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VEGETABLE OIL-BASED HYPERBRANCHED POLYOLS IN FLEXIBLE FOAMS

Z. S. Petrović^{*}, I. Cvetković

Kansas Polymer Research Center, Pittsburg State University, Pittsburg, KS 66762

Abstract: Novel polyols were synthesized by controlled polymerization of hydroxylated fatty acids from methyl soyate. Polymerization of methyl esters of hydroxy fatty acids gives a hyperbranched (HB) product with different content of hydroxyl groups depending on the degree of conversion. Molecular weights, functionality and hydroxyl equivalent of polyols can be controlled by controlling the degree of conversion but also using monofunctional components. A range of hyperbranched polyols with acceptable viscosities and functionalities, suitable for flexible applications, was obtained by stopping the reaction at different degrees of conversion. A polyol with 60% of hydroxylated soybean fatty acid methyl esters and 40% of methyl esters from castor oil was selected for detailed analysis and was used in flexible foams. Monte-Carlo simulation of the polymerization of hydroxylated methyl soyate gave molecular weights and distributions which were compared with experimental values. Flexible foams were obtained with 65% of HB polyol in a mixture with a petrochemical triol. Increasing concentration of the HB polyol improved load bearing properties but decreased mechanical strengths and in particular tear strength.

Keywords: hyperbranched, polyol, polyurethane, foam.

1. INTRODUCTION

The new interest in utilization of vegetable oils for industrial use is the result of the public awareness and insistence on sustainability and the need to save the environment. Vegetable oils have been successfully used for polyols in the polyurethane industry [1-7]. A serious issue with utilization of vegetable oil-based polyols in flexible polyurethane foams is presented by the limited incorporation (not more than 30%) in the mixture with petrochemical polyols. The limiting factors include inadequate molecular weight, high viscosity in some cases, large functionality distribution in natural oils and heterogeneous structure. Typical petrochemical polyols for flexible foams include triols having molecular weights between 3000 and 6000, while soybean polyols are usually in a 1000 range. Soybean polyols consist of triglycerides which may have zero to eight hydroxyl groups per triglyceride, causing uneven crosslinking density [8–9]. To resolve some of these issues, we studied the synthesis, structure and properties of polyols prepared from functionalized fatty acids rather than from triglycerides. This guarantees a better distribution of functional species and allows good control of molecular weights and functionality of polyols.

Another incentive for this work was to find new uses for methyl esters of fatty acids (bio-diesel) since the industry was hit hard after the governments recently reduced subsidies and the surplus of production capacities became evident.

Increasing molecular weight of polymers causes the increase of viscosity. However, branching reduces viscosity in comparison with linear molecules of the same molecular weight. Using the concept of hyperbranching [10] allows an increase in molecular weight without excessive increase in viscosity. Functionality of hyperbranched molecules increases quickly with increasing molecular weight reaching high values unacceptable for many applications, especially foaming [11]. To illustrate the effect of functionality on gelation we should review the effect of polyol functionality on gelation in a system with a diisocyanate at stoichiometric ratio. Conversion of functional groups of the component A, p_a, at the gel point [12] is given by eq.1:

$$p_{a} = [1/(f_{aw}-1)]^{0.5}$$
(1)

where f_{aw} is second moment of functionality distribution, sometimes called weighted average functionality and is defined as[13]

$$f_{w} = \sum (N_{i}^{*} f_{i}^{2}) / \sum (N_{i}^{*} f_{i}) ..$$
(2)

Here N_i is number of mols of species *i* in the mixture.

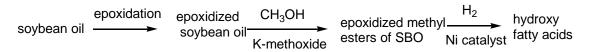
^{*} Corresponding author: zpetrovi@pittstate.edu

It is known that f_w correlates better with gel point than number average functionality. Table 1 illustrates dependence of conversion at the gel point, $p_{a(critical)}$, with functionality of polyols in a system with diisocyanate. We observe that gelation in a system with trifunctional polyol at stoichiometric ratio of components occurs at 70.7% conversion, 5functional polyol gels at 50% and 10-functional at 33.3% conversion. Early gelation in foam technology is not desirable because viscosity of the system becomes infinite and prevents normal foaming. The regulation of the functionality can be done by blocking some hydroxyl groups by different means. Another parameter important for the preparation of elastic networks is crosslinking density, which is closely related to the hydroxyl equivalent [14]. A typical value for the OH equivalent in polyols for flexible foams is about 1000 (triol of molecular weight of 3000 or tetrol of molecular weight 4000) or higher. When polyols are made by introducing OH groups at the position of double bonds in triglycerides their functionality is about 3-5 and molecular weight about 1000, thus their OH equivalents are in the 200-400 range, which is too low for application in flexible foams.

