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## Properties of polylactide reinforced with montmorillonite/multiwalled carbon nanotube hybrid

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### Abstract

Both montmorillonite (MMT) and multi-walled carbon nanotubes (MWCNT) are prominent nanofillers incorporated into polymers due to their unique properties. The realization of uniform dispersion of these reinforcing nanomaterials in polymeric matrices without agglomerates remains a key issue in polymer science. In this work, a lyophilized MMT/MWCNT hybrid was incorporated into polylactide (PLA) at varying low mass fractions (0.5, 1.0 and 2.0 wt%). The nanocomposites were prepared by a combined solution/melt blending method. The structure, thermal and mechanical behavior of the obtained nanocomposites were investigated. The morphological and structural studies revealed a strong hybrid-polymer interaction, while the thermal characterization indicated that the hybrid particles synergistically constrain the PLA segmental motions and promote the crystallization of the PLA matrix. The inclusion of the MMT/MWCNT hybrid into the PLA matrix showed an increase in the elastic modulus and tensile strength by more than 45% and 24%, respectively.

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*Keywords: Polylactide; montmorillonites; multiwalled-carbon nanotube; nanocomposites; mechanical properties*

### 1. Introduction

Polymer-based nanocomposites are attracting increasing attention in high-technology applications such as packaging, energy, sports, military and automotive due to their versatile properties [1-3]. The incorporation of nanomaterials into polymers to develop composites is extremely attractive due to their enormous interfacial areas [4]. All the properties of nanofillers lead to high thermal and mechanical properties, improve flame retardancy, electrical conductivity and reduce permeability of the composite, which is sought in advanced applications [5]. Montmorillonites (MMT) with carbon nanotubes (MWCNT) are the most studied nanoparticles that have been reported to improve the properties of polymers [6]. However, MWCNT easily form aggregates due to their large hydrophobicity, which makes their dispersion extremely difficult [7-9]. For MMT, the stacking of platelets combined with compatibility with most hydrophobic polymer matrices is a problem [10]. Therefore, researchers use the synergistic influences of MMT and MWCNT fillers in matrices [11] to correct the limitations of duo nanomaterial [12]. In previous studies, MMT and MWCNT were physically incorporated into polymers [13-15], but agglomeration of the particles still occurred, which was associated with increased filler content [13]. Some

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researchers prepared MMT/MWCNT hybrid particles by sol-gel approach (SGM) [16] and catalytic chemical vapor deposition (CCVD) of MWCNT on MMT [17]. SGM uses strong acids at high temperatures, which leads to environmental and hazard problems [18]. The growth of MWCNT on MMT by CCVD resulted in increased thermal degradation rates of nanocomposites, which is attributed to metallic residues used in expanding clay platelets during CCVD, causing high thermal conductivity [19].

In this work, MMT/MWCNT was prepared by a green, efficient and simple freeze-drying method, and the obtained hybrid nanofillers were mixed in polylactide (PLA) by a combined solution-melt mixing. Subsequently, the morphology, structure, thermal and mechanical properties of the resulting samples were analyzed.

## 2. Experimentation

### 2.1. Materials and methods

Poly(lactide) (PLA) (Ingeo™ Biopolymer 3052D, Plastica Kritis S.A.) with a molecular weight of 63,090 g/mol and an intrinsic viscosity of 1,055 dL/g was used as the matrix. The solvent used was reagent grade dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) (Scharlab S.L. Spain). The MMT/MWCNT hybrid used was synthesized by lyophilization [20] using Cloisite® MMT-10A nanoclay and pristine multi-walled carbon nanotube (MWCNT).

A combined solution/melt mixing was used to prepare the nanocomposites. The first phase consisted of the preparation of a masterbatch film by solution mixing, where the MMT/MWCNT hybrid nanoparticles were ultrasonically dispersed in dichloromethane. PLA was then dissolved in the solution with continuous stirring until the chloroform evaporated. The resulting slurry was dried at 50 °C to obtain masterbatch films. Then, the masterbatch was melt-mixed together with the remaining PLA at 180 °C, 30 rpm for 5 min to fabricate the nanocomposites, whose compositions are listed in Table 1.

