Research Article

Isocyanate Reduction by Epoxide Substitution of Alcohols for Polyurethane Bioelastomer Synthesis

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A phosphate ester-forming reaction was carried out by mixing epoxidized soybean oil with up to 1.5% o-phosphoric acid. *In situ* oligomerization took effect almost instantly producing a clear, homogeneous, highly viscous, and a low-acid product with a high average functionality. The resulting epoxide was used as a reactant for urethane bioelastomer synthesis and evaluated for rigid foam formulation. Results have shown that with a number of catalysts tested phosphoric acid significantly enhances a solvent-free oxirane ring cleavage and polymerization of the epoxidized soybean oil via phosphate-ester formation at room temperature. The resulting phosphoric acid-catalyzed epoxide-based bioelastomer showed an 80% decrease in extractable content and increased tensile strength at the same isocyanate loading relative to the noncatalyzed epoxide. The oligomerized epoxidized soybean oil materials exhibited ASTM hydroxyl values 40% less than the nonoligomerized starting material which translates to reduced isocyanate loadings in urethane applications.

1. Introduction

Polyurethane elastomers and industrial foams manufacturing rely significantly on fossil fuels and their derivatives as major reactants for the production of polyols. Nonrenewable resources are rapidly being exhausted, therefore, a growing worldwide research effort is focused on the understanding and using renewable resources to reduce dependence on petroleum-derived materials and to develop innovative technologies and competitive industrial products. Vegetable oils such as soybean oil (SBO) are increasingly replacing petroleum-derived products owing to its environment-friendly, biodegradable, and noncorrosive properties [1–3].

Although SBO-based polyols have shown promising results in the production of urethane-formulated products ranging from elastomers to flexible foams [3–5], replacement of substantial portions of polyol and isocyanate with soybean oil-derived epoxides is economically significant. SBO-derived epoxides which include epoxidized soybean oil (ESBO) and bodied ESBO are intermediates in much

of the chemistry to create soy-based polyols [4, 6–8], and so they are less expensive than many soy-based polyols. High reactivity through cleavage of the oxirane ring makes epoxides very versatile both as chemical intermediates and as end product. Epoxides are able to directly react with water to diols, with carboxylic acids to ester alcohols, and with alcohols to ether alcohols [9]. Moreover, epoxides have been reported to react with and partially displace isocyanate in urethane mixtures [6, 10, 11]; hence, urethane formulations with increased bio-based content can be developed. A multifunctional monomer containing one or more epoxide moieties may thus to some extent displace alcohol and isocyanate in the regular urethane formulation.

Phosphoric acid (o-H$_3$PO$_4$) has been extensively used in the preparation of a series of soybean oil phosphate esters for rigid polyurethanes, coatings, surfactants, and antiwear additives [1, 2, 12–15]. Guo et al. [2] reported that soy polyols having tunable hydroxyl content and phosphate ester functionality are possible by controlling the type and amount of polar solvent and phosphoric acid content added to the

reactants. The authors claimed that phosphoric acid does not only catalyze ring-opening reaction of ESBO with water but also chemically combine to become part of the polyol product. Much of the work done to produce soybean oil phosphate ester polyols used water and significant amount of polar solvents to obtain high hydroxyl functionality while keeping the final acid values low [1, 2, 14, 15].

The main objectives of this work were to (1) develop catalyst formulations to specifically promote solventless epoxide reaction in epoxide-substituted polyol (ESP) and effectively replace substantial amounts of the petroleum-based polyol and (2) develop urethane bioelastomer formulations using epoxides or ESP to reduce the total isocyanate content. Acid, hydroxyl, oxirane values, and viscosity of the epoxides or ESP were measured to evaluate the effect of o-H_3PO_4 on ring-opening hydrolysis and oligomerization of the monomers.

