Thermal and Mechanical Properties of Acrylated Expoxidized-Soybean Oil-Based Thermosets

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ABSTRACT: A series of epoxidized-soybean oil (ESO) with different epoxyl content were synthesized by *in situ* epoxidation of soybean oil (SBO). The acrylated epoxidized-soybean oil (AESO) was obtained by the reaction of ring opening of ESO using acrylic acid as ring opener. The acrylated expoxidized-soybean oil-based thermosets have been synthesized by bulk radical polymerization of these AESOs and styrene. The thermal properties of the resins were characterized by differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TG). The results showed that these resins possess high thermal stability. There were two glass transition temperature of each resin due to the triglycerides structure of the resins. The tensile strength and impact strength of the resins were also recorded, and the tensile strength and impact strength increased as the iodine value of ESO decreased. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2220–2225, 2010

Key words: AESO; thermoset; thermal-mechanical properties

INTRODUCTION

Polymers and polymeric composite materials have been widely used in aerospace, automotive, marine, infrastructure, and industrial fields. These lightweight materials exhibit excellent mechanical properties, high corrosion resistance, dimensional stability, and low assembly costs. Polymers and polymeric composites are derived from petroleum reserves and as the number of applications of polymeric materials continues to increase, an alternative source of these materials becomes more important.[1] Vegetable oils are the interesting alternative chemical feedstock, since they are renewable and widely available, albeit from different species. Moreover, their biodegradability makes them particularly attractive.[2,3]

Soybean oil (SBO) is one of many vegetable oils, triglycerides are composed of three fatty acids joined at a glycerol juncture. Soybean oil has double bonds, but it does not give homo- or copolymer by a radical-initiated polymerization. Therefore, to be useful as a monomer for radical polymerization, the triglyceride molecule has to be suitably functionalized. Many ways of modifying soybean oil have been explored including maleinization,[4] epoxidation,[5,6] acrylation,[7–9] and hydroxymethylation.[10]

The attention has been focused on the studies of soybean oil-based polyols and the polyurethanes. The reports about that using the acrylic acid as ring opener to react with epoxidized-soybean oil (ESO) for synthesizing acrylated epoxidized-soybean oil (AESO), and the latter copolymerizing with styrene by using free radical polymerization mechanism are rare.

Much of this effort has recently been devoted to modifications that could facilitate the subsequent polymerization of the soybean oil to produce solid films. The potential application for this kind thermoset are solid films and composite materials which can be used in aerospace, automotive, marine, infrastructure, military, sports, and industrial fields.[11,12] In this work, AESOs were synthesized from the reaction of acrylic acid with a series of ESOs with different expoxidation degree. Triphenyl phosphine was used as catalyst. AESOs used in this work contains different degree acrylate double bonds, these double bonds can be free radically polymerized or copolymerized with reactive diluents such as styrene, to give thermoset resins. Polymers with different glass transition temperatures (T_g) can be produced. The effect of iodine value of ESO on thermal and mechanical properties of resins has been studied by using differential scanning calorimetry (DSC), thermo-gravimetric analysis (TG), and mechanical tests.

EXPERMENTAL

Materials

Soybean oil with an iodine value 127.23 (g I/100 g oil) was kindly provided by Nanhai Oil Co.

(Guangzhou, China). Glacial acetic acid (99.5%), sodium carbonate, sodium hydroxide, hydrogen peroxide (30%), sulfuric acid (98%), acrylic acid, styrene, benzoyl peroxide, triphenyl phosphine, hydropninone, sodium thiosulfate pentahydrate, Iodine trichloride, ethyl ether were all purchased from Guangzhou Chemical Reagent Co. (Guangzhou, China). All the chemicals were AR grade and were used as supplied.

Methods

The epoxy oxygen content (EOC) was determined using the AOCS method (Cd9-57). The iodine value on triglycerides of ESO was determined according to the GB/T9104.1-1988 standard test method. The IR spectra were recorded on a Fourier transform infrared (FTIR) spectrometer (Prestige-21, Shimadzu, Japan). The samples were prepared as thin films on KBr salt plates.

NMR spectra were obtained on a 400-MHz model VNMRJ instrument (USA). The samples were dissolved in deuterated chloroform, and ^{1}H-NMR spectra were obtained at room temperature.

