

Soybean- and Castor-Oil-Based Thermosetting Polymers: Mechanical Properties

E. Can,¹ R. P. Wool,² S. Küsefoğlu³

¹Department of Materials Science and Engineering and Center for Composite Materials, University of Delaware, Newark, Delaware 19711-3144

²Department of Chemical Engineering and Center for Composite Materials, University of Delaware, Newark, Delaware 19711-3144

³Department of Chemistry and Polymer Research Center, Bogaziçi University, Istanbul, Turkey

Received 10 August 2005; accepted 25 February 2006

DOI 10.1002/app.24423

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Maleic anhydride modified soybean- and castor-oil-based monomers, prepared via the malination of the alcoholysis products of the oils with various polyols, such as pentaerythritol, glycerol, and bisphenol A propoxylate, were copolymerized with styrene to give hard rigid plastics. These triglyceride-based polymers exhibited a wide range of properties depending on their chemical structure. They exhibited flexural moduli in the 0.8–2.5 GPa range, flexural strength in the 32–112 MPa range, glass transition temperatures (T_g) ranging from 72 to 152°C, and surface hardness values in the 77–90 D range.

The polymers prepared from castor oil exhibited significantly improved modulus, strength, and T_g values when compared with soybean-oil-based polymers. These novel castor and soybean-oil-based polymers show comparable properties to those of the high-performance unsaturated polyester (UP) resins and show promise as an alternative to replace these petroleum-based materials. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1497–1504, 2006

Key words: thermosets; renewable resources; resins; structure–property relations; mechanical properties

INTRODUCTION

There is a worldwide potential demand for replacing petroleum-derived raw materials with renewable plant-based ones in production of valuable polymeric materials. Plant oils, which are found in abundance in all parts of the world and are easily replenished annually, have the potential to replace petroleum as a chemical feedstock for making polymers. In the majority of the prior work with plant oil triglycerides, triglycerides were used as the minor component of the main polymer matrix to improve the properties of the main matrix and the polymers derived from triglycerides were low molecular weight and lightly cross-linked materials with no significant structural strength. Within the past few years, there has been growing interest to use the triglycerides as the basic constituent of thermosetting polymers with the necessary rigidity, strength, and glass transition temperatures required for engineering applications.

Li et al. reported the preparation of polymers ranging from rubbers to hard plastics by cationic polymerization of a variety of oils: fish, tung, and soybean oil with petroleum-based comonomers such as styrene, divinyl benzene, and dicyclopentadiene in

the presence of boron trifluoride diethyl etherate as the initiator.^{1–3} Epoxidized vegetable oils were photo-polymerized in the presence of cationic initiators to prepare fiberglass-reinforced composites by Crivello et al.⁴ Plant oils are not reactive in radical polymerization; however, various functional groups that are reactive in radical polymerization can easily be attached to the triglyceride structure making them ideal crosslinking monomers for thermosetting liquid molding resins. This way plant oils can partially replace petroleum to make thermosetting polymers. Using this approach, our group has developed a number of chemically modified triglycerides to prepare rigid thermosetting polymers.^{5–8} As a part of this research, malinated soybean oil monoglycerides (SOMGMA) were prepared and copolymerized with styrene,⁷ neopentyl glycol, and bisphenol A maleate half esters.⁸ The plasticizing effects of the fatty acids in the SOMGMA monomers that do not participate in polymerization decrease the modulus and T_g of the resulting polymers.

To reduce this plasticizing effect, castor oil was used instead of soybean oil in alcoholysis reactions with both aliphatic alcohols such as glycerol, pentaerythritol, and an aromatic alcohol bisphenol A propoxylate. The resulting alcoholysis products were then reacted with maleic anhydride to form maleate half esters. Castor oil was directly malinated as well to see the effect of the alcoholysis step on the proper-

Correspondence to: R. P. Wool (wool@che.udel.edu).

ties of the resins. Soybean oil pentaerythritol glyceride maleates were also prepared for a direct comparison of the properties of the castor- and soybean-oil-based resins. Figure 1 shows the chemical structures of the

basic constituents of these triglyceride-based monomers: (a) soybean oil pentaerythritol glyceride maleates (SOPERMA), (b) castor oil pentaerythritol glyceride maleates (COPERMA), (c) castor oil monoglyceride (COGLYCMA), (d) castor oil pentaerythritol glyceride maleates (COPERMA), (e) castor oil monoglyceride (COGLYCMA).

