

Synthesis, Characterization, and Kinetics Study of Thermal Decomposition of Epoxidized Soybean Oil Acrylate

D. Behera, A. K. Banthia

Materials Science Centre, Indian Institute Of Technology, Kharagpur 721302, India

Received 5 April 2007; accepted 24 February 2008

DOI 10.1002/app.28350

Published online 9 May 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The synthesis of epoxidized soybean oil acrylate (ESOA) from epoxidized soybean oil (ESO) had been carried out by reacting acrylic acid with the oxirane group in ESO. The acrylated ESO products were characterized using a variety of analytical techniques. The oxygen value, iodine value, and acid value were obtained to know the amount of unsaturation in the synthesized product. Infrared and proton NMR spectra were carried out to confirm the participation of oxirane group in the acrylation reaction. Free-radical initiators, benzoyl peroxide and tertiary butyl peroxy benzoate, were used for the curing of ESOA resin. Thermal decomposition kinetics of ESOA was studied by the methods of Ozawa, Kissinger, and Horowitz-Metzger, and the kinetic parameters were compared.

The thermal decomposition data of the cured ESOA resin was analyzed by thermogravimetric analysis (TGA) at different heating rates. TG curves showed that the thermal decomposition of the ESOA system occurred in one stage. The apparent activation energies determined by the Ozawa, Kissinger, and Horowitz-Metzger methods are 122.69, 95.347, and 126.20 kJ/mol, respectively. The results show that there was a reasonably good agreement between the calculated activation energies for stage one in the above methods. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2583–2590, 2008

Key words: ESOA; activation energy; TGA; Kissinger; Horowitz-Metzger methods

INTRODUCTION

In the recent years, the environmental and economic concerns inherent in the manufacture of chemicals and materials from finite petroleum oil reserves have driven a search for the replacements derived from renewable and sustainable natural resources such as oilseed crops. In 2004, world production of oils from the seven major crops shown in Figure 1 totaled 380 million metric tons. Production continues to rise at the rate of about 3–4% per annum.¹

Soybean oil is a biodegradable vegetable oil dominating today's food oil market. About 65% of the soybean oil produced each year is used for human food. Another 8% is used for animal feed, while the remainder (27%) finds nonfood uses (soap, fatty acids, lubricants, coatings, etc.).²

Soybean oil contains a relatively high level of unsaturated groups and can be epoxidized by reaction with peracids and hydrogen peroxide.³ A preliminary study had shown that the internal double

bonds present on the unsaturated aliphatic chains were too unreactive for any viable polymerization process, chemical modifications were investigated involving the grafting of polymerizable moieties on epoxide groups present in epoxidized soybean oil. Acrylate moiety was successfully appended on these triacylglyceride molecules.⁴ Triglyceride-based polymers have been used as toughening agents in PVC and epoxy resins,⁵ and as the major component of a number of natural resins and,⁶ composites,⁷ and pressure-sensitive adhesives.⁸ In addition, it is copolymerized with a low molecular weight species, such as styrene, to modify the properties of the polymer and lower the resin viscosity.⁹ The low viscosities of this resin make it ideal for inexpensive polymer composite fabrication processes, such as vacuum-assisted resin-transfer molding.

ESOA resin is an attractive alternative to petroleum-based resins, because it is inexpensive, has good properties, and is derived from renewable resources. However, unlike petroleum-based resins, it has a wide distribution of functionality ranging from zero to nine polymerizable groups per molecule.¹⁰

The ESOA polymer is analogous to vinyl esters (VE) and unsaturated polyesters (UPE),⁹ and have multiple functional sites per molecule, which allow the resins to crosslink. Epoxidized soybean oil

Correspondence to: D. Behera (dibakar_polymer@yahoo.com).

Contract grant sponsor: Indian Institute of Technology, Kharagpur, India.

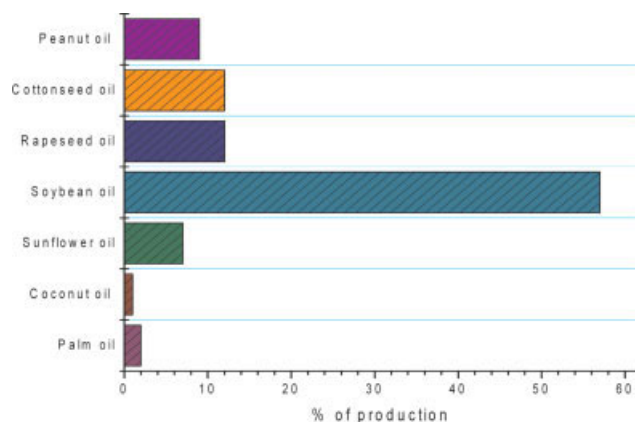


Figure 1 World production of oils from the seven major crops. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

acrylate (ESOA) can be cured through its reactive acrylate end groups using any appropriate free radical polymerization initiators, including ultraviolet initiators, electron beam curing, high-energy radiation, etc. In the open literature, some work has been conducted regarding its synthesis, characterization, and curing.^{11–14} We initiated a new approach, which is much simpler like other procedures. Thus, this work deals with the conversion of epoxidised soybean oil to its acrylate along with its characterization. Also in this study, the detailed investigation of thermal decomposition of cured ESOA resin was done to know its thermal stability. From the results of thermogravimetric analysis, the kinetic parameters were determined by various methods.

