Polymerization of Maleic Anhydride–Modified Plant Oils with Polyols

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ABSTRACT: In this study soybean oil triglycerides were reacted with maleic anhydride in an ene reaction to introduce more than two maleate residues per triglycerides. The maleinized soybean oil (SOMA) was then polymerized with diols to the half-ester stage only. Two different types of alcohols was used in this work: (1) short-chain polyhydroxy linear or cyclic alcohols having 2, 3, 4, or 6 hydroxyl groups; and (2) long-chain dihydroxy alcohols. The aim was to determine the effect of functionality and chain length by choosing alcohols with increasing number of hydroxyl groups and different chain lengths. The reaction of alcohols with anhydride functionalized soybean oil to give a polymeric half-ester is a reaction that proceeds without the formation of byproducts and is different from complete polyesterification of maleinized oils, which are well known. To improve the reaction yields, different catalysts and different reaction conditions were examined. The structural analysis of the products was done with ^{1}H-NMR and IR spectroscopy. All of the new polymers obtained were resilient and soft rubbers at room temperature. Castor oil polymer mixed with 60% $CaCO_3$ and 12% cork powder gave a resilient and nontacky linoleum composition. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 197–202, 2003

Key words: soybean oil; ene reaction; renewable resources; polyester; esterification

INTRODUCTION

The primary raw material used for the synthesis of commercially important polymers has been petroleum for the last 50 years. The synthesis of polymers from renewable resources such as plant and animal products is attractive because of diminishing reserves and the increasing price of petroleum. Social acceptance of polymers from renewable, agricultural raw materials is also high because they represent a high-tech use for traditional agricultural products. Usually biodegradable and inexpensive polymers are obtained from agricultural raw materials. In our efforts to use plant oil triglycerides as raw materials for polymer synthesis, we examined the polymerization of maleic anhydride–modified soybean oil. We studied the polymerization of soybean oil and epoxidized soybean oil chemistry in some depth and reported our results in earlier publications.[1–3]

Soybean oil, iodine number 135, contains internal double bonds in its oleic, linoleic, and linolenic acid components. The unsaturation is high enough to give the oil the classical terminology of "semidrying" but not high enough to allow its use as a traditional "drying oil" in alkyd manufacture by itself. The expected availability of genetically engineered soybeans from which oil with a high content of oleic esters and the cheap price makes soybean oil a good choice as a raw material for polymers. Efforts over the last century to produce a high molecular weight polymer by simple free-radical reactions of the naturally occurring unsaturation in plant oils have met with little success. Therefore, the strategy we employed was to convert the triglyceride to a maleic anhydride–modified oil that would polymerize by the polycondensation route rather than the polyaddition route.

Maleinization of plant oil has been known for a long time. Rheinecku and Khoe[4] report that in the case of monounsaturated fatty acid esters the maleinization reaction requires at least 200°C and follows an "ene" reaction path, resulting in the addition of a succinic anhydride group to the allylic position of the fatty acid. The mechanism involves an allylic shift of one double bond by transferring the allylic hydrogen to the enophile and bonding of the two molecules, as shown in Figure 1. Teeter et al.[5] report that in the case of diunsaturated, nonconjugated fatty acids, which are the naturally occurring isomers of most plant oils, the ene reaction also takes place, and results in conjugation of the two double bonds, to give the *trans–trans* isomer. This adduct now undergoes a Diels–Alder reaction with another mole of maleic anhydride. In the unusual case of the *trans–trans* conjugated diene containing fatty acids, only the Diels–Alder reaction is
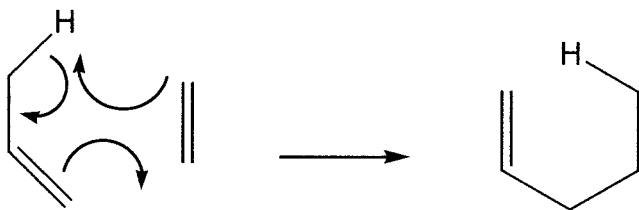
Figure 1 Schematic representation of ene reaction.

observed and it proceeds at the much lower temperature of 80°C. Bickford and Fischer[6] examined the reaction of maleic anhydride with methyl oleate and, more recently, Metzger and Biermann[7] deduced the structures of regioisomers obtained in the same reaction. The chemistry is shown in Figure 2.

