Development and Evaluation of Pressure Sensitive Adhesives from a Fatty Ester

Yili Wu, Anlong Li, Kaichang Li

Department of Wood Science and Engineering, Oregon State University, Corvallis, Oregon 97331
Correspondence to: K. Li (E-mail: kaichang.li@oregonstate.edu)

ABSTRACT: Novel pressure sensitive adhesives (PSAs) were developed from renewable methyl oleate (MO) and fully evaluated for their peel strength, tack force and shear resistance. MO was epoxidized and selectively hydrolyzed on the ester group to form epoxidized oleic acid (EOA) that is a bifunctional monomer containing both a carboxylic acid group and an epoxy group. EOA was step-growth polymerized to form a hydroxyl-containing polyester, which was then cured in the presence of a small amount of a polyfunctional epoxide [epoxidized soybean oil or trimethylolpropane triglycidyl ether (TMPTGE)] to afford PSAs. The PSAs from the polyester cured with TMPTGE exhibited high peel strength (2.4 N/10 mm), high tack force (5.8 N), and sufficient shear resistance (9.0 min). The PSAs can be fully based on renewable natural materials, and their preparations are environmentally friendly. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41143.

INTRODUCTION

Pressure sensitive adhesives (PSAs) are widely used in tapes and labels.[1,2] PSA-based tapes and labels can easily stick to numerous substrates such as metal, glass, plastics, and paper with a light pressure. PSAs are very easy to use because they do not have to be activated or cured by heat or radiation. Their uses are also very environmentally friendly because no organic solvents or chemicals are needed. However, the process for the preparation of PSAs may not be environmentally friendly. For example, an organic solvent such as toluene has to be used to dissolve natural rubber so that the natural rubber can be coated on films or paper for the production of tapes and labels. Natural rubber only accounts for a very small share of the PSA market. Most of existing PSAs are made of petrochemical-based polyacrylates and styrenic block copolymers. Petroleum is nonrenewable and thus not a sustainable resource for making PSAs. Therefore, it is desirable to develop PSAs from renewable materials such as fatty acids or fatty esters. Fatty acids or fatty esters can be readily derived from vegetable oils and the kraft pulping of wood and other plant-based biomass.[3] They are renewable, abundant, and readily available. Some work has been done in the development of PSAs from fatty esters.[4–6] Fatty esters were first epoxidized to form epoxidized fatty esters that were further reacted with acrylic acid to form acrylated fatty esters. The free radical polymerization of the acrylated fatty esters resulted in PSAs.[4–6] The resulting PSAs are still based on polyacrylates in

which the long fatty acid chains replace butyl and 2-ethylhexyl groups in butyl acrylate and 2-ethylhexyl acrylate, the two commonly used petrochemical-based monomers for PSAs. Petrochemical-based acrylic acid and acrylic comonomers such as methyl methacrylate are still required.[4–6]

In this study, novel PSAs were developed and evaluated from methyl oleate (MO), an abundant and readily available fatty ester. MO was first epoxidized and then selectively hydrolyzed on the ester group to form epoxidized oleic acid (EOA). The EOA self-polymerizes to form hydroxyl-functionalized polyesters. It was the first time to demonstrate that the hydroxyl-functionalized polyesters served as superior PSAs after being crosslinked with a small amount of a crosslinking agent.

EXPERIMENTAL

Materials

MO (99%), chromium (III) tris(acetylacetonate) (CTAA; 97%), hydrogen peroxide (35 and 50 wt % aqueous solution), oleic acid (OA) (99%), peracetic acid (32 wt % in dilute acetic acid), $N,N,N'N'$-tetramethyl-ethylenediamine (99%), tetraphenylphosphonium bromide (97%), dimethylbenzylamine (99%), and trimethylolpropane triglycidyl ether (TMPTGE; technical grade) were purchased from Sigma-Aldrich (St. Louis, MO). Formic acid (97%) was purchased from Alfa Aesar (Ward Hill, MA). N-Methylmorpholine (99%) was purchased from VWR International (West Chester, PA). Epoxidized soybean oil (ESO) (iodine

value of 2.0) was manufactured by Spectrum Chemical Mfg. Corp. (Gardena CA) and purchased from VWR International. The BOPP (biaxially oriented polypropylene)-based backing film (thickness: ∼50 μm), PET (polyethylene-terephthalate)-based release film (thickness: ∼50 μm), and a release liner were obtained from Avery Dennison Corp. (Pasadena, CA). All common chemicals and solvents were purchased from commercial sources and used as received.

Synthesis of EOA from OA

Epoxidation of OA with Hydrogen Peroxide. OA was epoxidized in the presence of formic acid and hydrogen peroxide according to a slightly modified literature procedure.[7] Hydrogen peroxide (50 wt % aqueous solution, 2.93 g) was added dropwise to a mixture of OA (5.00 g) and formic acid (5.48 g) in a 100-mL three-neck flask equipped with a mechanical stirrer, a thermometer, and an addition funnel under vigorous stirring at 4°C over 5 min. The reaction mixture was then stirred at room temperature for about 2 h, which resulted in the formation of a solid. The solid was collected by vacuum filtration, washed with chilled water (5°C, 4 × 150 mL), and dried under high vacuum. The resultant solid (4.79 g, 60% EOA, 34% unreacted OA, and 6% byproducts) was pale pink and slightly waxy and was characterized by nuclear magnetic resonance (NMR). Increase in the reaction time of the exactly same experiment as described previously from 2 to 3.5 h at room temperature resulted in a white powder (4.15 g; 70% EOA, 6% unreacted OA, 24% byproducts).

