Rheology of Chemically Modified Triglycerides

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ABSTRACT: The rheology of chemically modified plant oils was determined to aid in their processing for polymers and other applications. Epoxidized and acrylated triglycerides were derived from various plant oils and model triglycerides. The viscosity of the unmodified oils decreased as the level of oil unsaturation increased. However, the viscosity of the epoxidized oils increased slightly as the level of epoxidation increased. Furthermore, the viscosity of the acrylated oils increased exponentially as the level of acrylation increased because of increased polarity. In addition, the viscosity of the acrylated oils increased as the average distance of the acrylate groups from the fatty acid chain ends decreased. Chemically modified and unmodified oils did not exhibit any shear-thinning behavior or any memory of shear history. The temperature dependence of the viscosity followed the Arrhenius law, and the activation energy decreased linearly with the level of acrylation. The addition of comonomers, such as styrene, reduced the viscosity of the acrylated oils exponentially as the comonomer concentration increased. However, the glass-transition temperature and modulus of the triglyceride-based polymers decreased as the styrene content decreased. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 774–783, 2005

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INTRODUCTION

Refined oils, such as soybean oil, are composed of at least 99% triglyceride molecules.[1] Triglycerides are three fatty acids connected by a glycerol center (Fig. 1). Chemically modified plant oils have been used as additives in inks and coatings,[2] as toughening agents in poly(vinyl chloride) and epoxy resins,[3] and as the major components of a number of natural resins,[4] composites,[5] and pressure-sensitive adhesives.[6] In all these applications, the triglycerides are chemically modified (e.g., epoxidized or acrylated). Epoxidized and acrylated triglycerides (Fig. 2) are usually monomeric liquids but can be polymerized to form solid gels. Epoxidized triglycerides can be polymerized in the presence of a curing agent, such as a diamine.[7] Acrylated triglycerides can be free-radically polymerized with or without a comonomer, such as styrene.[4]

These chemically modified triglycerides are excellent candidates for use as liquid molding resins.[4] Thermosetting liquid molding resins contain monomers, an initiator, and possibly fillers and a promoter (a chemical that promotes initiator breakdown at low temperatures to allow for room-temperature curing of the monomers).[8] In free-radical systems, one monomer is a linear chain extender (e.g., styrene), whereas the other is a crosslinking agent (e.g., acrylated triglycerides or vinyl ester) with a functionality of 2 or greater.

Liquid molding is used to manufacture many thermosetting polymer composite parts, such as automobile parts.[8,9] Vacuum-assisted resin-transfer molding is among the many different manufacturing processes used to produce these composites.[8,9] In all these processes, a monomeric resin is injected into a mold containing fibers (e.g., glass fibers, carbon fibers, or flax fibers). The resin is driven into the mold with a pressure differential. This pressure difference also moves the resin into the gaps between the fibers. The resin is then cured for some time at room temperature or at elevated temperatures. The composite part is demolded and, if possible, postcured at higher temperatures to more completely react the monomers to maximize the properties of the composite part.

Currently, liquid molding resins are dominated by epoxy resins, vinyl ester resins, unsaturated polyester resins, and phenolic resins.[8,9] These resins are petroleum-derived, and they are not recyclable or biodegradable. On the other hand, triglyceride-based resins are derived from renewable sources and are potentially biodegradable.

The composites industry has established some guidelines for liquid molding resins.[8,9] Possibly the most stringent requirement is the resin's viscosity, which should be less than 500 cP. Higher viscosities can cause problems with fiber wetting, voids may occur in the part, and the time required for injection increases. Increased injection time is an issue for two
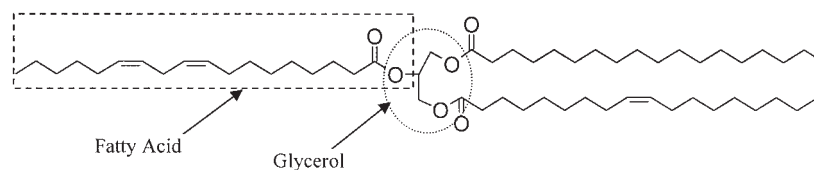
Figure 1 Molecular structure of a typical triglyceride molecule. Three fatty acids are connected to a glycerol center.

reasons. First, the longer it takes to mold a part, the lower the production rate is of the part. In addition, if a promoter is used, the resin could cure before it is fully injected into the mold.

The processing of chemically modified triglycerides is important to the production of numerous products, including liquid molding resins. Unmodified plant oils are Newtonian fluids with low viscosities (ca. 50 cP), but when they are chemically modified (e.g., epoxidized or acrylated), the viscosities of these oils can increase significantly. Triglycerides can be modified to contain various functional groups (Fig. 2) at different levels of functionality.[4] Virtually any plant oil, such as olive oil or soybean oil, can be used to make these chemically modified triglycerides. As a result of chemical modification, the polarities of triglyceride molecules change.[10] Differences in the molecular polarity can have very large effects on the rheology.[10,11] Furthermore, during chemical modification, unwanted side reactions, such as etherification (Fig. 3), increase the molecular weight of the modified triglycerides.[12–14] Etherification can lead to gelation and thus can have a very large impact on the rheology.[11–14] Changes in both the polarity and molecular weight can affect the zero-shear viscosity (η_0) and the viscosity's temperature dependence and can potentially induce shear-thinning behavior.

