

Hydroxymethylation and Polymerization of Plant Oil Triglycerides

Tarik Eren, Selim H. Küsefoğlu

Department of Chemistry and Polymer Research Center, Boğaziçi University, Bebek, Istanbul, 80815, Turkey

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ABSTRACT: The ene reaction between plant oil triglycerides (such as soybean and sunflower oils) and paraformaldehyde was used to introduce a homoallylic hydroxyl functionality on the triglyceride. Paraformaldehyde and triglyceride were reacted in the presence of a Lewis acid catalyst, ethylaluminum dichloride, and hydroxymethyl derivatives were obtained at yields of 42 and 55% for sunflower oil and soybean oil, respectively. In the next step, hydroxymethyl products were reacted with maleic anhydride at 100°C to produce the maleate half esters. The average number of maleate groups per triglycerides was found to be 1.7 for soybean oil and 1.3 for sunflower oil. In the final step, the free-radical-initiated copolymerization of the maleinized

triglycerides with styrene produced rigid polymers. Characterization of new monomers and polymers was done by ¹H-NMR, ¹³C-NMR, and infrared and mass spectrometries. The swelling behavior of the crosslinked network polymers was determined in different solvents. The glass-transition temperature of the cured resin was also determined by differential scanning calorimetry to be 40°C for soybean-based polymer and 30°C for sunflower-based polymer. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 4037–4046, 2004

Key words: ene reaction; renewable resources; biodegradable; esterification; copolymerization

INTRODUCTION

Synthesis of new mechanically rigid thermoset resins from plant oil triglycerides is attractive for both economical and social reasons. To use a plant oil triglyceride as a monomer it must first be suitably functionalized. Continuing with our efforts to functionalize triglycerides^{1–3} we report here the hydroxymethylation, followed by maleinization, of soy oil and sunflower oil. The resulting maleate half esters are then copolymerized with styrene by free-radical initiation to yield a thermoset resin comparable to unsaturated polyester resins, containing about 50% plant oil. The chemistry is shown in Figure 1.

The reaction between an alkene having an allylic hydrogen (an “ene”) and a compound containing an electron-deficient carbonyl compound or multiple bond (enophile) to form a new bond by a six-electron pericyclic process is called the ene reaction.⁴ The ene reaction of formaldehyde with alkenes containing allylic hydrogen is a good method of producing primary homoallylic alcohols. This reaction can be applied to unsaturated plant oil triglycerides to obtain their hydroxymethyl derivatives.

In plant oils, fatty acids are found as triesters of glycerol called triglycerides and their structures are shown in Figure 2.

Fatty acids are long chain alkyl monocarboxylic acids and they can be saturated or unsaturated. Short-chain acids (C₄–C₁₀) are present in milk fats, the medium-chain acids (C₁₂–C₂₄) are present in plant seed fats and animal fats, and the long-chain acids (up to C₃₈) are present in waxes. These fatty acids can have no double bonds, one double bond, or a number of methylene-interrupted double bonds, triple bonds, or conjugated double bonds.⁵ Double bonds naturally occur as the *cis* isomer.

Table I shows the fatty acid contents of some important seed oils, including soybean oil and high oleic sunflower oil, which were used in our study.

Thermal reactions of paraformaldehyde with acyclic and cyclic olefins were discussed by Blomquist et al.^{6,7} and the suggested ene mechanism can be seen in Figure 3.

Snider and Phillips⁸ studied the ene reaction of aldehydes (such as formaldehyde) with nonnucleophilic alkenes in the presence of a Lewis catalyst, such as ethylaluminum dichloride. Lewis acid-catalyzed ene reactions can proceed by a stepwise mechanism with a zwitterionic intermediate or a concerted mechanism with a polar transition state. It was also proven that the energetics of the two mechanisms were similar and that the lower energy process varied as a function of the ene, enophile, and the catalyst.⁹ It is worth noting that the ene reaction does not consume triglyc-

Correspondence to: S. Küsefoğlu (kusef@boun.edu.tr).

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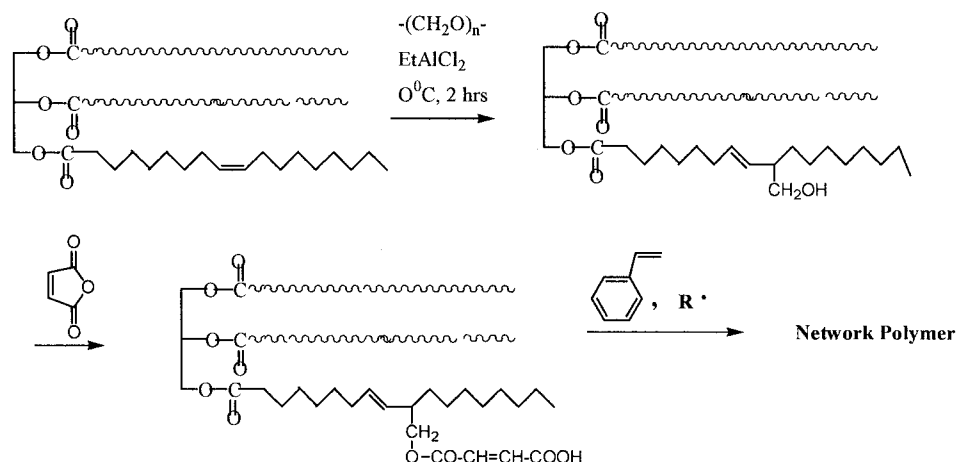


Figure 1 Synthesis and polymerization of maleate half ester-based plant oil triglycerides.

eride unsaturation, but rather causes only the double bond to shift to a new position. The migrating double bond ends up in the *trans*-geometry and is available for free-radical reactions during the polymerization step of our synthesis.

