

Development of New Green SMC Resins and Nanocomposites from Plant Oils

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Abstract

Sheet molding compound (SMC) is widely used in automotive parts, appliances, furniture, and construction. These materials heavily depend on the petroleum supply, which is depleting fast. The use of plant oils as an alternative source for SMC resins presents economic and environmental advantages over petroleum.

Two synthetic methods have been used to develop new resins from triglycerides. The double bonds presented on the fatty acid chains were first converted to epoxy or hydroxyl functionality; the hydroxyl groups were maleinized, while the epoxies were acrylated and then further maleinized. When these functionalized oils were combined with 33.3 wt% styrene, the polymers showed mechanical properties comparable to those of commercial unsaturated polyesters. In addition, these new resins exhibit adequate thermo-reversible thickening behavior with MgO.

These triglyceride-based resins have good compatibility with natural fibers, such as hemp and flax to form low-cost green composites. New bio-based nanocomposites were also developed using these new resins and organo-treated clays, and the nanocomposites showed considerable increase in modulus and toughness. These new green materials show the promise to be used in the automotive industry.

Introduction

The use of materials from renewable resources is of increasing importance as the world's leading industries and manufacturers seek to replace dwindling petrochemical-based feedstock with agricultural based materials. Sheet molding compound (SMC) is used extensively in the production of composite materials for use in automotive parts, appliances, furniture, and construction. For example, the automotive industry consumes more than 10^8 kg per year in the USA [1]. The molding compound consists of a mixture of fibers, fillers, additives, and a liquid molding resin. The most common resins used in SMC are the various unsaturated polyester resins, which are synthesized using raw materials derived from petroleum. Replacing some, or all, of these petroleum-derived raw materials with renewable plant-based raw materials, such as plant oils, is attractive, both economically and socially, as such raw materials are cheaper and their use contributes to global sustainability by not depleting scarce resources [2].

Plant oils are mainly composed of triglyceride molecules, which have the structure shown in Figure 1. Triglycerides are composed of three fatty acids connected by glycerol center through ester linkages. The fatty acids in most common triglycerides have 0 to 3 double bonds and vary from 14 to 22 carbons in length [3]. While double bonds is the main functionality present on a fatty acid, other functionalities, such as epoxies, hydroxides, cyclic groups, and furanoid groups also occur naturally [4]. Plant oils have been widely used in coatings, inks, plasticizers, lubricants and agrochemicals except in the food industry [5-9]. Some work has been done to use epoxidized plant oils as toughening agent in epoxy matrix [10, 11]. Interpenetrating networks (IPNs) based on functionalized triglycerides has also been extensively studied [12, 13]. In all these applications, triglyceride was just a minor component in the polymer matrix. In recent years, an extensive work has been done to develop polymers for engineering applications using

plant oils as main component [2, 14-23]. Li and his coworkers [20-22, 24] developed a series of polymers ranging from rubbery to rigid by cationic polymerization of different kinds of oils with styrene and divinyl benzene. Another approach to make plant oil-based polymers is to introduce polymerizable functionality onto the triglycerides molecule. In the past few years, the Affordable Composites from Renewable Sources (ACRES) group at the University of Delaware has developed many chemical routes to synthesize functionalized triglycerides as a basis for polymers and composites [2, 19]. In this work, we present two synthetic routes to functionalize the triglycerides to be used SMC applications, the development of all natural composites with natural fibers, and clay nanocomposites using these new resins.

SMC Resins

For a resin to be suitable for use in SMC technology, it requires the chemical functionality to undergo thickening reactions with divalent metallic oxides and /or hydroxides to form the sheet as well as unsaturation for the free radical polymerization during the molding process [25]. Figure 2 shows two chemical routes to synthesize triglyceride-based monomers matching the SMC requirement [17]. In the first synthetic route, the double bonds on triglycerides are converted to hydroxyl functionality, these hydroxyl groups react with maleic anhydride to form maleinized hydroxylated triglycerides. In the second method, the triglyceride molecules are epoxidized, the epoxy groups are reacted with ethylenically substituted carboxylic acids, such as acrylic acid to form acrylated epoxidized triglycerides. These acrylated triglycerides can be further modified with cyclic anhydride (e.g. maleic anhydride) which renders acid groups and adds more unsaturation on the molecules. When these functionalized triglycerides are combined with 33.3 wt% styrene, they form unsaturated polyester like resins which can be used for SMC applications.

Natural Fiber Composites

Using lightweight, strong and low cost natural fibers to replace glass and mineral fillers in composite production for interior parts has been a new trend in automotive industry, although it can be traced back to last decade when the European car makers used natural fiber composites for door panels, seat backs, headliners, package trays, etc. Obviously, the use of natural fibers has certain advantages, they are eco-friendly and readily available, and they have low density in the range of 1.25-1.50 g/cc, versus 2.6 g/cc for glass fiber, which can reduce the part weight, a key factor in automotive industry. Thus, natural fiber reinforced composites have been extensively studied using both thermoplastic and thermosets [26-30]. The combination of natural fibers with bio-based polymer matrix can be more attractive because of environmental and economic concerns. High performance composite materials from natural fibers and soybean oil-based resins have been developed by ACRES group at the University of Delaware [19, 31]. The SMC resins synthesized in this work have been tested for compatibility with natural fibers, and their mechanical properties are evaluated.

Clay Nanocomposites

Another interesting topic in the automotive industry is the use of nanocomposites for automobile parts. In contrast to conventional composites, a nanocomposite is formed when phase mixing occurs on a nanometer level. With relatively low loading of nanometer-sized particles, nanocomposites showed dramatically increased stiffness, HDT, dimensional stability, gas barrier, electrical conductivity and flame retardancy [32, 33]. The triglyceride-based resins are suitable to synthesize nanocomposites using either nanotubes or organo-treated clays [34, 35]. In this work, we focus on the synthesis and characterization of clay nanocomposites as the clay is favored for the principle of reducing material cost.

Experimental

Chemicals

Acrylated epoxidized soybean oil (AESO) was obtained in the form of Ebecryl-860 (UCB Radcure Inc.) This AESO is acrylated with approximately 3.4 acrylates per triglyceride and an average molecular weight of 1200 g/mol. An epoxidized linseed oil (Vikoflex 7190) from Elf Atochem was used as obtained. It has a molecular weight of approximate 974.2 g/mol and contains approximate 6.2 epoxy groups per triglyceride. Acrylic acid, maleic anhydride, N, N-Dimethylbenzylamine (BDMA), hydroquinone and styrene were used as received from the Aldrich Chemical Co. The catalyst AMC-2, supplied by Aerojet Chemicals, was used as received. The initiators used for polymerization were t-butyl peroxy benzoate (TBP) from Elf Atochem and methyl ethyl ketone peroxy (MEKP) (Witco Inc.).

