

Water-Blown Rigid and Flexible Polyurethane Foams Containing Epoxidized Soybean Oil Triglycerides

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ABSTRACT: Both rigid and flexible water-blown polyurethane foams were made by replacing 0–50% of Voranol[®] 490 for rigid foams and Voranol[®] 4701 for flexible foams in the B-side of foam formulation by epoxidized soybean oil. For rigid water-blown polyurethane foams, density, compressive strength, and thermal conductivity were measured. Although there were no significant changes in density, compressive strength decreased and thermal conductivity decreased first and then increased with increasing epoxidized soybean oil. For flexible water-blown polyurethane foams, density, 50% compression force deflection, 50% constant force deflection, and resilience of foams were measured. Density decreased first and then increased, no changes in 50% compression force deflection first and then

increased, increasing 50% constant force deflection, and decreasing resilience with increase in epoxidized soybean oil. It appears that up to 20% of Voranol[®] 490 could be replaced by epoxidized soybean oil in rigid polyurethane foams. When replacing up to 20% of Voranol[®] 4701 by epoxidized soybean oil in flexible polyurethane foams, density and 50% compression deflection properties were similar or better than control, but resilience and 50% constant deflection compression properties were inferior. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 537–544, 2008

Key words: rigid polyurethane foam; flexible polyurethane foam; epoxidized soybean oil

INTRODUCTION

With numerous advantages like light weight, good heat insulation, excellent strength and weight ratio, and good force and sound absorbing properties, the consumption of polyurethane foams has grown rapidly and they become indispensable part in our daily life.¹ Effort to use alternative resources to replace finite petroleum for making polyurethane foams has been accelerated in recent years. The major alternative and renewable resources are vegetable oils such as soybean oil. Soybean oil is a triglyceride which contains several unsaturated π bonds as shown in Figure 1. Several methods have been reported for converting soybean oil triglyceride into polyols. For example, the hydroxyl functionalities^{2–4} or the epoxy group^{5–7} can be attached directly to the unsaturated π bonds in the soybean oil triglyceride. Unlike the group with hydroxyl functionalities, the epoxy group does not react directly with the isocyanate.⁸ Therefore, the epoxy rings in the epoxidized soybean oil triglyceride will need to be converted further into hydroxyl groups through other methods.^{9–13} However, in a previous study, we found that epoxidized

soybean oil triglyceride can be blended with a commercial polyether polyol and used in polyurethane foaming directly. The epoxidized soybean oil triglyceride has a high hydroxyl number (403.8) and the resulting foam has excellent density versus compressive strength properties.¹⁴ Epoxidized soybean oil appears to have participated in the polyurethane foaming reaction and formed the crosslinking structure. The objective of this study is to further investigate the role of epoxidized soybean oil in both rigid and flexible water-blown polyurethane foams.

MATERIALS AND METHODS

Materials

Epoxidized soybean oil (Vikoflex[®] 7170) used in this study was supplied by ATOFINA Chemicals (Philadelphia, PA) with a hydroxyl number of 403.8.^{14,15} Voranol[®] 490 and Voranol[®] 4701 are petroleum-based polyether polyols with a hydroxyl number of 490 and 34 for rigid and flexible foam applications, respectively. PAPI[®] 27, a polymeric diphenylmethane diisocyanate (MDI) with 2.7 NCO functionality, has 340 average molecular weight, and 31.4% part by weight of NCO content. Voranol[®] 490, Voranol[®] 4701, and PAPI[®] 27 were obtained from Dow Chemical (Midland, MI). The catalysts for rigid polyurethane foaming were POLYCAT[®] 5 and POLYCAT[®] 8. A surfactant, DABCO[®] DC5357, was used

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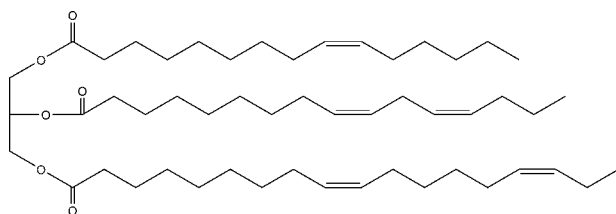