Alkylaluminum chloride-catalyzed ene reactions of formaldehyde with fatty acids and their methyl esters were studied by Metzger and Biermann.¹⁰ In this study ethylaluminum dichloride was used as a catalyst and gave good yields in the ene addition of formaldehyde to methyl 10-undecenoate (51%) and methyl oleate (63%). Paton et al.¹¹ studied the hydroxymethylation of jojoba oil, which is mostly fatty alcohol esters of fatty acids, in the presence of EtAlCl_2 , by using a 2.2 : 1M ratio of formaldehyde to jojoba oil. They isolated 1 : 1 adducts (32%) and 2 : 1 adducts (52%).

We report here the reaction of soybean oil and high oleic sunflower oil with paraformaldehyde in the presence of EtAlCl_2 to introduce hydroxymethyl groups at the allyl positions of the triglyceride molecules. The resulting alcohols were reacted with maleic anhydride to produce maleate half esters, which were then polymerized and copolymerized free radically.

EXPERIMENTAL

Reagents and instruments

The soybean oil (Marsa) used was food grade and was used without further purification. High oleic sun-

flower oil, methyl oleate (83% methyl oleate, 7% methyl linoleate), and methyl linoleate (64% methyl linoleate, 24% methyl oleate) were obtained from Henkel KgaA. EtAlCl_2 (Schering AG), paraformaldehyde (Merck, Darmstadt, Germany), and maleic anhydride (Fluka, Buchs, Switzerland) were used without purification. CDCl_3 (Aldrich, Milwaukee, WI) was used for $^1\text{H-NMR}$ analysis. The radical initiator methyl ethyl ketone peroxide (MEKP; Lucidol) was also used without further purification. Benzoyl peroxide (BPO) was obtained from Fischer and recrystallized from methanol before use.

The infrared (IR) analysis was performed on a Perkin-Elmer 1600FTIR spectrometer using NaCl windows. $^1\text{H-}$ and $^{13}\text{C-NMR}$ spectra were recorded on Varian 400-MHz NMR (Varian Associates, Palo Alto, CA) operating at a frequency of 399.986 MHz for proton and 100.587 MHz for carbon. Spectra were reported as ppm (δ) with TMS as internal standard. Mass spectra were obtained using a Micromass Zab-spec and Finnegan MAT 212 mass spectrometers. All differential scanning calorimetry (DSC) spectra were obtained on a TA Instruments Universal V2.5H (TA Instruments, New Castle, DE). Analyses were conducted under nitrogen gas at a gas flow rate of 10 mL/min and at a heating rate of $10^\circ\text{C}/\text{min}$. The sample weights used were about 10 mg. Analytical GC was performed on a Carlo Erba Fractovap 2150 with free-induction delay (FID; DB1-column, 13 m).

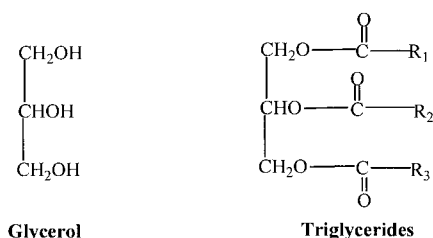


Figure 2 Structure of glycerol and triglycerides.

Hydroxymethylation of triglycerides (HMSU and HMSO)

In a typical reaction, triglyceride (8.8 g, ~ 10 mmol; assuming MW of 884 g/mol for sunflower oil and 878 g/mol for soybean oil triglyceride) and paraformaldehyde (2.7 g, 90 mmol) were mixed in CH_2Cl_2 under N_2 atmosphere for 5 min at 0°C . Then EtAlCl_2 (1M in hexane, 70 mL, 70 mmol) was added dropwise to the

TABLE I
Fatty Acids Content (%) in the Seed Oil of Common Oil Crops

Type	12:0[a]	14:0	16:0	18:0	18:1	18:2	18:3	20:1	22:1	Others
Soybean	—	—	11	4	23	54	8	—	—	—
Rapeseed	—	—	3	1	11	12	9	8	52	4
Sunflower ^a	—	—	7	5	19	68	—	—	—	1
Linseed	—	—	6	4	18	14	58	—	—	—
Olive	—	—	14	2	64	16	2	—	—	2

^a New sunflower oil: C₁₆ = 4.2%; C₁₈ = 4.3%; C_{18:1} = 82.3%; C_{18:2} = 7.7%; C₂₀ = 0.3%; C_{20:1} = 0.3%; C₂₂ = 0.7%.

reaction mixture. The samples were stirred 2 h at 0°C. The reaction was then quenched with 100 mL H₂O and 40 mL diethyl ether. Alumina precipitates were dissolved by addition of 5 mL 10% HCl. The organic layer was separated, dried (Na₂SO₄), and evaporated. Weights of sunflower oil and soybean oil triglyceride products were 9.27 and 9.14 g, respectively, and the products were yellow colored oils at room temperature (RT).

Maleinization of HMSU and HMSO

In a typical reaction, 2.15 g (~ 2.3 mmol) hydroxymethyl adduct of sunflower oil and 0.24 g (2.5 mmol) maleic anhydride were mixed in a three-neck flask and purged with N₂. The mixture was magnetically stirred at 100°C for 2 h. The color of the solution changed from yellow to orange. Maleic anhydride sublimation on the walls of the flask was observed throughout the reaction. At the end of this period, 40 mL of Et₂O was added to the mixture and the unreacted maleic anhydride was removed by extraction with 100 mL aq. HCl (10%). The organic layer was removed, dried (Na₂SO₄), and evaporated. A red-orange viscous liquid (2.35 g) was obtained. Spectral analysis indicated 100% conversion.

