Rigid Polyurethane Foams Based on Soybean Oil

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ABSTRACT: Both HCFC- and pentane-blown rigid polyurethane foams have been prepared from polyols derived from soybean oil. The effect of formulation variables on foam properties was studied by altering the types and amounts of catalyst, surfactant, water, crosslinker, blowing agent, and isocyanate, respectively. While compressive strength of the soy foams is optimal at 2 pph of surfactant B-8404, it increases with increasing the amount of water, glycerin, and isocyanate. It also increases linearly with foam density. These foams were found to have comparable mechanical and thermoinsulating properties to foams of petrochemical origin. A comparison in the thermal and thermo-oxidative behaviors of soy- and PPO-based foams revealed that the former is more stable toward both thermal degradation and thermal oxidation. The lack of ether linkages in the soy-based rather than in PPO-based polyols is thought to be the origin of improved thermal and thermo-oxidative stabilities of soy-based foams. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 467–473, 2000

Key words: rigid polyurethane foam; soybean oil; oleochemical polyol; compressive strength; thermal stability

INTRODUCTION

Rigid polyurethane (PU) foams are widely used in thermal insulation and packaging. They also have excellent strength and higher weight-carrying capacity than other commercial packaging foam materials. They are easy to process and can be formed to very complex shapes.[1] Most of the rigid PU foams on the market are based on polypropylene oxide (PPO) triols and MDI. About 1.5 billion pounds of rigid polyurethane foams was produced in 1996.[2] PPO polyols are relatively inexpensive material but have rather low oxidative stability. Foams based on PPO polyols are sensitive to hydrolysis and have moderate water absorption.[3] Replacing PPO-based rigid PU foams with vegetable oil–based PU foams would alleviate some of the problems, provided that mechan-
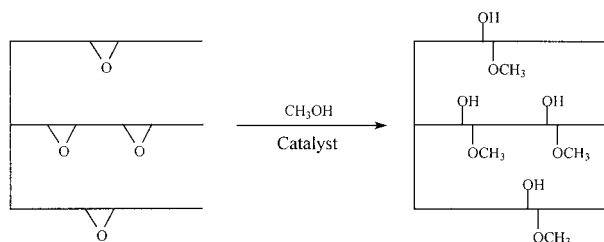
ical and thermoinsulating properties are comparable. A number of researchers have investigated the possibilities of converting vegetable oils into polyols for polyurethane foams.[4–11] While castor oil–based polyurethane foams have existed for many years,[9,11] other oils such as palm-, linseed-, safflower-, and rapeseed oil–based polyols have been known, some of which are even produced on a limited commercial scale.[7,8]

The driving force for such research is the availability of vegetable oils, replacement of petrochemicals with environmentally friendly renewable resource, and adding values to existing agricultural products to benefit farming and industry. The main issues in the application of vegetable oil–based polyols in industry are economics and properties of new polyols. Typical soybean oil from American origin has about 4.6 double bonds per molecule. Distribution of double bonds in the soybean oil molecule is uneven: two of these double bonds are located on one branch of the triglyceride, a few branches contain three double bonds, and one branch in about three molecules has no

Scheme 1

Table II Typical Soy Foam Formulation

Soy polyol	100 part
Glycerin	10–25
Water	1–5
Surfactant	2.0
DBTDL T-12	1.0
DABCO DMEA	1.0
Crude MDI index	1.1–1.3
Genetron-141b/cyclopentane	Vary

unsaturation. If typically 90% of the double bonds is converted to a single OH group, the hydroxyl number of the polyol would be ca. 200 mg KOH/g. Polyols having a higher OH number are possible but are unfortunately semigreases at room temperature. With the existing OH number, soy polyols would give semirigid foams. Thus, the OH number should be increased to 450–500 mg KOH/g in order to obtain necessary rigidity. This can be achieved by adding hydroxyl-containing crosslinkers or water or both. Oil-based polyols are much less polar than PPO-based polyols and thus require different formulation. The objective of this work was to prepare rigid foams from soy-based polyols synthesized in our laboratory and compare their mechanical properties, thermoinsulating properties, and thermal and thermo-oxidative stabilities with those of a commercial rigid foam system. This included the study of the effect of the type and amount of the surfactants, catalysts, crosslinker, blowing agents, and the effect of the NCO/OH ratio on foam properties.

EXPERIMENTAL

Preparation of Soy Polyol

The soy polyols were prepared via the oxirane ring-opening reaction of epoxidized soybean oil with methanol, as outlined in Scheme 1.[12] The

characteristics of some selected soy polyols are listed in Table I.