Table 1. Illustration of the dependence of gel point on functionality of polyols reacting with diisocyanate

junctionality of polyois reacting with allobeyanate					
Functionality, f _a	conversion at gel point, pac				
3	0.707				
4	0.577				
5	0.5				
10	0.333				
20	0.229				
100	0.101				

One efficient way to control molecular weight, functionality and viscosity is to use the concept of hyperbranching starting from hydroxy fatty acids rather than triglycerides. Soybean oil (SBO) fatty acids were hydroxylated by epoxydation and hydrogenation. The process was actually carried out by epoxidation of soybean oil then by preparation of methyl esters of epoxidized fatty acids by methanolysis in basic conditions and finally hydrogenation of epoxidized fatty acids after removal of glycerin. The process of converting soybean oil (SBO) to fatty acid methyl esters is illustrated below:



The process can be alternatively carried out by preparing first methyl esters of SBO (bio-diesel) followed by epoxidation and hydrogenation or to hydrogenate epoxidized oil first and then break it to fatty acid methyl esters as in this paper, with the same result.

In order to increase molecular weight and OH equivalent and keep functionality constant, we used castor oil fatty acids whose main component (~90%) is ricinoleic acid, and the rest (10%) are palmitic, oleic and linoleic acids.

The main fatty acids in soybean oil are saturated: palmitic (~10%) and stearic (~4%), and three unsaturated oleic (~25%), linoleic (~50%) and linolenic (3-9%), having one, two and three double bonds, respectively. By introducing hydroxyl groups at the position of double bonds one obtains hydroxy fatty acids with zero, one, two and three hydroxyl groups. The schematic representation of hydroxy fatty acids is shown in Figure 1. Simple heating of this mixture in the presence of a transesterification catalyst will cause polymerization resulting in a hyperbranched polyol whose conversion, molecular weight and functionality depend on heating time at a given temperature. At the complete conversion, the polymer will be a solid of infinite molecular weight and functionality. However, for all practical applications, a polyol of viscosity below 10 Pa.s, molecular weight below 10,000 and functionality between 3 and 5, is needed. The starting mixture consists of monomers of the type A, A-B, A-BB and ABBB, where A groups is an acid or methyl ester group and B is the hydroxyl group. Functionality is defined here as the number of B groups per molecule.

Preparation of A-BB type of hyperbranched polymers is well known [15]. The main component causing branching in our case is A-BB type, while A-B component just increases molecular weight, hydroxyl equivalent and viscosity while functionality remains unchanged. Fatty acids of the type A block chain growth, reduce functionality and reduce viscosity but increase molecular weight and OH equivalent. Using methyl esters of soybean fatty acids (bio-diesel) also have the same function and can be used to regulate functionality and hydroxyl equivalent. In this paper we have used fatty acids of castor oil instead in the mixture with hydroxylated methyl esters of SBO. The hydroxyl number is the highest at the beginning of the reaction and decreases to a constant value at the end of the reaction. However, the acid number, in the case of hydroxyl fatty acids instead of their methyl esters, decreases from an initial value to zero at full conversion. OH numbers of polyols for flexible foams should be below 100 mg KOH/g and OH equivalent above 1000 g/mol.

In this paper we have prepared polyols of controlled functionality by reacting the mixture of hydroxy fatty acids with methyl esters of castor oil to obtain minimal quantity of unreacted monomers in the final polyol. The polyols were used to make foams. For the preparation of foams they were mixed with petrochemical polyols in different ratios and the properties of foams were tested. The main objective for foams was to increase the content of bio-based polyol in the mixture above 50%, i.e., to the concentration when the hyperbranched polyol becomes the base polyol.

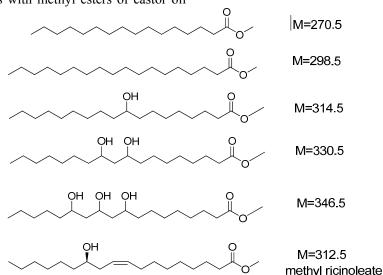


Figure 1. Schematic representation of fatty acid methyl esters from soybean oil with zero, one, two and three hydroxyl groups obtained by epoxidation and hydrogenation and methyl ricinoleate.

