Styrene–hydroxyethyl acrylate copolymer based alkyd resins with a comb-type structural morphology obtained with a high solid content

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ABSTRACT: Nowadays, so many studies are being carried out with the goal of obtaining environmentally friendly materials. In this study, styrene–hydroxyethyl acrylate copolymer (St-*co*-HEA) based alkyd resins with high solid contents and comb-type structural morphologies were synthesized from St-*co*-HEA and macromonomers [MMs; dimethylol propionic acid modified with different proportions of tall oil fatty acids (TOFAs)]. The molar mass and gloss values of St-*co*-HEA were lower than those of the alkyd resins, but the thermal stability, viscosity, and glass-transition temperature exhibited the opposite behavior. In all cases, the conversion percentage was higher than 80 %. The hydroxyl value and viscosity of the alkyd resins decreased with the TOFA content present in the MMrs, but the molar mass and the thermal stability increased. The rheological behavior of these resins was mainly pseudoplastic. Furthermore, the viscosity values were lower than 10 Pa s. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43996.

INTRODUCTION

Alkyd resins are widely used in the coating industry, and they are the most versatile binder used in architectural, industrial, and decorative coatings.[1] The development of environmental technologies and products has become interesting during recent years because of health and environmental concerns and also because of recent environmental legislation requirements.[2]

The possibility of obtaining cheap products from renewable materials, specifically, alkyd resins, as attractive materials in the coating industry is becoming more viable because of their good gloss, flexibility, and adhesion properties.[1] Usually, these materials are synthesized with a high content of volatile organic compounds (>60 wt%); this contributes to global warming and the creation of photochemical ozone, which is toxic to mammals, human, and plants.[1,2]

Recently, hyperbranched polyester polyols (HBPs) were obtained,[3–5] and they have acquired great importance in the preparation of new materials, for example, hyperbranched alkyd resins, which are synthesized with a higher solid content than conventional alkyd resins (linear structure).[6–12] Some hyperbranched alkyd resins have been obtained with a high solid content from HBPs;[10–12] these have been a good alternative for obtaining an environmentally friendly alkyd resin. A disadvantage of the use of HBPs to obtain alkyd resins is that a great amount of extender [dimethylol propionic acid (DMPA)] has to be used to synthesize these materials.[3–5]

Alkyd resins with a comb-type structural morphology and hyperbranched alkyd resins are materials with a high potential for obtaining solvent-borne resins with low volatile organic compound contents (<40 wt%). An important property of HBPs and comb-type polymers is that they present low viscosities with respect to linear polymers of the same molar mass;[12] this is desirable for obtaining coatings where a low volatile organic compound content is required. Polymers with a comb-type structural morphology have a lower branching degree than dendrimers, but they have a high number of terminal chains and a compact architecture, which present a low viscosity.[12] Polymers with a comb-type structural morphology can be prepared more quickly than HBPs; it makes that these materials be good alternatives for replacing HBPs (cores) in so many applications.[13]

In another study, styrene–hydroxyethyl acrylate copolymers (St-*co*-HEAs) were prepared[14,15] by the macroinitiator method with iodopolystyrene as the macroinitiator. St-*co*-HEA was prepared with a free-radical polymerization method in bulk. In this process, 2,2-azobisisobutyronitrile was used as the initiator.[15] Some copolymers with comb-type morphology have been synthesized from styrene (St). Comb copolymers consisting of a polystyrene

backbone and poly[*tert*-butyl methacrylate] side chains were synthesized by a combination of nitroxide-mediated polymerization and a photoinduced iniferter technique.[16] Amphiphilic poly(styrene-*co*-octadecyl maleamic acid salt) with a comb-like architecture was synthesized with a heterophase aqueous polymerization reaction.[17] A series of comb-type copolymers composed of poly(styrene–maleic anhydride) and 1-alcohols (C*n*OH with *n* = 14, 16, 18, or 26) were synthesized through a grafting reaction.[18] Lightly branched comb-structured polyesters containing oxazoline units as linker groups to reactive fatty acid side chains were synthesized through a scalable, solvent-free protocol and purified by simple recrystallization.[19] A terpolymer of polycaprolactone–St–vinyl trimethoxysilane was synthesized by free-radical polymerization with benzoyl peroxide (BPO) as the initiator, and then, the terpolymer was modified with sunflower oil partial glyceride via a sol–gel method.[20] Acrylic monomers were grafted onto alkyd resins by a free-radical polymerization method with BPO and azobisisobutyronitrile as initiators. The alkyds were composed of soybean oil, glycerol, phthalic anhydride, and tetrahydrophthalic anhydride.[21]

Acrylic-modified alkyds were prepared from the sequential polymerization of acrylic monomers in the presence of alkyd macro-reversible addition–fragmentation chain-transfer agents (reached by end-capping a soya-based alkyd with a carboxy-functional trithiocarbonate); the resulting material was then used as a chain-transfer agent to affix the acrylic blocks onto the alkyd backbone.[22] Rubber seed oil alkyd was postpolymerized with St by free-radical polymerization with as the initiator BPO to synthesize styrenated alkyds.[23]

A critical review of the literature revealed that there have been no studies on the synthesis of St-*co*-HEA-based alkyd resins with a comb-type structural morphology obtained with a high solid content. Therefore, in this study, we produced St-*co*-HEA by solution polymerization and then modified it with several macromonomers [MMs; obtained from DMPA and tall oil fatty acid (TOFA) by an esterification reaction][24] to prepare alkyd resins with a comb-type structural morphology with a high solid content. The effects of the MMs on the structural, thermal, rheological, and film properties of the alkyd resins were studied.

EXPERIMENTAL

Materials
St, hydroxyethyl acrylate (HEA), xylene, potassium hydroxide (KOH), phenolphthalein, pyridine, sodium hydroxide (NaOH) solution, sodium chloride (NaCl), hydrochloric acid (HCl), acetic anhydride/tetrahydrofuran and butanol, *p*-toluenesulfonic acid, BPO, and DMPA were supplied by Sigma-Aldrich. Cobalt, calcium and zirconium octoates, and TOFA were supplied from Colorquímica SA. DMPA modified with TOFA (MMs) were obtained in a previous work.[24] In all cases, the purity degree of the reagents was higher than 98 wt%.

