

# Synthesis of Reactive Soybean Oils for Use as a Biobased Thermoset Resins in Structural Natural Fiber Composites

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**ABSTRACT:** Biobased thermosets resins were synthesized by functionalizing the triglycerides of epoxidized soybean oil with methacrylic acid, acetyl anhydride, and methacrylic anhydride. The obtained resins were characterized with FTIR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectroscopy to confirm the functionalization reactions and the extent of epoxy conversion. The viscosities of the methacrylated soybean oil resins were also measured for the purpose of being used as a matrix in composite applications. The cross-linking capability was estimated by UV and thermally initiated curing experiments, and by DSC analysis regarding the degree of crosslinking. The modifications were successful

because up to 97% conversion of epoxy group were achieved leaving only 2.2% of unreacted epoxy groups, which was confirmed by <sup>1</sup>H-NMR. The <sup>13</sup>C-NMR confirms the ratio of acetate to methacrylate methyl group to be 1 : 1. The viscosities of the methacrylated soybean oil (MSO) and methacrylic anhydride modified soybean oil (MMSO) were 0.2 and 0.48 Pas, respectively, which indicates that they can be used in resin transfer molding process. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3137–3145, 2010

**Key words:** biofibres; biopolymers; crosslinking; modification; renewable resources

## INTRODUCTION

Biobased polymers are becoming more popular in many technical products such as plastics, composites, and construction materials. Polymers can be made from many raw materials available in nature. The most common raw material is lactic acid available by fermentation of carbohydrates, and the resulted polymer polylactic acid is used in thermoplastic applications such as packaging products and biomedical applications. Biobased thermosets have also been developed, and their application in aerospace, automotives, marine, and military is gaining interest. Triglycerides from plants, such as soy bean, palm, rapeseed or sun flower, can be utilized.<sup>1–9</sup> The triglyceride compound must be isolated and purified, and also functionalized to obtain the requested reactivity. Various chemical modification reactions are possible; the most common goes via an epoxidation reaction. Therefore, the use of plant oil based resins in liquid molding resins not only would reduce volatile organic compounds emissions, thereby reducing health and environmental risks, but it also would promote global sustainability.<sup>10,11</sup>

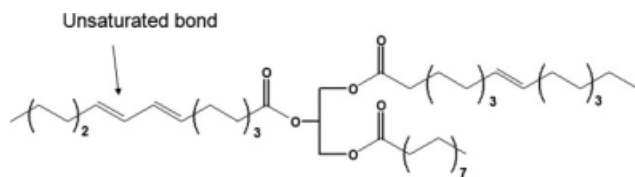
Plant oils are renewable raw materials for a wide variety of industrial products, including coatings,

inks, plasticizers, lubricants, and paints.<sup>8,9,12</sup> Recently, polymers developed from renewable resources have attracted much attention due to their environmental and economic advantages.<sup>13–15</sup> The growing environmental awareness and new rules and regulations are compelling the industries to seek more eco-friendly materials for their products.<sup>16</sup> Commercial markets for biodegradable and biobased polymers are expected to increase substantially in the coming years.<sup>16</sup> However, the physical and chemical properties of conventional soybean oil limit its use for many industrial applications. Soybean resins are based on triglycerides, which are the major component of plant and animal oils.<sup>6</sup> Triglycerides are composed of three fatty acid chains joined by a glycerol center.<sup>6,7,11,17–19</sup> (Fig. 1).

There is an on going research aimed at improving the industrial value of soybean oil through “green chemistry.”<sup>4,12</sup> Significant progress has been made in the development of chemical methods for enhancing the functionality of soybean oil.<sup>3,4,6–8,12,19</sup> One of the most notable examples of this research has been the discovery of methods for producing polyols from soybean oil.<sup>20</sup> For example, soybean oil has double bonds (iodine number 142), but it does not give homo- or copolymer by a radical-initiated polymerization.<sup>3</sup> Therefore, to be useful as a monomer for radical polymerization, the triglyceride molecule has to be suitably functionalized.<sup>2,3,6,8,18</sup>

Of the available plant oils, soybean oil appears to be most attractive alternative resource because of its

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**Figure 1** Chemical structure of a triglyceride molecule.

very low price and abundant supply.<sup>4,12,21,22</sup> Fatty acid monomers are excellent alternatives to styrene because of their low cost and low volatility.<sup>11</sup> Styrene and other commonly used reactive diluents are hazardous air pollutants and volatile organic compounds (VOC), so there has been legislation to limit styrene emissions from composite manufacturing.<sup>18,23</sup> The largest category of industrial soybean oil use includes plastics and resins.<sup>12</sup>

Epoxidized soybean oil can be used as a reactive modifier for epoxy resin systems.<sup>24</sup> The epoxy groups are however available for further chemical modification reactions.<sup>25</sup> The introduction of acrylate or methacrylate functions in a polymer or oligomer is generally made with the aim of polymerization or copolymerization of the double bonds leading to network or grafted copolymers.<sup>26</sup> More recently, researchers have begun to explore the feasibility of manufacturing polymer composites from epoxidized soybean oil and this is the background that motivated these studies, which investigate organic synthetic methods for epoxy functionalisation. The development of soy-based resins for structural applications is still a challenge for the polymer and composite industries.<sup>12</sup>

In this article, we will describe some synthetic attempts to functionalize epoxidized soybean oil (ESO) by reaction with methacrylic compounds. The goal of this research is to develop soybean oil based thermoset resins, which will subsequently be used as matrix in composite preparation.