Table 1. Composition of PLA nanocomposites.

	PLA (%wt)	MMT/MWCNT hybrid (%wt)
PLA	100	0
PLA0.5hyb	99.5	0.5
PLA1.0hyb	99	1
PLA2.0hyb	98	2

### 2.2. Characterizations

The distribution of MMT/MWCNT particles in PLA was investigated by transmission electron microscopy (TEM) (Jeol JEM -1010 electron microscope 100kV). TEM samples were prepared by obtaining thin sections of the samples using a Leica UCT Ultracut ultramicrotome and collected on Au grids of 400 mesh. X-ray diffraction (XRD) study was performed from 5 - 50°. Differential scanning calorimetry (DSC) studies were investigated using Perkin Elmer Pyris 6 DSC under 20 mL/min nitrogen. The experiment was performed using 8 g of the sample mass. The sample was tested from 20 - 190 °C and held at 190 °C for 1 minute; the sample was brought from 190 - 20 °C and held at 20 °C for 1 minute. The procedure was repeated twice with the heating/cooling rate fixed at 10 °C/min. The mechanical tensile test was carried out on dogbone-shaped specimens at a rate of 2 mm/min. The mechanical specimen was cut out of the pressed film web using a Wallace cutting press.

## 3. Results and discussions

Fig. 1 shows TEM images of PLA1.0hyb at various magnifications. The images show that MWCNT and MMT particles are homogeneously dispersed in the matrix. The images show that hybridization of MMT with MWCNT promotes the dispersion of both nanoparticles and inhibits the aggregation of MWCNT. In Fig. 1a, the arrows indicate individual dispersed MWCNT. Fig. 1b shows a magnified view of single carbon nanotubes connection and joining with an exfoliated MMT platelet, suggesting that the structure of the two particles affects the dispersibility of the other. This could mean that synergistic interactions occur between MWCNT and MMT particles. Therefore, the images imply that the adopted freeze-drying and nanocomposite fabrication route have a good influence on MMT/MWCNT dispersion in PLA.

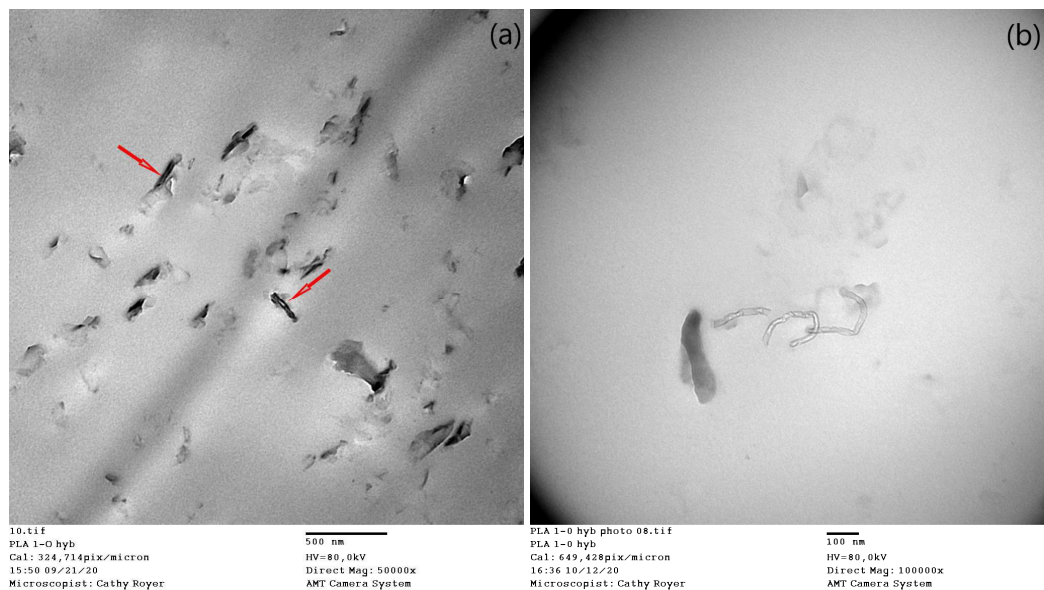


Fig. 1. TEM images of PLA1.0hyb at different magnifications (a) 500 nm; (b) 100 nm

