Synthesis of Palm Oil-Based Polyester Polyol for Polyurethane Adhesive Production

Khoon Poh Ang,[1] Choy Sin Lee,[2] Sit Foon Cheng,[1] Cheng Hock Chuah[1]

[1]Unit of Research on Lipids (URL), Department of Chemistry, Faculty of Science, University Malaya, 50603 Kuala Lumpur, Malaysia
[2]Department of Pharmaceutical Chemistry, International Medical University, No 126, Jalan Jalil Perkasa 19, Bukit Jalil, 57000 Kuala Lumpur, Malaysia
Correspondence to: L. C. Sin (E-mail: choysin_lee@imu.edu.my)

ABSTRACT: Palm oil-based polyester polyol is synthesized by ring opening reaction on epoxidized palm olein by phthalic acid. The reaction is carried out in a solvent free and noncatalyzed condition with the optimal reaction condition at 175°C for 5 h reaction time. The physical state of the product is a clear bright yellowish liquid with low viscosity value of 5700–6700 cP at 25°C and pour point of 15°C. The chemical structure and molecular weight of the polyester polyol were characterized by FTIR, ^{1}H-NMR, ^{13}C-NMR, and GPC. The optimal polyol with molecular weight of 36,308 dalton and hydroxyl value of 78.17 mg KOH/g sample was reacted with polymeric 4,4′-methylene diphenyl diisocyanate (pMDI) at isocyanate index of 1.3 to produce polyurethane adhesive. The lap shear strength of the polyurethane adhesive showed two times higher than the commercial wood adhesives. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39967.

INTRODUCTION

The conventional polyurethane adhesives are produced by reacting petroleum-based polyols with isocyanates.[1–3] However, the concern on oil crisis and its impact to the environment have driven the search for renewable sources to substitute petroleum-based products. Vegetable oil is one of the potential feedstock to replace petroleum-based polyols because of its availability, versatility, and feasibility. A number of reports have outlined the potential of vegetable oils towards polyurethane wood adhesives application. Somani and his co-workers reported on the use of castor oil to prepare polyurethane wood adhesives in which the adhesives product showed better lap shear strength than commercial wood adhesives.[4] Choi et al.[5] and Badri et al.[6] reported on the utilization of soybean oil and palm kernel oil-based polyols to prepare wood adhesives that showed good adhesion properties towards wood substrates. Apart from the mechanical strength itself, polyurethane wood adhesives prepared from vegetable oils also show improved hydrolysis resistance as compared to the petroleum-based polyurethane wood adhesives.[7,8] This is because of the dangling long fatty acid chains in vegetable oil-based polyols that protect the polyurethane adhesives from hydrolysis by preventing the penetration of water molecules into the adhesives that can hydrolyze the

ester bonds.[7] Polyols prepared from epoxidized canola oil and 1,3-propane had been used in polyurethane adhesives production and the adhesives exhibited superior hydrolysis resistance in hot water.[8]

Most vegetable oils do not have hydroxyl functional groups in its acyl chains except for castor oil. There are several approaches to introduce the hydroxyl group into the vegetable oils structure,[9,10] each of which produces polyols with different physical and chemical properties. Polyols with primary hydroxyl groups can be prepared via ozonolysis[11] and hydroformylation.[12,13] Polyols synthesized via ozonolysis has terminal hydroxyl structure, which results in short gel time to as low as 1 min. The extremely low gel time is unfavorable to polyurethane adhesives application as the adhesive gelled before it was applied onto the wood surfaces.[14] On the other hand; its high tendency to crystallize at room temperature has made the reaction with isocyanate during polyurethane formulation difficult.[14] Polyol with primary hydroxyl structure can also be synthesized by hydroformylation. The unsaturated fatty compounds were first allowed to undergo hydroformylation to form aldehyde functional compounds and were then hydrogenated to form polyols with the aid of rhodium or cobalt catalyst. Rhodium catalyst gave satisfactory conversion but it is relatively expensive and needed a

secondary nickel catalyst to obtain hydroxyl structure, whereas the use of cobalt catalyst has the drawback of low polyol conversion.[12] In view of this, vegetable oil-based polyols prepared by ring opening reaction on epoxidized vegetable oils seems to be the better option in polyurethane adhesive application. The secondary hydroxyl structures of polyols prepared from ring opening reaction offer sufficient gel time for adhesives application as compared to primary hydroxyl structures. Furthermore, it showed good mechanical strength and superior to hot water resistance as compared to commercial polyurethane adhesives.[8] Epoxidized soybean oil, canola oil, and palm oil had been reported to react with alcohols and acids to produce both polyether and polyester polyols with secondary hydroxyl functionality.[8,15–17]

In continuing our work, we synthesized palm oil-based polyester polyol via ring opening reaction of epoxidized palm olein (EPOo) in a solventless and catalyst free condition. The synthesized polyol showed low hydroxyl value, high molecular weight, and the secondary hydroxyl structures gave polyurethane a longer gel time that is beneficial for adhesive application as compared to polyol with primary hydroxyl groups.[18,19] In addition, the dangling hydrocarbon chains from fatty acid moieties reduced the brittleness of polyurethane adhesives that resulted in stronger polyurethane structure.[20] In formulating the palm oil-based polyester polyol with pMDI and additives, the synthesized palm oil-based polyurethane adhesive achieved a two folds higher in lap shear strength as compared to the commercial wood adhesives.

