



Hyperbranched alkyd resins obtained without volatile organic compounds

Resinas alquídicas altamente ramificadas obtenidas sin compuestos orgánicos volátiles

Rafael Enrique-Rangel^a, María Judith Percino-Zacarias^b, Edwin Alberto Murillo-Ruiz^{c*}

^aEstudiante de Tecnología Química, Universidad Francisco de Paula Santander, Cúcuta, Colombia. orcid.org/0000-0002-6934-5950

^bDoctora en Química de Polímeros, Benemérita Universidad Autónoma de Puebla, Puebla, México. orcid.org/0000-0003-1610-7155

^cDoctor en Ciencias Químicas, Universidad Francisco de Paula Santander, Cúcuta, Colombia. orcid.org/0000-0002-0617-2327

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ABSTRACT

Keywords:

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Background: Hyperbranched alkyd resins have usually been obtained from hyperbranched polyester polyols (HBP) of second, third and fourth generations. Objectives: In this work the influence of the proportion of TOFA on the structural, thermal, and rheological and films properties of hyperbranched alkyd resins (NRA) were evaluated. **Methodology:** In order to obtain the NRA, the respective amount of HBP of fifth generation (HBPIG), tall oil fatty acids (TOFA) and p-toluenesulphonic acid (0.1 wt%), were taken to the reactor. The temperature was kept at 200 °C. The system was kept under mechanical stirring (200 rpm) and the conversion of the reaction was evaluated by measurement of acid value (VA). The molar ratios of HBP:TOFA were as follows: 1:3 (NRA1), 1:4 (NRA2), 1:5 (NRA3) and 1:6 (NRA4). **Results:** VA of the NRA was lower than that of TOFA, the hydroxyl value (VOH) was minor compared to that of HBPIG. This is an indication that the esterification reaction between TOFA and HBPIG was carried out. The reaction conversion for obtaining the conversion to NRA was higher than 90 %. By nuclear magnetic resonance (NMR) analysis, the signals of the methylene protons joined to OH groups of the HBPIG were evidenced and decreased in their intensity in the NRA1, due to the reaction between HBPIG and TOFA. The hydrodynamic dimensions of the NRA1, NRA2 and NRA3 were nanometrics. **Conclusions:** The NRA presented the lowest viscosity. Furthermore all NRA, exhibited OH groups and double bonds, which allow that these materials be employed for obtaining hybrid materials and also as crosslinking agents. The NRA showed good film properties.

RESUMEN

Palabras Clave:

Ácidos grasos de tall
oil Poliéster poliol
altamente ramificado
Propiedades
Resinas alquídicas

Antecedentes: Las resinas alquídicas altamente ramificadas, usualmente han sido obtenidas a partir de poliésteres polioles altamente ramificados (HBP) de segunda, tercera y cuarta generación. **Objetivo:** En este estudio se evaluó la influencia de la proporción de TOFA en las propiedades estructurales, térmicas, reológicas y de película de unas resinas alquídicas altamente ramificadas (NRA). **Metodología:** Para obtener las NRA, las respectivas cantidades de un HBP de primera generación (HBPIG), ácidos grasos de tall oil (TOFA) y de ácido p-toluensulfónico (0.1 %), fueron llevadas al reactor. La temperatura fue mantenida a 200°C. El sistema se mantuvo bajo agitación mecánica (200 rpm) y la conversión de la reacción fue evaluada por mediciones de valor ácido (VA). Las relaciones molares de HBPIG: TOFA, fueron las siguientes: 1:3 (NRA1), 1:4 (NRA2), 1:5 (NRA3) y 1:6 (NRA4). **Resultados:** El VA de las NRA fue inferior al de TOFA, el valor hidroxilo (VOH) fue inferior al del HBPIG. Esto indica que se llevó a cabo la reacción de esterificación entre TOFA y el HBPIG. La conversión de la reacción para obtener las NRA fue superior al 90 %. Por análisis de resonancia magnética nuclear (RMN) fue evidenciada la señal de los protones metileno unidos a grupos OH del HBPIG disminuyó su intensidad en la NRA1, debido a la reacción entre el HBPIG y TOFA. Las dimensiones hidrodinámicas de las NRA1, NRA2 y NRA3 fueron nanométricas. Las propiedades de película fueron buenas. **Conclusión:** Las NRA presentaron baja viscosidad. Además, todas exhibieron grupos OH y dobles enlaces, los cuales permite que estos materiales sean empleados para obtener materiales híbridos y como agentes entrecruzantes. Las NRA presentaron buenas propiedades de película.

Introduction

Conventional alkyd resins (low branched structure) are widely used in the coatings industry and are the most versatile binders used in architectural, industrial and decorative coatings [1]. These materials are obtained with high levels of volatile organic compounds (VOCs) (generally > 60 %), that contribute to global warming and the creation of photochemical ozone, which is toxic to plants, animals and humans [2]. The possibility of obtaining low - cost versatile products with renewable materials, make alkyd resins very attractive materials in the coatings industry because they have excellent properties of gloss, flexibility and adhesion [1]. HBPs are a great alternative to obtain HBRA [3] because they have a large number of functional groups in their periphery and low viscosity in solution, and in melted in comparison with linear polymers [4].

