Synthesis and Properties of Bionanocomposites of Polyhydroxybutyrate-Polylactic Acid Doped with Copper and Silver Nanoparticles

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Received 12 December 2018; Revised 19 June 2019; Accepted 25 July 2019; Published 28 August 2019

Global pollution has caused a real interest on the use of biodegradable materials to the sustainable development. PLA and PHB are interesting materials due to their properties and their biodegradability, and their blends in different ratios are proposed in this study; also, Ag and Cu nanoparticles were incorporated to observe possible enhances and advantages on it. Blends were characterized through FTIR, TGA, tensile, and DMA tests. Theoretically, results obtained were coherent; FTIR spectra showed a characteristic band (around 1740 cm⁻¹) corresponding to the carbonyl bond at different intensities for each blend which is an evidence of the polymers. Likewise, TGA results showed different marked decomposition points (except for PLA/PHB 70/30), which is another indicative parameter. Regarding tensile tests, PLA/PHB/nanoparticle (NP) blends showed higher Young modulus value action improving exponentially some properties and they can act as a powerful complementary component even in small amounts. The NPs incorporated exhibited clustering due to the blending process with ranges from 93.24 nm for Cu to 123.71 nm for Ag.

1. Introduction

Currently, global pollution is being an important motivation in scientific research since the modern approach is focused on correcting and modifying harmful environmental practices and replacing them with sustainable and positive policies for our environment. It is known that the plastic industry has contributed significantly to the current state of pollution because the polymeric materials used so far in various applications are not biodegradable. Today, it is estimated that plastic solid waste reaches approximately 250 metric tons per year, a condition that generates highly negative impacts on the environment where they are located [1]. Thus, the need arises to find out and incorporate viable and sustainable solutions that reduce the environmental impact and have an ideally better performance than the options currently found in the market. In this regard, biodegradable polymers emerged as one of the solutions to take into account to reduce this problem; a biodegradable polymer has the ability to degrade or reduce in simple molecules under environmental conditions. Knowing this, we presented two biodegradable polymers that have been taken into account in recent years and that will be analyzed during this brief study: polyhydroxybutyrate (PHB) and polylactic acid (PLA). The PLA (polylactic acid) is synthesized from the fermentation of lactic acid, with amorphous morphology, offering attractive advantages such as biocompatibility, easy processing, hydrophobicity, low synthesis cost (requiring between 25 and 55% less energy than is needed to produce polyolefins), and high transparency. However, it has some disadvantages such as its sensitivity to thermal degradation and poor performance for barrier properties, among others [1–3]. On the other hand, the PHB is synthesized from the bacterial fermentation, has semicrystalline morphology, and
also offers advantages among which can be mentioned: good barrier properties and moderately good mechanical properties, but offers disadvantages such as low resistance to thermal degradation, high cost, and fragility [1, 3].

Given these characteristics, it can be said that these materials could complement each other to be used in a novel application. Arrieta et al. [1] and Zhang et al. [2] reported studies of PHB/PLA blends and discussed important improvements on them with 25% w/w of PHB; among other things, they mentioned an increase in crystallinity and mechanical properties and a decrease in oxygen permeability. Knowing this, we made the study using composition rates between 20, 25, and 30% w/w of PLA in order to evaluate the blend behavior. However, it is also remarkable that, most likely, the help of other components will be needed to achieve an optimal balance between the properties with which they are counted and the objective to be achieved. In this sense, materials have been progressively developed that have contributed a great development and exponential improvements in the scientific field; it is about the nanoparticles (NPs). These materials are very interesting because their small size and, therefore, their large surface area are able to provide large changes in the properties of a material using small proportions. Of course, one of the great challenges of science is to control the size and reactivity of them [4]. Silver nanoparticles (AgNPs) and copper nanoparticles (CuNPs) are widely known and used for their antimicrobial effects, which would make a great contribution to the aforementioned mixtures in food packaging applications, for example. However, previous studies suggest being quite careful as it has been shown that, depending on some factors such as particle size and aggregate amounts, the release of nanoparticles can occur, which can generate harmful effects for the human body and even for the environment.