EXPERIMENTAL

Materials

ESOA was prepared in our laboratory by using acrylic acid (Merck Chemical Company) and epoxidized soybean oil (SV Plasto Chem Pvt Ltd, epoxide equivalent 400 ± 5). Benzoyl peroxide (BPO; Fluka) was recrystallized from chloroform-methanol (1 : 1) mixture. Butylated hydroxy toluene, triphenylphosphine, other chemicals, and all solvents were used as received.

Synthesis of epoxidized soybean oil acrylate and its curing

To a three-necked 500-mL flask fitted with a condenser, thermometer and mechanical stirrer were added with 227.60 g of epoxidized soybean oil (0.40 mol) and 58.0 g of acrylic acid (0.80 mol). Next, 0.085 g of butylated hydroxy toluene (0.03% of the total weight resin) was added as a stabilizer or free

radical inhibitor along with 2.856 g of triphenylphosphine (1% by weight) as a catalyst. The reaction temperature was raised to 90–95°C and was carried out for 6 h (until 99% of the acid had reacted). The reaction was terminated by titrating the residual epoxy groups or by measuring the acid value of the mixtures by standard methods. The reaction scheme for ESOA synthesis was shown in Figure 2.

Predetermined quantities of ESOA along with 1.1 wt % benzoyl peroxide and 0.2 wt % tertiary butyl peroxy benzoate were taken in a plastic beaker and mixed by hand as an initial dispersion. The mixer was then placed for sonication process. During sonication, heat builds up. To avoid temperature rise during sonication, external cooling was used by submerging the mixing beaker in a mixture of ice and water. After degassing, the resin mixture was cured at 60°C temperature for 2 h under nitrogen atmosphere and then subjected for postcuring at 120°C for about 1 h. The postcured resin was then used for degradation kinetics study.

Methods of characterizations

Determination of oxirane content

The oxirane content (OC) of the ESOA was determined by the hydrogen bromide—acetic acid procedure (American Oil Chemists' Society, 1963).

Determination of iodine value

The American Oil Chemists' Society (AOCS) recommends the use of ASTM method D1959-97, also known as the Wijs method, for the determination of iodine value (IV) of the ESO and ESOA.

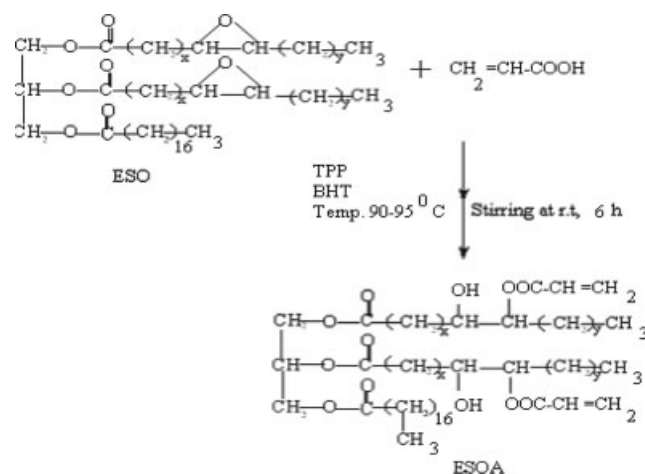


Figure 2 Synthesis of ESOA by the reaction of ESO with acrylic acid.

Determination of acid value

About 1–2 g resin was dissolved in 100 mL of acetone. A few drops of phenol red: bromothymol blue (1 : 1 in 90% ethanol) indicator was added. The solution was then titrated with standardized 0.1N KOH. The end point was achieved when the color of the solution changed from yellow to green and to blue.

The acid value (AV) was calculated using the following eq. (1),

$$\text{Acid value} = (56.1 \times T \times N)/W \quad (1)$$

where T is the titer (mL), N is the normality of potassium hydroxide solution, and W is the weight of sample (g).

Determination of refractive index

Refractive index (RI) was determined using an Abbe refractometer following the procedures given by ASTM and AOCS.

