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Mechanical and moisture barrier properties of titanium dioxide nanoparticles and halloysite nanotubes reinforced poly(lactic acid) (PLA)

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Abstract. Poly(lactic acid) (PLA) has been larger used in biomedical field due to its low toxicity and biodegradability. The aim of this study was to produce PLLA nanocomposites, by melt extrusion, containing Halloysite nanotubes (HNT) and/or titanium dioxide (TiO₂) nanoparticles. Immediately after drying, PLLA was mechanically homogenized with the nanofillers and then melt blended using a single screw extruder (L/D = 30) at a speed of 110 rpm, with three heating zones in which the following temperatures were maintained: 150, 150 and 160°C (AX Plásticos model AX14 LD30). The film samples were obtained by compression molding in a press with a temperature profile of 235 ± 5°C for 2.5 min, after pressing, films were cooled up to room temperature. The mechanical tests were performed according to ASTM D882-09 and the water vapor permeability (WVP) was measured according to ASTM E-96, in triplicate. The tensile properties indicated that the modulus was improved with increased TiO₂ content up to 1g/100g PLLA. The Young's modulus (YM) of the PLA was increased from 3047 MPa to 3222 MPa with the addition of 1g TiO₂/100g PLLA. The tensile strength (TS) of films increases with the TiO₂ content. In both cases, the YM and TS are achieved at the 1% content of TiO₂ and is due to the reinforcing effect of nanoparticles. Pristine PLA showed a strain at break (SB) of 3.56%, while the SB of nanocomposites were significant lower, for instance the SB of composite containing 7.5 g HNT/100g PLLA was around 1.90 %. The WVP of samples was increased by increasing the nano filler content. It should be expected that an increase of nanofiller content would decrease the mass transfer of water molecules throughout the samples due to the increase in the way water molecules will have to cross to permeate the material. However, this was not observed. Therefore, this result can be explained considering the molecular structure of both fillers, which contain several hydroxyl groups in the surface, making the end material more hydrophilic.

1. Introduction

Polymer nanocomposites refer to multiphase materials where at least one of the constituent phases, com-monly the nanofiller, has at least one dimension in thenanoscale range (<100 nm)¹. The advantages of nanocomposites over traditional composites are numerous, including but not limited to enhanced mechanical properties, gas barrier, increased flame retardancy and thermal stability. This can be accomplished at low loading levels due to the large surface area and high aspect ratio of the nanoparticles. This effect greatly depends on the shape/aspect ratio of the particle, the dispersion of the nanoparticles in the polymer matrix, and the interaction between the filler and the bulk polymer .

Poly(lactide) (PLA) is a biodegradable and bioresorbable polymer produced from corn. Because of its characteristics (mechanical properties, renewability, biodegradability and relatively low cost), it is successfully used in the packaging and textile industries as well as in medicine². For many

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applications of PLA, for example, as the bone internal fixation material, its mechanical performance should be improved in order to meet the requirement for strength and modulus³. Many types of nanoparticles, such as carbon nanotubes (CNT), hydroxyl-apatite (HA), nanoclay, silica, and zinc oxide, were incorporated into PLA to improve the physical and mechanical properties⁴

Halloysite (HNT) is a naturally occurring polymorph of kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, with a dominant hollow tubular morphology^{4, 5}. HNT has two different interlayer surfaces. The external surface is predominantly covered by siloxane (Si–O–Si) groups and some silanol (Si–OH) and aluminol (Al–OH) groups that are exposed at the edges of the tube, whereas aluminol groups are located in the internal surface⁵. HNTs have been widely used during recent years to reinforcing the polymer matrices such as epoxy resins⁶ polypropylene, polyamide, polyvinyl alcohol and styrene rubber. In addition, HNTs is far less expensive than carbon nanotubes (CNTs) and can be mined from deposits as a raw material⁶. Titanium dioxide (TiO_2) belongs to the family of transition metal oxides⁷. TiO_2 is an inexpensive and chemically stable inorganic filler. When irradiated with ultraviolet (UV) light, TiO_2 has great potential as a photocatalyst. Besides the afore mentioned advantages, the presence of nanofillers can also control the biodegradation rate⁸.