EXPERIMENTAL

Materials

EPOo (specification: OOC = 3.40%, acid value = 0.25 mg KOH/g sample, iodine value = 0.77 g I_2/100 g sample, moisture content = 0.08%) was purchased from Advanced Oleochemicals Technology Division of the Malaysian Palm Oil Board. Laboratory grade phthalic acid (99%) was purchased from Merck. Polymeric 4,4-methylene diphenyl diisocyante (pMDI) was obtained from Samchem Holding Berhad. All other chemicals used were of analytic grade and used as received.

Synthesis of Polyester Polyols

The reaction was carried out in a 2-L three-neck round bottom flask connected to a heating mantle. The flask was equipped with a magnetic stirrer, a thermometer, and a condenser. Various ratios of phthalic acid (7.5–20 wt %) were reacted with EPOo to produce different average molecular weights of polyester polyols. The reaction was carried out at a temperature ranging from 145°C to 190°C for 5 h. Equal amount of polyester polyols was withdrawn hourly in which acid value, oxirane oxygen content (OOC), hydroxyl value (OHV), average molecular weight (M_w), viscosity, and pour point of the reaction mixtures were determined.

Characterization of Polyester Polyols

Acid value, OOC, and OHV was analyzed according to American Oil Chemists' Society (AOCS) Te 2a-64, AOCS Cd 9–57, and AOCS Cd 13–60 method, respectively. Samples were analyzed in triplicate and the average values were recorded. The viscosity of the polyester polyols was measured by a programmable rheometer (Anton Parr Physica MCR301) at 25°C and 40°C. The pour point of polyester polyols was determined based on ASTM D 97-87. Samples were prepared in triplicates and the average values were rounded to the nearest degree. The measurement for pour point was done with resolution at specified 3°C increment. ^{1}H-NMR and ^{13}C-NMR spectra were recorded using BRUKER FT-NMR 600 machine. Five mg polyester polyol was dissolved in 1 mL chloroform-d in a sample vial. The solution was then transferred into a NMR sample tube with a minimum height of 4 cm prior to NMR analysis. FTIR spectroscopy analysis was carried out using Perkin Elmer Spectrum 400 machine with four scan times for each sample. Neat samples were placed onto a NaCl cell and subjected to FT-IR spectroscopy scanning. Gel permeation chromatography (GPC) analysis was carried out using Waters 600 machine with Waters 2414 RI detector. Samples were dissolved in tetrahydrofuran (THF) before analysis. THF was used as an eluent at a flow rate of 1.0 mL/min. The calibration curves for GPC analysis were obtained with polystyrene standards with Styragel column.

IR (KBr): $v = 3525.95$ (w, OH), 1281.98 (n, COO phthalic ester), 1580.46 (n, C=C phthalic acid). ^{1}H-NMR (400 MHz, CDCl₃, δ): 0.80 (t, 3H, CH₃), 1.20 (d, 2H, CH₂), 1.61 (s, 2H, COOCH₂**CH₂**), 2.25 (s, 2H, **CH₂**COO), 3.65 (s, 2H, C**H**OH), 4.20 (m, 2H, sn-1,3 H), 5.10 (s, 1H, C**H**CHOH), 5.24 (s, 1H, sn-2 H), 7.63 (m, 4H, Ar H). ^{13}C-NMR (400 MHz, CDCl₃, δ): 74.06 (COH), 79.00 (COO phthalate ester), 13.95 (CH₃), 125–130 (Ar C), 34.16 (COO**C**H₂), 25.29 (COOCH₂**C**H₂), 68.88 (sn-1,3C), 62.02 (sn-2C), 172 – 173 (C=O fatty acid moieties).

Polyurethane Adhesive Preparation

Polyurethane adhesives were prepared by reacting polyester polyol with pMDI at NCO/OH ratio of 1.3 and glycerol was added as a cross-linker. The reaction mixture was stirred at 180 rpm at room temperature for 3 min and subsequently the product was applied onto the wood surfaces using a brush. The gel time[21] for the adhesive system to remain in fluid condition in order to be applied to wood substrate was recorded.

Wood Specimens Preparation

Tectona grandis (teak wood) were cut into rectangular panels with dimension 100 x 25 x 4 mm³. The woods specimens were polished with sand paper grit number 60 prior to application of polyurethane adhesives.