2. EXPERIMENTAL

Materials

Epoxidized soybean oil (ESBO) FLEXOL EPO with epoxy oxygen content (EOC) of 7.02 % was obtained from Dow Chemical. KOCH₃ (purity) used for methylation of hydroxylated ESBO and castor oil (I.V. = 83 and OH# = 168) was obtained from Alfa Aesar. Sponge nickel catalyst (50% aqueous slurry) was purchased from Strem Chemicals. Titanium (IV) isopropoxide (purity >98%), used for transesterification polymerization was purchased from Acros Organics.

Methods

The hydroxyl numbers of the polyols were determined according to the ASTM E 1899-97 using a reaction with *p*-toluenesulfonyl isocyanate (TSI) and potentiometric titration with tetrabutylammonium hydroxide as well as with phthalic anhydride method. Acid values were determined by IUPAC 2.201 method, using a 1:1(V:V) toluene/isopropanol mixture as solvent.

Viscosity was determined by using AR 2000ex Rheometer (TA Instruments) at 25 $^{\circ}$ C, with cone/plate geometry (truncation height 55µm for the 40 mm diameter, 2° cone).

Swelling ratio and soluble fraction were measured according to ASTM C1247, using toluene as solvent.

Molecular Weights (MW) and MW distribution were determined using a Waters Gel Permeation Chromatograph (Waters Corporation, Milford, MA, USA) consisting of a 510 pump, a 410 differential refractometer and data collection system. Tetrahydrofurane (THF) was used as the eluent at 1.00 ml / min at 30 °C. Four Phenogel 5 μ m columns (50, 100, 1000 and 10,000 Å) plus Phenogel guard column from Phenomenex (Torrance, CA, USA) covering MW range of 10²-10⁶ were used.

Foam properties were measured according to the ASTM D 3574 for molded urethane foams. The

Q-Test2 machine from MTS was used for mechanical properties measurements. Compression strength is a modified Indentation Deflection Force (IDF). The force was measured at 25 and 50% deflection on cubes of 100 mm sides. <u>Preparation of hydroxyl fatty acid methyl</u> esters HMESBO and MECO

The scheme for preparing hydroxy fatty acids from epoxidized vegetable oil is given in Figure 2.

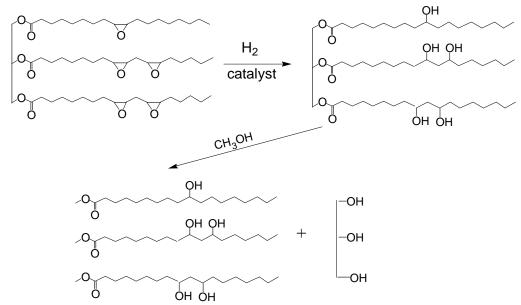


Figure 2. Schematic representation of the preparation of hydroxylated fatty acids from epoxidized oil (HMESBO) by hydrogenation and methylation

Hydrogenation of ESBO gives a polyol (HESBO). It was carried out as follows: 500 ml Parr reactor was charged with 100 g ESBO (FLEXOL EPO)+30g sponge nickel in 100 ml isopropanol. Pressure of hydrogen was maintained at 6.9 MPa (1000 psi). The reaction was run for 7 hours under vigorous stirring at 110 °C. Post-reaction treatment involved catalyst removal by filtration and removal of solvent on a rotary evaporator. Next step is to prepare methyl esters from the polyol (HMESBO) by heating the mixture with 15 times the stoichiometric amount of methanol in presence of 1% of CH₃OK for 3h at 65-68 °C. MECO was prepared by methylation of castor oil under the same conditions.

Synthesis of hyperbranched polyols

The synthesis of the hyperbranched polyol using methyl esters of soybean oil (HMESBO) and castor oil methyl esters (MECO) was carried out in a in 3-neck 250 ml glass, round bottom reactor, at 200 °C. The catalyst was 0.25% titanium isopropoxide. Total reaction time was 9. 5 hours. The HMESBO polyol had initial OH# (TSI) = 244 mg KOH/g. Methyl esters of castor oil fatty acids (MECO) had OH#=167.6 mg KOH/g,

3. RESULTS AND DISCUSSION

A series of polyols were prepared from the mixture of HMESBO and MECO of different ratios; only two at weight ratios 65:35 (designated as HMESBO-MECO-15) and 60:40 (designated as HMESBO-MECO-15) will be shown here. Changing the ratios of components was carried out to observe the effect of composition on viscosity and other properties and select the optimal ratio. It is estimated that higher MECO content would increase the distance between OH groups and give more favorable networks. It should be emphasized that ricinoleic acid has one double bond which gives a stronger color of the polyol and is prone to eventual oxidation, while HMESBO has no double bonds. The ricinoleic acid component also lowers viscosity of the final polyol. However, viscosity is also a function of the extent of reaction, i.e., of molecular weight. Table 2 shows characteristics of two polyols prepared from different ratios of HMESBO and MECO. Molecular weight distribution of two polyols is shown in Figure 3.