Thermal properties were measured on a differential scanning calorimeter (DSC 200PC NETZSCH, Germany) with a heating rate of 10 K/min from −50 to 100°C. Nitrogen was used as purge gas at a 50 mL/min flow rate. Ten milligrams of samples were used in sealed aluminum pans for each analysis. The analysis of thermogravimetry behavior of the samples were performed on a thermogravimetric instrument, (model STA 409PC NETZSCH, Germany), with a heating rate of 10 K/min from 25 to 600°C. Nitrogen was used as the purge gas at a 100 mL/min flow rate. About 10 mg of each sample was used in each test. The tensile properties were measured according to ASTM D 882-97 on a tensile tester, model WSM-100 Universal Electricity Computer Control Tester from Changchun Intelligent Instrument and Equipment Co. (Changchun, China). The extension rate is 100 mm/min and five specimens were used for each sample. The impact properties were measured on a JJ-20 Computer Control Memory System Impact-tester from Changchun Intelligent Instrument and Equipment Co. (Changchun, China). Six specimens were used for each sample in impact test.

Synthesis of the ESO and AESO

ESO was made through the reaction of SBO and peroxyacetic acid (was prepared *in situ* by reacting various mixtures of 35 g of 99.5% glacial acetic acid and 165 g of 30% H_2O_2 in the presence of small quantities of concentrated sulfuric acid for about 12 h[8,9]). The iodine value of the ESO was determined accord-

ing to the GB/T9104,1-1988. The prepared ESOs were used for the synthesis of AESOs.

AESO was synthesized from the reaction of acrylic acid with ESO. The molar ratio of epoxy groups of ESO and acrylic acid is 1 : 1.1. Triphenyl phosphine was used as catalyst and the concentration was 1.5% of the total weight of the ESO and acrylic acid. The reaction mixture was placed into a 500-mL three-necked round-bottom flask and held the temperature of the mixture at 110°C in oil bath for 8 h. After cooling to room temperature, the product was dissolved in ethyl ether and washed with aqueous sodium hydrogen carbonate until the pH of the solution was slightly alkaline, the oil phase was washed with sodium chloride solution for several times. Finally, the product was purified on a rotary evaporator under low vacuum at 50°C for 0.5 h, followed by 90°C for 1 h, respectively.

Resin preparation

Acrylated-based resin was prepared by mixing the AESO with the low-molecular-weight comonomer-styrene using benzoyl peroxide (BPO) as initiator. 5% BPO (based on the total weight of styrene and AESO) was dissolved in styrene and was blended with AESO in a beaker, stirring for a few minutes and then the mixture was poured into a mold and put into an oven for 2 h at 100°C to complete the reaction. The mass fraction of styrene and AESO is 70% and 30%, respectively. The sample was then cooled to room temperature and remolded. A series of resins were prepared using AESOs with different iodine value (I_V) of ESO. The used I_V are 71, 47, 32, 28, 15, and 4 g I_2/100 g oil, labeled as a, b, c, d, e, and f, respectively. Another series of resins with the mass ratio of AESO varies from 90% to 10% were also prepared. The AESO used in these experiments was synthesized from the ESO with EOC content of 0.3875 mol/100 g. The concentration of the BPO of all samples is 5% of the total weight of the AESO and styrene.