2. Materials

2.1. Synthesis of Epoxide-Substituted Polyol (ESP).
Ortho-H_3PO_4 85% aqueous from Fisher Scientific, ESBO (Vikoflex 7170) 7.0% oxirane from Arkema (King of Prussia, Pa, USA), polymeric methylene diphenyl diisocyanate or pMDI (PAPI 27) 31.4 wt% NCO from Dow Chemical (Midland, Mïch, USA), and castor oil (CO) from Alnor Oil (Valley Stream, NY, USA). Full epoxidized soybean oil was reacted with 0.5%–2.0% o-H_3PO_4 added dropwise in a beaker under vigorous mechanical stirring at room temperature. A homogeneous and highly viscous product is obtained after mixing for 5 min. The schematic of this reaction is shown in Figure 1. The next step was the preparation of a series of ESPs by varying the amount of epoxide (noncatalyzed or o-H_3PO_4-catalyzed ESBO) in castor oil. This was done by moderately mixing the epoxide and castor oil at room temperature until a homogeneous ESP is obtained.

2.2. Preparation of Urethane Bioelastomers.
Two types of bioelastomers were prepared: (1) ESPs using only 0.5% by weight o-H_3PO_4 with noncatalyzed ESP as control, and (2) acid-catalyzed ESBO using 0.5–1.5% by weight o-H_3PO_4 without castor oil and noncatalyzed ESBO as control. The preparation procedure of ESP bioelastomer consists of the following steps: (1) mixing 5.0 g ESP and 2.5 g pMDI in a 50 mL beaker on a hotplate equipped with stirrer (moderate stirring at room temperature was employed to obtain uniform phase and consistency and also avoid bubbles formation), (2) placing the samples in a 7 cm × 11 cm rectangular plastic mold and degassed for 10 min at 45°C vacuum oven to get rid of CO_2, air trapped, or gases evolved during reaction, and (3) postcuring samples for about 48 h at 45°C [3] in an oven with no vacuum applied. Extractability of unreacted oil phase of the finely cut samples was measured after 48 h of curing. The second type of bioelastomers was prepared the same way, but the amount of o-H_3PO_4 was varied (0.5, 1.0, 1.5%), and no alcohol source (castor oil) was added. Polymeric MDI was added at 10–30% by weight of the acid-reacted ESBO. After postcure, dumbbell-shaped specimens were cut from the bioelastomer samples using an ASTM D638 Type V cutter.

2.3. Characterization of ESPs and Bioelastomers.
Hydroxyl values of ESPs were determined according to an American Oil Chemists' Society (AOCS) Official Method Tx 1a-66 (1997). Acid numbers (mgKOH/g sample) of all reaction products were evaluated according to the AOCS official method (AOCS Te 1a-64, 1997). Epoxy content of the ESP samples was measured according to AOCS-official method (AOCS Cd 9–57, 1997). The dynamic viscosities (cP measured at 20°C) of the ESPs were determined using a Model RS100 Rheometer (Haake, Paramus, NJ, USA). The synthesized epoxides and ESPs displayed non-Newtonian behavior like many other polymer solutions as shown by their nonlinear shear stress and strain rate relationship plotted on the instrument program's data manager. Gardner color index was evaluated according to ASTM D1544-04 (Reapproved, 2010). Tensile properties of the bioelastomers were determined by a TA. HDi Texture Analyzer (Texture Technologies Corp., Scarsdale, NY, USA) following ASTM Procedure D 882-10. The test specimens were airtight sealed and conditioned at 23 ± 2°C (73.4 ± 3.6°F) and 50 ± 5% relative humidity for not less than 40 h prior to test. The initial gauge length of the sample was 7.62 mm, and the crosshead speeds were 12.5 and 50 mm/min depending on the percent elongation at break. DSC measurements were carried out on a TA Instruments (New Castle, Del, USA) DSC Q100. All DSC measurements were performed following the ASTM E 1356-08 standard. The specimens were airtightsealed prior to testing. About 10 mg of the bioelastomer samples were heated at a rate of 10°C/min from −60 to 100°C under dry nitrogen gas atmosphere.

