

## Pressure-Sensitive Adhesives Based on Epoxidized Soybean Oil and Dicarboxylic Acids

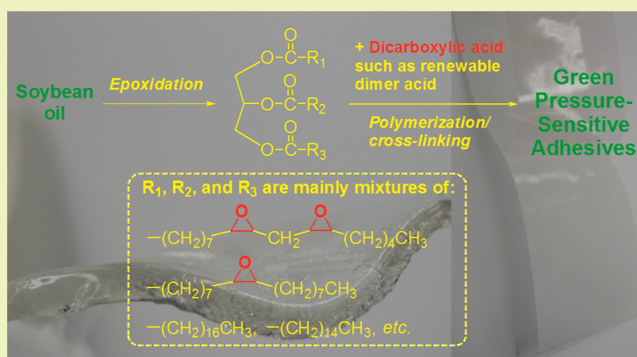
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## Supporting Information

**ABSTRACT:** Existing pressure sensitive adhesives (PSAs) are mainly derived from petrochemicals. This study describes a novel approach for development of biobased PSAs. Epoxidized soybean oil was polymerized and cross-linked with a dicarboxylic acid to generate superior PSAs. The dicarboxylic acids used in this study included dimer acid (DA), sebacic acid, adipic acid, and a difunctional polymeric carboxylic acid that was prepared from polymerization of bisphenol A diglycidyl ether (BPAGE) and an excess of DA. AMC-2, a chromium(III)-based organometallic compound, was found to be the most effective catalyst for the polymerization/cross-linking. The PSAs had a peel strength of 1.4–5.0 N/cm, a loop tack of 7.1–12.6 N, a shear strength of 34 min to more than 168 h, and a good aging resistance. The adhesive properties of the PSAs can be tailored for specific applications such as PSA tapes and labels through the selection of the dicarboxylic acid and its usage. Incorporation of a small amount of phenylene-containing monomer BPAGE into the PSAs significantly increases the peel and shear strengths of the resulting PSAs. This new class of PSAs can be fully based on renewable materials. The preparation of the PSAs does not use any organic solvent or toxic chemicals, thus being environmentally friendly.

**KEYWORDS:** Renewable materials, Pressure-sensitive adhesive, Hydroxyl-functionalized polyester, Soybean oil, Dimer acid, Aging resistance



## INTRODUCTION

Pressure-sensitive adhesives (PSAs) are tacky and form a bond at room temperature with a variety of dissimilar surfaces with light pressure. Their response to deformation is viscoelastic. They show liquid-like behavior to deform or flow in contact with a surface under light pressure, yet they have sufficient resistance to flow during a separation or debonding process.<sup>1,2</sup> PSAs find wide applications in our daily lives and in numerous industries, especially in the electric, automotive and medical industries. At present, commercial PSAs are mainly based on petrochemical-derived polymers such as acrylic copolymers, styrene-based block copolymers, and ethylene-vinyl acetate copolymers. Petroleum is nonrenewable and not sustainable. There is a pressing need for the development of PSAs from renewable materials.

Plant oils as triglycerides of long-chain unsaturated and saturated fatty acids are one of the most abundant and attractive renewable natural materials. Plant oils or their fatty acid derivatives as starting materials have many attractive features such as renewability, low cost, low toxicity, biodegradability, and fairly high purity. In addition, the long aliphatic chains from the fatty acids impart unique properties to the resulting polymeric materials such as elasticity, flexibility, hydrolytic stability, hydrophobicity and intrinsically low glass transition temperature ( $T_g$ ).<sup>3–5</sup> To date, plant oils have been

widely utilized as raw materials in applications such as elastomers, plastics, coatings, ink formulations, resins, and various thermosetting composites.<sup>3,6,7</sup> However, there are only a relatively few reports describing the use of plant oils or their derivatives for PSA applications. It has been demonstrated that PSAs could be developed from the free-radical polymerization of (meth)acrylates such as 1,4-butanediol diacrylate and acrylated epoxidized methyl oleate that was generated from epoxidization of methyl oleate followed by the ring-opening reaction of the resulting epoxy with (meth)acrylic acid.<sup>8–12</sup> This class of PSAs still requires the substantial amount of (meth)acrylic acid and (meth)acrylates. New PSAs were recently prepared from epoxidized soybean oil (ESO), dihydroxyl soybean oil and phosphoric acid.<sup>13–15</sup> These PSAs could be cleanly removed from a stainless steel panel for the peel test and have the peel strength comparable to that of Post-it notes.<sup>13–15</sup> However, the tack, the shear strength, and the aging resistance of these PSAs were not reported. It has also been demonstrated that polyesters from dimer acid and diols after being cured with maleic-anhydride-modified plant oils or epoxidized plant oils exhibited PSA properties.<sup>16,17</sup>

Received: June 18, 2014

Revised: July 15, 2014

Published: July 18, 2014

In our previous study, PSAs were successfully prepared from a mixture of epoxidized fatty acids (EFAs).<sup>18</sup> The mixture of EFAs was prepared from ESO via the selective hydrolysis of the ester groups in ESO. In this study, we report a novel and simple approach for development of PSAs directly from ESO without the extra hydrolytic step. The resulting PSAs were evaluated for their adhesive properties and aging resistance.

