

DEGRADATION OF A MECHANICALLY RECYCLED POLYLACTIDE/HALLOYSITE NANOCOMPOSITE IN AN ETHANOLIC FOOD SIMULANT

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Abstract:

This work aims to study the effect of immersion in a ethanolic food simulant in mechanically recycled poly(lactic acid) (PLAR) and its nanocomposites reinforced with halloysite nanotubes (HNT). PLAR was obtained by subjecting PLA to an accelerated ageing process, which includes photochemical, thermal and hydrothermal ageing steps, followed by a final demanding washing step. PLAR was further reinforced with 4 %wt. HNT to improve the properties of the PLAR films. The materials were melt compounded by melt extrusion and processed into films by compression molding. The resulting films were exposed to food simulant D1 (50 %vol. ethanol solution) for 10 days at 40 °C. The intrinsic viscosity, crystallization behavior, thermal stability as well as the mechanical performance were analyzed before and after the contact with the food simulant. The swelling, plasticizing and hydrolyzing effect of the food simulant led to an important decrease of the intrinsic viscosity of all the samples, along with a significant increase of the crystallinity. Thermal stability was negatively affected by the decrease of the molecular weight, while the high crystallinity values resulted in materials with higher Vickers hardness values after the immersion in the food simulant.

Keywords: poly(lactic acid); halloysite; nanocomposites; mechanical recycling; food simulant.

Cite as: Beltrán, F.R., Arrieta, M.P., Hortal, Y., Gaspar, G., de la Orden, M.U., Martínez Urreaga, J. (2021). Degradation of a mechanically recycled polylactide/halloysite nanocomposite in an ethanolic food simulant. *J Appl Res Eng Technol & Engineering*, 2(2), 63-70. <https://doi.org/10.4995/jarte.2021.15297>

1. Introduction

The use of bioplastics is a sustainable alternative to conventional based plastics in several applications, particularly in short term applications such as food packaging, which might help to mitigate the environmental issues related to the massive production, and consumption, of fossil-fuel based plastics. Bioplastics production have been increasing in recent years, reaching 2.11 million tonnes in 2019 (European Bioplastics, 2020). Among bioplastics, poly(lactic acid) (PLA) nowadays plays a prominent role in the food packaging field. Its good properties, availability and moderate cost are making PLA one of the most interesting alternative to conventional plastics in some short-term food packaging applications (Castro-Aguirre et al., 2016; Raquez et al., 2013). However, the increasing production of PLA could come along with environmental problems, mainly related to the possible competition with the food supply chain, since it comes from food grade renewable resources (mainly starch and sugar), and the slow degradation rate of PLA in non-industrial composting conditions (Arrieta et al., 2017; Haider et al., 2018; Kale et al., 2007; Niaounakis, 2019).

This slow degradation, and an inadequate management of the residues, could lead to the accumulation of PLA wastes (Farah et al., 2016). Therefore, it is necessary to recover and valorize PLA wastes, which would help not only to decrease the environmental impact of this bioplastic, but would also align with the circular economy model, one of the priorities of the European Union (European Comission, 2018; European Comission, 2019)

Nowadays, mechanical recycling represents one of the most important technology to recover post-consumer plastics waste and convert them into high value products. Initially, biopolymers were considered as potential impurities for traditional plastics recycling channels as they could act as impurities influencing the structural and thermal properties of recycled traditional plastic products (Samper et al., 2014; Samper et al., 2018). But, as the advantages of PLA-based materials became more developed and demanded, PLA became a new important waste in plastic recycling facilities. Thus, since the last decade academic and industrial sector are highly focused on the improvements of PLA recycled properties to extend its industrial applications (Agüero et al., 2019; Badia et al., 2012). In fact, among

