Thermomechanically modified ground tire rubber/zinc borate compositions as fillers for flexible polyurethane foams

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Due to the rapid development of the automotive sector, the global number of vehicles increases, implicating environmental threats. Except for the most discussed CO_2 emissions, one of the most severe threats is the generation of vast amounts of waste tires. They are considered dangerous waste with no safe possibility of landfilling, which is often prohibited (Chen *et al*, 2021). Therefore, efficient utilization methods are needed, which is a goal of many industrial and scientific works. Waste tires can be shredded, leading to the generation of ground tire rubber (GTR), which still lacks high-scale industrial applications. It could be applied in polymer technology as filler for polymer composites, but to ensure satisfactory performance, proper compatibility of GTR with polymer matrix is required (Hejna *et al*, 2020). Two main strategies of providing compatibility are applications of additional compatibilizer or filler modification. In the first case, the additive needs to show good miscibility with the polymer matrix and simultaneously create interactions with filler particles. Another possibility is the modification of filler particles, particularly their surface, to increase the specific surface area and possibly introduce reactive functional groups, enhancing the interfacial interactions with matrix (Aoudia *et al*, 2017).

GTR modifications are mainly realized by grafting chemical compounds on the particles' surface or its partial devulcanization and oxidation, which increases the surface area and enhances the GTR reactivity. Devulcanization results in partial degradation of rubber 3D network and can be realized using mechanical, thermomechanical, chemical, ultrasonic, microwave, and other methods (Seghar *et al*, 2019). One of the most promising and environmentally beneficial methods is reactive extrusion, which could be performed continuously, without solvents, with reduced heat demand, and using the equipment commonly available in polymer technology (Zedler *et al*, 2019). Moreover, it enables the application of additional GTR modifiers.

The presented study aimed to investigate the thermomechanical modification of GTR with zinc borate in twin-screw extrusion process as a novel, highly-effective treatment method, and further incorporation of modified GTR in flexible, foamed polyurethane (PU) matrix. The goal of zinc borate introduction was to provide additional friction during thermomechanical modification of GTR, which could enhance the specific surface area and reduce GTR particle size. These two factors are often crucial for the performance of polymer composites (Fu *et al*, 2008). Moreover, additions of inorganic modifiers may noticeably enhance the thermal stability of polymer materials (Morgan and Putthanarat, 2011). The zinc borate was used in the amount of 40 parts by weight with respect to the GTR, and the compositions were extruded at varying temperatures and screw speed. Then, they were introduced into foamed polyurethane matrix in the fixed amount of 15 wt%. Their impact on the cellular structure, insulation, mechanical and thermal performance of composite PU/GTR foams was evaluated.

As mentioned above, the size of filler particles and often associated specific surface area show the enormous impact on the performance of composite materials. In the case of polyurethane foams, this impact is even stronger, because it affects not only the mechanical properties but also the course and rate of the foaming process, as well as the cellular structure, which is critical, e.g., for thermal insulation or sound absorption performance (Li *et al*, 2014; Sung and Kim, 2017). Therefore, Figure 1 presents the changes in the particle size distribution of GTR/zinc borate compositions resulting from thermomechanical treatment in a twin-screw extruder. Initially, the composition was heterogeneous and consisted of two types of particles with noticeably different sizes in the range of 5-45 µm and 100-1500 µm, respectively. Depending on the applied parameters, extrusion affected the particle size distribution, which was attributed to the shear forces acting on the material and the friction between particles, which may cause their grinding and coalescence.

Thermomechanical treatment of GTR/zinc borate compositions and resulting changes in the particle size distribution provided beneficial changes in the interfacial adhesion between fillers and PU matrix. Such an effect was associated with the enhanced homogeneity of cellular structure and increased nucleating activity of treated GTR particles. Performed static and dynamic mechanical tests pointed to the increase in foams' tensile strength and stiffness, related to the enhanced interfacial interactions suggested by the decrease in the magnitude of loss tangent peak.

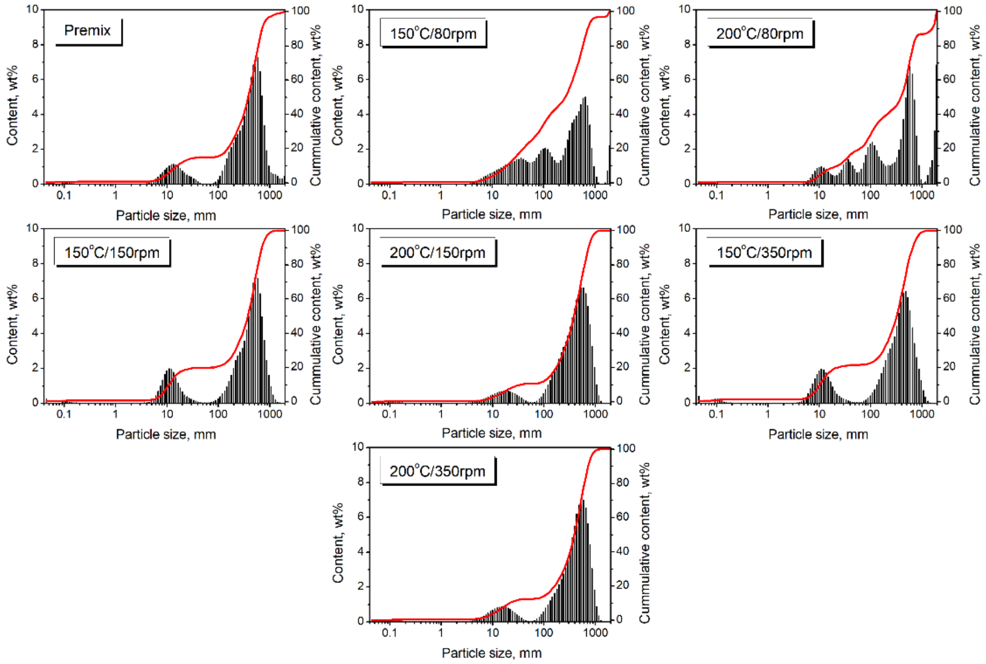

Figure 1. Particle size distribution of GTR/zinc borate compositions depending on treatment conditions.

Except for the mechanical performance, thermomechanical treatment enabled small enhancement of composite foams' thermal stability, shifting onset of decomposition by 4-7 °C towards higher temperatures. Such an effect also points to the increased compatibility of presented composites.

Generally, it was proven that proposed method of GTR thermomechanical treatment assisted by zinc borate particles may provide beneficial effects on the performance of flexible PU foamed composites, which could broaden the application range of GTR and provide novel ways for its efficient utilization.

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