Fig. 2 shows the wide angle X-ray diffraction (WAXD) of hyb nanoparticles, PLA and PLA/hyb nanocomposites. The three peaks ( $17.87^\circ$ ,  $20.25^\circ$  and  $23.44^\circ$ ) appearing in the diffractogram of PLA represent the orthorhombic crystalline  $\alpha$ -PLA form [21]. These are repeated in all the nanocomposites, indicating that the crystalline structure of PLA remained unchanged after incorporation of the prepared MMT/MWCNT hybrid [22]. Moreover, there is no obvious peak of graphitic carbon in hyb on any of the PLA/hyb nanocomposites, indicating a homogeneous distribution of MMT, thus preventing the MWCNT aggregation that occurs when normal MWCNT is used. This confirms the intercalation of MMT by the MWCNT and is in agreement with Bai et al [23].

The temperatures related to transition ( $T_g$ ), cold crystallization ( $T_c$ ) and melting ( $T_m$ ) with the percentage of crystallinity are briefly shown in Table 2. The  $T_g$  of PLA was found to be  $60^\circ\text{C}$ , where the equivalent  $T_c$  is  $119.6^\circ\text{C}$  and the melting temperature is  $\sim 150^\circ\text{C}$ . The properties are in agreement with previous work [24]. For the nanocomposites, the  $T_g$  remained approximately unchanged, while the  $T_m$  increased slightly compared to pure PLA. The minor changes in these thermal properties can be associated with PLA stereoregularity, which resulted in the matrix crystal structure exhibiting little change in melting temperature [25]. Chattopadhyay et al [26] reported a similar small change in  $T_g$ , which they attributed to a stronger filler-filler interaction rather than a filler-matrix interaction.

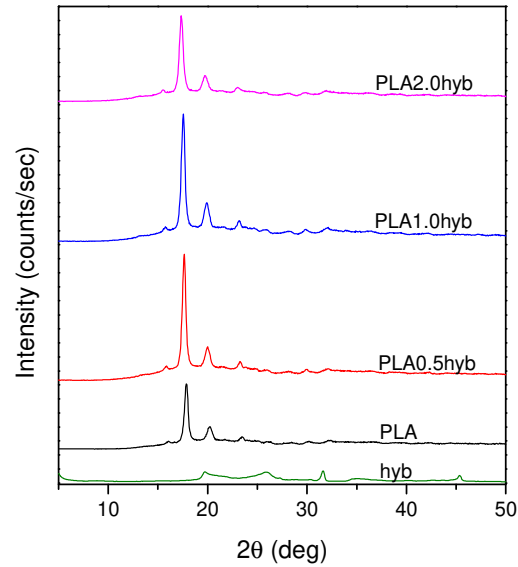


Fig. 2. WAXD of MWCNT/MMT hybrid and PLA nanocomposites.

PLA nanocomposites show a significant temperature increase upon crystallization ( $\sim 124 - 128$  °C) compared to PLA ( $\sim 119$  °C), confirming a good interaction of PLA with lyophilized nanoparticles. This suggests a restriction in the motion of PLA segments as a result of PLA/hyb interaction [27]. Moreover, the crystallinity increases with the hybrid concentration, which is attributed to uniform dispersion and better nucleation site generation by the MMT/MWCNT nanofillers [28]. MMT and MWCNT are nucleating agents [21][29], so their hybridization as MMT/MWCNT shows a synergistic role in improving  $X_c$ . Therefore, it can be concluded that freeze-dried MMT/MWCNT nanoparticles were well dispersed and increased the crystallinity in PLA, thus strengthening the matrix.

