



Soybean Oil-based Polyol as a Modified Natural Binder for Polyurethane Turf-adhesive

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Abstract

Polyurethane turf adhesive is a two-component system formed by reacting diisocyanate and petroleum-based polyether polyol. This polyol can be replaced by soybean oil as one of the main economical and common oils. In this article, soybean oil was epoxidized followed by oxirane ring-opening in the presence of methyl alcohol and orthophosphoric acid as a catalyst in order to create hydroxyl groups in the soybean oil which are responsible for reaction with the diisocyanate molecules. The epoxidation step was confirmed by ATR-FTIR spectroscopy and iodine value measurements. Iodine value was decreased from 135.6 g/100 g of neat soybean oil to be 5.98 g/100 g of epoxidized soybean oil. In addition, the effect of orthophosphoric acid contents (0.6%, 0.8%, 1.0%, 1.2%) on the ring-opening steps was investigated, considering the same reaction time, the same alcohol concentration and constant temperature. Successful oxirane ring-opening was confirmed by oxirane oxygen content (OOC) values which were decreased from 6.72% to 2.93%, 1.45%, 0.60% & 0.04% respectively. Hydroxyl value of oil-based polyols (OHV) were increased from 131, 180, 208 & 229 mg KOH/g respectively. Meanwhile, ATR-FTIR showed disappearance of the oxirane rings and appearance of hydroxyl groups as indication of polyol formation in the four samples. The four polyol samples were applied as modified natural binders in polyurethane turf adhesive formulations and showed comparable results against the standard and commercially used product SubFix 411.

Keywords: Polyurethane, Turf adhesive, Soybean oil, Epoxidation, Polyol, Oxirane ring-opening, Orthophosphoric acid

Introduction

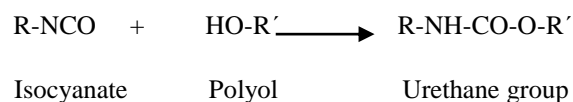
Artificial turf is a surface of synthetic fibers made to look like the natural grass. It should undergo good abrasion resistance, uniformity and lower maintenance management. It is most often used in landscape and athletic applications that are normally played on grass.

Polyurethane has a wide range of products which satisfy the architectural, building, construction, rigid foam, flexible foam, coatings, adhesives, sealants and elastomers industries ^[i, ii]. Turf adhesive is a two-component solvent-free polyurethane based material designed to provide superior bonds of synthetic turf during sports installations. The adhesive must give a flexible rubbery characteristic in adverse weather conditions like resistance to water, moisture and corrosive materials ^[iii].

The mechanical and thermal properties of polyurethanes depend on its chain structure and

cross-linking, which are affected by the hydroxyl value (OHV) of the polyols.

Polyols and diisocyanates are the principal raw materials used in synthesis of polyurethanes (chemical equation 1) ^[iv]. Polyols are polyether or polyester polyhydroxy compounds that reinforce special properties for the created polyurethane products ^[v, vi].



The production of polyols from petrochemicals is costly, requires great energy and also has adverse effects on the environment, which accordingly is related to the cost of polyurethane products ^[vii]. Meanwhile, the availability of natural vegetable oils

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is practically unlimited, eco-friendly and economically significant [viii, ix].

Chemical structures of vegetable oils are characterized by their fatty acid compositions. It contains two major functional moieties, carbon-carbon double bonds and ester linkages and do not contain hydroxyl groups with the exception of castor and lesquerella oils [x].

Starting from one of these two functional moieties, almost all synthetic routes for vegetable oil polyols production include epoxidation followed by oxirane ring-opening, hydroformylation followed by hydrogenation, ozonolysis, thiol-ene coupling, transesterification, or amidation [xi].

