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Optimization of foamed polyurethane/ground tire rubber composites manufacturing †

Adam Olszewski, Paulina Kosmela, Łukasz Zedler, Krzysztof Formela, Aleksander Hejna *

[1] Department of Polymer Technology, Gdańsk University of Technology, Narutowicza 11/12 80-233 Gdańsk, Poland; adam.olszewski@student.pg.edu.pl (A.O.); paulina.kosmela@pg.edu.pl (P.K.); lukasz.zedler@pg.edu.pl (Ł.Z.); krzform1@pg.edu.pl (K.F.); aleksander.hejna@pg.edu.pl (A.H)

* Correspondence: aleksander.hejna@pg.gda.pl;

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Abstract: The development of the automotive sector and increasing amount of vehicles all over the world poses multiple threats to the environment. One of them, probably not so emphasized as others, is the enormous amount of post-consumer car tires. Due to the potential fire threat, waste tires are considered as dangerous waste, which should not be landfilled, so it is essential to develop efficient methods of their utilization. One of the possibilities is their shredding and application of resulting ground tire rubber (GTR) as filler for polymer composites, which could take advantage of the excellent mechanical performance of car tires. Nevertheless, due to the poor compatibility with majority of polymer matrices, prior to the application, surface of GTR particles should be modified and activated. In the presented work, the introduction of thermo-mechanically modified GTR into flexible foamed polyurethane matrix was analyzed. Among the compounds applied during manufacturing of polyurethane foams can be found isocyanates, which are able to react and generate covalent bonds with the functional groups present on the surface of modified GTR. Such an effect can noticeably enhance the interfacial interactions and boost up the mechanical performance. Nevertheless, it requires the adjustment of formulations used during manufacturing of foams. Therefore, for better understanding of the process foams with varying isocyanate index (from 0.8 to 1.2) were prepared with and without taking into account the possible interactions with functional groups of GTR. For comparison, unfilled matrix and composite containing deactivated GTR were also prepared.

Keywords: Polyurethane foam; ground tire rubber; rubber modification; surface activation polymer composites

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1. Introduction

Polyurethane (PU) foams are commonly applied in various branches of the industry thanks to their wide range of easily adjustable performance [1]. Their properties strongly depend on the applied formulation, particularly on the ratio between isocyanate and hydroxyl groups present in the system, expressed by the isocyanate index. Hydroxyl groups are present in the structure of polyols, the major components of polyurethanes. Moreover, they can be found in water applied as a blowing agent and in the chemical structure of fillers introduced into the PU matrix [2]. Hydroxyls are primarily present in organic, plant-based fillers like cellulose, wood flour, or natural fibers [3]. However, they can also be found in materials previously subjected to oxidative conditions during different industrial processes [4]. An excellent example of such material is ground tire rubber (GTR) generated during the recycling of post-consumer car tires. During the shredding of tires, hydroxyl groups can be introduced onto the surface of GTR particles due to oxidation occurring during the reduction of particle size [5]. The incorporation of such materials affects the desired balance between isocyanate and hydroxyl groups in the PU formulation, which may influence performance of composite materials [6]. Członka et al. [7] reported that solid waste from the leather industry rich in hydroxyl groups might noticeably affect the foaming kinetics and cellular structure of PU foams. The unfavorable influence of natural fillers on the performance of PU foams was reported by Zieleniewska et al. [8].

The effect of additional hydroxyl groups is particularly noticeable for foams, characterized by the lower values of the isocyanate index. For rigid foams with values of isocyanate index around 2.0 or higher, the effect is not so strong [9]. On the other hand, for flexible foams, even a tiny amount of filler may noticeably affect the balance between functional groups, as reported by Silva et al. [10] for incorporation of waste rubber particles. Despite incorporating filler showing superior mechanical performance, composite foams' strength was lower than the unfilled matrix. It points to the weakness of the PU network, attributed to its reduced cross-linking [11]. The effect may be particularly significant for the fillers very rich in hydroxyl groups, which was reported in our previous paper when GTR was additionally oxidized with potassium permanganate [12].

