Noncatalytic Polymerization of Ethylene Glycol and Epoxy Molecules for Rigid Polyurethane Foam Applications

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ABSTRACT: The study investigated an approach to incorporate modified epoxidized soy-based vegetable oil polyol as a replacement for petroleum-based polyether polyol and to substantially reduce the isocyanate loading in the rigid foam formulation. Noncatalytic polymerization of epoxidized bodied soybean oil and ethylene glycol (EG) was carried out in a closed batch reaction. Cleavage of the oxirane rings and hydroxyl group attachment at optimum conditions provided the desired polyol products. The polyols were characterized based on its hydroxyl numbers, acidity, viscosity, iodine number, and Gardner color index for quality purposes. Reactions of oxirane ring and EG were verified by spectroscopic FTIR. Crosslinking performance was evaluated by extractability analysis on the poly-urethane (PU) elastomer wafers. Rigid foaming performed at 50 and 75% petroleum-based polyether polyol replacements have shown excellent thermoinsulating and mechanical properties compared with epoxidized soybean oil (ESBO) alone or petroleum-based polyether polyol alone. A reduction of up to 8% of the polymeric diphenylmethane diisocyanate was achieved using the synthesized ESBO-EG-based polyols. A higher average functionality polyol is key component to the reduction of isocyanate in PU synthesis. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2185–2194, 2009

Key words: crosslinking; degree of polymerization; oligomers; polyurethanes

INTRODUCTION

Polyols derived from vegetable oils have gained major commercial interest and significant attention in scientific research owing to the availability, biodegradability, and unique properties of the triglycerides. These triglycerides have at least one unsaturated fatty acid moiety, which can be modified by catalytic or noncatalytic means to introduce the desired hydroxyl functional groups in the polyol structure. A number of physicochemical approaches and even biological methods have been used to functionalize unsaturated vegetable oils to yield industrially useful polymer derivatives and polyols.[1,2] Soybean oil has been most promising as starting material for polyol conversion because of its volume and price stability in addition to its versatility for chemical modification.

More recently, epoxidized soybean oil (ESBO) has received increased attention because they are of interest both as chemical intermediates and as end-products. A wide variety of ring-opening reactions are possible because of the high reactivity of the oxirane group. Cleavage of the epoxy functional group by reaction with carboxylic acids leads to ester alcohols, with water to diols, and with alcohols to ether alcohols.[3] Different ESBO-based polyols were evaluated in terms of its potential to replace up to 50% of the petroleum-based polyol in waterborne rigid polyurethane (PU) foam applications. Results have shown that the PU foams not only had superior thermal conductivity but better density and compressive strength properties than had foams made from 100% petroleum polyol. The ESBO alone when used in a 50 : 50 blend with a petroleum-based polyol had similar density versus compressive strength properties with foams made from 100% petroleum-based polyol.[4]

Palm oil-based epoxidized diethanolamides were used to produce a new type of rigid PU foam. The epoxides retained in the diethanolamides reacted with isocyanate during foam production in the presence of AlCl$_3$-THF complex catalyst to form oxazolidone linkages in the PU network. The resulting foams had improved thermal and mechanical properties but required high isocyanate loading to produce quality rigid foams.[5] Rigid PU foams are polymers formed by the reaction of alcohol with two or more reactive hydroxyl functional groups per molecule (diols or polyols) and isocyanates that have more than one reactive isocyanate group per molecule (a diisocyanate or polyisocyanate).[4] Rigid foam formulation typically requires a high hydroxyl value (OH number) in the 400–500 mg KOH/g range to obtain the necessary rigidity.[6]

Based upon these previous studies, higher isocyanate loading was often required to react with vegetable oil-based polyols to obtain PU foams with comparable mechanical and thermoinsulating properties to that of petroleum-based polyols. The objectives of this study were to evaluate an approach for preparing a high average equivalent weight soy-based epoxy polyol, test its potential to replace up to 75% of the petroleum-based Voranol® 490 in waterborne rigid PU foam applications, and evaluate the reduction in isocyanate loading in the rigid foam formulation (pure ESBO compared with the synthesized soy-based epoxy polyol). ESBO is reacted with ethylene glycol (EG) at optimum reaction conditions without catalyst keeping the acid number <1 and a Gardner color index less 7 for product quality.

An increase in viscosity and a decrease in weight percentage of oxirane oxygen were observed with different EG loading (for the same reaction time and temperature), which is indicative of oxirane ring opening and polymerization. In this article, a series of polyols are presented based on variation in the amount of EG added to ESBO. Extractability characterization was performed in elastomer test-wafers. Rigid foams were prepared with characterization of density, compressive strength, and thermal conductivity.

