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# Property analysis of triglyceride-based thermosets

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## Abstract

Triglycerides with acrylate functionality were prepared from various oils and model triglycerides. The triglyceride-acrylates were homopolymerized and copolymerized with styrene. The cross-link densities of the resulting polymer networks were predicted utilizing the Flory–Stockmayer theory. Although the model predictions overestimated the cross-link density, the trends in the cross-link density predictions matched the experimental results. In both cases, the cross-link density was found to increase gradually at low levels of acrylation and then linearly at higher levels of acrylation. The deviation in the experimental results and model predictions were the result of intramolecular cross-linking. Approximately 0.5 and 0.8 acrylates per triglyceride were lost to intramolecular cyclization for homopolymerized triglyceride-acrylates and triglycerides copolymerized with styrene, respectively. The glass transition temperature ($T_g$) increased approximately linearly with the cross-link density from as low as $-50$ °C to as high as 92 °C. Simple models accurately predicted the effect of cross-link density on $T_g$. The tensile strength and modulus of triglyceride-based polymers increased exponentially at low levels of acrylate functionality, but increased linearly at higher levels of acrylate functionality, as predicted by vector percolation theory.

*Keywords:* Triglyceride-based thermosetting polymers; Vector percolation; Thermo-mechanical properties

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## 1. Introduction

Triglycerides are the main component of plant oils, such as soybean oil, corn oil, etc. Triglycerides are composed of three fatty acids connected by a glycerol center (Fig. 1). There are numerous ways of chemically modifying the unsaturated sites on the fatty acids [1,2], many of which can be used to make polymers. Triglyceride-based polymers have been used as toughening agents in PVC and epoxy resins [3], and as the major component of a number of natural resins [1,4], composites [5], and pressure-sensitive adhesives [6].

The triglyceride-based polymers studied in this work are analogous to vinyl esters (VE) and unsaturated polyesters (UPE) [7], such that chemically modified triglycerides have multiple functional sites per molecule, which allow the resins to cross-link. In addition, VE, UPE, and triglyceride resins are typically copolymerized with a low molecular weight species, such as styrene, to modify the properties of the polymer and lower the resin viscosity [7]. The low viscosities of these resins make them ideal for inexpensive polymer composite fabrication processes, such as vacuum assisted resin transfer molding.

Triglyceride-based resins are an attractive alternative to petroleum-based resins because they are inexpensive, have good properties, and are derived from renewable resources. Furthermore, the advent of genetic engineering technology, which can drastically change the fatty acid composition of triglycerides in plant oils, offers a large potential for inexpensively improving the properties of these polymers. However, unlike petroleum-based resins, triglyceride cross-linkers have a wide distribution of functionality ranging from zero to nine polymerizable groups per molecule [8].

Typically triglyceride-based polymers form gels, which can be hard or soft depending on the level of functionalization of the triglycerides, extent of polymerization, comonomer type, and comonomer content. In an effort to improve the properties of plant oil-based thermosetting resins, this work examines the effect of triglyceride molecular structure on the resulting polymer properties. The use of simple new models, such as vector percolation, to predict the

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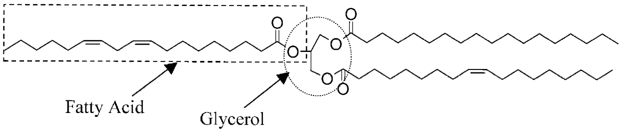

Fig. 1. The molecular structure of a typical triglyceride molecule. Three fatty acids are connected to a glycerol center.

mechanical properties of triglyceride-based polymers, are presented and assessed.

## 2. Experimental section

### 2.1. Monomer synthesis

Epoxidized samples (as shown in Fig. 2(a)) were made by reacting the unsaturated sites of oils and model triglycerides with a mixture of formic acid and hydrogen peroxide as presented elsewhere [6,9]. The oils used in this work have similar molecular weights, but different levels of unsaturation ranging from 2.8 to 6.4 sites per triglyceride [8]. Olive oil, cottonseed oil, canola oil, corn oil, soybean oil, safflower seed oil, linseed oil, and triolein (99%) were purchased from Sigma-Aldrich. These oils have considerably different fatty acid distributions, but have similar molecular weights [10]. DuPont Corporation (Wilmington, DE) provided the genetically engineered high oleic soybean oil (HOSO).

Acrylate monomers were prepared by reacting the epoxide groups of epoxidized oils and epoxidized triglycerides with acrylic acid as presented elsewhere [6,9] (Fig. 2(b)). The AMC-2 catalyst (Aerojet Chemicals, Rancho Cordova, CA), which is a proprietary mixture of 50% trivalent organic chromium complexes and 50% phthalate esters, was used to reduce the extent of epoxy homopolymerization [11]. The AMC-2 was used in every sample at a concentration of 0.02 g/ml. A concentration of 0.0033 g/ml hydroquinone was used to inhibit free-radical polymerization. The oils were maximally acrylated by adding 1.1 mol of acrylic acid per epoxide group to the reaction mixture. The effect of acrylation level on the polymer properties can also be determined by acrylating a single oil to different extents. Epoxidized high oleic soybean oil, 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 silicone oil bath on a hot plate while stirring vigorously. The acrylates were purified using an ether extraction [6,9]. The samples were dissolved in ether and washed with aqueous sodium bicarbonate until the pH of the solution was slightly alkaline. The contents were allowed to phase separate, and the aqueous layer was discarded. Finally, the solution was washed with aqueous sodium chloride and dried over sodium sulfate. The ether was removed by heating at 40 °C under vacuum. The extents of epoxidation and acrylation were measured using $^1$H NMR [9] (250.13 MHz, spectral window of $\pm$2000 Hz, 0.427 Hz/pt digital resolution, 16 scans at 293 K, 90° pulse width) with a Bruker (Billerica, MA) AC250 Spectrometer. Using both methods, the level of functionalization was varied from 0.6–5.8 acrylates per triglyceride.

