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The influence of rapeseed oil-based polyols on the foaming process of rigid polyurethane foams

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ABSTRACT

The foaming process of water-blown rigid polyurethane foams with different contents of a rapeseed oil-based polyol was analyzed. The present work reports for an analysis of the foaming process using foam qualification system FOAMAT—which allows recording characteristic parameters such as the dielectric polarization, rise height of a sample, pressure, temperature during a foaming process. A replacement of a petrochemical polyol by a rapeseed oil-based polyol (ROP) affects the foaming process of rigid polyurethane foams by reducing the reactivity of the system. Increasing the content of ROP resulted in a smaller decrease in the dielectric polarization which reflects slower gelling and foaming reactions.

1. Introduction

The deepening global warming and fluctuating prices of fossil fuels result in a greater interest of the polyurethane (PUR) industry in the application of polyols made from renewable raw materials. Most commercial polyols are derived from petrochemical resources which are diminishing and their price is not stable. The competitive cost, worldwide availability and structure of natural oils make them attractive raw materials in the polymer industry (Tu et al., 2007).

PUR are formed in a reaction of alcohol with two or more reactive hydroxyl groups and isocyanates that have more than one reactive isocyanate group (Tu et al., 2007). Rigid PUR foams have been widely utilized in the appliance and construction industry due to they have an excellent and unique combination of heat insulation and mechanical properties. Besides, such foams can be obtained in a wide range of apparent densities (30–200 kg/m^3) (Choe et al., 2004).

The expansion process is the most important step in the synthesis of rigid PUR foams. The method of foaming has an influence on the cellular structure of foam materials. The cellular structure has a decisive influence on the thermal insulation and mechanical properties of PUR foams. The conditions of the foaming process, a properly selected catalyst system and the reactivity of components used in the preparation of PUR materials also have a very significant impact on the foam cell structure and physical-mechanical properties. Choe et al. (2004) examined the effect of gelling and foaming catalysts as well as the chemical and physical foaming agents on the foaming reaction rate that may have an influence on the physical-mechanical properties of final foam materials. Increasing the amount of the foaming catalyst reduced the start time, and had also an influence on the gelling reactions. Increasing the amount of the gelling catalyst resulted in a decrease of the average cell size from 307 to 132 μm. The analysis of the structure showed that the rate of gas bubbles formation increased with an increasing amount of the catalyst as well as that the type of the investigated catalyst was not significant.

Another important factor of the PUR expansion process that affects the cellular structure of foams are blowing agents. Choe et al. (2004) conducted a study which showed that with the same amounts of the foaming and gelling catalysts, and higher content of water as a blowing agent, the gelling and tack free times were shorter. An increase in the reaction temperature is due to an exothermic reaction of isocyanate groups with polyols as well as with water. Park et al. (2013) observed that the rigid PUR foams obtained using cyclopentane as a physical blowing agent had smaller cells than in the case of foams blown by carbon dioxide generated in the reaction of water and isocyanate.

Bio-polyols can replace petrochemical polyols in the synthesis of rigid PUR foams (Tu et al., 2008). In recent years, researches have focused on using natural oil-based polyols for a preparation of PUR materials (Palanisamy et al., 2011; Stirna et al., 2008; Bandyopadhyay-Ghosh et al., 2010; Silva et al., 2013). Vegetable oils are triglyceride molecules which are fatty acid triesters of glycerol. Generally, natural oils are relatively non reactive and must

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be transformed into compounds containing at least two hydroxyl groups capable of reacting with diisocyanate (Rojek and Prociak, 2012). The epoxidation of the rapeseed oil followed by oxirane ring-opening is a widespread method of natural oils functionalization. Depending on the type of agents used to open oxirane rings, polyols are characterized by primary or secondary hydroxyl groups or both simultaneously. The position and number of OH-groups can affect reactivity of such bio-polyols.

Campanella et al. (2009) obtained flexible PUR foams from three types of soybean oil-based polyols with different positions of OH-groups and functionalities. The soybean oil-based polyol containing primary hydroxyl groups was the most reactive and the foams with this polyol had smaller and most uniform cells. Fan et al. (2013) analyzed the influence of soy-polyols with high viscosity on the properties of rigid PUR foams. They found that the maximal foaming temperature of the foams slightly decreased with an increasing soy-polyol content. Secondary OH-groups and a lower hydroxyl number in the soy-polyol resulted in its lower reactivity as well as a smaller exothermic effect when they reacted with an isocyanate comparing to the petrochemical polyol which contained primary OH-groups and a higher hydroxyl number.

The replacement of a petrochemical polyol by a bio-polyol requires the use of a suitable catalyst system during the synthesis of PUR foams. Therefore, the impact of new components of plant origin must be carefully analyzed. The foaming process of PUR can be investigated using foam qualification system FOAMAT. In this paper, a detailed analysis of the synthesis of rigid PUR foams using a rapeseed oil-based polyol has been carried out.

