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# Evaluation of the effect of a hyperbranched polyester on the thermal, rheological, morphological and mechanical properties of polyvinyl chloride/hemp fiber blends

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**Abstract.** The aim of this study was to investigate the effect of the hyperbranched polyester polyol from second generation content on the structural, thermal, rheological, morphological and mechanical properties of recycled polyvinyl chloride/hemp fiber/hyperbranched polyester polyol obtained from second generation blends. In all blends, the amounts of recycled polyvinyl chloride and hemp fiber were 70 wt% and 30 wt% respectively. The blends were obtained in a torque rheometer. The proportions of hyperbranched polyester polyol regards to those of the polyvinyl chloride and hemp fibers were 5 wt%, 10 wt%, 15 wt% and 20 wt%. Additionally, a recycled polyvinyl chloride /hemp fiber blend was prepared to be used as control blend. Infrared analysis was then used to evidence the interaction between components of the blends. The thermal stability of the recycled polyvinyl chloride/hemp fiber/hyperbranched polyester polyol blends was lower than that of the polyvinyl chloride. Furthermore, it was not observed a trend in the thermal behavior of the recycled polyvinyl chloride blends. Hyperbranched polyester polyol increased the glass transition temperature of the blends. Additionally, rheological analysis results indicated that the hyperbranched polyester polyol reduced the viscosity of the blends.

## 1. Introduction

Polyvinyl chloride (PVC) is a plastic material that is typically rigid at room temperature. Therefore, in order to improve some of its properties, PVC has to be mixed with additives. The additives include plasticizing agents, fillers, pigments, heat stabilizers, lubricants, etc. [1]. PVC is used in many applications such as, construction, medical, electrical, office, leisure and sports, packaging, cards, automobile and clothing [2]. In 2013 the production of PVC was about 61 million tones [2]. It is estimated that global demand will rise by about 3.2%/year to 2021 [2].

Once the PVC finishes its utility cycle, it may be incinerated or accumulated. In the case of the incineration for energy recovery, it produces toxic pollutants such sulfur and nitrogen oxides, heavy metals and particulates in both flue gas and solid residues though it can reduce the volume and produce energy [2]. Therefore, this process is not environmentally friendly. On the other hand, the accumulation contaminates the environment, since this material may be disposed in the rivers, oceans and land causing adverse effects on the wildlife, wildlife habitat and human beings. Thus, the recycling of this material is the main alternative to reduce the negative environmental impact.



Unfortunately, sometimes the properties of the recycled PVC are not appropriate for a specific application. An alternative to improve the properties of recycled PVC and to incorporate it again in the productive chain is by blending with natural fiber, which may improve the properties of this material [3]. Natural fibers of hemp are biomaterials and they can be an alternative to replace petroleum in polymer blends, mainly in the application as reinforcing materials, but may be inconvenient to employ as they make it difficult to process, since they reduce the flow. Therefore, plasticizing agents have to be employed to improve the processing of these blends [4]. The plasticizing agent employed to the PVC (phthalates) is derived from petrochemical sources, which are often toxic [5]. A hyperbranched polyester polyol obtained from second generation (HBP2G) could potentially be used as a plasticizing agent, as it has low viscosity in molten and solution state, it is not toxic, and has a high number of OH groups and carbonyl groups [6-9]. Today these formulations are widely employed to phthalates. However, the HBP2G could effectively replace to this material in these formulations. Currently there is still very limited research on the preparation of PVC/hemp fiber/HBP2G (PVCHH) blends. This study, therefore, investigates the use of HBP2G as plasticizing agent of these blends, and in the process makes an important contribution to the reduction of negative environment impact produced by polymeric residue, such as PVC. Consequently, for this study PVCHH blends were obtained and the effect of HBP2G amount on the structural, thermal, rheological, morphological and mechanical properties was studied. Comparison between the properties of PVCHH and PVC/hemp fiber (PVCH) was also done.