## EXPERIMENTAL

### Materials

Epoxidized soybean oil (EDENOL D81) was supplied by Cognis GmbH, Monheim, Germany. Methacrylic acid, (99 %), methacrylic anhydride (94 %), and acetic anhydride (99 %) were used for the modification. *N*-Methylimidazol (99 %) was used as a catalyst, and hydroquinone (99 %) was used as cross-linking inhibitor. All chemicals were purchased from Aldrich Chemical Company, USA. Chloroform (99 %) was supplied by Fisher Scientific, Sweden. *t*-Butyl peroxybenzoate was used as the free radical initiator for the curing experiments, and it was supplied by Adonox PB, Sweden. Silica gel

was used in the gel filtration for the purification of the products and was bought from Kebo lab, Sweden.

### Synthesis of methacrylate modified soybean oil (Scheme 1)

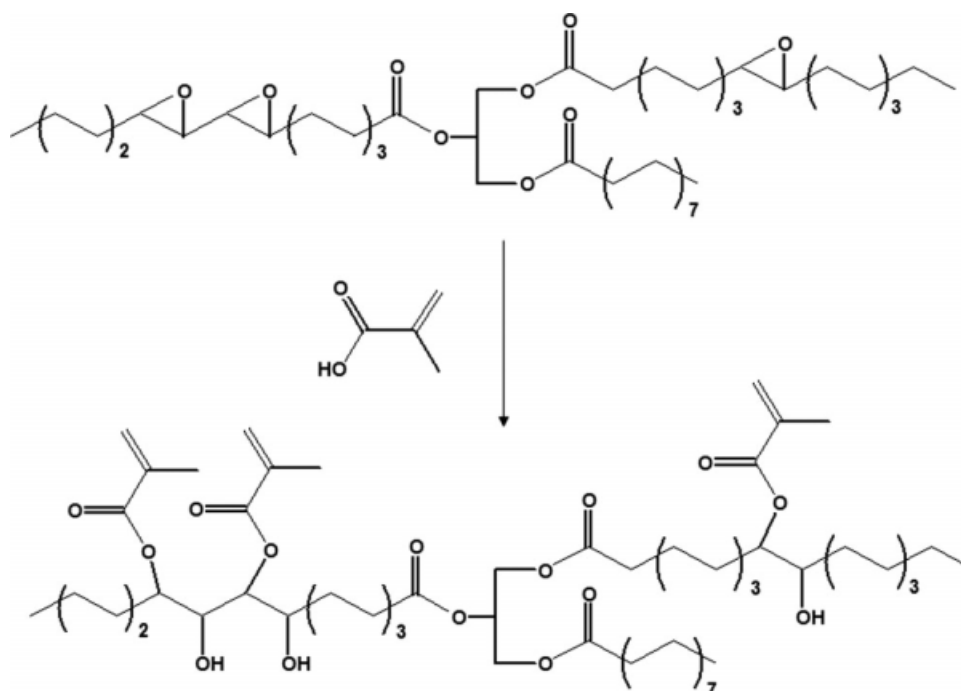
Epoxidized soybean oil, ESO (13.2 g) equivalent to 0.01 mol ESO was heated from room temperature while methacrylic acid (4.3 g, 0.05 mol) containing hydroquinone (0.01 g, 0.25 wt %) was added during 30 min. The reaction mixture was heated under reflux for 8 h at 120°C while being constantly stirred. Excess methacrylic acid (1.7 g, 0.02 mol) containing hydroquinone (0.004 g) was then added during 5 min and the reaction was allowed to proceed for another 4 h at the same temperature. The mixture was then cooled to room temperature and purified by extraction in chloroform and further washed with 5% anhydrous sodium carbonate. The organic layer was dried over anhydrous sodium sulfate and evaporated using rotational distillation. The obtained product, methacrylated soybean oil (MSO) was then isolated. The product weighed 14.9 g and was further purified by gel filtration. The initial synthesis was upscaled, first fourfold, and then 12-fold twice. The total amount of obtained MSO was therefore about 400 g.

