Properties of the thermoplastic starch/polylactic acid blends compatibilized by hyperbranched polyester

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Abstract. With the aim of to contribute to the employ of new compatibilizing agent and to the preparation of biodegradable materials, in this study were obtained thermoplastic starch/polylactic acid blends and was evaluated the compatibilizing effect of a hyperbranched polyester polyol of second generation modified with polylactic acid in these blends. The blends were prepared in a torque rheometer. In all cases the weight ratio of thermoplastic starch/polylactic acid was 50/50 wt%. The proportions of the compatibility were 5 wt%, 10 wt% 15 wt%, and 20 wt% regard to the total amount of thermoplastic starch and polylactic acid. The blends were characterized by infrared, thermogravimetric, differential scanning calorimetry, X-ray diffraction, scanning electron microscopy and rheological analyses. Torque value decreased with the proportion of compatibilizing. Therefore, the compatibilizing also acted as plasticizing. By infrared analysis was observed that the increasing on the compatibilizing content enhanced the intensity of the signals corresponding to OH and C=O groups. By X-ray diffraction and differential scanning calorimetry analyses was observed a reduction of the crystallinity of the blends obtained with compatibilizing. By rheological analysis was evidenced the formation of a microstructure, which is able to elastically deform.

1. Introduction

There is currently great concern about the accumulation of plastic materials derived from the petrochemical industry because these are not biodegradable. These pollute rivers, seas and spaces inhabited by humans, attracting rodents and diseases [1]. Non-biodegradable polymers such as low density polyethylene, polystyrene and polypropylene derived from petroleum are widely used in the Colombia packaging industry [2], this has motivated many investigations aimed at replacing them with biodegradable polymers, such as starch and polylactic acid (PLA). Starch is a renewable, biodegradable, low-cost, has high hydrophilicity and poor mechanical properties [3]. This material is not thermoplastic, thus to convert it into thermoplastic starch (TPS) it must be plasticized [4]. PLA is thermoplastic, hydrophobic and it has good mechanical properties [5–8]. However, TPS/PLA blends are incompatible, so it requires a compatibilizing agent that improves the interaction between them and prevents phase separation during mixing [9]. For these blends polyvinyl alcohol [6], maleic anhydride (MA) [7], acetylated thermoplastic starch [8] and toluene diisocyanate [6] have been used as compatibilizing, but the use of hyperbranched polyester of second generation (HBP) has been scarcely reported. In a study was obtained different HBP of second generation modified with PLA [10]. In another study a HBP2G (45 wt%) modified with PLA (55 wt%) was used as compatibilizing.
of TPS/PLA blends (50/50) [11]. The compatibilizing was named HBP2G45 and according to review of the literature this is the unique report about use of this type of compatibilizing in TPS/PLA blends. The physicochemical properties of the blends obtained with HBP2G45 were better than those obtained without it [11]. However, the high proportion of PLA (55 wt%) used in its synthesis makes it more expensive than that obtained with a proportion of 25 wt% of PLA. Therefore, in this study was prepared blends of TPS/PLA by using a compatibilizing obtained from HBP (75 wt%) and PLA (25 wt%). In this study this material is named HBP75. The aim of this study was to employ HBP75 as compatibilizer TPS/PLA blends and to evaluate the effect of this material on the structural, thermal, morphological and rheological properties, which has not been reported.

2. Materials and methods
The PLA was provided by the company Alico S.A. from Colombia. TPS (plasticized tapioca starch) was prepared in our laboratory, the preparation conditions were already reported by us [10]. The HBP75 and TPS were previously prepared by us, this material was named HBP75. The conditions of the preparation and the properties were already reported by us [10,11].

2.1. Preparation of the blends
The respective proportions of TPS, PLA and HBP75 were weighed and homogenized, and taken to torque rheometer Thermo Science. The rheometer was kept at a rotation speed of 50 rpm at 200 °C. The mixing time was 5 min. In all cases the weight ratio of TPS/PLA was 50/50 wt%. The amounts of HBP75 employed were 5 wt% (HBP75-5), 10 wt% (HBP75-10), 15 wt% (HBP75-15) and 20 wt% (HBP75-20) with respect to the total amount of TPS and PLA. In order to estimate the compatibilizing efficiency of the HBP75 in the TPS/PLA blends, a control sample (TPS/PLA 50/50 wt%) without HBP75 was prepared under the same conditions used for obtaining the TPS/PLA blends with HBP75.

