

Polyfunctional macromonomers obtained from 2,2-bis(hydroxymethyl) propanoic acid and tall oil fatty acids

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ABSTRACT: Macromonomers (MMs) were obtained with different proportions of dimethylolpropionic acid (DMPA) and tall oil fatty acid (TOFA). The MMs were characterized by their acid value (AV), their hydroxyl value (OHV), IR spectroscopy, NMR, electrospray ionization–mass spectrometry, UV spectroscopy, rheological, differential scanning calorimetry, thermogravimetric analysis, gloss, flexibility, and adherence analyses. The presence of hydroxyl and ester groups and double bonds were confirmed by IR and NMR analyses. IR analysis showed that the intensity of the OH groups decreased with the addition of TOFA. In all cases, the AVs of the MMs were lower than those of DMPA and TOFA. By electrospray ionization–mass spectrometry, the formation of the DMPA homopolymers and structures with molecular weights higher than that of DMPA were observed. All of the MMs were amorphous. The viscosity of the MMs decreased with the addition of TOFA. The gloss values of the MMs at 85° were higher than 100, and the flexibility was good. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42029.

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INTRODUCTION

During the last few years, research has been more focused toward the synthesis of friendly environmental materials obtained from renewable resources to reduce the dependence on the petrochemical industry.¹ So many monomers derived from the petrochemical industry have been used in the synthesis of polymers. Some of these monomers are toxic, irritating, and volatile. The most common monomers found in this type of industry are acrylics,^{2,3} styrene,⁴ and maleic anhydride.⁵

Dimethylolpropionic acid (DMPA) is a trifunctional material because it has two OH groups and an acid group.¹ This material has been used as an extender during the synthesis of hyperbranched poly(ester polyol).^{6–8}

Tall oil fatty acid (TOFA) is a mix of oleic (46 wt %), linoleic (35 wt %), linolenic (12 wt %), palmitic (4 wt %), and stearic acid (3 wt %). This material was obtained from renewable resources (wood pulp).⁹ This material has been used in the synthesis of hyperbranched alkyd resins.^{10–13}

Many materials with some degree of branching are required in applications for crosslinking reactions, as stabilizers, and for the synthesis of polymers with special performances or morphologies.¹⁴

There have been some reports of the synthesis of macromonomers (MMs) obtained from triglycerides.^{15,16} An MM triglyceride oil derivative is obtained; it has long chains containing acrylate in its structure. This material has been copolymerized with butyl acrylate, methyl methacrylate, and acrylic acid by miniemulsion polymerization.¹⁵ Another MM was obtained from triglycerides and methyl methacrylate, and this MM was copolymerized with styrene.¹⁶ The monomers usually used in the free-radical polymerization are derived from petrochemical resources. The MMs synthesized from DMPA and TOFA have the advantage that they can be obtained from renewable resources (TOFA). These MMs can contain acid groups, hydroxyl groups, and —C=C— bonds in their structures; these allow them to be used in other applications, such as crosslinking agents or monomers for condensation and addition reactions. Furthermore, they can be obtained with a low proportion of volatile organic compounds (<40 wt %); this makes these MMs environmentally friendly materials.

So far, no reports on the synthesis of DMPA modified with TOFA have been made. Therefore, this article makes an important contribution to the study of branched MMs. In this study, some MMs were obtained by the esterification reaction of

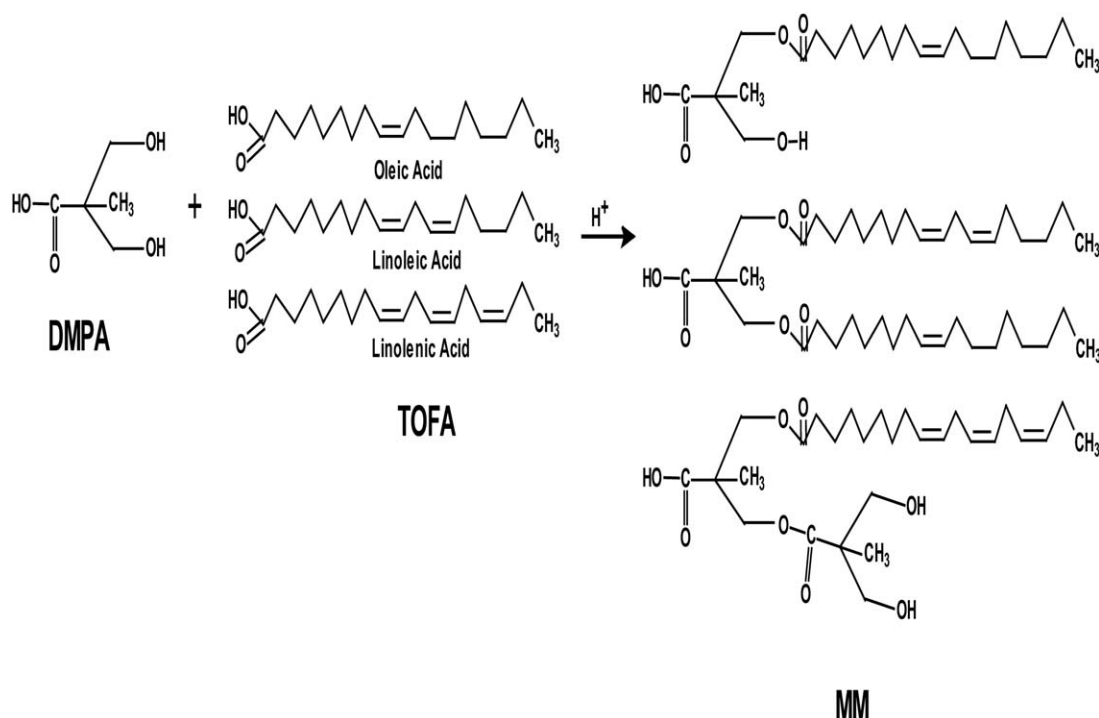


Figure 1. Schematic representation of an MM.

