

Jakub Smoleń^{1*}, Karolina Olszowska², Marcin Godzierz²

¹ Silesian University of Technology, Faculty of Materials Engineering, ul. Z. Krasińskiego 8, 40-019 Katowice, Poland

² Centre of Polymer and Carbon Materials, Polish Academy of Sciences, ul. M. Curie-Skłodowskiej 34, 41-819 Zabrze, Poland

*Corresponding author: jakub.smolen@polsl.pl

Received (Otrzymano) 4.12.2021

COMPOSITES OF RIGID POLYURETHANE FOAM AND SHREDDED CAR WINDOW GLASS PARTICLES – STRUCTURE AND MECHANICAL PROPERTIES

This publication describes the effect of shredded (milled) car windows on the structure and mechanical properties of rigid polyurethane (PUR) foam. The multi-stage shredding (crushing + milling) process for car windows provides an effective method for reusing the material as a filler. The proposed method of the mechanical recycling of windshields is energy-consuming, which increases the costs of recycling processes. At the same time, this method is scalable, which allows the processes to be transferred from the laboratory to the industrial scale. The mechanical properties of the foams reinforced with shredded glass were assessed by performing a compression test in accordance with standard PN EN 826. The obtained results demonstrate the effectiveness in increasing the compressive strength for the two-component polyurethane foam with densities of 30, 50 and 70 kg/m³. The addition of milled glass in the amounts of 10, 20, 30% by weight increases the compressive strength of the rigid foams from 10 to even 90%. The filler particles create areas where new pores form, resulting in the reinforced PUR foams having more small pores than the neat PUR foams. The sharp edges of the glass particles act as “cutting blades” for the pores that form, which is manifested by the foil effect on the filler surface.

Keywords: windshield glass, recycling, rigid foams, mechanical properties, waste

INTRODUCTION

The use of PUR foams is often found in the production of pipeline and tank insulation, door construction insulation and reinforcement, in cooling systems, the filling of buoyancy chambers in ships or the building of bee hives and others [1]. A significant advantage of this material is the two-component composition that allows in situ production. Porous foam fills the entire volume of the chamber into which it is introduced. Due to the two-component composition of the foams, it is possible to transport them in a liquid form to the place of production of the final product, which is beneficial for the environment as this reduces the carbon footprint (compared to the transport of polystyrene boards). The most important advantages of PUR foams include very good thermal insulation, easy application, good adhesion to many types of substrate, good mechanical parameters, in addition to high efficiency. It is also widely used for the acoustic insulation of mechanical devices [2, 3]. In addition, PUR foams are often used in mechanical energy-absorbing solutions, which are important in automotive or other branches [4, 5].

Among the numerous descriptions of PUR foam reinforcement with particles, fillers in the form of shredded waste materials can be found, e.g. solid waste from leather production [6], agricultural wastes (rapeseed straw, rice straw, wheat straw, corn stover) [7], steel slag waste [8, 9], textile wastes [10] or milled PET

waste [11]. Fibrous fillers, including ground GFRP and CFRP composites, are also common [12-14]. Organic particles are a popular filler for rigid PUR foams, e.g. walnut shells, egg shells, potato proteins and sugar beet pulp [15-18]. Organic particles generally result in ecological improvement of the materials [19, 20]. The last PUR filler often reported in the literature is ceramic particles [21, 22].

The aim of this article is to propose a method of managing waste car window glass, containing certain amounts of PVB foil, as a filler for rigid polyurethane foam. Reusing car windows is important as they are a source of large amounts of undeveloped waste. Car windows have a multi-material composition resulting from the presence of PVB film between the glass layers. The task of the foil is to ensure safety in the event of an accident by maintaining its integrity. The tear-resistant foil is strongly bonded to the glass surface, which means that the glass fragments do not injure passengers upon impact. The processing of such material waste poses technological problems. The current state of knowledge on car glass recycling is wide, as evidenced by numerous publications [23-25]. The method of car glass management proposed in this article may be a favorable method of mechanical recycling, contributing to improvement of the properties of rigid polyurethane foams used in various constructions [26, 27].