## 2. Materials and methods

Recycled PVC was supplied by Tubos de Oriente factory, the hemp fiber was provided by “Asociación Sembrando un Norte” and the HBP2G was supplied by our group. The properties of HBP2G were previously reported by Mesías *et al.* [10]. This material theoretically has 16 OH groups.

### 2.1. Preparation of the blends

Initially the hemp fiber was passed through mill and the granules obtained were passed through a net number 20 whose diameter was 0.841 mm. In order to prepare the blends, the respective amount of PVC (70 wt%), hemp fiber (30 wt %) and HBP2G were placed in a torque rheometer, which was kept under the following conditions: temperature; 180 °C, mixed speed; 50 rpm and mixed time: 6 min. The proportions of HBP2G regards to that of the recycled PVC and hemp fiber were as follows: 5 wt% (PVCHH5), 10 wt% (PVCHH10), 15 wt% (PVCHH15) and 20 wt% (PVCHH20). Additionally, a PVCH blend (70/30) was prepared and was used as a control.

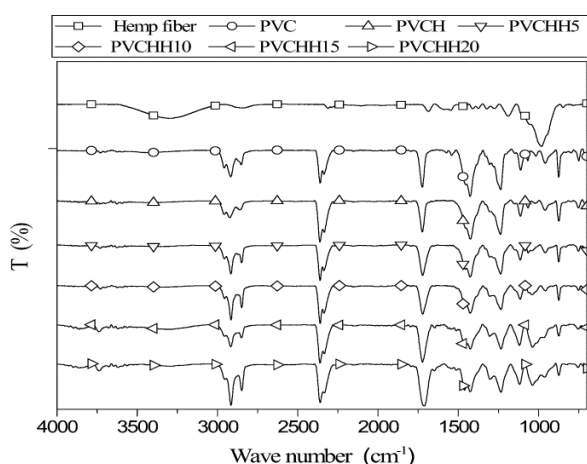
### 2.2. Characterization of the blends

In order to evidence the interactions between the materials, an infrared (IR) analysis was performed. This analysis was done by attenuating total reflectance in a Shimadzu Prestige 21 using ten scans and a range of frequency between 600  $\text{cm}^{-1}$  and 4000  $\text{cm}^{-1}$ . Thermogravimetric analysis (TGA) was also undertaken with the intention of knowing the thermal stability of the materials. This analysis was performed in a TA Instruments SDT Q600 equipment using a heating rate of 20 °C/min. from room temperature to 600°C while in a nitrogen atmosphere. In order to identify the thermal transitions of the blends, the differential scanning calorimetric (DSC) analysis was done. This analysis was executed in a TA Instruments Q-100 at heating rate of 10°C/min. in a range of temperature between -70°C and 200°C. Rheological analysis was performed in a rotational rheometer of TA instruments using a plate-plate geometry whose diameter was 20 mm and a temperature of 180°C. The spacing between plates was 1 mm. This analysis was done under dynamic conditions for angular frequency between 1.0 Hz and 100 Hz and a strain of 0.2 %. Scanning electron microscopy (SEM) analysis was done 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 realized using a beam acceleration voltage of 20 kV. Tensile test was done under standard methods ASTM D 638 [11] using specimens type I. This analysis was performed by using EMIC universal machine employing a deformation rate of 5 mm/min.