Copolymerization of HMSUM and HMSOM with styrene

Polymerizations of maleinated sunflower oil (HMSUM) and maleinated soybean oil (HMSOM) were run in closed vials. Each adduct was mixed with about 35% of its own weight of styrene to gave clear solu-

tions of 400 cps viscosity. MEKP (2%) and cobalt naphthenate (2%) initiator system was added and polymerization was carried out for 48 h at RT. Treatment with excess chloroform swelled and fragmented the sample but did not extract any unreacted monomers or oligomers.

Radical homopolymerization of the HMSUM and HMSOM

Homopolymerizations of the maleinized sunflower oil (HMSUM) and maleinized soybean oil (HMSOM) were also carried out in the presence of MEKP and BPO as radical initiators. In a sample procedure, 0.32 g maleinized triglyceride was mixed with 0.013 g MEKP and 0.011 g cobalt naphthenate and cured at RT. Polymerization was observed with a slow viscosity increase. Infrared (IR) analysis showed a decrease in maleate peak intensities, corresponding to 30% conversion. Increasing initiator concentration did not lead to a solid polymer.

Swelling tests

The swelling behaviors of the polymers were tested in CCl₄ by using a traveling microscope (Geartner 7109-46). Rectangular pieces (dimensions ~ 2 × 5 × 10 mm) were cut from the polymer samples. The samples were placed in a closed container containing the solvent CCl₄. The length of the samples was measured at certain time intervals. The procedure was continued until the solvent uptake ceased.

Water sorption was determined by soaking a polymer sample for 24 h in distilled water at RT. Water sorption (WS) was calculated as the relative sample weight increase, expressed as a percentage, according to eq. (1):

$$WS (\%) = \frac{m_2 - m_1}{m_1} \times 100$$

where m_1 is the initial mass (weight) of dry polymer and m_2 is the mass (weight) of swollen polymer.

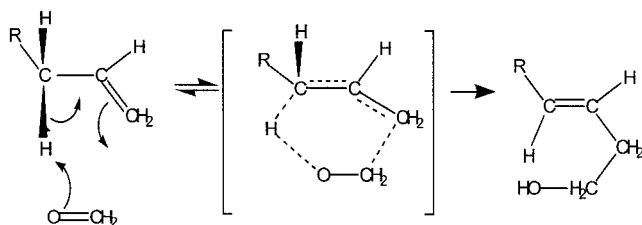


Figure 3 Mechanism of thermal addition of paraformaldehyde to olefins.

RESULTS AND DISCUSSION

Hydroxymethylation of soybean and sunflower oils

Table I shows that soybean oil contains 50–55% linoleic and 30% oleic acids and high oleic sunflower oil contains 84% oleic acids in their structures. Therefore as a model compound we decided to examine the reactivity of the methyl oleate and methyl linoleate with paraformaldehyde by the ene reaction pathway. The resulting products would also provide ene adducts that would be useful as models to identify the structure of hydroxymethyl triglycerides. Methyl oleate and methyl linoleate were reacted with paraformaldehyde in the presence of ethylaluminum dichloride by the procedure described by Metzger and Biermann.¹⁰ From this reaction a regioisomeric mixture of ene adducts, in a combined yield of 60% for methyl oleate and 62% for methyl linoleate, was obtained. The products were identified by GC, GC–mass spectrometry (MS), ¹H-NMR, ¹³C-NMR, and IR techniques and their structures were found to be in agreement with the reported results.

Different conditions were used to achieve higher yields for the hydroxymethylation of triglycerides. For one equivalent of triglyceride molecule, 9 equivalent paraformaldehyde and 7 equivalent of EtAlCl₂ were used to achieve high yields. Ene reactions require a stoichiometric amount of Lewis acid catalysts and a second equivalent of EtAlCl₂ is required especially where the alkene also contains ester, acid, or hydroxyl functionality in its structure.⁹

Soybean oil and high oleic sunflower oil have an average number of 4.2 and 2.7 double bonds per molecule, respectively, as determined by their iodine numbers. Thus soybean oil has more allylic positions per triglyceride to react with formaldehyde compared to high oleic sunflower oil. By comparing the intensities of the CH₂-α to the carbonyl and allylic hydroxymethyl NMR signal intensities in the final products, the yields of hydroxymethylated sunflower oil (HMSU) and of hydroxymethylated soybean oil (HMSO) were found to be 42 and 55 mol %, respectively. These correspond to 1.3 and 1.7 hydroxymethyl groups, on average, per triglyceride for sunflower and soybean oils, respectively. Yields were not very high because molecular packing of the triglyceride molecules prevented the attack of the formaldehyde–Lewis acid complex.

The IR spectra of hydroxymethylated sunflower oil (HMSU) are shown in Figure 4(a). Two new peaks may be observed in the HMSU spectrum: at 3468 cm⁻¹, attributed to O–H stretching vibration of the hydroxyl groups; and at 968 cm⁻¹, attributed to the *trans* alkenes produced by the ene reaction pathway.

¹H-NMR data of HMSU are seen in Figure 5(a) where the *trans* double bond signals may be observed at 5.10 and 5.50 ppm. Characteristic peaks for CH₂OH

are observed at 3.3 and 3.4 ppm. Allylic hydrogen (–CH=CH–CH) gives a peak at 2.1 ppm and the new allylic methylene signal of *trans* double bond is not observed because it is overlapped with the allylic signal of unreacted alkenes. Coupling of the hydrogens that belong to the *trans* double bond is at 15.3 Hz, thus confirming the *trans*-geometry for the alkene. There are also characteristic peaks for the hydroxymethylene group in the ¹³C-NMR spectrum, shown in Figure 6(a). *trans* Double bond isomers are seen at 133.4, 133.05, 131.4, and 131.1 ppm. Other characteristic carbons are at 65.8 ppm (–CH₂–OH), 45.7 ppm (–CH–CH₂OH), and 32.4, 32.5 ppm belonging to the allylic carbons (–CH=CH_{*trans*}–CH₂–). The doubling of some peaks in the ¹³C-NMR spectrum shows the formation of regioisomers. ¹H- and ¹³C-NMR spectra of the hydroxymethyl soybean oil were more complex than that of hydroxymethyl sunflower oil (high oleic) because formaldehyde has a greater number of sites to attack. The hydroxymethyl carbons (–CH₂–OH) are observed at 65.4, 65.6, and 65.8 ppm and allylic carbon of the type (–CH–CH₂OH) are observed at 45.5, 45.6, and 45.9 ppm. These suggested to us that at least three types of regioisomers were produced.

