

Effect of Tall Oil Fatty Acids Content on the Properties of Novel Hyperbranched Alkyd Resins

Edwin A. Murillo, Pedro P. Vallejo, Betty L. López

Grupo Ciencia de los Materiales, Universidad de Antioquia, Calle 62 52-59 Medellín, Antioquia, Colombia

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ABSTRACT: Hyperbranched alkyd resins (HBRA) were synthesized by modification of hydroxylated hyperbranched polyester (HBP1-4) with tall oil fatty acids (TOFA). The core is a hydroxylated hyperbranched polyester of fourth generation with OH groups in the periphery (18), which is endcapped with tall oil fatty acids. The occurrence of these reactions, HBP1-4 and TOFA, was determined by making use of acid value, nuclear magnetic resonance, and hydroxyl values. The effects of TOFA and HBP1-4 on properties of the HBRA resins were investigated by vapor pressure osmometry,

differential scanning calorimetry, thermogravimetric analysis, friction resistance, and hardness. The resins with higher modification percentage (HBRA4) presented the best thermal and hydrolytic stability, but lower friction resistance and hardness. All HBRA resins presented amorphous characteristics, OH groups, and double bonds in the periphery. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3151–3158, 2011

Key words: polyester; hyperbranched; resins; polymer synthesis; characterization

INTRODUCTION

Dendrimers are highly branched monodisperse macromolecules. Hyperbranched polymers are considered irregular analogues of dendrimers due to fact that they contain linear units in their structure. This leads to imperfections, and therefore they are considered polydisperse structures.^{1,2}

Contrary to linear polymers, hyperbranched polymers contain a large number of branching points and functional groups in the periphery, which gives them their unique physical and chemical properties.^{3–8} Hyperbranched polymers exhibit much lower solution and molten state viscosities than linear polymers. This is due to the lack of entanglements, which results from their packed structure.^{9–11} They often present very high solubility as a result of the large number of terminal functional groups available per macromolecule, as compared with those of linear polymers.⁵

Hyperbranched polymers that are based on bisMPA (extender) and ethoxylated pentaerythritol (core), are the commercially available Boltorn Hx polyesters: where x denotes the pseudogeneration number (Perstorp Specialty Chemicals AB, Sweden).^{4,12} One of the most widely investigated families of hyperbranched

polymers are the hydroxylated hyperbranched polyesters, which are synthesized from 2,2-bis(methylol)propionic acid and different core molecules (e.g., tris(methylol)propane or ethoxylated pentaerythritol^{3,14}).

The properties of hyperbranched polymers are strongly determined by the nature of their terminal groups.^{15–17} For instance, the solubility of this type of material may be regulated by the partial or total chemical modification of the terminal groups. Attractive properties can be obtained by blending hyperbranched polymers with other materials for specific applications such as rheology modifier¹⁰ coatings,^{18,19} thermosets,²⁰ and additives.²¹

Recently, the use of renewable sources in the preparation of various industrial materials has been revitalized because of petroleum scarcity and environmental concerns. The conventional alkyd resins (linear structure) are polyesters modified with fatty acids,²⁰ and are used extensively as a binder for making paints.^{22–24} These paints are usually resistant to UV-radiation, thermal fluctuations and high humidity.²⁴

These conventional alkyd resins are obtained generally from triglyceride oils, such as castor oil, linseed oil, soybean and tung oil, or glycerol and anhydrides.²² The triglycerides react with glycerol (transesterification) to produce monoglycerides and diglycerides, and then these react with anhydrides to obtain conventional alkyd resins.^{22–24} Hyperbranched alkyd resins (HBRA) can be obtained by an esterification reaction between hydroxylated hyperbranched polymers and TOFA. The advantage of using TOFA instead of triglycerides oils is that this process does

Correspondence to: E. A. Murillo (edwinalbertomurillo@gmail.com).