DMPA and TOFA using an acid catalyst. The effects of the amounts of DMPA and TOFA on the structural, thermal, rheological, and film properties of the MMs were studied.

EXPERIMENTAL

Materials

DMPA with an acid value (AV) of 418.82 mg of KOH/g of sample and a hydroxyl value (OHV) of 821.54 mg of KOH/g of sample, *p*-toluene sulfonic acid, pyridine, acetic anhydride, sodium hydroxide (NaOH), and xylene were supplied by Sigma Aldrich, and TOFA was supplied by Colorquímica SA.

Synthesis of the MMs

The synthesis of the MMs (Figure 1) was carried out according to the methodology reported by Murillo *et al.*⁶ The respective amounts of DMPA and TOFA were placed in the reactor, which was kept at 200°C under a nitrogen atmosphere, whereas the system was stirred at 200 rpm. Table I shows the proportions of DMPA, TOFA, and oil percentage (OP) used for obtaining the MMs.

The reaction conversion was monitored by measuring the AV until the wanted AV value was acquired. Finally, the solutions

Table I. DMPA, TOFA, and OP Proportions Used to Obtain the MMs

MMs	DMPA (g)	TOFA (g)	OP
MM1	75.40	69.60	48.00
MM2	51.04	69.60	57.69
MM3	33.80	69.60	67.31
MM4	20.00	69.60	77.68

of the MMs in xylene were obtained with a solid content of 65 wt %.

Characterization of the MMs

AV Analysis. The AV measurements were discerned in order, with the methodology reported by us⁸ to determine the reaction conversion percentage at different times and to corroborate the reaction between DMPA and TOFA.

OHV Analysis. The OHV analyses were done according to ASTM D 4274-05. A volume of 20 mL of an acetylation reagent (a mixture of 127 mL of acetic anhydride with 1000 mL of pyridine) were added to pressure bottles for the blank and sample determinations (ca. 1 g). The bottles were kept in a water bath at 100°C for 2 h under stirring. They were then removed from the bath and cooled to room temperature. The bottles were carefully opened to release any pressure. Then, between 20 and 30 mL of water and 1 mL of the phenolphthalein indicator solution were added, and the titration was realized immediately with the 0.5 N NaOH solution to the first faint pink end point that persisted for 15 s. This analysis was done in triplicate for every sample. The OHV was determined with the following equation:

$$\text{OHV} = \frac{(B-A)N \times 56.1}{g} \quad (1)$$

where *B* is the number of milliliters of NaOH solution required for the titration of the blank solution, *A* is the number of milliliters of NaOH solution required for titration of the sample, *N* is the normality of the NaOH solution, and *g* is the number of grams of the sample.

IR Analysis. This analysis was carried out in a PerkinElmer Spectrum One instrument. The sample was scanned eight times.

Table II. AV, OHV, and MP of the MMs

MM	AV (mg of KOH/g of sample)	OHV (mg of KOH/g of sample)	MP
MM1	79.37 ± 1.07	310.12 ± 1.02	62.25 ± 0.12
MM2	62.81 ± 1.15	271.13 ± 1.11	66.99 ± 0.13
MM3	63.37 ± 1.02	232.30 ± 1.23	71.72 ± 0.15
MM4	60.67 ± 1.20	181.00 ± 1.35	77.97 ± 0.16

For DMPA analysis, this was mixed with potassium bromide, and pellets were obtained. In the case of the MMs, a small drop was put on the zinc selenide window, and when the solvent was vaporized, analysis was performed.

NMR Analysis. ¹H-NMR and ¹³C-NMR analyses were done in a Bruker AC 300-MHz spectrometer with chloroform as a solvent. The concentration of the sample solutions was 3 wt %.

Electrospray Ionization/Mass Spectrometry Analysis. This analysis were performed with an Agilent 1200 mass spectrometer (Finnigan, MATTM) with an electrospray ionization interface under the following conditions: the solvent was a mix of chloroform and acrylonitrile (5:1), the gas was nitrogen, the solvent flow was 1.5 mL/min, the drying gas flow 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 negative scanning between 100 and 1500 mass/charge (*m/z*).

UV Spectroscopy Analysis. A PerkinElmer Lambda 35 was used at room temperature. The MMs were dissolved in xylol, and the concentration of these solutions was 1 wt %.

Rheological Analysis. The rheological measurements in solution (65 wt % MMs in xylene) were done in a Bohling HRNano rotational rheometer (TA Instruments) at a strain of 2% with concentric cylinder geometry.

Thermal Analysis. Differential scanning calorimetry (DSC) analyses were performed in a TA Instruments model Q100 instrument equipped with a refrigerated cooling system with a heating and cooling rate of 30°C/min under a nitrogen atmosphere.

The decomposition temperatures (*T_d*'s) of the MMs were determined by thermogravimetric analysis in a TA Instruments model Q500 at a rate of 10°C/min.

Film Properties. Studies of the MM film properties (gloss and flexibility) were performed according to methodologies we reported on previous studies.^{10,12} The adherence test was carried out according to ASTM D 3359.

RESULTS AND DISCUSSION

AV, OHV, and Modification Percentage (MP)

Table II shows the results of the AV, OHV, and MP. The AV of the samples was around 80 mg of KOH/g of sample; this was lower than the AV of DMPA (418.82 mg of KOH/g of sample). This is an indication that during the synthesis, DMPA was also polymerized because the acid and OH groups of DMPA reacted

between them. Furthermore, the esterification reaction between DMPA and TOFA or between the DMPA homopolymers and TOFA was carried out. The AV desired in this study was obtained because we wanted these MMs to have acid groups in their structures.