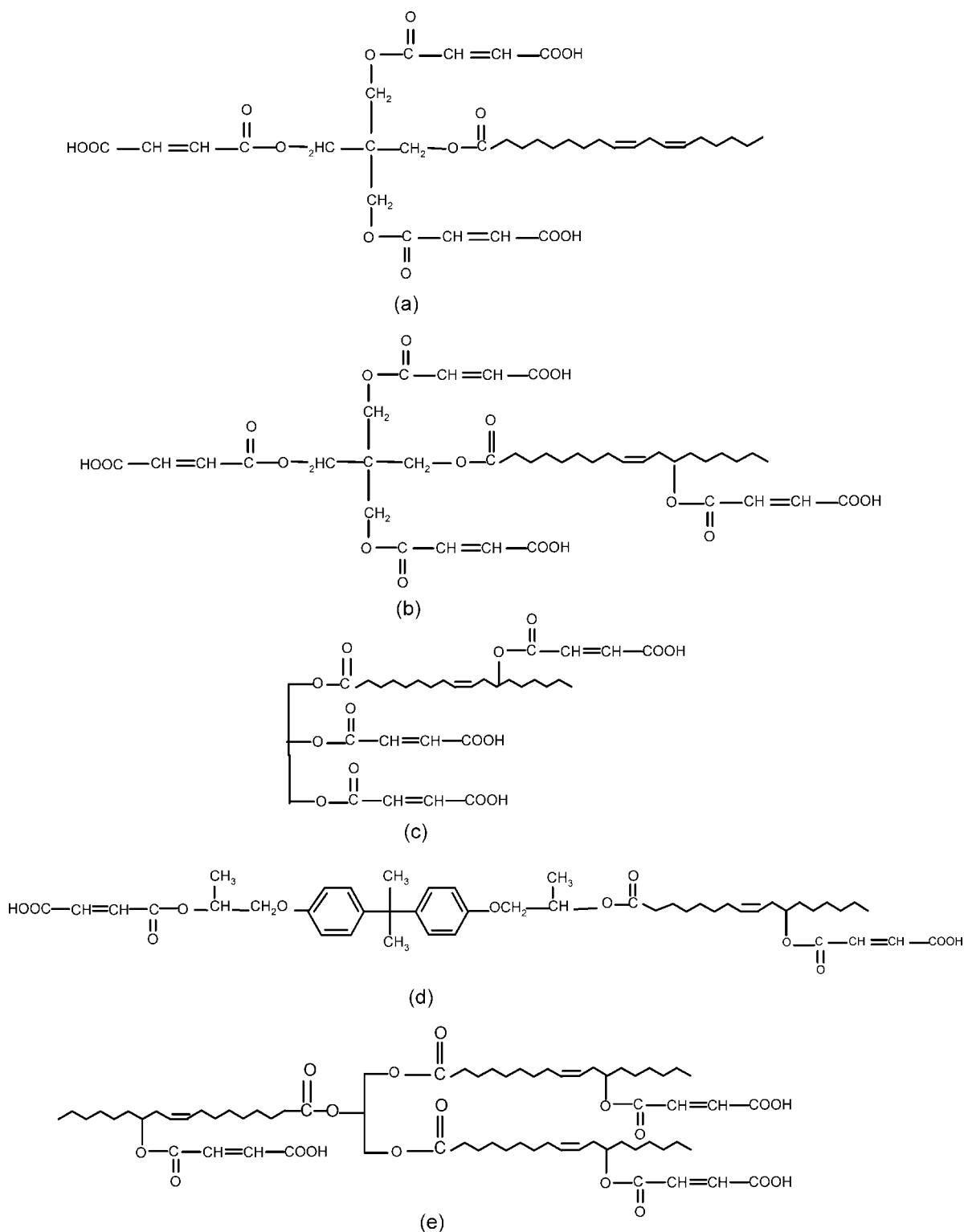


Figure 1 The chemical structures of the basic constituents of the (a) SOPERMA, (b) COPERMA, (c) COGLYCMA, (d) COBPAPRMA, and (e) COMA monomers.

maleates (COGLYMA), (d) castor oil bisphenol A propoxylate maleates (COBPAPRMA), and (e) castor oil maleates (COMA). The synthesis of these triglyceride-based monomers was reported and their copolymerization with styrene was analyzed via time resolved FTIR analysis in a previous work.⁹ This study presents the thermal and mechanical properties of these soybean and castor-oil-based polymers. The effect of chemical structure of the triglyceride-based monomers and comonomer styrene content on the mechanical properties is also presented. To our knowledge, triglyceride-based thermosetting resins based on the above-mentioned synthetic route have never been prepared before. Therefore, the polymers reported in this work are completely new and original.

EXPERIMENTAL

The soybean- and castor-oil-based monomers used in this study were prepared by the alcoholysis reactions of the oils with the specific polyol followed by malination of the alcoholysis products with maleic anhydride, according to the procedures described in reference.⁹ The chemical structures of the basic constituents of these soybean- and castor-oil-based monomers are shown in Figure 1.

