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Sustainable nanocomposites based on halloysite nanotubes and pectin/polyethylene glycol blend

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A B S T R A C T

This study was focused on the preparation and characterization of biofilms based on pectin/polyethylene glycol 20000 (PEG) blend and halloysite nanotubes (HNTs). The obtained blends loaded with a natural nanoclay are proposed as sustainable alternative to the polymers produced from non-renewable resources such as fossil fuels. Properties of technological interest have been monitored and they were correlated to the structural features of the nanocomposites. It turned out that the wettability of the films can be tuned by changing the composition and the distribution of HNTs into the material as well as the surface roughness. The tensile properties of the blend are enhanced by the presence of the nanoclays. The PEG crystallinity is reduced by the nanoparticles and preserved if a certain amount of pectin is added.

This work represents a starting point to develop new green composite material, which can be used for purposes such as in packaging, by employing the strategy of adding plasticizers and fillers within a full biocompatible approach.

1. Introduction

The largely used petroleum based plastics in several fields, such as in packaging, generates a relevant environmental impact in urban areas because of their non degradability. The disposal of plastic wastes by incineration produces an increase of carbon dioxide and, in some cases, toxic products which contribute to the global warming and the city pollution.

To the light of this situation, nowadays there is a growing interest on the development of biodegradable materials, sustainable alternative to the plastics produced from fossil fuel. Researchers have focused their attention on biopolymers and clay nanoparticles as renewable resources to process innovative green materials, such as polymer blends and bionanocomposites.

Pectin is a biodegradable polymer which is used to develop smart green materials useful for specific purposes. Blend based on pectin and chitosan may be used as carrier of pharmaceutical products [1]. Biofilms based on pectin and starch can be potentially employed in the food conservation because of their good mechanical properties [2] and oxygen barrier capability [3]. Gelatin-pectin films showed improved tensile characteristics and water resistance than the pristine polymers [4].

Polyethylene glycol (PEG) is a biocompatible, nontoxic polymer with good water solubility. It is an efficient plasticizer for biopolymers and nanocomposites. The mechanical properties of chitosan were improved by the addition of an appropriate amount of PEG [5,6]. The PEG content (C_{PEG}) is crucial to determine the effectiveness of the plasticization; a decrease of the glass transition temperature (T_g) of Poly(lactic acid) (PLA) was observed in polymer blends with C_{PEG} = 20 wt% [7]. PLA/PEG blends with C_{PEG} up to 30 wt% showed a decrease of the elongation at the break point [8] and an increase of T_g [9] because of the phase separation of PEG in the composite system.

Filling a polymer blend with clay nanoparticles represents an alternative route to develop new nanomaterials with unique properties from the physico-chemical view point [10–12].

Among the clay nanoparticles, halloysite nanotubes (HNTs) are newly promising filler. The size of HNTs is rather polydisperse ranging between 0.1 and 2 μm while the outer and inner diameters are ca. 30–50 nm and 1–30 nm, respectively [13]. The biocompatibility of HNTs makes these nanoparticles appropriate to develop composite materials with appealing perspective in several applications, such as biotechnology [14–17], water decontamination [18,19], anticorrosive coatings [20,21] and packaging [22,23]. Composite materials with humidity control ability were prepared by using HNTs as filler [24].

