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Synthesis of Polyurethanes Coatings From Renewable Resources - A State of Review

Dinesh Lonare[1], Manish Lonare[2] , Sanjana Gaikwad[3], Akhil Khedulkar[4], Pooja Kapse[5], Bhagyashree Dhargawe[6]

[1]Department of Paint Technology, Laxminarayan Institute of Technology, Amravati Road, Opposite Bharat Nagar, Ram Nagar, Nagpur-440033 ,Maharashtra, India.

[2]Higher and Technical Education Department ,Government of Maharashtra, India .

[3]University Department of Pharmaceutical Science ,RTM Nagpur University ,Nagpur-440033 Maharashtra, India.

[4]Department of Chemistry , Dr. Ambedkar College, Deeksha Bhoomi, Nagpur - 440010 , Maharashtra, India.

[5]Department of Chemistry , Government Institute of Science , R. T. Road, Civil Lines, Opp. Air India Office, Civil Lines, Nagpur-440008, Maharashtra, India

[6]University Department of Chemistry ,RTM Nagpur University ,Nagpur-440033, Maharashtra, India.

Abstract - Polyethylene, polypropylene, polystyrene, and polyvinyl chloride are all derived from petrochemical feedstock. The utilization of fossil fuels in the manufacture of plastics accounts for about 7% of worldwide oil and gas. These resources will arguably be depleted within the next one hundred years, and the peak in global oil production as estimated by some will occur within next few decades. We believe there is an urgent need to develop new synthetic routes to polymeric materials using renewable resources. Fats and oils are renewable resources that can chemically or enzymatically be treated to produce polymeric materials that can often act as a replacement for materials derived from petroleum. The most important oils are highly unsaturated oils, where, by using various chemical reactions, the double bonds are transformed into hydroxyl groups. In this category of highly unsaturated vegetable oils there are: soybean oil, sunflower oil, safflower oil, corn oil, linseed oil, olive oil, tung oil, castor oil. One of the important reactions that can be used to improve these fats and oils' performance is epoxidation. The synthesis of a polyol product from vegetable oil involves two key reaction steps, namely: epoxidation followed by hydroxylation. Vegetable oils have high contents of unsaturated fatty acid and can be converted into epoxy fatty acid by conventional epoxidation, catalytic acidic ion exchange resin, metal catalyst epoxidation or using chemo enzymatic epoxidation. This paper presents an overview of different synthesis methods of polyols and their application in polyurethanes.

Key words: Renewable resources, Epoxidation , Hydroxylation, Polyols, polyurethanes.

I. INTRODUCTION

Vegetable oils are important natural raw materials in the food industry as well as for the production of synthetic polymers. The increasing interest in their use is mainly due to their high availability, low cost and easy conversion to useful chemicals and new materials. Vegetable oils are mainly composed of triglycerides, which are characterized by having three fatty acids units esterified to a glycerol unit. Generally, these fatty acids can be saturated or unsaturated with chain lengths ranging from 16 to 20 carbon atoms. Castor oil, soybean oil, palm oil are the most widely used vegetable oil in the polymer industry because it is mainly formed of ricinoleic acid. This fatty acid contains a hydroxyl group at C12 that is usually useful for polyurethanes (PU) or polyesters synthesis. On the other hand, other vegetable oils need to be modified in order to be suitable for the same industrial purpose.

II. SOURCES OF OILS AND FATS

Naturally occurring oils and fats are obtained from two major sources:

1. Vegetable sources

2. Animal sources i.e. i) Land animals ii) Marine or Sea animals iii) Microorganisms.

Table 1. Sources of oils and fats

Fatty acid	**Common name**	**Sources**
Butanoic	Butyric (4:0)	Butter
Hexanoic	Caproic (6:0)	Butter
Octanoic	Caprylic (8:0)	Coconut
Decanoic	Capric (10:0)	Coconut
Dodecanoic	Lauric (12:0)	Coconut, Palm kernel
Tetradecanoic	Myristic (14:0)	Coconut ,Palm kernel, Butter
Hexadecanoic	Palmitic (16:0)	Palm, cotton, butter, animal and marine fats

Cis9hexadecanoic	Palmitoleic (16:1)	Butter, animal fats
Octadecanoic	Steric (18:0)	Butter, animal fats
Cis9octadecanoic	Oleic (18:1 9c)	Olive, tall, peanut, butter, animal and marine fat
cis, cis9,12octadecadienoic	Linoleic (18:2 9c,12c)	Safflower, sunflower, corn, soy bean, cotton.