Figure 1 The chemical structure of soybean oil triglyceride.

in rigid polyurethane foaming. DABCO[®] 33-LV, DABCO[®] BL-17, stannous octoate, and dibutyltin dilaurate were used as catalysts and DABCO[®] DC2585 was the surfactant for flexible polyurethane foaming. A crosslinker, diethanolamine, was used in flexible polyurethane foaming. POLYCAT[®] 5, POLYCAT[®] 8, DABCO[®] 33-LV, DABCO[®] BL-17, DABCO[®] DC5357, and DABCO[®] DC2585 were from Air Products and Chemicals (Allentown, PA) gratis. Both stannous octoate and dibutyltin dilaurate were obtained from Sigma-Aldrich Chemical (St. Louis, MO). Diethanolamine was from Fisher Scientific (Hanover Park, IL). Distilled water was used as the blowing agent.

Experimental design and formulations

The effects of replacing the B-side polyether polyols (Voranol[®] 490 and Voranol[®] 4701) with 0–50% of epoxidized soybean oil in the foam formulation on the properties of water-blown rigid and flexible polyurethane foams were studied. Other factors in the foam formulation such as water content, catalysts, surfactant, and isocyanate index were kept constant. Tables I and II show the foam formulations for water-blown rigid and flexible polyurethane foams, respectively. The amount of isocyanate was based on the total hydroxyl content of Voranol[®] 490, Voranol[®] 4701, epoxidized soybean oil, and distilled water.

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

Ingredients	Parts by weight
B-side materials	
Voranol [®] 490	100, 90, 80, 70, 60, 50
Epoxidized soybean oil	0, 10, 20, 30, 40, 50
Polycat [®] 5	1.26
Polycat [®] 8	0.84
DABCO [®] DC5357	2.5
Blowing agent (distilled water)	3.0
A-side material	
PAPI [®] 27	Index 110 ^a

^a The quantity of isocyanate was based on an isocyanate index 110, defined as the actual amount of isocyanate used over the theoretical amount of isocyanate required, multiplied by 100.

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

Ingredients	Parts by weight
B-side materials	
Voranol [®] 4701	100, 90, 80, 70, 60, 50
Epoxidized soybean oil	0, 10, 20, 30, 40, 50
DABCO [®] 33-LV	0.6
DABCO [®] BL-17	0.2
Stannous octoate	0.3
Dibutyltin dilaurate	0.3
Diethanolamine	2.2
DABCO [®] DC2585	1.0
Blowing agent (distilled water)	5.0
A-side material	
PAPI [®] 27	Index 80 ^a

^a 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.

Foam properties measurements

Rigid polyurethane foam properties

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 American Society of 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, 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 reported.

Flexible polyurethane foam properties

The density, 50% compression force deflection, 50% constant force deflection, and resilience (ball rebound test) of flexible polyurethane foams were measured according to ASTM procedure D 3574-05. Fifty percent compression force deflection was determined by a TA.HDi Texture Analyzer (Texture Technologies). For 50% constant force deflection or compression set, the initial foam thickness was measured first. The foam was then pressed to 50% of 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 foam was

removed from the constant temperature-humidity chamber and placed in ambient environment (23°C and 50% RH) for 30–40 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 thickness, t_o = original thickness of test specimen, and t_f = final thickness of test specimen.

Closed cell measurement of water-blown rigid polyurethane foams

A Quantachrome Instruments Ultrapycnometer 1000 (Boynton Beach, FL) was used to determine the closed cell percentage of water-blown rigid polyurethane foams. The specimen's dimension was one cubic inch and the uncorrected method was used. A total of six specimens from each treatment were tested and the average reported.

