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Physicochemical properties of organoclay filled polylactic acid/natural rubber blend bionanocomposites

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ABSTRACT

A novel toughened polylactic acid (PLA) bionanocomposite with tuneable properties was successfully prepared by melt mixing PLA with natural rubber and several montmorillonites (MMTs). The organoclays were preferentially located at the interface acting as compatibilisers between both polymer phases. This location resulted in a marked improvement of the physical and mechanical properties of the system. Moreover, these properties can be controlled as a function of the nanofiller nature and the mixing procedure used.

1. Introduction

Polylactic acid (PLA) is a sustainable alternative to petrochemical-derived polymers, since it is produced from renewable resources, possesses excellent physical properties and is easily processed [1]. However, several drawbacks such as its brittle behaviour, slow crystallisation rate or low gas barrier properties have limited its applications until now. In our previous study, we demonstrated that blending PLA with Natural Rubber (NR) presents a practical strategy to toughen PLA [2]. The addition of natural rubber allows straightforward production of ductile PLA. The optimal NR content in the blend was found to be 10 wt.%; at this concentration the rubber improves the brittleness and favours the crystallisation ability of PLA. However, a lack of compatibility between the two polymers was observed. It is well known that the final properties of immiscible polymer blends are strongly influenced by both the size and interface of the dispersed phase and, hence, compatibilisers are often required in order to improve the morphology. While organic molecules and block copolymers are most commonly used, recent studies have introduced inorganic solid particles as a new type of compatibilisers [3,4]. In particular, layered silicates have been reported to improve the morphology of immiscible blends [5–7]. Moreover, the addition of nanoclays to the PLA/NR blend could also present a practical way to improve the gas barrier properties of the material.

Thus, our approach is to develop a novel and industrially scalable organoclay filled PLA/NR blend bionanocomposite prepared by melt blending. This study is aimed at understanding the influence of several nanofillers, presenting different surface properties and hydrophilicity on the properties of an immiscible PLA/NR blend [8]. The control of the nanofiller surface property and the mixing procedure could force the location of the clay in the blend. Thus, this location and the interactions of the nanoparticles with the blended polymers will determine the ultimate physicochemical properties of the nanocomposite. We carried out a thorough study based on both experimental and theoretical approaches to understand the best strategy to attain the desired properties. Here, we specifically focused on optimising the mechanical and barrier properties since they will benefit PLA bionanocomposite applications.

2. Experimental part

2.1. Materials and sample preparation

PLA polymer 2002D was provided by NatureWorks® (D-content 4.25%, $\rho = 1.24$ g/cm^3). Natural Rubber (NR) was kindly supplied by Malaysian Rubber under the trade name CV60 (Mooney viscosity: ML(1 + 4) 100 °C = 60, $\rho = 0.91$ g/cm^3). Three montmorillonites, one

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Table 1
(a) Contact angle values for PLA and NR and (b) Surface energies and interfacial tension between the components. Equilibrium location of the clays in the PLA/NR blends.

	Water	Diiodomethane
(a)		
θ_{PLA} °	74 ± 1	45 ± 4
θ_{NR} °	92 ± 2	66 ± 2

	PLA	NR	CNa$^+$	C15A	C30B
(b)					
γ mJ m^{-2}	30.81	16.75	44.00	25.40	34.50
$\gamma_{PLA/NR}$	2.13				
$\gamma_{PLA/MMT}$			1.17	0.26	0.10
$\gamma_{NR/MMT}$			6.45	0.89	3.17
ω			−2.49	−0.30	−1.44
Location			PLA phase	Interface	PLA phase

un-modified, CNa$^+$, and two organo-modified, denoted as Cloisite C15A and C30B, provided by Southern Clay Products were used as fillers. C15A is modified with dimethyl dehydrogenated tallow alkyl ammonium cation while C30B is modified with bis(2-hydroxyethyl)-methyl tallow alkyl ammonium cation. PLA and clays were dried overnight at 80 °C in a desiccating dryer prior to use. Composites were prepared by melt blending in a Haake Minilab twin screw extruder. NR concentration was fixed at 10 wt.%, and the clay loading was varied from 1 to 5 wt.%. An optimal processing window was selected: temperature at 180 °C, rotor speed of 100 rpm, and a mixing time of 15 min, considering the dispersion of the clays and PLA degradation. Subsequently, the materials were compression-moulded into 0.4 mm thick sheets in a Collin P200P press resulting in amorphous samples.