Because styrene is a hazardous air pollutant and a volatile organic compound (VOC), the Environmental Protection Agency of the United States of America introduced legislation to limit styrene emissions from composite manufacturing.[15] Therefore, minimizing the styrene content in these resins is desirable, but knowledge of the rheology is required to ensure that the resin can be properly processed at minimal styrene contents.

In this work, we examine the rheological effects of epoxidizing and acrylating a series of different oils and model triglycerides with well-defined fatty acid

distributions in the hope of gaining a fundamental understanding of the rheology of triglyceride-based systems. In addition, this work will allow the resin viscosity to be tailored for any application and VOC emissions to be minimized.

EXPERIMENTAL

Synthesis of the epoxidized and acrylated plant oils

Epoxidized samples were made through the reaction of the unsaturation sites of oils and model triglycerides with a mixture of formic acid and hydrogen peroxide[16] [Fig. 2(a)]. The oils used in this work had similar molecular weights but different levels of unsaturation[1] (Table I). The amount of formic acid used was one-third the oil mass. The amount of hydrogen peroxide used was twice the molar ratio needed to produce the completely epoxidized sample. This amount of hydrogen peroxide was used to drive the epoxidation to completion. Olive oil, cottonseed oil, canola oil, corn oil, soybean oil, safflower seed oil, linseed oil, and triolein (99%) were purchased from Sigma–Aldrich (St. Louis, MO). DuPont Corp. (Wilmington, DE) provided the genetically engineered high oleic soybean oil (HOSO).

The unsaturated oils were added to an Erlenmeyer flask, which contained a magnetic stirring bar. The appropriate mass of hydrogen peroxide (Fisher Scientific, Fair Lawn, NJ; 30% aqueous solution) was added, followed by the formic acid (Fluka, Buchs, Switzerland; 98%). The flask was stoppered and stirred vigorously. The reaction was run at ambient temperature with a water bath for cooling. After 16 h of reaction, the samples were ether-extracted to recover purified epoxidized oils.[6,16] The ether was removed *in vacuo* during heating at 40°C. The extent of epoxidation (Table I) was measured
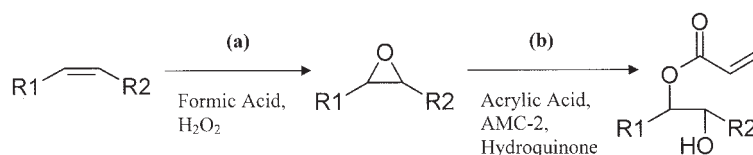

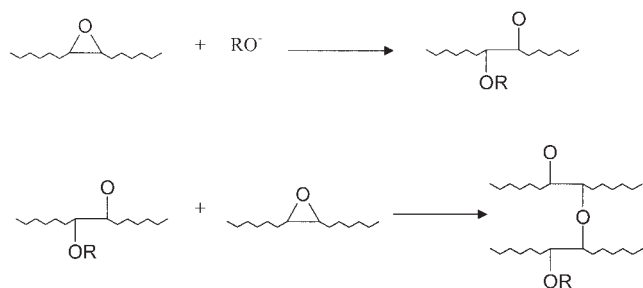**Figure 2** (a) Epoxidation and (b) acrylation of triglycerides.

Figure 3 Etherification reaction causing epoxy homopolymerization in the presence of acids.

with ^{1}H-NMR[16] (250.13 MHz, ±2000-Hz spectral window, 0.427 Hz/pt digital resolution, 16 scans at 293 K, 90° pulse width) with a Bruker (Billerica, MA) AC250 spectrometer. Epoxidized linseed oil (Elf Atochem, Philadelphia, PA) was used because we were unable to synthesize a highly epoxidized linseed oil.

Partially epoxidized soybean oil was prepared through the reaction of soybean oil with formic acid and hydrogen peroxide in the same concentrations used for maximally epoxidized oils, but for different reaction times. Epoxidized soybean oils with 1.1, 2.4, and 3.3 epoxides per triglyceride were reacted for 1, 2, and 4 h, respectively. These oils were purified and analyzed in the same manner as maximally epoxidized oils.

Acrylated samples were made through the reaction of the epoxide groups of epoxidized oils and epoxidized triglycerides with acrylic acid[17] [Fig. 2(b)]. The AMC-2 catalyst (Aerojet Chemicals, Rancho Cordova, CA) was used to reduce the extent of epoxy homopolymerization.[18] AMC-2 was used in every sample at a concentration of 0.02 g/mL. A hydroquinone concentration of 0.0033 g/mL was used to inhibit free-radical polymerization. The oils were maximally acrylated by the addition of 1.1 mol of acrylic acid per epoxide

group to the reaction mixture (Table I). The effect of the acrylation level on the polymer properties could also be determined by the acrylation of a single oil to different extents (Table II). Epoxidized HOSO, epoxidized soybean oil, and epoxidized linseed oil were acrylated to different extents. We selected the desired extent of acrylation and added 1.1 times the required amount of acrylic acid to the reaction mixture. The reaction was run at 70°C in a silicon oil bath on a hot plate with vigorous stirring. The acrylated oils were purified with ether extraction.[6,16] The extents of epoxidation remaining and acrylation added were measured with ^{1}H-NMR.[16] With both methods, the level of functionalization was varied from 0.6 to 5.8 acrylates per triglyceride.