The functional groups of the noncatalyzed and o-H_3PO_4-catalyzed ESBO bioelastomers were characterized by an attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy using Thermo Scientific Nicolet 4700 (Thermo Electron Corp., Madison, Wis, USA) equipped with Smart Detectors and multiple spectral range. The sample was pressed against an ATR diamond to have a good contact. A total of 64 scans from 4000–400 cm^{-1} wavenumber range were obtained at a resolution of 4 cm^{-1}. The functional groups present in the control bioelastomer (noncatalyzed with o-H_3PO_4), with peak intensities corresponding to the wavenumbers, were epoxy at 824 cm^{-1} (high intensity), epoxy at 920 cm^{-1} (present), phosphate ester at 1020 cm^{-1} (absent), urethane bonds at 1730 cm^{-1} (present), 2-oxazolidone at 1760 cm^{-1} (absent), NCO groups at 2280 cm^{-1} (present), and urethane bonds at 3340 cm^{-1} (high intensity). In comparison, the functionality groups present in the sample bioelastomer (catalyzed with o-H_3PO_4) were epoxy at 824 cm^{-1} (low intensity), epoxy at 920 cm^{-1} (present), phosphate ester at 1020 cm^{-1} (high intensity), urethane bonds at 1730 cm^{-1} (present), 2-oxazolidone at 1760 cm^{-1} (absent), NCO groups at 2280 cm^{-1} (present), and urethane bonds at 3340 cm^{-1} (low intensity).

The differentiation in structures of both unreacted and acid-reacted ESBO were confirmed by ^{13}C-NMR (Bruker DRX 500 MHz, CDCl$_3$). Both samples exhibited the spectra of epoxy groups present in the δ 56.9–58.5 ppm region. The unreacted ESBO was showed a slightly higher intensity in this region indicating more epoxy groups present compared with
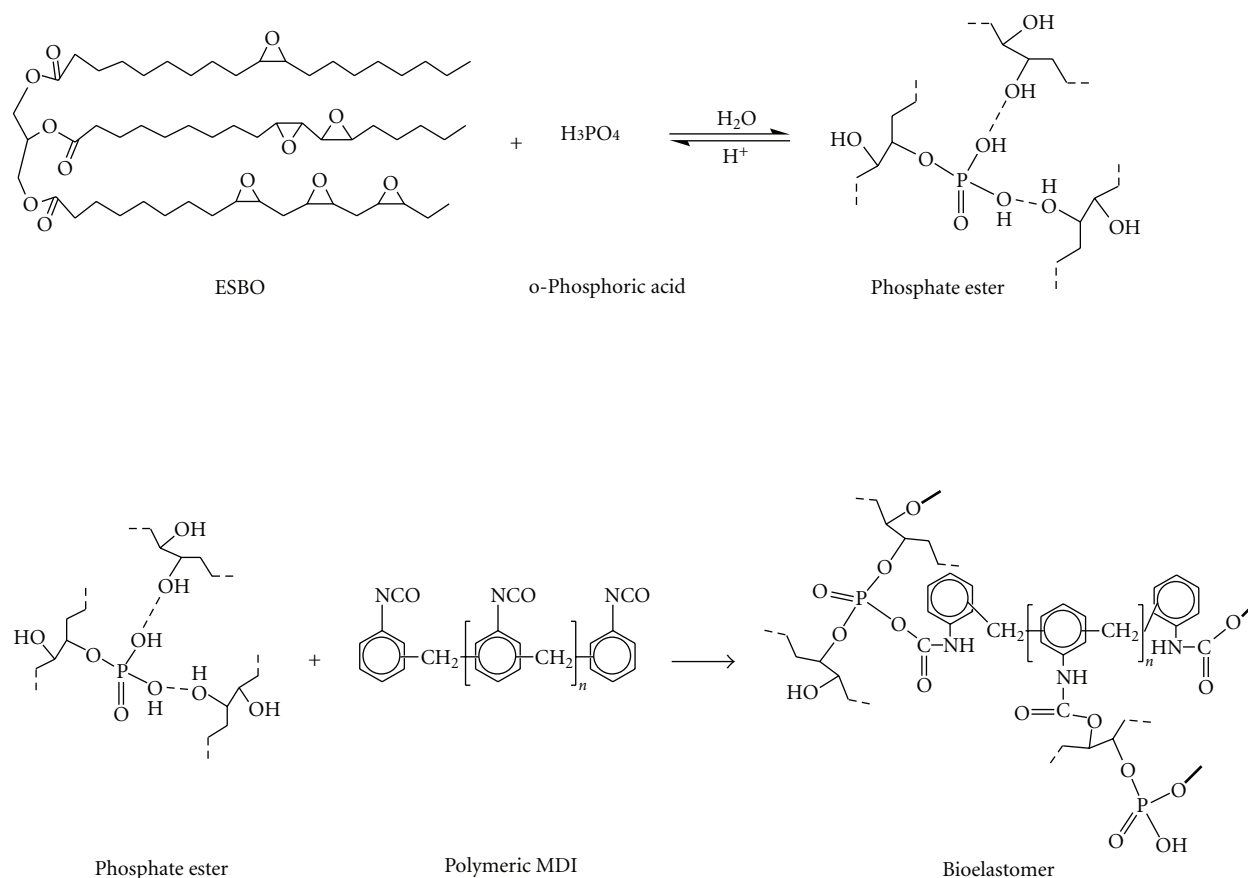
Figure 1: Overall schematic representation of phosphate ester and subsequent bioelastomer formation.