EXPERIMENTAL PROCEDURE

In this work, automotive glass waste from a local car dismantling and recycling company – KAPADORA (Żory, Poland) was used. The waste was collected as mixed broken glass particles (Fig. 1). In the first stage of using automotive glass, it is necessary to separate all the non-glazed objects, especially metal objects that may damage the milling equipment in the subsequent stages. After removing the undesirable objects from the glass cullet and drying the waste in a laboratory dryer (temperature 120°C, time 6 h), the waste was milled using a Retsch SK 300 cross beater mill with 0.5 mm separation sieves. The ground car glass was examined by means of scanning electron microscopy (SEM Hitachi S-4200) to ascertain the grain morphology of the material. The Thermo Noran System 7 was employed to determine the chemical composition of the glass particles (EDS).



Fig. 1. Contaminated glass cullet from car windows

The rigid polyurethane foams used in the study were purchased from Minova Ekochem (Siemianowice Śląskie, Poland). The U30, U50 and U70 foams were used, whose names refer to the foam density, respectively 30, 50 and 70 kg/m³. The foam system consists of two components A and B. Component A is a mixture of polyols, auxiliaries and a foaming agents. Component B is an isocyanate of the *p*-MDI type. The A and B components were mixed together in a weight ratio of 100:120. The ingredients were poured into a dry container in the appropriate proportions and intensively mixed with a mechanical stirrer at a rotational speed of 1200 rpm for about 10 seconds. Afterwards, the mixture was poured into the final growth space. In the study, the PUR foam was cast into plastic molds (HDPE) with the dimensions 120x120x70 mm. The molds were open at the top. Four series of samples were made for each foam density, whose compositions and designations are presented in Table 1.

Rigid polyurethane foam specimens were cut to 100x100x50 mm in size with an electric cutter. Compression tests were performed utilizing an INSTRON 4469 machine at the travel speed $v = 5$ mm/min. The compression tests were carried out in accordance

with the PN EN 826 standard and the structure of the material was described using a scanning electron microscope, Quanta 250 FEG (FEI).

TABLE 1. Compositions and designations of samples

	PUR foam (30 kg/m ³)	PUR foam (50 kg/m ³)	PUR foam (70 kg/m ³)
without additives	U30	U50	U70
+ 10 wt.% milled glass waste	U30 (+10%)	U50 (+10%)	U70 (+10%)
+ 20 wt.% milled glass waste	U30 (+20%)	U50 (+20%)	U70 (+20%)
+ 30 wt.% milled glass waste	U30 (+30%)	U50 (+30%)	U70 (+30%)

RESULTS AND DISCUSSION

The morphology (SEM) of the cullet grains after grinding is presented in Figure 2. The glass pieces are characterized by a rectangular shape with clear, sharp edges. Most of the glass particles are about 200÷300 µm in length and 50÷100 µm in width. On the walls, remnants of the PVB foil are visible, which is bonded to the glass by strong adhesive bonds. During grinding, the PVB foil melts and crumbles, which leads to its partial fragmentation.

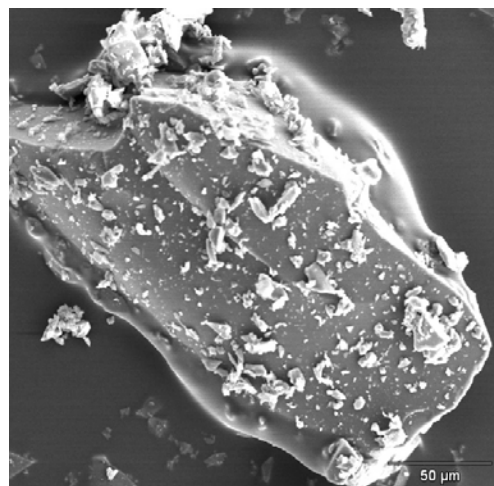


Fig. 2. Morphology of milled car windshield glass particles (SEM)

The results of the performed compression tests are presented in Figure 3. All the PUR foam specimens are characterized by an elastic behavior range of 5 mm, so they are elastic up to 10% compression. Further compression of the sample leads to its destruction. The transition from elastic deformation to destruction is the least marked in the series of foams with the density of 30 kg/m³ (Fig. 3a). The specimen of pure U30 foam does not show a typical inflection of the curve in the diagram; therefore, it can be assumed that it does not

exhibit any clear elasticity and its destruction occurs when it is loaded with a force of $1 \div 1.5$ kN. The course of the compression curve for the specimens with the addition of milled glass is similar, but different from the specimen without the addition of glass (Fig. 3a). The highest load value recorded in the compression test was obtained by the sample with the 10 wt.% glass content (U30 (+10%)), and the lowest load for the specimen without the addition of glass (U30).