TABLE II
Level of Acrylation of Partially Acrylated HOSO, Soybean Oil, and Linseed Oil and Molecular Weights of Those Oils due to Functionalization and Oligomerization

Oil	Acrylate groups per triglyceride	Molecular weight (g/mol)
HOSO	1.1	1070
HOSO	1.7	1100
HOSO	2.2	1140
HOSO	2.7	1190
Soybean	0.6	1020
Soybean	1.1	1060
Soybean	1.9	1110
Soybean	2.5	1150
Soybean	2.8	1180
Soybean	4.2	1290
Linseed	1.3	1090
Linseed	2.2	1170
Linseed	2.9	1210
Linseed	3.5	1260
Linseed	4.1	1310
Linseed	5.1	1390
Linseed	5.8	1700

TABLE I
Levels of Unsaturation, Epoxidation, and Acrylation of Maximally Functionalized Plant Oils and Model Triglycerides and Molecular Weights of Those Oils due to Functionalization and Oligomerization

Oil	Functional groups per triglyceride			Molecular weight of chemically modified oils (g/mol)	
	Unsaturation	Epoxides	Acrylates	Epoxidized	Acrylated
Olive	2.8	2.7	2.5	950	1150
HOSO	3.0	2.8	2.7	970	1190
Triolein	3.0	2.9	2.8	970	1190
Cottonseed	3.8	3.5	3.3	950	1190
Canola	3.9	3.7	3.5	970	1240
Corn	4.3	4.3	4.0	960	1260
Soybean	4.6	4.4	4.2	960	1290
Safflower Seed	4.7	4.5	4.2	1020	1350
Linseed	6.4	6.2	5.8	990	1700

SEC of modified and unmodified triglycerides

The oligomerization of triglycerides can occur during epoxidation and acrylation because of epoxy homopolymerization. Size exclusion chromatography (SEC) was used to quantify the concentrations of triglyceride monomers and oligomers.[19,20] A PerkinElmer (Boston, MA) series 200 gel permeation chromatograph was used with two 5-μm styrene/divinylbenzene columns in series. The columns were equilibrated and run at 45°C with tetrahydrofuran (THF) as the elution solvent at a flow rate of 1 mL/min. The column effluent was monitored by two detectors operating at 25°C: a refractive-index detector (Optilab) and a multi-angle laser light scattering detector (Minidawn) were coupled together in a system manufactured by Wyatt Technology Corp. (Santa Barbara, CA). The samples were prepared through the dissolution of 2.5 mg in 1 mL of THF. A repeat run was performed for every sample.

Resin preparation with the comonomers

Low-molecular-weight comonomers, such as styrene, can be used to modify the viscosity of the triglyceride-based resins. The rheological effect of four different comonomers were studied: styrene (Aldrich, Milwaukee, WI; 99%), methyl methacrylate (MMA; Fisher Scientific; 98%), ethyl methacrylate (Avocado Research Chemicals, Heysham, United Kingdom; 99%), and butyl methacrylate (Avocado Research Chemicals; 99%). These comonomers were added to acrylated oils in different concentrations ranging from 0 to 100% comonomer.

Rheology of the unmodified and chemically modified plant oils

The rheological character of the chemically modified triglycerides was measured with a TA Instruments (New Castle, DE) AR 1000 control stress rheometer. Parallel-plate geometry with 40-mm plates was used for all the samples. In addition, 25-mm plates were used to test the two most highly acrylated linseed oil samples at high shear rates. In these cases, the results for both plate geometries were within a 1% margin of error for the shear rates that were tested in common. A gap distance of 1000 μm was used for all samples. Gap spacings as low as 300 μm were used to test the samples at shear rates greater than 2500 s^{-1}. The maximum shear rate that could be obtained without gap failure was 3000 s^{-1}. TA Rheology Advantage Data Analysis software (version 3.0.24) was used to analyze the results. A repeat run was performed for every sample.

Steady-state shear experiments were used to determine η_0, the time-dependent viscosity, and the shear-thinning behavior of chemically modified and unmodified oils and model triglycerides. The samples were equilibrated at 25°C. The shear rate was then increased from 1 to 3000 s^{-1} and then reduced back to 1 s^{-1}, and 10 measurements per decade were taken. At a given shear rate, the shear stress was measured every 2 s. The shear rate and viscosity were recorded when the shear rate stabilized within a 5% tolerance for three consecutive points. The samples were tested at 25°C, and the temperature was maintained within 1% of the set point with liquid nitrogen for cooling. However, because triglycerides with one epoxide group per fatty acid are solid at this temperature, all the epoxidized samples were also measured at 45°C, at which temperature all the samples were completely liquid. To determine if there was memory of shear history, we sheared the samples at 50 s^{-1} for 5 min, and the viscosity was measured every 2 s.

The rheological effect of the comonomers was measured through the testing of mixtures of the acrylated oils and one of the comonomers: styrene, MMA, ethyl methacrylate, or butyl methacrylate. These mixtures were tested at 10 s^{-1} and 25°C. Steady-state shear experiments, as previously detailed, were performed on selected samples.

