

SYNTHESIS OF REACTIVE SOYBEAN OILS FOR USE AS BIOBASED THERMOSET RESINS IN STRUCTURAL NATURAL FIBRE COMPOSITES

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ABSTRACT

Biobased materials are becoming more and more popular in technical products such as plastics, composites and construction materials. Polymers can be made from biobased raw materials, the most common is polylactic acid, which is a thermoplastic material, and has found use in packaging products. Biobased thermosets have also been developed. Triglycerides from plants, such as soy bean, palm, rapeseed or sun flower, can be utilised. The triglyceride compound must be isolated and purified, and also functionalised to get reactivity. Various chemical modification reactions are possible; the most common goes via an epoxidation reaction. In this study we described some synthetic attempts to functionalize epoxidised soybean oil (ESO) by reaction with methacrylic and acrylic compounds. The functionalized soybean oil resins were purified and characterized using FT-IR, NMR spectroscopy and the extent of cure was done with DSC scanning. The obtained resins later used as matrices in composites preparation.

1. INTRODUCTION

In search of alternative raw materials for resins and polymers, the plant oils have been identified as versatile candidates. Plant oils, or natural triglyceride oils, are abundant in most parts of the world, and they are ideal alternatives to crude oil based feed stocks.[1-8] Triglycerides are esters of fatty acids and glycerol, and the fatty acid chain contains typically 14 to 22 carbons in length of which 0 to 6 are unsaturated. [6, 7, 9-12] There are many plants that can be used for oil production. Soybean, rapeseed, sunflower, linseed and sunflower are some examples. The exact chemical composition varies a lot between the plants, and there are also individual variations among the plants. The plant oils main use is in the food industry, but there is also a traditional use as binders for coatings and inks, lubricants as well as plasticizers. [8, 13] As such the plant oils cannot be used in rigid and structural plastic products, due to their low molecular weight. This is however possible, if the plant oil triglyceride is functionalized so it can undergo further chemical reactions. There are several chemical reactions available, which can be utilized for the functionalisation into a thermosetting resin. Maleinisation, acrylation, hydroxylation and anhydriation are some reported methods. [2, 8] The obtained resin can then be cross-linked by various methods, and a rigid plastic material is then obtained.

In this paper we will describe synthetic modification of epoxidised soybean oil by reaction first with methacrylic acid, and then with methacrylic anhydride or acetic anhydride. The reactions were characterized by FT-IR spectroscopy, ^1H and ^{13}C NMR spectroscopy. The curing of the resin was investigated by differential scanning calorimetry (DSC), after adding a free radical initiator.

2. EXPERIMENTAL

2.1 Materials.

Epoxidised soybean oil (EDENOL D81) was supplied by Cognis GmbH, Germany. Methacrylic acid, (99 %), methacrylic anhydride (94 %) and acetic anhydride (99 %) were used for the modification. N-methylimidazol (99 %) (GC) 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. tert-Butyl peroxy benzoate was used as the free radical initiator for the curing experiments and it was supplied by Adonox PB, Sweden.

2.2 Instrumentation.

The epoxidised soybean oil and the synthesized resins were characterized and analyzed by FT-IR and ^1H respective ^{13}C NMR spectroscopy. FT-IR analysis was carried out on Nicolet spectrometer (1Mw HeNe Laser 633nm), the DSC scanning was done using (DSC Q-200 seriesTM model) while the NMR analysis was performed by dissolving the samples in chloroform and run them on a 400 MHz instrument.

2.3 Synthesis of methacrylate modified soybean oil. (Figure 1, step 1)

Epoxidised soybean oil (13.2 g, 0.01 mol) 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 minutes. The reaction mixture was heated under reflux for 8 hours 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 minutes and the reaction was allowed to proceed for another 4 hours 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 sulphate, 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 up-scaled, first 4 fold, and then 12 fold twice. The total amount of obtained MSO was about 400g.

2.4 Further modification with methacrylic anhydride. (Figure 1, step 2a)

15.7 g of MSO was dissolved in chloroform and heated under reflux condenser in a 3 neck round bottomed-flask at 55°C. Methacrylic anhydride (7.7 g, 0.05 mol) was added in drop wise during 15 minutes, 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 a catalyst. The reaction proceeded for 3 hours being constantly stirred. The reaction mixture was allowed to cool to room temperature and the extraction was done as for step 1. The product MMSO obtained weighed 16.0 g. The synthesis was then upscaled 4 fold, and totally 55 g product was obtained.

