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Evaluation of the rheological properties in solution and molten state of hyperbranched polyester polyols obtained of first and second generation

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Evaluation of the rheological properties in solution and molten state of hyperbranched polyester polyols obtained of first and second generation

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Abstract. The hyperbranched polyesters have gain great attention since these materials have smallest hydrodynamic dimensions, high functionality, good solubility and they may be modified for obtaining compounds for specific applications. There are few reports about the rheological properties on the solution and molten state of the hyperbranched polyesters polyols obtained of the first and second generation, especially those prepared from dimethyl propionic acid and pentaerythritol. Thus, the aim of this study is to evaluate the rheological properties in solution and molten state of these materials. Furthermore, the hydrodynamic dimensions by dynamic light scattering by using dimethyl formamide and dimethyl sulfoxide as solvents also were analyzed. The hydrodynamic dimensions on volume of the hyperbranched polyesters polyols obtained of second generation by using dimethyl formamide as solvent were greater than those of first generation, but the behavior was different when was used dimethyl sulfoxide as solvent. Furthermore, these materials exhibited aggregations. The rheological behavior in solution showed that all samples exhibited lowest viscosity and a Newtonian region between 1 and 60 s^{-1}, then this behavior changed to shear thickening. By rheological analysis in molten state was evidenced a shear-thinning behavior to these materials.

1. Introduction

Hyperbranched polyesters (HBPs) are dendritic polymers (Figure 1) [1-3]. These materials exhibit high branching degree, low viscosity (η) in solution and molten state, high solubility, low hydrodynamic dimensions and high functionality [1-3]. These materials are synthetized from a core and an extender [1-6]. The core is a polyfunctional molecule (B_y) and the extender (AB_x) has various reactive groups [2]. The group B of the core reacts with the group A of the extender [1-3]. Every stoichiometric reaction between the core and extender produce a generation or shell [3-6]. HBPs are intermedium structures between linear polymer and dendrimers (perfect structure) [2]. The dendrimers are globular structures and it does not contain linear unit at difference of the HBPs, which contain these units [2]. These units have a functional group without reacted. Therefore, reduce the branching degree and produce a structural imperfection [2]. The HBPs can be synthetized by one step, by steps and by a combination of these methodologies [3-6]. These materials have lower cost and less synthesis time than a dendrimer [2]. With the aim of obtain specific applications, HBPs have been modified with several compound such as maleic anhydride [7], melamine-formaldehyde [8] and fatty acids [9,10]. These materials are used as plasticizer, functionalizing, crosslinker, etc. [7-10]. The HBPs exhibit lower η and disentanglement than linear polymers [2]. This is an aspect important to consider in so many applications, since this is an advantage

of HBPs on linear polymers. In the other hand, so many HBPs have been characterized. However, the rheological properties in solution and molten state have been less studied. Hsieh, *et al.* [11] evaluated the rheological behavior on molten state of commercial HBPs polyols of second (HBP2G), three (HBP3G), fourth (HBP4G) and fifth generation (HBP5G). They observed that the HBP2G and HBP3G exhibited shear-thinning behavior and highest activation energy (Ea). In the other hand, HBP4G and HBP5G showed a Newtonian behavior. In all cases η decreased with the temperature. In another study Hsied, *et al.* [12] studied the rheological behavior of commercial HBPs blends of different generation (HBP2G, HBP3G, HBP4G and HBP5G). In Newtonian/no-Newtonian polymer blends exhibited Newtonian characteristic under steady and oscillatory conditions. Nuñes, *et al.* [13] evaluated the rheological behavior of HBPs in solution. They used 1-methyl-2-pyrrolidinone as solvent. All HBPs exhibited a Newtonian behavior and η did not show dependence with the shear rate. Furthermore, η was slightly affected by the different generation. Murillo, *et al.* [14] studied the rheological behavior in solution and molten state of HBP4G and HBP5G. It was observed that η decreased with the increasing of the temperature and all HBPs exhibited a Newtonian behavior. HBPs in solution showed a shear-thickening behavior at a shear rate greater than 40 s^{-1}. In the case of the HBP1G and HBP2G, there are few reports about the rheological behavior in solution and molten state and their hydrodynamic dimensions in solution by using dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). In the case of the HBP2G, some rheological properties of this material were evaluated by us at 110 °C [7], this material exhibited a shear-thinning behavior and by dynamic light scattering analysis were observed aggregations of the solutions prepared by using DMF.
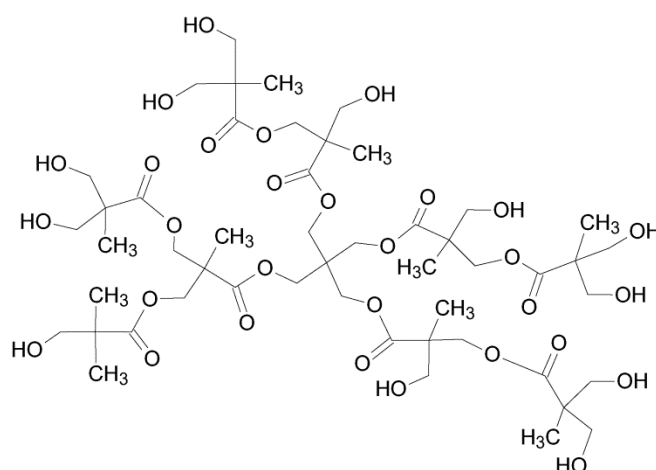