Wood Bonding and Testing

The adhesive was applied onto the surface of wood specimens with area of 30 mm x 25 mm and thickness around 0.1 mm. The two coated pieces of woods' surfaces were then placed together and cured at room temperature. A 2.5-kg load was placed on top of wood specimens for 24 h. After that, wood specimens were conditioned in a dry box at 30°C and relative humidity of 50 ± 5% for 7 days. The specimens were then subjected to lap shear strength test according to ASTM D906.[22] The average lap shear strength of the adhesives recorded was based on the average of five wood specimens prepared under the same formulation. The wood failure mode[21] for all the tested specimens were observed and recorded.
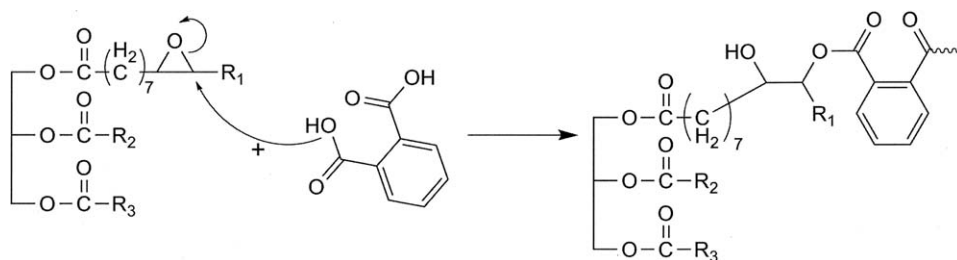
Figure 1. Ring opening reaction mechanism of EPOo by phthalic acid.

RESULTS AND DISCUSSION

Synthesis of Polyester Polyol

In our study, phthalic acid was selected to react with EPOo in consideration that aliphatic dicarboxylic acids produce polyol that solidified at room temperature; except for phthalic acid produces polyol that remains as liquid at room temperature.[23] The ring opening reaction of EPOo with phthalic acid was performed effectively in non-catalyzed condition despite report quoting that polyesterification reaction between acids and epoxides in non-catalyzed reaction is slower than that with amine catalyst such as 2-ethylhexylamine or benzyldimethylamine.[24,25] We favored the noncatalyzed reaction system to obviate amine catalyst that may catalyze the reaction between isocyanate and water resulting in the formation of urea and biuret hard segments that reduces the mechanical strength of the urethane.[26] The starting material, EPOo was prepared from palm olein that consists of approximately 40.9% palmitic acid (16:0), 41.5% oleic acid (18:1), 11.5% linoleic acid (18:2) and other minor fatty acid chains.[27] Thus, epoxidation of palm olein produced mainly monoepoxide (from oleic acid) and diepoxide (from linoleic acid). Reaction of monoepoxide and diepoxides with phthalic acid produced polyol with secondary hydroxyl group and ester bonding (Figure 1). The hydroxyl groups of the oligomer undergoes further reactions either esterification reaction with phthalic acid or etherification with epoxy groups to produce a mixture of polyol with various chain lengths of high molecular weight. The polyol was used without further separation and purification for PU adhesives preparation.

Effect of Reaction Temperature on Polyester Polyol. Ring opening reaction of epoxides with various organic and inorganic acids, such as acetic acid and phosphoric acid at reaction temperature ranging from 40°C to 90°C had been reported.[17,28] Nevertheless, in this study, high reaction temperature is essential to melt the phthalic acid powder in order to obtain phase homogeneity with liquid EPOo. The reaction was carried out by reacting EPOo with 7.5 wt % phthalic acid at temperature ranging from 145°C to 190°C for 5 h. Both acid value and OOC

were used to monitor the reaction kinetic of the epoxides ring opening by phthalic acid (Figure 2). The acid value and OOC of reaction mixtures reacted at 145°C and 160°C decreased hourly demonstrating that ring opening reaction by phthalic acid was progressing throughout the reaction. Nevertheless, for reactions carried out at 175°C and 190°C, the acid value and OOC of the reaction mixtures became constant after 1 h of reaction time. This suggested that the ring opening reaction was vigorous at higher reaction temperature (175°C and 190°C) and the polymer matrices achieved its maximum growth in molecular weight.

The OHV of the polyols synthesized at various reaction temperatures were similar and fell in the range of 70–80 mg KOH/g sample (Table I). However, the OHV of polyester polyol reacted at 160°C and 175°C were slightly higher than that at 145°C and 190°C. This can be attributed to the lower reaction
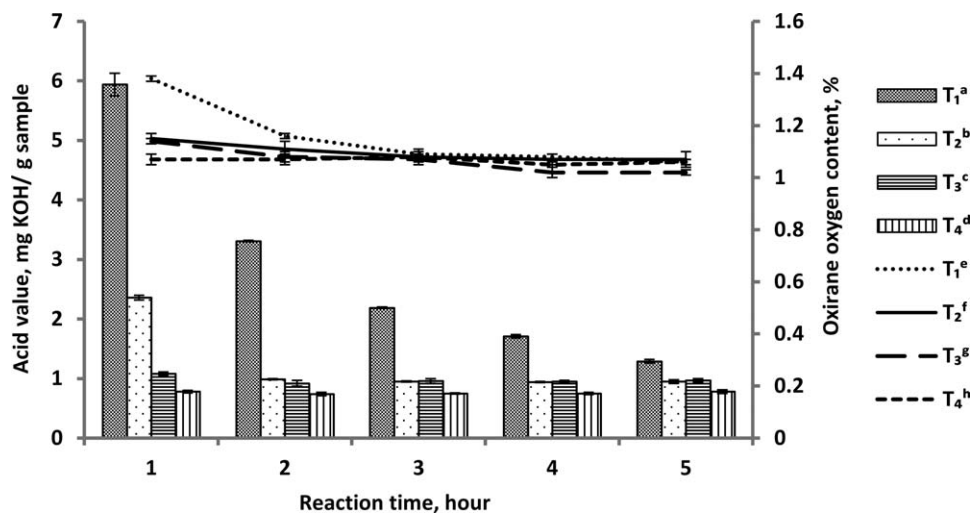

Figure 2. Effects of reaction temperatures and time on acid value and OOC of polyester polyols. T_1–T_4—reaction conducted by reacting 7.5 wt % phthalic acid with EPOo. T_1—145°C, T_2—160°C, T_3—175°C, T_4—190°C. [a, b, c, d] - acid value. [e, f, g, h] – OOC.