The effect of the temperature on the viscosity of oils was measured with a temperature step experiment on three maximally acrylated samples—acrylated HOSO, acrylated soybean oil, and acrylated linseed oil—and two partially acrylated linseed samples with 2.2 and 3.5 acrylates per triglyceride. The samples were equilibrated at 20°C. The temperature was increased from 20 to 80°C and then reduced to 20°C in increments of 2.5°C. Higher temperatures were not studied because of the risk of polymerization. When the set-point temperature was reached, each sample was allowed to equilibrate for 3 min. The viscosity was measured every 20 s during the equilibration time. After 2 min of equilibration, the samples reached a constant viscosity. No hysteresis of viscosity as a function of temperature was observed. In addition, the η_0 values and extent of oligomerization of these samples were measured before and after the temperature studies and found to be unaffected by the temperature step experiment. The acrylated HOSO, acrylated soybean oil, and acrylated linseed oil were tested at constant shear stresses of 6, 30, and 320 Pa, respectively. The partially acrylated linseed samples with 2.2 and 3.5 acrylates per triglyceride were tested at shear stresses of 8 and 30 Pa, respectively. These shear stresses corresponded to a shear rate of 1 s^{-1} at 25°C.

The AR 1000 rheometer could not accurately determine the viscosities of the pure comonomers (i.e., styrene). Therefore, literature values for their viscosities were used.[21,22] The viscosities of styrene, MMA, ethyl methacrylate, and butyl methacrylate were 7.0×10^{-4}, 6.0×10^{-4}, 6.5×10^{-4}, and 7.3×10^{-4} Pa s, respectively.

Polymer preparation

Acrylated oils were homopolymerized and copolymerized with 85 mol % styrene. The free-radical initiator was Hi Point 90 at a concentration of 0.015 g/mL. To prevent oxygen free-radical inhibition, we purged the resin with nitrogen gas before the curing. The resin was then poured into vertical molds. The vertical molds consisted of a silicon rubber mold (Dow Corning, Midland, MI) sandwiched between two aluminum plates with binder clamps. The rubber molds had four equally spaced slots 1.1 cm wide, 0.5 cm thick, and 8.3 cm high. A sheet of Kapton film was used on both sides of the silicon rubber to make a very flat surface. All mold components were sprayed with a poly(tetrafluoroethylene) release agent dry lubricant (Miller-Stephenson, Danbury, CT) to ease demolding.

   The samples were cured in an isotemp oven (Fisher Scientific). The temperature was ramped from 30 to 90°C at a rate of 5°C/min. The samples were cured at 90°C for 2 h. The temperature was then ramped to 120°C at 5°C/min. The samples were postcured for 2 h at this temperature. Finally, the temperature was allowed to decrease to room temperature. The samples were then demolded. The dynamic mechanical analysis samples were polished down to approximate dimensions of 5.5 cm $\times$ 0.9 cm $\times$ 0.4 cm on a polishing wheel.

Dynamic mechanical properties

The thermomechanical properties of the triglyceride-based polymers were tested with a Rheometrics Solids Analyzer II (Rheometrics Scientific, Inc., Piscataway, NJ). Before the testing, the exact sample dimensions were measured. The samples were tested in a three-point-bending geometry. The temperature was ramped from -60 to 180°C at a rate of 2°C/min, with a frequency of 1 Hz and a strain of 0.01%. The temperature was controlled with a Rheometrics environmental controller, and liquid nitrogen was used for cooling below room temperature. This experiment was repeated at least three times for each sample. The temperature corresponding to the maximum in the loss modulus was taken as the glass-transition temperature (T_g) of the polymer.[23]

RESULTS AND DISCUSSION

SEC characterization

The light scattering detector did not record any significant peaks during the SEC characterization of the modified and unmodified oil samples. Therefore, there were no polymeric molecules within these samples. The refractive-index detector observed a single peak for the unmodified samples (Fig. 4). This peak eluted at 13.30 mL and was due to individual triglyc-
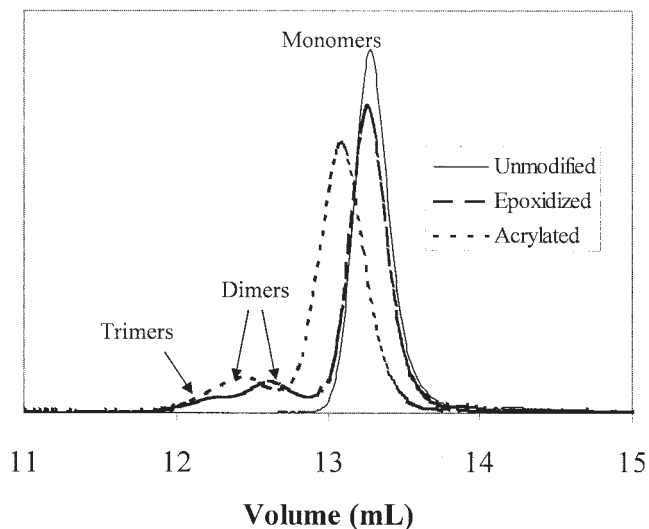

Figure 4 SEC refractive-index chromatograph of unmodified, epoxidized, and acrylated safflower seed oil. The SEC chromatographs of other oils were very similar.

eride molecules. No oligomers were observed in the unmodified samples. The refractive-index detector observed three peaks for the epoxidized samples (12.3, 12.65, and 13.28 mL) and two peaks for the acrylated samples (12.45 and 13.10 mL; Fig. 4). The peak that evolved at 12.3 mL represents trimers. This peak was only observed in the epoxidized HOSO and epoxidized safflower seed oil samples. The 12.45–12.65-mL peak represents dimers, and the last peak eluted represents monomers. The ether-extraction process removed the trimers from the acrylated product. The elution time of the peaks decreased as the samples went from being unmodified to epoxidized to acrylated because the molecular weight of the triglycerides increased as a result of these reactions.