2.2. Characterisation methods

The morphology of the samples was observed using a Philips XL30 environmental scanning electron microscopy (ESEM) at 15 kV. All the samples were cryo-fractured in liquid nitrogen and the fracture surface was sputter coated with gold/palladium (Au/Pd 80/20). The nanoclay dispersion was also studied by transmission electron microscopy (Philips Tecnai 20 microscope at an acceleration voltage of 200 kV). Ultra thin sections of the samples were prepared by cryo-ultramicrotomy at −140 °C (Leica EM UC6). The rubber droplet size was determined by image analysis using ImageJ [9]. Typically, 200 droplets were analysed per sample and the average Feret's diameter was calculated.

Contact angle measurements were carried out in a Krüss G10 optical contact angle meter. Distilled water and diiodomethane were used as testing liquid. Contact angles of 10 droplets at equilibrium were considered in order to obtain an average value.

Rheological measurements were performed using an Advanced Rheometer AR2000 from TA Instruments with parallel plate geometry of 25 mm of diameter. Tests were carried out in dynamic mode of shearing at 180 °C from 0.01 rad/s to 100 rad/s frequency range in nitrogen atmosphere.

Dynamic mechanical analysis was performed on a TA instruments (model Q800) in tensile mode at 3 Hz as a function of temperature from −90 °C to 150 °C at a heating rate of 2 °C/min.

Tensile tests of the samples were measured according to ASTM D 3379-75 specifications on an Instron dynamometer (model 3366) at 23 °C, and at a cross-head speed of 10 mm/min. At least five specimens of each sample were tested.

Gas barrier properties were determined using a barometric permeation method at a constant temperature of 30 °C. The upstream and downstream pressures were kept at 3 bar and below 10^{-2} mbar, respectively. For the permeation experiments, helium,

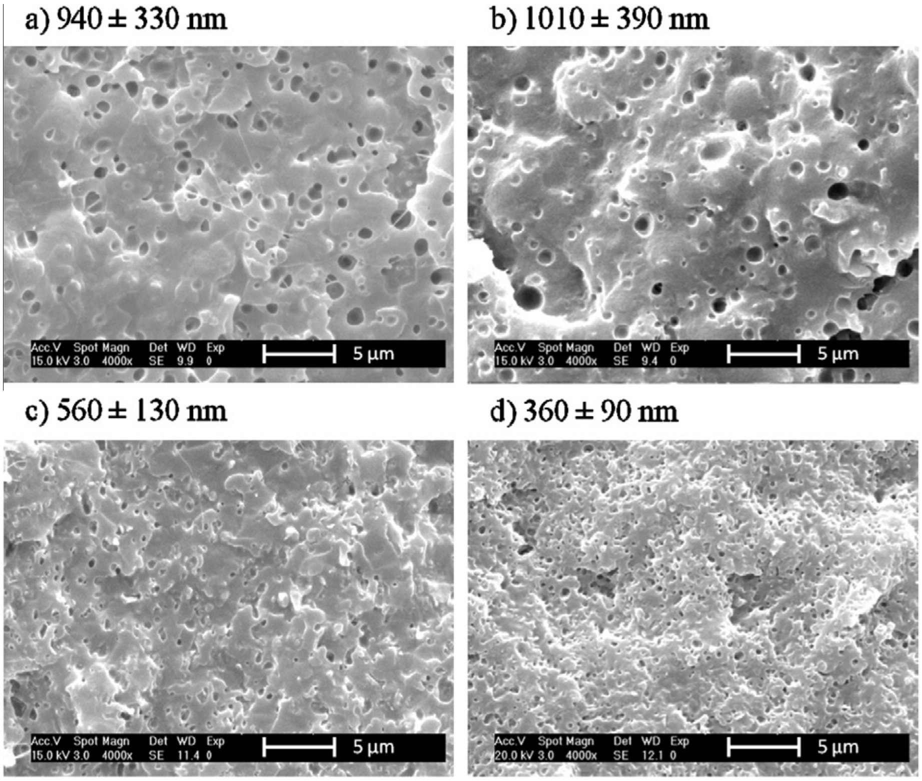
a) 940 ± 330 nm
b) 1010 ± 390 nm
c) 560 ± 130 nm
d) 360 ± 90 nm

Fig. 1. Scanning electron microscopy images of (a) the PLA/NR blend and its composites at 3 wt.% of filler, (b) PLA/NR/CNa$^+$, (c) PLA/NR/C15A and (d) PLA/NR/C30B.