## ■ EXPERIMENTAL SECTION

**Materials.** Epoxidized soybean oil (ESO, epoxy equivalent weight (EEW), ~7.0 wt %; iodine value, 2.0) was purchased from Spectrum Chemical Manufacturing Corp. (New Brunswick, NJ) and used as received. Chromium(III) tris(acetylacetonate) (97%), zinc stearate (purum, 10–12% Zn basis), zinc acetylacetonate hydrate (23–26% Zn), aluminum acetylacetonate (99%), triethylamine (99+%), *N,N*-dimethylbenzylamine (99+%), tetrabutylammonium iodide (98%), hexadecyltrimethylammonium bromide (99+%), tetraphenylphosphonium bromide (97%), dimer acid (DA) (hydrogenated, average  $M_n$  ~ 570, 99+%), adipic acid (AA, 99%), sebacic acid (SA, 98%), and bisphenol A diglycidyl ether (BPAGE) (EEW, ~174) were purchased from Sigma-Aldrich Corp. (St. Louis, MO) and used as received. AMC-2 (a solution of 50% chromium(III) 2-ethylhexanoate in a mixture of di(heptyl, nonyl, undecyl) phthalates) was kindly provided by Ampac Fine Chemical LLC (Rancho Cordova, CA) and used as received. The release paper (silicone coated paper) was obtained from ChemInstruments, Inc. (Fairfield, OH). Fasson 54# Semi-Gloss Facestock (a paper backing material, ~ 68  $\mu\text{m}$  thick), biaxially oriented polypropylene (BOPP)-based backing film (~50  $\mu\text{m}$  thick) and the poly(ethylene terephthalate)-based release film were obtained from Avery Dennison Corp. (Pasadena, CA).

**Analyses.** FTIR spectra were recorded with a Thermo Nicolet Nexus 470 FTIR spectrometer (Thermo Nicolet Corp., Madison, WI) coupled with Smart Golden Gate diamond ATR accessory in a scanning range of 650–4000  $\text{cm}^{-1}$  for 64 scans at a spectral resolution of 2  $\text{cm}^{-1}$ . <sup>1</sup>H NMR spectra were recorded at room temperature (~23 °C) using a Bruker DPX400 spectrometer (Rheinstetten, Germany) operating at 400 MHz; CDCl<sub>3</sub> (99.8% D, Cambridge Isotope Laboratories, Inc., Andover, MA) was used as a solvent for preparation of sample solutions.

**Prepolymerization of ESO and a Dicarboxylic Acid.** A typical procedure that used DA as the dicarboxylic acid was described as follows. DA (14.936 g), ESO (12.102 g), and AMC-2 (0.298 g) were placed in a 50 mL, round-bottom flask equipped with a silicone oil bath and a magnetic stirrer. The resulting mixture was bubbled with nitrogen for 2 min while being stirred at 300 rpm and heated to 85 °C. The reaction mixture was then stirred at 85 °C for 25 min to give a light green, homogeneous, and viscous resin. FTIR (neat,  $\text{cm}^{-1}$ ): 3456  $\text{cm}^{-1}$  (OH stretching), 2950 and 2870 (CH<sub>3</sub> stretching), 2922 and 2853 (CH<sub>2</sub> stretching), 1737 (ester carbonyl stretching), 1710 (carbonyl stretching of the carboxylic acid (–COOH) groups), 1460 (CH<sub>2</sub> bending), 1239 (ester C–O stretching), 1165 and 1106 (ester C–O–C stretching), 1026 (C–OH stretching), 858–809 (“12 micron band” of the epoxy ring<sup>19,20</sup>), 723 (CH<sub>2</sub> rocking motions, characteristic for at least four linearly connected CH<sub>2</sub> groups).

**Prepolymerization of ESO and a Difunctional Polymeric Carboxylic Acid (DPCA).** (i) *Preparation of DPCA.* DA (14.722 g) and AMC-2 (0.256 g) were placed in a 50 mL, round-bottom flask equipped with a silicone oil bath and a magnetic stirrer. The resulting mixture was stirred while being heated to about 80 °C. When the mixture turned homogeneous, BPAGE (3.356 g) was added to the flask. The resulting mixture was bubbled with nitrogen for 2 min while being heated to 135 °C. The reaction mixture was then stirred at 135 °C for 60 min to give a light green, homogeneous, and viscous resin. The resulting polymer or oligomer was designated as DPCA. FTIR (neat, in  $\text{cm}^{-1}$ ): 3450  $\text{cm}^{-1}$  (OH stretching), 2950 and 2870 (CH<sub>3</sub> stretching), 2922 and 2852 (CH<sub>2</sub> stretching), 1739 (ester carbonyl stretching), 1708 (–COOH carbonyl stretching), 1608, 1582, and 1510 (benzene ring vibrations), 1460 (CH<sub>2</sub> bending), 1169 and 1113 (ester C–O stretching), 1245, 1180 and 1045 (ether C–O stretching),

829 (vibrations of the *para*-substituted benzene ring), and 723 (CH<sub>2</sub> rocking motions).