   The ratios of the peak areas (Fig. 4) were used to determine the molar fraction of oligomerized triglycerides (O):

$$O = \frac{A_{\text{oligomers}}}{A_{\text{oligomers}} + A_{\text{monomers}}} \qquad (1)$$

where A_{monomers} and $A_{\text{oligomers}}$ are the areas of the monomer and oligomer peaks, respectively. The extent of oligomerization was low, except for acrylated linseed oil, and was not a function of the level of functionalization. The percentages of oligomerized triglycerides in the epoxidized and acrylated oils, not including maximally acrylated linseed oil, were 7.4 $\pm$ 4.3 mol % and 9.6 $\pm$ 3.7 mol %, respectively; 45 mol % of the triglycerides were oligomerized in linseed oil with 5.8 acrylates per triglyceride. The extent of oligomerization was similar for the epoxidized and acrylated samples, with the exception of maximally ac-

rylated linseed oil. This was expected because the AMC-2 catalyst was used during the acrylation step to prevent oligomerization. Therefore, most of the oligomerization occurred during the epoxidation step. A significant amount of oligomerization took place during the acrylation step for maximally acrylated linseed oil because of the long reaction times involved, causing a higher likelihood of epoxy homopolymerization (Fig. 3).

Rheology

Effect of the unsaturation level on the viscosity of the unmodified triglycerides

The viscosity of the unmodified oils decreased from 65 to 40 cP as the level of unsaturation increased from 2.8 to 6.4 unsaturation sites per triglyceride. The standard error in the viscosity was no more than 5% for any given sample. Equation (2) shows the dependence of η_0 on the level of unsaturation (U) at 25°C:

$$\eta_0 = 0.115 U^{-0.60} \quad [\text{Pa s}] \quad (2)$$

This trend was caused by the conformation of the fatty acid chains. The cis character of the carbon–carbon double bonds in these oils put kinks in the fatty acid chains, which increased the average distance between fatty acid chains. Therefore, intermolecular interactions decreased as the level of unsaturation increased. Evidence of this effect can be seen in the inverse relationship between the melting point and level of unsaturation for the triglycerides.[24] No shear thinning was observed in the range of tested shear rates.

Effects of the extent of epoxidation

The viscosity of the epoxidized oils increased slightly with the extent of epoxidation. The viscosity increased monotonically from approximately 50 cP for unmodified plant oils to as high as 750 cP for oils with 6.2 epoxide groups per triglyceride at room temperature. At 45°C, the viscosity increased monotonically with the level of epoxidation as high as 180 cP at 6.2 epoxides per triglyceride. The error in η_0 was no more than 5% for any level of epoxidation.

Increases in the molecular weight[11,19,20] and polarity[10,11] can cause such effects. Each epoxide group added to a triglyceride molecule increased its molecular weight by about 1.8%. This molecular weight change could be observed in the SEC results, in that the peak representing the triglyceride monomers shifted to lower elution times when the sample was epoxidized (Fig. 4). However, SEC results confirmed that there was only about 7% oligomerization during the epoxidation reaction.
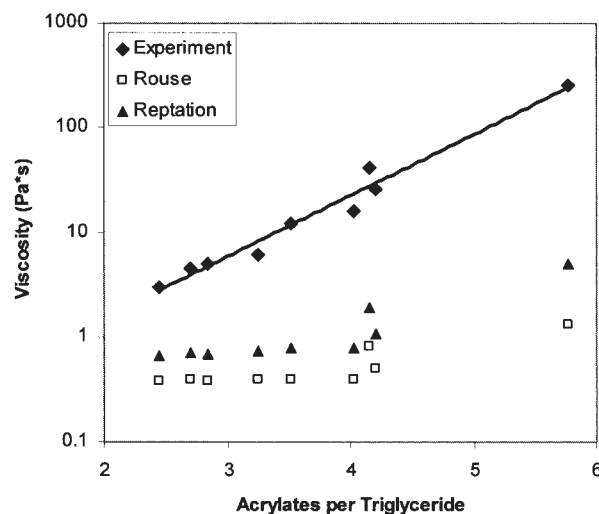

Figure 5 Viscosity as a function of the level of acrylation for maximally acrylated oils determined experimentally and predicted by Rouse and reptation theories.

