

MANUFACTURING AND COMPATIBILIZATION OF BINARY BLENDS OF POLYETHYLENE AND POLY(BULYLENE SUCCINATE) BY INJECTION MOLDING

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Abstract:

In this study was analyzed the effect of three different compatibilizers polyethylene-graft-maleic anhydride (PE-g-MA), unmodified halloysite nanotubes (HNTs), and HNTs treated by silanization with (3-glycidyloxypropyl) trimethoxysilane (GLYMO) (silanized HNTs) in blends of bio-based high-density polyethylene (bioPE) and poly(butylene succinate) (PBS) with a weight ratio of (70/30). Each compatibilizer was added in a proportion of (3 phr regarding PBS). Standard samples were obtained by extrusion and subsequent injection molding. The analyzes of the samples were performed by mechanical tests, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), field emission scanning electron microscopy (FESEM), and wettability (θ_w). Results suggest that the addition of modified HNTs (silanized HNTs) allowed to obtain better properties than samples compatibilized with unmodified HNTs and PE-g-MA, due to it contributes with the improvement in mechanical properties regarding bioPE/PBS blend, for instance, the tensile modulus and elongation at break increase about 8% and 13%, respectively. In addition, it was determined through FESEM images and that silanized HNTs particles were better dispersed over the matrix, which in fact contribute to the enhance in mechanical properties. TGA showed that silanized HNTs delay the degradation temperature regarding the uncompatibilized blend. While DMTA indicated the reduction in the mobility of the chains in samples with unmodified and modified HNTs. Therefore, it was successfully obtained compatibilized bioPE/PBS blends, which constitutes an interesting option to develop new sustainable polymers.

Keywords: blends; halloysite nanotubes; PE-g-MA; compatibility.

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1. Introduction

In recent years, the production and consumption of plastics in our society have increased significantly, thanks mainly to the low price of plastics. In 2019 there was a global production of 368 million tonnes of plastic, increasing by 9 million tonnes compared to 2018 (PlasticsEurope, 2020). Some of the problems related to the massive use of plastics include the use of fossil fuels due to it contributes to the increase in emission of greenhouse gases, in addition, the large amount of non-biodegradable waste that is generated, a small part of which is recycled or incinerated to produce energy (Lochab, Varma, & Bijwea, 2012). However, a large proportion of such waste ends up in controlled landfills or, in the worst case, spread in the environment (e.g. rivers, seas, oceans, etc.). It is estimated that by 2050 around 12 billion tonnes of plastic waste could end up in the natural environment (Riechers et al., 2021). The environmental problems caused by the increased consumption of plastics together with society's growing environmental awareness have led to an increase in research into more environmentally friendly polymers. These polymers include polymers obtained

from renewable sources, such as bio-polyethylene (BioPE), bio-polyethylene terephthalate (BioPET) or bio-polyamide (BioPA); biodegradable polymers such as polycaprolactone (PCL), polybutylene succinate (PBS) or polybutylene adipate terephthalate (PBAT); or polymers that are both bio-based and biodegradable, which include polylactic acid (PLA), thermoplastic starch (TPS) or polyhydroxyalkanoates (PHAs). All of them are known as biopolymers (Hassan, Bai, & Dou, 2019)

Bio-based polyethylene (BioPE) is one of the most studied and most interesting biopolymers for industrial use, as it has properties identical to its petrochemical counterpart, comes from renewable resources, it is easy to process, and costs less than other biopolymers (Siracusa & Blanco, 2020). BioPE is a polymer that is synthesized from ethylene monomer derived from the dehydration of bioethanol obtained from the glucose of different biological raw materials such as sugar cane, sugar beet, corn or wheat starch, and lignocellulosic materials (Tsiropoulos et al., 2015). This material can reach up to 95% bio-based content, which makes it more environmentally friendly than petroleum-based polyethylene (Jorda et al.,

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2019). Furthermore, CO₂ emissions from petrochemical PE are estimated to be 2.1 tonnes per tonne of polymer whereas for BioPE the emissions are -2.5 tonnes of CO₂, indicating that it binds carbon, thus reducing CO₂ emissions to the atmosphere and the environmental impact compared to its petroleum-based counterpart (Garcia-Garcia, Carbonell-Verdu, Jordá-Vilaplana, Balart, & Garcia-Sanoguera, 2016; Samper-Madrigal, Fenollar, Dominici, Balart, & Kenny, 2015). However, one of its main drawbacks is that it is not a biodegradable polymer, leading to environmental problems after its life cycle. In order to reduce its final environmental impact, BioPE has been blended with different biodegradable polymers such as PLA (Ferri, Garcia-Garcia, Rayón, Samper, & Balart, 2020; Quiles-Carrillo, Montanes, Jorda-Vilaplana, Balart, & Torres-Giner, 2019), PCL (Bezerra, França, Morais, Siqueira, et al., 2019; Bezerra, França, Morais, Silva, et al., 2019) or TPS (Samper-Madrigal et al., 2015). One of the most interesting biopolymers to reduce the environmental impact of BioPE is PBS. PBS is a biodegradable polyester obtained from the polymerization of butanediol and succinic acid, both of which can be obtained from petroleum or renewable resources (Tecchio, Freni, De Benedetti, & Fenouillot, 2016). PBS has good mechanical properties, similar to polypropylene and polyethylene, and ease of processing, making it a good candidate for use in BioPE blends (Liu, Yu, Cheng, Qu, 2009; Liu, Yu, Cheng, Yang, 2009). However, studies have shown that blending PBS with petrochemical PE results in blends with poor mechanical properties due to the lack of miscibility between both polymers (Darshan, Veluri, Kartik, Yen-Hsiang, & Fang-Chyou, 2019). This lack of miscibility is due to the polarity difference between both polymers. On the one hand, PE is a non-polar and therefore highly hydrophobic polymer while PBS is a more hydrophilic, polar polymer, due to the presence of ester groups and other oxygen-based groups in its structure (Quiles-Carrillo et al., 2019).

