

# Oxirane Cleavage Kinetics of Epoxidized Soybean Oil by Water and UV-Polymerized Resin Adhesion Properties

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**Abstract** Di-hydroxylated soybean oil (DSO), a biobased polyol synthesized from epoxidized soybean oil (ESO) could be used to formulate resins for adhesives; however, current DSO synthesis requires harsh reaction conditions that significantly increase both cost and waste generation. In this paper, we investigate the kinetics of oxirane cleavage in ESO to DSO by water and elucidate the role of different process parameters in the reaction rate and optimization of reaction conditions. Our kinetic study showed that ESO oxirane cleavage was a first-order reaction and that the ESO oxirane cleavage rate was greatly influenced by tetrahydrofuran (THF)/ESO ratio, H<sub>2</sub>O/ESO ratio, catalyst content, and temperature. Optimized reaction parameters were THF/ESO of 0.5, H<sub>2</sub>O/ESO of 0.25, catalyst content of 1.5 %, and reaction time of 3 h at 25 °C. DSO with hydroxyl value of 242 mg KOH/g was obtained under these conditions. We also characterized the structure, thermal properties, adhesion performance, and viscoelasticity of UV-polymerized resins based on this DSO. The resin tape exhibited peel adhesion strength of 3.6 N/in., which is comparable to some commercial tapes measured under similar conditions.

**Keywords** Epoxidized soybean oils (ESO) · Di-hydroxylated soybean oil (DSO) · Polyol · Oxirane cleavage kinetics · UV-curing · Pressure-sensitive adhesives (PSA) · Biobased product

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## Introduction

Plant oils, such as soybean oil, have been used to produce polyol that is an important monomer used to synthesize polyurethanes and other polymers [1–3]. Most soybean polyols are produced by oxirane cleavage of ESO with proton donors (alcohols, carboxylic acid, amines, amino alcohols, thiols, water, etc.) [1]. The oxirane cleavage reaction and resulting polyol properties are affected by several factors, including reactants, catalysts, solvents, reaction time, and temperature. Kinetics studies have been conducted to optimize reaction conditions to reduce operating costs and waste generation [4–7].

We prepared di-hydroxylated soybean oil (DSO) from ESO in a water/tetrahydrofuran (THF) system catalyzed by perchloric acid and found that DSO could be a critical component in developing pressure-sensitive adhesives (PSA) when co-polymerized with ESO [8, 9]. Bio-based and biodegradable PSA might be alternatives to some petrochemical-based PSA products such as removable labels, tapes, and protective films; however, the DSO process requires long reaction times, high reaction temperatures, or large amounts of perchloric acid and solvents [8, 10, 11]. These harsh reaction conditions are evident in [10], who used a high temperature (100 °C), took a long time (48 h), and required high HClO<sub>4</sub> content (20.45 wt% based on ESO) to synthesize DSO. The methods reported by [11] and [8] required high ratios of THF/ESO (12, v/w), H<sub>2</sub>O/ESO (8, v/w), perchloric acid/ESO (33.2 %, v/w), and a reaction time of 20 h. Cost-effective production of DSO necessitates studying ESO oxirane cleavage to DSO kinetics by water and understanding how the reaction rate is related to the THF/ESO ratio, H<sub>2</sub>O/ESO ratio, catalyst ratio, and temperature.

This research focuses on: (1) investigating the kinetics of oxirane cleavage in ESO to DSO by water, hence

**Table 1** Experimental design for the study of ESO oxirane cleavage kinetics

Variables	Range	Fixed factors			
		THF/ESO (v/w)	H <sub>2</sub> O/ESO (v/w)	Acid/ESO (v/w)	Temperature (°C)
THF/ESO (v/w)	0–1	n/a	0.5	1 (%)	25
H <sub>2</sub> O/ESO (v/w)	0–0.75	0.5	n/a	1 (%)	25
Acid/ESO (v/w)	1–2 %	0.5	0.5	n/a	25
Temperature (°C)	25–60	0.5	0.5	1 (%)	n/a

elucidating the role of the different process parameters on the reaction rate; (2) synthesizing DSO based on optimized parameters; and (3) studying the performance of PSA formulated with the optimized DSO.

## Experimental Procedures

### Materials

ESO (VIKOFLEX<sup>®</sup>7170, oxirane oxygen ~7.0 %, viscosity at 25 °C 0.42 Pa, molecular weight ~1,000 g/mol) was provided by Arkema Inc. PC-2506 (diaryliodonium hexafluoroantimonate) was used as cationic photo initiator (PI) for the UV curing of adhesives and was obtained from the Polysset Company (Mechanicville, NY, USA). Rosin ester (SR, SYLVALITE<sup>®</sup> RE 80 HP) was from Arizona Chemical (Jacksonville, FL, USA). Perchloric acid (70 % solution in water) and other chemicals were all purchased from Fisher Scientific (Pittsburgh, PA, USA) and used as received.

### Oxirane Cleavage and Hydroxylation of ESO

Oxirane cleavage and hydroxylation reactions were carried out in a flask equipped with a magnetic stirrer. For a typical reaction, 60 g ESO was placed in the flask, and a determined volume of tetrahydrofuran (THF) was pipetted to dissolve the ESO. A determined amount of perchloric acid and distilled water was mixed in another container and dropped into the flask gradually (within 2 min) while stirring. The course of the reaction was followed by withdrawing samples at regular intervals and considering the completion of adding acid/water mixture to be the zero time. Collected samples were immediately extracted with ethyl acetate in a separating funnel, washed with distilled water, neutralized with saturated sodium bicarbonate solution, and finally evaporated with a rotary evaporator first under low vacuum (~100 torr) for 1 h, then under high vacuum (~0.1 torr) for 1 h to remove any residual solvent and water. The collected products were analyzed for oxirane content. For the reactions conducted under temperatures higher than room temperature, a water bath was used to control the temperature within  $\pm 1$  °C. The flask was also connected to a condenser to reflux THF. Other steps were remained

the same. The experimental design for the study of ESO oxirane cleavage kinetics is shown in Table 1.