In this study, PLA filled HNT and/or TiO_2 nanocomposites were prepared through melt blending and characterized with the aim of to assess the mechanical and barrier properties of PLA films containing these nanoparticles.

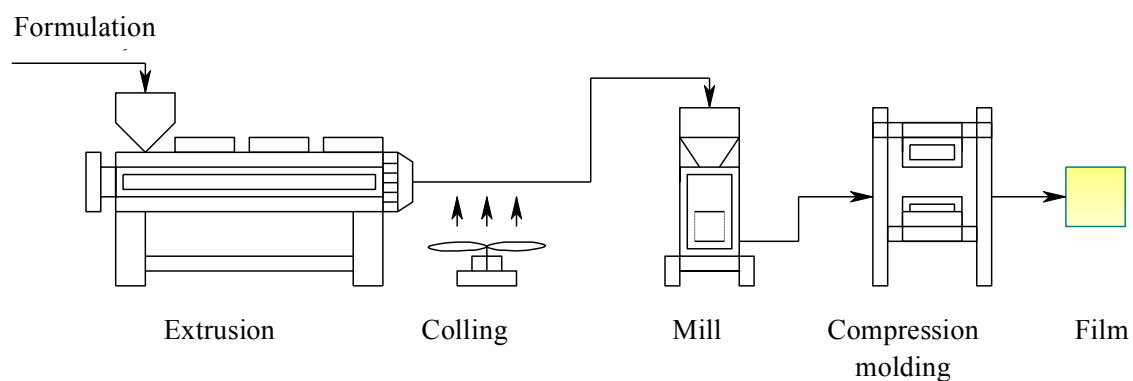
2. Material and Methods

Poly(L-Lactide) (PLLA) was supplied by Cargill Dow SA (Minnetonka, MN, EUA) under commercial name NatureWorks[®] PLA polymer 2002D. The PLLA is composed by > 95% de L-lactide and < 5% de D-lactide. PLLA pellets have been dried for 2 hs at 90 °C before use. Titanium dioxide (TiO_2 , anatase, 79.87 g/mol, nanopowder, <25 nm particle size, 99.7% trace metals basis) and Halloysite nanoclay ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, 294.19 g/mol, diam. x L 30-70 nm × 1-3 μm, surface area of 64 m²/g, nanotube) were supplied by Sigma-Aldrich (Saint Louis, MO, EUA). Thirteen nanocomposites formulations were prepared according with Table 1.

PLLA nanocomposites were prepared according with the composition presented in Table1. Immediately after drying, PLLA was mechanically homogenized with the nanofillers and then melt blended using a single screw extruder (L/D = 30) at a speed of 110 rpm, with three heating zones in which the following temperatures were maintained: 150, 150 and 160°C (AX Plásticos model AX14 LD30). After extrusion, PLLA nanocomposites powder were obtained by grinding the polymer using a mill (Marconi, model MA 048). The resulting material was compression molded (235±10°C for 5 min) using a mold (Figure 1) in an thermoforming press (Ico Comercial SA (PHS Model 15t) with pressure control between 0-15 tones. Films were then cooled to room temperature and stored for further characterization. The mechanical tests were performed according to ASTM D882-09 and the water vapor permeability (WVP) was measured according to ASTM E-96, in triplicate.

Table 1. Formulations of nanocomposites based on PLLA

Sample	Nanoparticles (g/100g PLLA)	
	TiO ₂	HNT
1	0	0
2	0.5	0
3	1.0	0
4	2.5	0
5	5.0	0
6	7.5	0
7	0	0.5
8	0	1.0
9	0	2.5
10	0	5.0
11	0	7.5
12	0.25	0.25
13	0.50	0.50

**Figure 1.** Film production

3. Results and Discussion

Mechanical and barrier properties of nanocomposites are listed in Table 2. As it can be seen, the Young's modulus (YM) of composites had a significant increase ($p \leq 0.05$) with the addition of TiO₂ up to 2.5g TiO₂/100 g PLLA. Regarding the TS, the better results were also achieved when adding 2.5g TiO₂/100 g PLLA (an increase of 13.5 % in relation to pristine PLLA). When adding more TiO₂ in the matrix the SB was drastically reduced (up to 39.3% for sample containing 7.5g TiO₂/100 g PLLA). The YM also presented an increase up to a 2.5g of filler /100g PLLA. The TS and YM increased up to 2.5g/100 g PLLA load and then decreased. Similar results were reported by Zhu et al.