The EOA content was estimated by the ratio of the peak area of the two C$\underline{H}$-protons of the epoxy ring at 2.91 ppm over the peak area of the α-C$\underline{H}_2$ adjacent to the carbonyl group at 2.34 ppm (i.e., the epoxy/COOR ratio) in the ^{1}H-NMR spectrum. The content of unreacted OA was estimated by the ratio of the peak area of two C$\underline{H}$-protons of the double bond at 5.35 ppm over the peak area of the α-C$\underline{H}_2$ adjacent to the carbonyl group at 2.34 ppm in the ^{1}H-NMR spectrum.

Epoxidation of OA with Peracetic Acid. Epoxidation of OA with peracetic acid was conducted in accordance with a literature procedure.[8] The usage of OA was proportionally scaled down from 500 g in the literature procedure to 2 g in this study. OA (2.01 g) was added to a well-stirred solution of peracetic acid (32 wt % in dilute acetic acid, 2.02 g) and de-ionized water (6.31 g) in a 50-mL round-bottom flask over 15 min at 18°C with an icy-water bath. The reaction mixture was stirred for 3 h at 18°C and then poured into a separation funnel which contained chilled water (5°C, 50 mL). A layer of a solid was formed on top of the aqueous phase and collected by draining the lower aqueous phase. The solid was further washed with chilled water (5°C, 2 × 50 mL) and dried under high vacuum to afford a waxy white solid (1.61 g, 9% EOA, 90% unreacted OA, and 1% byproducts) that was characterized by NMR.

Synthesis of EOA from MO

Preparation of Epoxidized Methyl Oleate. Epoxidation of MO was performed according to a modified literature procedure.[9] MO (12.00 g) and formic acid (6.00 g) were placed in a 100-mL round-bottom flask equipped with a magnetic stirrer and thermometer. After the resulting mixture was cooled to 0°C in

a salty-ice water bath, hydrogen peroxide (35 wt % aqueous solution, 8.32 g) was added dropwise over 15 min while stirring. The mixture was stirred at 5°C for 2 h and then at 23°C for about 11.3 h. The resulting mixture was then extracted with hexane three times (3 × 50 mL). The combined organic phases were washed successively with saturated sodium bicarbonate solution (2 × 100 mL) and brine (2 × 150 mL). The resulting neutral mixture was dried over anhydrous magnesium sulfate and then filtered. Evaporation of the hexane afforded clear, colorless oil (12.55 g, 91% of EMO). ^{1}H-NMR (400 MHz, CDCl$_3$, δ): 3.67 (s, C$\underline{H}_3$O—), 2.91 (m, C$\underline{H}$— of the epoxy ring), 2.34 (t, —C$\underline{H}_2$—COO—), 1.2–1.8 (methylene protons other than α-CH$_2$ to the carbonyl group), 0.88 (t, —CH$_2$C$\underline{H}_3$). The EMO content was estimated by the ratio of the peak area of —CH protons of the epoxy ring at 2.91 ppm to the peak area of the α-CH$_2$ adjacent to the carbonyl group at 2.34 ppm (the epoxy/carbonyl ratio) in the ^{1}H-NMR spectrum.

Preparation of EOA by Selective Hydrolysis of EMO on the Ester Group. The crude epoxidized methyl oleate (EMO) (12.45 g) obtained as described above was dissolved in acetone (300 mL), followed by addition of 0.4 N NaOH (300 mL). The resulting mixture was vigorously mixed with a mechanical stirrer at room temperature for 2 h to generate a homogeneous clear solution. After evaporation of the acetone, the remaining aqueous solution was extracted with ethyl acetate (110 mL), cooled to about 1°C in a salty-ice water bath, and then acidified to a pH of 4 with efficient agitation. The resulting acidified mixture was extracted with ethyl acetate three times (3 × 100 mL). The combined organic phases were washed with brine (2 × 150 mL). The resulting organic phase was dried over anhydrous magnesium sulfate and then filtered. Removal of the ethyl acetate afforded a white powder (11.60 g). The crude EOA (91% purity, 11.00 g) was dissolved in hexane (33 mL) in a 250-mL round-bottom flask equipped with a condenser at 60°C. The solution was kept at 5°C overnight and crystallization occurred. The crystal was collected by vacuum filtration, washed with chilled hexane (3 × 20 mL), and dried under high vacuum to provide 9.88 g (86% overall yield based on MO) of white fine powder which was confirmed by ^{1}H-NMR analysis to be EOA having a purity of 93%. ^{1}H-NMR (400 MHz, CDCl$_3$, δ): 10 (broad, –COOH), 2.91 (m, C$\underline{H}$– of the epoxy ring), 2.34 (t, —C$\underline{H}_2$—COOH), 1.2–1.8 (methylene protons other than α-CH$_2$ to COOH), 0.88 (t, —CH$_2$C$\underline{H}_3$). ^{13}C-NMR (100 MHz, CDCl$_3$, δ): 179.57 (HOO$\underline{C}$—CH$_2$–), 57.31 and 57.27 (carbons of the epoxy ring), 20–35 (methylene carbons), 14.10 (—CH$_2\underline{C}$H$_3$). Fourier-Transfer Infrared (FTIR; neat, cm^{-1}): 3050 and 2985 (C—H stretching of epoxy ring[10]), 2944 and 2871 (CH$_3$ stretching), 2911 and 2849 (CH$_2$ stretching), 1692 (COOH carbonyl stretching), 1469 (CH$_2$ bending), 1298, 1261, 1226, and 1194 (epoxy ring symmetrical stretching, or ring breathing[10,11]), 918 (presumably due to carboxyl O—H[11]), 889 (C—C asymmetrical stretching of epoxy ring[10,12]), 856, 840, and 825 (12 micron band, typical for epoxy ring[11,12]), and 719 (CH$_2$ rocking motions, characteristic for at least four linearly connected CH$_2$ groups). The EOA content was estimated by the epoxy/carbonyl ratio in the ^{1}H-NMR spectrum.