Soybean oil has 55% linoleic acid and methyl linoleate was used as a model compound for the ene reaction of soybean oil. Methyl linoleate, used in this reaction, contains approximately 24% methyl oleate and 64% methyl linoleate. The expected ene adducts of methyl linoleate are given in Figure 7.

We expected to find some conjugated isomers in the ene adducts of methyl linoleate or soybean oil. Schäfer et al.¹² studied the conjugation of methyl linoleate and assigned the NMR signals for conjugated double bond as δ 5.87–5.94 ppm (m, 3J = 11.0 Hz, 1H, =CHCH = *cis*) and 6.21–6.31 ppm (m, 3J = 15.0 Hz, 1H, =CHCH = *trans*). The ¹H-NMR spectra of ene reaction products of both soybean oil and methyl linoleate with paraformaldehyde synthesized in our work showed that there were no signals for conjugation. If doubly allylic hydrogens were reacted, the conjugation should be observed. We conclude that structures **c** and **a** are favored over structure **b**, as shown in Figure 7. In methyl linoleate there are four singly allylic and two doubly allylic hydrogens; therefore, the probability of attack of paraformaldehyde to the singly allylic hydrogen is higher. We conclude that the ene reaction occurs at the singly allylic hydrogen and is kinetically controlled.

Triglycerides have a complex mixture of fatty acids in their structure. We used high oleic sunflower oil (average molecular weight ~ 884) and hydroxymethyl sunflower oil should show at least mono addition in MS results. The mass spectrum showed the mono-, di-, and triaddition of methylol (–CH₂OH–) products at 914, 944, and 976 *m/e*, respectively. Water elimination [M⁺ – H₂O] from the monoaddition fragment is seen

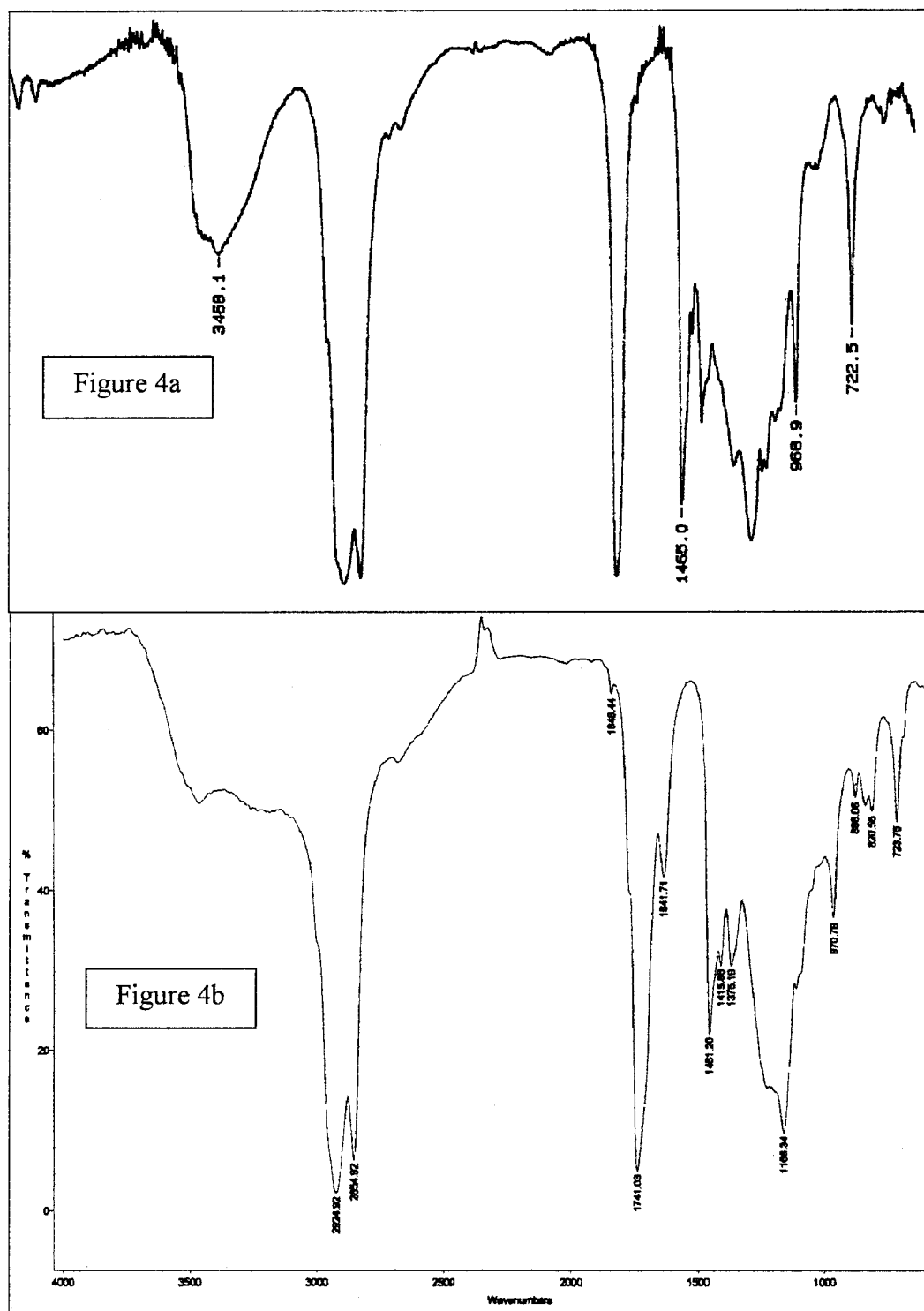


Figure 4 IR spectra of (a) the paraformaldehyde adduct of sunflower oil and (b) maleinization adduct of that product.