MATERIALS AND METHODS

Materials

Voranol® 490 polyether polyol (a petroleum-based polyol made from propylene oxide and a sucrose/glycerin base with the following properties: 4.3 alcohol functionality, 460 average molecular weight, and 490 hydroxyl number) and PAPI® 27 [a polymeric diphenylmethane diisocyanate (MDI) with 2.7 NCO functionality, 340 average molecular weight, and 31.4 wt % of NCO content] were obtained from Dow Chemical (Midland, MI). ESBO (Vikoflex® 7170) was supplied by ATOFINA Chemicals (Philadelphia, PA). EG (≥99% ReagentPlus) was purchased from Sigma Aldrich (St. Louis, MO). Catalysts (POLYCAT® 5 or pentamethyldiethylenetriamine is a liquid tertiary amine mainly used as a blowing catalyst; and POLYCAT® 8 or dimethylcyclohexylamine is a standard liquid amine catalyst used in rigid foaming formulation) and a silicone surfactant (Dabco® DC 5357) were from Air Products and Chemicals (Allentown, PA) gratis. Distilled water was used as the blowing agent.

Standard analytical methods

Hydroxyl values of polyols were determined according to an American Society for Testing and Materials (ASTM) Procedure E222-00 (reapproved 2005) Method A.[7] Another method of hydroxyl content determination was performed according to American Oil Chemists' Society (AOCS) Official Method Tx 1a-66.[8] Acid numbers (mg KOH/g sample) of all reaction products were evaluated according to the AOCS official method (AOCS Te 1a-64, 1997).[9] Iodine values (centigram, cg I_2/g sample) of the polyol samples were determined using ASTM Designation: D1959-97.[10] Epoxy content of the samples were measured according to AOCS official method (AOCS Cd 9-57, 1997).[11] The dynamic viscosities (centipoise, cP measured at 200°C) of the samples were determined using Model RS100 Rheometer (Haake-Thermoelectron, Newington, NH). Gardner color index of the polyol samples were evaluated according to ASTM D1544 (edited D6166, 1998).[12]

A Fox 200 heat flow meter instrument (Laser-Comp, Wakefield, MA) was used to measure the thermal conductivity of the PUs according to ASTM Procedure C518-04.[13] Densities of foam samples were determined according to ASTM Procedure D 1622-03.[14] Compressive strengths of foam samples were measured using a TA-Hdi Texture Analyser (Texture Technologies, Scarsdale, NY) according to ASTM Procedure D 1621-04a.[15] Thermal conductivity measurements were performed after curing the foams for 24 h, whereas density and compressive strength measurements were performed after 7 days sample storage.

Soy-based polyol synthesis

Noncatalytic batch synthesis of ESBO-EG polyols was carried out in a 300-mL Bench Top Model 4561 Parr stirred vessel. About 200 g of ESBO was poured into the Parr reactor vessel. Pure EG was added to the same vessel at varying quantities (0, 2, 7, and 9% by weight based on ESBO). The mixture reacted in a closed Parr vessel with constant stirring at a temperature range of 150–300°C at 1–10 h reaction times. Kinetic studies were performed on the samples to evaluate the effects of EG concentration and reaction conditions on the chemical properties of the ESBO-EG polyol products. Table I presents relevant chemical physicochemical properties of these polyol products.

Extractability test

A single-step plastic extraction method was used to determine the extent of polymer crosslinking between the polymeric MDI (PAPI® 27) and polyol products. Polymeric MDI and the sample polyol in a weight ratio of 1 : 2 was well mixed in a small disposable aluminum pan. The resulting product was left to dry for 10 h in a convection oven at 110°C. The dry sample was then cooled to room temperature and cut into thin sheets for unreacted oil extraction. About 1 g of

TABLE I
Physicochemical Properties and Reaction Conditions for the Synthesized Polyols

Polyol code	Description[a]	Acid value (mg KOH/g) (±0–5%)	Percentage oxirane oxygen (±0.2–3%)	Viscosity (cP) (±0.2–1%)	Gardner color index[b]	Percentage unreacted oil phase (±0–38%)	AOCS hydroxyl value (mg KOH/g) (±2–4%)	ASTM hydroxyl value (mg KOH/g) (±0.3–5%)
Ctrl A	Pure ESBO	<0.20	7.18	362	1	17.8	11.0	352
Ctrl B	Voranol® 490	<0.20	<0.10	>10,000	1	0.38	484	484
EG-3	ESBO + 7%EG, 250°C/1 h	0.18	5.71	467	4	1.83	153	370
EG-4	ESBO + 7%EG, 250°C/3 h	0.20	5.59	512	5	1.65	158	363
EG-5	ESBO + 2%EG, 250°C/5 h	0.45	5.98	530	3	5.28	81.0	320
EG-6	ESBO + 7%EG, 250°C/5 h	0.66	4.86	600	6	1.34	169	322
EG-7	ESBO + 9%EG, 250°C/5 h	0.68	4.22	647	6	0.92	202	325
EG-8	ESBO + 9%EG, 250°C/10 h	0.72	2.53	1360	6	0.47	211	268

[a] Reactions in a closed Parr reactor. All reaction products were one-phase.
[b] Gardner color index of water is 1 and carbon black is 16.

the cut sample was soaked in a 1 : 4 by volume n-hexane-cyclohexanol solution for 15 min after which the mixture was 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.

Fourier-transform infrared spectroscopic analyses

A thermo scientific Nicolet™ 380 FT-IR equipped with Smart Orbit diamond ATR Attachment (Thermo Electron Corp., Madison, WI) was used to characterize the functional groups in ESBO-EG polyols. A total of 64 scans of each sample from 4000 to 400 cm^{-1} wavenumber range were obtained at a resolution of 2 cm^{-1}.