Table I. Physicochemical Properties of Polyester Polyols after 5 hours Reaction

| Samples | OHV (mg KOH/ g sample) | Viscosity (cP) | | Pour point (°C) | Physical form | Color |
		25°C	40°C			
T_1[a]	74.88	6210	2160	15	liquid	Pale yellowish
T_2[b]	80.45	5930	2020	15	liquid	Yellowish
T_3[c]	80.57	6720	2260	15	liquid	Yellowish
T_4[d]	73.66	5750	1960	15	liquid	Brown

T_1-T_4—reaction conducted by reacting 7.5 wt % phthalic acid with EPOo.
[a] T_1—145°C.
[b] T_2—160°C.
[c] T_3—175°C.
[d] T_4—190°C.

kinetics at lower reaction temperature (145°C). Besides, sublimation of phthalic acid occurred at higher reaction temperature when phthalic anhydrides were determined in the reaction mixture at 190°C. This reduced the amount of phthalic acid reacting with EPOo and therefore producing polyol with lower OHV.

GPC was used to study the effects of reaction time and temperature on average molecular weight (M_w) and polydispersity index (PDI) of the reaction mixture. The M_w and PDI of the reaction mixture were increasing with longer reaction time (Table II). The increment of PDI indicates the increasing of side reactions, such as further esterification with dicarboxylic or etherification with epoxides, in producing mixture of polyester polyol with inconsistent chain length. Polyol with high hydrocarbon chain length contribute to the soft segments of PU matrices.[18] Thus, higher molecular weight and non-uniform chain length of polyester polyol give flexibility to the PU matrices and prevent brittleness in PU adhesives. As for the physical form, all polyols synthesized were liquid in nature (Table I). However, the color of the synthesized polyols became darker with the increasing reaction temperature, especially for polyol synthesized at 190°C that showed obvious unfavorable brown color. Based on the physicochemical properties, reaction temperature of 175°C was selected as the optimal reaction temperature as it gave high reaction kinetic, at the same time producing light color polyol with high M_w.

Effect of Phthalic Acid Concentration on Polyester Polyol. Reactions coded as P1 to P6 were conducted by reacting EPOo with different wt % of phthalic acid at 175°C for 5 h to prepare polyester polyol with different molecular weight range. Acid value and OOC were used to monitor the reaction (Table III). The increment in phthalic acid concentration used in reactions P3 to P6 yielded reaction mixture with higher acid value but lower OOC. A more complete conversion of OOC into ester linkages was observed when 10 wt % of phthalic acid (P3) was used to react with EPOo to produce polyester polyol with acid value of 2.74 mg KOH/g sample. The conversion of free carboxylic group to ester linkages was not efficient beyond 10 wt % phthalic acid as the amount of phthalic acid used was in excess, thus produced polyester polyol with high acid value.

The OHV of all synthesized polyols was in the range of 60–82 mg KOH/g sample (Table III). Polyols with low OHV are suitable in producing CASE (coating, adhesive, sealant, and elastomer) PU.[18] The OHV of the polyester polyol increased with the increasing amount of phthalic acid (7.5–12.5 wt %) used to react with EPOo. However, further increment in the phthalic acid (15–20 wt %) produced polyols with lower OHV. The theoretical OHV calculated based on OOC of the EPOo were higher than the actual measured OHV. This is because of the subsequent cross-linking reaction between the hydroxyl groups of the polyol with the phthalic acid added.

Table II. Effects of Reaction Temperature and Time on M_w and PDI of Polyester Polyols

| Reaction time (h) | M_w (Da) | | | | PDI | | | |
	T_1[a]	T_2[b]	T_3[c]	T_4[d]	T_1[a]	T_2[b]	T_3[c]	T_4[d]
1	8920	12,330	14,482	14,551	1.64	2.04	2.17	2.18
2	12,511	14,211	14,604	14,457	2.02	2.10	2.17	2.15
3	14,245	14,600	14,649	14,391	2.14	2.17	2.17	2.13
4	14,546	14,636	14,646	14,466	2.15	2.16	2.17	2.10
5	14,575	14,571	14,694	14,632	2.15	2.16	2.20	2.14

T_1-T_4 - reaction conducted by reacting 7.5% phthalic acid with EPOo.
[a] T_1—145°C.
[b] T_2—160°C.
[c] T_3—175°C.
[d] T_4—190°C.