Synthesis of St-*co*-HEA
The respective amounts of St (80 g), HEA (20 g), and xylene (100 g) were placed in a reactor with a condenser (vertical position) and mechanical stirring. The system was heated under
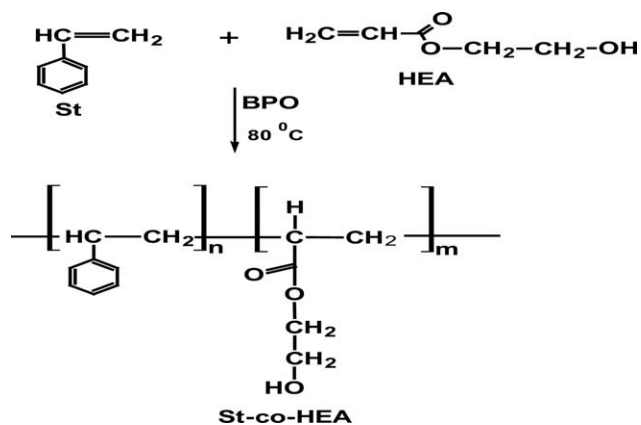

Figure 1. Schematic representation of the synthesis of St-*co*-HEA.

constant stirring (200 rpm) until a temperature of 80 °C was reached; then, 2 g of BPO was added. The system was kept at low reaction conditions for 5 h. The solid content of this copolymer was 50 wt%. Figure 1 shows a schematic representation of this reaction. In the IR and NMR analyses, this copolymer was precipitated in acetone (the HEA homopolymer was soluble, but St-*co*-HEA was insoluble), and then, the samples were subjected to Soxhlet extraction with acetone for 12 h (the extraction of the HEA homopolymer) followed by drying in an oven at 50 °C for 12 h *in vacuum*.

Synthesis of the St-*co*-HEA-Based Alkyd Resins with a Comb-Type Structural Morphology via a Grafting-To Method
St-*co*-HEA (80 wt%) synthesized previously was placed in the reaction system (the same used for synthesizing St-*co*-HEA), but in this case, the condenser was used in the horizontal position to extract the xylene and water. The system was heated at 150 °C until 25 wt% of the xylene contained in the copolymer was extracted, and then, in every case, the respective amounts (20 wt%) of macromonomer 1 (MM1; prepared from 75.40 g of DMPA and 69.60 g of TOFA), macromonomer 2 (MM2; obtained from 51.04 g of DMPA and 69.60 g of TOFA), macromonomer 3 (MM3; synthesized from 33.80 g of DMPA and 69.60 g of TOFA), and macromonomer 4 (MM4; prepared from 20 g of DMPA and 69.6 g of TOFA) and 0.4 wt% of *p*-toluenesulfonic acid were added to the reactor. Finally, the system was monitored until the acid value (AV) reached a value around 10 mg of KOH/g of sample. All of resins were obtained with a solid content of 65 wt%. The resins obtained from MM1, MM2, MM3, and MM4 were named R1, R2, R3, and R4, respectively. Figure 2 shows the schematic representation of the four structures present in the MMs, which were evidenced in previous studies with electrospray ionization–mass spectrometry.[24] Figure 3 shows a schematic representation of possible reactions between St-*co*-HEA and MMs.

Characterization of the Materials
AV Analysis. The AV analysis was done with the same methodology reported in a previous article.[7] Approximately 1 g of the sample was weighted, and then, the sample was dissolved with 20 mL of the neutralized solvent mixture (1:1 xylene/isopropyl alcohol) and titrated with a 0.4120 *M* KOH standard solution with phenolphthalein as an indicator.
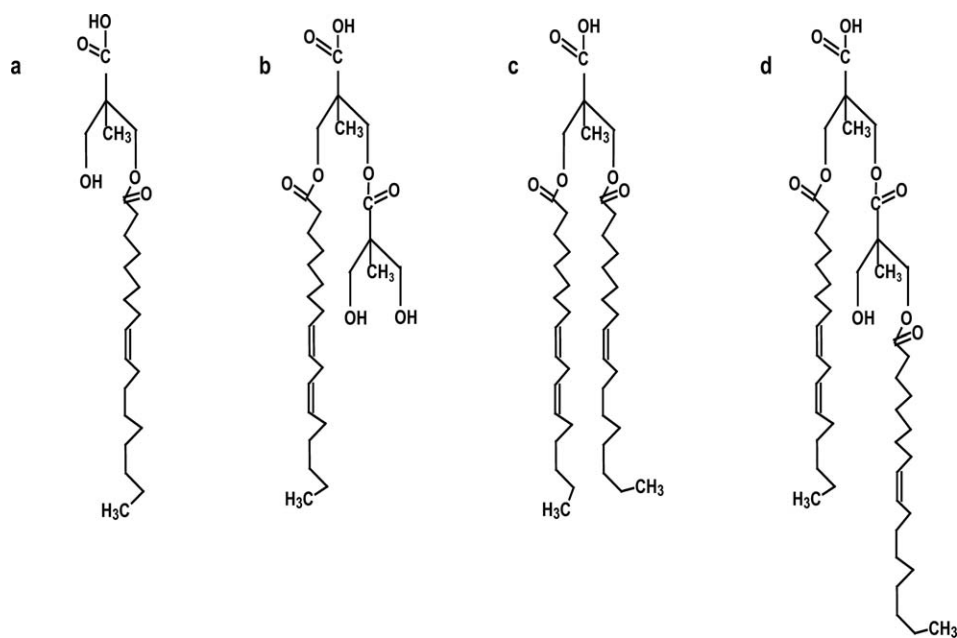
Figure 2. Schematic representation of the structures present in the MMs: (a) a DMPA molecule modified with a mole of fatty acid, (b) a DMPA molecule that reacted through OH groups with one fatty acid molecule and another DMPA molecule, (c) a DMPA molecule that reacted with 2 mol of fatty acids, and (d) the structure in panel B that reacted with one molecule of fatty acid.
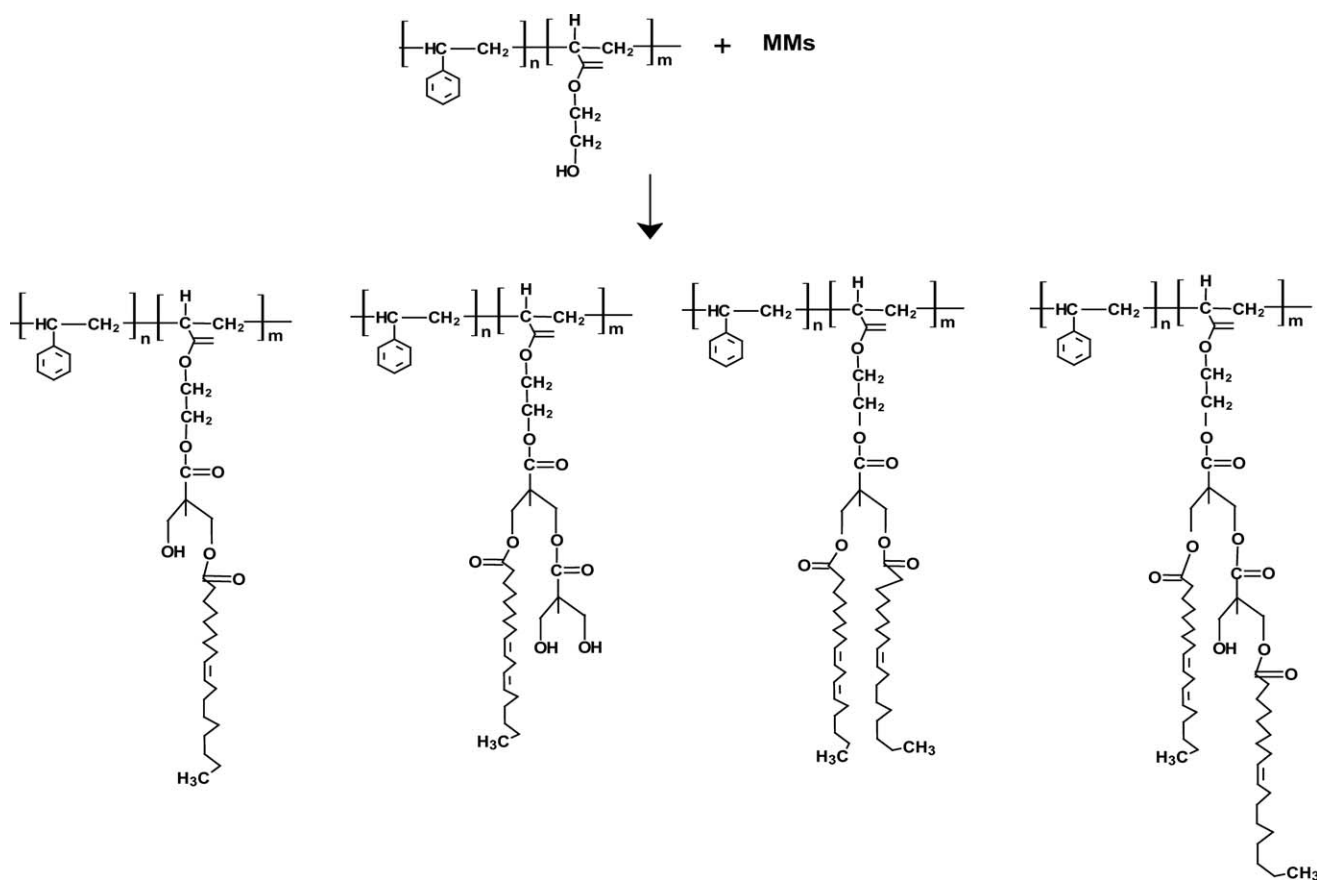