For the series of specimens with densities of 50 and 70 kg/m³, the compression test behavior is different from that of the 30 kg/m³ series, and the compression curves are similar to each other, regardless of the addition of glass. In both series, there is a difference in the maximum load, which was recorded for the pure PUR foam, both U50 (Fig. 3b) and U70 (Fig. 3c) as the lowest load. For the U50 series (Fig. 3b) the maximum load is the highest for the samples with the 20 and 30 wt.% glass addition. For the U70 series (Fig. 3c) the maximum load was recorded for the specimen with the 30 wt.% glass addition.

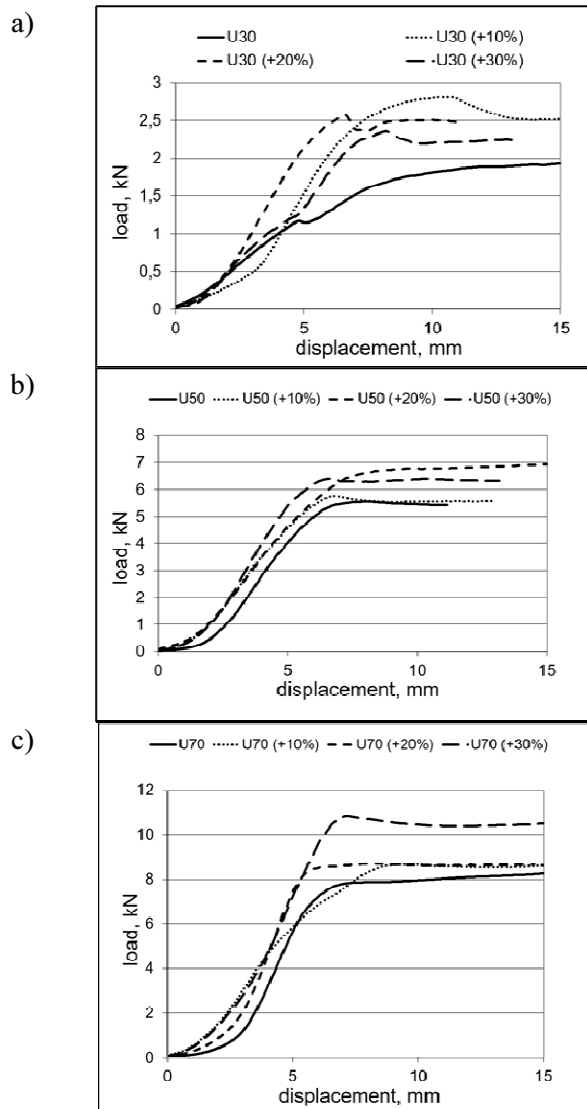


Fig. 3. Results of static compression test for PUR foams with densities of: a) 30 kg/m³, b) 50 kg/m³, c) 70 kg/m³

Figure 4 presents the results of the compressive strength. The compressive strength increases with the density of the foam; thus, the lowest values were recorded in the U30 series (Fig. 4a) and the highest values in the U70 series (Fig. 4c). For the U30 series of specimens, the highest increase in shear strength was recorded for the specimen with 10% by weight of glass (Fig. 4a), where the growth in the value was 91%. The addition of 20 wt.% causes an increase of 76 and the 30 wt.% content results in a rise of 61%. The high value of the compressive strength in the U30 (+10%) specimen may indicate a favorable distribution of glass particles in the volume of polyurethane foam, contributing to a significant increment in stiffness. Higher levels of glass additive also raise the compressive strength, but not as much as the 10 wt.% additive, which may be due to the reduced possibility of pore growth caused by the increased proportion of glass particles.