Table III. Effect of Phthalic Acid Concentration on the Physicochemical Properties of Polyester Polyols

Polyol code	Acid value (mg KOH/g sample)	OOC (%)	Percentage conversion[a] (%)	OHV (mg KOH/g sample) Theoretical value	Experimental value	GPC analysis M_w (Dalton)	PDI	Viscosity, (cP) 25°C	40°C	Pour point (°C)	Physical state[b]	Color
P1[c]	0.97±0.01	1.03±0.01	69.7±0.21	83.10	63.62±4.31	14694	2.20	5710	1940	15	Liquid	Light yellowish
P2[d]	1.09±0.06	0.67±0.01	80.3±0.21	95.37	72.34±2.33	26051	3.33	20800	6310	15	Liquid	Yellowish
P3[e]	2.74±0.14	0.36±0.01	89.4±0.21	106.94	78.17±3.24	36308	4.21	41000	11800	15	Liquid	Yellowish
P4[f]	7.57±0.11	0.21±0.01	93.8±0.21	111.84	81.58±2.80	41619	3.53	90500	23600	18	Semi-solid	Yellowish
P5[g]	22.60±0.13	0.07±0.03	97.9±0.85	116.76	74.12±4.74	22641	2.88	53500	13200	18	Semi-solid	Brown
P6[h]	42.86±0.33	0.03±0.01	99.1±0.01	118.16	63.85±4.94	17978	2.42	123000	25800	18	Semi-solid	Dark brown

[a] Percentage conversion[h] = [(OOC$_{EPOo}$ -- OOC) / OOC$_{EPOo}$] × 100%.
[b] Physical state—observation after 6 months of storage.
[c] P1—EPOo react with 7.5 wt % phthalic acid at 175°C for 5 h.
[d] P2—EPOo react with 8.75 wt % phthalic acid at 175°C for 5 h.
[e] P3—EPOo react with 10 wt % phthalic acid at 175°C for 5 h.
[f] P4—EPOo react with 12.5 wt % phthalic acid at 175°C for 5 h.
[g] P5—EPOo react with 15 wt % phthalic acid at 175°C for 5 h.
[h] P6—EPOo react with 20 wt % phthalic acid at 175°C for 5 h.

Table IV. Comparisons of PU Average Lap Shear Strength and Gel Time with Commercial Adhesives

Product name	Average lap shear strength (MPa)	Locus of failure	Gel time (min)
PU[a]	5.3 ± 0.2	SF[b]	90
Titebond™	2.7 ± 0.2	CF[c] + AF[d]	53
Weldbond™	2.6 ± 0.3	CF[c] + AF[d]	67

[a] PU—PU adhesive prepared by reacting polyester polyol P3 and 3 wt % glycerol with pMDI at NCO/OH ratio of 1.3.
[b] SF: substrate failure.
[c] CF: cohesive failure of adhesive.
[d] AF: adhesive failure of adhesive.

GPC results exhibited that the M_w and PDI of the polyester polyols were increasing when higher concentration of phthalic acid was used in the reaction. However, the M_w and PDI were leveled off beyond 10 wt % of phthalic acid used (Table III). This is attributed to the addition of excessive phthalic acid (12.5, 15, and 20 wt %) that causes intermolecular forces, such as hydrogen bonding and dipole attraction between the unreacted phthalic acid with the hydroxyl group of the polyol compound, resulting in lower reactivity of the reaction mixture. Similar phenomena was observed in the viscosity measurement of the polyester polyol, where higher viscosity was recorded for samples prepared by reacting excessive amount of phthalic acid (12.5, 15, and 20 wt %) with EPOo. Polyester polyols P1 to P3 remained as liquid while the others were in semi-solid state at room temperature.

The evaluation based on acid value, OOC, OHV, M_w, and physical appearance concluded that 10 wt % phthalic acid concentration (P3) was the optimal ratio for preparing polyester polyols with low acidity, low OOC, and moderate OHV. Besides, the liquid polyol with sufficiently high molecular weight and acceptable viscosity makes it suitable and convenient to be used in adhesive application.

Characterization of Polyester Polyol

FTIR was used to determine the functional groups of the optimal polyester polyol P3 that was synthesized by reacting EPOo with 10 wt % phthalic acid at 175°C for 5 h. The appearance of the broad OH band at 3525.95 cm^{-1} in the polyol samples was observed (Figure 3). Low OH band intensity suggested that the polyol synthesized possessed low OHV that is in agreement with the OHV determination test. Meanwhile, the disappearance of C-O epoxides at 822–840 cm^{-1} and the appearance of phthalic acid ester linkage at 1281.98 cm^{-1} indicated the occurrence of ring opening reaction.[29] Two small peaks at regions 1580–1598 cm^{-1} corresponded to the phenyl ring of phthalate were noted.[30]