RESULTS AND DISCUSSION

Characterization of AESOs

The reaction for the preparation of AESOs by expoxidation of soybean oil followed by ring opening was shown in Figure 1. The iodine value and the epoxy value of ESO were shown in Table I. As the epoxidation time of soybean oil increases the iodine value decreases. The iodine value shows that there are still double bonds in the ESO molecules. The FTIR spectra of the AESOs were shown in Figure 2. The peak at 3500 is attributed to the OH groups. The peak at 1630 cm^{-1} shows the stretching vibration of the
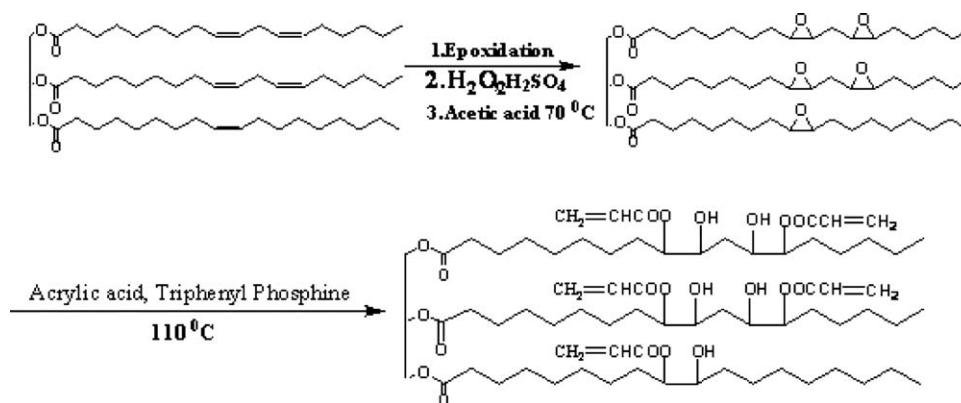
Figure 1 Scheme of epoxidation and acrylation of soybean oil.

C=C. The peaks at 1400, 985, and 810 cm^{-1} are attributed to the —CH=CH$_2$ vibration in acrylate. In ESO curve, the peak at 822 and 845 cm^{-1} are attributed to the residual epoxyl groups.

The ^{1}H-NMR spectra of AESO and ESO were shown in Figure 3. The fatty acid protons to the carbonyl (a triplet peak in the 2.2–2.4 ppm, peak 3) and methyl protons (peak 4) were remained unchanged during the course of the modification of ESO (Fig. 3). The peaks from 5.8 to 6.7 ppm (peak 5) represent the three protons attached to the carbon–carbon double bond of the acrylate esters. According to the NMR spectrum, there are ~3.4 acrylates per triglyceride.

Thermal properties

Figure 4 shows the similar decomposition behavior of the AESO-based resins. The TG and DTG data were obtained under N$_2$ atmosphere for all samples. The decomposition of the resins starts around 350°C. The maximum rate of decomposition is reached at 420°C. The whole weight-loss region is due to random scission of the linear chains of the polymers.

DSC curves of the AESO-based resins, as shown in Figure 5, show clear glass transitions for samples. There were two glass transition temperature (T_g) of each samples, this may be due to the samples are

the block copolymers. The samples are triglyceride molecular structure. The long fatly chain of the triglyceride has good flexibility, when the temperature rises, the glass transition happens, the T_g is between −20°C and 2.6°C. As to the acrylic-styryl, the rigid copolymerization fragment, the glass transition happens at higher temperature, the T_g increases from 23.5°C to 52.3°C with the increasing of acrylate content in AESOs.

The TG and DTG curves of the resins with 30%, 50%, 70%, and 90% AESO (mass ratio) was shown in Figure 6. The decomposition starts around 350°C, and the maximum rate of decomposition is reached at 420°C. The result is similar to the result of resins based different iodine value of AESO.

The DSC curves of resins with 30%, 40%, 50%, 60%, 70%, and 80% AESO (mass ratio), as shown in Figure 7, also is similar to the result of resins based different iodine value of AESO, each samples have two glass transition region. The AESO gave the

TABLE I
The Iodine Value and the Epoxy Value of ESO

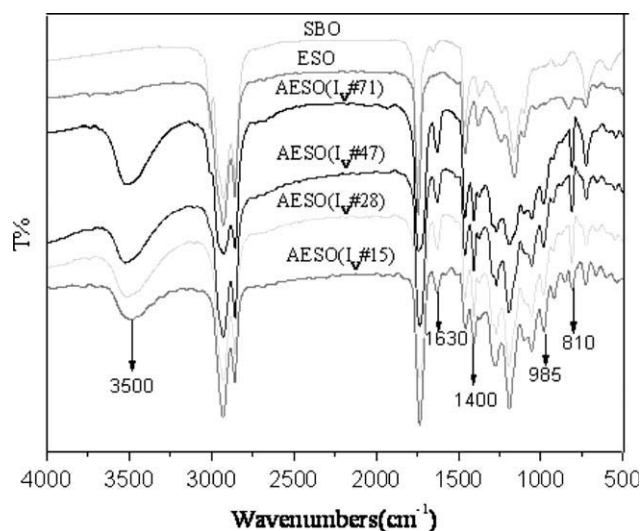| Epoxidation time (h)	Epoxy value (mol/100 g)	Iodine value (g I$_2$/100 g)
1	0.1980	71
2	0.2682	47
3	0.3097	32
4	0.3405	28
5	0.3746	15
5.5	0.4012	4