We observed that the OHV values of all of the MMs were lower than those of the DMPA. This was an indication that the OH groups of DMPA or DMPA homopolymers were modified with TOFA. This verified that the esterification reaction between DMPA and TOFA took place. The main reaction occurred between DMPA and TOFA because, initially, these materials were taken to the reactor at the same time. This reduced the possibility of the DMPA homopolymerization. The MP of DMPA was calculated with the results of DMPA and MM OHV with the methodology reported by Murillo *et al.*⁸ These results are presented in Table II. MP increased with the amount of TOFA used in the synthesis of the MMs. This was expected because, as the amount of TOFA increased, a higher number of OH groups of DMPA could react with the acid groups of TOFA.

IR Analysis

Figure 2 presents the IR spectra of the TOFA and DMPA [Figure 2(a)] and the IR spectra of the MMs [Figure 2(b)]. The TOFA spectrum [Figure 2(a)] presented a signal at 3009 cm⁻¹, which corresponded to the stretching of —CH=CH—. At 1707 cm⁻¹, a signal due to the carbonyl group (C=O) of the acid groups appeared, and around 2900 cm⁻¹, two peaks were visible and were assigned to C—H symmetric and asymmetric stretching. The DMPA spectrum [Figure 2(a)] presented a signal at 3368 cm⁻¹ due to acid and OH groups. The signal at 1688 cm⁻¹ was attributed to C=O groups.

In the MM spectra [Figure 2(b)], several signals appeared. At around 3500 cm⁻¹, a signal appeared; this was attributed to the stretching of OH groups. At 1738 cm⁻¹, a signal appeared. This corresponded to a carbonyl group (—C=O) of ester groups. The DMPA and TOFA spectra were different than those of the MMs. The signal, due to the OH groups (ca. 3500 cm⁻¹), decreased its intensity with the amount of TOFA used in the synthesis. The presence of signals due to ester groups, the stretching of —CH=CH—, and the reduction in the intensity of OH groups (with the TOFA amount) were indications that the OH groups of DMPA reacted with the acid groups of TOFA. These results were in accordance with those obtained from MP.

NMR Analysis

Figure 3 shows the ¹H-NMR spectrum of the DMPA [Figure 3(a)] and the sample MM2 [Figure 3(b)]. In the DMPA spectrum [Figure 3(a)], the signal at 3.43 ppm was due to the —CH₂ joined to OH groups. The signal at 2.5 ppm was attributed to the solvent (DMSO), and the signal around 1.0 ppm was due to aliphatic protons of —CH₂ and —CH₃.

In the spectra of the sample MM2 [Figure 3(b)], the signal at 5.25 ppm was due to the —CH=CH— protons of fatty acid joined to DMPA. The signal at 4.35 ppm was assigned to the CH₂OCOR protons, whereas the signals at 3.70 ppm were due to the CH₂ joined to OH groups. The signals between 0.5 and 3

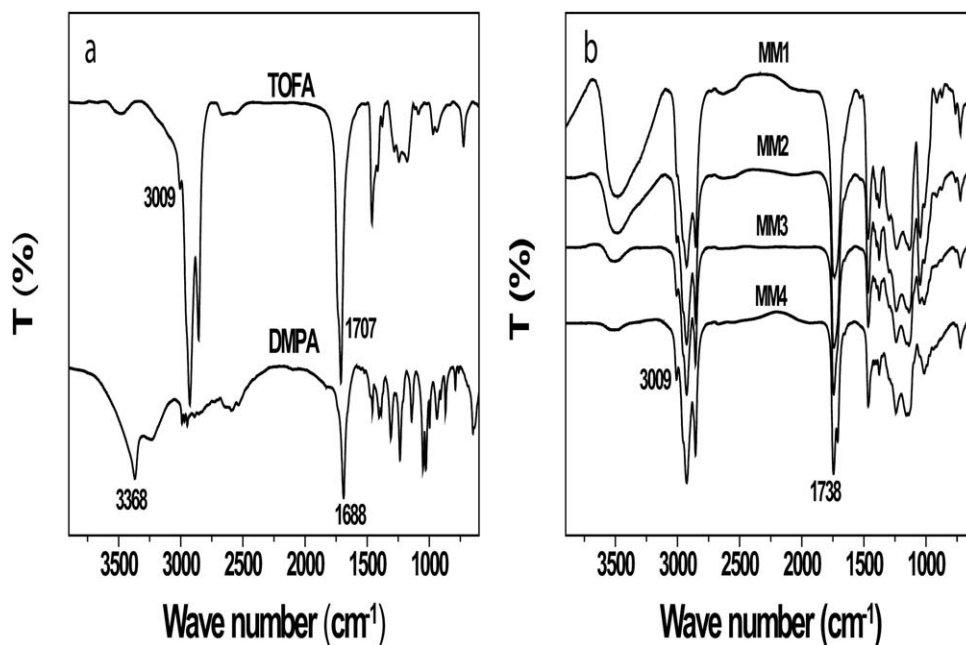


Figure 2. IR spectra of the samples: (a) TOFA and DMPA and (b) MMs.

ppm corresponded to the aliphatic protons of $-\text{CH}_3$, $-\text{CH}_2$ and $-\text{CH}$. The presence of the signals of the $-\text{CH}=\text{CH}-$ protons of fatty acid and the reduction in the intensity of the signal due to $-\text{CH}_2$ joined to OH groups in the MM2 spectrum was evidence that DMPA reacted with TOFA. The reduction in the intensity due to $-\text{CH}_2$ joined to OH groups was in accordance with the results obtained by IR analysis.

