHB (wt%)	PCL (wt%)	CNC (wt%)
PHB	100	0	0
PHB_{75}/PCL_{25}	75	25	0
3% CNC	72.75	24.25	3
5% CNC	71.25	23.75	5
7% CNC	69.75	23.25	7