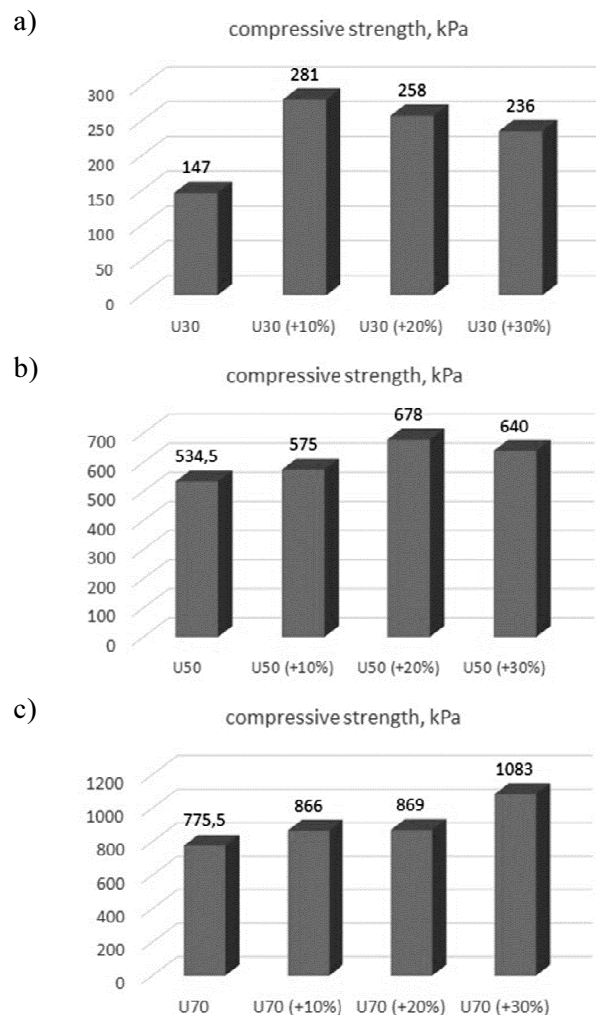


Fig. 4. Compressive strength of rigid PUR foams for: a) U30, b) U50, c) U70 series, according to PN EN 826

For the U50 series (Fig. 4b), the highest increase in compressive strength was recorded for the U50 (+20%) specimen, where the value increased by 27%. A similar rise in value was recorded for the 30 wt.% glass addi-

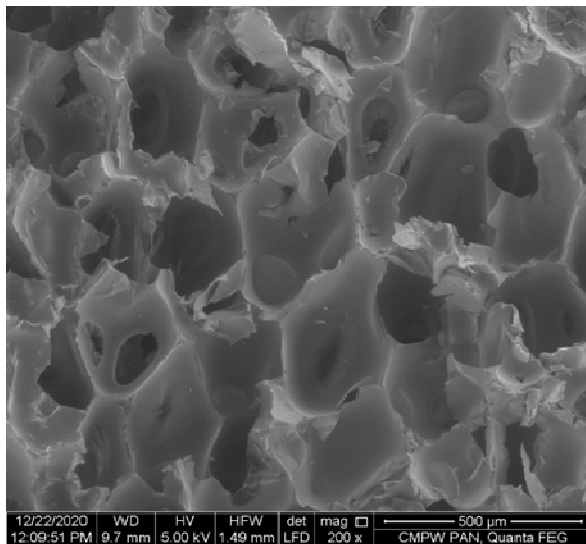
tion, where the growth in strength was 20%. Only the U50 (+10%) specimen has a slight increase in compressive strength, less than 10%, which can be considered ineffective. The U70 series specimens (Fig. 4c) exhibit an increment in compressive strength with an increase in glass content. The highest value was registered for the sample with the 30 wt% glass addition (1083 kPa), and the growth in the value in relation to the U70 specimen was about 40%. The specimens with the 10 wt.% and 20 wt.% glass additions have an approximate increase of 12%.

Figure 5 shows the foam morphology recorded by scanning electron microscopy for the intermediate series of U50 specimens. The glass-free specimen (Fig. 5a) has pores of a regular, elongated shape with the dimensions $200 \times 400 \mu\text{m}$, following the direction of PUR foam growth in the mold. The specimens with the addition of glass are characterized by a regular, round

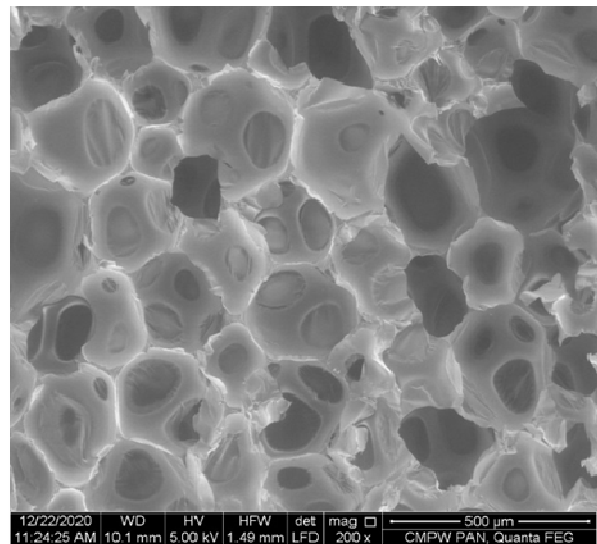
shape of pores, which proves that the ground glass affects the process of foaming and foam growth. As the glass content increases, the number of small pores inside the large pores rises, possibly because the particles are the nucleation sites for new pores. The largest amount of small porosities is visible in the U50 specimen with 20% by weight of glass (Fig. 5c). At the same time, the large pores in the foam tend to break as the glass content increases, possibly be due to the morphology of the ground glass particles, which have sharp edges that act as a cutting blade.