### Oxirane Oxygen Content Determination

The oxirane oxygen content was measured according to ASTM D 1652-97 (Test Method A).

### Hydroxyl Number Determination

The hydroxyl number of selected products was measured according to ASTM D 4274-99 (Test Method A-Acetylation).

### Gel Permeation Chromatography (GPC) Analysis

The weight ( $M_w$ ) and number-average molecular ( $M_n$ ) weight as well as the molecular weight distribution (PDI, equal to  $M_w/M_n$ ) of selected products were determined through GPC (Waters 2695 Separation Module). Samples were dissolved in dimethylformamide (DMF). Measurements were performed at room temperature and a flow rate of 1 ml/min. The molecular weight was calibrated according to the polystyrene standard.

### PSA Preparation

The DSO synthesized under optimized parameters was used to prepare PSA, and four different formulations were prepared to understand the function of DSO in the PSA system: (1) EP (ESO/PI = 1/0.03), (2) EDP (ESO/DSO/PI = 1/1/0.03), (3) ESP (ESO/SR/PI = 1/0.7/0.03), and (4) EDSP (ESO/DSO/SR/PI = 1/1/0.7/0.03). The first part of each label is the abbreviation for the PSA formulation, and the portion in parentheses indicates the composition and weight ratio of each component. The PSA component ratio was based on the optimized results as reported in our previous work [9]. No solvents were used in the PSA preparation. For a typical process, 1 g ESO was transferred into a 25-mL glass vial, and other components were accurately weighed and added to the vial. The vial was sealed and placed in a sonicator filled with heated water (~70 °C). A heat gun and vortex mixer were also used to help melt rosin ester and mix the ingredients. The mixing step was

completed when photo initiator particles could not be observed by naked eyes.

The adhesive mixture was coated onto PET film with a EC-200 Drawdown Coater with #6 wire-wound rod (Chem Instruments, Fairfield, OH, USA). The coating amount was calculated to be 14.58 g/m<sup>2</sup>, and coating thickness was 15.2 μm. The PSA coatings were cured using a Fusion 300S 6" UV system (300 W/in. power, D bulb, UVA radiation dose 215–231 mJ/cm<sup>2</sup>) equipped with an LC6B benchtop conveyor at 7 ft/min.

#### Fourier-Transform Infrared (FTIR) Spectroscopy of Cured PSA Resins

FTIR spectra were acquired with a PerkinElmer Spectrum 400 FT-IR/FT-NIR spectrometer (Waltham, MA, USA). Reins scratched from cured PSA tapes were used. Spectra were collected in the region of 4,000–380 cm<sup>-1</sup> with a spectral resolution of 4 cm<sup>-1</sup> and 64 scans co-added.

#### Differential Scanning Calorimetry (DSC) of Cured PSA Resins

Thermal transitions of cured PSA resins were measured with a Q200 DSC (TA Instruments, New Castle, DE, USA) in an inert environment using nitrogen with a gas flow rate of 50 ml/min. The cured resin was carefully scratched from the PSA tapes with a blade and collected. About 10 mg of resin was sealed in a stainless steel pan. An empty pan was used as a reference. The sample was heated from -80 to 100 °C at a rate of 10 °C/min, equilibrated at 100 °C, quenched to -80 °C, equilibrated at -80 °C, then heated again to 100 °C at the same heat rate. Data from the second heating scan was used to eliminate the processing/thermal history. Phase transition temperatures, including glass transition, cold crystallization, and melting were obtained.

#### Thermogravimetric Analysis (TGA) of Cured PSA Resins

Thermal stability of cured resins was determined with a Pyris1 TGA (PerkinElmer, Waltham, MA, USA). About 5 mg of cured resin scratched from the PSA tapes was placed in a platinum TGA pan and heated from 40 to 600 °C at a heating rate of 20 °C/min under a nitrogen atmosphere. The thermal decomposition temperatures were recorded.

#### PSA Peel Strength, Tack, and Shear Strength Determination

The PSA tapes were cut into 1-in. × 5-in. stripes. The peel strength was measured following ASTM D3330/D3330 M-04 (2010), and loop tack strength was measured following

ASTM D6195-03(2011) using an MV-110-S tester (IMADA Inc., Northbrook, IL, USA) with stressing clamp moving speed of 5.0 mm/s. At least three specimens were measured for each PSA type. The shear test was conducted following ASTM D3654/D3654 M-06 (2011) with slight modifications. Specimen size of 1-in. × 1-in. and test mass of 1,000 g were used. The time between the application of the load to the specimen and its separation from the panel was recorded. The peel strength of several commercial PSA tapes was also measured similarly and compared with our PSA tapes.

#### Viscoelasticity of Cured PSA

The viscoelasticity of cured PSA was measured using a Bohlin CVOR 150 rheometer (Malvern Instruments, Southborough, MA, USA) with a PP 20 parallel plate. The PSA specimen was taped to the stationary base of the rheometer with the adhesive side facing the parallel plate probe. The strain amplitude was set at 0.1 % (within the linear viscoelastic region), and oscillatory frequency sweep was performed from 0.01 to 100 rad/s at 25 °C. All measurements were made in the linear viscoelastic region.