2.5 Further modification with acetic anhydride (Figure 1, Step 2 b)

10.2 g MSO 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. 10.6 g of product AMSO was obtained. The synthesis was then upscaled 4 fold, and this gave 55g of the wanted product.

2.6 Purification of products.

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 were analyzed.

2.7 Viscosity measurements

The viscosity of the neat uncured resin was determined using a Bohlin rheometer CS30 from Malvern Instruments Ltd. All measurements were done with a cone plate configuration with a truncated cone (Ø15 mm, 5.4°). The characterisation was done by stress viscometry. For each temperature, three different levels of the stress were chosen and the viscosity was calculated.

2.8 Curing experiments

The resins were mixed with t-Butyl peroxybenzoate as free radical initiator and placed in an oven heated to 160 °C (thermal curing). Samples were withdrawn at 5 min, 10 min, 1 hour, 2 hours, 4 hours, 19 hours and 24 hours and analyzed by DSC and FT-IR. The data from the first dynamic DSC scans were analyzed for possible exothermic peaks.

For the photocuring, the resins were blended with the photoinitiator, Irgacure 819, and exposed by blue light for 0s, 6s and 90s, using a Heraflash light curing unit. The remaining heat exotherm was analysed by dynamic DSC scans.

3. CHARACTERISATION

The characterisations of these thermoset resins were done using FT-IR and NMR spectroscopy. By using these methods the obtained structures could be characterized and verified. Thermal and photocuring were done on the obtained resins and the crosslinked resins were also characterized by FT-IR spectroscopy.

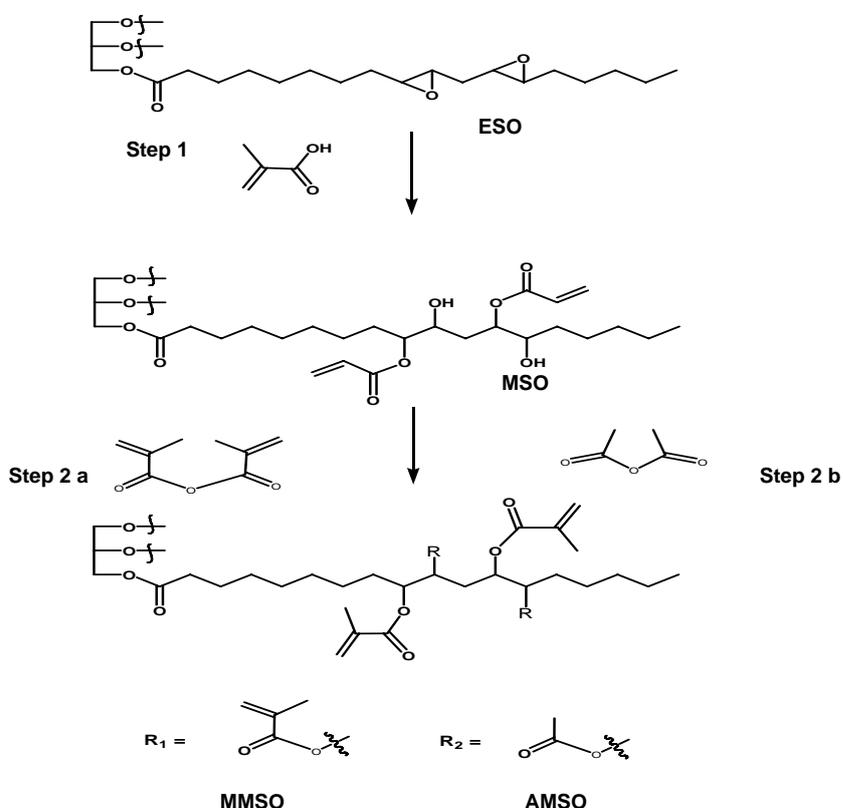


Figure 1. Reaction scheme for the modification of epoxidised soybean oil

4. RESULTS AND DISCUSSIONS

4.1 Fourier-transform IR spectroscopy.

Table 1 gives the summary of the functional groups identified from the FT-IR spectra of all the samples available for analysis.

