

Hyperbranched Polyester Polyol Modified with Polylactic Acid

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ABSTRACT: In this study the modification of a hyperbranched polyester polyol of second generation (HBP2G) with polylactic acid (PLA) was carried out. The proportions employed of PLA were: 10 (HBP2G90), 25 (HBP2G75), 40 (HBP2G60), and 55 wt % (HBP2G45). The materials obtained were characterized by acid value, hydroxyl value, infrared, nuclear magnetic resonance (NMR), chromatography exclusion size (SEC), dynamic light scattering, thermogravimetric, differential scanning calorimetry, and rheology analyses. The analyses of the acid values and hydroxyl values showed that the reaction between HBP2G and PLA occurred. The greater modification degree was 92.00%. The NMR spectrum shows that evidently the PLA was grafted onto the HBP2G. The SEC analysis revealed that all samples presented values of average molecular weight (M_n) and weight average molecular weight (M_w) higher than the HBP2G. The thermal stability of the materials increased with respect to HBP2G and it was independent of the modification degree. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41589.

KEYWORDS: dendrimers; functionalization of polymers; hyperbranched polymers and macrocycles; properties and characterization

Received 20 July 2014; accepted 2 October 2014

DOI: 10.1002/app.41589

INTRODUCTION

Hyperbranched polyester polyols (Figure 1) with dendritic architecture contain a large number of branching points and terminal functional groups. Although the structure of these polymers is not as perfect as that of dendrimers, they have properties that resemble those of the dendrimers.^{1,2} They are synthesized by one step or pseudo-one-step polymerization procedures.³ At the moment, the most intriguing and well-known properties of hyperbranched polymers are their high reactivity, low viscosity in solution and molten state as a result of their packed structure, the absence of entanglements, and good compatibility with other materials.³

The hyperbranched polymers can be modified through the terminal functional groups with other compounds to obtain new materials with specific applications. Mishra and coworkers⁴ modified a hyperbranched aliphatic polyester polyol (HBP) of second generation with isoforonedisocyanate to obtain urethane-urea polyester. Kutyreva and coworkers⁵ modified a HBP of second generation with succinic anhydride to obtain a chelating agent. Murillo and coworkers⁶ modified a HBP of fourth generation with tall oil fatty acids to obtain hyperbranched alkyd resins.

Polylactic acid (PLA) is an aliphatic polyester, biodegradable, compostable, and thermoplastic.⁷ This material presents good

mechanical properties, and it is employed on industrial applications such as biocompatible/bioadsorbable packages, medical disposables, films, and fibers.⁸ PLA can be degraded by hydrolysis of ester bonds. Degradation rate depends on size, proportion of isomers and temperature.⁸ PLA can be processed by injection molding, thermoformed, blow and extrusion, but this material is degraded at temperatures higher than 200°C. This process affect the mechanical properties of PLA.⁹ PLA degradation is depending of the time, temperature, and catalyst concentration.⁹ PLA have a glass transition and melting temperature around 55 and 175°C, respectively. PLA with high molecular weight is colorless, glossy and tough. This material has been modified with some compounds. PLA was modified by esterification reaction with poly(hydroxyethyl methacrylate) by using stannous octoate as catalyst to obtain a stimulus-responsive biocompatible carrier with good drug release properties.¹⁰ In another study,¹¹ PLA was modified with maleic anhydride (MA), with a concentration between 0.29 and 8.70 wt %. The 2,5-bis(tert-butylperoxy)-2,5-dimethyl hexane (between 0.2 and 8.03 wt %) was used as initiator and grafting degree of MA was between 0.45 and 0.65 wt %. The application of the material obtained (PLA-g-MA) was as a compatibilizer in production of PLA blends with various components. A huge challenge with this material is the low grafting degree of MA. A thermoplastic polyolefin elastomer-graft-poly lactide (TPO-PLA) was prepared by

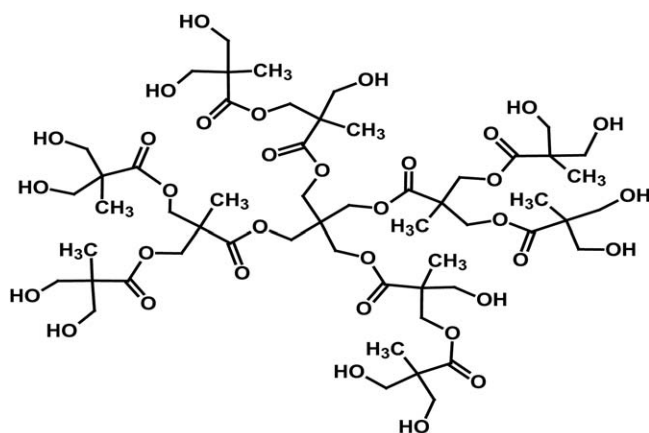


Figure 1. Schematic representation of the HBP.

grafting polylactide onto maleic anhydride-functionalized TPO (TPO-MA). The material obtained was employed as compatibilizer of TPO/PLA blends.¹²

In this work, we have synthesized and characterized a hyperbranched polyester polyol of second generation modified with different proportions of PLA. The influence of proportions of PLA on the structural, thermal, and rheological properties of the materials obtained was determined.

EXPERIMENTAL

Materials

The second generation polyester polyol was synthesized stepwise using the methodology reported by Murillo and coworkers.² The PLA was supplied by the company ALICO from Colombia and it has a number average molecular weight of 68,000 g/mol. Para-toluenesulfonic acid, acetone, pyridine, acetic anhydride, tetrahydrofuran, xylol, phenolphthalein, and potassium hydroxide were supplied by Sigma-Aldrich.