Depending on the number of carbon-carbon double bonds, epoxidation can be carried out to form oxirane rings with versatile oxirane oxygen content values (OOC) [xii, xiii]. The oxirane ring is a favor for nucleophilic attack [xiv] and hence, the additional hydroxyl group via ring-opening reaction can be attached to an aliphatic fatty acid chain using a broad range of active hydrogen-containing compounds such as alcohols, inorganic and organic acids, amines, water, and hydrogen forming the oil polyol [xv, xvi].

Soybean oil has a relatively medium iodine value (I.V) from 123-139 which is related to the degree of unsaturation [xvii]. It can be modified to form epoxidized soybean oil (ESBO) then a variety of chemical modifications are possible through the reactive oxirane functionality. The reaction of alcohol with ESBO produces polyols, depending upon the oxirane contents.

The content of hydroxyl groups in polyols is expressed as hydroxyl value (OHV). Conversion from oxirane rings to hydroxyl groups may be partially or completely which decide well the final hydroxyl value of soybean oil-based polyols. Soybean oil-based polyols may have different hydroxyl values according to the reagent and catalyst used in the ring-opening reaction [xviii].

In this article, we focused on preparation of polyurethane turf adhesive from soybean oil-based polyols. We also reported the effect of orthophosphoric acid, which is a weak acid that catalyzes, on the ring-opening hydrolysis of ESBO [xix].

Experimental

Materials:

RBD Soybean oil (Refined, Bleached, Deodorized) was supplied by Oil Tec Egypt. Glacial Acetic Acid 99.8% from LOBA CHEMIE PVT. LTD., Hydrogen Peroxide 30% H₂O₂ from Diachem Chemicals, Sulfuric Acid 95-97% from Merck KGaA Germany, Methanol from local source, Orthophosphoric acid 85% from S D Fine-Chem Limited, calcium carbonate from Green Egypt Group, EgyDisp 2000

(polymeric hyperdispersant) and SubFix 411 A&B (it is a commercial two-components polyurethane turf adhesive) from Egy Polymers for Chemicals. Component A consists of petroleum-based polyether polyol, and component B consists of MDI (a mixture of 4,4'- diphenyl methane diisocyanate and 2,4'-diphenyl methane diisocyanate).

Characterization:

- Iodine value (I.V) in grams of iodine per 100g of oil, was determined using the Wij's method according to ASTM D 1959-97 Standard Test Method for Iodine Value of Drying Oils and Fatty Acids.
- Oxirane oxygen content (OOC) was measured by the direct titration method using hydrobromic acid solution in glacial acetic acid and calculated according to ASTM D1652-11.
- Hydroxyl Value of Oil-based polyols (OHVs) were determined following ASTM D1957-86. This test method determines the total amount of residual hydroxyl groups present in oils and other fatty acid-containing materials. The hydroxyl value is expressed as milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of the oil.
- Viscosity was measured @ 25°C using The Brookfield Dial Viscometer.
- Density was measured @ 20°C using Stainless Steel Liquid Pycnometer.
- Attenuated Total Reflection – Fourier Transform Infrared spectroscopy (ATR-FTIR) was recorded on JASCO instrument. Samples were scanned at resolution of 4 cm⁻¹ over a wavenumber range of 600-4000 cm⁻¹.
- Isocyanate content (NCO%) was measured according to ASTM D2572 - 19. This test method covers the determination of the isocyanate group (NCO) content of a urethane intermediate or pre-polymer. The urethane pre-polymer is allowed to react with an excess of di-n-butylamine in toluene (Note 1). After the reaction is complete, the excess of di-n-butylamine is determined by back titration with standard hydrochloric acid.
- Seam strength was measured according to peel (Method 2) BS EN 12228:2013. It describes a procedure for reinforced butt joints in which a peel force is applied.
- Open time is referring to the curing time of turf adhesive after mixing the two components. The greater the open time value, the better the adhesive property. This value can be influenced by the ambient conditions. Using of a plastic cup, the prepared component A was mixed with the commercial product SubFix 411B at (w/w) ratio of 7:1 and compared to the commercial

product SubFix 411 A & B. At almost NCO% = 0, the time was recorded for all polyurethane prepared samples.

