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Preparation and characterisation of rigid polyurethane foams using a rapeseed oil-based polyol

Milena Zieleniewska[a,*], Michał K. Leszczyński[b], Maria Kurańska[c], Aleksander Prociak[c], Leonard Szczepkowski[d], Małgorzata Krzyżowska[e], Joanna Ryszkowska[a]

[a] Warsaw University of Technology, Faculty of Materials Science and Engineering, Wołoska 141, 02-507 Warsaw, Poland
[b] Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
[c] Cracow University of Technology, Faculty of Chemical Engineering and Technology, Warszawska 24, 31-155 Cracow, Poland
[d] FAMPUR Adam Przekurat Company, Gersona 40, 85-305 Bydgoszcz, Poland
[e] Military Institute of Hygiene and Epidemiology, Kozielska 4, 01-163 Warsaw, Poland

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ABSTRACT

Rigid polyurethane foams (RPUF) were fabricated using rapeseed oil-based polyol and polyols of petrochemical origin, which were tested using differing weight ratios. The aim of this study was the determination of the influence of the plant-based polyol content on the properties of obtained RPUF leading to the selection of the optimal product for the application as a pumice for the cosmetics industry. The synthesis of the polyurethane foams was conducted using a single-step procedure. The chemical structure and degree of phase separation of obtained materials were characterised by the infrared absorption spectroscopy. The thermogravimetric analysis was employed in order to determine the thermal degradation of analysed products. The temperatures of phase-transitions and accompanying heat effects were analysed using differential scanning calorimetry. Powder X-ray diffraction techniques were used in order to verify the presence of crystalline domains in obtained materials while the porous structure of RPUF was examined using scanning electron microscopy. Additionally, the dimensional stability, apparent density, water absorption, friability, compressive strength and aging effects were determined for synthesised materials. The biological properties of the obtained RPUF were examined using the toxicity test employing human monocyte cell line. As a result, the RPUF synthesised using 50% of plant-based polyol was selected as the optimal product for the cosmetics industry due to the regular porous structure, good mechanical and biological properties, high dimensional stability, high resistance to aging and low water absorption.

1. Introduction

The rigid polyurethane foams (RPUF) have been attracting an increasing attention over the recent years mainly due to the exceptional thermal insulating properties, high resistance to weather conditions, good mechanical properties and low apparent density (Tan et al., 2011). According, to the statistical data published in 2013 the total value of global polyurethane foams market amounts to 401 billion dollars and is estimated to grow to 619 billion dollars in 2018 (Rohan, 2013). Polyurethane foams are commonly used in a variety of industries e.g. construction, automotive, furniture and cosmetics industry (Beltrán and Boyacá, 2011; Nikje et al., 2015). RPUF are usually employed as lightweight construction and insulation materials in order to manufacture a great variety of products including the cores of floor-ceiling constructions, parts of door and window frames as well as the refrigeration equipment (Prociak et al.,2014).

The RPUF available on the current market are usually made from petroleum-based polyether or polyester polyol and polyisocyanate, in presence of a blowing agent, surfactants and catalysts (Cinelli et al., 2013). One of the problems related to the production of polyurethane foams is their dependence on petroleum-derived products (Prociak et al., 2014), as the petrochemical resources utilised worldwide in a large-scale production of the chemical and building industry are gradually being depleted (Fridrihsone et al., 2013; Dworakowska et al., 2014). In this regard, the tendency to substitute the petroleum-based polyols with polyols obtained from renewable sources is supported by both economical and ecological reasons (Alam et al., 2014; Ribeiro da Silva et al., 2013). Vegetable oils are non-toxic, non-volatile, non-depletable, domestically abundant, and biodegradable resource (Alam et al., 2014). Additionally,

* Corresponding author.
E-mail address: milenazieleniewska@wp.pl (M. Zieleniewska).

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their availability as well as the low production and derivatisation cost make the vegetable oils one of the most important renewable resources for use in industry as a promising competition for petrochemical polyols (Miao et al., 2014; Pietrzak et al., 2014).

Vegetable oils are composed of triglycerides of long-chain fatty acids. The most common chain lengths of in fatty acids in these oils are 18–20 carbon atoms, which can be saturated or unsaturated with the double bonds located at the 9th, 12th and 15th carbons (Zhang et al., 2014). Since 1960, the highly unsaturated vegetable oils are being investigated in order to transform the double bonds into hydroxyl groups by chemical reactions (Kairyte and Vejelis, 2015; Zieleniewska et al., 2014). Epoxidation and ring opening reaction with haloacids or alcohols or hydration and ozonolysis are some of the most frequently used methods for functionalisation of unsaturated vegetable oils (Petrovic et al., 2005; Yeganeh and Hojati-Talemi, 2007). The most common vegetable oils used for the production of polyols, depending on the geographical location, include: in Europe – rapeseed and sunflower oils, in Asia – palm and coconut oils, in America – soybean oil (Petrović, 2008; Prociak, 2007; Yeganeh and Mehdizadeh, 2004). The amount of publications concerning synthesis of polyurethanes by utilization of plant-based polyols is consistently growing. Triwulandari et al. (2011) presents effect of NCO/OH ratio and mould system on mechanical and physical properties of the RPUF based on palm oil. It was found out that NCO/OH ratio and the mold type had a significant effect on the properties of the obtained RPUF. In another example polyurethane foams were prepared using modified castor-oil-based polyols. The authors have shown that castor-oil-based polyols could be used as a raw material for preparing polyurethane foams after alcoholysis and condensation (Zhang et al., 2014). The palm kernel oil-based polyol was also successfully utilised as the renewable raw material for synthesis of RPUF with good mechanical and thermal insulation properties (Septevani et al., 2015).