Synthesis of Hyperbranched Polyester Polyol Modified with PLA (HBP2G-g-PLA). Different proportions of a hyperbranched polyester polyol obtained by the methodology of steps and of second generation (HBP2G) and (PLA) (Table I), were taken to a reactor, which was kept in an inert atmosphere with nitrogen and at 200°C. Once the system reached the reaction temperature, it was stirred at 200 rpm for 5 hours. The conversion of the reaction was assessed by measurement of acid value.

Characterization of the HBP2G-g-PLA

Acid Value (AV). This analysis was performed based on ASTM D1639-90 method as follows. A small amount of the samples (around 1.0 g) were dissolved in a xylol-isopropanol mix

Table I. Proportions of HBP2G and PLA Employed on the Preparation of HBP2G-g-PLA

HBP2G-g-PLA	HBP2G (wt %)	PLA (wt %)
HBP2G90	90	10
HBP2G75	75	25
HBP2G60	60	40
HBP2G45	45	55

1 : 1 (previously neutralized), to this solution one drop of phenolphthalein was added and the titration was done with ethanolic solution of KOH 0.5 N. This analysis was done in triplicate. The acid value (AV) was determined using the following equation:

$$AV = \frac{C_{KOH} \times (V_{KOH}) \times 56.1}{m} \quad (1)$$

where, C_{KOH} , is the concentration of the KOH ethanolic solution, V_{KOH} is the spent volume of the KOH solution in the titration and m is the mass of the sample.

Hydroxyl Value (OHV). For this analysis, infrared (IR) and nuclear magnetic resonance (NMR) analyses, the samples were previously purified by soxhlet extraction in xylol during 24 hours, to eliminate the residual PLA. This analysis allowed determining the modification percentage of the HBP2G with PLA, and it was performed according to AOCs Cd 13-60 method. The hydroxyl value (OHV) was determined using the following equation:

$$OHV = \frac{C_{KOH} \times (V_B - V_{KOH}) \times 56.1}{m} + AV \quad (2)$$

where, V_B is the volume of KOH solution used in the blank, V_{KOH} is the spent volume of the KOH solution in the titration of the sample, (AV) is the acid value of the sample, and m is the mass of the sample.

Infrared Analysis

This analysis was performed in a Perkin Elmer spectrometer Spectrum One model. The number of scans was 8 and the resolution was 4 cm^{-1} .

Proton Nuclear Magnetic Resonance Analysis

This analysis was done only for the HBP2G and HBP2G45 samples. This analysis was achieved on a Bruker AC 300 MHz spectrometer. For it, a solution (3 wt %) of the samples in deuterated dimethyl sulfoxide was prepared.

Size Exclusion Chromatography Analysis

This analysis was carried out in a Waters 600 chromatograph, by using polystyrene standards for the quantification.

Dynamic Light Scattering Analysis

This analysis was performed in a Zetasizer Nano S series Malvern Instrument. For it were prepared solutions of the samples (1 wt %) in tetrahydrofuran.

Thermogravimetric Analysis

The thermal degradation of the samples was determined in nitrogen atmosphere at heating rate of 10°C/min using TA Instruments model Q-500.

Differential Scanning Calorimetric Analysis

The differential scanning calorimetry (DSC) analysis was performed in a TA Instrument model Q100 equipped with a refrigerated cooling system, at the heating and cooling rate of 30°C/min under nitrogen atmosphere.

Rheological Analysis

A rotational rheometer of Malvern Instruments was employed, using a cone-plate geometry (two degrees) and employing a strain of 0.01%.

Table II. AV, CP, OHV, and MP of the Samples

Samples	AV (mg KOH/g sample)	CP	OHV (mg KOH/g sample)	MP
HBP2G	42.23	-	448.20	-
HBP2G90	4.14	93.91	333.32	25.63
HBP2G75	4.44	93.90	293.08	34.61
HBP2G60	7.25	92.28	227.23	49.30
HBP2G45	8.99	90.43	172.48	61.52
PLA	51.72	-	-	-

RESULTS AND DISCUSSION

Acid and Hydroxyl Values

The results AV and OHV of the samples are presented in Table II. It can be seen that the acid value of the HBP2G-g-PLA samples is lower than the AV of the PLA and HBP2G. Therefore this provides evidence that in all cases modification of the HBP2G with PLA occurred (esterification reaction). Conversion percentage (CP) of the reaction was calculated using the following equation:²

$$CP = \frac{AV_t - AV_f}{AV_t} \times 100 \quad (3)$$

where AV_t is the total acid value (HBP2G and PLA AV, this value is 93.95 mg KOH/g sample) and AV_f is the acid value of the HBP2G-g-PLA samples. In all cases conversion percentage of the reaction was higher than 90%. The calculations of the conversion percentage were done based on the

acid value of PLA, and HBP2G because both compounds can react due to their acid groups. The acid value of HBP2G is due to residual DMPA and DMPA oligomers are present in the HBP2G. Since the acid value of the HBP2G-g-PLA samples is lower than HBP2G and PLA. These compounds participated in the esterification reaction. The schematic representations of these reactions are presented in the Figure 2. Despite the fact that the PLA also has OH groups in its structure the probability that they reacted is low because the electron-withdrawing effect of the carbonyl group of PLA contributes to the higher reactivity of OH groups of the HBP2G than those OH groups of the PLA. Furthermore the OH groups of the PLA are sterically hindered. Therefore the main reaction that occurs in this process is between acids groups of PLA and OH groups of HBP2G.

The results of conversion percentage of the reaction are presented in the Table II. It is observed that when the content of PLA employed in the synthesis is 40 (HBP2G60) and 55 wt % (HBP2G45), the conversion percentage is lower than when high proportions of HBP2G are used (HBP2G90 and HBP2G75), this is because when the amount of PLA is high, the reaction system increases the viscosity and it makes the elimination of water and other diffusional processes (collision between HBP2G and PLA molecules, for the reaction to be carried out) more difficult. In all cases, the VOH of the HBP2G-g-PLA samples was lower than HBP2G (Table II), this indicates that the esterification reaction between HBP2G and PLA was performed, and this increased with the amount of PLA.