HBRA have low molar mass and may be the result of high content of solids [4]. These resins have good gloss, adhesion, flexibility and drying time [4]. Some studies report the synthesis of these resins. In a study, HBRA were prepared from a fourth-generation HBP and TOFA and were obtained with a solids content of 50 % [5]; they had good properties of gloss, flexibility and adhesion. In another study, the synthesis of solvent-free HBRA was reported, which were obtained from first, second and third generation HBPs, and fatty acids from soybean and flaxseed oil [6].

HBP was obtained from 1, 3, 5 - tris (2-hydroxyethyl) cyanuric acid (trifunctional) and dimethylol propionic acid (DMPA). The obtained materials showed low viscosity (< 5.5 Pa.s) and good film properties [6].

*Corresponding author.

E-mail address: edwinalbertomr@ufps.edu.co (Edwin Alberto Murillo Ruiz).



An HBRA was synthesized from a second generation HBP and flaxseed fatty acids, with a solids content of 70 %. The resin showed low viscosity (17.7 Pa.s), and good film properties [7].

The advantage of obtaining alkyd resins from a first-generation HBP, is that the amount of DMPA (non-renewable) used to obtain HBP is low, compared to higher-generation HBP. In addition, according to the review of the literature, there are no reports of the synthesis of HBRA that have been obtained by modification of a first-generation HBP produced from pentaerythritol and DMPA, and modified with TOFA. Therefore, in this work the synthesis of four HBRA was performed, starting from HBP1G and TOFA. For the obtained materials, the effect of different proportions of TOFA in the structural, thermal, rheological and film properties was evaluated.

Materials and Methods

Materials DMPA, pentaerythritol, potassium hydroxide, phenolphthalein and p-toluenesulfonic acid provided by Sigma Aldrich were used in this research. TOFA was supplied by the Colombian company Colorquímica SA.

Materials preparation

Synthesis of first generation HBP (HBP1G) With regard to the preparation of material, the methodology reported by Muriillo et al. [8], [9] was used. Specific amounts of pentaerythritol (one mole) and DMPA (4 mole), were taken to a reactor under a nitrogen atmosphere at 140 °C; then, the respective amount of p-toluenesulfonic acid (0.4%) was added. The system was maintained under mechanical stirring (200 rpm), suspending it when the desired AV was reached. The reaction conversion was evaluated by AV measurements. In (Figure 1) the schematic representation of the chemical reaction for the synthesis of HBP1G is shown.

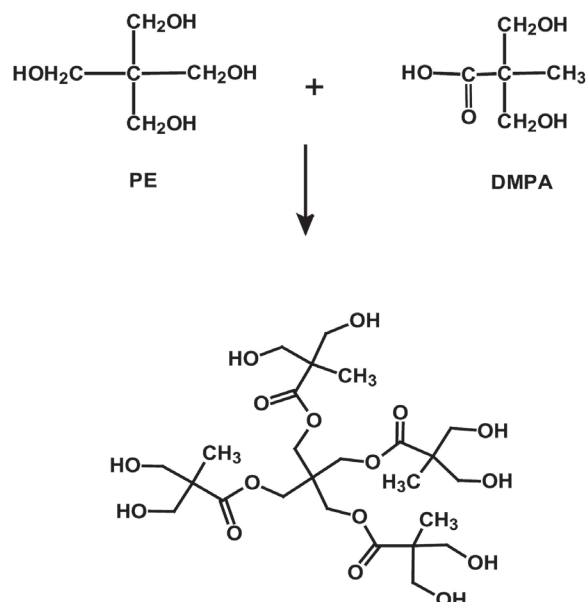


Figure 1. Schematic representation of the synthesis of a HBP1G

Synthesis of HBRA To obtain HBRA (Figure 2), the HBP1G was mixed with the respective proportions of TOFA, maintaining the same conditions as in the synthesis of HBP1G, but at a temperature of 200 °C and using 0.1 % p-toluenesulfonic acid. The conversion of the reaction was carried out by AV measurements until obtaining a value of less than 10 mg KOH/g sample. The molar ratios of HBP1G:TOFA were: 1:3 (HBRA1), 1:4 (HBRA2), 1:5 (HBRA3) and 1:6 (HBRA4).

