Polymer Testing 59 (2017) 478–486

Contents lists available at ScienceDirect

Polymer Testing

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

Rapeseed oil as main component in synthesis of bio-polyurethane-polyisocyanurate porous materials modified with carbon fibers

Aleksander Prociak [a], Maria Kurańska [a, *], Ugis Cabulis [b], Mikelis Kirpluks [b]

[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

ARTICLE INFO

Article history:
Received 21 December 2016
Received in revised form
24 January 2017
Accepted 5 March 2017
Available online 7 March 2017

Keywords:
Rapeseed oil
Carbon fibres
Particle-reinforced composites
Thermal properties
Thermogravimetric analysis TGA
Flammability
Thermal conductivity
Compressive strength

ABSTRACT

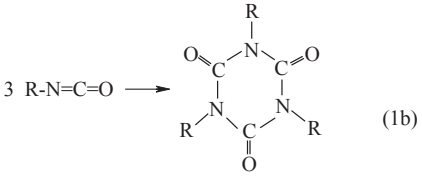
Porous polyurethane-polyisocyanurate (PUR-PIR) composites have been synthesized using two types of rapeseed oil-based bio-polyols. The bio-polyols from rapeseed oil were synthesized using two methods: (i) transesterification and (ii) epoxidation followed by oxirane ring opening. The PUR-PIR porous materials were prepared with two isocyanate indices, 150 and 250, and were modified with carbon fibres (CF) in an amount of 3 and 6 wt% of the total foam mass. The structure of the composites was examined using scanning electron microscopy. Thermal and mechanical properties of the composites were determined through a thermogravimetric analysis and measurements of the thermal conductivity, compressive strength, and Young modulus. The influence of CF on the composite flammability was analyzed using oxygen index and cone calorimeter tests. The investigations of the mechanical properties have shown that the compressive strength is the most beneficial in the case of the PUR-PIR foams modified with 6 wt % of CF. The studies have shown that the oxygen index of the composites increases with an increasing CF content and isocyanate index. An addition of CF reduces the heat rate release, especially for the materials with an isocyanate index of 250. An introduction of CF into the PUR-PIR foam structure is a way to improve the thermal stability and to decrease the flammability of final porous composites.

1. Introduction

Polyurethane (PUR) materials are attractive due to their structural versatility as rigid and flexible foams, elastomers and coatings, as well as the fact that they can be obtained using hydroxyl derivatives of vegetable oils [1–7]. The synthesis of PUR from renewable materials is currently interesting for environmental and economic reasons. Efforts to use renewable raw materials and to replace synthetic petrochemical polyols for making PUR foams have been accelerated in recent years [8–11]. Rigid PUR foams are applied mainly as heat insulating materials because they have one of the lowest thermal conductivity coefficients among such commercially available materials [12,13].

The thermal stability, fire resistance and dimensional stability of PURs can be improved by incorporating isocyanurate rings into their polymer matrix [14–16]. PUR-PIR foams are manufactured in the reaction of polyols with an excess of polyisocyanates in the presence of special catalysts for promoting a formation of isocyanurate rings. The hydroxyl groups of the polyols react with the isocyanate groups to form urethane linkages (1a), and because of the excess of isocyanate groups and the presence of special catalysts of the trimerization reaction a formation of isocyanurate rings occurs (1b).

(1a)



(1b)

* Corresponding author.
E-mail address: maria.kuranska@gmail.com (M. Kurańska).

http://dx.doi.org/10.1016/j.polymertesting.2017.03.006
0142-9418/

It is known that carbon nanotubes and carbon fibres may improve the physical and mechanical properties and increase the fire resistance of polymers based on petrochemical raw materials [17–19]. In the literature, various studies on the effect of carbon fibres in polymeric composites are described. Karsli et al. [17] studied the effects of initial fibre length and fibre length distribution on the properties of polypropylene composites. Their results showed that the mechanical strength of short fibre-reinforced polymers increases rapidly with an increase of the fibre mean length. Regardless of the initial carbon fibre length used, the tensile strength and modulus values of the composites increased with an increasing carbon fibre content. Yakushin et al. [18] investigated the influence of carbon fibres on the properties of rigid PUR foams. They found that the carbon fibres improved the mechanical properties of the porous PUR materials.

Xiong et al. [19] studied the influence of multi-walled carbon nanotubes on the thermal and mechanical properties of PURs. The results of a thermal analysis showed that the glass transition temperature of the composite was increased by about 10 °C and its thermal stability was clearly improved in comparison with a pure PUR. The investigation of the mechanical properties indicated that the modulus and tensile strength increased after adding 2 wt% carbon nanotubes to the PUR matrix [19].

In all the publications cited, the influence of carbon fillers on the selected properties of polymer materials was analyzed for composites synthesized using only petrochemical raw materials. In this paper, the influence of the carbon fibre content on the cell structure, physical and mechanical properties, and flame retardancy of PUR-PIR porous composites based on two types of bio-polyols is determined.

