Honey Bee:
Polyols for Diverse Applications

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ABSTRACT

MCPU has developed novel plant oil based polyols (Honey Bee) which can be used in diverse applications. These materials have 100% primary hydroxyl functionality, allowing their use in high concentrations in applications as diverse as rigid foams and elastomeric roof coatings. The utility of these products and the physical properties of these formulations will be demonstrated.

INTRODUCTION

The manufacture of polyurethanes from polyisocyanates requires readily available co-reactants at reasonable prices. As the price of oil has increased, so has the price of polyether polyols. Alternative sources of polyols, such as agriculturally derived products, have therefore become attractive.

Plant oils are primary metabolites of many higher plants [1] that are economically important as sources of food and industrial oils. Chemically, plant oils are triglycerides of mixtures of fatty acids. Typically, they contain some unsaturated fatty acids. Soybean oil, for example, contains 54% linoleic acid, 23% oleic acid, 10% palmitic acid, 8% linolenic acid, and 5% stearic acid (Figure 1). On average, soybean oil contains 4.65 sites of unsaturation (olefin groups, carbon-carbon double bonds) per molecule.

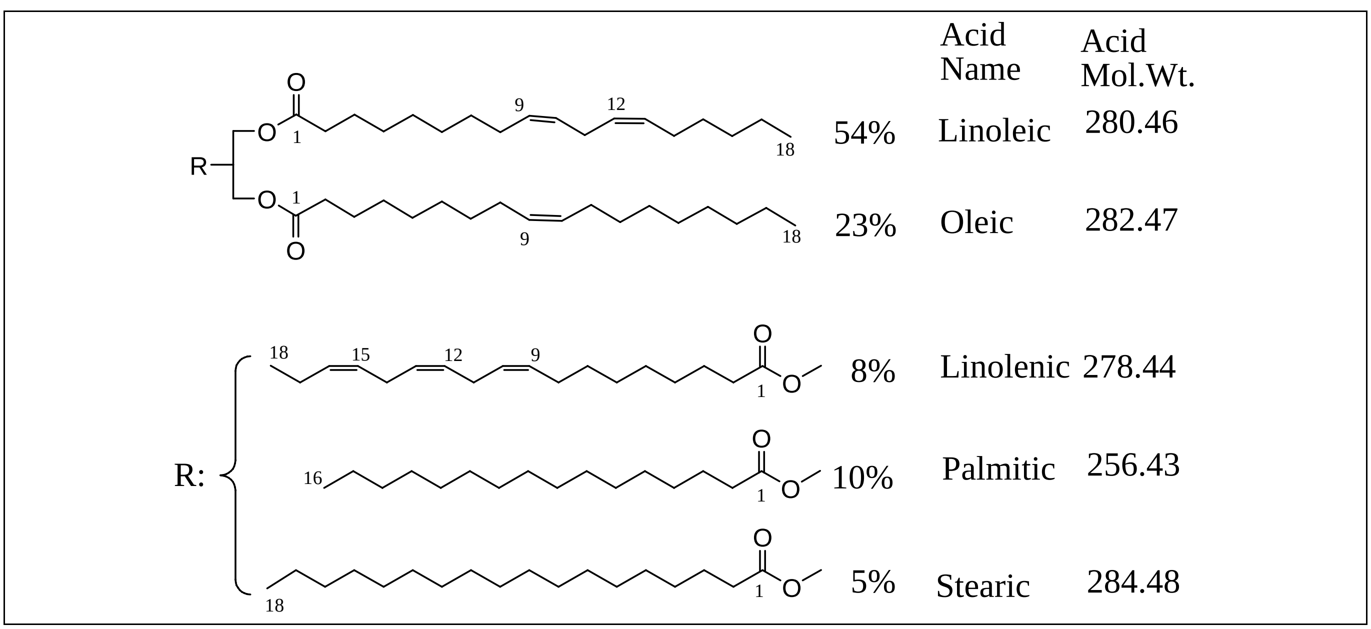


Figure 1. *Structure of Soybean Oil.*

If active hydrogen functional groups, such as alcohols, are introduced onto the molecule of plant oil, the product can be used as a polyol to make polyurethane. Scientists have made soy-based polyols from biodiesel [2] and hydroformulation [3] and the products of oxidized soybean oil, epoxidized soybean oil, for example. The epoxidation process of unsaturated hydrocarbon is well known [4]. Hydroxyl groups can be introduced onto the molecule of soybean oil in a second step by opening the oxirane of epoxidized soybean oil to form soy polyol. U.S. Pat. No. 2,882,249 describes the soy polyol formed by ring opening epoxidized soybean oil with ricinoleic acid. U.S. Pat. No. 4,025,477 describes the soy polyol obtained by ring opening epoxidized soybean oil with acrylic acid. U.S. Pat. Nos. 5,266,714 and 5,302,626 describe soy polyols obtained by ring opening epoxidized soybean oil with carboxylic acids. U.S. Pat. No. 6,891,053 B2 describes the soy polyol obtained by ring opening epoxidized soybean oil with acid leached clay. U.S. Pat. Nos. 4,508,853 and 4,742,087 describe the soy polyol obtained by ring opening epoxidized soybean oil with alcohols. U.S. Pat. Nos. 6,433,125 B1 and 4,551,517 describe the soy polyols obtained by ring opening epoxidized soybean oil with higher alcohols. U.S. Pat. No. 4,886,893 describes the soy polyol obtained by ring opening epoxidized soybean oil with polyfunctional alcohols. U.S. Pat. Nos. 6,107,433, and 6,433,121 B1, and 6,573,354 B1, and 6,686,435 B1 describe the soy polyols obtained by ring opening epoxidized soybean oil with a mixture of water, alcohol, and fluoroboric acid.

Hydroxylation of hydrocarbons can also be accomplished by biological methods [5-7]. To date, however, these processes have proven unsatisfactory. The maximum amounts typically suggested run to 30 – 40% [8], and products available are either expensive, or have high color, viscosity, and variable reactivity.

We have developed the Honey Bee polyols from plant oils by inserting guest molecules onto and between molecules of plant oils. Figure 2 shows synthetic route of our soy-based polyols. The guest molecules can be designed as bearing primary hydroxyl and secondary hydroxyl groups. Therefore, we can control reactivity of our soy-based polyols. For example, Honey Bee 230 and Honey Bee 150 function as 100% EO polyols, Honey Bee 105 functions as 71% EO and 29% PO polyol.