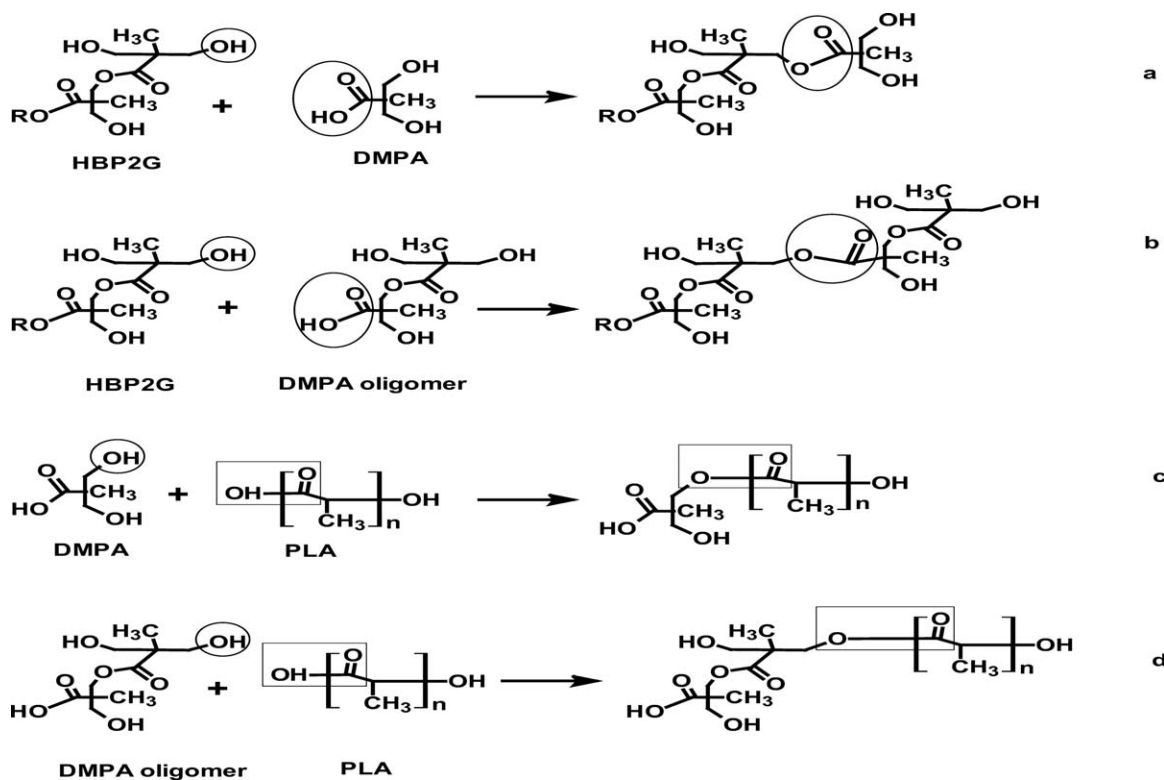


Figure 2. Schematic representation of side reactions related with DMPA and DMPA oligomers (a) HBP2G and DMPA, (b) HBP2G and DMPA oligomers, (c) DMPA and PLA, and (d) DMPA oligomer and PLA.

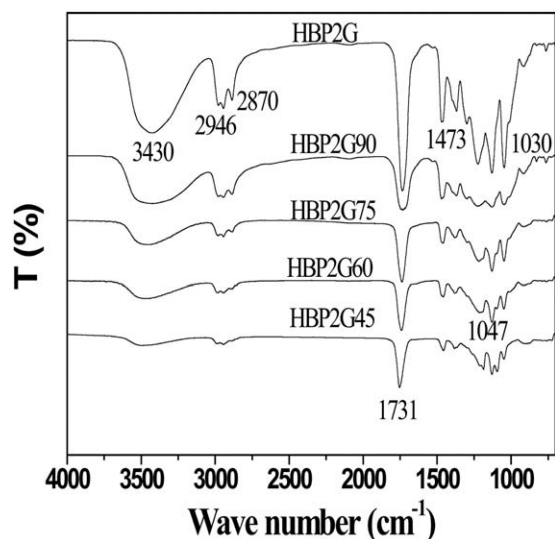


Figure 3. IR spectra of the samples.

The modification percentage (MP) of the HBP2G was calculated using the following equation:

$$MP = \frac{HV_{\text{HBP2G}} - HV_{\text{HBP2G-g-PLA}}}{HV_{\text{HBP2G}}} \times 100 \quad (4)$$

where HV_{HBP2G} and $HV_{\text{HBP2G-g-PLA}}$ are the HBP2G and HBP2G-PLA hydroxyl value, respectively. The results of MP of the HBP2G are presented in Table II. The MP value of the samples augmented with the content of PLA employed on the synthesis, and this result was expected because when the PLA amount is increased, the number of acid groups is greater; therefore, the number of hydroxyl groups that reacted is

increased. These results are in agreement with the obtained acid value.

IR Analysis (IR)

Figure 3 shows the IR spectra obtained for the HBP2G and HBP2G-g-PLA samples. An absorption around 3430 cm^{-1} is observed, which is due to stretching of the OH groups, and such signal also was observed for the HBP2G-g-PLA samples, but with a lower intensity. In the case of the HBP2G-g-PLA samples the intensity of stretching of OH groups decreased with the proportion of PLA, indicating that the modification of HBP2G rises, this is consistent with the results of the conversion percentage and hydroxyl value discussed in previous section. The reduction of this signal (OH groups), suggests that the reaction between the HBP2G and PLA occurred, through OH groups of HBP2G and $-\text{COOH}$ groups of PLA. Figure 4 illustrates this reaction. The signals at 2870 and 2946 cm^{-1} are due to C—H stretching (aliphatic), at 1731 cm^{-1} appear a signal which corresponds to carbonyl groups of ester.