Figure 3. Schematic representation of the synthesis of an alkyd resin with a comb-type structural morphology.

Hydroxyl Value (OHV) Analysis. The OHV analysis was done according to ASTM D 4274-05. We reported this methodology in a previous article.[24] These analyses were performed in duplicate.

IR Analysis. To realize this analysis, a small amount of the sample (ca. 20 mg) was applied in a cell of zinc selenide and placed in an oven at 50 °C with a vacuum system. Once the solvent evaporation was finished, we performed the analysis in a Perki-nElmer Spectrum One instrument with eight scans with a resolution of 4 cm^{-1}.

NMR Analysis. For the NMR analysis, a sample solution in deuterated chloroform (3 wt%) was used. This analysis was done in a Bruker AMX 300 spectrometer equipped with a tube with a 5-mm inner diameter and operated at a frequency of 300 MHz.

Electrospray Ionization–Mass Spectrometry Analysis. Electrospray ionization–mass spectrometry analysis was performed with an Agilent 1200 mass spectrometer (Finnigan, MAT) with an electrospray ionization interface under the following conditions; the solvent was a mix of chloroform and acrylonitrile (5:1), the gas used was nitrogen, the solvent flow rate was 1.5 mL/min, the drying gas flow rate was 12 L/min, the nebulizer pressure was 60 psi, the capillary voltage was 2500 V, and the drying gas temperature was 350 °C. This analysis was executed with a negative scan at a mass-to-charge ratio (m/z) between 100 and 1500.

Gel Permeation Chromatography (GPC). The samples were dissolved in tetrahydrofuran, and the analysis was performed in a Waters high-performance liquid chromatography instrument with Millennium 2000 software for the data-acquisition system equipped with a refractive-index detector. The mobile phase was tetrahydrofuran, the flow rate was 0.4 mL/min, and the temperature of the column was 28 °C. To make the quantification, linear polystyrene standards were used.

Thermal Analysis. Thermogravimetric analysis (TGA) was performed with a TA Instruments Q-500. This analysis was achieved at a heating rate 10 °C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis was done with a TA Instrument Q-100 at a heating and cooling rate of 30 °C/min under a nitrogen atmosphere.

Rheological Analysis. The rheological behavior of the materials dissolved in xylene (solid content = 65 wt%) was studied with a rotational rheometer from Malvern Instruments. This study was done at a strain of 0.1% at room temperature.

Film Properties. The film properties of the materials were studied by gloss, flexibility, and chemical resistance analyses with the same methodologies previously reported.[10] In the case of adherence, this analysis was performed with a crosscut tape method on the basis of ASTM D 3359 method B.

RESULTS AND DISCUSSION

AV, Conversion Percentage (CP), and OHV

The conversion of the reaction to produce St-co-HEA was 99.22%. The reaction presented a high conversion; this was attributed to the high amount of initiator used in this study to

Table I. AV, CP, and OHV of the Samples

Sample	AV (mg of KOH/g of sample)	CP (%)	OHV (mg of KOH/g of sample)
St-co-HEA	—	—	102.4
R1	10.96	86.19	145.4
R2	5.67	90.97	132.1
R3	11.19	82.34	121.3
R4	5.99	90.12	105.4

synthesize a copolymer with a low molecular weight. In all cases, the AV of the resins were lower than the respective MMs (MM1: 79.37 mg of KOH/g of sample, MM2: 62.81 mg of KOH/g of sample, MM3: 63.37 mg of KOH/g of sample, and MM4: 60.67 mg of KOH/g of sample).[24] This was an indication that the esterification reaction was carried out. The CP of the reaction was determined on the basis of the AV of the MMs and alkyd resins with a methodology reported previously.[7] The CP (Table I) was higher than 80%. This value was high, but it could not be increased because the system presented gelation at an AV lower than 5 mg of KOH/g of sample.