The objective of this study is to characterize PHB/PLA blends in different proportions to propose or verify their industrial applicability of the composite. However, it has also been decided to incorporate Cu and Ag nanoparticles in small percentages (1%) to observe their effect and to corroborate if a bonding or doping of this type is really useful to improve bactericidal properties as well [5, 6] that can be used for packaging.

### 2. Materials and Methods

#### 2.1. Materials

2.2. PHB/PLA and PHB/PLA/NP Blends. Physical mixture was made between the components of the different samples; it is necessary to note that the PHB, the silver nanoparticles and, the copper nanoparticles 50 nm (CuNPs) were initially in powder form, while the PLA was in the form of pellets (the main properties of PHB and PLA are summarized in Table 1). Approximately, 100 g of mixture was made for each one. The nomenclature was created according to the ASTM D638 standard. Table 2 shows the conditions to which the molding of specimens was carried out.

#### 2.3. Thermogravimetric Analysis (TGA).

The sample was characterized in a TGA analyzor, TA Instruments model Q50. The behavior and thermal stability of the sample were evaluated in the range of 25°C to 600°C, using a heating rate of 10°C/min. The analysis of each trial was approximately 60 minutes.

#### 2.4. Infrared Spectroscopy (FTIR).

IR studies were made using a Fourier-transform infrared spectroscopy spectrometer, PerkinElmer Model Spectrum Two with accessories dedicated to the study of polymers, with the ATR (attenuated total reflectance) system. The FTIR test was performed in the range between 450 and 4000 cm⁻¹, with a resolution of 4 cm⁻¹ and a laser incidence of 20 repetitions.

#### 2.5. Tensile Tests.

For tensile tests, the test pieces (type IV) and the procedure were made according to the ASTM D638 [7]. Test pieces were made through a mini injection molding machine (Thermo Scientific brand, model HAAKE Minijet II, was used as a molding tool). Tests were made in an Instron machine at 1 mm/min speed. Table 3 shows the conditions to which the molding of specimens was carried out.

#### 2.6. DMA Tests.

DMA (dynamic mechanical analysis) tests were performed on a PerkinElmer DMA 7e mechanical

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**Table 1: Polyhydroxybutyrate (PHB) and polylactic acid (PLA) main properties.**

<table>
<thead>
<tr>
<th>Material</th>
<th>MFR (g/10 min)</th>
<th>Density (g/cc)</th>
<th>Company name</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHB</td>
<td>8-15</td>
<td>1.25</td>
<td>Ningbo Tianan Biologic Mat.</td>
<td>Injection molding/thermoforming</td>
</tr>
<tr>
<td>PLA 4032</td>
<td>7*</td>
<td>1.24</td>
<td>NatureWorks</td>
<td>Extrusion</td>
</tr>
<tr>
<td>PLA 7001D</td>
<td>6*</td>
<td>1.24</td>
<td>NatureWorks</td>
<td>Injection stretch blow molded bottles</td>
</tr>
</tbody>
</table>

*210°C, 2.16 kg

**Table 2: Proportions of components used for each blend obtained.**

<table>
<thead>
<tr>
<th></th>
<th>PLA (%wt)</th>
<th>PHB (%wt)</th>
<th>AgNPs (%wt)</th>
<th>CuNPs (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA/PHB</td>
<td>70.0</td>
<td>30.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PLA/PHB</td>
<td>75.0</td>
<td>25.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PLA/PHB</td>
<td>80.0</td>
<td>20.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PLA/PHB/Ag</td>
<td>74.5</td>
<td>24.5</td>
<td>1.0</td>
<td>—</td>
</tr>
<tr>
<td>PLA/PHB/Cu</td>
<td>74.5</td>
<td>24.5</td>
<td>—</td>
<td>1.0</td>
</tr>
</tbody>
</table>
dynamic rheometer. For the test, a sample piece of each blend was used using a cup plate method at 1 Hz of frequency, heated from 25°C to 200°C at a heat rate of 10°C/min. The static force was 550 mN and the dynamic force 500 mN.