### Further modification with methacrylic anhydride (Scheme 2)

MSO (15.7 g) was dissolved in chloroform and heated under reflux condenser in a three-neck round-bottomed flask at 55°C. Methacrylic anhydride (7.7 g, 0.05 mol) was added drop wise during 15 min, after which the temperature rose a little above 60°C, the boiling point of chloroform. *N*-Methylimidazol (1 wt %, 0.25 g) was used as catalyst. The reaction proceeded for 3 h being constantly stirred. The reaction mixture was allowed to cool to room temperature and the extraction was done as for step 1. The product, methacrylic anhydride modified soybean oil (MMSO), weighed 16.0 g. The synthesis was then upscaled fourfold, and totally 55 g product was obtained.

### Further modification with acetic anhydride (Scheme 3)

MSO (10.2 g) was dissolved in chloroform and heated under reflux in the presence of *N*-methylimidazol (1 wt %, 0.25 g), acetic anhydride (5.1 g, 0.05 mol) was then added drop wise. The synthesis proceeded as previously described. The product acetic anhydride modified soybean oil (AMSO; 10.6 g) was obtained. The synthesis was then upscaled fourfold,

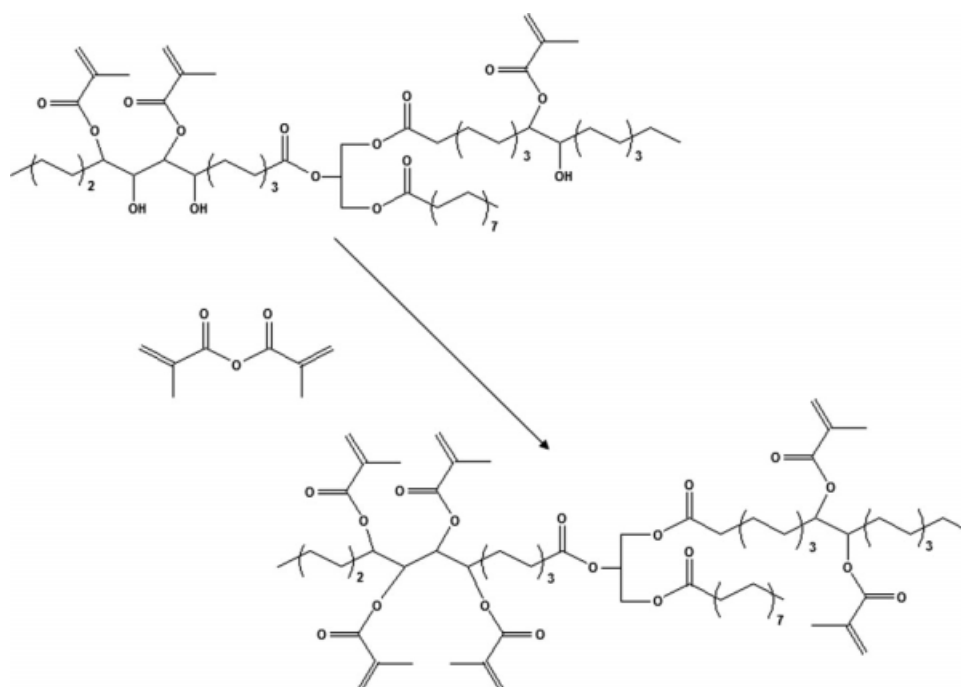


**Scheme 1** Reaction of epoxidized soybean oil (ESO) with methacrylic acid to yield a methacrylated soybean oil (MSO).

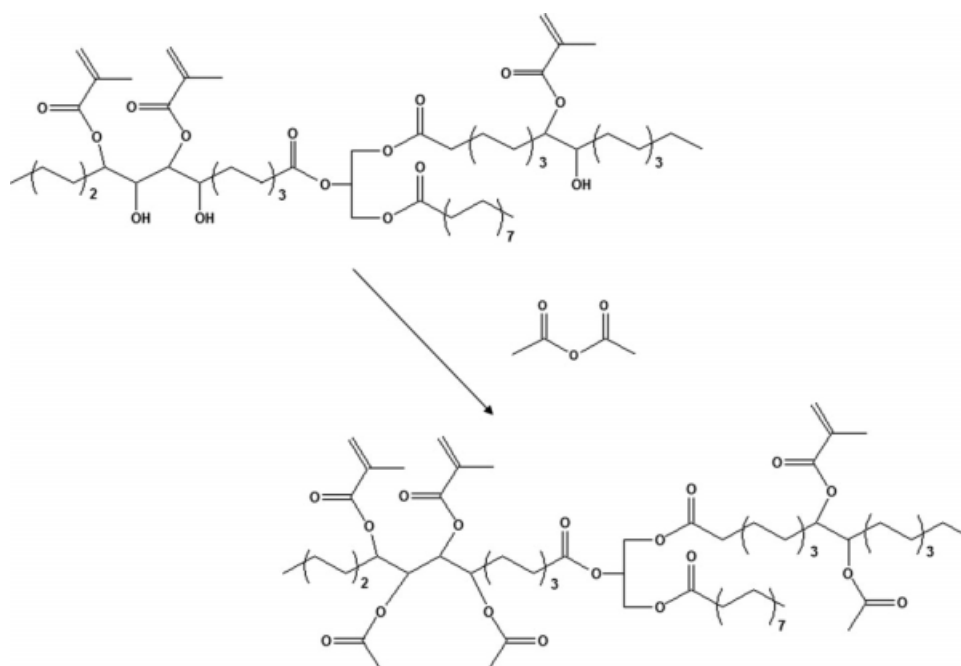
and this gave 55 g of the wanted product. Gel filtration of the various products of the syntheses was done using silica gel 60. The products were dissolved differently in chloroform and filtered through the column. Isolation of the various products was done using rotational distillation and the purified products analyzed.