### 2.2. Polymer preparation

Each triglyceride-acrylate was polymerized without comonomer, using 0.015 g/ml Hi Point 90 (Witco, Marshall, TX) as the free-radical initiator. Hi Point 90 is composed of a mixture of methyl ethyl ketone peroxides with relatively low molecular weights and different decomposition temperatures. In addition, every oil was copolymerized with 87.5 mol% styrene (Aldrich Chemicals, Milwaukee, WI; 99%) and a Hi Point 90 concentration of 0.015 g/ml.

Triglyceride-based polymer samples were made for dynamic mechanical analysis and tensile testing. To prevent oxygen free-radical inhibition, the resin was purged with nitrogen gas prior to curing. The resin was then poured into vertical molds. The vertical molds consisted of a silicone rubber mold (Dow Corning, Midland, MI) sandwiched between two aluminum plates using binder clamps. The silicone molds had four equally spaced slots 1.1 cm wide, 0.5 cm thick, and 8.3 cm tall for DMA samples. For tensile samples, the silicone rubber mold was 0.12 cm thick and the space for the liquid resin was 7 cm wide and 5 cm tall. A sheet of Kapton film was used on both sides of the silicone rubber to help make a very flat surface. All mold components were sprayed with PTFE 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 and 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 post-cured for 2 h at this temperature. The DMA samples were polished down to

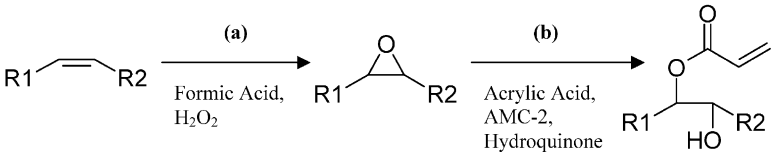

Fig. 2. The (a) epoxidation and (b) acrylation of triglycerides.

approximate dimensions of 5.5 cm long × 0.9 cm wide × 0.4 cm thick using 320 grit sandpaper on a polishing wheel. The samples that were molded to make tensile samples were cut into dog-bone samples using a die press (Dewes Gumbs Die Co., NY, NY). Samples that were very rigid were heated with a heat gun to facilitate the cutting process. The resulting samples had a gage length of 10.0 mm, a gage width of 4.05 mm, and a thickness of 1.2 mm. The exact sample dimensions were measured before testing.

### *2.3. Mechanical and thermo-mechanical testing*

The thermo-mechanical properties of the triglyceride-based polymers were tested using a Rheometrics Solids Analyzer II (Rheometrics Scientific Inc.). Before testing, the exact sample dimensions were measured. The samples were tested in three-point bend 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 rubber modulus was calculated from values of the DMA storage modulus that were within the plateau region of the modulus. The exact point selected was at the temperature where the modulus started to increase with temperature. Comonomer content had a large effect on this temperature relative to the tan $\delta$ maximum. For samples without styrene, the rubber modulus increased with temperature at ~100 °C above the maximum in tan $\delta$. For samples with 87.5 mol% comonomer, this temperature occurred at ~50 °C above the maximum in tan $\delta$. The experimental cross-link density values were calculated from the rubber moduli of the polymers. Rubber elasticity theory shows that the molecular weight between cross-links, $M_c$, and cross-link density are related to the modulus of elasticity, $E$, of rubbers [12,13] (Eq. (1)):

$$E = 3RT\rho/M_c = 3RT\nu \tag{1}$$

where $R$ is the ideal gas constant, $T$ is the absolute temperature, $\nu$ is the cross-link density, and $\rho$ is the polymer density. The polymer densities increased slightly with the acrylation level and ranged from 1.04 to 1.11 g/cm$^3$. Styrene content had little effect on the density. The temperature corresponding to the maximum in the loss modulus was taken as $T_g$ of the polymer [14].

The samples were tested in tensile mode on a 4201 Instron (Canton, MA) using ASTM D 638M [15]. A cross-head speed of 0.5 mm/min was used. The temperature was 26 °C ± 1 °C, and the relative humidity was 50% ± 5% during sample testing. Pneumatic grips were used to hold the sample. The maximum grip pressure that did not deform the sample was used. At least five repeat runs were performed for each sample.

