

# HYPERBRANCHED ALKYD RESINS OBTAINED FROM A HYPERBRANCHED POLYESTER POLYOL OF THE FIFTH GENERATION AND TALL OIL FATTY ACID

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## ABSTRACT

The first aim of this study was to synthesize hyperbranched alkyd resins from tall oil fatty acids and a hyperbranched polyester polyol via an esterification reaction. The second aim was to evaluate the effect of the fatty acid proportion on the properties of the resins. The modification percentage of the hyperbranched polyester polyol was between 47.68 and 66.02%. Infrared analysis shows that the alkyd resins decreased the intensity of the OH group's vibration. This decrease depends on the amount of TOFA used. Thermogravimetric and differential scanning calorimetry analyses showed that the modification of the hyperbranched polyester improved the thermal stability and the mobility of the macromolecules of the alkyd resins respectively. The viscosity of the alkyd resins was less than 10 Pa.s. They exhibited Newtonian behavior and had the highest gloss values at 60° (between 90.1 and 91.6).

**Keywords:** Hyperbranched Polyester Polyols, Esterification, Hyperbranched Resins, Tall Oil Fatty Acids, Properties.  
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## INTRODUCTION

Alkyd resins (ARs) are used in the coating industry because they have high performance, good adhesion, and are low cost.<sup>1</sup> ARs are polyesters modified with unsaturated fatty acids, these materials are usually prepared from triglyceride oils, polyfunctional alcohols, and anhydrides.<sup>2,3</sup> ARs are generally prepared with high amounts of volatile organic compounds (VOCs), which contribute to global warming.<sup>4</sup> The hyperbranched polyester polyols (HBPs) have attracted much research attention because these materials have low viscosity ( $\eta$ ) and the highest functionality<sup>5</sup>. These materials are prepared by polycondensation from a core (usually polyfunctional alcohol) and an extender (generally dimethylolpropionic acid).<sup>5,6</sup> The HBPs offer the possibility to obtain coatings with high solid content and low VOC amount. Thus, hyperbranched alkyd resins (HARs) have emerged as an environmentally friendly solution as these materials have the lowest viscosity compared to ARs.<sup>7,8</sup> Furthermore, they exhibit low drying times and high gloss<sup>4,9</sup>. Other advantages of the HARs over ARs are the high functionality and that they can be obtained in one step.<sup>10,11</sup> Some studies have reported the synthesis of HARs from HBPs and fatty acids such as ricinoleic, linseed, and tall oil fatty acids (TOFA).<sup>9-12</sup> However, there is little information about the synthesis and characterization of the HARs obtained from an HBP of fifth-generation (HBP5P). Therefore, it is important to explore new materials and evaluate their properties. Thus, the aim of this study is to synthesize HARs from HBP5P and TOFA and to study the effect of the TOFA quantity on the properties of the HBARS.

## EXPERIMENTAL

### Material and Methods

TOFA was supplied by Colorquímica SAS (Colombia). TOFA is composed mainly of linolenic (12% w/w linoleic (35% w/w) and oleic acid (46% w/w).<sup>13</sup> HBP5P was prepared by us and the properties were previously reported.<sup>10,14</sup> Potassium (KOH) and sodium (NaOH) hydroxides, and acid (HCl) and sodium (NaCl) chlorides were provided by Merck.

## General Procedure

In order to synthesize the HARs, the respective amounts of HBP5P, TOFA, and tosylic acid (TA) were placed in the reactor with an inlet and outlet of nitrogen, a thermocouple, a condenser, and a mechanical stirrer. The reaction temperature and stirrer speed were 200 °C and 200 rpm, respectively. The proportions of HBP5P to prepare the HARs were kept constant (0.025 mol), but those of the TOFA were 0.16 mol (HAR1), 0.23 mol (HAR2), and 0.33 mol (HAR3). The amount of TA was 1% w/w. The solid content of the HARs was 50% w/w.