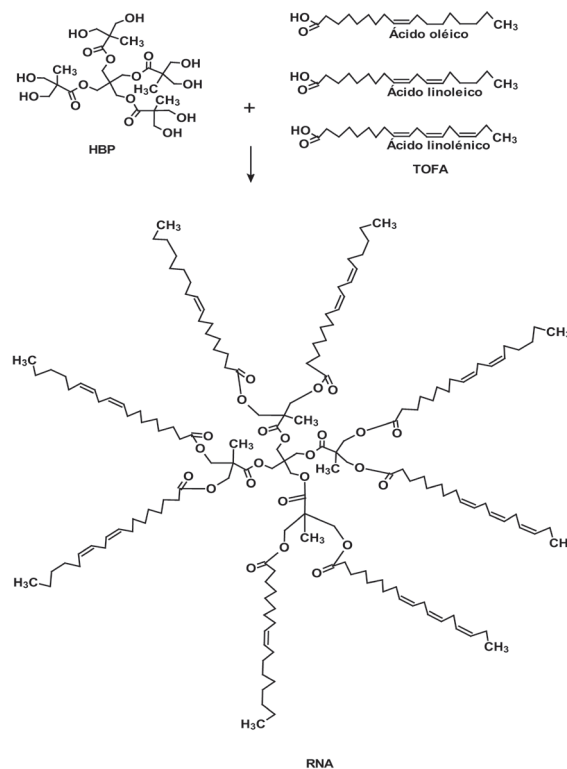


Figure 2. Schematic representation of the synthesis of an HBRA

Materials characterization The AV analyses were carried out twice using the ASTM D 1639-90 standard. The method used for the determination of HV was the described in the AOCS Cd 13-60 standard, and two repetitions were made. The infrared (IR) analyses were performed on a Perkin Elmer Spectrum One spectrometer using 8 sweeps and a resolution of 4 cm⁻¹. The ¹H NMR analyses were performed on a Bruker AC 300 MHz spectrometer. The ¹H NMR spectrum of the HBP1G was obtained in 3% solutions in DMSO-d₆; for the HBRA1, a 3% solution in deuterated chloroform was used. An Agilent 1200 series electrospray ionization mass spectrometer with a MQ quadrupole mass detector was used to analyze HBRA and HBP. A mixture of 0.1 % ammonia in methanol/water (8:2) was used as the mobile phase with a flow rate of 0.8 mL/min for HBP1G and chloroform-acrylonitrile (5:1) for HBRA.

The injection volume was 20 L. The conditions for mass spectrometry were: temperature of the drying gas 350 oC, drying gas flow rate of 12 L/min, 30 V capillary voltage and 6 psi nebulizer pressure. A negative run was obtained between 100 and 1500 m/z.

The hydrodynamic dimensions of the HBP1G and the HBRA were determined by dynamic light scattering (DLS), using a Malvern Instruments zetazizer equipment at a wavelength of 633 nm, using an angle of incidence of 173°. For this, solutions of HBP1G in dimethyl formamide (1 %) and HBRA in 1% xylol at a temperature of 25 °C were used.

The rheological analyses were carried out in an Anton Paar rotational rheometer, using a parallel plate geometry of 20 mm in diameter for the HBRA1 and a concentric cylinders geometry for the other HBRA. The differential scanning calorimetry (DSC) analyses were carried out in a TA Instruments Q-100 equipment at a heating rate of 20 °C/min using a nitrogen atmosphere. The thermogravimetric analyses (TGA) were performed in a TA Instruments SDT 600 equipment using a heating speed of 10 °C/min and a nitrogen atmosphere.

For the evaluation of film properties, thicknesses of 52 µm were achieved and a mixture of siccatives (0.6 % calcium, zirconium and aluminum octoates) was used. Flexibility measurements were made using the ASTM D 522 standard and the adhesion ones were carried out using the ASTM D 3359 method B. The gloss measurements were performed using the ASTM D 523 standard, using lenetas. The chemical resistance to solvents of the resins was evaluated against water and 0.1 M hydrochloric acid (HCl) solutions, 0.1 M sodium chloride (NaCl) and 0.1 M sodium hydroxide (NaOH).

Results and analysis

The AVs of the HBRA were lower than those of TOFA and HBP1G (Table I). In the same way, it was observed that the AVs of the HBRA are much lower than the TOFA ones, this means that the chemical reaction between the HBP1G and TOFA occurred, since the only cause of the decrease in the AV of TOFA is attributed to the esterification reaction between the acid groups in TOFA with the OH groups in the HBP1G.

The CP of the esterification reaction was determined according to a method previously reported in the literature [8]. In (Table II) the obtained results are shown; it can be seen that the CPs were higher than 90% and there was no significant increase in this with the amount of TOFA used in the synthesis.

The HV for the HBP1G was higher than in the case of the HBRA; this indicates that the number of OH groups present in the HBP1G is higher than in the HBRA, which shows the esterification reaction between the HBP1G and TOFA. Similarly, the HV of the HBRA was reduced with the amount of TOFA used in the synthesis, which was expected. The modification percentage of HBP1G (% M) was determined according to a method previously reported in the literature [10].

The % M of the HBRA (Table I) increased with the TOFA content used in the materials preparation, so it can be interpreted as a higher degree of esterification.

In addition, it can be inferred that all HBRA still have unreacted OH groups in their structures; the same behavior has been observed for alkyd resins obtained from sorbitol, where a reduction of the AV of fatty acids was evidenced [11]. HBRA also presented lower AV than TOFA and a reduction of HV with TOFA content [5].