- Green strength, handling strength or initial tack time is referring the time that the processed adhesive takes to build up its initial tack at 25 N/100mm relative to the cohesive strength in the wet state which is usually considerably lower than the final ultimate adhesive bond strength.
- Full cure time or full strength time is referring to the time that the adhesive takes to build up its full and final bond strength at seam strength more than 125 N/100mm.

Methods:

Epoxidation of soybean oil and its ring-opening reaction:

The reaction system consists of a 2-L four-neck reaction flask equipped with a mechanical stirrer, a thermometer, a water cooled condenser and a dropping funnel. A heating mantle and cooling system was introduced to keep the reaction between 68 – 70°C during the epoxidation reaction.

Briefly, Soybean oil was charged into the flask followed by heating at 60°C, then a mixture of acetic acid (as an oxygen carrier on epoxidation reaction), hydrogen peroxide and concentrated sulfuric acid was added dropwise into the flask over a period of 90 min. The acetic acid : hydrogen peroxide : carbon-carbon double bonds molar ratio was equal to 0.5 : 1.5 : 1 [xx]. After addition was completed and at a slow rate of mechanical stirring, the temperature of the reaction was kept at 70°C for 3 hours. At the end of the reaction, the mixture was subjected to successive washings using distilled water around 7-8 times by using a separating funnel till acid value was < 0.5, followed by heating the solution at 100°C for 30 minutes under vacuum till water content < 0.1%.

The formed ESBO was charged into 500-ml three-neck flask then methanol was added at ESBO : methanol weight ratio 1:1.5. Different polyols were prepared by using orthophosphoric acid at different concentrations keeping the reaction temperature at

60°C for 3 hours under continuous stirring. The OOC of the sample was periodically tested during the reaction. The product was purified to remove the excess methanol and the unreacted acid by condensation followed by vacuum then washing with distilled water using a separating funnel, followed by drying.

A series of reactions with varying amounts of orthophosphoric acid were investigated, whereas the ratios were 0.6%, 0.8%, 1.0% and 1.2% (w/w) as shown in table 1.

Table 1 Concentrations of orthophosphoric acid during ring-opening

Experiment	Orthophosphoric acid conc. (w/w) %
Polyol (1)	0.60%
Polyol (2)	0.80%
Polyol (3)	1.00%
Polyol (4)	1.20%

Preparation of polyurethane turf adhesive:

The commercial polyurethane turf adhesive (SubFix 411) is a two-component system (A&B). In this research, the component A (polyether polyol) of SubFix 411 was replaced by the modified soybean oil-based polyol prepared samples of different OOC values. Component A was formulated by mixing the modified soybean oil-based polyol samples with calcium carbonate and a polymeric dispersant (EgyDisp 2000). The mixtures were vigorously mixed at 1200 rpm using high speed mixer for 30 minutes. Component B consists of MDI-50 (a mixture of 4,4'- diphenyl methane diisocyanate and 2,4'- diphenyl methane diisocyanate). The final product was obtained by mixing A & B at weight ratio w/w 7:1.

Table 2 shows the formulations of the prepared polyols used for preparation of component A against the standard product to investigate the effect of the formed soybean oil-based polyols on the properties of the polyurethane turf adhesive.

Table 2 Formulation of component A of polyurethane turf adhesive

Items	Component A1	Component A2	Component A3	Component A4
Calcium Carbonate	76	76	76	76
EgyDisp 2000	1	1	1	1
Polyol 1	23	-	-	-
Polyol 2	-	23	-	-
Polyol 3	-	-	23	-
Polyol 4	-	-	-	23
SUM	100	100	100	100

The prepared component A samples were tested against component B of the standard.

Results and Discussion

Soybean oil (figure 1) contains more than four double bonds per molecule (4.6 double bonds per molecule)^[xxi]. It showed iodine value of 135.6 g iodine /100 g of oil which can be modified partially or completely to form oxirane rings then followed by partially or completely ring-opening reaction to introduce hydroxyl groups.