Preparation of Foams

A typical soy foam formulation is shown in Table II. The formulations involve B-8404 and B-8462 (Goldschmidt, Hopewell, VA) or DC-5454 (Air Products, Allentown, PA) as surfactant; DBTDL T-12 (Air Products) as main catalyst; DABCO DMEA (Air Products) as co-catalyst; Genetron-141b (Allied Signals, Morristown, NJ) or cyclopentane (Philips Petroleum, Bartlesville, OK) as blowing agents; distilled water and glycerin (USP 99.5%, HUMCO, Texarkana, TX) as crosslinkers, and PAPI-2901 (Dow Chemicals, Midland, MI) as isocyanate. The commercial foam samples included are prepared under the same conditions using PPO-based polyol Elastopor P 12600R (a mixture of polyol with catalysts, water, surfactant, and blowing agent HCFC-141b) and isocyanate Epor P 1046U (polymeric MDI), both of which are samples of commercial products from BASF (Carrollton, TX). Since this two-component system has a nominal free-rise cup density of 22 kg/m^3, the polyol was preevacuated to remove excess blowing agent so as to obtain a foam density of 30 kg/m^3.

Soy polyol was first mixed in a plastic cup with proper amounts of crosslinkers, catalysts, surfactant, and blowing agent. After the addition of

Table I Properties of Soy Polyols

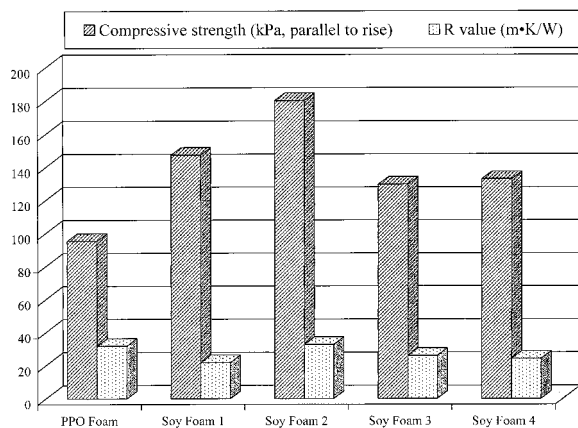| Soy Polyol	No. 1	No. 2	No. 3
Hydroxyl number (mg KOH/g)	184	196	215
Equivalent weight	305	286	261
Viscosity (mPa · s at 30°C)	7,200	6,000	10,400
Density (g/cm^3)	1.018	1.018	—
Color	Pale yellow	Pale yellow	Yellow

Figure 1 Mechanical and insulating properties of soy-based foams vs. PPO-based foam. PPO Foam and Soy Foams 1 and 2 are HCFC-blown, whereas Soy Foams 3 and 4 are cyclopentane-blown. Surfactant B-8462 was used for Soy Foam 3, whereas B-8404 was used for all others. An isocyanate index of 1.3 is used for all soy foams. All foam density is at ca. 30 kg/m^3.

isocyanate, the mixture was agitated up to 10 s using a high-speed mixer, and afterwards the content of the cup was allowed to foam and set. Samples were cut 1 week later into specific shapes, and the foam properties were then measured. These properties include apparent density, compressive strength, and thermoinsulating property (k and R values). The apparent density of the foams was measured according to ASTM D1622-93. The compressive strength of foams was evaluated on a MTS QTEST II tensile tester (Research Triangle Park, NC) according to ASTM D1621-94. The k and R factors of the foams were tested between two plates (10 and 35°C) on a LaserComp FOX 200 heat flow meter instrument (Wakefield, MA) according to ASTM C518-91. The thermal and thermo-oxidative properties of the foams were examined on a thermogravimetric analyzer (TGA, Model 2050; TA Instruments, New

Castle, DE) either in air or under nitrogen at a heating rate of 10°C/min. The foam samples were powdered and compressed prior to analysis. Each run was repeated, with identical results being produced.

RESULTS AND DISCUSSION

Soy-based polyols do not have high enough hydroxyl content to obtain a sufficient degree of crosslinking required for a rigid foam. Thus, water and a multifunctional crosslinker are added to adjust the OH number of the polyol to be about 450–500 mg KOH/g (equivalent weight of 110–120 g/Equiv.). Even with a single OH group per double bond, soy polyols have relatively high viscosity, typically about 6,000–11,000 mPa · s. However, the viscosity of the soy polyols has been brought to the normal working range (below 1000 mPa · s at 23°C) after all ingredients are blended in, including blowing agent. The effect of formulation variables on foam properties was studied by varying the amounts and/or types of catalyst, surfactant, water, crosslinker, blowing agent, and isocyanate, respectively.