At 1473 cm^{-1} a band due to the angular deformation of CH_2 group appears, signals at 1130 and 1047 cm^{-1} are attributed to asymmetric stretching C—O and $-\text{C}-\text{O}-\text{C}-$ groups, respectively. These signals are attributed to ester groups and have been reported by Jang and coworkers to hyperbranched aliphatic polyesters.¹³

The same behavior has been observed by some authors in the modification of hyperbranched polyester polyol of fourth generation modified with fatty acids of tall oil (TOFA)¹⁴ and a study of the improvement of the properties of the polyurethanes with the incorporation of polydimethylsiloxane to its chain using the

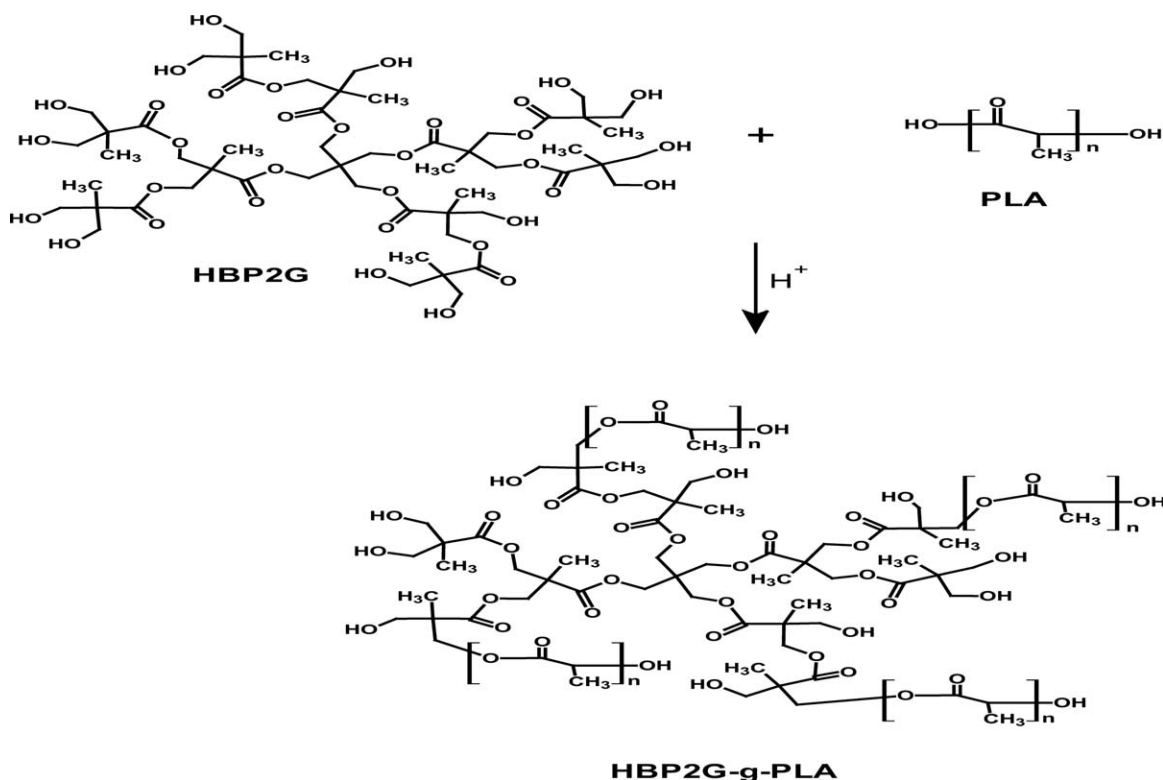


Figure 4. Schematic representation of the formation of a HBP2G-g-PLA.

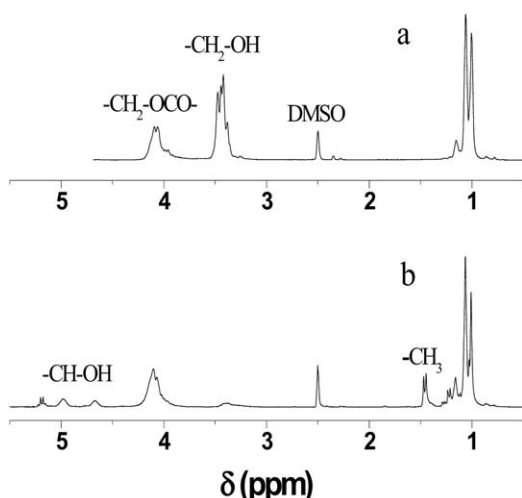


Figure 5. NMR analysis (a) HBP2G and (b) HBP2G45.

highly branched aliphatic polyesters of fourth generation as branching agents.¹⁵

Analysis of Nuclear Magnetic Resonance (NMR)

Figure 5 shows the ¹H NMR spectra for the HBP2G [Figure 5(a)] and to the HBP2G45 [Figure 5(b)]. In HBP2G spectrum [Figure 5(a)], three signals at 1.0, 1.06, and 1.16 ppm were observed, which are due to the protons of the methyl groups of dendritic (D) terminal (T), and linear (L) units. At 2.50 ppm, the signal corresponding to the solvent (dimethyl sulfoxide) appears, the signal at 3.40 ppm is due to methylene protons attached to OH groups (—CH₂OH). The signal at 4.1 ppm is attributed to protons of methylene groups adjacent to hydroxyl groups that reacted (—CH₂OR). These signals have been reported by other authors.^{16–23}