Given that each double bond has two allylic positions and one or the other but not both can undergo an ene reaction, many positional isomers of the succinyl derivative were obtained. Thus, in a hypothetical triglyceride containing two mono- and one diunsaturated fatty acid, the maximum number of anhydride groups that can be introduced per triglyceride is four.

Alcoholysis of a cyclic anhydride is a relatively easy reaction and in the case of primary alcohol, the reaction goes to completion in a short time at room temperature. Secondary alcohols require higher temperatures, longer times, and usually a base catalyst. The reaction proceeds without any byproduct and would lead to a polymer in the case of a triglyceride with at least two anhydride functionalities, together with a polyol with at least two hydroxyl groups. If the functionality of the monomers is higher than two, a crosslinked polymer should be obtained. In a Japanese patent[8] the anhydride group of the maleinized oil was opened with hydroxyalkyl methacrylate and the molecule was free-radically polymerized to give a rapid-hardening varnish. However, in this study, we deal only with polymerization by the monoesterification route with diols. Such a scheme would be ideal for the
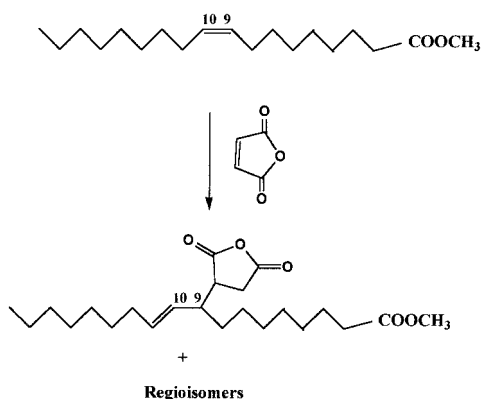
reaction injection molding (RIM) type process in which a liquid polyol and a liquid multiply maleinized plant oil would be coinjected into a mold and heated to give a thermoset polymer without any byproducts. Polymer formation with a diol is shown in Figure 3. Similar reactions with polyols containing higher numbers of hydroxyl groups should lead to higher connectivity and to more rigid polymers. Here, we report our efforts to polymerize maleinized soybean oil to different extents with polyols having 2, 3, 4, and 6 hydroxyl groups.

EXPERIMENTAL

Reagents and instruments

The soybean oil (Marsa, Adana, Turkey) used was food grade and was used without further purification. Maleic anhydride (MA) from Fluka (Buchs, Switzerland) was used without purification. Catalysts used in the polymerization reactions were 2-methylimidazole (Aldrich, Milwaukee, WI), $SnCl_4$ (Fisher Scientific, Pittsburgh, PA), and p-toluene sulfonic acid (Fisher Scientific). The polyols ethylene glycol, glycerol, pentaerythritol, mesoerythritol, D-ribose, D-arabinose, D-sorbitol, myoinositol, polyethylene glycol (PEG) 160, PEG 400, PEG 600, and castor oil were used without purification. CCl_4 (Merck, Darmstadt, Germany) and $CDCl_3$ (Aldrich) were used for ^{1}H-NMR analyses.

The IR analysis was performed on a Perkin–Elmer 1600 FTIR spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT) using NaCl windows. ^{1}H-NMR spectra were obtained on a Varian T-60A and Varian 400 MHz NMR spectrometer (Varian Associates, Palo Alto, CA). Melting points were obtained by hot-stage microscope apparatus (Bristoline, NY).

Maleinization of soybean oil

Soybean oil (100 g, 115 mmol, assuming an average molecular weight 870) was placed in a flask under N_2 fitted with a condenser, magnetic stirrer, and thermometer. Maleic anhydride (9 g, 91 mmol) was added and the mixture was heated to 180°C. The color of solution changed from yellow to orange. After 1 h, a
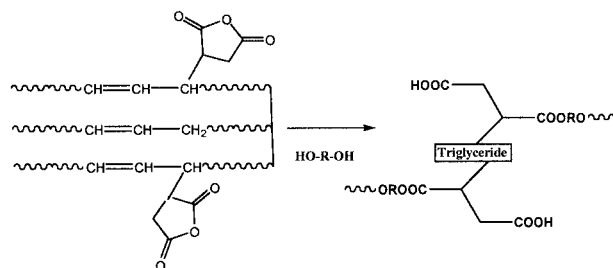

Figure 2 Ene reaction product of oleic methyl ester and maleic anhydride.