## Results and Discussion

### Kinetics Model of ESO Hydroxylation by H<sub>2</sub>O

Oxirane cleavage of ESO by water is essentially a nucleophilic attack of H<sub>2</sub>O on an electrophilic site formed by protonation of oxirane oxygen by an acid catalyst (Fig. 1) [12]. Under these conditions, the ring-opening hydrolysis reaction results in the formation of 1, 2-diol compounds (DSO).

Because water was used in excess throughout the experiments, the general form of the rate equation for oxirane cleavage can be written as:

$$-\frac{d[\text{Ep}]}{dt} = k[\text{Ep}]^n \quad (1)$$

where  $-\frac{d[\text{Ep}]}{dt}$  is the rate of oxirane cleavage, mol/h;  $t$  is time, h;  $k$  is rate constant;  $[\text{Ep}]$  is the molar concentration of the epoxy component, mol/L; and  $n$  is the reaction order with respect to the epoxy component.

If the oxirane cleavage reaction was first order with respect to  $[\text{Ep}]$ , then (1) was integrated to be:

$$\text{Ln} \frac{[\text{Ep}]_0}{[\text{Ep}]} = k't \quad (2)$$

Then curves of  $\text{Ln} \frac{[\text{Ep}]_0}{[\text{Ep}]}$  vs  $t$  were plotted at different THF/ESO, H<sub>2</sub>O/ESO, acid/ESO, and temperature values, and  $k'$  and correlation coefficient ( $R^2$ ) were obtained.

If the oxirane cleavage reaction as second order with respect to  $[\text{Ep}]$ , then (1) was integrated to be:



**Table 2** Rate constant ( $k'$ ) and correlation coefficient ( $R^2$ ) of oxirane cleavage reaction based on first-order fitting

THF/ESO (v/w)	$k'$	$R^2$	H <sub>2</sub> O/ESO (v/w)	$k'$	$R^2$
0	0.14 ± 0.02	0.92	0	0.31 ± 0.05	0.89
0.25	0.50 ± 0.03	0.98	0.25	1.36 ± 0.08	0.98
0.5	0.55 ± 0.02	0.99	0.5	0.55 ± 0.02	0.99
0.75	0.38 ± 0.02	0.99	0.75	0.15 ± 0.01	0.98
1	0.30 ± 0.02	0.99			
Acid/ESO (v/w) (%)	$k'$	$R^2$	Temperature (°C)	$k'$	$R^2$
1	0.55 ± 0.02	0.99	25	0.55 ± 0.02	0.99
1.5	1.09 ± 0.09	0.96	40	2.10 ± 0.10	0.99
2	1.96 ± 0.12	0.98	60	7.34 ± 0.79	0.93

the cleavage reaction of ESO by water was more successfully modeled as a first-order reaction in oxirane; in fact, the reaction order was closely related to the ESO oxirane cleavage agent. For example, oxirane cleavage by formic acid was found to be a second-order reaction with respect to oxirane concentration [5], but it was a first-order reaction by acetic acid [4].

#### Effects of THF/ESO Ratio on Oxirane Cleavage Rate

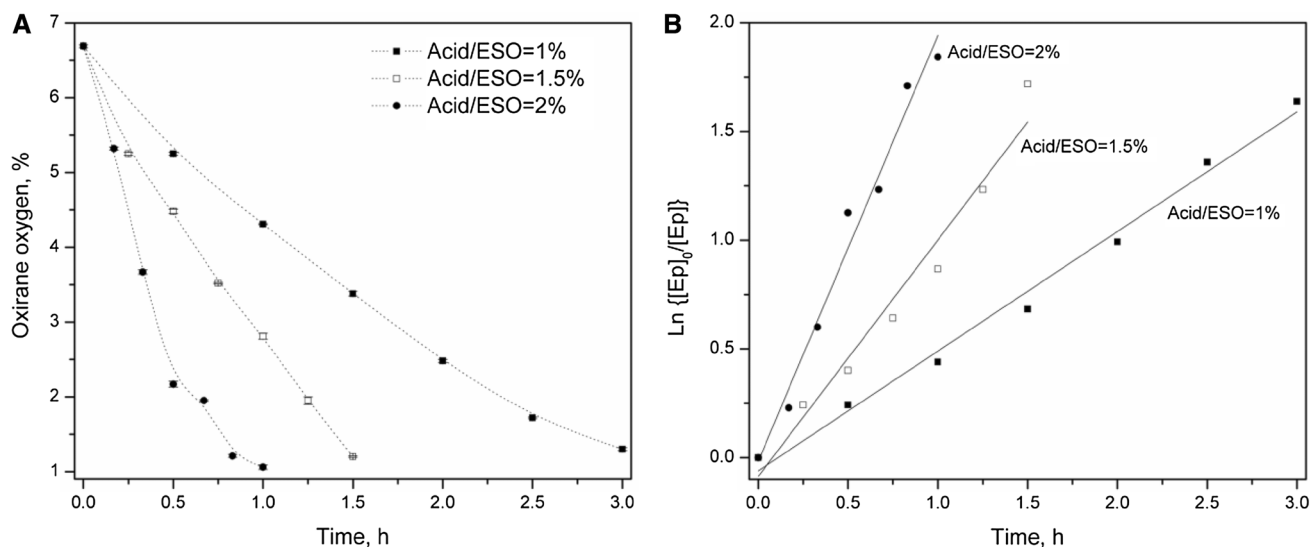
Oxirane cleavage rate first increased, then decreased with an increased THF/ESO ratio (Fig. 2a). The data were further converted according to Eq. (2) and plotted as scatters (Fig. 2b). The data were also fitted in straight lines using regression analysis, and the slope of each line was obtained as rate constant  $k'$  and summarized (Table 2). Maximum  $k'$  of 0.55 was obtained for the reaction at THF/ESO of 0.5. Without THF (THF/ESO = 0),  $k'$  was only 0.14,

showing that the oxirane cleavage rate was only 1/3 of that at THF/ESO of 0.5. With a THF/ESO ratio of 1, the rate was reduced to about half that of THF/ESO of 0.5.