Although HMESBO-MECO-16 was made at higher conversion and it had wider molecular weight distribution, the viscosity of this sample and OH number were lower and thus more favorable for application in foams. Further characterization will be limited to this polyol and its application in flexible foams.

The sample designated as IC-HB-MECO 16 was made from the mixture HMESBO (60%) and MECO (40%) containing 13.7% non hydroxylated fatty acid methyl esters, 51.4% monohydroxyl components (ricinoleic and hydroxylated oleic methyl esters), 33.4% of methyl esters with two OH groups and 3.4% with three OH groups. The number average molecular weight was calculated from the composition to be 317. The calculated OH number was 218 mg KOH/g, close to the measured initial OH number of the mixture of 214 mg KOH/g. The calculated number average functionality is 1.233. The measured OH number of the polyol was 56 mg KOH/g. The extent of the reaction (conversion) was calculated from the initial and final OH number $[(OH\#_0-OH\#)/OH\#_0]$. The calculated conversion of OH groups was 74%, viscosity was 7 Pa.s at 25 °C and unreacted monomer content 1.5%. GPC chromatograms of the polyol and starting components are given in Figure 2. Maximum conversion of OH groups is 81% at 100% conversion of ester groups (molar ratio of hydroxyl/ester=1.233).

Figure 3 shows the presence of some residual monomers, which are not detrimental to properties of the polyol. The initial mixture can selfpolymerize to a very high molecular weight forming hyperbranched polyols. The degree of polymerization (conversion) determines the functionality of the polyol, its molecular weight and molecular weight distribution, viscosity, hydroxyl and acid number (if one starts from the hydroxyl fatty acids rather than hydroxylated methyl esters). Three major components of the hydroformylated methyl soyate are species with one hydroxyl (51.4%), two hydroxyls (~33%), and saturated fatty acids (14%). Addition of methyl ricinoleate increases molecular weight and hydroxy equivalent but preserves functionality. Schematic representation of a polyol from these three components is given in Figure 4. The effect of adding ricinoleic acid is the same as adding hydroxylated oleic acid since both are A-B type, thus the mixture behaves as one with a higher content of oleic acid.

Table 2. Some characteristics of two hyperbranched polyols from different ratios of HMESBO and MECO

Polyol	HMESBO/ MECO	Initial OH#, mg KOH/g	Final OH# mg KOH/g	Hydroxyl conversion, %	Viscosity at 25° C, Pas	Unreacted monomer, %
HMESBO-MECO-15	65:35	217	71	67	11	1
HMESBO-MECO-16	60:40	214	56	74	7	1.8

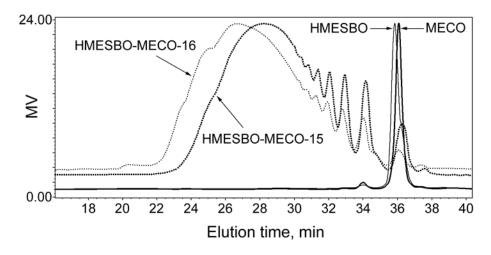


Figure 3. GPC curves polyols HMESBO- MECO 15 and HMESBO- MECO 16 together with starting components-MECO and HMESBO.

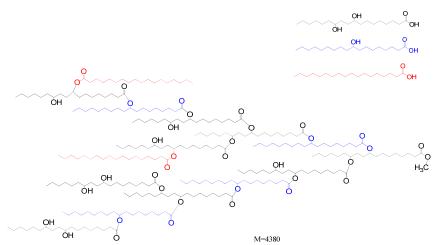


Figure 4. Schematic representation of a hyperbranched polyol from hydroxylated methyl soyate of molecular weight 4380 and eight OH groups.