Synthesis of Acrylated Epoxidized Triglycerides

The acrylated epoxidized soybean oil (AESO) was used as received. The acrylated epoxidized linseed oil (AELO) was synthesized based on the following steps. The epoxidized linseed oil was reacted with excess acrylic acid to maximize the level of acrylation. An excess of 0.1 mole acrylic acid per mole of epoxy group was used. In a 125 ml Erlenmeyer flask, 70 g epoxidized linseed oil, 0.14 g AMC-2, and 0.23 g hydroquinone were vigorously stirred at 75 °C. The acrylic acid was added in aliquots during the course of the reaction to reduce the amount of epoxy homopolymerization. The first aliquot was added when the temperature reached 70 °C. Upon addition of the acrylic acid, the solution became a bright green color. This was probably due to the interaction of the acid with the chromium-based catalyst. When the acid was consumed, as measured by pH paper, the reaction mixture became brown in color. When the reaction mixture turned brown, the next aliquot of acrylic acid was added. An aliquot of acrylic acid was added after 2 hours even if the reaction mixture was not brown. The overall reaction was kept for 12 hours. The product was analyzed using ¹H-NMR to determine the extent of acrylation and epoxy consumption. A Bruker AM250 NMR spectrometer was used to collect all spectra.

Synthesis of Maleinized Acrylated Epoxidized Triglyceride (MAESO & MAELO)

The acrylated epoxidized triglyceride was further modified with maleic anhydride (MA). Different molar ratios of MA to acrylated epoxidized triglyceride were examined as shown in Table I. In a typical maleinization of AESO, 50 g of AESO and 0.05 g of hydroquinone were first heated to 70 °C at a rate of approximately 1-2 °C/min, while being stirred. The necessary amount of MA was ground up finely and added at 70 °C. The mixture was then heated up to 80-90 °C, at which point the maleic anhydride dissolved, forming a homogeneous solution. The BDMA catalyst was then added in the amount of 1g. The reaction was stopped after 2 hours.

Synthesis of Maleinized Hydroxylated Soybean Oil (MHSO)

1000 ml of soybean oil was mixed with 1000 ml of 97% formic acid and 550 ml 30% H₂O₂; ice water was required to keep temperature below 45 °C. The reaction was vigorously stirred overnight. The emulsion was poured into a separator funnel and extracted with ether. The water layer was discarded, and the ether layer was washed with water, diluted sodium bicarbonate solution, and saturated sodium chloride solution, respectively. The resulting ether solution was dried over magnesium sulfate, and the ether was removed by a rotary evaporator. The resulting product is hydroxylated soybean oil with an average 6.8 hydroxyl groups per triglyceride from ¹H-NMR analysis.

Hydroxylated soybean oil was further maleinized. 400 g of hydroxylated soybean oil and 0.2 g hydroquinone were added in a 1 L round-bottom flask. 144.4 g of MA was added when the mixture was warmed to 60 °C under stirring. The temperature was further raised to 80 °C and 15 ml of BDMA was added in two portions. The reaction was maintained at 80 °C for 5 hours under stirring to obtain the maleinized product with a 4:1 molar ratio of MA to hydroxylated triglyceride (MHSO).

Polymer Synthesis and Mechanical Tests

Resins were prepared by blending triglyceride-based monomers with styrene and a free radical initiator. The maleinized triglycerides were mixed with styrene in the ratio of 100 g monomer to 50 g styrene. The free radical initiator (TBP for MAESO and MHSO system, and MEKP for MAELO) was then added in the amount of 1.5 wt % of the total resin weight. Polymer samples were prepared by casting the resin into a vertical gasket mold, cured at 110 °C for 2 hours and post-cured at 150 °C for 2 hours. To prevent oxygen free radical inhibition, the resin was purged with nitrogen gas prior to curing. Samples for dynamic mechanical analysis were prepared to dimensions of 48 x 10 x 2.5 mm. Dynamic mechanical analysis was conducted in a three-point bending geometry on a Rheometrics Solids Analyzer II (Rheometric Scientific Inc.). Temperature scans were run from approximately 25 °C to 180 °C at a heating rate of 5 °C/min with a frequency of 1 Hz and strain of 0.01%. The flexural and tensile properties were measured using ASTM method D790-95a and ASTM 638, respectively.

Preparation of Thickened Resins and Viscosity Measurement

The mixture of triglyceride-based monomers and styrene were thickened with magnesium oxide paste (PLASTIGEL[®] liquid thickener PG-9033, Plasticolors, Inc.), which is a dispersion of 38 wt % magnesium oxide in an unsaturated, non-monomer containing polyester vehicle. In a 600 ml beaker, 100 g of triglyceride-based monomer was well mixed with 50g styrene and the desired amount of MgO paste; the mixture was well sealed and kept at room temperature. To inhibit the polymerization, 1 wt % of hydroquinone was also added. The viscosity change during the maturation and heating process was monitored using a Brookfield DV-I+ viscometer. When the viscosity of the resin was low, a HB1 spindle was used, and T-bar spindles (TA91-96) were used for the high viscosity. All measurements were done at room temperature. For the heating process, the beaker with thickened resin was put in a 150 °C silicon oil bath, the temperature and viscosity changes were recorded.

Manufacturing of Flax and Hemp Composites

Composites were manufactured using woven hemp and flax mat with MAESO2-based polymer. MAESO2 was blended with 33.3 wt% styrene, and 1.5 wt% TBP based on the total weight of resin was added as the initiator. The composite was manufactured using a resin transfer molding process. Two layers of the oriented mats were placed with their orientation perpendicular to each other in the mold, the resin was injected into the mold, and the composite was cured at 110 °C for two hours followed by a post cure of 150 °C for two hours. Dynamic mechanical analysis was conducted as mentioned above, and the flexural properties were measured in accordance with ASTM D 790-95a.