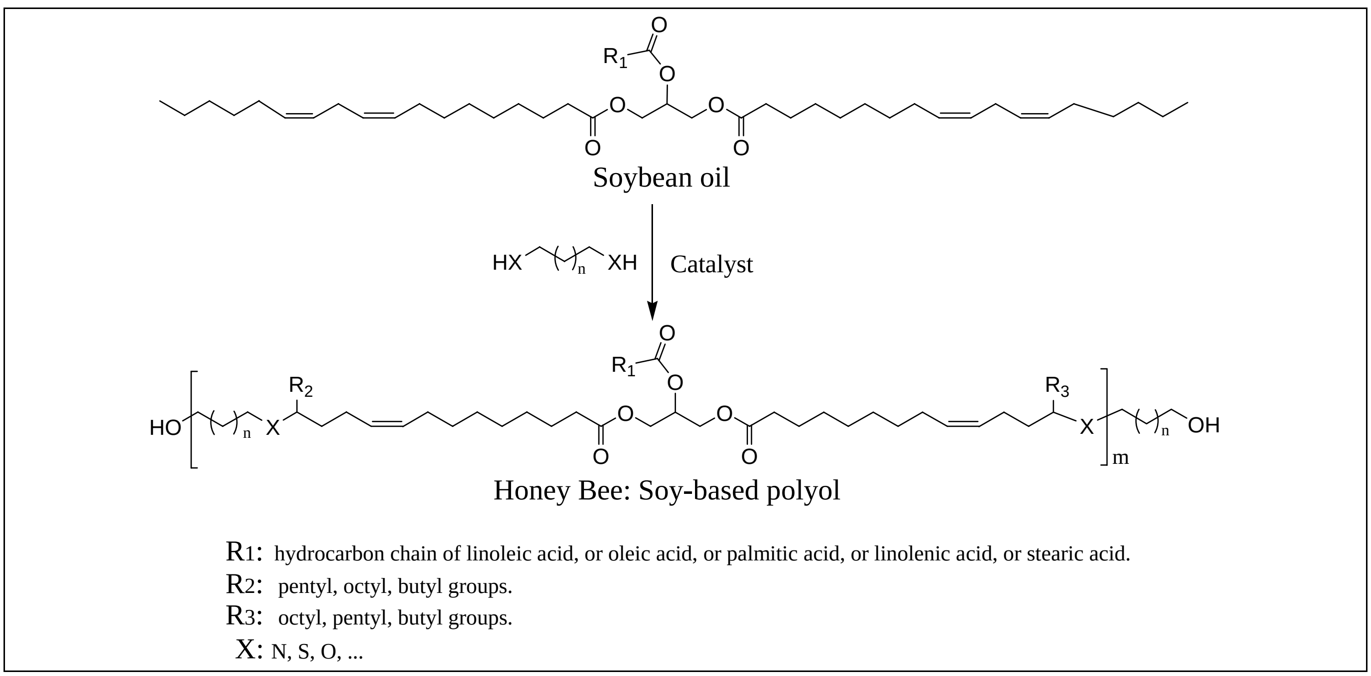


Figure 2. *Synthetic Route of MCP Soy-Based Polyols.*

Honey Bee soy-based polyols are directly produced from soybean oil in one step without going through the oxirane. As the hydroxyl groups of the polyols are on the end portion of guest molecules, they remain primary hydroxyls as polyols. In comparison with soy polyols made from epoxidized soybean oil, therefore, the HoneyBee has less steric-hindrance, viscosity, color and a higher reactivity. Honey Bee polyols react with every commercially available type of isocyanate, generating a potentially unlimited universe of polyurethanes for diverse applications.

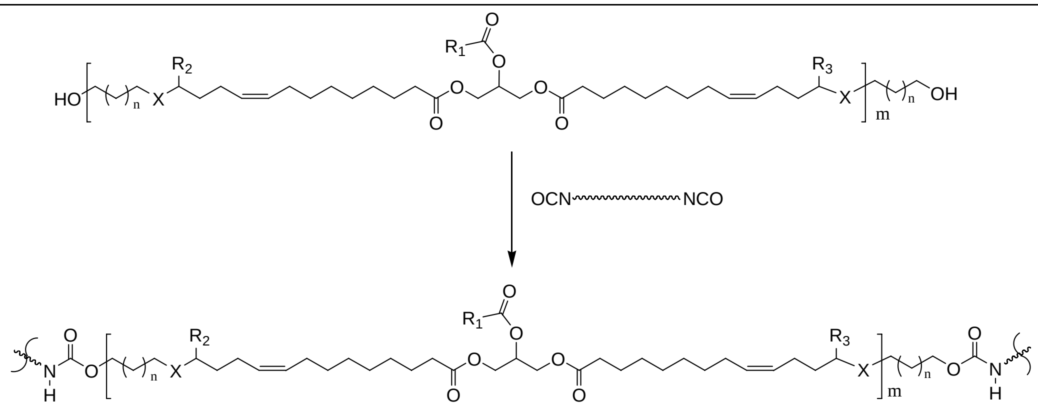
EXPERIMENTAL

Honey Bee polyols were used as manufactured by MCPU Polymer Engineering, the preparation of which is a trade secret, patents pending. Non cellular elastomers were made by reaction of Honey Bee and isocyanate terminated pre-polymers. Rigid non cellular urethanes were prepared by reaction of Honey Bee and MDI. Polyurethane foam samples were prepared by the reaction of Honey Bee and MDI.

Tests of tensile strength, elongation, compression set, shore durometer, density and resistance to tear were conducted according to ASTM D412, ASTM D395, ASTM D2240, ASTM D1622and ASTM D1938, respectively [9].