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the methods for the valorization of PLA wastes, mechanical recycling represents a very interesting alternative since it allows to reduce the amount of raw materials, energy and emissions related to the manufacture of PLA (Cosate de Andrade et al., 2016; Maga et al., 2019; Rossi et al., 2015). However, the mechanical recycling process of PLA has some inherent difficulties. Previous works have reported that mechanical recycling leads to the degradation of PLA, resulting in low molecular weight polymeric chains, along with a reduction of some key properties such as gas barrier, mechanical and thermal properties (Beltrán et al., 2018a). In the recent years some upgrading options such as thermal treatments (Beltrán et al., 2020), chain-extendors and crosslinking agents (Tuna & Ozkoc, 2017), and the incorporation of reinforcements of inorganic nature [i.e.: halloysite nanotubes (HNTs) (Beltrán et al., 2018b)]. In this context, nanoparticles are typically employed in improving biopolymers thermal stability, mechanical and gas/water vapor barrier properties, as well as to enhance their disintegration rate under industrial composting conditions (Villegas et al., 2019). Among other nanoparticles, HNTs possess interesting properties for food packaging materials such as its natural origin, abundant availability, low cost, low density, high rigidity as well as non-toxic characteristics (Rojas-Lema et al., 2020). HNTs possess low hydroxyl density in their surface with respect to other nanoparticles, making the hydrogen bonding interaction between HNTs are relatively weaker (Liu et al., 2008).

In this context, in a previous work natural halloysite nanotubes (HNTs) as well as silane-modified HNTs were used as filler for recycled PLA (PLAR). Both nanoparticles showed the ability to block the -COOH terminal groups generated during ageing and recycling of PLA, which could catalyze degradation reactions, and thus reduce the degradation of recycled PLA during melt processing (Beltrán et al., 2018a). However, there is limited scientific data about the degradation of PLA nanocomposites due to food simulants

Nevertheless, there are limited scientific data reporting the loss of properties of PLA-based packaging materials after migration tests. Fortunati et al. (2012) studied the effects of ethanol 10 %vol. on PLA nanocomposites reinforced with cellulose nanocrystals (CNC) after the overall migration tests and observed that similar migration levels were observed for neat PLA and for the nanocomposites, but CNC provides significant improvements to the PLA matrix such as improved barrier, thermal and mechanical performance (Fortunati et al., 2012). Arrieta et al. studied the performance of active packaging materials based on PLA-catechin after the release of catechin into a fatty food simulant (ethanol 50 %vol.) and observed that it was necessary to increase the crystallinity of the system by incorporating another more crystalline polymer, such as poly(hydroxybutyrate) (PHB), to maintain the structural and mechanical properties of the packaging material after 10 contact days with the food simulant (Arrieta et al., 2014). Iñiguez-Franco et al. studied the hydrolytic degradation of PLA in water as well as in ethanol 50 %vol. and in ethanol 95 %vol. solutions and observed that PLA showed faster hydrolytic degradation in contact with 50 %vol. ethanol than with 95 %vol. ethanol or pure water. While water produce the hydrolytic degradation of PLA, with a consequent decrease in molecular weight, ethanol swells the polymer matrix which increase the free volume allowing more water

molecules to diffuse into PLA matrix. Thus, ethanol at 50 %vol. concentration provides the optimal competitive balance between swelling and hydrolysis of PLA matrix (Iñiguez-Franco et al., 2016). Iñiguez-Franco et al. then studied PLA loaded with organo-modified montmorillonite in the same food simulants (50 %vol. ethanol, 95 %vol. ethanol and pure water) and observed that the nanoparticles did not have an effect on the hydrolysis rates (Iñiguez-Franco et al., 2017). To the best of our knowledge there are not studies reporting the performance of recycled PLA and recycled PLA loaded with HNTs after migration test. Thus, in the present work the effect of a ethanolic food simulant, namely simulant D1 (50 %vol. ethanol), on the overall performance of recycled PLA and PLA/HNT nanocomposites was studied. Therefore, the structural, thermal and mechanical properties of nanocomposites were measured after 10 days of immersion in the ethanolic food simulant. Special focus was paid on the crystallization phenomenon of the materials.