Synthesis and Characterization of Clay Nanocomposites

Cloisite[®] 30B (C30B), a natural montmorillonite modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium chloride was obtained from Southern Clay Products. The desired amount of clay was added to the resin and mechanically stirred for 24-48 h with the flask well sealed to protect against the evaporation of styrene. Both room temperature and high

temperature curing were used to cure the sample. For the high temperature curing, 1.5 wt% TBP was added and the mixture was cured at 110 °C for 3 hrs and post cured at 150 °C for 2 hrs. For room temperature curing, 3 wt% of trigonox 239A (Akzo Nobel) and 0.8 wt% of Cobalt Naphthalate was added. Samples were cured at room temperature for 24 hrs and then post cured at 150 °C for 2 h. Wide-angle X-ray diffraction (XRD) measurements were performed on solid samples with a Philips X'Pert diffractometer using Cu K α radiation (40 kV, 40 mA) in the 2 θ range 0-10°. Transmission electron microscopy (TEM) was performed on a JEOL 2000 FX electron microscope on 100 nm thick sections. The flexural strength and modulus were measured according to ASTM D 790-95a. The fracture test was performed in single edge notched bend (SENB) geometry according to ASTM D 5045-99. A TA Instruments Thermogravimetric Analyzer Q500 was used to measure the weight loss of the cured sample in air.

Results and Discussion

Physical and Mechanical Properties

In this work, both soybean oil and linseed oil were used to synthesize resins for SMC applications. Soybean oil is the cheapest and most available oil, while linseed oil, which is from flax, although quite expensive, has the second highest molecular unsaturation among plant oils, which gives the high potential to synthesize rigid polymers with high stiffness. Table I shows the number of polymerizable vinyl groups (acrylate and maleate groups) added to the triglycerides, compared to the original number of double bonds. Soybean oil has 4.6 double bonds per triglyceride, while linseed oil has 6.6 double bonds. In an ideal case, two functional groups could be added per double bond. As shown in Table I, the functional groups added is much less than expected due to side reactions and oligmerization during the course of modification. These functionalized triglycerides are soluble in styrene. When combined with 33.3 wt% styrene, they exhibit reasonable viscosity in the range of 800-2400 cP, as shown in Table II. The room temperature viscosity of the resin for SMC applications can range from 300 to 3000 cP, although the low viscosity is favored because the resin can better wet the fiber surface [1]. These functionalized triglycerides copolymerize with styrene to form hard, rigid polymers by free radical polymerization.

Figure 3 shows the dynamic mechanical behavior of a typical SMC resin from plant oils (MAELO2). It has a storage modulus of 2.34 GPa at 30 °C and the tan δ peak shows at 120.55 °C. It is well known that the tan δ peak at a frequency of 1 Hz generally is at a temperature 15 to 20 °C above the glass transition temperature as measured by dilatometry or differential thermal analysis, thus the glass transition temperature for MAELO2 is above 100 °C, which is very similar to unsaturated polyesters. In general, it shows a broad transition from the glassy to the rubbery state, which is mainly due to the plasticizing characteristics of triglycerides and chemical heterogeneity in which there are differences in overall chemical composition from different molecular structure in the system. Here there is MAELO which has long fatty acid bones and aromatic styrene. Table II summaries the themomechanical properties of these new SMC resins. The storage moduli for these new polymers at 30 °C are in the range of 1.5-2.5 GPa, and the glass transition temperatures are in the range of 103-130 °C. Based on the kinetic theory of rubber elasticity, the experimental cross-link density (v_e) of a polymer can be determined from the rubber moduli by the following equation [36]:

$$E' = 3v_e RT \quad (1)$$

Where E' is the storage modulus of the cross-linked polymer in the rubbery plateau region above T_g , R is the gas constant, and T is absolute temperature (K). As shown in Table II, the typical value of cross-link density for these new SMC resins is above 4000 mol/m^3 , which corresponds to a cross-link molecular weight M_c 275 g/mol.

Figure 4 shows the mechanical behavior of the triglyceride-based polymers from the flexural test. Basically they all show a typical deformation of brittle plastics in terms of the stress and strain. Beyond the yield point, the deformation of MHSO polymers cease to be elastic, but the failure of other polymers is very quick with a strain less than 7.0%. These new SMC polymers have a flexural strength in a range of 61-100 MPa and moduli in a range of 1.9-2.8 GPa. The tensile stress-strain behavior of these new polymers also show a typical deformation of brittle plastics with tensile strength in a range of 27 ~ 44 MPa, and tensile modulus in a range of 1.6-2.5 GPa. The Poisson ratio is approximately 0.4, which is in the range of typical plastics. The Poisson ratio slightly decreases with increasing functional groups on triglycerides. Figure 5 compares the mechanical properties of triglyceride-based polymers with those of commercial resins, such as ortho-unsaturated polyester, and iso-unsaturated polyester, which are commonly used in the SMC industry. We can see their properties are comparable; also, the advantage gained here is in the amount of renewable material in the resins, which contains up to 50 wt % triglycerides.

The mechanical properties of triglyceride-based polymers increase with increasing the number of functional groups on triglycerides. As shown in Figure 6, the tensile strength (σ) of these polymers can be predicted by percolation theory in the form of [37]

$$\sigma = \sqrt{ED_0\nu(P - P_c)} \quad (2)$$

where E is Young's modulus, D_0 is the bond dissociation energy, ν is the cross-link density, and $P - P_c$ is the percolation fraction of bonds that must be broken to cause fracture in the network. Thus, using the starting oils bearing high unsaturation such as linolenic acid is favored for making rigid thermosetting polymers; the properties of these triglyceride-based polymers can be improved by increasing the functional groups on the triglycerides.

Thickening Behavior

The thickening process is an essential step in SMC applications. The carboxylic acid groups in unsaturated polyester are able to react with magnesium ions, which causes at least a 1000-fold increase in viscosity in 2-3 days. Figure 7 shows the viscosity changes of MAESO2 and MHSO system when thickened with 1.5 wt % MgO paste. The starting viscosity for both resins is approximately 1200 cP. It takes less than 40 hours for the viscosity of resins to reach more than 10^6 cP, which is in a common moldable viscosity range during SMC processes. After that, the viscosity fluctuates a little, which may result from the humidity change in the environment, as the water content can affect the thickening behavior [38]. Compared to the thickening behavior of the commercial unsaturated polyesters, the triglyceride-based resins need a smaller amount of thickener and less time to achieve the same saturated viscosity. The possible reasons can be, first, the acid number of these new resins are in the range of 40-100 mg of KOH/g, which is higher than that of unsaturated polyester, but they have higher molecular weight than unsaturated polyester; in addition, due to the distribution of carboxylic acid groups on fatty acid backbones, some triglyceride molecules may have dicarboxylic functionalities, or even tricarboxylic acid, which results in the formation of a cross-linked network as shown in Figure 8.

