



Modified Palm Oil for Polyurethane Laminating Adhesives Used in Flexible Packaging Application

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Abstract

Starting from palm oil, as bio-based platform, polyurethane laminating adhesive was successfully prepared. Initially, the palm oil was epoxidized using formic acid and hydrogen peroxide. The degree of epoxidation was controlled by governing the reaction time. Then, the ring opening was carried out by diethylene glycol to obtain the corresponding polyols. The resultant polyol was incorporated in polyurethane prepolymer and then the laminating adhesive was formulated using the prepared polyurethane prepolymer and a suitable commercial polyol. The epoxidation and ring opening processes were monitored by ATR-FTIR in addition to iodine and oxirane oxygen content (OOC%). The effect of the degree of epoxidation of palm oil on the hydroxyl values and hence the performance of palm oil polyol as ingredient in laminating adhesive was carefully investigated. The peel strength results show enhancing of the adhesion performance as the degree of epoxidation increase.

Keywords: laminating adhesives, polyurethane, palm oil, bio-based materials.

1. Introduction

Laminating adhesives are widely spread in plastics, paper, foil laminates[1–3]. Based on their superior properties, polyurethane laminating adhesives are currently the most type used in flexible packaging[3, 4]. These unique characteristics include good peel strength, adhesion, heat seal strength and resistance to aggressive filling conditions. The polyurethane laminating adhesives can be one or two component systems. In two component system, the polyurethane prepolymer as one component is typically an isocyanate-terminated polymer prepared by reaction of diisocyanate and suitable polyether or polyester polyol[5–8]. The polyurethane prepolymer is mixed in a predetermined ratio with the second component which consists of a suitable polyol directly before applying on plastic or foil substrate and then laminated to the second substrate.

Generally, these kinds of adhesives are based on nonrenewable resources generated from crude oil. Both the limited availability and environmental concerns of petrochemicals motivated researchers from all over the world to do potential effort for finding the renewable alternatives[9–15]. Nowadays, some polymeric materials including laminating adhesives are based totally or partially on bio-based materials. Particularly, vegetable oils are considered as one of the promising renewable resources widely used in many applications[5, 7, 16, 17].

Palm oil as one of these vegetable oils is produced largely and accounted for one-third of vegetable oil production[18]. It is mainly used in food products to substitute natural butter in addition to other non-food products such as personal care, cleaning products and recently in polyurethane applications[19–25]. Also, reasonable amounts of

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palm oil are converted to biofuels[26]. The palm oil as triglyceride is chemically composed of approximately 50 % saturated fatty acids and the rest is unsaturated fatty acids[18].

Introducing of palm oil in polyurethane products such as foams and adhesives attracted the interest of many researchers[27–29]. Converting palm oil into suitable polyol by chemical modification is carried out and considered a critical issue as every application needs polyol with different criteria. Basically, the chemical modification includes epoxidation of the unsaturated fatty acids followed by ring opening using convenient alcohol or glycol[30–32].

In this work, the chemically modified palm oil as alternative renewable polyol was prepared and applied in polyurethane laminating adhesives. The structure of bio-based polyols as well as the properties of laminating adhesives was thoroughly investigated.

2. Experimental

2.1. Materials

Palm oil (PO) was supplied by Oil Tec Egypt. Formic acid, 97.5% and Hydrogen Peroxide 30% were purchased from Diachem Chemicals. Mixture of 4,4'- diphenyl methane diisocyanate and 2,4'- diphenyl methane diisocyanate (MDI-50), Diethylene glycol, dibutyltindilaurate (95%), glacial acetic acid, hydrobromic acid, and Sulfuric Acid 95-97% were obtained from Merck. Other solvents and salts were supplied by local source. Eglyol-110 and Polypropylene films with thickness 20 μm used as adhesive substrates were a gift from Eglypolymers for chemical industries.