Extractable oil of water-blown rigid polyurethane foams

The determination of extractable oil in polyurethane foams was based on ASTM Procedure C 613-97 (Reapproved 2003) using the Soxhlet procedure. Rigid foams containing 0% (control) and 50% of epoxidized soybean oil were prepared and aged at ambient environment for 12, 36, 60, 84, 108, 132, and 156 h, respectively. Hexane, obtained from Fisher Scientific (Hanover Park, IL), was used as the extraction reagent. The extraction time was 6 h at the room temperature (23°C). The extraction thimble was placed into a 100°C-oven overnight to remove hexane and then cooled to room temperature to determine the sample weight after extraction. The extractable oil was calculated as follows:

$$\text{Extractable oil (\%)} = \frac{W_o - W_e}{E} \times 100\%$$

where W_o = sample weight before extraction, W_e = sample weight after extraction, and E = weight of B-side polyols in sample.

Morphology of water-blown rigid polyurethane foams

A Hitachi S-4700 field emission scanning electron microscope (FESEM, Tokyo, Japan) was used to examine the surface of water-blown rigid polyurethane foams containing 0–50% of epoxidized soybean oil. The water-blown rigid polyurethane foams were first cut into 3-mm cubes and then attached to the sub-

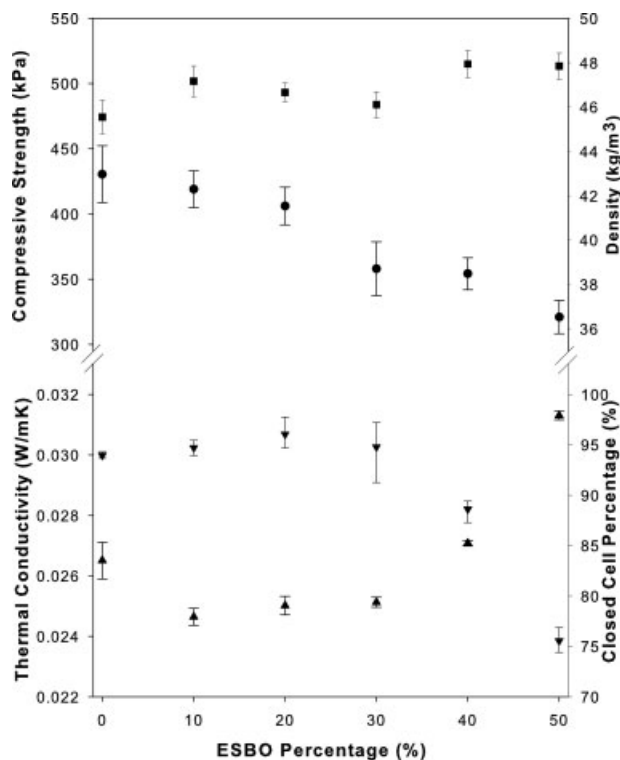


Figure 2 Effect of epoxidized soybean oil on compressive strength (●), density (■), thermal conductivity (▲), and closed cell percentage (▼) of water-blown rigid polyurethane foams.

strate with silver glue. Each sample was coated with gold by plasma sputter due to the nonconductivity of polyurethane. Samples were placed into the outer vacuum chamber and vacuumed after coated with gold. They were then moved into the inner chamber and under an electron gun after the pressure was balanced between outer and inner chambers. The accelerating voltage and emission current of FESEM were 5000 V and 9700 nA, respectively.

RESULTS AND DISCUSSION

Density and compressive strength of rigid foam

Figure 2 shows the effect of epoxidized soybean oil on the density of water-blown rigid polyurethane foams. As shown, there was no significant difference in foam density as epoxidized soybean oil was increased from 0 to 50%. The density of plastic foam is determined by the weight and volume of the plastics making up the foam matrix and the gases trapped in the foam cells. The plastic phase includes polyol, epoxidized soybean oil, isocyanate, and all additives such as surface active agents, stabilizers, crosslinking agents, or processing aids (catalysts). The gas phase includes carbon dioxide, generated from the chemical reaction between the blowing agent (water) and isocyanate, and air which is either intro-