The Rouse theory predicts that that the viscosity will scale with the molecular weight ($\eta_0 \sim M$) and applies to molecules below their critical entanglement molecular weight (M_c).[25] Reptation theory predicts that the viscosity will be a stronger function of the molecular weight ($\eta_0 \sim M^{3.4}$) but applies to entangled polymers with a molecular weight above M_c.[25] M_c is approximately 10^4 g/mol for most polymers and is much higher than the molecular weight of these chemically modified triglycerides,[11] so the Rouse theory should be valid. Anyway, the viscosity increases predicted by the Rouse and reptation theories were only 10 and 40%, respectively, at the maximum epoxidation of the oils used. These increases were considerably lower than the experimentally observed increases in the viscosity by over an order of magnitude. Thus, the increase in the molecular weight was not the main factor for the increased viscosity. In fact, the failure of the Rouse and reptation theories was expected because the chemical nature of the triglycerides changed as a result of epoxidation, and these theories do not account for changes in the molecular polarity. Epoxidized triglycerides are more polar than unmodified triglycerides. As a result, the polar nature of the epoxide groups increased intermolecular interactions, causing an increase in the viscosity.

Effects of acrylation on the triglyceride viscosity

The extent of acrylation had a large effect on the viscosity of acrylated oils (Fig. 5). η_0 of the acrylated oils increased exponentially with the level of acrylation (A) at 25°C:

$$\eta_0 = 0.104 \exp(1.34A) \quad [\text{Pa s}] \quad (3)$$

Acrylated triglyceride molecules contain a very polar hydroxyl group and ester linkage for every acrylate group added. These groups increase intermolecular interactions via hydrogen bonding and dipole–dipole interactions and thus cause an increase in the viscosity. The dipole moment of acrylated triglycerides was calculated with the Debye equation and a group contribution method.[26,27] The calculated dipole moments increased linearly from 0.95 to 1.25 debye/mol$^{0.5}$ as the acrylation level increased from 2.5 to 5.8. Therefore, the increase in the oil viscosity with the level of acrylation could at least partially be attributed to increases in the molecular polarity. Furthermore, it is possible that differences in the polarity between the very polar functional groups and the nonpolar triglyceride backbone induced clustering of the functional groups in these oils. Neutron scattering studies would need to be performed to determine if these oils have such a microstructure.

The molecular weight can also have an effect on the viscosity of acrylated oils. For every acrylate that was attached to the triglyceride, its molecular weight increased by approximately 8%. Therefore, the molecular weight of acrylated oils (~1300 g/mol) was up to 45% greater than that of epoxidized oils (~900 g/mol; Table I). The extent of oligomerization was fairly low (~10%) and did not change significantly with the level of acrylation. However, the molecular weight changes associated with the addition of acrylate groups and oligomerization could not cause the observed increases in the viscosity with the level of acrylation. The Rouse and reptation theories severely underpredicted the increase in the viscosity (Fig. 5). The Rouse theory predicted that the viscosity of maximally acrylated linseed oil (5.8 acrylate groups per triglyceride) should double with respect to that of epoxidized linseed oil, and the reptation theory predicted that the viscosity should increase by 1 order of magnitude. Yet, the experiment showed that the viscosity increased by 3 orders of magnitude as a result of acrylation. The failure of the Rouse and reptation models indicates that polarity effects caused the observed viscosity increase with the acrylation level.

The oil type had a small effect on the viscosity of the acrylated oils. η_0 of individual oils increased exponentially with the level of acrylation (Fig. 6), just as it did for maximally acrylated oils. Figure 6 also shows that η_0 of acrylated samples increased as the oil went from HOSO to soybean oil to linseed oil. Error bars were omitted because the error in the viscosity was only approximately 5% for each sample. Oligomerization did not cause this effect because the samples had similar molecular weights for the same level of acrylation (Table II). Polar groups at the end of a fatty acid chain are more likely to induce intermolecular interactions, which cause an increase in viscosity, whereas polar groups nearer the glycerol center mainly in-
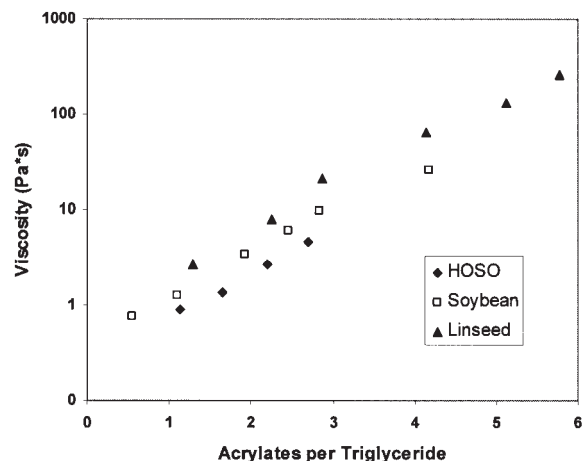

Figure 6 Viscosity as a function of the level of acrylation for acrylated HOSO, acrylated soybean oil, and acrylated linseed oil.

crease intramolecular interactions. The distance of the polar groups (i.e., hydroxyl and acrylate groups) from the glycerol center increased from acrylated HOSO to acrylated linseed oil. HOSO contains mostly oleic acid, and the unsaturation sites are located at the 9 and 10 carbon atoms with respect to the glycerol center.[1,24] Linseed oil contains mostly linolenic acid, and the unsaturation sites are located up to the 15 and 16 carbon atoms.[1,24] Soybean oil is between the two oils.[1,24] Because these oils are functionalized at the unsaturation sites, the distance of the functional groups from the glycerol center increased from HOSO to soybean oil to linseed oil. Therefore, linseed oil has the most functional groups at the end of its fatty acid chains, which induce intermolecular interactions, causing the viscosity to increase more than for the other oils.