PU formation

A foaming procedure described by Tu et al.[4] detailed in Table II was used in this study. Voranol® 490, ESBO-EG polyol, catalysts, surfactant, and blowing agent were added by weighing into a 500-mL disposable plastic drinking cup and mixed at 3450 rpm for 10–15 s. The mixture was allowed to degas for 120 s and then PAPI® 27 was rapidly added while continuously stirring for another 10–15 s at the same speed. The mixture was poured immediately into a wooden mold (11.4 × 11.4 × 21.6 cm^3) with aluminum foil lining and the foam was allowed to rise and set at ambient conditions (23°C). Fifty and seventy-five percent replacements of Voranol® 490 by the ESBO-EG polyol were performed using isocyanate index of 100 (where both alcohol and epoxy is used to calculate the index). Modification in the foaming was done to evaluate the effect of heating the polyols prior to foaming. The polyols were placed in a microwave oven for 9 s at high power. Higher peak foaming temperatures were achieved (measured by infrared temperature sensor). Catalysts, surfactant, and water were then

TABLE II
Water-Blown Rigid Polyurethane Formulation

Materials	Parts by weight
B-side	
Voranol® 490	50
ESBO-EG Polyol	50
Polycat® 5	1.26
Polycat® 8	0.84
DABCO DC 5357	2.5
Blowing Agent (Water)	3.0
A-side	
PAPI® 27	100[a]

[a] Isocyanate index is the percentage of the actual amount of isocyanate used over the theoretical amount of isocyanate required.
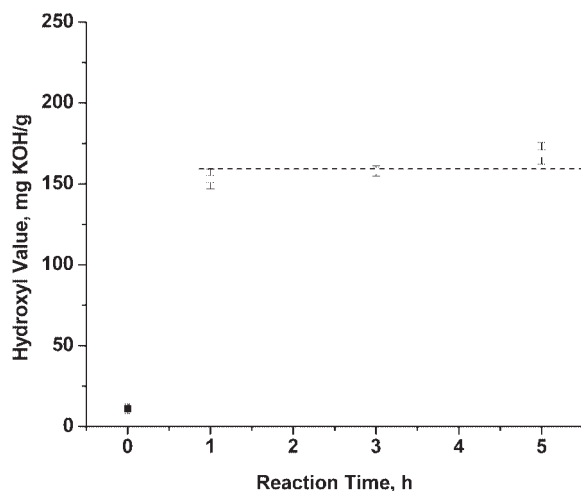
Figure 1 Dependence of hydroxyl value on reaction time for the batch processing of ESBO-EG polyols. EG loading (7%) and reaction temperature (250°C) were kept constant (■, pure ESBO; □, ESBO-EG polyols).

added and mixed. The plastic cup containing the B-side components was then subjected to a 50°C convection oven for 5 min before adding the A-side component.

RESULTS AND DISCUSSION

Polyol physicochemical properties

High residual acidity is an undesirable polyol property. Acid numbers >10 mg KOH/g polyol will have a significant impact on PU foam synthesis as it competes with hydroxyls to react with isocyanates and consumes catalysts.[16] Industry standard requires acid numbers <4. Table I shows that a reaction temperature of 250°C yields a polyol with an acid number <1 even at longer reaction times up to 10 h. EG-5, EG-6, EG-7, and EG-8 polyols were selected for foaming studies. Two methods of polyol hydroxyl value determination were used in the study as mentioned earlier. ASTM Procedure E222-00 Method A measures both the epoxy and the hydroxyl group content of the polyol. This hydroxyl value is used in the calculation of the amount of polymeric MDI (PMDI) to be added in the rigid foam formulation. AOCS Official Method Tx 1a-66 measures only the hydroxyl group content of the polyols which evaluates the quantity of the hydroxy functionality of the polyols. Only the latter method was used to explain the kinetics of polymerization via oxirane opening.

Oxirane opening polymerization

Near-constant hydroxyl values were observed with respect to time as shown in Figure 1 for polyol products obtained from a starting mixture of 7% EG load-

ing in ESBO at 250°C reaction temperature. Longer reaction times did not significantly affect the hydroxyl values of the polyols with EG loading and reaction temperature kept constant. The polyols underwent oxirane opening polymerization to some extent as evidenced by the reduction of oxirane oxygen content from 7% (no reaction, 0 h) to 4.86% (5 h reaction time), which is about 30% decrease in oxirane oxygen content confirmed by wet analytical method. Viscosity values of these polyols have also increased with pure ESBO as reference. Longer reaction times will mean more oxirane-ring opening (decrease in epoxy group content) and higher conversion to ESBO-EG complex with conservation in hydroxyl group content. An EG molecule with two terminal hydroxyls reacts with ESBO and yields two hydroxyls.