Determination of viscosity

The viscosity of the ESO and the acrylated ESO samples was measured at 25°C using a Brookfield viscometer (American Society for Testing and Materials, 1969).

Determination of FTIR spectra

FTIR spectra were recorded with a Thermo-Nicolet-870-FTIR spectrophotometer using KBr pellets.

Determination of ^1H NMR spectrum

^1H NMR spectrum of ESOA sample was recorded on a Bruker AC270 MHz NMR spectrometer in CDCl_3 at room temperature using tetramethylsilane as internal standard. A 90° pulse width, 4.096 s acquisition time and 2 s pulse delay were used.

Kinetic studies of degradation reactions

In this study, the detailed investigation of thermal decomposition of ESOA resin is mainly concerned. From the results of thermogravimetric analysis, the kinetic parameters have been determined by various methods. Based on the aforementioned equations, different kinetic methods (differential and integral) were applied in this study.

In the nonisothermal experiments carried out with a thermobalance, the sample mass is measured as a function of temperature. The rate of degradation or conversion, $d\alpha/dt$, is a linear function of a tempera-

ture-dependent rate constant, k , and a temperature-independent function of conversion, α , that is

$$d\alpha/dt = kf(\alpha) \quad (2)$$

The reaction rate constant, k , has been described by the Arrhenius expression

$$k = A \exp(-E/RT) \quad (3)$$

where A is the pre-exponential factor, E is the activation energy, R is the gas constant, and T is the absolute temperature. The combination of eqs. (2) and (3) gives

$$d\alpha/dt = Af(\alpha) \exp(-E/RT) \quad (4)$$

If the temperature of the sample is changed by a controlled and constant heating rate, β , dT/dt , the variation in the degree of conversion can be analyzed as a function of temperature, this temperature being dependent on the time of heating. Therefore, the rearrangement of eq. (4) gives

$$d\alpha/dT = [A/\beta] f(\alpha) \exp(-E/RT) \quad (5)$$

The integrated form of eq. (5) is generally expressed as

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(\frac{E}{RT}\right) dT \quad (6)$$

where $g(\alpha)$ is the integrated form of the conversion dependence function.

Based on the aforementioned equations, different kinetic methods (differential and integral) were applied in this study.

Differential method

Analysis of the changes in thermogravimetric data brought about by variation of the heating rate, β , is the basis of the most powerful differential method for the determination of kinetic parameters.

Kissinger method involves the maximum temperatures (T_{\max}) of the first derivative weight loss curves at multiple heating rates.¹⁵ The activation energy can be determined by the Kissinger's method without a precise knowledge of the reaction mechanism, using the following equation:

$$\ln(\beta/T_{\max}^2) = \left\{ \ln AR/E + \ln[n(1 - \alpha_{\max})^{n-1}] \right\} - E/RT_{\max} \quad (7)$$

where T_{\max} is the temperature corresponding to the inflection point of the thermodegradation curves,

which corresponds to the maximum reaction rate, α_{\max} is the conversion at T_{\max} , and n is the reaction order.

Taking into account the Kissinger's approximation, which states that $f^1(\alpha_{\max}) = n(1 - \alpha_{\max})^{n-1}$ [equiv] constant, the activation energy E can be determined from a plot of $\ln(\beta/T_{\max}^2)$ against $1/T_{\max}$.

Integral methods

The integral method involves an approximate integration of eq. (6). Two kinds of integral methods are applied in this article.

Flynn-Wall-Ozawa method,^{16,17} using the Doyle's approximation¹⁸ for the integration, has been expressed as

$$\log \beta = \log[AE/g(\alpha)R] - 2.315 - 0.4567E/RT \quad (8)$$

Using eq. (8), the linear representation of $\log \beta$ versus $1/T$ allows us to determine the activation energy with a given value of the conversion.

Horowitz-Metzger method¹⁹ simplifies the exponential integral, obtaining the following equation

$$\ln[\ln(1 - \alpha)^{-1}] = E\theta/RT_{\max}^2 \quad (9)$$

where θ is the difference between T and T_{\max} . The activation energy can be determined from a linear fit to the plot of $\ln[\ln(1 - \alpha)^{-1}]$ versus θ for the main (first) stage of thermal degradation.

RESULTS AND DISCUSSION

Synthesis and characterization of ESOA

Figure 2 shows the reaction of epoxidized soybean oil with acrylic acid to prepare epoxidized soybean oil acrylate (ESOA) resin, which was the most widely industrially, used oil based vinyl ester resin. ESOA was not highly viscous and showed a constant viscosity at different shear rates (Table I) indicating, Newtonian behavior. Therefore, it is not necessary to use reactive diluents to reduce the viscosity of acrylated oils, which is a highly desirable feature for composite application.