III. CHEMISTRY OF VEGETABLE OILS

Fats and oils are water insoluble, hydrophobic substances of vegetable or animal origin (land or marine), which consist predominantly of triglycerides. Fats are Solids and oils are liquids at ordinary temperatures. Chemical modification of vegetable oils is an important route to obtain industrial products using renewable feedstock. There is still a high potential to develop new efficient and environmentally friendly reaction pathways leading to new products or to find new applications for already existing oleo chemicals. This strategy can contribute to decrease our dependence on nonrenewable, and therefore limited, natural resources such as mineral oil. In order to give some structure to this content, the reactions were classified in three groups.

1. Reaction on hydrocarbon chain

2. Reaction on carbonyl function

3. Reaction on unsaturated position

The double bonds in the hydrocarbon chain of oleo chemicals exhibit a higher chemical potential than the paraffinic methyl and methylene groups. On the industrial level, chemical reactions on the unsaturations are in second place after the reactions involving carboxylic/ester groups. In industry the most extensively applied reactions on the unsaturations are hydrogenation and epoxidation.

IV. EPOXIDATION OF OIL

Epoxides, also known as oxiranes, are cyclic ethers with three member ring. The highly strained ring in their molecule makes them more reactive than other ethers. Epoxidation reaction is an important reaction in organic synthesis because the formed epoxies are intermediates that can be converted to a variety of products. Additionally, the formation of epoxide is attractive in asymmetric synthesis since it can lead to two chiral carbons in one step. Generally, four technologies are employed for the production of epoxide from olefinic molecules.

V. METHODS OF EPOXIDATION OF OIL

1. Epoxidation by Conventional Method

2. with organic and inorganic peroxides

3. with halohydrins for the epoxidation of olefins with electron deficient double bonds

4. with molecular oxygen

In general, per-acetic acid are used in epoxidation processes for oxygen transfer to the double bonds. The use of these acids is prone to loss of yield and side reactions.

Dinda et al. [1] worked on the epoxidation kinetics of cottonseed oil using a hydrogen peroxide catalysed by liquid inorganic acids i.e. HCl, H_2 SO_4 , HNO_3 and H_3PO_4 .They used carboxylic acid i.e.CH_3COOH and HCOOH as oxygen carrier but they found that acetic acid is more effective oxygen carrier than formic acid.Out of all liquid inorganic acid studied as catalyst,H_2 SO_4 was found to be most efficient and effective.

Cai et al. [2] worked on the kinetics of in situ epoxidation of soybean oil, sunflower oil and corn oil by peroxyacetic acid catalysed H_2SO_4. In this work they found that soybean oil has greatest conversion rate and lowest activation energy for epoxidation using peroxyacetic acid.

Goud et al. [3] worked on in situ epoxidation of karanja oil with aqueous hydrogen peroxide and acetic acid in presence of Amberlite IR120 acidic ion exchange resin as catalyst. The variables studied were stirring speed, hydrogen peroxide to ethylenic unsaturation molar ratio, acetic acid to ethylenic unsaturation molar ratio, temperature and catalyst loading. The effects of this parameter on the conversion to epoxidized oil were studied at the optimum condition for the maximum oxirane content was established. They reported that the intermediate temperature in the range of 55^0 C to 65^0 C gives maximum conversion of double bonds to oxirane groups and the reaction time was minimized. Further they added that molar ratio of acetic acid to karanja oil is 0.5 mol and a mole ratio of 1.5 for hydrogen peroxide to oil was the optimal concentration for the epoxidation reaction.