2.7. TEM. By transmission electron microscopy (TEM) and electron diffraction (ED), the micrographs of transmission were obtained using a copper grid covered with a sheet of carbon. A drop of the colloid was placed in a grid of 150-mesh copper and dried. The electron diffraction was also performed in the cases of nanoparticles. The micrographs and the diffractions are obtained with the following specifications, 120 kV, 60 cm, and K = 4.209. The calibration is carried out with a film of gold (Aldrich Chemical, 99.99%) that is evaporated in a copper grid. Evaporation was performed using an Edwards 5150 Evaporator.

3. Results

3.1. Thermogravimetric Analysis. Table 4 shows results obtained for thermogravimetric analysis. It can be seen that the PLA has a decomposition temperature between 387.46 and 390.65°C while the PHB decomposes at approximately 282.56°C. The results are coincident with trends of previous studies; for example, Abdelwahab et al. [8] also made tests of TGA with PLA and PHB and obtained decomposition temperatures of 324°C for PLA and 260°C for PHB, helping to understand the phenomena that occur in the other curves, since if it is observed in detail, the appearance of two (and up to three) decomposition temperatures that exhibit the mixtures coincides with the temperatures of the pure components (PHB and PLA) and with the proportion in which they are present. For example, in the PLA/PHB 75/25 mixture, two decomposition temperatures are observed: one at 293.81°C and the other at 357.30°C. For the similarities that these temperatures have to those of the pure components (PHB and PLA) and also knowing that it is a binary mixture in which these temperatures produce a mass reduction approximate to the proportion they are in, it can be said that the thermogravimetric analysis shows coherent results. Similar results can be observed in the mixtures PLA/PHB 80/20 and PLA/PHB/Cu 74.5/24.5/1 where the appearance of two decomposition temperatures that produce temperature losses approximate to the proportion in which each component is found is observed. Last but not least, it is necessary to highlight the PLA/PHB 70/30 and PLA/PHB/Ag 74.5/24.5/1 mixes in which the behavior of the thermograms deviates slightly from the strictly expected theoretical results. In the case of the PLA/PHB 70/30 mixture, three decomposition temperatures are observed and although there are two of them quite similar to that of the pure polymers, the appearance of a third temperature (300.81°C) can be observed between the previous two; in addition, a marked range of difference of mass losses is not observed, which may be due to synergistic effects of the mixture in the said proportion and rheological effects produced by the interaction between the components or miscibility of the system. On the other hand, the PLA/PHB/Ag mixture, although it has two decomposition temperatures similar to those of pure polymers, exhibits higher than expected mass loss ranges (see Table 4); this may be due to existing molecular interactions between the mixture and the added nanoparticles.

3.2. Infrared Spectroscopy (FTIR). The band assignments are shown in Table 5.

As can be seen in Figure 1, the chemical structure of PLA and PHB has groups: a carbonyl group (C=O), a C-O bond, and C-H and C-C bonds. In the middle infrared spectra of
the samples, different characteristic bands appear that show the presence of the bonds mentioned before through the vibrational frequencies characteristic of each one of them.

All mixtures show in broad bands the following: two bands were slightly pronounced at 2980 cm⁻¹ and 2920.44 cm⁻¹ approximately corresponding to the stretching frequency of the CH bond in -CH₃ groups; later, at 1747.49 and 1730 cm⁻¹ approximately, an acute and high-intensity peak characteristic of the carbonyl bond (C=O) is observed; then, at 1453.06 and 1384.55 cm⁻¹, the presence of two peaks corresponding to the asymmetric and symmetric flexion of the group can be noted CH₃. Then, a band is observed at 1358.66 cm⁻¹ corresponding to the deformation of the CH bond in the CH₃ group, and subsequently, a series of peaks are observed between 1182.06 and 870.49 cm⁻¹ attributable to the stretching of the bonds C-C and CO [11, 12].

