

Physical Properties of Water-Blown Rigid Polyurethane Foams Containing Epoxidized Soybean Oil in Different Isocyanate Indices

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ABSTRACT: To explore the potential of isocyanate usage reduction, water-blown rigid polyurethane foams were made by replacing 0, 20, and 50% of Voranoll[®] 490 in the B-side of the foam formulation by epoxidized soybean oil (ESBO) with an isocyanate index ranging from 50 to 110. The compressive strength, density, and thermal conductivity of foams were measured. The foam surface temperature was monitored before and throughout the foaming reaction as an indirect indication of the foaming temperature. Increasing ESBO replacement and/or decreasing isocyanate index decreased the foam's compressive strength. The density of the foam decreased while decreasing the isocyanate index to 60. Further decrease in isocyanate index resulted in foam shrinkage causing a sharp increase in the foam density. The thermal conductivity of foams

increased while decreasing the isocyanate index and increasing the ESBO replacement. Mathematical models for predicting rigid polyurethane foam density, compressive strength, and thermal conductivity were established and validated. Similar to compressive strength, the foaming temperature decreased while decreasing the isocyanate index and increasing the ESBO replacement. Because of the lower reactivity of ESBO with isocyanate, the rate of foaming temperature decrease with decreasing isocyanate index was in the order of 0% > 20% > 50% ESBO replacement. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2577–2583, 2009

Key words: rigid polyurethane foam; epoxidized soybean oil; foaming temperature; physical properties

INTRODUCTION

The crude oil price reached a historic high record of 140 to 150 US dollars per barrel briefly in summer 2008.¹ This resulted in a significant price increase in petroleum-based raw materials needed to make many consumer plastic products. For example, polyols and isocyanates, the two major raw materials of polyurethane, derived from the petroleum feedstock, have become increasingly more expensive in the past few years.^{2,3} Because of the wide range of properties and applications of polyurethane plastics,⁴ the global consumption of polyurethane polymer shows a steady increasing trend during the past decade.^{5,6} As a result, there are more green house gases resulting from the petroleum refining process while making polyols and isocyanate, which aggravate the global warming effect. Moreover, the petroleum is a finite resource and its supply will certainly be exhausted sooner or later. Because of these disadvan-

tages, researchers have been looking for alternative resources that are cleaner, renewable, and lower in cost to replace the petroleum. One potential candidate that has received significant attention in recent years is vegetable oil.

The basic chemical structure of vegetable oil is unsaturated triglyceride. To make polyols from unsaturated triglyceride, one commonly used method is to epoxidize the double bonds in the triglyceride structure and then convert the epoxy groups to hydroxyl groups by methanolysis.^{7–11} We have shown that the epoxidized soybean oil (ESBO) might be able to participate in the polyurethane foaming reaction without converting the epoxy groups to hydroxyl groups first.^{12–14} Because of its lower reactivity with isocyanate than polyether polyols in polyurethane foaming, replacing polyether polyols partially with ESBO may reduce the foaming temperature and the isocyanate in the foam formulation. Therefore, the objectives of this study were to investigate the effect of ESBO replacement and isocyanate index on the foaming temperature and the physical properties such as compressive strength, density, and thermal conductivity of water-blown rigid polyurethane foams.

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TABLE I
Formulations for Water-Blown Rigid Polyurethane Foam with Different Percentages of Epoxidized Soybean Oil and Isocyanate Indices

Ingredients	Parts by weight
B-side materials	
Voranoll [®] 490	100, 80, 50
Epoxidized soybean oil	0, 20, 50
POLYCATI [®] 5	1.26
POLYCATI [®] 8	0.84
DABCOI [®] DC 5357	2.5
Blowing agent (distilled water)	3.0
A-side material	
PAPII [®] 27	Index 110, 100, 90, 80, 70, 60, 50

MATERIALS AND METHODS

Materials

Voranol[®] 490 (Dow Chemical, Midland, MI), a commercial petroleum-derived polyether polyols with 4.3 functionality, prepared using sucrose and glycerine initiator, having an equivalent weight about 115 and a hydroxyl number of 490, is used in this study. PAPI[®] 27 (Dow Chemical), a polymeric diphenylmethane diisocyanate (MDI) with 2.7 NCO functionality, 340 average molecular weight, and 31.4% part by weight of NCO content. Vikoflex[®] 7170, an ESBO with a hydroxyl number of 403.8 was obtained from Arkema Chemicals (Philadelphia, PA). POLYCAT[®] 5 and POLYCAT[®] 8 were used as catalysts, and DABCO[®] DC5357 was used as the surfactant. POLYCAT[®] 5, POLYCAT[®] 8, and DABCO[®] DC5357 were obtained from Air Products and Chemicals (Allentown, PA) gratis.