### *2.4. Fourier transform infrared spectroscopy (FTIR)*

A Nicolet Magna 860 Fourier FTIR operating in transmission mode with 4 cm$^{-1}$ resolution was used. The set-up of the FTIR cell is explained elsewhere [16]. A drop of the resin was sandwiched between two 25 mm diameter NaCl disks (International Crystal Labs) separated by a 0.025 mm thick Teflon™ spacer (International Crystal Labs). One sodium chloride disk was 2 mm thick while the other was 4 mm thick. The salt plate assembly was placed in a cell holder. The temperature of the cell holder can be controlled to within ±0.1 °C of the set-point. The cell holder was kept at room temperature until the salt plate assembly was placed in the holder. Then, the set point temperature of the cell holder was increased to the cure temperature and the first FTIR scan was taken. All resin mixtures were cured at 90 °C for 2 h and post-cured at 120 °C for an additional 2 h. An FTIR spectrum, comprised of 16 scans, was taken every 10 min during the cure reaction.

The styrene and acrylate conversions were measured as a function of time by relating the absorbance of the peak of interest to the peak heights of internal standards as a function of time [16] (Eq. (2)):

$$\alpha = 1 - \left(\frac{\mathrm{ABS}(t)_{\mathrm{peak}}}{\mathrm{ABS}(t=0)_{\mathrm{peak}}}\right)\left(\frac{\mathrm{ABS}(t=0)_{\mathrm{standard}}}{\mathrm{ABS}(t)_{\mathrm{standard}}}\right) \tag{2}$$

The peak at 990 cm$^{-1}$ represents a vibrational mode of the vinyl group on acrylate groups [17,18]. The peak at 910 cm$^{-1}$ represents both the acrylate [17,18] and styrene carbon–carbon double bond [16]. The internal standards used were the peaks at 1744 cm$^{-1}$, corresponding to the ester groups on the triglycerides [17], and the peak at 700 cm$^{-1}$, representing the aromatic C–H stretch on styrene [16]. Neither of these groups were affected by the polymerization reaction.

## 3. Results and discussion

### *3.1. Extent of cure*

The ultimate conversion of styrene ($x_u^S$) was greater than 0.90 and the ultimate conversion of acrylate groups ($x_u^A$) was over 0.94 for all samples (Table 1). The ultimate conversion of acrylate groups decreased slightly as the level of acrylate functionality increased for samples without comonomer. This occurred because diffusion limitations of growing radicals became more severe as the cross-link density of the network increased. When comonomer was used, the level of acrylation had no effect on the acrylate conversion. The presence of comonomer was expected to increase the conversion of acrylate groups because the comonomer delays the gel point and reduces diffusion limitations. The conversion of styrene did not change as the comonomer

Table 1
The ultimate conversion of styrene and acrylated oils in triglyceride-based polymers

| Oil | Acrylates per triglyceride | Styrene mole fraction | Acrylate conversion | Styrene conversion |
|---|---|---|---|---|
| HOSO[a] | 2.7 | 0 | 0.96 | – |
| Soybean | 4.2 | 0 | 0.95 | – |
| Linseed | 5.8 | 0 | 0.94 | – |
| HOSO | 2.7 | 0.85 | 0.99 | 0.91 |
| Soybean | 4.2 | 0.85 | 0.99 | 0.93 |
| Linseed | 5.8 | 0.85 | 0.98 | 0.95 |

[a] HOSO—a genetically engineered high oleic soybean oil.

content was increased, but it did increase slightly as the level of acrylate functionality increased.

These results suggest that the sol content of these polymers is low. Sol contents are expected to increase as the comonomer content increases and acrylate functionality decreases. Regardless of the sol content, there was no evidence of phase separation in the DMA plots, and all samples were clear and homogeneous.

### 3.2. Cross-link density

The cross-link density increased with the level of acrylate functionality for samples with and without styrene (Fig. 3). The cross-link density was higher for samples without styrene because styrene is a linear chain extender and therefore does not contribute to cross-linking. For samples with styrene, the cross-link density increased slowly at low levels of acrylate functionality (i.e. up to about 2.5 acrylates per triglyceride) (Fig. 3(a)). At higher levels of acrylate functionality, the cross-link density increased linearly. This was a result of the fact that at low levels of acrylate functionality, the functional groups mainly linearly extended the polymer chains rather than cross-linking them. However, at higher levels of acrylate functionality, each additional functional group increased the cross-link density. For samples without styrene, the cross-link density increased with the number of acrylates per triglyceride (Fig. 3(b)). Samples with very low acrylate functionality ($<2$ acrylates per triglyceride) could not be tested because they were too brittle or did not cure. The molecular weight between cross-links, as calculated using Eq. (1), ranged from 80 to 20,000 g/mol, and indicates that some of these networks were very highly cross-linked while some were only lightly cross-linked. The plant oils used in this work had highly varied fatty acid compositions, which results in significantly different acrylate distributions. However, the distribution of acrylate groups did not have a significant effect on the cross-link density, as can be seen by the fact that cross-link density was a single function of acrylation (Fig. 3).