Figure 3 Polyester formation from SOMA and polyalcohols.

second portion of maleic anhydride (9 g, 91 mmol) was added and the temperature was increased to 195–200°C. Some sublimation of maleic anhydride was observed. After 1 h, the final portion of maleic anhydride (9 g, 91 mmol) was added and the temperature was increased to 220–230°C. The mixture was stirred for 1 h at 220°C and then cooled to room temperature. The solution became reddish and the viscosity increased. NMR analysis showed that no maleic anhydride was left in the reaction medium.

IR (NaCl): 3006.2, 723.9 cm^{-1} (C=C); 2926.1, 2854.0, 1458.0 cm^{-1} (C—H); 1860.8, 1781.9, 918.6 cm^{-1} (O=C—O—C=O); 1224.4, 1161.1, 1062.8 cm^{-1} [C—C(=O)—O]; 1742.4 cm^{-1} (C=O).

^{1}H-NMR (CCl$_4$) δ: 0.95 (CH$_3$—); 1.2 (—CH$_2$—); 2.3 [—CH$_2$—C(=O)—O]; 2.8 (—CH=CH—CH$_2$—CH=CH—); 3.1 [—CH—CH—(CH$_2$—)—C(=O)—O]; 4.2 [—O—CH$_2$—CH(O)—]; 4.1 [—O—CH$_2$—CH(O—)—CH$_2$—O—]; 5.2 (—HC=CH—).

Polymerization of SOMA with polyols

The general procedure is given for maleinated soybean oil (SOMA) polymer. In a typical run, SOMA (4.11 g, 3.7 mmol, assuming an average molecular weight of 1110) and glycerol (0.25 g, 2.7 mmol) were placed in a vial and 2-methylimidazole (0.05 g, 0.6 mmol) was added as a catalyst and the mixture was continuously stirred at 105°C for 2 hrs. The reaction temperature was kept constant at 105°C for 3 h and then the mixture was cooled to room temperature. The product was a semirigid solid at room temperature. When the sample was extracted with pentane a weight loss of 16% was observed. IR and NMR analyses showed that the extract consisted of unreacted soybean oil and SOMA adduct with only one maleic anhydride substitution.

IR analysis of the polymeric products showed the disappearance of an anhydride peak at 1849.9, 1776.9, 939.8 cm^{-1}, the appearance of a carboxylic OH band at 3285.9 cm^{-1}, and a new carbonyl peak (—COOH) at 1708.5 cm^{-1}.

The sample did not dissolve in common NMR solvents.

Preparation of a linoleum composition

SOMA (3.38 g, 3.0 mmol), castor oil (2.5 g, 2.9 mmol), and 2-methylimidazole (0.06 g, 0.7 mmol) were mixed in a vial and continuously stirred at 85°C for 5 h and then cooled to room temperature. The product was a highly viscous oil. This product was then mechanically mixed with 60% CaCO$_3$ and 12% cork powder to give a resilient and nontacky linoleum composition.

Ha ⟶ 2.84 ppm
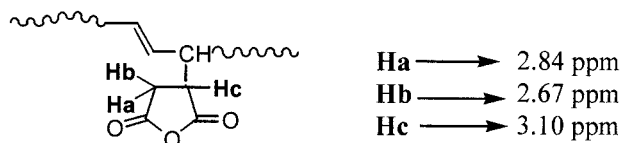Hb ⟶ 2.67 ppm
Hc ⟶ 3.10 ppm

Figure 4 NMR chemical shifts of succinic anhydride protons.

