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Thermosetting Allyl Resins Derived from Soybean Oil

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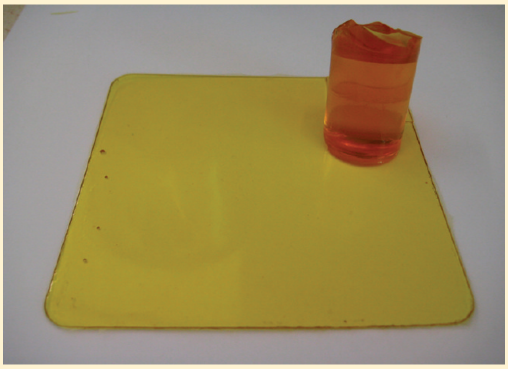
ABSTRACT: A new class of biopolymers based on plant oils with allylic double bonds was prepared from vegetable oils by oxirane ring-opening. Investigation of model systems revealed that the main side reactions during ring-opening were formation of intramolecular cyclic ethers in epoxidized linoleic fatty ester and oligomerization. Side reactions in the epoxidized oleic fatty ester were insignificant. Allyl alcohol ring-opened epoxidized soybean oil (AESBO) was then copolymerized with maleic anhydride (MA) to prepare thermosetting resins by free radical polymerization and esterification. In the best case, high gel content (99%), low water absorption (~1%), and low swelling ration in toluene (~4%) were achieved. Glass transition temperatures of these resins ranged from below room temperature to about 123 °C depending on the loading of MA. Tensile modulus varied from few MPa to 1.1 GPa, with the highest tensile strength of 29 MPa.



1. INTRODUCTION

Utilization of natural products such as plant oils and natural fats has attracted great attention in both scientific and industrial areas in recent years due to growing economic, environment, and sustainability concerns. Common plant oils are triglycerides containing five major fatty acids: oleic (C18:1), linoleic (C18:2), linolenic (C18:3); palmitic (C16:0), and stearic (C18:0). Soybean oil has typically 25% of oleic, 50% of linoleic, 3−9% linolenic, and around 15% of palmitic and stearic acids. Internal double bonds in plant oils are less reactive to free radical polymerization. Cationic polymerization of plant oils in the presence of Lewis acids, such as BF_3, has been described in the literature and patents.[1−6] However, only viscous or rubbery polymers were obtained. Polymerization of plant oils by metathesis gave low molecular weight oligomers.[7] All mentioned processes did not yield solid products with useful engineering properties. Typical methods of making solid polymers from triglycerides involve functionalizing oils to polyols, polyacids, or polyamines and then reacting them with isocyanates or other compounds to make polyesters, polyureas, or polyurethanes.[8−15] Such techniques, although very useful in many applications, may involve multistep syntheses, utilization of toxic and expensive reactants such as isocyanates, and sacrificing useful properties (for example, increasing dielectric constant and dielectric loss compared to the starting oils). The ideal vegetable oil casting resins would allow radical or other types of polymerization directly into polymeric products at low or moderate temperatures with high biomass content and without byproduct. Such systems may involve terminal or lateral double bonds which are easily polymerized by standard polymerization techniques: radical, anionic, cationic, or coordinative polymerization.

So far, radical polymerization has been investigated on acrylated oils prepared from epoxidized vegetable oils or fatty acids.[16−25] In this work, plant oils with lateral allylic double bonds obtained by oxirane ring-opening with excess allyl alcohol were investigated. Main side reactions and main side products of oxirane ring-opening were investigated using a model compounds. Allylic groups are not easily polymerized by radical mechanism due to the strong chain transfer of the allylic hydrogen but could be copolymerized with maleic anhydride by free radical polymerization. Maleic anhydride in the presence of hydroxyls may undergo esterification and increase cross-linking density. The extent of esterification under resin curing conditions was studied. Derived from these modified plant oils, a variety of novel thermosetting materials ranging from rubbery to tough or rigid glassy resins were prepared. Thermal and mechanical properties of resins were explored and discussed.

2. EXPERIMENTAL SECTION

2.1. Materials. Hydrogen peroxide solution in water (30 wt %), deuterated chloroform, *tert*-butyl peroxide (*t*-BP), and tetrafluoroboric acid (54 wt %) in ether were purchased from Aldrich (Milwaukee, WI). Maleic anhydride (>99%) was purchased from Acros Organic (Morris Plains, NJ). Allyl alcohol (>99%) was purchased from Alfa Aesar (Ward Hill, MA). Anhydrous magnesium sulfate, glacial acetic acid, tetrahydrofuran, toluene, and methylene chloride were purchased from Fisher Scientific (Pittsburgh, PA). Epoxidized soybean oil was obtained from American Chemical Service, Inc. (Griffith, IN). It has epoxy oxygen content 7.1%, corresponding to around 4 epoxy rings per triglyceride. Mold release agent E155 was obtained from Wacker Chemical Corp. (Adrian, MI). Lewatit MP64 ion-exchange resin was obtained from Sybron Chemical Inc. (Torrance, CA). Methyl oleate (MO) and methyl linoleate (ML) with purity of >99% were bought from Nu-Chek Prep, Inc. (Elysian NM). Amberlite IR-120 in acid form was purchased from

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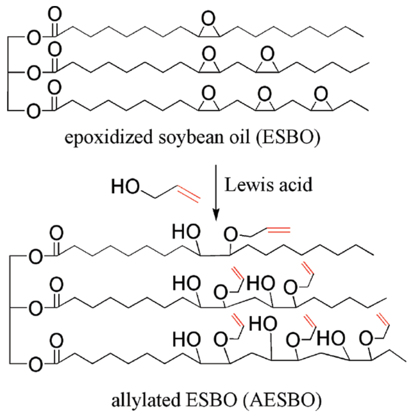
Scheme 1. Preparation of AESBO



Supelco (Bellefonte, PA). All chemicals were used as received except that epoxidized soybean oil was filtered before use.

2.2. Methods. Hydroxyl numbers were determined according to ASTM D 1957-86.

Fourier transform infrared (FTIR) spectroscopy was recorded on a Perkin-Elmer, Waltham, MA, Spectrum-1000 Fourier transform infrared spectrometer, scanning from 700 to 4000 cm^{-1}.