It should be noted that the before-mentioned bands were considered the most representative of the mixtures and that, as mentioned above, they did not show significant differences in terms of the spectra; in fact, the bands appear approximately in the same percentage of transmittance. Regarding the specific differences mentioned at the beginning of the discussion of this topic (FTIR), it is necessary to note that all PLA/PHB mixtures show, at an approximate frequency of 1720 cm⁻¹, for example, two peaks corresponding to the carbonyl group (C=O) that, by difference of intensities (% transmittance), can be said that one corresponds to signals generated by the PLA and PHB, respectively. This is confirmed because if the spectra of the PLA and the PHB are observed separately, it is noted that for the PLA (4032), the carbonyl band is emitted between 24 and 22% at a frequency of 1747 cm⁻¹ approx. while for pure PHB, the signal is emitted at a higher percentage between 99 and 85% at a frequency of 1731 cm⁻¹, considering that the PLA is the majority phase in all samples, it has to be in the spectra of the mixtures, and the peak with greater intensity appears at a maximum percentage of 22% and is always the lowest frequency which is consistent with the peak generated by the PHB.

3.3. Tensile Tests. The results obtained for the tensile tests are shown in Table 6.

As can be seen in Table 6, as the PLA content in PLA/PHB binary mixtures increases, an increase in stiffness (Young's modulus) is observed. Comparing the results obtained for binary mixtures (PLA/PHB) with higher and lower PLA content, respectively, can corroborate what is stated in the previous idea: if the Young modulus is taken from the sample PLA/PHB 70/30 (4805.00 ± 501.00 MPa) and compared with the results obtained for the 80/20 PLA/PHB mixture (6386.80 ± 189.11 MPa), an increase of 132.91% is observed. These results are theoretically expected since if both polymers are compared in their pure state, the PLA has a rigidity (3600 MPa) [11] greater than that of the PHB (2045 MPa) [12]. Also, it can be seen that when the nanoparticles are added in the binary mixtures, the module increases considerably. Given that PLA/PHB/NP ternary samples were made with proportions of major components (PLA and PHB) quite similar to the binary mixture PLA/PHB 75/25, comparative relationships can be established regarding this mixing ratio. Therefore, if we observe the value of the modulus of elasticity shown by the mixture PLA/PHB 75/25 (5603.25 ± 594.29 MPa) with respect to that of the ternary mixture PLA/PHB/Ag 74.5/24.5/1 (14824.00 ± 508.45 MPa), an approximate increase of 264.56% is evidenced, whereas if it is compared with that of PLA/PHB/Cu 74.5/24.5/1 whose Young modulus was 15726.00 ± 456.21 MPa, an approximate increase of 280% is shown.

Regarding the final strength, behavior marked by a pattern does not occur as in the case of the Young modulus. Regarding this property, it is observed that the values vary independently of the content of PLA or PHB; however, it can be noted that ternary mixtures with NPs exhibit higher values than binary mixtures. Given that the PLA/PHB mixtures with NPs are more rigid than the PLA/PHB mixtures, this result is consistent.

3.4. DMA Tests. The results obtained from the DMA test are shown in Figure 2.

3.4.1. Storage Modulus. When observing Figure 2, it can be noted that mixtures that exhibit the highest stiffness values or storage modulus are the mixtures that contain NPs as part of their components. Regarding binary PLA/PHB mixtures,
there is no clear pattern of behavior related to the content of any of the components of the mixture. Regarding the shape of the curve in general and continuing with the ideas discussed above, this module is indicative of the rigidity of the material; therefore, it is consistent that the values of $G'$ decrease to increase the temperature because when receiving thermal energy, the material has more molecular movement and less resistance to deformation; also, due to the nature of the material, (polymeric) vibrational particle movements are experienced that also favor this decrease. It is important to point out that this decrease occurs around the range between 70 and 60°C, a temperature previously reported by other authors [13] such as the Tg of the PLA, as well as the slight increase in the module near 100 and 120°C since similarly these temperatures are reported as the range of recrystallization of the material. On the other hand, it can be noted that the pure PLA curve has no marked transitions and, as is theoretically expected, has the lowest stiffness of the total sample population.