(ii) *Prepolymerization of ESO and DPCA.* Into the flask containing DPCA and AMC-2, ESO (6.336 g) was added. The resulting mixture was then stirred at 300 rpm at 70 °C for 30 min to afford a light green, homogeneous, and highly viscous resin. FTIR (neat,  $\text{cm}^{-1}$ ): 3450  $\text{cm}^{-1}$  (OH stretching), 2950 and 2870 (CH<sub>3</sub> stretching), 2922 and 2852 (CH<sub>2</sub> stretching), 1739 (ester carbonyl stretching), 1710 (–COOH carbonyl stretching), 1608, 1582, and 1510 (benzene ring vibrations), 1460 (CH<sub>2</sub> bending), 1168 and 1113 (ester C–O stretching), 1245, 1180, and 1045 (ether C–O stretching), 829 (vibrations of the *para*-substituted benzene ring), and 723 (CH<sub>2</sub> rocking motions).

**Curing of the Prepolymers and Preparation of PSAs.** The prepolymers as prepared previously were coated onto a sheet of release paper at a coating thickness of  $4.0 \pm 0.5 \text{ mg/cm}^2$  with an HLCL-1000 hot-melt coater/laminator (ChemInstruments, Inc., Fairfield, OH). The resin coating on the release paper was then mated with a sheet of a release film using the laminator, resulting in a “sandwich”-like assembly. The resins between the two release liners were subjected to further polymerization and curing reaction in an air-circulating oven maintained at 160 °C. The assembly was taken out of the oven after a predetermined time. The release film was peeled off without taking away any adhesive residue (the release film has better repellence against the adhesive than the release paper). The exposed adhesive layer on the release paper was then mated with a sheet of paper or BOPP backing using the laminator to give a PSA assembly.

**Measurements of the Peel Strength, Loop Tack, and Shear Strength of the PSAs.** The 90° peel, shear, and loop tack tests were performed at  $23 \pm 1$  °C and  $50 \pm 5\%$  RH. Five specimens were tested for each sample and the averaged values were reported. The peel and loop tack tests were performed with an Instron Testing Machine (model 5582, Instron, Norwood, MA).

(i) *Peel Test.* The 90° peel strength test was performed on a stainless steel panel (type 302) in accordance with Test Method F of ASTM D3330/D3330M-04 (Reapproved 2010). PSA tape specimens with a width of 25 mm were applied to the panel with the adhesive contacting the panel and pressed twice with a 2-kg rubber-coated roller. The tapes applied were allowed to dwell for 1 min. The tapes were then peeled off at a crosshead speed of 30 cm/min. The peel strength data were collected after the first 25 mm of the tapes was peeled. The averaged value in newtons per centimeter was obtained for peeling the rest of the tape specimens.

(ii) *Shear Test.* Shear tests were performed on a stainless steel panel (type 302, mirror polished) in accordance with the Procedure A of ASTM D3654/D3654M-06. The PSA tape specimens were applied to the panel with a contact area of 25 mm  $\times$  25 mm and pressed twice with a 2-kg rubber-coated roller. After the tapes applied were dwelled for 15 min, the free end of the tapes was attached to a mass of 1000 g. The test panel (and the tapes applied) was held by the test stand at an angle of about 1° relative to the vertical. The time to failure, i.e., the time from the attachment of the mass until the complete separation of the tape from the test panel, was recorded and used as an indication of the shear strength of the PSA tapes.

(iii) *Loop Tack Test.* The Loop Tack test was performed on a stainless steel panel (type 302) in accordance with Test Method A of ASTM D6195-03 (Reapproved 2011). The PSA specimens were looped and attached to the grip of the tester. The crosshead was allowed to move downward at a speed of 30 cm/min until the loop was brought into contact to the test panel surface with a contact area of 25 mm  $\times$  25 mm. Immediately after the contact, the crosshead was allowed to move upward at a speed of 30 cm/min until the loop was completely separated from the test panel. The maximum force in newtons required to break the adhesive bond was recorded.

**Statistical Analysis.** Peel strength, loop tack, and shear strength data were statistically analyzed with a two-sample *t* test using Microsoft Excel (version 2010, Microsoft Corp., Redmond, WA). All comparisons were based on a 95% confidence interval.