The OHVs of the resins (Table I) were higher than that of St-co-HEA and lower than those of the respective MMs (MM1: 310.12 mg of KOH/g of sample, MM2: 271.13 mg of KOH/g of sample, MM3: 232.30 mg of KOH/g of sample, and MM4: 181.00 mg of KOH/g of sample).[24] This phenomenon could be explained as follows. During the synthesis of every one of the MMs, a possibly side reaction occurred because macromolecules with several repetitive units of DMPA, which contained OH groups and fatty acids, were formed so that the OHV increased in the alkyd resins. The resins showed the same behavior with respect to the OHVs of the MMs (OHV decreased with TOFA content used in the synthesis of the MMs). The reaction that took place in the synthesis of the resins was thought to be between acid groups of the MMs and OH groups of St-co-HEA (esterification reaction). A possible side reaction occurred between MM macromolecules, but this reaction was hindered sterically. Furthermore because the MMs had OH groups in their structure, the probability that they reacted was low because the electron-withdrawing effect of the carbonyl groups of the MMs contributed to the higher reactivity of the OH groups of St-co-HEA compared to that of the OH groups of the MMs.

IR Analysis

Figure 4 presents the IR spectra of the samples. Figure 4(a) presents the IR spectra of HEA, St, and St-co-HEA. The HEA spectrum showed a signal at 3416 cm^{-1} that corresponded to the stretching of the C—OH bonds. The signal that appeared at 1725 cm^{-1} was attributed to the adsorption of the carbonyl groups (—C=O). The signal at 1638 cm^{-1} was due to the stretching of the —CH=CH— bonds, and that at 1410 cm^{-1} corresponded to the bending of —CH$_2$. In the St spectrum, a signal appeared at 3030 cm^{-1}; this corresponded to the C—H stretching of aromatic compounds. The signal around 2955 cm^{-1} was attributed to aliphatic C—H stretching, and the signals at 1595 and 1628 cm^{-1} were assigned to the C=C
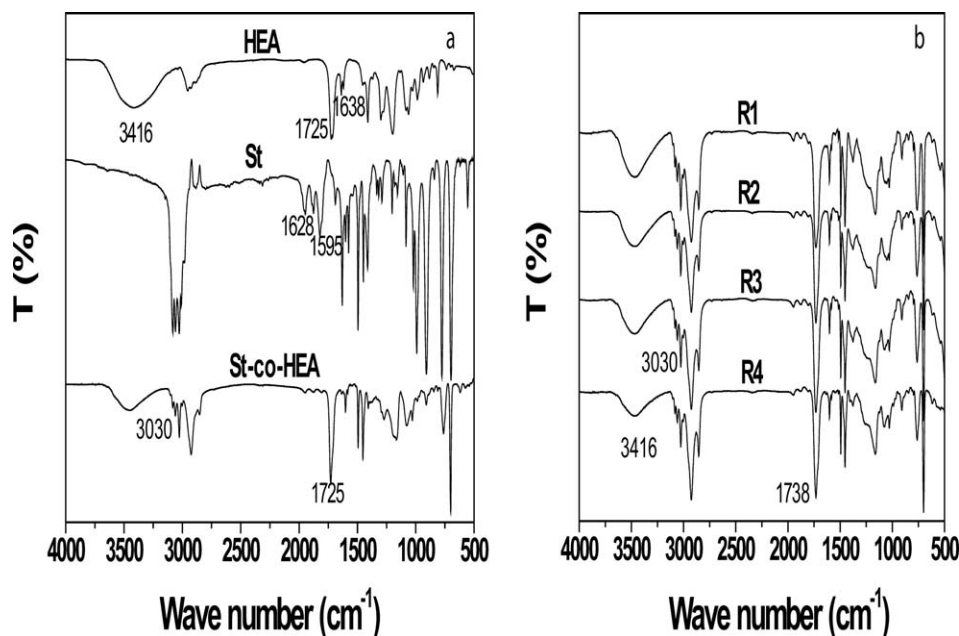
Figure 4. IR spectra of (a) HEA, St, and St-*co*-HEA and (b) alkyd resins.

stretching of aromatic rings. The signals corresponding to C—H and C=C stretching at 3030 and 1595 cm^{-1}, which were present in the St spectrum, and the signal of the stretching of C—OH bonds in the HEA spectrum were also in the spectrum of St-*co*-HEA. Therefore, we concluded that the copolymers were formed during the reaction.

Figure 4(b) shows the IR spectrum of the alkyd resins. These spectra presented a signal around 3400 cm^{-1} due to the stretching of OH groups. At 1738 cm^{-1}, a signal appeared that corresponded to the carbonyl group (—C=O) of ester groups. These signals also appeared on the MMs' spectra.[24] The signal due to C—H and C=C stretching at 3030 and 1595 cm^{-1} for St-*co*-HEA also appeared in all of the spectra of the alkyd resins.

Additionally, the IR spectra of the MMs[24] showed that the intensity of the stretching due to OH groups in the resins (Figure 4) was intermediate between the intensity of the MMs[24] and that of St-*co*-HEA. Therefore, this was another indication that the OH groups of St-*co*-HEA participated in the esterification reaction. The intensity of the absorption due to OH groups decreased with the TOFA content used in the synthesis of the MMs; this was in accordance with the behavior exhibited for these materials on OHV.

NMR Analysis

In Figure 5, the ^{1}H-NMR spectra of St-*co*-HEA [Figure 5(a)] and R2 [Figure 5(b)] are presented. The NMR spectrum of St-*co*-HEA [Figure 5(a)] presented a signal around 7 ppm, which
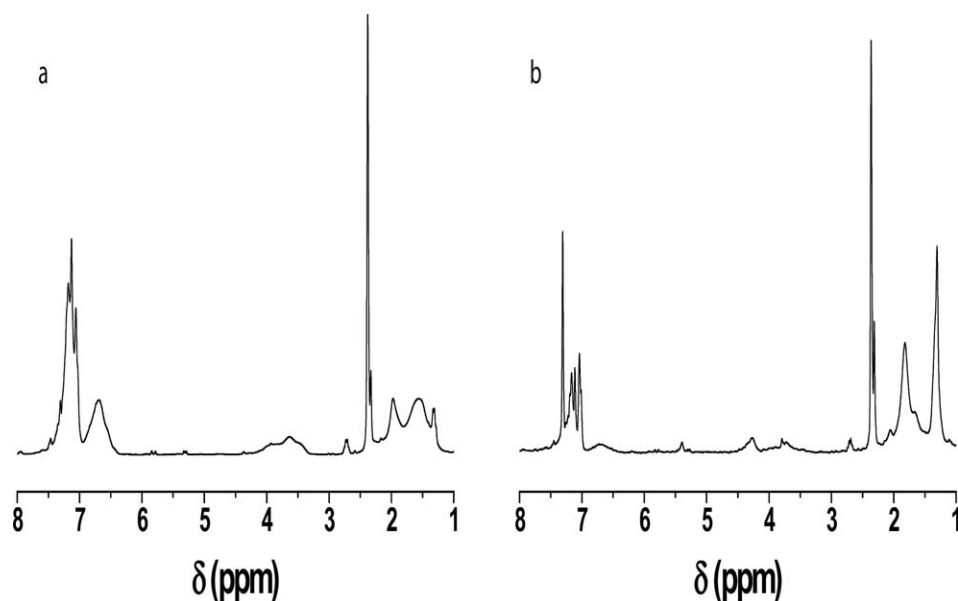