Polymerization (curing) of the resins

For all the maleic anhydride modified soybean- and castor-oil-based monomers whose chemical structures are shown in Figure 1, a similar curing procedure was employed. The maleic anhydride modified oil was first heated to a temperature around 60–70°C to reduce the viscosity and then mixed with the specified amount of styrene. The styrene used was obtained from Aldrich Chemicals and was 98% pure. After completely mixing, *tert*-butyl peroxy benzoate was added as initiator. The amount of initiator used was 2% of the total resin weight for the SOPERMA, COMA, and the COBPAPRMA resins and 1.5% for the COPERMA and the COGLYCMA resins. Nitrogen gas was then passed through the resins for ~ 5 min to remove residual oxygen. The resins were then poured into the appropriate molds. The resin-filled molds were placed in an oven at 30°C. For the SOPERMA, COMA, and the COBPAPRMA resins, the temperature was increased to 120°C at the rate of 5°C/min and the resin was cured at this temperature for 3 h and postcured at 160°C for 1 h. For the COPERMA and the COGLYCMA resins, a slower curing cycle was employed. The resins were heated to 90°C at a heating rate of 2°C per minute, cured at this temperature for 2 h, and then postcured at 120°C for 1 h and at 160°C for 1 h. The polymer samples were then polished to the desired dimensions.

Characterizations

Dynamic mechanical analysis (DMA) was conducted in three-point bending geometry on a Rheometrics Solids Analyzer II (Rheometric Scientific). The dynamic temperature ramp default test was performed on samples with dimensions of 57 × 10 × 2.6 mm³. The temperature ramps were run from 25 to 200°C, at a ramp rate of 5°C/min with a frequency of 1 Hz and a strain of 0.01%. The flexural tests were conducted in accordance with ASTM D790 on an Instron model 4484 operating at a constant cross-head speed of 1.27 mm/min. The specimens were in 65 × 12.7 × 3.17 mm³ in dimension. Surface hardness was determined using a 307L Type D durometer. For the determination of the polymer densities, samples prepared for DMA analysis were used. The mass of the polymer samples were measured using a digital balance capable of measuring to the nearest 0.0001 g. The dimensions of the samples were measured using a caliper capable of measuring to the nearest 0.01 mm in three different positions on the sample and the average value was used for the volume calculations. The densities of the polymer samples were then determined using the mass and the volume of each sample.

RESULTS AND DISCUSSION

Dynamic mechanical analysis

The typical DMA behavior of the SOPERMA–styrene polymer (40 wt % styrene) is shown in Figure 2. All the other polymers based on modified castor oil and styrene showed similar DMA behavior. A distinct feature for all the triglyceride-based polymers is that these polymers show a very broad transition from glassy to rubbery state. At room temperature these polymers are already in transition from the glassy region to the rubbery plateau. Most common thermoset polymers show a distinct glassy region in which modulus is independent of temperature. This

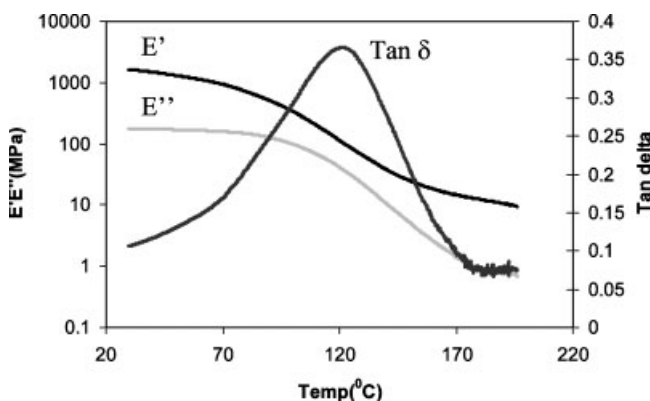


Figure 2 Typical DMA behavior of the SOPERMA–styrene polymer (40 wt % styrene).