2.2. Characterization

ATR-FTIR spectra were recorded by JASCO instrument. Samples were scanned at a resolution of 8 cm^{-1} over a wavenumber range of 600–4000 cm^{-1} . The transmittance of laminated films was measured using UV-Vis spectrophotometer (JASCO V630). Viscosity of prepared polyol and polyurethane prepolymers was measured by Anton Paar viscometer (ViscoQC 100) using proper spindle. The OH value and NCO % were determined according to ASTM-D4274 and ASTM-D5155, respectively. Iodine value was measured using Wij's method according to ASTM-1959 and the oxirane oxygen content (OOC) was determined according

to ASTM-1652 by direct titration method using hydrobromic acid solution in glacial acetic acid. The peel test 180° was carried out for peel strength measurement according to ASTM F904. Gel content of the prepared laminating adhesives were determined by Soxhlet extraction of fully cured samples using THF as eluent and calculated using the following equation:

$$\text{Gel content \%} = (W_f/W_s) \times 100$$

Where W_f is the weight of the dried sample after extraction and W_s is the initial weight of the laminating adhesive sample.

Pot life of the laminating adhesives was determined as time required for the duplication of initial viscosity.

2.3. Epoxidation of palm oil

Epoxidized Palm oil (EPO) was synthesized as previously described[25] using constant molar ratio PO:HCOOH: H_2O_2 (1:3:5). In brief, the reaction was carried out in three-necked flask under magnetic stirring at constant temperature (50 °C). The flask was equipped with thermometer, dropping funnel, and reflux condenser. The hydrogen peroxide was gradually added into the reaction mixture using the dropping funnel. The in situ generated peroxy acid causes the epoxidation to the double bond of fatty acids. After certain time (30, 60, 120 min) the reaction was terminated and the reaction mixture was thoroughly washed with sodium bicarbonate (3 wt%) and distilled water (3X). then, the sample was dried under vacuum overnight at 50 °C. The prepared sample was then analyzed for iodine value and oxirane oxygen content (OOC).

2.4. Ring opening of epoxidized oil

The prepared epoxidized palm oil (EPO) was charged into three-necked round flask equipped with thermometer and condenser then diethylene glycol (DEG) was added at molar ratio (EPO : DEG) of 1:4. The reaction was catalyzed by sulfuric acid (0.5 % based on the weight of EPO) and kept for 4 hours at 70 °C. By the end of reaction the mixture washed several times with sodium bicarbonate solution (3%) and then with brine solution (5X) before drying of sodium sulfate. later, the samples were dried overnight under vacuum at 60 °C. Then samples were evaluated by measuring their OOC, OH values, and viscosity.

2.5. Prepolymer preparation

The prepared palm oil polyol was used to synthesize prepolymer-terminated NCO. Where, 80g of palm oil polyol was mechanically mixed at 70°C

with 100g of diisocyanates MDI-50 (IEW)=127). The NCO% was monitored by titration according to ASTM D5155 every hour till becomes stable.

2.6. Lamination process

Lamination between the two PP films was carried out by mixing the synthesized prepolymer as component A and the commercial polyol (Egyol110) as component B in proper ratio (NCO:OH, 1.05:1). Then, the prepared adhesive was poured onto the PP substrate surface and was spread by hand coater to obtain thickness of about 10 μm (wet film). After that, the other PP film was placed on top of the adhesive layer and rubber roller was rolled over the laminated films many times to confirm the adhesion of the laminated films.

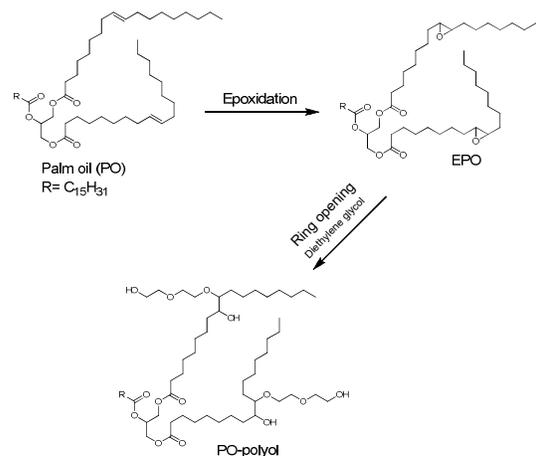
2.7. Adhesion properties

The bond strength of laminated films was evaluated according to ASTM-F904. The specimen was cut from laminated films in certain dimension (2.5 x 15cm). The peel test 180° was performed for the laminated films after 8 hours from the lamination process and the peel speed was set at 200 mm/min. The average load required to separate the laminated was recorded and expressed as the bond strength in (N/20mm). The measurement was taken as average for five samples.