at 896 m/e and CH elimination $[(M^+ - H_2O) - CH]$ is observed with elimination of 13 from 896 m/e . The average molecular weight of soybean oil is assumed to be 879 g. The mass spectrum of hydroxymethyl soybean oil showed the monoaddition peak cluster ($-CH_2OH-$) at 909 m/e , and diaddition and triaddition molecular peaks at 939 and 969 m/e , respectively.

Maleinization of the hydroxymethylated soybean and sunflower oils (HMSUM and HMSOM)

Maleic anhydride, like most other anhydrides, undergoes a nucleophilic ring-opening reaction. Reaction with an alcohol leads to a half ester. Siegel and Moran¹³ studied the reaction of lower primary alcohols

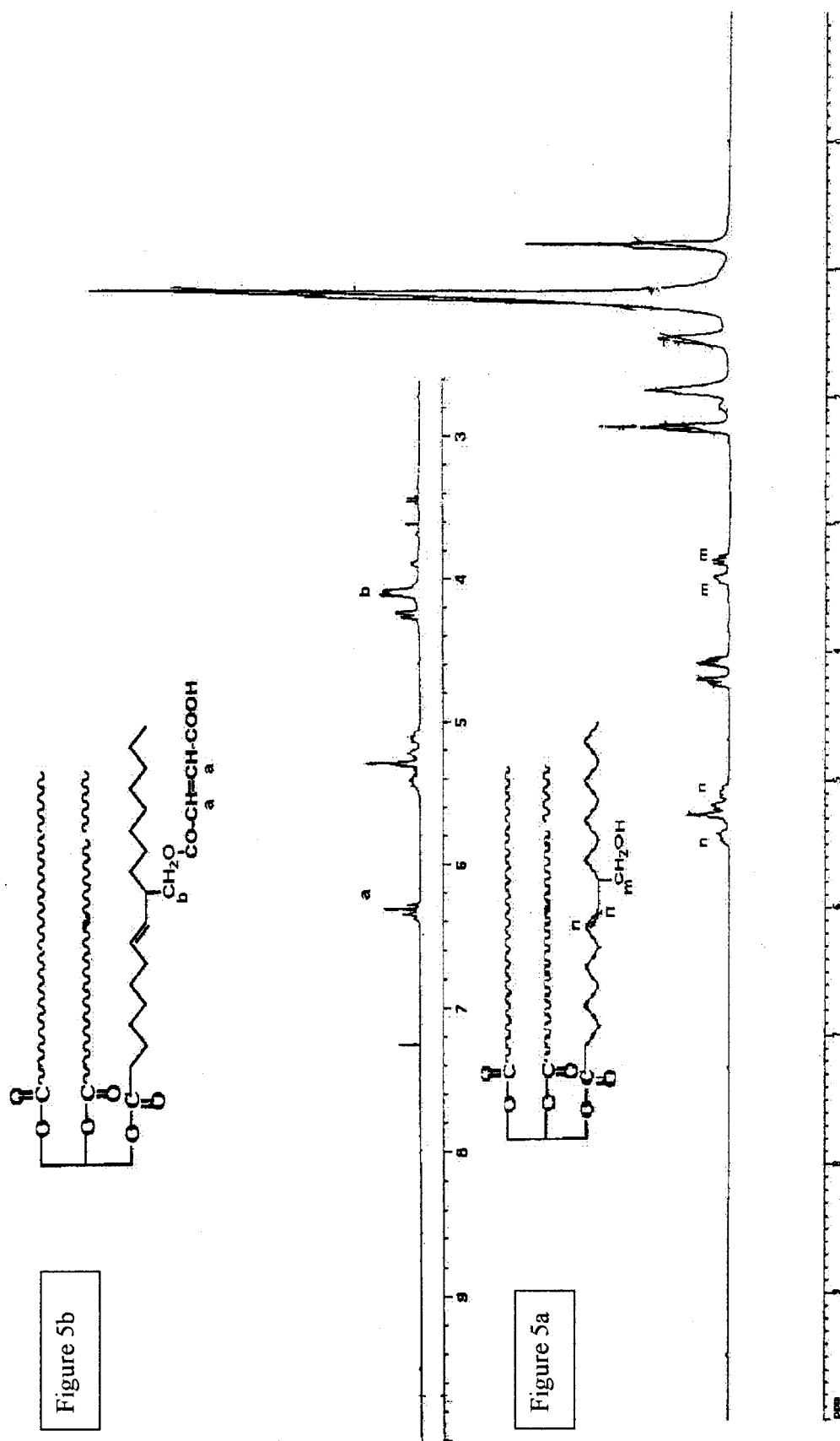


Figure 5 $^1\text{H-NMR}$ spectra of (a) the paraformaldehyde adduct of sunflower oil and (b) maleinized product.