the acid-reacted sample. A ^{1}H-NMR analyses of the samples showed no significant difference in chemical shifts.

2.4. Extractability Test and Catalyst Evaluation. A single-step unreacted oil-phase extraction method was used to determine the extent of polymer cross-linking between pMDI and ESP. Polymeric MDI and the sample ESP were well mixed in a small disposable aluminum pan. The resulting elastomeric wafer product was left to cure for 24 h in a convection oven for 48 h at 45°C for ESP bioelastomers. The cured wafer samples were then cooled to room temperature and cut into thin sheets for unreacted oil extraction. About a gram of each cut sample was soaked with occasional stirring in a 1 : 4 by volume *n*-hexane-cyclohexanol solution for 15 min after which the mixture is filtered. Both permeate and retentate were dried in a vacuum oven at 110°C for 2 h. The percentage of unreacted oil phase was calculated by mass balance. This test is a straightforward reaction of epoxides and pMDI. This basic polymerization reaction is described elsewhere [16].

Different organic and inorganic chemicals (acids, bases, alcohols, polymers, surfactants, metal salts, amides, amines, etc.) were initially evaluated according to their catalytic effect on the reaction between ESBO and pMDI. Table 1 showed a list of the catalysts and their corresponding catalytic performance based on the extractability test described above.

About 0.5% by weight of each catalyst was added to ESBO and mixed well at room temperature. The catalyzed ESBO was reacted with pMDI in a 2 : 1 mass ratio, and the resulting PU mixture was then cured in a 140°C convection oven for 24 h. The PU wafers were tested for unreacted oil phase. Lower extractable content correlates with better catalytic performance for the PU-forming reaction. Phosphoric acid showed the lowest extractable content and was, therefore, used to produce the epoxide-substituted polyols.

3. Results and Discussion

In this work, a urethane bioelastomer formulation is studied following the epoxide-substituted polyol (ESP) and polymeric diphenylmethane diisocyanate (pMDI) reaction, including physicochemical characterization of the elastomer products. Catalysts were evaluated to specifically promote epoxide reaction. *Ortho*-phosphoric acid lowered the oxirane concentration of the epoxide even at room temperature with no solvents added. A simplified scheme of the process is shown in Figure 2.

ESP reacted in an open glass vessel with the acid catalyst added dropwise until a homogeneous phase is obtained. Proper mixing was crucial in attaining a uniformly catalyzed product. After the completion of reaction, pMDI was added

TABLE 1: Catalysts evaluation by extractable content method. A sample elastomeric wafer was a mixture of catalyzed ESBO (0.5% catalyst) and pMDI at 2 : 1 mass ratio then cured at 140°C/24 h in a convection oven.