The glass particles are located at the pore border, as shown in Figure 6. Individual pieces of glass are covered with polyurethane, which forms a thin film on the surface of the glass. The foil is frayed as a result of cutting the polyurethane with the glass edge during PUR foaming. The formation of pores very often begins at the corners of the glass grains.

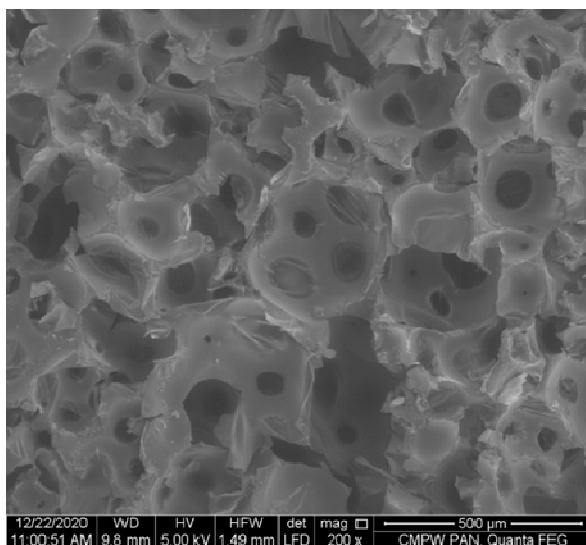
a)



b)



c)



d)

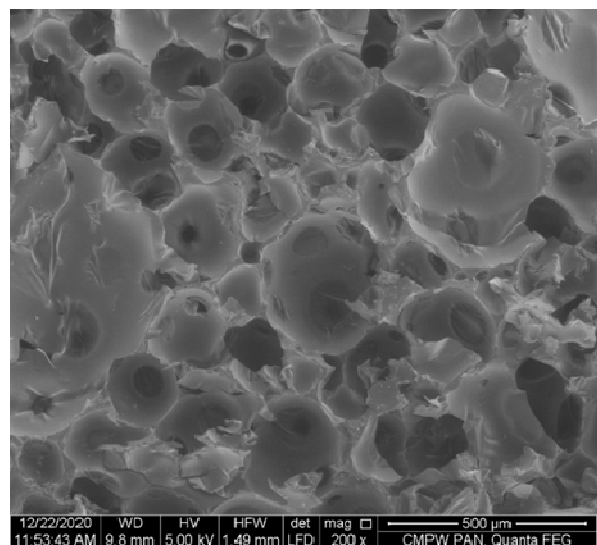


Fig. 5. Morphology of rigid PUR foams in U50 series, SEM: a) U50, b) U50 (+10%), c) U50 (+20%), d) U50 (+30%)