Therefore, to prepare PU composite foams efficiently, it is important to consider the influence of the chemical structure of fillers and the presence of functional groups, which may affect the overall isocyanate index. The presented work aimed to investigate the effect of GTR hydroxyl groups on the mechanical performance of flexible PU foams prepared with varying isocyanate index. The tensile and compression tests were performed to assess the foam modifications' impact and describe it qualitatively and quantitatively.

2. Materials and Methods

2.1. Materials

The materials used in the presented study are listed in Table 1.

Table 1. The list of materials used in the presented work.

Material	Producer	Properties/Additional information
	Polyurethane foams preparation	
Rokopol®F3000	PCC Group (Brzeg Dolny, Poland)	Polyether polyol, propoxylated glycerol, hydroxyl value – 53–59 mg KOH/g
Rokopol®V700	PCC Group (Brzeg Dolny, Poland)	Polyether polyol, propoxylated glycerol, hydroxyl value – 225–250 mg KOH/g
Glycerol	Sigma Aldrich (Poznań, Poland)	Hydroxyl value – 1800 mg KOH/g
SPECFLEX NF 434	M. B. Market Ltd. (Baniocha, Poland)	Polymeric methylenediphenyl-4,4′-diisocyanate, free isocyanate content – 29.5%
PC CAT® TKA30	Performance Chemicals (Belvedere, UK)	Potassium acetate catalyst
Dabco33LV	Air Products (Allentown, USA)	Catalyst, 3 wt% solution of 1,4-diazabicyclo[2.2.2]octane in dipropylene glycol
Dibutyltin dilaurate	Sigma Aldrich (Poznań, Poland)	Organic tin catalyst
Distilled water	-	Chemical blowing agent
Ground tire rubber	Recykl S.A. (Śrem, Poland)	Filler, average particle size – 0.6 mm, hydroxyl value – 61.7 ± 3.0 mg KOH/g
	Deactivation of hydroxyl groups in GTR	
Acetone	Sigma Aldrich (Poznań, Poland)	Solvent
Toluene diisocyanate	Sigma Aldrich (Poznań, Poland)	Free isocyanate content – 42%
Dibutylamine	Sigma Aldrich (Poznań, Poland)	Analyte solution
Chlorobenzene	Sigma Aldrich (Poznań, Poland)	Solvent
Hydrochloric acid	Sigma Aldrich (Poznań, Poland)	Titrant
3′,3″,5′,5″-Tetrabromophenol-sulfonphthalein	Sigma Aldrich (Poznań, Poland)	Indicator

Table 2. Formulations applied during preparation of PU foams.

Component	Neat Foam							GTR deactivated /Not considered							GTR considered						
	Content, wt%																				
F3000	35.4	34.2	33.7	33.2	32.7	32.2	31.2	29.5	28.5	28.1	27.6	27.2	26.8	26.0	28.3	27.3	26.8	26.4	25.9	25.5	24.6
V700	35.4	34.2	33.7	33.2	32.7	32.2	31.2	29.5	28.5	28.1	27.6	27.2	26.8	26.0	28.3	27.3	26.8	26.4	25.9	25.5	24.6
Glycerol	0.9	0.8	0.8	0.8	0.8	0.8	0.8	0.7	0.7	0.7	0.7	0.7	0.6	0.6	0.7	0.7	0.6	0.6	0.6	0.6	0.6
DBTDL	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.4
33LV	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
TKA30	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Water	0.4	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
pMDI	26.6	28.9	30.0	31.1	32.2	33.2	35.2	22.1	24.1	25.0	25.9	26.8	27.7	29.3	24.5	26.6	27.7	28.7	29.6	30.6	32.3
GTR/modified GTR	-	-	-	-	-	-	-	16.7	16.7	16.7	16.7	16.7	16.7	16.7	16.7	16.7	16.7	16.7	16.7	16.7	16.7
Isocyanate:hydroxyl ratio	0.8	0.9	0.95	1.0	1.05	1.1	1.2	0.8	0.9	0.95	1.0	1.05	1.1	1.2	0.8	0.9	0.95	1.0	1.05	1.1	1.2

2.2. Deactivation of Ground Tire Rubber hydroxyl groups

To prepare GTR with deactivated hydroxyl groups, the equivalent amounts of GTR and TDI were placed in a glass flask in acetone. Components were mechanically mixed and left for 24 hours in a dark place at room temperature. Then, GTR was taken out, washed with acetone to remove the excess of TDI, and dried to remove the solvent. To ensure the successful deactivation of hydroxyl groups, the hydroxyl value of GTR was determined according to the method based on the modified test method for isocyanate groups, as described in our previous work [13].