After the conversion of carbon-carbon double bonds to oxirane rings, the iodine value of the modified soybean oil reached to 5.98 g iodine/100 g of oil. It

Table 3 Physico-chemical properties of soybean oil, epoxidized soybean oil and the prepared soybean oil-based polyol samples

Sample name	Iodine value g iodine /100 g of oil	OOC %	OHV# mg KOH/g	Viscosity cP @ 25°C	Density g/ml @ 20°C
Soybean oil	135.6	—	—	80	0.917
ESBO	5.98	6.72	—	325	0.988
Polyol 1	9.22	2.93	131	760	0.993
Polyol 2	9.41	1.45	180	1,440	0.999
Polyol 3	9.75	0.60	208	2,070	1.003
Polyol 4	9.88	0.04	229	2,630	1.006

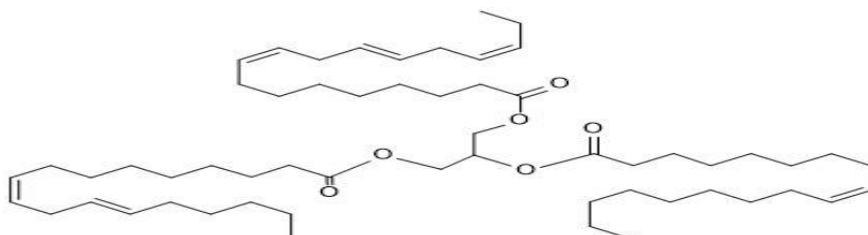
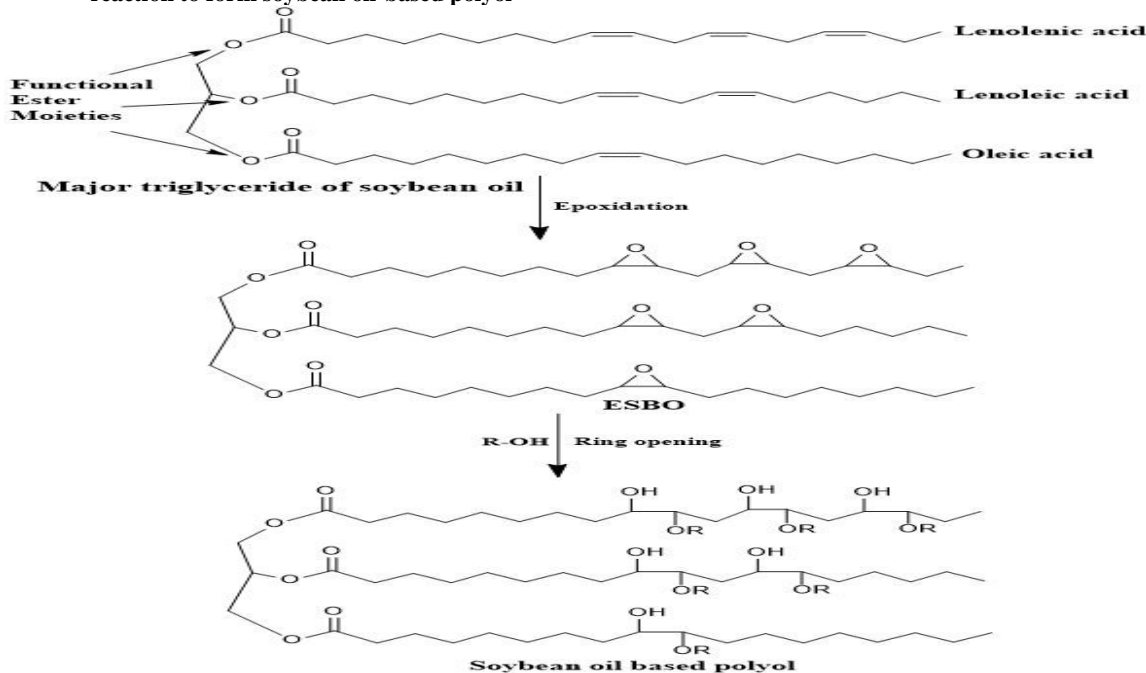