Figure 1. Schematic representation of an HBP.

Despite that there some reports about the rheological behavior of the commercial HBPs (Perstorp) [11,12], there is not information about of the rheological behavior of HBP1G and the comparison with rheological behavior of HBP2G in solution and molten state. Furthermore, there is no report about the study of the hydrodynamic dimensions of these materials using DMSO as solvent. Therefore, the primary focus of the present study is to investigate the rheological behavior in solution and molten state of HBP1G and HBP2G and compare their hydrodynamic dimensions in solution. Furthermore, to contribute to art state of these materials.

2. Materials and methods
HBP1G and HBP2G were provided by our research group. The synthesis and thermal, structural properties of these materials were previously reported [7,10]. In the case of the HBP2G the rheological properties under steady conditions in molten state (at 110 °C) were already reported [7]. DMF and DMSO were provided by Sigma Aldrich.

2.1. Characterization of the samples

The dynamic light scattering (DLS) analysis was made to determine the hydrodynamic dimensions of the materials. This analysis was executed on a Zetasizer of Malvern instruments employing a wavelength of 633 nm and an incidence angle of 173 nm. For this analysis were used solutions of HBP1G and HBP2G in DMF and DMSO, whose concentrations were 1 wt%. The rheological analysis in solution and molten state was performed in an Anton Paar rheometer. For the solution analysis were prepared solutions in DMF and DMSO (25 wt%). The analysis in solution was done by using a concentric cylinder geometer and at room temperature. The shear rate was between 0.1 s^{-1} and 1000 s^{-1}. In the case of the analysis in molten state, this was performed under steady and oscillatory conditions. For it was used a parallel plate geometer and the spacemen between plates was of 0.5 mm. The temperatures used for this analysis were 110 °C, 120 °C, 130 °C and 140 °C. The analysis under steady conditions was done at shear rate between 0.1 s^{-1} and 1000 s^{-1}. The analysis under oscillatory conditions was performed at 0.2% of strain and the angular frequency was between 0.1 and 100 Hz.

3. Results and discussion

The size distributions of the samples are displayed in the Figure 2 and Figure 3. Figure 2 shows the volume distribution. It can be seen that the distribution of the samples prepared using DMF is monomodal and those obtained with DMSO are polymodal. This mean that possibly for these samples DMF is better solvent than DMSO, since the hydrodynamic dimension on volume of the samples obtained with this solvent were smaller than those prepared with DMSO (Table 1). The hydrodynamic dimension (d) of the HBP2G on volume by using DMF as solvent were higher than those of the HBP1G, but the behavior was different when was used DMSO as solvent. This phenomenon was caused by the aggregation process exhibited by these macromolecules through OH groups [2], since HBP1G has lower molar mass than HBP2G [2]. Figure 3 shows the intensity distribution of the samples by using DMF and DMSO. The samples presented the same behavior exhibited on volume distribution, since was observed the same trend on size. In the other hand, appear other distributions which were not evidenced in the volume distribution, this is a proof of the presence of aggregations. The reason of the absence of the new distributions that appear on intensity is that that all samples contained aggregates which have higher radiation dispersion than small molecules. This behavior already has been reported [2,5,7].
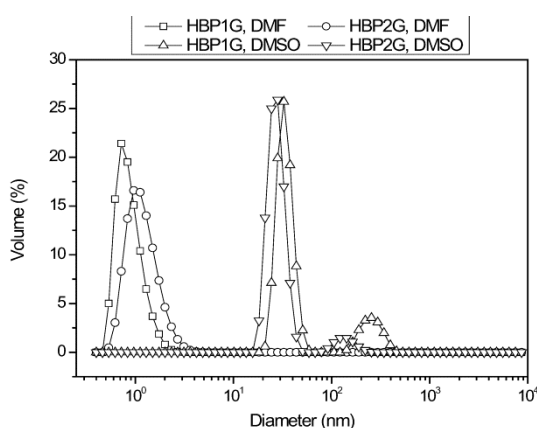