RESULTS AND DISCUSSION

Thermal maleinization of soybean oil

Maleinization of soybean oil was carried out at 220°C and proceeded as expected. The IR spectrum of the product shows characteristic peaks at 1685, 1782, and 918 cm^{-1} attributed to the succinic anhydride group and at 699 cm^{-1}, attributed to the unreacted maleic anhydride disappeared. The absence of a carboxylic acid band indicates that the anhydride was intact. ^{1}H-NMR of the product shows that the peak at 7.1 ppm attributed to the residual maleic anhydride disappeared and allows peak assignment of the succinic anhydride group, as shown in Figure 4. Unfortunately, unreacted (—CH=CH—CH$_2$—CH=CH—) methylene-interrupted hydrogen signals coincide with succinate hydrogen signals, which makes it impossible to determine the extent of maleinization by NMR. Many positional isomers of the succinyl derivative were obtained that also obscured the NMR signal. However, when maleic anhydride loss attributed to sublimation is prevented by a slight overpressure, the unreacted maleic anhydride can be determined by NMR spectroscopy, and thus the extent of maleinization can be calculated. The best experimental procedure resulted in a SOMA adduct, obtained as a brown viscous oil that contains, on average, 2.4 succinate groups per triglyceride, and this product was used for the rest of this study.

Lewis acid–catalyzed maleinization of soybean oil

Because the thermal ene reaction of soybean oil with maleic anhydride requires a high temperature we attempted to use a Lewis acid catalyst to lower the reaction temperature. There are numerous reports in the literature about catalysts of ene reactions. Eslami[9] studied the ene reaction of maleic anhydride with oleic acid catalyzed by hydrochloric and phosphoric acids and claimed to obtain higher yields. A recent Japanese patent[10] claims the use of zeolite for the same reaction and discloses that a shorter contact time and lower temperatures were possible.

We chose BF$_3$–ethylamine complex as a catalyst for this reaction and indeed observed much faster consumption of maleic anhydride. However, the product proved to be considerably different from the one obtained without a catalyst. ^{1}H-NMR showed that tri-

glyceride unsaturation, with vinyl proton peaks at 5.2δ, decreased in intensity, probably because of cationic oligomerization by the BF$_3$ catalyst. The IR spectrum also showed the presence of a new carbonyl group that was neither an ester nor an anhydride, but was most probably an α,β-unsaturated acid carbonyl group at 1709 cm^{-1}, and the appearance of a broad hydroxyl band at 3200 cm^{-1}. These findings led us to believe that an acylation reaction took place in addition to the ene reaction. The competing acylation reaction is shown in Figure 5.

The acylation product may be interesting in its own right, but because it has reduced anhydride content, it was not used in the rest of this study.

## Maleinization of soybean oil in the presence of organic peroxide

Reactions of maleic anhydride with linoleic and oleic acid in the presence of organic peroxide were investigated by Nagakura and Yoshitomi.[11] Di-*tert*-butyl peroxide and dicumyl peroxide were the best initiators of the maleinization reaction at 130°C. In this work *tert*-butyl peroxybenzoate was used in the maleinization of soybean oil. The product was more viscous than thermally initiated or Lewis acid–catalyzed maleinated adducts of soybean oil. This could be the result of copolymerization of maleic and triglyceride double bonds leading to higher molecular weight products. The thermal reaction in the absence of a peroxide gave only maleic addition products but no polymers were observed. The Hc proton of SOMA appears at 3.1 ppm (as shown in Fig. 4) because of the close proximity of the double bond on the fatty acid. This signal is missing in the radical-initiated products because the double bond is no longer there. This fact and the unexpectedly high viscosity of the product leads us to agree with Yoshitomi's claim that maleic anhydride copolymerizes with the triglyceride. The reaction product can be seen in Figure 6. The radical-initiated maleinated product was more difficult to characterize and was not used for the subsequent reaction with polyols.

Reaction of SOMA with polyols

The expected reaction of SOMA with diols is given in Figure 3. The diols and polyols used in this study are
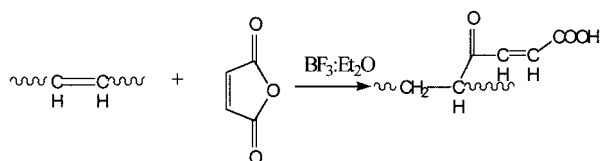
Figure 5 Acylation product of maleic anhydride with BF$_3$: Et$_2$O.
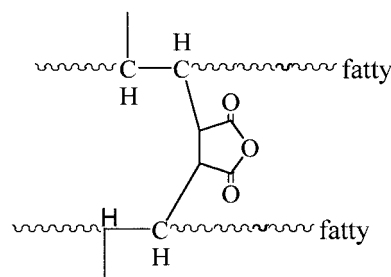
Figure 6 Copolymerization of maleic anhydride and triglycerides.