Proton nuclear magnetic resonance was performed on a Bruker Advance DPX-300 spectrometer at 300 MHz with a 5 mm broadband probe. Deuterated chloroform was used as solvent.

A differential scanning calorimeter (DSC) model Q100, from TA Instruments, New Castle, DE, was used for thermal analysis of monomers and polymers. Calibration and measurements were carried out at a heating rate of 10 °C/min.

A thermogravimetric analyzer (TGA) model Q50 (TA Instruments) was used for examining thermal stability of cured resins. Calibration and experiments were carried out under the nitrogen gas with a heating rate of 10 °C/min from room temperature up to 600 °C.

Dynamic mechanical analysis was carried out on DMA 2980 from TA Instruments, at 1 Hz, at a heating rate of 2 °C/min in a temperature range between −90 and 250 °C.

Gel permeation chromatography (GPC) was useful for following the formation of dimers or trimers during oil molecule modifications. A Waters GPC model 510, equipped with 4 Phenomenex columns covering molecular weight range 10^2−10^6 and differential refractometer model 410 (Waters, Milford, MA), with tetrahydrofuran as the eluent was used to follow the molecular weight variation. The flow rate of tetrahydrofuran was 1 mL/min at room temperature.

Viscosity was measured on an AR 2000 dynamic stress rheometer from TA Instruments, New Castle, DE, at 25 °C with 25 mm in diameter parallel plate configuration, having a gap of 55 μm.

Tensile properties were measured according to ASTM D638-01 using a tensile tester model 4467 from Instron, Canton, MA.

Epoxy oxygen content (EOC) determination was carried out according to the standard procedure for oils and fats.[26]

Iodine value (IV) was determined by the Hanus method.[27]

ASTM D570 was followed to measure water absorption of cured resins by immersing cured resins in water at 23 °C for 24 h. Specimens were taken out and both surfaces were dried with paper before weighing. Water absorption was calculated from the difference in the weights of the swollen and dry sample.

ASTM D543 was followed to measure swelling ratio of cured resins by immersing cured resins in toluene at 23 °C. Specimens were taken out and both of the surfaces were dried with paper before weighing every 24 h until constant weight. The swelling ratio was calculated from the difference in equilibrium weights of the swollen and dry sample.

Table 1. Properties of Modified Oils

oil ID[a]	viscosity (Pa s)	IV	OH# mg KOH/g	EOC (%)
ESBO	0.41	1.0	5.0	7.0
AESBO	5.4	56.5	182	0.02
AEMO		70.6	154	0.02
AEML		54.8	208	0.04

[a] ESBO = epoxidized soybean oil, AESBO = allylated epoxidized soybean oil, AEMO = allylated epoxidized methyl oleate, and AEML = allylated epoxidized methyl linoleate.

Gel content of cured resins was determined after Soxhlet extraction. Specimens of 3−5 mm long and about 1 mm thick were cut from bulk resins and were extracted with 100 mL of refluxing methylene chloride using a Soxhlet extractor until dry weight of resins did not change (24 h was enough in all of the cases). The extracted materials were then dried in vacuum oven at 100 °C for 1 h. Gel content was calculated from the difference in weight of the dry samples before and after extraction.

2.3. Epoxidation of Methyl Oleate and Methyl Linoleate. Methyl ester of oleic acid and methyl ester of linoleic acid were epoxidized according to our previously published method.[28] The reaction was monitored by GC and stopped when the peak of the starting material completely disappeared.

2.4. Ring-Opening of Epoxidized Oils. Epoxidized oils were ring opened by a one-pot, one-step process. Scheme 1 illustrates the synthetic pathway. A typical reaction is as follows: a predetermined amount of allyl alcohol was mixed with tetrafluoroboric acid catalyst in a three-neck round flask, which was equipped with a magnetic stirrer, nitrogen inlet and outlet, and an addition funnel. The flask was heated in an oil bath. After the desired temperature was reached, a calculated amount of epoxidized oil (epoxidized soybean oil, epoxidized methyl oleate, or epoxidized methyl linoleate) was added into the flask dropwise. The molar ratio of allyl alcohol to epoxy group was between 6 and 8. After all of the epoxidized oil was added, the epoxy oxygen content of the reaction mixture was tracked by GC or standard measurement procedures of epoxy oxygen content for oils and fats. When epoxy oxygen content is not detectable, ion-exchange resin, MP64, was added to neutralize the mixture. The ion-exchange resin was separated from the liquid part by filtration through paper filter. Excess allyl alcohol was removed and recycled with a rotary evaporator. The crude oil was then washed with large amount of distilled water 3 times and dried with anhydrous magnesium sulfate.

2.5. Preparation of AESBO-*co*-MA Resins. Stoichiometric amounts of AESBO and maleic anhydride were mixed in a 25 mL vial sealed with a rubber stopper. The mixture was placed under vacuum to get rid of dissolved water and gas and then heated to ~120 °C. The pressure was then increased to atmospheric pressure with nitrogen. A calculated amount of the free radical initiator (*tert*-butyl peroxide) was injected. The mixture was magnetically stirred until viscosity was high enough. Vacuum was applied to remove gas bubbles produced in the process. The pressure was brought back to atmospheric pressure with nitrogen. The viscous mixture was then poured into a hot mold in nitrogen an atmosphere to cast a sheet with dimension of 100 mm × 100 mm × 1 mm. The mold was then heated in oven at 120 °C for 2 days.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of AESBO Monomer.

