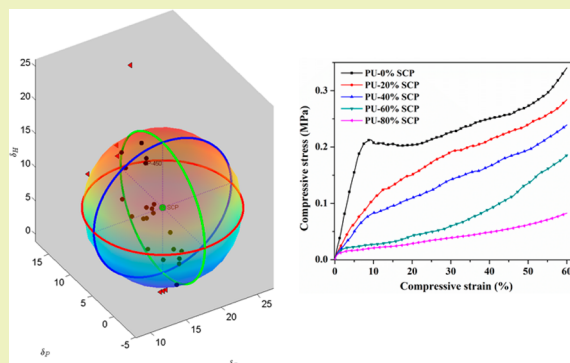


Bio-based Polyurethane Foam Made from Compatible Blends of Vegetable-Oil-based Polyol and Petroleum-based Polyol

Chaoqun Zhang[†] and Michael R. Kessler^{*‡}[†]Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, United States[‡]School of Mechanical and Materials Engineering, Washington State University, Pullman, Washington 99164, United States

ABSTRACT: The Hansen solubility parameters of a soy-castor oil-based polyol and a petroleum-based polyol are investigated to evaluate their miscibility for polyurethane blends. The two polyols were found to be miscible at different ratios over a temperature range from 25 to 90 °C. Blends with different ratios of these two polyols were used to prepare polyurethane foams. With increasing levels of bio-based polyol content, the density of the open cell foams increased. The thermal stability of the polyurethane foams improved, and their thermal conductivity increased, with increasing bio-content, while the foam's compression strength decreased. This study provides a method to evaluate polyol blends for the preparation of polymeric materials that balances economic and environmental considerations.

KEYWORDS: Polyurethane foam, bio-based polyol, epoxidized soybean oil, Hansen solubility parameters, thermal conductivity



INTRODUCTION

Rigid and flexible polyurethane (PU) foams are widely used in building construction and in the automotive, bedding, packaging, and medical device industries because they offer numerous advantages, including lightweight, excellent strength, low thermal conductivity, and high weight-carrying capacity.^{1,2} In general, PU foams are made from a reaction between polyisocyanate and polyol in the presence of a catalyst, which produce the PU matrix, and of a reaction between isocyanate and water, which produces urea and carbon dioxide that acts as a blowing agent to create the foam cells. Historically, petroleum has been the feedstock for polyols and isocyanates for the production of PU foams. Over the past decade, depleting fossil reserves, fluctuating petroleum prices, and environmental concerns have triggered growing interest in the development of bio-renewable feedstocks to substitute petrochemically derived counterparts in the production of some polymeric materials, including PU.

Currently, some of the most widely studied renewable resources for the polymer industry include plant oils, starch, woods, and cellulose.^{3,4} Vegetable oils are one potential sustainable resource for polyols in the PU foam industry because they are inexpensive, readily available, and renewable.^{5,6}

Several vegetable-oil-based polyols were developed for the manufacture of PU foams, ranging from flexible to rigid, with a broad range of properties. Guo prepared bio-polyols from epoxidized soybean oil ring-opened by methanol and the resulting rigid PU foam exhibited comparable mechanical, and insulating properties, and better thermal resistance properties than foams from petrochemical feedstocks.⁷ Dworakowska

developed polyols from rapeseed oil through microwave-assisted synthesis for flexible PU foams. The effects of the renewable content on the cell structure, tensile strength, and resilience values of foam were investigated.⁸ Veronese synthesized polyols with high functionalities from castor oil by transesterification with triethanolamine and glycerin. The corresponding rigid PU foam exhibited slightly lower mechanical properties than rigid foams from petroleum-based polyols.⁹ Lee prepared epoxidized diethanolamides as polyols by reacting epoxidized palm oil with diethanolamine, and produced PU foam with acceptable dimensional stability.¹⁰ Moreover, Tu reported that epoxidized soybean oil can directly react with isocyanate and that blends of epoxidized soybean oil and petroleum-based polyether polyols can be used for preparation of rigid and flexible PU foams.¹¹ However, the preparation methods of vegetable-oil-based polyols often caused high viscosity, secondary functional groups (relative low reactivity), and low hydroxyl numbers, resulting in PU foams with inferior properties, such as heterogeneous cell structure¹² and difficulty in density control.¹³ Also, the controversy over food-grade feedstocks being used for the production of polymeric materials impedes their wide application on an industrial scale. Therefore, a partial replacement of petroleum-based polyols with bio-based polyols is a widely accepted approach to the preparation of PU foam. Another motivation for the partial substitution of petroleum-based polyols is the opportunity to tailor mechanical, thermal,