shown in Table I. The anhydride can be esterified at either end by the polyols used. The alcohols used can be linear or cyclic and their functionality is changed as stated earlier in the Experimental section. NMR spectroscopy was not very useful because most samples became insoluble in NMR solvents very early in the reaction, which suggests that a hyperbranched and crosslinked structure is formed. In some cases IR spectroscopy was also difficult to perform because the flexible solid products could not be dissolved, powdered, or formed into a thin film.

The general procedure for reaction of polyols with SOMA was to mix a stoichiometric amount of each and to heat in a closed container. Catalysts such as SnCl$_4$, 2-methylimidazole, and *p*-toluene sulfonic acid are known to increase the rate of alcoholysis of anhydrides and 2-methylimidazole was used in this work in most reactions in catalytic amounts. The product was initially examined by IR analysis and in all cases diminishing of the anhydride peak and formation of a carboxyl peak could be observed. The end points of these reactions were determined by observing the disappearance of the anhydride peaks in the IR.

The alcohol that gave the best physical properties was glycerol. The product was a semirigid, reddish material and the color of the polymer was reddish. It had a melting decomposition temperature of 150–155°C. The IR spectrum of the reaction mixture is given in Figure 7. After the addition of catalyst, 2-methylimidazole, the disappearance of anhydride peaks at 1849.9, 1776.9, and 939.8 cm^{-1} was observed in 3 h. A new carbonyl band of the carboxylic acid at 1708.5 cm^{-1} and a broad carboxylic OH at 3285.9 cm^{-1} were also observed. A new ester peak caused a broadening at the carbonyl region. A good IR spectrum was not taken for the product at room temperature because the solid could not be powdered. A sample of the polymer was taken and melted at 220°C and was drawn into a thin film on a KBr window. It was observed that all anhydride peaks were consumed.

Nadkarni and Uphade[12] studied the kinetics of the polyesterification reaction between the series of polyethylene glycol (PEG) 200, 300, 400, and maleic anhydride. They concluded that the rate of the reaction

TABLE I
Polyols Used to Polymerize SOMA and Qualitative Properties of the Polymeric Products

Alcohols	Structure	Functionality	Comments for SOMA adduct
Ethylene glycol	$HOCH_2CH_2OH$	2	Soft solid
Glycerol		3	Semirigid material
Pentaerytritol		4	Soft solid
Mesoerytritol		4	Soft solid
D-Ribose		4	Sticky and rubbery
D-Arabinose		4	Sticky and rubbery
D-Sorbitol		6	Soft-flexible solid
Myo-inositol		6	Soft solid
PEG 160	$HO—(CH_2CH_2O)_3—CH_2CH_2OH$	2	Soft-flexible solid
PEG 400	$HO—(CH_2CH_2O)_9—CH_2CH_2OH$	2	Resilient soft solid
PEG 600	$HO—(CH_2CH_2O)_{13}—CH_2CH_2OH$	2	Rubbery soft solid
Castor oil	—[a]	2,7	Highly viscous oil

[a] Castor oil is a typical example of triglycerides and has an 89% ricinoleic acid ($C_{18}H_{31}O_3$) in its structure.

decreased considerably with increasing the chain length of polyether and so it was found that PEG 200 was the most reactive, whereas PEG 400 was the least reactive. The same trend was observed in the reaction of SOMA with PEG of different molecular weights. PEG 160 reacted with SOMA in the presence of 2-methylimidazole catalyst at 100°C. A new carbonyl band of the carboxylic acid peak formed at 1707.6 cm^{-1} and a broadening at the carboxylic OH band was also observed. At the end of the reaction anhydride peaks at 1851.0, 1775.1, and 939.5 cm^{-1} were consumed. The product was a soft reddish solid at room temperature, with a melting decomposition at 95–105°C. The reaction of PEG 400 and SOMA produced a resilient soft polymer, whereas the PEG 600 adduct was a rubbery soft solid.