In the simple case of self-condensation of dihydroxylated linoleic acid (A-BB case), which is similar to the generation of a family tree (Figure 5), the properties are related to the generation, g, as in dendrimers, although the shape of molecules is irregular and the molecular weight distribution is wider. Thus, we can talk about equivalent rather than a true generation as in dendrimers. While it is easy to analyze the properties of polyols obtained in this simple case the presence of non-hydroxy and mono hydroxy acids complicates the case and using simulation allows calculation of some molecular parameters. The conversion or extent of the reaction, p_a , can be related to the acid number which varies from an initial value to zero at the end of the reaction. Conversion calculated from acid (or ester) groups, p_a, is related to the conversion of hydroxyl groups, p_b, by the initial molar ratio of the acid (or ester) and hydroxyl groups, r_a or r_{OH}:

$r_a = 1/r_{OH} = p_b/p_a = [COOH]/[OH]$

In our case $r_a=1/1.233$, maximum conversion of ester (or acid) groups, p_a , is 100% but maximum conversion of hydroxyl groups is 100/1.233=81%. Molecular weights at 100% conversion are infinite making the product unsuitable for practical application. In our case the reaction was stopped at 74% of OH groups reacted, corresponding to conversion of ester groups of 74*1.233=91.2%. generation

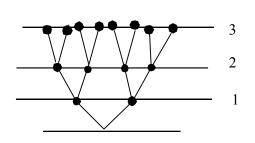


Figure 5. Growth of a branched polymer from A-BB monomers

Polydispersity (M_w/M_n) increases with increasing conversion. The starting mixture of hydroxylated fatty acids is practically monodisperse. OH equivalent weight of the polyol having OH number 56 mg KOH is 56100/56=1000, suitable for flexible applications. The weight loss at the end of the reaction due to the removal of methanol is 10%, and at 91% ester conversion is 9.1%. Calculation of molecular properties of the synthesized polyol was carried out using Monte-Carlo simulation. Although we carried out polymerization by transesterification of methyl esters of hydroformylated soybean fatty acids, the simulations were carried out with the acid form for simplicity. The measured and simulated properties of the final polyol are given in Table 3.

Table 3. Parameters of the initial polyol mixture and the final product HESBO-MECO-16

Sample	Functional	OH#	Acid#	M _n	M_w	Conversion of	Conversion of	OH
	ity, f_n/f_w	mg KOH/g	mg KOH/g			OH groups, %	acid groups, %	equiv
Initial	1.233/						0.0	
mixture	1.68	214	177	317	319	0.0		257
HESBO-	2.65ª/			2654 ^a	7686 ^a		91.2	
MECO-16	3-6 ^c	56	15.50	3350 ^b	23800^{b}	74		1000

^aGPC measurement; ^bsimulation; ^crough estimate

Reaction simulation

Reaction simulation was carried out using a commercial Drv Add+ program (DrvAdd, Intelligensys Ltd, UK, 2003), starting from 200,000 molecules, ignoring cyclization reactions. No cyclization usually results in higher molecular weights. It should be pointed out that GPC results are not quite correct since a special procedure for calibration did not extend to very high molecular weights. The results are summarized in Table 1. The overestimation of simulation results could occur if the extent of reaction (conversion) was also overestimated. For example, if the OH number of the final polyol is only two units higher, i.e., at 58 mg KOH/g, which is within experimental error, conversion would be 72.8% and M_n and M_w would be 2890 and 17800, respectively. Thus, molecular weights show the approximate range rather than precise values. The number average functionality, fn, is obtained by dividing M_n by OH equivalent. However, the second moment of distribution, fw, cannot be determined directly. If the hyperbranched polyol was to be made from a single A-BB component then it would be possible to calculate f_w by dividing M_w by hydroxy equivalent, which in our case would give a range 7-23. However, due to the large presence of monoxydoxy and some non-hydroxylated acids $(\sim 65\%)$ the estimated values are 3-6.

Polyurethane foams from the hyperbranched polyol

The intention of preparing hyperbranched polyols was to use them as base polyols in flexible foams, i.e., with more than 50% in the mixture with petrochemical polyols. The hyperbranched polyol

was used in this formulation in spite of the fact that it contains only secondary OH groups and thus would have lower reactivity. Polyols for molded foams always contain some primary groups. The description of properties and methods of measurements for flexible foams are described in a book [16].

The selected petrochemical polyol was Multranol M3900 (Bayer) having OH#=28 mg KOH/g and nominal molecular weight of 6000. Multranol is the polypropyleneoxide triol modified with ethylene oxide. The polyol component in foams was 0, 10, 30, 50, 65 and 70% of the hyperbranched polyol in the mixture with the petrochemical polyol. The general formulation is given in Table 4. Foams were prepared by pouring mixed components in a closed mold heated to 45 °C. The foams were crushed with hands to open the cells. All foams were successfully made except one with 70% HB, which lost integrity.