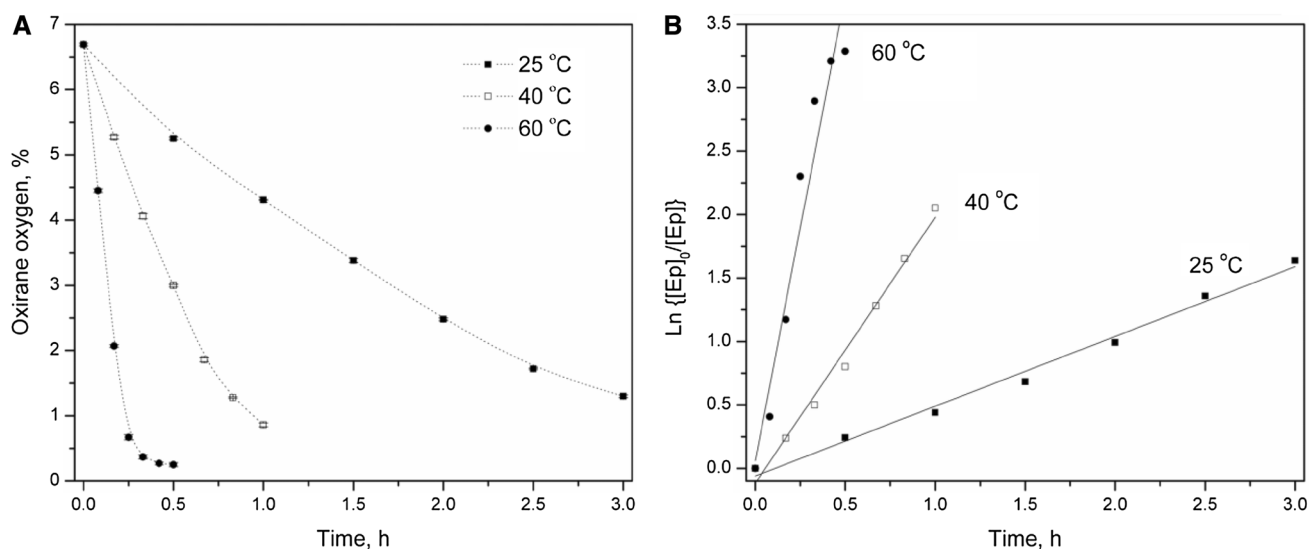
In this reaction system, THF was used as a water-miscible solvent to dissolve ESO and to achieve a homogeneous reactant mixture of ESO, H<sub>2</sub>O, and an acid catalyst. Without THF or with a lower THF/ESO ratio, mixing of reactants and the catalyst was poor, leading to a lower reaction rate. When THF was overloaded, the reactants and catalyst were over-diluted, leading to a lower reaction rate; therefore, an optimal THF/ESO ratio of 0.5 is necessary to achieve the maximal reaction rate.

#### Effect of H<sub>2</sub>O/ESO Ratio on Oxirane Cleavage Rate

The oxirane cleavage rate first increased, then decreased with an increased H<sub>2</sub>O/ESO ratio (Fig. 3a). The data were also converted according to Eq. (2) and plotted as scatters



**Fig. 4** a ESO oxirane oxygen percentage versus reaction time at various acid/ESO ratios (H<sub>2</sub>O/ESO, THF/ESO, and temperature were fixed as shown in Table 1); b first-order reaction fitting at various acid/ESO ratios (scatters represent experimental data)



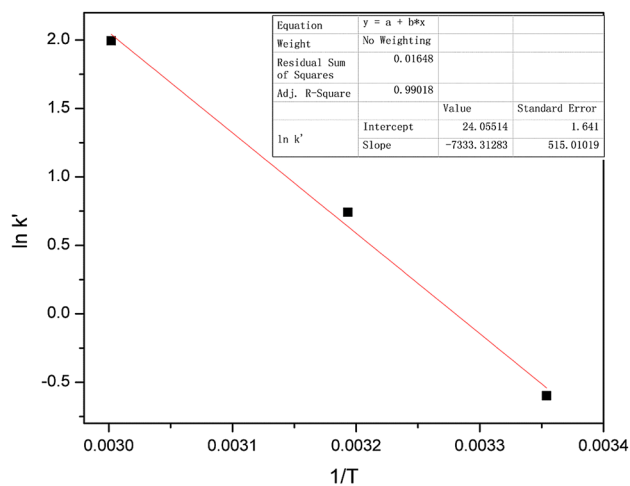
**Fig. 5** a ESO oxirane oxygen percentage versus reaction time at various temperatures (THF/ESO, H<sub>2</sub>O/ESO, and acid/ESO were fixed as shown in Table 1); b first-order reaction fitting at various at various temperatures (scatters represent experimental data)

(Fig. 3b). Linear fitting of the scatters was conducted, and rate constant  $k'$  was obtained and summarized (Table 2). Maximum  $k'$  of 1.36 was obtained for the reaction at H<sub>2</sub>O/ESO of 0.25. Without the addition of extra water (H<sub>2</sub>O/ESO = 0),  $k'$  was only 0.31. The oxirane cleavage reaction could still occur because perchloric acid was supplied as 70 % (v/v) solution, and little H<sub>2</sub>O was introduced into the reactant during the acid addition. With an H<sub>2</sub>O/ESO ratio of 0.5 and 0.75,  $k'$  was greatly reduced to 0.55 and 0.15, respectively.