Polymerization of EOA with *N*-Methylmorpholine. A mixture of EOA (70% purity, 10.06 g) and *N*-methylmorpholine

(0.14 g) in a 50-mL round-bottom flask was purged with N_2 for 10 min and stirred at 180°C for 6 h, which generated a light yellow oil that had similar viscosity to soybean oil and was not sticky felt by hand.

Polymerization of EOA with *N,N,N'N'*-Tetramethylethylenedi-amine. A mixture of EOA (70% purity, 8.00 g) and *N,N,N'N'*-tetramethylethylenediamine (0.10 g) in a 50-mL round-bottom flask was purged with N_2 for 10 min and stirred at 120°C for 7.5 h, which generated a brown oil that was slightly more viscous than soybean oil and showed some stickiness felt by hand.

Polymerization of EOA with Dimethylbenzylamine. A mixture of EOA (70% purity, 10.01 g) and dimethylbenzylamine (0.21 g) in a 50-mL round-bottom flask was purged with N_2 for 10 min and stirred at 160°C for 9 h, which generated a brown oil that had similar viscosity to soybean oil and was not sticky felt by hand.

Polymerization of EOA with Tetraphenylphosphonium Bromide. A mixture of EOA (70% purity, 2.62 g) and tetraphenylphosphonium bromide (0.14 g) in a 50-mL round-bottom flask was purged with N_2 for 10 min and stirred at 140°C for 12.5 h, which generated a dark brown oil that had similar viscosity to soybean oil and was not sticky felt by hand.

Polymerization of EOA with CTAA. A mixture of EOA (70% purity, 0.53 g) and CTAA (0.011 g) in a 50-mL round-bottom flask was purged with N_2 for 5 min and stirred at 160°C for 4 h, which generated a viscous and sticky purple resin.

Preparation of PSAs

Preparation of PSA91A. A mixture of EOA (91% purity, 4.53 g) and CTAA (0.09 g) in a 50-mL round-bottom flask was purged with N_2 for 5 min and stirred at 160°C for 9 min when the mixture was too viscous to be stirred with a magnetic stirring at 400 rpm. The reaction mixture was subsequently coated onto a release liner and covered by a PET release film by hand. The resulting laminate was cured in an air-circulating oven at 160°C for 50 min to give a dry, tacky adhesive film. This adhesive film was then transferred onto a paper backing material and was designated as PSA91A. PSA91A was evaluated for its peel strength.

Preparation of PSA91B. A mixture of EOA (91% purity, 1.00 g), CTAA (0.020 g), and succinic anhydride (0.20 g) in a 10-mL round-bottom flask was purged with N_2 for 5 min and stirred at 130°C for 52 min. The reaction mixture was subsequently coated onto a release liner and covered by a PET release film by hand. The resulting laminate was cured in an air-circulating oven at 160°C for 120 min only to give a wet and slightly tacky adhesive film. This adhesive film was designated as PSA91B and was not further evaluated as a PSA.

Preparation of PSA91C. A mixture of EOA (91% purity, 4.05 g), CTAA (0.082 g) and ESO (0.40 g) in a 25-mL round-bottom flask was purged with N_2 for 5 min and stirred at 130°C for 42 min. The reaction mixture was subsequently coated onto a release liner and covered by a PET release film by hand. The resulting laminate was cured in an air-circulating oven at 160°C for 50 min to give a dry, tacky adhesive film.

This adhesive film was then transferred onto a paper backing material and was designated as PSA91C. PSA91C was evaluated for its peel strength.

Preparation of PSA93A. A mixture of EOA (93% purity, 1.81 g), CTAA (0.037 g) and ESO (0.17 g) in a 10-mL round-bottom flask was purged with N_2 for 5 min and stirred at 130°C for 37 min. The reaction mixture was subsequently coated onto a release liner and covered by a PET release film by hand. The resulting laminate was cured in an air-circulating oven at 160°C for 75 min to give a dry, tacky adhesive film. This adhesive film was then transferred onto a paper backing material and was designated as PSA93A. PSA93A was evaluated for its peel strength.