Epoxidized soybean oil is an inexpensive commercial product with an average of 4 epoxy groups per triglyceride. Incorporation of lateral allylic double bonds into fatty acid chains was achieved by ring-opening of epoxidized soybean oil with allyl alcohol in the presence of fluoroboric acid as catalyst. After ring-opening, allyl

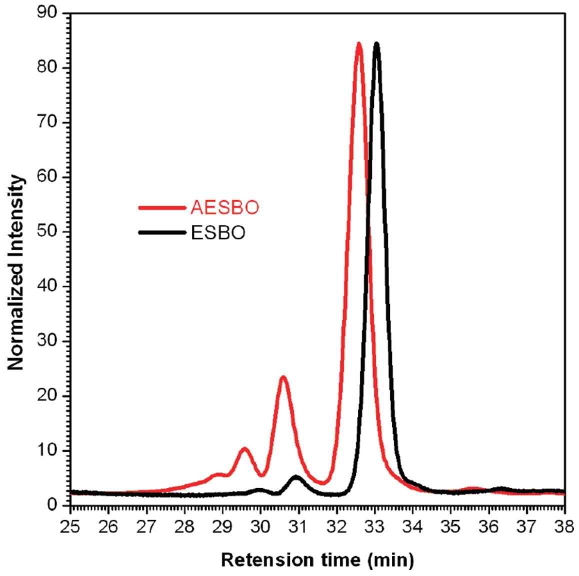


Figure 1. GPC of ESBO (black) and AESBO (red).

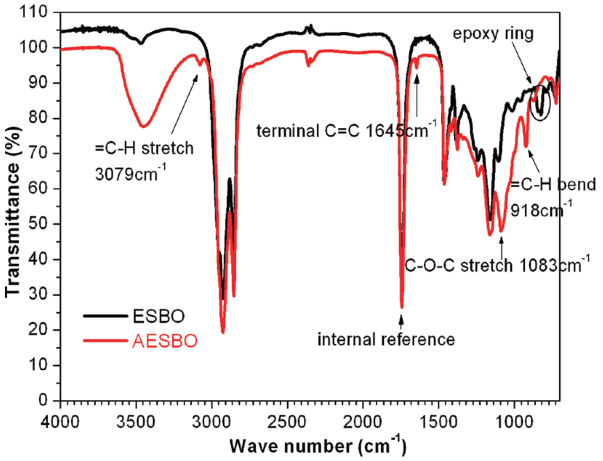


Figure 2. FTIR spectra of ESBO (black) and AESBO (red).

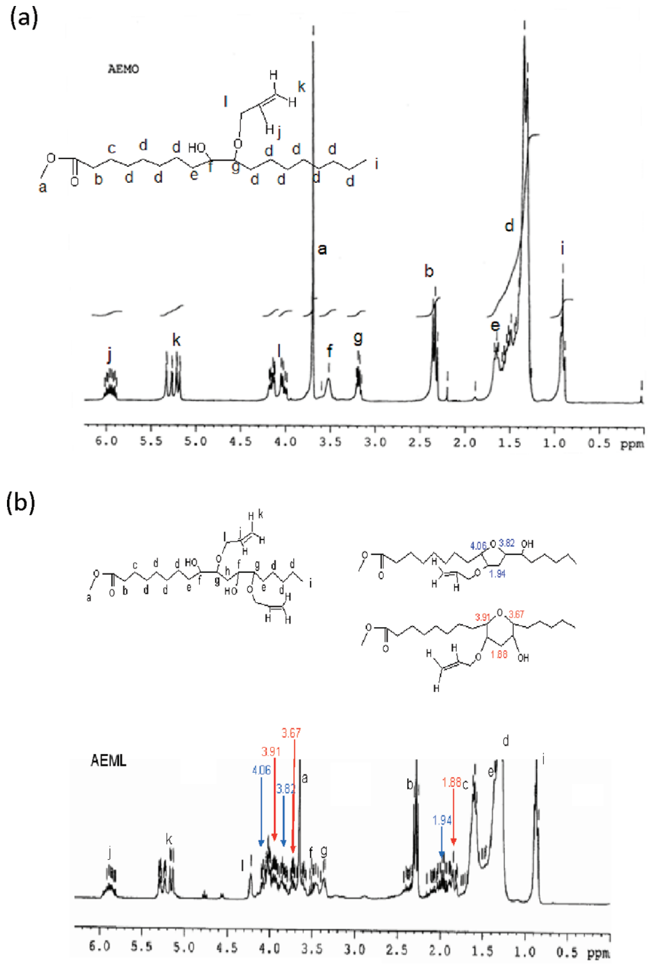


Figure 3. (a) ^{1}H NMR of AEMO and (b) ^{1}H NMR of AEML.

ether and secondary hydroxyl groups were formed, as shown in Scheme 1. The measured OH number of AESBO is 182 mg KOH/g oil, as shown in Table 1. It is lower than the theoretical value of 192 mg KOH/g. Epoxy oxygen content also decreased from 7.1% to essentially zero after ring-opening.

GPC in THF (Figure 1) showed the main peak shifted to a shorter retention time due to the molecular weight increase by incorporation of allyl alcohol moiety. The GPC also demonstrated that significant amounts of dimers and trimers were produced by homopolymerization of ESBO, i.e., the ring-opening of epoxy groups by secondary hydroxyl groups. In fatty acids with two or three epoxy groups the formation of intramolecular cyclics also occurs as proved later. These are the main reasons that theoretical hydroxyl number cannot be reached.

FTIR spectra in Figure 2 show the disappearance of the doublet epoxy ring peak at 822 and 839 cm^{-1}. The appearance of terminal double bond =C−H stretching at 3079 cm^{-1}, terminal double bond C═C− stretching at 1645 cm^{-1}, terminal double bond =C−H bending at 918 cm^{-1}, and a strong broad −OH peak centered around 3450 cm^{-1} illustrated the successful incorporation of allyl groups into oil molecules.[29] The allyl ether C−O−C stretching peak at 1083 cm^{-1} is overlapped with the ester C−O−C stretching peak at the same position. However, the significant increase in intensity after the ring-opening due to the formation of allyl ether demonstrates the incorporation of allyl moiety into oil molecules too. Based on the epoxy oxygen content and ^{1}H NMR presented later, ring-opening of ESBO was very efficient, but the measured iodine value (IV) was only 56.5, corresponding to the average number of double bonds per triglyceride of around 2.7. The iodine value was much lower than the theoretical value of 87.8, indicating that a significant part of epoxy groups was involved in side reaction(s). In order to investigate possible side reaction(s), high purity methyl oleate (containing one double bond) was epoxidized and then ring-opened with allyl alcohol under the same conditions. The measured iodine value of allylated epoxidized methyl oleate (AEMO) is 70.6 and close within experimental error to the theoretical value of 69.1. The measured hydroxyl number was 154 mg KOH/g, close within experimental error to the theoretical value of 151 mg KOH/g, as listed in Table 1. The ^{1}H NMR of AEMO in Figure 3a shows that no significant side reactions took place in the case of the ring-opening of epoxidized methyl oleate with allyl alcohol. Since soybean oil contains about 50% of linoleic acid, side reactions may have occurred due to the existence of two epoxy groups separated by one methylene group. High purity methyl linoleate was epoxidized and ring-opened