For HBP2G45 [Figure 5(b)], additional signals were observed with respect to HBP2G [Figure 4(a)], which appeared at 1.8 ppm and around of 5 ppm. The signal at 1.8 ppm is attributed to —CH₃ protons of the PLA. The signals around 5 ppm are

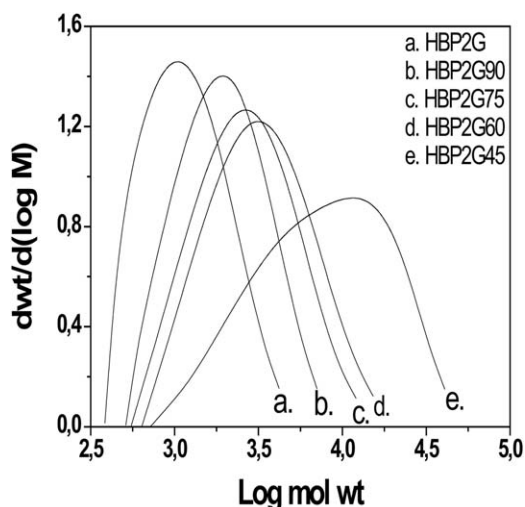


Figure 6. SEC analysis of the samples.

Table III. M_n , M_w , and PI Values of the Samples

Samples	M_n (g/mol)	M_w (g/mol)	PI
HBP2G	1001	1361	1.36
HBP2G90	1617	2285	1.41
HBP2G75	2131	3313	1.55
HBP2G60	2554	4091	1.60
HBP2G45	5049	10,820	2.14

due to protons of —CH of PLA, these signals have been previously reported in other studies.^{24,25}

In the spectrum of the HBP2G45 sample, the methylene proton signal joined to OH groups (—CH₂OH) was not observed, this is an indication that these groups reacted. Another important aspect is that an increase in the signal at 4.1 ppm for methylene groups adjacent to the hydroxyl groups that reacted (—CH₂OR) was observed. Therefore it can be concluded that the HBP2G was modified with the PLA, which also is corroborated by the results of IR, AV, and OHV analyses.

Analysis by Size Exclusion Chromatography (SEC)

Figure 6, shows the chromatograms of the HBP2G-g-PLA samples. Table III, shows the number (M_n) and (M_w) weight average molecular weight and the polydispersity index (PI) of the molecular weight of the samples.

It is observed that the molar mass of the modified HBP2G is greater than that of HBP2G, suggesting that the PLA was grafted in the HBP2G. The M_w and M_n increased with the content of PLA used on the modification, which was expected. Similar behaviors have been reported by Murillo and coworkers on modification of HBP with tall oil fatty acids¹⁷ and alkyd resins modified with silicone.²⁶ The analysis of SEC was used only to make a comparative analysis between the samples because the standard employed is a linear polymer (styrene) and the polymers obtained in this study are hyperbranched. Therefore this method is not quantitative.

Analysis of Dynamic Light Scattering (DLS)

Figure 7 presents hydrodynamic dimensions on number [Figure 7(a)], volume [Figure 7(b)], and intensity [Figure 7(c)] of HBP2G and HBP2G90. It can be observed (Figure 7) that the hydrodynamic dimensions of HBP2G are about 10 nm and that none of the number and volume distributions of the HBP2G90 is observed. The presence of the HBP2G distribution indicates that the PLA was grafted in the HBP2G. Also in these Figure 7(a,b) a distribution around 10^3 nm is observed, this is due to the formation of HBP2G90 (larger hydrodynamic dimensions than HBP2G). The other HBP2G-PLA samples were not studied because for those, the hydrodynamic dimensions were high and they were not in the range of the measure of the equipment.

Volume and number distributions are monomodal for both samples (HBP2G and HBP2G90), but the intensity distribution [Figure 7(c)] is bimodal for HBP2G90 and trimodal for HBP2G. Indicating that both samples showed agglomerations, which are due to interaction between OH groups (hydrogen bonds). This has been observed by some authors to HBP