Water had two functions in this reaction system. One was to act as an oxirane cleavage reactant, and the other was to act as a solvent to disperse the acid catalyst and maintain the homogeneity of the reactant mixture similar to THF. With little H<sub>2</sub>O, the oxirane cleavage agent was insufficient and the reaction rate was lower. With overaddition of H<sub>2</sub>O, ESO and the catalyst were too diluted, which also resulted in a lower reaction rate. Therefore, an optimal H<sub>2</sub>O/ESO ratio of 0.25 is necessary to achieve the maximum reaction rate.

#### Effects of Perchloric Acid/ESO Ratio on Oxirane Cleavage Rate

Oxirane cleavage experiments were further carried out at 25 °C with three levels of perchloric acid/ESO ratio, 1, 1.5, and 2 %, to investigate how the catalyst content affected the reaction. The optimized THF/ESO ratio of 0.5 was used, and the H<sub>2</sub>O/ESO ratio of 0.5 was used. We did not use the optimized H<sub>2</sub>O/ESO ratio of 0.25 because the reaction needed to be mild so we had enough time to collect the appropriate number of samples before the reaction was complete.

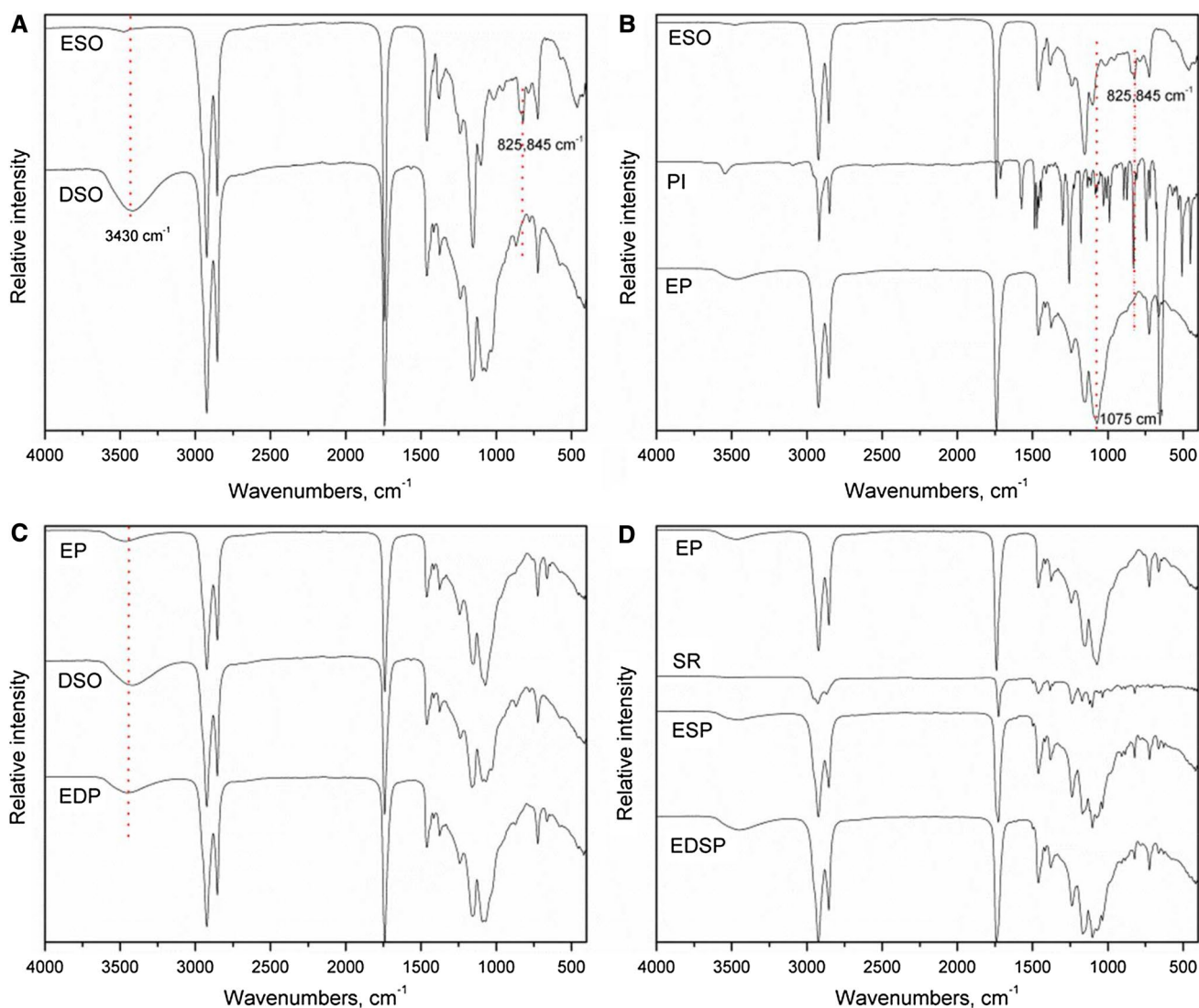


**Fig. 6** Arrhenius plot of ESO oxirane cleavage reaction by H<sub>2</sub>O

The oxirane cleavage rate greatly increased as acid content increased (Fig. 4a). The data were further analyzed by fitting into the rate Eq. (2) (Fig. 4b), and rate constant,  $k'$ , was 0.55, 1.09, and 1.96 at an average concentration of perchloric acid of 1, 1.5, and 2 %, respectively (Table 2).

