### Thermal and Mechanical Behavior of Flexible Polyurethane-Molded Plastic Films and Water-Blown Foams with Epoxidized Soybean Oil

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**ABSTRACT:** Water-blown flexible polyurethane foams and molded plastic films were made by replacing 0 to 50% of Voranol<sup>®</sup> 4701 in the B-side of foam and plastic film formulation by epoxidized soybean oil (ESBO). Physical properties of foams including density, 50% compression force deflection (CFD), 50% constant deflection compression (CDC), and resilience were determined. A dynamic mechanical spectrometer (DMS) and a differential scanning calorimeter (DSC) were used to characterize the hard segment (HS) and soft segment (SS) ratio and thermal properties of plastic. Various functional groups in both flexible polyurethane foam and plastic film were characterized using Fourier transform-infrared spectroscopy with attenuated total reflectance (FTIR-ATR). When increasing the ESBO content,

#### INTRODUCTION

For many years, the derivatives from petroleum are the major feedstock or raw materials for the polymer industry. Polyurethane polymer is one of the most versatile plastic materials derived from the petroleum resource. Depending on the reactants and process methods, polyurethane polymer can be an elastomer, viscoelastic gel, foam, or plastic with a wide range of applications such as construction materials, automotives seating, furniture, packing materials, and medical devices.<sup>1-4</sup> The global consumption of polyurethane polymer shows an over 7% average growth rate annually in the past decade.<sup>5,6</sup> The petroleum price also shows a steady increase at the same time and a drastic increase within last year. Additionally, the petroleum is a finite and not environment-friendly resource. Therefore, finding a new and renewable resource to fully or partially replace the petroleum resource is urgent for both environmental and economic considerations.<sup>7</sup>

both density and 50% CFD of water-blown polyurethane foams decreased first, then increased. On the other hand, the 50% CDC and resilience of foams showed a sharp increase and decrease, respectively. When increasing the ESBO content, the peak of tan  $\delta$  in DMS analysis and  $\Delta c_p$  in DSC analysis of plastic films both decreased indicating the hard segment increased and the soft segment decreased in plastic film, respectively. The FTIR-ATR results also show the hydrogen-bonded urethane group increased in plastic films with increasing ESBO content. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1311–1317, 2009

**Key words:** flexible polyurethane foam; epoxidized soybean oil; DMS; DSC; FTIR

Because of lower cost, more environment-friendly and also bio-renewable, polyols derived from vegetable oils have a great potential to partially replace the petroleum resource. For the triglycerides, the major component of vegetable oils, to react with isocyanate and synthesize polyurethane, it is believed that the hydroxyl functional groups would have to be attached to them first and one of the common methods is through alcoholysis of epoxidized vegetable oils.<sup>8,9</sup> In this method, the triglycerides of vegetable oils were epoxidized first. Methanol was then used to open the oxirane ring and attach the hydroxyl groups, a process called alcoholysis. We have reported in our previous studies, however, that the epoxidized soybean oil (ESBO) can directly participate in the polyurethane foaming reaction without opening the oxirane ring first despite there is no hydroxyl functional group in ESBO.<sup>10,11</sup> The reaction mechanism between ESBO and isocyanate has yet to be elucidated and the effect of ESBO on the thermal, mechanical, and chemical properties of the resulting final products-polyurethane foams-has not been well studied and characterized. Therefore, a series of water-blown flexible polyurethane foams and molded plastic films were prepared in this study where 0–50% of a petroleum-based polyether polyol was replaced by ESBO. The objectives of this study

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TABLE I
Formulations for Water-Blown Flexible Polyurethane
Foam with Different Percentages of Epoxidized
Soybean Oil

Ingredients	Parts by weight		
B-side materials			
Voranol <sup>®</sup> 4701	100, 90, 80, 70, 60, 50		
Epoxidized Soybean Oil	0, 10, 20, 30, 40, 50		
DABCO <sup>®</sup> 33-LV	0.6		
DABCO® BL-17	0.2		
Stannous octoate	0.3		
Dibutyltin dilaurate	0.3		
Diethanolamine	2.2		
DABCO <sup>®</sup> DC 2585	1.0		
Blowing Agent (distilled water)	5.0		
A-side material			
PAPI <sup>®</sup> 27	Index 80 <sup>a</sup>		

<sup>a</sup> The quantity of isocyanate was based on an isocyanate index 80, defined as the actual amount of isocyanate used over the theoretical amount of isocyanate required, multiplied by 100.

were to investigate the effect of ESBO on the physical properties of water-blown polyurethane foams and on the thermal, mechanical, and chemical properties of water-blown polyurethane foams and molded plastic films.