Table I. Values for AV, CP, HV and % M

	TOFA	HBP1G	NRA1	NRA2	NRA3	NRA4
VA (mg de KOH/g sample)	192.19	40.23	8.21	8.18	7.90	7.70
PC	-	-	95.72	95.74	95.88	95.99
VOH (mg KOH/g sample)	-	650.23	321.14	258.78	200.65	136.29
%M	-	-	-	60.20	69.14	79.04

(Figure 3) shows the IR spectra of the samples. HBP1G presented an absorption at 3396 cm⁻¹ associated with the OH stretching vibration; in addition, the HBP1G had other signals at 2930 cm⁻¹ (-CH₂ asymmetric stretch), 2851 cm⁻¹ (-CH₂ symmetric stretch), 1733 cm⁻¹ (ester C=O stretch), 1474 cm⁻¹ (C-CH₃ asymmetric bending) and 1228 and 1142 cm⁻¹ (C-C-O stretch). In the IR spectra of the HBRA a decrease in the intensity of the signal of the OH groups (3396 cm⁻¹) with the content of TOFA and % M is observed; this is because of the esterification reaction between HBP1G and TOFA.

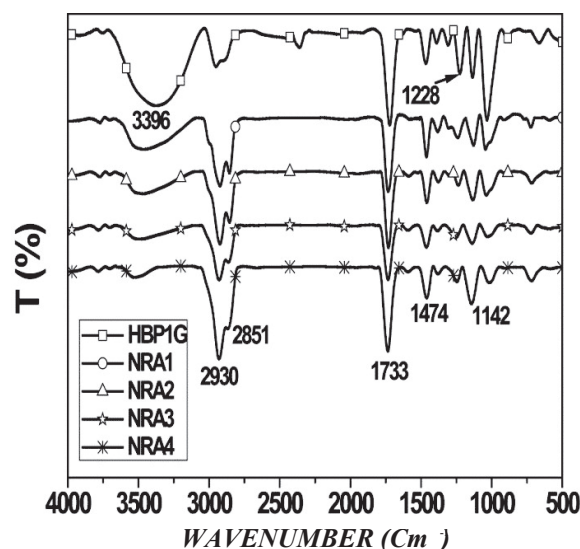


Figure 3. IR spectrum of the samples

These results are consistent with those obtained for AV and HV, since it is expected that the greater the number of TOFAs, the lower the number of residual OH groups and the greater the % M. Likewise, HBRA spectra presented a shoulder band around 3030 cm⁻¹, which is attributed to the presence of -CH=CH- bonds. HBRA obtained from third and fourth generation HBPs also showed a reduction in the intensity of the absorption of the OH groups [5], [6].

(Figure 4) shows the ^1H NMR spectra of the HBP1G (Figure 4a) and the HBRA1 (Figure 4b). In the NMR spectrum of HBP1G, different signals are observed (Figure 4a).

Around 4.0 ppm, there is a signal due to methylene protons attached to ester groups ($-\text{CH}_2\text{OOR}$); this confirms that the esterification reaction between pentaerythritol and DMPA occurred. In addition, another evidence of that fact is the presence of $-\text{CH}_3$ protons of linear, terminal and dendritic units that appear around 1 ppm.

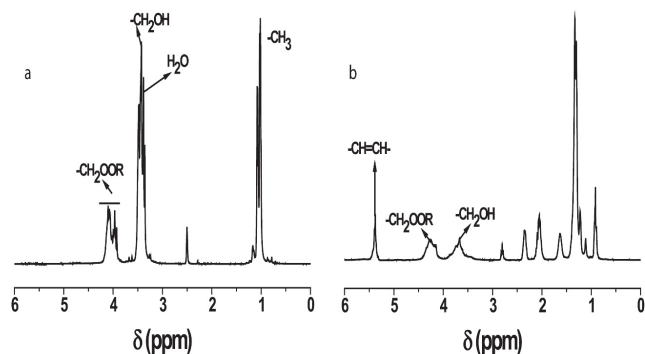


Figure 4. NMR spectra a) HBP1G and b) HBRA1

A signal around 3.5 ppm is observed (Figure 4), due to H_2O protons and to methylenes attached to OH groups ($-\text{CH}_2\text{OH}$).

The above signals have already been observed for HBPs [12]. In the ^1H NMR spectrum of HBRA1 (Figure 4b), a signal at 5.36 ppm is observed, which is attributed to protons of $-\text{CH}=\text{CH}-$; this signal is absent in the HBP1G spectrum (Figure 4a), what is an evidence that HBRA1 was produced since this type of protons are present in fatty acids [5], [6].

Another important aspect is that there is a reduction in signal intensity due to the methylene protons attached to OH groups ($-\text{CH}_2\text{OH}$) in HBRA1 compared to those of HBP1G (around 3.5 ppm), that indicates that the OH groups have reacted [13].