TABLE I
Viscosity of ESOA by the Reaction of ESO with Acrylic Acid after 6 Hours

Sample	Shear rate (s ⁻¹)	Viscosity (Pa s)
ESOA	8.4	25.425
	16.72	25.345
	25.03	25.313
	41.65	25.305
	49.96	25.294

TABLE II
Analytical Data of the ESO and the Acrylated ESO

Properties	ESO	Acrylated ESO
Oxirane oxygen content	6.4	0.012
Iodine value (g I ₂ /100 g)	6	8
Acid value (mg KOH/gm)	1.0	1.15
Colour (Gardner)	3	4
RI η_D^{20}	1.4627	1.4873
Viscosity (25°C) (Pa s)	0.258	25.336

Analytical data of the ESO and the ESOA were shown in Table II. It could be seen from the table that ESOA had an oxirane oxygen content of 0.012 compared to 6.4 found in the ESO. This indicated that almost all oxirane oxygen in the ESO had participated in the reaction to yield ESOA.

On the other hand, ESOA had an increased iodine value (8 g I₂/100 g in ESOA compared to 6 g I₂/100 g in ESO). This indicated that the acrylated groups had been successfully attached to the triglyceride molecules of ESO to give ESOA.

Upon acrylation of the ESO, the acid value of the sample increased slightly from 1.0 mg KOH/g to 1.15 mg KOH/g. This is due to the unreacted acrylic acid content in the ESOA that results in a subsequent increase of acid value.

The color of the ESO was found to be 3G. However, after acrylation, it was found that ESOA had a color at 4G (slightly yellowish in color). In addition, the refractive index of the ESO and the uncured ESOA were found to be 1.4627 and 1.4873, respectively. The viscosity of the ESO and the uncured ESOA, measured at 25°C, were 0.258 and 25.336 Pa s, respectively, indicating that acrylated groups may be attached to the triglyceride molecules of ESO. Sample was further characterized by infrared and proton NMR spectra to confirm the participation of oxirane group in the acrylation reaction.

FTIR analysis of ESO, ESOA, and cured ESOA resin

Table III presents the IR data relevant to ESO, uncured ESOA, and cured ESOA. There were three important functional groups in terms of the structural information. These were the oxirane group in the ESO sample, the acrylate group, and the hydroxyl (—OH) group in the ESOA samples (uncured and cured).

The ESO sample (Fig. 3) had several absorption peaks at 912 and 882 cm⁻¹, which represented oxirane groups in the triglyceride group. No oxirane group absorption peak was found in the ESOA sample, due to the reduction of the oxirane oxygen content after acrylation. The success of acrylation was further confirmed by the appearance of FTIR peaks at 1637, 1461, and 1406 cm⁻¹ corresponding to

TABLE III
IR Absorption Peaks of ESO, ESOA, and Cured ESOA

ESO		ESOA		Cured ESOA	
Absorption peak, cm^{-1}	Functional group	Absorption peak, cm^{-1}	Functional group	Absorption peak, cm^{-1}	Functional group
3478	OH str (weak)	3470	OH str (strong)	3468	OH str (strong)
2944	CH str	2927,2856	CH str	2925	CH str
1740	C=O str	1740	C=O str	1745	C=O str
–	–	1637	H ₂ C=CH str	–	–
1378	CH sym band	1378	CH sym band	1378	CH sym band
1282	C–O str	1270	C–O str	1247	C–O str
1142	C–C–O str	1189,1057	C–C–O str	1122	C–C–O str
912,882	C–O–C oxirane groups	967,810	C–C–O Asy band	–	–
1468	CH scissoring band	1461	CH scissoring band	1462	CH scissoring
–	–	1406	H ₂ C=CH scissoring band for terminal alkene	–	–

acrylate groups (Fig. 4). The presence of the OH group was confirmed by the peaks at 3478 (very weak band), 3470, and 3468 cm^{-1} for ESO, uncured ESOA and cured ESOA, respectively.

¹H NMR spectrum of ESOA resin

Figure 5 shows the ¹H NMR spectrum of acrylated soybean oil. The peaks at 4.1–4.4 ppm originate from the protons in the methylene groups of the triglyceride. The vinylic hydrogens are detected at 5.2–5.5 ppm. The protons in the CH₂ groups between two carbon–carbon double bonds appear at 2.0–2.5 ppm. The methylene and methyl protons of acrylate end group showed signal at 6.34 and 5.87 ppm. All the ¹H NMR peaks supported the formation of ESOA.

Determination of kinetic parameters of ESOA resin

For obtaining the kinetic information, such as the activation energy, the TGA study was conducted

with the variation of the heating rates in this article. Figure 6 shows the TGA thermograms of the ESOA resin corresponding to dynamic experiments carried out at different heating rates (1, 5, 10, and 30°C/min). For the sample, the TGA curves shift to higher temperatures at higher heating rates, although their shapes are quite similar.

