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Evaluation of a hyperbranched polyester polyol as plasticizing agent for composites of recycled polystyrene and rice husk

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Abstract. This study makes a contribution to the preparation of composites from recycled polystyrene and rice husk (it is mainly incinerated producing environmental contamination in Norte de Santander department-Colombia), which will contribute to reduce the accumulation of waste derivatives from polymeric and rice industries in this region. Hence, the aim of this work was to use a hyperbranched polyester as plasticizing agent and to evaluate its influence on the properties of the composites. The proportions of the recycled polystyrene and rice husk were 60 wt% and 40 wt% respectively. In the case of the polyester, were employed amount of 10 wt%, 20 wt%, 30 wt% and 40 wt%. Also was prepared a control sample (0 % of polyester). The results of infrared analysis evidenced changes in the absorption of the hydroxy groups. The thermogravimetric analysis showed that the first thermal decomposition of the composites decreased with the polyester content, but it did not follow the same trend on mechanical properties. The results of scanning electronic microscopy analysis allowed evidence that the fracture mechanism of the composite was fragile. The viscosity of the control sample was lower than that of the composites obtained with the polyester.

1. Introduction

Polystyrene (PS) is a thermoplastic polymer [1]. It presents good resistance to acids and bases, excellent optical clarity, good hardness, high flammability, very good electric insulator, heat and moisture resistant, cushioning, can be easily machined and it is dimensionally stable [1,2]. The PS is widely used in packing industry, electronics industry, toys and home appliances [3]. The consumption of PS has increased so much, this material is non-biodegradable. Therefore, once this material is used it produces environmental problems. This material persists in the environment, which leads to contamination of groundwater, soil, oceans and rivers [4-6]. The recycling of thermoplastic polymer is a good alternative to reduce the environmental contamination, since it conserves non-renewable natural sources and also decrease the emission of gases during the manufacture, transport and disposal of solid waste [7]. Recycled polymers exhibit usually lower impact resistance, melt viscosity and mechanical properties than virgin polymers, which is possibly due to that during its use or the mechanical recycling, the polymer suffer a degradation resulting in reduction of its average molecular weight [8]. With the aim of improved the mechanical properties of the recycled polymers, these polymers have been blended with reinforcement agent.

The natural fibers such as sisal, wood flour, coir, flax, jute and rice husk (RH) have been used as reinforcement agent since these materials have a number of advantages over traditional synthetic fibers, such as glass fibers and carbon fibers, since they are renewability, have high specific strength

and modulus, low density, wide availability, relative nonabrasiveness to processing equipment, biodegradability, cheapness and energy recovery (when incinerated) [9]. Between the natural fibers, the RH has gained great attention due to need to overcome environmental problems caused by agricultural by-products [10]. RH is a major agricultural residue [10], this material is composed by 25 wt.% lignin, 20 wt.% inorganics, 33 wt.% cellulose and 22 wt.% hemicellulose [11]. This material has been used as fertilizer, animal food, chipboards and substrate in greenhouse crops and production of energy or heat (fuel), landfill, etc., [11].

The Norte de Santander department in Colombia had 34.755 ha planted of rice between 2015 and 2016 [12]. It has been reported that for every ton of rice produced, about 0.23 tons of RH are formed [13]. The RH produced in this region is mainly used in the production of energy (incineration of RH) and fertilizer. The incineration of RH produces fumes, ash and toxic gases, leading to serious air pollution [13]. In addition, in Norte of Santander department, RH has been scarcely employed as reinforcement or filler in the polymeric industry. Therefore, it is very important to find pathways to fully use the RH in the packing industry, toys and home appliances and to reduce the use of the non-biodegradable materials in these industries, since with the incorporation of RH will be used less amount of PS and these materials will be more biodegradable than neat PS. Furthermore, in Colombia the RH has been scarcely used in the polymeric industry. Therefore, this study may be attractive because RH is doing used as an alternative to reduce the use of non-biodegradable plastics in the polymeric industry. Some thermoplastic polymer such as low-density polyethylene [13], PS [14], high density polyethylene [15], polypropylene [16], polyvinyl chloride [17], polylactic acid [18], have been blended with RH. All these composites presented better thermal, mechanical, physical and chemical properties than those of the neat polymers [13].