HCFC-Blown Foams

Soy-based rigid polyurethane foams prepared using Genetron-141b have comparable mechanical and insulating properties to commercial foams. This is illustrated in Figure 1, where all soy foams actually possess a higher compressive strength than the PPO-based foam sample, while the thermoinsulating factors are at the same level. Typical values of compressive strength for a rigid foam at a density of 30 kg/m^3 is in the range of 100–150 kPa, and typical R value at the same density is in the range of 40–60 m · K/W.[1] The lower R values in Figure 1 (20–40 m · K/W) are the consequence

Table III   Effect of Catalyst Amounts on Soy Foam Properties

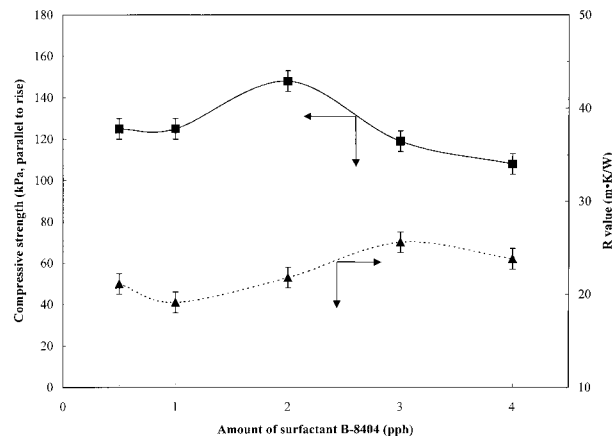| Sample ID	DBTDL T-12 (pph)	DABCO DMEA (pph)	Density (kg/m^3)	Compressive Strength (kPa)	R Value (m · K/W)
Soy foam 5	0.5	0.5	30.6 (0.5)	125 (0)	19.1 (0)
Soy foam 6	1.0	1.0	31.6 (0.7)	140 (4)	27.3 (0)
Soy foam 7	1.5	1.0	27.9 (0.6)	116 (1)	33.9 (0)
Soy foam 8	2.0	1.5	30.3 (1.1)	91 (4)	30.4 (0)
Soy foam 9	2.0	2.0	29.3 (0.2)	79 (0)	33.2 (0)

Values in parentheses are SDs.

Figure 2 Amount of surfactant on soy foam properties. Formulation conditions: water 2 pph, glycerin 23.5 pph, isocyanate index 1.3. Foam density is at ca. 30 kg/m³.

Figure 4 Effect of water amount on soy foam properties. Formulation conditions: glycerin 23.5 pph, isocyanate index 1.3. Foam density is at ca.30 kg/m³.

of a small-scale preparation and aging effect (all foams were aged before testing for 1 week under ambient conditions, and no extra wrapping measure was taken). Indeed, the foam sample prepared through a twofold enlargement and measured after 1 day of preparation exhibited an R value of 51 m · K/W, which is comparable to that of a commercial PPO-based foam (49 m · K/W).

Cyclopentane-Blown Foams

Compatibility of the blowing agent with the polyol is important in foam formulation. Cyclopentane should be more compatible with soy-based than with the PPO-based polyols, owing to closer po-
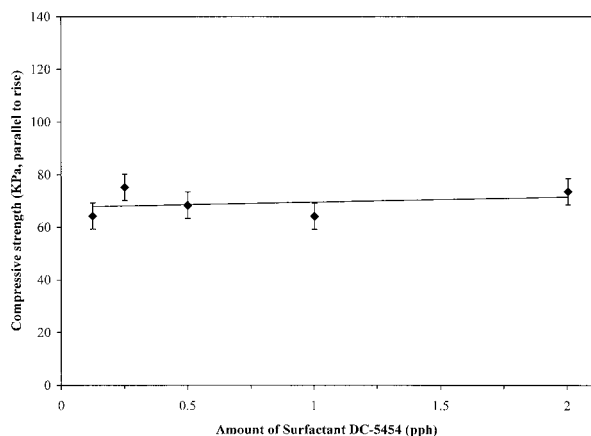
larity to the former. Soy foams using cyclopentane as the blowing agent were prepared. These foams were found to be comparable in both strength and insulating properties to those of HCFC-blown soy foams, and both surfactants B-8404 and B-8462 worked well for this system (Fig. 1). Surfactant B-8404 was used for Soy Foam 4, while B-8462 was used for Soy Foam 3. According to the supplier, B-8404 is a general-purpose surfactant for rigid foams, and B-8462 is a surfactant for pentane-blown foams.