RESULTS AND DISCUSSION

Our experimental results show MCP soy-based polyols can completely react with isocyanates and isocyanate terminated pre-polymer to yield polyurethanes (Figure 3). The results show the reactivity of HoneyBee is higher than that of petroleum based polyols. Honey Bee polyols can be used in both CASE and foam markets.



Soy-based Polyurethane

Figure 3. *Reaction of Honey Bee and Isocyanates to Form Polyurethanes.*

Table 1 shows a starting point formulation for a moisture curing binder [10]. The isocyanate terminated pre-polymer MCP1411B is made from reaction of petroleum based polyol and MDI. The cured film has 1200 PSI tensile strength, 300% elongation, and 40 lbs/in tear resistance.

Table 1. Soy Based Moisture Cure Polyurethane Elastomer.

Polyol:	Honey Bee 230	Soy Based Polyol
Isocyanate:	MCP 1411B	Isocyanate Terminated Pre-Polymer
Tensile:	1200 psi	
Elongation:	300%	
Tear:	40 pli	
Durometer:	55 A	
Compression Set:	1.1%	

Table 2 is a starting point formulation for a roof coating elastomer. Isocyanate reacts with the soy-based polyol and partial petroleum based polyol to give flexible non cellular material. The roof coating demonstrates good physical properties.