Composite of the PS and RH were prepared, and the effect of the size and proportions of RH were evaluated. The results showed that at lower sizes of RH, the tensile strength increased to some extent and then decreased. In all micrograms obtained by scanning electronic microscopy (SEM) were observed aggregations of the RH [14]. RH is a material that not is thermoplastic [9,14]. Thus, it remains in solid state during the processing, this increase the viscosity of the composite. Therefore, for improving the processing may be used a plasticizing agent. Hyperbranched polyester polyol (HBP) may be an alternative to be employed as plasticizing agent, since it presents low viscosity in solution and molten state [19-21]. So far there are not reports about the use of HBP obtained of first generation (HBP1G) as plasticizing agent of composite of PS and RH. This study makes a contribution important to art state of this material type, to reduction of the environmental impact caused for PS waste and the used of materials derived from agro-industrial waste. Therefore, in this work were prepared composites of recycled PS and RH by using a HBP1G as plasticizing agent. Furthermore, was evaluated the effect of HBP1G amount in the properties of the composites of recycled PS and RH.

2. Materials and methods

Recycled PS was supplied by Ecostretch factory, the RH was provided by the "Arrocera Gelvez, Colombia" factory and the HBP1G was supplied by our group. The properties of HBP1G were previously reported by Rangel, *et al.* [22]. This material theoretically has 8 OH groups in the periphery.

### 2.1. Preparation of the composites

Initially the RH was passed through mill and the granules obtained were passed through a net number 20 whose diameter was 0.841 mm. The composites were prepared in an extruder, by using a mixed speed of 50 rpm. The extruder presented three heating zones; zone 1: 160 °C, zone 2: 170 °C and zone 3: 180 °C. The proportions of the recycled PS and RH were 60 and 40 wt% respectively. In the case of the HBP1G were employed amount of 10 wt%, 20 wt%, 30 wt% and 40 wt% regards to those of recycled PS and RH. These samples were named as 10%, 20%, 30% and 40% respectively. In order to determine the effect of the HBP1G on the properties of the composites was prepared a sample without HBP1G (control sample), which was named as 0 %.

2.2. Characterization of the samples

In order to evidence the interactions between the materials, was done infrared (IR) analysis. This analysis was realized by attenuating total reflectance in a Shimadzu Prestige 21 using ten scans and a range of frequency between 600 cm^{-1} and 4000 cm^{-1}. Thermogravimetric analysis (TGA) was also executed with the aim of determine the thermal stability of the materials. This analysis was performed in a TA Instruments SDT Q600 equipment employing a heating rate of 20 °C/min from room temperature until 600 °C using a nitrogen purge. Tensile test was realized under standard methods ASTM D 638 [23] using specimens type I. This analysis was done by using universal testing machine EMIC employing a deformation rate of 5 mm/min. SEM analysis was executed on cryofractured surfaces by using a Jeol JSM-6490LV. Samples obtained were made conductive by the deposition of a layer of gold. The analysis was performed using a beam acceleration voltage of 20 kV. Rheological analysis was done in a rotational rheometer of Anton Paar using a plate-plate geometer whose diameter was 20 mm and a temperature of 180 °C. The gap used was of 1 mm. This analysis was done under dynamic conditions for angular frequency from 1.0 Hz until 100 Hz and a strain of 0.2%.

3. Results and discussion

Figure 1 presents the IR spectra of the samples. Neat PS spectrum presents a signal at 3024 cm^{-1} which is associated with C-H stretching of aromatic compounds. The signal at 2916 cm^{-1} is attributed to asymmetric stretching of $-CH_2$. The RH spectrum exhibited a signal between 3200 cm^{-1} and 3600 cm^{-1}, which is due to stretching of OH bonds. The signal at 1045 cm^{-1} corresponds to C-O stretching. The same signals have been observed to RH [24]. The sample 0 % exhibited the same signals of the neat PS and RH. However, the signal due to stretching of the OH groups presented a lowest intensity. The samples obtained with HBP1G exhibited the signals of stretching of OH bonds and carbonyl groups. These signals also are present into HBP1G spectrum [22]. The signal attributed to stretching of the OH groups in the samples obtained with HBP1G was of highest intensity to samples prepared with greatest proportion of HBP1G, which was expected since the HBP1G has high number of OH groups (theoretically 8) [22] and the intensity of this signal can increase with its proportion. It was not observed some shift of the signals, which indicates that, was not carried out an interaction between HBP1G and RH through OH groups.
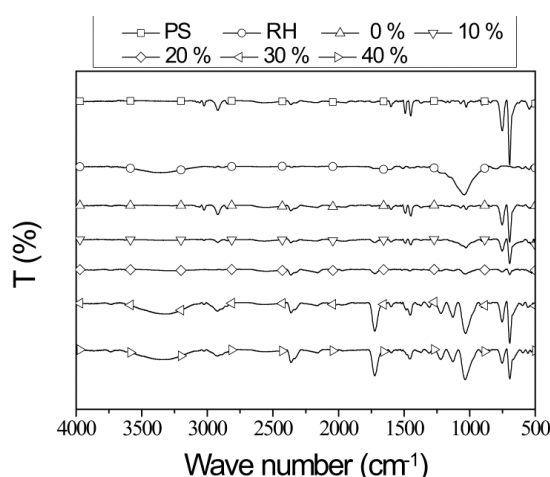
Figure 1. IR Spectra of the PS, RH and the composites.