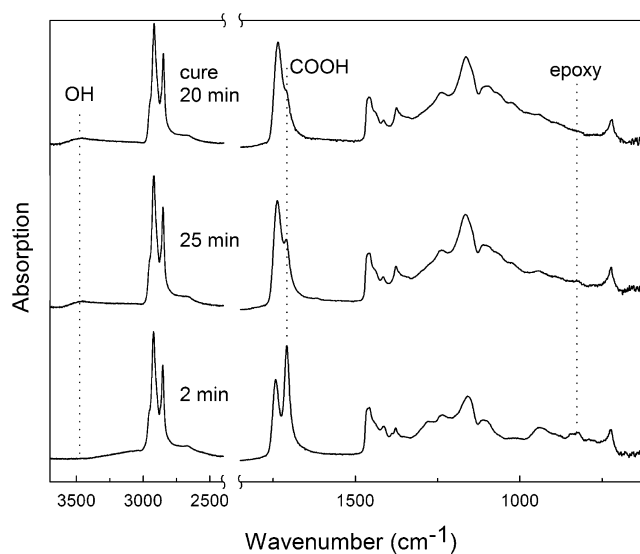
## RESULTS AND DISCUSSION

**Polymerization of ESO and DA.** Soybean oil can be efficiently epoxidized with a conversion rate of up to 98%.<sup>13,21</sup> Characterization of ESO with <sup>1</sup>H NMR spectroscopy (Figure S1 of the Supporting Information) reveals that the molar ratio of the epoxy to ester carbonyl groups is 1.4 based on the ratio of the peak area of the epoxy protons at 2.9–3.2 ppm<sup>22,23</sup> to that of the CH<sub>2</sub> α to the carbonyl at 2.3–2.4 ppm. Therefore, ESO has an average of 4.2 (i.e., 1.4 × 3) epoxy groups per molecule of ESO (Figure S2 of the Supporting Information). DA is a long-chain dicarboxylic acid derived from unsaturated fatty acids.<sup>24</sup> As a monomer, DA can impart unique properties to the resulting polymers such as elasticity, flexibility, hydrolytic stability, hydrophobicity, and intrinsically low *T*<sub>g</sub>.<sup>24</sup> Theoretically, a mixture of ESO and DA would polymerize to form hydroxyl-functionalized polyesters via the ring-opening of the epoxy groups with the –COOH groups.

As expected, polymerization of a mixture of ESO and DA (ESO–DA mixture) with an equivalent amount of –COOH and epoxy groups at 125 °C for about 110 min generated a tacky gel. For accelerating the polymerization, various catalysts such as organometallic compounds<sup>10,25,26</sup> (AMC-2, chromium(III) tris(acetylacetonate), zinc stearate, zinc acetylacetonate and aluminum acetylacetonate), tertiary amines<sup>25,26</sup> (triethylamine and *N,N*-dimethylbenzylamine), ammonium salts<sup>25</sup> (hexadecyltrimethylammonium bromide and tetrabutylammonium iodide), and a phosphonium salt<sup>25</sup> (tetraphenylphosphonium bromide) that have been demonstrated as effective catalysts for accelerating the reaction between the –COOH and epoxy groups were then investigated (see the Supporting Information for a typical procedure). Results on the investigation (Table S1 of the Supporting Information) showed that AMC-2 effectively and efficiently accelerated the polymerization of the ESO–DA mixture, resulting in a transparent and tacky gel in about 50 min. CTAA that is also a chromium(III)-based organometallic compound was less effective than AMC-2, requiring about 80 min for the formation of a similar gel. Therefore, AMC-2 was used as the catalyst for the polymerization of ESO–dicarboxylic acid mixtures in this study.

The polymerization of the ESO–DA mixture gave a tacky gel, which is a good indication for potential PSA applications. The gel was infusible and could only be swollen and partially dissolved in ethyl acetate, chloroform, tetrahydrofuran, toluene, acetone, ethyl ether, *N,N*-dimethylformamide, and hexane (see the Supporting Information for the details), which suggested the cross-linking nature of the gel. For further evaluating the adhesive properties of such a gel, a special procedure was designed for preparation of the gel in a form of film. The ESO–DA mixture in the presence of AMC-2 remained spreadable at 85 °C for up to 3 h although it gelled at 125 °C in about 50 min. Therefore, the mixture was first prepolymerized at 85 °C for 25 min. The resulting prepolymer was then coated on a sheet of release paper to give a uniform layer, and the coating was mated with a sheet of release film to afford a “sandwich”-like assembly that was further cured in an oven. The resulting adhesive film can be directly used for characterization or transferred to a backing material for preparation of PSA products such as tapes and labels.