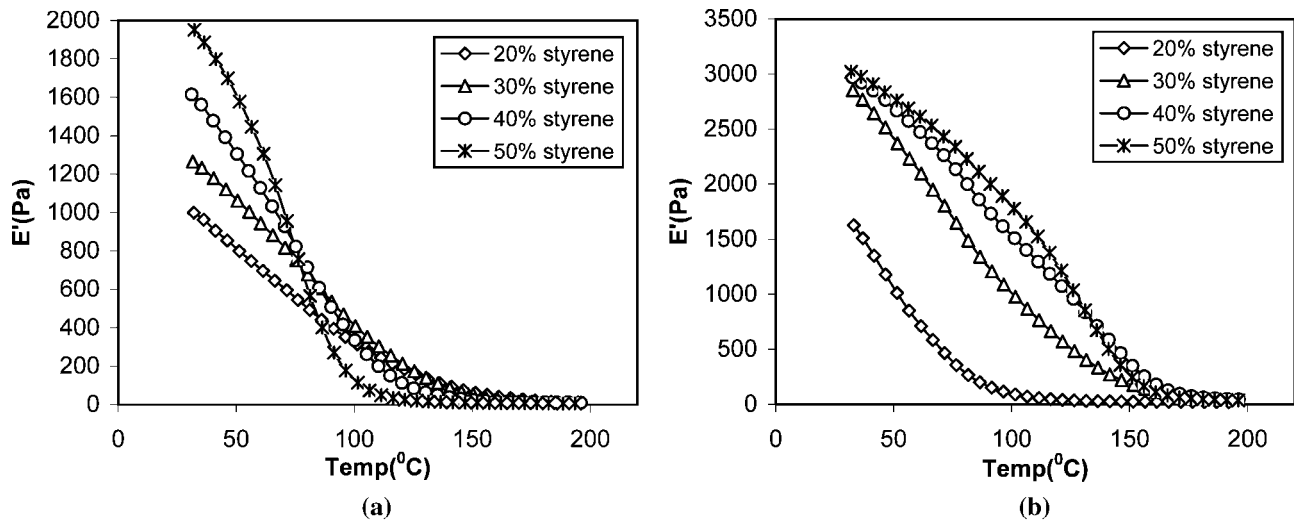


Figure 3 The change of storage modulus values with temperature for the (a) SOPERMA and (b) COPERMA polymers at increasing styrene concentrations.

is not observed for these triglyceride-based polymers. Because of this broad transition, these polymers do not show a clear peak in the loss modulus E'' . Thus the $\tan \delta$ curve is also very broad. One possible effect that results in this broad glass transition behavior is the formation of triglyceride-rich and styrene-rich regions with variable compositions in the polymer, spanning the range of the different phase transitions. This behavior is commonly observed for interpenetrating polymer networks.¹⁰ Another effect that may result in a broad glass transition is the plasticizing effect of the fatty acids present in these triglyceride-based monomers. These long alkyl chains act as plasticizers for the polymer network. This effect should be more pronounced for the SOPERMA polymers in which the fatty acid chains do not participate in polymerization. For the castor-oil-based polymers that have polymerizable maleate functionality on C-12 position, the rest of the fatty acid chain that is six carbons long should still have a plasticizing effect. The transition from glassy to rubbery state

drastically broadens with the addition of small amounts of plasticizers to polymers.¹¹

The effect of styrene concentration on mechanical properties of the SOPERMA and COPERMA polymers

The effect of comonomer styrene concentration on the properties of the SOPERMA and COPERMA polymers was explored, and a comparison of the properties of the two polymers was made. The change in storage modulus with temperature in changing styrene concentrations as determined by DMA for the SOPERMA and COPERMA polymers is given in Figure 3(a,b) respectively. As described above, at room temperature, both the SOPERMA and the COPERMA polymers are already in transition from the glassy region to the rubbery plateau. This behavior is consistent in all the styrene concentration range studied. For both of the polymers, the room temperature storage modulus values increase as the styrene

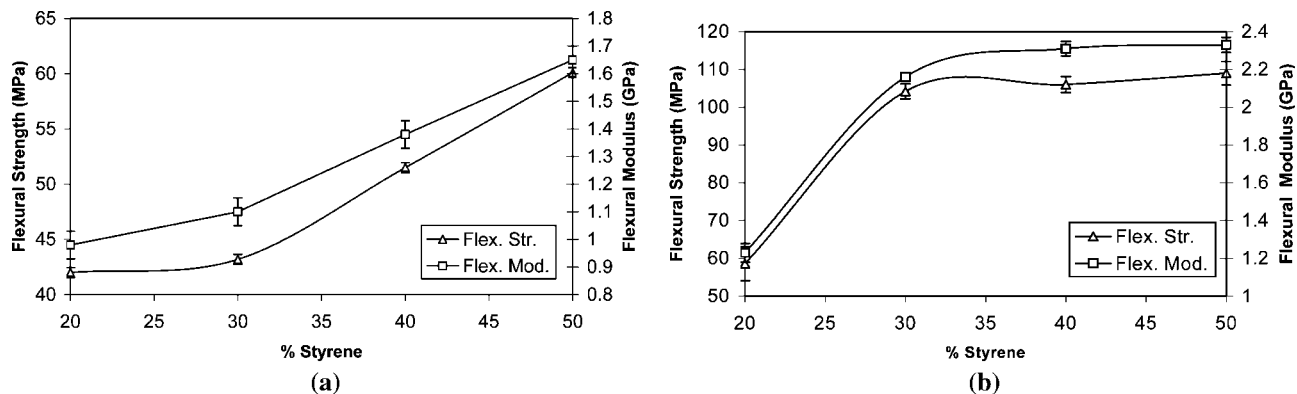


Figure 4 The change in the flexural modulus and flexural strength of the (a) SOPERMA and (b) COPERMA polymers with increasing concentrations of styrene.