TABLE I
TOFA and HBP1-4 Content of the HBRA Resins

Resins	HBP1-4 (mol)	TOFA (mol)
HBRA1	0.025	0.16
HBRA2	0.025	0.23
HBRA3	0.025	0.33
HBRA4	0.025	0.63

not require transesterification reactions, since the fatty acids in TOFA are not forming triglycerides and they are in a free state. Therefore the esterification reaction is direct. TOFA is a mix of oleic (46%), linoleic (35%), linolenic (12%), palmitic (4%), and stearic acid (3%).²⁵ The oleic, linoleic, stearic, and linolenic fatty acid have 18 carbon atoms in their structure, while palmitic acid has 16 carbon atoms.²⁵ Hydroxylated hyperbranched polyesters obtained from tris(methylol)propane have been modified with TOFA and employed by Perstorp Company on paint products, but the influence of TOFA on the structural, hydrolytic, thermal, and tribological properties of these materials have not been studied.²⁶ The HBP1-4 cannot act as a crosslinking agent for reactions of polycondensation through OH groups on a hydrophobic medium, due to its high hydrophilicity. Hydroxylated hyperbranched polyester has been used as a crosslinking agent for polyurethane on a hydrophilic medium.¹¹ In this work, the HBP1-4 is modified with different amounts of TOFA and the effect of TOFA in the structural, hydrolytic, thermal, and tribological properties of the hyperbranched alkyd resins is studied.

EXPERIMENTAL

Materials

The HBP1-4 was synthesized in our group and the procedure to obtain this polymer, was reported in previous publications.^{27,28} TOFA was supplied by Chemical Arizona and has a molar mass of 290 g/mol, an iodine value of approximately 130 g I₂/100 g, and an acid value of 197.92 mg KOH/g. Tetrahydrofuran, *p*-toluenesulfonic acid (PTAS), potassium hydroxide (KOH), acetone, ethanol, xylene, phenolphthalein, isopropyl alcohol, cobalt, calcium, and zirconium octoate were purchased from Aldrich and they were used as received.

Syntheses of HBRA resins

HBP1-4 was obtained by bulk polymerization of 2,2-Bis(hydroxymethyl)propanoic acid and pentaerythritol²⁷ and it was modified by an esterification reaction with TOFA using *p*-toluenesulfonic acid (PTAS) as a catalyst. The respective amounts of

HBP1-4 and TOFA were mixed under nitrogen atmosphere, into a reactor equipped with a mechanical stirrer, a condenser, and a regulated heating device. The system was heated (140–220°C) and then the respective amount of PTAS (0.1–5%) was added. The conversion of the reaction was monitored by measuring the acid value until obtaining the wanted acid value, and then a determined amount of xylene was added to obtain a solid content of 50%. The composition of HBRA resins on mol basis is given in Table I. The Figure 1 shows a schematic representation of the synthesis of a HBRA resin obtained from HBP1-4 and TOFA.

Acid value

To determine the reaction conversion percentage at different times, and to evidence the reaction between HBP1-4 and TOFA, the acid value measurements was performed. Around 1 g of the sample were weighted and then the sample was diluted with 20 mL of the neutralized solvent mixture (xylene/isopropyl alcohol 1:1) and titrated with 0.4601M KOH standard solution using phenolphthalein as an indicator.

Nuclear magnetic resonance analysis

¹³C nuclear magnetic resonance analysis (NMR) was done, in a Bruker AC 300 MHz spectrometer using chloroform as a solvent.

Hydrolytic stability

To study the hydrolytic stabilization, the HBRA resins were mixed with water until it formed an emulsion. Afterwards, they were stored at 50°C during 28 days. To determine the acid value, the resins were taken out of the oven and kept at room temperature, and then the sample was diluted with 10 mL of the neutralized solvent mixture (xylene/isopropyl alcohol) and titrated with 0.4601M KOH standard solution using phenolphthalein as an indicator. To study the modification percentage of HBP1-4, analyses of hydroxyl value according to the ASTM D-4274 standard test method were done.

Vapor pressure osmometry analyses

The vapor pressure osmometry analyses (VPO) were done to determine the number average molar mass. The measurements were done in Knauer vapor pressure osmometer using tetrahydrofuran (THF) as a solvent in a concentration range of 1.14 and 9.04 g/kg at 45°C. Benzyl was used for calibration. The experiments were repeated five times and the data reported was the average of the five measurements.