The TG curves (Fig. 6) of degradations showed that investigated resin degraded with the formation of residues stable up to 300°C. The percentage of decomposed polymer increased with decreasing heating rate (Table IV), and the 100% weight loss was observed at $\beta = 1^\circ\text{C}/\text{min}$.

The degradation behavior of the ESOA resin had been read from the DTG thermograms. Based on the number of peaks in the DTG curves, the weight loss processes of the ESOA resin was considered. As shown in Figure 7, the DTG curve shows clearly single-stage degradation.

For the ESOA resin, the onset being above 300°C, the maximum rate of weight loss being in the range

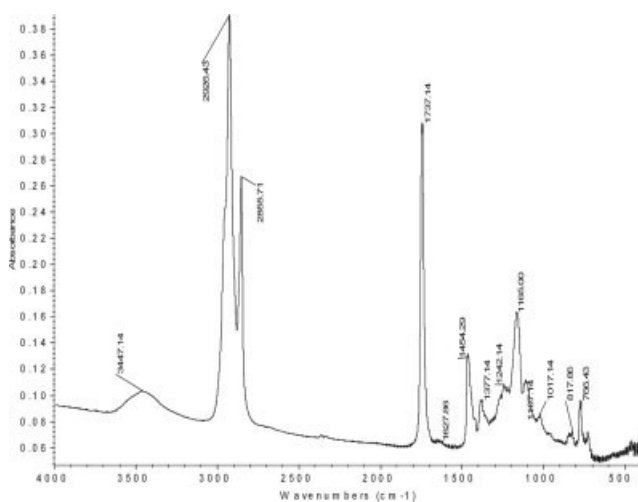


Figure 3 FTIR spectrum of ESO at room temperature.

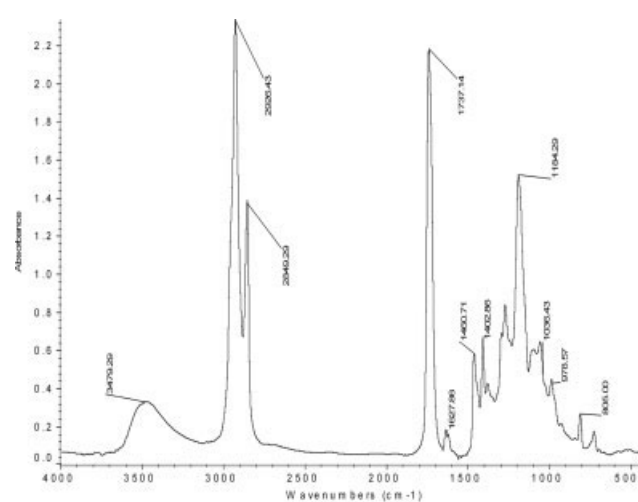


Figure 4 FTIR spectrum of ESOA at room temperature.

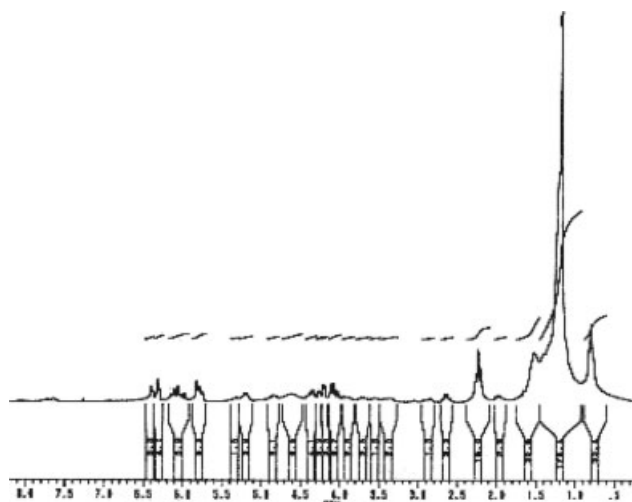


Figure 5 ^1H NMR spectrum of ESOA at room temperature.

