Industrial Crops and Products xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Innovative porous polyurethane-polyisocyanurate foams based on rapeseed oil and modified with expandable graphite

Maria Kurańska[a,*], Aleksander Prociak[a], Ugis Cabulis[b], Mikelis Kirpluks[b], Joanna Ryszkowska[c], Monika Auguścik[c]

[a] Cracow University of Technology, Department of Chemistry and Technology of Polymers, Warszawska 24, 31-155 Cracow, Poland
[b] Latvian State Institute of Wood Chemistry, Dzerbenes 27, LV-1006 Riga, Latvia
[c] Warsaw University of Technology, Faculty of Materials Science and Engineering, Wołoska 141, 02-507 Warsaw,, Poland

ARTICLE INFO

Article history:
Received 15 June 2016
Received in revised form
29 September 2016
Accepted 22 October 2016
Available online xxx

Keywords:
Bio-foams
Cellular structure
Mechanical properties
Porosity
Bio-polyols

ABSTRACT

Rigid polyurethane-polyisocyanurate (PUR-PIR) foams were synthesized with the use of bio-polyols based on rapeseed oil. The bio-polyols were synthesized using two distinct methods oil epoxidation followed by oxirane ring opening (ROPep) and oil transesterification with triethanolamine (ROPtr). In this study, the PUR-PIR systems based on bio-polyols ROPep and ROPtr with the isocyanate indices 150 and 250 were modified with expandable graphite (3, 6 and 9 wt.%). The effects of expandable graphite on the foaming process, cellular structure and selected properties of the foams such as the apparent density, compressive strength as well as water absorbance and brittleness were described. The modification of the PUR-PIR system with EG slowed down the reaction of the polymer matrix formation. The PUR-PIR system modified with EG had a lower maximum temperature and exhibited a slower decrease of the dielectric polarization during the foaming process. The apparent density of the PUR-PIR foams with EG was higher than in the case of the unmodified foams. EG did not have any significant effect on the thermal conductivity of the materials obtained. A tendency to get a smaller average cross-sectional area of cells in the foams modified with EG was observed.

1. Introduction

Polyurethanes (PUR) are versatile polymers with a broad range of applications. Foams are among the most important commercial PUR products and can be classified as rigid, semi-rigid and flexible (Zia et al., 2007). Applications of porous PUR materials are highly dependent on their cellular structure. Rigid PUR foams, due to their excellent properties, such as a closed-cell structure, low thermal conductivity and low moisture permeability, find various applications as heat insulating materials in construction, pre-insulated pipelines and refrigeration industry (Zhang et al., 2014; Pillai et al., 2016a,b,c).

Heat insulating properties of PUR foams are mainly dependent on their cellular structure and the type of blowing agents used in the system. Currently, there is a need to search for new blowing agents to replace HFCs (hydrofluorocarbons), which have a high greenhouse warming potential (GWP) (Prociak et al., 2014). Many researchers develop PUR systems with environmentally friendly blowing agents, such as cyclopentane and carbon dioxide, generated in the reaction of water with isocyanates. The influence of the use of such blowing agents on selected properties of cellular materials has been studied (Han et al., 2009). Seo et al. (2003) investigated the effect of the water content on the selected properties of rigid PUR foams. They found that water importantly affects the apparent density, mechanical properties and morphology of the foams. Jung et al. (2001) found that the average cell size of rigid PUR foams blown with distilled water increased from 150 to 290 μm with an increasing water content. The apparent density of those PUR foams decreased from 175.7 to 28.2 kg/m^3 with the content of water increasing from 0.5 to 3 php. In the formulations of PUR foams, other components such as surfactants, catalysts and nucleating agents could also have a significant effect on the cell size of the foams. In the case of PUR foams, smaller cell sizes result in lower thermal conductivity (Mondal and Khakhar, 2004). However, the thermal conductivity increases with an increasing apparent density of PUR foams (Thirumal et al., 2008a,b).

One of the two main components for the preparation of rigid PUR foams are polyols. Alternative sources to produce a new class of polyols from a renewable raw material are natural fats and oils (Kurańska et al., 2013; Jia et al., 2015 and Pillai et al., 2016a,b,c).

* Corresponding author.
E-mail address: mkuranska@chemia.pk.edu.pl (M. Kurańska).

http://dx.doi.org/10.1016/j.indcrop.2016.10.039
0926-6690/

Vegetable oils have to be functionalized and this can be done through double bond reactions, such as epoxidation followed by opening oxirane rings, hydroformylation, metathesis, or through ester bond reactions (transesterification, transamidization) (Stirna et al., 2013; Mosiewicki and Aranguren, 2013 and Pillai et al., 2016a,b,c).

Despite good heat insulating properties, rigid PUR foams are intrinsically highly flammable and have a high potential for fire growth due to their low heat capacity, and a large internal surface area. In the past decades, intumescent flame retardants have attracted a lot of attention due to their low toxicity, low amount of smoke, halogen-free nature and high efficiency. An incorporation of intumescent flame retardants into foams by simple mechanical mixing is the most popular approach to improve the flame retardancy of rigid PUR foams (Gao et al., 2013). One of them is expandable graphite (EG) which exposed to heat expands and generates a voluminous insulating layer thus providing a fire barrier to the polymeric matrix (Walid et al., 2010 and Kirpluks et al., 2014).

The influence of expandable graphite on thermal properties and flammability of PUR-PIR foams based on two types of rapeseed polyol was presented in our previous research work (Kurańska et al., 2016). Excellent results associated with a decrease of flammability motivated further research concerning physical and mechanical properties of bio-based PUR-PIR foams modified with EG.