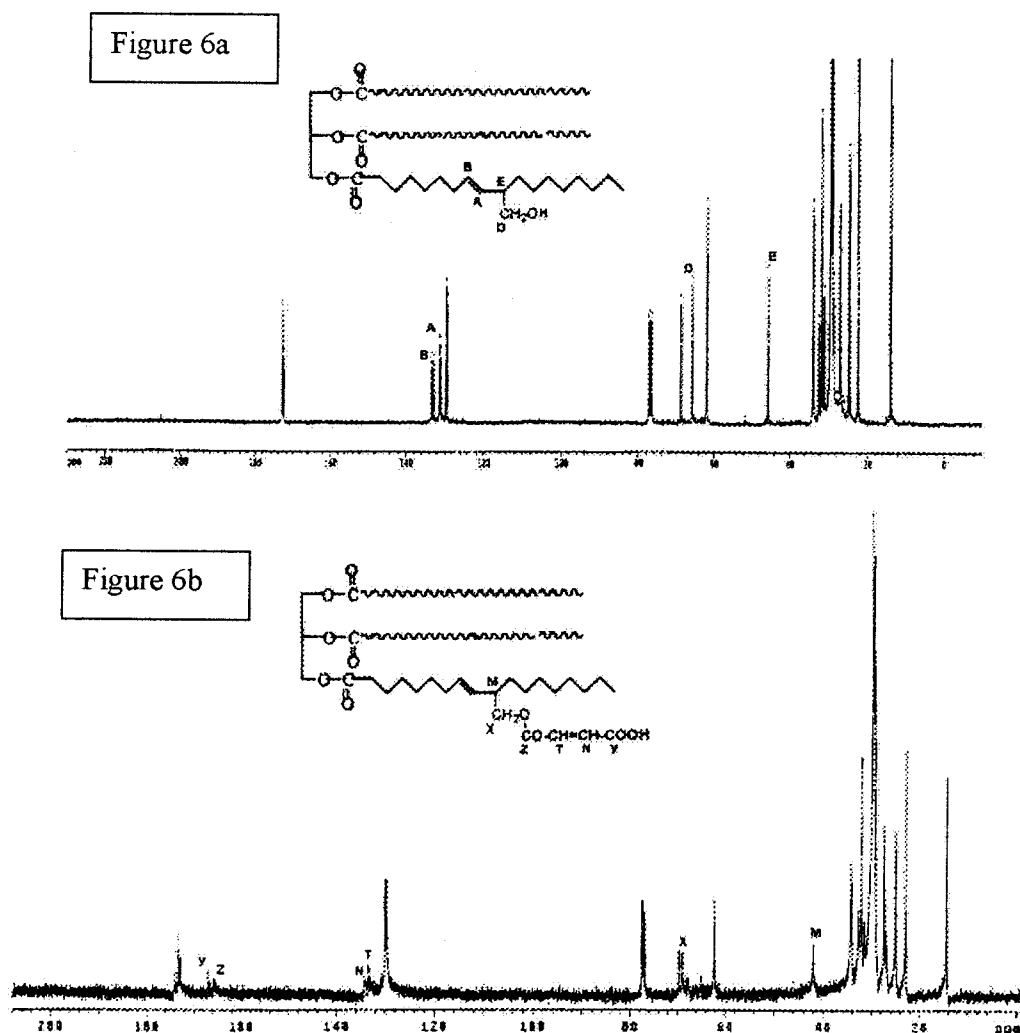


Figure 6 ¹³C-NMR spectra of (a) the paraformaldehyde adduct of sunflower oil and (b) maleinized adduct.

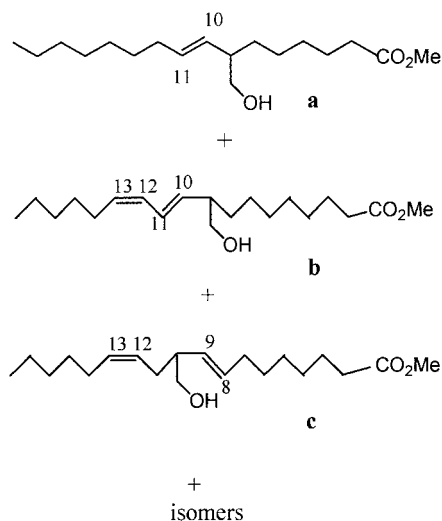


Figure 7 Isomers of hydroxymethyl products of linoleic methyl ester.

and maleic anhydride and reported that the reaction proceeds quantitatively at RT without any catalyst. Friedman and Garti¹⁴ and Can et al.² studied the maleate half esters of monoglycerides in terms of reaction conditions. In our work maleinization of hydroxymethyl triglycerides was carried out without any catalyst at 100°C and gave quantitative yields.

Figure 4(b) shows the IR spectrum of the maleated hydroxymethyl sunflower oil (HMSU). A broad carboxylic OH band may be observed at 2500–3600 cm⁻¹; a low intensity O—H out-of-plane bending vibration of the acid groups appeared at 820 cm⁻¹; C=C stretching of the maleate half ester group may be observed at 1643 cm⁻¹. New ester and acid carbonyl peaks overlapped with the carbonyl of the triglycerides molecules, causing broadening of the signal. New ester stretching may be seen at 1240 cm⁻¹.

NMR spectroscopy provides further clues for the maleinization of hydroxymethyl products of triglycerides. Figure 5(b) shows the respective signals of the

maleated hydroxymethyl product of sunflower oil (HMSUM). Characteristic peaks for CH_2OH at 3.3 and 3.4 ppm disappeared and maleate vinylic protons ($\text{HOOC}-\text{CH}=\text{CH}-\text{COO}-$) may be observed at 6.3 ppm. The methene signals at 4.0 ppm ($\text{HOOC}-\text{CH}=\text{CH}-\text{COO}-\text{CH}_2-$) overlapped with one of the glycerol part of the triglycerides [$-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{O}-$]. Analysis of NMR indicates that, on average, there are 1.3 and 1.7 maleate groups on the sunflower oil and soybean oil triglycerides, respectively.