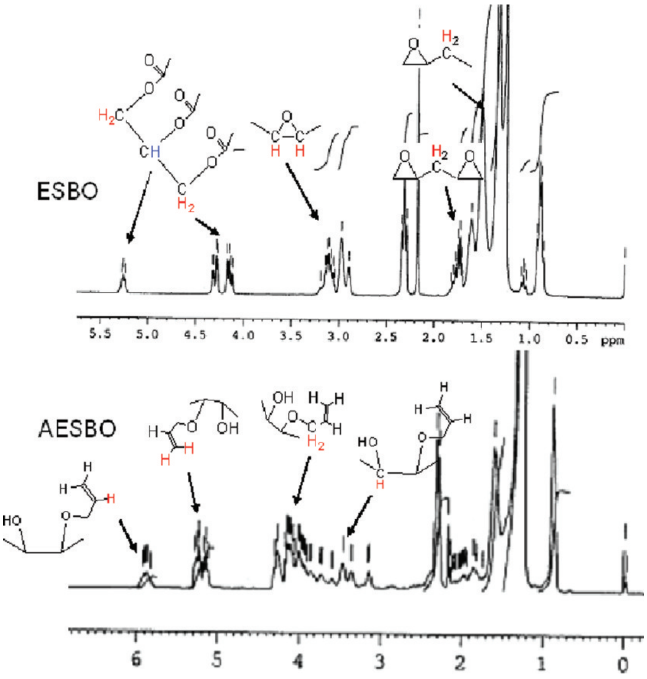


Figure 4. ^1H NMR of ESBO and AESBO.

under the same conditions to produce allylated epoxidized methyl linoleate (AEML). The measured iodine value of allylated epoxidized methyl linoleate (AEML) was 55, which is only about half of the theoretical value of 115. The hydroxyl number was 208 mg KOH/g compared to the theoretical value of 253 mg KOH/g, as listed in Table 1. ^1H NMR of AEML in Figure 3b illustrated that five-member ring and six-member ring compounds were formed as the main side reaction products. This suggests that the cyclization reaction limited incorporation of allyl groups and formation of hydroxyls in AESBO and decreased the iodine value.

^1H NMR spectra of ESBO and AESBO are presented in Figure 4. They show the proton shift in the epoxy ring (−CH−) between 3.2 and 2.9 ppm and the methylene proton (CH_2) between two epoxy rings at around 1.7 ppm. The α-methylene proton to the epoxy ring is around 1.5 ppm.[30] After the epoxy ring was opened with allyl alcohol, several new peaks appeared including a peak around 5.9 ppm corresponding to methylene proton in terminal double bonds, the peak around 5.2 ppm corresponding to the methine proton in terminal double bonds, the peak around 4 ppm corresponding to the allyl proton (α-CH_2) of the double bond, and the peak around 3.5 ppm corresponding to methine group adjacent to the hydroxyl group. The peak at around 2.9 ppm disappeared. Peaks around 1.5 and 1.7 ppm corresponding to the residual epoxy were significantly weaker if not completely disappeared.

Based on the above analyses, lateral double bonds were successfully incorporated into triglycerides of soybean oil by ring-opening with allyl alcohol with formation of dimers, trimers, and intramolecular cyclic ethers.

3.2. Properties of AESBO-*co*-MA Resins. Homopolymerization of AESBO with free radical initiator was attempted. Soft gels were obtained only at a very high initiator concentration of 10 wt %. It is well-known that allylic double bonds are not efficient in free radical homopolymerization, producing low molecular weight oligomers due to the high chain transfer ratio.[31,32] However, when allylic compounds are copolymerized with maleic anhydride in presence of a free radical initiator, high molecular weight can be achieved by alternating polymerization of allylic and maleic double bonds,[33] as shown in Scheme 2. In this study, AESBO was copolymerized with different amounts of maleic anhydride in the presence of a peroxide free radical initiator, and good thermosetting resins were obtained.

Scheme 2. Reactions between AESBO and Maleic Anhydride

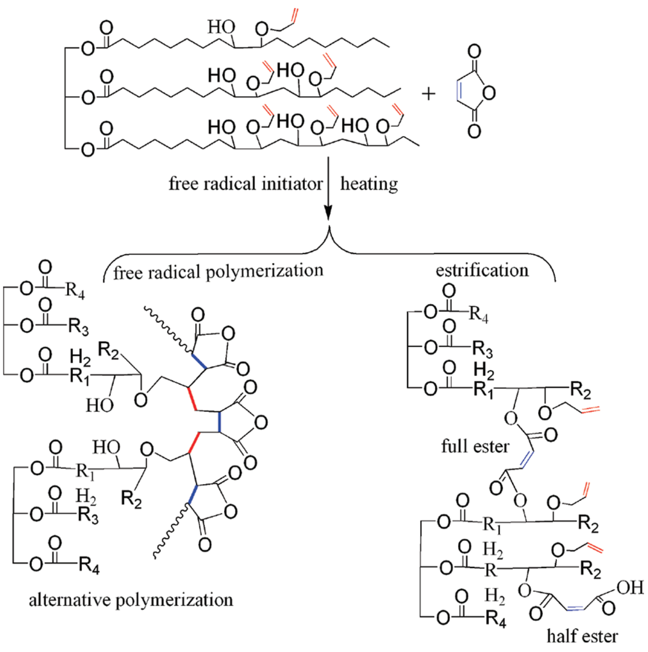


Table 2. Acid Number of AESBO + MA Mixture after Heating at 120 °C for 48 h[a]

AESBO	MA	−OH/anhydride	acid no. (48 h)
6.2 g	1.975 g	1:1 (mol)	159
6.2 g	0.987 g	2:1 (mol)	25

[a] Theoretical acid numbers after all hydroxyl groups reacted are 138 mg KOH/g for the first and zero for the second mixture.