Figure 2 FTIR spectra of SBO, ESO, and AESOs.
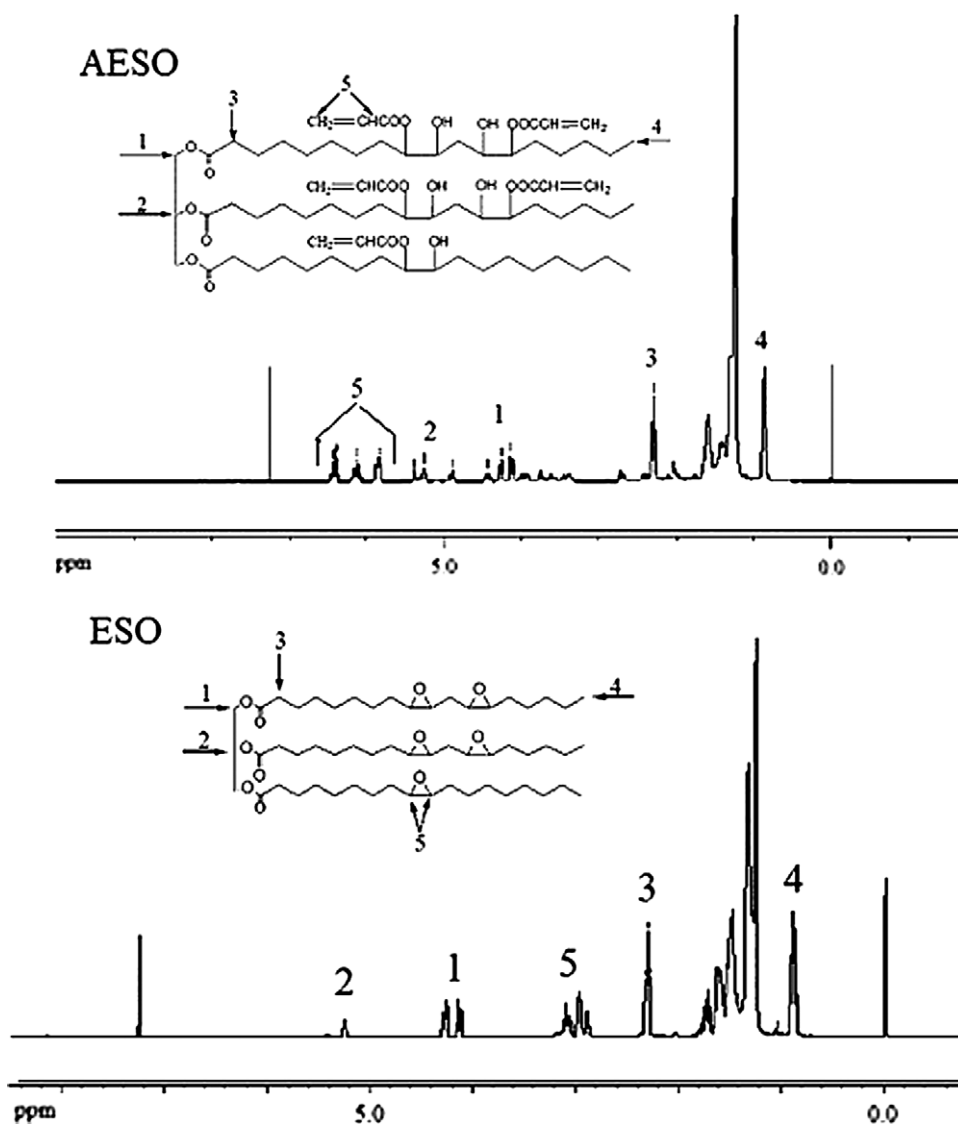
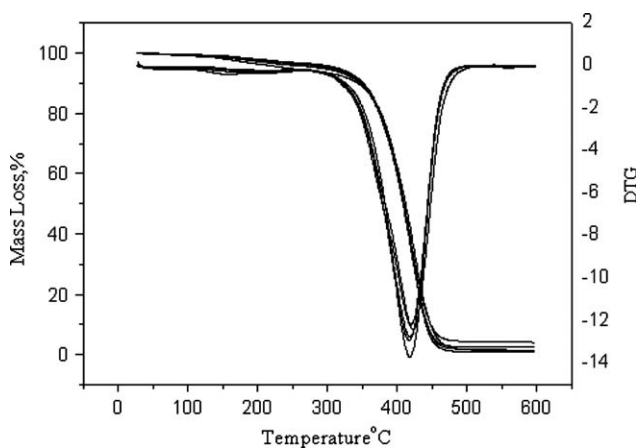**Figure 3** The ^{1}H-NMR spectra of AESO and ESO.