The polymerization and the subsequent curing were monitored with FTIR. As shown in the FTIR spectra (Figure 1), a new broad peak of hydroxyl groups at 3450 cm<sup>-1</sup> and a new peak of ester groups at 1732 cm<sup>-1</sup> developed, and the peak

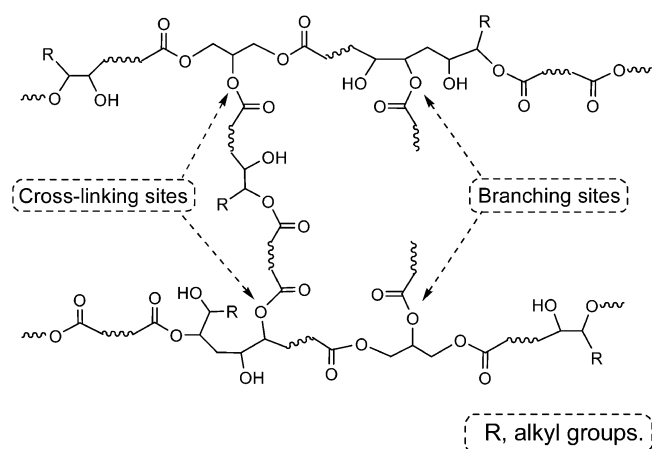


**Figure 1.** FTIR spectra of the prepolymers from polymerization of the ESO–DA mixture in the presence of AMC-2 at 85 °C for 2 min (bottom) and 25 min (middle), respectively, and the cured product (top) from the curing of the prepolymer (that was prepolymerized for 25 min) at 160 °C for 20 min.

of the epoxy groups between 820 and 850 cm<sup>-1</sup> and that of –COOH at 1700 cm<sup>-1</sup> decreased during the polymerization, which confirmed that the ring-opening of the epoxy groups with the –COOH groups took place, producing new ester linkages and hydroxyl groups. After curing at 160 °C for 20 min, the epoxy groups virtually disappeared, while a small amount of –COOH groups was still present in the cured product (Figure 1, top). Increasing the curing time from 20 to 85 min did not change the intensities of peaks of the unreacted –COOH groups, the remaining epoxy groups, and other functional groups (Figure S3 of the Supporting Information), which implied that the curing reactions were complete in 20 min. The monitoring with FTIR also revealed that the epoxy groups were consumed faster than the –COOH groups throughout the polymerization, which suggested that the epoxy groups were also involved in side reactions in addition to their reactions with –COOH groups. The faster consumption of the epoxy groups than –COOH groups was also observed in the polymerization of epoxidized oleic acid.<sup>27,28</sup> The possible side reactions might include those of the epoxy groups with secondary hydroxyl groups and water, respectively.<sup>28</sup>

ESO contains an average of about four epoxy groups per single molecule. At the beginning of the polymerization, ESO reacts with DA via the epoxy–COOH reaction to form hydroxyl-functionalized oligomeric chains, the remaining epoxy groups of ESO can react with DA or –COOH containing oligomers to form branches (Figure S4, top, of the Supporting Information). As the step-growth polymerization proceeds, the branches lead to formation of new oligomeric/polymeric chains that can lead to more branches, thus forming a mixture of branched or highly branched oligomers and polymers. Along with the consumption of the epoxy groups, the reaction mixture became viscous and eventually led to the formation of a gel at which cross-linked polymer networks form from the branched or highly branched oligomers and polymers (Figure S4 of the Supporting Information). A representative structure of possible networks with typical functional groups, branching and cross-

linking sites is proposed in Figure 2. In addition, the final polymeric mixture also contains sol fractions that are soluble in



**Figure 2.** Schematic representation of a possible polymeric network resulting from the polymerization of ESO and a dicarboxylic acid and typical functional groups, branching, and cross-linking sites.

the solvents described previously (see the Supporting Information for the solubility test of the gel). The sol fractions could consist of hydroxyl-functionalized polymers and oligomers, and possible loops and unreacted monomers. As discussed later, this polymeric mixture turned out to be a suitable material for PSAs.

**Effect of the  $-\text{COOH}/\text{Epoxy}$  Ratio on the PSA Properties of the Polymers.** The tacky film prepared from the polymerization of the ESO–DA mixture (Table 1, entry 1) was readily transferred to a backing such as paper and BOPP film to form PSA tapes. The resulting tapes were evaluated for their  $90^\circ$  peel strength, loop tack, and shear strength. The PSA on the paper backing exhibited a good peel strength of 2.1 N/cm, a good tack of 7.1 N, and a sufficient shear strength of 34 min (Table 1, entry 1). The PSA left no adhesive residues on the panel surface after the peel and tack tests, which indicated that the PSA had the desirable property of adhesive failure for commercial applications. Increasing the curing time from 20 to 85 min (Table 1, entry 2) did not significantly change the peel

strength of the PSA. These results suggest that the tacky film can potentially be used for PSA products. It should be noted that the PSA on the BOPP backing (Table 1, entry 3) has a lower peel strength of 1.6 N/cm but a higher shear strength of 174 min than that on the paper backing. The discrepancy between the two PSA tapes could be due to the backing materials, since the peel and shear strengths of a PSA tape are not only dependent upon the properties of PSA layer itself but are also strongly influenced by the properties of the backing materials such as the thickness and modulus.<sup>2</sup>