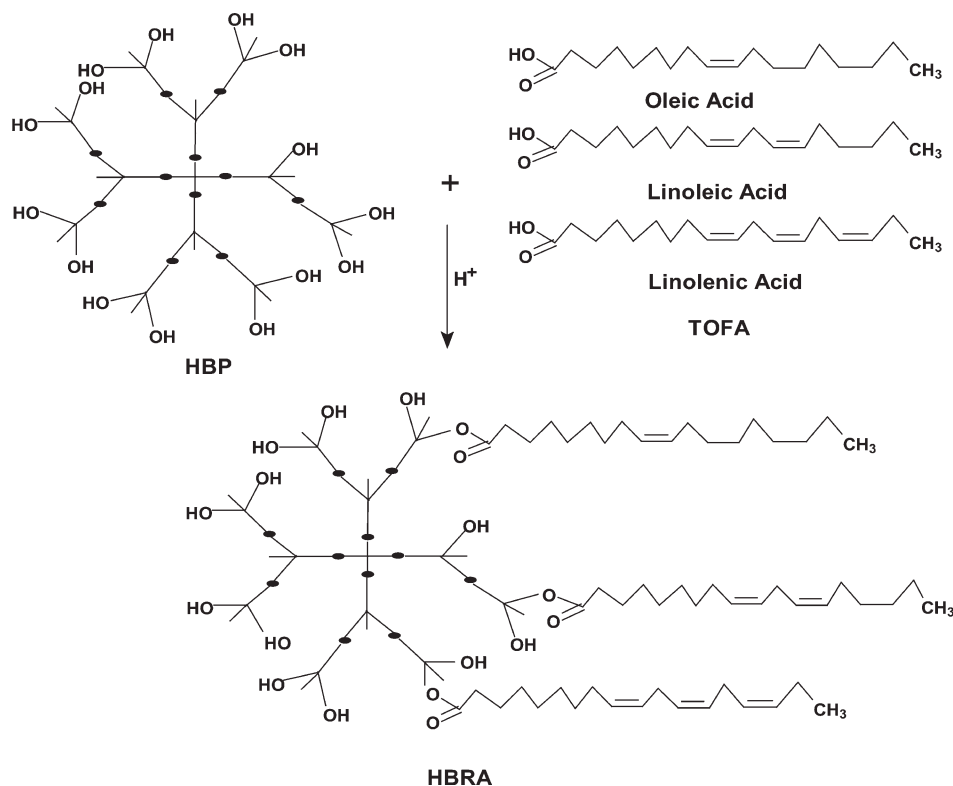


Figure 1 Schematic representation of the synthesis of a HBRA resin.

Differential scanning calorimetry

The glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC) in a TA Instrument model Q100 equipped with refrigerated cooling system, using a heating and cooling rate of 30°C/min, under nitrogen atmosphere.

Thermogravimetric analyses

To determine the thermal stability of the HBRA resins, thermogravimetric analyses (TGA) were done in a TA instrument model Q500 under nitrogen atmosphere at a rate of 10°C/min were done.

Friction resistance and hardness

For analysis of microhardness, the HBRA resins were mixed with solutions of cobalt octoate (0–4%), calcium octoate (0–4%), and zirconium octoate (0–4%). By using a film applicator, the resin films were formed on a plate, dried at 25°C at relative humidity of 40% and then the Vickers hardness was measured using the Shimadzu HMV-mIII hardness tester at one load of 100 g. The application time of load was 5 s. The friction coefficient was determined using the pin on disk test with the universal test SINTECH of MTS systems Corp; with the following parameters: disk speed, 100 rpm; pin diameter, 4.0 mm; revolutions, 2000 and applied load, 2.0N.

RESULTS AND DISCUSSIONS

Acid value of the HBRA resins and reaction conversion percentage

The determination of the acid value is evidence that the esterification reaction between TOFA and HBP1-4 took place, and it is expected that with the increase of the reaction time the acid value (AV) will reduce due to the esterification reaction between acid group of TOFA and OH group of HBP1-4. The probability of a reaction between two terminal OH groups of HBP1-4 on the periphery is very low, since the electron-withdrawing effect of the carbonyl group of TOFA favored the reaction between terminal OH groups of HBP1-4 and acid groups (COOH) of TOFA. OH groups of linear units do not suffer chemical reaction with TOFA because they have high steric hindrance, due to the fact that they are inside of the HBP1-4 macromolecule.

The Table II presents the acid value of the HBRA resins and the reaction conversion percentages based on TOFA content. The reaction conversion percentage was determined from the difference in acid value of TOFA (197.92 mg KOH/g sample) and the acid value of the sample divided by the acid value of TOFA. The acid value of HBRA resins varied between 15.91 and 17.17 mg KOH/g sample, which are very low compared to the acid value of TOFA; this is an indication that the acid group of TOFA has

TABLE II
Acid Value of HBRA Resins and Reaction Conversion Percentage

Resins	AV (mg KOH/g sample)	Conversion percentage
HBRA1	17.17	91.25
HBRA2	15.91	91.89
HBRA3	16.90	91.39
HBRA4	16.77	91.45

reacted. The reaction conversion percentage based on TOFA content was high, indicating that the double bonds of TOFA were grafted in the HBP1-4 polyester.

