



Bio-based polyurethane-polyisocyanurate composites with an intumescent flame retardant



Maria Kurańska^a, Ugis Cabulis^{b,*}, Monika Auguścik^c, Aleksander Prociak^a,
Joanna Ryszkowska^c, 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

^c Warsaw University of Technology, Faculty of Materials Science and Engineering, Woloska 141, 02-507 Warsaw, Poland

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ABSTRACT

Rigid polyurethane and polyisocyanurate (PUR-PIR) foams are one of the most effective thermal insulation materials applied in a wide range of industries. A sustainable solution for the production of these materials is to substitute one of their petrochemical components with a component produced from bio-based resources, like vegetable oils.

The biggest disadvantage of this type of thermal insulation is its high flammability which usually is reduced by an addition of halogen-based flame retardants. Halogenated flame retardants are getting out of use due to potential health risks. Two different bio-based polyols obtained from rapeseed oil were applied to develop rigid PUR-PIR foams with isocyanate indices of 150 and 250. Flammability of these materials was decreased using an intumescent expandable graphite (EG) filler; 0%; 3%; 6% and 9% contents of EG were used. Flammability (Cone calorimeter), combustion (limited oxygen index, thermal imaging), thermal stability (TGA/DTG) were studied for the developed PUR-PIR foams. The addition of EG did not change the ignition behaviour of the developed materials but it had a significant influence on other flammability properties. Due to the development of a stable char layer, the peak value of the heat release in the Cone Calorimeter test was reduced from 240 to 136 kW/m², the released smoke was also reduced from 560 to 288 m²/m². TGA graphs showed a significant char formation (sample with 9% of EG) that was stable at high temperatures, over 400 °C. The addition of EG to the PUR-PIR system had a positive effect on the burning process which was confirmed by thermal imaging camera results. The formation of the char layer moderated the combustion of the PUR-PIR foams and increased the burning time.

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1. Introduction

Rigid polyurethane (PUR) foams are widely used as heat insulating materials in building and construction industries, civil engineering and machinery due to their low thermal conductivity in comparison to other commercial products of this type [1,2]. Conventional rigid PUR foams are prepared from petrochemical polyols. It is necessary to adopt renewable resources and partially replace petrochemical polyols in order to increase the sustainability of rigid PUR foams. Hydroxyl derivatives of vegetable oils can be potential replacements for petrochemical polyols in the synthesis

of rigid PUR foams [3,4]. Vegetable oils, before being applied in PUR systems, have to be transformed into hydroxyl derivatives [5]. A number of methods to synthesize natural oil-based polyols is known, e.g. hydroformylation and hydrogenation, epoxidation followed by oxirane ring-opening, microbial conversion, thermal polymerization followed by transesterification, ozonolysis and hydrogenation or halogen addition and nucleophilic substitution [6,7].

Unfortunately, rigid PUR foams based on petrochemical and bio-polyols are ignitable and can be additional fire fuel sources in case of a fire disaster. An improvement in the thermal stability of PUR foams may be achieved through an introduction of isocyanurate trimerization structures into the PUR matrix [3]. Isocyanurates, from the thermodynamic point of view, are more thermally stable than urethane bonds (urethane dissociates at approx. 200 °C as

* Corresponding author.

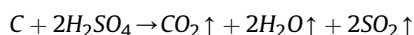
E-mail address: cabulis@edi.lv (U. Cabulis).

opposed to 350 °C for polyisocyanurates). The thermal stability of isocyanate-based polymers is provided in the following order: isocyanurate (350 °C) > urea (250 °C) > urethane (200 °C) > biuret (135–140 °C) > allophanate (106 °C) [8,9].

Another method of decreasing the flammability of rigid polyurethane–polyisocyanurate (PUR–PIR) foams is introducing flame retardants (FRs). The most widely used FRs are compounds containing halogen, phosphorus, nitrogen etc. Halogenated additives release corrosive, obscuring and toxic smokes which pollute the environment, erode instruments and can seriously endanger human health [10,11]. Intumescent halogen-free FRs can be good substitutes for halogenated ones due to the formation of a protective char layer that covers the surface of the polymer matrix and prevents its further decomposition, and as a consequence decreases the transition of a volatile compound into the gas phase [12,13]. Moreover, such an intumescent layer makes a thermal barrier protecting the foam core from high temperatures and is used as a smoke suppressant [14,15]. Expandable graphite (EG) can be used as a good intumescent halogen-free FR in rigid PUR–PIR foams.

EG has a special graphite flake structure, i.e. stacked layers of the hexagonal sp^2 hybridized carbon structure. EG is treated with a sulphuric acid, nitric acid or acetic acid which are intercalated into the graphite crystal structure. Such intercalated graphite particles can expand or exfoliate under heat. This flame retardant works mainly in the condensed phase thereby reducing the smoke density.

