Synthesis of polyols from rapeseed oil

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Keywords

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Abstract

In this work, vegetable polyols as a potential replacement of petroleum polyols were investigated. The two-stage method of preparation natural oil-derived polyols was presented.

Introduction

Polyols plays an important role in polyurethane industry. The use of petrochemical polyols is disadvantageous in terms of production, energy and costs. From both economic and environmental point of view, it is desirable to replace petroleum polyols with renewable resources [1-3]. Vegetable oils are triglycerides of fatty acids, which have a number of excellent properties, so they could be utilized in producing valuable polymeric materials and probably will become potential bio-renewable feedstock for polyurethanes.

Results and discussion

The rapeseed oil was epoxidized using peracetic acid obtained in situ from the reaction between 30 wt% hydrogen peroxide and glacial acetic acid (Fig.1). Then ring opening of the epoxy groups to hydroxyls has been done (Fig. 2) [4]. The process of oxirane ring opening was carried out under microwave irradiation. It allowed to reduce reaction time and led to energy savings [5].

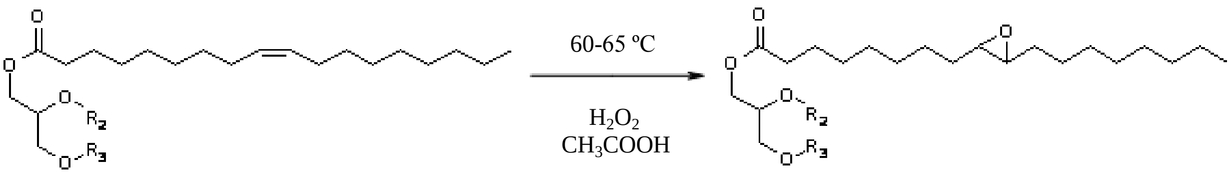

Fig. 1. Oxidation of rapeseed oil using hydrogen peroxide. R_1 and R_2 – the residues of fatty acids.

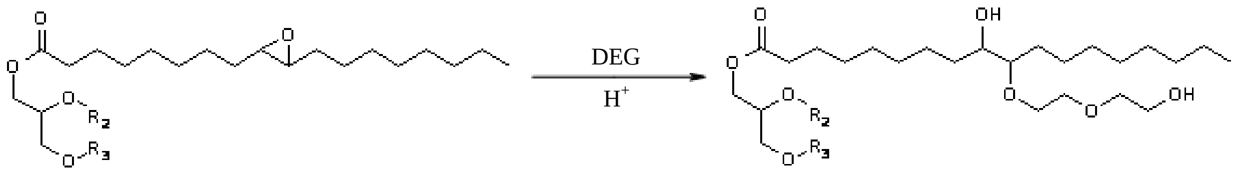

Fig.2. Oxirane rings opening in epoxidized rapeseed oil. R_1 and R_2 – the residues of fatty acids.

The course of reactions was monitored by the determination of iodine number (LI) [6], epoxy number (LEP) [7], hydroxyl number (LOH) [8], IR spectra and changes of molecular weights of the samples.

Changes of the iodine, epoxy and hydroxyl numbers are presented in table 1 and 2.

Table 1. Properties of: rapeseed oil 1, epoxidized oil (REPOX 1) and polyol (RDEG 1).

Sample	LI [g I_2/100 g]	LEP [mol/100g]	LOH [mg KOH/g]
Rapeseed oil 1	99	-	-
REPOX 1	48,9	0,198	53
RDEG 1	48,8	0	196

Table 2. Properties of: rapeseed oil 2, epoxidized oil (REPOX 2) and polyol (RDEG 2).

Sample	LI [g I_2/100 g]	LEP [mol/100g]	LOH [mg KOH/g]
Rapeseed oil 2	80,3	-	-
REPOX 2	65,4	0,123	28
RDEG 2	65,1	0	114

Fourier-transform infrared (FT-IR) spectroscopy was used to follow the chemical structure of the substances. The analysis of spectra (Fig. 3,4) indicated an increase of the absorbance of the peaks at 3464 cm^{-1} and 3473 cm^{-1} suggesting appearance of broad absorption bands assigned to the vibrations of OH groups.