Received: January 20, 2015

Revised: March 2, 2015

Published: March 6, 2015

Table 1. Properties of SCP and P-450

	OH number (mg KOH/g)	acid number (mg KOH/g)	number-average molecular weight	polydispersity index	viscosity (Pa·s) at 25 °C, shear rate of 30/s
SCP	148	3.7	2611	1.32	8.24
P-450	355		702	1.05	0.29

Table 2. Formulations for PU Foam

polyol blends	Polycat 5	Polycat 8	Dabco DC5357	water	PMDI
100	1.26	0.84	2.5	3.0	index ×1.1

and physical properties of PU foams by blending vegetable-oil-based polyols and petroleum-based polyols.^{11,14}

This approach is feasible only as long as the two polyols are compatible given their differences in molecular weight, density, and molecular structure. Incompatibility of the blend partners may not only cause phase separation during prolonged storage and/or shipment, but it also strongly influences the performance of the corresponding PU foams, such as physical instabilities, heterogeneous structure, and poor properties.^{15,16} Tu indicated that the incompatibility between epoxidized soybean oil and petroleum polyol caused phase separation, leading to large bubbles in rigid PU foam.¹¹ However, this issue has not received further attention. It is necessary to develop a method to evaluate the compatibility between blends of polyols in order to design novel polyols and to determine appropriate formulations for the manufacture of PU foams.

Traditionally, Hansen solubility parameters are used to estimate the compatibility of two materials.^{17,18} The idea is based on the assumption that two materials that have matched solubility parameters will have balanced intermolecular forces resulting in miscibility. The solubility parameter describes interaction between molecules^{17,19} and can be calculated from the cohesive energy (E_t) per unit volume (V), which is called the cohesive energy density.²⁰ The cohesive energy is the sum of internal energy that holds the materials intact, consisting of dispersion cohesion energy (E_d), polar cohesion energy (E_p), and hydrogen bonding cohesion energy (E_h).

$$\delta_t = \sqrt{\frac{E_t}{V}} \quad (1)$$

$$E_t = E_d + E_p + E_h \quad (2)$$

Therefore, Hansen defined three parameters affecting a solvent's solubility: the dispersion parameter (δ_d), meant to quantify the London dispersion forces of the solvent; the polar parameter (δ_p), which is attributed to a molecule's fixed dipole moment; the hydrogen bonding parameter (δ_h), which accounts for a molecule's hydrogen bonding forces.²¹

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3)$$

Upon calculation of all three solubility parameters, any solvent can be plotted on a three-dimensional plot called a solvent map. Each solvent has a fixed radius on the map. Any species whose parameters reside within the resulting sphere (the solubility region) should be soluble in the solvent, whereas those whose parameters are excluded from the resulting sphere should be nonsoluble in the solvent. The most common method for the prediction of Hansen solubility parameter values of materials was proposed by Krevelen and Hofzyer based on the contributions of functional groups.²² However,

this method is not suitable for vegetable-oil-based polyols that contain a complex combination of multiple fatty acid structures.

In this research, the Hansen solubility parameters of a soy-castor oil-based polyol (SCP) and a petroleum-based polyol (P-450) were determined using dissolution tests. Compatibility between these two polyols was evaluated by theoretical prediction and experimental confirmation in the temperature range between 25 and 90 °C, relevant for PU foaming. Finally, PU foams were prepared from blends with various ratios of vegetable-oil- and petroleum-based polyols. The morphologies of the PU foams were characterized by scanning electron microscopy (SEM). In addition, the thermal, physical, and mechanical properties of the PU foams were characterized using thermal conductivity tests, thermogravimetric analyses, and compression tests. The effects of bio-polyol content on the thermal-mechanical properties of the resulting PU foams are discussed.