Therefore, it is another reliable evidence of the esterification reaction between HBP1G and TOFA. In the NMR spectrum of the HBRA1 (Figure 4b) the presence of signals between 0.5 and 2.5 ppm is observed, which are due to aliphatic protons present in the fatty acids that were incorporated into the HBRA1.

(Figure 5) shows the mass spectrum of HBP1G (Figure 5a), of HBRA1 (Figure 5b), HBRA2 (Figure 5c), HBRA3 (Figure 5d) and of HBRA4 (Figure 5e). For the HBP1G, intense peaks of molecular ions of acyclic species are observed at a distance of 116 ($M_{\text{DMPA}} - M_{\text{agua}}$) between two peaks, which correspond to the repetitive units. These signals have high intensity (m/z : 249, 365, 481, 597, 713 and 829).

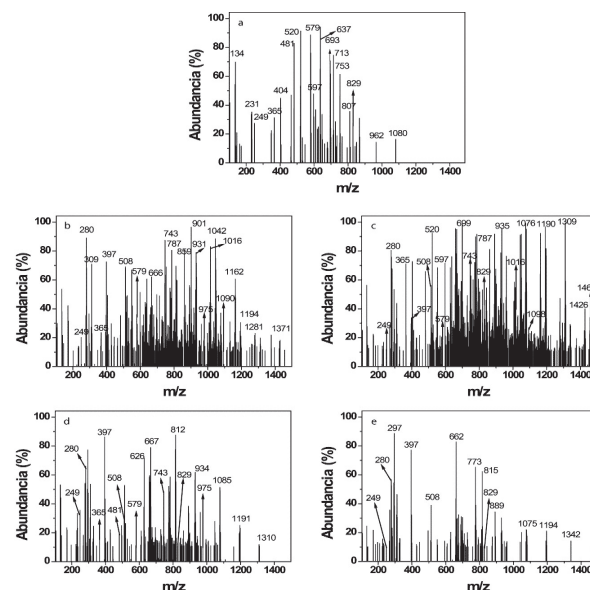


Figure 5. Mass spectra of the samples a) HBP1G and b) HBRA1, c) HBRA2, d) HBRA3 y e) HBRA4

The molar mass of acyclic (M_1) and cyclic (M_2) macromolecules were calculated using equations (1) and (2) [12]:

$$M_1 = M_{\text{DMPA}} + (\text{DP} - 1) (M_{\text{DMPA}} - M_{\text{water}}) \quad (1)$$

$$M_2 = (\text{DP})_{\text{RMN}} (M_{\text{DMPA}} - M_{\text{water}}) \quad (2)$$

Where:

DP , is the degree of polymerization.

M_{DMPA} , is the molar mass of DMPA (134 g/mol).

M_{water} , is the molar mass of water (g/mol).

In the HBP1G spectrum (Figure 5a) appear the peaks associated with the acyclic signals of the repetitive units of the DMPA (m/z : 249 (DP=2), 365 (DP=3), 481 (DP=4), 597 (DP=5), 713 (DP=6) and 829 (DP=7)); these signals have already been observed for HBP obtained from several generations [12]. The signal at $m/z = 579$ is due to cyclic units whose DP is 5.

On the other hand, the mass spectrum of the HBRA1 (Figure 5b) has some peaks of acyclic units that were observed for the sample of HBP1G; likewise, there are new signals at $m/z = 280$ due to fragments of fatty acid (R) (Figure 6a), at $m/z = 397$ associated with a fragment containing modified DMPA with one mole of R (Figure 6b), at $m/z = 508$ attributed to a fragment containing units of DMPA and RCOOH (Figure 6c). Over $m/z = 700$, other peaks were observed for HBRA1 that are attributed to acyclic units modified with TOFA. At $m/z = 743$ (acyclic unit whose DP = 4 modified with one mole of TOFA), at $m/z = 975$ (acyclic unit whose DP = 6 modified with one mole of TOFA), at $m/z = 1016$ and at $m/z = 1090$ (acyclic unit whose DP = 7 modified with one mole of TOFA), etc.

HBRA2 showed peaks at $m/z = 280, 397, 508, 743, 1016$ and 1090 , that are also present for HBRA1. HBRA3 (Figure 5d) and HBRA4 (Figure 5e) also presented additional peaks that do not appear in the mass spectrum of the sample of HBP1G; these peaks appear at $m/z = 280, 397$ and 508 . The intensity of the peaks observed for the HBRA were different, which indicates that the amount of these fragments is different for each of the samples. The presence of these new peaks in the mass spectra of the HBRA is an evidence of their formation.