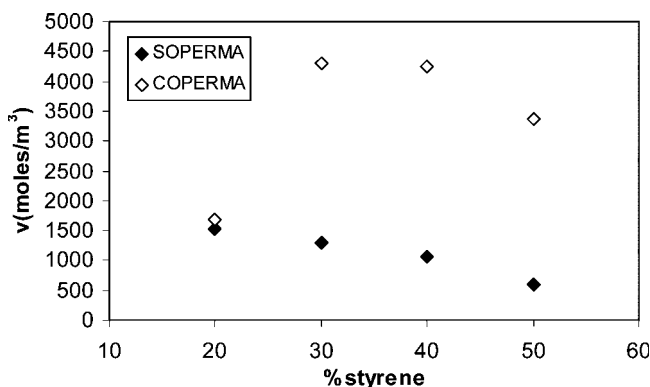


Figure 5 The crosslink densities of the SOPERMA and COPERMA polymers at increasing styrene concentrations.

concentration increases. For the COPERMA polymer, the polymer containing 20% styrene by weight shows a considerably lower modulus than the polymer containing 30% styrene by weight. The increase in styrene concentration above 30% has a less pronounced effect on the modulus. For the SOPERMA polymer, the room temperature storage modulus values show a continuous increase with the increase in styrene concentration. The change in flexural modulus and flexural strength of the SOPERMA and COPERMA polymers at increasing styrene concentrations is shown in Figure 4(a,b) respectively. The increase in flexural modulus and strength with styrene concentration follows a similar trend as observed for the storage modulus. To explain the effect of styrene concentration on the mechanical properties of these polymers, it is useful to determine the crosslink densities of the polymers at different styrene concentrations. It is possible to calculate the crosslink density, ν , and the effective molecular weight between crosslinks, M_c , from experimental data using rubber elasticity theory. At higher

temperatures (20–30°C above T_g), thermoset polymers behave as rubbers and the rubber elasticity theory can be applied. At small deformations, the rubber elasticity theory predicts that the modulus E , of an ideal elastomer with a network structure is proportional to the crosslink density ν , the average number of crosslinks per unit volume, according to the following equation.¹²

$$E = 3\nu RT = \frac{3dRT}{M_c}$$

where R is the gas constant, T is the temperature, d is the density of the polymer, and M_c is the effective molecular weight between crosslinks. Using this equation and the value of E in the rubbery region as determined by the DMA analysis, the crosslink densities of the SOPERMA and COPERMA polymers at different styrene concentrations were determined. Figure 5 shows the crosslink densities (ν) of the SOPERMA and COPERMA polymers at increasing styrene concentrations. For the COPERMA resin, which has much higher maleate content per triglyceride than the SOPERMA resin, at 20% styrene, the styrene concentration is too low to incorporate all the maleates into polymerization, since the maleates do not homopolymerize.¹³ Thus, the 20% styrene COPERMA polymer has the lowest crosslink density. At 30–40% styrene, the styrene–maleate copolymerization reaches its optimum value, and after this point, the increase in styrene concentration decreases the crosslink density as the increase in styrene concentration increases the length of the linear segments between the crosslinks. Thus, at this point it is the effect of the rigidity of the styrene molecules that increases the modulus and strength. For the SOPERMA polymers, which show considerably lower crosslink densities than the

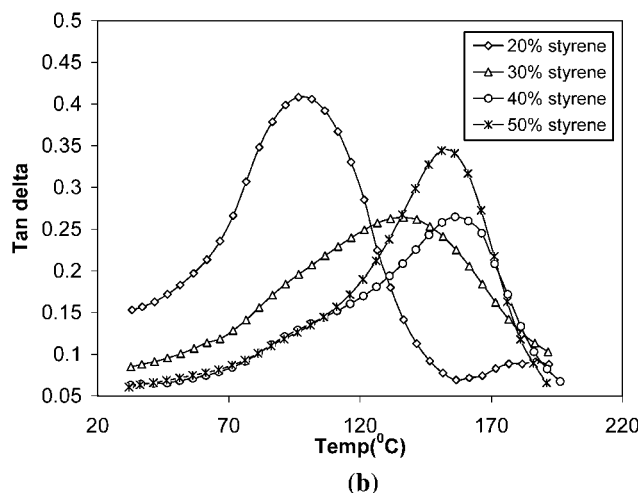
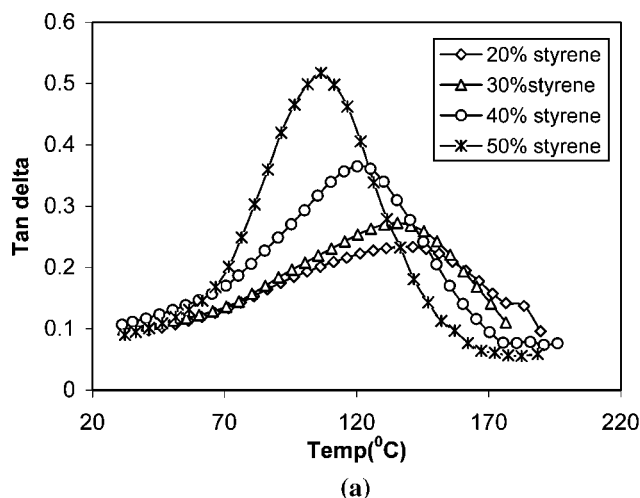