2. Experimental

2.1. Materials

Two different rapeseed oil-based polyols were prepared: the first one in the Department of Chemistry and Technology of Polymers in Cracow University of Technology (P1 with the hydroxyl number 256 mg KOH/g and a water content of 0.47 wt%) and the second one in the Latvian State Institute of Wood Chemistry (P2 with the hydroxyl number 365 mg KOH/g and a water content of 0.07 wt%). Bio-polyols P1 and P2 were obtained on the basis of rapeseed oils, products of Kruszwica SA and Iecavnieks SIA, respectively. The bio-polyols were synthesized using two methods: epoxidation with opening oxirane rings (P1) and transesterification with triethanolamine (P2). In the first step of the P1 synthesis, unsaturated fatty acids in triglycerides reacted with an acetate peroxyacid to form epoxidized oil. Through the epoxidation, the double bonds of the triglycerides were transformed into oxirane rings. In the second step, the epoxidized oil was converted into a polyol using a diethylene glycol. The transesterification (P2) of the rapeseed oil with triethanolamine was carried out using the molar ratio 1: 2.9.

Petrochemical polyetherol with the trade name Lupranol 3422 having the hydroxyl number ca. 490 mgKOH/g and a water content of 0.10 wt% was supplied by BASF, Germany. Polymeric methylene diphenyldiisocyanate (PMDI) containing 31.5 wt% of free isocyanate groups was supplied by Minova Ekochem S.A. Poland. Polycat5 produced by Air Products and Chemicals, USA, and PC CAT TKA 30 produced by Performance Chemicals, Germany, were used as catalysts. A silicone surfactant with the trade name Niax Silicone L-6915 produced by Momentive Performance Materials Inc. Germany, was used as a stabilizer of the foam structure. Tris (chloropropyl) phosphate (TCPP) produced by Lanxess, Germany, was used as a flame retardant. Water was used as a blowing agent which generated carbon dioxide while reacting with isocyanate groups. The foam PUR-PIR systems were filled according to the specification with Tenax A milled carbon fibres (CF) (Fig. 1), that had been manufactured by Toho Tenax Europe GmbH, Germany.

The length of type 383 fibres was 50–150 μm. The average diameter of the fibres was 7 μm.

2.2. Preparation of the PUR–PIR/CF porous composites

The PUR-PIR/CF composites were obtained by mixing two components (A and B). Component A was prepared using two types of rapeseed oil-based polyols, the petrochemical polyol, water, catalysts and the surfactant. The chemical compositions of component A used for the preparation of rigid PUR-PIR foams are presented in Table 1.

These formulations were modified by an addition of CF. The fibre concentrations were 3 and 6 wt% with respect to the total weight of the PUR-PIR system. The amount of the fibres introduced was limited due to increasing viscosity of component A. The composites were marked with respect to the type of bio-polyol, isocyanate index and fibre content. The isocyanate indices were 150 and 250 for the formulations prepared. The pre-selected amount of fibres was added to the polyol premix (polyols, flame retardant, catalysts, surfactant and water) and stirred to obtain a homogeneous mixture. In the next stage, component B (isocyanate) was added to component A and, after stirring the mixture for 7 s, poured into an open mould (200 × 200 mm^2). Free rise foaming took place in a vertical direction.

3. Measurements

The thermal stability was tested through a thermogravimetric analysis using a Mettler Toledo TGA/SDTA 851e under a nitrogen flow and at a heating rate of 10 °C/min from room temperature to 1000 °C. FTIR spectroscopy was used to confirm the structural features of the sample foams.

The thermal conductivity factors were determined using a Laser Comp Heat Flow Instrument Fox 200. Measurements were made at an average temperature of 10 °C (temperature of cold plate 0 °C and warm plate 20 °C).

The behaviour of the rigid PUR-PIR foams and PUR-PIR/CF foam composites under a heat flux of 35 kW/m^2 was tested using an FTT Dual Cone Calorimeter (Fire Testing Technology Ltd.). The tests were done according to the ISO 5660-2 standard. The materials were exposed to the heat flux for 300 s. During the experiments the

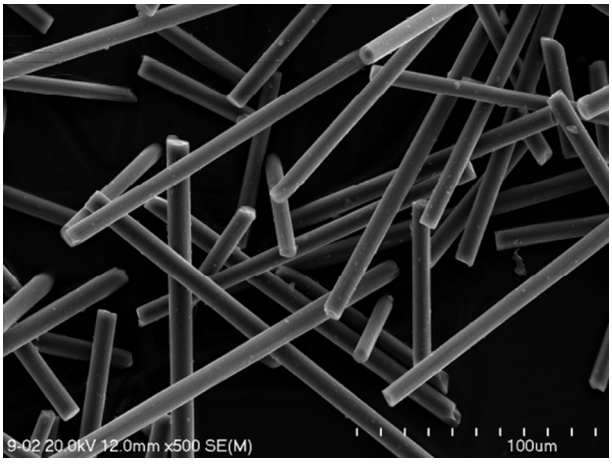


Fig. 1. A SEM image of CF.