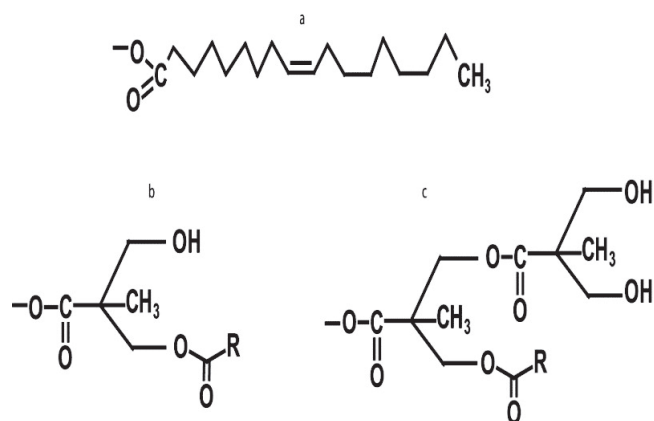


Figure 6. Mass spectra of the samples. Fragments of some structures a) $m/z = 280$, b) $m/z = 397$ y c) $m/z = 508$

(Figure 7) shows the size distributions in intensity (Figure 7a) and number (Figure 7b). The behavior presented by the samples HBP1G, HBRA1, HBRA3 and HBRA4 in intensity were bimodal (Figure 7a). The hydrodynamic dimensions in intensity of HBP1G were higher than HBRA2 and HBRA3 (Table II), possibly due to the fact that HBP1G is presenting a molecular aggregation through hydrogen bonds, which has been evidenced when DMF is used that is an excellent solvent for HBPs [13].

It was expected that the samples HBP1G and HBRA1 had smaller hydrodynamic dimensions than the other samples, since the HBP1G is unmodified and the HBRA1 presented the lowest degree of modification; this behavior is attributed to the aggregation of the macromolecules, since they have the greater number of OH groups (higher HV) which can interact through hydrogen bonds. The hydrodynamic dimensions in intensity of the samples HBRA3 and HBRA4 (Table II) were higher than those of the other HBRA; this was expected because they presented the highest degree of modification.

Table II. Hydrodynamic dimensions of the samples

Size		HBP1G	NRA1	NRA2	NRA3	NRA4
Intensity (nm)	d1	339	57.12	99.28	311.8	1.831
	d2	5507	435.2	-	5441	681
	d3	-	4467	-	-	4599
Number (nm)		295.10	23.65	89.64	273.5	857

The distribution in number of the samples was unimodal (Figure 7b). This behavior is different from that presented by the size distribution in intensity (Figure 7a), because the larger molecules scatter more light; due to this, some distributions (aggregates) that appear in (Figure 6a) are not observed in the number distribution, indicating that their number is small.

The hydrodynamic dimensions of the HBRA increased with % M (Table II) and these were nanoscale for HBRA1, HBRA2 and HBRA3 (Table II). Observing the results of the number distribution of the samples, it can again be seen that the HBP1G presented a greater hydrodynamic dimension than the HBRA1 and HBRA2.

Our results are very important because they allow to verify that three out of four HBRA obtained presented nanometric hydrodynamic dimensions, which is very useful in the coatings industry since this allows a greater coverage area.

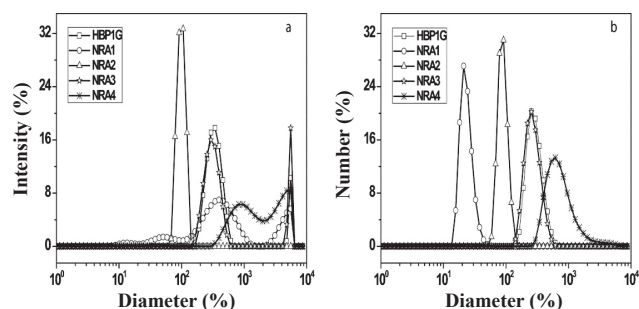


Figure 7. Sample distributions a) Intensity and b) Number

The hydrodynamic dimensions of HBP1G are greater than those of obtained fourth- (229 nm) and fifth- generation (165-278 nm) HBPs [9], possibly due to the fact that this material had a great interaction through their OH groups. Except for the HBRA4, the hydrodynamic dimensions of the HBRA are lower than those of alkyd resins obtained from a fourth generation HBP and TOFA [5].

The viscosity of the pure HBRA (free of solvents) at a shear rate of 0.56 s^{-1} were: HBRA1 (18.88 Pa.s), HBRA2 (6.89 Pa.s), HBRA3 (4.20 Pa.s) and HBRA4 (3.50 Pa.s) (Figure 8). According to the results, the viscosity decreased with the amount of TOFA used in the HBRA synthesis. HBRA1 and HBRA2 samples presented a pseudoplastic behavior, above all for HBRA1.

The greater pseudoplastic behavior exhibited by HBRA1 was due to the greater dissociation of hydrogen bonds, between OH groups that were not modified with TOFA, since this resin was obtained with the lowest % M. Another important aspect is that the lower amount of TOFA used for the synthesis of this resin, possibly made the TOFA substitutions to be produced at certain distances from each other so this facilitated the entanglement of the TOFA chains in the HBRA1. An evidence of this fact is the behavior exhibited by HBRA2, which presented a less pseudoplastic behavior than HBRA1.

The rheological behavior of HBRA3 and HBRA4 is mainly Newtonian between 1 and 375 s⁻¹, becoming pseudoplastic later, possibly due to the dissociation of interactions or unraveling of the TOFA chains present in the HBRA.