Figure 6 The change of $\tan \delta$ values with temperature for the (a) SOPERMA and (b) COPERMA polymers at increasing styrene concentrations.

TABLE I
The Mechanical Properties of the COPERMA and SOPERMA Polymers at 30 wt % Styrene

Property	COPERMA	SOPERMA
Flexural strength (MPa)	104.23 (± 4.2)	43.86 (± 3.1)
Flexural modulus (GPa)	2.16 (± 0.008)	1.1 (± 0.056)
T_g ($^{\circ}\text{C}$)	144	135
Storage modulus (GPa)	2.88 (± 0.01)	1.24 (± 0.001)

COPERMA polymers, the crosslink density continuously decreases as styrene concentration increases. Thus, the room temperature modulus and strength of the SOPERMA polymers increase considerably with increasing styrene concentrations despite the decrease in crosslink density. The introduction of the rigid aromatic rings of the styrene comonomer into the SOPERMA monomer with long flexible fatty acid chains results in a net increase in both the modulus and strength of the network. This effect is less pronounced for the COPERMA polymers, since the fatty acids present in the COPERMA monomer are functionalized and incorporate in polymerization.

The $\tan \delta$, which is a measure of the internal friction or damping in the material is very sensitive to crosslink density. The $\tan \delta$ curves for the SOPERMA and the COPERMA polymers at different styrene concentrations are shown in Figures 6(a) and 6(b) respectively. For the SOPERMA polymer, the 50% styrene polymer has the narrowest $\tan \delta$ peak, at the lowest temperature. The $\tan \delta$ maximum shifts to higher temperatures, the peaks broaden and the values decrease as styrene concentration is decreased. The increase in crosslink density with the decrease in styrene concentration increases the T_g and broadens the $\tan \delta$ curve. The increased crosslink density is known to decrease the $\tan \delta$ value and have a broadening effect on the $\tan \delta$ curve.¹¹ Another possible effect for the decrease of the width of $\tan \delta$ curves with increasing styrene content can be the better solubilization of the malinated glycerides in styrene that should lead into the formation of a less heterogenous system. For the COPERMA polymers, this trend is more complex. The 20% styrene polymer with the lowest crosslink density shows the $\tan \delta$ maximum at the lowest temperature, and the $\tan \delta$ maximum shifts to higher temperatures with increases

up to 40% styrene. After this point, the increase in styrene concentration decreases the crosslink density and the T_g starts to decrease again.

Comparison of the mechanical properties of the COPERMA and SOPERMA-styrene polymers

Table I shows the properties of the 30% styrene SOPERMA and COPERMA polymers for a direct comparison. It can be seen that the modulus values nearly double, and the flexural strength even shows a larger increase with the change from soybean oil to castor oil. The glass transition temperature of the COPERMA polymer is about 9°C higher than that of the SOPERMA polymer. The incorporation of the fatty acid chains into polymerization both increases the crosslink density and reduces the plasticization effect of the fatty acid chains in the COPERMA polymer that in turn leads a considerable increase in modulus, strength, and T_g when compared with those of the SOPERMA polymer.

The mechanical properties of castor-oil-based polymers

The increase in styrene concentration generally improves the mechanical properties of these triglyceride-based polymers. One can choose the right concentration based on the necessary requirements for the targeted application using these resins. However, since the scope of this research is to keep the renewable content of these new materials high, we used 33 wt % styrene concentration for the other castor-oil-based polymers. This concentration gives optimum properties for the COPERMA polymer, and it gives us a chance to compare the properties of these materials to the commercially available unsaturated polyesters (UPs), which use similar formulations.