Amounts of Catalysts

The amounts of catalysts DBTDL T-12 and DABCO DMEA were varied, but special attention

Figure 3 Amount of surfactant on soy foam strength. Formulation conditions: water 2 pph, glycerin 23.5 pph, isocyanate index 1.1. Foam density is at ca. 30 kg/m³.
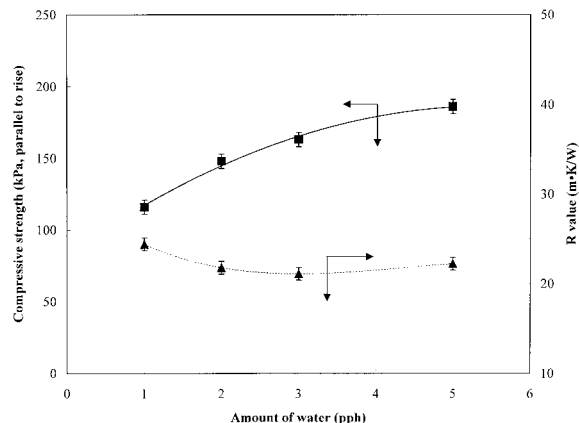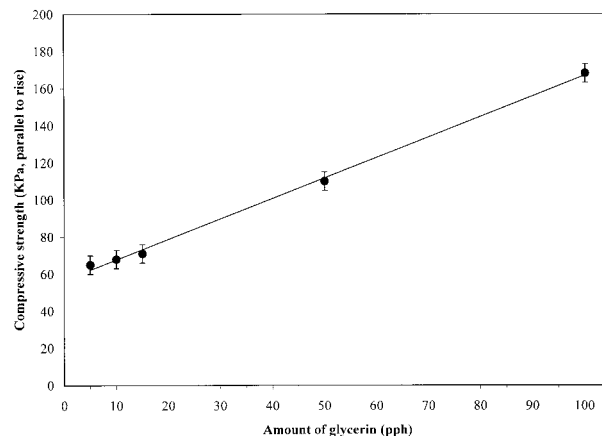

Figure 5 Effect of amount of glycerin on soy foam strength. Formulation conditions: water 1 pph, isocyanate index 1.1. Foam density is at ca. 30 kg/m³.
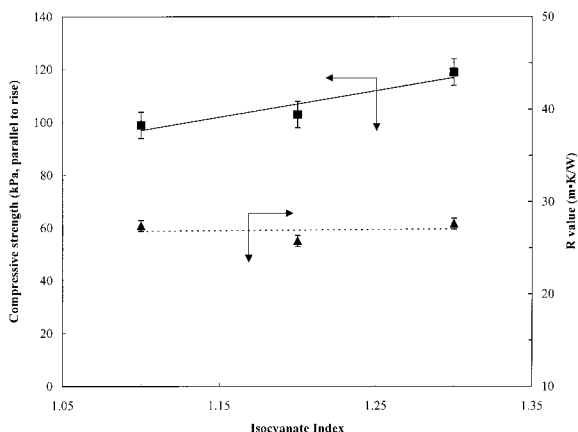
Figure 6   Effect of isocyanate index on soy foam properties. Formulation conditions: water 2 pph, glycerin 23.5 pph. Foam density is at ca. 30 kg/m³.

was paid to balance the amounts of the two catalysts so as to obtain a desired cream time, gel time, and tack-free time. Normally the cream time is adjusted to about 10 s, gel time 30–45 s, and tack-free time 45–60 s. It was found that as the catalyst concentration changes, foam strength optimized at 1.0 part per hundred of polyol in weight (pph) for both catalyst, while R value remains essentially constant if the catalyst amounts were above 1.0 pph (Table III). The optimized amount for both catalysts at about 1.0 pph is at the same level as for conventional rigid foam systems.