The viscosity of the unmodified and chemically modified triglycerides was independent of the shear rate and time. This was expected because the acrylated triglycerides were not polymeric.

Effect of the temperature on the viscosity of acrylated triglycerides

As the temperature increased, the viscosity of the resin decreased exponentially (Fig. 7). As a result, increasing the temperature of these oils slightly could reduce their viscosities significantly, and this made them easier to process. The temperature dependence was accurately modeled (Fig. 7) with an Arrhenius relationship:[28]

$$\eta = \eta_\infty \exp\left(\frac{E_\eta}{RT}\right) \quad [\text{Pa s}] \qquad (4)$$

where η_∞ is the prefactor, E_η is the activation energy for viscous flow, R is the ideal gas constant, and T is
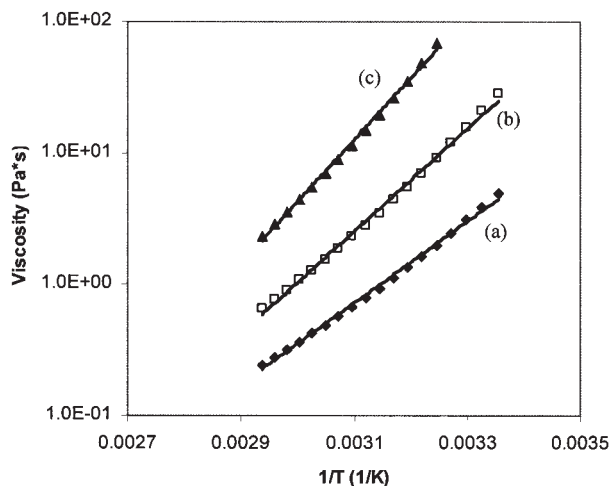
Figure 7 Experimental temperature dependence (symbols) of the viscosities of (a) maximally acrylated HOSO, (b) maximally acrylated soybean oil, and (c) maximally acrylated linseed oil and their Arrhenius fits (lines).

the absolute temperature. The deviation in the viscosity was less than 5% at a given temperature. On the basis of the Arrhenius fits, the activation energies were calculated. Increasing the level of acrylation caused the activation energy to increase linearly:

$$E_\eta = 10.4A + 29.8 \text{ (kJ/mol)} \quad (5)$$

In fact, the addition of a single acrylate group caused the activation energy to increase 10 kJ/mol. The increase in the activation energy with the level of acrylation was expected because temperature disrupts intermolecular interactions, and this has a larger effect on oils with more acrylate groups. On the basis of the small molecular weight increase of these oils with the acrylation level alone, this large change in the activation energy should not be observed. This is further evidence that polar interactions are the main cause for the increase in the oil viscosity as a function of the level of acrylation.

Effect of the comonomer on the viscosity of the triglyceride-based resins

The comonomers had a very large effect on the rheological character of the acrylated triglycerides. The sample viscosity (η) was normalized with respect to the pure comonomer viscosity ($\eta_{comonomer}$) and pure acrylated oil viscosity (η_{oil}):

$$\eta_{normalized} = \frac{\eta}{\eta_{comonomer} \eta_{oil}} \quad \left[\frac{1}{\text{Pa s}}\right] \quad (6)$$

where $\eta_{normalized}$ is the normalized viscosity. As the volume fraction of the comonomer ($\phi_{comonomer}$) in-

creased, $\eta_{normalized}$ decreased in an exponential manner (Fig. 8). This result was very encouraging, in that a small amount of the comonomer could be used to make these resin systems much easier to process. Furthermore, $\eta_{normalized}$ was not a function of the oil or comonomer (Fig. 8). $\eta_{normalized}$ was only a function of $\phi_{comonomer}$:

$$\eta_{normalized} = 1.2 \times 10^3 \exp(-14\phi_{comonomer}) \quad \left[\frac{1}{\text{Pa s}}\right] \quad (7)$$

Equation (7) can be used to predict the viscosity of any given solution of an oil and a comonomer. The viscosity dependence of mixtures of vinyl esters and unsaturated polyesters with styrene[29] and the viscosity dependence of concentrated polymer solutions[30] are similar to the results observed for the acrylated oils. The error in the viscosity was approximately 5% at all comonomer concentrations, as determined by repeat runs.

Triglyceride-based resins are similar in viscosity to commercial resins. In comparing resins with 33 wt % styrene, for example, we find that Dow Derakane 441-400 (400 cP)[31] has a viscosity similar to that of acrylated linseed oil. Therefore, using oils with fewer than 5.8 acrylates per triglyceride is desirable to reduce the styrene content in thermosetting resins with respect to that of Derakane 441-400. In fact, 25 wt % styrene is all that is necessary to reduce the viscosity of acrylated soybean-oil-based resins to 500 cP and results in an 8% reduction in hazardous content with respect to Derakane 441-400.
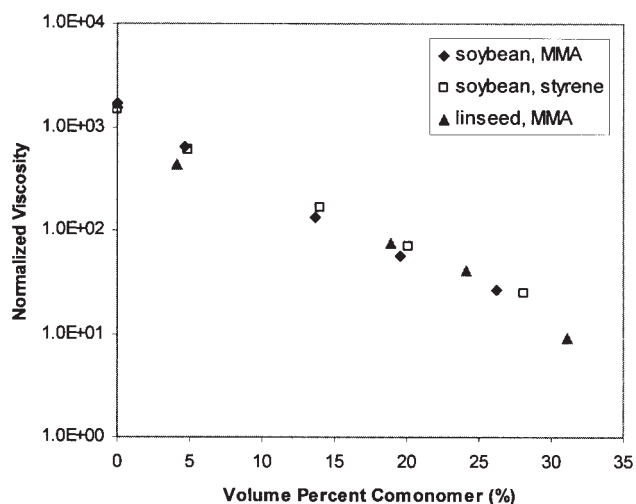