#### MATERIALS AND METHODS

#### Materials

The petroleum-based polyether polyol and isocyanate used in this study were Voranol® 4701 with a hydroxyl number of 34 and PAPI® 27, a polymeric diphenylmethane diisocyanate (MDI) with a functionality (the average number of reactive functional group which is NCO) of 2.7, an average molecular weight of 340, and 31.4% part by weight of NCO (isocyanate) content. Voranol® 4701 and PAPI® 27 were obtained from Dow Chemical Co. (Midland, MI). The epoxidized soybean oil, Vikoflex® 7170, with a hydroxyl number of 403.8,<sup>10,11</sup> was supplied by Arkema Chemicals (Philadelphia, PA). DABCO® 33-LV, DABCO® BL-17, stannous octoate, dibutyltin dilaurate were used as catalysts and DABCO® DC2585 and diethanolamine, as a surfactant and a crosslinker, respectively, for flexible polyurethane foaming. DABCO® 33-LV is a gelling catalyst containing 33% triethylenediamine (TEDA) and 67% dipropylene glycol. DABCO® BL-17 is an acidblocked delayed-action blowing catalyst containing 70% bis (dimethylaminoethyl) ether diluted with 30% dipropylene glycol. DABCO® DC2585 is a silicone type nonionic surfactant. DABCO® 33-LV, DABCO® BL-17, and DABCO® DC2585 were from Air Products and Chemicals (Allentown, PA). Both stannous octoate and dibutyltin dilaurate were

obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO). Diethanolamine was from Fisher Scientific (Hanover Park, IL). Distilled water was used as the blowing agent.

#### Flexible polyurethane foam

Water-blown flexible polyurethane foams were made by replacing 0–50% B-side polyether polyols (Voranol<sup>®</sup> 4701) with ESBO in the foam formulation and the foaming procedure was the same as reported previously.<sup>10</sup> B-side materials contained a blend of polyols, chain extender, crosslinker, catalysts, surfactants, and blowing agent (water), whereas A-side contained the isocyanate only. Other factors in the foam formulation such as water content, catalysts, surfactant, and isocyanate index were kept constant. Table I shows the foam formulations for water-blown flexible polyurethane foams and Figure 1 shows typical foam specimens with 10 to 50% ESBO replacement. The amount of isocyanate was based on the total hydroxyl content of Voranol<sup>®</sup> 4701, epoxidized soybean oil, and distilled water.

#### Flexible polyurethane-molded plastic film

Flexible polyurethane plastic films were made by replacing 0–50% polyether polyol (Voranol<sup>®</sup> 4701) with ESBO. The isocyanate index was 100. Both polyol (Voranol<sup>®</sup> 4701 and ESBO) and PAPI<sup>®</sup> 27 were placed into a 500 mL plastic cup and mixed with a high speed mixer (3450 rpm) for 10 s. The mixture was then placed into a vacuum chamber and degassed for 15 min. The mixture was then poured into a vacuum chamber to



**Figure 1** Water-blown flexible polyurethane foams and plastic films. The upper image shows flexible water-blown polyurethane foams with 10 to 50% ESBO. The lower image shows polyurethane plastic films with 0 to 50% ESBO from left to right. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley. com.].