2. Material and Methods

2.1. Materials

PLA (Ingeo™ 2003D) with a melt mass-flow rate of 6 g/10 min (2.16 kg at 210 °C) was purchased from NatureWorks. Raw halloysite was supplied by Sigma-Aldrich.

2.2. Preparation of the recycled PLA-halloysite nanocomposites

The ageing and mechanical recycling of PLA, along with the preparation of the nanocomposites was carried out according to the following procedure: (i) PLA pellets were dried for 2 h and 85 °C in a vacuum oven, and then melt processed at 60 rpm in a Rondol Microlab twin-screw extruder with a L/D ratio of 20. The temperature profile, from hopper to die, was: 125, 160, 190, 190 and 180 °C; (ii) the obtained material was then compression molded, at 190 °C, into films with a thickness of 200 ± 10 µm using an IQAP-LAP hot plate press (PLAV); (iii) the PLAV films were subjected to an accelerated ageing process which included a 40 h photochemical degradation stage, carried out in a ATLAS UVCON chamber equipped with eight F40UVB lamps, a 468 h thermal degradation stage carried out in an oven at 50 °C and a 240 h hydrolytic degradation stage carried out in demineralized water at 25 °C; (iv) the aged samples were washed during 15 min at 85 °C in a NaOH (1 %wt.) and surfactant (Triton X-100, 0.3 %wt.) solution, as it was reported in previous works (Beltrán et al., 2018a); (v) the washed samples were grinded, dried and melt processed in the same conditions that PLAV. 4 %wt. of raw halloysite nanotubes were added to selected PLA batches during this second processing stage. The obtained materials are summarized in Table 1.

Table 1: Materials obtained after the mechanical recycling process.

Sample	Description
PLAV	PLA subjected to the first extrusion and compression molding steps.
PLAR	PLA subjected to the whole simulated mechanical recycling process.

PLAR-HNT Nanocomposite of mechanically recycled PLA (PLAR) loaded with 4 wt.% of halloysite.

2.3. Degradation conditions

Immersion was performed in a 50 %vol. ethanol solution (simulant D1). Four samples, with dimensions of 1.5×1.5 mm, were immersed in 9 mL of food simulant (area-to-volume ratio = 1 dm²/100 mL) contained in glass vials, which were kept at 40 °C for 10 days. After 10 days, the films were removed and thoroughly dried at 40 °C for their characterization.

2.4. Characterization techniques

The changes on the molecular weight of the samples were estimated by means of intrinsic viscosity (IV) measurements. The measurements were conducted according to the ISO 1628 standard, using an Ubbelohde viscometer at 25 °C and chloroform as a solvent.

Fourier transform infrared (FTIR) spectroscopy was used to analyze the chemical and structural changes in the different samples as a consequence of their exposition to the food simulants. Spectra were recorded in a Nicolet iS10 spectrometer equipped with an attenuated total reflectance (ATR) accessory. Each spectrum was recorded with a resolution of 4 cm⁻¹ and averaging 16 scans. Each sample was analyzed by triplicate. The crystallinity can be estimated from the variations in the band at 955 cm⁻¹ according to Equation 1 (Meaurio et al., 2006):

$$X_c = \frac{I_0 - I_f}{I_0} \times 100 \quad (1)$$

where I_0 is the intensity of the absorption band at 955 cm⁻¹ of the PLA-based materials before the immersion in the food simulants and I_f is the intensity of the band after 10 days of immersion in the food simulants.

Changes on the crystalline pattern of the samples were also followed by means of X-ray diffraction (XRD) using a PANalytical X'Pert PRO Powder system using $K\alpha$ ($\lambda = 1.5406 \text{ \AA}$) for values of 2θ from 1° to 10° range and a X'PERT MPD with conventional Bragg-Brentano geometry for values of 2θ from 1.8° to 35°. Scanning was performed on square film surfaces (15×15 mm) mounted in an appropriate sample holder. The crystallinity degree was calculated by means of Equation 2:

$$X_c = \frac{I_c}{I_c + I_a} \times 100 \quad (2)$$

where I_c and I_a are the diffraction intensities of crystalline and amorphous regions, respectively.