Table 1. Summary of the FT-IR spectra

Wave number (cm ⁻¹)	Functional Group Assignment	Samples
3491	-OH	MSO
1740	C=O	ESO, MSO
1630	C=C	MSO, MMSO, AMSO
823 and 841	Epoxy group	ESO
1200 and 1275	Acetyl group	AMSO

The absorption bands of the epoxy group at 823 and 841 cm⁻¹ present in ESO disappear in the IR spectra of MSO, while double bands appear at 1739 and 1716 cm⁻¹, see figure 2. The hydroxyl absorption was around 3491 cm⁻¹ and 3472 cm⁻¹ in the spectra of MSO respectively, while this was absent in the spectrum of ESO. The absorption at about 1630 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 resins MMSO and AMSO, show that the hydroxyl peaks disappear and the absorptions at about 1715 and 1730 cm⁻¹ characteristic of carbonyl group and the carbon double bond also at 1636 cm⁻¹ are visible, which indicates a successful reaction. The IR spectrum of AMSO shows absorptions at 1217 and 1235 cm⁻¹ which could be due to acetyl functional group.

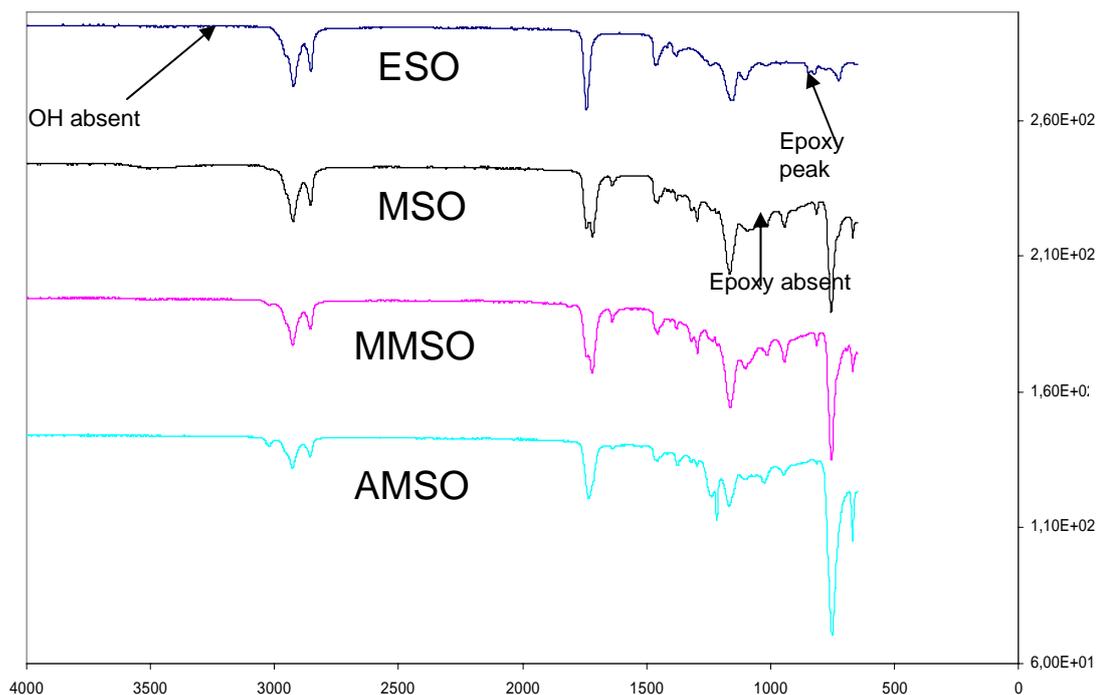
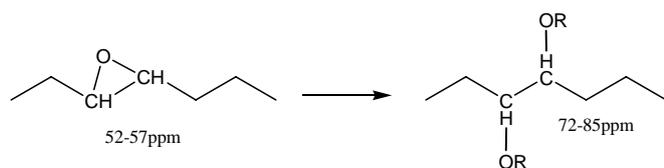


Figure 2. FT-IR Spectra comparison of ESO, MSO, MMSO and AMSO

4.2 NMR spectroscopy.

The NMR analysis verified that the wanted reactions occurred. The epoxy carbons in the ESO sample are in the 52 - 57 ppm region. These signals are missing in the AMSO sample and several new peaks around the 72-85 ppm area can be seen. These are presumed to be due to the following reaction:



R = H or acetate or methacrylate

The ^{13}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.