3.4.2. Loss Modulus. Regarding the loss modulus, it can be observed (in Figure 3) that the mixture that exhibits the
highest values for this property is the PLA/PHB 80/20 while the mixture that exhibits the lowest values is the PLA/PHB 70/30. Regarding the general shape or trend of all the curves, it is clear that there is a peak between 60 and 80°C for all the mixtures; this happens because, as mentioned above, around this temperature range, it has instead the glass transition phenomenon of the PLA which represents the majority component of the mixture; therefore, a decrease in the resistance to flow is experienced causing an increase in the loss modulus that represents the viscous component of the material [14]; in fact, it can be observed that the PLA shows a fairly marked transition in this curve, which is theoretically expected.

3.4.3. Delta Tangent ($\tan \delta$). Figure 4 shows analysis curves, and it can be noted that analogous to the loss modulus, the mixtures exhibit a behavior in which they have a slight peak in the glass transition zone of the material; this shows that the
material has an important viscous component and that when reaching values between 0 and 1, the material behaves mostly as a viscoelastic material [14].

3.5. Transmission Electron Microscopy (TEM). Micrographs obtained act as evidence of CuNP and AgNP presence in PHB/PLA blends. The average size for CuNPs in PHB/PLA/CuNP blends was 93.24 nm. On the other hand, the average size for AgNPs in PHB/PLA/AgNP blends was 123.71 nm. Even in a PHB/PLA micrograph, it can be seen too. Figure 5 summarizes those mentioned above.

It can be observed in PLA/PHB micrography, a two-phase blend, where PLA as a matrix has a clear grey color and PHB seems being black dark particles. On the other hand, AgNPs and CuNPs can be noted for their black color, respectively. Both NPs have an average size around 100 nm which is an acceptable size to get interesting properties in composites.

4. Conclusions

The FTIR spectra of the PLA/PHB and PLA/PHB/NP mixtures showed two bands of the carbonyl bond (C=O) at different frequencies (1747 and 1731 cm⁻¹ approximately) and different intensities (between 20 and 26% of transmittance) evidencing, of course, the presence of the two main components of the mixtures (PLA and PHB) and above all giving indications of immiscibility in the system.

Likewise, the TGA tests of the PLA/PHB and PLA/PHB/NP mixtures show at least two different decomposition temperatures for all the mixtures, which in addition to being similar to those of the pure polymers show a proportional mass loss to the percentage in which the pure components are found in each mixture; however, in the case of the PLA/PHB mixture in a 70/30 ratio, no decomposition ranges were observed, so it can be said that this mixture showed some miscibility.

Regarding tensile results, PLA/PHB/NP mixtures showed a significant increase in their stiffness or Young modulus. The mixture PLA/PHB/Cu was the mixture that showed the highest Young modulus among all with a value of 15.726 ± 0.456 GPa; this exceeded (in the value of the elastic modulus) the binary mixture PLA/PHB 80/20 by 246.23%. The 80/20 mixture showed a value of 6.388 ± 0.189 GPa exceeding the PLA/PHB 70/30 mixture by 132.90%, which was the one with the lowest Young modulus with 4.805 ± 0.501 GPa. Evidently, the content of PLA and NPs caused increased rigidity.

The DMA results show the glass transition zone of the PLA (around 60°C); in addition, the results obtained from tan δ confirm that the material is of the viscoelastic type.

The particle size of the blends are as follows: the particle size of PHB/PLA/CuNP blends was 93.24 nm. On the other hand, the average size for AgNPs in PHB/PLA/AgNP blends was 123.71 nm.

It is very interesting to note that the significant property changes can be achieved adding small amounts of nanoparticles.

Data Availability

The supplementary data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

The authors would like to thank the financial support from the ProyectMacroFacultad 2030 CORFO código 14ENI2-26866 from Universidad del Bio-Bio.

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