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Research Paper

Structural, thermal and physico-mechanical properties of polyurethane/brewers' spent grain composite foams modified with ground tire rubber

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ABSTRACT

In this work, brewers' spent grain (BSG) and ground tire rubber (GTR) waste fillers were applied as low-cost reinforcement phase in rigid polyurethane foam (PUR). PUR/BSG/GTR composites were prepared by a single step method, using polyglycerol as partial substitute of commercially available petrochemical polyols. Foaming parameters, chemical structure, dynamic mechanical properties, thermal stability, physico-mechanical properties and morphology of obtained composites were evaluated as function of BSG/GTR ratio (in range: 20/0; 15/5; 10/10; 5/15; 0/20 parts by weight – pbw). Modification of PUR/BSG composite foams with GTR accelerated foaming reactions, which resulted in decrease of rise time and tack free time. Higher content of GTR in PUR/BSG/GTR composites significantly enhanced their physico-mechanical properties and thermal stability. Compressive strength of PUR modified with BSG/GTR in ratio 5/15 pbw was more than 50% higher than for PUR/BSG composite foam without GTR, which correspond to 37% increase of density. Additionally, it was observed that temperatures corresponded to a 2% and 5% weight loss were for 9 °C and 24 °C higher for composite with BSG/GTR hybrid filler than for pure polyurethane matrix. Presented results indicate better compatibility between polyurethane matrix and GTR than with BSG, confirmed also by ATR-FTIR, DMA, swelling behavior and SEM analysis. Conducted investigations showed that performance properties of polyurethane/brewers' spent grain composite foams could be successfully tailored using GTR, which consequently extend their potential industrial applications.

1. Introduction

Rigid polyurethane foams (PUR) and their composites possess a wide range of performance properties such as low apparent density, good mechanical properties, low thermal conductivity and excellent damping abilities. This results in their frequent applications in various branches of industry, such as automotive and furniture industry or in production of thermal insulation materials (Cornille et al., 2015; Xie et al., 2017; Yang et al., 2015). Growing interest in polyurethane foams is related to their relatively simple processing and a wide spectrum of properties, which can be easily tailored by changing the chemical structure of polyurethane or application of specific modifying additives. Therefore, the investigations of structure-property relationships in various polyurethane foams are nowadays very popular among various research groups (Estravís et al., 2016; Rastin et al., 2016; Zou et al., 2015).

On the other hand, law regulations, limited petroleum resources and higher ecological awareness of the society enforced the industry and academic research groups to search and develop of environmentally friendly polyurethane technologies based on a low-cost and pro-ecological components, mainly renewable raw materials (Bryśkiewicz et al., 2016; Hejna et al., 2017; Tavares et al., 2016), recycled materials (Kopczyńska and Datta, 2016; Zieleniewska et al., 2016Kopczyńska and Datta, 2016; Zieleniewska et al., 2016) or their combinations (Beneš et al., 2012; Carriço et al., 2016).

It seems that the application of used tires as a source of secondary

Abbreviations: ATR-FTIR, attenuated total reflectance mode Fourier transform infrared spectroscopy; BSG, brewers' spent grain; DSC, differential scanning calorimetry; DMA, dynamic mechanical analysis; GTR, ground tire rubber; pbw, parts by weight; PUR, rigid polyurethane foam; SEM, scanning electron microscopy; TGA, thermogravimetric analysis; TGA/DSC-FTIR, simultaneous thermogravimetric/differential scanning calorimetry analyzer coupled with Fourier transform infrared spectroscopy

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raw materials could be a very promising route in this field. At present, the size reduction method in the form of grinding is the most commonly applied technology used in the field of waste tires recycling. Ground tire rubber (GTR), with desired particle shape and size, is prepared during mechanical grinding of the used tires at ambient temperature or cryogenic conditions. Many attempts have been focused on application of GTR as a fillers or modifiers of variable polymers, which were comprehensively described in review papers published by Karger-Kocsis et al. (2013) and Ramarad et al. (2015). Higher content of ground tire rubber in polymer composites usually results in deterioration of mechanical properties, which is due to weak adhesion between the cross-linked rubber and the surface of polymer matrix. It should be mentioned that the low compatibility between polymer matrix and GTR phase has smaller impact on the properties of a polymeric materials with cellular structure, what could be their advantage (Karger-Kocsis, 2013). However, only few recently published research works concerning preparation and characterization of polyurethane foams containing GTR. Tran et al. (2015) performed oxidative cleavage of GTR to obtain telechelic carbonyl oligomers, which were reduced to hydroxyl oligomers. These products were successfully used as new polyols during polyurethane foams preparation. On the other hand, GTR can be used directly in polyurethane foam composites as reinforcement filler. In this case additional chemical reactions between polyurethane component highly reactive isocyanate groups and functional groups on the surface GTR (e.g. hydroxyl, carboxyl, etc.) may occur during their processing. These reactions enhance the interface adhesion between polyurethane and GTR phases, which was confirmed in our previous studies (Piszczyk et al., 2015a,b,c). Furthermore, cross-linked structure of GTR makes this filler perfectly suited for the production of vibration absorbers, dampers, buffers, gaskets or sealing elements based on polyurethane foams (Cachaço et al., 2013; Zhang et al., 2013).