| Sample	Catalyst used	Extracted oil phase, %
Control	None	16.0
1	K_2HPO_4	17.2
2	Tin(II) 2-Ethylhexanoate	10.0
3	Triethanolamine	15.1
4	o-Phosphoric acid	**2.85**
5	Glycerol	15.6
6	1,4-diazabicyclo[2.2.2]octane (DABCO) 8154	21.1
7	Polycat SA-1	22.6
8	DABCO BL-17	21.6
9	Propylamine	18.9
10	Propionamide	17.9
11	Octadecanamide	19.5
12	N-Methyl-N-nitroso-p-toluenesulfonamide (Diazald)	14.0
13	N-Bromo-succinimide	15.4
14	N,N-Dimethylformamide	15.9
15	KH_2PO_4	14.4
16	Calcium carbonate	15.1
17	n-Butanol	15.6
18	Methanol	16.2
19	Methanol + sulfuric acid	17.0
20	Perfluoric acid-PTF prepolymer	13.8
21	Cobalt acetate	15.2
22	Phthalic acid	13.1
23	Acetic acid	19.8
24.	Formic acid	11.3
25	p-Toluenesulfonic acid	11.0
26	Titanocene dichloride	10.2
27	1-Naphthol-3,6-disulfonic acid disodium salt hydrate	12.7
28	Phenylenediamine	22.1
29	Potassium hydroxide	41.5
30	Ammonium chloride	16.1
31	Sulfuric acid	15.2
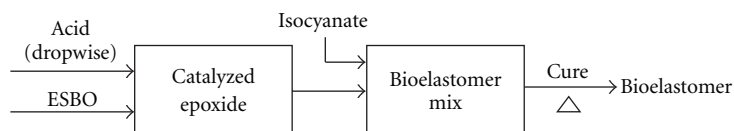
FIGURE 2: Schematic of bioelastomer synthesis. Oxirane opening reaction is performed at room temperature with constant stirring.

to ESP and the product degassed, then postcured in a convection oven. The postcured bioelastomer products displayed a range of physical properties from viscous and tacky to hard and brittle. Variations in the elastomer properties are attributed mainly to the isocyanate index used and hydroxyl equivalent weight of the ESP [7, 17, 18].

3.1. Extractability for Evaluation of Catalysts. An extractability analysis method was established in our previous work [19] to evaluate the reactivity of the polyol products with

the polymeric MDI. The test determined the percentage of the unreacted oil phase in the elastomer. Low extractability is believed to correlate with high cross-linking, whereas high extractability is believed to correlate with the presence of nonfunctional or single-functional components in the B-side (alcohol side) of the urethane formulation.

In this study, the extractability method was used to evaluate the effect of different catalysts added in epoxidized soybean oil for promoting reaction with polymeric MDI. A lower extractable content value indicates higher cross-

linking and better catalyst performance. Table 1 shows the extractability values of samples using different catalysts. While presented as catalysts, in some instances, the materials may participate in reaction.

More than 30 catalysts were evaluated as shown in Table 1. About half-promoted minor increases in reactivity with pMDI as shown in their extractable content. Phosphoric acid showed the lowest extractable content at 2.85% followed by a metal-based catalyst Tin (II) 2-ethylhexanoate at 10.0%. The former was the catalyst of choice owing to its effect in the reactivity of epoxide or ESP with pMDI.

3.2. Mixing of Epoxide and Alcohol.

Two mixing sequences were performed to investigate any changes in properties of the final ESP. In the first sequence, ESBO was made to react with o-H_3PO_4 separately before castor oil, was added. The other sequence was performed by mixing ESBO, castor oil and o-H_3PO_4 simultaneously. All reactions were performed at room temperature. The chemical properties of the final ESPs are summarized in Table 2.

Based on Table 2 results, there were no significant changes in the chemical properties of the final ESPs using different mixing sequences; therefore, the alcohol did not significantly interfere in the phosphate-epoxy ring reaction. Under the conditions of the reaction, the o-H_3PO_4 is believed to react directly with the oxirane group as shown in Figure 1 causing an increase in viscosity and decrease in the oxirane oxygen concentration. Slight increases in hydroxyl values are attributed to the increasing o-H_3PO_4 percentages where o-H_3PO_4 reacts to from an alcohol.

3.3. Extractability of ESPs.

The schematic representation of the reaction of ESP/phosphate esters with pMDI is shown in Figure 1. For ESPs with higher alcohol concentration, it is expected that the unreacted oil extractability is lower because the hydroxyl groups of castor oil readily react with the NCO-functional group of pMDI forming cross-linked urethane polymer network. The effect of catalysis and reaction of ESBO with o-H_3PO_4 is more pronounced at mass fractions between 0.5 to 1.0 ESBO in castor oil as shown in Figure 3.