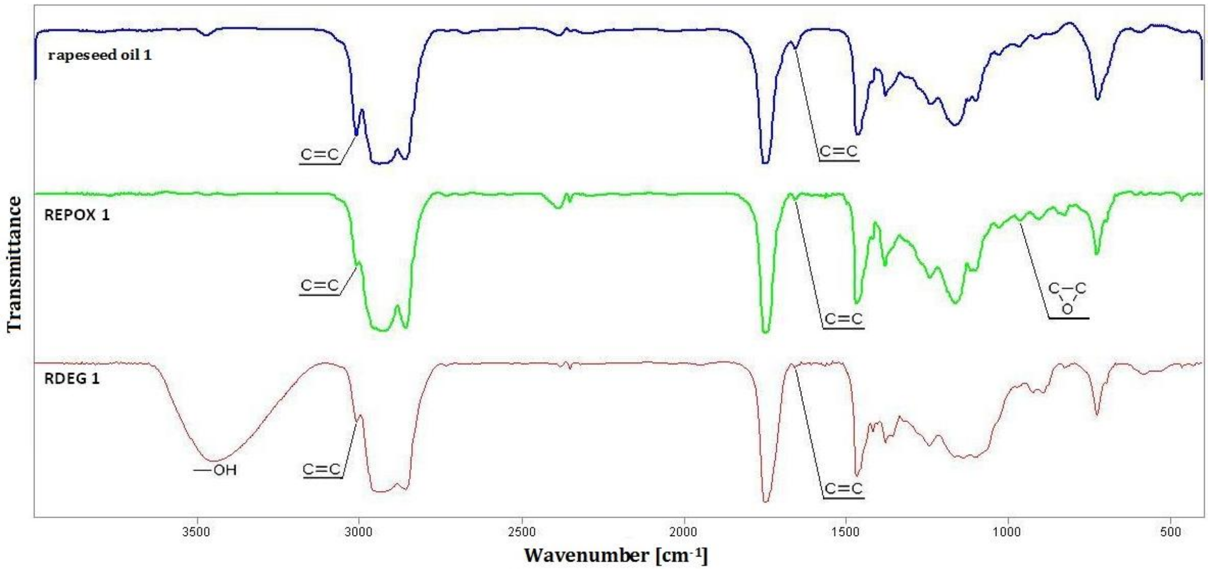

Fig. 3. The FT-IR spectra of: rapeseed oil 1, epoxidized oil (REPOX 1) and polyol (RDEG 1).

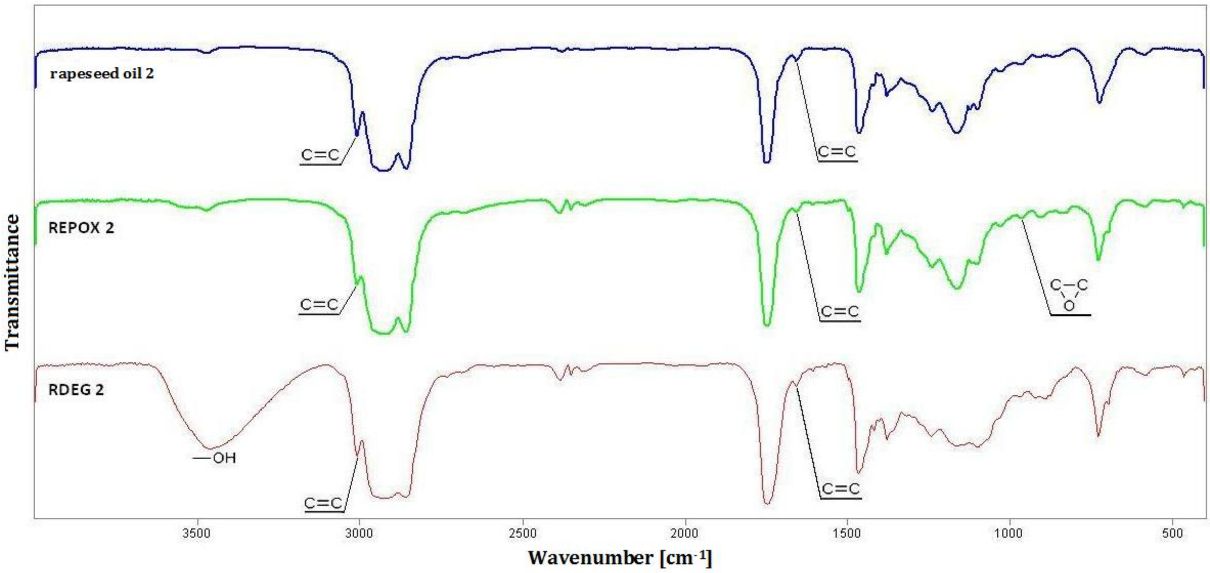

Fig. 4. The FT-IR spectra of: rapeseed oil 2, epoxidized oil (REPOX 2) and polyol (RDEG 2).