350–445°C and the amounts of residue at 500°C being relatively small (Fig. 7). The TG curves of degradation showed that the investigated resin degraded with the formation of residues. The obtained result suggested that resin degraded by an initial random chain scission followed by branching and crosslinking. Nevertheless, the quite sharp DTG peak observed at high heating rates indicated that, in these conditions, the two processes are about simultaneous and that branching and crosslinking rates are comparable with the scission rate, as also supported by the high amount of residue found. By contrast, at low heating rate, the scission process was quicker than branching, crosslinking processes,

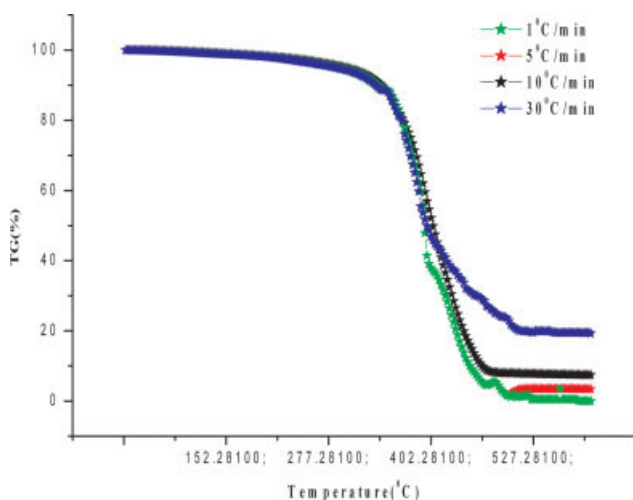


Figure 6 TG curves of ESOA with heating rates 1, 5, and 10°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Weight Loss (%) of Polymer at the Various Used Heating Rate

Φ (°C/min)	Weight loss (%)
1	100.00
5	97.00
10	93.23
20	85.80
25	80.72

and the complete or about complete degradation of resin was observed.^{20–24} The apparent activation energy value associated with the first degradation stage of our resin was then evaluated by the Kissinger equation, using the data of Table V. Single linear regression was found for the resin ESOA. The regression coefficients and the apparent activation energy were listed in Table VI, and in Figure 8, the corresponding straight line was plotted.

The occurrence of single Kissinger linear relationship was found for this resin. This behavior has been attributed to kinetically slow diffusion processes. Because O_2 was not present in our experimental conditions, it can only be due to the slow diffusion of the degradation products in the melt, so that, at higher heating rates, the kinetics of process was under diffusion control, in agreement with the corresponding high- E_a values. Therefore, we considered true E_a values as those obtained at lower scanning rates.

Another procedure for calculating the activation energy is to take the Flynn-Wall-Ozawa eq. (8). At a given value of the conversion, the activation energy can be obtained from a logarithmic plot of heating rates as a function of the reciprocal of temperature,

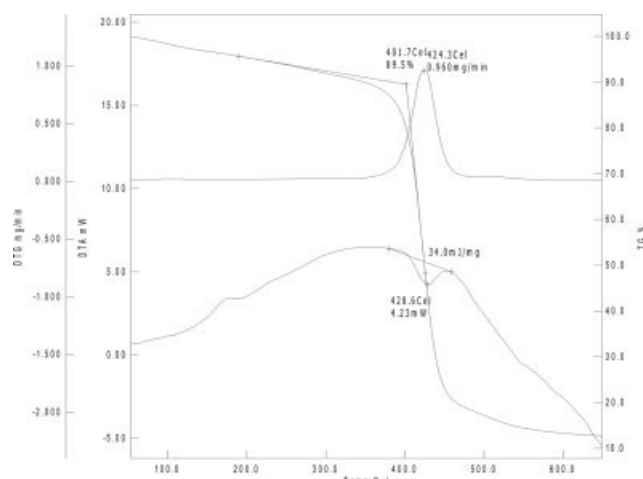


Figure 7 Thermogravimetric curve for ESOA under nitrogen atmosphere at a heating rate of 20°C/min.

TABLE V
Temperatures at Maximum Rate of Weight Loss (T_m) for the First Degradation Stage of Resin ESOA at the Various Heating Rates Used (Φ)

Φ ($^{\circ}\text{C min}^{-1}$)	T_m ($^{\circ}\text{C}$)	T_m (K)	Ln (Φ/T_m^2)	$[1000/T_m]$ (K^{-1})
1	350	623	-12.86	1.61
5	356	629	-11.27	1.53
10	387	660	-10.68	1.49
20	402	675	-10.03	1.45
30	419	692	-9.86	1.44

because the slope of such a line is given by $-0.4567 E_a/R$. For this work, the conversion values of 2, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, and 98%, and 5, 10, 20, and 30 heating rates were used. Figure 9 shows the fitting lines of ESOA resin at the selected conversion values. All the calculated activation energies are listed in Table VII. The activation energies implies that this stage of decomposition result from the destruction of ESOA structures.

Compared to others, the aforementioned two methods present the advantage that they do not require the previous knowledge of the reaction mechanism for determining the activation energy. The Flynn-Wall-Ozawa results were considered for comparison purposes, because the Kissinger method takes only one point of the thermodegradation curve whereas the Flynn-Wall-Ozawa method takes different points corresponding to different conversion values. In this study, the two methods show good agreement when used to determine the decomposition activation energies at certain conversion values.