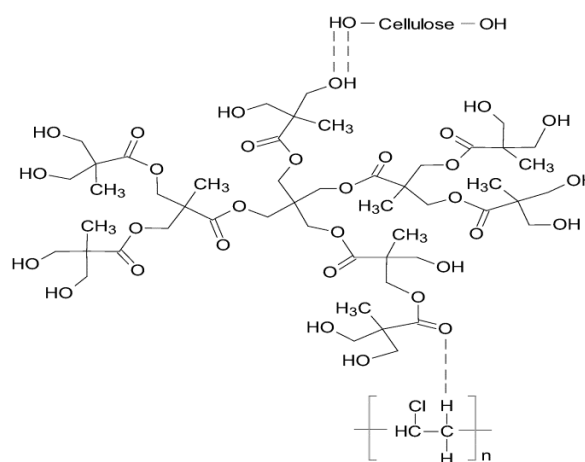
### 3. Results and discussion

Figure 1 presents the IR spectra of the samples. Hemp fiber exhibited a signal at  $3300\text{ cm}^{-1}$  corresponding to stretching of OH bonds. On the other hand, in the PVC spectrum was observed a signal at  $2972\text{ cm}^{-1}$  associated with asymmetric stretching of  $-\text{CH}_3$ . The signals at  $2920\text{ cm}^{-1}$  and  $2852\text{ cm}^{-1}$  are due to asymmetric and symmetric stretching of  $-\text{CH}_2$  respectively. At  $1724\text{ cm}^{-1}$  a signal appears corresponding to stretching of carbonyl group of esters ( $-\text{C}=\text{O}$ ). This signal is related with the presence of plasticizing agent in the PVC [12]. The signal at  $1454\text{ cm}^{-1}$  is attributed to asymmetric bending of  $\text{C}-\text{CH}_3$  bonds. At  $1430\text{ cm}^{-1}$  appears the signal of bending of  $-\text{CH}_2-$ . The signals at  $1236\text{ cm}^{-1}$  and  $1112\text{ cm}^{-1}$  are corresponding to ester bonds ( $\text{C}-\text{C}-\text{O}$ ) of the plasticizing agent. The signal at  $750\text{ cm}^{-1}$  is due to  $\text{C}-\text{Cl}$  bonds. The PVCH blend exhibited all signals observed to the PVC, but the absorption of OH group was not observed as shown by the hemp fiber, which was possibly due to interaction of PVC with the plasticizing agent.

The PVCHH blends presented the same signals observed to the PVCH blend, but some signals ( $2972\text{ cm}^{-1}$ ,  $2920\text{ cm}^{-1}$ ,  $1458\text{ cm}^{-1}$  and  $1112\text{ cm}^{-1}$ ) increased your intensities; which is associated with the presence of functional groups of the HBP2G. The signals that appeared at  $1724\text{ cm}^{-1}$ ,  $1454\text{ cm}^{-1}$  and  $1430\text{ cm}^{-1}$  in the PVC are shifted at  $1722\text{ cm}^{-1}$ ,  $1458\text{ cm}^{-1}$  and  $1425\text{ cm}^{-1}$  respectively. It means that was carried out an interaction between the components of the PVCHH blends (Figure 2). Another proof of this interaction is that the HBP2G presented absorption at  $3300\text{ cm}^{-1}$  associated with the OH groups [10], but this was not observed in the PVCHH blends.