duced during mixing or diffuses into the cells during the aging process. The blowing agent (water) was set at 3% for all foams. Although the isocyanate index was set at 110, the quantity of PAPI[®] 27 (isocyanate) in the foam formulation decreased slightly (about 6%) when increasing the epoxidized soybean oil from 0 to 50%. This was because the hydroxyl number of epoxidized soybean oil (403.8) is less than 490 of Voranol[®] 490. The reduction in isocyanate content might have not been sufficient to cause changes in foam density. On the other hand, the compressive strength of foams decreased with increasing epoxidized soybean oil percentage ($r = -0.98$) as shown in Figure 2. This was most likely caused by the following: (1) the slight reduction in isocyanate content when increasing epoxidized soybean oil lowered the foam crosslinking density and (2) a weaker three-dimensional foam network when increasing epoxidized soybean oil content due to a lower reaction rate of epoxidized soybean oil (containing secondary reactive functional groups) with isocyanate than Voranol[®] 490 (containing primary hydroxyl groups).^{14–16}

Thermal conductivity and closed cell percentage of rigid foam

Figure 2 also shows the effect of replacing Voranol[®] 490 with 0–50% of epoxidized soybean oil on thermal conductivity and closed cell percentage of water-blown rigid polyurethane foams. It is interesting to note that the foam thermal conductivity decreased while closed cell percentage was not affected with increasing epoxidized soybean oil up to 30%. This might be due to decreased polymer phase or solid structure with increasing epoxidized soybean oil content. As explained earlier, when increasing epoxidized soybean oil, the corresponding isocyanate content in the foam formulation decreased because epoxidized soybean oil had a lower hydroxyl number than Voranol[®] 490. When epoxidized soybean oil content was more than 30%, the polyurethane solid structure might have decreased to such an extent that the foam cells became more open and trap less carbon dioxide inside the foams. In addition, the reaction rate of epoxidized soybean oil with isocyanate was slower than Voranol[®] 490. This could lead to a weaker three-dimensional network causing cells to become more open.^{14,17} Figure 2 indeed confirms the foam closed cell percentage decreased when the epoxidized soybean oil content exceeded 30%. As a result, the thermal conductivity would increase.

SEM images of rigid foam

Figure 3(a–f) shows the SEM images of water-blown rigid polyurethane foams with different epoxidized

soybean oil contents. As shown, the bubbles appeared on the polyurethane foam when epoxidized soybean oil was incorporated. In addition, the number of bubbles increased with increasing epoxidized soybean oil up to 30%. Beyond 30%, the bubble size increased although the bubble number did not change. Figure 4(a–d) shows the effect of epoxidized soybean oil on the bubbles size. The bubble size increased from 3 μm at 10 and 20% epoxidized soybean oil to 5 μm at 30% and 5–6 μm at 40% epoxidized soybean oil. Thus, both number and/or size of bubbles increased with epoxidized soybean oil content. The presence of bubbles in the polyurethane foam structure seemed to indicate poor miscibility between epoxidized soybean oil and petroleum polyol which caused phase separation. In addition, epoxidized soybean oil reacted with isocyanate in much slower rate than Voranol[®] 490. Both poor miscibility and slower reaction rate might have weakened the three-dimensional network of the polyurethane foam, in particular, when epoxidized soybean oil was more than 30% in the foam formulation. Therefore, decreases in foam compressive strength and increases in thermal conductivity were observed as shown in Figure 2.