Figure 1 Chemical structure of soybean oil containing unsaturated fatty acids connected to a glycerol center
Scheme 1 Epoxidation of soybean oil and ring-opening reaction to form soybean oil-based polyol



Effect of orthophosphoric acid ratio on oxirane ring-opening reaction:

Orthophosphoric acid (OPA) is used as an acidic catalyst for the ring-opening reaction of epoxy resins. In this study, the effect of Orthophosphoric acid on the oxirane oxygen content (OOC) and oxirane ring conversion % was investigated. As shown in Table 4, it is clear that OOC and oxirane conversion were greatly affected by increasing OPA concentration in the reaction medium. The ratios of orthophosphoric acid showed a significant effect on OOC which had an effect on the characteristics of the final product. The highest concentration of orthophosphoric acid in polyol 4 led to complete ring-opening with OOC of 0.04% under the same reaction time, alcohol concentration and temperature 60°C.

The commercial product SubFix 411 A showed OHV of 162 mg KOH/g. OHV of the prepared polyol samples were shown in Table 3. Polyol 4 had the highest hydroxyl value (229 mg KOH/g) and lowest OOC% (0.04%). As OOC values decrease, the hydroxyl values increase which increases the reactivity of polyurethane reaction.

Effect of the prepared polyols on polyurethane properties:

To study the effect of the prepared polyols on the turf polyurethane adhesive, different soybean polyols were used for preparation of component A which mixed with SubFix 411B with the (w/w) ratio of 7:1 and compared to the standard product SubFix 411 A & B.

Table 4 Effect of orthophosphoric acid ratios on the OOC values and oxirane ring conversion:

Polyol	Orthophosphoric acid conc. (w/w) %	OOC values (%)	Oxirane rings conversion%
Polyol 1	0.60%	2.93	56.40%
Polyol 2	0.80%	1.45	78.42%
Polyol 3	1.00%	0.60	91.07%
Polyol 4	1.20%	0.04	99.40%

Table 5 The properties of polyurethane turf adhesive products against the standard one

Polyurethane Turf adhesive		Open time (Minutes)	Green strength time (hours)	Full Cure time (hours)
Component A	Component B			
SubFix 411A	SubFix 411B	80	2	7.5
Polyol 1	SubFix 411B	190	7	17
Polyol 2	SubFix 411B	140	6	13
Polyol 3	SubFix 411B	100	4	10
Polyol 4	SubFix 411B	85	2.5	8

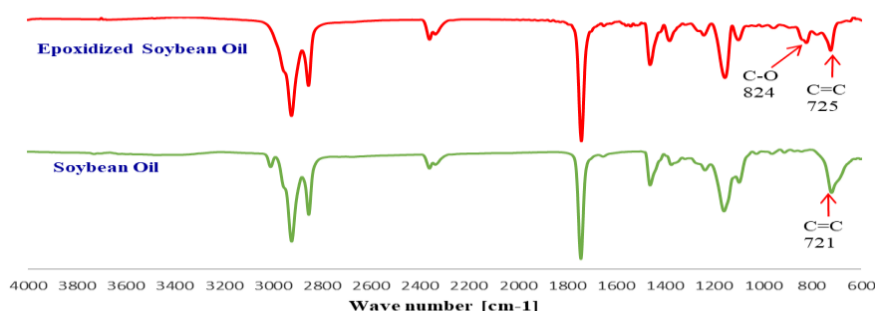


Figure 2 ATR-FTIR spectra of soybean oil and ESBO

It was noted that by decreasing OOC values and consequently increasing hydroxyl values affected positively the polyurethane turf adhesive properties that showed higher initial and final cure time and relatively higher bond strength and shorter open time.