Figure 4 presents the ^{13}C -NMR spectrum of the sample DMPA [Figure 4(a)], the sample MM2 without magnification [Figure 4(b)], and magnification of the quaternary carbon region [Fig-

ure 4(c)]. In the ^{13}C -NMR spectra of the sample DMPA, a signal at 17.26 ppm appeared; this was due to the carbons of $-\text{CH}_3$. The signal at 49.75 ppm was attributed to the carbons of $-\text{CH}_2\text{OH}$, and the signal at 176.76 ppm corresponded to carbon of $-\text{COOH}$ groups.

Between 0 and 40 ppm, different signals [Figure 4(b)] appeared; these were due to the carbons of CH_3- (ca. 15 ppm), CH_3-CH_2- (23.12 ppm), $-\text{CH}_2\text{COO}-$ (27.2 ppm), $\text{CH}_3-(\text{CH}_2)_2-$ (30.14 ppm), and $-\text{CH}_2\text{COOR}$ (34.72 ppm). Between 40 and 50 ppm [Figure 4(c)], the signals of lowest intensity of

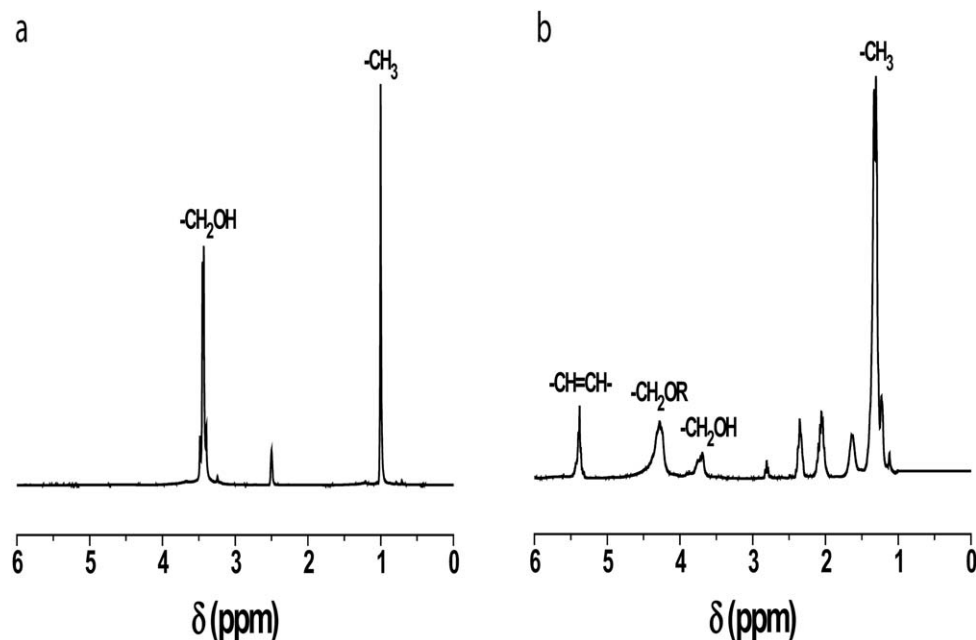


Figure 3. ^1H -NMR spectra of (a) DMPA and (b) MM2.

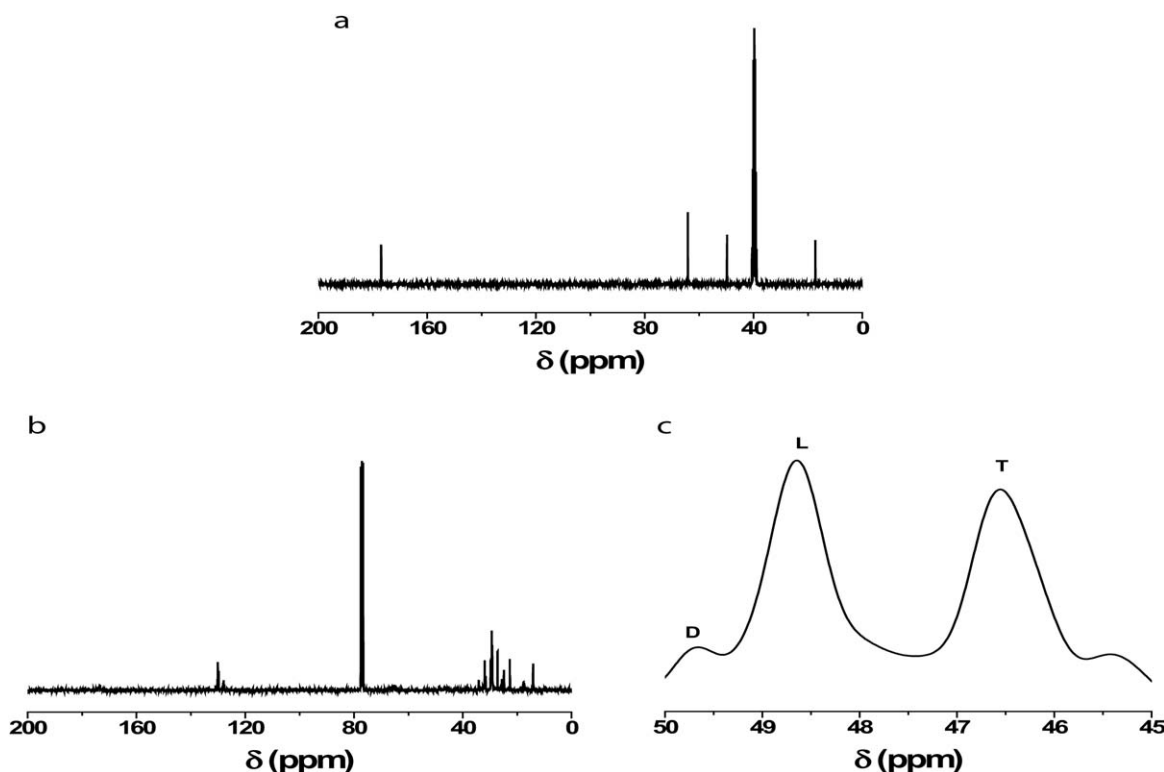


Figure 4. ^{13}C -NMR spectra of (a) DMPA, (b) sample MM2 without magnification, and (c) sample MM2 with magnification of the quaternary carbon region.