#### Effect of Temperature on Oxirane Cleavage Rate

The effect of temperature on the course of ESO oxirane cleavage was investigated at three different temperatures, 25, 40, and 60 °C. THF/ESO ratio of 0.5, H<sub>2</sub>O/ESO of 0.5, and acid content of 1 % were used. We did not use the optimal H<sub>2</sub>O/ESO ratio and higher catalyst ratio because the reaction needed to be mild so we had enough time to



**Fig. 7** FTIR spectra of ESO, DSO, rosin ester (SR), and cured PSA resins (hydroxyl at  $3,430\text{ cm}^{-1}$ , epoxy at  $825\text{--}845\text{ cm}^{-1}$ , and ether at  $1,075\text{ cm}^{-1}$  were indicated as dotted lines)

collect samples before the reaction was complete. Temperatures above  $60\text{ }^{\circ}\text{C}$  were not considered because the boiling temperature of THF is  $66\text{ }^{\circ}\text{C}$ . The rate of oxirane cleavage increased greatly as temperature increased (Fig. 5a). The data were further analyzed by fitting into the rate Eq. (2) (Fig. 5b). At  $60\text{ }^{\circ}\text{C}$ ,  $k'$  was 13 times higher than at  $25\text{ }^{\circ}\text{C}$ , and the reaction was completed in only 30 min, even under mild reaction conditions (Table 2).

The activation energy of the cleavage reaction,  $E_a$ , by  $\text{H}_2\text{O}$  can be predicted according to the Arrhenius equation:

$$k' = Ae^{\frac{E_a}{RT}} \quad (4)$$

where  $k'$  is the reaction rate constant,  $A$  is the frequency factor for the reaction,  $R$  is the universal gas constant ( $8.314\text{ J/mol K}$ ), and  $T$  is temperature (in Kelvin).

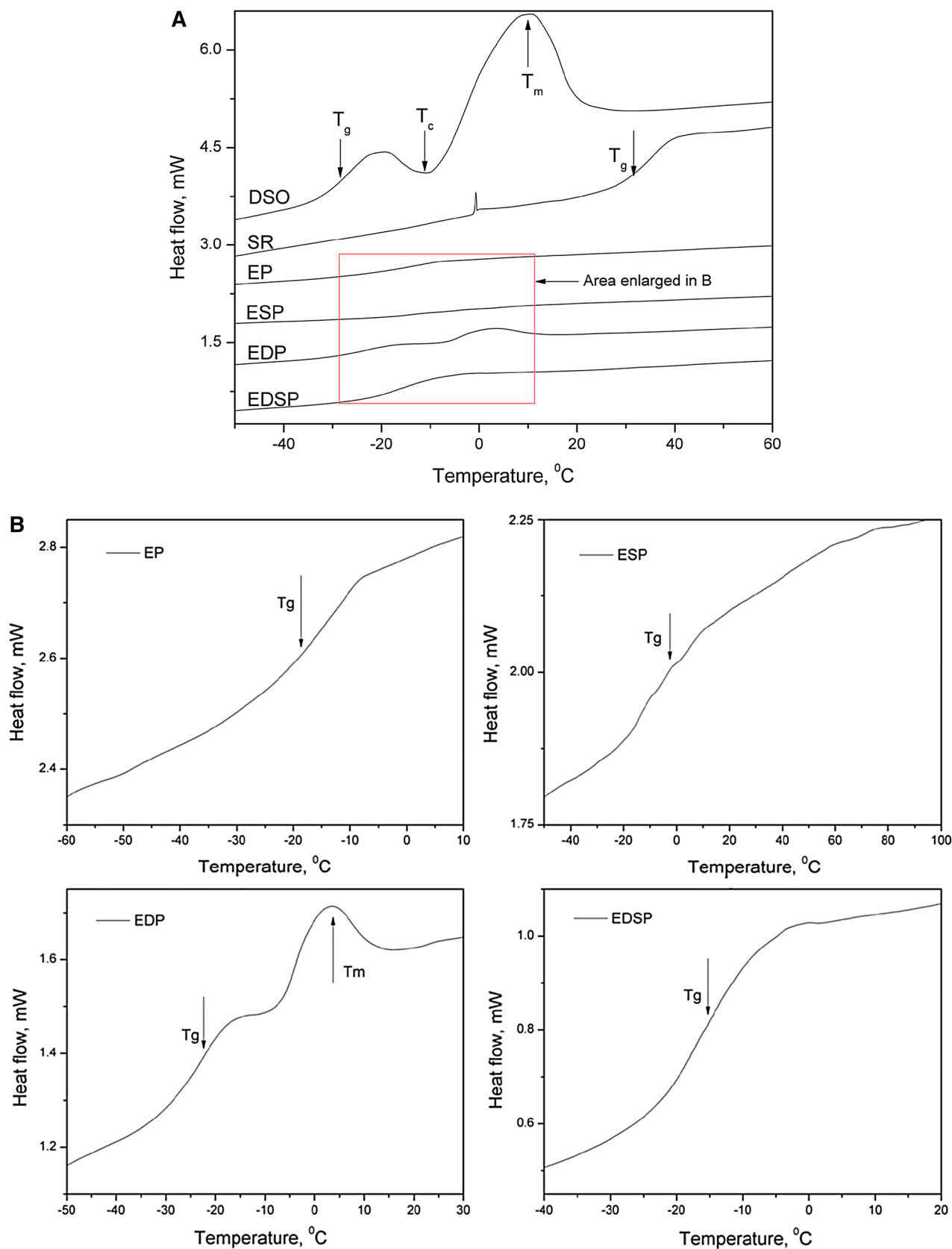
Equation (4) was converted into the following form:

$$\ln k' = \ln A - \frac{E_a}{RT} \quad (5)$$

The relationship of  $\ln k'$  vs  $1/T$  was plotted (Fig. 6). Activation energy  $E_a$  and frequency factor  $A$  were found to be  $60.97\text{ kJ/mol}$  and  $2.80 \times 10^{10}\text{ h}^{-1}$ , respectively.