Oil extraction of rigid foam

According to Table I, Voranol[®] 490 and epoxidized soybean oil were the sources of oil present in the water-blown rigid polyurethane foam. If the reaction between Voranol[®] 490 or epoxidized soybean oil and isocyanate were complete, extractable oil would be nil in the foam system. Figure 5 shows the effect of aging time of water-blown rigid polyurethane foams containing 0 and 50% of epoxidized soybean oil in the B-side of foam formulation on the percentage of extractable oil. As shown, most of Voranol[®] 490 (~92%) reacted with isocyanate at first 12 h for the foam containing 100% Voranol[®] 490 (i.e., 0% epoxidized soybean oil) in the B-side.¹⁸ The extractable oil percentage decreased with aging time and Voranol[®] 490 almost fully reacted with isocyanate after 7 days. For foams containing 50% epoxidized soybean oil and 50% Voranol[®] 490 in the B-side, about 80% of them reacted with isocyanate at first 12 h. In addition, the extractable oil percentage also decreased with aging time and it took about 170 h for all epoxidized soybean oil and Voranol[®] 490 to complete their reaction with isocyanate. These results indicate that (1) similar to the petroleum polyol, Voranol[®] 490, epoxidized soybean oil also participated in the polyurethane reaction and contributed to the properties of polyurethane foam and (2) the reaction rate of epoxidized soybean oil with isocyanate was slower than Voranol[®] 490. The latter