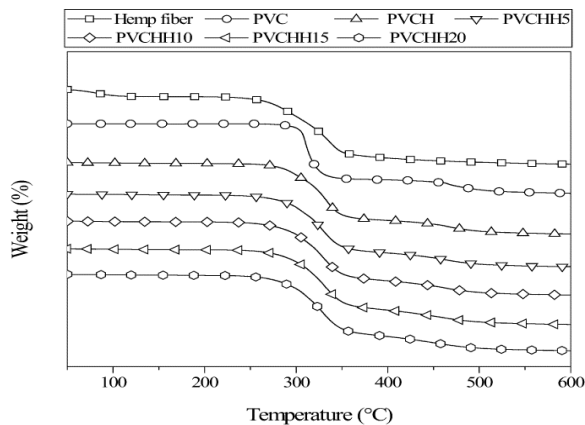


**Figure 1.** IR Spectra of the hemp fiber, PVC and PVCHHs samples.

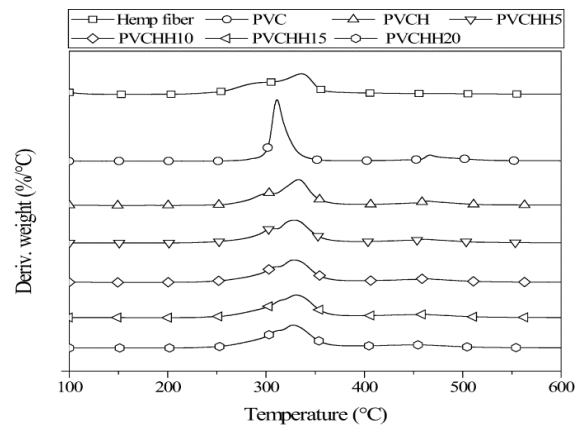


**Figure 2.** Schematic representation of the possible interactions.

Figure 3 (weight vs temperature) and Figure 4 (derivative weight vs temperature) exhibit the TGA thermograms of the samples. Hemp fiber showed a loss weight between  $30^\circ\text{C}$  and  $175^\circ\text{C}$  ( $T_1$ ) corresponding to 7.90 wt% ( $P_1$ ), which is likely associated with the water evaporation and volatile compounds present in this sample [13,14]. At  $216^\circ\text{C}$  ( $T_2$ ) another weight loss of 60 wt% ( $P_2$ ) is observed, corresponding to hemicellulose present in the hemp fiber [13]. In the case of the PVC, this showed two weight losses ( $P_1$  and  $P_2$ ), which are attributed to thermal decomposition of the plasticizing agent and the PVC respectively [15]. PVCH blend also exhibited this reduction in weight, which happened at different temperatures ( $T_1$  and  $T_2$ ) to those of the hemp fiber and PVC (Figure 3, Figure 4 and Table 1). This indicates that there was an interaction between the functional groups of these materials, which possibly occurred through plasticizing agent present in PVC, as  $T_1$  of the PVCH blend is higher than  $T_2$  of the hemp fiber and lower than  $T_1$  of the PVC. Furthermore,  $T_2$  of the PVCH blend is lower than that of the PVC, which could be due to the presence hemp fiber that affected the interaction between PVC and the plasticizing agent as they can interact through hydrogen bond. Another evidence of this interaction is that carbonaceous residue (R) of PVCH has an intermedium value between hemp fiber and PVC.



**Figure 3.** Weight vs temperature.



**Figure 4.** Derivative weight vs temperature.

In the case of the PVCHH blends it can be observed that the  $T_1$  values are lower than that of PVCH blend (Figure 3, Figure 4 and Table 1), thus meaning that the presence of HBP2G reduces thermal stability. This may be due to the fact that HBP2G has a  $T_1$  of 218°C [10] and possible interactions of the HBP2G and the hemp fiber.  $P_1$  value of the PVCH blend is greater than that of the PVCHH blends, which could be interpreted as the lowest interaction between PVC and hemp fiber or plasticizing agent into PVC and hemp fiber, or highest interaction between HBP2G and hemp fiber, since this material has high number of OH groups [10]. The interaction between carbonyl and OH groups has been reported for PVC/bagasse fiber [16]. The  $T_2$  of the PVCH blend is similar to those of the PVCHH5, PVCHH10 and PVCHH15 blends; but it is greater than that of the PVCHH20. This result indicates that the interactions of the HBP2G in the PVCHH blends are mainly affected when the concentration of HBP2G is 20 wt%. On the other hand, the  $P_2$  value of the PVCH blend was similar to those of the PVCHH blends (Table 1). The R values exhibited by the PVCHH blends were slightly higher than that of the PVCH blend largely as a result of the presence of HBP2G in these blends.