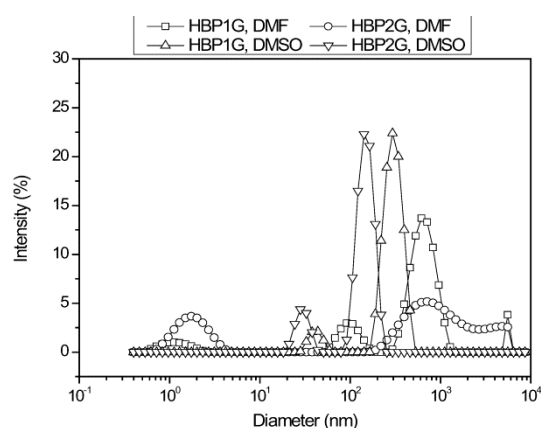**Figure 2.** Size distribution on volume of the samples.

Figure 3. Size distribution on intensity of the samples.

According to the results, DMF is better solvent than DMSO for these materials. Since the results obtained with this solvent are in agreement with the molar mass (HBP2G > HBP1G) of these samples. The results obtained for HBP2G using DMF as solvent are comparable with those obtained by other authors (d values around 2 nm) [7,15]. However, those obtained by employing DMSO as solvent are higher than those reported [7,15].

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

Samples	Volume (DMF)	Volume (DMSO)		Intensity (DMF)			Intensity (DMSO)	
	d_1 (nm)	d_1 (nm)	d_2 (nm)	d_1 (nm)	d_2 (nm)	d_3 (nm)	d_1 (nm)	d_2 (nm)
HBP1G	0.89	39.06	298.1	1.21	99.73	663.8	41.79	304.6
HBP2G	1.23	27.61	139.2	1.86	977	4015	29.88	150.5

Figure 4 shows the rheological behavior of the samples in solution under steady conditions. It can be observed that all samples exhibited a Newtonian region between 1 s^{-1} and 60 s^{-1}, and then this behavior changed to shear-thickening. The Newtonian behavior has been related to the absence of disentanglement [11]. The increasing off η with shear rate have been assigned to the formation of a thermolabile network due to the strong self-association of polar groups [16,17]. The same behavior was observed to HBP4G and HBP5G, whose solutions were prepared by using DMF as solvent [14]. Another hand, it can be seen that when was used DMF as solvent, η of the HBP1G was lower than that of the HBP2G. In the case of the solutions prepared by using DMSO, the behavior was opposite. It is important note that the η value increases with the generation [13]. However, there are some deviations of this behavior, since the interactions between macromolecules through OH groups have an important rheological effect [11-13], which explain the behavior exhibited by the samples when was used DMSO as solvent. The rheological behavior presented in solution is in accordance with those obtained by DLS analysis. A remarkable result obtained in this study is the lowest viscosity exhibited by these materials. The η values obtained in the present work are lower than that reported to solutions of HBP3G, HBP4G and HBP5G (> 20 mPa.s), which was obtained by using 1-methyl- 2-pyrrolidinone as solvent [13] and for those of HBP4G and HBP5G prepared by using DMF as solvent, whose η values were higher than 20 mPa.s.
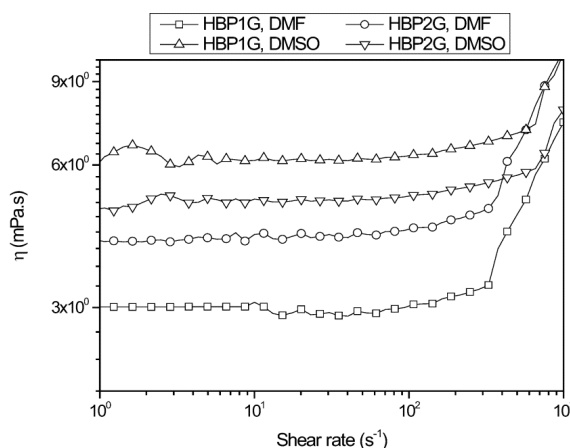

Figure 4. Flow curve of solutions of the samples.