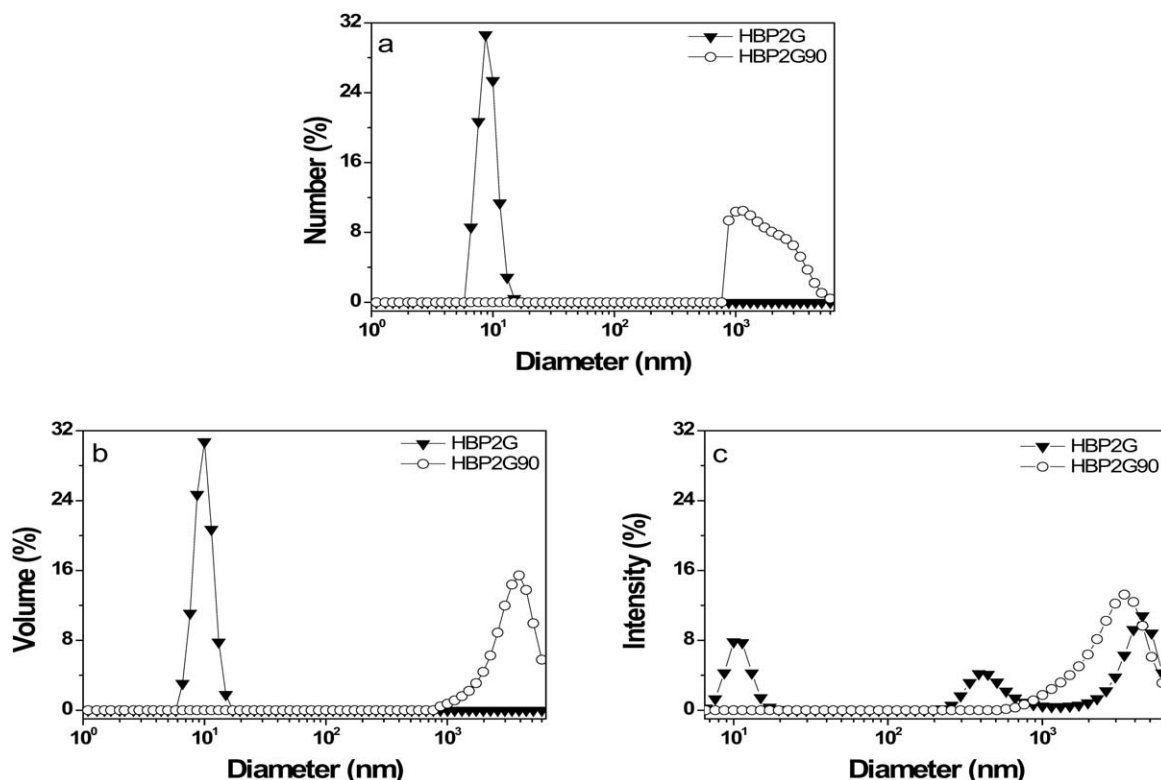


Figure 7. Dynamic light scattering (a) number (b) volume, and (c) intensity.

samples include utilizing good solvents, such as dimethylformamide and dimethylsulfoxide.²⁷ The presence of other distributions in the intensity distribution is attributed to large particles scatter more light.²⁸

Thermogravimetric Analysis (TGA)

Figure 8 shows the results of the TGA. It is noted that the HBP2G-g-PLA samples have a similar behavior on thermal stability, but these have an intermediate value between the HBP2G and PLA. For all samples, a weight loss around at 150°C appeared. This is due to decomposition of com-

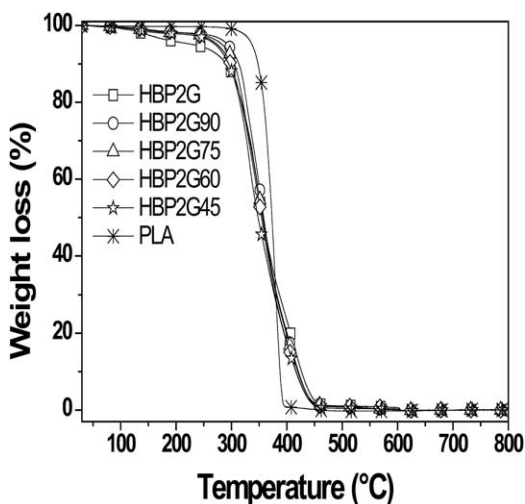


Figure 8. TGA thermograms of the samples.

pounds of low molecular weight, but this weight loss is higher for HBP2G (5.2%) than HBP2G-PLA samples (around 3.1%).

According to the degradation temperatures (T_d) shown in Table IV, one can infer that the thermal stability is independent of the amount of PLA used in the synthesis and the molecular weight of the samples. This behavior can be attributed to the fact that during synthesis, side reactions mentioned above (Figure 2) and other factors such as intramolecular etherification and hydroxy-ester exchange through of HBP2G-g-PLA occurred (Figure 9). This has already been reported by Murillo and Zagar^{29,30} to hyperbranched polyester polyols. Another important aspect is that the PLA possibly suffered chain scission during the synthesis of the materials and form low molecular weight compounds, it is associated with the synthesis temperature and reaction time employed in this study.^{31,32}

Table IV. T_d , T_g , T_c , T_m , and ΔH_m of the Samples

Samples	T_d (°C)	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m (J/g)
HBP2G	218.8	24.9	82.6	107.8	7.3
HBP2G90	249.1	34.5	-	-	-
HBP2G75	255.9	32.4	-	-	-
HBP2G60	247.6	28.8	-	-	-
HBP2G45	243.1	42.8	-	-	-
PLA	295.3	57.6	105.6	156.9	24.3