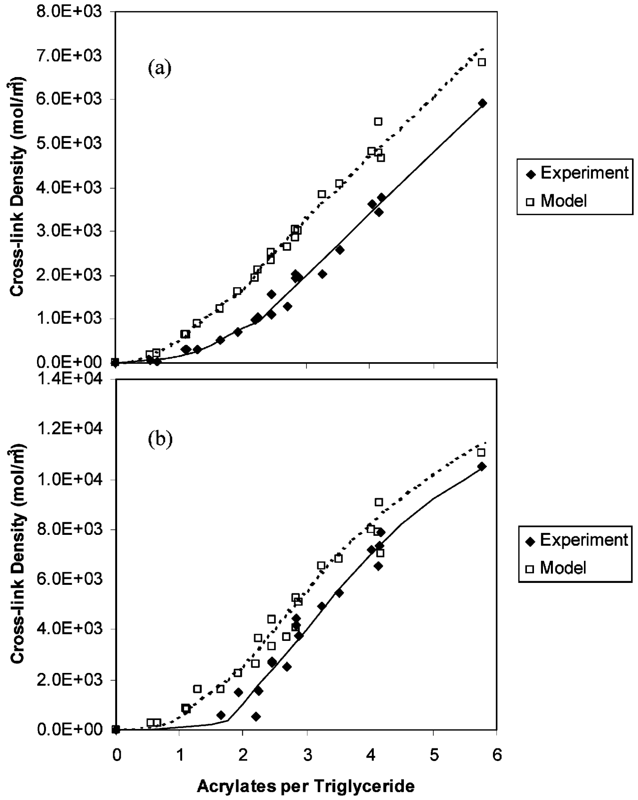

Fig. 3. The cross-link density determined experimentally and predicted from the Miller and Macosko model for triglyceride-based polymers (a) with 87.5 mol% styrene and (b) without styrene.

The cross-link density as defined by Eq. (1) is the density of chains or segments that connect two infinite parts of the polymer network, rather than the density of cross-link junctures. The cross-link density is affected by the functionality of the cross-linker molecule. Vinyl polymers are typically represented as having two functional groups, $f$, per vinyl group, $n$ [19] (Eq. (3)):

$$f = 2n \tag{3}$$

The number of functional groups on a cross-linker that polymerizes and leads to another cross-linked molecule is $m$, where $m \leq f$. For examples, triglycerides with $m=1$ functional group are dangling chain-ends. The functionality, $m$, and the number of cross-linked chains, $N_x$, per triglyceride are related (Eq. (4)):

$$N_x = 3m/2 - 3 = 3n - 3 \tag{4}$$

Therefore, with $m$ in the range 0–18, the number of cross-link chains varies from 0 to 24 per triglyceride, depending on the functionality. The positional distribution of the functional groups does not affect $N_x$. Therefore, the structure of the triglyceride (i.e. three chemically linked fatty acids) has no effect on the cross-link density except that it allows each triglyceride molecule to have a different number of functional groups and cross-links.

Flory and Stockmayer used the principles of branching and cross-linking to derive the cross-link density for addition polymers [19]. The number of cross-links per molecule in divinyl polymers is (Eq. (5)):

$$c = \theta c_0 \tag{5}$$

where $\theta$ is the extent of polymerization (as determined by FTIR) and $c_0$ is the fraction of polymerizable groups on the cross-linking agent. Eq. (5) is defined for cross-link sites rather than cross-link segments. Eq. (6) accounts for this and generalizes Eq. (5) for a mixture of cross-linking agents with $n$ polymerizable groups (i.e. vinyl groups):

$$c = \theta \sum_{n=2}^{n=9} \Phi_n(3n - 3) \tag{6}$$

where $\phi_n$ is the fraction of triglycerides with $n$ polymerizable groups. The molecular weight between cross-links is simply the average molecular weight of the monomers, $M_{\mathrm{av}}$, divided by the number of cross-links per molecule (Eq. (7)):

$$M_{\mathrm{c}} = M_{\mathrm{av}}/c \tag{7}$$

The cross-link density resulting from chemical cross-link chains can then be calculated by dividing the polymer density by $M_{\mathrm{c}}$.

Intramolecular cyclization in finite species causes the delayed gel point relative to the predictions of Flory–Stockmayer [19]. However, intramolecular cyclization only affects the cross-link density when a growing polymer chain polymerizes with functionality on the same triglyceride before it polymerizes with functionality on another cross-linking agent. Other forms of intramolecular cyclization reactions must occur for gelation and stiffening of the thermosetting polymer to occur. Intramolecular cyclization of functional groups on the same triglyceride reduces the number of effective attachment points of this triglyceride to the rest of the network. When a triglyceride reacts with itself, it forms a loop that is not attached to the rest of the polymer network. Consequently, this reduces the cross-link density of the resulting polymer. Every time two functional groups react in this way, the effective number of functional groups per triglyceride is reduced by 2. Therefore, Flory–Stockmayer model should overestimate the cross-link density because of intramolecular cyclization. Similar theories, such as Miller–Macosko [20], predict similar results.