The thermal behavior of the different samples was studied by means of differential scanning calorimetry (DSC) using TA Instruments DSC Q20 calorimeter. Samples of approximately 5 mg were placed in aluminum pans and subjected to a thermal cycle consisting of a first heating scan, at 5 °C/min, from 10 to 180 °C; an isothermal step for 3 min; a cooling scan, at 5 °C/min, until 0 °C; an isothermal step for 1 min and a second heating scan, at

5 °C/min, until 180 °C. A Nitrogen flow of 50 mL/min was used. Crystallinity was calculated using Equation 3:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_\infty} \times 100 \quad (3)$$

where ΔH_m and ΔH_{cc} are the melting and cold crystallization enthalpies respectively, and ΔH_∞ is the melting enthalpy of a perfect PLLA crystal, 93.1 J/g (Beltrán et al., 2016)

Thermogravimetric analysis (TGA), using a TA Instruments TGA 2050 thermobalance, was used to study the thermal stability. Samples of approximately 12 mg were heated, under nitrogen atmosphere, from room temperature to 800 °C at 10 °C/min.

The Vickers hardness of the different samples was measured using a Shimadzu Type M microhardness tester, equipped with a Vickers pyramidal indenter. A load of 25 g and a loading time of 10 s were used. Each sample was measured six times.

3. Results and discussion

3.1. Effect of immersion on the intrinsic viscosity

It is well known that PLA is susceptible to suffer hydrolytic degradation during its immersion in aqueous medium, which leads to the generation and subsequent release of low molecular weight compounds to the immersion media (lactic acid and lactic acid oligomers). This phenomenon plays a very important role in food packaging applications. Therefore, the effect of the different PLAR-based formulations immersion in the ethanolic food simulant during 10 days on the molecular weight of PLA was measured by means of solution viscometry.

It can be seen on Figure 1 that mechanical recycling leads to a decrease of the intrinsic viscosity of PLA. This behavior has been reported in a previous study (Beltrán et al., 2018a), and has been attributed to the degradation

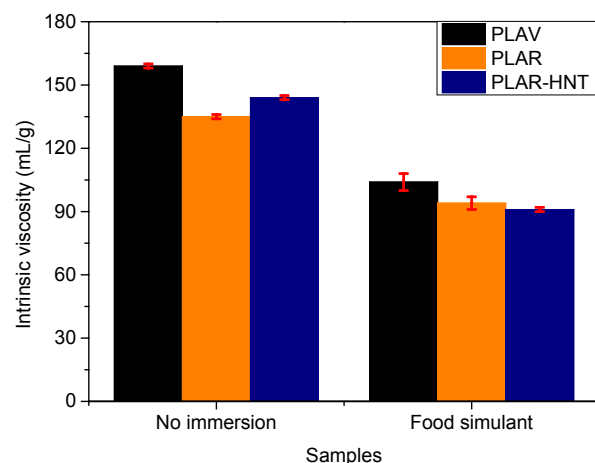


Figure 1: Intrinsic viscosity values before and after immersion of the different samples.

reactions that take place during accelerated ageing, washing and especially reprocessing, resulting in a decrease of the molecular weight of the polymer. It is also worth to note that the addition of HNTs resulted in a slight increase of the intrinsic viscosity. A similar result was reported by Beltrán et al. (Beltrán et al., 2018b), which found that the functional groups present in HNTs had a blocking effect on the -COOH and -OH groups present in aged and washed PLA, which could catalyze degradation reactions during the melt reprocessing step. The blocking effect of both nanotubes resulted in a reduced degradation during reprocessing and slightly higher intrinsic viscosity values.