The molecular weights of samples used in this study were measured by gel permeation chromatography (GPC) at room temperature. GPC chromatograms are displayed in Figure 5 and 6.

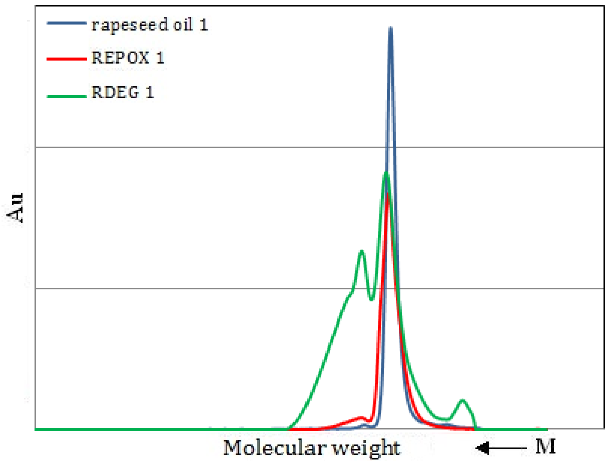

Fig. 5. Distribution of molecular weights of: rapeseed oil 1, epoxidized oil (REPOX 1) and polyol (RDEG 1).

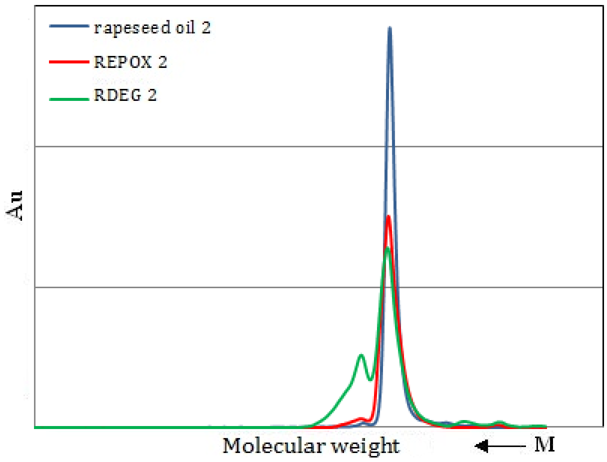

Fig. 6. Distribution of molecular weights of: rapeseed oil 2, epoxidized oil (REPOX 2) and polyol (RDEG 2).

The calculated M_n of RDEG 1 is 1488 g/mol, polydispersity index (PDI) = 1,99 and f_n = 5,2. Respectively M_n of RDEG 2 is 1235 g/mol, polydispersity index (PDI) = 1,49 and f_n = 2,5.

On the basis of obtained results it was found that there were second broad peaks in GPC traces of polyols. It was probably due to both variations in fatty acid substituents and oligomerizations of fractions of RDEG 1 and RDEG 2 during modifications.

Conclusions

Biopolyols represent a significant investment opportunity. It is important to replace petro-polyols with more environmentalfriendly analogs based on vegetable oils, such as rapeseed oil which is low cost and readily available renewable feedstock.

Experimental part

Rapeseed oil, manufactured by Zakłady Tłuszczowe "Kruszwica" S.A., Kruszwica, was used in the studies. The following raw materials were used in the syntheses: glacial acetic acid (99,5 wt%, POCh Gliwice), toluene (99,5 wt%, POCh Gliwice), hydrogen peroxide (30 wt% aqueous solution, POCh Gliwice), sulfuric acid (95 wt%, POCh Gliwice), and diethylene glycol (POCh Gliwice).

Epoxidation of the rapeseed oil was carried out with the use of peracetic acid obtained in situ as a result of the reaction of hydrogen peroxide and glacial acetic acid in acidic environment. The resulting mixture was neutralized with water. The remains of toluene and water were distilled under vacuum.

The epoxidized rapeseed oil was converted into the polyol using diethylene glycol in the presence of sulfuric acid under microwave irradiation.

The course of epoxidation and oxirane ring-opening process was represented by changes in the iodine, epoxy and hydroxyl numbers. Samples were also characterized by Fourier transform infrared (FTIR) spectroscopy and gel permeation chromatography (GPC).

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