Figure 5 and Figure 6 displaying the rheological behavior under steady conditions of the HBP1G and HBP2G on molten state at different temperatures. It can be observed that all materials exhibited a shear-thinning behavior. This was due to dissociation of the interactions through OH groups. This behavior also was reported to commercial HBP2G produced by Perstorp [12]. Another hand in the range of shear rate studied, η of the HBP1G was lower than that of the HBP2G at the same temperature. The enhancing of the η values with the increasing in the generation has been observed to HBP2G, HBP3G, HBP4G and HBP5G [11].

The flow activation energy of the materials was obtained from η values at different temperatures at shear rate of 1 s^{-1}. Ea can be obtained since η showed dependence with the temperature [11]. Therefore, it may follow an Arrhenius type equation, see Equation (1) [11].

$$\eta = A \times e^{Ea/RT}. \qquad (1)$$

Where A is a constant, R is the gas constant and T is the temperature. Ea can be calculated from the slope of a graph of ln η vs 1/T (Figure 7). Since the slope is Ea/R. In Figure 7, it can be seen that the graphs have a good linearity. The values of Ea, correlation factor and slope appear in the Table 2. The Ea value of the HBP2G was higher than that of the HBP1G. This means that HBP1G flow easier than HBP2G, this behavior may be attributed to various factors such as, highest molar mass of the HBP2G and greatest interaction through OH groups. The Ea value obtained for HBP1G is comparable with the observed to commercial HBP2G (139 kJmol^{-1}) [11]. Furthermore, the Ea value of the HBP2G is highest regards to those of the commercial HBP2G, HBP3G (174 kJmol^{-1}), HBP4G (103 kJmol^{-1}) and HBP5G (91 kJmol^{-1}) [11]. The correlation factors of the graphs were high (Table 2), this means that the aggregation did not affected the linearity.
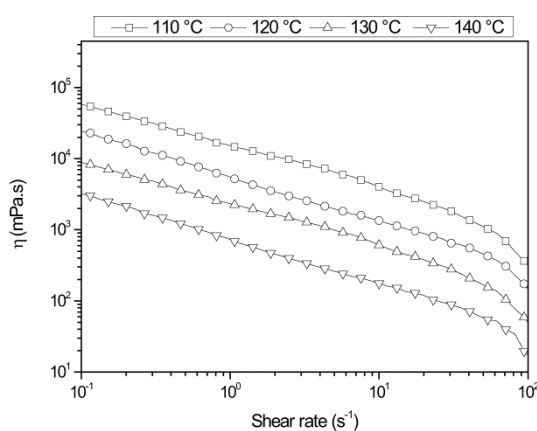

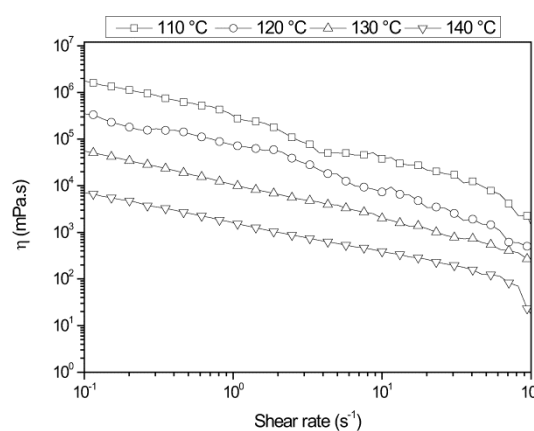**Figure 5.** Flow curve on molten state of HBP1G.

Figure 6. Flow curve on molten state of HBP2G.

Table 2. Results of the thermal and mechanical properties of the samples.

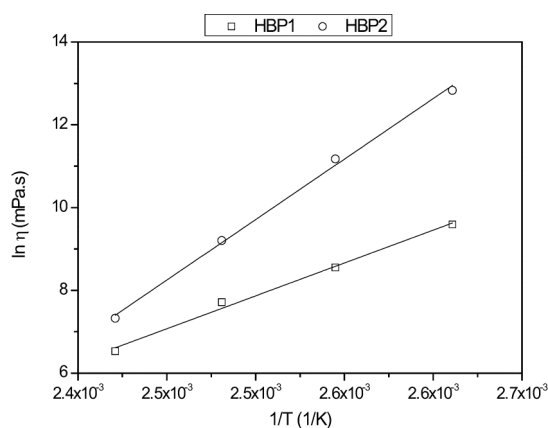| Samples	Ea (kJmol^{-1})	Correlation factor	Slope
HBP1G	130.24	0.9962	15884
HBP2G	239.64	0.9988	29224

Figure 7. Graph of ln η vs. 1/T.