Physical Properties of Flexible Polyurethane Foams Containing 0 to 50% Epoxidized Soybean Oli						
	Control	10% ESBO	20% ESBO	30% ESBO	40% ESBO	50% ESBO
Density (kg/m <sup>3</sup> ) 50% CFD (kPa) 50% CDC (%) Resilience (%)	44.83 <sup>a</sup> 8.78 <sup>b</sup> 5.54 <sup>f</sup> 44.89 <sup>a</sup>	37.88 <sup>b</sup> 8.88 <sup>b</sup> 29.85 <sup>e</sup> 34.39 <sup>b</sup>	31.98 <sup>d</sup> 7.63 <sup>b</sup> 36.91 <sup>d</sup> 31.39 <sup>c</sup>	30.88 <sup>d</sup> 7.84 <sup>b</sup> 39.54 <sup>c</sup> 27.95 <sup>d</sup>	$\begin{array}{c} 33.60^{\rm c,d} \\ 9.81^{\rm b} \\ 45.70^{\rm b} \\ 25.39^{\rm e} \end{array}$	36.22 <sup>b,c</sup> 14.64 <sup>a</sup> 47.10 <sup>a</sup> 21.78 <sup>f</sup>

 TABLE II

 Physical Properties of Flexible Polyurethane Foams Containing 0 to 50% Epoxidized Soybean O

<sup>a,b,c,d,e,f</sup>Values with the same superscript within the same row are not significantly different at 5% level.

degas for 15 min. The mold was made of PTFE (Polytetrafluoroethylene) and it has six rectangular cells of 1 mm in depth, 15 mm in width, and 50 mm in length. Excess mixture with small bubbles was then scraped off from the PTFE mold. The plastic films, free from bubbles, were cured at 105°C overnight by placing the mold into a vacuum oven. After cooling at 23°C and 50% RH, the films were peeled off from the mold. Typical flexible polyurethane plastic film specimens made by replacing 0–50% polyether polyol with ESBO are shown in Figure 1.

#### Flexible polyurethane foam properties

Based on ASTM procedure D 3574-05, the density, 50% compression force deflection (CFD), 50% constant force deflection (CDC) or compression set, and resilience (ball rebound test) of flexible polyurethane foams were measured. The ASTM procedure D 3574-05 describes the standard test methods for flexible cellular materials including slab, bonded, and molded urethane foams. Fifty percent CFD was determined by a TA.HDi Texture Analyzer (Texture Technologies Corp., Scarsdale, NY). For 50% CDC or compression set, the initial foam sample thickness was measured first. The sample was then clamped between two flat plates and compressed to 50% of its initial thickness and placed into a VersaTenn III Temperature-Humidity Chamber (Tenney Engineering, Williamsport, PA) set at 70°C and 6% RH for 22 h. The final thickness was measured after the sample was removed from the constant temperature-humidity chamber and flat plates and placed in ambient environment (23°C and 50% RH) for 30 to 40 min. The compression set was calculated by the following equation:

$$C_t = \left(\frac{t_o - t_f}{t_o}\right) \times 100\%$$

where:

 $C_t$  = compression set expressed as a percentage of the original specimen thickness,

 $t_o$  = original thickness of test specimen, and

 $t_f$  = final thickness of test specimen.

#### Dynamic mechanical analysis

The dynamic mechanical properties of flexible polyurethane films were determined under a sinusoidal oscillation tension mode by a dynamic mechanical spectrometer (DMS 6100, Seiko Instruments, Kotoku, Japan). The dimensions of film samples were 20 mm  $\times$  5 mm  $\times$  1 mm. The strain amplitude, initial force, and minimum tension force were 10 µm, 400 g, and 20 g, respectively. The storage modulus (*E'*), loss modulus (*E''*) and tan  $\delta$  were recorded at a frequency of 1 Hz from -140 to 300°C at a ramp rate 2°C/min.

#### Differential scanning calorimetry

A differential scanning calorimeter (DSC 7, Perkin– Elmer, Waltham, MA) was used to determine the glass transition temperatures ( $T_g$ ) and specific heat change ( $\Delta c_p$ ) of polyurethane films. Approximately, 6 to 7 mg of polyurethane film was loaded into an aluminum sample holder and sealed. The sample was cooled to  $-140^{\circ}$ C and equilibrated for 5 min first and then heated to 300°C at 10°C/min.