Nuclear magnetic resonance (NMR) analysis

The Figure 2(a) shows the ^{13}C RMN spectrum of the HBRA2 resin. Different signals can be observed: between 0 and 40 ppm they are due to CH_3 (15.21 ppm), $\text{CH}_3 - \text{CH}_2$ (23.3 ppm), CH_2COO^- (26.3 ppm), $\text{CH}_3-(\text{CH}_2)_2$ (32.6 ppm), CH_2COOR (34.6 ppm); between 46 and 52 ppm a signal due to quaternary carbons of terminals (T), linear (L) and dendritic units (D) appears [the magnification of this region is shown in Fig. 2(b)]; the signal observed at 72.66 ppm is due to chloroform (solvent); and between 171–175 ppm signals due to $\text{C}=\text{O}$ group. The presence of signals due to $\text{C}=\text{C}$ bonds is an indication of the reaction between HBP1-4 and TOFA. Furthermore this signal does not appear in the typical spectra of HBPs.²⁷

Modification percentage of the HBP1-4 sample

The modification percentage of the HBP1-4 sample (M) was determined using the following equation:

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

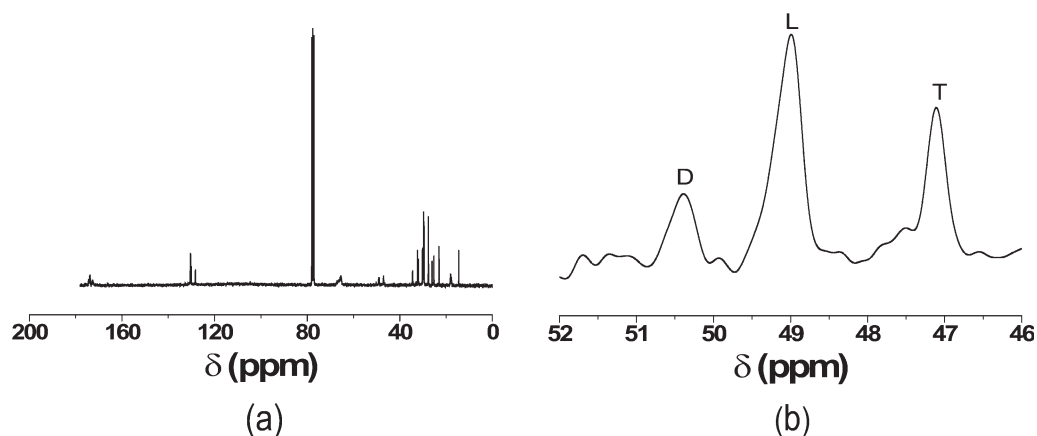


Figure 2 (a) ^{13}C -NMR spectrum of the HBRA2 resin and (b) Magnified quaternary carbon region.

TABLE III
Results of Hydroxyl Value and Modification of Terminal OH Group (HBP1-4)

Resins	B (mg KOH/g sample)	M	K	H
HBRA1	280.53	37.15	6.69	11.31
HBRA2	230.52	48.35	8.70	9.30
HBRA3	208.52	53.34	9.60	8.40
HBRA4	139.44	68.75	12.38	5.62

where A and B is the hydroxyl value (VOH) of the HBP1-4 (446.34 mg KOH/g sample) and the HBRA resins respectively. The number of modified OH groups per molecule of HBP1-4 (K) is given by:

$$K = \frac{M - OH_T}{100} \quad (2)$$

where, OH_T is the number of terminal OH groups of the HBP1-4 sample in the periphery, which was calculated by NMR (18).²⁷ The number of OH groups without modification per molecule of HBP1-4 (H) was calculated using the following equation:

$$H = OH_T - K \quad (3)$$

The Table III presents the hydroxyl values, modification percentage, number of modified OH groups, and unmodified OH groups of the samples. With the increase of the TOFA content, the hydroxyl value decreases, while the modification percentage and number of modified OH groups of the HBRA resins increase. This is coherent due to the fact that there are high amount of COOH groups that may react with OH groups of the HBP1-4 polyester. The HBP1-4 polyester, despite having been modified, still presented OH groups in the periphery, which are susceptible for modification with other reactive groups (for example OH, NH_2) to obtain hybrid materials.