In addition to the above heating rate method, we also applied another integral method, Horowitz-Metzger equation, to calculate the kinetic parameters. This method can determine the decomposition activation energy using only one heating rate. In this study, the TGA curve at a heating rate of $20^{\circ}\text{C}/\text{min}$ was used to calculate the degradation kinetics. The plot was shown in Figure 10, with the chosen T_0 from $T_{\text{max}} - 15$ to $+15^{\circ}\text{C}$ in a step of 5°C . The slope data was obtained with good correlation coefficients, and the calculated activation energy was listed in Table VIII. A comparison of these results with those previously obtained by the Kissinger method shows

TABLE VI
Regression Coefficients and Apparent Activation Energies by the Kissinger Equation

Φ ($^{\circ}\text{C min}^{-1}$)	$\ln(nRA)$ (W_m^{n-1}/E_a)	E_a/R 3×10^{-3} (K)	r	E_a (kJ mol^{-1})
1-10	14.86	11.47	0.9993	95.347 (± 4)
10-30	37.86	16.41	0.9987	136.281 (± 11)

r , Product moment correlation coefficient.

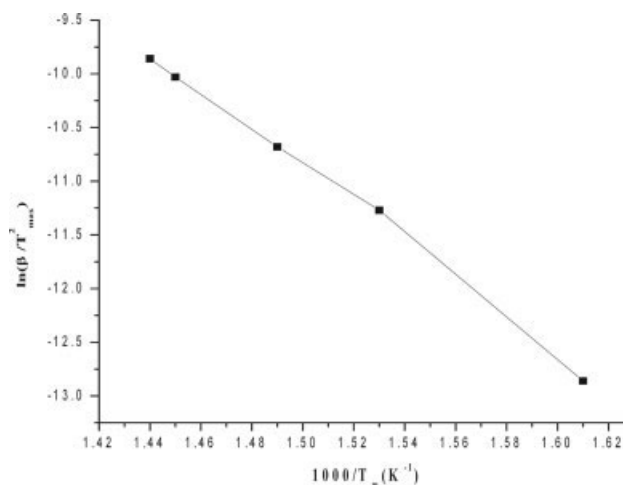


Figure 8 Kissinger plots for the first degradation stage of the resin ESOA.

that there was a reasonably good agreement between the calculated activation energies for stage one.

Generally, the multiple heating rate technique seems more realistic for studying the kinetic mechanism of the thermal degradation of polymers. The Kissinger method and Flynn-Wall-Ozawa method are very useful to study the material whose degradation mechanism was not precisely described. The Horowitz-Metzger method, using another approximation for the integration of eq. (6), presents the problem of the arbitrary selection of the referenced temperature.

CONCLUSIONS

The synthesis of acrylated epoxidized soybean oil derived from epoxidized soybean oil had been carried out successfully. The oxygen value, iodine

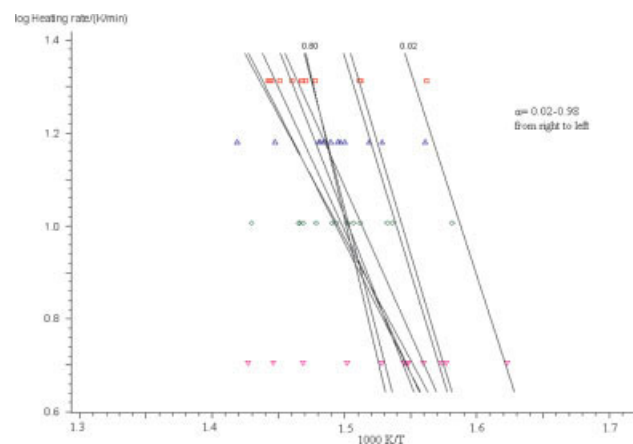


Figure 9 Plots of $\log \Phi$ versus $1/T$ of for calculating the activation energies by Flynn-Wall-Ozawa. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE VII
Calculated Activation Energies at Various Conversions of the Decomposition by FlynnWalleOzawa Method

Conversion (α)	E_a (kJ mol ⁻¹)	R
0.020	92.69	0.9993
0.050	94.11	0.9990
0.100	94.43	0.9987
0.200	99.48	0.9981
0.300	104.37	0.9977
0.400	107.34	0.9970
0.500	109.24	0.9967
0.600	113.91	0.9950
0.700	119.71	0.9944
0.800	120.83	0.9928
0.900	122.69	0.9917
0.950	111.53	0.9897
0.980	112.16	0.9890