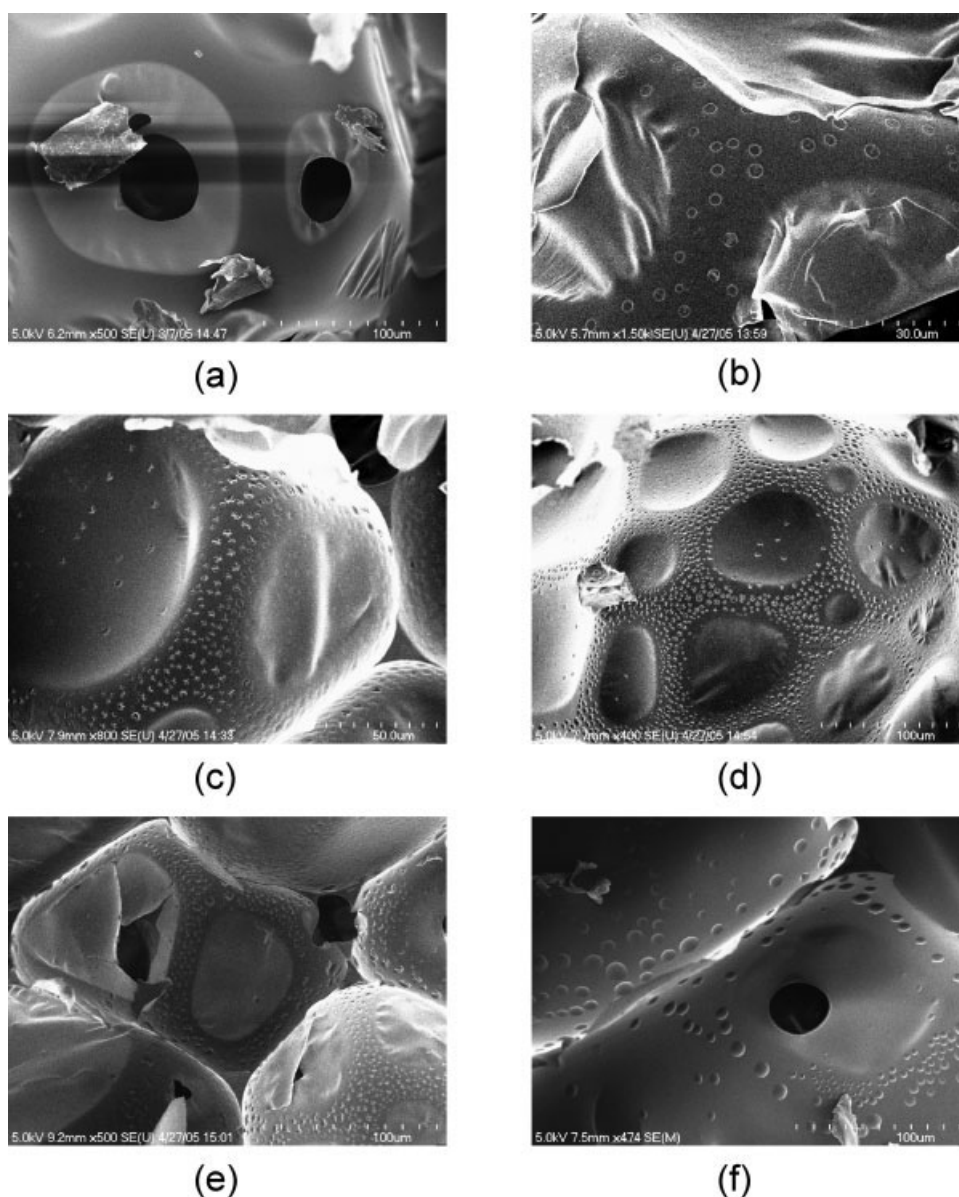


Figure 3 SEM images of water-blown rigid polyurethane foams with (a) 0%, (b) 10%, (c) 20%, (d) 30%, (e) 40%, and (f) 50% of epoxidized soybean oil.

was not unexpected because the reactive functional groups in epoxidized soybean oil were secondary and less reactive than the primary hydroxyl groups in Voranol[®] 490.

Density of flexible foam

Figure 6 shows the effect of epoxidized soybean oil on the density of water-blown flexible polyurethane foams. The density decreased with increasing epoxidized soybean oil up to 30% and then increased. Because the hydroxyl number of epoxidized soybean oil (403.8) was much greater than Voranol[®] 4701 (34) and the isocyanate index was fixed at 80 (Table II), the quantity of isocyanate (PAPI[®] 27) used in the foam formulation increased with epoxidized soybean

oil. Thus, the foam matrix would weigh more with increases in epoxidized soybean oil. At the same time, foam volume would also increase due to more carbon dioxide from the reaction of isocyanate with the blowing agent (water) and maybe better gas retention of the foam matrix. The volume increase was indeed observed during foam making. The increase of foam volume exceeded the increase of foam weight up to 30% epoxidized soybean oil. Thus, the foam density decreased. Above 30% epoxidized soybean oil, the volume increase effect might have reached its limit and the gas retention deteriorated in the foam matrix. Both could be caused by the slower reaction rate of epoxidized soybean oil with PAPI[®] 27 than Voranol[®] 4701. Therefore, the foam density increased.