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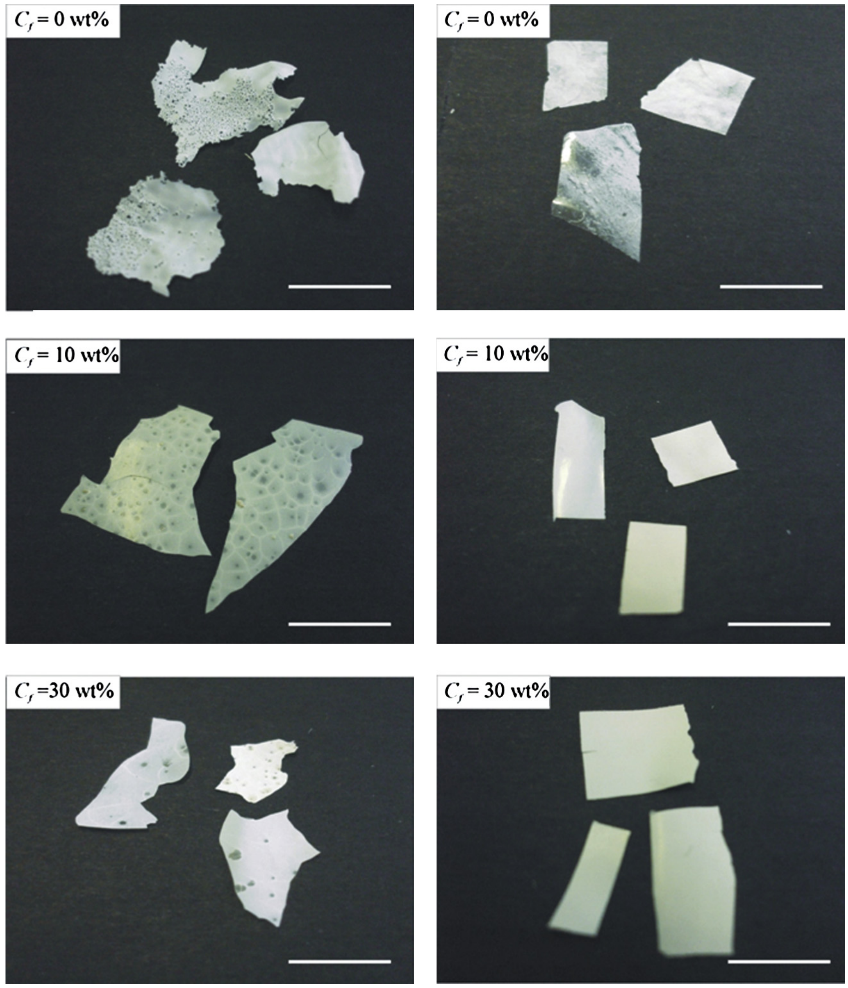

Fig. 1. Photos of bionanocomposites at variable C_f for $R_{pp} = 1$ (on the left) and $R_{pp} = 4$ (on the right). The bar is 10 mm.

Literature reports that the addition of HNTs prevents the cracking in the drying latex films [25]. Filling pectins with HNTs caused an improvement of the thermal and the mechanical properties in a large clay loading regime. [23] The hydroxypropylcellulose/HNTs showed an enhancement of the polymer degradation temperature only for small nanoclay concentration, while the peculiar sandwich-like structure observed at the high filler loading caused a thermal destabilization [22]. It was observed [26] that PEG/HNTs is thermally more stable than the pristine polymer in the low filler regime where the nanomaterial presents a compact morphology, while the opposite thermal behavior occurred over the high HNTs loading region because of the more open structure.

Furthermore, it is known that the physical properties of blend polymers [27] and nanocomposites [26,28] depend on their supramolecular morphology that is controlled by the crystallization process in melt processing for crystalline and semicrystalline polymers. In many cases the nucleation and the overall crystallization may be enhanced by the presence of nanofillers which act as a nucleating agent [28]. Nevertheless, it was found that for plasticized PEG/PLA/cloisite nanocomposites [29] and for the PEG/halloysite nanotubes (HNTs) nanocomposites [26] the nanoclay did not play such a role.

In this work, we prepared blend films based on pectin and PEG 20000 as precursors of new plasticized bionanocomposites containing also HNTs. All biofilms were extensively investigated from the physico-chemical view point by determining the thermal and mechanical properties, the wettability and the water uptake behavior. The morphological study was crucial to explain the nanomaterial features.

The acquired knowledge represents a basic point for designing new hybrid sustainable materials.

2. Experimental

2.1. Materials

Pectin (degree of methyl esterification, 24%, Mw = 30–100 kg mol^{-1}), halloysite nanotubes ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$, HNTs) are from Aldrich. Polyethylene glycol (PEG) 20,000 g mol^{-1} is from Fluka. All the materials were used without further purification. Water from reverse osmosis (Elga model Option 3) with a specific resistivity greater than 10^5 Ω m was used.

Table 1
The water contact angle at $\tau = 0$ for pectin, PEG 20000 and the pectin/PEG 20000 blend ($R_{pp} = 4$).

	θ_i (°)
Pectin[a]	75 ± 1
PEG 20000	28 ± 1
Pectin/PEG 20000 ($R_{pp} = 4$)	80 ± 2

[a] From Ref. [22].