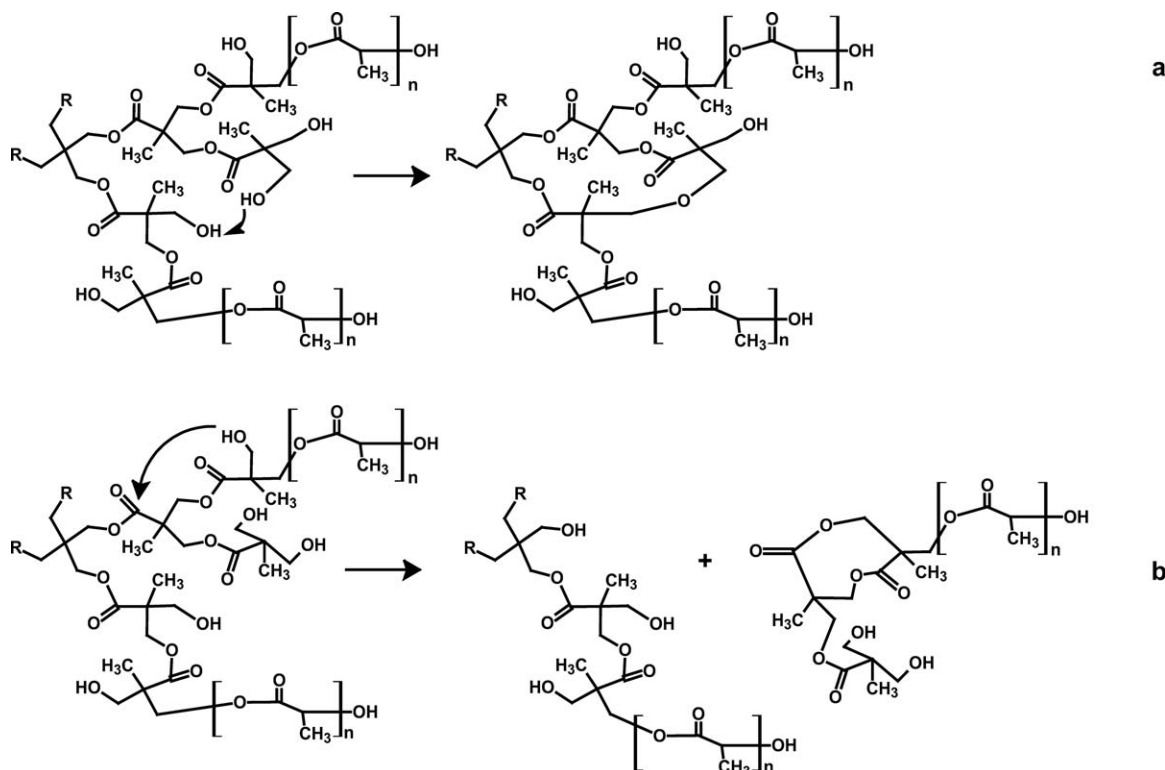


Figure 9. Side reactions of the HBP2G-g-PLA (a) intramolecular etherification and (b) hydroxy-ester exchange.

Differential Scanning Calorimetry (DSC)

The DSC thermograms of the samples are presented in Figure 10. Figure 10(a) shows the modulated DSC thermograms obtained to pure PLA, HBP2G90, and HBP2G75, where it can be seen that PLA exhibit a crystallization temperature (T_c) and melting temperature (T_m) (semicrystalline compound). None of the samples of HBP2G-g-PLA had a crystallization and melting

temperature [Figure 10(b)]. The behavior exhibited by the HBP2G90 and HBP2G75 samples was completely amorphous indicating that the reaction between HBP2G and PLA was carried out.

Figure 10(b) shows the DSC thermogram obtained from the conventional samples. The HBP2G sample has a glass transition temperature (T_g), T_c and T_m , the presence of crystallinity in

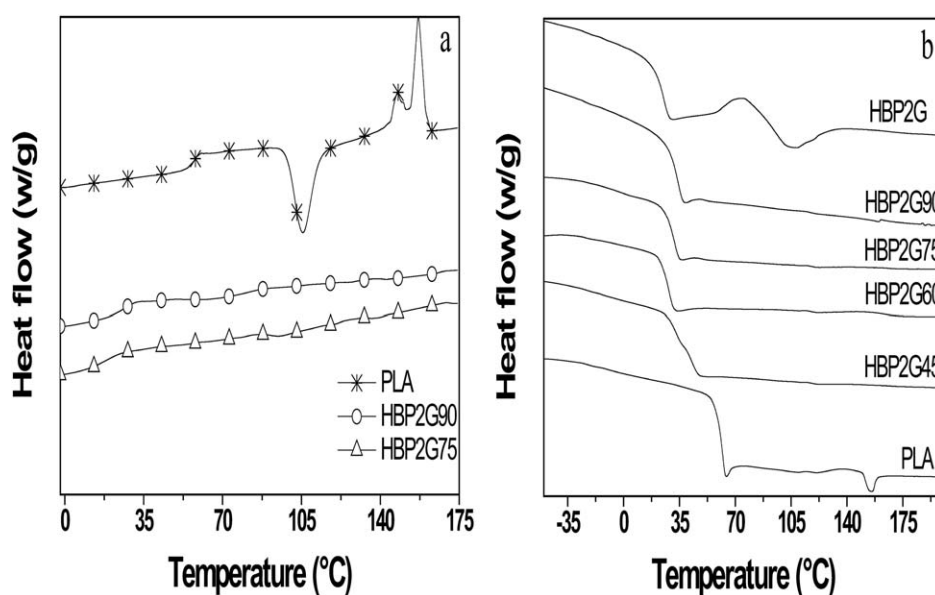


Figure 10. DSC thermograms of the samples (a) Modulated (b) Conventional.

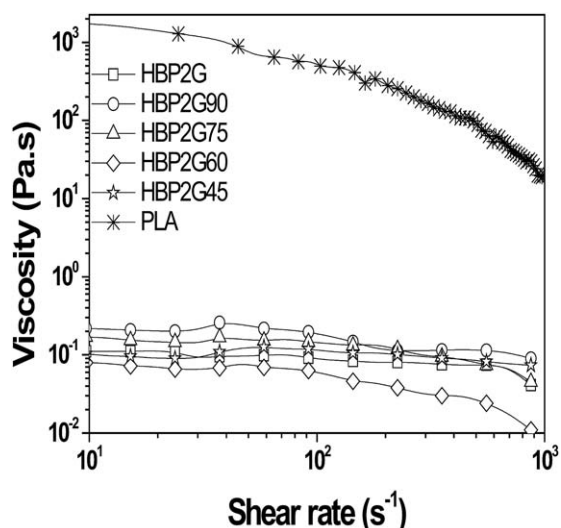


Figure 11. Viscosity versus shear rate of the samples.

these materials has been attributed to the formation of a crystalline structure, which is formed by the interaction between OH groups through hydrogen bonds.^{26,29,33}

As demonstrated in Figure 10(b), in the HBP2G-*g*-PLA samples, only one T_g is observed and there doesn't appear to be any crystallization of the HBP2G, which indicates that during the synthesis of the HBP2G-*g*-PLA samples, the interaction between OH groups through hydrogen bonds have been broken by the modification of terminal OH groups of the HBP2G. Table IV shows the values of the representative temperatures: T_g , T_c and T_m , and melting enthalpy (ΔH_m). It is noted that the T_g values of the samples are greater than the HBP2G and lower than that PLA. A trend is observed in the behavior of the T_g with the amount of PLA and HBP2G used in the synthesis, or the molecular weight, which was probably due to the random man-

ner of the process of the HBP2G modification and possibly during the synthesis side reactions occurred, which were mentioned above.