The storage modulus values at 30°C and the T_{gs} , as determined from DMA as well as the flexural modulus, flexural strength, and the surface hardness values of the castor oil polymers are given in Table II. The styrene content of each resin is 33% by weight. The mechanical property, hardness, is the ability of the material to resist scratching, abrasion, cutting, and penetration.¹¹ This property may be important for structural materials, which require a high resistance to

TABLE II
The Mechanical Properties of the Castor Oil Polymers

Resin type	E' (30°C) (GPa)	T_g ($^{\circ}\text{C}$)	Flexural modulus (GPa)	Flexural strength (MPa)	Surface hardness (D)
COPERMA (1 : 2 : 10.7)	2.94 (± 0.02)	149	2.17 (± 0.070)	104.6 (± 3.1)	89.3 (± 0.40)
COGLYMA (1 : 2.2 : 9.2)	2.40 (± 0.01)	124	1.76 (± 0.076)	78.89 (± 2.74)	86.1 (± 0.45)
COBPAPRMA (1 : 2 : 6.7)	2.69 (± 0.01)	86	2.19 (± 0.072)	83.20 (± 3.76)	88.5 (± 0.58)
COMA (1 : 3)	1.15 (± 0.005)	72	0.78 (± 0.059)	32.83 (± 1.64)	77 (± 0.71)
Ortho-UP	–	100–130	3.45	80	–
Iso-UP	–	100–130	3.59	100	–

indentation or abrasion. The hardness of a polymer reflects, all or in part, other qualities such as resilience, durability, uniformity, strength, and abrasion resistance. As can be seen in Table II, the surface hardness of the castor-oil-based polymers changes proportionally with the strengths of the polymers. The observed mechanical properties of the castor-oil-based polymers can be explained in terms of both the crosslink density and the chemical structures of the polyols used. Table III shows the crosslink densities of the castor-oil-based polymers, which are determined using the value of E in the rubbery region of the polymers as determined by DMA. The effective molecular weight (M_c) values were calculated using the polymer densities (d) determined as described in the experimental section. The COPERMA has the highest crosslink density, followed by COGLYMA, COMA, and COBPAPRMA. The $\tan \delta$ values of the castor oil polymers as a function of temperature as determined by DMA is shown in Figure 7. As mentioned above, the damping is a sensitive indicator of crosslinking. As crosslink density increases, the $\tan \delta$ maximum shifts to higher temperatures, the peak broadens and a decrease in the $\tan \delta$ value is observed.¹¹ These effects reflect themselves on the $\tan \delta$ curves of the castor oil polymers. Thus, the COPERMA polymer with the highest crosslink density shows the broadest peak at the highest temperature with the lowest $\tan \delta$ value. The broadening of the $\tan \delta$ curves as going from COMA to COPERMA polymer can also be attributed to the increasing maleate content of the resin. The system should become more heterogeneous with the increasing maleate content of the resin. The COBPAPRMA shows the lowest crosslink density, which can partially be attributed to the bulkiness of the bisphenol A propoxylate moiety. It shows the highest $\tan \delta$ values as expected; however, its $\tan \delta$ max temperature is about 14°C above than that of the COMA polymer. The higher T_g observed for the COBPAPRMA may be explained by the presence of the rigid aromatic backbone of bisphenol A propoxylate when compared with the aliphatic fatty acid backbone of the COMA polymer. The same effect reflects itself on other mechanical properties. The COPERMA polymer with the highest crosslink density exhibits the highest modulus, strength, and T_g . The COBPAPRMA polymer's modulus, strength, and surface hardness values are higher than those of both COMA and COGLYMA polymers and approach those of COPERMA

TABLE III
Crosslink Densities of the Castor Oil Polymers

Resin type	M_c (g/mole)	v (moles/m ³)
COPERMA	314	3621
COGLYMA	681	1654
COMA	732	1511
COBPAPRMA	753	1474

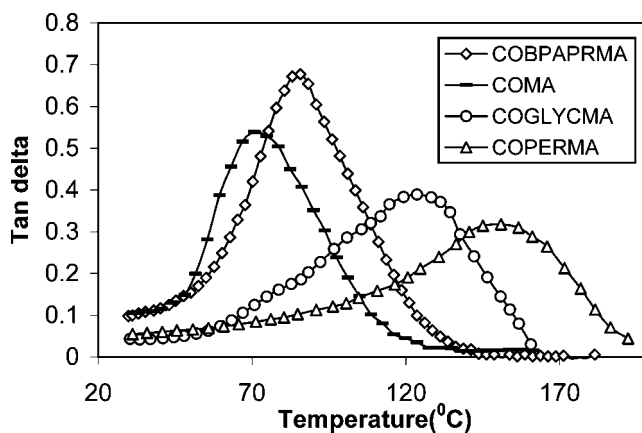


Figure 7 The $\tan \delta$ values of the castor oil polymers as a function of temperature.

polymer, although its crosslink density is slightly lower than these two polymers. The aromatic structure of the bisphenol A propoxylate moiety brings both rigidity and strength to the polymer network. Thus, this resin shows both high modulus and strength with a reasonable T_g despite its lower maleate content, which is beneficial for the formulation, since it decreases the non-renewable content of the polymer. The COMA polymer, on the other hand shows the lowest modulus, strength, surface hardness, and T_g values due to its low crosslink density and also showing that a multifunctional unit at the center of the triglyceride monomer structure is essential for improved properties for these polymers. Table II also shows the mechanical properties of two common use UP resins: Orthophthalic (Ortho-UP) and Isophthalic (Iso-UP) UP resins. As can be seen, the properties of castor-oil-based polymers are in a comparable range with those of the commercially successful UP resins.