The linkages between magnesium ions and carbonyl oxygens are weak, they break up at high temperature. To understand the viscosity changes during heating, the thickened sheet was placed in a 150 °C silicon oil bath and the viscosity of the sheet was followed by the Brookfield

viscometer. Figure 9 shows the viscosity and temperature changes vs. time during heating. With the temperature of the resins increasing, the viscosity decreases dramatically from 10^7 cP to the initial value of un-thickened resins, which means all the thickening bonds are broken, and this whole process takes approximately 15 minutes. In the real case, the viscosity may not drop that much as the curing reaction starts.

Natural Fiber Composites

When bio-based resins derived from natural oils are combined with natural fibers, new low-cost composites are produced that are economical in many high-volume applications. These triglyceride-based SMC resins are compatible with natural fibers. The carboxylic acid groups on triglycerides can improve adhesion of fiber and matrix. Table III shows some of properties for SMC composites with flax and hemp. Figure 10 shows the first John Deere Round Hay Baler panel made with triglyceride-based resins.

Clay Nanocomposites

Clay nanocomposites have been successfully synthesized from these triglyceride-based resins and organo-treated clay [35]. XRD data shows the formation of an exfoliated structure at low clay concentration, but an intercalated structure at high clay loads (>5 wt%). The morphology of triglyceride-based nanocomposites was further confirmed by TEM. Table IV summarizes the properties of nanocomposites compared to the pristine polymer. The flexural modulus increases significantly with increasing clay content up to 7.5 wt%, which only corresponds to 4.0 vol%, the increase in modulus is 30%. After that, the modulus slightly decreases. There is no significant effect on the flexural strength, and glass transition temperature. The formation of an intercalated clay nanocomposite has a significant effect on the fracture toughness. The G_{1C} value is doubled at 5 wt% of clay load, which is possible due to the tactoids of intercalated organoclay acting as a toughening phase [39]. TGA showed the thermal degradation is slightly hastened by the formation of nanocomposites.

Conclusions

The use of natural resources such as triglyceride oils and natural fibers in polymers and composites area offers economic and environmental advantages. Green SMC resins were successfully synthesized from triglyceride by introducing polymerizable functional group and acid functionality onto triglyceride molecules. When combined with styrene, they form rigid polymers with mechanical properties comparable with those of commercial unsaturated polyesters. Experimental evidence has shown that these functionalized triglycerides can be used for SMC applications. When the resins were thickened with MgO paste, the viscosity increases fast during the maturation process and keeps a stable value during room temperature storage. Upon heating, the viscosity of the thickened resins is reduced quickly as the temperature increased. The formation of nanocomposites based on these triglyceride-based resins has been confirmed both by the X-ray and transmission electron microscopy data. The morphology shows a mix of intercalated and partially exfoliated sheets. The formation of nanocomposites greatly increases flexural modulus and fracture toughness, but no significant effect on flexural strength and glass transition temperature.

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References

1. H. G. Kia, Hanser/Gardner Publications, Inc., Cincinnati, OH, 1993.
2. R. P. Wool, S. H. Kusefoglou, G. R. Palmese, R. Zhao, and S. N. Khot, U.S. Patent 6,121,398, 2000.
3. K. Liu, *Soybeans: Chemistry, Technology, and Utilization*, Chapman and Hall, New York, 1997.
4. F. Gunstone, *Fatty Acid and Lipid Chemistry*, Blackie Academic and Professional, New York, 1996.
5. A. Cunningham and A. Yapp, U.S. Patent 3,827,993, 1974.
6. G. W. Bussell, Inmont Corporation, U.S. Patent 3,855,163, 1974.
7. L. E. Hodakowski, C. L. Osborn, and E. B. Harris, Union Carbide Corporation, U.S. Patent 4,119,640, 1975.
8. D. K. Salunkhe, J. K. Chavan, R. N. Adsule, and S. S. Kadam, *World Oilseeds: Chemistry, Technology, and Utilization*, Van Nostrand Reinhold, New York, 1992.
9. D. J. Trecker, G. W. Borden, and O. W. Smith, U.S. Patent 3,931,075, 1976.
10. I. Frischinger and S. Dirlikov, *Advances in Chemistry Series*, 451 (1993).
11. I. Frischinger, P. Muturi, and S. Dirlikov, *Interpenetrating Polymer Networks*, 1994.
12. S. Qureshi, J. A. Manson, L. H. Sperling, and C. J. Murphy, *Polymer Applications of Renewable-Resource Materials*, New York, 1983, pp 249.
13. L. W. Barrett, L. H. Sperling, and C. J. Murphy, *Journal of the American Oil Chemists' Society*, 70, 523 (1993).
14. E. Can, S. Kusefoglou, and R. P. Wool, *Journal of Applied Polymer Science*, 81, 69 (2001).
15. E. Can, S. Kusefoglou, and R. P. Wool, *Journal of Applied Polymer Science*, 83, 972 (2002).
16. A. Guo, D. Demydov, W. Zhang, and Z. S. Petrovic, *Journal of Polymers and the Environment*, 10, 49 (2002).
17. R. P. Wool, J. Lu, and S. N. Khot, U.S. Patent pending, 2002.
18. R. P. Wool, *Abstracts of Papers of the American Chemical Society*, 223, 082 (2002).
19. S. N. Khot, J. J. Lascala, E. Can, S. S. Morye, G. I. Williams, G. R. Palmese, S. H. Kusefoglou, and R. P. Wool, *Journal of Applied Polymer Science*, 82, 703 (2001).
20. F. K. Li and R. C. Larock, *Journal of Polymer Science Part B-Polymer Physics*, 38, 2721 (2000).
21. F. K. Li and R. C. Larock, *Journal of Applied Polymer Science*, 78, 1044 (2000).
22. F. K. Li, A. Perrenoud, and R. C. Larock, *Polymer*, 42, 10133 (2001).
23. Z. S. Petrovic, W. Zhang, A. Zlatanic, C. C. Lava, and M. Ilavsky, *Journal of Polymers and the Environment*, 10, 5 (2002).
24. F. K. Li and R. C. Larock, *Journal of Polymer Science Part B-Polymer Physics*, 39, 60 (2001).
25. R. Burns, K. S. Gandhi, A. G. Hankin, and L. B.M., *Plastics & Polymers* (1975).
26. H. J. Li and M. M. Sain, *Polymer-Plastics Technology and Engineering*, 42, 853 (2003).
27. A. Keller, *Composites Science and Technology*, 63, 1307 (2003).
28. M. M. Thwe and K. Liao, *Composites Science and Technology*, 63, 375 (2003).
29. A. Hodzic, R. A. Shanks, and M. Leorke, *Polymers & Polymer Composites*, 10, 281 (2002).
30. L. K. Belcher, L. T. Drzal, M. Misra, and A. K. Mohanty, *Abstracts of Papers of the American Chemical Society*, 222, U310 (2001).
31. G. I. Williams and R. P. Wool, *Applied Composite Materials*, 7, 421 (2000).
32. M. Alexandre and P. Dubois, *Materials Science & Engineering R-Reports*, 28, 1 (2000).
33. P. C. LeBaron, Z. Wang, and T. J. Pinnavaia, *Applied Clay Science*, 15, 11 (1999).