Type and Amount of Surfactants

Despite the presence of polar hydroxyl groups, soy polyol molecule remains largely nonpolar, because its backbone is made of long hydrophobic aliphatic chains. Crosslinkers (water and glycerin) are highly polar, whereas blowing agents (Genetron-141b or cyclopentane) are nonpolar. Therefore, a highly efficient surfactant is needed for the soy foam system to ensure proper mixing of all ingredients apart from its regular function to reduce surface tension during the formation of a fine cellular structure. High-speed agitation also was applied during mixing, and a milky emulsion, accompanied by a moderate exotherm, resulted in all cases (this emulsion will turn clear if allowed to stand). Among all the five surfactants tested, Goldschmidt surfactants B-8404 and B-8462 were found to be satisfactory. Compressive strength of the soy foams is optimal at 2 pph of B-8404 (Fig. 2), which is in excellent agreement

with the supplier-recommended amount for this surfactant. Although sufficient amount of surfactant is essential to form microcells with optimized rigidity, the excess surfactant acts as plasticizer and thus decreases this property. All other surfactants tested were found to be much less effective, including DC-5454, DC-198, and DC-193 from Air Products. As shown in Figure 3, foam strength shows no improvement in the range of 0.125–2 pph of DC-5454, indicating the surfactant is inefficient for the soy foam system.

Amount of Water

The compressive strength of soy foams increases continuously with increasing the amount of water (Fig. 4). Water reacts with isocyanate to form very rigid polyurea structures in the foam, which accounts for the increase in foam strength. The R value of the foams decreases with increasing water quantity but seems to level off when this quantity exceeds 2 pph. This means that the foam strength can be adjusted by varying the water quantity in the formulation without sacrificing the thermoinsulating property.

Type and Amount of Crosslinkers

Crosslinker is an essential component for vegetable oil–based foam systems since it brings in the required rigidity. A number of crosslinkers have been used, including sorbitol, trimethanolylpropane (TMP), triethanolamine, tripropanolamine, and glycerin.[9,10,13–18] We tested three crosslinkers: triethanolamine, TMP, and glycerin. The first
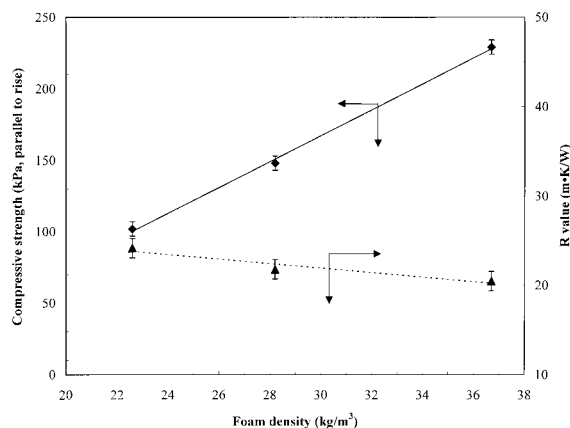

Figure 7   Effect of density on soy foam properties. Formulation conditions: water 2 pph, glycerin 23.5 pph, isocyanate index 1.3.

Table IV   Effect of Foam Structural Anisotropy on Compressive Strength

		Compressive Strength		
Sample ID	Density (kg/m^3)	Parallel to Rise (kPa)	Perpendicular to Rise (kPa)	Difference (%)
Soy foam 10	28.9 (0.4)	148 (3)	89 (0)	−40
Soy foam 11	36.8 (0.6)	229 (12)	196 (0)	−14
Soy foam 12	32.4 (0.6)	192 (0)	100 (0)	−48
PPO foam	33.5 (0.1)	204 (0)	146 (0)	−28

Values in parentheses are SDs.

crosslinker also acted as a catalyst, thus leading to a very short cream time (<10 s), and foams formed were found to have low rigidity. TMP, being a solid, was difficult to mix in. Glycerin was found to be the best crosslinker to work with for soy-based foam systems. This substance has a high hydroxyl content (calculated OH number of 1828 mg KOH/g) and a compact backbone, both of which are advantageous to the rigidity of the foams. It is also a liquid, with a viscosity convenient to blend with the soy polyols. At 5–10 pph of glycerin (with 2 pph of water), the foam had minimal visual shrinkage. Although compressive strength is observed to increase linearly with the amount of glycerin (Fig. 5), foams formed were found to be brittle if the glycerin amount exceeded ca. 25 pph. The optimal amount of this crosslinker is thus in the range of 10–25 pph. Glycerin at 30 pph has been used for a castor oil–based foam system.[9]

Isocyanate Index

Compressive strength of soy foams was observed to vary proportionally with isocyanate index (Fig.