Figure 4 DTG, TG curves in N_2 of the AESO-based resins with different I_V.
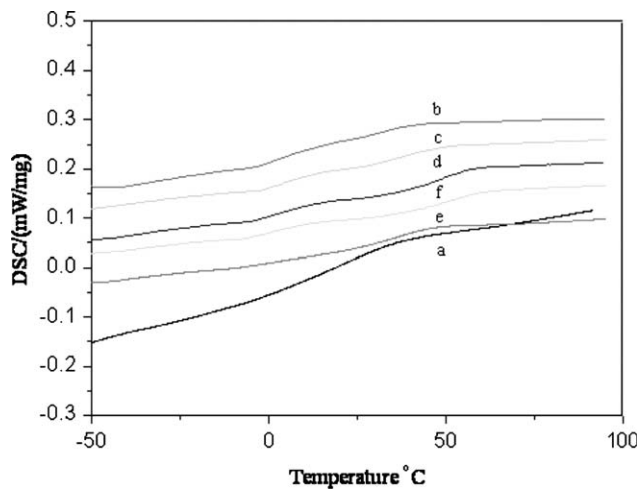

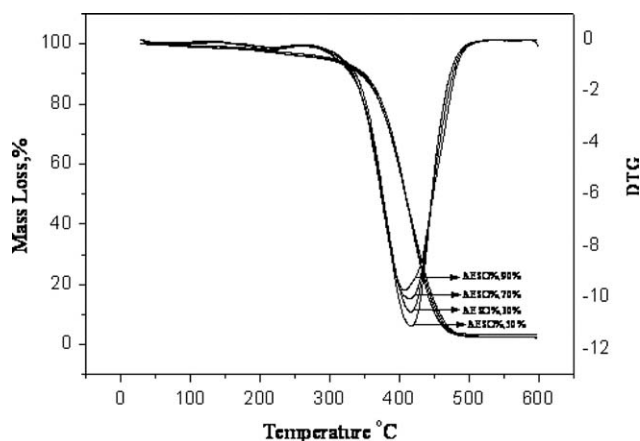**Figure 5** DSC curves in N_2 of the AESO-based resins with different I_V.

Figure 6 TG, DTG curves in N_2 of the resins with different mass ratio of AESO.

flexibility property as the styrene gave the rigidity property to the resins. As mass ratio of the AESO increased, the T_g at low temperature decreased from 8.1°C to 1.6°C, the T_g at high temperature decreased from 43.6°C to 36.4°C.