Figure 2 shows a steep increase in hydroxyl values of the resulting polyol products as the concentration of EG was increased from 2 to 9%. It is important to note that these products (EG-5, EG-6, and EG-7) were reacted completely as observed by the polyols' uniform phase appearance. Viscosity values were observed to have increased and oxirane oxygen decreased as well. This phenomenon was still attributed to the ring-opening reaction of the epoxy groups in ESBO and the simultaneous formation of an ESBO-EG complex suggested in the reaction scheme shown in Figure 3. An epoxy ring reacts with EG to form an ether alcohol. In the bigger scheme, simultaneous conversion of the reacting species into ether alcohol will effect a complexation between ESBO and EG, thus the polymerization. The resulting increase in viscosity and consumption of oxirane oxygen content were mainly attributed to this complexation which is suggested to be the main product.
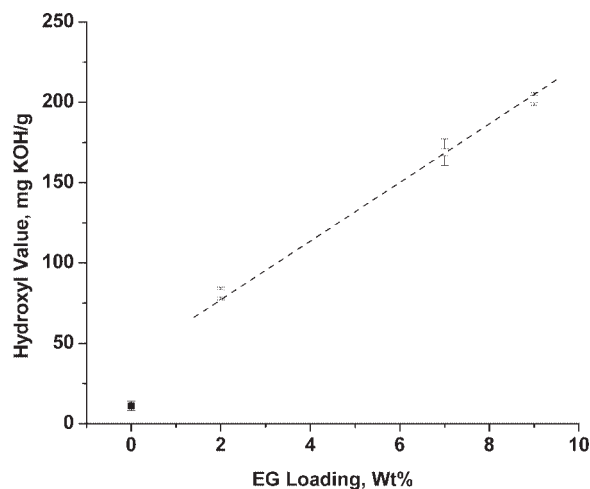

Figure 2 Dependence of hydroxyl value on EG loading for the batch processing of ESBO-EG polyols. Reaction time (5 h) and reaction temperature (250°C) were kept constant (■, pure ESBO; □, ESBO-EG polyols).
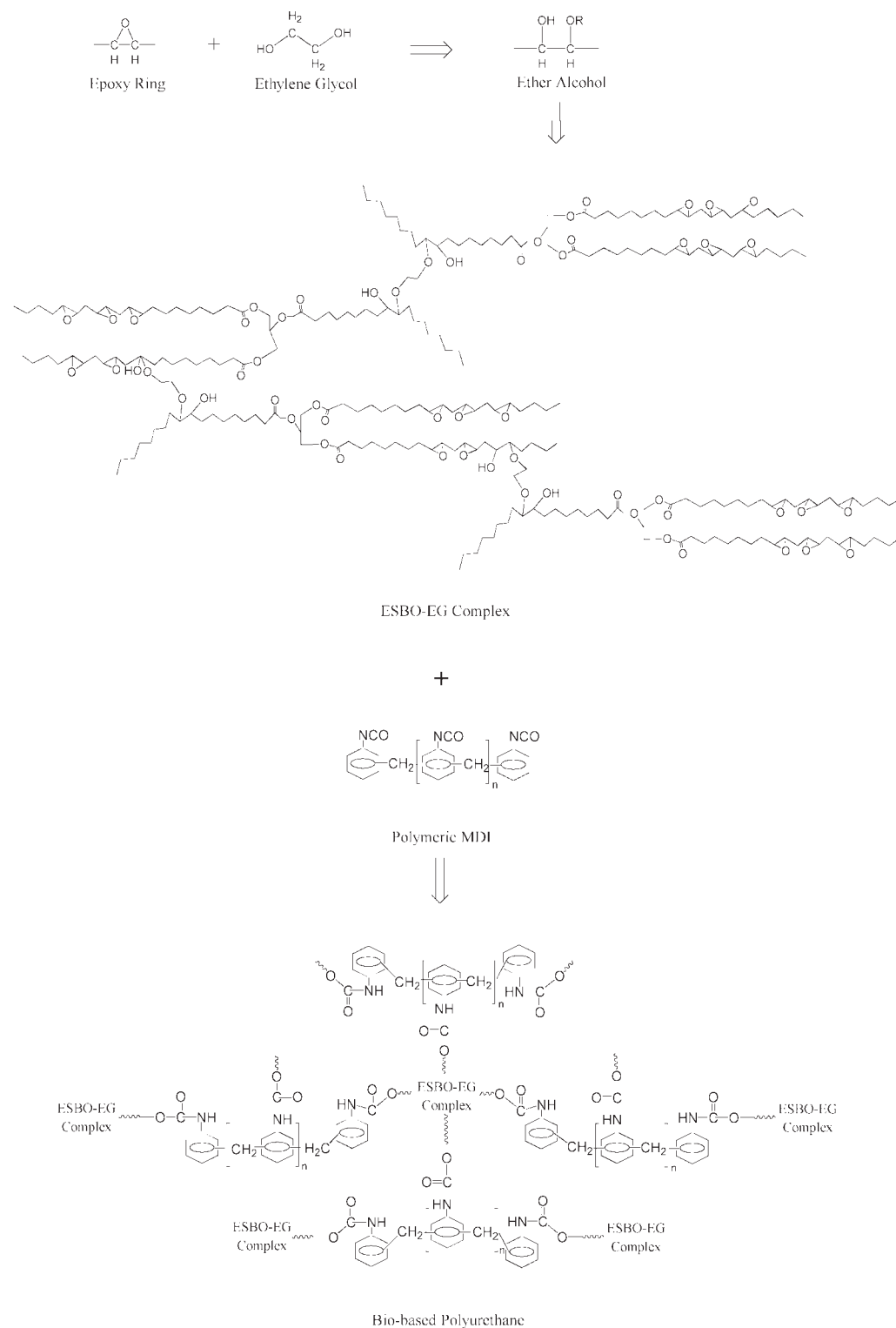
Figure 3 Two-step reaction schemes from the formation of ESBO-EG complex to the synthesis of bio-based polyurethane foam.