Goud et al. [4] worked on the epoxidation reaction of mahua oil using hydrogen peroxide. In order to optimize the process they studied various parameter and factors including catalyst type, temperature, and reactants molar ratio and mixing speed on the epoxidation reaction. Also they stated that the economic value of mahua oil could be increased by converting oil to epoxidized mahua oil. They used H_2 O_2 as oxygen donor and glacial acetic acid as oxygen carrier in the presence of catalytic inorganic acid i.e. H_2SO_4 and HNO3 but they concluded that sulphuric acid is the best inorganic catalyst for this system producing a high conversion of double bonds to oxirane groups when the epoxidation reaction performed at the intermediate temperature of 55^0 C to 65^0 C to reduce the hydrolysis reaction.

Lian Kun Jia al. [5] worked on the synthesis of vegetable oil based polyether polyols via epoxidation followed by ring opening reaction. In this study, epoxidation of cottonseed oil with epoxy oxygen content from 5.25 wt% to 6.15 wt% was first produced by peroxyformic acid generated insitu from hydrogen peroxide and formic acid, they used HBF_4 (40 wt%) The presence of strong mineral inorganic acid such as H_2SO_4 as acid catalyst leads to many side reactions such as oxirane ring opening to diols, hydroxyl esters, estelloids and other dimer formation.

Mungroo et al. [6] worked on the epoxidation of canola oil with H_2O_2 as oxygen donor, acetic acid as oxygen carrier and AIER (22 % loading) as catalyst. The heterogeneous catalyst, AIER, was found to be reusable and exhibited a negligible loss in activity. The formation of epoxy adduct of canola oil was confirmed by FTIR and $_1$ H NMR spectral analysis.

Petrovic et al. [7] worked on the epoxidation kinetics and side reactions of soybean oil in toluene with peroxyacetic acid and peroxy formic acid in the presence of AIER as a catalyst. They found that peroxyacetic acid is less efficient than peroxy formic acid. Acidic ion exchange resin can be used as catalyst to synthesize peroxy acids followed by in situ epoxidation of vegetable oils. While studying the kinetics of in situ epoxidation of soybean oil in bulk catalyzed by ion exchange resin, they find that AIER has prominent advantages over conventional chemical method of epoxidation of vegetable oil is that by improving the selectivity and undesirable side reactions can be reduced to certain level.

SinadinovicFiser et al. [8] worked on the kinetics of epoxidation of soybean oil in bulk by per acetic acid formed in situ, in the presence of an ion exchange resin as the catalyst. The catalytic reaction of the per acetic acid formation was characterized by adsorption of only acetic acid and per acetic acid on the active catalyst sites and irreversible surface reaction was the overall rate determining step. They investigated that increasing the catalyst concentration, reaction temperature and acetic acid to ethylenic unsaturation molar ratio increases the reaction rate and oxirane content.

Dinda et al.[9] investigated the kinetics of epoxidation of cottonseed oil by peroxyacetic acid (PAA) generated in situ from hydrogen peroxide and glacial acetic acid (AA) in the presence of acidic ion exchange resin (AIER) catalysts, namely Amberlite IR120. The effect of several variables including temperature, stirring speed, catalyst loading, and particle size, concentration of hydrogen peroxide and AA on oxirane conversion was studied. A satisfactory level of oxirane conversion (greater than 65%) with high selectivity (greater than 90%) could be obtained if the epoxidation was carried out at optimum conditions, using in situ generated PAA. The Langmuir–Hinshelwood–Hougen–Watson (L–H–H–W) kinetic model approach has been adopted for the development of overall reaction rate equations, and the proposed kinetic model includes the major side reactions for the estimation of kinetic parameters. Kinetic parameters were estimated by fitting experimental data using a nonlinear regression method. From the estimated kinetic constants, the activation energy for the AIER catalysed epoxidation of cottonseed oil was found to be 10.1 kcal mol^{-1} .

Annelise E. Gerbase et.al. [10] studied the methyl trioxorhenium (MTO)CH_2Cl_2 /H_2O_2 biphasic system for epoxidizing soybean oil. The reactions were optimized (reactant ratio, time, and temperature), which resulted in a better performance (higher conversion and selectivity) than those described in the literature. Total double bond conversion and 95% selectivity were obtained in 2 h at room temperature. Furthermore, it was possible to reach desired epoxidation degrees by changing the oxidant and MTO amounts. The rhenium epoxidized soybean oil remained stable in the absence of stabilizers for up to 30 d when stored at mild conditions.