Experimental design and formulations

The experimental design included replacing the B-side polyether polyols (Voranol[®] 490) with 0, 20, and 50% of ESBO and using seven isocyanate index levels ranging from 50 to 110 in the foam formulation. Other factors in the foam formulation, such as water content, catalysts, and surfactant, were kept constant. Table I shows the foam formulations for water-blown rigid polyurethane foams, and Table II shows the isocyanate usage in different isocyanate indices and different percentages of Voranol[®] 490 and ESBO. The amount of isocyanate was based on the total hydroxyl content of Voranol[®] 490, ESBO, catalysts, surfactant, and distilled water.

Rigid polyurethane foaming procedures

A standard laboratory mixing and pouring procedure for making water-blown polyurethane foams was used.¹⁵ The petroleum polyol (VORANOL[®]

490), vegetable oil-based polyol, catalysts, surfactant, and blowing agent (B-side materials) were added by weighing into a 500-mL disposable plastic cup and mixed at 3450 rpm for 10–15 s. The mixture was allowed to degas for 120 s. PAPI[®] 27 (A-side material) was then added rapidly and stirring was continued for another 10–15 s at the same speed. The mixtures were poured immediately into a wooden mold (11.4 cm × 11.4 cm × 21.6 cm) with aluminum foil lining, and then the foam was allowed to rise and set at ambient conditions (23°C).

Rigid polyurethane foaming temperature measurement

An Omega Engineering OS552A-MA-4 (Omega Engineering, Stamford, CT) infrared thermometer equipped with a wireless transmitter and receiver was used to measure the surface temperature of water-blown rigid polyurethane foams in different ESBO contents and isocyanate indices. The temperature measurement covered an area of 2.54 cm in diameter up to 76.2 cm between the subject and infrared thermometer. The infrared thermometer was held at 40.64 cm above the wooden mold and focused on the center of mold. The temperature recording was started 10 s before the polyurethane mixture was poured into the wooden mold and stopped after 500 s. The response time of the temperature recording was 1 s.

TABLE II
The Isocyanate Usage in Different Isocyanate Indices and Different Percentages of Voranol[®] 490 and ESBO

Voranoll [®] 490 (pbw)	ESBO (pbw)	Isocyanate index	Isocyanate amount ^a (pbw)
100	0	110	176.6
100	0	100	160.6
100	0	90	144.5
100	0	80	128.5
100	0	70	112.4
100	0	60	96.34
100	0	50	80.28
80	20	110	172.4
80	20	100	156.7
80	20	90	141.0
80	20	80	125.3
80	20	70	109.7
80	20	60	94.01
80	20	50	78.34
50	50	110	165.9
50	50	100	150.8
50	50	90	135.8
50	50	80	120.7
50	50	70	105.6
50	50	60	90.51
50	50	50	75.42

^a The isocyanate usage of water (3 pbw), catalysts (2.1 pbw), and surfactant (2.5 pbw) were also included.

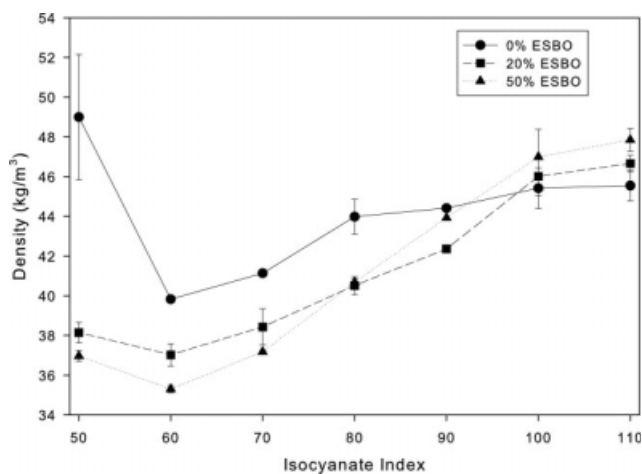


Figure 1 Effect of isocyanate index and ESBO replacement percentage on the density of water-blown rigid polyurethane foams.