As shown in Table 1, the peel strength had the following order: entry 4 < entry 1 < entry 5, which implied that the peel strength of the PSAs from the polymerization of the ESO–DA mixtures increased with increase in the  $-\text{COOH}/\text{epoxy}$  molar ratio of the reaction mixtures. The peel strength is measured by peeling the PSA samples from a stainless steel (type 302). The stainless steel is an iron-based alloy containing at least 11% of chromium and contains a chromium-rich oxide film on the surface.<sup>29</sup> It is demonstrated that the  $-\text{COOH}$  groups can improve the wetting onto the surface of the stainless steel adherend and increase the adhesion strength of the PSA layer to the adherend via formation of hydrogen bonding and other noncovalent interactions at the adhesive/adherend interface.<sup>17,30,31</sup> The FTIR spectra (Figure 1, top) of the PSAs from our study revealed that a small amount of  $-\text{COOH}$  groups was still present in the PSAs after the completion of the curing reactions, and that the reaction mixtures with a higher  $-\text{COOH}/\text{epoxy}$  ratio resulted in a greater amount of unreacted  $-\text{COOH}$  group remaining in the PSAs. The increase in the amount of  $-\text{COOH}$  groups remaining in the PSAs could thus result in the increase in their peel strength.

**Effect of the Dicarboxylic Acid on the PSA Properties of the Polymers.** The chemical structure of a dicarboxylic acid influences the reactivity of the  $-\text{COOH}$  groups and the rigidity/flexibility of its molecular chain that may subsequently affect the cross-linking density,  $T_g$ , adhesion and cohesion strengths, and modulus of the resulting polymers. The following dicarboxylic acids with different molecular weights and backbone flexibilities were investigated: DA, SA, AA and DPCA. A mixture of ESO and each of the dicarboxylic acids was polymerized and completely cured under the same

**Table 1.** Polymerization of ESO and Dicarboxylic Acids in the Presence of AMC-2 and the PSA Properties of the Cured Polymeric Products<sup>a</sup>

entry	prepolymerization			cure time (min) <sup>c</sup>	peel adhesion (N/cm) <sup>d</sup>		loop tack (N) <sup>d</sup>		shear strength (min) <sup>d</sup>	
	dicarboxylic acids (ratio <sup>b</sup> )	temp (°C)	time (min)		average	SD	average	SD	average	SD
1	DA (1.00)	85	25	20	2.1	0.2	7.1	0.9	34	15
2	DA (1.00)	85	25	85	1.8	0.3	n.m.		n.m.	
3	DA (1.00)	85	25	20	1.6	0.1	n.m.		174	97
4	DA (0.85)	85	25	35	1.7	0.2	n.m.		n.m.	
5	DA (1.18)	85	25	30	2.9	0.3	n.m.		36	20
6	SA (1.00)	100	25	18	1.5	0.2	n.m.		n.m.	
7	AA (1.00)	130	20	15	1.4	0.2	n.m.		n.m.	
8	DPCA (1.18)	70	30	35	5.0	0.5	12.6	2.5	181	96
9	DPCA (1.18)	70	30	115	4.7	0.5	n.m.		n.m.	
10	DPCA (1.18)	70	30	35	3.3	0.5	n.m.		>168 h	

<sup>a</sup>The amount of AMC-2, 1.1 wt % relative to the reaction mixture; PSA layer thickness,  $4.0 \pm 0.5$  mg/cm<sup>2</sup>; paper ( $\sim 68$   $\mu\text{m}$  thick) is used as the backing except that BOPP film ( $\sim 50$   $\mu\text{m}$  thick) is used instead in entries 3 and 10. <sup>b</sup>The  $-\text{COOH}/\text{epoxy}$  molar ratio of the resulting mixture. <sup>c</sup>The prepolymer was cured in an oven at  $160$   $^\circ\text{C}$  until completion of the curing reactions. <sup>d</sup>The failure mode in peel, tack, and shear tests is adhesive failure; SD, standard deviation; n.m., not measured.

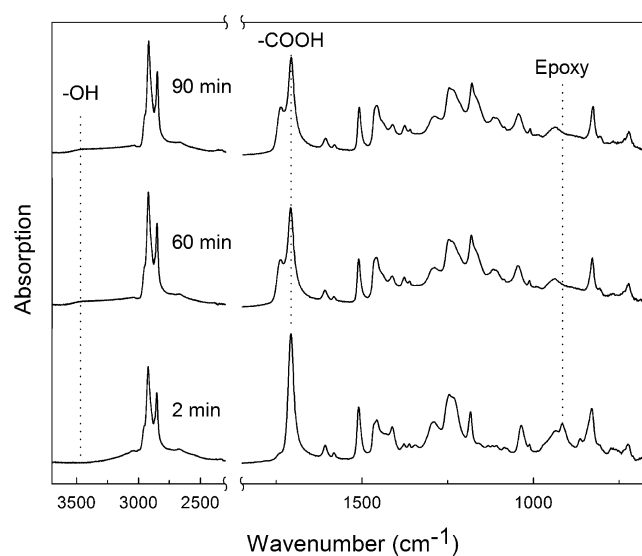
experimental conditions, and the results are summarized in Table 1.