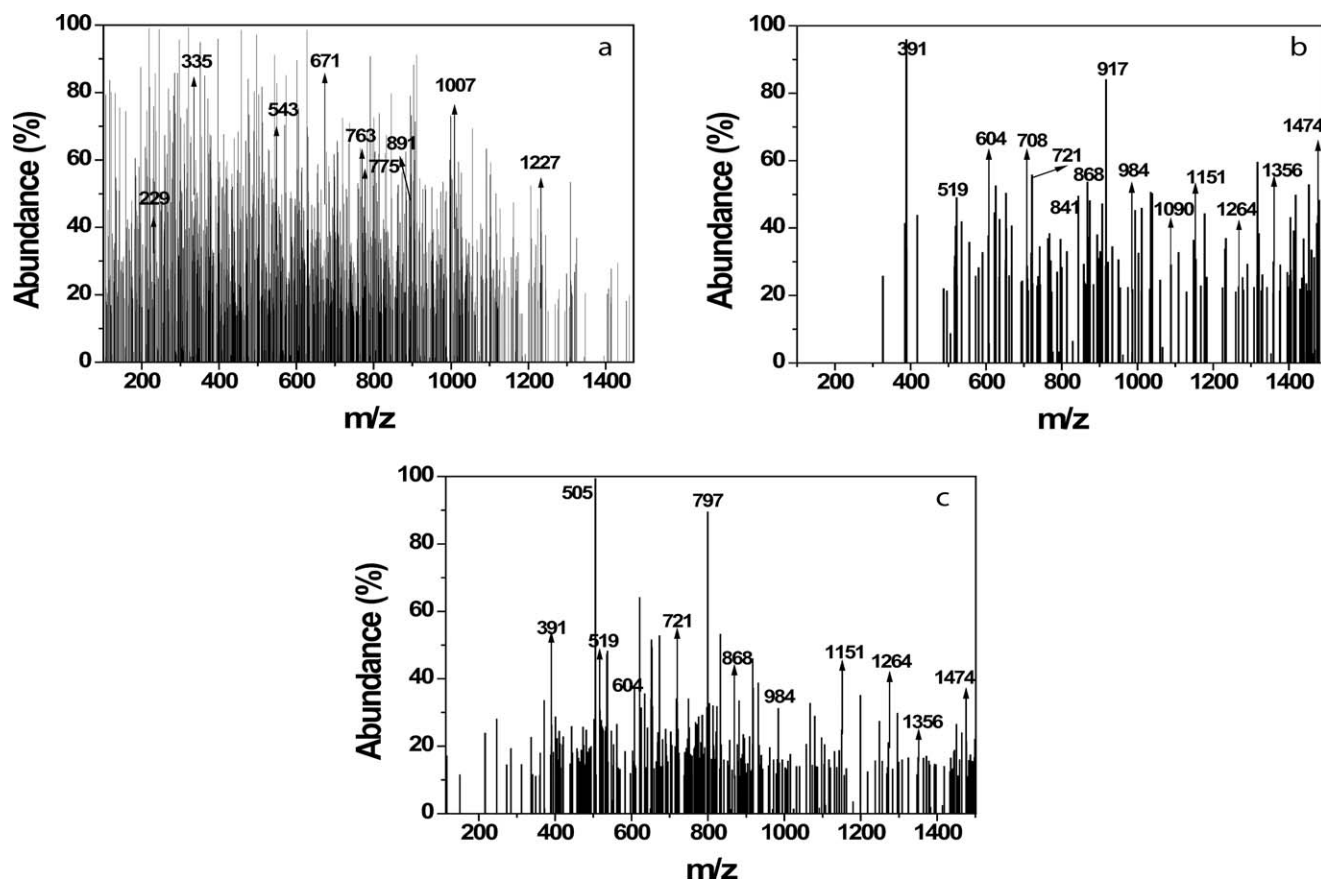**Figure 5.** ^{1}H-NMR spectra of (a) St-*co*-HEA and (b) R2 resins.

Figure 6. Mass spectra of (a) St-*co*-HEA, (b) R1 resin, and (c) R2 resin.

was due to protons of the CH of the aromatic ring. Around 6.5 ppm, a signal appeared that corresponded to the protons of CH joined to benzene (St). The wide signal around 3.5 ppm was attributed to methylene protons of HO—CH₂— and —CH₂OCO—R.[25] Between 1 and 2.5 ppm, signals appeared that were due to other protons of CH and CH₂. The same signals have been observed by others authors.[26,27] In this spectrum, a signal corresponding to —HC≡CH— protons did not appear; this suggested that the purification process was good.

Figure 5(b) presents an important signal at 5.30 ppm, which was due to —CH=CH— protons of fatty acids; these were presents in the MM structures.[24] This was an indication that the reaction between MM2 and St-*co*-HEA was carried out. The same signal was observed in HBP modified with TOFA.[8] This spectrum showed the same signals of St-*co*-HEA between 6 and 7.5 ppm, but the signal around 3.5 ppm that appeared in the St-*co*-HEA spectrum was now resolved into two signals, which appeared at 3.6 and 4.1 ppm and were attributed to OH groups joining with the methylene protons of HO—CH₂— and —CH₂OCO—R, respectively.

Electrospray Ionization–Mass Spectrometry Analysis
The molar mass of the repetitive unit of St-*co*-HEA was 230 g/mol. Figure 6 shows the mass spectra of the samples. Figure 6(a) presents the St-*co*-HEA mass spectrum; in this spectrum, there appeared different peaks of the St-*co*-HEA repetitive units containing different number of units of St and HEA. At $m/z = 229$ (one St unit and another HEA unit), $m/z = 335$ (one St unit and two HEA units), $m/z = 451$ (one St unit and three HEA units), $m/z = 543$ (two HEA units and three St units), $m/z = 567$ (one St unit and four HEA units), $m/z = 671$ (two St units and four HEA units), $m/z = 763$ (four St units and four HEA units), $m/z = 775$ (three St units and four HEA units), $m/z = 891$ (three St units and five HEA units), $m/z = 1227$ (four St units and seven HEA units), and $m/z = 1295$ (four HEA units and eight St units). The presence of theses peaks showed that the copolymerization process was random.