quaternary carbons were observed; these corresponded to dendritic units (D), linear units (L), and terminal units (T). The presence of these signals were an indication that during the synthesis the reaction between the DMPA units was carried out. The signal at approximately 80 ppm [Figure 4(b)] was due to the solvent (chloroform). The signals at 130.12 ppm [Figure 4(b)] corresponded to the carbons of $-\text{HC}=\text{CH}-$ bonds (fatty acids), and at 176.76 ppm, a signal due to carbons of $-\text{COOH}$ groups appeared. This signal's intensity decreased with respect to the same signal, which appeared in the DMPA spectrum; this was due to the reaction between the acid and OH groups of DMPA.

The presence of the signal of the carbons of $-\text{CH}=\text{CH}-$ was evidence that the fatty acid reacted with the OH groups of the DMPA or its dimer.

Electrospray Ionization/Mass Spectrometry Analysis

Figure 5 exhibits the mass spectra of the MMs. The molecular weight of the DMPA was 134 g/mol. The molar mass of the acyclic macromolecules (M_1) and the molar mass of the cyclic macromolecules (M_2) were determined with the following equations:^{17,18}

$$M_1 = X(M_{\text{DMPA}} - M_{\text{water}}) + M_{\text{water}} \quad (2)$$

$$M_2 = X(M_{\text{DMPA}} - M_{\text{water}}) \quad (3)$$

where X , M_{DMPA} , and M_{water} are the DMPA unit number in the macromolecule, DMPA molar mass, and water molar mass, respectively. The intense peaks at $m/z = 116$ at the same distance between two peaks corresponded to the molecular ions of

acyclic species of DMPA repetitive units ($m/z = 134, 249, 365, 481, 597, 713, 829, 945, 1051$).^{1,17}

All of the samples exhibited a peak at $m/z = 134.1$ ($X = 1$); this peak was due to DMPA. The samples MM1 [Figure 5(a)], MM2 [Figure 5(b)], and MM3 [Figure 5(c)] presented peaks at $m/z = 249$ and 365 ; these corresponded to acyclic species with two and three repetitive units of DMPA, respectively. This was an indication that DMPA was homopolymerized. In all of the spectra, a peak appeared at an m/z value of around 280; this was possibly due to the fatty acids because the molecular weight of the components of TOFA were as follows: 282.46 g/mol (oleic acid), 280.45 g/mol (linoleic acid), and 278.43 g/mol (linolenic acid). The MM1 [Figure 5(a)] and MM2 [Figure 5(b)] samples showed a high number of molecular fragments with respect to MM3 [Figure 5(c)] and MM4 [Figure 5(d)]. This behavior possibly occurred when the DMPA amount was high (MM1 and MM2). The possibility of the compound formation with several DMPA units, therefore, increased. In all cases, the molecular weight of the MM was greater than DMPA. This was an indication that the formation of MMs occurred.

Figure 6 shows the schematic representations of some compounds that were formed during the synthesis of these materials, which had fatty acids as their structures. The peak around $m/z = 398$ was due to one DMPA unit modified with a mole of fatty acid [Figure 6(a)]. This peak appeared in all of the spectra. The peak at $m/z = 509$ of the samples MM1 [Figure 6(a)], MM2 [Figure 6(b)] and MM3 [Figure 6(c)], is due to one molecule of DMPA that reacted through one of the OH groups, with one fatty acid molecule and another DMPA [Figure 6(b)].