(2011) where the TS of PLA composites increased up to a limit of 2 g TiO₂/100g of PLA, due to the reinforcing effect of nanoparticles and after this load the TS was reduced (5 and 10 g TiO₂/100g PLA), probably related to the aggregation of the nanoparticles in the polymer matrix ⁹.

Table 2. Mechanical Properties of PLA/TiO₂/HNT nanocomposites

Sample PLA/TiO ₂ /HNT	Tensile Strength (MPa)	Strain at break (%)	Young's modulus (MPa)	WVP (g mm/m ² d kPa)
100/0/0	53.66 ^f ± 0.84	3.56 ⁱ ± 0.08	3048 ^f ± 43	1.88
100/0.5/0	57.69 ^{g,h} ± 1.18	3.36 ^h ± 0.09	3111 ^f ± 35	1.99
100/1.0/0	58.28 ^h ± 0.83	3.00 ^f ± 0.08	3237 ^g ± 31	3.24
100/2.5/0	57.10 ^{g,h} ± 0.99	2.61 ^d ± 0.13	3335 ^h ± 39	3.35
100/5.0/0	56.49 ^g ± 0.89	2.35 ^c ± 0.10	3213 ^g ± 32	0.96
100/7.5/0	52.74 ^f ± 0.75	2.16 ^b ± 0.10	2945 ^e ± 33	0.89
100/0/0.5	43.06 ^c ± 0.64	3.21 ^g ± 0.09	2099 ^a ± 48	3.52
100/0/1.0	40.06 ^d ± 1.09	2.84 ^e ± 0.07	2140 ^{a,b} ± 49	3.62
100/0/2.5	38.48 ^c ± 0.85	2.52 ^d ± 0.10	2181 ^{b,c} ± 50	--
100/0/5.0	36.54 ^b ± 1.09	2.12 ^b ± 0.11	2228 ^c ± 40	--
100/0/7.5	32.77 ^a ± 1.17	1.90 ^a ± 0.08	2298 ^d ± 48	--
100/0.25/0.25	41.40 ^d ± 0.94	2.50 ^d ± 0.09	2220 ^c ± 40	2.88
100/0.50/0.50	38.55 ^c ± 0.93	2.78 ^e ± 0.10	2335 ^d ± 53	3.24

**Means and standard deviations of triplicates.

a-h Mean values in the same column with different letters are significantly different ($p \leq 0.05$).

The addition of HNT in the PLLA matrix did not provided any improvement in the mechanical properties of nanocomposites. The results showed a significant decrease in the TS, SB and YM values of samples. Studies of PLA composites prepared by injection molding showed an improvement of TS and YM properties when HNT was added to the polymer ^{4, 10}, which is different from the results obtained by the films prepared by hot pressing. As the shear rate in the hot pressing are extremely low compared to injection molding, the mechanical properties observed in the films can be related to the random orientation of the HNT into the PLLA matrix. In one of the references cited above ¹⁰, the results also showed a slight reduction in SB of composites when increasing the nano filler content. The addition of both TiO₂ and HNT did not presented a positive effect on the mechanical properties of composites.

The WVP of films loaded with TiO₂ increased up to a load of 2.5 g/100g PLLA and then decreased. The WVP of samples containing HNT increased by adding the nano filler. It should be expected that an increase of filler content would decrease the mass transfer of water molecules throughout the samples due to the increase in the way water molecules will have to cross to permeate the material. However, this was not observed. Therefore, this result can be explained considering the

molecular structure of both fillers, which contain several hydroxyl groups in the surface, making the end material more hydrophilic.

4. Conclusions

In this study PLLA was filled with two different nano fillers, TiO₂ (nanoparticles) and HNT (nanotubes). The results showed significant differences in the mechanical and WVP properties of PLLA composites when loading different types and amounts of fillers. Comparing the TiO₂ and HNT, we could observe a higher performance of TiO₂ as filler for PLLA, in relation to the mechanical properties of the films.

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