Regarding the intrinsic viscosity reduction after the immersion in the ethanolic food simulant, Figure 2 shows that all the samples present significantly lower intrinsic viscosity values after the immersion. This result could be attributed to the synergistic effect of ethanol and water. Ethanol has a swelling effect on PLA, which generates free volume and allows water molecules to diffuse more easily through the polymer bulk, thus promoting the hydrolytic degradation (Iñiguez-Franco et al., 2016). This noticeable decrease of the intrinsic viscosity, and thus molecular weight, could lead to structural changes in the different samples after immersion, which will be analyzed in the following sections.

3.2. Structural changes after the immersion

Besides the changes observed in the intrinsic viscosity it is known that the immersion of PLA in ethanol solutions leads to the formation of crystalline structures in PLA based materials (Arrieta et al., 2014; Iñiguez-Franco et al., 2017). The crystallizing effect of the ethanol solution could be explained, mainly, by several phenomena: (i) ethanol has a swelling effect on PLA, facilitating the diffusion of water molecules inside the polymer matrix (Iñiguez-Franco et al., 2016); (ii) water causes the hydrolytic degradation of the polymer, generating shorter polymer chains which promotes the packing in ordered structures (Badia et al., 2012); (iii) water has a well-known plasticizing effect, resulting in an increase of the mobility of the polymer chains which cause a molecular rearrangement and the formation of crystalline structures (Iñiguez-Franco et al., 2016; Iñiguez-Franco et al., 2017), that has been related with the accelerated spherulite formation (Fortunati et al., 2012). The study of crystalline structures formed after the immersion in food simulants was analyzed by means of DSC, XRD and FTIR-ATR spectroscopy. Figure 2 shows the results obtained from the first heating DSC scans of the different samples, while Table 2 summarizes the crystallinity values obtained by each technique.

It can be seen on Figure 2 that the samples before immersion show the characteristic thermal behavior of PLA, with a glass transition temperature around 60 °C, an exothermic cold-crystallization peak above 100 °C and a melting endotherm above 140 °C. However, there are some differences between the samples. The cold crystallization peak (T_{cc}) of PLAV takes place at around 124 °C suggesting that the processing conditions used did not allow the crystallization of PLA and an amorphous material was obtained. The mechanical recycling process

led to a reduction of the T_{cc} value ($T_{cc}=110$ °C), since the shorter polymer chains, resulting of the polymer matrix degradation, promote the crystallization at lower temperatures (Beltrán et al., 2018a). Meanwhile, the nanocomposite showed a T_{cc} value below 110 °C. Previous works (Beltrán et al., 2016) reported that 2 %wt. of natural halloysite did not have a nucleating effect on PLA. However, in this work, a larger amount of halloysite is added to the polymer, which could have a nucleating effect on PLA. Regarding the melting behavior, a double melting peak is observed in nanocomposites, as it was already reported for PLA and PLAR loaded with HNTs and is related to a melt recrystallization mechanism (Rojas-Lema et al., 2020).

Figure 2b shows that immersion in the food simulant led to important changes in the thermal behavior of the samples. It can be seen that, after immersion, all the samples show no cold crystallization peak. This behavior suggests that all regions available for crystallization crystallized during the exposition to the food simulant.

Regarding the crystallinity values after the immersion in the food simulant, it is worth to note that each technique provides different information. While DSC and XRD