Mechanical properties

The mechanical properties of AESO-based thermosets were shown in Figure 8. As seen from Figure 8, the tensile and impact strength decrease with the increasing of iodine value of ESOs. The lower the iodine value of ESO the higher the acrylic double bond is in AESO. The higher the acrylic double bond in AESO gives more perfect network of the final thermoset which result in the tensile strength increasing. The more carbon–carbon double bonds of triglyceride skeleton structure of resins contenting, the more flexibility of the resins, leads to the decrease of mechanical strength. So, the tensile
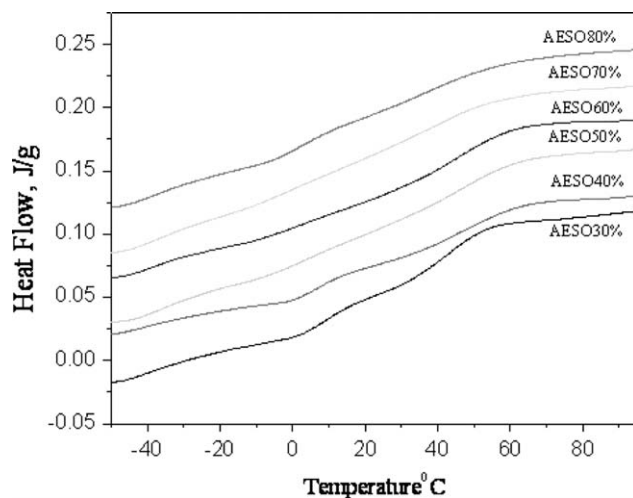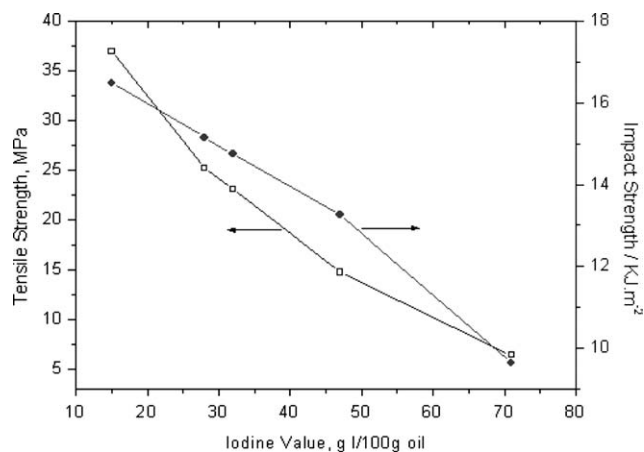

Figure 8 The effect of iodine value of triglyceride skeleton structure of resins on the tensile strength and impact strength.

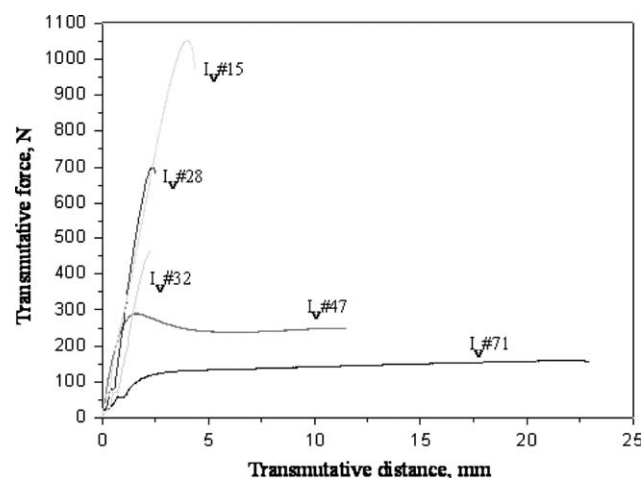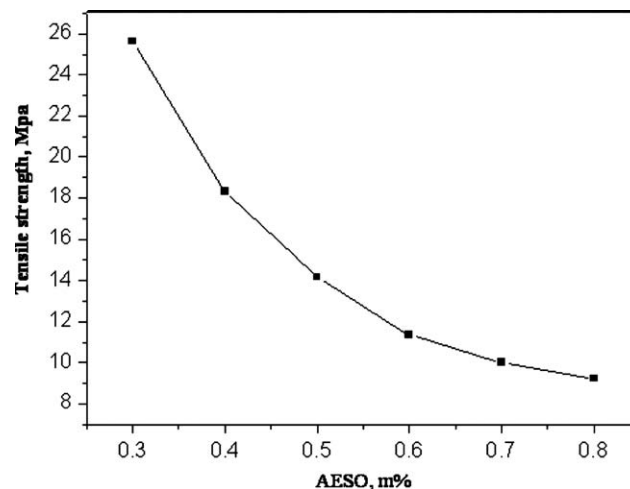**Figure 9** Stress–strain curves of AESO-based resins with different I_V.

Figure 7 DSC curves in N_2 of the resins with different mass ratio of AESO.

Figure 10 The effect of the mass ratio of AESO of resins on the tensile strength.