2.3. Preparation of Polyurethane/Ground Tire Rubber Composite Foams

Samples were prepared on a laboratory scale by a single-step method. The predetermined amount of GTR particles was mixed with polyols at 1000 rpm for 60 s to ensure proper distribution. Then, all components were mixed for 10 s at 1800 rpm and poured into a closed aluminum mold with dimensions of 20 × 10 × 4 cm^3. All analyses were performed after 24-hour conditioning of samples at room temperature and average humidity of 60%.

As mentioned above, for a better understanding of the interactions between isocyanates and functional groups of GTR filler, foams with varying isocyanate index (from 0.8 to 1.2) were prepared. Except for neat foams without the GTR addition (named PU_X), three series of composite foams were prepared, which were named D-GTR_X, N-GTR_X, and C-GTR_X, where D indicated deactivated GTR, N not considered, and C considered in the isocyanate index calculation. For all samples, X indicates the isocyanate index applied in the formulation. Table 2 shows the formulations of prepared composite foams. All foams were characterized by a similar level of apparent density – 205 ± 6 kg/m^3.

2.4. Characterization Techniques

The tensile strength of microporous polyurethane elastomers was estimated following ISO 1798. The beam-shaped samples with 10 × 10 × 100 mm^3 dimensions were measured with a slide caliper with an accuracy of 0.1 mm. The tensile test was performed on a Zwick/Roell tensile tester at a 500 mm/min constant speed.

The compressive strength of studied samples was estimated following ISO 604. The cylindric samples with dimensions of 20 mm × 20 mm (height and diameter) were measured with a slide caliper with an accuracy of 0.1 mm. The compression test was performed on a Zwick/Roell Z020 tensile tester (Ulm, Germany) at a constant speed of 15%/min until reaching 60% deformation.

3. Results and discussion

Figure 1 presents the impact of the isocyanate index on the tensile strength of prepared foams. It can be seen that the mechanical performance significantly depends on the isocyanate index applied during the preparation of foams. It is associated with the development of a polyurethane network during reactions between hydroxyl and isocyanate groups. Typically, increasing the isocyanate index is beneficial for the tensile performance of flexible polyurethane foams. Such an effect was noted by Prociak et al. [14] or Lee et al. [15]. In the presented case, the tensile strength was almost directly proportional to the isocyanate index. For higher values of isocyanate index, especially exceeding 1.0, the excess of isocyanate may react with hydroxyl groups present on the surface of filler and strengthen the interface.

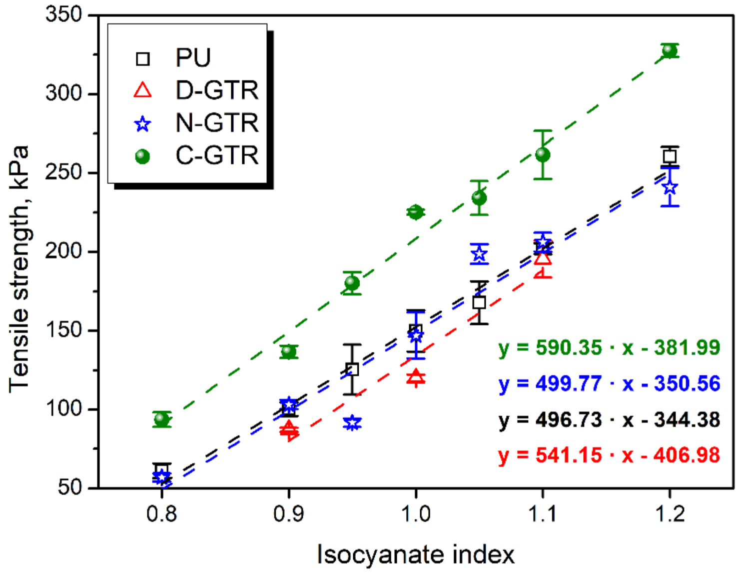

Figure 1. The impact of isocyanate index on the tensile strength of prepared PU foams.