There are different methods for improving the miscibility between polymers. One of the most employed is the use of compatibilizers, mainly prefabricated copolymers (block or grafted). These copolymers are characterized by a dual functionality that allows them to interact with both polymers in the blend, acting as a bridge between them and establishing interactions, thus improving their compatibility and their final mechanical properties (Ferri et al., 2020). Samper-Madrigal et al. (2015) studied the effect of incorporating different contents (1, 3, and 5 wt%) of graft copolymer poly(ethylene-g-maleic anhydride) (PE-g-MA) in BioPE/TPS blends (70/30). Morphologically, the authors observed that the presence of the copolymer in the blend leads to a noticeable reduction in the size of the phases in the matrix due to the improved polymer's compatibility. Regarding mechanical properties, the authors observed that the presence of PE-g-MA in the BioPE/TPS blend significantly improved the elongation at break without hardly affecting the tensile strength, demonstrating the effectiveness of this compatibilizer.

Another more recent approach to improve miscibility between polymers is the use of nanoparticles. Several studies have demonstrated how the incorporation of small amounts of nanoparticles such as carbon nanotubes (CNT) (Darshan et al., 2019), calcium carbonate nanoparticles (de Oliveira et al., 2020; Vrsaljko, Macut, & Kovačević,

2014), montmorillonite (Abdolrasouli, Nazockdast, Sadeghi, & Kaschta, 2015) or sepiolite (Nuñez et al., 2012), unmodified and modified, in PE blends has led to an increase in the miscibility between both polymers. One of the most promising nanoparticles for use as a nanofiller is halloysite nanotubes (HNT). Halloysite is a natural aluminosilicate, chemically similar to Kaolin, from natural deposits in countries such as China, Brazil, and France, among others (Du, Guo, & Jia, 2006). Depending on its origin, halloysite can be found in the form of spheres, plates, elongated prisms, or nanotubes, being the last ones the most used as reinforcements in polymers (Peres & Oréfica, 2020). HNT are hollow tubular structures consisting of multiple layers with dimensions ranging from 500 to 1000 nm in length, 15 to 100 nm in inner diameter and 40 to 120 nm in outer diameter (Pal, Kundu, Malas, & Das, 2014; Schmitt, Prashantha, Soulestin, Lacrampe, & Krawczak, 2012)

One of the most important characteristics of HNTs is the difference in chemical structure between the inner and outer surface, on the one hand, the outer surface is composed of siloxane while the inner layers are composed of aluminum groups (Carli, Daitx, Soares, Crespo, & Mauler, 2014). The high aspect ratio of HNTs, high mechanical strength, biocompatibility, chemical difference between the inner and outer surface, and low cost, among others, make HNTs interesting nanoparticles for use as nanofiller in polymer blends (Sharma, Singh, Majumdar, & Butola, 2019). However, HNTs have high hydrophilicity due to the presence of numerous hydroxyl groups on their surface, which favors the aggregate formation and thus a poor dispersion in the polymer matrix, which has a negative effect on the overall properties of the sample (Garcia-Garcia, Garcia-Sanoguera, Fombuena, Lopez-Martinez, & Balart, 2018a; Krishnaiah, Ratnam, & Manickam, 2017)

One of the most commonly used methods to increase the hydrophobicity of HNTs and improve their dispersion in the polymer matrix is the chemical surface modification with silanes (Yang et al., 2017).

The main objective of the present work is to study the effect of different compatibilizers such as PE-g-MA, unmodified and silane-modified halloysite nanotubes, and the combination of both on the compatibility of the BioPE/PBS (70/30) blend. The effectiveness of the different compatibilizers used has been evaluated by studying the mechanical, thermal and morphological properties.

2. Materials and Methods

2.1. Materials

Poly(butylene succinate) (PBS) of injection grade Bionolle 1020MD supplied by Show Denko Europe (Munich, Germany) was used as the load, while bio-based high-density polyethylene (bioPE) SHA7260 grade, with a density of 0.955 g cm⁻³ was used as the matrix, it was provided by Braskem (São Paulo, Brazil) and supplied in pellet form by FKUR Kunststoff GmbH (Willich, Germany). In addition, three different compatibilizers were used halloysite nanotubes (HNTs), ((3-glycidioxypropyl) trimethoxysilane (GLYMO)), and the copolymer polyethylene-graft-maleic anhydride (PE-g-MA) which

were supplied by Sigma Aldrich (Madrid, Spain). Ethanol 96 %v/v with analytical grade was supplied by Scharlau (Barcelona, Spain). Acetic acid (99.7%) supplied by PanReac Applichem (Barcelona, Spain).

2.2. Silanization of HNTs

Halloysite nanotubes (HNTs) were functionalized with silanes (GLYMO) following the procedure indicated by (Garcia-Garcia et al., 2018a). For this, 14.4 g of GLYMO were dissolved in 600 mL of ethanol then, this dissolution was stirred for 15 min at 60 °C. Subsequently, acetic acid was added drop by drop to adjust the pH at 5, once reached the pH required 60 g of HNTs were added and the resultant dissolution was stirred for 2 h at 60 °C. The HNTs treated were obtained by filtration and later washed with ethanol. In order to remove the residual moisture in the silanized HNTs, nanotubes were dried at 70 °C overnight.

2.3. Preparation of samples

BioPE and PBS were pre-homogenized in a zipper bag with each additive PE-g-MA, HNTs, silanized HNTs. Then, materials were processed by melt compounding in a co-rotating twin-screw extruder from Construcciones Mecánicas Dupra, S.L., (Alicante, Spain). The screw diameter is 25 cm and its length-to-diameter ratio (L/D) is 24. During melt processing the temperature profile was set as follows: 145 °C (hopper) – 150 °C – 155 °C – 160 °C (die), since the matrix is a polyethylene, whereas screw rotation speed was adjusted to 19 rpm. The extruded strands were pelletized with an air-knife unit. The resultant pellets were dried at 60 °C for 72 h to remove moisture. The final samples were obtained by injection molding process in a Meteor 270/75 from Mateu & Solé (Barcelona, Spain). The temperature profile for the injection process was set to 120 °C – 125 °C – 130 °C – 135 °C (from hopper to the injection nozzle), the cavity filling was set to 1 s and the compacting pressure was maintained during 10 s. Table 1 shows the set of compositions prepared for each sample considering the amount (phr) of the PE-g-MA, unmodified HNTs, and silanized HNTs in respect of the PBS that is the load of the blend.