Vaibhav V. Goud et.al. [11] Jatropha (Jatropha curcas) oil with iodine value 104 g I2/100 g, and containing 44.7% oleic acid and 31.4% linoleic acid, was epoxidised in situ with hydrogen peroxide (30%) and acetic/formic acid in the presence of catalytic amounts of sulphuric acid. We have compared the kinetics of epoxidation of jatropha oil (JO) by peroxyacetic and peroxyformic acids, in or without toluene at 30, 50, 70, and 85 °C. The effects of temperature and various mole ratios on epoxidation rate, oxirane ring stability, and iodine value of the epoxidised oil were studied, and optimum conditions were established. The rate constants for epoxidation of JO were found to be in the range 0.22–69.4 × 10−6 $l.mol^{-1}.s^{-1}$ and activation energies were found to be 64.46 $KJ.mol^{-1}$, 72 $KJ.mol^{-1}$, 59 $KJ.mol^{-1}$, and 68.24 $KJ.mol^{-1}$, for peroxyacetic and peroxyformic acids in or without toluene, respectively.

Srikanta Dinda et.al. [12] The epoxidation reactions were carried out in a fully baffled mechanically agitated contactor or reactor made of glass (6.5 cm i.d. and 250 ml capacity), equipped with a 2.5 cm diameter six bladed turbine type glass stirrer. The contactor assembly was immersed in a thermostatic Water bath, with a temperature control ±1 0 C. A suitable amount of cottonseed oil was taken in the reactor. Calculated amount of carboxylic acid (CH_3COOH/ HCOOH) and liquid inorganic acid catalyst (H_2 SO_4 / HNO_3 / H_3PO_4 / HCl) was added to the reactor and the mixture was stirred for about half an hour. Then the required amount of 50% aqueous H_2 O_2 was added drop wise at a rate such that the addition was completed in half an hour and the reaction was continued further for the desired time duration. Samples were withdrawn intermittently, considering the completion of H_2O_2 addition as zero time. The collected samples were then extracted with diethyl ether in a separating funnel, washed with cold and slightly hot water successively to remove free acid, and then analyzed for iodine value, oxirane content, Alfa glycol content.

P. Saithai et.al.[13] A solution of soybean oil (100g) and glacial formic acid (13.97g) was heated at a 45–55°C. Sulphuric acid (0.5mL) was added into the solution. Then, 116.98g of 30wt% H^2O^2 solution was added slowly from a dropping funnel and reacted at 45, 50 and 55°C for 1–7h. The molar ratio of soybean oil: formic acid: hydrogen peroxide was 1:2.64:8.9. The crude product was filtered and washed with distilled water repeatedly until a pH of 7.0 was obtained. The oil phase was dried with anhydrous sodium sulphate then filtered. Finally, the residue (water) was removed using an evaporator at 45–50°C under pressure. The number of epoxide groups per molecule of ESO was calculated from the $_1$ HNMR spectrum by using the peak at 4.0–4.4ppm for the glycerol backbone and the peak at 0.9ppm for the methyl group as an internal standard, and using the peak intensity ratio between the peak at 2.8–3.2 and 4.0–4.4ppm.

Yong shang Lu and Richard C. Larock et.al. [14] Vegetable oils contain carbon–carbon double bonds capable of being polymerized through a free radical mechanism. However, the free radical polymerization of triglyceride double bonds has received relatively little attention as a result of the presence of chain transfer processes, which can occur in the allylic positions of the fatty acid chains. However, drying oils, such as tung oil, can react with atmospheric oxygen to form polymeric materials with a network structure. The oxidation of drying oils by air involves hydrogen abstraction from a bis-allylic group between two double bonds in a polyunsaturated fatty acid chain, which leads to peroxidation, per-epoxidation, hydro peroxidation, epoxidation, and crosslinking through radical recombination. This procedure is commonly used to prepare alkyd resins as well as in the synthesis of linoleum floor covers.