Given the influence of applied formulation, a significant difference was observed between samples which formulation considered or not considered the hydroxyl values of GTR. When applied filler was not taken into account during isocyanate index calculation, the tensile strength of composites was slightly lower than the neat matrix. It suggests that for N-GTR foams, rubber particles were at least to some extent bonded with polyurethane matrix. However, it also indicates that the interfacial interactions between matrix and filler were relatively poor because the tensile strength of GTR itself is in the range of MPas [16]. At the same time, the worst results were noted when deactivated GTR particles were introduced. It indicates that when the inert filler is incorporated into the polyurethane matrix, its development during foaming is affected, and the resulting strength of the final composite is reduced [17].

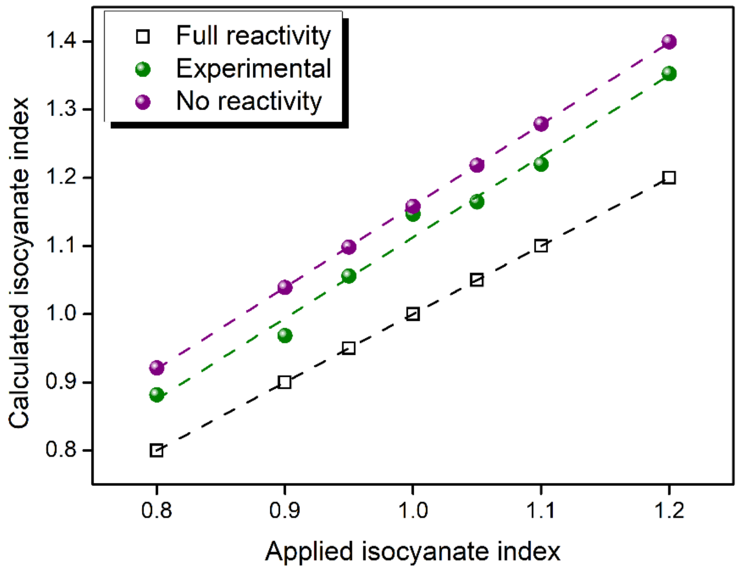

Figure 2. Calculated and applied values of isocyanate index based on the tensile tests and used formulations.

Significantly the best results were observed for C-GTR foams, attributed to the higher amount of isocyanate used. Compared to N-GTR foams, considering the hydroxyl value of GTR filler in calculation of isocyanate index required ~10% more isocyanate. As a result, more covalent linkages in the polyurethane network were developed, which strengthened the material. Figure 2 shows plots aimed to provide more quantitative information about the amount of GTR hydroxyls reacted with isocyanate. It shows the dependence between applied and calculated isocyanate index assuming different reactivity of GTR functional groups. Full reactivity means that all hydroxyl groups present on the surface of GTR particles reacted with isocyanates during foaming. Therefore, applied and calculated values of the isocyanate index are equal. No reactivity means that the isocyanates theoretically reacted only with polyols and water. In such a case, the actual values of the isocyanate index (calculated ones) would be substantially higher since more isocyanate was introduced into formulations. Experimental data points are obtained by applying tensile strength-isocyanate index dependence for PU samples presented in Figure 1 ($y = 496.73 \cdot x - 344.38$) to analyze the C-GTR samples. All data points lie between full reactivity and no reactivity, indicating that only part of GTR hydroxyls involved reactions with isocyanates. It was affected mainly by the lower reactivity of these groups compared to polyols' hydroxyls and steric hindrance caused by bulk GTR particles [18]. Presented data indicate that from 7 to 51% of GTR hydroxyls reacted with isocyanates depending on the sample. For most samples, the average value was 28±5%.