3.2.1. Extent of Esterification. Since esterification also occurs during curing, the extent of esterification under the applied curing conditions was studied, except there is not free radical initiator. AESBO and maleic anhydride were mixed at 1:1 and 2:1 molar ratios of hydroxyl group to anhydride. The mixtures were then stirred and heated at 120 °C for 48 h. In the case of −OH: anhydride = 2:1, an aliquot of reaction mixture was withdrawn every hour until a gel formed. Acid numbers were measured and presented in Table 2 and Figure 5.

When the molar ratio of hydroxyls to anhydrides was 2 to 1 (hydroxyl to acid = 1:1), acid numbers decreased almost linearly until gelation occurred after 4 h of curing. Further measurements were difficult because of gelation. Gel after 48 h of curing at 120 °C was then grinded into fine powder, and the acid number was titrated. Because of the fading end point, the rough acid value in the gel state was 25 mg KOH/g, indicating that most of anhydride groups reacted with hydroxyls. At a hydroxyl to anhydride molar ratio of 1:1 (OH:carboxyl = 1:2), after 48 h at 120 °C, the mixture did not turn solid but stayed as very viscous liquid. Ideally, half ester will form if one hydroxyl group reacted

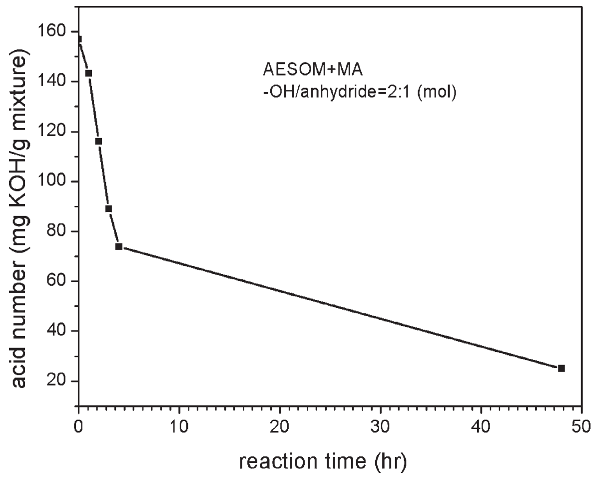


Figure 5. Acid number vs reaction time for the system OH/MA = 2:1.

Table 3. Gel Contents (in %) of Cured AESBO(70 wt %) + MA(30 wt %) Initiated by Different Amounts of *t*-BP at 120 °C

t-BP	1.5	3	4.5	6	8
sol fraction	21	15	12	1	1

with one anhydride group, and the theoretical acid number in this case would be 138 mg KOH/g. The measured acid number was 159 mg KOH/g, relatively close to the theoretical value, suggesting that most of hydroxyl groups reacted with anhydride to form half esters. Thus, it is reasonable to believe that under the curing conditions, at the molar ratio of hydroxyls to anhydride less than 1, half esters were the main product, and when the molar ratio is higher than 2:1, a significant amount of full esters was produced.

3.2.2. Effect of Initiator Concentration. It is well-known that molecular weight of thermosetting polymers is theoretically infinite and independent of initiator concentration. Increasing initiator concentration will not decrease molecular weight as occurred in linear thermal plastics but will increase reaction rate and may affect cross-linking density. Because of the autoinhibition of allyl monomers,[32] the rate of propagation is low, which at the end resulted in very low conversion of double bonds. Since each allylated triglyceride contains multiple double bonds, it is enough for maleic anhydride to bridge two molecules to form a network. However, copolymerization of maleic anhydride with double bonds in the same triglyceride would decrease the efficiency of cross-linking. A simple and direct method to enhance the rate of propagation is to increase initiator concentration. Unfortunately, high initiator concentration has disadvantages such as low initiator efficiency, gas bubbles, and rapid heat buildup. Because of the degradative chain transfer of allylic double bonds in AESBO, relatively high initiator concentrations are necessary in order to produce materials with high gel content. In this study, copolymerization of AESBO (70 wt %) and maleic anhydride (30 wt %) initiated with different amount of *t*-BP from 1.5 to 8 wt % was conducted to find the optimal initiator concentration.

Table 3 shows that sol fraction of cured resins went up from 21% to 1% as *t*-BP increased from 1.5 to 6 wt %. Thus, the further increase of *t*-BP was not necessary.

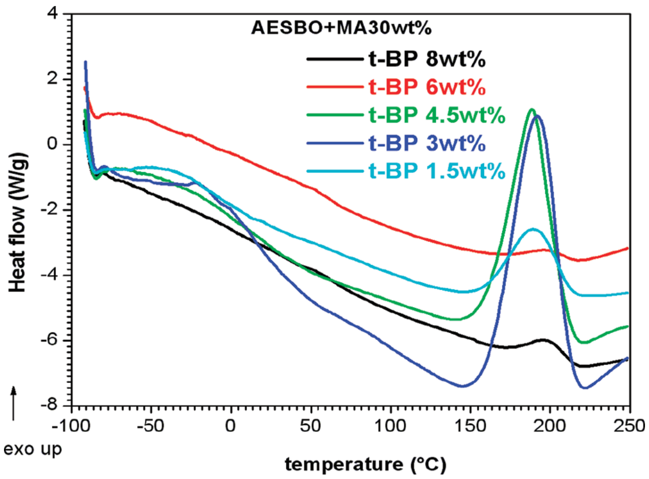


Figure 6. DSC thermograms of AESBO-*co*-MA with different amounts of *t*-BP (black: 8 wt %; red: 6 wt %; green: 4.5 wt %; blue: 3 wt %; cyan: 1.5 wt %).