#### Characteristics of DSO Synthesized Under Optimized Conditions

Based on the kinetics data and considering cost, the following optimized parameters were used to synthesize DSO: THF/ESO of 0.5,  $\text{H}_2\text{O}/\text{ESO}$  of 0.25, acid/ESO of 1.5 %,  $25\text{ }^{\circ}\text{C}$ , and 3 h reaction time. The hydroxyl value of DSO was determined to be  $242.3 \pm 1.3\text{ mg KOH/g}$  and

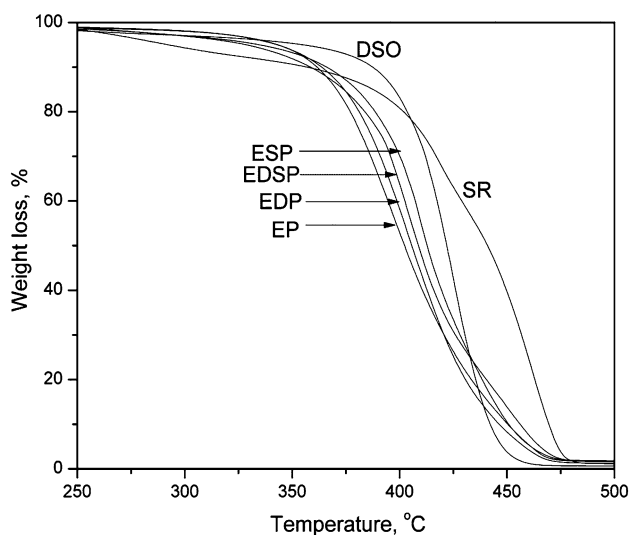


**Fig. 8** DSC thermograms (2nd heating scan) of DSO, rosin ester (SR), and UV-cured PSA resins. The area enclosed in the rectangle in (a) is enlarged in (b) to better view glass transition temperature



**Table 3** Thermal properties of DSO, rosin ester (SR), and UV-cured PSA resin derived from DSC and TGA thermograms

Sample ID	$T_g$ (°C)	$\Delta C_p$ (J/g) (°C)	$T_c$ (°C)	$T_m$ (°C)	$T_{onset}$ (°C)
DSO	-27.6	0.45	-9.9	10.1	381.0
SR	34.5	0.33	/	/	422.4
EP	-14.3	0.33	/	/	355.4
EDP	-23.6	0.39	/	2.7	363.5
ESP	0.5	0.76	/	/	398.2
EDSP	-15.1	0.47	/	/	386.5

**Fig. 9** TGA thermograms of DSO, rosin ester (SR), and cured PSA resins

epoxy oxygen content of  $0.16\% \pm 0.02$ . The  $M_n$  and  $M_w$  of ESO were determined to be 1,006 and 1,291 g/mol by GPC, respectively. The molecular weight of DSO increased greatly compared with that of ESO, with a  $M_n$  of 2,257 g/mol and  $M_w$  of 4,311 g/mol. Oligomerization during ring opening reaction of epoxidized oils was a common side reaction, as reported previously [13, 14].

**FTIR.** The epoxy group band ( $822$  and  $842\text{ cm}^{-1}$ ) disappeared, and the intensity of the OH group band ( $\sim 3,400\text{ cm}^{-1}$ ) significantly increased in DSO (Fig. 7a), indicating successful oxirane cleavage of ESO in generating hydroxyl groups in DSO. Compared with the spectrum of ESO, the epoxy group band disappeared and a new peak at  $1,075\text{ cm}^{-1}$  (ether group) was noted in cured ESO (EP)

(Fig. 7b). The UV-curing of ESO was attributed to the formation of ether linkages between epoxy groups catalyzed by a photo initiator during cationic polymerization [15, 16]. The spectra of EP, DSO, and cured resin from both ESO and DSO (EDP) are also presented (Fig. 7c). Copolymerization was believed to occur between epoxy groups of ESO and hydroxyl groups of DSO in forming ether linkages during UV-curing based on the previous study [9, 17], although FTIR could not provide such information.

### Thermal Properties

In general, all the components in a PSA resin system need to be compatible. DSC was conducted to study the compatibility of PSA resins. DSO had a  $T_g$  of  $-27.6\text{ }^\circ\text{C}$  and  $T_m$  of  $10.1\text{ }^\circ\text{C}$ , rosin ester (SR) showed a  $T_g$  of  $34.5\text{ }^\circ\text{C}$ , and  $T_g$  of cured ESO alone (EP) was  $-14.3\text{ }^\circ\text{C}$  (Fig. 8; Table 3). A small endothermic peak was observed at  $0\text{ }^\circ\text{C}$  for SR, which was probably caused by the melting of moisture residue of rosin. EDP had a single  $T_g$  of  $-23.6\text{ }^\circ\text{C}$  and reduced  $T_m$  of  $2.7\text{ }^\circ\text{C}$ , indicating good compatibility between cured ESO and DSO. ESP also exhibited only one  $T_g$  at  $0.5\text{ }^\circ\text{C}$ , showing that the cured ESO and rosin ester are compatible as well. We found a single  $T_g$  at  $-15.1\text{ }^\circ\text{C}$  for EDSP, which shows that all these PSA components are compatible. DSO had a  $T_{onset}$  of  $381\text{ }^\circ\text{C}$ , rosin ester (SR)  $422\text{ }^\circ\text{C}$ , and the  $T_{onset}$  of all the polymers ranged from  $355$  to  $400\text{ }^\circ\text{C}$  (Fig. 9; Table 3). Therefore, the PSA resins possessed very good thermal stability.