Figure 3 presents the compressive performance of prepared foams depending on the isocyanate index. The increase in compressive strength was associated with better development of polyurethane network and higher cross-link density of a material. Such a strengthening effect was observed by other researchers [14, 19]. Presented data also indicate that functional groups of GTR affect the performance of the PU matrix. For N-GTR samples, strength deterioration was noted, despite the superior performance of filler compared to polyurethane.

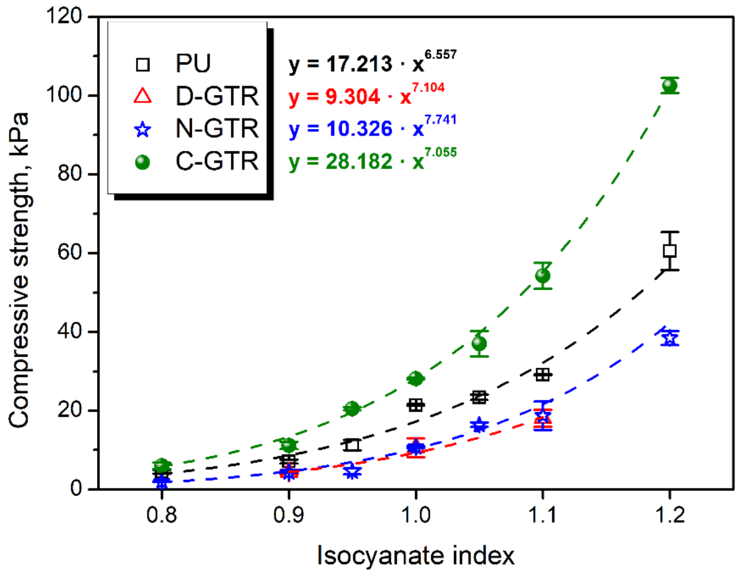

Figure 3. Compressive strength of prepared foams depending on the isocyanate index.

Figure 4, similar to Figure 2, presents the quantitative information about the interaction of GTR particles with the PU matrix. The experimental data points for C-GTR samples were calculated from the compressive strength-isocyanate index curve described by the power equation ($y = 17.213 \cdot x^{6.557}$). Like tensile-based dependence, all data points indicate partial reactivity between isocyanate groups and hydroxyls on the GTR surface. However, compression data indicates higher reactivity in the range of 43-74% for most samples 48-57%. Around twice as high reactivity compared to the tensile-based dependence is attributed to the different deformation mechanisms and GTR particles' contribution. During tension, the cohesion of material is crucial so that it can withstand deformation. Therefore, heterogeneity and insufficient interfacial adhesion result in discontinuity of material and reduced tensile strength. The filler itself may enhance the strength of the composite. However, such an effect is usually noted for fibrous fillers, which can transfer stress during tension rather than particulate fillers [20]. Considering compression, the force is acting on the material in the opposite direction. Hence, the impact of filler is different. For an efficient reinforcement, the filler itself should withstand high compressive forces, and essential is its impact on the PU foams' cellular structure [4,6,12]. Due to GTR particles' characteristics (shape, aspect ratio, mechanical performance), their impact on the foams' compressive performance was more substantial than for tensile strength. Therefore, compression-based dependence suggested a greater extent of GTR reaction with isocyanates compared to tension.