3. Results and Discussion

3.1. Epoxidation of palm oil

The epoxidation reaction of palm oil is illustrated in scheme 1. It was carried out successfully as indicated from ATR-FTIR spectra where the band of oxirane was appeared in epoxidized palm oil (EPO) samples at around 820 cm^{-1} (Figure 1). Additionally, iodine and OOC values measurements (table 1) confirmed the epoxidation reaction. It is important to state that palm oil composed of around 50% palmitic acid which is saturated, 40% oleic acid, and 10% linoleic acid.



Scheme 1: epoxidation reaction of palm oil (oleic acid is taken as major unsaturated fatty acid)

Only oleic and linoleic acids as unsaturated acids represent the active sites for the epoxidation process. After treatment of palm oil with epoxidation reagent the double bond was converted to oxirane ring. Chemically, the epoxidation reaction is based on generation of in situ peroxy acid (in this work, by reaction of formic acid and hydrogen peroxide as oxygen donor) which unstable and chemically bonded to the double bond of the palm oil forming the oxirane ring in addition to the starting acid. Based on literature [31], formic acid: hydrogenperoxide: double bond ratio is suggested to be 0.5:1.5:1. Obviously, time of reaction is a critical factor in controlling the epoxidation degree. Based on reaction time, three different samples of EPO were obtained (see table 1). Iodine and the OOC values confirm the oxidation of double bonds in the unsaturated chains into oxirane ring that is suitable for polyol formation. Clearly, the epoxidation reaction time has potential impact on the reaction progress where the iodine values, as an indicator of double bond content, decreased gradually by increasing the reaction time. Similarly, the oxirane oxygen content (OOC) increased gradually by increasing the time of reaction. Table 1 summarizes the effect of reaction time on the epoxidation and other physicochemical properties.

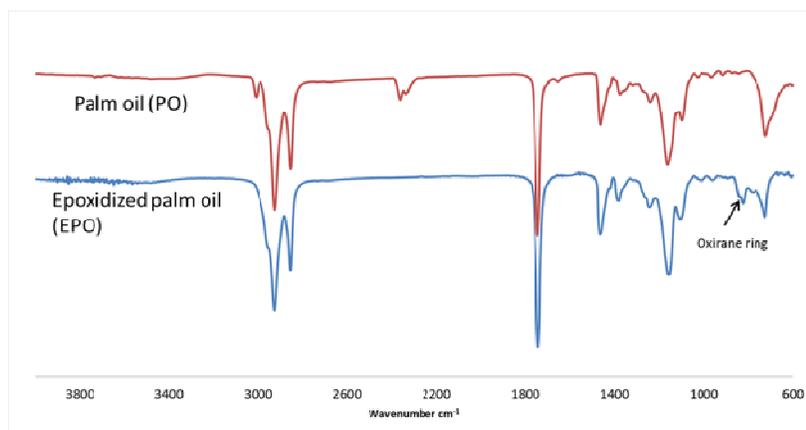


Figure 1: ATR-FTIR spectra of palm oil and epoxidized palm oil (EPO300)

Table 1
physicochemical properties of epoxidized palm oil (EPO)

sample	Reaction time (min)	Iodine value (g/100g oil)	OOC %	Viscosity mPas@25 °C	Density g/cm ³
PO	---	56	---	80	0.885
EPO100	30	11	2.1	100	0.891
EPO200	60	5.2	3.0	150	0.901
EPO300	120	4.9	3.5	170	0.921

*OOC: oxirane oxygen content

3.2. Ring opening of epoxidized palm oil

The ring opening of EPO was carried out using diethylene glycol in the presence of sulfuric acid as catalyst (Scheme 1). The three samples with different degree of epoxidation were treated with the glycol to obtain different hydroxyl values.

