

CHEMISTRY AND MATERIALS SCIENCE

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THE IMPACT OF GROUND TIRE RUBBER TREATMENT ON THE THERMAL CONDUCTIVITY OF FLEXIBLE POLYURETHANE/GROUND TIRE RUBBER COMPOSITES

Abstract: Waste car tires are burdensome waste, and their utilization is crucial for the natural environment. In many countries, the primary method of their recycling is energy recovery, performed by simple combustion. However, material recycling is much more effective and significantly more beneficial for the natural environment. It results in the generation of ground tire rubber, which can be used to produce polymer-rubber composites. It should be considered as a method of waste rubber utilization. Moreover, it may significantly reduce the use of petroleum-based polymers. Therefore, the environment's total impact could be noticeably reduced, which should be

considered a convenient step towards more “green” polymer composites. In the presented paper, the impact of ground tire rubber treatment on the structure and insulation properties of flexible polyurethane/ground tire rubber composite foams was evaluated.

Keywords: *Ground tire rubber; polyurethane foams; recycling; thermal conductivity*

Introduction

Polyurethane (PU) foams are a versatile group of materials commonly applied in various industry branches due to the very broad spectrum of potential properties [1]. Polyurethane foams may be divided into rigid and flexible foams [2]. They are used in different applications, but both groups are very perspective and prone to potential innovations. The PU foams are often applied as matrices for polymer composites [3]. It is very beneficial to look for the waste materials, whose introduction could significantly reduce the use of conventional, petroleum-based raw materials required to manufacture polyurethanes, which would be very beneficial for the economics and ecology [4]. Among the potential filler candidates are polyurethane foam scraps [5], waste lignocellulose fillers [6,7], textiles [8], eggshell waste [9], or rubber wastes [10]. The last material is an auspicious one, due to the excellent mechanical properties of many primary rubber materials, e.g., car tires. They are commonly utilized through mechanical recycling resulting in the production of ground tire rubber (GTR). This material can be efficiently introduced into various polymer matrices, including also polyurethane foams [11].

In the presented research work, we aimed to investigate the influence of GTR treatment on the structure and thermal insulation properties of flexible PU/GTR composite foams. We modified the GTR with two types of rapeseed oil, including waste from a local restaurant.

Materials and methods

Ground tire rubber obtained by ambient grinding of used tires (a combination of passenger car and truck tires in 50:50 mass ratio), whose average particle size is approximately 0.6 mm, was produced and provided by Recykl S.A. (Śrem, Poland).



Two types of rapeseed oil were applied as modifiers for ground tire rubber. Fresh rapeseed oil (FO) was acquired from Lidl (Poland), while waste oil (WO) was obtained from a local restaurant (Gdańsk, Poland).

Polyurethane foams were prepared using Rokopol®F3000 and Rokopol®V700 polyols obtained from the PCC Group, with the addition of glycerol. The polymeric methylenediphenyl-4,4'-diisocyanate (pMDI) SPECFLEX NF 434 was used as an isocyanate component. The solution of potassium acetate PC CAT® TKA30 from Performance Chemicals, 33 wt% solution of triethyl diamine in dipropylene glycol (Dabco33LV from Air Products), and dibutyltin dilaurate (DBTDL) from Sigma Aldrich were applied as catalysts. Distilled water was used as a chemical blowing agent.

Applied modifications of ground tire rubber were described in our previous work [12]. Briefly, treatment of GTR was performed with EHP 2x20 Sline co-rotating twin-screw extruder from Zamak Mercator (Poland) with a screw diameter of 20 mm and an L/d ratio of 40. Before the modification, GTR was premixed with 20 or 40 phr (parts per hundred of rubber) of selected oil. Then, it was dosed into the extruder with a constant throughput of 2 kg/h. Barrel temperature in all zones was set at 200 °C. The screw speed was set at 50 or 150 rpm, depending on the oil content. For each set of parameters, extrusion was carried out for at least 5 min after stabilizing the extruder's motor load, indicating the stabilization process.

