INJECTED BOTTLES BASED ON BIOPOLYMERS REINFORCED WITH MODIFIED NANONOCLAYS.

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Abstract. During the last decade, the use of clays for polymer reinforcement has attracted a lot of attention since it is possible to get an enhancement in mechanical, thermal, barrier and barrier properties compared to raw materials. In packaging, huge amounts of plastics materials are used, and therefore efforts are focused towards biodegradable/biocompatible polymers. Some biopolymers have already an application in food packaging industry but these applications would be increased if materials were reinforced. One approach to such improvement is the use of nanofillers in bioplastics leading to biopolymer nanocomposites. In this work, large quantities of optimized additives have been produced, and PLA masterbatch has been prepared in order to obtain bottles at industrial scale. The obtained bottles have been characterized by mechanical, barrier and thermal properties as well as their biodegradability and the toxicity of the modified nanoclay. Results have been compared with a PLA bottle without being reinforced.

Introduction. An important source of environmental concern related to food processing industry is the generation of large quantities of packaging wastes. The use of bio-based materials is a promising alternative in the packaging segment to reduce the disposal and the use of non-renewable material [1]. Bio-based biodegradable materials have two main advantages [2], they are derived from renewable resources and are biodegradable or compostable. Unfortunately, so far the use of biodegradable polymers [3] has been strongly limited because of the poor barrier properties and weak mechanical properties shown. With the aim of extending their application, biodegradable polymers are reinforced with different types of modified nanoclays.

Experimental.

Materials

Purified sodium montmorillonite (MMT) (Cloisite®Na+) was purchased from Southern Clay Products. The quaternary ammonium salt Hexadecyltrimethyl-ammonium bromide (HDTA) was supplied by CYMITQUIMICA S.L. with 99 % of purity, used for the preparation of the modified nanoclays. Polylactide pellets were purchased from Cargill Dow (NatureWorks® PLA polymer 7032) for the preparation of filled biopolymers.

Organo-modified nano-clay preparation

Organo-modified nano-clay was prepared by conventional cation exchange reaction between MMT and an excess amount of HDTA as previously described [4]. The large scale reaction was carried out in a 200 liters capacity tailored reactor from INOXPA S.A, and it was filtered and purified in a RINA 200U 250x150 PI centrifuge (Riera Nadeu S.A). After that, the additive was dried at 70ºC, and following milled in a planetarium ball mill, and finally, separated in different particle sizes by sieving. The organo-modified nano-clay has been called Clay1.

PLA masterbach preparation

Different compositions of PLA masterbach were produced using PLA pellets (dried overnight at 60ºC) blended with 3, 4 and 5% of the modified nanoclay prepared. To produce the large scale compound, a Coperion twin screw extruder DSE 20/40 equipped with a side feeder for powder dosing was used.

Bottle injection

Bottles were processed in the injection–blowing equipment settled at B.U. Plastics Bormioli Rocco Facilities (Saint Sulpice, France). The process used to obtain the bottle consisted of one step injection-blowing procedure. Processing temperatures profile was set between 200 and 230 ºC.

Results and conclusions.

Thermal stability. A test of thermal resistance was performed over the samples. They were conditioned at 60 ºC in an air convection furnace during 24 hours. Results of the test are shown in Figure 1. It can be seen that PLA bottle suffered a big distortion after the heat treatment, whereas the reinforced bottles maintained their original shape, showing an improvement in thermal behavior.

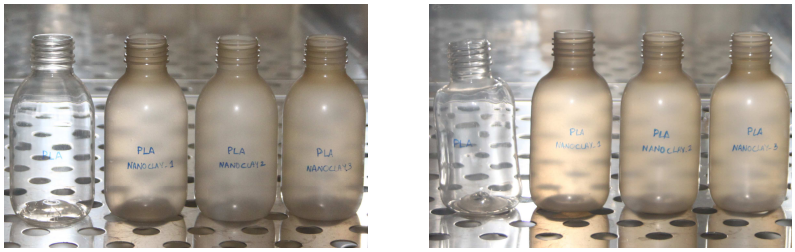

Figure 1. Picture of the PLA, PLA_3%Clay1, PLA_4%Clay1 and PLA_5%Clay1 bottles from left to right before (left side) and after (right side) a thermal treatment at 60 ºC.

Mechanical properties. Compression properties were determined using a universal testing machine MTS 2/ME, according to ASTM D2659-95. The results of this characterization are showed in Figure 2. It can be seen that the addition of 4% of Clay1 leads to the highest increase in the stiffness of the bottle.

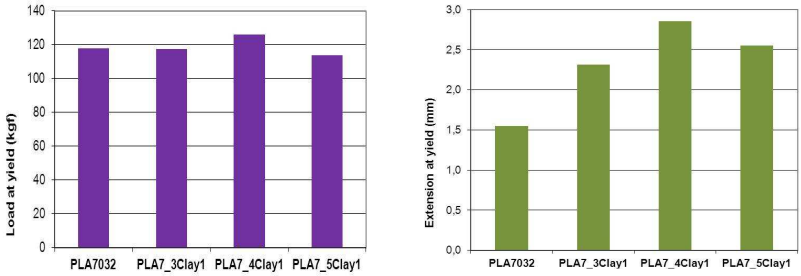

Figure 2. Compression tests results of injected bottles. Load at yield (left side) and Extension at yield (right side).

Water vapour transmission rate. These tests were performed following standard ASTM E96. Seven bottles were filled with 100 grams of calcium chloride, previously dried at least 4 hours at 240ºC, and were closed using the torquemeter settled at 15 lbf.in. Measurement conditions were 23ºC and 75 % relative humidity. Results are shown in Table 1. It can be observed the difference between the raw PLA bottles and the bottles with the additive, reaching in the best case an improvement of 15%.

Table 1. Water Vapour Transmission Rate Results for the PLA bottles.

Sample	WVTR (grH_2O/bottle·day)
PLA Bottle	0,070
PLA_3%Clay1	0,066
PLA_4%Clay1	0,062
PLA_5%Clay1	0,060

Biodegradability. Aerobic Biodegradability in mature compost according to UNE EN 13432-2000 was carried out in PLA and PLA_4%Clay1 bottles. As it can been shown in Table 2, after 101 days, the samples reached an average biodegradation value higher than 90% as required by UNE EN 13432-2000.

Table 2. Biodegradability Results for the PLA samples.

Sample	Average %Biodegradation	Standard Deviation
Reference, Avicel Cellulose	104,1	3,6
PLA_4%Clay1	100,2	6,2
PLA raw	110,8	5,1

Organo-modified nano-clay toxicity. The cytotoxic effect of the Clay1 in the human hepatic cell line HepG2 was studied. Different endpoints (total protein content, neutral red uptake and methylthiazol tetrazolium salt metabolization) were determined after 24 and 48 hours of exposure to a wide range of concentrations (up to 8 µg/mL). Cytotoxicity was only observed in the HepG2 cells at the highest concentration used. Mean effective concentration (EC50) values, this is the concentration that modifies each biomarker by 50% in comparison with untreated controls, could not be calculated due to the low effects induced by Clay1.

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