The PSA prepared from the polymerization of the ESO-SA mixture (Table 1, entry 6) had a peel strength of 1.5 N/cm that was lower than that (2.1 N/cm) from the ESO-DA mixture (Table 1, entry 1). The same amount of ESO and the same -COOH/epoxy molar ratio were used in the polymerizations of the ESO-SA mixture and the ESO-DA mixture, respectively. The ESO-SA mixture thus contained the same number of -COOH groups as the ESO-DA mixture. The -COOH groups of SA were assumed to have the same reactivity toward the epoxy groups as those of DA. The polymers from the ESO-SA mixture were thus expected to have the same number of cross-links from the reactions of -COOH groups and the epoxy groups (Figure S4, bottom, of the Supporting Information) as those from the ESO-DA mixture after the curing reactions were complete. SA has a molecular weight of 202 g/mol that is much lower than that (~570 g/mol) of DA. For having the same number of -COOH groups, the ESO-SA mixture would have a mass smaller than the ESO-DA mixture. In other words, the PSA from the ESO-SA mixture had a smaller mass than that from the ESO-DA mixture. Therefore, the cross-linking density, i.e., the number of cross-links per gram,<sup>32</sup> of the PSA from the ESO-SA mixture was higher than that from the ESO-DA mixture. Our results are consistent with reports that increase in the cross-linking density of a PSA can decrease its peel strength.<sup>9,33</sup>

Contrary to the big difference in the molecular weights between SA and DA, the molecular weight (146 g/mol) of AA is only slightly lower than that (202 g/mol) of SA. Therefore, the PSA from the ESO-AA mixture would have a similar cross-linking density to that from the ESO-SA mixture, which explains that a peel strength of 1.4 N/cm for the PSA from the ESO-AA mixture (Table 1, entry 7) was comparable to that (1.5 N/cm) for the PSA from the ESO-SA mixture.

DPCA was prepared from polymerization of a mixture of DA and BPAGE with the -COOH/epoxy molar ratio of 2.68. After the mixture was polymerized for 60 min, the epoxy groups of BPAGE were completely consumed as evidenced by disappearance of the characteristic peak of the epoxy groups at 916 cm<sup>-1</sup> in the FTIR spectrum (Figure 3, middle), while a considerable amount of -COOH groups remained in the product. Increasing the reaction time from 60 to 90 min (Figure 3, top) did not change the intensities of the peaks of the remaining -COOH groups and other functional groups in the FTIR spectrum, which implied that the reactions were complete in 60 min. Since DA was used in excess and the epoxy groups were completely consumed by the -COOH groups, the product was expected to be a mixture of dicarboxylic acids containing at least two DA units per polymer/oligomer in addition to some unreacted DA.

A mixture of DPCA and ESO was prepolymerized at 70 °C for 30 min. The curing of the prepolymer at 160 °C resulted in a PSA (Table 1, entry 8). The monitoring of the curing process with FTIR (Figure S5 of the Supporting Information) revealed that the curing reactions completed in 35 min. The PSA on the paper backing had a very good peel strength of 5.0 N/cm, a very good tack of 12.6 N, and a good shear strength of 181 min. Increase in the curing time from 35 to 115 min (Table 1, entry 9) did not significantly change the peel strength of the PSA. DPCA is a polymer/oligomer that has an average molecular weight much higher than DA. Therefore, the PSA from the ESO-DPCA mixture was expected to have a much lower cross-



**Figure 3.** FTIR spectra of the prepolymers from polymerization of the DA-BPAGE mixture in the presence of AMC-2 at 135 °C for 2 (bottom), 60 (middle), and 90 min (top), respectively.

linking density than that from the ESO-DA mixture, which explains that the peel strength (5.0 N/cm) of the PSA from the ESO-DPCA mixture (Table 1, entry 8) was much higher than that (2.9 N/cm) of the PSA from the ESO-DA mixture (Table 1, entry 5). The shear strength (181 min) of the PSA from the ESO-DPCA mixture (Table 1, entry 8) was also higher than that (36 min) of the PSA from the ESO-DA mixture (Table 1, entry 5), which could be explained as follows. The average molecular weight ( $M_c$ ) of the chains between cross-links (Figure S4, bottom, of the Supporting Information) is related to the cross-linking density ( $\nu$ ) by the equation,  $\nu M_c = 1/2$ , i.e.,  $M_c$  is inversely proportional to  $\nu$ .<sup>32</sup> The PSA from a DPCA-ESO mixture has a much lower  $\nu$  than that for the PSA from a ESO-DA mixture and, thus, has a much higher  $M_c$  than the latter. The significant increase in the molecular weight could enhance the entanglement among the polymer chains, thus increasing the cohesion strength of the PSAs.<sup>32,34</sup> In addition, it has been demonstrated that the incorporation of rigid phenylene moieties into the polymer backbones that are sufficiently mobile for allowing ordered chain packing could result in physical cross-links among the polymer chains, thus increasing the cohesion strength of the resulting polymer.<sup>32,35</sup> In the PSA from a ESO-DPCA mixture, phenylene moieties from BPAGE that had been incorporated into the flexible polymer backbones could potentially pack together through  $\pi$ -electron stacking, thus increasing the cohesion strength and subsequent shear strength of the PSA.