#### Curing experiments

The thermal curing was done by first mixing the resins with *t*-butyl peroxybenzoate and then placing them in an oven heated to 160°C. Samples were withdrawn at 5 min, 10 minutes, 1 h, 2 h, 4 hours, 19 h and 24 h after addition of the peroxide, and



**Scheme 2** Reaction of methacrylated soybean oil (MSO) with methacrylic anhydride to yield a twice methacrylated soybean oil (MMSO).



**Scheme 3** Reaction of methacrylated soybean oil (MSO) with acetic anhydride to yield an acetic anhydride modified methacrylated soybean oil (AMSO).

analyzed by DSC and FT-IR. The data from the first dynamic DSC scans were used for determination of possible exothermic peaks.

The photocuring was done with Irgacure 819, and the resin was exposed to blue light for 0 second, 6 s and 90 seconds, using a Heraflash light curing unit. The remaining heat exotherm was analyzed by dynamic DSC scans.

### Characterization

The synthesized resins were characterized by FTIR and  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy in order to verify the chemical modification reactions. The FTIR analysis was carried out on Nicolette 6700 spectrometer, supplied by Thermo Fisher Scientific, Massachusetts, USA. The cured specimens were also analyzed, in order to determine the degree of conversion. The NMR analysis was performed with a CMX400 infinity spectrometer supplied by Chemagnetics, Colorado, USA. The samples were dissolved in chloroform and then run at a frequency of 400 MHz. The number of scans acquired was 32, using a 90 degrees excitation pulse and a 20 s recycle delay.

The average side chain length, the epoxy density on the chain and the amount of methacrylate and acetyl groups reacted with them, as well as the residual alcohol groups were determined by the NMR analysis. These analyzes were done to investigate the reactions of the epoxy groups and to determine the ratio of acrylate to acetate group.

The DSC analysis was done on a TA Instruments Q series (DSC Q 1000) TM model supplied by Waters LLC, New Castle, USA. Samples of  $\sim 10$  mg were heated at  $10^\circ\text{C}/\text{min}$  in a nitrogen purge stream between  $-20^\circ\text{C}$  and  $200^\circ\text{C}$ , fast cooling applied and then heated again at the same rate between  $-20^\circ\text{C}$  and  $200^\circ\text{C}$ . The data from the first scan was used.

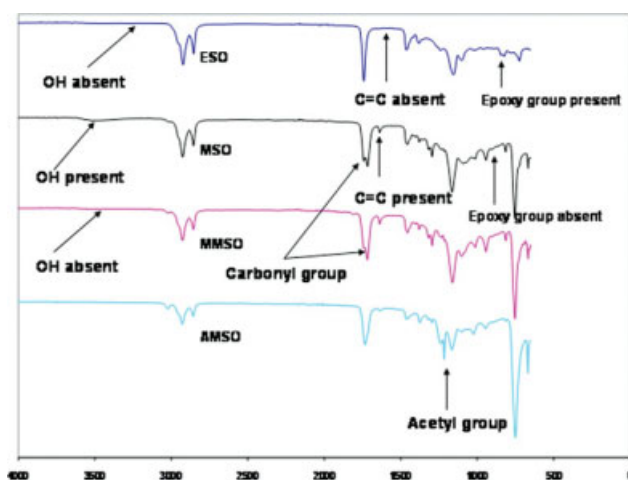
The thermogravimetric analysis was done using TA instrument (TGA Q 500) supplied by Waters LLC, New Castle, USA. Samples of  $\sim 15$  mg were heated at  $20^\circ\text{C}/\text{min}$  in a nitrogen purge stream between  $30^\circ\text{C}$  and  $650^\circ\text{C}$ . The flow rate of the nitrogen stream was  $50\text{ mL}/\text{min}$ .