### Fourier-transform infrared spectroscopy with attenuated total reflectance

A thermo scientific Nicolet<sup>TM</sup> 380 FTIR equipped with smart orbit diamond ATR attachment (Thermo Electron Corp., Madison, WI) was used to characterize the functional groups in both flexible polyurethane films and foams. The flexible polyurethane foams were ground first and then placed into a 105°C oven for 4 h to remove water that might have been absorbed. Both flexible foam powder and film samples were pressed against ATR diamond to ensure complete contact between them. A total of 64 scans of each sample from 4000 to 400 cm<sup>-1</sup> wave number were obtained at a resolution of 2 cm<sup>-1</sup>.

#### **RESULTS AND DISCUSSION**

#### Physical properties of flexible polyurethane foams

Table II shows the effect of epoxidized soybean oil on the density, 50% CFD, 50% CDC, and resilience of water-blown flexible polyurethane foams. The density decreased with increasing ESBO up to 30% and then increased. Because of the hydroxyl number difference between ESBO (403.8) and Voranol® 4701 (34), the quantity of isocyanate (PAPI® 27) used in the foam formulation increased with ESBO. At the same time, foam volume would also increase due to more carbon dioxide generation from the reaction of isocyanate with the blowing agent (water). The foam volume increase exceeded the weight increase resulting in a decrease in density. Above 30% ESBO, the volume increase effect might have reached its limit because the blowing agent (water) was exhausted. In addition, the gas retention might have deteriorated in the foam matrix. Both could be caused by the slower reaction rate of ESBO with PAPI® 27 than Voranol<sup>®</sup> 4701.<sup>11</sup>

Table II also shows the effect of ESBO on 50% compression force deflection of water-blown flexible polyurethane foams. The 50% CFD was almost identical at 0 and 10% ESBO replacement, and then slightly decreased at 20%. At 30% ESBO replacement, the 50% CFD was also almost identical to that at 20% replacement. A sharp increase in 50% CFD, however, was observed at 40 and 50% replacement. This could be explained by changes in foam density and hard segment. As ESBO increased from 0 to 30%, foam density decreased which would reduce the 50% CFD. However, the hard segment (HS) might have increased because ESBO had a higher hydroxyl number than Voranol® 4701 resulting in using more isocyanate in the foam formulation, which would increase the 50% compression force deflection.<sup>12</sup> These two effects (density decrease and hard segment increase) might have counteracted and cancelled each other. Thus, there was no significant change in 50% compression force deflection. When ESBO in foam exceeded 30%, both foam density and crosslinking density increased resulting in firmer foams.

The constant deflection compression set (50% CDC) of foams increased sharply when increasing ESBO (Table II). On the contrary, the resilience of foams decreased with increasing ESBO (Table II). It appears that the foams became less flexible and less resilient with increasing ESBO. This might be due to the difference in equivalent weight between Voranol<sup>®</sup> 4701 and ESBO. The equivalent weight of a polyol relates to or gives an indication of the length or distance between two adjacent hydroxyl functional groups in a polyol molecule. The polyol with a higher equivalent weight is expected to have a greater length or distance between two adjacent hydroxyl groups resulting in a longer "soft segment" in the polyurethane foam. When ESBO was introduced into the foaming system, the HS increased and SS decreased because the equivalent weight of ESBO (139) is only about one-twelfths of Voranol® 4701 (1650). A lower equivalent weight of ESBO



**Figure 2** Storage modulus (E') and loss modulus (E'') of flexible polyurethane films containing 0 to 50% ESBO. Note that the noise in 100% V4701 sample at higher temperature range was due to loss of elastic behavior when close to the film melting temperature.

would result in shorter polymer chains causing stiffer foams. Moreover, the backbone of ESBO is a triglyceride while Voranol<sup>®</sup> 4701 is linear in chemical structure. Thus, foams containing more ESBO would contain polymers with shorter chains. They would be more easily crushed or damaged by compression and less resilient than foams with more Voranol<sup>®</sup> 4701 in the foam formulation.<sup>11</sup>