Figure 2 and Figure 3 exhibit the graphs of the weight vs temperature and derivative weight vs temperature respectively, which was obtained by TGA analysis. Neat PS exhibited only one decomposition temperature (T_d). All composites showed various T_d, which was expected, because the PS and RH are not miscible, since PS is no polar [1,4] and RH is polar [25]. The thermal stability of

the neat PS was higher than that of the RH (Figure 2, Figure 3 and Table 1). RH exhibited a T_d around 100 °C, which is lower than 3 wt%. It is due to the mass loss of water [25]. Furthermore, appeared others two T_d, which are important and it will be the focus of the discussion of the thermal results. The behavior exhibited by RH was due to it contains various compounds and they have different thermal stability, this was mentioned before. The first T_d (T_{d1}) exhibited by RH was lower than that of the sample 0%, but the second T_d (T_{d2}) of these samples were similar. This behavior means that the presence of PS improved the thermal stability of the sample 0%. Another hand, composites obtained from RH and recycled high-density polyethylene and recycled polyethylene terephthalate also exhibited various T_d [25] and the thermal stability did not increase with the amount of RH, but it was higher than that of the composites of PS and RH obtained in this study. Hypothetically, this phenomenon may be due to protection effect done by PS on RH during the heating. In the composites obtained with HBP1G, T_{d1} is associated with RH and T_{d2} with PS. The T_{d1} values of the composites prepared with HBP1G decreased with the amount of the HBP1G, but the T_{d2} did not follow this behavior (Table 1). This may be interpreted as a low interaction between HBP1G and RH, which would occur through OH groups. In the thermograms of the composites was not observed the T_d of the HBP1G (378 °C) [22]. This means that possibly the T_d is overlapped with that of the PS. According to the thermal results, it can be concluded that the thermal stability (T_{d1}) of the composites was affected by the presence of HBP1G, but T_{d2} did no showed a dependence with HBP1G, which is due to PS is no polar [1,4] and HBP1G and RH are polar [22,26], since there is a great number of OH groups in these materials. Furthermore, possibly the HBP1G may participate in the dissociation of interactions between compound present into RH.
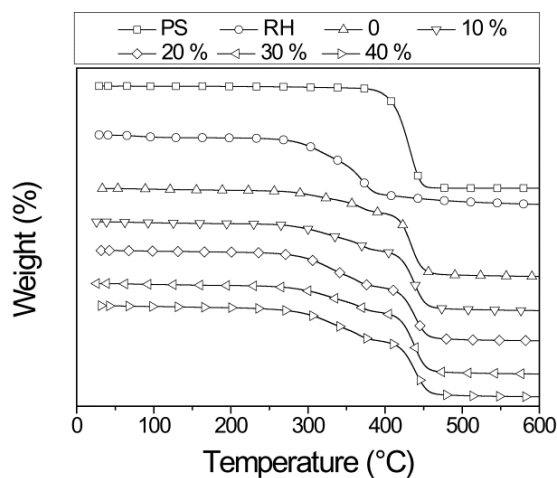

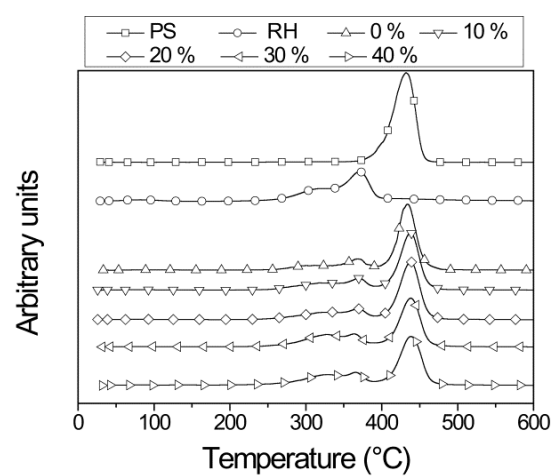
Figure 2. Weight vs temperature.