## Characterizations

AV was determined using the methodology reported by Murillo *et al.*<sup>11</sup> Hydroxyl value (OHV) analysis was carried out based on AOCS CD 13-60. The proton nuclear magnetic resonance (<sup>1</sup>H NMR), infrared (IR) thermogravimetric (TGA), differential scanning calorimetry (DSC), rheological analyses, and film properties (gloss, flexibility chemical resistance and adhesion) were performed using the methodologies previously reported.<sup>11,12</sup>

## RESULTS AND DISCUSSION

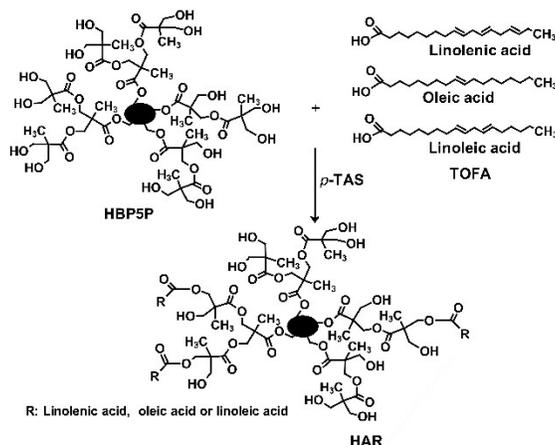
The results of AV, conversion percentage (*CP*), OHV, and *M* are displayed in Table-1. The AV of the HARs was between 23.16 and 24.61 mg KOH/g sample, these values were lower compared to that of the TOFA (197.92 mg KOH/g sample), this means that the acid groups of TOFA reacted with OH groups of HBP5P to form the HARs (Scheme-1). On the other hand, the *CP* of the HARs were determined from equation (1):

$$CP = \frac{A}{B} \times 100 \quad (1)$$

Where *A* and *B* are the AV of HARs and TOFA respectively. From the *CP* results, it may be concluded that the reaction conversion was high. This is confirmed by OHV results because the HAR OHVs were lower than that observed for the HBP5P (448.03 mg KOH/g).<sup>14</sup> Additionally, it is important to determine the modification percentage (*M*) of the HBP5P. Therefore, equation(2) was used as follows:

$$M = \frac{C - D}{C} \times 100 \quad (2)$$

Where *C* and *D* are the OHV of the HBP5P and HARs respectively. The *M* was enhanced and this increased as the TOFA proportion increased, which was the result of the higher number of acid groups that participated in the reaction (Scheme-1). Furthermore, the *M* results mean that in the same manner, the molar mass of the HARs increased. From the OHV results, it can be inferred that the HARs can be posteriorly modified with other reactive groups through OH groups to obtain different structures for specific applications.



Scheme-1: Schematic Representation of the HAR Synthesis

In the HBP5P <sup>1</sup>H NMR spectrum (Fig.-1) some signals appeared at displacements ( $\delta$ ) 4.90 ppm, 4.15 ppm, 3.35 ppm, and around 1 ppm, which correspond to protons of OH, -CH<sub>2</sub>OR, -CH<sub>2</sub>OH (methylenes) and -CH<sub>3</sub> respectively. These signals have already been observed in HBPs.<sup>15</sup> On the other hand, the <sup>1</sup>H NMR spectrum of the HAR3 sample (Fig.-2) exhibited some signals which are absent in the HBP5P spectrum

and others appeared with reduced intensities. The signal at 5.4 ppm (-CH=CH-) in Fig.-2 did not appear in the HBP5P spectrum, it means that TOFA reacted with HBP5P. The signal due to -CH<sub>2</sub>OH visibly reduced its intensity due to the OH groups' participation in the esterification reaction. This is consistent with the AV and OHV results.

Table -1: AV, CP, OHV and M of the HARs

HARs	AV (mg KOH/g)	CP	OHV (mg KOH/g)	M
HAR1	24.61	87.57	233.32	47.48
HAR2	23.27	88.24	215.45	51.92
HAR3	23.16	88.30	152.23	66.02

The IR spectrum of the TOFA, HBP5P, and HARs are displayed in Fig.-3. The HBP5P exhibited a signal at 3401 cm<sup>-1</sup> due to OH groups. The signals at 2922 and 2821 cm<sup>-1</sup> correspond to the stretching of C-H bonds. The signal at 1730 cm<sup>-1</sup> is due to the absorption of -C=O bonds of esters. At 1229 and 1129 cm<sup>-1</sup> two signals appeared due to the bending of the C-O bonds of esters. The TOFA spectrum showed signals at 3500, 3030, 2922, and 1715 cm<sup>-1</sup>, which are associated with the stretching of -COO-H, -CH=CH-, C-H, and carbonyl groups of acids respectively. The HARs presented the signal exhibited by HBP5P and TOFA, but in some cases the intensities were different. On the other hand, the signal associated with the stretching of O-H bonds into HARs reduced its intensity with the TOFA proportion. This result is in accordance with that observed in the OHV. The same behavior was reported for HARs.<sup>8,9</sup>