EXPERIMENTAL DETAILS

Materials. Polyol 450 (P-450), a reaction product of propylene oxide and glycerin, and polymeric diphenylmethane-4,4'-diisocyanate (PMDI, NCO content: 31 wt %) were provided by Kumho Petrochemical Co. The catalysts (POLYCAT 5 and POLYCAT 7) and surfactant (Dabco DC 5357) were kindly provided by Air Products (Allentown, PA). Distilled water was used as a blowing agent. Soy-castor oil-based polyol (SCP) was prepared by a ring-opening reaction of epoxidized soybean oil by castor oil fatty acid using a procedure previously reported.²³ All solvents used to determine the Hansen solubility parameters of the polyols were common laboratory solvents of high purity obtained from commercial chemical suppliers (Sigma-Aldrich, Milwaukee, WI) and were used as received (see Table 1 for properties of SCP and P-450).

Determination of Solubility Parameters for SCP and P-450. The Hansen solubility parameters for both polyols (SCP and P-450) were determined by qualitatively measuring the dissolution of the polyols in various common organic solvents (28 types) with well-known parameters. A predetermined amount of 0.4 g of polyol was added to a 20 mL vial containing 4 mL of the respective solvent. The mixture was sealed and mixed vigorously for 7 h, and subsequently kept at room temperature for 3 days. After visual inspection, the dissolution test results were classified into two categories: soluble and nonsoluble. With the dissolution information for SCP and P-450 in various solvents, the Hansen solubility parameters and the interaction radii were calculated using HSPiP software. Finally, the compatibility between SCP and P-450 was predicted by determining whether the Hansen solubility parameters of SCP and P-450 were in each other's solubility sphere.

Also, the compatibility of SCP and P-450 was confirmed by experimental dissolution tests. The blends with different weight percentages of SCP (0%, 20%, 40%, 60%, 80%) were mixed vigorously for 7 h. The mixtures were put in oven at different temperatures (25, 50, 75, 90 °C) for 1 day, after which the miscibility of the blend partners was determined by visual inspection.

Preparation of PU Foam. Polyurethane foams were prepared according to a reported foam formulation,²⁴ as shown in Table 2. The

Table 3. Miscibility Test Results for SCP and P-450: Soluble (+), and Nonsoluble (–)

solvent name	solubility parameters ^a			P-450	SCP	relative polarity ^b
	δ_d (MPa) ^{1/2}	δ_p (MPa) ^{1/2}	δ_h (MPa) ^{1/2}			
methylene chloride	17	7.3	7.1	+	+	0.309
isophorone	17	8	5	+	+	
toluene	18	1.4	2	+	+	0.099
1-butanol	16	5.7	15.8	+	+	0.586
acetonitrile	15.3	18	6.1	+	–	0.46
tetrahydrofuran	16.8	5.7	8	+	+	0.207
chlorobenzene	19	4.3	2	+	+	0.188
dimethylformamide	17.4	13.7	11.3	+	+	0.386
1-propanol	16	6.8	17.4	+	+	0.617
cyclohexane	16.8	0	0.2	–	+	0.006
chloroform	17.8	3.1	5.7	+	+	0.259
pyridine	19	8.8	5.9	+	+	0.302
methyl ethyl ketone	16	9	5.1	+	+	0.327
dimethyl sulfoxide	18.4	16.4	10.2	+	–	0.444
ethyl acetate	15.8	5.3	7.2	+	+	0.228
water	15.5	16	42.3	+	–	1.0
formic acid	14.6	10	14	+	–	
acetic acid	14.5	8	13.5	+	+	0.648
ethylene glycol	17	11	26	+	–	0.79
diethyl ether	14.5	2.9	4.6	+	+	0.117
styrene	18.6	1	4.1	+	+	
acetone	15.5	10.4	7	+	+	0.355
N-hexane	14.9	0	0	–	–	0.009
heptane	15.3	0	0	–	–	0.012
pentane	14.5	0	0	–	–	0.009
p-xylene	17.8	1	3.1	+	+	0.074
nitrobenzene	20	10.6	3.1	+	+	0.324
diethyl sulfide	16.8	3.1	2	+	+	

^aThe values for solubility parameters were extracted from HSPiP software. ^bThe relative polarity values were reported by Reichardt (Reichardt, 2003).

polyols were premixed in specific weight percentages. The polyol blends, catalysts (Polycat 5 and Polycat 8), surfactant (Dabco DC5357), and blowing agent (distilled water) were mixed in a plastic cup for 30 s using a high speed mixer. The PMDI was added quickly into the mixture using a syringe and the mixture was mixed for another 12 s. Subsequently, the mixture was allowed to foam and settle for 8 days prior to analysis.