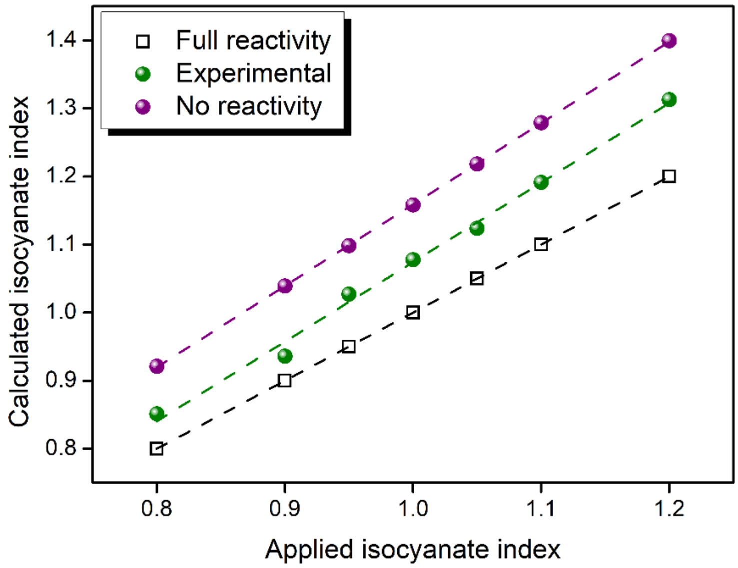

Figure 4. Calculated and applied values of isocyanate index based on the compression tests and used formulations.