Table 1: Summary of compositions according to the weight (wt%) of bioPE, PBS and the (phr) of PE-g-MA, unmodified HNTs, and HNTs treated with silane that were added.

| Sample | bioPE (wt%) | PBS (wt%) | PE-g-MA (phr) | HNTs (phr) | HNTs-sil (phr) |
|----------------------------|-------------|-----------|---------------|------------|----------------|
| bioPE/PBS | 70 | 30 | 0 | 0 | 0 |
| bioPE/PBS/PE-g-MA | 70 | 30 | 3 | 0 | 0 |
| bioPE/PBS/HNTs | 70 | 30 | 0 | 3 | 0 |
| bioPE/PBS/HNTs-sil | 70 | 30 | 0 | 0 | 3 |
| bioPE/PBS/PE-g-MA/HNTs | 70 | 30 | 3 | 3 | 0 |
| bioPE/PBS/PE-g-MA/HNTs-sil | 70 | 30 | 3 | 0 | 3 |

2.4. Characterization of samples

2.4.1. Mechanical tests

Mechanical tests were carried out in a universal test machine Elib 30 S.A.E. Ibertest, (Madrid, Spain) following the ISO 527-1:2012 guidelines. A load cell of 5 kN and a cross-head speed of 5 mm min⁻¹ were used during the tests. Measurements were performed at room conditions and, at least five samples were analyzed. The hardness was measured using the Shore D scale with a durometer model 676-D from J. Bot Instruments (Barcelona, Spain) using ISO 868:2003. Finally, impact strength was obtained in a Charpy pendulum (1-J) on notched (0.25 mm radius V-notch) in rectangular samples from Metrotec (San Sebastián, Spain) following the ISO 179-1:2010. Five different sample values were averaged.

2.4.2. Microscopy characterization

Fracture surface morphologies of the samples after Charpy test were observed by field emission scanning electron microscopy (FESEM). A ZEISS ULTRA 55 FESEM microscope from Oxford Instruments (Abingdon, UK) was used at an acceleration voltage of 2 kV. Then, samples were coated with a gold-palladium alloy in a Quorum Technologies Ltd. EMITECH mod. SC7620 sputter coater (East Sussex, UK).

2.4.3. Thermal tests

Differential scanning calorimetry (DSC) was performed on the samples, with an average weight sample of 5–7 mg in a Mettler-Toledo 821 calorimeter (Schwerzenbach, Switzerland). The samples were placed in 40-µL aluminum-sealed crucibles. Values were analyzed through a thermal cycle, which started with initial heating from 30 to 180 °C, then a cooling to -50 °C, and finally a second heating to 250 °C, all of this at a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere with a constant flow rate of 66 mL min⁻¹. From the second heating it was obtained the melting enthalpies and temperatures.

Thermogravimetric analysis (TGA) was also conducted samples using an average weight of 15–25 mg in a PT1000 from Linseis (Selb, Germany). Samples were first placed in standard 70-µL alumina crucibles and subjected to a heating program in a nitrogen atmosphere with a constant flow rate of 66 mL min⁻¹ from 30 to 700 °C at a heating rate of 10 °C min⁻¹. The temperature measured for a mass loss of 5% (T_{5%}) was considered as the onset degradation temperature, while the temperature at the maximum degradation rate (T_{deg}) was determined from the first derivative thermogravimetry (DTG) curves. All the thermal tests were performed in triplicate.

2.4.4. Thermomechanical test

The dynamic mechanical thermal analysis (DMTA) was conducted in a DMA-1 model from Mettler-Toledo S.A. (Barcelona, Spain), working in Single Cantilever mode. The pieces were subjected to a temperature sweep program from -150 °C to 120 °C at a heating rate of 2 °C min⁻¹. The DMTA tests were run in triplicate to obtain reliable data.

2.4.5. Wettability

The water contact angle of bioPE/PBS blend and compatibilized bioPE/PBS blends was obtained with the use of an optical goniometer EasyDrop-FM140 from Kruss Equipment (Hamburg, Germany), and analyzed at room temperature. The liquid used for the analysis was distillate water with a volume of approximately 5 µL. All contact angles were measured at 7 s after the droplet was dropped into the surface. At least, five different measurements for each film were obtained and averaged.

2.4.6. Color measurements

To determine color coordinates and color changes a colorimetric spectrophotometer Konica CM-3600d Colorflex-DIFF2, from Hunter Associates Laboratory, Inc. (Reston, VA, USA) was used. This employs a standard light D65 and a 10° standard observation angle to determine the CIE Lab color space coordinates L*, a*, and b*. For its part, coordinate L* represents luminance, being L*=0 (darkness) and L*=100 (lightness), in addition, a* represents the color change from red to green, while b* indicates the color change from yellow to blue, and finally, the color variation is indicated by ΔEab*, which was calculated using Equation 1. Five different measurements were performed for each sample

$$\Delta E_{ab}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

3. Results and Discussion

3.1. Mechanical properties

Figure 1 summary the mechanical properties of the bioPE/PBS blend and the compatibilized bioPE/PBS blend with PE-g-MA, unmodified HNTs, and silanized HNTs. For its part, bioPE/PBS blend presents a tensile modulus of 734.9 MPa, a tensile strength of 15.2 MPa, and elongation at break of 6.7%. Similar values were obtained in the study performed by (Darshan et al., 2019) for PBS/HDPE blends with a value of 676 MPa for young modulus and a value between 5% to 7% for elongation at break. With the addition of PE-g-MA, unexpected results were obtained, it was observed a decrease in their mechanical properties with a reduction of tensile modulus, tensile strength, and elongation at break in 12%, 8%, and 31%, respectively, regarding the values of bioPE/PBS blend, respectively, which indicate that it was not obtained a compatibilizing effect in the bioPE/PBS blend, this variation in the effect compared to other similar studies such as (Darshan et al., 2019) could be related to the proportions of bioPE and PBS used, since in the mentioned study the relation considered was (PBS/HDPE) (70/30) while in this study the proportions were the opposite (bioPE/PBS) (70/30).