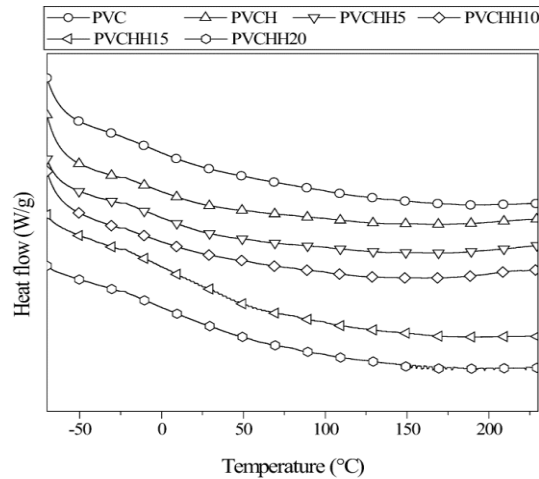
**Table1.** Values of  $T_1$ ,  $P_1$ ,  $T_2$ ,  $P_2$ , R and  $T_g$  of the samples.

| Samples    | $T_1$<br>(°C) | $P_1$<br>(%) | $T_2$<br>(°C) | $P_2$<br>(%) | R<br>(%) | $T_g$<br>(°C) |
|------------|---------------|--------------|---------------|--------------|----------|---------------|
| Hemp fiber | 0-175         | 7.904        | 208           | 70.20        | 21.9     | -             |
| PVC        | 271           | 60.22        | 370           | 14.26        | 25.52    | - 4.41        |
| PVCH       | 246           | 61.74        | 367           | 14.12        | 24.14    | - 3.21        |
| PVCHH5     | 232           | 57.25        | 369           | 14.86        | 27.89    | - 2.81        |
| PVCHH10    | 222           | 58.42        | 366           | 13.72        | 27.86    | -2.42         |
| PVCHH15    | 230           | 59.20        | 367           | 15.31        | 25.49    | 8.87          |
| PVCHH20    | 222           | 59.10        | 362           | 15.13        | 25.77    | 9.18          |

Figure 4 shows the shift of the  $T_1$  and  $T_2$ . This shows that the kinetic energy of the thermal decomposition of hemp fiber is lower as compared to that of the PVC. The decomposition kinetic energy of the PVCH blend is similar to that of the hemp fiber and PVCHH blends, which means that the HBP2G slightly affects the decomposition kinetic energy of the PVCHH blends. This behavior may be as a result of low thermal decomposition of the HBP2G.

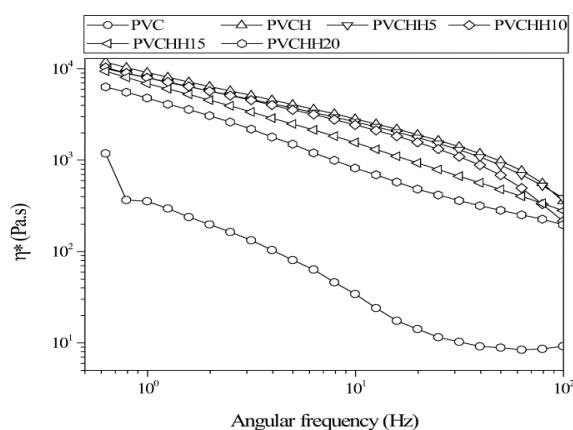
Figure 5 shows the DSC thermograms of the samples. It can be observed that PVC presents a glass transition temperature ( $T_g$ ) value slightly lower than that of the PVCH, this means that the presence of hemp fiber reduces slightly the mobility of the chains of PVC. The PVCHH blends exhibited higher  $T_g$  values than the PVCH blend, this indicates that the presence of HBP2G increased the interactions between hemp fiber and HBP2G or HBP2G and the PVC (Figure 2). On the other hand,  $T_g$  values of the PVCHH blends increased with the HBP2G content, but this increase was abrupt to the PVCHH15 and PVCHH20, it can be interpreted as high restriction of the chain movement of the PVC due to

interaction between hemp fiber and HBP2G or between PVC and HBP2G when the concentrations of HBP2G are 15 wt% and 20 wt%.