### Dynamic mechanical analysis of polyurethane films

Dynamic mechanical analysis is often used to investigate the mechanical and thermal properties of polymers. Figure 2 shows both storage modulus and loss modulus and Figure 3 shows tan  $\delta$  of flexible polyurethane films containing 0 to 50% of ESBO from -100 to 200°C. Although the experiments were carried out from -140 to 300°C, no significant change in tan  $\delta$  was observed either in the temperature range lower than -100°C or higher than 200°C. This was also observed in the DSC results to be discussed later. The glass transition temperature was



Figure 3 Tan  $\delta$  versus temperature of flexible polyurethane films containing 0 to 50% ESBO.

determined from the maximum or peak in tan  $\delta$  or loss modulus. It is interesting to note that the glass transition temperatures for all films were about  $-48^{\circ}$ C, not affected by the percentage of ESBO. This is not unexpected as the soft segment (SS) of these polyurethane films was essentially the same<sup>13</sup> forming from the reaction of Voranol<sup>®</sup> 4701, a long and linear polyether polyol, with isocyanate. At temperatures lower than the glass transit temperature  $(T_g)$ , the storage moduli, E', were high ( $\sim 10^9$ ) indicating these films behave like a solid material. For the film made with 100% Voranol® 4701 and isocyanate, the storage modulus decreased rapidly and reached a plateau when the temperature exceeded  $T_g$ . This decrease was due to the dramatic increase in molecular motion.<sup>13</sup> When ESBO was introduced replacing some Voranol® 4701 in the polyurethane film, the decay or decrease in film's storage modulus was reduced and the reduction became more pronounced with increasing ESBO (Fig. 2). Also, instead of a plateau the storage modulus decreased gradually with temperature. Moreover, the storage modulus increased with increasing ESBO at temperatures higher than  $T_g$ . All of these phenomena indicate that the films became stiffer with increasing ESBO.<sup>14–16</sup>

Similar conclusions can be drawn based on the results of loss modulus, E", and tan  $\delta$ . The magnitude of maximal loss modulus (Fig. 2) and tan  $\delta$  (Table III) decreased with increasing ESBO indicating these films became less soft.<sup>13,14</sup> Because of the low equivalent weight and nonlinear triglyceride backbone chemical structure of ESBO, its reaction with

isocyanate is expected to form more hard segment (HS) than the reaction between Voranol<sup>®</sup> 4701 and isocyanate. Therefore, as ESBO increased and Voranol<sup>®</sup> 4701 decreased, HS would increase resulting in stiffer or firmer films.

# Differential scanning calorimetry analysis polyurethane films

Figure 4 shows the DSC heating curves of polyurethane films containing 0 to 50% ESBO from -100 to 200°C. All curves show a discontinuity in specific heat indicating a second-order transition. The glass transition temperature,  $T_{g}$ , of the polyurethane films was determined by taking the middle of the change in baseline which is the inflection point. They were about -54°C, independent of the percentage of ESBO in the film and slightly lower than that determined from the dynamic mechanical analysis method. This might be due to differences in heating rate (2°C/min by DMS versus 10°C/min by DSC) and/or due to using peak tan  $\delta$  value which is several degrees higher than peak E" in DMS.<sup>17</sup> The specific heat changes at  $T_g$ ,  $\Delta c_p$ , of the polyurethane films are listed in Table III. They decreased with increasing ESBO percentage. The specific heat change  $(\Delta c_{\nu})$  is an indication of the energy consumed for the phase change of the soft segment in polyur-ethane films at  $T_g$ .<sup>13</sup> As discussed in the previous section, the soft segment in the polyurethane films was formed from the reaction between Voranol® 4701, a long and linear polyether polyol, with isocyanate. Therefore, as more and more Voranol<sup>®</sup> 4701 was replaced by ESBO in the polyurethane film, the soft segment fraction in the film would decrease leading to the decrease in  $\Delta c_{p.}^{18-20}$ 