CONCLUSIONS

Polymers based on malinated soybean and castor oil alcoholysis products were prepared using styrene as the comonomer. The formulations contained both aliphatic alcohols such as glycerol, pentaerythritol, and an aromatic alcohol bisphenol A propoxylate. These triglyceride-based polymers exhibited a wide range of properties. They exhibited flexural moduli in the 0.8–2.5 GPa range, flexural strength in the 32–112 MPa range, T_g ranging from 72 to 152°C, and surface hardness values in the 77–90 D range. The mechanical properties of the polymers were significantly influenced by the type of the oil and the alcohol as well as the styrene content. The effect of styrene concentration on the properties of SOPERMA and COPERMA polymers was explored. The mechanical properties of both of the polymers generally improved with increasing concentrations of styrene; however, for

the COPERMA polymer, it was found out that the styrene concentration should be in the 30–40% range to reach optimum properties. The COPERMA polymers, which showed higher crosslink densities than the SOPERMA polymers, exhibited superior properties when compared with the SOPERMA polymers due to the incorporation of the fatty acids into polymerization. The fatty acid chains present in the SOPERMA monomer are not functionalized, and therefore act as a plasticizer, reducing the overall modulus and strength of the polymers. For the castor-oil-based polymers, at the same styrene concentration, the polymers made from COPERMA exhibited the highest modulus, strength, surface hardness, and T_g values, since it has the highest crosslink density as determined by DMA analysis. The polymers prepared from castor oil bisphenol A propoxylate glyceride maleates, COBPAPRMA, on the other hand exhibited higher modulus and strength than both of the polymers based on COMA and castor oil glyceride maleates, COGLYCMA, although it possesses the lowest crosslink density. The modulus and surface hardness values of the COBPAPRMA approached those of the COPERMA polymer. This result was attributed to the presence of rigid aromatic rings on the backbone of the COBPAPRMA polymer.

These novel castor-oil-based polymers show comparable properties to those of the high-performance UP and show promise as an alternative to these

petroleum-based materials. Their thermal and mechanical properties are compared with those of many other bio-based composites resins in reference.¹⁴

References

1. Li, F.; Marks, D. W.; Larock, R. C.; Otaigbe, J. U. *Polymer* 2000, 41, 7925.
2. Li, F.; Larock, R. C. *J Appl Polym Sci* 2000, 78, 1044.
3. Li, F.; Larock, R. C. *J Appl Polym Sci* 2001, 80, 658.
4. Crivello, J. V.; Narayan, R.; Sternstein, S. S. *J Appl Polym Sci* 1997, 64, 2073.
5. Wool, R. P.; Kusefoglu, S. H.; Palmese, G. R.; Zhao, R.; Khot, S. N. U.S. Pat 6,121,398 (2000).
6. Khot, N. S.; Lascalea, J. J.; Can, E.; Morye, S. M.; Williams, G. I.; Palmese, G. R.; Kusefoglu, S. H.; Wool, R. P. *J Appl Polym Sci* 2001, 82, 703.
7. Can, E.; Kusefoglu, S.; Wool, R. P. *J Appl Polym Sci* 2001, 81, 69.
8. Can, E.; Kusefoglu, S.; Wool, R. P. *J Appl Polym Sci* 2002, 83, 972.
9. Can, E.; Kusefoglu, S.; Wool, R. P. *J Appl Polym Sci*, to appear.
10. Sperling, L. H. *Physical Polymer Science*; Wiley-Interscience: New York, 2001.
11. Nielsen, L. E.; Landel, R. F. *Mechanical Properties of Polymers and Composites*; Marcel Dekker: New York, 1994.
12. Van Krevelen, D.W.; Hoftyzer, P. J. *Properties of Polymers: Their Estimation and Correlation with Chemical Structure*; Elsevier: Amsterdam, 1976.
13. Triverdi, B. C.; Culbertson, B. M. *Maleic Anhydride*; Plenum: New York, 1985.
14. Wool, R. P.; Sun, X. S. *Bio-Based Polymer and Composites*; Elsevier: Burlington, MA, 2005.