Preparation of PSA93B. A mixture of EOA (93% purity, 1.25 g), CTAA (0.027 g) and TMPTGE (0.055 g) in a 10-mL round-bottom flask was purged with N_2 for 5 min and stirred at 130°C for 47 min. The reaction mixture was subsequently coated onto a release liner and covered by a PET release film by hand. The resulting laminate was cured in an air-circulating oven at 160°C for 70 min to give a dry, tacky adhesive film. This adhesive film was then transferred onto a paper backing material and was designated as PSA93B. PSA93B was evaluated for its peel strength.

Preparation of PSA93C. A mixture of EOA (93% purity, 1.02 g) and CTAA (0.021 g) in a 10-mL round-bottom flask was purged with N_2 for 3 min and stirred at 140°C for 30 min. ESO (0.11 g) was then added to the reaction mixture and the resulting reaction mixture was further stirred at 140°C for 10 min. The reaction mixture was subsequently coated onto a release liner and covered by a PET release film by hand. The resulting laminate was cured in an air-circulating oven at 160°C for 35 min to give a dry, tacky adhesive film. This adhesive film was then transferred onto a paper backing material and was designated as PSA93C. PSA93C was evaluated for its peel strength.

Preparation of PSA93D. A mixture of EOA (93% purity, 1.10 g) and CTAA (0.022 g) in a 10-mL round-bottom flask was purged with N_2 for 3 min and stirred at 140°C for 70 min. TMPTGE (0.082 g) was then added to the reaction mixture and the resulting reaction mixture was further stirred at 140°C for 7 min. The reaction mixture was subsequently coated onto a release liner and covered by a PET release film by hand. The resulting laminate was cured in an air-circulating oven at 160°C for 20 min to give a dry, tacky adhesive film. This adhesive film was then transferred onto a paper backing material and was designated as PSA93D. PSA93D was evaluated for its peel strength.

Preparation of PSA93E. A mixture of EOA (93% purity, 4.12 g) and CTAA (0.083 g) in a 10-mL round-bottom flask was purged with N_2 for 3 min and stirred at 140°C for 70 min. TMPTGE (0.33 g) was then added to the reaction mixture and the resulting reaction mixture was further stirred at 140°C for 13 min. The reaction mixture was subsequently coated onto a PET release film by hand. The resulting adhesive-coated film was cured in an air-circulating oven at 160°C for 30 min to
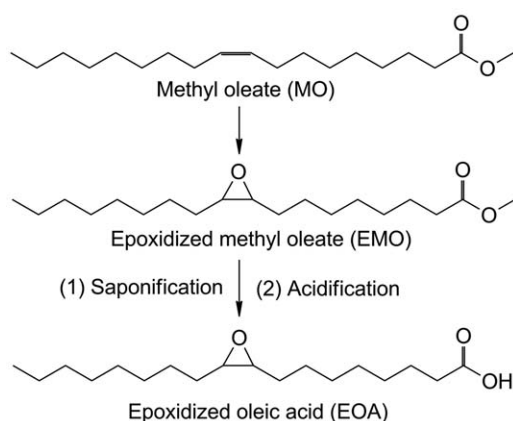
Scheme 1. Preparation of EOA from MO.

give a dry, tacky adhesive film. This adhesive film was then transferred onto a BOPP backing film and was designated as PSA93E (coating rate: 25 g/m^2). PSA93E was evaluated for its peel strength, tack, and shear resistance.

Characterizations with NMR and Fourier-Transfer Infrared

All NMR experiments were performed at room temperature with a Bruker 400 MHz spectrometer with CDCl$_3$ as solvent and internal reference. FTIR spectra were recorded on a Nexus 470 FTIR spectrometer equipped with a Golden Gate diamond ATR (attenuated total reflectance) accessory (Thermo Fisher Scientific, Waltham, MA).

Measurements of Adhesive Properties of the PSAs

The 90° peel and loop tack tests were performed with an Instron Testing Machine (model 5582, Instron, Norwood, MA). Test panel was stainless steel (type 302). Adhesive properties were measured at 23 ± 1°C and 40 ± 5% RH. Three specimens were tested for each sample and the averaged values were reported.

90° Peel Test. The 90° peel strength test was performed in accordance with Test Method F of ASTM D3330/D3330M-04 (Reapproved 2010). The PSA specimen tape with a width of 24 mm was applied to the test panel by rolling a roller (2040 g) on the tape once in each lengthwise direction at the rolling rate of 10 mm/s. After 1 min of contact, the specimen was peeled off by the tensile tester at a speed of 5 mm/s. Data were collected after the first 25 mm of specimen tape was peeled, and average peel strength (in N/10 mm) was obtained by peeling the rest of the tape.

Loop Tack Test. The Loop Tack test was performed in accordance with Test Method A of ASTM D6195-03 (Reapproved

2011). A loop of adhesive tape was attached to the grip of the tensile tester and formed a tear drop shape. The crosshead moved downward at a speed of 5 mm/s. The adhesive loop was then brought into contact to the surface of the test panel with a contact area of 24 by 24 mm. Immediately after the contact, the crosshead moved upward at a speed of 5 mm/s and the loop was separated from the test panel. The maximum force required to break the adhesive bond was recorded.