Characterization of Polyols and PU Foam. The OH values of the polyols were titrated according to the Unilever method.²⁵ The acid numbers of the polyols were determined by AOCS Official Method Te 1a-64. Rheological tests of polyols were conducted using an AR2000ex stress-controlled rheometer (TA Instruments) with parallel plate geometry at room temperature.

The apparent density of the PU foam was measured according to ASTM D 1622-08. Four samples per foam formulation were measured, and the average result was reported. The compressive properties of the PU foams were evaluated on an Instron universal testing machine with a crosshead speed of 4 mm/min according to ASTM D 1621-10. At least three samples were tested to obtain average values. The test specimens were cylinders with a diameter of 60 mm and a thickness of 40 mm.

Solvent extraction tests were conducted using the following procedure: 0.1 g samples cut from the middle of the PU foam samples were immersed in 15 mL of dimethylformamide for 4 days at room temperature followed by oven drying at 70 °C for 2 days. The weight loss after solvent extraction was recorded based on an average of 4 samples per foam formulation. The transient plane source technique (ASTM C518-91) was employed to measure the thermal conductivity of the PU samples, using a hot disk TPS 1500 system (ThermTest Inc.) with 80 s measure time and 15 mW heating power. The experiments were carried out at room temperature by placing the

sensor between two cylindrical samples with a diameter of 60 mm and a thickness of 20 mm. The cellular structure of the samples was investigated using a field emission scanning electron microscopy instrument (FE-SEM, FEI Quanta 250) operated at 8 kV. The foams were frozen in liquid nitrogen and cut with a razor blade into rectangular samples with the dimensions of 10 × 5 × 3 mm. The top surface of each sample was sputter coated with 5 nm iridium to avoid electrostatic charging during examination. Thermogravimetric analyses were carried out using a TA Instrument Q50 (New Castle, DE). Samples with a weight of approximately 4 mg were heated from room temperature to 800 °C at a rate of 20 °C/min in air.

RESULTS AND DISCUSSION

Hansen Solubility Parameters of SCP and P-450. The outcomes of the dissolution tests with SCP and P-450 in different solvents are shown in Table 3. The dissolution tests were conducted in 28 solvents, 20 of which were good solvents and 8 bad solvents for SCP, whereas 24 were good and 4 were bad for P-450. For example, SCP dissolved in acetic acid, forming a uniform solution, whereas SCP was not miscible with ethylene glycol, demonstrating a clearly visible phase separation as shown in Figure 1. It is noteworthy that SCP did not dissolve in water because of the hydrophobic nature of its triglycerides and the lower polarity of oil-based polyols. Therefore, pure SCP was not used to prepare PU foams in this study. The solubility parameters of SCP and P-450 were calculated based on the dissolution test results. Water was excluded from the determination of the solubility parameters because of its very high δ_h and its tendency to form a special structure with other

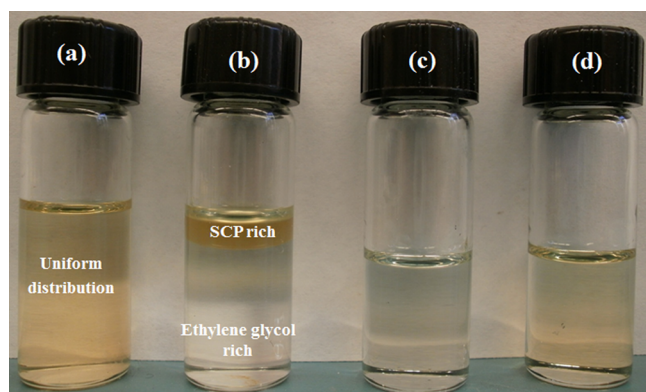


Figure 1. SCP in acetic acid (a), SCP in ethylene glycol (b), blends of 20% SCP with P-450 (c), and 40% SCP with P-450 (d).

substances.^{19,26} Hansen solubility parameters and the interaction radius are calculated for polyols by including the dissolving solvents inside the solubility sphere and excluding the nondissolving solvents outside the solubility sphere.