FTIR analysis of ESBO-EG polyols

A comparison of FTIR spectra[17–19] of both pure ESBO and EG is shown in Figure 4. Symmetric/asymmetric methyl or C—H stretching for both ESBO and EG are shown at different but closer wavenumbers. The absorption intensity of hydroxyl groups at 3000–3700 cm^{-1} which represents the OH vibration band is much stronger in EG spectra than ESBO which showed a flat line in this region, indicative of less or absence of H-bonded OH and other —OH groups.
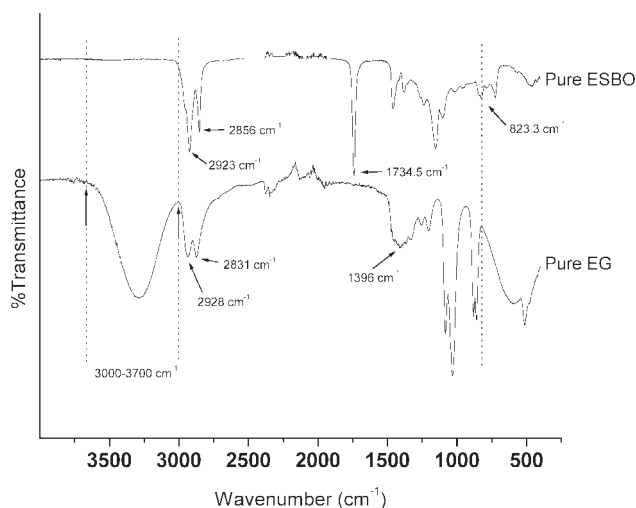
Figure 4   FTIR spectra of pure ESBO and EG.

Most of the -OH groups found in EG were attributed to the terminal alcohol groups, which also exhibit COH bending at 1396 cm^{-1}. The characteristic oxirane absorption peak at 823.3 cm^{-1} and the ester carbonyl band (C=O) centered at 1734.5 cm^{-1} of the ESBO spectra are obviously not present in EG.

Figure 5 shows the spectra of ESBO-EG polyols processed at different times (1, 3, and 5 h, corresponding to EG-3, EG-4, and EG-6) but the same EG loading and reaction temperature of 7% and 250°C, respectively. The oxirane absorption peaks and the OH vibration bands of these ESBO-EG polyols have shown almost the same intensity. This seems to indicate reaction time does not significantly affect oxirane opening polymerization as reflected by close hydroxyl
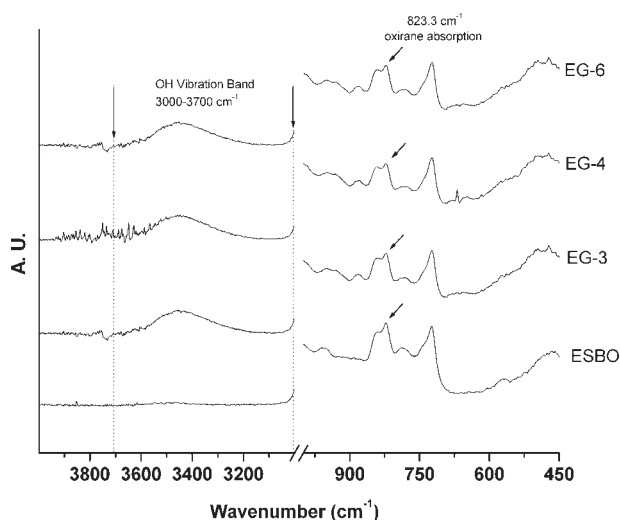
(Fig. 1), viscosity and oxirane oxygen content (Table II) values of the polyols.

Figure 6 shows the spectra of ESBO-EG polyols processed at different EG loading (2, 7, and 9%, corresponding to EG-5, EG-6, and EG-7) but the same reaction times and temperature of 5 h and 250°C, respectively. The reaction products were observed to be one-phase, indicative of a complete reaction. At higher EG loading such as sample EG-7 (at 9%) it seems there is greater tendency for oxirane ring polymerization compared to EG-5 (at 2%). This is consistent with their corresponding oxirane absorption band at 823.3 cm^{-1} wavenumber. A steep change in both viscosity and hydroxyl values of these samples indicate a high degree of polymerization, thus, a high average functionality of the polyols. The plot of hydroxyl values versus EG loading shown in Figure 3 is consistent with the OH vibration band at 3000–3700 cm^{-1} which showed the highest intensity for EG-7 and lowest intensity with EG-5.