With no alcohol loading, an increase from 4.1% (catalyzed) to 18.6% (noncatalyzed) unreacted oil phase is observed which suggests that the extent of ESP-pMDI reaction can be increased by increasing the amount of o-H_3PO_4. Lower extractability can be obtained by either increasing the alcohol loading in the bioelastomer mix or increasing the hydroxyl functionality (increase the hydroxyl equivalent weights at the same hydroxyl number) of the ESP which can be achieved by epoxy reaction with o-H_3PO_4.

The ASTM hydroxyl value of the polyol is used to calculate the amount of isocyanate needed to react with the polyol. The acid-catalyzed epoxide sample C in Table 3 shows an ASTM hydroxyl value of 240 mg KOH/g. The amount of isocyanate can be reduced to about 40% relative to the control with a hydroxyl value of 404 mg KOH/g. o-H_3PO_4-catalyzed ESBO presents the following potential advantages: increased polymeric network (high average functionality), displayed relatively higher tensile properties, and reduced
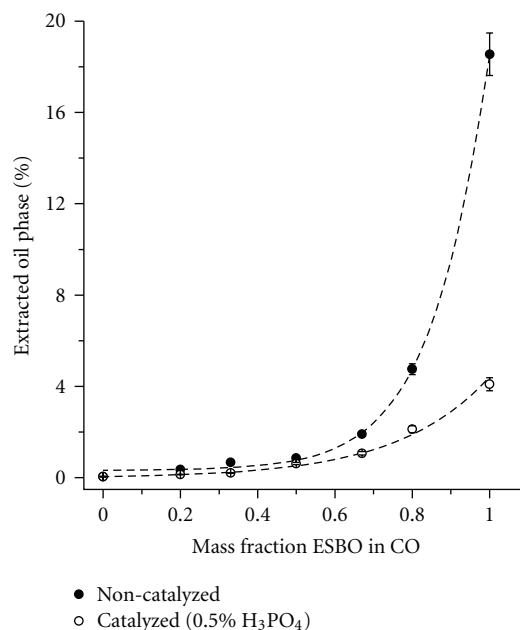

FIGURE 3: Extractability trend of urethane elastomers based on catalyzed and noncatalyzed ESBO. Urethane materials were formed from the reaction of ESPs (epoxide and castor oil) and polymeric MDI. Curing conditions were at 45°C for 48 h in a convection oven.

pMDI loading for both urethane bioelastomer and rigid foaming formulations.

3.4. Acid-Catalyzed Epoxide.

Urethane bioelastomers were also prepared by reacting ESBO with o-H_3PO_4 without solvent or alcohol source. Table 3 presents the chemical properties of these samples with untreated ESBO as a control. A reduction of about 25% oxirane oxygen content was observed upon reacting ESBO with 1.5% phosphoric acid. Gelation was observed at 2.0% acid loading.

An increase in viscosity was observed as the amount of phosphoric acid added to ESBO was increased. Guo et al. [2] made the same observation and attributed the increase of viscosity and molecular weight to an increased tendency for oligomerization reaction due to higher acid concentration and the presence of increasing amount of higher phosphate esters and other reaction products. This established reaction which mainly involves epoxy ring opening forms polymeric or oligomeric species which results to an increase in molecular weight from the intermolecular phosphates di-and triester formation. Oligomerization through epoxy-epoxy and/or hydroxy-epoxy reaction is also highly possible in an acid catalysis of epoxy compounds. [1].

The epoxy ring-opening reaction was verified by FTIR with the untreated ESBO showing a more intense peak compared with acid-treated sample at wavenumber 824 cm^{-1}, a characteristic of an epoxy signal. A steep increase in viscosity was also observed from 362 cP for untreated ESBO to about 4000 cP for the 1.5% acid-treated sample. This was indicative of the formation of phosphate esters which was verified by FTIR spectral intensity at wavenumber 1020 cm^{-1}. This characteristic signal was not observed with the untreated ESBO sample. The acid number did not increase significantly

TABLE 2: Chemical properties of ESPs using two different mixing sequences. The Gardner color indices of the samples range from 1 to 3. All reacted samples composition: 1 : 1 by wt ESBO and CO. "Separate" indicates that acid reaction was done first before alcohol addition while "Simultaneous" that indicates acid and alcohol reactions were done at the same time.