# FTIR-ATR analysis of polyurethane foams and films

The FTIR-ATR results of polyurethane films containing 0 to 50% of ESBO are shown in Figure 5 (wave number range 4000 to 500 cm<sup>-1</sup>) and Figure 6 (wave number range 1900 to 800 cm<sup>-1</sup>). The details of spectra interpretation and band assignments are provided in Table IV.<sup>21-23</sup> It is interesting to note that there are two peaks between 1000 and 800 cm<sup>-1</sup> one is 818 cm<sup>-1</sup> indicating the in-plane bending or scissoring (C—H) aromatic ring and the other, 923 cm<sup>-1</sup>, indicating the out-of-plane bending or

TABLE III	
Tan $\delta$ Maximum and $\Delta c_p$ of Flexible Polyurethane Molded Plastic	Containing 0 to 50% Epoxidized Soybean Oil

	Control	10% ESBO	20% ESBO	30% ESBO	40% ESBO	50% ESBO
Tan $\delta$ maximum	1.771	0.962	0.584	0.314	0.191	0.143
$\Delta c_p$ (J/°C g)	0.332	0.323	0.286	0.230	0.181	0.109

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**Figure 4** DSC analysis results of flexible polyurethane films containing 0 to 50% ESBO. These curves were vertically shifted to simplify comparisons.

wagging (C-H) aromatic ring.<sup>22</sup> No change in transmittance was found at wave number 863 and 916  $cm^{-1}$ (Fig. 6), the transmittances of the epoxy ring.<sup>22</sup> This seems to indicate all epoxy rings in ESBO were consumed when reacting with isocyanate in the presence of Voranol® 4701. The transmittance at wave number 1097 cm<sup>-1</sup> represents the aliphatic ether which is present in Voranol® 4701, but not in ESBO. Therefore, the transmittance at wave number 1097 cm<sup>-1</sup> became less pronounced with increasing ESBO. As shown by the transmittances at 1411, 1508, and 1592 cm<sup>-1</sup> (due to aromatic ring from isocyanate) and at wave number 2281 cm<sup>-1</sup> (due to the cyanate group from isocyanate), the residual or unreacted isocyanate in the polyurethane film increased with increasing ESBO. This was because the hydroxyl number of ESBO (403.8) is much



**Figure 5** FTIR-ATR results of flexible polyurethane films containing 0 to 50% ESBO from wave number 4000 to 500 cm<sup>-1</sup>.



**Figure 6** FTIR-ATR results of flexible polyurethane films containing 0 to 50% ESBO from wave number 1900 to 800 cm<sup>-1</sup>.

greater than Voranol<sup>®</sup> 4701 (34). Thus, the amount of isocyanate used in the film formulation increased with increasing ESBO. In addition, the hydroxyl groups in Voranol<sup>®</sup> 4701 are primary and are much more reactive with isocyanate than ESBO. The transmittance at wave number 2923 cm<sup>-1</sup> shows the stretching mode (C—H) in CH<sub>2</sub> became more pronounced with increasing ESBO. This is not unexpected because CH<sub>2</sub> was abundant in the chemical structure of ESBO, but not in Voranol<sup>®</sup> 4701 which

TABLE IV Assignments of Functional Groups in FTIR-ATR Spectra

Wave number (cm <sup>-1</sup> )	Possible interpretation
1097	$\upsilon$ (C—O—C) aliphatic ether <sup>22</sup>
1305	$\delta (N-H)^{22}$
1373	$\omega$ (C-H) in CH <sub>2</sub> <sup>22</sup>
1411	$\upsilon$ (C=C) aromatic ring (1410) <sup>22</sup> , $\upsilon$ (C-C)
	aromatic ring $(1412-1414)^{22}$ or
	deformed (C—H) epoxy (1414)? <sup>21</sup>
1457	$\delta$ (C-H) in CH <sub>2</sub> <sup>22</sup>
1508	$\upsilon$ (C–C) aromatic ring <sup>22</sup>
1540	$\upsilon$ (C–N) + $\delta$ (N–H) Amide II <sup>22</sup>
1592	$\upsilon$ (C=C) aromatic ring <sup>22</sup>
1716	$\upsilon$ (C=O) urethane Amide I, H-bonded <sup>22</sup>
1729	υ (C=O) urethane Amide I, nonbonded <sup>22</sup>
2281	Cyanate group (2280) <sup>23</sup>
2856	$v_s$ (C-H) in $CH_2^{22}$
2923	υ <sub>a</sub> (C—H) in CH <sub>2</sub> (2925) <sup>22</sup> , υ (C—H)
	epoxy (2929)? <sup>21</sup>
2969	$v$ (C–H) in CH <sub>3</sub> (2970) <sup>22</sup> , $v_a$ (C–H)
	in CH <sub>3</sub> (2970) <sup>22</sup> , $v_a$ (CH <sub>3</sub> ) +
	$v_a (OCH_2) (2968)?^{21}$
3351	υ (N—H) H-bonded <sup>22</sup>