Rigid polyurethane foam property measurements

Apparent thermal conductivity of samples was determined in duplicate, after curing at room temperature (23°C) for 24 h by a Fox 200 heat flow meter instrument (LaserComp, Wakefield, MA) using the American Society for Testing and Materials (ASTM) procedure C 518-04. The dimension of the foam samples was 20 cm × 20 cm × 2.5 cm. Density of foam samples was measured according to ASTM procedure D 1622-03. Compressive strength of foams was determined by a TA.HDi Texture Analyzer (Texture Technologies Corp., Scarsdale, NY) following ASTM procedure D 1621-04a. Both density and compressive strength were conducted after foams were stored for 7 days at room temperature (23°C and 50% RH), and the dimension of the foam sample was 6.35 cm × 6.35 cm × 3.81 cm. Five measurements were made for each treatment, and the average was reported.

Modeling of compressive strength, density, and thermal conductivity

Based on the data from a previous study¹³ and this work, three mathematical models were established by regression to describe the effect of ESBO fraction and isocyanate ratio on compressive strength, density, and thermal conductivity of water-blown rigid polyurethane foams. The ESBO fraction is defined as the ESBO amount used in foaming divided by the total polyol amount, and the isocyanate ratio is the actual amount of isocyanate used in foaming divided by the theoretical amount of isocyanate. Thus, the isocyanate index is equal to the isocyanate ratio multiplied by 100. These mathematical models were based on second-order polynomial equations using the statistical software SAS 9.1 (SAS Institute, Cary,

NC). The dependent variables were compressive strength, density, and thermal conductivity, and the independent variables were the ESBO fraction from 0.1 to 0.5 and the isocyanate ratio from 0.5 to 1.1. The second-order polynomial equation is as follows:

$$y_n = a_{n0} + a_{n1}e + a_{n2}i + a_{n3}ei + a_{n4}e^2 + a_{n5}i^2$$

where y_n = compressive strength (when $n = 1$), density (when $n = 2$), and thermal conductivity (when $n = 3$); e = ESBO fraction; i = isocyanate ratio; ei = interaction between ESBO fraction and isocyanate ratio; and a_{n0} to a_{n5} = intercept and regression coefficients based on the second-order polynomial equations.

RESULTS AND DISCUSSION

Density

Figure 1 shows the effect of ESBO replacement and isocyanate index on the density of polyurethane foams. The mathematical model is given as follows:

$$y_2 = 57.149 - 48.725e - 39.541i + 37.689ei + 24.964e^2 + 27.316i^2 \quad (R^2 = 0.8093)$$

This model is depicted in Figure 2.

As shown in Figures 1 and 2, the density of polyurethane foams decreased when decreasing the isocyanate index from 110 to 60. This was because, first of all, the isocyanate in the polyurethane formulation