The properties of foams are displayed in Table 5. The density of all foams was somewhat higher than planned. Indentation force deflection is a quantity that measures load bearing of foams, which is important for car seats where the support of a sitting person is required. Higher values are preferred. A higher comfort factor, CF, is also preferable. Most of the properties fall in the same range of the pure petrochemical foam except for tensile strength at 50 and 65%, elongation at 65% and tear at 30, 50 and 65%, which are well below acceptable values. The air flow in all foams is poor but open cell content is excellent. Better properties could be obtained with optimization of the formulation since even the reference foam did not satisfy all requirements for a good molded foam.

component	%
Multranol	Х
Hyperbranched polyol	100-x
Low-activity, silicone glycol copolymer	0.75
Silicone stabilizer	0.15
High-potency silicone glycol copolymer.	0.15
33% triethylene diamine in propylene glycol (efficient gelation catalyst)	0.55
70% bis(dimethyleaminoethyl)ether and 30% dipropylene glycol- (strong blowing agent)	0.15
water	4.2
TDI index	100

 Table 4. Formulation of the molded foam

Property	Unit		% HB in the polyol mixture					
	%HB->	0	10	30	50	65		
density	kg/m ³	36	36	34	36	36		
ball rebound	%	24	24	26	26	26		
IFD	25%, N	27	25	30	53	43		
	65%, N	56	49	61	97	97		
	25%R, N	21	20	23	34	24		
	CF	2.1	2.0	2.0	1.8	2.3		
tensile strength	KPa	87	67	86	67	54		
elongation	%	95	109	45	30	9		
tear strength	N/m	108	110	45	30	9		
air flow	L/min	0.12	0.31	0.25	0.38	0.05		
open cell content	%	98	98	97	98	94		

Table 5. Properties of molded foams obtained from mixture of Multranol 3901 and HESBO-MECO-16

4. CONCLUSIONS

-Hyperbranched polyols were prepared from the hydroxylated fatty acid methyl esters of soybean oil and fatty acids of castor oil methyl esters. The selected ratio for application in foams was 60:40. Molecular weights, functionality and polydispersity of the polyol were determined by GPC and simulation. The polyol was used to prepare foams at different concentration in a mixture with a petrochemical polyol.

- HB polyols significantly increased load bearing properties of the foams, measured by the IFD values. Decrease in trend is noticeable for the foams with 65% HB polyol added. Comfort factor is in a range of 1.8-2.2

- Tensile strength was good up to 30% HB, but further increase in HB content caused deterioration. Elongation showed a similar trend. Tear strength rapidly decreases when incorporating more than 10% of HB polyol.

- The study indicated that HB polyols can be used in molded foams but both structure adjustment (introduction of primary OH groups) and optimization of the formulations is required in order to satisfy all requirements.

5. ACKNOWLEDGMENT

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ХИПЕРРАЗГРАНАТИ ПОЛИОЛИ НА БАЗИ БИЉНИХ УЉА У ОБЛИКУ ФЛЕКСИБИЛНЕ ПЈЕНЕ

Сажетак: Новел полиоли су синтетизовани контролисаном полимеризацијом хидрокси-масних киселина из метил-сојата. Полимеризација метил естера хидрокси масних киселина даје хипер-разгранат (XP) производ са различитим садржајем хидроксилних група, у зависности од степена конверзије. Молекулске масе, функционалности и хидроксилни еквивалент полиола може се контролисати контролом степена конверзије, али исто тако и употребом мултифункционалних компоненти. Палета хипер-разгранатих полиола са прихватљивим вискозитетима и особинама, подесних за флексибилне примјене, добијена је заустављањем реакције на различитим степенима конверзије. Полиол са 60% хидрокси-метил-естера сојиних масних киселина и 40% метил-естера из рицинусовог уља изабран је за детаљну анализу и употребљен је у флексибилним пјенама. Монте-Карло симулација полимеризације хидроксилних метил-сојата дала је молекулске масе и дистрибуције које су упоређене са експерименталним вриједностима. Флексибилне пјене добијене су са 65% ХВ полиолом у смјеси са петрохемијским триолом. Повећавање концентрације XB полиола побољшало је својства ношења терета (носивости), али је умањило механичку чврстоћу, а нарочито чврстоћу цијепања.

Кључне ријечи: хипер-разгранат, полиол, полиуретан, пјена.

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