34. W. Thielemans and R. P. Wool, Manuscript in preparation (2004).
35. J. Lu, C. K. Hong, and R. P. Wool, *Journal of Polymer Science Part B-Polymer Physics*, 42, 1441 (2004).
36. L. E. Nielsen and R. F. Landel, *Mechanical Properties of Polymers and composites*, Marcel Dekker, Inc., New York, 1994.
37. R. P. Wool, *Polymer Interfaces: Structure and Strength*, Hanser Publishers, New York, 1995.
38. F. Alve, *Journal of Polymer Science A-1*, 9, 2233 (1971).
39. C. Zilg, R. Mulhaupt, and J. Finter, *Macromolecular Chemistry and Physics*, 200, 661 (1999).

Table I: The parameters for the resulting maleinized triglyceride

	Initial double bonds	Molar ratio (TG:MA)	Weight ratio (TG:MA)	Functional groups
MAESO2	4.6	4.4	100:16.3	5.2
MAESO3	4.6	1:3	100:24.5	5.9
MAELO2	6.6	1:2	100:14.1	7.3
MAELO3	6.6	1:3	100:21.6	8.18

Table II: Physical characteristics for triglyceride-based resins

	Viscosity (cP)	Density (g/cm ³)	E' at 30 °C (GPa)	(tan δ) _{max} (°C)	Cross-link density ((mol/m ³))
MHSO	~1376	1.10	1.50	103	---
MAESO2	~800	1.11	1.91	114	4658
MAESO3	~1500	1.14	2.15	130	6322
MAELO2	~2200	1.13	2.34	120	8659
MAELO3	~2200	1.14	2.50	133	8848

Table III: Mechanical and dynamic mechanical properties of natural fiber composites

	fiber wt%	Flexural Strength (MPa)	Flexural Modulus (GPa)	(tan δ) _{max} (°C)	E' at 30 °C (GPa)
MAESO+hemp	10.3	44.069	2.595	115.8	1.77
MAESO+flax	14.7	45.63	2.894	116.5	2.52

Table IV: Mechanical properties of triglyceride-based clay nanocomposites

Clay Content (%)	Flexural Modulus (GPa)	Flexural Strength (MPa)	G _{1C} (J/m ²)
0	2.06±0.10	82.3±2.4	171.0±32.7
3	2.31±0.11	85.4±1.4	187.1±26.3
5	2.45±0.05	86.1±0.8	383.5±77.4
7.5	2.63±0.03	81.7±2.4	365.7±34.9
10	2.47±0.09	81.0±2.0	175.1±26.1

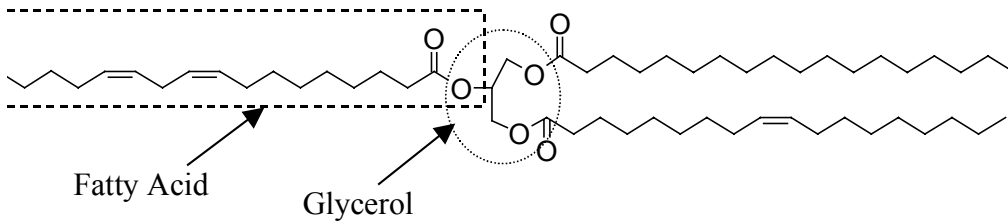


Figure 1: The molecular structure of a typical triglyceride molecule.