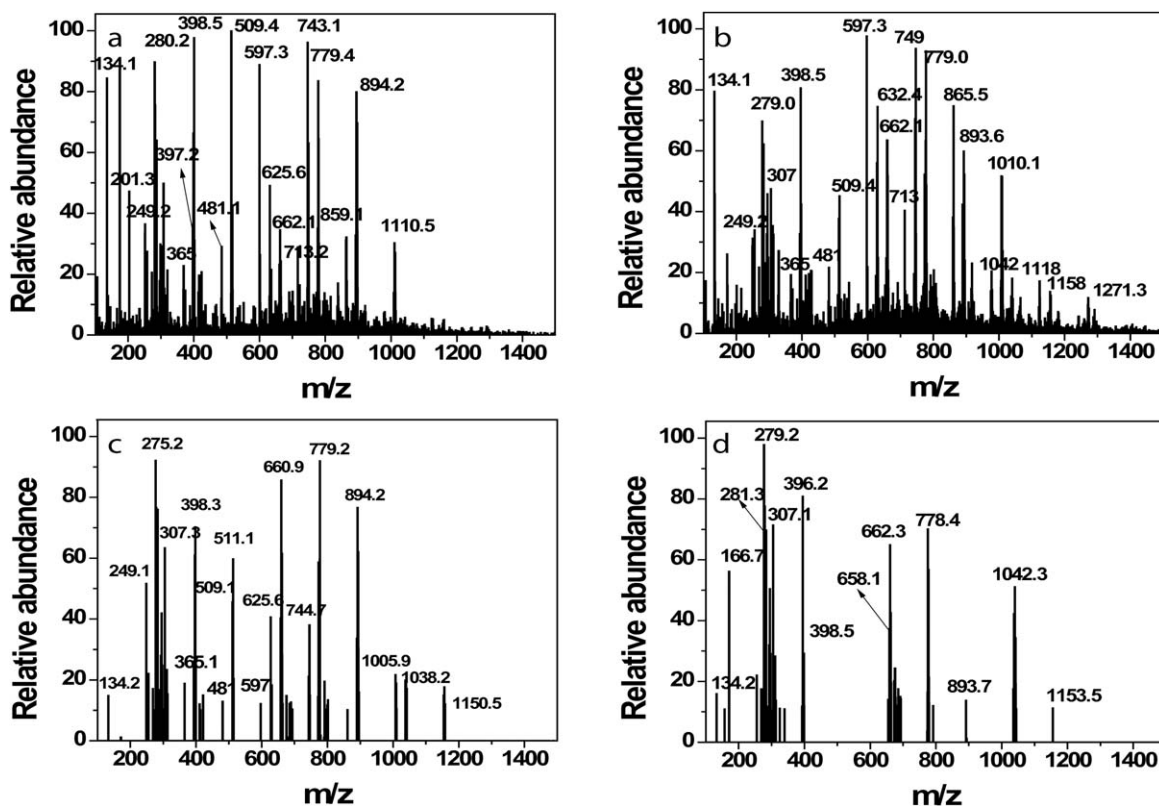


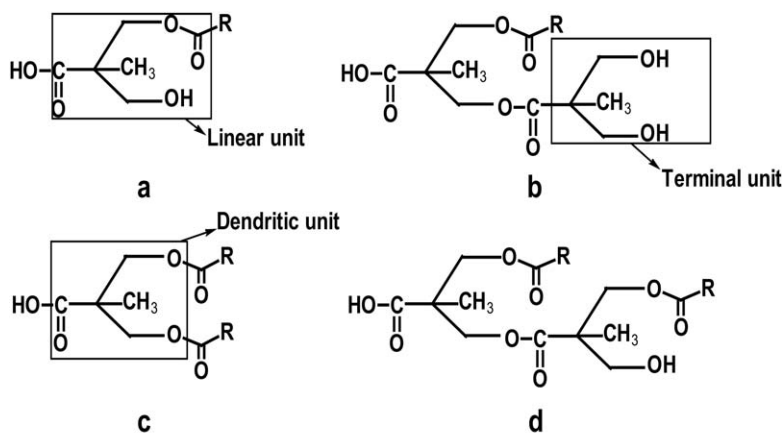
Figure 5. Mass spectra of the MMs: (a) MM1, (b) MM2, (c) MM3, and (d) MM4.

The peak around $m/z=662$ was attributed to the reaction between 1 mol of DMPA and 2 mol of fatty acids [Figure 6(c)]. The peaks at $m/z=778$ and 779 corresponded to the previous structure, which appeared in Figure 5(b) modified with 1 mol of fatty acid [Figure 6(d)]. At values higher than $m/z=780$, other peaks become visible; these were due to the formation of species with high molecular weights containing molecules of fatty acids. Furthermore, we observed that during the synthesis, various structures were formed, and the presence of free DMPA

decreased with the amount of TOFA. This was in accordance with the obtained AV. The mass spectrometry results agreed with the obtained ^{13}C -NMR results because the formation of structures with D, L, and T were observed.

UV Spectroscopy

Figure 7 presents the results of this analysis. At 291 nm, an absorption appeared that was attributed to —C=C— bonds. This increased with the content of TOFA used in the synthesis.



R: Aliphatic chain of fatty acids

Figure 6. (a) DMPA molecule modified with a mole of fatty acid, (b) molecule of DMPA that reacted with one fatty acid molecule and another of DMPA, (c) 1 DMPA molecule modified with two fatty acid molecules, and (d) molecule formed in panel b modified with a fatty acid molecule.

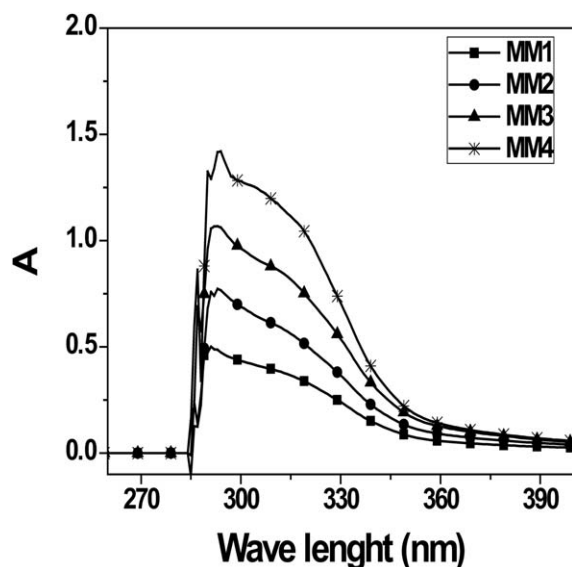


Figure 7. UV spectra of the MMs.

This results was expected because the $-\text{CH}=\text{CH}-$ bond number also increased. These results were consistent with those obtained by IR analysis.

Rheological Analysis

The viscosity of the MMs decreased with the amount of TOFA used on the synthesis (Figure 8). The viscosity decreased with content of TOFA. The viscosity values of the MMs at a 100-s^{-1} shear rate were as follows: MM1, 2.39 Pa.s; MM2, 0.73 Pa.s; MM3, 0.11 Pa.s, and MM4, 0.039 Pa.s.