Alternative route to produce environmental-friendly polyurethane composite foams is application of natural fillers/fibers, which has become a matter of growing interest during the last years (Chang et al., 2014; Gu et al., 2013; Kurańska and Prociak, 2012). From economical point of view, the most promising sources of natural fillers/fiber are cellulose rich by-products generated from agriculture industry, such as brewers' spent grain (BSG). This major by-product of brewing industry was recently used as filler in polymer composites (Berthet et al., 2015; Cunha et al., 2015; Hejna et al., 2015).

However, according to our best knowledge, there is no information about the polyurethane/natural fillers (or fibers) composite foams modified with GTR.

In this work we aimed to examine the impact of brewers' spent grain/ground tire rubber (BSG/GTR) hybrid filler ratio on chemical structure (FTIR), thermal properties (TGA/DSC-FTIR), dynamic mechanical properties (DMA), physico-mechanical properties (compression strength, apparent density), swelling behavior (swelling degree, sol fraction), and morphology (SEM) of rigid polyurethane foam composites.

2. Experimental

2.1. Materials

Rigid polyurethane foams (PUR) were prepared from commercially available polyols from PCC Rokita company, Rokopol G441 (trifunctional polyether based on glycerol) and Rokopol RF55 (high functional polyether based on sorbitol). Additionally, to limit petroleum based polyols in composites, crude glycerol bio-based polyol prepared according to patent application (Haponiuk et al., 2015) was used. The physico-chemical properties of the aforementioned polyols are presented in Table 1.

Isocyanate used in the reaction was polymeric 4,4′-methylene diphenyl diisocyanate (pMDI) characterized by a 31.5% content of NCO groups (Borsodchem). Fyrol® PNX produced by ICL Industrial Products was used as a flame retardant. Two types of tertiary amines (Dabco® 1027 and Dabco® TMR-2) were applied as a catalyst. Both were purchased from Air Products and Chemicals, Inc. Tegostab® B 8465 (Evonik Industries AG) was used as a silicon-based surfactant. The physical blowing agent was liquid hydrofluorocarbon blend Solkane® 365/227 from Solvay. Distilled water was used as a chemical blowing agent.

Table 1
The physico-chemical properties of polyols used in study.

Property	Polyol type		
	Rokopol G441	Rokopol RF55	Biopolyol based on crude glycerol
Density (g/cm^3)	1.07	1.09	1.18
Hydroxyl number (mg KOH/g)	345	495	460
Viscosity at 25 °C (mPa s)	280	9200	1300
Water content (wt.%)	< 0.100	< 0.100	0.207

Two types of waste fillers were used for modification of polyurethane foams: brewers' spent grain (BSG) and ground tire rubber (GTR). BSG was provided by home brewery Dno Bojlera (Poland). It was a by-product from the production of Christmas Ale and its initial composition contained (wt.%): 3.7% Chocolate wheat malt; 3.7% Special B malt; 6.7% Biscuit malt; 6.7% Carawheat malt; 19.4% Pilsner malt; 22.4% Munich malt type II and 37.3% Pale wheat malt. Almost half of malts (47.7 wt.%) were wheat malts, while the rest (52.3 wt.%) were barley malts. Prior to processing, BSG was dried at 80 °C and then mechanically grinded in a co-rotating twin-screw extruder at 120 °C to obtain particles with a narrow size distribution. GTR, fraction to 1.0 mm, was prepared from whole used tires (mix of car and truck tires) grinded at ambient temperature by Grupa Recykl S.A. (Poland).

2.2. Rigid polyurethane foam composites preparation

Rigid polyurethane composites foams were produced on a laboratory scale by a single step method from a two-component (A and B) system with the ratio of NCO/OH groups ratio of 2:1. The component A (polyol mixture) consisting of the proper amounts of Rokopol RF55, Rokopol G441 and biopolyol based on crude glycerol, flame retardant, catalysts, surfactant, foaming agents and pro-ecological fillers (BSG, GTR or their mixture in different ratio) was weighed and placed in a 500 mL polypropylene cup. Next, the polyol mixture was homogenized with a mechanical stirrer at 2000 rpm for 60 s. Such prepared component A was mixed with component B (pMDI) at a predetermined mass ratio and stirred at 2000 rpm for 20 s. The resulting reaction mixture was left in cup for a free rise. Obtained PUF samples were seasoned at room temperature for at least 24 h. Table 2 contains the details of PUR composites formulations. The samples were coded as PUR/BSGX/GTRY, where X means amount of BSG and Y is content of GTR. For example, PUR/BSG15/GTR5 is a sample of PUR with 15 pbw (parts by weight) of BSG and 5 pbw of GTR. It is worth to noticed that application of waste fillers could affect storage stability of PUR systems, which should be evaluated during further studies on this field. The PUR without fillers formed in the same conditions was used as a reference sample.

2.3. Measurements

Elemental analysis (C, H, N, S) of fillers was carried out using a Flash 2000 CHNSO Analyser from Thermo Scientific (USA).

Macro- and microelements content in fillers was determined by wavelength dispersive X-ray fluorescence spectrometry (WD-XRF) using a spectrometer S8 Tiger 1KW from Bruker (USA).

Reaction kinetics of polyurethane composite foams were evaluated