Shear Test. Shear tests were performed in accordance with the Procedure A of ASTM D3654/D3654M-06. A strip of PSA tape was applied to the test panel by rolling a roller (2040 g) on the tape twice in each lengthwise direction at the rolling rate of 10 mm/s, with a contact area of 24 by 24 mm. The panel was at an angle of 2° vs. the vertical direction. After 1 min of contact, the free end of the specimen was attached to a mass of 1 kg. The time to failure (i.e., the time between the attachment of the mass and the complete separation of the tape from the test panel) was recorded by a timing system and was used as the indication of shear resistance (holding power). The shear resistance is a measurement of the internal strength or cohesive strength of the adhesive itself.

Determination of Degree of Cohesive Failure

In the 90° peel test and the loop tack test, the failure mode (adhesion failure or cohesive failure) was also recorded. The Degree of Cohesive Failure (DCF) was used for quantifying cohesive failure and was defined as the ratio of the surface area covered by adhesive residues to the total contact area of the adhesive. The surface area covered by adhesive residues was estimated by visual inspection. The reported DCF was an average of all the test specimens.

RESULTS AND DISCUSSION

Preparation and Characterization of EOA

It would be ideal if EOA could be prepared from direct epoxidation of OA. The direct epoxidation of OA was first attempted with formic acid and hydrogen peroxide in accordance with a literature procedure.[7] When the reaction was conducted at room temperature for 2 h, the resulting crude product contained 60% EOA, 34% unreacted OA, and 6% ring-opening byproducts. Increase in the reaction time from 2 to 3.5 h resulted in a crude product containing 70% EOA, 6% unreacted OA, and 24% byproducts. At the short reaction time of 2 h, a substantial amount of unreacted OA remained. Increase in the reaction time significantly decreased the amount of unreacted OA, but also significantly increased the amounts of byproducts. Extensive studies through variations of reaction time and
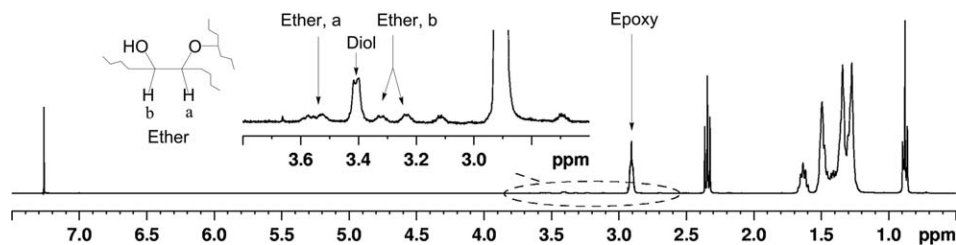
Figure 1. ^{1}H-NMR spectrum of EOA with 93% purity and the close-up views (32× original intensity) of the proton absorption signals related to the epoxy, ether, and diol groups.
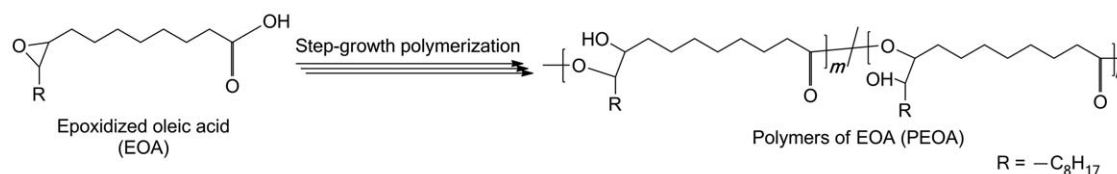
Scheme 2. Proposed step-growth polymerization of EOA.

temperature failed to generate EOA with its purity of higher than 70%. Epoxidation of OA with peracetic acid was also investigated in accordance with a literature procedure.[8] However, we were not able to reproduce the purity and the yield of EOA indicated in the literature.[8] The purity of EOA was never higher than 70% in our hands.

Attempts for increasing the purity of EOA through crystallization in various organic solvents were not successful. Pure EOA could be obtained from liquid column chromatography. However, it was too time-consuming and too expensive to use liquid column chromatography for preparation of gram scales of pure EOA. As discussed later in the preparation of PSAs, 70% purity was not high enough for generation of a polymer with adequate PSA properties. It was speculative that the carboxylic acid group in the OA was responsible for the high amount of byproducts during the prolonged epoxidation reaction. Therefore, our attention was turned to the extensively studied epoxidation of MO.[4,13]

Preparation of EOA from MO is shown in Scheme 1. Epoxidation of MO with hydrogen peroxide in the presence of formic acid readily generated EMO with 91% purity (according to ^{1}H-NMR analysis). The impurities were mainly byproducts that included esters (3%) and diols (2%) from the ring opening of the epoxy group with formic acid and water, respectively (the content of the esters was estimated from the ratio of the peak area of —CH protons α to the ester linkages at 5.0 ppm to the peak area of the α-CH$_2$ adjacent to the carbonyl group at 2.34 ppm; and the content of the diols was estimated from the ratio of the peak area of the two —CH— protons of the diols at 3.4 ppm to the peak area of the α-CH$_2$ adjacent to the carbonyl group). The crude epoxidized product was directly hydrolyzed with a NaOH solution at room temperature, followed by acidification to generate EOA. The ^{1}H-NMR spectrum of the crude