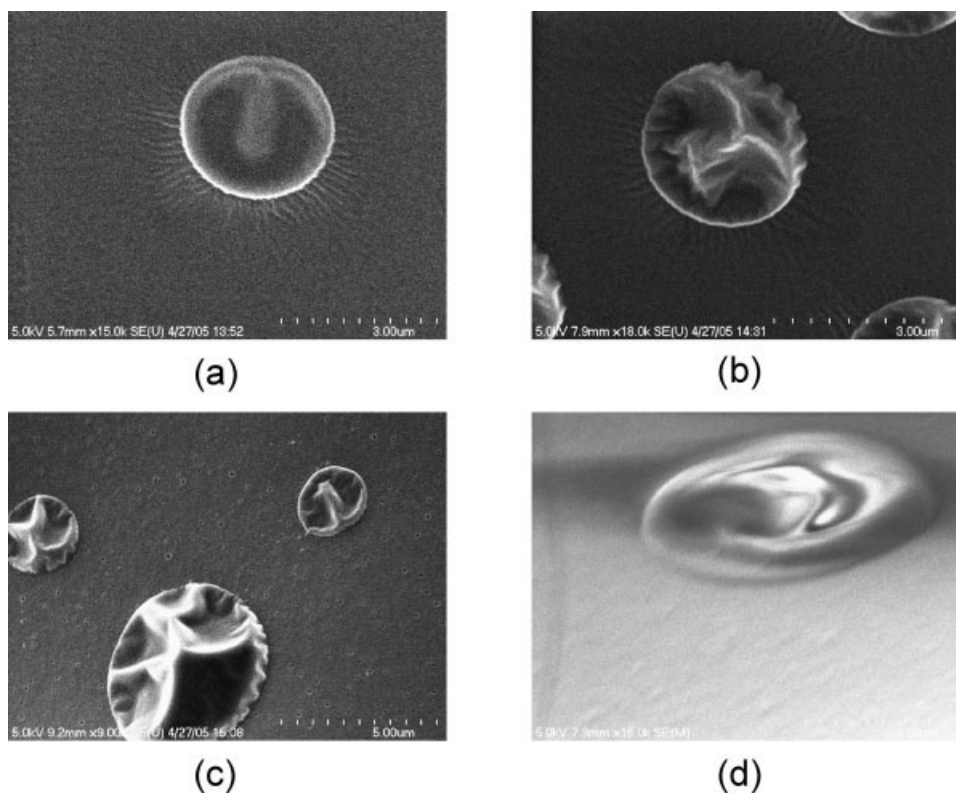


Figure 4 SEM images of water-blown rigid polyurethane foams with (a) 10%, (b) 20%, (c) 40%, and (d) 50% of epoxidized soybean oil [the magnification of (d) was the same as (a)].

Compression force deflection of flexible foam

This test measures the force necessary to produce a 50% compression over the entire top surface area of the foam specimen. A higher compression force deflection indicates the foam is firmer resulting from either a higher crosslinking density or a higher foam density or both. Figure 6 also shows the effect of epoxidized soybean oil on 50% compression force deflection of water-blown flexible polyurethane

foams. Similar 50% compression force deflection was observed for foams containing 0–30% epoxidized soybean oil. This could be explained by changes in foam density and crosslinking density. As epoxidized soybean oil increased from 0 to 30%, foam density decreased which would reduce the 50% compression force deflection. However, the crosslinking density increased (data not shown), because epoxidized soybean oil had a higher hydroxyl number than Voranol[®] 4701 leading to using more isocya-

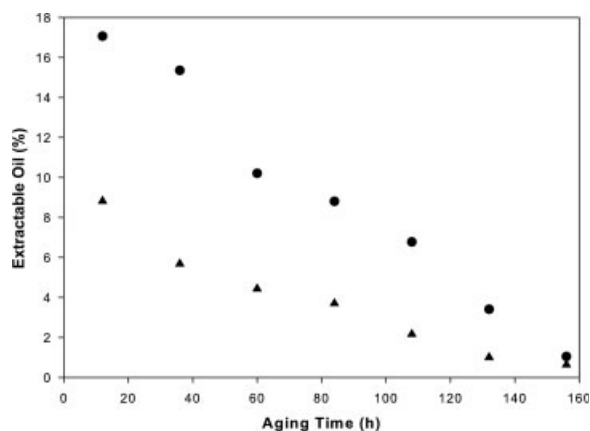


Figure 5 Effect of aging time on the extractable oil of water-blown rigid polyurethane foams containing 0% (▲) and 50% of epoxidized soybean oil (●).

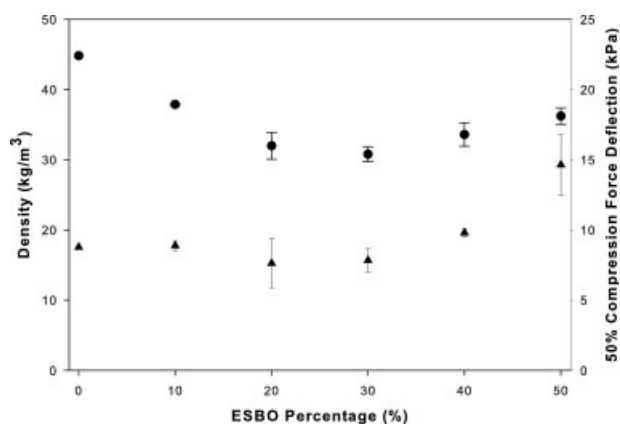


Figure 6 Effect of epoxidized soybean oil on density (●) and 50% compression force deflection (▲) of water-blown flexible polyurethane foams.