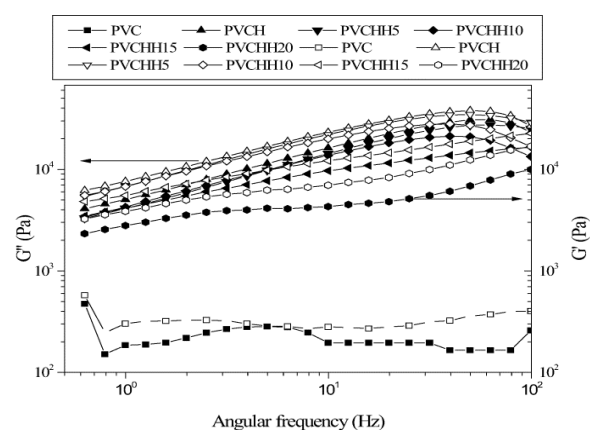


**Figure 5.** DSC thermograms of the blends.

Figure 6 and Figure 7 exhibit the rheological behavior of the samples. Figure 6 and Figure 7 display the results of the curves of complex viscosity ( $\eta^*$ ) vs angular frequency and storage ( $G'$ ) and loss ( $G''$ ) modulus vs angular frequency respectively. All samples exhibited a pseudoplastic rheological behavior (Figure 6), which was due to disentanglement of the chains or disassociation of the interactions. PVCH presented higher  $\eta^*$  than PVC, it was due to presence of hemp fiber. The  $\eta^*$  of PVCHH blends was lower than that of the PVCH blend, this shows that despite the interactions between hemp fiber and HBP2G, it has a plasticizing effect in these blends, which improved with the increase of the HBP2G content, since the viscosity of these blends was reduced in the same sense. This behavior is due to the low viscosities that present the hyperbranched polymers in molten and solution state [7,17]. The  $\eta^*$  values of the PVC, PVCH and the PVCHH blends at angular frequency of 1 Hz are as follow: PVC: 356 Pa.s, PVCH: 9164 Pa.s, PVCHH5:8015 Pa.s, PVCHH10:8001 Pa.s, PVCHH15:6923 Pa.s y PVCHH20:4788 Pa.s.