This was also confirmed by ^1H NMR spectrum of the ESO, see figure 3. The epoxy groups give signals around 3 ppm, and in the modified resin samples these have disappeared, and subsequently new signals are formed around 4.0 and 5.0 ppm. The peaks around 4.0 ppm are probably due to CH-OH groups, while the ones around 5.0 ppm are due to the CH-OR groups (R = acetate or methacrylate).

The degree of epoxy group conversion determined from the ^1H NMR data is given in Table 2.

Table 2. Loss of epoxy protons from the samples

Sample	Epoxy H/molecule	Loss of epoxy H's	Residual epoxy H's
ESO	7.95	-	100%
MSO	0.46	94.2%	5.8%
MMSO	0.43	94.6%	5.4%
AMSO	0.64	92.0%	8.0%

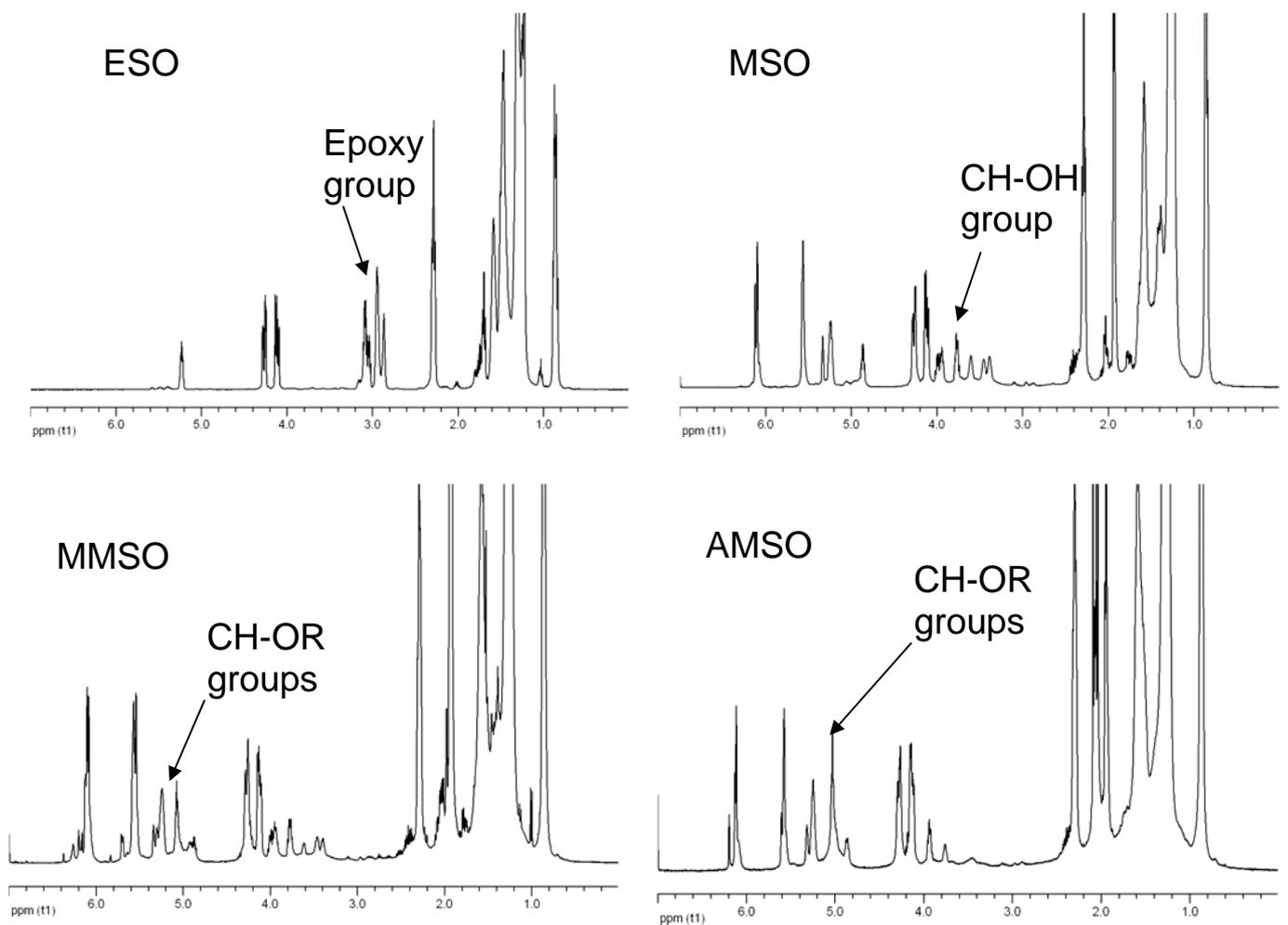


Figure 3. ^1H - NMR Spectra comparison of ESO, MSO, MMSO and AMSO

4.3 Curing results

The DSC scan for the sample withdrawn up to 10 min showed an exotherm peak indicating incomplete cure. Longer curing times gave no exothermic peaks, meaning that the curing was complete. The FT-IR spectra of the samples drawn at 5 and 10 min showed carbon-carbon double bond peak at about 1635 cm^{-1} which indicates that the samples are not fully cured, while no carbon-carbon double bonds could be seen in the samples drawn at intervals between 1 hour and 24 hours, see figure 4.