The viscosity of the neat uncured resin was determined using a Bohlin rheometer CS30 from Malvern Instruments Ltd, United Kingdom. All measurements were done with a cone plate configuration with a truncated cone ( $\text{Ø}15\text{ mm}$ ,  $5.4^\circ$ ). The characterization was done by stress viscometry. For each temperature, three different levels of the stress were chosen and the viscosity was calculated.

## RESULTS AND DISCUSSION

### FTIR spectroscopy analysis of the thermoset resins

Figure 2, shows the FTIR spectra of all the samples available for analysis. The absorption bands of the epoxy group at  $823$  and  $841\text{ cm}^{-1}$  present in ESO disappear in the IR spectra of MSO, while double bands appear at  $1739$  and  $1716\text{ cm}^{-1}$  which



**Figure 2** FTIR spectra comparison of ESO, MSO, MMSO, and AMSO resins. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

represent the carbonyl group. The hydroxyl absorption was around  $3491\text{ cm}^{-1}$  and  $3472\text{ cm}^{-1}$  in the spectra of MSO respectively, while this was absent in the spectrum of ESO. The absorption at about  $1630\text{ cm}^{-1}$  which is characteristic of carbon double bond can be seen in the spectra of MSO, while this is absent in the spectrum of ESO. The IR spectra of the MMSO and AMSO show that the hydroxyl peaks disappear and the absorptions at about  $1715$  and  $1730\text{ cm}^{-1}$  characteristic of carbonyl group and the carbon double bond also at  $1636\text{ cm}^{-1}$  are visible, which indicates a successful reaction. The IR spectrum of AMSO shows absorptions at  $1217$  and  $1235\text{ cm}^{-1}$ , which could be due to acetyl functional group.

### $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy analysis of the thermoset resins

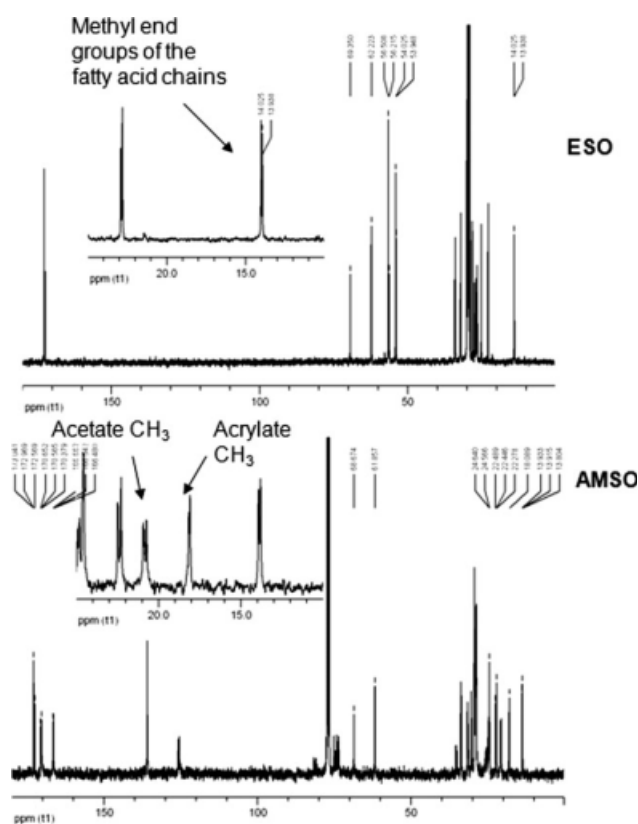
The NMR spectroscopic analysis verified that the wanted reactions occurred. The epoxy carbons in the ESO sample are in the 52 to 57 ppm region. These signals are missing in the AMSO sample and several new peaks around the 72 to 85 ppm area can be seen. These are presumed to be due to the ring-opening reaction of the epoxide group, (Fig. 3). The  $^{13}\text{C-NMR}$  spectra of ESO and AMSO were also used to confirm the methyl group assignments and also to determine the ratio of acetate and methacrylate methyl groups (and therefore mole ratio of acetate and methacrylate groups) in the AMSO sample. The ratio of acetate and methacrylate methyl groups in the AMSO sample was found to be 1 : 1 (Fig. 3).

This was also confirmed by  $^1\text{H-NMR}$  spectrum of the ESO, see Figure 4. The epoxy groups give signals around 3 ppm, and in the modified resin samples these have disappeared, and subsequently new sig-

nals are formed around 4.0 and 5.0 ppm. The peaks around 4.0 ppm are probably due to  $\text{CH-OH}$  groups, while the ones around 5.0 ppm are due to the  $\text{CH-OR}$  groups ( $R = \text{acetate or methacrylate}$ ).