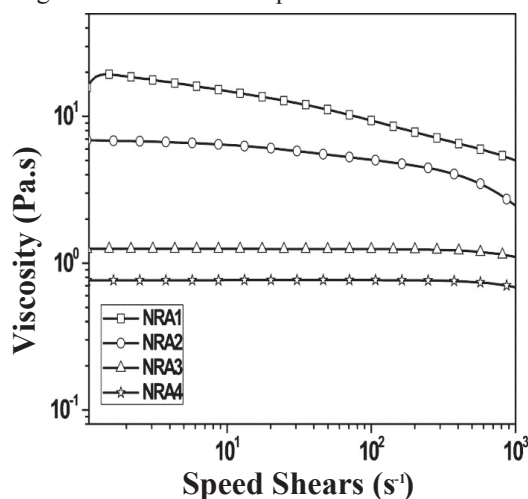


Figure 8. Rheological behavior of the HBRA

The viscosity values obtained for HBRA2, HBRA3 and HBRA4 were lower than those of an HBRA prepared from a second-generation HBP (using dipentaerythritol as the nucleus and DMPA as an extender) and castor fatty acids, which presented a viscosity of 17.5 Pa.s [7]. On the other hand, the viscosity value of the HBRA1 is comparable with the value for conventional alkyd resins (linear structure) with high solids content that had viscosity values of 26 Pa.s [3].

(Figure 9) shows the DSC (Figure 9a) and TGA (Figure 9b and 9c) thermograms of the samples. The HBP1G (Figure 9a) presented a glass transition temperature (T_g); besides, it has a crystallization temperature at 54.1 °C and a melting temperature at 86.75 °C. The presence of crystallinity (structural ordering) in this sample is associated with the interaction of OH groups through hydrogen bonds, making this sample acquiring a certain organization [14].

The same behavior has been observed for HBPs [9,14]. The HBRA did not present neither a crystallization nor a fusion temperature; this means that there was a dissociation of the hydrogen bonds causing the crystallinity, due to the modification with TOFA. The T_g of the HBRA (Figure 9a) decreased with the proportion of TOFA (Table III), and it was less than that presented by the HBP1G, because of the lubricating effect of TOFA. In addition, the T_g for HBP1G was not observed in any of these samples.

All these results are an evidence that in all cases the modification of HBP1G with TOFA occurred, being consistent with the results obtained from HV, AV, IR and NMR. The T_g value of HBRA1 is comparable to the value for an HBRA ($T_g = -14.8$ °C) whose oil length was 50%, which was obtained from a fourth-generation HBP and TOFA [10].

The T_g values of HBRA1 and HBRA2 were lower than that of the reported alkyd resin [10], due to the higher TOFA content. These results are analogous to those obtained by rheology, where a reduction in viscosity was observed with the increase in the proportion of TOFA, which was attributed to the plasticizing effect of TOFA in these resins.

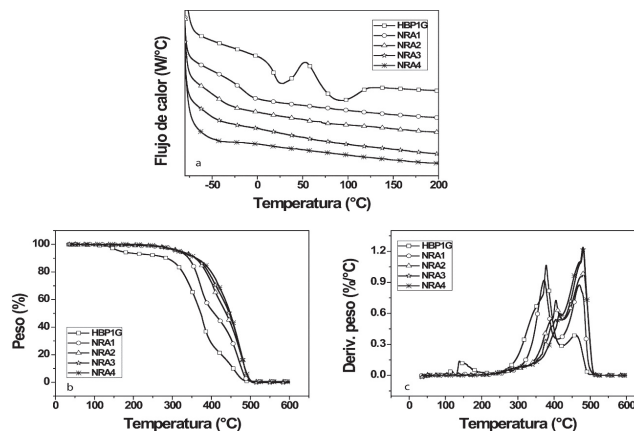


Figure 9. Thermograms of the samples a) DSC, b) TGA, Weight vs temperature and b) TGA, Derivative of weight vs temperature

The thermal stability of HBP1G (Figure 9b and 9c) is lower than that of the HBRA, attributed to an increase in the molar mass of the HBRA. In (Table III), the values of the temperatures of thermal decomposition of the samples (T_d) that were obtained from the onset are shown. In (Figure 9b and 9c), it can be seen that HBP1G presents a first loss (T_{d1}) possibly associated with the water evaporation.

In addition, two other losses (T_{d2}) and (T_{d3}) can be observed, may be associated with structures that were formed due to hydroxy-ester exchange reactions, intermolecular etherifications or structures containing a different number of units of pentaerythritol and/or DMPA.

Likewise, the third loss that appears for HBP1G is possibly due to high molecular weight molecules that underwent interaction through hydrogen bonds. The HBRA had two weight losses that appeared at a higher temperature than the second and third loss exhibited by the HBP1G (Table III), due to the modification with TOFA. The area of the first loss (T_{d1}) for HBRA1 is similar to the area of the second loss for HBP1G (T_{d2}), because of the greater amount of HBP used for the synthesis of this resin.