The solubility spheres of SCP and P-450 on three mutually perpendicular axes are shown in Figure 2. The brown circles, inside the solubility spheres, represent polyols soluble in this solvent, while the red triangles, outside the solubility spheres, indicate that the polyols are nonsoluble in the solvent. The solubility parameters and the interaction radius for SCP were obtained as 17.58, 4.40, 8.68 (MPa)^{1/2} (for solubility parameters δ_d , δ_p , and δ_h , respectively), and 9.7 (MPa)^{1/2} (interaction radius). For P-450, they were determined as 17.20, 7.80, and 13.31 (MPa)^{1/2} (for solubility parameters δ_d , δ_p , and δ_h , respectively), with an interaction radius of 13.1

(MPa)^{1/2}. It can be seen that the Hansen solubility parameters of SCP reside inside the solubility sphere of P-450 and the Hansen solubility parameters of P-450 also reside inside the solubility sphere of SCP, indicating that bio-polyol is compatible with petroleum-based polyol. The calculation results were confirmed by experimental dissolution tests shown in Table 4. All polyol blends were compatible in the temperature range between 25 and 90 °C. Figure 1 shows the homogeneous distribution of SCP in P-450.

Table 4. Miscibility Tests of SCP in P-450 (wt) at Different Temperatures: Soluble (+), and Nonsoluble (–)

	25 °C	50 °C	70 °C	90 °C
SCP:P-450 = 20:80	+	+	+	+
SCP:P-450 = 40:60	+	+	+	+
SCP:P-450 = 60:40	+	+	+	+
SCP:P-450 = 80:20	+	+	+	+

Characterization of PU Foams. In general, rising time is related to the rate of expansion and gelation. Figure 3 shows that with increasing SCP content, the rising time of the respective PU foams increased because of low reactivity OH groups in SCP. The vegetable-oil-based SCP contained secondary hydroxyl groups located in the middle of the triglyceride chains, whereas the petroleum-based P-450 contained highly reactive primary hydroxyl groups and had a much higher hydroxyl number than SCP. The reaction rate of the primary hydroxyl group toward isocyanate is about 3 times higher than that of the secondary hydroxyl group.^{24,27}

Solvent extraction was conducted to determine the degree of polymerization and polymer network connectivity in the