Figure 6(b) shows the ^{13}C -NMR data of the maleated adduct of hydroxymethyl sunflower oil (HMSUM): 168.1 ppm is the characteristic peak for the ($-\text{C}=\text{C}-\text{COOH}$) and 164.0 ppm is the characteristic peak for the ($-\text{O}-\text{CO}-\text{C}=\text{C}-\text{COOH}$). The hydroxymethyl carbon signal ($-\text{CH}_2-\text{OH}$) at 65.8 ppm for hydroxymethyl sunflower oil disappeared. A new signal for the ($-\text{CH}_2-\text{O}-\text{CO}-\text{C}=\text{C}-$) carbon may be observed at 70.0 ppm. A new signal of the carbon type ($-\text{CH}-\text{CH}_2-\text{O}-\text{CO}-\text{C}=\text{C}-$) may be observed at 42 ppm. Maleate double-bond carbons ($-\text{HC}=\text{CH}-$) were expected to be seen at 132 and 134 ppm but one of them (132 ppm) is not well observed because it overlaps with the *trans* double bonds of the fatty acid.

Mass spectra of the maleinated hydroxy methyl mixtures reveal a multitude of peaks around specific mass number clusters. This is typical behavior of plant oil-based compounds because there are a multitude of different fatty acid esters with different molecular weights and positional isomers in the mixture. Indeed, it was impossible to assign every peak, although peaks attributed to 1, 2, and 3 maleate adducts at 1012, 1141, and 1271 *m/e*, respectively, were seen as prominent peaks. Water elimination was observed at 994 *m/e* [$\text{M}^+ - \text{H}_2\text{O}$]. The molecular fragmentation peak at 914 *m/e* was attributed to [$\text{M}^+ - \text{H}_2\text{O}-\text{C}(\text{O})\text{C}=\text{C}-\text{C}(\text{O})$]. Assignment of the maleated soybean oil mass spectrum peak clusters is given in Table II.

TABLE II
Peak Clusters in the Mass Spectrum of Maleinated Soybean Oil Adduct

Peak	ΔMass	Number of $-\text{CH}_2\text{O}-\text{CO}-\text{C}=\text{C}-\text{COOH}$ (maleate) residues	Number of $-\text{CH}_2\text{OH}$ residues
1036	158	1	1
1066	188	1	2
1096	218	1	3
1136	258	2	0
1166	288	2	1
1190	312	2	2
1288	410	3	1

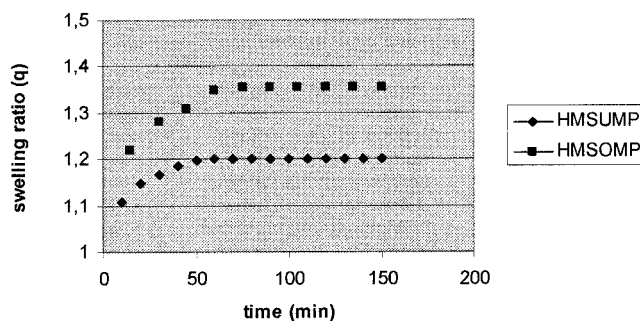


Figure 8 Swelling behaviors of the copolymers of sunflower (HMSUMP) and soybean-based monomers (HMSOMP) with styrene.

Polymerization of the maleated triglycerides

Copolymerizations of HMSUM and HMSOM with styrene were carried out by using MEKP and cobalt naphthenate accelerator. Soybean oil has a higher maleate half ester ratio than that of sunflower oil, so it reached a gelled state more quickly. The liquid solution of the HMSOM and styrene was transformed into a soft rubber and after 1 h, the cured product was a transparent, light green-yellow colored semirigid solid polymer. Meanwhile, the copolymer of HMSUM and styrene gelled in 2 h and the cured product was a soft solid. Unfortunately it was impossible to analyze the polymers with ^1H -NMR, given that the polymers were insoluble in common solvents.

The free-radical-initiated copolymerization of maleinated soybean oil with styrene was also carried out in the presence of BPO at 85°C and in solvent [$(\text{CDCl}_2)_2$] to facilitate NMR analysis. NMR integral analysis of vinyl protons of the solution-polymerized sample shows that 20% of the triglyceride double bonds were also consumed during the polymerization at this higher temperature. Therefore, we conclude that the level of unsaturation of the oil used has an important role in the final properties of the cured product. The IR spectrum shows the disappearance of $\text{C}=\text{C}$ stretching bands, although the complete disappearance of maleate double bonds at 1643 cm^{-1} could not be observed because of the fact that benzene group stretching bands are at the same region. Residual maleate unsaturation in the polymerized sample can be characterized by the small band at 1346 cm^{-1} . This band is still visible in this region, suggesting that still unreacted maleate residues are present in the final polymer. A similar behavior was observed in commercial unsaturated polyesters where at complete cure, about 15% of the maleate unsaturation remains unreacted, whereas all the styrene unsaturation is consumed.

Swelling behavior and insolubility in common solvents verified the crosslinked structure. Figure 8 shows the swelling behaviors of the copolymers.