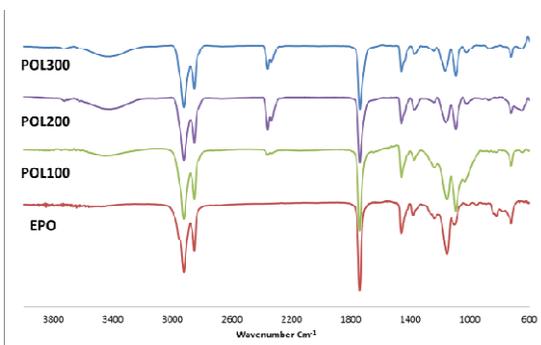


Figure 2: ATR-FTIR spectra of palm oil polyol after ring opening process.

ATR-FTIR spectra confirm the ring opening of oxirane ring where a new band appeared at 3500-3330 cm⁻¹ which ascribed to the stretching mode of OH bond (Figure 2). Additionally, a decrease in oxirane ring peak intensity at 840 cm⁻¹ was observed. Additionally, the hydroxyl value was determined chemically by indirect titration according to ASTM-4274 and their values in addition to hydroxyl equivalent weight (HEW) are tabulated in table 2.

Table 2
physicochemical properties of polyol prepared from EPO

Polyol	Starting EPO	OH value	OOC%	HEW*	Viscosity (mPas**)
POL100	EPO100	75	0.42	748	900
POL200	EPO200	110	0.53	510	1100
POL300	EPO300	150	0.61	374	1500

*HEW=56100/OH value ** measured at 25°C

3.3. Prepolymer and laminating adhesive preparation

The corresponding prepolymers are prepared by mixing the MDI-50 and the prepared palm oil polyol (see table 3). It is worth mentioning that, a constant weight of polyol having different OH value had been used. As a result, the measured NCO % values of the prepared prepolymers are different as the used polyols have distinct OH values. Where the prepolymer (PRE100) has the highest NCO% due to the low OH value of the contributed polyol (OH=75). The NCO% and the isocyanate equivalent weight (IEW) in addition to the viscosity of the prepared prepolymers are stated in table 3.

Table 3
properties of the synthesized prepolymer based on PO polyol

Prepolymer	Starting PO-Polyol	NCO %	IEW	Viscosity mPas@25 °C
PRE100	POL100	18	233	1350
PRE200	POL200	13	323	1850
PRE300	POL300	10.5	400	2200

The corresponding laminating adhesives were prepared using a commercial polyether polyol (Egyol110, OH =110) as a second component.

The NCO: OH mixing ratio was 1.05:1 to guarantee the complete utilization of hydroxyl groups and hence full crosslinking. After preparation of laminated films the peel test was conducted to study the effect of epoxidation degree on the performance of laminated adhesives. Obviously, the laminated adhesive containing prepolymer with higher NCO % (PRE100), based on polyol with lower OH value, shows the less bond strength (2.5 N/20mm as tabulated in table 4). This observation could be explained by the presence of inactive chains inside the adhesive that weaken the bond. On the other side, laminated adhesives containing prepolymer with less NCO% (PER300) have the higher bond strength value (5.6 N/20mm). In addition, the pot life (time needed for duplication of initial viscosity) is another evidence for the presence of inactive alkyl long chains where the pot life of laminated adhesives is proportional to the NCO% of the prepolymer.

Table 4 properties of the laminating adhesives prepared using the bio-based prepolymer

Prepolymer (component A)	NCO %	Component B	Pot life (min)	Gel content	Transmittance %	Peel strength (N/20mm)
PRE100	18	Egyol110	56	93	99	2.5
PRE200	13	Egyol110	50	97	98	4.1
PRE300	10.5	Egyol110	35	99	99	5.6

4. Conclusions

Three types of polyol based on palm oil as renewable resource were prepared successfully and applied in polyurethane laminating adhesives. The degree of epoxidation was controlled to obtain polyol with different OH values. Incorporating such bio-based polyol in isocyanate prepolymer and subsequently in the laminating adhesive was studied in terms of physical and chemical properties. Interestingly, increasing the degree of epoxidation led to higher OH value and hence higher crosslinking density when incorporated in polyurethane laminating adhesive. Additionally, the peel strength measurements confirm the deteriorated effect of unepoxidized chains in palm oil that reduce the crosslinking density and increase the plasticization effect.

5. Conflicts of interest

There are no conflicts to declare.

6. Acknowledgments

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