The rheological behavior in the molten state of the samples under oscillatory conditions is presented in the Figure 8 and Figure 9. The complex η (η*) decreased with the temperature, the same behavior was observed under steady conditions. In the range of angular frequency studied, the sample HBP1G at

120 °C, 130 °C and 140 °C exhibited a reduction on $\eta*$, but then it increased, this was due to the formation of a thermolabile network. At 110 °C, the sample HBP1G exhibited a shear-thinning rheological behavior. These behaviors indicate that the formation of the thermolabile network is favored at temperatures higher than 110 °C. In the case of the HBP2G, only was observed an increasing on $\eta*$ at 140 °C, but it was less abrupt than that observed to the sample HBP1G at 130 °C and 140 °C. The behavior exhibited by the sample HBP1G is probably due to the high mobility of the macromolecules and highest interaction between OH groups and distribution of the OH groups. It has been reported that with the increasing of the generation number, the dendritic units become more flexible and fold back into the macromolecules and less polar end groups will be exposed to other molecules [11].
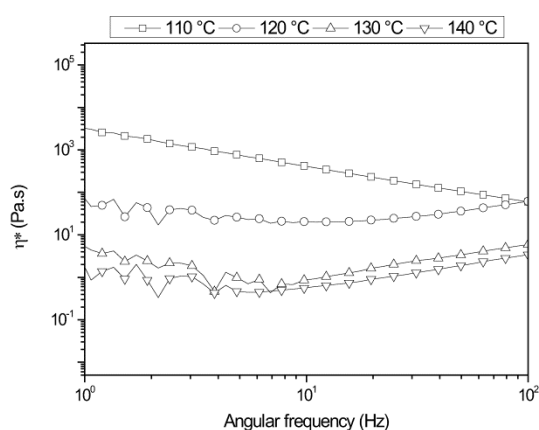

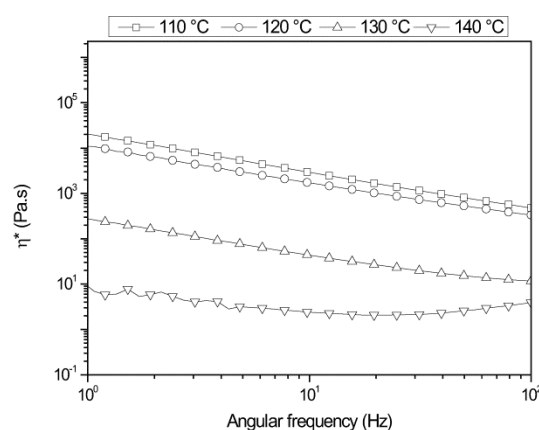**Figure 8.** Graph of $\eta*$ vs angular frequency of the HBP1G.

Figure 9. Graph of $\eta*$ vs angular frequency of the HBP2G.

The difference of the behavior exhibited by the samples under steady and oscillatory conditions is due to under steady conditions the material is not in the linear viscoelastic region, which if occur under oscillatory conditions. Therefore, the material is deformed but elastic recovery is total. The results obtained in this study are different that those obtained to commercial HBP2G, HBP3G, HBP4G and HBP5G [11]. On the other hand, these materials did not follow the Cox-Merz rule [11], since in none case was observed a superposition of the curves of η vs shear rate and $\eta*$ vs angular frequency at any temperature. This behavior was due to interactions between OH groups.

4. Conclusions

In this study was evaluated the rheological properties in solution and molten state of the samples HBP1G and HBP2G. Furthermore, the hydrodynamic dimensions of the solutions of HBP1G and HBP2G also were analyzed by DLS using DMF and DMSO as solvents. By DLS was evidenced that DMF was better solvent than DMSO. Another hand, when was used DMF as solvent, η of the HBP1G was lower than HBP2G, but the solutions prepared by using DMSO exhibited an opposite behavior. The rheological behavior presented in solution is in accordance with those results obtained by DLS analysis. By rheological analysis in molten state was observed that at the same temperature, η of the HBP1G was lower than that of the HBP2G. HBP2G exhibited higher flow resistance than HBP1G since *Ea* of HBP2G was greater than that of the HBP1G. In the range of angular frequency studied the sample HBP1G at 120 °C, 130 °C and 140 °C exhibited a reduction on $\eta*$, but then it increased, this was due to the formation of a thermolabile network. The difference of the behavior exhibited by the samples under steady and oscillatory conditions is due to under steady conditions the material is not in the linear viscoelastic region, which if occur under oscillatory conditions. HBP1G and HBP2G did not follow the Cox-Merz rule, since in none case was observed a superposition of the curves of η vs shear rate and $\eta*$ vs angular frequency at any temperature.

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