Table 2. Soy Based Elastomeric Roof Coating.			
Polyols:	80%	Honey Bee 230	Soy Based Polyol
	20%	3000 mw PPO Triol	Petroleum Based Poyol
Isocyanate:		MCP 1611B	Isocyanate Terminated Pre-Polymer
Tensile:	2200 psi		
Elongation:	200%		
Tear:	45 pli		

Table 3 shows a starting point formulation for a rigid non cellular polyurethane casting or potting compound. In this formulation, 100% of the petroleum based polyols have been replaced with bio-based materials. The cured material demonstrated the typical properties of a polyurethane.

Table 3. Soy Based Molding Compound.			
Polyols:	90%	Honey Bee 230	Soy Based Polyol
	10%	Honey Bee 105	Soy Based Polyol
Isocyanates:	20 – 50%	4,4'-MDI	
	50 – 80%	Polymeric MDI	
Tensile:	4200 psi		
Elongation:	20%		
Durometer:	70 D		

Table 4 is a starting point formulation for a flexible foam. 4,4'-MDI reacts with a mixture of soy-based Honey Bee polyols and petroleum based polyols to yield a polyurethane flexible foam. Approximately 80% of polyol component in the flexible foam shown in Table 4 is made by using bio based materials. Again the physical properties are similar to those obtained with conventional polyether polyols.

Table 4. Soy Based Flexible Foam.			
Polyols:	50%	Honey Bee 230	Soy Based Polyol
	30%	Honey Bee 105	Soy Based Polyol
	20%	3000 mw PPO triol	Petroleum Based Polyol
Isocyanate:		4,4'-MDI	
Density:	24 kg/m^3		
Tensile:	18 psi		
Elongation:	190%		
Tear:	2.4 pli		

Table 5 contains a starting point formulation for a rigid polyurethane foam. Honey Bee 230 and Honey Bee 105 are allowed to react with polymeric MDI to give polyurethane rigid foam using only water as a blowing agent. Our results suggest that petroleum based polyols can be completely replaced by Honey Bee polyols with good effect and at any density.

As the carbon/oxygen ratio is much higher for Honey Bee than for other soy or petroleum based polyols, the fire resistance would be expected to be greater.

Table 5. Soy Based Rigid Foam.			
Polyols:	70%	Honey Bee 230	Soy Based Polyol
	30%	Honey Bee 105	Soy Based Polyol
Isocyanate:		Polymeric MDI	
Density:	28 kg/m^3		
T_g:	145 °C		
Tensile:	165 psi		
Elongation:	7%		

Table 6 is a starting point formulation for an isocyanurate foam made with 100% bio based materials. Water was used as the only blowing agent. Our results suggest that the trimer content may be easily adjusted. It is expected that this will allow the temperature resistance of the foam to be dialed in to customer requirements.

Table 6. Soy Based Isocyanurate Foam.			
Polyols:	65%	Honey Bee 230	Soy Based Polyol
	35%	Honey Bee 105	Soy Based Polyol
Additives:	0.8%	Water	
	0.4%	Amine Catalyst	
	2.0%	Potassium acetate	
	2.0%	Surfactants	
Isocyanate:		Polymeric MDI	
Density:	25 kg/m^3		
T_g:	175 °C		
Tensile:	200 psi		

CONCLUSIONS

Cost effective, low color, low viscosity soy-based polyols have been produced by a novel method. These Honey Bee polyols demonstrated high reactivity with a variety of MDI based isocyanates and prepolymers. Elastomers, coatings, rigid, flexible and isocyanurate foams were all produced using concentrations of bio based materials of up to 100%. Physical properties of these materials were typical of polyurethanes.

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BIOGRAPHIES

Thomas M. Garrett

Tom Garrett is President and Research Director at MCPU Polymer Engineering, A Division of MCP Industries, Inc. Also known as MCP Urethanes, MCPU was founded in 1937 as the research arm of the WS Dickey Clay Company with the hiring of chemistry professor Elmer R. Ligon. MCPU has been manufacturing polyurethanes since the late 1950's and has received over 25 patents. Dr. Garrett holds a B.S. with honors from Stanford University and a Ph.D. from the University of California at Berkeley, both in chemistry. Prior to joining MCPU, Dr. Garrett was a postdoctoral fellow at the Université Louis Pasteur in Strasbourg. The author of over 30 papers and patents, Dr. Garrett is a graduate of Harvard Business School in Boston.

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Frank Du is Principal Scientist at MCPU Polymer Engineering. Dr. Du holds a B.S. from Sichuan University, a M.S. from Concordia University, and a Ph.D. from the University of Montreal, all in chemistry. Prior to joining MCPU, Dr. Du was a research scientist at Los Alamos National Laboratory.