Table I also shows some cyclic alcohols. A cyclic structure can increase the rigidity between molecule segments, so it should be possible to obtain a rigid material at the end of the reaction. Unexpectedly, the adducts were soft, flexible, or rubbery solids at room temperature.

CONCLUSIONS

In this study maleinized soybean oil (SOMA) was polymerized with different alcohols that can be classified as low molecular weight polyols and long-chain diols. The SOMA–alcohol polymers were soft, flexible solids or viscous oils. The insolubility of the products is attributed to the crosslinking because of the presence of triglycerides with multiple maleates and because of the polyfunctional alcohols used. The solubility of the polymers obtained in common solvents, like acetone and chloroform, leaves no doubt about crosslinking because the material became jellylike and
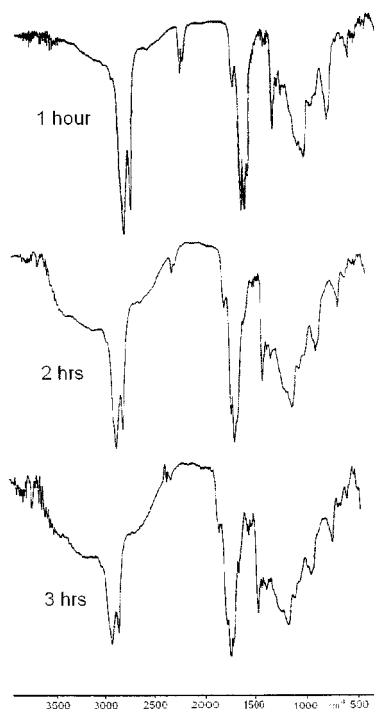
Figure 7 IR spectra of glycerol–SOMA polymer at different stages of its synthesis.

sticky and did not dissolve but swelled. In the course of this work we found that succinic anhydride groups on the triglyceride molecule is less reactive than maleic anhydride toward alcohols. The effect of various transesterification catalysts such as $SnCl_4$, *p*-toluene sulfonic acid, and 2-methylimidazole were tried, and 2-methylimidazole was found to be the best catalyst for the reaction of anhydride with alcohols.

Although maleinized soybean oil has been known for some time, its half-ester polymers with multifunc-

tional alcohols are new. Unfortunately, none of these new polymers was a rigid solid. All of them were soft tacky solids that could not be used as a structural polymer. No increase in connectivity and crosslink density could be observed by increasing the functionality of the polyol. However, these new polymers may have applications such as adhesives, film formers, textile and paper sizes, and tackifiers. For example, when SOMA–castor oil polymer was mechanically mixed with 60% $CaCO_3$ and 12% cork powder, an excellent, resilient, and tough material resembling linoleum was observed.

References

1. Wool, R.; Küsefoğlu, S.; Palmese, G.; Khot, S.; Zhao, R. U.S. Pat. 6,121,398, 2000.
2. Can, E.; Küsefoğlu, S. H.; Wool, R. P. J Appl Polym Sci 2001, 81, 69.
3. Can, E.; Küsefoğlu, S. H.; Wool, R. P. J Appl Polym Sci 2002, 83, 972.
4. Rheinecku, A. E.; Khoe, T. H. Fette-Seifen Anstrichmit 1969, 71, 644.
5. Teeter, M. T.; Geertz, M. J.; Cowan, J. C. J Am Oil Chem Soc 1948, 25, 158.
6. Bickford, G. W.; Fischer, G. J. J Am Oil Chem Soc 1948, 25, 254.
7. Metzger, O. J.; Biermann, U. Fat Sci Technol 1994, 96, 321.
8. Hitachi Chemical Co. Ltd., Japan. Jpn. Pat. 57136310, 1996; Chem Abstr 98, 35715.
9. Eslami, E. In: Maleic Anhydride; Trivedi, B. C.; Culbertson, B. M., Eds.; New York/London: Plenum Press, 1985; Chapter 5.
10. Agency of Industrial Science Technology. Jpn. Pat. 7, 8012-494, 1978.
11. Nagakura, M.; Yoshitomi, K. Yukagaku 1972, 21, 83; Chem Abstr 1972, 76, 139717b.
12. Nadkarni, V. M.; Uphade, B. S. J Polym Sci Part A: Polym Chem 1994, 32, 2003.