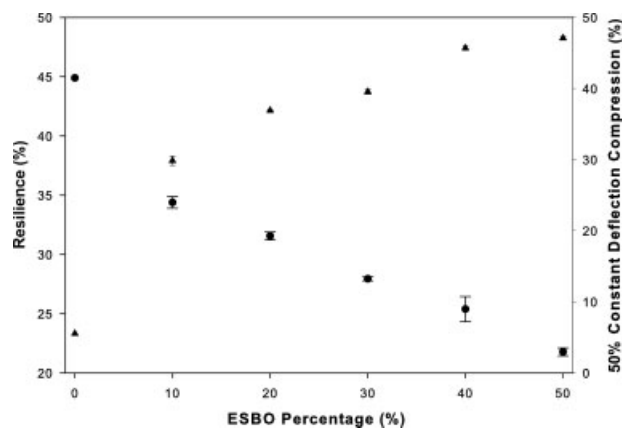


Figure 7 Effect of epoxidized soybean oil on the resilience (■) and 50% constant deflection compression (▼) of water-blown flexible polyurethane foams.

nate in the foam formulation, which would increase the 50% compression force deflection.¹⁸ These two effects might have counteracted and cancelled each other. Thus, there was no significant change in 50% compression force deflection. When epoxidized soybean oil in foam exceeded 30%, both foam density and crosslinking density increased resulting in firmer foams. Therefore, the 50% compression force deflection would increase as shown.

Constant deflection compression set of flexible foam

This test consists of deflecting the foam specimen to 50% initial thickness, exposing it to 70°C and 6% RH for 22 h and measuring the change in the thickness of the specimen after recovery at 23°C and 50% RH for 30–40 min. A lower constant deflection compression set indicates the foam is more flexible and recovers its thickness better after deflection compression. Figure 7 shows the constant deflection compression set increased sharply when increasing epoxidized soybean oil from 0 to 10%. The increase then became less and the change was almost linear when increasing epoxidized soybean oil from 20 to 50%. It appears that the foams became less flexible and lost more of their initial thickness after deflection compression with increasing epoxidized soybean oil replacement of Voranol[®] 4701 in the foam formulation.¹⁹

The equivalent weights of Voranol[®] 4701 and epoxidized soybean oil are 1650 and 139, respectively. Equivalent weight is the molecular weight of polyol divided by its functionality, or 56,100 divided by the hydroxyl number of polyol. The equivalent weight of 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. In addition, the backbone of the epoxidized soybean oil is a triglyceride while Voranol[®] 4701 is linear in chemical structure. Because of the significant differences in the distance between two adjacent hydroxyl groups and the chemical structure, it is expected that the cell walls and struts in the polyurethane foam became stiffer, due to much shorter “soft segments” in the foam structure, and more easily be crushed or damaged by compression when more Voranol[®] 4701 is replaced by epoxidized soybean oil in the foam formulation. Therefore, constant deflection compression set increased with epoxidized soybean oil content in the foam.

Resilience (ball rebound test) of flexible foam

Figure 7 also shows effect of epoxidized soybean oil on the resilience of water-blown flexible polyurethane foams. It is apparent that the resilience of foams decreased steadily with increase in epoxidized soybean oil. Again, the loss of resilience was most likely due to significant differences in the equivalent weight between Voranol[®] 4701 and epoxidized soybean oil and their chemical structure. As a result, the foam containing more epoxidized soybean oil became stiffer and less resilient under the ball rebound testing conditions.

CONCLUSIONS

In conclusion, water-blown rigid and flexible polyurethane foams were successfully prepared by introducing epoxidized soybean oil in the foaming system. There were no significant changes in density, compressive strength decreased and thermal conductivity decreased first and then increased with increasing epoxidized soybean oil replacement of Voranol[®] 490 from 0 to 50% in the rigid polyurethane foam system. It appears that up to 20% of Voranol[®] 490 could be replaced by epoxidized soybean oil in rigid polyurethane foams without compromising the properties of rigid foams. It remains to be challenging when replacing up to 20% of Voranol[®] 4701 by epoxidized soybean oil in flexible polyurethane foams. Although density and 50% compression deflection properties were similar or better than control flexible foams, resilience and 50% constant deflection compression properties were inferior.

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