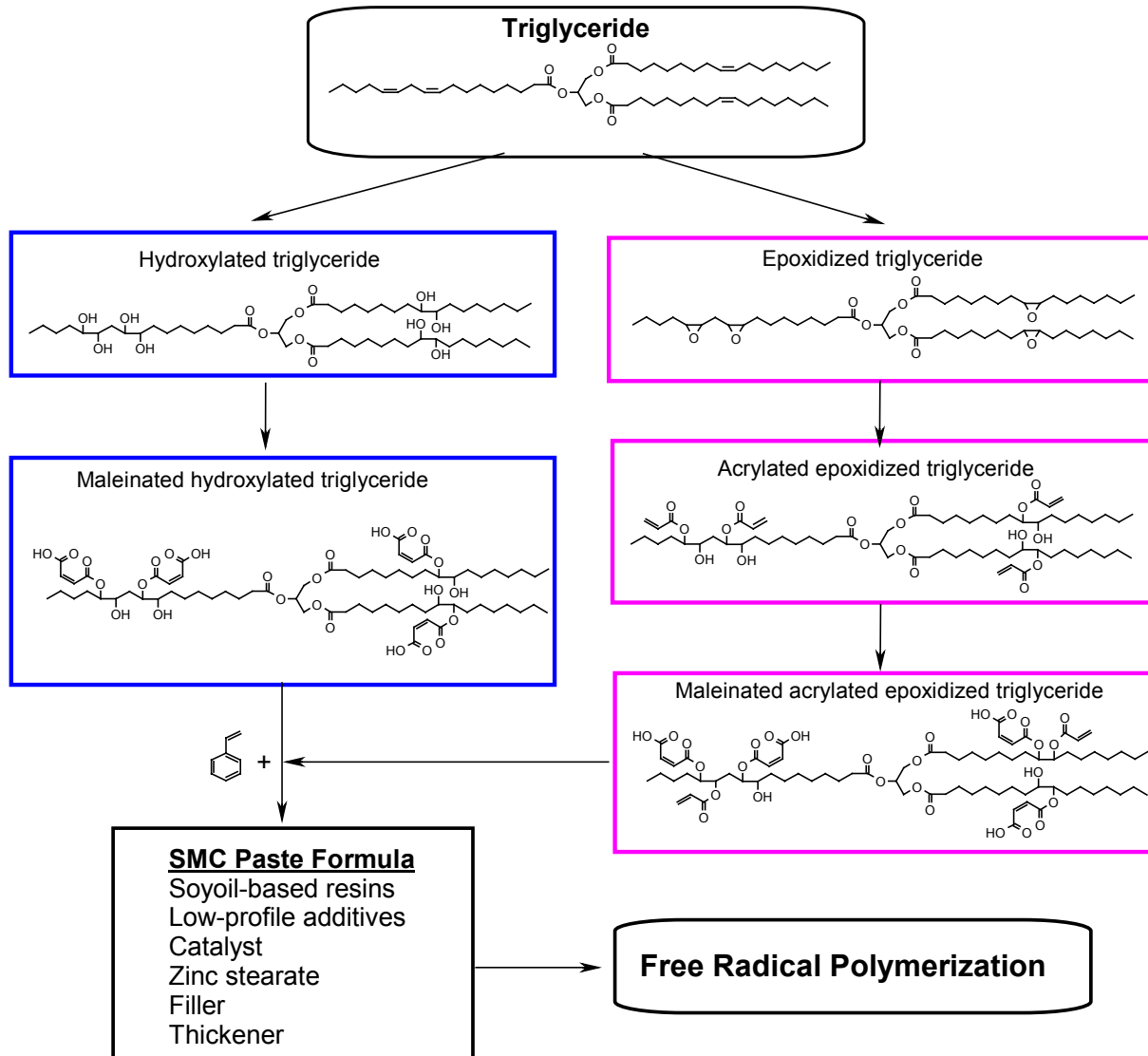


Figure 2: Chemical pathways to prepare thermosetting resins for SMC applications.

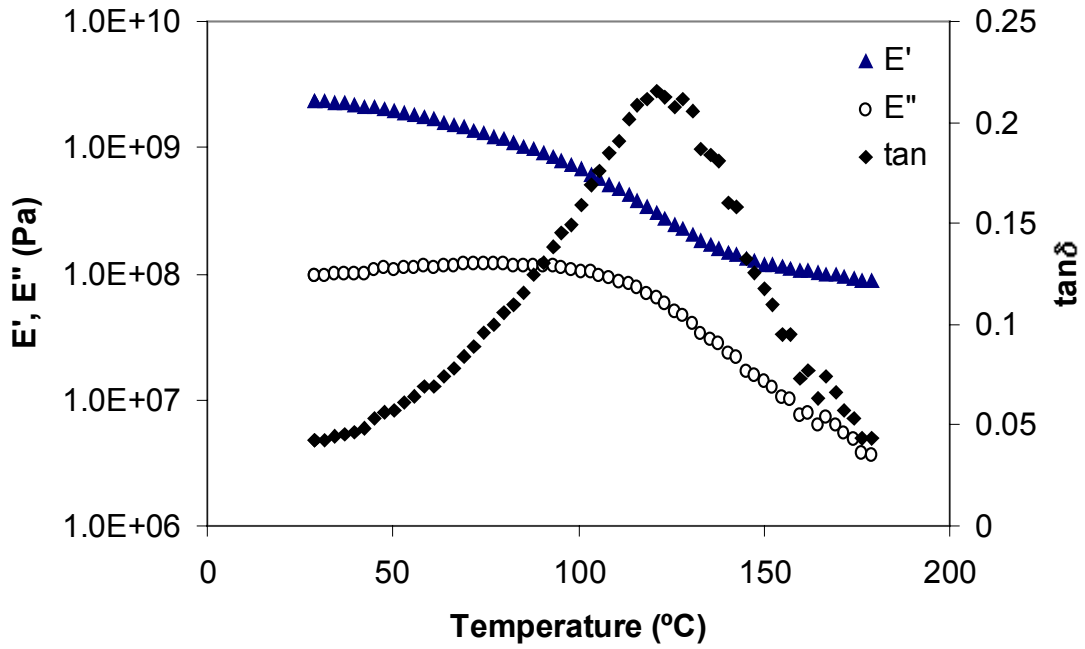


Figure 3: Dynamic mechanical behavior of MAELO2 system as a function of temperature.

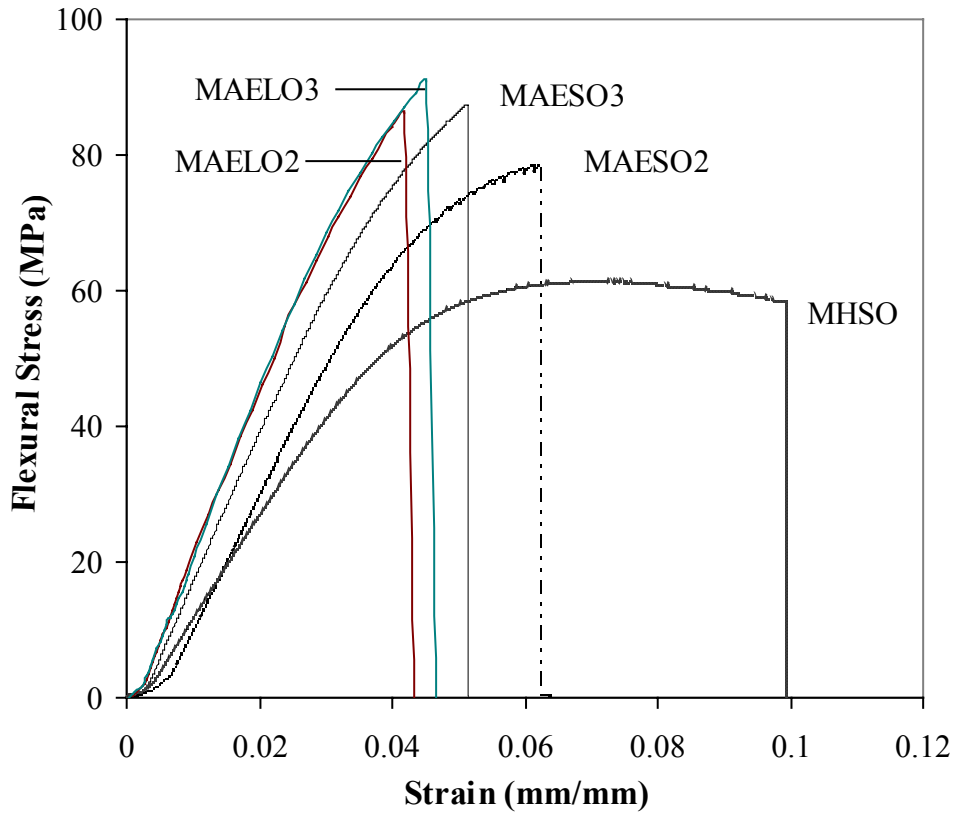


Figure 4: Flexural behavior of the triglyceride-based polymers.