When HNTs were added to the uncompatibilized blend, the material becomes more brittle regarding the uncompatibilized blend due to the HNTs aggregates and poor particle dispersion that can cause stress concentration (Garcia-Garcia et al., 2018a), therefore, the tensile modulus decreases but in less proportion that in the sample with PE-g-MA. A similar trend was observed in blends of bioPE/PBS compatibilized with

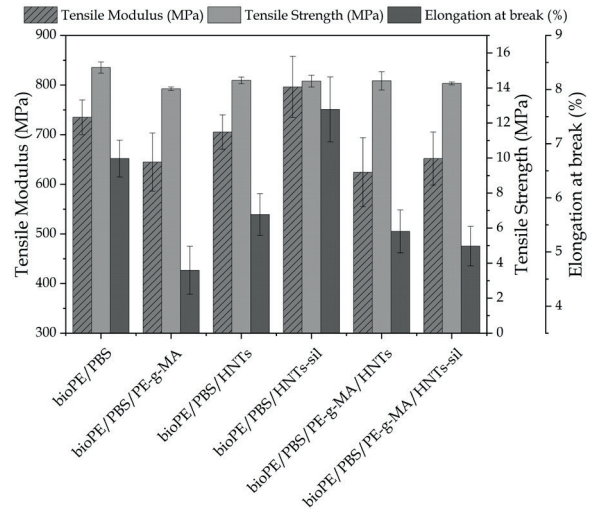


Figure 1: Mechanical properties of bioPE/PBS blend and compatibilized bioPE/PBS blends: tensile modulus (E), tensile strength (σ), and elongation at break (εb).

PE-g-MA and HNTs, possibly caused by the less mobility of the polymeric chains. However, in blends reinforced with silanized HNTs results showed an increase in tensile modulus and elongation at break of 8.3% and 13.4%, respectively, regarding bioPE/PBS blend, this increase in the properties could be related to the increase of the hydrophobicity (this will be discussed later) of the particles in the sample, therefore the particle aggregation decreases and as a result the particles can be better dispersed compared to the samples with unmodified HNTs, which can contribute with the compatibility and adhesion with bioPE/PBS blend, this could indicate that nanotubes reinforce the polymer matrix (Chrissafis, Paraskevopoulos, Tsiaoussis, & Bikiaris, 2009; Garcia-Garcia et al., 2018a; Krishnaiah et al., 2017). According to (Frankland, Caglar, Brenner, & Griebel, 2002) the increase in the modulus is due to the chemical bonding between nanotubes and polymer during processing which allowed to enhance stress transfer. A similar behavior was reported by (Abd El-Rahman, Ali, Khalil, & Kandil, 2020) in which study the HDPE matrix presented a strong interfacial interaction with nanoparticles of calcium carbonate (NPCC).

Regarding tensile strength it is observed that uncompatibilized bioPE/PBS blend presented the highest value (15.2 MPa), nevertheless, after the incorporation of the PE-g-MA, HNTs unmodified, and silanized HNTs, the value hardly changes from 14.4 MPa except for the sample with PE-g-MA that presents a slight decrease with a value of 13.9 MPa. Hence, Figure 1 indicates that this property is not greatly affected by the compatibilizer, in addition, this could indicate a low interaction between compatibilizers and the polymer blend (Tanniru, Yuan, & Misra, 2006).

Figure 2 indicates that the impact strength hardly changes with the incorporation of coupling agents in the bioPE/PBS blend, which implies a low interaction between polymer matrix and compatibilizers (Abd El-Rahman et al., 2020). While the hardness decreases in the samples that have

incorporated PE-g-MA, HNTs unmodified, and silanized HNTs, being the lowest value the sample with PE-g-MA and silanized HNTs that present a decrease of 73% regarding uncompatibilized blend, which indicates that the use of these two compatibilizers worsen this property.

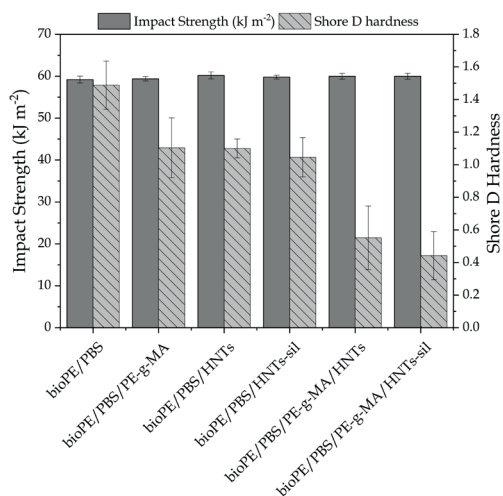


Figure 2: Mechanical properties of bioPE/PBS blend and compatibilized bioPE/PBS blends in terms of impact strength (kJ m^{-2}) and Shore D hardness.