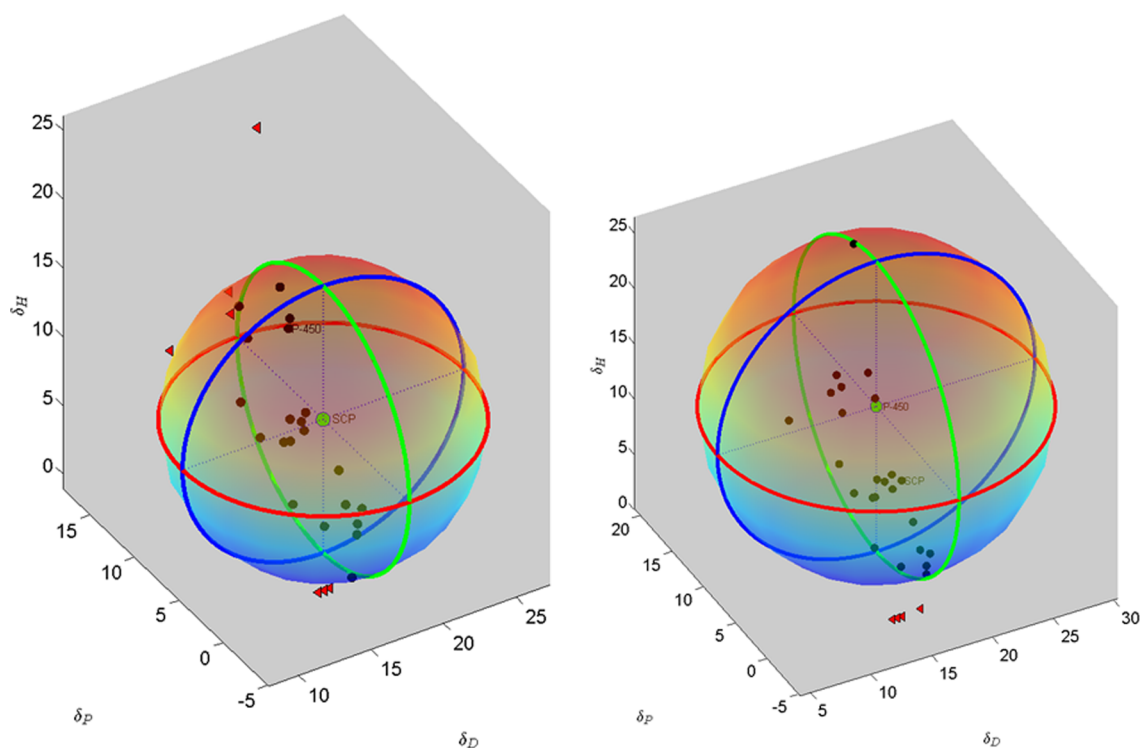


Figure 2. Solubility spheres of SCP (left) and P-450 (right), (solubility sphere of SCP: $\delta_d = 17.58$, $\delta_p = 4.40$, $\delta_h = 8.68$, $R_1 = 9.7$ (MPa)^{1/2}; solubility sphere of P-450: $\delta_d = 17.20$, $\delta_p = 7.80$, $\delta_h = 13.31$, $R_2 = 13.1$ (MPa)^{1/2}. Red triangles represent solvents with Hansen solubility parameter outside solubility sphere, brown circles represent solvents with Hansen solubility parameters inside solubility sphere).

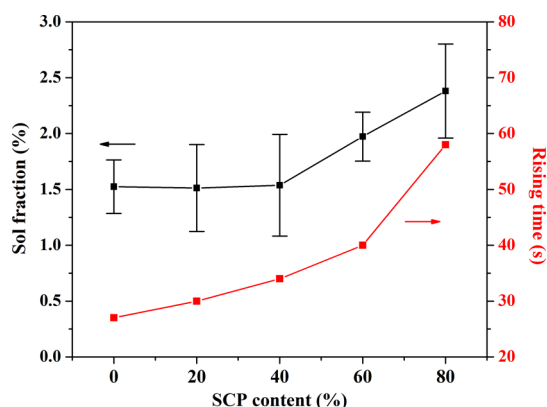


Figure 3. Sol fraction and rising time of PU foams prepared from blends with different ratios of P-450 and SCP.

investigated foams. The measured sol fractions of the foams are shown in Figure 3. With increasing SCP content, the sol fraction of the resulting PU foams increased, indicating lower reactivity of SCP with isocyanate because of its secondary hydroxyl groups. However, all foams exhibited remarkable low extractable content (less than 3%), indicating that with long curing times, the secondary hydroxyls in SCP had sufficient reactivity to incorporate the polyols into the PU network. Tu¹¹ reported that 92% of the polyol reacted with isocyanate within the first 12 h in foam containing pure Voranol 490 (a petroleum-based polyol with terminal hydroxyl groups), whereas foams containing 50% soy-polyol (secondary functional groups) and 50% Voranol 490 incorporated 80% of the polyol into the PU network over the same time period. Both systems occurred fully cure after 7 days. The results indicate 8 days was a suitable aging time for foam preparation in the study.

The apparent density of the PU foams prepared from blends with different ratios of P-450 and SCP is shown in Figure 4.

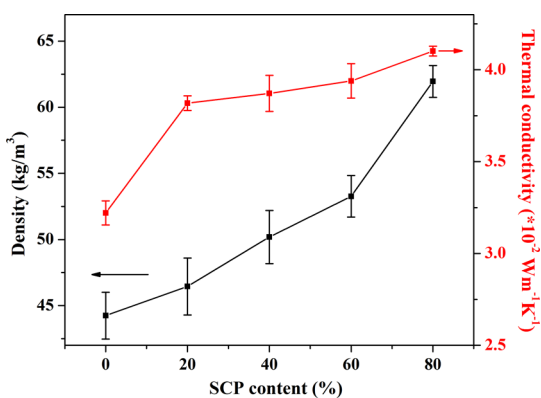


Figure 4. Apparent density and the thermal conductivity of PU foams prepared from blends with different ratios of P-450 and SCP.

With increasing SCP content, the density of the PU foams increased. The density of PU foam is determined as its weight-to-volume ratio. Here, the weight of the foam matrix includes the weight of the polyols, isocyanates, and all additives, while the weight of air and carbon dioxide (the reaction product of water and isocyanate) trapped in the foam cells is negligible. The measured volume is determined by the foam matrix and the foam cells. Although the weight of the foam matrix decreased because less isocyanate was used with increasing SCP

content, the density of the resulting foams increased. This was attributed to the fact that with increasing SCP content, the polymer-forming reaction rate decreased, leading to a weak three-dimensional PU network. The cell walls were not strong enough to trap the carbon dioxide generated by the blowing reaction, so that the cells ruptured and carbon dioxide was emitted. The PU matrix expanded less and the volume of the PU foams decreased. These explanations were confirmed by SEM investigations. The thermal conductivity of the PU foam is shown in Figure 3. With increasing SCP content, the thermal conductivity of the resulting PU foams increased, because more open and ruptured cell were present in the foam network, leading to more air convection and increased thermal conductivity.²⁴ Also, the increased density of the foams promoted thermal conductivity.⁷