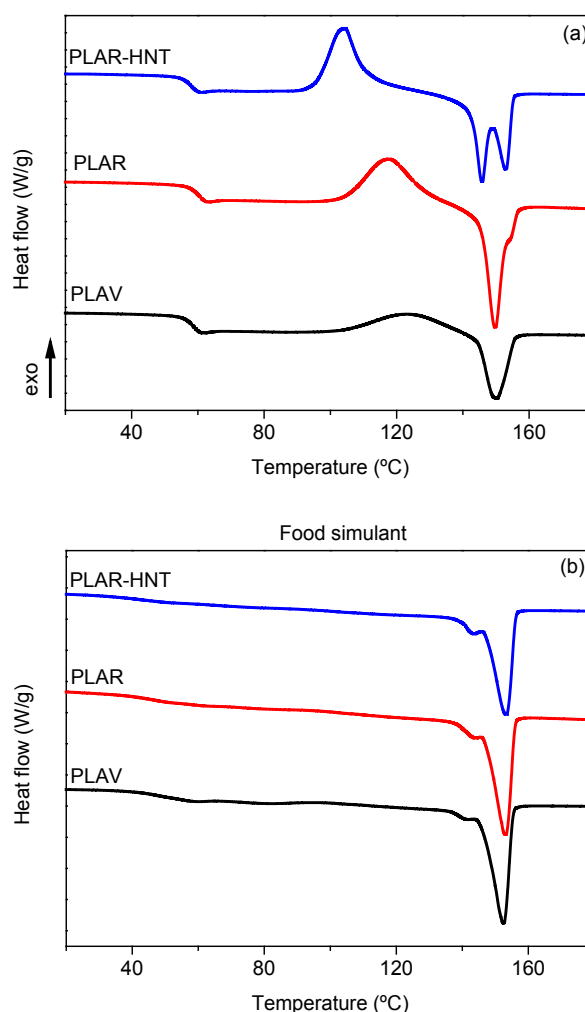


Figure 2: DSC first heating scans (a) before immersion and (b) after 10 days of immersion in the food simulant.

provide information about the crystallinity of the bulk material, FTIR-ATR provides information about the surface of the samples. Table 2 shows that, DSC and XRD results have a similar trend, in which all the samples present a similar crystallinity degree after immersion. Nevertheless, the crystallinity values calculated by means of XRD are significantly higher than those obtained by DSC. This could be due to the fact of DSC calculations being affected by the crystal morphologies present in the samples, while XRD calculations are independent of the crystal morphologies (Beltrán et al., 2016). Table 2 also shows that, according to FTIR-ATR, the PLAR-HNT sample has a higher Xc value than its unfilled counterparts. This result might be explained by the nucleating effect of the HNTs on PLA, and also by the hydrophilicity of the clay. The presence of the clays could facilitate the absorption and diffusion of water in the surface of the sample, enhancing their plasticizing and swelling effect and thus favoring the formation of crystalline structures.

Table 2: Crystallinity values of the samples after immersion, according to different experimental techniques.

Sample	Xc ^{DSC}	Xc ^{XRD}	Xc ^{FTIR}
PLAV	28	46	31
PLAR	33	45	29
PLAR-HNT	32	45	42

3.3. Effect of immersion on the thermal stability

The effect of the immersion in the food simulant on the thermal stability of the samples was studied by means of TGA. Table 3 summarizes the results obtained for the different samples. Table 3 shows that PLAR has a lower T₁₀ and T₅₀ values than PLAV, thus indicating that the degradation that took place during recycling resulted in the decrease of the thermal stability of the material. This behavior could be attributed to the presence of shorter polymer chains which decompose at lower temperatures, as it has been previously reported in mechanically recycled PLA. Regarding the behavior of the nanocomposite with halloysite, it can be seen on Table 3 that PLAR-HNT shows higher thermal stability than PLAR, even reaching T₁₀ values close to that of PLAV. These results are rather frequent in PLA based nanocomposites, since the nanotubes might act as barrier, hindering the liberation of the degradation product, thus increasing the thermal stability of the material (Risyon et al., 2020; Rojas-Lema et al., 2020).

Table 3: TGA results of the different samples before and after immersion in the food simulant.

Sample	T ₁₀ (°C)	T ₅₀ (°C)	T _{max} (°C)
Before immersion			
PLAV	334.3	358.4	365.7
PLAR	322.7	354.0	366.3
PLAR-HNT	332.6	358.2	367.3
After immersion			
PLAV	325.2	350.7	358.6
PLAR	320.8	348.6	356.6
PLAR-HNT	323.0	355.7	364.8

Regarding the behavior of the immersed samples in the food simulant, Table 3 show that all the materials present a decrease on the thermal stability after 10 days of immersion in the ethanolic food simulant. This decrease of the thermal stability could be related to the degradation of the samples, as it was observed by means of solution viscosimetry, since the shorter polymer chains decompose at lower temperature.