Extractability tests

An initial crosslinking performance test or extractability test was done on the ESBO-EG polyols as well as the controls. This test is a straightforward reaction of the polyol and PMDI described in the Methods section. The basic polymerization reaction of this test is described elsewhere[20] and is shown in the reaction scheme-second step in Figure 3. Figure 7 shows a strong correlation of the percentage unreacted oil phase of the polyol and its viscosity. A high viscosity polyol product indicates a higher degree of oligomerization or complexation between ESBO and EG. The trend shows that the higher the viscosity of the ESBO-
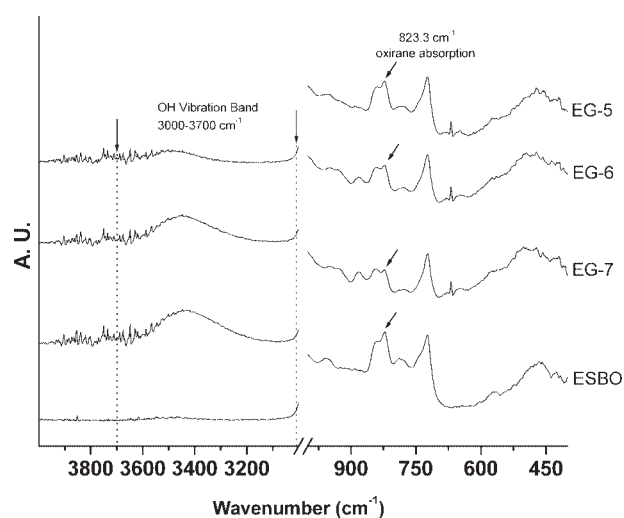

Figure 5   FTIR spectra of ESBO-EG polyols processed at different times with EG loading (7%) and reaction temperature (250°C) kept constant.

Figure 6   FTIR spectra of ESBO-EG polyols processed at different EG loading with reaction time (5 h) and reaction temperature (250°C) kept constant.
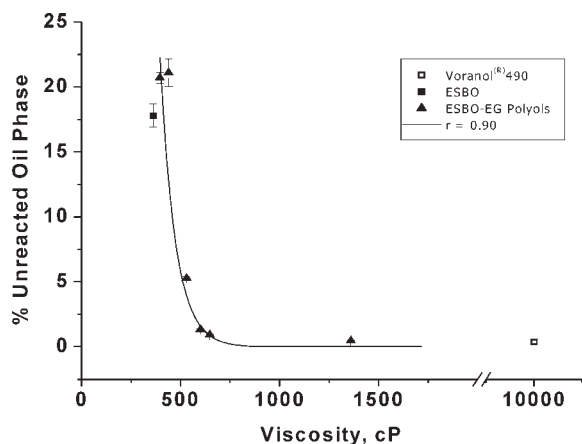
Figure 7 Crosslinking performance and viscosity relationship of ESBO-EG polyols.

EG polyol the lower its extracted unreacted oil phase. Viscosity is significantly related to the hydroxyl content of the polyol as shown in Figure 8. Viscosity increases with an increase in the hydroxyl content of the polyol. At the same quantity of PMDI, there are more reactive hydrogen sites for the isocyanate to react with in the case of EG-8 (OH# = 211) than with EG-5 (OH# = 81.0) to form the polymer network, therefore, higher hydroxyl content means lower unreacted oil extractability. Both the unreacted polyol and unreacted PMDI will be extracted by hexane-based solution as weight percentage of unreacted oil phase. For the ESBO-EG polyols tested, the highest hydroxyl content of EG-8 achieved the lowest mass percentage of the unreacted oil phase at 0.47%, whereas EG-5 achieved the lowest mass percentage at 5.28%. The control Voranol® 490 presents the lowest (0.38%) extractability not only due to its high hyroxyl content (484 mg KOH/g) but that most of its hydroxyl groups are primary, which is 3.3 times more reactive than secondary hydroxyl groups which made up most of the ESBO-EG polyols. ESBO has the lowest hydroxyl content (11.0 mg KOH/g) of all polyols tested, which translates to its highest (17.78%) unreacted oil extractability value.

Polyol average equivalent weights (average molecular weights at the same hydroxyl content) increase with increasing complexation of the starting components. A more efficient crosslinking performance is related to higher average weights of the ESBO-EG polyols. Higher viscosity ESBO-EG polyols have higher average equivalent weights achieved by increasing the degree of oligomerization reflected in the increased hydroxyl content of the polyols as shown in Figure 8. Voranol® 490 exhibits the highest viscosity of about 10,000 cP and highest hydroxyl content most of which are primary as oppose to ESBO with the lowest viscosity of 362 cP and hydroxyl content (lowest average equivalent weight).