The change of the backing material from paper (Table 1, entry 9) to BOPP film (Table 1, entry 10) reduced the peel strength from 5.0 to 3.3 N/cm but dramatically raised the shear strength from 181 min to more than 168 h. The true shear strength for the PSA on the BOPP backing was not known because the shear test was terminated at 168 h. As discussed previously, the discrepancy between the two PSA tapes could be due to the backing materials, since the peel and shear strengths of a PSA tape are not only dependent upon the properties of PSA layer itself but are also strongly influenced by the properties of the backing materials.<sup>2</sup>

**Aging Resistance of the PSAs.** The PSA from the AA-ESO mixture (Table 1, entry 7) was evaluated for its aging

resistance at ambient humidity and temperature. The peel strength of the PSA after the aging was  $1.4 \pm 0.1$  N/cm after 9 months and  $1.5 \pm 0.1$  N/cm after 42 months, respectively, and was essentially the same as that ( $1.4 \pm 0.2$  N/cm) of the PSA without aging (Table 1, Entry 7). There were no adhesive residues left on the stainless steel panel after the peel test, which implied that the PSA did not disintegrate after an aging time of up to 42 months. These results revealed that the PSA was very stable during the storage at ambient environment.

PSAs obtained in this study are tacky, soft, and flexible, which is partly due to the inherent flexibility of long hydrocarbon chains in the starting monomers such as DA and ESO.<sup>24</sup> The flexible long hydrocarbon chains allow the PSAs to readily deform and wet adherends under light pressure, thus facilitating establishment of an adhesive bond with the adherends. The cross-links in the PSAs impart the PSAs sufficient cohesion strength. In addition, the PSAs contain hydroxyl groups (–OH) and a small amount of unreacted –COOH groups. It has been well demonstrated that these functional groups in PSAs can significantly improve the adhesion strength of the PSAs through formations of hydrogen bonds between the PSAs and adherends.<sup>30,31,36</sup> The –OH and –COOH groups can also improve the wetting of the PSAs on various adherends such as stainless steel, paper, glass, and skin, thus facilitating the intimate contact between the PSAs and the adherends.<sup>17,30,31</sup> The –OH and –COOH groups also allow formations of hydrogen bonds among molecular chains and within the same molecular chain of the PSA, thus increasing the cohesive strength of the PSA.<sup>17,30,31,36</sup>

Commercially available office PSA tapes typically have a peel strength in the range of 3.5–8.8 N/cm, and labels such as Post-it notes require a peel strength as low as 0.2 N/cm.<sup>10</sup> The PSAs from this study can be tailored through the selection of a dicarboxylic acid and its usage for a different peel strength ranging from 1.4 to 5.0 N/cm (Table 1). The PSAs described in this study could potentially be used for office tapes and labels. In addition, the PSAs described in this study can be solely based on renewable biomaterials because ESO, DA,<sup>24,37</sup> SA,<sup>37</sup> and AA<sup>38</sup> can be derived from renewable natural resources. The process for the preparation of the PSAs does not require organic solvents or toxic chemicals, thus being very environmentally friendly.

## CONCLUSIONS

Prepolymerization of ESO with DA, SA, AA, or DPCA followed by a thermal curing afforded cross-linked hydroxyl-functionalized polyesters. AMC-2 was found to be the most effective catalyst for the prepolymerization. The polyesters as PSAs had superior peel strength, good loop tack, high shear strength and good aging resistance. The PSA properties of the hydroxyl-functionalized polyesters can be tailored to meet requirements of different PSA products through changing the dicarboxylic acid and its usage. Incorporation of a small amount of phenylene-containing monomer BPAGE into the polymers significantly increased the peel and shear strengths of the resulting PSAs. The new PSAs can be fully based on renewable materials. The process for the preparation of the PSAs is simple and environmentally friendly.

## ASSOCIATED CONTENT

### Supporting Information

Screening of a catalyst for the polymerization of ESO and DA, solubility test of the gel, <sup>1</sup>H NMR spectrum and structure of

ESO, and additional FTIR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This research was supported by the royalty fee income of patented technologies from K.L.'s research group.

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