The cellular structure and morphology of the PU foams were studied by SEM. Figure 5 shows SEM micrographs (in the rise

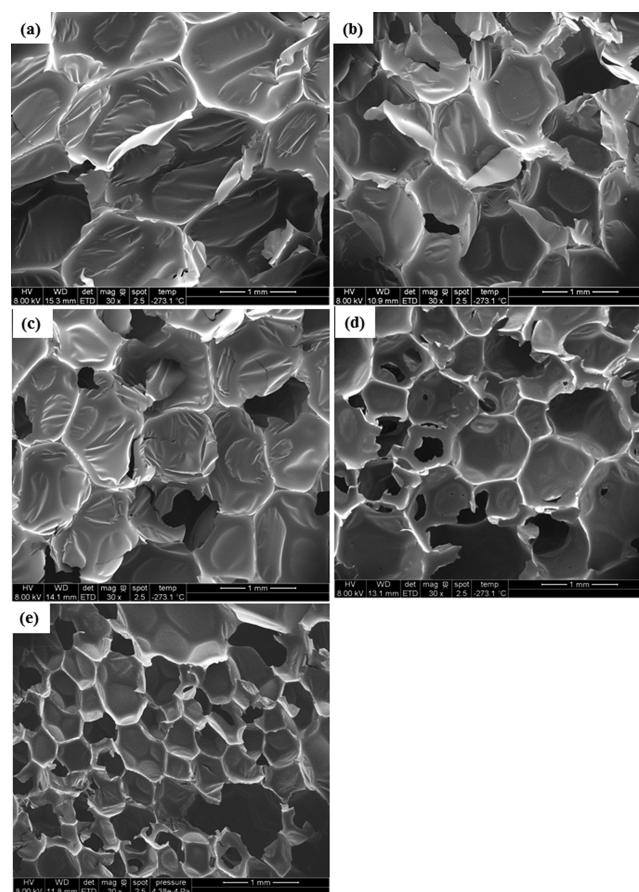


Figure 5. Microphotographs of PU foams prepared from blends with different ratios of P-450 and SCP (a) 0% SCP, (b) 20% SCP, (c) 40% SCP, (d) 60% SCP, and (e) 80% SCP.

direction) of PU foams based on blends of SCP and P-450 in different ratios. The PU foams were composed of various open and closed elliptical cells. With increasing SCP content, the cell size gradually decreased while the number of cells increased. This was attributed on the one hand to the fact that with increasing SCP content, the viscosity of the reacting liquid mixture increased, because of higher viscosity of SCP than that of P-450 (see Table 1), which led to less coalescence among bubbles.²⁸ On the other hand, the prevalence of pendant groups in the SCP backbone provided more nucleation sites

that facilitated the formation of bubbles, as compared to petroleum-based polyol with terminal functional groups.²⁹ With increasing SCP content, the number of open cells in the PU foams increased and the cell sizes were less uniform. This was attributed to the fact that the low reaction rate between SCP and isocyanate produced weak cell walls during foam reaction, which in turn led to more open cells under the pressure of carbon dioxide inside the cells.

The thermo-oxidative behavior of the PU foams prepared from polyol blends with different SCP content is shown in Figure 6, and the corresponding data are summarized in Table

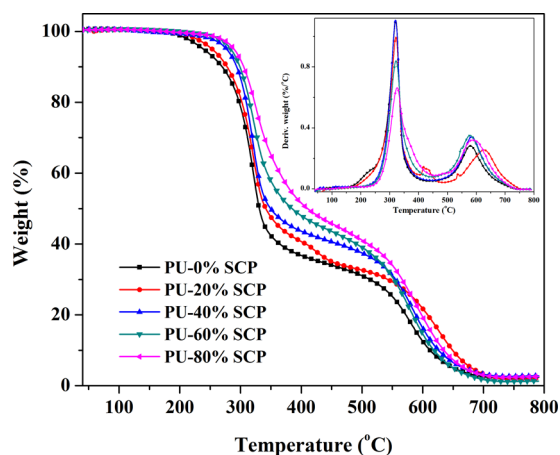


Figure 6. Thermo-oxidative behavior of PU foams prepared from blends with different ratios of P-450 and SCP.