3.4. Effect of the immersion on the Vickers hardness

Mechanical properties of the different samples were measured by means of microhardness tests. Figure 3 shows the Vickers hardness of the different materials, before and after immersion in the food simulant. Firstly, it can be seen that, prior to immersion, PLAR shows a slightly lower hardness value than PLAV. This small difference could be attributed to the degradation of the polymer during aging and recycling, although, previous studies have shown that intrinsic viscosity have a limited effect on the mechanical properties of recycled or reprocessed PLA (Beltrán et al., 2018a; Perego et al., 1996). Regarding the effect of the addition of the halloysite nanotubes, Figure 3 shows that the nanocomposite filled with HNT shows a slightly higher hardness value than PLAR, and even PLAV. This could be explained by two factors, namely the increase of the intrinsic viscosity and the reinforcing effect of the halloysite nanotubes well dispersed in the PLA matrix. Similar results were obtained by Beltrán et al. in recycled PLA nanocomposites filled with 2 %wt. of halloysite nanotubes (Beltrán et al., 2018b).

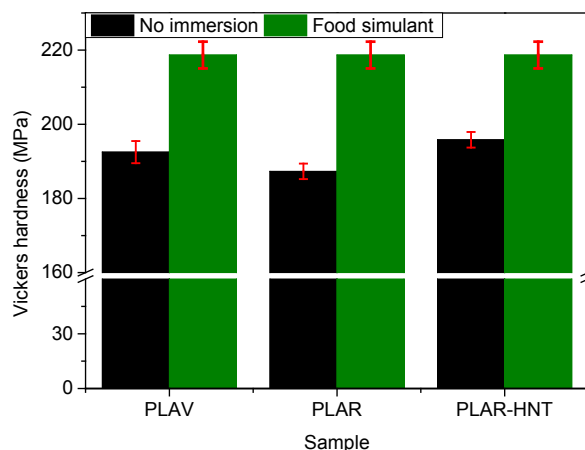


Figure 3: Vickers hardness values of the samples before and after immersion in the food simulant.

Secondly, it can be seen on Figure 3 that the immersion in the food simulant resulted in an increase of the Vickers hardness of the samples. This result might seem surprising if only the intrinsic viscosity values are considered, since the severe degradation of the polymer should result in an important decrease of the mechanical properties. However, there are other factors which affect the hardness of polymeric materials, such as the crystallinity degree. DSC, FTIR and XRD results indicate that the immersion of the materials in the ethanolic food

simulant led to an important crystallization of PLA, which results in an increase of the hardness values of all the samples.

4. Conclusions

The effect of the immersion in an ethanolic food simulant on the structure and properties of PLAR and PLAR-HNT nanocomposites was studied. Intrinsic viscosity measurements point out that all the samples show important degradation after only 10 days of immersion in the food simulant. DSC, XRD and FTIR results indicate that the ethanolic food simulant causes a significant increase on the crystallinity of all the samples. Regarding the effect of the immersion on the thermal and mechanical properties of the samples, TGA results show that all the samples present a reduced thermal stability after being exposed to the ethanolic food simulant, as a consequence of the degradation of the polymer matrix. Meanwhile, Vickers hardness results suggest that crystallinity degree plays a crucial role in the mechanical properties of the

samples, since all the materials showed higher Vicker hardness values after immersion, despite the important decrease of the molecular weight.

The addition of HNTs to mechanically recycled PLA leads to an improvement of the performance of the recycled polymer matrix. However, the presence of the clay nanotubes does not seem to significantly affect the behavior of PLA matrix after being exposed to a ethanolic food simulant.

5. Acknowledgements

This work was supported by European Union's Horizon 2020 research and innovation program [grant agreement No. 860407 BIO-PLASTICS EUROPE], by MINECO-Spain [project CTM2017-88989-P] as well as Universidad Politécnica de Madrid [project UPM RP 160543006].

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