High temperatures cause the oxidization of the graphite in the following reaction with H_2SO_4 :



The released gases cause expansion of the graphite, which acts as a physical barrier for the heat and mass transfer [16]. EG forms a worm-like thermal insulating layer structure on the surface of a sample that prevents a heat and oxygen transfer giving a good fire retardant performance. Ultimately, the carbon coating prevents the PUR foams from burning [17,18].

EG keeps most of the natural graphite attributes, such as a low price and high porosity, making it very useful as a functional carbon material that can be applied in various fields of the polymer industry, but especially as FR [19]. Modesti et al. studied the influence of EG on the properties of rigid PUR foams with an apparent density of 35 kg/m³ and concluded that a higher filler content gives a significant improvement in the fire resistance of the materials [20]. Bian et al. prepared rigid PUR foams of different apparent densities filled with various contents of EG. The results showed that the FR efficiency was better with an increase in the apparent foam density at a fixed EG content or with an increase in the EG content at a fixed apparent foam density [10]. The sizes of EG particles also have an influence on the flame retardant efficiency. EG particles of a smaller size did not produce enough char to cover the whole surface of the burning sample resulting in a poor fire retardant property of rigid PUR foams [21]. The effect of passive protection of rigid PUR foams using an intumescent mat prepared from glass fibers on their fire performance was also investigated. EG was applied as a filler in both PUR foams as well as in the intumescent mat as an alternative to the EG added into the PUR material. Kirpluks et al. obtained the following four types of PUR foam samples: an unmodified PUR foam; a PUR foam filled with different amounts of EG (3%; 9% and 15%); a PUR foam protected with an intumescent mat and a PU foam with EG (3%; 9% and 15%) and an intumescent mat. The addition of EG into the PUR foams caused a decrease of the heat rate release peak (pHRR) from 327 kW/m² in the case of the unmodified material to 61 kW/m² for the PUR foam with 15% of EG, which was protected with the intumescent mat. Incorporation of an

intumescent mat boosts this effect even more [22].

The cumulative effect of an introduction of isocyanurate structures into the polyurethane matrix and an additive of EG as a FR is a prospective solution to decrease the flammability of rigid PUR–PIR foams. The literature does not describe the effect of EG on the properties of PUR–PIR foams based on bio-polyols from rapeseed oil. In this work, the influence of different contents of EG on the properties of rigid PUR–PIR foams obtained from two different bio-polyols and with various isocyanate indices is presented.

2. Experimental

2.1. Materials

Bio-polyols were obtained on the basis of rapeseed oils using two methods: epoxidation with opening oxirane rings (ROPep) and transesterification (ROPtr) with triethanolamine [23]. Two different rapeseed oil-based polyols were synthesized in the Department of Chemistry and Technology of Polymers at the Cracow University of Technology (ROPep with a hydroxyl number of 265 mgKOH/g and a water content of 0.5 wt%) and Latvian State Institute of Wood Chemistry (ROPtr with a hydroxyl number of 365 mg KOH/g and a water content of 0.1 wt%). A petrochemical polyol with the trade name Lupranol 3422 with a hydroxyl number ca. 490 mg KOH/g and a water content of 0.10 wt% was supplied by BASF. A polymeric methylene diphenyldiisocyanate (PMDI) containing 31.5 wt% of free isocyanate groups was supplied by Minova Ekochem S.A. An amine containing a catalyst with the trade name Polycat 5 produced by Air Products and Chemicals and a potassium acetate produced by Performance Chemicals were used as catalysts. A silicone surfactant with the trade name Nix Silicone L-6915 produced by Momentive Performance Materials Inc. was used as a stabilizer of the composite structure. Carbon dioxide generated in the reaction of water with isocyanate groups was used as a blowing agent. Expandable graphite with the trade name EG096 was supplied by Sinograf. The granulation and expansion of the expandable graphite were 0.2–0.6 mm and 200–300 ml/g, respectively.

2.2. Foam preparation

In all formulations, the petrochemical polyol in an amount of 70 wt% was replaced by the rapeseed oil-based polyols (ROPep or ROPtr). A two-component PUR system was applied to obtain rigid PUR–PIR foams. The reference formulation of the polyol premix consisted of the petrochemical polyol, a rapeseed oil-based polyol, the catalysts, the surfactant and water. These formulations were modified with EG in an amount of 3 or 6 or 9 wt% per total foam mass. The amount of the introduced EG was limited due to the increased viscosity of the polyol premix. The isocyanate indices were 150 and 250 for the prepared formulations. In the next stage, the isocyanate component was added to the polyol component and, after stirring the mixture for 10 s, poured into an open mould (200 × 200 mm²). Free rise foaming took place in a vertical direction. The rigid PUR–PIR foams were marked with respect to the rapeseed oil-based polyol, isocyanate and filler content. The chemical compositions of component A and the symbols of samples are shown in Table 1.

2.3. Test methods

The thermal stability was tested via the thermogravimetric (TG) 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. A TGA/FTIR analysis of the selected samples was carried out using TGA Q500 coupled to a Nicolet 6700 FTIR

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