EOA revealed that the characteristic peak of the methyl group from EMO completely disappeared, and the epoxy–carbonyl ratio remained at 0.91, which implied that the ester group was selectively hydrolyzed to form a —COOH group and the epoxy group remained intact during the hydrolysis. The byproduct esters derived from the ring opening of the epoxy group were also hydrolyzed to form diols in the hydrolysis process, which increased the diol content from about 2% to about 4% in the crude EOA. In addition, a small amount of ethers (2%) was present in the crude EOA, which could be derived from the ring opening of the epoxy group with hydroxyl groups in the presence of acids such as hydrochloric acid and formic acid[14,15] (the content of the ethers was estimated from the ratio of the peak area of the protons β to the ether linkages at 3.23 and 3.33 ppm (Figure 1, Ether b)[14,15] to the peak area of the α-CH$_2$ adjacent to the carbonyl group at 2.34 ppm). After crystallization of the crude product in hexane, EOA with 93% purity was obtained with an overall yield of about 86% (based on MO). The impurities in the purified EOA were mainly diols (4%) and ethers (1%) according to the ^{1}H-NMR spectrum (Figure 1).

Screening of a Catalyst for the Polymerization of EOA
EOA is a bifunctional monomer containing a —COOH and an epoxy group and can polymerize through the ring-opening reaction between the epoxy and —COOH groups, generating linear hydroxyl-functionalized polyesters (PEOA; Scheme 2).

The thermal polymerization of EOA in the absence of any catalyst has been previously reported.[16] However, the polymerization without a catalyst took several days to reach a satisfactory conversion of the functional groups, and no study on applications of the resulting polymers has been reported. For accelerating the polymerization of EOA, initial efforts were focused on screening of a catalyst for the polymerization of EOA. Various catalysts such as tertiary amines, an organometallic

Table I. Investigation of Suitable Catalysts for the Polymerization of EOA

Catalysts	Product appearance	Product viscosity	Peel test[a]	
			Stickiness	DCF (%)
N-Methylmorpholine	Light yellow; oil	Not viscous	Not sticky	100
N,N,N′N′-Tetramethylethylenediamine	Brown; oil	Slightly viscous	Slightly sticky	100
Dimethylbenzylamine	Brown; oil	Not viscous	Not sticky	100
Tetraphenylphosphonium bromide	Dark brown; oil	Not viscous	Not sticky	100
Chromium (III) tris(acetylacetonate) (CTAA)	Dark purple; resin	Viscous	Sticky	100

[a] At the end of the polymerization reaction, the resulting product was coated onto a piece of printing paper by hand. The coated paper was stuck on and then peeled off different substrates such as skin, paper, glass, plastic, and stainless steel.
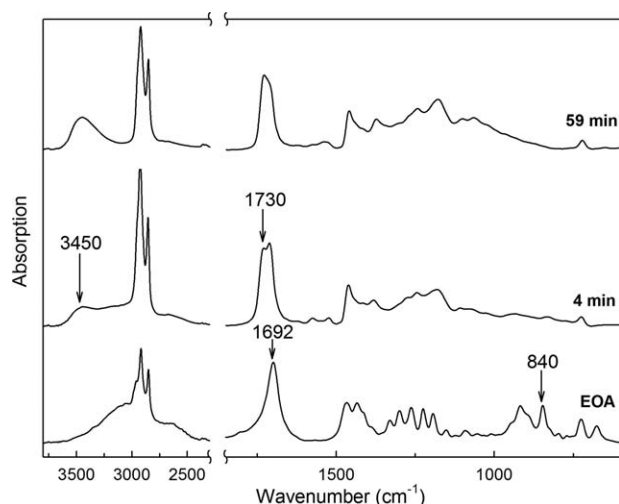
Figure 2. FTIR spectra of EOA (bottom), and the polymers from the polymerization of EOA in the presence of CTAA for 4 min (middle) and 59 min (top), respectively.

compound,[17] and a phosphonium salt[18] that have been demonstrated as effective catalysts for accelerating the reaction between a —COOH group and an epoxy group were investigated for the polymerization of EOA (Table I). N-Methylmorpholine failed to serve as an effective catalyst for the polymerization of the EOA; only a nonviscous, nonsticky oil was formed after the polymerization at 180°C for 6 h. The ineffective catalysis of N-methylmorpholine might be due to its evaporation from the reaction mixture during the polymerization reaction because the boiling point of N-methylmorpholine was 113–116°C. Lowering the reaction temperature from 180 to 120°C and use of a tertiary amine (N,N,N′N′-tetramethyl-ethylenediamine) with a similar boiling point of 120–122°C were still not able to significantly polymerize the EOA (Table I). In this reaction, the reaction temperature might be too low for the polymerization and was close to the boiling point of the amine, which might result in substantial loss of the amine from the reaction mixture. For eliminating the concerns over the low reaction temperature and evaporation of the catalyst, the reaction temperature of 160°C, and dimethylbenzylamine with its boiling point (180°C) being higher than the reaction temperature were investigated and also did not result in substantial polymerization of the EOA (Table I). Tetraphenylphosphonium bromide, an effective catalyst for the

step-growth polymerization of 10,11-epoxyundecanoic acid that has a terminal epoxy group,[18] was also not an effective catalyst for the polymerization of EOA. CTAA, an organometallic catalyst, effectively and efficiently accelerated the polymerization of EOA, affording a viscous and sticky resin. Therefore, CTAA was used as a catalyst in this study.