In Poland, the most common raw material for production of polyols is the rapeseed oil, which is a triglyceride of higher unsaturated fatty acids containing 61% of oleates, 21% of linoleates, 10% of linolenates and 8% of higher saturated fatty acid carboxylates (Lappi and Alén, 2011; Piszczyk, 2011). The rapeseed oil derivatives are also used as reagents in the production of polyamides, polyesters and polyurethanes (Ronda et al., 2013; Wei et al., 2012).

The RPUF are gradually, replacing the natural pumices in the cosmetics industry mainly due to the possible control over the mechanical and physical properties as well as the availability of the RPUF in a great variety of shapes and colours. Moreover, the RPUF pumices are non-toxic, which allows for the application in contact with the skin tissue. The increasing expectations towards the cosmetic products are forcing the manufacturers towards the constant technological modernisations and frequent introduction of new products to the market. However, the limited number of publications concerning application properties and synthesis of the cosmetic pumices produced using renewable substrates results in the low commercial availability of the natural polyol-based products. Therefore, the current modifications of the commercial products are mainly limited to the design changes resulting in a variety of shapes and colours of the products and the packaging. In this regard the introduction of the new ecological products manufactured using renewable substrates would be a significant improvement of in the merchandise competitiveness for many cosmetic companies.

This study was designed towards the development of new RPUF using the rapeseed oil-based polyol and the petrochemical polyols, which were tested using differing weight ratios. The aim of the study was the determination of the influence of the rapeseed oil-based polyol content on the properties of obtained RPUF as well as the evaluation of the obtained products with respect to industrial applicability. The selection of the optimal product was based on the optimisation of the renewable substrate content and the application properties in order to develop an environmentally-friendly material with the most valuable characteristics. The desired properties were estimated based on the investigation of the commercially available cosmetic pumices as well as the general requirements of the cosmetics industry, which was assumed as the potential application of the developed products.

2. Materials and methods

2.1. Materials

Rapeseed polyol (RP) having a hydroxyl value 282 mg KOH/g, acid value 3.4 mg KOH/g, iodine value 25.7 g J_2/100 g, number average molar mass of 1027 g/mol and water content of 0.32 wt% was produced using rapeseed oil as substrate at the Cracow University of Technology.

Polyoxyalkylene triol based on glycerine with the trade name Rokopol G500 (PP) having a hydroxyl value 300 mg KOH/g, number average molar mass of 560 g/mol and a water content of 0.10 wt% was supplied by PCC Rokita, Poland.

Aromatic polyester with the trade name Polios 420 PTA (PP) having a hydroxyl value 420 mg KOH/g, number average molar mass of 330 g/mol and a water content of 0.10 wt% was supplied by Purinova, Poland.

JEFFCAT® DPA and JEFFCAT® ZF-10 produced by Huntsman Corporation were used as catalysts.

A silicone surfactant with the trade name TEGOSTAB® B4900 produced by Evonik Industries, Germany was used as a stabilizer of composite structure.

Carbon dioxide generated during the foam growth process in the reaction of water with isocyanate groups was used as a blowing agent.

Mixture of methylene diphenyl diisocyanate (MDI) isomers and oligomeric MDI with the trade name Ongronat® TR 4040 containing 32.6 wt% of free isocyanate groups was supplied by BorsodChem company.

2.1.1. Synthesis of the rapeseed polyol

Rapeseed oil, manufactured by Kruszwica S.A. (Poland) was used as received. Glacial acetic acid, hydrogen peroxide as 30 wt% aqueous solution (H_2O_2), sulfuric acid (95 wt%), and diethylene glycol (DEG) were purchased from Avantor Performance Materials Poland S.A. (Poland).

Rapeseed polyol was synthesised by a two-step method: epoxidation of the double bonds of rapeseed oil and reaction of opening the oxirane rings by using diethylene glycol. The corresponding reaction schemes were presented in Fig. 1.

The epoxidation of rapeseed oil was performed using peracetic acid generated in situ as a result of the reaction of H_2O_2 and glacial acetic acid at 60 °C in the presence of concentrated sulfuric acid as a catalyst. The resulting mixture was washed with water and the separated organic phase was dried under vacuum. Epoxidized oils were converted into the polyols using diethylene glycol. The amount of DEG was used stoichiometrically to the epoxide groups and the reaction was carried out at 105 °C. Obtained rapeseed oil-based polyol was characterised by determination of the hydroxyl and acid values, water content as well as the average molar mass. Gel permeation chromatography (GPC) measurements were performed using the 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 at room temperature. The chromatogram of the resulting vegetable polyol was presented in Fig. 2.