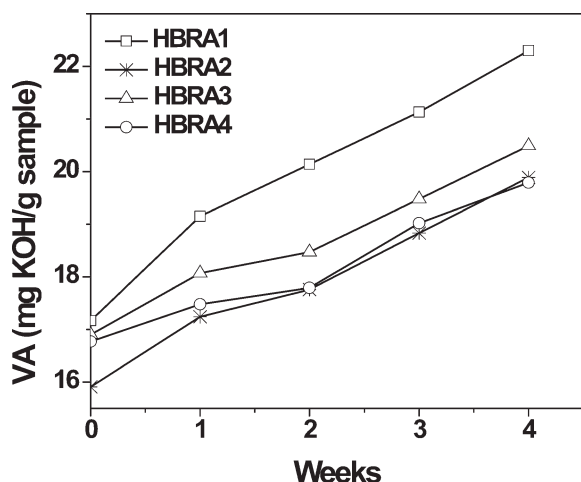


Figure 3 Variation of acid value with the time.

Hydrolytic stability of the Hbra resins

Polyesters are susceptible for hydrolysis reactions in water.²⁹ The hydrolysis enhances the acid value because the degradation produces the initial materials, in this case free fatty acids^{29,30} and HBPI-4.

The acid value variation of the HBRA resins (AVV) was determined by the difference between initial and final acid value. The variation percentage with respect to initial acid value was also calculated. The Figure 3 shows the behavior of acid value of the HBRA resins with time.

In the Table IV, the acid value variations (AVV) and acid value variation percentage (AVVP) of the HBRA resins are observed. The variations on acid value and variation percentage of the HBRA resins are between 3.02 and 5.13 mg KOH/g and 18.04–29.90% respectively. Degradation stability by hydrolysis of the HBRA resins enhances with the modification percentage, due to increase of hydrophobic character of the HBRA resins. The order of stability

TABLE IV
Acid Value and Variation of Acid Value of the HBRA Resins

Resins	AV (final) (mg KOH/g sample)	AVV (mg KOH/g sample)	AVVP (%)
HBRA1	22.30	5.13	29.90
HBRA2	19.89	3.99	25.06
HBRA3	20.48	3.59	21.23
HBRA4	19.79	3.02	18.04

is the following: HBRA4 > HBRA3 > HBRA2 > HBRA1. These results are good compared with the one obtained by Wang et al.²⁹ who reported percentage of variation on acid value of 34%, for an alkyd emulsion. The good hydrolytic stability of the HBRA resins is due to ester bonds, which are not in the surface of a macromolecule, and the access of water and acid species is difficult due to, steric hindrance.³⁰

Determination of number average molar mass of the HBRA resins by VPO

In this method, the vapor pressure of a solution is lower than that of the pure solvent at the same conditions of temperature and pressure. The decrease of the vapor pressure is directly proportional to the molar concentration of the dissolved polymer, which can be used to obtain molar mass.³¹ The determination of number average molar mass of hyperbranched polymers and dendrimers by vapor pressure osmometry (VPO) is a better method than gel permeation chromatography (GPC), since the calibration on GPC is realized using linear standard (usually polystyrene). This can cause errors in the measurements because hyperbranched polymers (densely packed structure) have a different relation between hydrodynamic radio and the molar mass

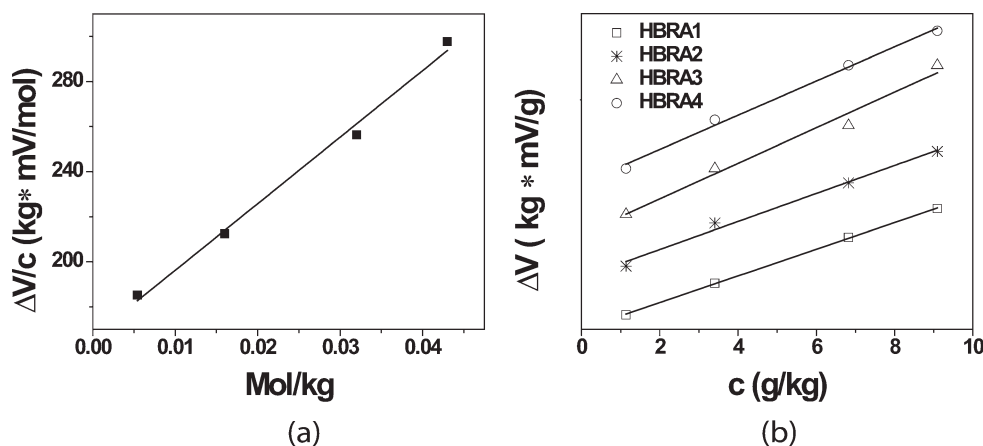


Figure 4 VPO measurements; (a) Benzyl and (b) HBRA resins.