Copolymerization of EOA with Other Monomers and Preparation of PSAs from the Copolymers

The polymerization product of EOA with 70% purity was a viscous and sticky resin, a good sign for PSA applications. However, 100% of cohesive failure, i.e., DCF of 100%, indicated that the cohesive strength of this product was still insufficient for PSA applications (Table I). The low purity of EOA was speculated to be the main reason for the inadequate PSA properties. As expected, the polymerization of EOA with 91% purity afforded a dry and tacky product. Monitoring of the polymerization by FTIR spectroscopy (Figure 2) showed a development of a new peak of the hydroxyl group at 3450 cm^{-1} and a new peak of the ester group at 1730 cm^{-1} during the polymerization, with a concomitant decrease in the peak of the epoxy group at 840 cm^{-1} and that of the —COOH group at 1692 cm^{-1} over time, which confirmed that the ring-opening reaction of the epoxy groups with the —COOH groups took place in the polymerization, producing new hydroxyl groups and new ester linkages under the experimental conditions used in this study. The resultant adhesive (PSA91A) from the polymerization of the EOA with 91% purity without a comonomer was dry and tacky, and had a good peel strength of 2.5 N/10 mm (Table II). However, the product still had a DCF of about 50%, which implied that the cohesive strength of the product was still not desirable. The cohesive failure typically implied the cohesive strength of the adhesive was lower than the adhesive strength, i.e., the bonding strength between the adhesive and the adherend. The insufficient cohesive strength typically implied that the molecular weight of the adhesive was not high enough for providing sufficient entanglement and adhesion among molecular chains of the adhesive.

For increasing the molecular weight, the EOA was copolymerized with various comonomers. Succinic anhydride was first investigated as a comonomer, hoping that succinic anhydride could crosslink newly generated hydroxyl groups in the polymerized EOA (Scheme 2), thus increasing the molecular weight

Table II. Copolymerization of EOA with Different Comonomers

PSA ID	Comonomer	Curing time[a] (min)	90° peel test	
			Peel strength (N/10 mm)[b]	DCF (%)
PSA91A	–	50	2.5 ± 0.8	50
PSA91B	Succinic anhydride	120	Adhesive film not dry	100
PSA91C	ESO	50	3.6 ± 1.1	25
PSA93A	ESO	75	2.5 ± 1.2	20
PSA93B	TMPTGE	70	3.9 ± 1.7	25

[a] The curing was considered finished when the resultant adhesive film was dry and left no residues on fingers.
[b] With paper backing.

Table III. Crosslinking of Prepolymer of EOA with 93% Purity with Different Crosslinkers

PSA ID	Crosslinker	Curing time[a] (min)	90° peel test	
			Peel strength (N/10 mm)[b]	DCF (%)
PSA93C	ESO	35	3.5 ± 0.4	<5
PSA93D	TMPTGE	20	4.0 ± 0.5[c]	0
PSA93E	TMPTGE	30	2.4 ± 0.8[d]	0

[a] The curing was considered finished when the resultant adhesive film was dry and left no residues on fingers.
[b] With paper backing material unless otherwise noted.
[c] The paper backing material split during peel test.
[d] With BOPP film as the backing material.

of the adhesive. However, the resultant adhesive (PSA91B) was not dry and had the DCF of 100% (Table II).

The ratio of the epoxy group to the carboxylic acid group was 0.91 for the EOA with 91% purity, which implied that about 9% of the impurities contained a carboxylic acid group, but did not contain an epoxy group. The impurities could react with the epoxy group of the EOA and oligomeric EOA, thus terminating the chain growth and lowering the molecular weight of the product. ESO had multiple epoxy groups on each ESO molecule, and could consume the carboxylic acid groups of the impurities and crosslink the carboxylic acid groups at the chain end of PEOA. ESO was theoretically able to increase the molecular weight. The adhesive (PSA91C) from the copolymerization of the EOA with ESO indeed had a higher peel strength and a lower DCF than PSA91A (Table II). The DCF for commercially viable PSA-based products should be zero. Therefore, the DCF of PSA91C was still too high. The purity of the EOA was believed to have great impacts on the properties of the resultant PSAs. Our attention was turned to polymerization of EOA with a higher purity than 91%.

Increase in the purity of the EOA from 91 to 93% in the copolymerization of the EOA and ESO resulted in a PSA (PSA93A) that had a slightly lower DCF than PSA91C (Table II). However, PSA93A had a lower peel strength than PSA91C, which was still poorly understood. TMPTGE had three epoxy groups on each TMPTGE molecule and could play the same role as ESO. PSA93B from the copolymerization of the EOA with 93% purity with TMPTGE had comparable peel strength and DCF to PSA91C, but had a higher peel strength and a slightly higher DCF than PSA93A. In summary, the strategy of copolymerization of the EOA with various comonomers only had limited success in terms of enhancing the peel strength and lowering the DCF (Table II). A different strategy that involved the prepolymerization of the EOA with 93% purity followed by crosslinking of the resultant prepolymer with various crosslinking agents was investigated (Table III).