2.2. Characterization of the blends
Infrared analysis (IR) was performed in a Perkin Elmer equipment using height scans and a resolution of 4 cm\(^{-1}\). The thermal stability of the samples was determined by thermogravimetric analysis (TGA) on a TA Instruments Model Q-500 using a nitrogen purge. The heating rate used in this analysis was 10 °C/min. For this analysis were weighted around 15 mg of sample. Differential scanning calorimetry (DSC) measurements were executed on a TA Instruments model Q100, the rate of cooling and heating was of 20 °C/min. and a nitrogen purge was used to keep an inert atmosphere. For this analysis was weighted around 6 mg of sample.

The X-ray diffraction (XRD) analysis was realized on a PANalytical X’Pert PRO MPD diffractometer by employing Cu-K alpha radiation (\(\lambda=1.5406\) Å). The operating current and voltage were 40 mA and 45 kV, respectively. The samples for scanning electron microscopy (SEM) analysis were coated with gold. This analysis was performed employing a microscope JEOL JSM 6490LV at an acceleration voltage of 5 kV. The rheological analysis was done in a rotational rheometer of Malvern Instruments, by employing a cone-plate geometry and a gap of 1 mm. The oscillatory analysis was executed by using strain of 0.01%.

3. Results and discussion
Figure 1 shows the graph of torque vs time to the control sample and TPS/PLA blends obtained with HBP75. The control sample exhibited a higher torque value than the blends obtained with HBP75. This means that HBP75 acted as a plasticizing or compatibilizing. In all cases, the torque stabilizes around 4.0 min. indicating that this is the optimal mixing time. The final torque value of the samples decreased with the HBP75 content, which was due to the low viscosity of this material [10]. Figure 2 shows the temperature curve as a function of time. The reduction on temperature is due to the material is initially cold and the system transfer heat to the materials to melt. Therefore, once the material (PLA) is melted the temperature become stable. It explains the reduction on temperature with the increasing of the HBP75 content, which is due to more energy, is required to melt the materials, which
was not observed to the control sample. The same behavior was observed to TPS/PLA blends using the same proportions of TPS, PLA and the HBP2G45 [10] and composites of TPS, lignocellulosic fiber and calcium carbonate [12].

Figure 1. Graphs of torque vs time.
Figure 2. Graph of temperature vs time.

Figure 3 presents the IR spectrum of the samples. For the control sample, the signal at 3430 cm\(^{-1}\) corresponds to the OH groups and the signals at 1850 cm\(^{-1}\) and 2940 cm\(^{-1}\) are due to the symmetrical and asymmetric stretching of -CH\(_2\) and -CH\(_3\) respectively. The signal at 1758 cm\(^{-1}\) is associated to the stretching of the carbonyl group (C = O) present in the PLA. The absorption at 1640 cm\(^{-1}\) is attributed to OH groups and the signals at 1082 cm\(^{-1}\) and 1025 cm\(^{-1}\) correspond to asymmetric stretching C-O of the C-OH and C-O-C (ester groups) respectively [13]. The increase in the percentage of HBP75 enhanced the intensity of the signals to 3430 cm\(^{-1}\), 2940 cm\(^{-1}\), 1758 cm\(^{-1}\) and 1640 cm\(^{-1}\), because these materials have a high percentage of OH and C=O groups in their structures.

Figure 4 shows the difractograms of the PLA, control sample and blends. Some peaks appear at 2\(\theta\) = 16.45º, 18.8º and 22.0º for neat PLA associated with the \(\alpha\) crystalline system [14]. The increase in HBP75 (amorphous) produces a reduction in the peak intensity, which indicates less crystallinity. The blends HBP75-15 and HBP75-20 exhibited better performance since were obtained more amorphous materials. This means that these samples presented highest compatibilization degree. The same behavior was observed to these blends obtained with a HBP2G45 [11].

Figure 3. IR spectra of the samples.
Figure 4. Difractograms of the samples.

Figure 5 presents the DSC thermograms. A glass transition temperature (\(T_g\)) and a melting temperature (\(T_m\)) were observed for the control sample. In the blends, was observed a reduction on \(T_g\) (Table 1), with the increasing on HBP75 content. This means that the HBP75 acted as compatibilizing
for these blends and that the mobility of the chains enhanced with the proportion of this material. The Tm values of the blends was higher than that of the control sample, this is an indication that the structural packing or reduction on lamellar thickness of the control sample were lower than those of the blends. In the other hand, it was not observed a trend on the behavior of $T_m$ with the content of HBP75; this means that the interaction between the PLA chains was different. Another hand, the melting enthalpy ($\Delta H_m$) of the blends HBP75-5 and HBP75-10 were higher than the control sample; this means that for these samples the HBP75 acts as nucleating agent to PLA. This behavior was not followed by the others samples (HBP75-15 and HBP75-20), which indicates that the proportion of HBP75 affected the molecular order of the samples. Highest amorpicity degree was to samples obtained with greatest HBP75 content (HBP75-15 and HBP75-20). The behavior of $\Delta H_m$ obtained in this study is different to that reported to the HBP2G45 [10] using the same proportion of this material. This means that the proportion of the PLA used in the synthesis of HBP2G45 and HBP75 affect the crystallinity of these materials of different manner.