Composite foams were prepared on a laboratory scale by a single-step method with the ratio of isocyanate to hydroxyl groups of 1:1. Content of modified ground tire rubber in composite foams was fixed at 20 wt%. Prior to polymerization, filler was mixed with the polyol components to enhance its distribution in the final material. Table 1 contains the details of foam formulations.

Table 1

Composition of prepared polyurethane foams

Component	Sample code					
	1	2	3	4	5	6
	Content, wt%					
F3000	32.6	26.1	26.1	26.1	26.1	26.1
V700	32.6	26.1	26.1	26.1	26.1	26.1

Table 1 (continued)

Component	Sample code					
	1	2	3	4	5	6
	Content, wt%					
Glycerol	0.8	0.6	0.6	0.6	0.6	0.6
DBTDL	0.6	0.5	0.5	0.5	0.5	0.5
33LV	0.4	0.3	0.3	0.3	0.3	0.3
TKA30	0.4	0.3	0.3	0.3	0.3	0.3
Water	0.3	0.3	0.3	0.3	0.3	0.3
pMDI	32.3	25.8	25.8	25.8	25.8	25.8
Neat GTR	-	20.0	-	-	-	-
GTR/20 phr FO	-	-	20.0	-	-	-
GTR/40 phr FO	-	-	-	20.0	-	-
GTR/20 phr WO	-	-	-	-	20.0	-
GTR/40 phr WO	-	-	-	-	-	20.0

After, the samples were conditioned at room temperature for 24 hours. Then, they were checked for the open cell content and thermal conductivity coefficient.

The content of open cells in foamed PU/GTR composites was determined using Ultrapyc 5000 Foam gas pycnometer from Anton Paar (Poland). Following measurement settings were applied: gas – helium; target pressure – 3.0 psi; foam mode – on; measurement type – corrected; flow direction – sample first; temperature control – on; target temperature – 20.0 °C; flow mode – monolith; cell size – small, 10 cm³; preparation mode – flow; time of the gas flow – 0.5 min.

The thermal conductivity coefficient was determined using the heat flow meter HFM 446 from Netzsch (Poland). Samples were tested in the range of 1-19 °C for an average temperature of 10 °C.

Results and discussion

Figure 1 presents the impact of the applied ground tire rubber treatment on the structure and insulation performance of prepared PU/GTR composite foams. It can be seen that the unmodified polyurethane matrix was characterized by the open cell content of 84.67%. Modifications of GTR caused slight decrease of the open cell content, which could be associated with the disruption of the cellular structure, also noted in our previous works [13,14]. As a result, the standard deviation was increased, which points to the reduced homogeneity of cellular structure. Such effects are often associated with the introduction of solid particles into polyurethane foams.