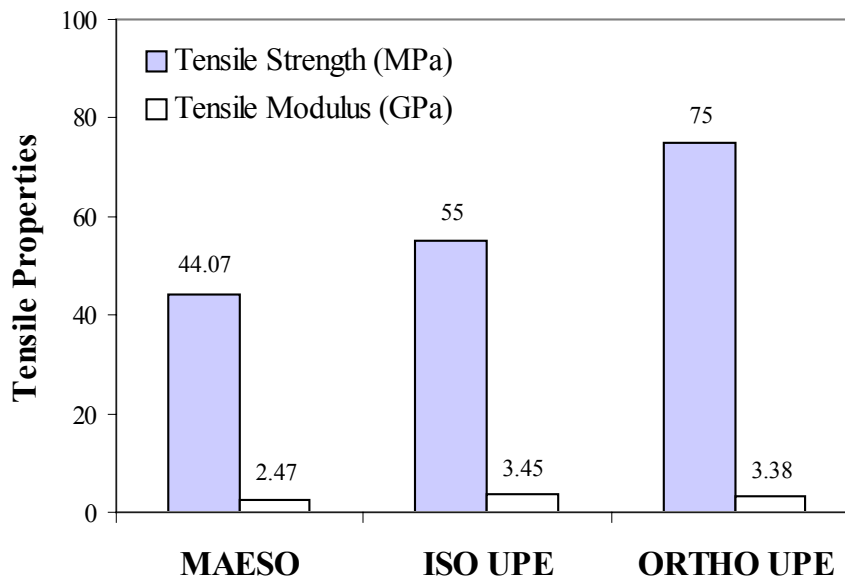
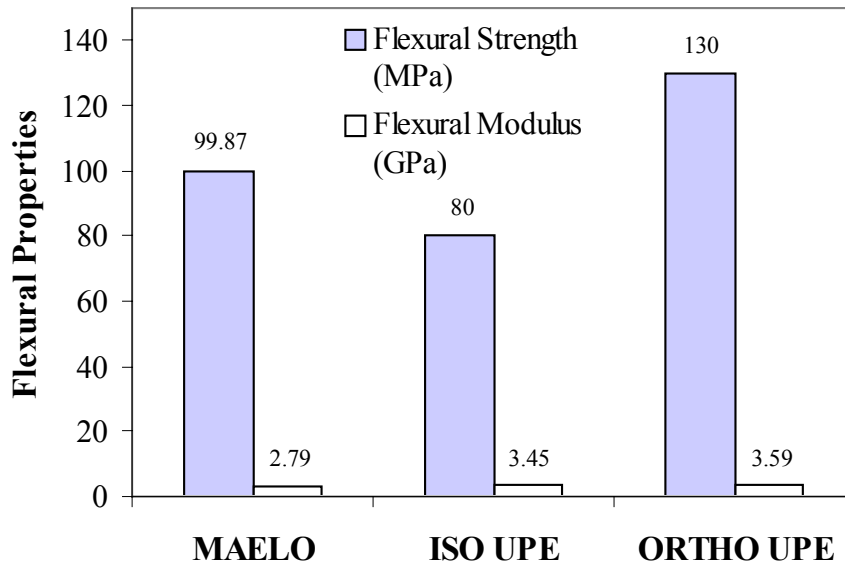


Figure 5: Comparison of mechanical properties of triglyceride-based polymers with the isophthalic unsaturated polyester (ISO UPE) and orthophthalic unsaturated polyester (ORTHO UPE).

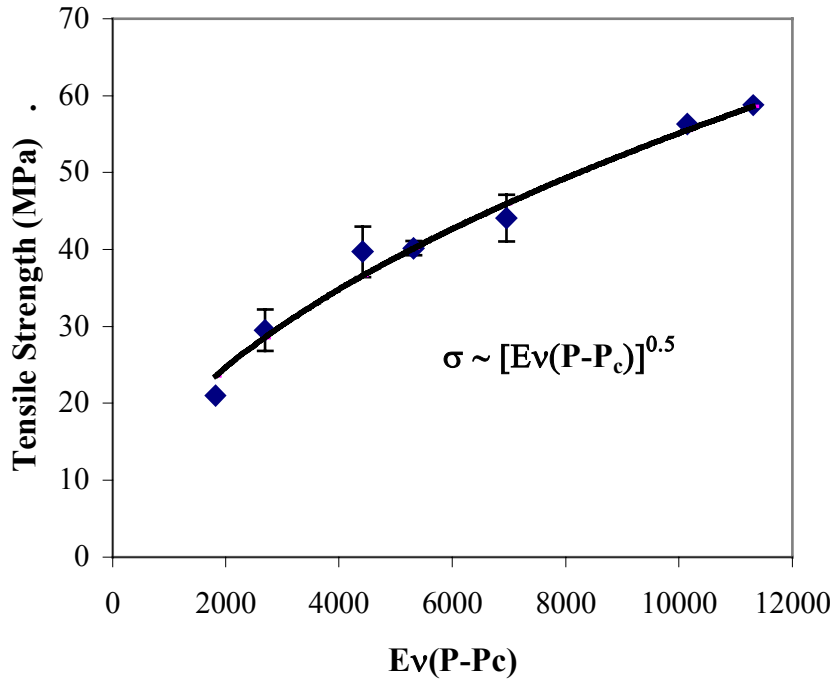


Figure 6: The tensile strength of triglyceride-based polymers is following percolation prediction.