The degree of epoxy group conversion was determined from the  $^1\text{H-NMR}$  analysis. The starting material ESO contains 100% epoxy group but this was consumed to a reasonable extent after the first synthesis with excess methacrylic acid (MSO) bringing the residual epoxy to about 5.8% and loss of epoxy to 94.2%. Further modification with methacrylic anhydride shows further consumption of the epoxy group, thus leaving only 2.2% residual epoxy while the total loss of epoxy was 97.8%. Modification with acetic anhydride shows the same trend leaving 3.8% residual epoxy and loss of epoxy was 96.2%. Higher consumption of the epoxy groups in subsequent modifications could be due to more reaction time and acid anhydride monomers added.

Table I shows the functional groups that are represented on the fatty acid chain of the triglyceride oil. The epoxy carbons per chain in the starting material, the epoxidized soybean oil, which was 3.8, reduced to a very low value due to the modification of the oil. The trend follows that the higher the level of epoxy conversion the lower the epoxy carbons per chain. The only resin having the acetate group



**Figure 3** Comparison of the quantitative  $^{13}\text{C-NMR}$  of ESO and AMSO resins.

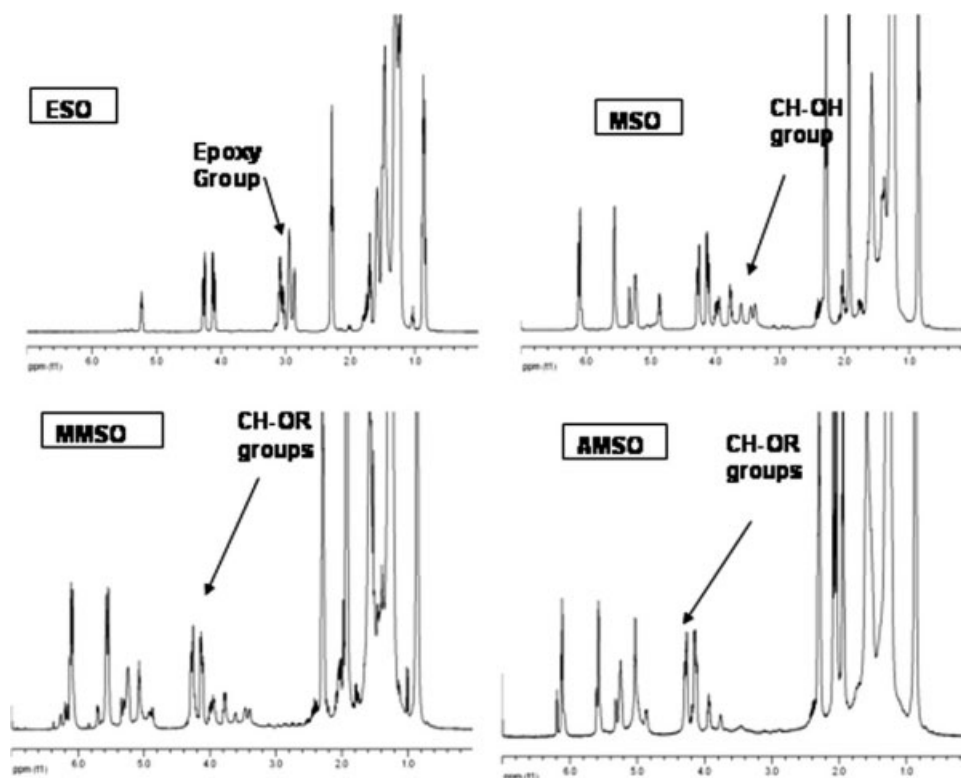


Figure 4  $^1\text{H-NMR}$  spectra comparison of ESO, MSO, MMSO, and AMSO resins.

present on its chain was the AMSO and this was due to the fact that the synthesis was further done using acetic anhydride as a monomer. Acrylate group per chain was higher in the MMSO and this was due to the further modification with methacrylic anhydride. The reason for modification with methacrylic acid in this experiment was to introduce cross-link-able functionalities (methacrylate groups) and further modification with methacrylic anhydride was to introduce additional functionalities (methacrylate groups), while further modification with acetic anhydride was to reduce polar functionality (OH groups) in the resin.

#### Cure investigation results

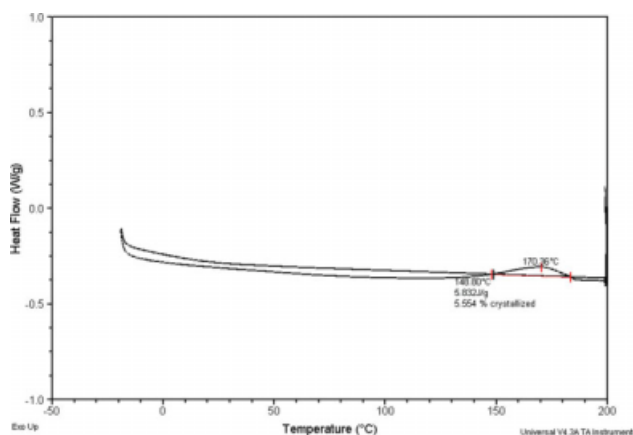
The DSC scan for the sample cured thermally for 10 min showed an exotherm peak indicating incomplete cure, see Figure 5. Longer curing times gave no exothermic peaks, meaning that the curing was complete. The FTIR spectra of the samples cured at 5 and 10 min showed a carbon-carbon double bond peak at  $1635\text{ cm}^{-1}$ , which indicates that the samples were not fully cured, while no carbon-carbon double bonds could be seen in the samples cured between 1 h and 24 h.