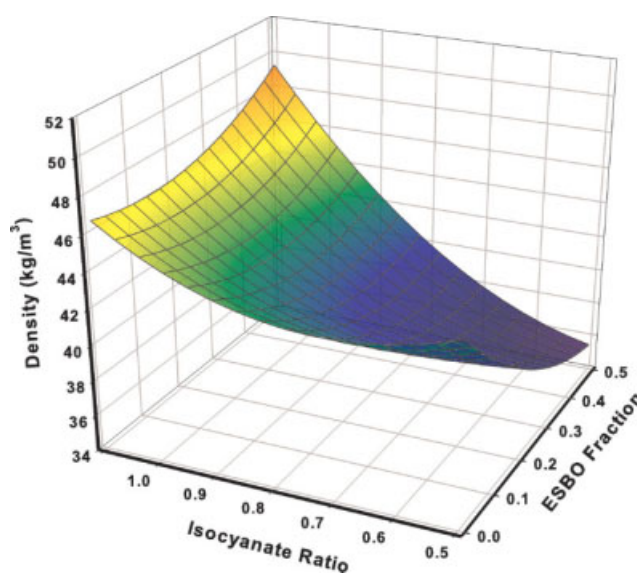


Figure 2 The regression plane ($R^2 = 0.8093$) of density of water-blown rigid polyurethane foams with different ESBO fractions and isocyanate ratios. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was less when decreasing the isocyanate index resulting in less polymer solid in the foam structure.¹⁶ Second, the amount of blowing catalyst (POLYCAT[®] 5) in this experiment was higher than that of the gelling catalyst (POLYCAT[®] 8). Most of the water in the polyurethane formulation might have reacted with isocyanate producing carbon dioxide regardless of the isocyanate index. It was also likely that the effect of reducing isocyanate index has less effect on the reaction between water and isocyanate. Thus, the reduction in foam volume was less than the reduction in foam weight while reducing the isocyanate index from 110 to 60. Therefore, the density of foams reduced while reducing the isocyanate index. When the isocyanate index was lower than 60, however, the structure of the polyurethane foam was probably too weak to hold its shape because of insufficient isocyanate in the foam formulation and the foam showed significant shrinkage within 24 h after the foam was made. As a result, the density of foam showed a sharp increase while reducing the isocyanate index from 60 to 50.

It is interesting to note that the density of foams increased with the percentage of ESBO replacement when the isocyanate index was 100 or higher, but decreased with the percentage of ESBO replacement when the isocyanate index was less than 80. We showed in a previous study that ESBO could react with isocyanate in the presence of a polyether polyol, but the reactivity between ESBO and isocyanate was lower than that between polyether polyol, which contains primary hydroxyl groups and isocyanate.¹⁴ When the isocyanate index was 100 or higher, the isocyanate in the foam formulation was sufficient to react with catalysts, water, polyether polyol, and ESBO. Because of the lower reactivity between ESBO and isocyanate, the polyurethane foam structure was weaker with more open cells at a higher percentage of ESBO replacement.¹³ Therefore, the volume of foams was less, leading to higher foam density. When the isocyanate index was less than 80, catalysts, water, polyether polyol, and ESBO would compete for a reaction with isocyanate. The higher the ESBO replacement percentage, the less was the polyether polyol in the foam formulation to compete with water for reacting with isocyanate. In addition, the hydroxyl number of ESBO is less than that of Voranol[®] 490. The foam with a higher ESBO replacement would weigh less at the same isocyanate index. Therefore, the higher the ESBO replacement percentage, the lower was the foam density when the isocyanate index was less than 80.

When the isocyanate index was 50, the foam density at 0% ESBO replacement was much higher than at 20 and 50%. It was observed that the foam at 0% ESBO replacement had severe shrinkage within 24 h after foaming, whereas the foams at 20 and 50%

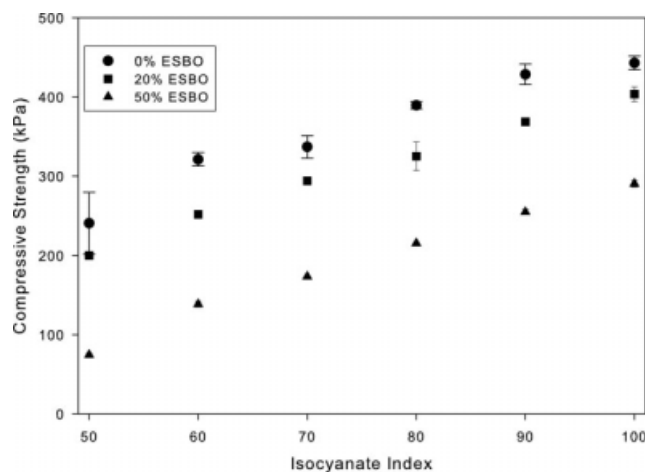


Figure 3 Effect of isocyanate index and ESBO replacement percentage on the compressive strength of water-blown rigid polyurethane foams.

ESBO replacement had moderate shrinkage. This was because the foam with a higher ESBO replacement would have a lower closed cell percentage.¹³ When the isocyanate index was 50, the foam structure was too weak to hold its shape. Thus, all the foams shrank within 24 h after foaming. Foams with a higher ESBO replacement containing more open cells, however, would shrink less because of the less pressure difference between the inside and outside of foams.