3.2. Morphological characterization

Figure 3 shows the FESEM images from the different samples after the impact test. In Figure 3a it is observed the fracture surface of bioPE/PBS blend, which indicates the immiscibility of the two polymers due to the formation of the two well-differentiated phases: the matrix, which corresponds to the bioPE due to it has the highest proportion in the blend, and the small spherical particles being pulled out that present distribution in the range of (1–6.5) μm correspond to the PBS (Ferri et al., 2020). Then, in Figure 3b, it can be seen that PE-g-MA causes a slight improve in the compatibilization between the two polymers in some areas of the blend due to some boundaries between bioPE and PBS phases became less discernible, it can also be said that the size of the PBS particles decrease, however, this effect was not enough to contribute with the improvement of mechanical properties when comparing with the uncompatibilized blend as was indicated before. Figure 3c and Figure 3d contain unmodified HNTs and silanized HNTs, respectively, in the first case, it can be seen some HNTs agglomerates (see yellow arrows), this could be related to the lack of interactions between the HNTs (hydrophilic particles) and the blend (hydrophobic), while in the second one silanized HNTs are more dispersed over the blend and it is observed that spherical particles of PBS are more embedded into the matrix (see yellow arrows), which indicates a better interaction between polymers. Later with the addition of unmodified HNTs and silanized HNTs in blends with PE-g-MA Figure 3e and Figure 3f, respectively, it is possible to evidence a decrease in the domain size of PBS, this due to a possible interaction of PE-g-MA with the ester linkage of PBS, which could improve the adhesion between the two phases (Darshan et al., 2019), in which study it was reported a similar trend in the morphology obtained in PBS/HDPE/PE-g-MA blend when adding

carbon nanotubes (CNT). In another study carried out by (Rafiee et al., 2016) it was observed that the incorporation of organo-modified layered double hydroxides (LDH) as nanoparticles and maleated polypropylene (PP-g-MA) as compatibilizer into de polypropylene (PP)/ethylene-vinyl acetate copolymer (EVA) blend promote the reduction of EVA domain size.

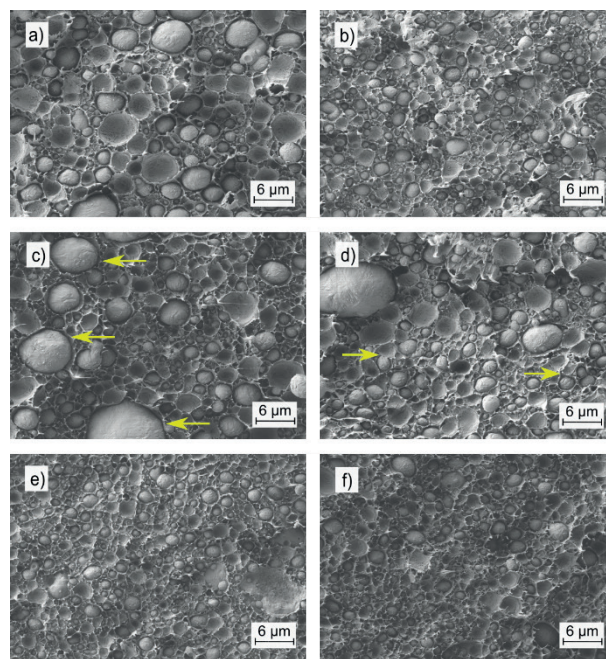


Figure 3: Field emission scanning electron microscopy (FESEM) micrographs of the fractured surfaces of the bioPE/PBS blend and compatibilized bioPE/PBS blends: (a) bioPE/PBS, (b) bioPE/PBS/PE-g-MA, (c) bioPE/PBS/HNTs, (d) bioPE/PBS/HNTs-sil, (e) bioPE/PBS/PE-g-MA/HNTs, (f) bioPE/PBS/PE-g-MA/HNTs-sil. Images were taken at 2500x with scale markers of 6 μm .

3.3. Thermal properties

Figure 4 shows the differential scanning calorimetry (DSC) thermograms of the bioPE/PBS blend, and the compatibilized bioPE/PBS blends. It can be observed that melting point occurs in two steps, which indicates the existence of the two phases due to the immiscibility of the polymers, these values are presented in Table 2, the first peaks in each sample correspond to the peak of PBS at around of 115 °C and the second one with the peak of bioPE that was determined at around 135 °C, both values were previously obtained in the studies performed by (Liminana, Garcia-Sanoguera, Quiles-Carrillo, Balart, & Montanes, 2019; Rojas-Lema et al., 2021a). However, since these two temperatures are close, the transitions present some overlapping, this can be corroborating with the curve of neat bioPE presented in Figure 4, this does not allow to obtain an accuracy melting enthalpy value and therefore the crystallinity degree cannot be either determined. The addition of the unmodified HNTs and silanized HNTs hardly changes the melting point of the blends considering both temperatures regarding the peaks identified in bioPE/PBS blend.

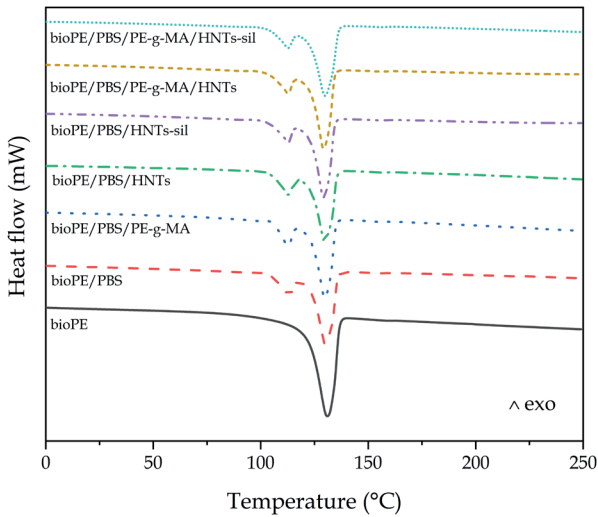


Figure 4: Heating curves obtained by differential scanning calorimetry (DSC) of bioPE/PBS blend and compatibilized bioPE/PBS blends.