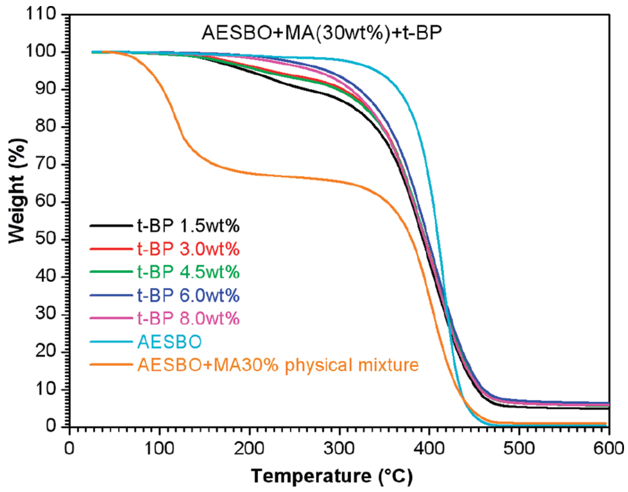


Figure 7. TGA curves of AESBO-*co*-MA resins cured with different amounts of *t*-BP (black: 1.5 wt %; red: 3 wt %; green: 4.5 wt %; blue: 6 wt %; magenta: 8 wt %; cyan: AESBO; orange: AESBO + MA(30 wt %) physical mixture).

All of the cured resins with different t-BP showed residual reaction heat when scanned in DSC to 250 at 10 °C/min, as shown in Figure 6. With 1.5 wt % *t*-BP, the residual *t*-BP after curing was low. Even with relatively large sol fraction, heating the resin above curing temperature produced limited postcuring. As a result, the residual heat of reaction was only 67 J/g. When *t*-BP was 3 and 4.5 wt %, both residual *t*-BP and unreacted allylic double bond contents were relatively high, and a large amount of residual heat (108 and 120 J/g, respectively) was released when the resins were scanned to high temperature. Further increase of the initiator content to 6 wt % resulted in lower residual heat of 7 J/g, apparently because most of double bonds were consumed during regular curing, which was also reflected in the low sol fraction. Similar results were obtained with 8% *t*-BP. This again proved that a very small amount of allylic double bonds were left unreacted at high initiator concentrations.

Sol fraction and DSC demonstrated that low concentrations of free radical initiator led to relatively large amounts of starting materials in the final product. As shown in Figure 7, AESBO is relatively stable up to 300 °C. MA is less stable, and almost all of it

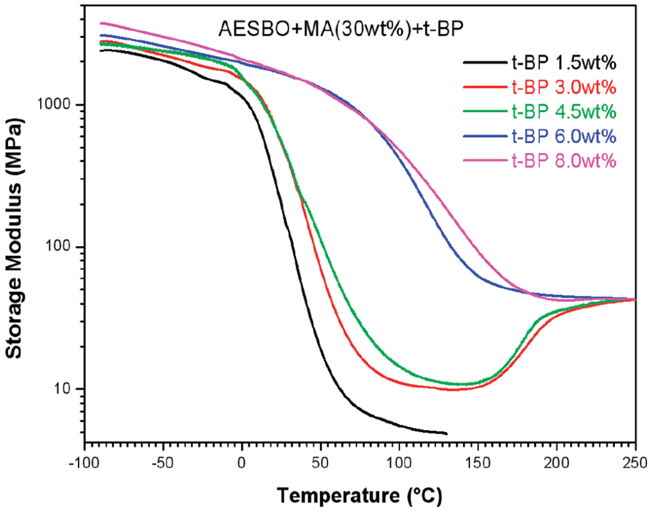


Figure 8. Storage modulus of copolymer AESBO + MA(30 wt %) resins initiated with different amount of *t*-BP (black: 1.5 wt %; red: 3 wt %; green: 4.5 wt %; blue: 6 wt %; magenta: 8 wt %).

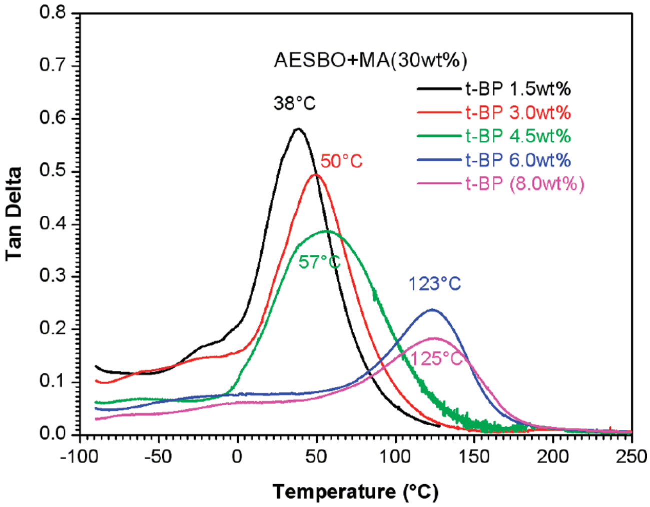


Figure 9. Tan delta of copolymer AESBO + MA(30 wt %) resins initiated with different amount of *t*-BP (black: 1.5 wt %; red: 3 wt %; green: 4.5 wt %; blue: 6 wt %; magenta: 8 wt %).

was lost upon heating to 200 °C. If unreacted materials remained in products initiated with low initiator concentrations, a large weight loss would be observed in the corresponding products upon heating. The TGA thermogram in Figure 7 shows a larger initial loss between 150 and 300 °C in resins cured with less *t*-BP; i.e., a relatively large amount of unreacted MA existed in these resins.

DMA data further verified that higher initiator concentration resulted in better curing, as shown in Figure 8. An interesting phenomenon was observed that at low *t*-BP concentration. Heating of the resins above 150 °C increased rubbery storage modulus of the resins in the case of 3 and 4.5 wt % of *t*-BP. In the case of 1.5 wt % of *t*-BP, the material was too weak under the testing conditions and broke prematurely. The increase of rubbery storage modulus upon heating was the indirect proof of a further reaction of residual starting materials. The same phenomenon was absent in the case of resins initiated with higher concentration of *t*-BP; apparently, most of double bonds were consumed at the initial curing process. Figure 9 demonstrates that when *t*-BP concentration was low, the glass transition temperature was low and the glass transition temperature range was narrow. At high *t*-BP concentration, T_g was high and the transition temperature range was wide.