Ma´rcia Campos Brasil et.al [15] Four different HSO were synthesized to be used as organic precursors in the preparation of the hybrid films: HSO F198 (soybean oil fully hydroxylated with formic acid/hydrogen peroxide, having an OH value of 198 mg of KOH/g), HSO F75 (soybean oil partially hydroxylated with formic acid/hydrogen peroxide, having an OH value of 75 mg of KOH/g), HSO EG (HSO from epoxidized soybean oil and ethylene glycol), and HSO meso (HSO from epoxidized soybean oil and meso erythritol). Refined soybean oil (70 g, 0.37 mol of double bonds) was mixed with 43 mL (1.11 mol) of formic acid. A solution of 32% H_2 O_2 (50.5 mL, 0.56 mol) was added drop wise to the mixture at room temperature for 30 min, under strong mechanical stirring. When the H_2 O_2 addition was completed, the mixture was heated to 65 ^{0} C, and stirred strongly for different times depending on the hydroxylation level to be reached. After the required time, the product was washed, firstly with a sodium bisulfide 10% w/v solution to remove peroxide, followed by a sodium bicarbonate 10% w/v solution until the pH of the aqueous layer was neutral. Afterwards, ethyl ether was added and the organic phase was separated and dried overnight with sodium sulfate. After filtration, the solvent was removed in vacuum.

Cecilia OrellanaCoca et.al [16] The effect of reaction parameters on lipase mediated chemo enzymatic epoxidation of linoleic acid was investigated. Hydrogen peroxide was found to have the most significant effect on the reaction rate and degree of epoxidation. Excess of hydrogen peroxide with respect to the amount of double bonds was necessary in order to yield total conversion within a short time period, as well as at temperatures above 50 ^{0} C to compensate for hydrogen peroxide decomposition. However, prolonged incubation with high excess of hydrogen peroxide leads to the accumulation of peracids in the final product. The reaction rate increased also with increasing hydrogen peroxide concentration (between 10 and 50 wt%) ; however, at the expense of enzyme inactivation. Linoleic acid was completely epoxidized when used at a concentration of 0.5–2 M in toluene at 30 ^{0}C, while in a solvent free medium; the reaction was not complete due to the formation of a solid or a highly viscous oily phase, creating mass transfer limitations. Increasing the temperature up to 60 ^{0}C also improved the rate of epoxide formation.

Wei He, Zheng Fang et.al [17] In the study, the epoxidation process of soybean oil by micro flow system (MFS) was investigated. With formic acid as oxygen carrier and EDTA2Na as stabilizer, the optimal result (epoxidized soybean oil (ESO) with an epoxy number (EN) of 7.3) was obtained in such conditions: Temperature 75°C, H_2 SO_4 concentration 3%, EDTA2Na dosage 3%, residence. time 6.7 min, ratio of formic acid to hydrogen peroxide 1:1, and H_2 O_2 to double bond molar ratio 8:1.

Z.S.Petrović, I. Cvetković [18]* 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 mono functional 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.

VI. CONCLUSION

In this review, we have summarized various epoxidation methods followed by various polyol synthesis methods. Most importantly here we have focused on renewable resources, as we know that petroleum feed stocks are depleting everyday and it was urgently needed to developed some new synthetic routes to polymeric materials. All of these various synthesis methods of polyols and polyurethanes that we have observed above an Efficient epoxidation of vegetable oils has been done by the maintaning the reaction temperature of the reactor , stirring speed, selection of vegetable oils having iodine value high (unsaturation groups in oil) and selection of inorganic and organic acid . Epoxidation with per carboxylic acids and epoxidation with organic and inorganic peroxides can gives best results .

REFERENCES

[1] Dinda S, Goud VV, Patwardhan AV, Pradhan NC (2008) Epoxidation of cottonseed oil byaqueous hydrogen peroxide catalysed by liquid inorganic acids. Bioresour Technol. doi:10.10.16/ j.biotech.2007.07.15.

[2] Cai C, Dai H, Chen R, Su, C, Xu X, Zhang , S and Yang L 2008, Studies on the kinetics of in situ epoxidation of vegetable oil , 'European Journal of Lipid Science and Technology' vol.110, no.4, pp.341-346.

[3] Goud, V. V., Patwardhan, A. V., Dinda, S. AndPradhan, N. C. (2007), Epoxidation of karanja (Pongamiaglabra) oil catalysed by acidic ion exchange resin, European Journal of Lipid Science and Technology, 109: 575–584.