TABLE V
 M_n Value and Correlation Factor of the HBRA Resins

Resins	Intercept ($\times 10^2$ mV \times kg/g)	M_n (g/mol)	Correlation factor
HBRA1	2.99	5576	0.9995
HBRA2	2.80	5954	0.9863
HBRA3	2.30	7249	0.9707
HBRA4	2.08	8015	0.9921

as compared with linear polymers of the same molar mass.³²

The number average molar mass (M_n) of the HBRA resins was determined using this equation:³²

$$\frac{\Delta V}{C} = \frac{Kc}{M_n} + A\rho C Kc \quad (4)$$

where ΔV , C , Kc , A and ρ are respectively, the potential change measured by the change in resistance of the thermistor, the concentration of the solution in g/kg, calibration constant, second virial coefficient, and the density of the solvent. The value of Kc is 166.73 mV*kg/mol, which was determined from the intercept of the benzyl calibration curve [Fig. 4(a)]. From equation 4 and Fig. 4(b) and the intercept, the M_n values of the HBPs were determined.

The Table V presents the correlation factor and M_n value of the HBRA resins. The M_n value increases with the increase of TOFA content. These results are in accordance with the hydroxyl value, modification percentage, and number of modified OH groups. The M_n value of HBP1-4 polyester (5087 g/mol) determined by VPO²⁸ is lower than HBRA resins, which indicates that the reaction between HBP1-4 and TOFA occurred.

None of the HBRA resins presented aggregation due to hydrogen bonding since the slopes always increase with the concentration; this is evidence of

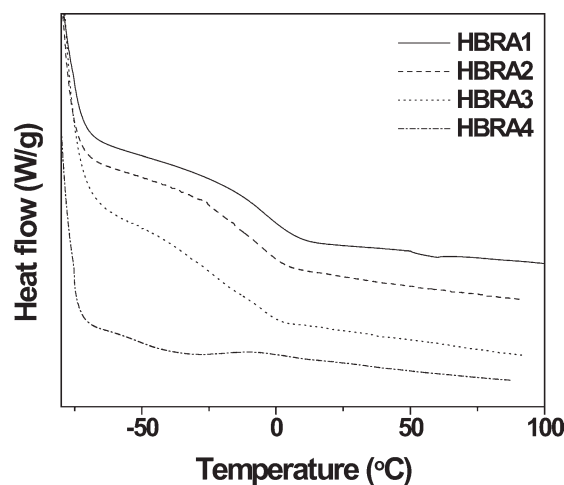


Figure 5 DSC Thermograms of the HBRA resins.

an absence of aggregation in the concentration range employed for preparing the solutions of the HBRA resins.³⁴ The correlation factor was good in all cases.

DSC of the HBRA resins

In Figure 5 it can be observed that the HBRA resins are amorphous because all resins presented glass transitions (T_g). The T_g values were the following: HBRA1, -4.9 ; HBRA2, -14.8 ; HBRA3, -24.9 and HBRA4, -49.8 °C. T_g decreased with the modification percentage of the HBP1-4 polyester and M_n values of the HBRA resins. This indicates that TOFA has a plasticant effect in these materials. Some oil has been used as plasticizer in polymers with the objective of reducing the viscosity to facilitate the processing.³⁵

TGA of the HBRA resins

The thermal stability of the HBRA resins [Fig. 6(a,b)] enhanced with the modification percentage of the