The applicability of the three resins for photocuring was examined. The neat resins were blended with a photoinitiator and the resins were exposed to blue light. All the resins can be cured to completion by photocuring, see Table 3. The MSO resin seems to be the most reactive and goes to almost completion with 6 seconds 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 the resins contain one carbon-carbon double bond one would expect both resin to have a similar heat exotherm after 0 seconds 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 as well. It would take more tests to completely characterize these resins in terms of photocuring.

Table 3. Dynamic DSC scans after different exposures.

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

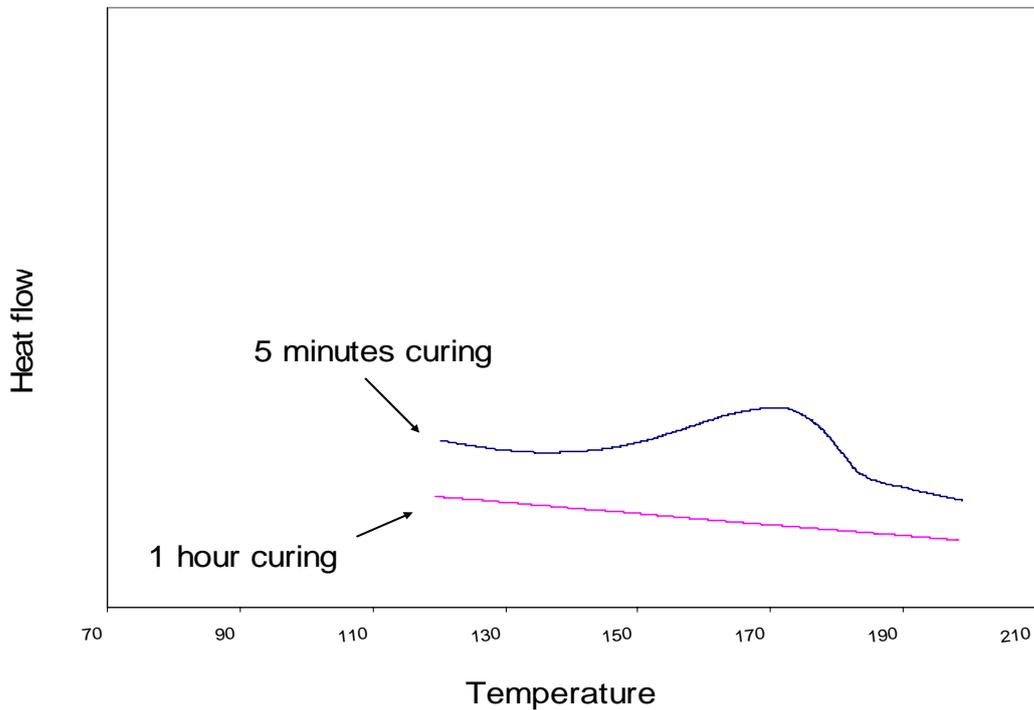


Figure 4. Cured with 2 wt-% tert-Butylperoxybenzoate at 160 °C

4.4 Viscosity

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 5. Both the MMSO resin and the MSO resin have low viscosities at room temperature. Especially the MSO resin which have a viscosity of about 0.22 Pas at 25°C. Commercial petroleum 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 moulding with only a small addition styrene or eventually without styrene.