Foam thermal conductivity

Thermal conductivity of the foam samples can be affected by many factors including the polyol's OH_m, or the combined ASTM hydroxyl values of the polyol and Voranol® 490 replacement. For a 50% Voranol® 490 replacement, the OH_m of the polyol blend is computed as follows:

$$OH_m = \frac{[(\text{ASTM OH value of Voranol}^®490)50] + [(\text{ASTM OH value of Polyol})50]}{100} \quad (1)$$

The OH_m values of the ESBO-EG polyols ranges from 376 to 463 mg KOH/g compared to pure Voranol® 490 with 484 mg KOH/g and ESBO with an OH_m of 418 mg KOH/g. A higher OH_m means higher reactivity of the polyols with isocyanate because of a higher concentration of the active hydrogen sites. Rigid foam made with 100% Voranol® 490 exhibits lower thermal conductivity (0.026 W/mK) than ESBO-EG and ESBO foams (0.026–0.030 W/mK). This could be attributed to the fact that in addition to the petroleum-based polyol's higher OH_m, it has also most of its hydroxyl functional group as primary compared to the soy-based polyols which have mostly secondary. A faster reaction rate could be expected with Voranol® 490 and PMDI resulting in a stronger three-dimensional PU network capable of holding up most of the carbon dioxide evolved in the reaction of PMDI and water. Secondary hydroxyl group has slower reaction rate with PMDI resulting in a weaker polymer network and increased number of open cells which would be susceptible to air convection and escape of carbon dioxide, both of which contribute to a higher thermal conductivity.[4] Other factors that affects foam thermal conductivity includes thermal conductivity of gas trapped inside the foam cells, thermal conductivity of the foam cell membrane material, convection of cell gas, cell size and orientation,
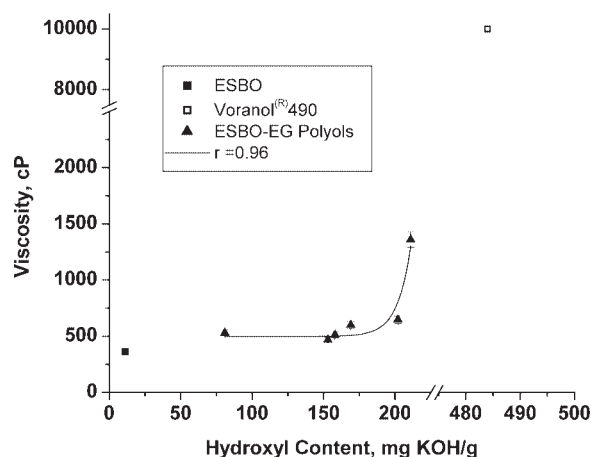

Figure 8 Hydroxyl content dependence of the viscosities of ESBO-EG polyols.

closed cell content, foam density, and thermal radiation.[21] ESBO presenting the highest thermal conductivity (0.032 W/mK) can be attributed to its chemical structure which contains the lowest hydroxyl groups (all secondary) at 12 mg KOH/g. ESBO has the potential to form oxazolidone with PMDI but at a higher temperature.

Foaming reaction rates can be evaluated by measuring the peak foaming temperatures of the polyols. Higher peak foaming temperature reflects higher heat generation of the polyols foamed at the same isocyanate index. ESBO-EG polyols foamed at 50% Voranol® 490 replacement and 100 isocyanate index have lower peak temperatures (range = 88.3–93.3°C) than the peak temperature of Voranol® 490 (104°C). This can be attributed to the presence of primary hydroxyls as the majority of its hydroxyl functional group which react faster with PMDI than do polyols with most of its hydroxyl functional groups as secondary hydroxyls. In addition, Voranol® 490 has a higher OH_m value than any of the ESBO-EG polyols as mentioned earlier, therefore a higher tendency of the PMDI to react with the hydrogen reactive sites. ESBO has the lowest peak foaming temperature (78°C) of the polyols tested and is therefore suggested to have the lowest PMDI reactivity and is reflected in its high thermal conductivity.

Foam density

ESBO-EG polyols have a foam density values in the range of 42.4–46.6 kg/m^3, lower than the control Voranol® 490 (46.7 kg/m^3) and ESBO (47.3 kg/m^3). An increase in density may be governed by the rate of reaction of the polyol and isocyanate that would eventually make up the PU network after curing of the rigid foams. A faster reaction and higher conversion rate would make up a denser crosslinked three-dimensional PU network that eventually gives a higher foam density and volume. A slower reaction and conversion rate translates to a weak three-dimensional PU network which consequently results in a higher density of the final foam due to the shrinkage of the dimensions making it heavier for the same volume. OH_m alone does not give enough information as to the type of hydroxyls present in the polyols or polyol blends. In the case of Voranol® 490 which has most of its hydroxyls as primary, a higher foam density is expected. ESBO presenting the highest foam density can be attributed to poor polymer network causing shrinkage of the structure.

Foam compressive strength

Like foam density, compressive strength is also governed by the rate of reaction of the polyol and isocyanate.[22] A faster reaction and higher conversion of the

A-side and B-side reactants would make up a denser and stronger crosslinked three-dimensional PU network that eventually gives a denser and stronger final foam property as exemplified by the petroleum-based control Voranol® 490. Figure 9 presents a strong correlation ($r = 0.80$) between the extractability of the starting ESBO-EG polyol and the compressive strength of its resulting rigid foam. The lower the unreacted oil phase of the starting polyol the higher compressive strength of its rigid foam (at 50% Voranol® 490 replacement and 100 isocyanate index) will be expected. Lower extractability translates into a higher viscosity ESBO-EG polyol (higher degree of polymerized ESBO and EG proposed in Fig. 3) resulting in a complex with the hydroxyl groups distributed throughout the macromolecule. This high equivalent weight complex will react with PMDI forming an even denser complex that consequently gives a stronger structure in the final rigid foam. Higher compressive strength rigid ESBO-EG foam can be achieved by increasing the average equivalent weight of its starting polyol. Initial crosslinking test was necessary to predict the final compressive strengths of the rigid foam. The highest compressive strength achieved by the ESBO-EG polyol tested was 387 kPa with percentage unreacted oil phase of 0.92. Comparatively, Voranol® 490 has a compressive strength of 459 kPa with 0.38% unreacted oil phase. Although, these two polyols have close extractability values, their hydroxyl content (primary and secondary alcohol content) varies which made a significant impact in the final compressive strength.