Figure 8 $\eta_{normalized}$ as a function of the volume percentage of the comonomer for three samples: acrylated soybean oil with MMA, acrylated soybean oil with styrene, and acrylated linseed oil with MMA.
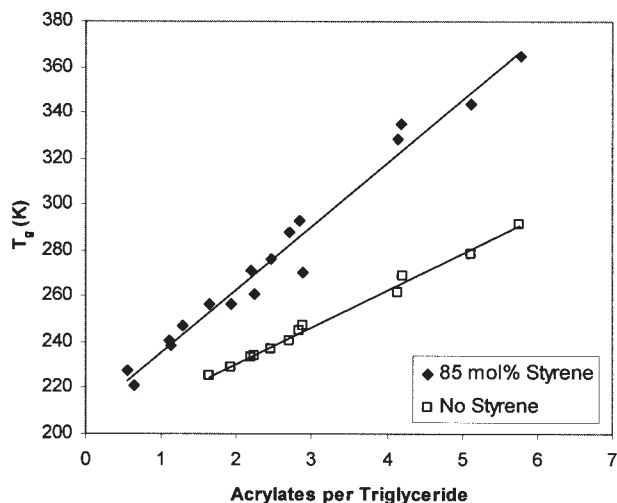
Figure 9 T_g as a function of the acrylation level for homopolymerized acrylated triglycerides and acrylated triglycerides copolymerized with 85 mol % styrene.

Dynamic mechanical effects

The dynamic mechanical properties of triglyceride-based polymers were affected by the acrylation level and styrene content. T_g increased linearly with the level of acrylation and was not a function of the particular oil used (Fig. 9). T_g was below 100°C at all levels of acrylation. At room temperature, the storage moduli ranged from 1 MPa to 2 GPa as the acrylation level increased from 0.5 to 4 acrylates per triglyceride and leveled off thereafter for samples with 85 mol % styrene. For homopolymerized triglycerides, the modulus increased from 4 MPa to 1 GPa as the acrylation level increased from 2 to 4 per triglyceride. T_g and the modulus increased with the acrylation level because the polymer was becoming more heavily crosslinked. The polymer properties improved as the styrene concentration increased (Fig. 9). For example, for oils with 4.2 acrylates per triglyceride, T_g increased from −4 to 40°C to 62°C as the styrene concentration increased from 0 to 20 to 33 wt %. Although increasing the styrene concentration reduced the crosslink density, the polymer properties increased because polystyrene has a higher modulus (~3 GPa) and T_g (~100°C)[32] than pure triglyceride-based polymers. Unlike the resin viscosity, high styrene contents are necessary to improve the properties of triglyceride-based polymers. However, for composites that will not be used at elevated temperatures, fairly stiff materials can be produced using resins with low styrene concentrations.

CONCLUSIONS

The viscosity of triglycerides increased as a result of chemical modifications that increased the intermolecular interactions among the molecules. The epoxi-dized triglycerides were slightly polar and had a higher viscosity than the unmodified triglycerides. The acrylated triglycerides were considerably more polar and, as a result, had a significantly higher viscosity. Oligomerization only occurred to a small extent in these oils, and the resulting increases in the molecular weight were too small to account for the observed increases in the viscosity and E_η. The viscosities of the acrylated oils were predicted accurately on the basis of their level of acrylation alone. Furthermore, the temperature dependence of the viscosity was accurately modeled with an Arrhenius relationship, and the activation energy could be predicted from the level of acrylation of the triglycerides alone.

Added comonomers acted like solvents and drastically reduced the viscosity of the triglyceride-based resins. In addition, the viscosity of a resin containing any acrylated plant oil and any comonomer was accurately predicted with only $\phi_{comonomer}$ and the viscosities of the pure components. Overall, the viscosity of these oils decreased exponentially as the distance between the acrylate and hydroxyl groups increased, whether this occurred through the addition of a comonomer or a reduction in the acrylation level. As the distance between the functional groups and the glycerol center increased, the viscosity of the acrylated oils increased slightly because intermolecular interactions increased.

At high levels of acrylation and at styrene concentrations of 30 wt % or greater, triglyceride-based polymers have good properties suitable for use in composite applications. Styrene concentrations in these resins can be reduced with respect to commercial resins using plant oils with five or fewer acrylates per triglyceride. However, polymer properties decrease significantly with the styrene concentration and acrylation level. Therefore, low-VOC, acrylate, triglyceride-based polymers may be best suited for use in gel coatings and other nonstructural applications.

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