4. Conclusions

The presented research aimed to investigate the impact of hydroxyl groups present on the surface of ground tire rubber particles on balance between the isocyanate and hydroxyl groups in the polyurethane system applied to produce flexible PU composite foams. Tensile-based dependences indicated that around 23-33% of GTR hydroxyls reacted with isocyanates, while compression tests suggested higher values in the range of 48-57%. The differences were associated with the filler performance and different modes of deformation. Nevertheless, despite the lack of chemical analysis, mechanical tests and calculations of foams' formulations pointed to partial reactivity of applied filler with isocyanates, which should be considered, especially during the development of flexible PU composite foam-based products on an industrial scale.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Hejna, A.; Kosmela, P.; Kirpluks, M.; Cabulis, U.; Klein, M.; Haponiuk, J.; Piszczyk, Ł. Structure, Mechanical, Thermal and Fire Behavior Assessments of Environmentally Friendly Crude Glycerol-Based Rigid Polyisocyanurate Foams. *J. Polym. Environ.* **2017**, *26*(5), 1854–1868. https://doi.org/10.1007/s10924-017-1086-2
2. Gosz, K.; Kosmela, P.; Hejna, A.; Gajowiec, G.; Piszczyk, Ł. Biopolyols obtained via microwave-assisted liquefaction of lignin: structure, rheological, physical and thermal properties. *Wood Sci. Technol.* **2018**, *52*(3), 599–617. https://doi.org/10.1007/s00226-018-0991-4
3. Hejna, A.; Barczewski, M.; Andrzejewski, J.; Kosmela, P.; Piasecki, A.; Szostak, M.; Kuang, T. Rotational Molding of Linear Low-Density Polyethylene Composites Filled with Wheat Bran. *Polymers* **2020**, *12*, 1004. https://doi.org/10.3390/polym12051004
4. Kosmela, P.; Olszewski, A.; Zedler, Ł.; Burger, P.; Formela, K.; Hejna, A. Structural Changes and Their Implications in Foamed Flexible Polyurethane Composites Filled with Rapeseed Oil-Treated Ground Tire Rubber. *J. Compos. Sci.* **2021**, *5*, 90. https://doi.org/10.3390/jcs5030090
5. Hejna, A.; Korol, J.; Przybysz-Romatowska, M.; Zedler, Ł.; Chmielnicki, B.; Formela, K. Waste tire rubber as low-cost and environmentally-friendly modifier in thermoset polymers – A review. *Waste Manage.* **2020**, *108*, 106–118. https://doi.org/10.1016/j.wasman.2020.04.032
6. Piszczyk, Ł.; Hejna, A.; Formela, K.; Danowska, M.; Strankowski, M. Effect of ground tire rubber on structural, mechanical and thermal properties of flexible polyurethane foams. *Iran. Polym. J.* **2015**, *24*, 75–84. https://doi.org/10.1007/s13726-014-0301-4
7. Członka, S.; Bertino, M.F.; Strzelec, K.; Strąkowska, A.; Masłowski, M. Rigid polyurethane foams reinforced with solid waste generated in leather industry. *Polym. Test.* **2018**, *69*, 225–237. https://doi.org/10.1016/j.polymertesting.2018.05.013
8. Zieleniewska, M.; Przyjemska, K.; Chojnacki, P.; Ryszkowska, J. Modification of flexible polyurethane foams by the addition of natural origin fillers. *Polym. Degrad. Stabil.* **2016**, *132*, 32–40. https://doi.org/10.1016/j.polymdegradstab.2016.05.002
9. Piszczyk, Ł.; Hejna, A.; Danowska, M.; Strankowski, M.; Formela, K. Polyurethane/ground tire rubber composite foams based on polyglycerol: Processing, mechanical and thermal properties. *J. Reinf. Plast. Compos.* **2015**, *34*(9), 708–717. https://doi.org/10.1177/0731684415579089
10. Silva, N.G.S.; Cortat, L.I.C.O.; Orlando, D.; Mulinari, D.R. Evaluation of rubber powder waste as reinforcement of the polyurethane derived from castor oil. *Waste Manage.* **2020**, *116*, 131–139. https://doi.org/10.1016/j.wasman.2020.07.032
11. Hejna, A.; Haponiuk, J.; Piszczyk, Ł.; Klein, M.; Formela, K. Performance properties of rigid polyurethane-polyisocyanurate/brewers' spent grain foamed composites as function of isocyanate index. *e-Polymers* **2017**, *17*(5), 427-437. https://doi.org/10.1515/epoly-2017-0012
12. Hejna, A.; Olszewski, A.; Zedler, Ł.; Kosmela, P.; Formela, K. The Impact of Ground Tire Rubber Oxidation with H2O2 and KMnO4 on the Structure and Performance of Flexible Polyurethane/Ground Tire Rubber Composite Foams. *Materials* **2021**, *14*, 499. https://doi.org/10.3390/ma14030499
13. Zedler, Ł.; Kosmela, P.; Olszewski, A.; Burger, P.; Formela, K.; Hejna, A. Recycling of Waste Rubber by Thermo-Mechanical Treatment in a Twin-Screw Extruder. *Proceedings* **2021**, *69*, 10. https://doi.org/10.3390/CGPM2020-07195
14. Prociak, A.; Malewska, E.; Bąk, S. Influence of Isocyanate Index on Selected Properties of Flexible Polyurethane Foams Modified with Various Bio-Components. *J. Renew. Mater.* **2016**, *4*(1), 78–85. https://doi.org/10.7569/jrm.2015.634129
15. Lee, C.S.; Ooi, T.L.; Chuah, C.H.; Ahmad, S. Effect of isocyanate index on physical properties of flexible polyurethane foams. *Malaysia. J. Sci.* **2007**, *26*(2), 91–98
16. Zedler, Ł.; Kowalkowska-Zedler, D.; Colom, X.; Cañavate, J.; Saeb, M.R.; Formela, K. Reactive Sintering of Ground Tire Rubber (GTR) Modified by a Trans-Polyoctenamer Rubber and Curing Additives. *Polymers* **2020**, *12*, 3018. https://doi.org/10.3390/polym12123018
17. Hejna, A.; Kopczyńska, M.; Kozłowska, U.; Klein, M.; Kosmela, P.; Piszczyk, Ł. Foamed Polyurethane Composites with Different Types of Ash – Morphological, Mechanical and Thermal Behavior Assessments. *Cell. Polym.* **2016**, *35*(6), 287–308. https://doi.org/10.1177/026248931603500601
18. Vilar, W.D. Química e Tecnologia dos Poliuretanos, 2nd ed.; Vilar Consultoria Técnica Ltda.: Rio de Janeiro, Brazil, 1998.
19. Abdel Hakim, A.A.; Nassar, M.; Emam, A.; Sultan, M. Preparation and characterization of rigid polyurethane foam prepared from sugar-cane bagasse polyol. *Mater. Chem. Phys.* **2011**, *129*(1-2), 301–307. https://doi.org/10.1016/j.matchemphys.2011.04.008
20. Olcay, H.; Kocak, E.D. The mechanical, thermal and sound absorption properties of flexible polyurethane foam composites reinforced with artichoke stem waste fibers. J. Ind. Textile. **2020**, 152808372093419. https://doi.org/10.1177/1528083720934193