TABLE II
Degradation Rate of the Thermosets with Different AESO Content after 45 and 55 Days

AESO content in the sample/%	20	40	60	80
Degradation rate after 45 days/%	2.85	3.36	3.39	5.13
Degradation rate after 55 days/%	9.52	11.25	14.37	13.80

strength and impact strength increases as the iodine value of ESO decreases.

The stress–strain curves of the final thermosets with different double bonds content were given in Figure 9. As can be seen from Figure 9, the final thermosets with lower acrylic content (higher iodine value of ESO) gives rubbery behavior and higher acrylic content (lower iodine value of ESO) gives plastic behavior.

The tensile strength of final thermosets with different AESO content was shown in Figure 10. The tensile strength also decreased as the mass ratio of AESO increased.
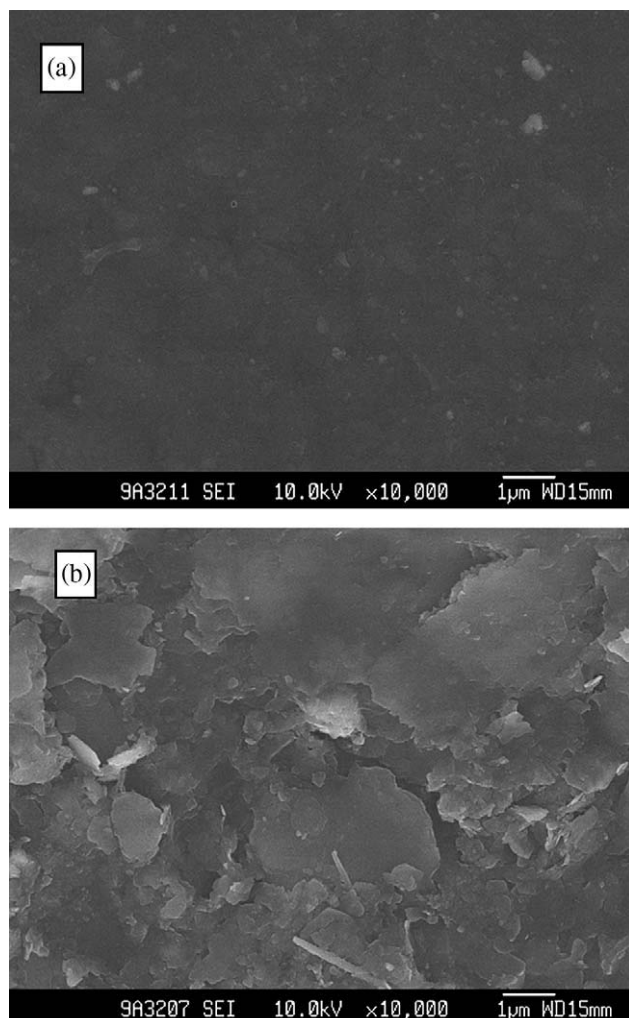

Figure 11 The SEM micrographs of the thermoset before (a) and after burying in soil for 45 days (b) of the thermoset with 60% AESO.

Environment degradation

The environment degradation property was evaluated by soil burying.[13] The degradation rate was defined as the ratio of the lose weight to the original weight of the sample. The results were shown in Table II. As can be seen from Table II, the degradation rate was increasing with the increasing of AESO content in the thermoset. This is due to AESO is the degradable segments in the polymer chain. The higher AESO content in the thermosets is the higher the degradation rate is. The SEM micrographs of the thermoset before and after burying in soil for 45 days were shown in Figure 11. The sample's surface clearly shows the degradation took place.

CONCLUSIONS

In this work, the acrylated epoxidized-soybean oil-based resins were synthesized and the effect of iodine value on the thermal and mechanical properties of the resins was studied. As a result, the tensile strength and impact strength of the resins decreased with the increasing of iodine value. When the iodine value of the ESO lower than 30 g I/100 g oil, the tensile strength and impact strength of the thermosets which made from the corresponding AESO higher than 23 MPa and 15 kJ m^{-2}, respectively. This resins possess high thermal stability, the decomposition happens at about 350°C.

The advantages of these plant oil-based resins are their low cost, availability from a renewable natural resource and their possible biodegradability.

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