2. Experimental

2.1. Materials

The petrochemical polyol Rokopol RF-551 (ROK) was supplied by PCC Rokita SA. The rapeseed oil-based polyol (ROP) was prepared in the Department of Chemistry and Technology of Polymers in Cracow University of Technology. The characteristics of polyols are shown in the part “Results and discussion”. The polymeric methylene diphenyldiisocyanate (PMDI) containing 31.5 wt.% of free isocyanate groups was supplied by Minova Ekochem S.A. Amine containing catalyst (Polycat 5) produced by Air Products and Chemicals and potassium acetate produced by Performance Chemicals were used as catalysts. A silicone surfactant with the trade name Niax Silicone L-6915 produced by Momentive Performance Materials Inc. was used as a stabilizer of the foam structure. Carbon dioxide generated in a reaction of water with isocyanate groups act in foaming reaction as a chemical blowing agent.

2.2. The characterization of bio-polyol

Hydroxyl value and content of water of rapeseed oil-based polyol obtained were determined according to following standards PN-93/C-89052/03 and PN-81/C-04959, respectively. Fourier transform infrared spectroscopy measurements were performed on a Perkin Elmer spectrometer equipped with ZnSe crystal attenuated total reflectance unit. Spectra were recorded with a resolution of 4 cm^{-1} from 4000 to 400 cm^{-1} with an average of 32 scans.

GPC measurements were performed using a Knauer chromatograph equipped with the Plgel MIXED-E column for the analysis of oligomers and refractometric detector. The calibration was performed using polystyrene standards. Tetrahydrofuran was used as an eluent at 0.8 mL/min flow rate. Number-average functionalities of polyols were calculated basing on hydroxyl values and experimentally determined number-average molecular weight.

Table 1
The chemical compositions of polyurethane systems.

Raw materials	Rok-100	Rok-70	Rok-50	Rok-30
ROK	100	70	50	30
ROP	–	30	50	70
H_2O	4.10	4.02	3.96	3.90
$\sum H_2O$	4.10	4.10	4.10	4.10
Polycat 5	0.90	0.90	0.90	0.90
L6915	1.50	1.50	1.50	1.50
PMDI	195	177	165	153

$$f_n = \frac{M_n \times OH_{val}}{56110}$$

where f_n—number-average functionality, M_n—number-average molecular weight and OH_{val}—hydroxyl value of polyol

2.3. Preparation of samples

Rigid PUR foams with different contents of ROP were prepared using a one step method. The polyurethane foams based on only rapeseed oil-based polyol were not dimensional stable. The polyol, amine catalyst, surfactant and water were mechanically stirred for 15 s to ensure their complete homogenization. After that the PMDI was added to the polyol premix to obtain the ratio NCO/OH = 1.1:1.0 (the contributions of the polyols and water were considered in the OH calculation). Next, such system was mechanically mixed for 7 s and poured into a tube with a diameter of 10 cm. The formulations and marking PUR system are presented in Table 1.

2.4. The characterization of foaming process

The foaming process was analyzed using the foam qualification system FOAMAT (Fig. 1), which allows determining characteristic parameters, such as the foam rise height, reaction mixture temperature, pressure, dielectric polarization and mass loss during foaming. Additional information such as viscosity, gelling and curing times can also be determined. The rise profile was measured with an ultrasonic sensor. The temperature was measured with a use of thin thermocouples. The rise pressure was measured using a Foam Pressure Measurement device (FPM). Dielectric polarization measured using a Curing Monitor Device (CMD) which gives an insight into the electrochemical processes occurring during a

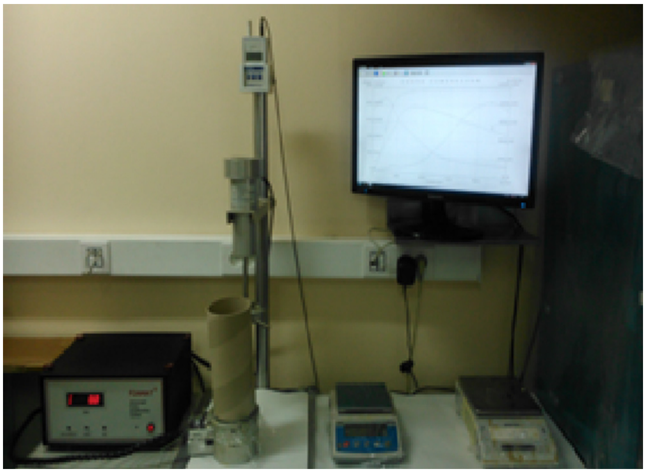

Fig. 1. Foam qualification system FOAMAT.