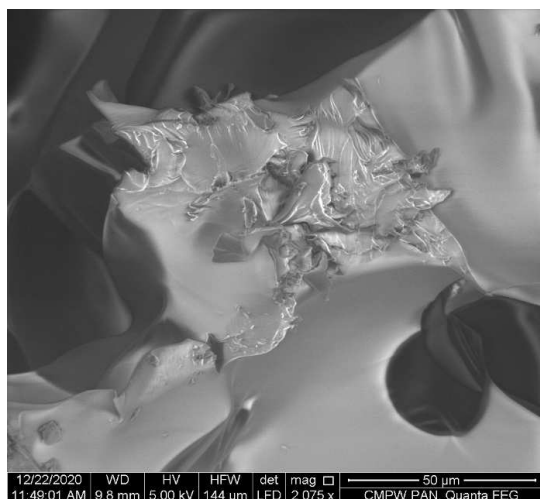


Fig. 6. Single glass grain in U50 (+30%) specimen, SEM

CONCLUSIONS

The proposed method of recycling car windshield glass, contaminated with PVB foil, is effective and enables effective waste management. The mechanical recycling of car windows is a multi-stage process that requires the use of high-energy mills to obtain grains below 0.5 mm. The use of milled glass as reinforcement in rigid PUR foams intended for sealing and filling constructions is beneficial and raises the compressive strength. The most significant growth in foam strength was achieved by the PUR foams with the density of 30 kg/m³, which results from the favorable distribution of glass particles in the foam. For the PUR foams with the density of 50 kg/m³, the best effect was achieved with the 20 and 30% by weight additions of glass. For the foam with the density of 70 kg/m³, the best effect of augmenting the compressive strength was exhibited by the specimen with 30% by weight of glass. The glass grains are located at the pore boundaries and during PUR foaming, the pores are cut by the sharp glass edges, which contributes to an increment in the number of small pores in the material. It is believed that increasing the number of small pores at the boundaries of the large pores contributes to the effective rise in the compressive strength. The addition of ground automotive glass to PUR foams is a cost effective and eco-friendly method for improving the strength of the foams.

Acknowledgements

The study was realized at Faculty of Materials Engineering, Silesian University of Technology, within statutory research project BK-231/RM3/2021.

REFERENCES

- [1] Gama N.V., Ferreira A., Barros-Timmons A., Polyurethane foams: Past, present, and future, *Materials* 2018, 11, 10, 1841, DOI: 10.3390/ma11101841.
- [2] Asadi Khanouki M., Ohadi A., Improved acoustic damping in polyurethane foams by the inclusion of silicon dioxide nanoparticles, *Advances in Polymer Science* 2018, 37, 8, 2799-2810, DOI: 10.1002/adv.21952.
- [3] Figlus T., Koziol M., Kuczyński Ł., The effect of selected operational factors on the vibroactivity of upper gearbox housings made of composite materials, *Sensors* 2019, 19, 4240, DOI: 10.3390/s19194240.
- [4] Linul E., Serban D.A., Voiconi T., Marsavina L., Sadowski T., Energy-absorption and efficiency diagrams of rigid PUR foams, *Key Engineering Materials* 2014, 601, 246-249, DOI: 10.4028/www.scientific.net/kem.601.246.
- [5] Koziol M., Evaluation of classic and 3D glass fiber reinforced polymer laminates through circular support drop weight tests, *Composites Part B* 2019, 168, 561-571, DOI: 10.1016/j.compositesb.2019.03.078.
- [6] Członka S., Bertino M.F., Strzelec K., Strąkowska A., Masłowski M., Rigid polyurethane foams reinforced with solid waste generated in leather industry, *Polymer Testing* 2018, 69, 225-237, DOI: 10.1016/j.polymertesting.2018.05.013.
- [7] Zhang J., Hori N., Takemura A., Reinforcement of agricultural wastes liquefied polyols based polyurethane foams by agricultural wastes particles, *Journal of Applied Polymer Science* 2021, 138(23), 50583, DOI: 10.1002/app.50583.
- [8] Tang G., Liu X., Zhou L., Zhang P., Deng D., Jiang H., Steel slag waste combined with melamine pyrophosphate as a flame retardant for rigid polyurethane foams, *Advanced Powder Technology* 2020, 31(1), 279-286, DOI: 10.1016/j.apt.2019.10.020.
- [9] Tang G., Liu X., Yang Y., Chen D., Zhang H., Zhou L., Zhang P., Jiang H., Deng D., Phosphorus-containing silane modified steel slag waste to reduce fire hazards of rigid polyurethane foams, *Advanced Powder Technology* 2020, 31(4), 1420-1430, DOI: 10.1016/j.apt.2020.01.019.
- [10] Tiuc A.E., Vermeşan H., Gabor T., Vasile O., Improved sound absorption properties of polyurethane foam mixed with textile waste, *Energy Procedia* 2016, 85, 559-565, DOI: 10.1016/j.egypro.2015.12.245.
- [11] de Mello D., Pezzin S.H., Amico S.C., The effect of post-consumer PET particles on the performance of flexible polyurethane foams, *Polymer Testing* 2009, 28(7), 702-708, DOI: 10.1016/j.polymertesting.2009.05.014.
- [12] Xue B.L., Wen J.L., Sun R.C., Lignin-based rigid polyurethane foam reinforced with pulp fiber: synthesis and characterization, *ACS Sustainable Chemistry & Engineering* 2014, 2(6), 1474-1480, DOI: 10.1021/sc5001226.
- [13] Barczewski M., Kurańska M., Sałasińska K., Michałowski S., Prociak A., Uram K., Lewandowski K., Rigid polyurethane foams modified with thermoset polyester-glass fiber composite waste, *Polymer Testing* 2020, 81, 106190, DOI: 10.1016/j.polymertesting.2019.106190.
- [14] Kim S.H., Park H.C., Jeong H.M., Kim B.K., Glass fiber reinforced rigid polyurethane foams, *Journal of Materials Science* 2010, 45(10), 2675-2680, DOI: 10.1007/s10853-010-4248-3.
- [15] Członka S., Strąkowska A., Kairyte A., Effect of walnut shells and silanized walnut shells on the mechanical and thermal properties of rigid polyurethane foams, *Polymer Testing* 2020, 87, 106534, DOI: 10.1016/j.polymertesting.2020.106534.
- [16] Zieleniewska M., Leszczyński M.K., Szczepkowski L., Bryśkiewicz A., Krzyżowska M., Bień K., Ryszkowska J., Development and applicational evaluation of the rigid polyurethane foam composites with egg shell waste, *Polymer Degradation and Stability* 2016, 132, 78-86, DOI: 10.1016/j.polyimdegradstab.2016.02.030.
- [17] Członka S., Bertino M.F., Strzelec K., Rigid polyurethane foams reinforced with industrial potato protein, *Polymer*