According to the obtained results one can infer that HBP2G modification with the PLA effectively occurred. The PLA ΔH_m is much greater than that of HBP2G, which is due to the highest crystallinity of this.

Rheological Analysis

The HBP2G-*g*-PLA samples exhibited a Newtonian behavior at a shear rate range between 10^1 and 10^2 s^{-1} (Figure 11), due to its, low hydrodynamic volume. After of 10^2 s^{-1} , the samples presented a pseudoplastic behavior, which is possibly due to the disruption of interactions (due to hydrogen bonds through of OH groups) or disentanglement (attributed to PLA chain in the HBP-PLA). Behavior of PLA is pseudoplastic; this is attributed to the disentanglement. The PLA bulk viscosity is attributed to the fact that it is a high molecular weight polymer.

The viscosities at a shear rate of 10^1 s^{-1} were the following: PLA:1679.4, HBP2G:0.110, HBP2G90:0.217, HBP2G75:0.161, HBP2G45:0.097, and HBP2G60:0.079 Pa.s. It was expected that increasing the proportion of PLA also will increase the viscosity of the HBP2G-*g*-PLA samples, but this was not observed. Furthermore some samples (HBP2G90 and HBP2G75) had higher viscosity than HBP2G. The HBP2G45 sample has lower viscosity than HBP2G. In the case of the HBP2G60 sample, this presented a viscosity very similar to HBP2G. The behavior exhibited by the samples is possibly related with the aforementioned side reactions before named in this study and PLA chain degradation.

The behavior of the elastic (G') and viscous (G'') modulus versus frequency is shown in Figure 12, for the HBP2G, HBP2G90, and HBP2G75 samples [Figure 12(a)] and HBP2G60 and HBP2G45 samples [Figure 12(b)].

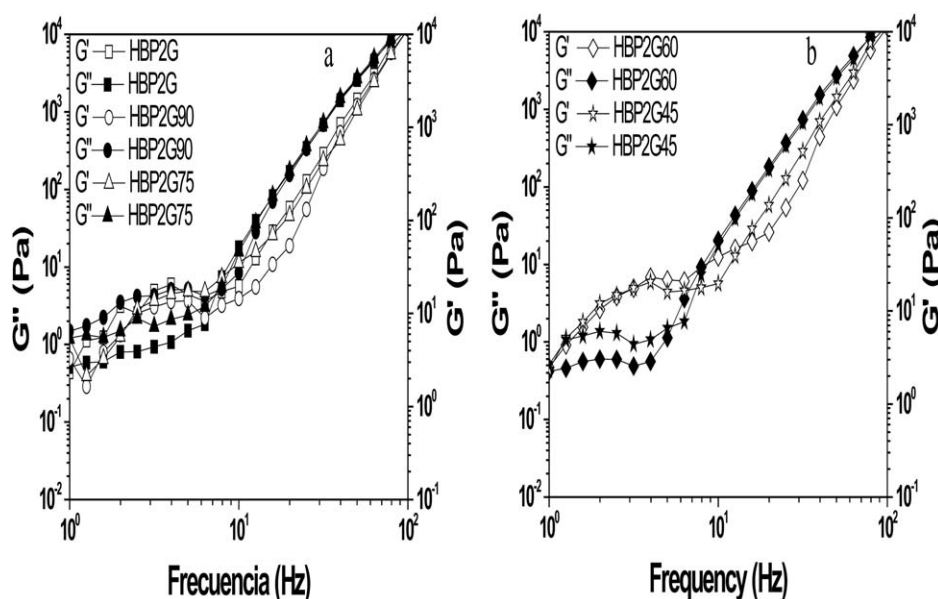


Figure 12. Elastic and viscous modulus (a) HBP2G, HBP2G90, HBP2G75, and (b) HBP2G60, HBP2G45.

It can be observed that the initial rheological behavior of all samples is elastic (about 8 Hz), but at a frequency >8 Hz, the behavior is viscous. Therefore in the frequency range examined, the rheological behavior is mainly viscous. This behavior has been observed for hyperbranched polyester polyols.³⁴

CONCLUSIONS

In this study HBP2G modified with PLA was obtained. This contributed to the development of new materials, which can be employed as compatibilizer on starch-PLA blends or PLA blends with hydrophilic polymers, since they presented a high degree of PLA in the HBP2G and they contain OH groups and PLA chains in their structures. Furthermore due to the low viscosity, these materials can be used as plasticizer in these systems.

The hydroxyl value, IR, NMR, and DLS analyses performed to HBP2G-g-PLA evidenced the reaction between HBP2G and PLA. The modification percentage of HBP2G increased with the content of PLA employed on the synthesis. The DSC analyses exhibited changes in the glass transition temperature and also the absence of crystallization and melting temperature in the functionalized materials. The DSC and TGA analysis showed no evidence of the presence of residual PLA in the HBP-PLA samples. Therefore it is an indication that the final acid value is due to mainly residual DMPA and DMPA oligomers. The rheological analyses showed evidence that the materials showed Newtonian behavior in a range dependent on shear rate. Furthermore a mainly viscous behavior was exhibited. The rheological and thermal properties of the HBP2G-g-PLA samples were independent of the amount of PLA and HBP2G used in the synthesis, which was possibly due to side reactions. The samples exhibited agglomerations due to interaction between OH groups (through hydrogen bonds). The hydrodynamic dimensions of the HBP2G-g-PLA were higher than HBP2G.

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