The area of the third loss for HBP1G is lower than the second loss for the HBRA and also appears at a lower temperature, which is due to the modification of HBP1G with TOFA. The area of the second loss for HBRA increases with the degree of modification of HBP1G, only for HBRA1, HBRA2 and HBRA3, since the area of HBRA3 and HBRA4 are very similar; the same goes for the T_d . The HBRA exhibited greater thermal stability than HBP1G due to the modification with TOFA.

The thermal stability of the HBRAs is higher than that of alkyd resins obtained from polyglycerol and fatty acids [15], and that of HBRA obtained from HBP and castor oil fatty acids whose values were between 395 and 460 °C [7].

Table III. T_g and T_d values of HBP1G and HBRAs

	HBP1	NRA1	NRA2	NRA3	NRA4
T _g (°C)	19.02	-14.46	-40.50	-66.04	-71.89
T _{d1} (°C)	112.69	373.16	405.27	405.37	414.74
T _{d2} (°C)	378.36	470.19	482.06	481.66	479.43
T _{d3} (°C)	459.79	-	-	-	

The thermal stability of the NRAs did not follow a trend with % M, possibly due to hydroxy-ester exchange reactions, interactions through hydrogen bonds or intermolecular etherification reactions.

On the other hand, the film properties of the VOC-free HBRAs are reported in (Table IV). In this sense, all the films passed the flexibility test, since none of them showed rupture in the area where the bending was performed, due to its amorphous nature. The same behavior has been observed for HBRAs [6,7].

The adherence was higher for the HBRA1, possibly because of its greater T_g and its greater rigidity. The adherence of the NRAs was equal to that of NRA reported in other studies, whose values were 5B [7].

The gloss of the samples was good and the values were very similar, although a slight increase was observed related to the proportion of TOFA used in the synthesis. It has been reported that if the gloss value measured at 60° is greater than 70, the gloss is considered high [7].

The gloss values obtained in this study are higher than those obtained for conventional alkyd resins, whose values were between 70 and 85 [16]. In addition, the gloss values of the HBRAs are also comparable with those of HBRA previously reported [3].

Tabla IV. Flexibilidad, adhesión y brillo de las HBRA

	HBRA1	HBRA2	HBRA3	HBRA4
Flexibility	Pasa	Pasa	Pasa	Pasa
Adhesion	5B	5B	5B	5B
Brightness	89.23	90.32	90.57	91.22

The chemical resistance of the HBRAs against water, NaCl and HCl was acceptable (Table V), due to the hydrophobic nature of the resins. At the same time, the chemical resistance of the HBRAs to the NaOH solution was regular, since there was a partial removal of the films; this is associated with the chemical structure of the HBRAs which are polyesters, being susceptible to a basic hydrolysis caused by NaOH. Alkyd resins obtained from sorbitol and fatty acid from soybean oil, [11] and HBRA, showed the same behavior [5].

Table V. Chemical resistance of the HBRAs

	HBRA 1	HBRA 2	HBRA 3	HBRA 4
H ₂ O	A	A	A	A
NaCl 0.1 M	A	A	A	A
NaOH 0.1 M	C	C	C	C
HCl 0.1 M	A	A	A	A

Conclusions

HBRAs were obtained without VOCs. These materials can be an alternative for reducing VOCs in the paint industry and as reactive diluents for conventional alkyd resins. The HV of the HBRAs decreased with the proportion of TOFA used in the synthesis. Likewise, it was possible by IR analysis to demonstrate a reduction in the intensity of the OH groups of the HBRAs, by increasing the proportion of TOFA; nevertheless, all the HBRAs showed residual OH groups. The ¹H NMR spectra allowed observing the presence of the signals due to the protons attached to the carbons of the double bonds (-CH=CH-).

By mass spectrometry, it was possible to prove the presence of the acyclic units of HBP1G and fragments of the HBRAs with fatty acid units in their structure. The hydrodynamic dimensions (in intensity) of HBP1G were greater than those of the HBRAs, because of an aggregation process of HBP1G, which occurred through the hydrogen bonds of the OH groups. The HBP1G presented a semicrystalline behavior, since one T_g, crystallization and fusion temperatures was observed. The HBRAs presented an amorphous behavior because they only exhibited one T_g which was lower than that of the HBP1G. The rheological analysis of the HBRAs obtained with a 100 in solids showed that these materials had viscosities lower than 20 Pa.s. Taking into account the used stoichiometric ratios of TOFA and HBP1G and the very low AVs that were obtained for these materials, it can possibly be inferred that the stoichiometric relationship of the TOFA grafted in the HBP1G was the same. The HBRA1 and HBRA2 showed a pseudoplastic behavior, which is possibly associated with an unraveling of the chains and/or dissociation of interactions through hydrogen bonds. The chemical resistance to 0.1 M NaOH solution was regular, but against water, 0.1 M NaCl and 0.1 M HCl was good.

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