The applicability of the resins for photocuring was examined. The neat resins were blended with a

TABLE I  
Characterization of the Functional Groups in the Soybean Oil resins

	ESO	MSO	MMSO	AMSO
Chain length	15.8	a	a	a
Residual C=C carbons/chain	0.1	a	a	a
Epoxy carbons/chain	3.8	0.18	0.06	0.1
Acetate groups/chain	—	—	—	0.81
Acrylate groups/chain	—	0.66	0.99	0.64
Alcohol groups/chain	—	1.77	1.57	1.07
% epoxy carbons/chain	16.5	1.1	0.4	0.6
% acetate groups/chain	—	—	—	4.9
% acrylate groups/chain	—	4.2	6.3	3.9
% alcohol groups/chain	—	11.2	9.9	6.5
TOTAL% of groups substituted on chain	16.5	16.5	16.5	15.9

<sup>a</sup> Assumed to be the same as in the ESO sample.



**Figure 5** DSC curve of MSO, MMSO, and AMSO resins cured with 2 wt % tert-butylperoxybenzoate at 160°C for 10 min. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

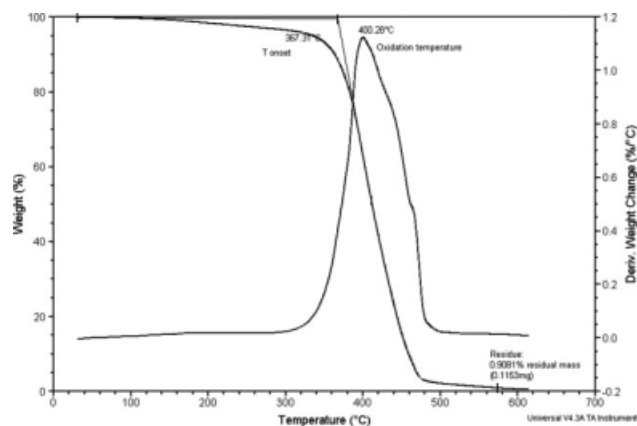
photoinitiator and the resins were exposed to blue light. All the resins can be cured to completion by photocuring (see Table II). The MSO resin seems to be the most reactive and cures to almost completion with 6 s of exposure. The MMSO resin also seems to be feasible for photocuring. The AMSO resin only shows about half of the heat exotherm in comparison to the MSO resin. Considering that both resins contain one carbon–carbon double bond one would expect both resin to have a similar heat exotherm after 0 s exposure. Besides, considering that the MMSO resin contains two double bonds in contrast to the other two resins, one would expect a higher heat exotherm for this resin in terms of photocuring.

### Thermogravimetric analysis of the cured resins

The percentage weight loss of the cured samples is recorded while the sample is being heated at a uniform rate in an appropriate environment. The loss in weight over a specific temperature ranges (30 to 650°C) provides an indication of the composition of the samples, including volatiles and inert fillers, as well as indications of thermal stability. The thermogravimetric curves (Fig. 6) represented the MSO resin cured between 10 min and 1 h at 160°C. They show that there was only a single degradation process for

**TABLE II**  
Heat of Exotherms Detected by DSC after Different UV Exposures

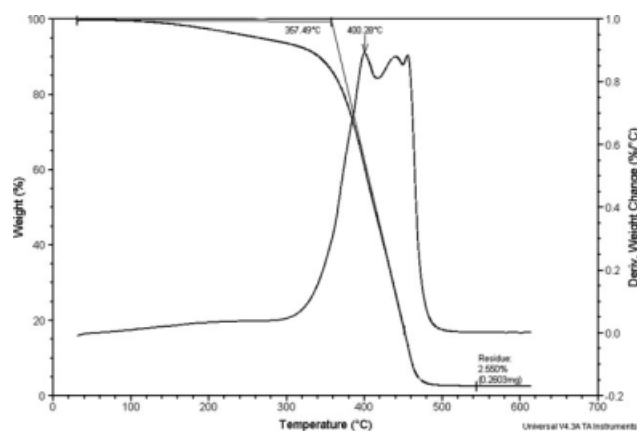
Resin + 4% Irgacure 819	0 s exposure (J/g)	6 s exposure (J/g)	90s exposure (J/g)
MSO	36.77	2.1	0
MMSO	34.57	8.00	0
AMSO	16.2	0	0