An introduction of EG into the matrix affects the PUR cellular structure as well as the mechanical properties of foams. Bian et al. found that a modification of PUR foams with EG led to an increase of the cell sizes (Bian et al., 2007). A similar effect was observed by Modesti et al. They also found that an addition of graphite affects the deterioration of the mechanical properties as well as an increase in the thermal conductivity coefficient of modified foams (Modesti et al., 2002).

In this paper, an impact of expanded graphite on the cellular structure and physical-mechanical properties of rigid PUR-PIR foams based on two different bio-polyols has been studied. Distilled water was used as a chemical blowing agent that generates carbon dioxide having a very low value of GWP.

2. Experimental part

2.1. Materials

In this work the following raw materials were used: Lupranol 3422 (polyether polyol based on sorbitol) having a hydroxyl number ca. 490 mg KOH/g and a water content of 0.10 wt.%, supplied by BASF; polymeric methylene diphenyldiisocyanate (PMDI) containing 31 wt.% of isocyanate groups, supplied by Minova Ecochem SA, Poland; Polycat 5 (amine catalyst) produced by Air Products and Chemicals and potassium acetate produced by Performance Chemicals; silicone surfactant with the trade name Niax Silicone L-6915 produced by Momentive Performance Materials Inc. as a stabilizer of the composite structure; carbon dioxide generated in the reaction of water with isocyanate groups as a chemical blowing agent.

Moreover, two different rapeseed oil-based polyols were prepared: the first one (ROPep with the hydroxyl number 256 mg KOH/g and a water content of 0.47 wt.%) in the Department of Chemistry and Technology of Polymers of Cracow University of Technology and the second one (ROPtr with the hydroxyl number 365 mg KOH/g and a water of content 0.07 wt.%) in the Latvian State Institute of Wood Chemistry. The viscosities of obtained bio-polyol ROPep and ROPtr were 2260 and 190 mPas, respectively. The bio-polyols were synthesized using two methods: epoxidation with opening oxirane rings (ROPep) (Pat Pol 205405, 2009 and Pat Pol 206376, 2010) and transesterification with triethanolamine (ROPtr) (Kirpluks et al., 2013). Expandable graphite with the trade name EG096 was supplied by Sinograf. The average size and expansion of the expandable graphite were 0.2–0.6 mm and 200–300 ml/g, respectively.

2.2. Foam preparation

The rigid PUR-PIR foams were prepared using two-component (A and B) systems. Firstly, the bio-polyol (70 wt. parts) was mixed with the petrochemical polyol (30 wt. parts), catalysts (2.5 and 3.5 for the foams with bio-polyol ROPep with the isocyanate index 150 and 250, respectively; 2 and 3 php for the foams with bio-polyol ROPtr with the isocyanate index 150 and 250, respectively) water (3.2–6 php) and surfactant (1.5 php) (component A). PMDI was added as component B to component A and these reaction mixtures were stirred vigorously for 7 s with an overhead stirrer. Then, the prepared mixtures were dropped into an open mould where they expanded freely in the vertical direction. The influence of both rapeseed polyols, various contents of EG (3, 6 and 9 wt%.) and different isocyanate indices (150 and 250) on the foaming process, as well as the cell structure and selected properties of the foams obtained was investigated. Information about the type of a bio-polyol (ROPep or ROPtr), value of isocyanate index (150 or 250) and content of expandable graphite (3, 6 or 9) was included in the symbol of a given sample.

2.3. Testing methods

The foaming process of various PUR-PIR systems was analyzed using a FOAMAT® Format-Messtechnik device. The morphology of cells was analyzed using an optical and a scanning electron microscope (Hitachi S-4700). The samples were sputter coated with graphite before testing to avoid charging. The PUR foam samples were cut into slices using a microtome in two cross-sections, parallel and perpendicular to the foam rise direction. Three photos (using optical microscopy) of each foam's cross-section were taken in order to estimate the cell parameters (the average cell cross-section area and anisotropy index of cells) on the basis of more than one hundred cells. The foam morphology in each photo was analyzed using the same procedure in the Aphelion software. The anisotropy index expresses the circularity of the cells. It was calculated as the ratio of the parameters measured: height and width of the rectangular in which a cell is inscribed.

Cell structures of selected foams were also analyzed using computer microtomography, the study was performed using a CT scanner Xradia 410CT. Cubic samples having dimensions of $1 \times 1 \times 1$ cm were tested. For the analysis, a beam with acceleration voltage of 40 kV and power of 7W was used. The exposure time for the samples was 9 s, and ca. 1200 images were made to the 180° rotation. The filters with the signature #LE1 (for samples ROPep/150, ROPep/150/3 and ROPep/150/9) and #LE2 (for samples ROPtr/150, ROPtr/150/9) were used. For the reconstruction of the images obtained the X-Radia reconstructor software was used. The images obtained in the reconstruction were processed by the CTvol software. The porosity and pore sizes were identified using the binarization threshold, closing of grain boundaries and possibility of removing defects.

The following properties of all the foams were measured in accordance with the ISO Standard tests: ISO 845 apparent density (kg/m^3); ISO 844 compressive strength 10% (MPa), ISO 4590 closed cells content (%). The mechanical properties of the foams were estimated in two directions, parallel and perpendicular to the foam

Please cite this article in press as: Kurańska, M., et al., Innovative porous polyurethane-polyisocyanurate foams based on rapeseed oil and modified with expandable graphite. Ind. Crops Prod. (2016), http://dx.doi.org/10.1016/j.indcrop.2016.10.039