Compressive strength

Figure 3 shows the effect of ESBO replacement and isocyanate index on the compressive strength of water-blown rigid polyurethane foams. The second-order mathematical model is given as follows:

$$y_1 = -106.188 - 347.720e + 906.726i + 156.864ei - 198.899e^2 - 364.087i^2 \quad (R^2 = 0.9715)$$

This model is shown in Figure 4. As shown in Figures 3 and 4, the compressive strength of water-blown rigid polyurethane foams decreased not only while decreasing the isocyanate index but also while increasing the ESBO replacement. This was because both decreasing isocyanate index and increasing ESBO replacement would reduce the amount of isocyanate usage in the polyurethane foams. The latter was because the hydroxyl number of ESBO (403.8) is less than that of Voranol[®] 490 (490).

In polyurethane reaction, polyols reacts with isocyanate and generates polyurethane, which react with isocyanate further to generate allophanate. Water reacts with isocyanate generating carbon dioxide and amine, and then amine reacts with

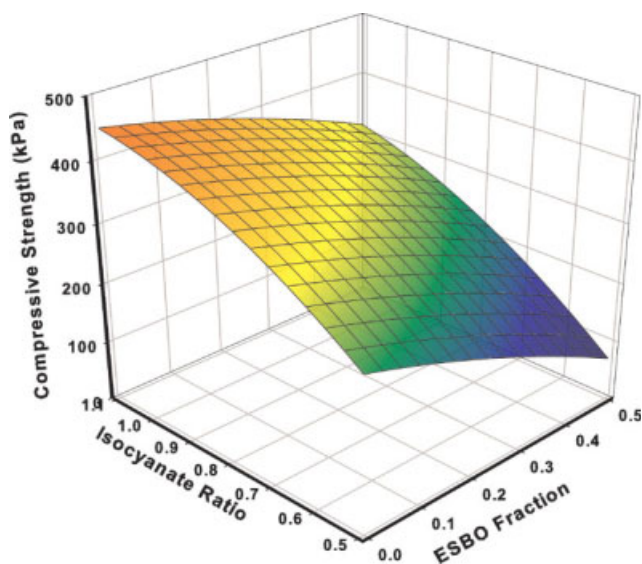


Figure 4 The regression plane ($R^2 = 0.9715$) of compressive strength of water-blown rigid polyurethane foams with different ESBO fractions and isocyanate ratios. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

isocyanate and generate disubstituted urea,¹⁷ which may further react with isocyanate to generate biuret.¹⁷ The more allophanate, disubstituted urea, and biuret are present in the polyurethane polymer, the higher is the polymer's crosslinking density.¹⁷ Therefore, the lower the isocyanate index or the less the isocyanate usage in the polyurethane foam, the lower is the foam's crosslinking density, which leads to a lower compressive strength.¹²

Thermal conductivity

Figure 5 shows the effect of ESBO replacement and isocyanate index on the thermal conductivity of foams. The mathematical model is given as follows:

$$y_3 = 0.04612 - 0.00943e - 0.03719i + 0.03750e^2 + 0.01718i^2 \quad (R^2 = 0.8405)$$

This model is shown in Figure 6. The thermal conductivity of foams with 0% and 20% ESBO replacement increased gradually with decreasing isocyanate index and most foams had a thermal conductivity lower than 0.028 W/mK. This might be due to a high percentage of closed cells in these foams.¹³ While decreasing the isocyanate index, more polyols would remain unreacted, which might cause a slight decrease in the closed cell percentage leading to a slight increase in the thermal conductivity. When the isocyanate index was 50, the foams at 0% and 20% ESBO replacement showed shrinkage within 24 h after foaming. In fact, the thermal conductivity

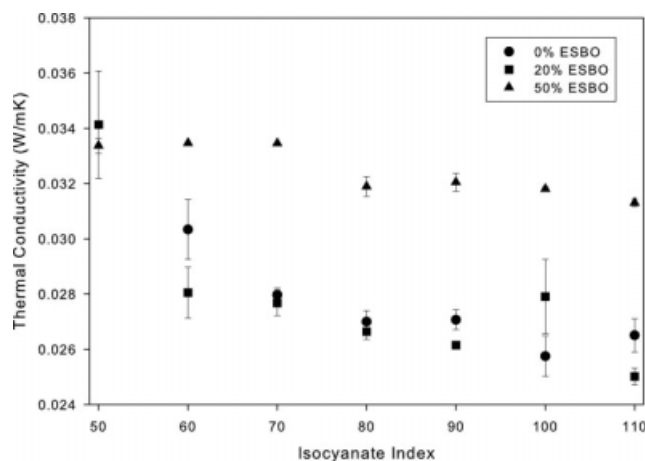


Figure 5 Effect of isocyanate index and ESBO replacement percentage on the thermal conductivity strength of water-blown rigid polyurethane foams.