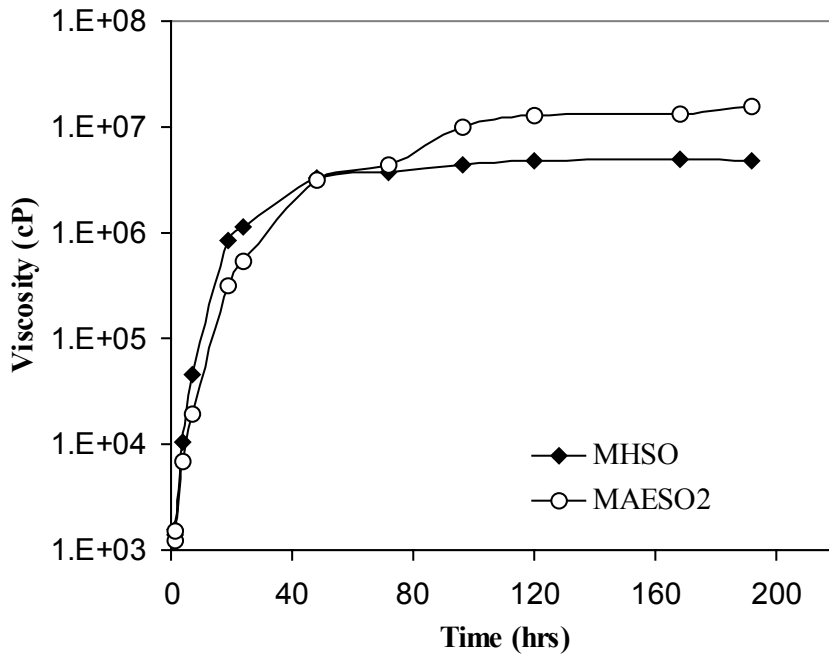


Figure 7: Viscosity changes during the maturation process of triglyceride-based resins with 1.5 wt % MgO.

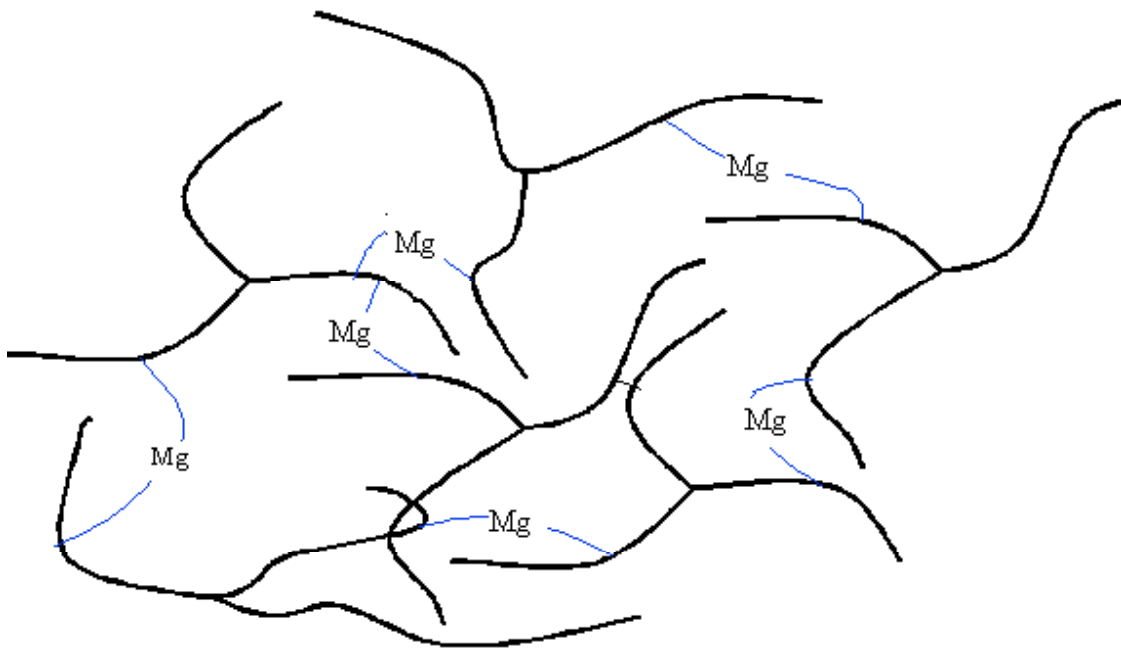


Figure 8: The formation of cross-linked structure during thickening.

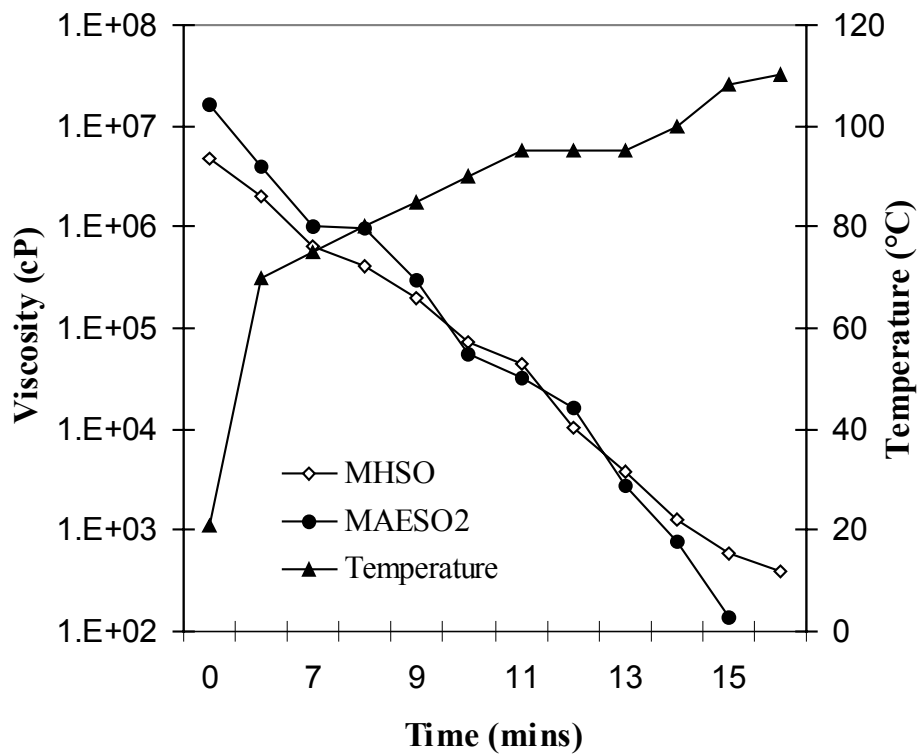


Figure 9: Viscosity changes during heating.



Figure 10: The first John Deere Round Hay Baler panel made with triglyceride-based resins.