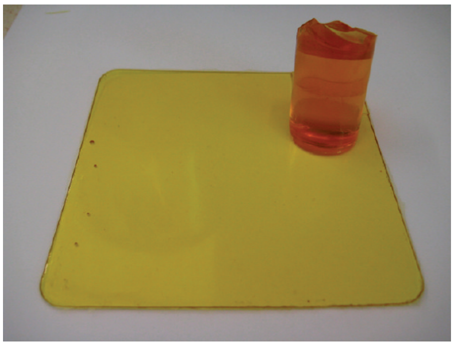


Figure 10. Copolymer of AESBO + MA(30 wt %) + *t*-BP(6 wt %) cast in different forms.

Based on the above tests, 6 wt % of *t*-BP was thought to be the optimal amount for copolymerization of AESBO and maleic anhydride and was adopted for copolymerization.

3.2.3. Effect of Maleic Anhydride Loading. In order to study the effect of maleic anhydride loading on properties of copolymer resins, AESBO was copolymerized with different amounts of maleic anhydride from 10 to 30 wt %. The thermosetting resins of AESBO-*co*-MA can be cast into thin sheets or cylinder shapes, as shown in Figure 10.

The equilibrium swelling of thermosetting polymers in solvent could be a good indicator of cross-linking density since a higher cross-linking density leads to a lower swelling ratio. The swelling behavior of the copolymer reins in toluene was examined by following ASTM D543. Specimens were immersed in a sealed wide mouth jar containing toluene. Wet weight after wiping surfaces dry with paper napkins was checked every 24 h until solvent uptake was not detectable.

Table 4 shows the ultimate swelling ratios of the copolymerized resins. Resins with higher polar maleic anhydride concentration have lower swelling ratios. A sharp decrease of swelling ratio from ∼30% to ∼4% was observed when maleic anhydride loading increased from 20 to 30 wt %. During the test, all of the specimens reached the equilibrium after 2 days in toluene except the resin containing 30 wt % of maleic anhydride, which took 7 days to equilibrate. In a double check test, an equilibrated swelling ratio of 4.3% was achieved in 6 days. This slow swelling and low swelling ratio are possibly the result of higher cross-linking density and higher content of polar compounds.

Water absorption measurement results presented in Table 4 show that the presence of unreacted maleic anhydride and free acid groups in the product did not increase the polymer sensitivity to water significantly. Low water absorption is possibly due to the hydrophobicity of the vegetable oil moiety.

Table 4 also shows that gel content measured by Soxhlet extraction increased from 87% to 99% when maleic anhydride loading increased from 10 to 30 wt %, indicating a higher cross-linking density of the resins with higher maleic anhydride loading. Two different reactions occurred under applied curing conditions in this study. One is the free radical polymerization of double bonds. The other is the esterification of hydroxyl groups

Table 4. Properties of AESBO-*co*-Maleic Anhydride Initiated with 6% of *t*-BP

sample	double bond ratio	OH/anhydride	swelling ratio (%)	water absorption (%)	gel content (%)
AESBO + MA(10%)	1.9	2.9	49.8	1.1	87
AESBO + MA(15%)	1.2	1.8	37.3	0.9	92
AESBO + MA(20%)	0.9	1.3	29.8	0.7	97
AESBO + MA(30%)	0.5	0.7	4.3	1.0	99

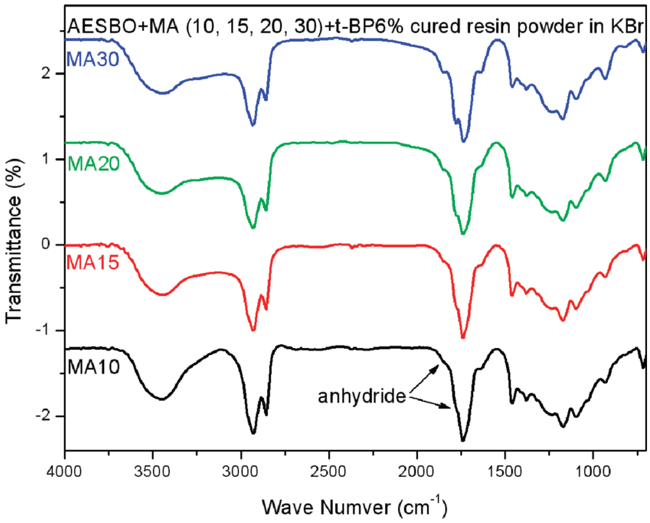


Figure 11. FTIR of AESBO + MA resin cured with *t*-BP. Resin powder in KBr.

in AESBO with the anhydride in maleic anhydride, as shown in Scheme 2. Based on the iodine value and hydroxyl number in Table 1, every 100 g of AESBO will consume 21.4 g of maleic anhydride (18 wt %) via free radical polymerization if an ideal alternating copolymer is formed and will consume 16.4 g of maleic anhydride (14 wt %) for full esterification, giving a cross-linked product. If only half esterification happened, which means one maleic anhydride molecule only reacted with one hydroxyl group and no cross-linking took place, the consumption of maleic anhydride would be 32.8 g (25 wt %). Because the mechanism of curing is complex involving partial reaction of anhydrides, formation of half and full esters, radical homopolymerization of oil, and copolymerization with MA, optimal concentration of MA could be determined only from experimental trials. DMA and tensile test demonstrated that strongest resin was the one with 30 wt % of maleic anhydride, suggesting that most of maleic anhydride did not undergo both free radical polymerization and full esterification. FTIR in Figure 11 also shows that even with the excess of hydroxyl groups (black spectrum), there are still unreacted anhydride groups. With a larger amount of maleic anhydride (= 15 wt %), free carboxyl groups resulting from half esters formed during curing showed up in FTIR at about 3250 cm^{-1}. In this study, the highest maleic content applied was 30 wt %, participating in both free radical polymerization and esterification. Further increasing of maleic anhydride will cause higher extent of half esterification, which will lower cross-linking density.