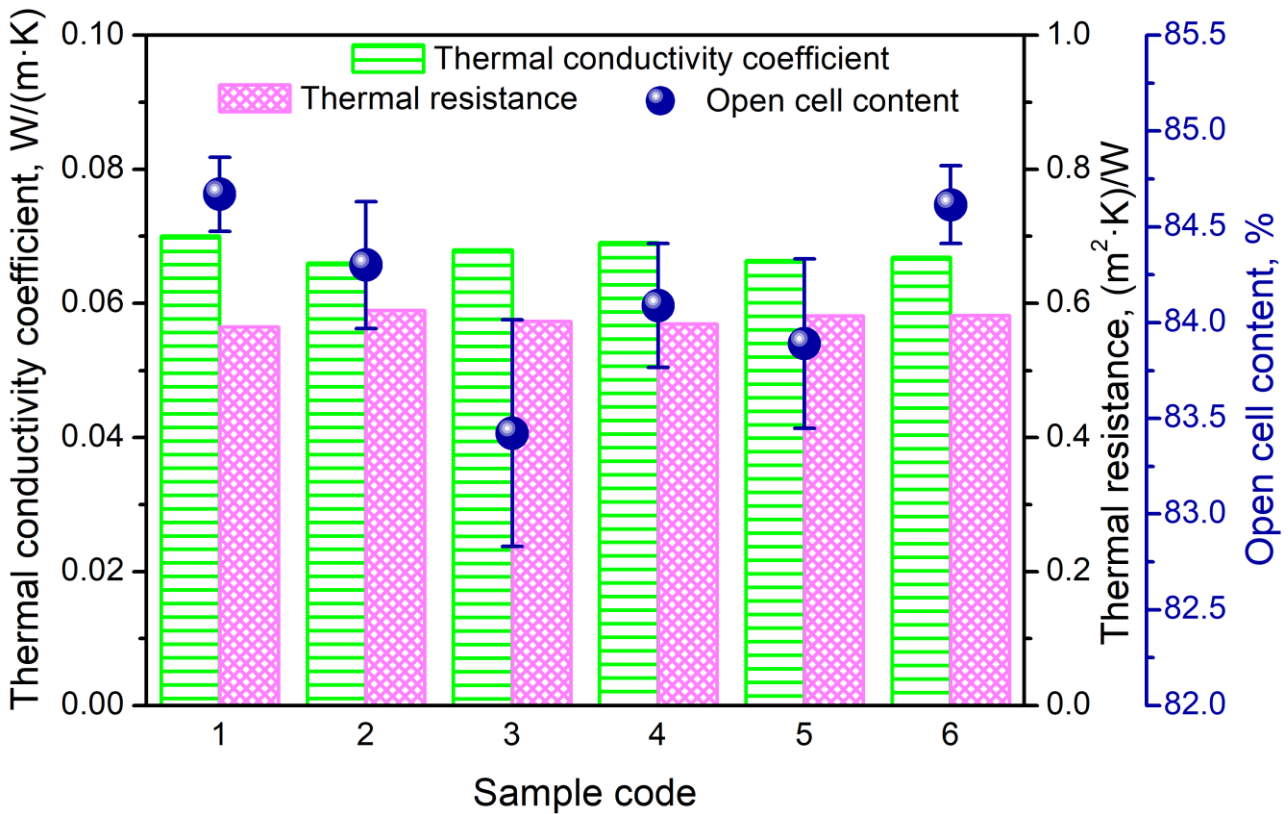


Fig. 1. Open cell content, thermal conductivity coefficient and thermal resistance of prepared PU/GTR composite foams.

The open cell content is a very important parameter for the insulation properties of polyurethane foams. It directly affects the heat convection through the material. It is related to the movement of a substance in a liquid or gaseous state under the influence of a temperature gradient in a given volume. Convection can be described by the following equation (1):

$$q = hA\Delta T \quad (1)$$

where: q is the amount of heat transported per unit of time, h is the heat transfer coefficient, A is the surface area of heat transport, and ΔT is the temperature difference causing convective heat transport.

The convective heat transport is closely related to the surface of the heat transport. Thus, another very important parameter is the content of open and closed cells in the foam. The higher content of closed cells significantly limits the convective heat movement and also hinders the gaseous exchange between the volatile hydrocarbons



used in foaming and the air surrounding the material, which has a higher value of thermal conductivity coefficient. In the case of very high closed cell contents, the influence of convection on the total value of the thermal conductivity coefficient is neglected [15].

It can be seen that in the presented case, the drop of the open cell content resulted in a decrease in the thermal conductivity coefficient, pointing to the enhanced insulation properties. For the unmodified matrix, the coefficient equaled 70.1 mW/(m·K). The introduction of neat GTR caused the biggest drop of its value to 66.0 mW/(m·K), which was associated with the lower thermal conductivity coefficient for rubber comparing to the solid polyurethane (~160 vs. ~220 mW/(m·K)) [16]. After performed modifications of ground tire rubber, the insulation properties of foams were slightly deteriorated because the coefficient was increased to 66.4 and 66.8 mW/(m·K) (for waste oil), and to 68.0 and 69.0 mW/(m·K) (for fresh oil). Except for slightly higher open cell content, such an effect could be associated with the higher thermal conductivity of oil comparing to the rubber, which is around 170-180 mW/(m·K) [17]. Moreover, the application of waste oil resulted in better insulation properties, which is very beneficial from the environmental point of view. Generally, prepared composite foams showed similar insulation properties compared to the neat matrix, which is very beneficial. Changes in thermal resistance of foams showed the opposite trend.

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