measurement of foam at 0% ESBO replacement was not possible due to severe shrinkage. The density of foam at 20% ESBO replacement was high due to foam shrinkage. Because foam solid conducts heat better than gases, a denser foam would result in higher thermal conductivity. The thermal conductivity change of foams at 50% ESBO replacement with decreasing isocyanate index followed the same trend as foams at 0 or 20% ESBO replacement and all foams had a thermal conductivity of 0.032 W/mK or slightly higher. This was because the closed cell percentage was lower or cells were more open than foams at 0 or 20% ESBO replacement. As a result,

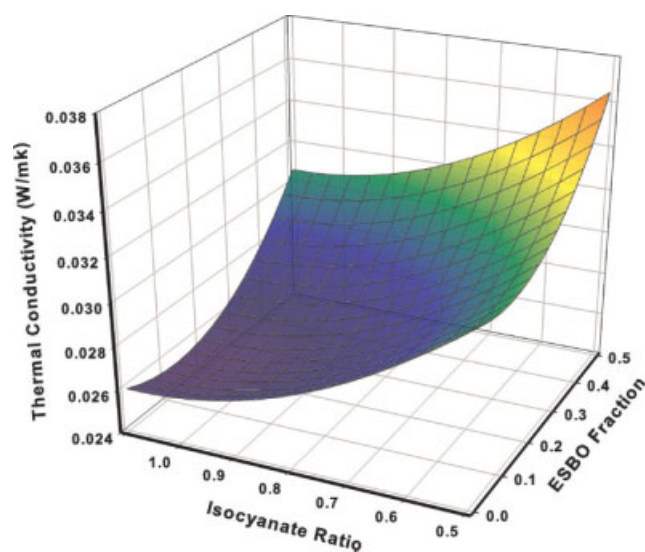


Figure 6 The regression plane ($R^2 = 0.8405$) of thermal conductivity of water-blown rigid polyurethane foams with different ESBO fractions and isocyanate ratios. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Experimental and Predicted Thermal Conductivity,
Density and Compressive strength

ESBO fraction	Isocyanate ratio	Experimental	Predicted	$ \varepsilon $ (%)
Density (kg/m³)				
0.1	1.0	44.1	44.1	0.00
0.1	0.8	40.0	41.4	3.34
0.3	1.0	43.9	43.9	0.00
0.3	0.8	38.8	39.7	2.10
Compressive strength (kPa)				
0.1	1.0	410.7	415.4	1.12
0.1	0.8	366.0	362.0	1.11
0.3	1.0	354.0	361.3	2.02
0.3	0.8	294.2	301.6	2.44
Thermal conductivity (W/mK)				
0.1	1.0	0.02589	0.02554	1.36
0.1	0.8	0.02584	0.02680	3.56
0.3	1.0	0.02664	0.02666	0.06
0.3	0.8	0.02717	0.02791	2.65

less carbon dioxide was trapped in the foam and it had more convection heat transfer leading to a higher thermal conductivity.

Model validation

To validate the reliability of the mathematical models of density, compressive strength, and thermal conductivity, four rigid polyurethane foams with different ESBO fractions and isocyanate ratios were made, and the properties of the foam were determined according to the methods mentioned previously. The results are shown in Table III. It can be seen that the absolute errors between predicted and experimental value were less than 3.34, 2.44, and 3.56% for density, compressive strength, and thermal conductivity values, respectively. Thus, the mathematic models for these three physical properties appear to be adequate.