The mass spectra of samples R1 [Figure 6(b)] and R3 [Figure 6(c)] presented some peaks that did not appear in the St-*co*-HEA mass spectrum. In the R1 mass spectrum, the peak at $m/z = 391$ was due to fragments of a DMPA unit modified with a mole of fatty acid. The peak at $m/z = 604$ corresponded to the St-*co*-HEA oligomer, whose polymerization degree was one and which reacted with a DMPA unit modified with a mole of fatty acid. This structure is presented in Figure 7(a). Other copolymer units were modified with the same structure, and these peaks appeared at $m/z = 708$ (fragments containing one repetitive unit of St and two repetitive units of HEA), $m/z = 841$ (fragments containing one repetitive unit of St and three repetitive units of HEA), $m/z = 1264$ (fragments containing three repetitive units of St and five repetitive units of HEA), and $m/z = 1356$ (fragments containing four repetitive units of HEA and five repetitive units of St).
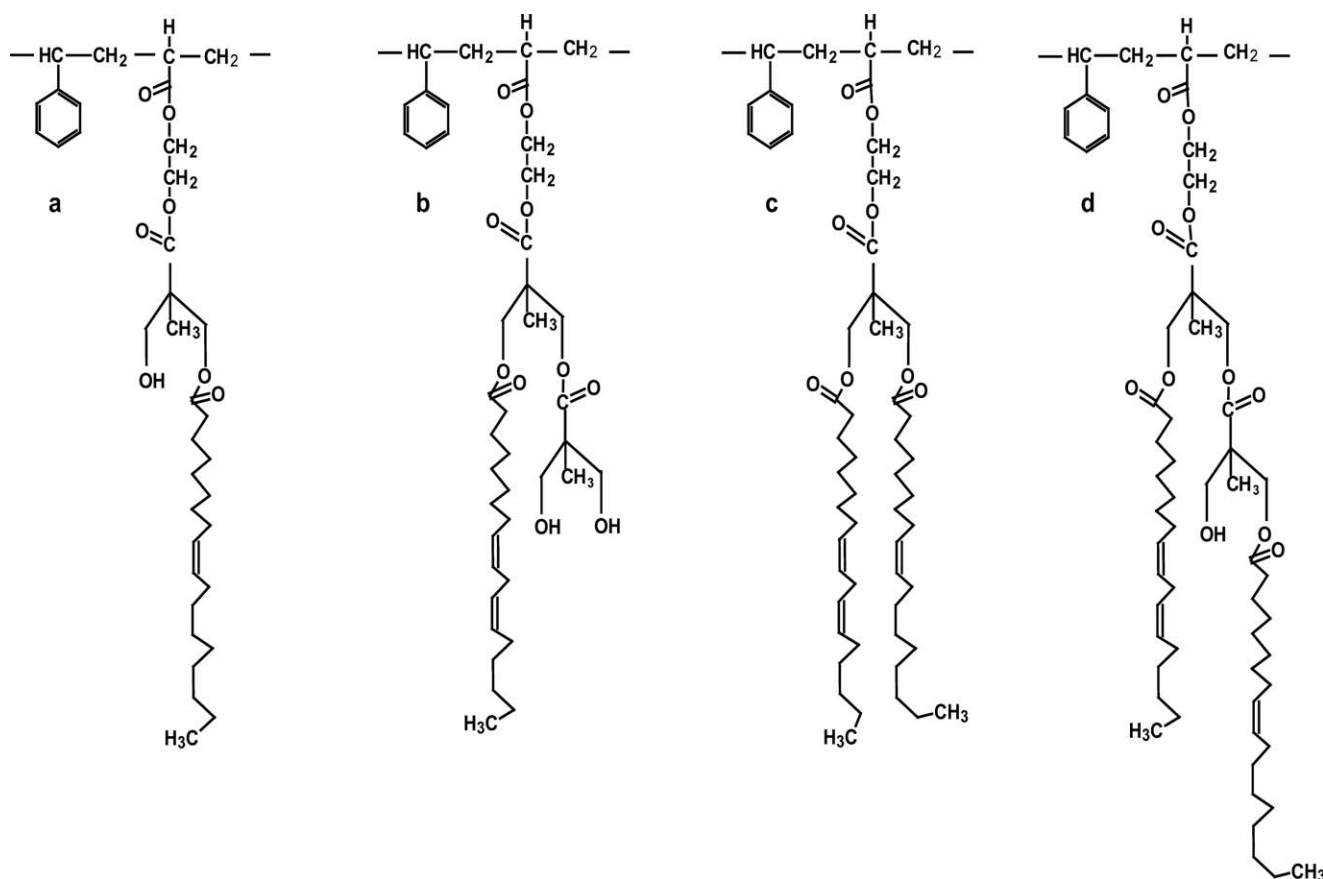
Figure 7. Schematic representation of the structures that were formed and presented peaks at m/z values of (a) 604, (b) 721, (c) 868, and (d) 984 in the mass spectra.

The peak at $m/z = 721$ corresponded to the St-co-HEA oligomer, whose polymerization degree was one and which was modified with the following structure: one molecule of DMPA that reacted through OH groups with one fatty acid molecule and another DMPA molecule. The schematic representation of this structure is shown in Figure 7(b). The peaks at $m/z = 1151$ and 1474 were possibly due to fragments of the resins that were formed by a reaction between the compound of Figure 7(b) with St-co-HEA. At $m/z = 868$, a peak appeared that was due to fragments that contained one St-co-HEA repetitive unit that reacted with the MM formed from 1 mol of DMPA and 2 mol of fatty acids. The schematic representation of this structure is presented in Figure 7(c). At $m/z = 984$, a peak was observed that was due to the structure shown in Figure 7(b) and which was modified with 1 mol of fatty acid. This structure is shown in Figure 7(d). The mass spectrum of resin R2 exhibited peaks at $m/z = 391$, 721, 868, 984, 1151, and 1264; these peaks also appeared in the R1 mass spectrum.

This analysis showed that during the synthesis of these materials, different structures were formed because St-co-HEA was modified with four types of structures, which were (1) a DMPA molecule modified with a mol of fatty acid, (2) a DMPA molecule that reacted through OH groups with one fatty acid molecule and another DMPA molecule, (3) one DMPA molecule that reacted with 2 mol of fatty acid, and (4) the second struc-

ture, which reacted with one molecule of fatty acid. These four structures were present in the sample of the MMs studied (Figure 3).[24]

This analysis allowed us to confirm the explanation given to the OHV and IR analyses because the formation of St-co-HEA modified with MMs containing one or several OH groups was observed; this increased the OHV and the intensity of OH groups in the IR spectra.