The behavior of these materials was mainly Newtonian, but only sample MM1 exhibited a reduction in the viscosity at a 514-s^{-1} shear rate. This was due possibly to a higher reduction of interac-

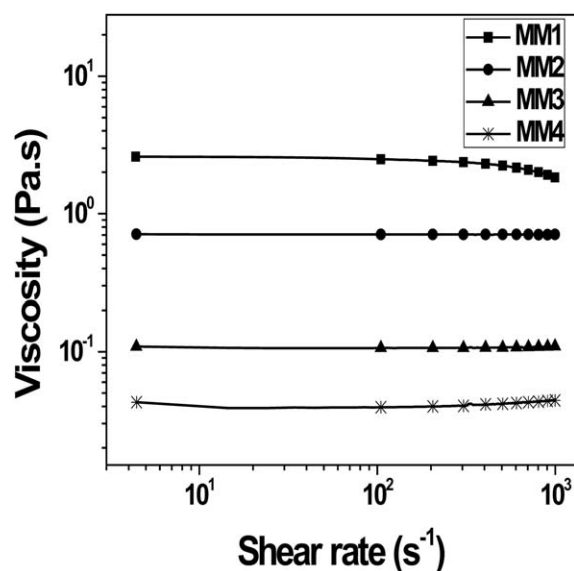


Figure 8. Viscosity versus the shear rate for the MMs.

tions between the OH groups because this sample presented a lower modification degree of DMPA. The same rheological behavior has been observed to hyperbranched alkylid resins.^{7,19}

Thermal Analysis

Figure 9 presents the thermal stability of the MMs. Figure 9(a) exhibits the behavior of weight loss with the temperature, and Figure 9(b) shows the derivate weight with the temperature. The thermal stability of the MMs was higher than those of TOFA and DMPA (Table III), and this means that the incorporation of TOFA on DMPA improved the thermal stability. The same behavior was observed for hyperbranched poly(ester polyol) modified with castor and linseed fatty acid.¹⁹ We observed that around 220°C [Figure 9(a,b)], weight loss occurred. This

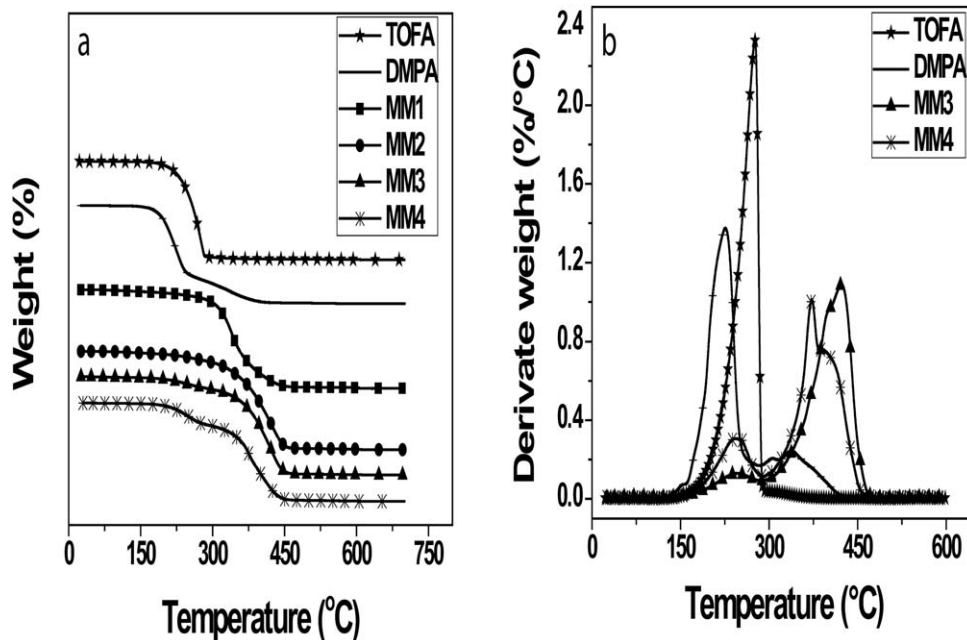


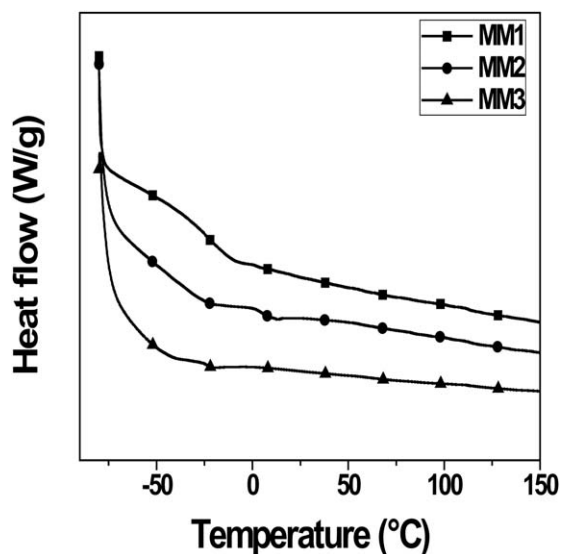
Figure 9. Thermogravimetric analysis of the samples: (a) weight versus temperature and (b) derivate weight versus temperature.