Figure 3. Derivative weight vs temperature.

The tensile modulus of the neat PS was higher than that of the sample 0%, but the tensile strength followed an opposite behavior (Table 1). The neither tensile modulus nor tensile strength followed a trend with the amount of HBP1G, the same happened with the elongation at break. These behaviors were possibly due to the presence of aggregations or different dispersion degree of the RH and HBP1G. Furthermore, this behavior also has been assigned to the poor dispersion of the fibers and reduced interfacial adhesion to the polymer matrix and poor interfacial adhesion between components [27]. The tensile modulus obtained in the present study is higher than those found for polylactide/starch/rice husk blend whose values were lower than 304 MPa [24]. Tensile modulus and tensile strength of the composites obtained in the present study are comparable with some flour RH biocomposites based on recycled high-density polyethylene/polyethylene terephthalate blends, but the elongation at break is lowest [25]. In another study was reported values of the tensile strength between 21 MPa and 44 MPa for composites obtained from PS and RH (particle size between 350 μm and 310 μm) [14].
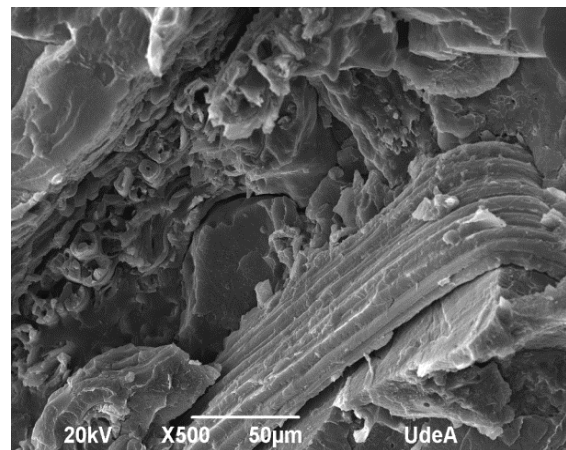
The micrographs of the samples 0% (Figure 4) and 10% (Figure 5) obtained by SEM analysis of the cryofractured surfaces of the composites showed that the mechanism of fracture is fragile (brittle), since the surface was roughness. Furthermore, it can be observed that there is a low adhesion between PS and RH, this is associated with the chemistry nature of these materials [26,27], which was previously mentioned. Furthermore, were observed aggregates of RH, which indicates the low dispersion presented by these samples. It explains the behavior showed by these composites on mechanical properties. In the other hand, all materials exhibited microcavities, which are associated with the extraction of the RH during tensile test. The same behavior has been saw to RH biocomposites, which was attributed to the low interaction between the polymer and RH [25]. The interaction or adhesion between PS and RH can be improved by using a compatible agent.

Table 1. Results of the thermal and mechanical properties of the samples.

| Samples	T_{d_1} (ºC)	T_{d2} (ºC)	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PS	368		3310	24.61	0.75
RH	248	393	-	-	-
0%	269	394	4525	10.09	0.39
10%	264	390	4907	14.68	0.49
20%	249	390	1730	9.18	0.77
30%	246	388	950	3.37	0.64
40%	236	387	1072	5.06	0.41
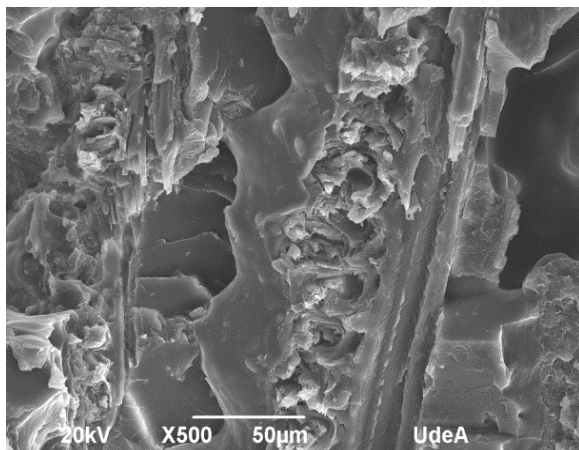
Figure 4. Micrographs of the sample 0%.


Figure 5. Micrographs of the sample 10%.