Note:  $\upsilon =$  stretching mode,  $\upsilon_a =$  asymmetric stretching,  $\upsilon_S =$  symmetric stretching,  $\delta =$  in-plane bending or scissoring,  $\omega =$  out-of-plane bending or wagging,  $\tau =$  out-of-plane bending or twisting,  $\rho =$  in-plane bending or rocking

is a polyether polyol. The transmittances at wave numbers 1716 cm<sup>-1</sup> and 3351 cm<sup>-1</sup> represent hydrogen-bonded urethane amide (C=O) and (*N*-H), while that at wave number 1729 cm<sup>-1</sup> represent nonbonded urethane amide (C=O) (Table IV). It is interesting to note that the hydrogen-bonded urethane amide was absent in the polyurethane film containing 100% Voranol<sup>®</sup> 4701 and appeared only after some of the Voranol<sup>®</sup> 4701 was replaced by ESBO. On the other hand, the nonbonded urethane amide remained the same with or without ESBO. It is expected that the presence of more hydrogenbonded urethane amide would result in firmer or stiffer polyurethane film. Thus, the results were consistent with those obtained from DMS analysis.

The epoxy functional group in ESBO can react with isocyanate and produce oxazolidone.<sup>5</sup> This reaction, however, takes place at a much higher temperature ( $\sim 250^{\circ}$ C)<sup>24</sup> and a longer reaction time than those of typical polyurethane foaming reactions. The infrared absorbance or transmittance of oxazolidone is at wave number 1750 cm<sup>-1</sup>.<sup>24,25</sup> This was absent in the FTIR-ATR results (Fig. 6). Thus, oxazolidone was not present in the polyurethane film.

The FTIR-ATR results of polyurethane foams containing 0 to 50% ESBO (data not shown) were similar to those of polyurethane films containing 0 to 50% of ESBO. The transmittances at wave numbers 2856 and 2923 cm<sup>-1</sup> became more pronounced with increasing ESBO. These two wave numbers are assigned to the symmetric and asymmetric stretching mode (C-H) in  $CH_2$  which is present in the triglyceride structure of ESBO. In addition, increasing residual isocyanate in the polyurethane foam with increasing ESBO was evident as shown by the transmittances at wave numbers 1411, 1508, 1592, and 2281 cm<sup>-1</sup>. Similar to the FTIR-ATR results of polyurethane film, the transmittances at wave numbers 863, 916, and 1750 cm<sup>-1</sup> in all polyurethane foams indicate that these foams did not have any residual epoxy ring or containing any trace of oxazolidone. Further studies are needed to elucidate the reaction mechanism between ESBO and isocyanate.

#### CONCLUSIONS

The physical properties of water-blown flexible polyurethane foams containing 0 to 50% ESBO were studied. The density and 50% compression deflection properties were similar to or better than control flexible foams up to 30% ESBO, whereas the resilience and 50% constant deflection compression properties were inferior to control flexible foams. These were due to increase in hard segment with increasing ESBO resulting in firmer foams. In DMS analysis of plastic films, decreasing maximal tan  $\delta$  and increasing E' indicates the hard segment in plastic film increased with increasing ESBO. In DSC analysis, decreasing  $\Delta c_p$  indicates the soft segment in plastic film decreased with increasing ESBO. In FTIR-ATR experiment, hydrogen-bonded urethane group (HS) was found once ESBO was introduced into the molded plastic films, the films became firmer or stiffer. In addition, the epoxy ring and oxazolidone were absent in both flexible mold plastic and foams.

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