Table III. T_d and T_g Values of the Samples

Sample	T_d (°C)	T_g (°C)
TOFA	276	—
DMPA	226	8
MM1	340	-24
MM2	425	-52
MM3	418	-68
MM4	377	—

weight loss was due to TOFA because T_d of TOFA was the same as that of the first weight loss, which appeared for the MMs [Figure 9(b)]. This same weight loss was observed for hyperbranched alkyd resins obtained from TOFA.⁸

Figure 10 shows the differential scanning calorimetry thermograms of the MMs. The glass-transition temperature (T_g) of the MMs was lower than that of DMPA (Table III). This indicated that the MMs were more amorphous than DMPA. An important aspect to take into account was that TOFA acted as a plasticizing agent (and reduced the T_g value)²⁰ and this reaction was random (it was demonstrated with the results obtained by mass spectrometry). Various structures were obtained, as is shown in Figure 5. In the synthesis of hyperbranched alkyd resins, we observed that with the content of TOFA, the T_g value decreased.⁸ Between the MMs, the MM1 sample exhibited a highest T_g value (Table III). This was due to this sample that less TOFA was obtained. The T_g value of the MMs increased with the amount of TOFA only for the samples MM1, MM2, and MM3. The sample MM4 did not exhibit a T_g because this was lower than -80°C , which was out of the range of temperature for the analysis. The samples MM2 and MM3 exhibited T_g 's with a low inflection at 8 and -24°C , respectively. It was possibly due to the formation of others structures, which were independent of the proportions of DMPA and TOFA used because the samples obtained with a high amount of DMPA (MM1) and TOFA (MM4) did not present this behavior.

**Figure 10.** Differential scanning calorimetry thermograms of the MMs.**Table IV.** Gloss, Adhesion, and Flexibility of the MMs

MM	Gloss (85°)	Adherence (%)	Flexibility
MM1	102.4	4B	Pass
MM2	108.3	4B	Pass
MM3	115.5	4B	Pass
MM4	120.7	5B	Pass

Film Properties

Table IV shows the results of the gloss, adhesion, and flexibility of the MMs. The gloss value of the MMs increased with the amount of TOFA used in the synthesis. These results were possibly due to the branched structure of these materials. Furthermore, TOFA had a higher gloss compared to DMPA. The same behavior was found in a previous study of hyperbranched alkyd resins.¹⁰ Furthermore, this result indicated that with the content of TOFA, the surface of the MM films was smoother because rougher films reduced the gloss.²¹ All of the MMs presented high gloss because of the obtained values that were higher than 70 when measured at an incidence angle of 60° .¹⁹ The sample MM4 presented the best adhesion. The adhesion of the others MMs was acceptable. The flexibility of the MMs was good because none of the films suffered rupture. This behavior was expected because these materials are amorphous.

CONCLUSIONS

This study made an important contribution to the synthesis of biobased MMs, which can be an alternatively used as diluent reactives to coating and plasticizers because these materials present a low viscosity and good thermal stability. The OHV of the MMs decreased with amount of TOFA but the absorption attributed to $-\text{C}=\text{C}-$ bonds was augmented. The mass spectra showed that during the synthesis, the formation of different structures of TOFA-DMPA and DMPA repetitive units with grafted fatty acids took place.

The rheological behavior of the MMs was mainly Newtonian in the range of shear rate studied. The thermal stability of the MMs was higher than those of TOFA and DMPA.

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REFERENCES

- Murillo, E. A.; Vallejo, P. P.; López, B. L. *e-Polymers* **2010**, *1*, 1347.
- López, B. L.; Murillo, E.; Hess, M. *e-Polymers* **2004**, *4*, 288.
- López, B. L.; Zapata, R.; Murillo, E.; Hess, M. *Mater. Res. Innovat.* **2005**, *9*, 59.
- Kim, J.; Lee, J.; Son, Y. *Mater. Lett.* **2014**, *126*, 43.
- Guzmán, M.; Murillo, E. A. *Polímeros* **2014**, *24*, 162.
- Murillo, E. A.; Vallejo, P. P.; Sierra, L.; López, B. L. *J. Appl. Polym. Sci.* **2009**, *112*, 200.

7. Murillo, E. A.; Cardona, A.; López, B. L. *J. Appl. Polym. Sci.* **2010**, *119*, 929.
8. Murillo, E. A.; Vallejo, P. P.; López, B. L. *J. Appl. Polym. Sci.* **2011**, *120*, 3151.
9. Simon, S. L. *Encyclopedia of Polymer Science and Technology*; John Wiley & Sons Inc., **2001**; Vol. 1, p 1.
10. Murillo, E. A.; Vallejo, P. P.; López, B. L. *Prog. Org. Coat.* **2010**, *69*, 235.
11. Murillo, E. A.; López, B. L.; Brostow, W. *J. Appl. Polym. Sci.* **2011**, *72*, 3591.
12. Murillo, E. A.; López, B. L. *Prog. Org. Coat.* **2011**, *74*, 731.
13. Murillo, E. A.; Lopez, B. L.; Brostow, W. *Prog. Org. Coat.* **2011**, *72*, 292.
14. Mckee, M. G. *Prog. Polym. Sci.* **2005**, *30*, 507.
15. Quintero, C.; Mendon, S. K.; Smith, O. W.; Thames, S. F. *Prog. Org. Coat.* **2006**, *57*, 195.
16. Akbas, T.; Beker, U. G.; Guner, F. S.; Erciyes, A. T.; Yagci, Y. *J. Appl. Sci.* **2003**, *88*, 2373.
17. Žagar, E.; Žigon, M.; Podzimek, S. *Polymer* **2006**, *47*, 166.
18. Chikh, L.; Tessier, M.; Fradet, A. *Polymer* **2007**, *48*, 1884.
19. Bat, E.; Gündüz, G.; Kısakürek, D.; Akhmedov, M. *Prog. Org. Coat.* **2006**, *55*, 330.
20. Kalogeras, I. M.; Hagg Lobland, H. E. *J. Mater. Ed.* **2012**, *34*, 69.
21. Trezza, T. A.; Krochta, J. M. *J. Appl. Sci.* **2001**, *79*, 2221.