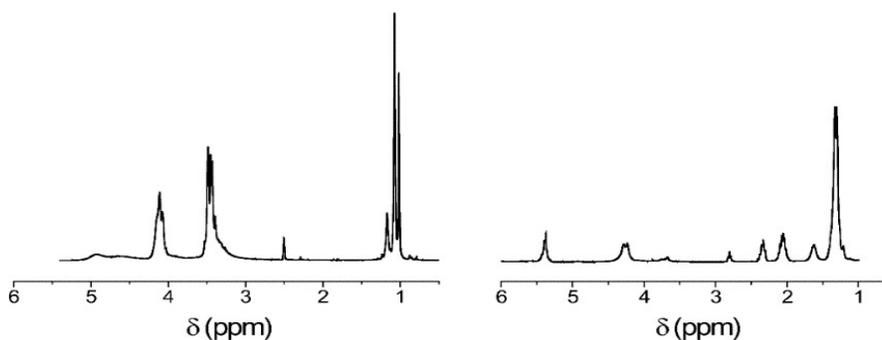
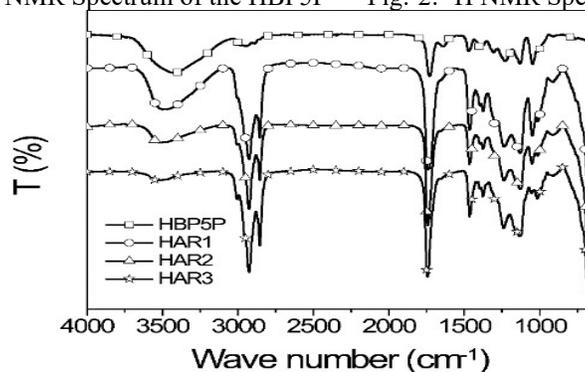
Fig.-1: <sup>1</sup>H NMR Spectrum of the HBP5P Fig.-2: <sup>1</sup>H NMR Spectrum of the HAR3

Fig.-3: IR Spectrum of the HBP5P and HARs

The TGA thermograms of the HARs are shown in Fig.-4. HARs displayed the highest thermal stability. This behavior was the result of the increase in molar mass and modification of end groups of HBP5 with TOFA, which is confirmed by the same compartment observed in *M* values. The degradation onset temperatures (*T*<sub>onset</sub>) of the HARs were: HAR1: 265.8 °C, HAR2: 288.5 °C, and HAR3: 310.6 °C. All these values were higher than that of the HBP5P (244.6 °C).<sup>14</sup> This suggests that the modification of HBP5P with TOFA increased thermal stability. The *T*<sub>onset</sub> values of the HARs are higher than those reported for HARs obtained from HBP2 and ricinoleic acid whose values were lower than 193 °C.<sup>7</sup> The glass transition temperature (*T*<sub>g</sub>) values of the HARs obtained from Fig.-5 were: HAR1: -13.5 °C, HAR2: -28.5 °C, and

HAR3:  $-46.2\text{ }^{\circ}\text{C}$ . The  $T_g$  values of the HARs decreased with the content of TOFA and it was lower than that reported for HBP5P ( $30.5\text{ }^{\circ}\text{C}$ ).<sup>14</sup>

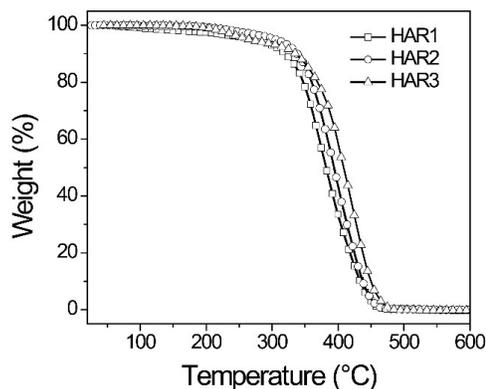


Fig.-4: TGA Results of the HARs.