GPC Analysis

Table II presents the number-average molar mass (M_n), weight-average molar mass (M_w), and polydispersity index. This study was used to make a comparative study because the determination of M_n and M_w used a calibration curve obtained from a standard whose structure was linear (polystyrene), and this polymer was not branched. In the MMs, the molecular weight increased with the TOFA content and modification degree[24] (reduction of the OHV). Therefore, we expected that the same behavior would be observed for the resins, and this did occur. These results once more proved the reaction between the MMs and St-co-HEA.

Thermal Analysis

Figure 8 presents the TGA thermograms of the samples. The values of the decomposition temperature (T_d) of the alkyd resins are presented in Table II. The thermal stability of the alkyd

Table II. Results of GPC and Thermal Analyses

Sample	M_n (g/mol)	M_w (g/mol)	Polydispersity index	T_d at onset (°C)	T_g (°C)
St-co-HEA	4554	8897	1.95	423.1	87.3
R1	5746	11,432	1.99	429.9	64.0
R2	6673	14,322	2.14	432.4	62.9
R3	7667	16,985	2.21	434.4	55.8
R4	8981	20,551	2.29	430.7	38.2

resins [Fig. 8(a,b) and Table II] was higher than that of St-co-HEA and the MMs (339–424 °C).[24] This shows that between the MMs and St-co-HEA existed synergies. The behavior presented for the alkyd resins on the thermal stability with respect to St-co-HEA was due to the increase in the molecular weight (Table II). Only for resins R1, R2, and R3 did the thermal stability increase with the TOFA content used in the preparation of the MMs; this was expected because the same behavior was exhibited by MMs.[24] Therefore, resin R4 did not follow a trend with respect to the thermal stability with the TOFA content. Another possible cause of the behavior showed by the R4 resin was that the resins were grafted on the St-co-HEA structures of low molar mass. St-co-HEA presented a weight loss around 131 °C that corresponded to 7.3 wt%. The same occurred in the alkyd resins but the weight loss value was lower than 2 wt%. This loss was possibly due to the thermal decomposition of oligomers with low molecular weight, although the reduction of the weight loss in the alkyd resins may have been due to some oligomer chains modified with the MMs.

Figure 8(b) shows the distribution of the thermal decomposition of the alkyd resins; we observed that the resin R4 exhibited two peaks. This suggested that the sample presented a higher polydispersity than the other alkyd resins. This might have been

due to steric hindrance because the resin was obtained with MM4, which was synthesized with highest TOFA content.[24] This may also have explained the behavior exhibited by this resin with respect to thermal stability.

The mechanism of pyrolysis of the ester involved a cis elimination (the nucleophilic attack of the oxygen on the β-hydrogen atoms).[28] In a study of the modification of pentaeritritol with erucic acid, it was observed that monoesters and diesters were thermally less stable than triesters and tetraesters; this was associated with the presence of OH groups in the structures because monoesters and diesters have higher OH group numbers that triesters and tetraesters.[29] From these results, we can hypothetically comment that the thermal stability of the resins was influenced by the type of structure that reacted with St-co-HEA because the thermal stability did not follow a trend with the OHV and M_n.

The TGA results allowed us to demonstrate that the reaction between the respective MMs and St-co-HEA was carried out in all cases. Furthermore, we could also infer that the composition of the MMs had an important effect on the thermal stability.

Figure 9 presents the DSC thermograms of the samples. All of the alkyd resins were amorphous, and their glass-transition
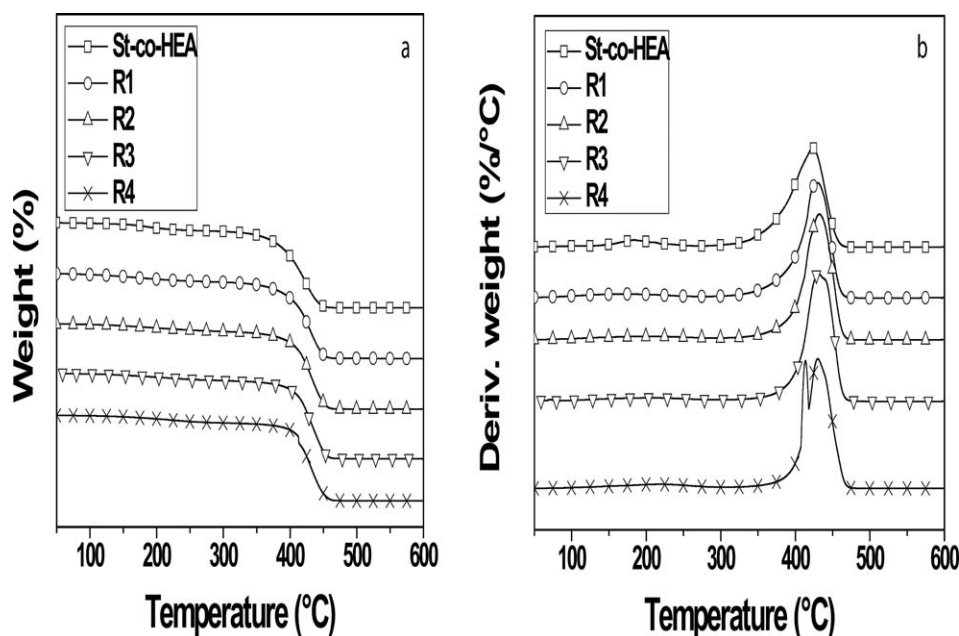
Figure 8. TGA thermograms: (a) weight versus temperature and (b) derived weight versus temperature.
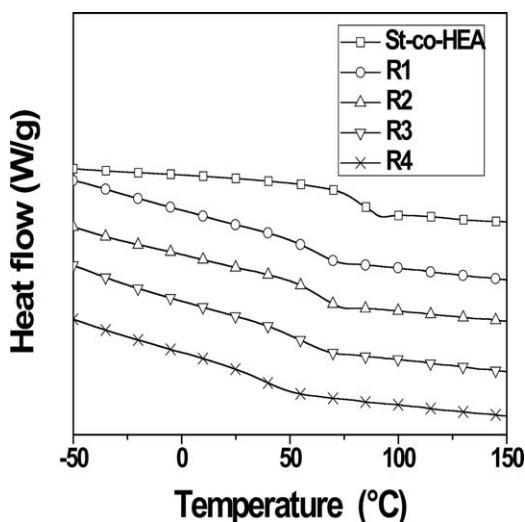
Figure 9. DSC thermograms of the samples.

