

Epoxyed soybean oil 로 제조된 하이드록시 폴리올의 합성

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Polyols with High Hydroxyl Value Prepared from Epoxyed Soybean Oil

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1. Introduction

There is a growing urgency to develop novel bio-based products and other innovative technologies that can reduce the widespread dependence on fossil fuels. In the search for sustainable chemistry, considerable importance is being attached to the polymers prepared from biological sources, and interest has focused on the use of cheap, biodegradable, and annually renewable starting materials such as starch, cellulose, carbohydrates, proteins, and vegetable oils for synthesizing a wide range of bioplastics [1]. Rigid polyurethane (PU) foams are widely used in thermal insulation and packaging. Most of the rigid PU foams on the market are based on polypropylene oxide (PPO) triols and MDI. Soybean oils are one of the cheapest and most abundant biological sources, and their use as starting materials has numerous advantages, for example, low toxicity, inherent biodegradability, and high purity. Therefore, soy-based polyols provide an interesting alternative to petroleum based synthetic polyols. In recent years there has been a considerable research effort focused on producing polyols from vegetable oils. Many researchers prepared natural polyols through epoxidation of vegetable oils, specifically soybean oil, followed by ring opening reaction. Urethane Soy Systems Company (USSC) and Maskimi produce vegetable polyols in the large scale. But the hydroxyl number of all these oil polyols are below 250mg KOH/g that is not high enough for rigid foam. Polyols of industrial importance are usually required to have low viscosity and high hydroxyl content [2]. The present study aims to develop novel, biobased, low viscosity and high hydroxyl value polyols prepared from epoxyed soybean oils (ESO). This natural polyols is suitable to prepare rigid polyurethane foam.

2. Experiment

ESO with 6.91% epoxy oxygen content was purchased from SINWON CHEMICAL CO., LTD. ESO, glycerol, 1, 2-propanediol and KOH were mixed into a flask. The molar ratio of ESO to polyfunctional alcohol is 1:4. The mixture was stirred at about 170°C for a certain time, and then cooled. The hydroxyl value, viscosity, epoxy value, and pH value were determined according to Chinese standard method.

3. Results and discussion

The ring-opening reactions of the oxiranes in ESO and transesterification with alcohol are illustrated in Figure 1. Addressing prior research efforts using ESO for natural polyols preparation, there has been a considerable research effort focused on oxirane ring opening with monofunctional alcohol such as methanol in the presence of an acid catalyst [3]. In that condition there is only oxirane ring opening reaction and no

transesterification, so the final natural polyols keep a triglyceride molecule structure and the hydroxyl value must be below 250 mgKOH/g and the hydroxyl groups of the soybean-based polyol are more located in the inner regions of the backbone that is not suitable for rigid polyurethane foam. In this paper the ESO was reacted with polyfunctional alcohol in the presence of basic catalyst, thus it is easy to get polyols with a high hydroxyl value. The glycerol and 1, 2-propanediol was used as polyfunctional alcohol and KOH as basic catalyst. Table 1 shows the properties of natural polyols. The glycerol is chosen as raw material because it is cheap and natural, but when the glycerol content is too high, increasing the OH content caused an increase in viscosity and an eventual transition into grease. The physical state of the polyols was largely determined by hydrogen bonding and crystallization. The polyols with low viscosity and high hydroxyl content are important for the industrial application in large scale especially for the rigid polyurethane foam. 1, 2-propanediol is used as polyfunctional alcohol because it contains a relative low hydroxyl content and nonpolar methyl which inhibits the molecule interaction and hydrogen bonding. Table 1 shows the viscosity of polyols decreased when the content of 1, 2-propanediol increased. Meanwhile the viscosity also influenced by side reaction such as crosslink reaction.

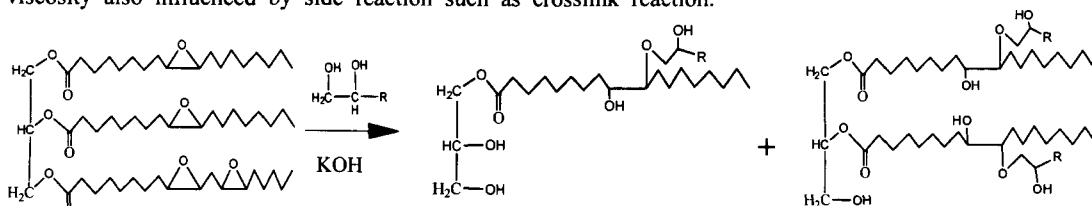


Figure 1 The ring opening reactions and transesterification of epoxidized soybean oil

Table 1 Properties of the natural polyols prepared

ID	Molar ratio		Properties			
	Glycerol	1, 2- propanediol	Hydroxyl value (mgKOH/g)	Epoxy value (%)	Viscosity (25 °C, mPa·s)	pH value
1	100	0	503	0.82	waxes	8.1
2	75	25	465	1.03	waxes	8.3
3	50	50	432	0.75	6070	8.5
4	25	75	380	0.56	4210	7.8
5	0	100	355	0.84	2500	8.5

4. Conclusions

The natural polyols was synthesized by oxirane ring opening in ESO and transesterification with glycerol and 1, 2-propanediol, and the properties were characterized by hydroxyl value, viscosity, epoxy value, and pH value. The viscosity of polyols decreased with when the content of 1, 2-propanediol increased and determined by the hydrogen bonding and crystallization. This kind of novel, high hydroxyl and natural polyols is suitable for the rigid polyurethane foams.

Reference

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