- Testing 2018, 68, 135-145, DOI: 10.1016/j.polymertesting.2018.04.006.
- [18] Strąkowska A., Członka S., Kairyte A., Rigid polyurethane foams reinforced with poss-impregnated sugar beet pulp filler, *Materials* 2020, 13(23), 5493, DOI: 10.3390/ma13235493.
- [19] Hejna A., Korol J., Kosmela P., Kuzmin A., Piasecki A., Kulawik A., Chmielnicki B., By-products from food industry as a promising alternative for the conventional fillers for wood-polymer composites, *Polymers* 2021, 13, 6, 893, DOI: 10.3390/polym13060893.
- [20] Toroń B., Sziperlich P., Koziol M., SbSI composites based on epoxy resin and cellulose for energy harvesting and sensors – The influence of sbSI nanowires conglomeration on piezoelectric properties, *Materials* 2020, 13, 4, art. 902, DOI: 10.3390/ma13040902.
- [21] Cimavilla-Román P., Pérez-Tamarit S., Santiago-Calvo M., Rodríguez-Pérez M.Á., Influence of silica aerogel particles on the foaming process and cellular structure of rigid polyurethane foams, *European Polymer Journal* 2020, 135, 109884, DOI: 10.1016/j.eurpolymj.2020.109884.
- [22] Kim M.W., Kwon S.H., Park H., Kim B.K. Glass fiber and silica reinforced rigid polyurethane foams, *eXPRESS Polymer Letters* 2017, 11(5), DOI:10.3144/expresspolymlett.2017.36.
- [23] Smoleń J., Pawlik T., Sopicka-Lizer M., Michalik D., Structure and properties of lightweight ceramic aggregates based on local silesian waste materials, *Arch. Metall. Mater.* 2018, 63(3), 1321-1328, DOI: 10.24425/123807.
- [24] Godzierz M., Adamczyk B., Pawlik T., Sopicka-Lizer M., Mechanical and physical properties of light-weight ceramic aggregates prepared from waste materials, *Waste Biomass, Valorization* 2020, 11(5), 2309-2319, DOI: 10.1007/s12649-018-0464-x.
- [25] Tupy M., Mokrejs P., Merinska D., Svoboda P., Zvonicek J., Windshield recycling focused on effective separation of PVB sheet, *Journal of Applied Polymer Science* 2014, 131(4), DOI: 10.1002/app.39879.
- [26] Mutlu T., Yegin S.K., Sen G., Dirikolu M.H., Design and implementation of a glass fiber reinforced hybrid polymer matrix composite washing machine drum support replacing cast aluminum alloy, *Composites Theory and Practice* 2021, 21(1-2), 54-58.
- [27] Dhotre P.K., Chikkol S.V., Free vibration studies on skew sandwich plates, *Composites Theory and Practice* 2020, 20(3-4), 118-127.