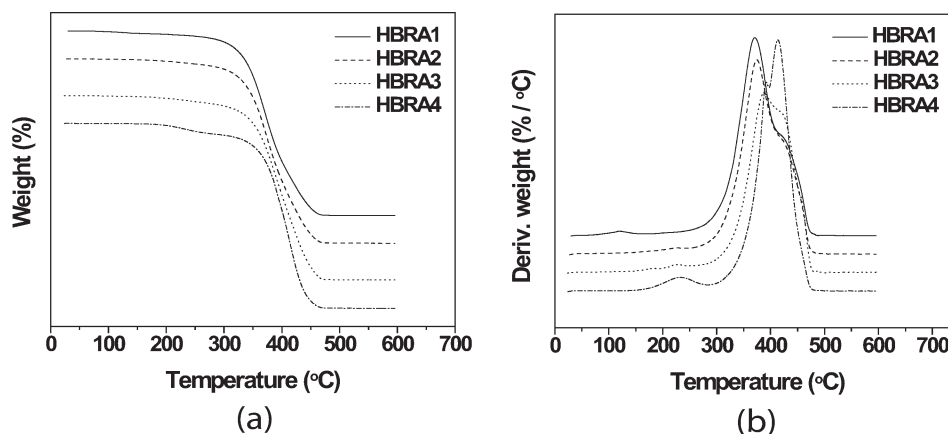


Figure 6 Thermograms of the HBRA resins; (a) Weight versus temperature and (b) Deriv. weight versus temperature.

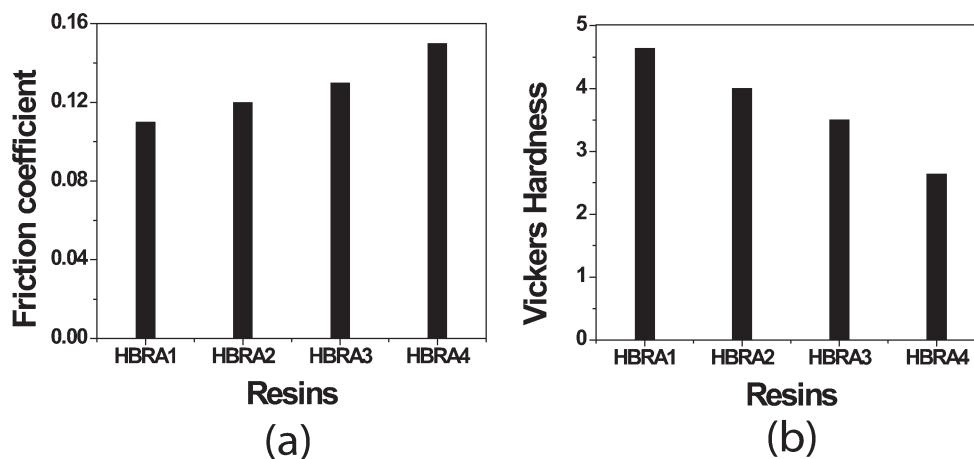


Figure 7 (a) Friction coefficient and (b) Hardness of the HBRA resins.

HBP1-4 polyester and M_n value of the HBRA resins. The decomposition temperature of the HBRA resins are: HBRA1, 252.7; HBRA2, 267.3; HBRA3, 279.8, and HBRA4 295.7°C.

The increase on thermal stability of the HBRA resins was as expected, due to the increment of the modification percentage of the HBP1-4 sample.

HBRA4 resin presented an additional decomposition temperature around 240°C, since the amount of TOFA employed for this sample was higher; this is possibly due to the decomposition of fatty acids or dimers.

Friction resistance and hardness of the HBRA resins

The friction coefficient is inversely proportional to friction resistance.³⁶ The behavior of friction resistance and Vickers hardness of the HBRA resins are presented in Figure 7. The friction resistance [Fig. 7(a)] increased with the proportion of HBP1-4 employed in the synthesis; this is due to the increase on number of fatty acids units in the macromolecule, which facilitate the interaction between them. The Vickers hardness [Fig. 7(b)] decrease with the proportion of TOFA employed in the synthesis, since the HBRA resins become softer. This result is according with the behavior presented on DSC.

CONCLUSIONS

TOFA content employed on the synthesis has high influence on the properties of the HBRA resins. The hydrolytic and thermal stability and number average molar mass of the HBRA resins enhance with the TOFA content employed in the synthesis, but friction coefficient and hardness decrease. These resins can be used in formulation of coatings with high hydrolytic stability. All plot obtained for determi-

nation of number average molar mass by VPO presented a good linearity. After the modification with TOFA all resins presented residual OH groups and double bond in the periphery. Therefore it can be modified with other materials for obtaining hybrid materials or crosslinking reactions through OH groups or double bonds.

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