The viscosity curve of the AMSO resin does not look very reliable. The rheological behaviour of this resin needs to be further investigated.

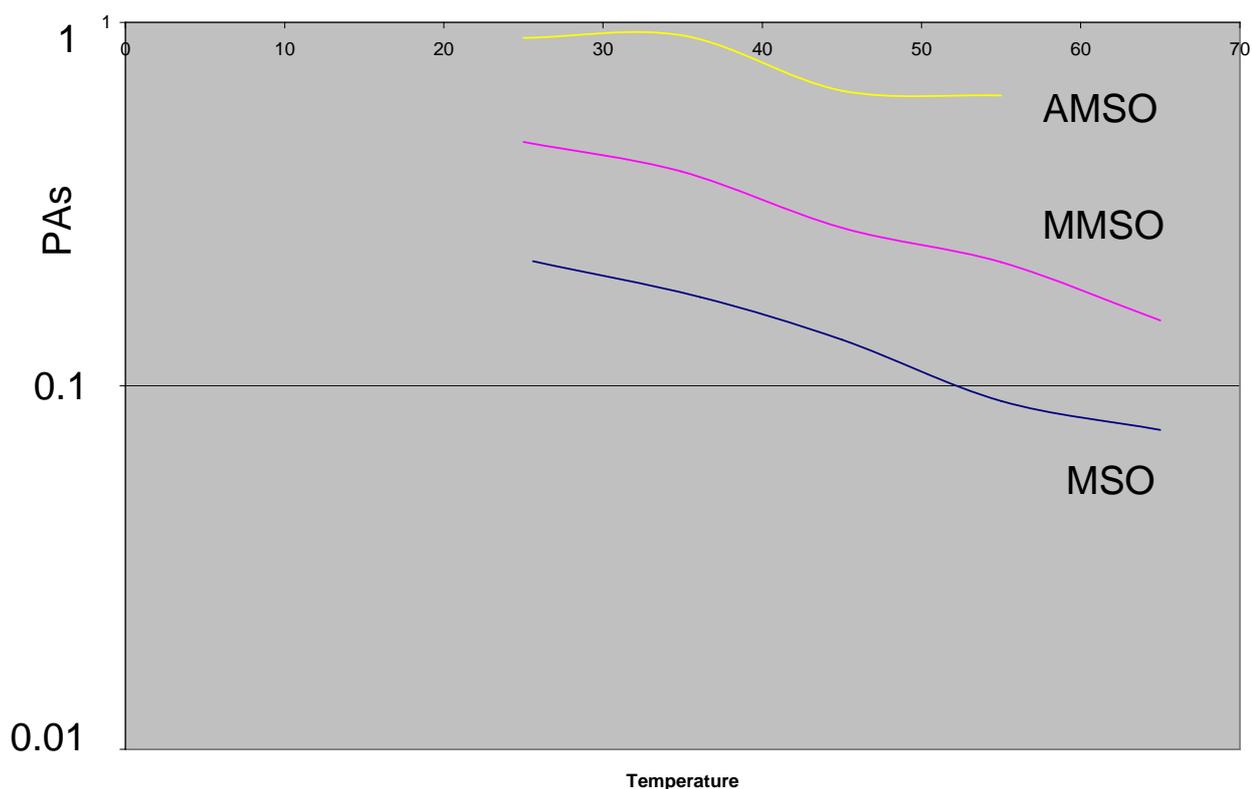


Figure 5. Viscosity measurements

5. CONCLUSIONS

Bio-based resins for use in thermoset composites were synthesized from soybean oil. The epoxidised 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 triglyceride but also reduces the number of free hydroxyl groups, which have a viscosity increasing effect. The methacrylation of the epoxidised 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 95 % in the MMSO sample, this was confirmed by the ^1H 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}C -NMR.

The methacrylated epoxidised soybean oil MSO was mixed with 2 wt % tert-butylperoxybenzoate and was cured thermally at 160 °C for 24 hours, however a fully crosslinked thermoset polymer was achieved after 1 hour, and this was confirmed by the DSC. No structural changes observed in the crosslinked polymer inspite of the prolonged cure in the oven, this was also confirmed by the FT -IR.

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