[4] Goud, V.V.; Patwardhan, A.V.; Pradhan, N.C. Studies on the epoxidation of Mahua Oil (Madhumica Indica) by hydrogen peroxide. Biores. Technol. 2006, 97, 1365–1371.

[5] Lian Kun Jia, Li Xiang Gong, Wen Jiao Ji, Cheng YouKan 2011, Synthesis of vegetable oil based polyols with cottonseed oil and sorbitol derived from natural source, Chinese Chemical Letters (2011).

[6] Mungroo R., Narayan C. Pradhan., Goud V.V., Dalai AK. Epoxidation of canola oil with hydrogen peroxy decatalysed by acidic ion exchange resin. J Am Oil Chem Soc (2008) 85:887-896.

[7] Petrovic, ZS Zlatanic, A Lava, CC and Sinadinovic Fiser, S 2002; Epoxidation of soybean oil in toluene with peroxy acetic and peroxy formic acids kinetics and side reactions, European Journal of Lipid Science and Technology, Vol 104, no.5, pp. 293-299.

[8] SinadinovicFiser., Jankovic, M. Petrovic. Z.S. Kinetics of insitu epoxidation of soybean oil in bulk catalysed by ion exchange resin. J.Am.Oil Chem.Soc.2008.85, 887-896.

[9] Dinda S, Patwardhan AV, Goud VV & Pradhan NC 2008, 'Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids' Bioresource Technology, vol.99 , no.9, pp. 37373744.

[10] Annelise E. Gerbase*, José R. Gregório, Márcia Martinelli, Márcia C. Brasil, and Ana N.F. Mendes, Epoxidation of Soybean Oil by the MethyltrioxorheniumCH2Cl2/ H_2O_2 Catalytic Biphasic System, Paper no. J10060 in JAOCS 79, 179–181 (February 2002).

[11] Vaibhav V. Goud, Srikanta Dinda, Anand V. Patwardhan3 and Narayan C. Pradhan, Epoxidation of Jatropha (Jatropha curcas) oil by peroxyacids, asia pacific journal of chemical engineering ,Asia Pac. J. Chem. Eng. 2010; 5: 346–354.

[12] Srikanta Dinda, Anand V. Patwardhan , Vaibhav V. Goud, Narayan C. Pradhan, Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids, Bioresource Technology 99 (2008) 3737–3744.

[13] P. Saithai, J. Lecomte, E. Dubreucq, V. Tanrattanakul, Effects of different epoxidation methods of soybean oil on the characteristics of acrylated epoxidized soybean oil co poly(methyl methacrylate) copolymer, e- XPRESS Polymer Letters Vol.7, No.11 (2013) 910–924.

[14] Yongshang Lu and Richard C. Larock , N ovel Polymeric Materials from Vegetable Oils and Vinyl Monomers: Preparation, Properties, and Applications, ChemSusChem2009, 2, 136 – 147.

[15] Ma´rcia Campos Brasil ,Annelise Engel Gerbase ,Maria Augusta de Luca ,Jose´ Ribeiro Grego ´rio, Organic–Inorganic Hybrid Films Based on Hydroxylated Soybean Oils, J Amer Oil Chem Soc (2007) 84:289–295.

[16] Cecilia Orellana Coca ,Samuel Camocho ,Dietlind Adlercreutz ,Bo Mattiasson, Rajni HattiKaul, Chemoenzymatic epoxidation of linoleic acid:Parameters influencing the reaction, D OI 10.1002/ejlt.200500253 Eur. J. Lipid Sci. Technol. 107 (2005) 864–870.

[17] Wei He, Zheng Fang, Dong Ji, Ketao Chen, Zhidong Wan, Xin Li,Haifeng Gan, Shigui Tang,Kai Zhang, and Kai Guo, Epoxidation of Soybean Oil by Continuous MicroFlow System with Continuous Separation, dx.doi.org/10.1021/op400050n Org. Process Res. Dev. 2013, 17, 1137−1141.

[18] Z. S. Petrović, I. Cvetković, Vegetable oilbased hyperbranched polyols in flexible foams Contemporary Materials, III1 (2012) Page 63 of 71.