6), which means the foam strength can be adjusted by regulating the amount of isocyanate used in the formulation. In other word, although soy foam strength is satisfactory at an index of 1.1, a better product can be achieved using a higher index. The excess isocyanate used in the foam formulation should result in a more complete conversion of OH groups in the polyol and should react over time with moisture in the air, leading to more rigid polyurea structures in the foam.

Effect of Foam Density

Although the compressive strength of soy-based foams increases linearly with foam density, the insulating property varies inversely. This is shown in Figure 7, which illustrates a decrease in R value with increasing foam density. This is understandable, since more blowing agent is needed at a lower foam density and blowing agents have significantly lower conductivity than the polymer matrix (e.g., 0.0089 W/m · K for Gen-
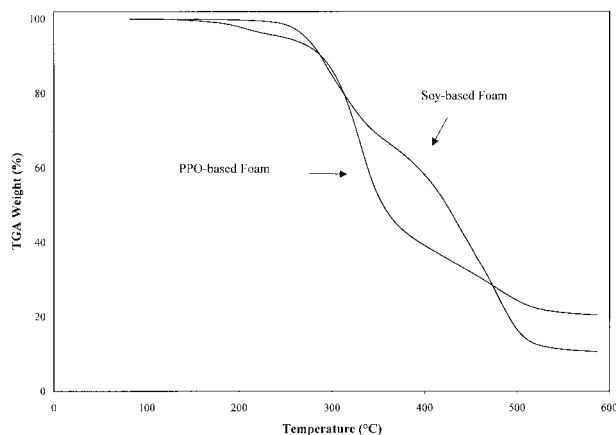

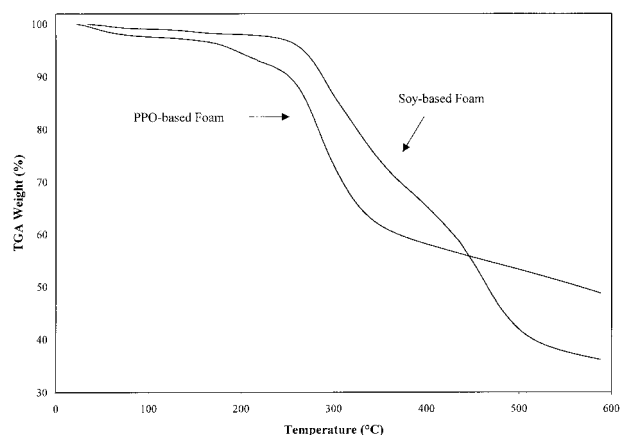**Figure 8** Thermal behavior of soy-based foam vs. a PPO-based foam (TGA under N$_2$).

Figure 9 Thermo-oxidative behavior of soy-based foam vs. a PPO-based foam (TGA in air).

etron-141b; 0.2–0.5 W/m · K is typical for solid polymers).[1,19] Similar relationships also have been observed with some conventional rigid foams.[20]

Structural Anisotropy

Compressive strength anisotropy (parallel- vs. perpendicular-to-rise) was observed with these soy foams. It was found that the perpendicular strength is lower than the parallel strength. Soy oil–based foams are 14–48% lower in strength in the perpendicular direction, compared with 28% lower for the PPO-based foam. This is illustrated in Table IV. This difference is also comparable to rigid urethane foams based on some other vegetable oil polyols.[11,21]

Thermal and Thermo-oxidative Stability

A comparison in the thermal and thermo-oxidative behaviors of soy- and PPO-based foams revealed that the former is more stable toward both thermal degradation and thermal oxidation, as is clearly seen from thermograms shown in Figure 8 (under N_2) and Figure 9 (in air). The first downturn of these thermograms (at about 260°C) is characteristic of urethane bond decomposition, followed by the degradation of the polyol backbone (at about 400°C). The PPO-based polyol contains ether linkages in the molecule, which are apparently less stable toward thermal degradation and thermal oxidation than hydrocarbon and ester linkages present in the soy polyol.[3] This is therefore thought to be the origin of improved thermal and thermo-oxidative stabilities of soy-based foams, the latter being more distinctive. The soy polyols are therefore thermo-oxidatively much more stable than PPO-based polyols. Similar results were obtained in this laboratory based on a comparison in the thermal stabilities of vegetable oil– and PPO-based cast polyurethanes.[22]

CONCLUSIONS

Both HCFC- and cyclopentane-blown rigid polyurethane foams using soybean oil–based polyols have been successfully prepared. These foams were found to have comparable mechanical and insulating properties and higher thermal and thermo-oxidative stabilities than the foams of petrochemical origin.

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