Fig. 3 shows the predictions of the Flory–Stockmayer model along with the experimentally determined cross-link densities. The model over-predicted the cross-link density at all levels of acrylate functionality for polymers with and without styrene. This was expected because the model did not account for intramolecular cyclization of triglycerides. In addition, rubber elasticity theory is not expected to completely apply to these highly cross-linked polymers, but at least should show general trends in how cross-link density is affected by the acylation level. In fact, the model's predictions matched the trends in the experimentally determined cross-link densities. Both plots show that the predicted and experimentally determined cross-link densities increased linearly as the acrylate functionality level increased above a certain value. Therefore, for the most-part, the cross-link density is proportional to the number of acrylates per triglyceride. Both plots show that the model accurately predicted that the cross-link density increased at a lower rate at low levels of acrylate functionality. However, the model and experiment disagree on the point where the cross-link density should increase linearly because of the over-prediction of the cross-link density.

The model predicted that there was some level of cross-linking regardless of the level of acrylate functionality. However, monomers with low functionality ($<0.5$ acrylates per triglyceride with styrene and $<1.5$ acrylates per triglyceride without styrene) did not cure. Again, this was due to the effect of intramolecular cyclization. The extent of intramolecular cyclization can be quantified by fitting the model results to the experimental results. The shift required to equate the model cross-link density, $\nu_{\mathrm{model}}(A)$, to the experimentally determined cross-link density, $\nu_{\mathrm{exp}}(A)$, was $A_{\mathrm{lost}}$ (Eq. (8)):

$$\nu_{\mathrm{model}}(A - A_{\mathrm{lost}}) = \nu_{\mathrm{exp}}(A) \tag{8}$$

The number of acrylate groups lost towards intramolecular cyclization, $A_{\mathrm{lost}}$, is plotted as a function of the level of acrylate functionality in Fig. 4 for triglyceride-acrylates copolymerized with styrene. The amount of intramolecular cyclization increased with the number of acrylates per triglyceride at low levels of functionality. After $\sim 2$

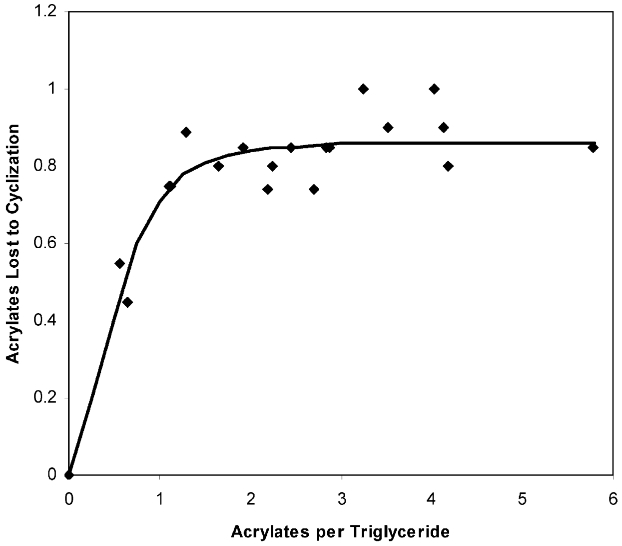

Fig. 4. The number of acrylate groups lost due to intramolecular cyclization of the triglycerides for polymers copolymerized with styrene (87.5 mol%).

acrylates per triglyceride, the amount of intramolecular cyclization was constant. Overall, the model predicted that the amount of intramolecular cyclization reduced the effective functionality by approximately 0.7–0.9 acrylates per triglyceride for polymers copolymerized with styrene. The presence of styrene in samples with low acrylate functionality levels actually decreased the extent of intramolecular cyclization, as expected. The concentration of triglycerides with two or more acrylates per triglyceride was very low in samples with low functionality levels. As a result, the probability of intramolecular cyclization should be high relative to the probability for cross-linking. However, the presence of styrene reduced the rate of cyclization at low levels of functionality by propagating the growing radical away from the triglyceride molecule. In addition, samples with low levels of acrylate functionality were more likely to terminate by chain transfer, which lowers the cross-link density [21].

The amount of acrylate groups lost to intramolecular cyclization was approximately 0.5 for homopolymerized triglycerides at all levels of functionality. Any trends in the amount of intramolecular cyclization were obscured because of the scatter in the cross-link density as a function of acrylates per triglyceride. In all cases, the amount of intramolecular cyclization was less than 1 acrylate per triglyceride. This could indicate that 1 cyclization event per triglyceride was a maximum. After this cyclization event occurs, further intramolecular cyclization of acrylate groups on the same triglycerides may be sterically hindered. However, more work needs to be done to verify this.

The rubber modulus determined from dynamic mechanical analysis is a measure of the effective cross-link density of polymers. The effective cross-link density takes into account chemical and physical cross-links [13,22]. Chain entanglements can increase effective cross-linking. However, for chain entanglements to occur in branched and linear polymer systems, the molecular weight of the polymers chains must be greater than the entanglement molecular weight, which is on the order of at least $10^4$ g/mol [23]. Only the resins with 0.56 and 0.65 acrylates per triglyceride copolymerized with styrene had molecular weights between cross-links that were on that order of magnitude. Therefore, it was possible that chain entanglements increased the effective cross-link density and decreased the calculated extent of intramolecular cyclization for polymers with low levels of acrylate functionality. However, it was unlikely that chain entanglements had much of an effect on the other samples.