^{1}H-NMR and ^{13}C-NMR was used to elucidate the molecular structure of the polyol. Comparison was done between the ^{1}H-NMR spectrum of EPOo with polyester polyol P3 (Figure 4). In both spectra, proton of *sn-1,3* and *sn-2* of glycerol were observed at peak 5 (4.00–4.30 ppm) and peak 6 (5.23 ppm), respectively. The highest peak, peak 2 (1.00–1.30 ppm) was corresponded to the CH_2 proton in the fatty acid moiety. Triplet
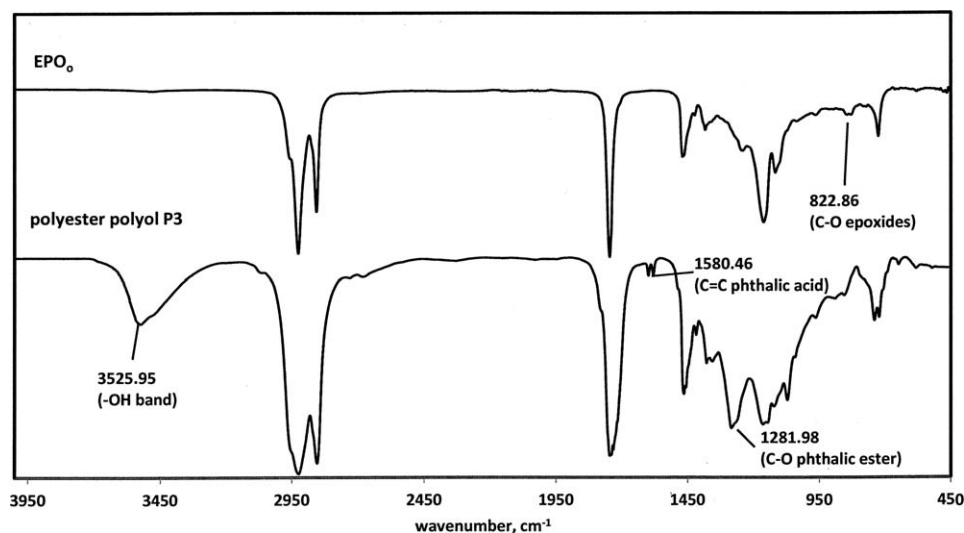
Figure 3. FTIR of EPOo and polyester polyol P3. P3—10 wt % phthalic acid reacted with EPOo at 175°C.

observed at peak 1 (0.70–0.80 ppm) which was corresponded to terminal CH_3 proton of the fatty acids structure.[31] Methylene carbon at α position to triacylglycerol carbonyl was assigned to peak 4 (2.25 ppm), whereas β-methylene carbon was assigned

Figure 4. ^{1}H-NMR spectra of EPOo and polyester polyol P3.