% o-H_3PO_4 based on ESBO	Acid value, mg KOH/g ($\pm$0–5%)	Viscosity, cP ($\pm$0.2–1%)	%Oxirane oxygen ($\pm$0.2–3%)	AOCS Hydroxyl value, mg KOH/g ($\pm$2–4%)
Control				
0	1.54	434	3.44	84.10
Separate				
0.5	1.75	501	3.22	84.30
1.0	1.65	665	3.12	89.56
2.0	1.63	1240	2.69	95.36
Simultaneous				
0.5	1.90	507	3.30	87.70
1.0	1.80	660	3.04	89.30
2.0	1.90	1100	2.73	98.24

TABLE 3: Chemical properties of o-H_3PO_4-reacted ESBO (at RT) without solvent or alcohol source.

Sample code	% o-H_3PO_4 based on ESBO	Acid value, mg KOH/g ($\pm$0–5%)	% Oxirane oxygen ($\pm$0.2–3%)	AOCS Hydroxyl value, mg KOH/g ($\pm$2–4%)	ASTM Hydroxyl Value, mg KOH/g ($\pm$0.3–5%)	Viscosity, cP ($\pm$0.2–1%)
Control	0	<0.20	7.06	11.0	404	362
A	0.5	0.77	6.77	23.0	—	559
B	1.0	0.89	6.30	32.2	—	1020
C	1.5	0.95	5.34	38.4	240	3950

with increasing phosphoric acid loading. This indicates that the phosphate molecules completely react with the epoxy molecules up to at most 1.5% phosphoric acid loading.

Higher residual acidity is an undesirable polyol property as it competes with hydroxyls to react with isocyanates and consumes catalysts when these samples are further processed to produce bioelastomers and urethane foams. All samples maintained nonproblematic acid values less than 1.0. An increase in AOCS hydroxyl values from 11.0 to 38.4 was attributed mainly to an alcohol gain in the phosphate formation or partly on residual water from the aqueous o-H_3PO_4.

3.5. Bioelastomer Formation. The physicochemical properties of the bioelastomers synthesized from the treated epoxides in Table 3 are presented in Table 4. Urethane bond formation was verified by FTIR spectra at wavenumber 3340 cm^{-1} with a higher peak intensity observed with the bioelastomer synthesized from nontreated epoxide.

The greatest extent of cross-linking in elastomers will tend to occur when the A-side and B-side monomers are reacted in stoichiometric quantities. For urethane reactions, and especially for urethane reactions with epoxy moieties present, a complex network of reactions occurs, and reaction stoichiometry is not straightforward. However, even with this uncertainty, it is evident that at 10% pMDI there is an inadequate amount of isocyanate to completely react with the B-side alcohol and epoxy moieties. At 10% pMDI loading, the bioelastomeric materials were too soft to be

measured with its tensile properties. NCO concentration was less compared to the available alcohol/epoxy reacting groups which leave more unreacted soy-phosphate molecules.

At 30% pMDI, the isocyanate will tend to exhaust reaction with the alcohol moieties and undergo reactions that form undesirable brittle elastomers. At 30% pMDI loading, bioelastomers were observed to be hard and brittle. This seemed to be the opposite of the 10% loading at the same curing temperature. Excess amounts of pMDI relative to the epoxy/alcohol groups may result in the formation of the hard segment composed of isocyanurate, biurets, and allophanates which would lead to brittleness and fragility of the urethane product. The T_g values of the bioelastomers in Table 4 show a consistent trend; an increasing T_g value as OH/NCO molar ratio increases. Each bioelastomer sample shows one glass transition temperature which reflects a high degree of phase mixing between the hard segment and the soft-segment domains. Relatively higher combination of strength and strain performances was attained at about 25% pMDI loadings.