Table 2. Thermal properties of samples

	$T_g$ (°C)	$T_c$ (°C)	$T_m$ (°C)	$X_c$
PLA	60.00	119.57	150.00	44.78
PLA0.5hyb	60.99	128.19	151.93	33.19
PLA1.0hyb	59.12	124.73	150.79	56.67
PLA2.0hyb	55.72	126.22	151.12	62.61

Fig. 3 represents the stress/strain plots of samples, and the summary of the samples' mechanical properties are reported in Table 3. The stress-strain curves present an initial linear elastic deformation, trailed by the non-linear trend before breaking. PLA0.5hyb with only 0.5 wt% hybrid nanofillers recorded the maximum tensile strength improvement ( $>24\%$ ) when compared with neat PLA. PLA1.0hyb and PLA2.0hyb achieved  $\sim 19.4\%$  and  $\sim 24.2\%$  tensile strength enhancement, respectively. This gives a clear indication that low loading of the lyophilized hybrid influences tensile strength of PLA matrix, and the enhancement suggests homogenous and cluster-free dispersion of the MMT/MWCNT hybrid particles, as observed in TEM images [30]. The entire hybrid reinforced PLA showed significant improvement in elastic modulus with about 45% peak increment in PLA1.0hyb. The achieved mechanical improvements in the samples can be related to transfer of stress from PLA to the evenly distributed rigid nanoparticles [31], and the restriction in mobility imposed on polymer chains by hybrid nanofillers [32].

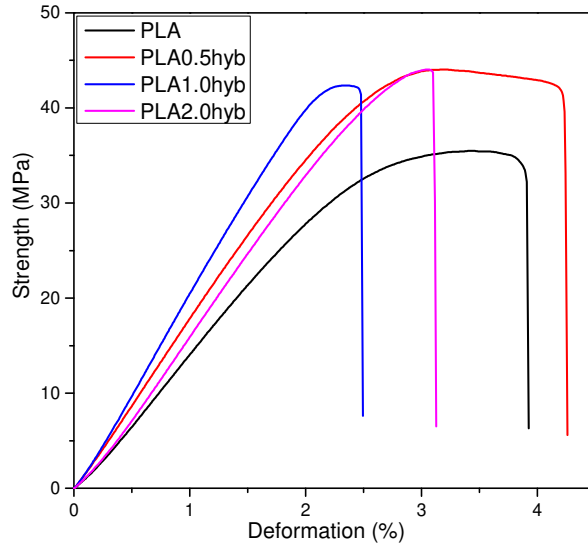


Fig. 3. Stress/strain plots for PLA/hyb nanocomposite.

Table 3. Mechanical parameters of samples.

	Tensile stress (MPa)	Elastic modulus (MPa)	Tensile strain break (%)
PLA	35.50	1443.49	4.0
PLA0.5hyb	44.05	1750.75	4.3
PLA1.0hyb	42.39	2086.69	2.5
PLA2.0hyb	44.07	1724.67	3.2

#### 4. Conclusion

The hybrid of MMT and MWCNT incorporated into the PLA matrix influenced the crystallization and improved the mechanical behavior of this matrix. The morphological and structural studies showed a good interaction of MMT/MWCNT and the matrix without changing the structure of PLA. Moreover, the morphological studies show that the lyophilized MMT/MWCNT forms a 3D-structured network of MWCNT and MMT within PLA, which can serve as a good material candidate for conductive applications. The incorporation of the lyophilized MMT/MWCNT into the matrix resulted in increased crystallinity, crystallization temperature and melting temperature of the matrix. Moreover, the addition of a small mass fraction of MMT/MWCNT hybrid resulted in more than 45% and 24% increase in the elastic modulus and tensile strength of PLA, respectively.

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