In a study of the compatibilization of starch/PLA blends using MA [7] was obtained a reduction lower than 6 °C in $T_g$. However, in this study was obtained a maximum reduction of $T_g$ of 20.2 °C regards to that of the control sample. Therefore, the HBP75 is better compatibilizing to these blends than MA. The reduction on $T_g$ values obtained in the present study are higher than those obtained using a HBP2G45 whose maximum reduction was of 16.3 °C [11].

Figure 6 shows the thermograms of the blends, the thermal decomposition ($T_d$), are listed in Table 1. All materials exhibited decomposition kinetic in a one step, this allow inferring that the compatibilization process was carried out, since were not observed other inflections in these curves. It was not evidenced a trend of the thermal stability with the amount of HBP75. It is possibly associated to different interaction degree and degradation mechanism [15,16]. The $T_d$ values observed in this study are higher than those obtained using HBP2G45 as compatibilizing of TPS/PLA blends, which is due to highest interaction exhibited by TPS and PLA in the present study [11]. Furthermore, these results also are higher than those observed to TPS/PLA blends prepared by using glycidyl methacrylate as compatibilizing, which present $T_d$ values lower than 280 °C [17]. The TGA results obtained in this study allow inferring that these materials can be process at temperatures lower than 299 °C.
of TPS/PLA using starch modified with MA since these samples did not show homogeneous morphology [5].

Table 1. Values of $T_g$, $T_m$, $\Delta H_f$ and $T_d$ of the samples.

| Samples  | $T_g$ ($^\circ$C) | $T_m$ ($^\circ$C) | $\Delta H_f$ (J/g) | $T_d$ ($^\circ$C) |
|----------|-----------------|-----------------|-----------------|----------------|
| Control  | 59.6            | 153.1           | 2.6             | 301.8          |
| HBP75-5  | 61.3            | 157.7           | 6.2             | 303.4          |
| HBP75-10 | 55.3            | 154.8           | 6.6             | 299.4          |
| HBP75-15 | 41.5            | 153.7           | 0.3             | 312.6          |
| HBP75-20 | 39.4            | 156.8           | 0.4             | 299.4          |

Figure 7. Micrographs of the control sample.

Figure 8. Micrographs of the HBP75-20 blend.

Figure 9. Schematic representation of the interactions between PLA, TPS and the compatibilizing.

The rheological analysis was carried out only to the control sample and the blends HBP75-15 and HBP75-20. Figure 10 shows the graph of complex viscosity ($\eta^*$) as a function of frequency.

Highest viscosity was observed for the control sample. All samples exhibited a reduction on $\eta^*$ with the angular frequency, but then $\eta^*$ increased. The reduction on $\eta^*$ is due to interaction dissociation and disentanglement of the chains. The same behavior was observed to TPS/PLA [18].

The increasing on viscosity is related to the formation of a microstructure able of elastically deforming when exposed to external stress [19]. The formation of this microstructure has been assigned to the complexation reaction between amylose and lipids [20]. In the other hand, between 0.1 Hz and 20 Hz, the $\eta^*$ values of the control sample were higher than those of the HBP75-15 and HBP75-20. It means that the HBP75 also acted as plasticizing agent.
4. Conclusions

In this study were obtained TPS/PLA blends and was evaluated the compatibilizing effect of the HBP75 on the properties of these materials. The control sample exhibited highest final torque value; the optimal mixing time was 4 min. The thermal stability did not show dependence with the amount of compatibilizing; this possibly was due to different interaction degree and degradation mechanism. By SEM analysis was observed that the control sample exhibited a less homogenization degree than the blend obtained with 20 wt% of compatibilizing.

By rheological analysis also was evidenced the plasticizing effect of the compatibilizing, since the complex viscosity decreased with the amount of compatibilizing. The glass transition temperature and melting enthalpy decreased with the compatibilizing content. The blends prepared with a proportion of 20 wt% exhibited highest reduction on crystallinity. This was also confirmed by DSC analysis. The maximum reduction on $T_g$ was of 20.2 °C.

The results of this study are very important since the HBP75 acted as plasticizing and compatibilizing agent, this phenomenon has been scarcely reported.

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