PSA93C had a higher peel strength and much lower DCF (<5%) than PSA93A, indicating that the cohesive strength for the PSA prepared with the new strategy increased significantly (Table III). PSA93D had a higher peel strength than PSA93C and zero DCF, i.e., no cohesive failure (Table III), which implied that TMPTGE was a more effective crosslinking agent than ESO. These results were consistent with the fact that the epoxy

groups in TMPTGE were terminal and more reactive than the internal epoxy groups in ESO. As a matter of fact, the adhesive strength and the cohesive strength of PSA93D were so strong that the paper backing material broke instead of the test specimens being peeled off the stainless steel panel during the 90° peel tests. BOPP film, a stronger backing material than the paper backing material, was employed for the preparation of PSA93E that had the same PSA composition as PSA93D. PSA93E had zero DCF, i.e., no cohesive failure. PSA93E had a lower peel strength than PSA93D, which was probably due to the change in backing material, because the peel strength results from the combined effects of three works: the work required to deform the backing layer, the work to deform the PSA layer, and the work to debond the PSA from an adherend.[19] In addition, the loop tack force and shear resistance of PSA93E were 5.8 ± 1.3 N and 9.0 ± 1.4 min, respectively.

The PSAs can be solely based on renewable raw materials because both EOA and TMPTGE can be derived from renewable material-based chemicals (TMPTGE can be derived from epichlorohydrin and trimethylolpropane. Epichlorohydrin can be derived from renewable glycerol[20] and trimethylolpropane can be derived from starch and sugars[21]). The preparation of the PSAs did not require the use of an organic solvent or a toxic chemical, thus being environmentally friendly.

CONCLUSIONS

EOA was successfully prepared in high purity from the epoxidization of MO followed by the selective hydrolysis and crystallization. CTAA was found to be the most effective catalyst for the polymerization of the EOA to afford hydroxyl-functionalized polyesters. While the strategy of copolymerization of the EOA with various comonomers only had limited success, the strategy of prepolymerization of the EOA followed by crosslinking of the resultant prepolymers successfully generated superior PSAs. TMPTGE was a more effective crosslinker than ESO in terms of enhancing the peel strength, tack force, and cohesive strength of the resulting PSAs.

ACKNOWLEDGMENTS

REFERENCES

1. Creton, C. *MRS Bull.* **2003**, *8*, 434.

2. Satas, D. In Handbook of Pressure Sensitive Adhesive Technology, 2nd ed.; Satas, D., Ed.; Van Nostrand Reinhold: New York, NY, **1989**; p 1.

3. Biermann, C. J. In Handbook of Pulping and Papermaking, 2nd ed.; Academic Press: San Diego, CA, **1996**; p 39.

4. Bunker, S. P.; Wool, R. P. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 451.

5. Bunker, S.; Staller, C.; Willenbacher, N.; Wool, R. *Int. J. Adhes. Adhes.* **2003**, *23*, 29.

6. Klapperich, C. M.; Noack, C. L.; Kaufman, J. D.; Zhu, L.; Bonnaillie, L; Wool, R. P. *J. Biomed. Mater. Res. Part A* **2009**, *91A*, 378.

7. Salimon, J.; Salih, N. *Eur. J. Sci. Res.* **2009**, *32*, 216.

8. Findley, T. W.; Swern, D.; Scanlan, J. T. *J. Am. Chem. Soc.* **1945**, *67*, 412.

9. Dailey, O. D.; Prevost, N. T.; Strahan, G. D. *J. Am. Oil Chem. Soc.* **2009**, *86*, 1101.

10. Silverstein, R. M.; Webster, F. X. In Spectrometric Identification of Organic Compounds, 6th ed.; John Wiley & Sons: New York, NY, **1998**; p 90.

11. Shreve, O. D.; Heether, M. R.; Knight, H. B.; Swern, D. *Anal. Chem.* **1951**, *23*, 277.

12. Moser, B. R.; Erhan, S. Z. *Eur. J. Lipid Sci. Technol.* **2007**, *109*, 206.

13. Doll, K. M.; Erhan, S. Z. *J. Agric. Food Chem.* **2005**, *53*, 9608.

14. Ahn, B. K.; Kraft, S.; Wang, D.; Sun, X. S. *Biomacromolecules* **2011**, *12*, 1839.

15. Ahn, B.-J. K.; Kraft, S.; Sun, X. S. *J. Mater. Chem.* **2011**, *21*, 9498.

16. Swern, D.; Billen, G. N.; Eddy, C. R. *J. Am. Chem. Soc.* **1948**, *70*, 1228.

17. Khot, S. N.; Lascala, J. J.; Can, E.;Morye, S. S.; Williams, G. I.; Palmese, G. R.; Kusefoglu, S. H.; Wool, R. P. *J. Appl. Polym. Sci.* **2001**, *82*, 703.

18. White, J. E.; Earls, J. D.; Sherman, J. W.; López, L. C.; Dettloff, M. L. *Polymer* **2007**, *48*, 3990.

19. Satas, D. In Handbook of Pressure Sensitive Adhesive Technology, 2nd ed.; Satas, D., Ed.; Van Nostrand Reinhold: New York, NY, **1989**; p 63.

20. Fourcade, D.; Ritter, B. S.; Walter, P.; Schönfeld, R.; Mülhaupt, R. *Green Chem.* **2013**, *15*, 910.

21. Fleischer, M.; Blattmann, H.; Mülhaupt, R. *Green Chem.* **2013**, *15*, 934.