5. The weight loss derivative curves of the PU foams revealed that all foams underwent three main degradation steps: the initial degradation of PU foams is characteristic of urethane bond decomposition (50–360 °C), followed by chain scission of the polyol backbone (360–520 °C), and the final degradation region above 500 °C that is contributed to further thermo-oxidation of the PU foams. Increasing SCP content led to a decrease in the OH number of the polyol blends, resulting in a decreased number of urethane bonds in the PU foam, and therefore improved the thermal stability in the first region. The ether linkages in P-450 are less resistant to thermal degradation than the ester linkages in SCP.^{2,7} Therefore, the thermal stability of the respective PU foams improved with increasing SCP content.

Figure 7 shows compressive stress–strain curves of PU foams prepared from different blends of SCP and P-450. The compression strength (10% compression strain) of PU foams is summarized in Table 5. PU foam prepared from 100% P-450 shows typical stress–strain behavior of a rigid foam. Initially, the foam exhibits linear-elastic deformation at low strain, which is then followed by a sustained plateau of deformation, likely a

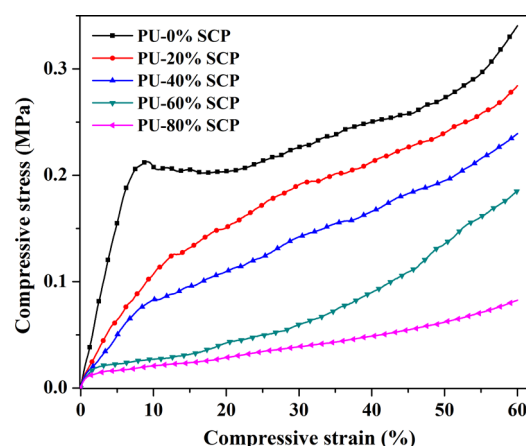


Figure 7. Compressive stress–strain curves of PU foams prepared from blends with different ratios of P-450 and SCP.

result of buckling plastic yielding and brittle fracture of the cell wall struts. At high strains, the eventual densification of the foam resulting from the compacted structure triggered a steady increase in stress.¹² As the SCP content increased to 60%, the foams exhibited only two regions, without the plateau of deformation. When the SCP content increased to 80%, the PU foams showed linear elastic behavior of a flexible foam. The compressive modulus and the compressive stress decreased with increasing SCP content. SCP with low OH number (compared to P-450) produced PU foams with low cross-linking densities, and therefore decreased mechanical properties of PU foams. Also, the plasticizing effect of dangling chains in the SCP molecule contributed to the inferior mechanical properties.

CONCLUSIONS

The Hansen solubility parameters of bio-polyol (SCP) and petroleum-based polyol (P-450) and the compatibility of these two polyols were evaluated using dissolution tests. Polyol blends with different ratios were used to prepare PU foam. With increasing SCP content, the number of open cells in the PU foams increased and the cell size became smaller. The thermal stability of the PU foams improved. The thermal conductivity of the PU foams increased and their compression strength decreased with increasing SCP, because SCP has a lower reactivity (lower hydroxyl number) and higher viscosity than P-450.

AUTHOR INFORMATION

Corresponding Author

*M. R. Kessler. E-mail: MichaelR.Kessler@wsu.edu.

Notes

The authors declare no competing financial interest.

Table 5. Properties of PU Foams

	density (kg/m ³)	thermal conductivity (10 ⁻² W·m ⁻¹ ·K ⁻¹)	sol fraction (%)	TGA in air (°C)		compression strength (MPa)
				T ₁₀	T ₅₀	
PU-0% SCP	44.2 ± 1.8	3.22 ± 0.07	1.52 ± 0.24	270	331	0.210 ± 0.005
PU-20% SCP	46.4 ± 2.2	3.82 ± 0.04	1.51 ± 0.39	278	342	0.083 ± 0.025
PU-40% SCP	50.2 ± 2.0	3.87 ± 0.10	1.54 ± 0.46	294	350	0.075 ± 0.007
PU-60% SCP	53.3 ± 1.6	3.94 ± 0.10	1.97 ± 0.22	299	385	0.060 ± 0.026
PU-80% SCP	62.0 ± 1.2	4.10 ± 0.03	2.38 ± 0.42	305	411	0.025 ± 0.07

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