Reduction in PMDI

Table III presents the summary of the foam properties of the controls and the synthesized ESBO-EG polyol specifically EG-8. EG-8 was evaluated at 50
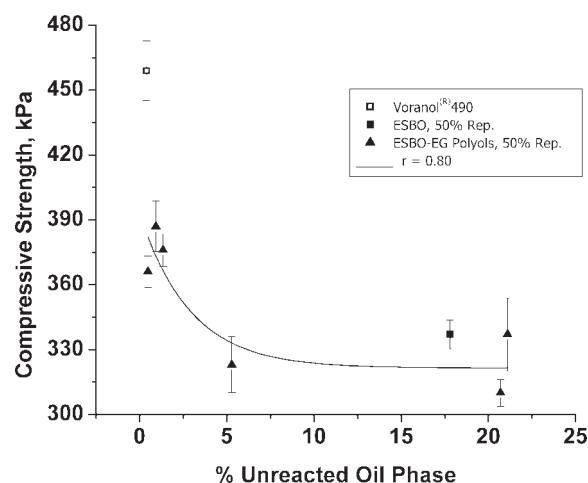

Figure 9 Compressive strength and polyol extractability relationship of the rigid polyurethane foams.

TABLE III
Comparison of Polyurethane Foam Properties

Polyols	Percentage PMDI used (100 iso-index)	Thermal conductivity (W/mK)	Density (kg/m^3)	Compressive strength (kPa)
Voranol® 490	61.6	0.026	46.6	459
ESBO (50R)[a]	60.0	0.032	47.3	337
EG-8 (50R)	57.4	0.027	42.0	366
EG-8 (50R), heated	57.4	0.028	41.5	336
EG-8 (75R)[b]	55.0	0.030	41.8	311

[a] 50R = 50% Voranol® 490 replacement.
[b] 75R = 75% Voranol® 490 replacement.

and 75% Voranol® 490 replacement and a modification in the foaming procedure was done on EG-8 at 50% replacement by heating the polyol blend as described in the Methods section. In the regular foaming of EG-8 at 50% replacement, better foam properties were achieved: a lower thermal conductivity value at 0.027 W/mK, a value close to the thermal conductivity of Voranol® 490 (0.026 W/mK), and a higher compressive strength than ESBO. A higher density was measured for ESBO, although there was no evident collapse of the foam observed after curing. The ESBO may act as a "filler" for the interaction between the highly reactive primary hydroxyl groups of Voranol® 490 and PMDI. Oxazolidone formation between the epoxy rings and isocyanate is unlikely at lower temperatures. A 5% reduction of PMDI was achieved for the regular foaming of EG-8 with ESBO as the basis.

The heated EG-8 polyol produced rigid foam with almost similar thermal conductivity and density values with the unheated EG-8 polyol. The objective of the polyol heating was to achieve a higher peak foaming temperature to boost the reaction rate between the A-side and B-side components. A significant drop in the compressive strength value was observed for the heated EG-8 foam. This might be due to the collapse of the PU cells caused by an imbalance of gelling and blowing rates. Foaming of EG-8 at 75% replacement of the Voranol® 490 was also possible and displayed better thermal conductivity than ESBO foam. There was no significant change in the density of the foam with respect to EG-8 at 50% replacement but the compressive strength dropped to about 15%. As the Voranol® 490 replacement increases, there is also a corresponding decrease in the amount of primary hydroxyl functional group which made up most of the petroleum-based polyol. This will slow down the reaction rate between the polyol blend and PMDI resulting in a less dense and weaker PU network that will cause a weaker compressive strength. A reduction of about 8% was achieved for EG-8 foams at 75% replacement.

CONCLUSIONS

In summary, high average equivalent weight polyols were synthesized by noncatalytic polymerization of ESBO and EG. A high molecular weight ESBO-EG complex was the major component of the polyols tested for waterblown rigid PU foams. EG-8 polyol at 50% Voranol® 490 replacement displayed closer thermal conductivity (0.027 W/mK) compared with that of 100% Voranol® 490 and better compressive strength compared with that of ESBO foam at 50% replacement. EG-8 polyol at 75% replacement was also possible and displayed a better thermal conductivity (0.030 W/mK) compared with that of ESBO at 50% replacement. The compressive strength dropped significantly by about 15% which was mainly attributed to a slower reaction rate of the polyol blend and PMDI (decreased primary hydroxyl content). The variation in hydroxyl content (primary and secondary alcohol content) of the polyols made a significant impact in the final compressive strength. EG-8 polyols at 50 and 75% replacement reduced PMDI quantity used by about 5 and 8% based on ESBO foam (at 50% replacement). Heating the polyols did not significantly improve foam properties.

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