Figure 5a,b indicates the thermogravimetric (TGA) curves of the bioPE/PBS blends, the main thermal transitions are summarized in Table 3. Results show that the onset degradation temperature ($T_{5\%}$) of the bioPE/PBS blend compatibilized with PE-g-MA, HNTs, and the combination of both decrease regarding the uncompatibilized blend, however, considering the temperatures obtained it can be said that the values of onset degradation temperature ($T_{5\%}$) in the different samples are within the range from the neat PBS (336 °C) to the neat bioPE (343 °C), which could indicate that those samples are thermally stables (Liminana et al., 2019; Rojas-Lema, Ivorra-Martinez, Lascano, Garcia-Garcia, & Balart, 2021b). On the other hand, the bioPE/PBS reinforced with HNTs treated with silane allow an increase in this value in 12 °C. It can be observed the decomposition occurs in two steps due to the immiscibility of the polymers. In Figure 5b it is evident the improvement in both decomposition temperatures, especially in samples that contain unmodified HNTs or silanized HNTs, being the blend that contains silanized HNTs the one with the major increase (27 °C) in the T_{deg2} regarding the bioPE/PBS blend.

According to (Pöllänen, Pirinen, Suvanto, & Pakkanen, 2011), the addition of unmodified HNTs and silanized HNTs promote the increase in the decomposition temperature, which indicates that the presence of nanotubes hinders the decomposition of the blends at high temperatures.

Table 2: Main thermal parameters of bioPE/PBS blend and compatibilized bioPE/PBS blends in terms of melting temperature (T_m).

| Sample | T_{m1} (°C) | T_{m2} (°C) |
|----------------------------|---------------|---------------|
| bioPE/PBS | 113.2 | 129.9 |
| bioPE/PBS/PE-g-MA | 112.6 | 130.1 |
| bioPE/PBS/HNTs | 112.9 | 129.3 |
| bioPE/PBS/HNTs-sil | 112.6 | 129.6 |
| bioPE/PBS/PE-g-MA/HNTs | 112.6 | 129.1 |
| bioPE/PBS/PE-g-MA/HNTs-sil | 112.6 | 129.9 |

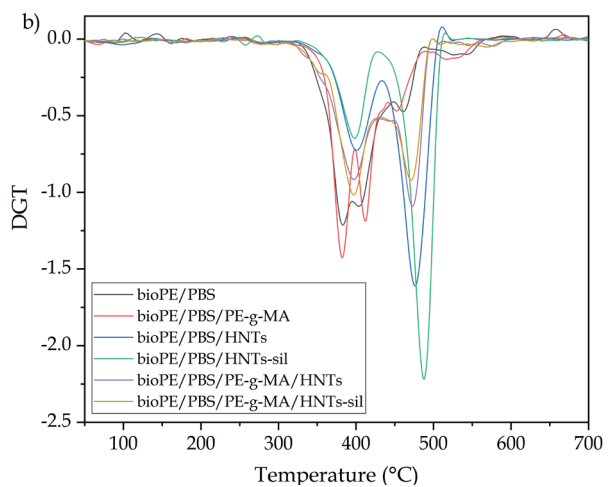
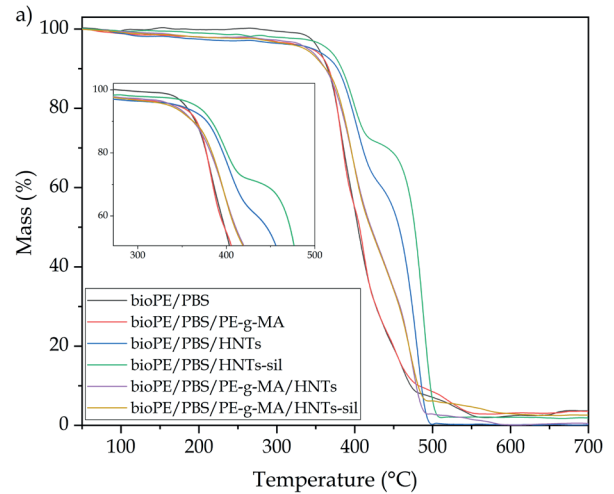


Figure 5: a) Thermogravimetric analysis (TGA) and (b) first derivative (DTG) curves of bioPE/PBS blend and compatibilized bioPE/PBS blends.

The same conclusion was stated by (Krishnan & George, 2014) in which study it was obtained an increase in the decomposition temperature at low clay loading until 4 wt% in blends of polypropylene/polystyrene. On the other hand, (Krishnaiah et al., 2017) state that the thermal

Table 3: Main thermal parameters of bioPE/PBS blend and compatibilized bioPE/PBS blends in terms of onset degradation temperature ($T_{5\%}$), temperature of maximum degradation (T_{deg1} , T_{deg2}), and residual mass at 700 °C.

| Sample | $T_{5\%}$ (°C) | T_{deg1} (°C) | T_{deg2} (°C) | Residual mass (%) |
|----------------------------|----------------|-----------------|-----------------|-------------------|
| bioPE/PBS | 353.2 | 382.3 | 460.3 | 3.7 |
| bioPE/PBS/PE-g-MA | 344.3 | 381.8 | 452.3 | 3.5 |
| bioPE/PBS/HNTs | 345.6 | 400.8 | 475.8 | 0.2 |
| bioPE/PBS/HNTs-sil | 364.8 | 397.8 | 487.3 | 1.9 |
| bioPE/PBS/PE-g-MA/HNTs | 339.9 | 397.3 | 472.8 | 0.5 |
| bioPE/PBS/PE-g-MA/HNTs-sil | 335.8 | 397.3 | 471.3 | 2.5 |

and also the mechanical properties of the samples with modified HNTs and the polymer matrix will depend on the reaction between the functional groups of organo-silane and the carbonyl groups of the matrix, in this case, the bonds could be between silanized HNTs and the PBS that is the polymer with carbonyl groups in its structure.

3.4. Dynamic mechanical thermal analysis

The DMTA allows to characterize mechanical properties in dynamic conditions as a function of a heating cycle, it provides information about storage modulus and damping factor. The curve of storage modulus as a function of temperature is shown in Figure 6a. Results indicate that samples with silanized HNTs presented high values of storage modulus regarding bioPE/PBS blend, which indicates a decrease in the molecular mobility in samples with unmodified and modified HNTs, which is related to the change in the tensile modulus indicated previously. In the study performed by (Montava-Jorda, Chacon, Lascano, Sanchez-Nacher, & Montanes, 2019) it was also observed that the addition of HNTs in the PLA matrix caused an increment in the storage modulus.