### 3.3. Glass transition

The DMA behavior of these polymers was similar to that of other thermosetting polymers [7]. However, the glass transition region was very broad and the glassy modulus was a strong function of temperature relative to other thermosetting resins because of the large amount of relaxation modes available to triglyceride-based polymers [4]. The breadth of the glass transition decreased as the styrene content in the resin increased and as the acrylate functionality level decreased [24]. However, DMA studies show no evidence of phase separation within these materials.

The glass transition temperature increased linearly with the number of acrylates per triglyceride. $T_g$ was related to the level of acrylate functionality, $A$, for polymers without styrene (Eq. (7)):

$$T_g = 16.1A - 74.7[°\mathrm{C}] \tag{9}$$

and for polymers with styrene (Eq. (8)):

$$T_g = 27.5A - 65[°\mathrm{C}] \tag{10}$$

$T_g$ of these polymers with styrene ranged from −50 to 92 °C over the range of 0.6–5.8 acrylates per triglyceride. Without styrene, $T_g$ ranged from −50 to 18 °C over the range of 1.7–5.8 acrylates per triglyceride. Therefore, the level of acrylate functionality can be varied to make very soft through very rigid materials. The glass transition temperature was significantly higher for the samples with styrene because the aromatic nature of styrene imparted rigidity to the network. $T_g$ increased linearly through 5.8 acrylates per triglyceride. However, it would be expected that $T_g$ would not increase higher than $T_g$ of the copolymer (i.e. $T_g \sim 100$ °C for polystyrene [25]). We would expect $T_g$ to level off at ~100 °C after some level of functionalization, but we have not seen the point where this occurs. $T_g$ was not dependent on the oil type, in that different oils acrylated to the same level had similar $T_g$. Furthermore, $T_g$ of maximally acrylated oils and partially acrylated oils with the same level of functionalization were similar.

Because the cross density is mainly proportional to the level of acrylate functionality, $T_g$ also increased in a linear fashion with the cross-link density (Fig. 5) because tightening of the polymer network reduced the mobility of the polymer chains. $T_g$ increased approximately linearly with the cross-link density for homopolymerized triglycerides (Fig. 5) (Eq. (11)):

$$T_g[\mathrm{K}] = 0.0055\left[\frac{\mathrm{K\ m^3}}{\mathrm{mol}}\right]\nu + 225[\mathrm{K}] \tag{11}$$

The $y$-intercept, 225 K, was the theoretical glass transition temperature of the triglyceride-based polymers with no cross-linking, $T_g^u$. This value closely matched the $T_g$ of linear polymers made from fatty acid methyl esters [6]. For triglyceride polymers copolymerized with styrene, $T_g^s$ ($T_g$ for samples copolymerized with styrene) increased at a high rate at low cross-link densities, then increased at a lower rate at mid to high cross-link densities (Fig. 5). At low cross-link densities, $T_g^s$ deviated from linearity because triglycerides with low functionality were able to cure with styrene, while they did not cure when there was no styrene present. At higher cross-link densities, $T_g^s$ deviated from linearity

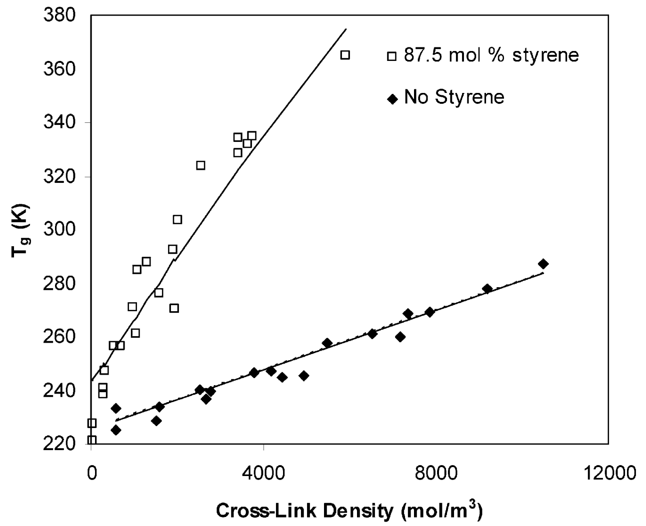

Fig. 5. The effect of cross-link density on the glass transition temperature of homopolymerized triglyceride polymers and triglycerides copolymerized with 87.5 mol% styrene. The experimental results are shown as the data points, while the predictions of the Fox and Loshaek model [26] are the solid lines.

because $T_g$ was approaching that of poly(styrene), and therefore, could not continuously increase with cross-link density. As a result, $T_g^{u,s}$(actual) = 225 K was lower than expected for these polymers. However, a linear relationship did an adequate job of approximating $T_g$ at all cross-link densities (Eq. (12)):

$$T_g^s[\mathrm{K}] = 0.024\left[\frac{\mathrm{K\,m^3}}{\mathrm{mol}}\right]\nu + 243[\mathrm{K}] \qquad (12)$$