**Figure 6.**  $\eta^*$  vs. angular frequency.

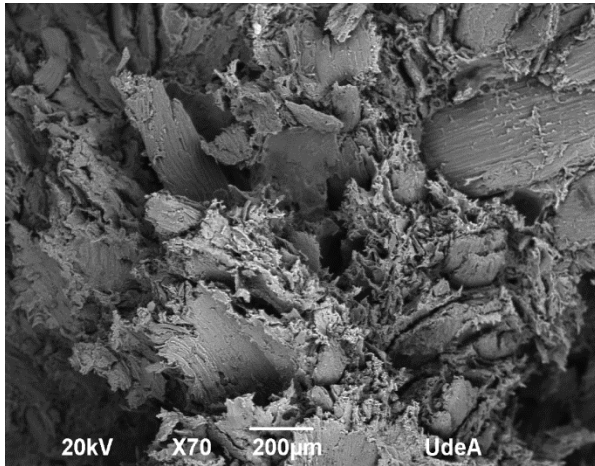


**Figure 7.**  $G''$  and  $G'$  vs. angular frequency.

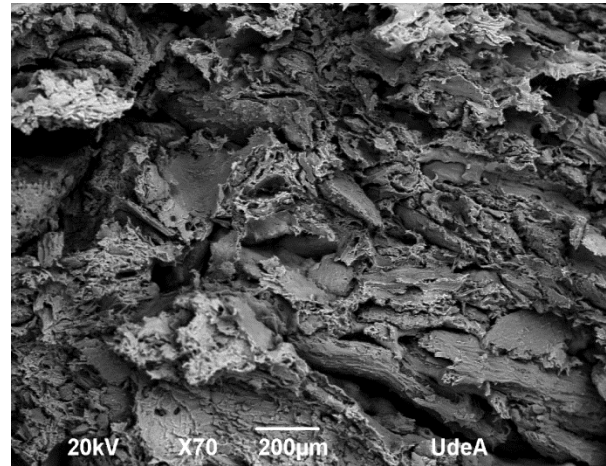
No sample exhibited a transition from viscous to elastic ( $G' > G''$ ) in the range of angular frequency studied (Figure 7). All samples showed a rheological behavior mainly viscous ( $G'' > G'$ ). The viscous behavior increased with the proportion of HBP2G used. This result is very important since the HBP2G

improved the processing of these blends, reducing so the viscosity and the energy employed for the mixture.

In the micrographs obtained by SEM analysis, samples of hemp fiber, spacing and aggregations of the hemp fiber for the PVCH and PVCHH20 blends were observed (Figure 8 and Figure 9). Smooth regions and other high rugosity with small microcavities, which are due to extraction of the hemp fibers during tensile test, were seen. The PVCH (Figure 8) and PVCHH20 (Figure 9) presented a fragile fracture since none showed a smooth surface. This behavior is typical for thermoplastic polymers.



**Figure 8.** Micrographs of the sample PVCH.



**Figure 9.** Micrographs of the sample PVCHH20.

In the case of the PVCHH20, smallest areas of the microcavities were detected. A possible explanation of the behavior showed by PVCHH20 blends is that HBP2G is fragile and the interaction between HBP2G and hemp fiber is high when its concentration is 20 wt%. Finally, the results showed that the adherence between the PVC and hemp fiber is low for the PVCH blend, but it was improved with the presence of the HBP2G in the PVCHH20 blend. However, all samples displayed aggregations of hemp fiber.

**Table 2.** Elastic modulus, tensile strength and elongation at break of the samples.

| Blends  | Elastic modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) |
|---------|-----------------------|------------------------|-------------------------|
| PVCH    | 205                   | 5                      | 14                      |
| PVCHH5  | 278                   | 4                      | 13                      |
| PVCHH0  | 274                   | 3                      | 13                      |
| PVCHH15 | 355                   | 3                      | 12                      |
| PVCHH20 | 250                   | 3                      | 15                      |

Table 2 presents the tensile modulus, tensile strength and elongation at break values of the blends. The tensile modulus of the PVCHH blends were higher than that of the PVCH blend, this was probably due to the presence of HBP2G, which improved the interaction between hemp fiber and PVC. Another reason of this behavior is the aggregation exhibited by the hemp fiber into the PVCH blend, which reduced the number of micro concentrators of efforts. On the other hand, tensile strength and the elongation at break of PVCH blend were very similar to those of the PVCHH blends. No material exhibited a trend in the mechanical properties, which was as a result of the aggregations or distribution of hemp fiber in these blends and the number of interactions between HBP2G and other components.

#### 4. Conclusions

This study makes a ground-breaking contribution with this blend type, as there are no prior reports in literature of a similar study being done. The displacement of some of the signals of the PVCHH blends observed by IR similar to those seen in the PVCH spectrum is a proof of the best interaction between the components when presenting the HBP2G. The thermal stability and mechanical properties of the PVCHH blends did not show dependence with the HBP2G amount. However,  $T_g$  and  $\eta^*$  exhibited a trend with HBP2G content. The PVCHH20 blend presented highest  $T_g$  value, which indicates that it possibly exhibited the greatest interaction degree between the components. On the other hand, HBP2G improved the interaction between PVC and hemp fiber, since the PVCHH20 blends exhibited the lowest aggregation of the hemp fiber and lower number of microcavities than the PVCH blend. Elastic modulus of the PVCH blend was lower than that of the PVCHH blends, but in the case of the elongation at break and tensile strength, was not observed a difference remarkable.

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