Figure 10. Viscosity versus the shear rate of the materials.

temperature (T_g) values were lower than that of St-co-HEA (Figure 9). The T_g values of the alkyd resins were between those of the MMs (MM1: $-24.2\,°C$, MM2: $-52.2\,°C$, MM3: $-68.5\,°C$, and MM4: $< -70\,°C$)[24] and St-co-HEA (Table II). None of the DSC thermograms of the alkyd resins showed T_gs of the MMs or St-co-HEA; this indicated once more that the reaction between them was completed. The T_g values of the alkyd resins followed the same trends presented by the MMs because the T_g values increased with the proportion of TOFA used in the synthesis. The R1 and R2 resins exhibited similar T_g values; this was an indication that the structural arrangement of them also was the same. The process of the grafting of the MMs onto St-co-HEA was random; this made the free volumes of the alkyd resins different. The reduction of the T_g value with increasing TOFA content was observed in hyperbranched alkyd resins.[6]

According to the results, the MMs had a plasticizer effect on the resins. This was due to the presence of TOFA in the MM structures. The same result was obtained in the modification of HBP with TOFA.[8]

Rheological Analysis

Figure 10 shows the rheological behavior of the materials. The rheological behavior of St-co-HEA was mainly Newtonian; the cause of this behavior may have been the facts that the copolymer was obtained with a high amount of initiator (2 wt%) and a copolymer with a low molecular weight and entanglement degree was easily obtained. The alkyd resins presented a higher viscosity than St-co-HEA, and this was a result of the modification of this copolymer and the increasing of molar mass. The viscosity values of all of these materials were lower than 10 Pa s. The viscosity values of the samples measured at a shear rate of 10 s^{-1} were as follows: 0.49 Pa s for St-co-HEA, 5.34 Pa s for R1, 3.35 for R2, 2.12 Pa s for R3, and 1.51 Pa s for R4. These values were lower than those obtained from the alkyd–silicone hyperbranched resins synthesized with a high solid content (65 wt%), which were higher than 6.0 Pa s.[10] The viscosity values of a high-solids alkyd resin with a conventional structure and a commercial conven-
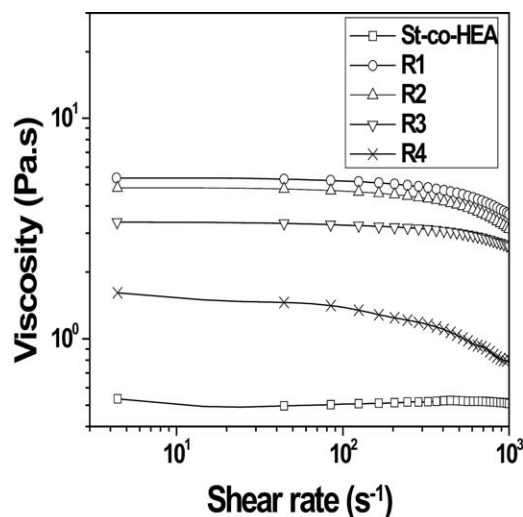
tional resin obtained in a previous study were 26 and 1000 Pa s, respectively.[12]

The increase in the viscosity was not proportional to the molar mass of the resins; this may have been due to the plasticizer effect (this was evidenced by DSC analysis because the resins exhibited lower T_gs than St-co-HEA) of the MMs in the resins and the interaction degree through hydrogen bonds between the macromolecules.

The R1, R2, and R3 resins exhibited steady regions on shear rates between 0.52 and 100 s^{-1}. The R4 resin presented a reduction in the viscosity with increasing shear rate. The rheological behavior of the alkyd resins was mainly pseudoplastic. These behaviors were related to the presence of TOFA in the MMs and the dissociation of interactions between OH groups because MM1 and MM2 were obtained with lower proportions of TOFA than in MM3 and MM4. Therefore, the numbers of fatty acid chains in the R1 and R2 alkyd resins were more minor than those in R3 and R4 (with a high probability of exhibit entanglement through the fatty acids), but R1 and R2 had a high possibility of suffering interaction ruptures through the OH groups (hydrogen bonds) because they showed the highest OHV.

St-co-HEA possibly exhibited a lower entanglement and interaction through OH groups than the alkyd resins because its rheological behavior was less pseudoplastic (Figure 10).

Table III. Results of Gloss, Flexibility, and Adherence Analyses of the Samples

Sample	Gloss (85°)	Flexibility	Adherence
St-co-HEA	60.1	Pass	5B
R1	75.4	Pass	5B
R2	76.3	Pass	5B
R3	75.6	pass	5B
R4	76.9	Pass	5B

Table IV. Results for the Chemical Resistance of the Samples

Sample	H$_2$O	NaOH (0.1 M)	HCl (0.1 M)	NaCl (5%)
St-co-HEA	A	D	A	A
R1	A	D	A	A
R2	A	D	A	A
R3	A	D	A	A
R4	A	D	A	A

A, without removal; B, totally removed; C, partially removed; D, blister.

The rheological results were very good because the alkyd resins were obtained with high solid contents and with low viscosities; this allowed us to obtain environmentally friendly materials.

Film Properties

Table III presents the gloss, flexibility, and adherence results. The values of gloss of the alkyd resins were higher than that of St-co-HEA. This was an indication that the incorporation of the MMs improved this property. This behavior was due to the fact that the MMs were obtained from TOFA, and it is known that oils have good gloss. The same behavior was reported previously.[30] The gloss values obtained in this study were lower than those of alkyd resins obtained in other studies.[8,9] According to the results obtained from the film properties, we observed that the modification of St-co-HEA with the MMs improved the gloss.

According to the results, the gloss did not show dependence on the MM type because similar behavior was observed with hyperbranched alkyd resins obtained from different proportions of TOFA.[8] All of the samples passed the flexibility test; this was expected because of the amorphous character of the samples. The adherence of the samples was good; this is an important quality exhibited by acrylic polymers and alkyd resins.[2,31]

The chemical resistance of the St-co-HEA and alkyd resins was good against water, HCl, and NaCl, but this was regular in a solution of NaOH (Table IV). This behavior was attributed to the fact that the esters could be hydrolyzed by the NaOH solutions.

CONCLUSIONS

This study allowed environmentally friendly alkyd resins to be obtained. The alkyd resins showed a synergy between the properties of St-co-HEA and the MMs. The reaction between St-co-HEA and the MMs was examined IR spectroscopy, NMR, mass spectrometry, DSC, and GPC analyses. All of the structures had residual OH groups, which could be modified with other compounds, such as anhydrides, to obtain waterborne hybrid alkyd resins. Mass spectrometry showed that in the MMs, there were several structures that were grafted onto St-co-HEA. The gloss values of the resins were very similar. The molar mass of St-co-HEA was lower than those of the alkyd resins. The chemical resistance of the resins against NaOH solution was lower than that of St-co-HEA. The flexibility of the alkyd resins and St-co-HEA were good because all of them passed this proof. The materials obtained may be alternatives for use in the coating industry.

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