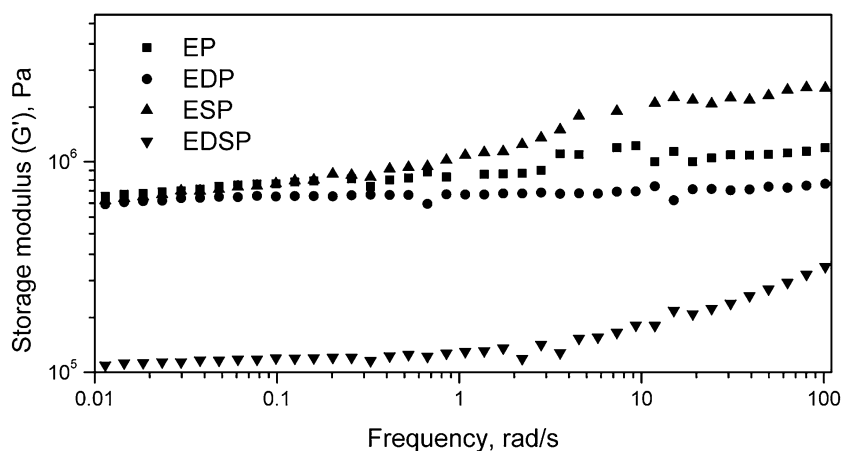
### PSA Performance

The performance of PSA tapes was evaluated in terms of peel strength, tack strength, and shear value (Table 4). UV-cured ESO alone (EP) or ESO with rosin ester did not possess any adhesion properties. The cured films were transparent coatings without any tackiness. After addition of DSO alone (EDP), the cured film exhibited some adhesion strength and tackiness, although the values of peel, tack, and shear were very low. Adding DSO and rosin ester (EDSP) significantly increased adhesion strength and tackiness of PSA films. The PSA tapes had a peel strength of  $3.6\text{ N/in.}$ , tack strength of  $7.04\text{ N/in.}$ , and shear strength of over  $10,000\text{ min}$  with adhesion failure for all these tests. After comparing EDSP with EP, ESP, and EDP, we can conclude that the significantly stronger adhesion

**Table 4** Peel strength, tack strength, and shear strength of PSA tapes

Sample ID	Peel strength (N/in.)	Tack strength (N/in.)	Shear strength (min)	Notes
EP	0	0	0	Coating film
ESP	0	0	0	Coating film
EDP	$0.54 \pm 0.05$	$0.66 \pm 0.31$	$1,680 \pm 240$	Adhesion failure
EDSP	$3.60 \pm 0.25$	$7.04 \pm 1.58$	$>10,000$	Adhesion failure

**Fig. 10** Storage modulus ( $G'$ ) of the PSA



performance of EDSP occurred because of the synergistic contribution from DSO and rosin ester, which contain polar groups including hydroxyl, ester, etc. We further compared the adhesion strength of our PSA with some commercial 3M PSA tapes and found that the peel strength of EDSP was greater than that of Post-It<sup>®</sup> Notes ( $0.95 \pm 0.09$  N/in.), Scotch<sup>®</sup> Magic<sup>™</sup> Tape ( $1.84 \pm 0.29$  N/in.), and Scotch<sup>®</sup> Transparent Tape ( $2.45 \pm 0.22$  N/in.).

Viscoelasticity of PSA is critical to its mechanical performance. Viscous behavior is needed to generate tack (adhesion), whereas elasticity is needed to enable clean removal and to sustain loads (cohesion). The PSA bonding process occurs at a slow rate of deformation (0.01 rad/s) and requires a low storage modulus ( $G'$ ) of adhesive so it has enough flowability to wet the substrate. The PSA debonding process occurs at a much higher rate (100 rad/s) and requires a higher  $G'$  of the adhesive so that it can sustain the deformation [18]. According to Dahlquist's criterion, a PSA needs to have a plateau modulus lower than  $3.3 \times 10^5$  Pa, so that it could wet the substrate and exhibit tack during bonding [19, 20].  $G'$  of EP, EDP, and ESP are all above  $3.3 \times 10^5$  Pa at bonding frequency (0.01 rad/s) (Fig. 10), which is consistent with their zero or low tack values as shown in Table 4.  $G'$  of EDSP were  $1.1 \times 10^5$  Pa at 0.01 rad/s and  $3.2 \times 10^5$  Pa at 100 rad/s, respectively, corresponding to its good tack and shear performances.

## Conclusion

In conclusion, the oxirane cleavage reaction of ESO with water was found to be first-order with respect to oxirane concentration. The reaction rate first increased, then decreased with the increasing of either the THF/ESO ratio or H<sub>2</sub>O/ESO ratio. The reaction rate increased significantly with increases in either perchloric acid content or temperature. DSO was synthesized from ESO based

on the optimized parameters, and UV-curable PSA resins were developed from ESO and DSO. The bio-based PSA (EDSP) exhibited peel adhesion properties comparable to some commercial tapes (e.g., Scotch magic tape) [8].

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