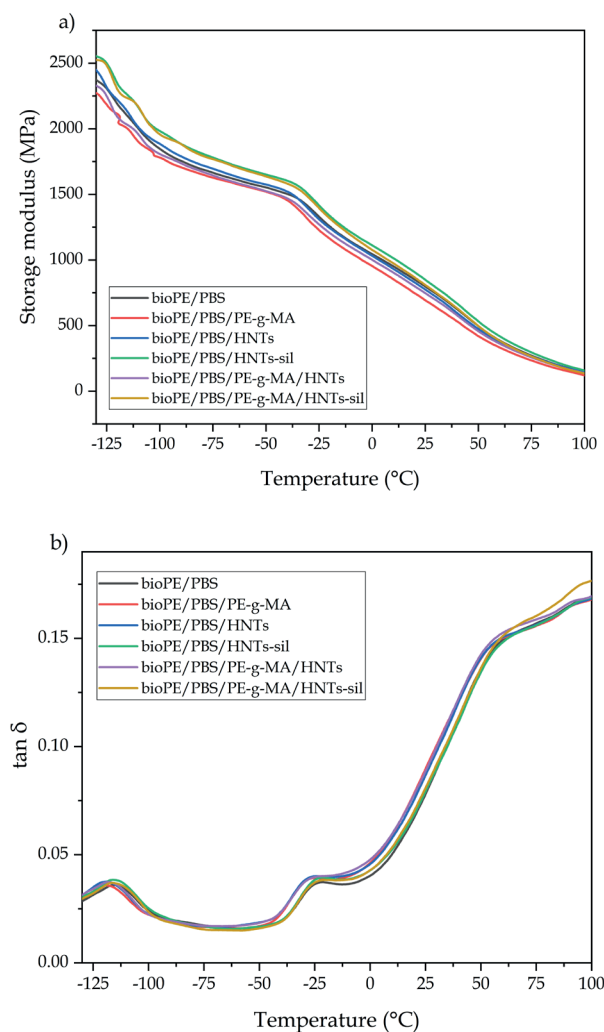


Figure 6: Dynamic mechanical thermal analysis (DMTA) curves of bioPE/PBS blend and compatibilized bioPE/PBS blends: (a) Storage modulus (E') and (b) Dynamic damping factor ($\tan \delta$).

With respect to glass transition temperature (T_g) according to works previously performed of bioPE and PBS the values obtained were around -114.6°C and -236°C , respectively (Liminana, Quiles-Carrillo, Boronat, Balart, & Montanes, 2018; Rojas-Lema et al., 2021a). These values are close to the peaks presented in Figure 6b for the different blends, the first peak (T_{g1}) has moved and decreased from -114.96°C for bioPE/PBS blend to a value of -119.56°C for compatibilized bioPE/PBS blend with PE-g-MA as it is indicated in Table 4, meanwhile, values in the second peak (T_{g2}) show an increase from -24.86°C for bioPE/PBS blend to -20.76°C for samples with PE-g-MA and silanized HNTs, which indicates that the compatibilizers added can slightly hinder the mobility of bioPE/PBS blend. This behavior also indicates that there was not optimal miscibility between the two polymers (Hassan, Wei, Jiao, & Muhuo, 2013; Zhu et al., 2018).

3.5. Wettability

The water contact angle (θ_w) can reflect the hydrophobic or hydrophilic character of the surface of the blends. In general, hydrophobic materials such as polymers present higher water contact angles. According to (Aldas, Pavon, Ferri, Arrieta, & López-Martínez, 2021) the range θ_w higher than 65° indicates hydrophobic surfaces, while θ_w lower than 65° is indicative of hydrophilic surfaces. The resulting blend of bioPE/PBS is hydrophobic, this due the bioPE matrix (the majority phase in the blend) is a hydrophobic material. In Table 5, it is observed that the addition of unmodified HNTs as was expected promote the major decrease of the water contact angle around 67.5° , which represent a decrease of the 28% regarding uncompatibilized blend. Nevertheless, the use of the silanized HNTs as compatibilizer allows a considerable improvement in the hydrophobicity reaching a value of 82.7° . Therefore, it can be stated that the addition of nanotubes provides some hydrophilicity to the blends due to the hydroxyl groups present in HNTs, so the hydrophobicity of the bioPE/PBS blend was affected, however, this could be balanced by the addition of silanized HNTs to the blends. In the study performed by (Platnieks et al., 2020) it is observed that the addition of 40 wt% of nanofibrillated cellulose (NFC) or microcrystalline cellulose (MCC) to the PBS matrix cause a slight

Table 4: Dynamic mechanical thermal analysis (DMTA) parameters of bioPE/PBS blend and compatibilized bioPE/PBS blends.

| Sample | T_{g1} ($^\circ\text{C}$) | T_{g2} ($^\circ\text{C}$) |
|----------------------------|-------------------------------|-------------------------------|
| bioPE/PBS | -114.9 | -24.8 |
| bioPE/PBS/PE-g-MA | -119.5 | -21.9 |
| bioPE/PBS/HNTs | -118.6 | -23.8 |
| bioPE/PBS/HNTs-sil | -116.2 | -21.1 |
| bioPE/PBS/PE-g-MA/HNTs | -118.3 | -22.0 |
| bioPE/PBS/PE-g-MA/HNTs-sil | -116.7 | -20.7 |

Table 5: Wettability through water contact angle measurements in bioPE/PBS blend and compatibilized bioPE/PBS blends.

| Sample | Water contact angle (θ_w) |
|----------------------------|------------------------------------|
| bioPE/PBS | 93.3 ± 1.4 |
| bioPE/PBS/PE-g-MA | 89.4 ± 1.1 |
| bioPE/PBS/HNTs | 67.5 ± 0.6 |
| bioPE/PBS/HNTs-sil | 82.7 ± 2.0 |
| bioPE/PBS/PE-g-MA/HNTs | 84.7 ± 2.1 |
| bioPE/PBS/PE-g-MA/HNTs-sil | 89.0 ± 0.3 |

decrease in the water contact angle. In other study carried out by (Garcia-Garcia, Lopez-Martinez, Balart, Strömberg, & Moriana, 2018) it is possible to note that the incorporation of pine cone cellulose nanocrystals (CNCs) causes a decrease in the θ_w from 80° in blends of poly(3-hydroxybutyrate)/poly(ϵ -caprolactone) (PHB₇₅/PCL₂₅) to 72.3° in blends with 7% of CNCs.