to peak 3 at 1.61 ppm. The epoxy ring (peak 8; 2.87 ppm) and methylene proton adjacent to epoxy ring (peak 7; 1.47 ppm) were observed in EPOo and P3 polyol samples indicated the presence of unreacted epoxides in polyol samples (OOC = 0.36%).[32] For P3 polyol, peak 11 (3.65 ppm) was assigned to methane proton attached to hydroxyl carbon indicated the presence of hydroxyl bond, whereas the multiplet at peak 9 (7.53–7.73 ppm) was assigned to the phenyl ring of phthalate.
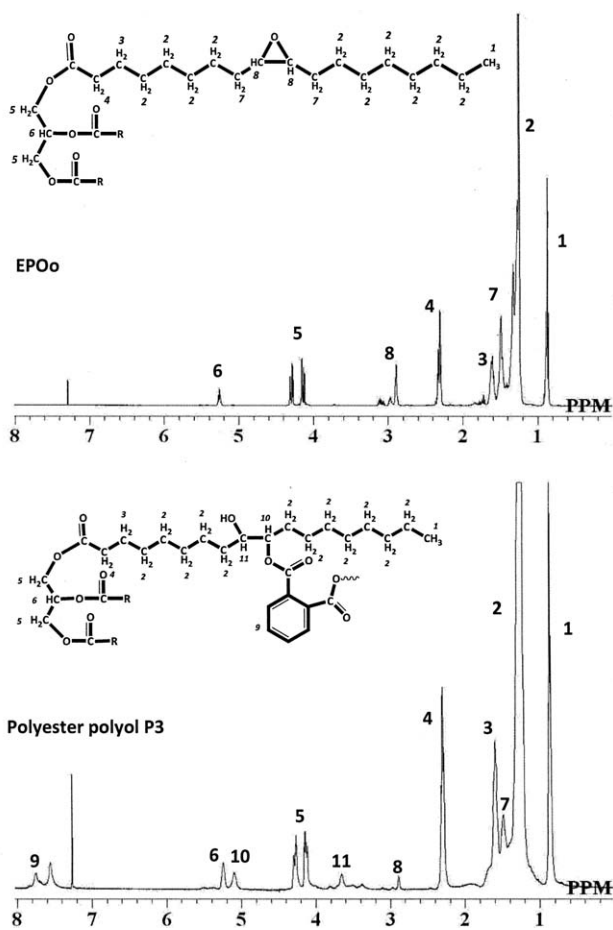
^{13}C-NMR spectra of EPOo and P3 polyol are shown in Figure 5. For EPOo, carbon attached to epoxy ring was assigned to peak 8 at 54.26 and 57.08 ppm.[32] Methylene carbon adjacent to epoxy ring was assigned to peak 7 (28–29 ppm). As for P3 polyol, decrement of relative height of epoxy ring and methylene carbon adjacent to epoxy ring indicated that the epoxy ring had reacted with phthalic acid. However, the reaction was not complete as weak epoxy peaks were still detected. Peak of carbon attached to hydroxyl group at peak 12 (74.06 ppm)[33] and carbon attached to ester linkage at peak 13 (79.00 ppm) indicated the formation of ester linkage resulted from ring opening reaction. Peak 15 at 168.00 ppm was assigned to the carbonyl bonding from the phthalic acid. Multiplet at region 125–130 ppm (peak 14) was corresponded to the phthalic acid aromatic ring. Peaks of fatty acid moieties remained unchanged throughout the ring opening reaction. Terminal CH_3 was assigned to peak 1 (13.95 ppm) and methylene carbons from fatty acid moieties were assigned to peak 3 (29–30 ppm). Peak 2 (22.64 ppm) and peak 6 (31.87 ppm) were assigned to the methylene carbon at both α and β positions of the terminal CH_3 carbon. Meanwhile, methylene carbon at α position to triacylglycerol carbonyl was assigned to signal resonated at 34.16 ppm (peak 5), whereas β-methylene carbon was assigned to signal at 25.29 ppm (peak 4). Carbon at sn-1,3 positions in glycerol backbone was assigned to peak 9 at 68.88 ppm, whereas carbon at sn-2 position was assigned to peak 10 at 62.02 ppm. Carbonyl carbon from the fatty acid moieties was resolved in 172–173 ppm (peak 11).
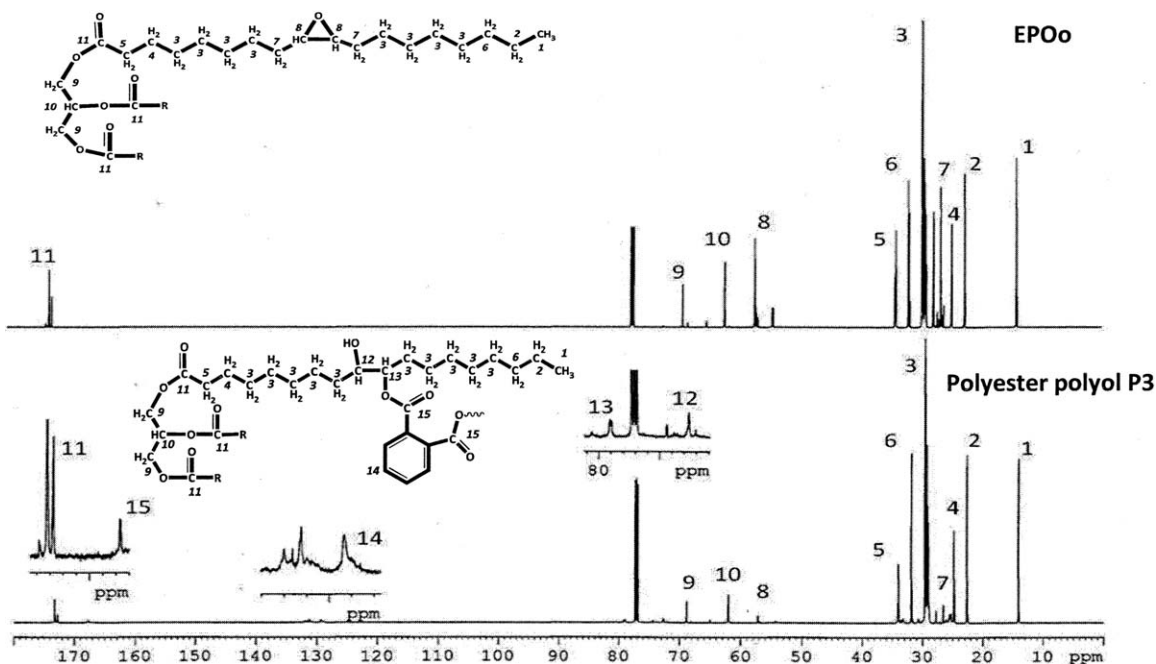
Figure 5. ^{13}C-NMR Spectra of EPOo and polyester polyol P3.

Comparison of Polyurethane Adhesives Prepared from Palm-Oil-Based Polyester Polyol with Commercial Wood-bonding Adhesives

The palm oil-based polyester polyol with secondary hydroxyl groups gave sufficient gel time to the PU adhesives. Formulation based on alteration of various amount of cross-linker, NCO/OH ratio and gel time had been carried out to obtain an optimal formulation for PU adhesives preparation. The PU adhesives were prepared by reacting polyester polyol P3 and 3 wt % glycerol cross-linker with pMDI (NCO content = 31%) at NCO/OH ratio of 1.3. The mechanical strength of PU adhesives were compared with two commercially available wood bonding adhesive, i.e. Titebond^{TM} and Weldbond^{TM}. The lap shear strength of the PU adhesives (5.3 MPa) showed two folds stronger as compared to the commercial adhesives. The locus of failure for wood specimens bonded by PU adhesives was observed as substrate failure, whereas the locus of failure for specimens bonded by Titebond^{TM} and Weldbond^{TM} were cohesive failure plus adhesive failure. This indicated that PU adhesives prepared from the newly synthesized polyester polyol not only possessed strong adhesion force with wood specimens, but also demonstrating a strong adhesive matrices thus causing the wood specimens to break during the lap shear strength test.