The prepared polyurethane sample using polyol 1 showed Open time of 190 minutes, green strength time of 7 hours and full cure time of 17 hours, which may be attributed to low OHV. From the other hand, oxirane rings that was indicated by OOC of 2.93%, do not contribute in the polyurethane reaction. It

might have a plasticizing effect on the prepared sample [xxii].

The prepared polyurethane samples using polyol 2 and polyol 3 showed lower open time, green strength time and full cure time values for the same reason.

The prepared polyurethane sample using polyol 4 showed comparable results as noted from its physico-mechanical properties compared to the commercial product SubFix 411 A/B.

Attenuated total reflection - Fourier transform infrared spectroscopy (ATR-FTIR):

Figure 2 shows the FT-IR spectra of soybean oil (SBO) and epoxidized soybean oil (ESBO). It is clear that SBO has a peak at 721 cm^{-1} corresponding to carbon-carbon double bonds (C=C) meanwhile after epoxidation the peak was still present but its intensity was decreased which was confirmed by iodine value measurements. The iodine value of SBO was 135.6 g iodine / 100 g of oil, confirming the consumption of the double bonds and the formation of the ESBO.

Here, it was interesting to note the appearance of the epoxide group peak at 824 cm^{-1} which confirm the results of OOC measurement at 6.72%.

Figure 3 outlines a comparison between the prepared soybean oil-based polyols using different ratios of orthophosphoric acid starting from 0.6%, 0.8%, 1.0% to 1.2% respectively. It was noted that the formation of hydroxyl groups in all prepared samples was almost appeared at 3450 cm^{-1} . Meanwhile, the peak of epoxide group of ESBO prepared at 824 cm^{-1} was gradually diminished upon the formation of polyol 1 to polyol 4, confirming the consumption of oxirane ring by the ring-opening reaction.

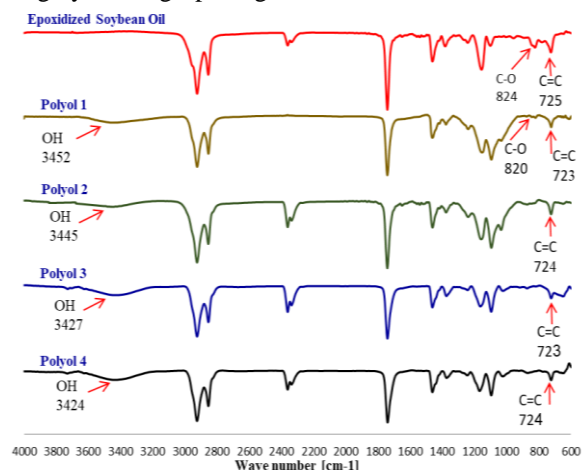


Figure 3 FT-IR spectra of ESBO and its polyol-based derivatives

These FT-IR results are consistent with OOC value measurements (Table 3). On the other hand, the intensity of OH group increased starting from polyol 1 to polyol 4 confirming the increase of hydroxyl number upon increasing OPA catalyst concentration

in the reaction medium. The intensities OH group peaks increase from polyol 1 to polyol 4.

Conclusion

Soybean oil-based polyol as a natural vegetable material from epoxidized soybean oil followed by ring opening with methanol in presence of orthophosphoric acid was successfully synthesized. It can replace petroleum-based polyols in polyurethane turf-adhesive application upon evaluating physico-mechanical and chemical properties. Higher contents of orthophosphoric acid showed complete ring-opening under the same reaction ambient conditions. Viscosities and densities of soybean oil-based polyols were increased by decreasing the OOC values. As OOC values of ESBO were decreased and hydroxyl values were increased, the polyurethane samples showed shorter full strength time and open time. This research incites the bio-based resources for the synthesis of polyols to replace the petroleum-based polyols in polyurethane turf-adhesive applications.

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