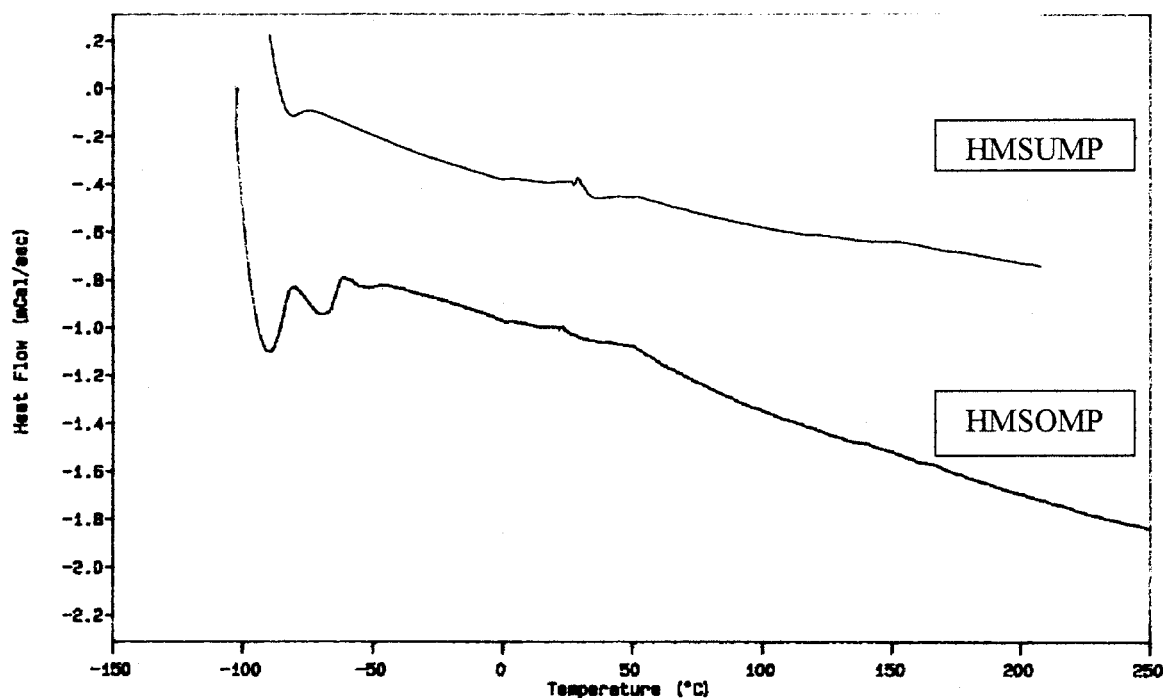


Figure 9 DSC spectrum of the soybean-based polymer (HMSOMP) and sunflower-based polymer (HMSUMP).

Swelling behavior is also a good indicator of the crosslinking density: a higher swelling ratio indicates a lower crosslinking density. In both copolymers no unreacted monomer could be detected in the swelling solvent so we concluded that the copolymer ratio is the same as the feed ratio. Water absorption of cured resins depended on the amount of maleic anhydride used. Water absorption values for sunflower-based polymer and soybean oil-based polymer were 1.78 and 2.10%, respectively.

Thermal properties of the cured resins were tested by DSC at a heating rate of 10°C/min at temperatures ranging from -100 to 250°C. It is well known that crosslinking density affects glass transition of the networks. Soybean-based polymer has more maleate residues and as a result showed higher T_g (40°C) than that of sunflower-based polymer (30°C), as shown in Figure 9. Mechanical properties of the new polymers are currently under investigation.

Homopolymerizations of the maleinized triglycerides were also carried out in the presence of MEKP and BPO as radical initiators. In each system, the polymerization of the maleinized triglycerides was observed with a slow viscosity increase. IR spectra of the products showed that the radical polymerization of the maleate groups was incomplete. We believe that the tocopherols present in the oil, the allylic hydrogens acting as chain-transfer agent, and the inherent inability of maleate groups to homopolymerize precluded high conversion.

CONCLUSIONS

Hydroxymethyl adducts of triglycerides were obtained by ene reaction with paraformaldehyde in the presence of EtAlCl_2 . Hydroxymethylation yields for sunflower oil and soybean oil were 42 and 55%, respectively. After maleinization, these correspond to 1.3 and 1.7 maleate groups per triglyceride for sunflower oil and soybean oil, respectively. The maleated adducts were copolymerized with styrene. Soybean oil-based copolymer achieved solid state quicker than sunflower-based polymer. Examination of swelling behavior showed that sunflower oil-based copolymer had higher swelling behavior because of lower crosslink density. This result coincided with DSC analysis that the sunflower-based copolymer showed a lower T_g than that of the soybean-based copolymer. Mechanical properties of the new thermoset resins are now under examination. There was also clear evidence of participation of the double bonds of the triglycerides in the styrene copolymerization reaction.

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References

1. Wool, R.; Küsefođlu, S.; Palmese, G.; Khot, S.; Zhao, R. U.S. Pat. 6,121,398, 2000.

2. Can, E.; Küsefođlu, S. H.; Wool, R. P. *J Appl Polym Sci* 2001, 81, 69.
3. Can, E.; Küsefođlu, S. H.; Wool, R. P. *J Appl Polym Sci* 2002, 83, 972.
4. Hoffmann, H. M. R. *Angew Chem Int Ed Engl* 1969, 8, 556.
5. Gunstone, F. D. *An Introduction to the Chemistry and Biochemistry of Fatty Acids and Their Methyl esters*; Chapman & Hall: London, 1967.
6. Blomquist, A. T.; Verdol, J.; Adami, C. L.; Wolinsky, J.; Philips, D. D. *J Am Chem Soc* 1957, 79, 4976.
7. Blomquist, A. T.; Passer, M.; Schollenberger, C. S.; Wolinsky, J. *J Am Chem Soc* 1957, 79, 4972.
8. Snider, B. B.; Phillips, G. B. *J Org Chem* 1983, 48, 464.
9. Snider, B. B. *Acc Chem Res* 1980, 13, 426.
10. Metzger, J. O.; Biermann, U. *Synthesis* 1992, 463.
11. Paton, R. M.; McLellan, J. F.; Mortier, R. M.; Orszulik, S. T. *J Am Oil Chem Soc* 1994, 71, 231.
12. Schäfer, H.; Kahmen, J.; Fett, M. *Lipids* 1998, 100, 207.
13. Siegel, E. F.; Moran, M. K. *J Am Oil Chem Soc* 1947, 69, 1457.
14. Friedman, M.; Garti, N. *J Am Oil Chem Soc* 1983, 60, 000.