Various models predict $T_g$ based on the cross-link density. For example, Fox and Loshaek derived an expression relating $T_g$ to the cross-link density by assuming the specific volume of the polymer at the glass transition to be a linear function of $T_g$ (Eq. (13)) [26]:

$$T_g = T_g^u + \frac{K_n}{M_c}[\mathrm{K}] \qquad (13)$$

where $K_n$ is a material constant. For homopolymerized triglycerides, the model accurately predicted $T_g$ for all cross-link densities and predicted a linear dependency that matched Eq. (11) (Fig. 5). The parameter $K_n = 5.2 \times 10^3$ K g/mol was used to fit the model to the experiment results. The values of this parameter indicate that moderately cross-linked triglyceride-based polymers with $M_c =$ 500 g/mol would have a value of $T_g$ 10 °C higher than that of uncross-linked homopolymerized triglycerides. For triglycerides copolymerized with styrene, the Fox and Loshaek model predicted a linear fit (Fig. 5) that matched Eq. (12) when $K_n = 2.5 \times 10^4$ K g/mol. Other more complex models, such as the Stutz model [27], can be used to capture the non-linear effects at lower cross-link densities. These results show that $T_g$ for triglyceride-based polymers were predictable based on their cross-link densities.

The prediction for the dependence of $T_g$ on the cross-link density $\nu$, is also given by vector percolation theory [28] as the linear relation (Eq. (14)):

$$T_g(\nu) = T_g^0 + (T_g^0 M_{ox}/p_c\rho)\nu \qquad (14)$$

where $\rho$ is the density, $M_{ox}$ is the molecular weight per backbone atom of the cross-linking chain structure, $T_g^0$ is the $T_g$ of the linear polymer extrapolated to $\nu = 0$ and $p_c$ is the thermal vector percolation threshold when the glassy modulus approaches zero. This relation is in qualitative and quantitative accord with our $T_g$ vs. $\nu$ data, and the Fox–Loshack theory. The slope of 0.0055 [K m$^3$/mol] in Eq. (11) for the pure triglycerides should be determined by the factor $(T_g^0 M_{ox}/p_c\rho)$ in Eq. (14); with $T_g^0 = 225$ °K, $p_c = 0.5$, $M_{ox} \approx 14$ g/mol and $\rho = 1.1 \times 10^6$ g/m$^3$, we calculate the slope to be about 0.0057 [K m$^3$/mol], which is good agreement with the experimental value.

### 3.4. Tensile properties

The mechanical properties of triglyceride-based polymers were strong functions of the number of acrylates per triglyceride. The tensile properties of these polymers increased exponentially with the level of functionality up to 3 acrylates per triglyceride (Figs. 6 and 7). The properties then leveled off beyond 3 acrylates per triglyceride. To an excellent first approximation, the oil type did not have a significant effect on the modulus or strength of these polymers, as linseed-, soybean-, and HOSO-based polymers with similar functionality levels had similar properties. The mechanical properties were very low at low levels of acrylate functionality because the cross-link density was very small (Fig. 3). As the cross-link density increased, the polymer chains became more tightly bound to each other, which increased the properties. This was indicative of a percolation phenomenon [29,30]. Obviously, the fact that $T_g$ increased as the acrylate functionality level increased was also a reason that the modulus increased.

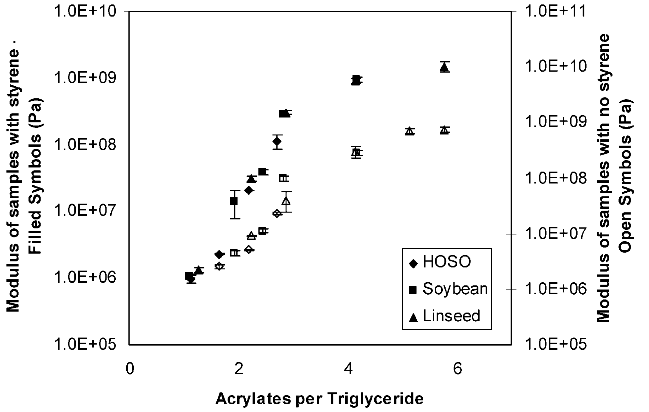

Fig. 6. The tensile modulus as a function of the level of acrylate functionality for polymers with 87.5 mol% styrene (filled symbols) and without styrene (open symbols) using oils acrylated to different extents.

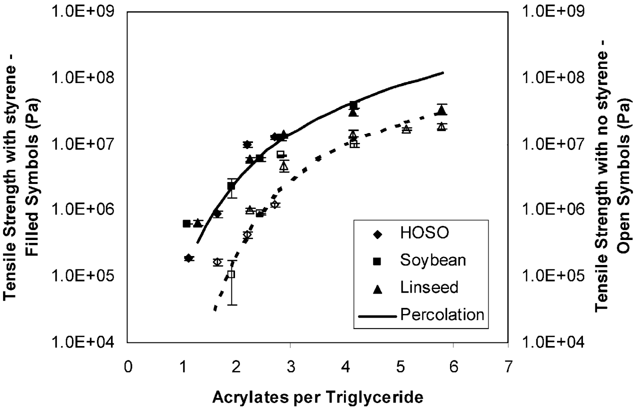

Fig. 7. The tensile strength as a function of the level of acrylate functionality for polymers with 87.5 mol% styrene (filled symbols) and without styrene (open symbols) using oils acrylated to different extents. The predictions of the vector percolation model are also shown (solid line for samples with styrene, dashed line for samples without styrene).