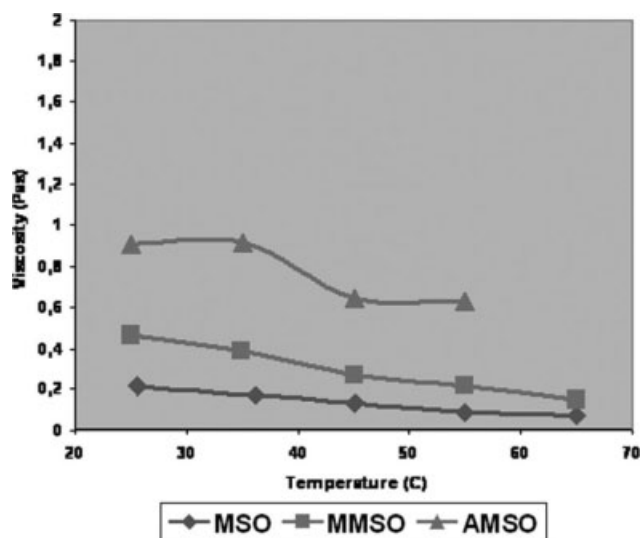
**Figure 6** TGA curve of the MSO resin cured between 10 min and 1 h at 160°C.

the thermoset polymer. The degradation occurred in the temperature region of 320–480°C, with the maximum rate of decomposition which is also referred to as the temperature of the maximum rate of oxidation, reached at about 400°C and the residual mass around 0.11 mg. Figure 7 represented thermogravimetric curves of the MMSO resin cured between 10 min and 1 h at 160°C, there were some peaks which could be due to some volatile components in the polymer, one would have expected the same result as in the MSO, although the degradation occurred in the same temperature region of 320–480°C and the maximum rate of decomposition reached at 400°C.

However, a MMSO resin that was cured in a different way (for instance at room temperature for 2 h and post cured at 125°C for 1.5 h) does not show any multiple peaks, which could mean that no volatile substance present in this resin, possible explanation could also be that the technique employed in the crosslinking might have effect on resulted cured polymer. The degradation is as a result of the



**Figure 7** TGA curve of the MMSO resin cured between 10 min and 1 h at 160°C.



**Figure 8** Soybean oil resin viscosities at different temperatures.

decomposition of the crosslinked polymer network and random scission of the linear chains. Oxidative temperature is basically a measure of the thermal stability of the polymers in air. Thermal stability is however a good measure of the overall quality of the samples tested. Higher oxidation temperature is always associated with purer, less defective samples.

### Viscosity measurements

The viscosity of a thermoset resin is very important since it will determine how the resin can be processed. The result of the viscosity measurements are shown in Figure 8. Both the MMSO resin and the MSO resin have low viscosities at room temperature especially the MSO resin which has a viscosity of about 0.22 Pas at 25°C. Commercial crude oil based resins, such as unsaturated polyester resins are invariably diluted with styrene in order to lower the viscosity. These tests indicate, however, that both the MMSO and the MSO resin can probably be processed with infusion techniques such as resin transfer molding with only a small addition of styrene or eventually without styrene. The viscosity curve of the AMSO resin does not look very reliable. The rheological behavior of this resin needs to be further investigated.

### CONCLUSIONS

Biobased resins for use in thermoset composites were synthesized from soybean oil. The epoxidized soybean oil was functionalized with methacrylic acid (methacrylation) and the resulted product was further modified using acid anhydrides, the aim was not only to increase the crosslink sites per triglycer-

ide but also reduces the number of free hydroxyl groups, which have a viscosity increasing effect. The viscosity of the MSO and MMSO resins is quite promising in composite manufacturing. The methacrylation of the epoxidized soybean oil using a 0.2 molar excess of methacrylic acid could maximize the conversion of epoxide groups to more than 90%. The further modification with methacrylic anhydride proved to be more effective than with acetic anhydride. A higher conversion of epoxy groups was achieved up to 97% in the MMSO sample, this was confirmed by the  $^1\text{H-NMR}$  and the ratio of acetate and methacrylate methyl groups in the AMSO sample was found to be 1 : 1, this was confirmed by the  $^{13}\text{C-NMR}$ .

The methacrylated soybean oil MSO was mixed with 2 wt % *t*-butyl peroxybenzoate and was cured thermally at 160°C for 24 h; however, a fully cross-linked thermoset polymer was achieved after 1 h, which was confirmed by the DSC analysis. No structural changes observed in the crosslinked polymer in spite of the prolonged cure in the oven, this was also confirmed by the FTIR. The thermogravimetric analysis (TGA) curve of the MSO sample showed a single degradation in the range of 320–480°C, which corresponded to the decomposition of the cross-linked structure.

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