3.6. Optical characterization

Figure 7 shows the appearance for the different samples, as it can be seen there is no apparent color difference between the samples, and this can be corroborated by the ΔE_{ab^*} presented in Table 6, this due to both polymers present similar luminance, in addition, the rest of compatibilizers PE-g-MA, unmodified HNTs, and silanized HNTs did not contribute with a considerable color variation.

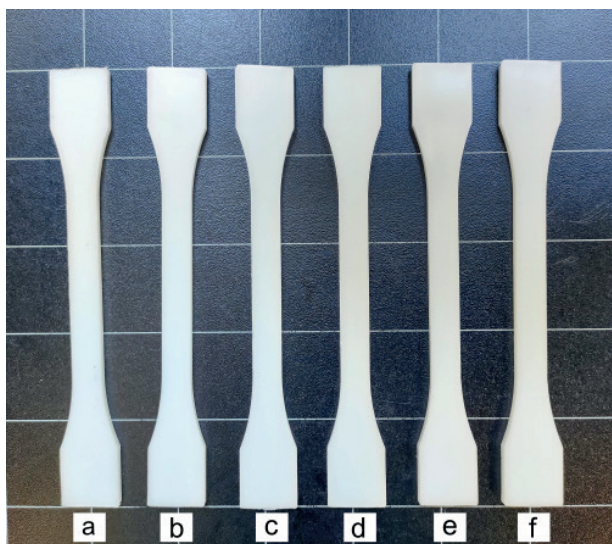


Figure 7: Injection-molded samples of bioPE/PBS blend and compatibilized bioPE/PBS blends: a) bioPE/PBS; b) bioPE/PBS/PE-g-MA; c) bioPE/PBS/HNTs; d) bioPE/PBS/HNTs-sil; e) bioPE/PBS/PE-g-MA/HNTs, and f) bioPE/PBS/PE-g-MA/HNTs-sil.

Table 6: Color parameters (L*, a*, b*) and color difference (ΔE_{ab^*}) of the injection-molded samples.

| Sample | L* | a* | b* | ΔE_{ab^*} |
|----------------------------|------------|------------|-----------|-------------------|
| bioPE/PBS | 79.9 ± 0.3 | -1.7 ± 0.0 | 1.3 ± 0.4 | - |
| bioPE/PBS/PE-g-MA | 81.1 ± 0.2 | -1.6 ± 0.0 | 1.3 ± 0.1 | 1.2 ± 0.2 |
| bioPE/PBS/HNTs | 79.9 ± 0.3 | -1.4 ± 0.1 | 1.7 ± 0.5 | 0.8 ± 0.2 |
| bioPE/PBS/HNTs-sil | 80.4 ± 0.3 | -1.6 ± 0.1 | 0.9 ± 0.3 | 0.6 ± 0.3 |
| bioPE/PBS/PE-g-MA/HNTs | 80.9 ± 0.5 | -1.4 ± 0.0 | 1.2 ± 0.2 | 1.1 ± 0.5 |
| bioPE/PBS/PE-g-MA/HNTs-sil | 81.2 ± 0.2 | -1.6 ± 0.1 | 1.4 ± 0.4 | 1.3 ± 0.2 |

4. Conclusions

This study reports the effect of the use of three different compatibilizers PE-g-MA, unmodified HNTs, and silanized HNTs in the blend of bioPE and PBS. According to the results, the bioPE/PBS blend reinforced with silanized HNTs allowed an important increase in the tensile modulus and elongation at break regarding bioPE/PBS blends of about 8% and 13%, respectively, which indicate an improvement in the interaction between the blend and the silanized HNTs, these results were supported by FESEM images, since the blend compatibilized with silanized HNTs presented a better dispersion over the matrix comparing to the blend with unmodified HNTs, this could be related to the hydrophobicity achieved by the HNTs particles treated by silanization because it could avoid the particles agglomeration. This increase in hydrophobicity of the compatibilized blend was verified by the wettability analysis that indicated an increase in the water contact angle of around 23% in samples with silanized HNTs regarding those with unmodified HNTs. In addition, impact strength did not present variation between the samples, which indicates that the incorporation of the compatibilizers did not change the toughness of the materials regarding bioPE/PBS blend. The effect of unmodified and silanized HNTs in thermal properties was observed through TGA analysis with the increase in the degradation temperatures identified, the first one (T_{deg1}) for PBS and the second one (T_{deg2}) for bioPE. In particular, the composite with silane-treated HNTs was the one that presented the higher temperatures for both peaks, allowing an improvement of 4% and 6%, regarding T_{deg1} and T_{deg2} of uncompatibilized bioPE/PBS blend, respectively. DMTA confirmed the immiscibility of the two materials in the blend due to the existence of two glass transition temperatures that correspond to bioPE and PBS, however, there was identified an increase in the T_{g2} (that correspond to the PBS phase) of about 4 °C in blends compatibilized in the first place with silanized HNTs and in the second place with PE-g-MA and silanized HNTs. In brief, it can be said that the incorporation of HNTs and especially silanized HNTs allowed to enhance the compatibilization in bioPE/PBS blends and as a consequence the improvement of mechanical and thermal properties, which can expand the use of this type of materials and contribute to optimizing them to meet customer demands.

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