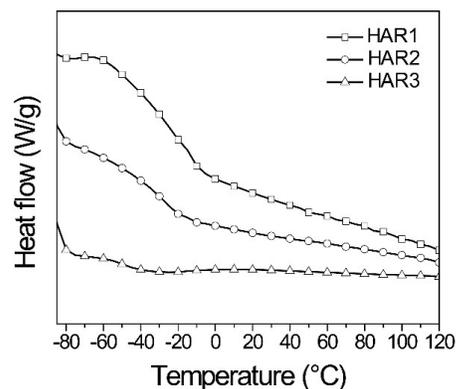


Fig.-5: DSC Results of the HARs.

This suggests that TOFA enhanced the mobility of the macromolecules and these materials are mainly amorphous because melting or crystallization processes were not observed.<sup>16</sup> Another reason for this behavior is that TOFA is a liquid. Thus, it improved the mobility of the macromolecules acting as lubricants.  $T_g$  values of the HAR1 and HAR2 are comparable with those reported for HARs whose values<sup>17</sup> were between  $-4.98$  and  $-22.93\text{ }^{\circ}\text{C}$ . The rheological behavior of the HARs is displayed in Fig.-6. All HBARS exhibited a Newtonian behavior because  $\eta$  did not show a dependence on the shear rate, this behavior is associated with the absence of entanglements into the HARs, which has already been observed in HBPs.<sup>18</sup> On the other hand, TOFA acted as a lubricant to the HARs, because  $\eta$  was reduced with the TOFA content. This behavior confirms the explanation given in the discussion of the DSC results. The  $\eta$  values of the HARs are lower than those reported for other HARs (higher than  $10\text{ Pa}\cdot\text{s}$ ).<sup>9</sup>

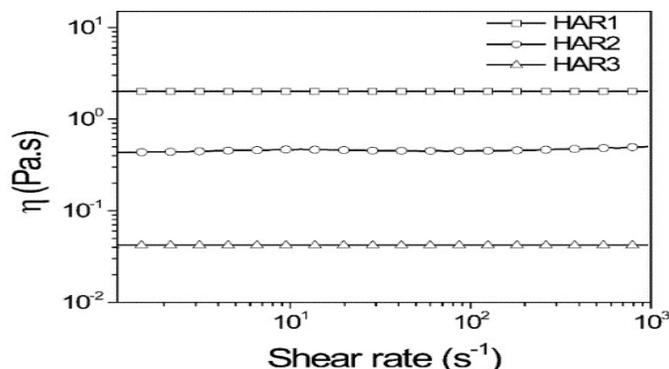


Fig.-6:  $\eta$  Dependence of Shear Rate of the HARs.

The gloss values at  $60^{\circ}$  of the HARs were the highest (HAR1: 91.2, HAR2: 90.1, and HAR3: 91.6) but they did not show a dependence on the TOFA proportion. This behavior was possibly due to the different roughness of the films.<sup>19</sup> On the other hand, the gloss values of these HARs were higher than those reported for other HARs, whose values at  $60^{\circ}$  were between 67-72 and 88.2-89.9.<sup>7,12</sup> The flexibility of the HARs was good because none of the films exhibited cracking. The adherence did not show a dependence on TOFA content (HAR1: 100 %, HAR2: 90 %, and HAR3: 90 %). This is associated with different structural arrangements of the HARs and the molar mass. This is because it has been demonstrated that during the synthesis, reactions of hydroxy-ester interchange may occur, and this affects the molar mass.<sup>5</sup> However, the HAR1 sample has the best performance due to its high  $T_g$  value (lowest flexibility). The stability of the HARs was excellent in  $\text{H}_2\text{O}$  and  $\text{HCl}$  and  $\text{NaCl}$  solutions, which was the result of the hydrophobic nature of the HARs. The chemical resistance in the  $\text{NaOH}$  solution was low because all films were partially removed. This behavior is associated with the low resistance of the ester groups against alkaline hydrolysis.<sup>20</sup> The same behavior has been observed for HARs.<sup>1,20</sup>

## CONCLUSION

In this study, HARs were prepared and the properties were evaluated. The  $CP$  values of the HARs were higher than 86 %. The OHV decreased with the TOFA content. The HARs exhibited the highest  $T_{onsets}$ , but the  $T_g$  followed the opposite behavior. All HARs exhibited an amorphous nature and displayed a low  $\eta$  value. The chemical resistance to NaOH solution was low because the ester groups were hydrolyzed in the presence of this solution. On the other hand, the HARs may be modified with other compounds to obtain specific properties for specific applications due to the presence of unreacted OH groups.

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## CONFLICT OF INTERESTS

We declare that there is no conflict of interest.

## AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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