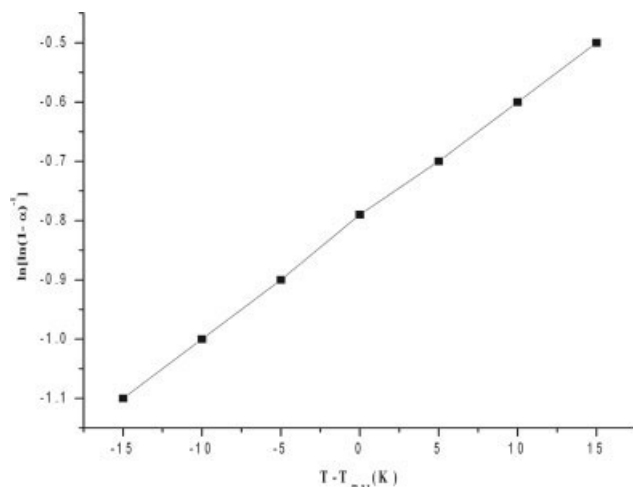


Figure 10 Determination of activation energy for the thermal degradation of ESOA with 20°C/min heating rates.

value, and acid value indicated that acrylated groups had been successfully attached to the triglyceride molecules of ESO. From FTIR analysis, no oxirane group absorption peak was found in the ESOA sample, which confirms the acrylated product of epoxidized soybean oil. All the ¹H NMR peaks supported the formation of ESOA. The Kissinger, Flynn-Wall-Ozawa, and Horowitz-Metzger methods were successfully used to study its thermal stability as well as to determine the apparent activation energy (E_a) associated with the first-degradation stage. The results show that there is a reasonably good agreement between the calculated activation energies for stage one in the above methods. The obtained results

TABLE VIII
Apparent Activation Energy by the Horowitz Metzger Equation

$T - T_{max}$ (K)	$\ln[\ln(W_0/W_T)]$	E_a (kJ mol ⁻¹)
-15	-1.1	126.208
-10	-1.0	
-5	-0.9	
0	-0.79	
5	-0.7	
10	-0.6	
15	-0.5	

also suggested that degradations occurred through random chain scission followed by branching and crosslinking, which partially superimposed with the initial process.

References

- Smith, W. Third Green Chemistry and the Consumer Symposium SCI, Vol. 1; NNFCC: London, 2006; p 6.
- Wang, H. Hunan Ind J 1998, 6, 15.
- Scala, J. L.; Wool, R. P. J Am Oil Chem Soc 2002, 79, 59.
- Wool, R. P.; Kusefoglu, S. H.; Palmese, G. R.; Zhao, R.; Khot, S. N. U.S. Pat. 6,121,398 (2001).
- Kirschenbauer, H. G. Fats and Oils, an Outline of their Chemistry and Technology; Reinhold: New York, 1960; p 146.
- Khot, S. N.; Scala La, J. J.; Can, E.; Morye, S. S.; Williams, G. I.; Palmese, G. R.; Kusefoglu, S.; Wool, R. P. J Appl Polym Sci 2001, 82, 703.
- Williams, G. I.; Wool, R. P. Appl Compos Mater 2000, 7, 421.
- Bunker, S. P.; Wool, R. P. J Polym Sci Part A: Polym Chem 2002, 40, 451.
- Malik, M.; Choudhary, V.; Varma, I. K. J Macromol Sci Polym Rev 2000, 40, 139.
- Liu, K. Soybeans. Chemistry, Technology, and Utilization; Chapman and Hall: New York, 1997; p 27.
- Scala La, J. J Appl Polym Sci 2005, 95, 87.
- Pelletier, H. Eur J Lipid Sci Technol 2006, 108, 54.
- Lu, J.; Khot, S.; Wool, R. P. Polymer 2005, 46, 71.
- Muhua, X.; Lihua, Z.; Ling, J. Hunan Ind J 2001, 21, 40.
- Kissinger, H. E. Anal Chem 1957, 29, 1702.
- Flynn, J. H.; Wall, L. A. J Res Natl Bur Stand A Phys Chem 1996, 70, 487.
- Ozawa, T. Bull Chem Soc Jpn 1965, 38, 1881.
- Doyle, C. D. Nature 1965, 207, 290.
- Horowitz, H. H.; Metzger, G. Anal Chem 1963, 35, 1464.
- Hay, J. N.; Kemmish, D. J. Polymer 1987, 28, 2047.
- Day, M.; Cooney, J. D.; Wiles, D. M. J Appl Polym Sci 1989, 38, 323.
- Day, M.; Sally, D.; Wiles, D. M. J Appl Polym Sci 2003, 40, 1615.
- Howell, B. A.; Betso, S. R.; Meltzer, J. A.; Smith, P. B.; Debney, M. F. Thermochim Acta 1990, 166, 207.
- Lee, J. Y.; Shim, M. J.; Kim, S. W. J Appl Polym Sci 2001, 81, 479.