Figure 6 display the results of the curves of complex viscosity (η^*) vs. angular frequency. Neat PS showed lowest viscosity. The rheological behavior of the composites was pseudoplastic, which is due to disentanglement of the chains. The same behavior has been observed to flour RH as filler in block copolymer polypropylene [28]. All composites prepared by using HBP1G showed lower η^* than sample 0%. This means that the HGBP1G acted as plasticizing agent in these composites. None sample exhibited a trend with the proportion of HBP1G, this possibly was result of the lower dispersion of these materials, which was evidenced by SEM results. Figure 7 and Figure 8 show the storage (G') and loss (G'') modulus vs angular frequency respectively. G' is related with the elastic behavior of the material and G'' represents the dissipated energy. G' and G'' increased with the angular frequency value. This is attributed to the fact that at high angular frequency, the time is short enough to raveling of the entanglements so a small amount of relaxation occur, resulting in a high value of G' and G'' [29]. G' and G'' of the sample 0 % were lower than those of the samples prepared with HBP1G, this means that in these composites was not carry out an interaction between PS and RH.
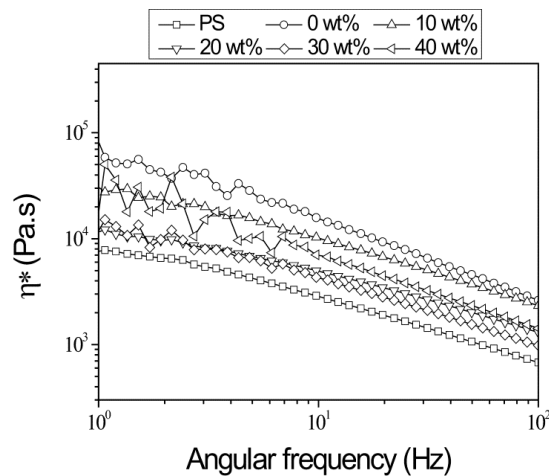
Figure 6. Curve of η* vs angular frequency of the samples.
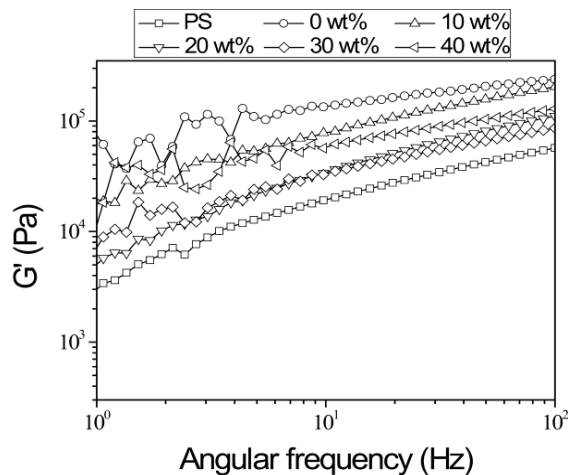
Figure 7. G' vs. angular frequency.
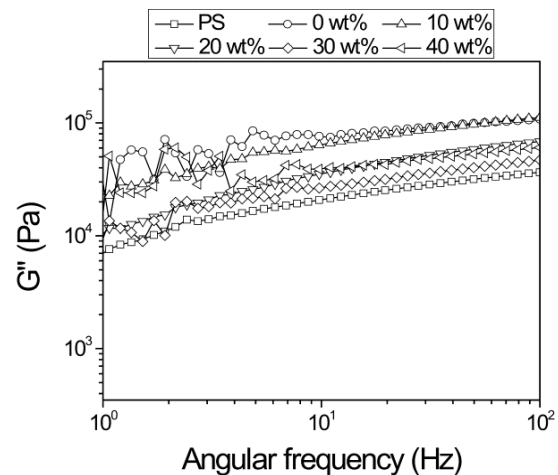
Figure 8. G" vs. angular frequency.

4. Conclusions

This study makes a contribution to reduction the environmental impact of polymer and agro-industrial wastes. Furthermore, it is reported the use of HBP1G as plasticizing agent of composites of recycled PS and RH, which so far has not been stated. By IR analysis was not evidenced some shifted of the signals. Therefore, the PS and RH did not interact. Possibly HBP1G participated in the dissociation of some interactions between components of the RH, since was observed a reduction on T_{d1} with the increasing of the HBP1G content. The composites obtained with HBP1G did not exhibit a trend on properties mechanical; this behavior was due to low dispersion of the RH. By SEM analysis was observed that the PS and RH exhibited a low adhesion, which was attributed to these materials not chemically interaction. However, it can be improved by using a compatibilizing agent. By rheological analysis was observed that the HBP1G acted as plasticizing agent since the η* values of the composites obtained with this material were lower than that of the sample 0%.

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