DMA can be used to obtain storage modulus and loss modulus as a function of temperature at a given frequency. The ratio of the loss modulus and storage modulus is tan δ, which relates the ratio of the energy dissipated by heat to the energy stored in the material upon periodic deformation.[34] In this study, homopolymerization of AESBO gave a very weak gel material which could not be tested by DMA under the applied testing conditions. Copolymerization of maleic anhydride with AESBO resulted in stronger thermosetting resins. Figure 12 shows that the storage moduli at rubbery and glassy regions increased as maleic anhydride loading rose from 10% to 30%. Rubbery and storage moduli increased significantly when maleic anhydride loading went up from 10 wt % to 15 wt %. Further increase of glassy moduli was not as significant even when the maleic loading was doubled from 15 to 30 wt %. Postcuring was not observed when maleic anhydride loading was 30 wt %, but insignificantly existed when maleic anhydride loading was 20 and 15 wt %; DMA did show increase of rubbery modulus upon heating. In the case of 10 wt % of loading, the material is too weak to stand up to the test conditions and broke prematurely. Temperatures of tan delta peak (Figure 13) of cured resins did increase from 18 to 123 °C when maleic anhydride loading increased from 10% to 30%. The peak values of tan delta decreased and the α-transition temperature range widened with more maleic anhydride.

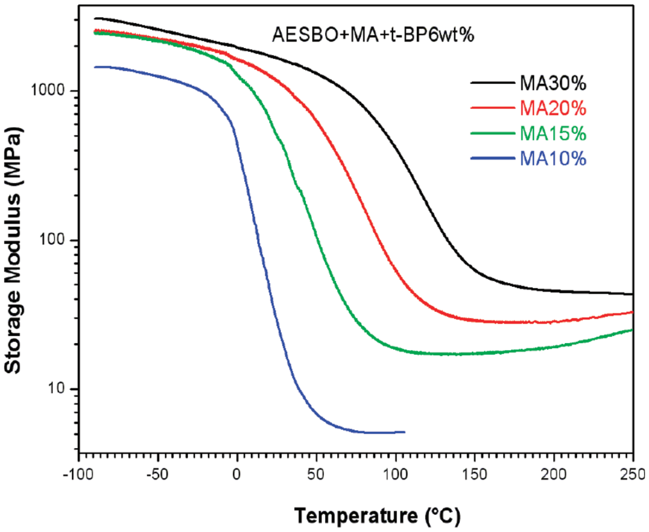


Figure 12. Storage modulus of AESBO + MA + *t*-BP(6 wt %) resins cured with different MA loading (black: 30 wt %; red: 20 wt %; green: 15 wt %; blue: 10 wt %).

Since neat AESBO cured with peroxide was too weak for mechanical testing, no comparison of copolymer to homopolymer networks is possible. Mechanical properties of the copolymers with different loading of maleic anhydride are presented in Table 5. The material containing 10 wt % of maleic anhydride was weak with tensile strength of hundreds of kilopascals and modulus of 6 MPa. This was due to the low cross-linking density and low glass transition temperature since

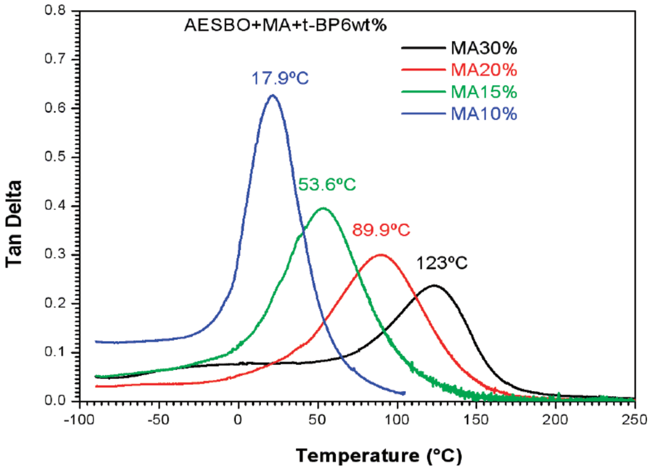


Figure 13. Tan delta of AESBO + MA + *t*-BP(6 wt %) resin cured with different MA content (black: 30 wt %; red: 20 wt %; green: 15 wt %; blue: 10 wt %).

Table 5. Tensile Properties of AESBO-*co*-Maleic Anhydride Initiated with 6% of *t*-BP

sample	modulus (MPa)	elongation (%)	tensile strength (MPa)
AESBO + MA(10%)	6 ± 0	15 ± 1	0.90 ± 0.07
AESBO + MA(15%)	75 ± 5.7	20 ± 1	6.2 ± 0.8
AESBO + MA(20%)	395 ± 64	18 ± 3	15.6 ± 0.5
AESBO + MA(30%)	1080 ± 40	7 ± 2	29 ± 3.3

tensile test was conducted at room temperature, which is higher than measured glass transition temperature by tan delta and the material was tested in rubbery state. Plasticization of a relatively large amount of small molecules as shown in Table 4 aslo contributes to mechanical weakness of the material. Increasing maleic anhydride loading to 15 wt % enhanced Young modulus, elongation at break, and strength. Further increasing maleic anhydride content to 20 wt % increased Young modulus and strength significantly while elongation decreased slightly. When 30 wt % of maleic anhydride was applied, Young modulus increased above 1 GPa and strength went up to 29 MPa. Elongation at break continuously went down to 6.6%, characterizing a brittle fracture behavior typical for highly cross-linked polymers.

4. CONCLUSIONS

Allylic double bonds were successfully incorporated into triglycerides of ESBO through a ring-opening nucleophilic addition reaction of allyl alcohol. The reaction is facile with high conversion under mild conditions. Side reactions in epoxidized soybean oil lowered the incorporation of allylic groups due to the high content of epoxidized linoleic acid. This novel monomer readily undergoes alternating copolymerization with maleic anhydride in the presence of a free radical initiator and forms polymers of different cross-linking densities depending on the amount of MA and peroxide. These polymers showed low water absorption, low solvent swelling ratio, and high gel content. Glass transition temperatures ranging from about room temperature to 123 °C can be tailored by varying maleic anhydride loading. When maleic anhydride loading was 30 wt %, high gel content (99%), low water absorption (∼1%), and low swelling ratio in toluene (∼4%) were achieved, and the resin possessed modulus and tensile strength of 1 GPa and 29 MPa, respectively.

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