At the same pMDI loading, tensile strength increased with increasing mass percentage of phosphoric acid added to ESBO. The higher o-H_3PO_4 loading in ESBO led to increased viscosities which are associated with increased average molecular weights. The higher average molecular weight of the B-side monomer translates to more cross-linking and increased tensile strength.

At different pMDI loadings (e.g., samples 15C and 25A), the Young's modulus of the samples are comparatively

TABLE 4: Tensile and thermal properties of bioelastomers from acid-catalyzed epoxides of Table 3. Bioelastomers were evaluated at 10%–30% by weight pMDI based on acid-treated ESBO.

| Sample code	Description	Strength at break, MPa	Strain at Break, %	Young's modulus, MPa	T_g(DSC), °C
10A	A + 10% pMDI		Material too soft		—
10B	B + 10% pMDI		Material too soft		—
10C	C + 10% pMDI		Material too soft		—
15A	A + 15% pMDI		Material too soft		−10.2
15B	B + 15% pMDI	0.29 ± 0.01	4.34 ± 2.96	0.22 ± 0.03	−13.8
15C	C + 15% pMDI	0.42 ± 0.14	5.10 ± 2.89	0.47 ± 0.34	−17.4
25A	A + 25% pMDI	0.94 ± 0.12	9.00 ± 1.54	0.46 ± 0.09	−11.5
25B	B + 25% pMDI	1.32 ± 0.14	5.93 ± 0.83	0.95 ± 0.07	−15.9
25C	C + 25% pMDI	1.47 ± 0.12	5.13 ± 0.48	2.04 ± 0.36	−18.4
30A	A + 30% pMDI		Material too brittle		—
30B	B + 30% pMDI		Material too brittle		—
30C	C + 30% pMDI		Material too brittle		—
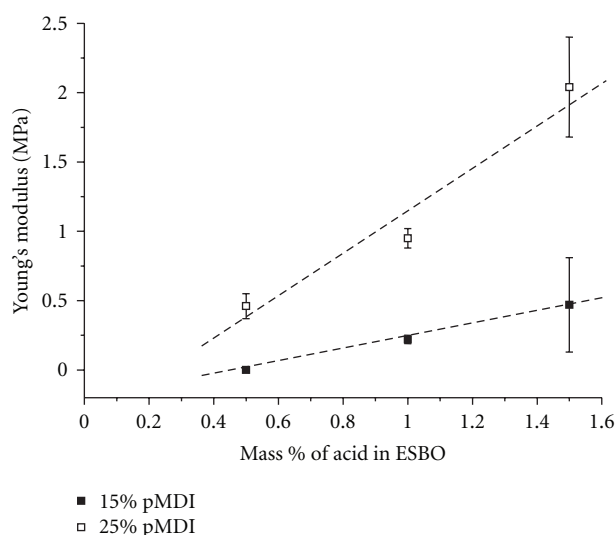
FIGURE 4: Effect of the amount of o-H_3PO_4 on Young's modulus of bioelastomers with 15% and 25% pMDI loading.

similar, which means that both samples have the same resistance to elastic deformation under load as shown in Figure 4.

4. Conclusion

Polymerized epoxidized soybean oil was synthesized by phosphate ester formation carried out by mixing epoxidized soybean oil with up to 1.5% o-phosphoric acid at room temperature. The product was homogeneous, highly viscous, low acid, and with a high average functionality. The resulting phosphoric acid-catalyzed epoxide-based bioelastomer showed up to 80% decrease in extractable content and increased tensile strength at the same isocyanate loading relative to the noncatalyzed epoxide.

With the same catalyzed epoxide used as a B-side reactant in the rigid foam formulation, the amount of isocyanate can be reduced to about 40% compared with the noncatalyzed epoxide reactant. There was no significant increase in the

hydroxyl number of the polyols, but its relatively lower extractable content indicates a higher hydroxyl equivalent weight due to its high molecular weight.
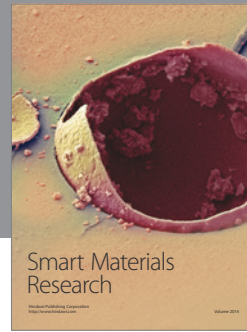
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