Foaming temperature

Figure 7 shows the foaming temperature profiles of rigid polyurethane foams containing 0% to 50% ESBO at isocyanate index 110. The effect of ESBO replacement and isocyanate index on the foaming temperature of water-blown polyurethane foams is shown in Figure 8. As shown, the foaming temperature decreased with both decreasing isocyanate index and increasing ESBO replacement percentage. In the water-blown polyurethane foaming reaction at isocyanate index 100, catalysts, water, and polyols reacted with isocyanate and released heat. At isocyanate index less than 100, less isocyanate was present to react with catalysts, water, and polyols, and thus less heat was released leading to a lower foaming temperature. At isocyanate index 110, the 10% excess

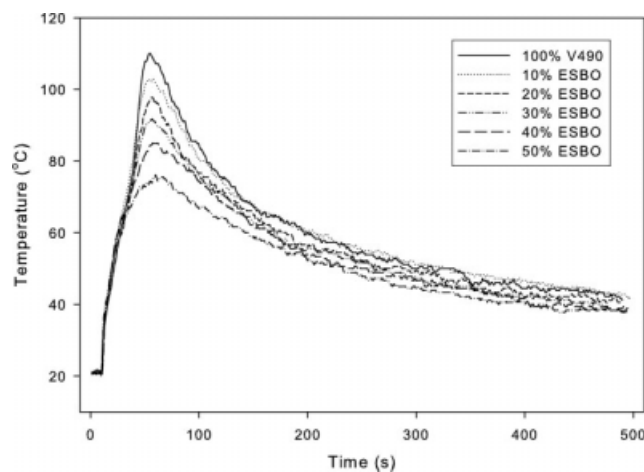


Figure 7 Temperature profiles of water-blown rigid polyurethane foams containing 0% to 50% ESBO at isocyanate index 110.

amount of isocyanate in the foaming system could react with amine, the byproduct from the reaction of water and isocyanate, and generate disubstituted urea. This chemical reaction is also exothermic raising the foaming temperature.

The foaming temperature decreased while increasing the ESBO replacement percentage and could be explained by the fact that the reactivity of isocyanate with ESBO is lower than that with polyether polyol, which contains primary hydroxyl groups.¹⁴ Regardless of the isocyanate index, a lower reactivity of isocyanate with ESBO would cause either a slower release of heat generated from this exothermic reaction or partial release if insufficient isocyanate was present in the foaming system because of lower isocyanate index.

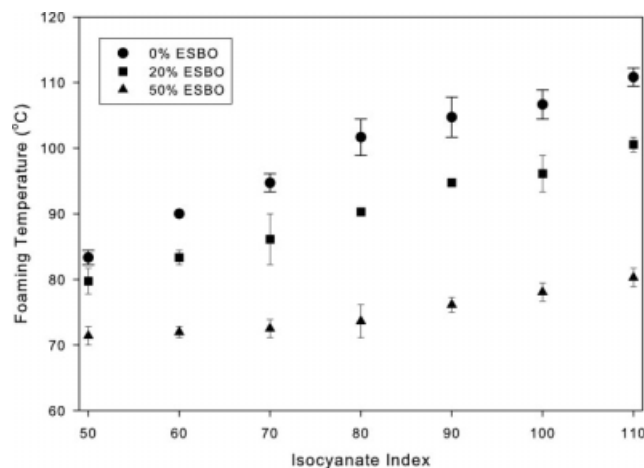


Figure 8 Effect of isocyanate index and ESBO replacement percentage on the foaming temperature of water-blown rigid polyurethane foams.

It is also interesting to note that the foaming temperature decreasing rate with decreasing isocyanate index at various ESBO replacement percentages differed. At 0% ESBO replacement, the decreasing rate was the highest, followed by at 20% and then at 50% ESBO replacement. This could also be explained by the slower reaction rate between isocyanate and ESBO than that between isocyanate and polyether polyol. The presence of ESBO in the foaming system, because of its lower reaction rate with isocyanate, would lessen the impact of reducing isocyanate index causing the reduction in the foaming temperature.

CONCLUSIONS

In this work, the effect of ESBO replacement and isocyanate index on the foaming temperature and physical properties of water-blown rigid polyurethane foams was investigated. Changes in foaming temperature and physical properties could be essentially attributed to the lower reactivity between ESBO and isocyanate than between polyether polyol and isocyanate. It is worth noting that when 20% of the polyether polyol (Voranol[®] 490) was replaced by ESBO, the foam at isocyanate index 90 had slightly favorable (lower) density and thermal conductivity values than the control foam (containing 100% polyether polyol) at isocyanate index 110, although the compressive strength value was slightly less favorable. Therefore, replacing 20% of the polyether polyol offers the possibility of reducing isocyanate in the foam formulation in applications in which compressive strength is not as critical.

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