Percolation theory is a simple way to predict the strength of polymers as a function of cross-link density. Percolation theory relates the polymer properties to the connectivity of the polymer network. The critical stress, $\sigma_c$, required to break a thermoplastic network is (Eq. (15)) [31]:

$$\sigma_c = [\sigma_0 E \nu_c (P - P_c)]^{1/2} \tag{15}$$

where $E$ is the tensile modulus, $\nu_c$ is the critical entanglement density, $\sigma_0$ is a constant of proportionality representing the energy to disentangle or break bonds, $P$ is the level of perfection of the entangled network (i.e. $P=1$ for a perfect network), and $P_c$ is the percolation threshold. For thermosetting systems, there is no critical cross-link density. The cross-link density can theoretically increase to as high as found in graphite, but will more likely level off at a value of $\sim 10^4$ mol/m$^3$ for most cross-linked polymer systems. The extent of cross-linking exceeded the percolation threshold for all of the polymers tested, considering that the polymers had gelled and had enough mechanical integrity for mechanical testing. For examining the effect of different extents of cure, the term $P$–$P_c$ would be important. However, for fully cured thermosetting systems, this value is likely to be constant. The level of perfection is affected by the morphology of the system, but DMA traces indicated no differences in phase behavior and cure studies indicated that the level of triglyceride functionality has no significant effect on reactivity ratios. Therefore, the strength of these triglyceride polymers can be estimated as (Eq. (16)):

$$\sigma_c = [\sigma_0 E \nu]^{1/2} \tag{16}$$

Percolation theory has also been used to predict the modulus [29,30]. However, these theories do not account for $T_g$ effects. As seen by Fig. 5, $T_g$ increased from below to above room temperature as the level of acrylate functionality increased, which caused the steep increase in the modulus from 2 to 3 acrylates per triglyceride (Fig. 6). Therefore, percolation theory was not used to predict the modulus. On the other hand, Eq. (15) is expected to be valid regardless of varying $T_g$ because the equation separates out stiffness effects and bond energy effects.

Fig. 7 shows that vector percolation theory adequately described the tensile strength as a function of acrylation level. Thus, the strength improvements with functionality level are indeed percolation phenomena. The vector percolation predictions of tensile strength were calculated using the experimentally determined cross-link densities. For both samples with and without styrene, vector percolation predictions at high functionality levels overestimated the strength. This may have occurred because other failure mechanisms were beginning to dominate at high cross-link densities for this triglyceride-based polymer system.

The constant of proportionality, $\sigma_0$, was $5\times10^3$ J/mol for samples with 87.5 mol% styrene and $1.4\times10^2$ J/mol for samples without styrene. This indicates that styrene improves the mechanical integrity of the network through means other than simply increasing the modulus or affecting the cross-link density. Similar thermosetting systems, such as unsaturated polyesters and vinyl esters, typically form microgels of high cross-link density at the initial stages of cure, which link up at higher extents of cure [32]. The cracks that form during failure need not travel in a straight line through the material, but instead could travel through the path of least resistance. In other words, the crack can travel through regions of much lower cross-link density and stiffness than the average across the whole polymer. Therefore, a possible explanation for the values of $\sigma_0$ is that homopolymerized triglycerides have greater microscopic variance in the stiffness and cross-link density than triglycerides polymerized with high styrene contents.

## 4. Conclusions

Triglyceride-acrylates were prepared from various oils and model compounds. The cross-link densities of the resulting polymers were calculated using the extent of cure as measured with FTIR and Flory–Stockmayer theory. The cross-link density was found to increase gradually at low functionality and linearly at higher functionality levels, and the trends in the cross-link density predictions matched the experimental results. The deviation in the experimental results and model predictions were the result of intramolecular cross-linking. Approximately 0.5 and 0.8 acrylates per triglyceride were lost to intramolecular cyclization for homopolymerized triglycerides and triglycerides copolymerized with styrene, respectively.

The level of acrylate functionality affected the properties of triglyceride-based polymers in a manner that can be predicted using simple models. The glass transition temperature increased in a linear fashion with the cross-link density. Simple models, such as those proposed by Fox and Loshaek, can be used to accurately predict $T_g$ of triglyceride-based polymers. In addition, $T_g$ as well as the tensile strength of triglyceride-based polymers were accurately predicted using vector percolation theory. The vector percolation behavior of these polymers was a result of the polymer chains becoming more tightly bound to each other as the cross-link density increased with increasing network perfection. Overall, triglyceride-based polymers are very complex, containing cross-linker molecules with a range of functionality. Yet, the polymer properties are well-behaved and predictable using fairly simple models based on only the level of functionalization of the oils.

From this work, it is evident that plant oils with high unsaturation levels should be used to make rigid thermosetting polymers and composites. Alternatively, for tryglycerides with intermediate levels of unsaturation, the extent of functionalization can be increased by adding two functional groups per double bond, such as acrylation followed by maleinization of the hydroxyl group [1]. These oils would provide a large number of attachment points for chemical functionality that would be used to increase the cross-link density and other polymer properties. However, very low levels of unsaturation are required to produce good triglyceride-based elastomers. Specifically, most triglycerides should have one unsaturation site, while a small percentage should have two or more to provide some cross-linking to make soft and flexible elastomers.

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