CONCLUSIONS

Liquid-based polyester polyol with low viscosity was synthesized by reacting EPOo with phthalic acid in noncatalyzed and solvent-free condition. The optimal weight ratio of EPOo to phthalic acid was determined as 9 : 1 at the optimal reaction temperature of 175°C for 5 h. The synthesized polyol with high molecular weight and low hydroxyl functionality has potential to be used in wood adhesive applications. This is mainly because of its good spreadability on wood surface, strong lap shear strength, and low gel time ($\sim$90 min) that are suitable to be used for adhering large wood surfaces with a longer work life.

REFERENCES

1. Jean-Pierre, L. D. I.; Amar, M.; Manjusri, M.; Lawrence, D. Biobased Polyurethanes and their Composites, Natural Fibers, Biopolymers, and Biocomposites; CRC Press: New York, **2005**.

2. Lligadas, G.; Ronda, J. C.; Galià, M.; Cádiz, V. *Polym.* **2010**, *2*, 440.

3. Lee, C. S.; Ooi, T. L.; Chuah, C. H.; Ahmad, S. *J. Am. Oil Chem. Soc.* **2007**, *84*, 1161.

4. Somani, K. P.; Kansara, S. S.; Patel, N. K.; Rakshit, A. K. *Int. J. Adhes. Adhes.* **2003**, *23*, 269.

5. Choi, S. W.; Seo, D. W.; Lim, Y. D.; Jeong, Y. G.; Mollah, M. S. I.; Park, H.; Tae, W. H.; Whan, G. K. *J. Appl. Polym. Sci.* **2011**, *121*, 764.

6. Badri, K. H.; Ujar, A. H.; Othman, Z.; Sahaldin, F. H. *J. Appl. Polym. Sci.* **2006**, *100*, 1759.

7. Petrović, Z. S. *Polym. Rev.* **2008**, *48*, 109.

8. Kong, X.; Liu, G.; Curtis, J. M. *Int. J. Adhes. Adhes.* **2011**, *31*, 559.

9. Carlson, K.; Chaudhry, A.; Bagby, M. *J. Am. Oil Chem. Soc.* **1990**, *67*, 438.

10. Trân, N. B.; Vialle, J.; Pham, Q. T. *Polymer* **1997**, *38*, 2467.

11. Tran, P.; Graiver, D.; Narayan, R. *J. Am. Oil Chem. Soc.* **2005**, *82*, 653.

12. Guo, A.; Demydov, D.; Zhang, W.; Petrovic, Z. S. *J. Polym. Environ.* **2002**, *10*, 49.

13. Petrović, Z. S.; Guo, A.; Javni, I.; Cvetković, I.; Hong, D. P. *Polym. Int.* **2008**, *57*, 275.

14. Petrović, Z. S.; Zhang, W.; Javni, I. *Biomacromolecules* **2005**, *6*, 713.

15. Lin, B.; Yang, L.; Dai, H.; Yi, A. *J. Am. Oil Chem. Soc.* **2008**, *85*, 113.

16. Guo, A.; Cho, Y.; Petrović, Z. S. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 3900.

17. Guo, Y.; Hardesty, J.; Mannari, V.; Massingill, J. *J. Am. Oil Chem. Soc.* **2007**, *84*, 929.

18. Ionescu, M. Chemistry and Technology of Polyols for Polyurethanes; Rapra Technology Limited: *Shropshire*, **2005**.

19. Descroches, M.; Escouviois, M.; Auvergene, R.; Caillol, S.; Bouvin, B. *Polym. Rev.* **2012**, *52*, 38.

20. Petrović, Z. S.; Cvetković, I.; Hong, D.; Wan, X.; Zhang, W.; Abraham, T.; Malsam, J. *J. Appl. Polym. Sci.* **2008**, *108*, 1184.

21. Sandip, D. D.; Jigar, V. P.; Vijay, K. S. *Int. J. Adhes. Adhes.* **2003**, *23*, 393.

22. ASTM D906. 1998.

23. Malinovski, M. S. Epoxides and their Derivatives; Daniel *Davey* & Co Inc: New York, **1965**.

24. Blank, W.; He, Z.A.; Picci, M.*J. Coating Technol.* **2002**, *74*, 33.

25. Boquillon, N.; Fringant, C. *Polymer* **2000**, *41*, 8603.

26. Gürtler, C.; Danielmeier, K. *Tetrahedron Lett.* **2004**, *45*, 2515.

27. Gunstone, F. D.; Harwood, J. L.; Dijkstra, A. J. The Lipid Handbook, 3rd ed.; CRC Press: New York, **2007**.

28. Guo, R.; Ma, C.; Sun, S.; Ma, Y. *J. Am. Oil Chem. Soc.* **2011**, *88*, 517.

29. Adhvaryu, A.; Erhan, S. Z. *Ind. Crop. Prod.* **2002**, *15*, 247.

30. Ismail, E. A.; Motawie, A. M.; Sadek, E. M. *Egypt. J. Pet.* **2011**, *20*, 1.

31. Miao, S.; Zhang, S.; Su, Z.; Wang, P. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 243.

32. Chandu, S.; Madankar, S.; Ajay, K. D.; Naik, S. N. *Ind. Crop. Prod.* **2013**, *44*, 139.

33. Souza, V.; Silva, S.; Ramos, L.; Zawadzki, S. *J. Am. Oil Chem. Soc.* **2012**, *89*, 1723.