Blackcurrant pomace as a biodegradable filler for rigid polyurethane foams

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Abstract

The dynamically rising costs of heating result in an increased interest in thermal insulation materials. The best thermal insulation material available on the market is a rigid polyurethane foam. The rise in mining prices of raw materials is disrupting the polyurethane industry, so it is imperative to reduce the amount of petrochemicals in foams. The aim of the article was to check the possibility of using blackcurrant pomace as a filler for polyurethane foams. First, rigid foam composites containing 10 wt.% of fruit processing waste were produced. The obtained materials were analyzed in terms of structure, basic parameters such as water absorption, dimensional stability, apparent density, mechanical properties and the impact of the aging process on the content of C, H, N elements. The conducted research showed that the pomace has antioxidant properties and has a positive effect on the mechanical properties. In addition, this type of filler has a positive effect on the delay in ignition of the foams.

Keywords: blackcurrant pomace, rigid polyurethane foam, biodegradable filler, fruit processing waste

I. INTRODUCTION

The price of heating and fuels in the European Union has risen sharply and has reached an unprecedented level. Therefore, it is necessary to perform thermal insulation for new buildings as well as for the existing ones. There are many products available on the building materials market, such as: mineral wool, polystyrene and polyurethane foams [1]. The main differences between these materials are the thermal conductivity coefficient (λ) and the price.

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Rigid polyurethane foam (RPUF) is the insulator most indicated due to the lowest heat conduction parameters. The λ value for commercial polyurethane foams ranges 0.02–0.04 $W \cdot m^{-1} \cdot K^{-1}$ [2]. RPUF is also popular for its other good properties: low density, biological and chemical inertness, as well as superior mechanical and hydrophobic properties [3][4]. In addition to insulating partitions of buildings, polyurethane foam is also used for pipes and refrigerators as an insulator [5], [6]. RPUFs are also used as light construction elements and in commercial refrigeration devices, but also in everyday objects, such as furniture and cars [7]–[11]. The biggest disadvantage of RPUF is its high price [12]. It is expensive due to fluctuations in the prices of the raw materials it is made of. Therefore, changes in the demand and supply of these raw materials can have a significant impact on the RPUF products. Therefore, many studies are conducted to reduce the amount of petrochemical products by partially replacing them with solid fillers. The use of fillers not only reduces the price of the polyurethane product, but also affects its properties and may increase the possibilities of its application. The use of waste as fillers is very popular. As a result, the by-product is additionally recycled. The used waste fillers can be divided according to their origin. An example of a filler of animal origin is feathers. Due to the issues of their disposal, they have been used in RPUF and have had a positive effect on the improvement of thermal and acoustic properties of the material [13], [14]. Fruit seeds and nut shells are also very popular fillers. Plant-based fillers are another group of fillers used in the RPUF industry. This type of filler includes fruit and vegetable pomace, fruit seeds[15] and nut shells [16], [17]. The above-mentioned natural fillers are characterized by the fact that their chemical composition often positively influences the mechanical, physical and thermal properties of foams [18]. Other fillers are those that come from the energy or steel industries. An example is fly ash from coal combustion, which has a positive effect on the reduction of flammability and reduces the rate of polymer degradation [19][20].

In this study, blackcurrant pomace was used as a filler. The evaluation of the application of this filler was based on the results showcased in the article. Namely - the results of research on the structure, physical properties, and strength properties of obtained composites. The novelties presented in the paper are the aging tests performed together with the determination of the elements C, H, N, and O, which allowed to assess the influence of blackcurrant pomace on the oxidation process of polyurethane foams. It should be emphasized that the currant pomace is a rich source of polyphenolic compounds with confirmed antiradical properties [21]. In the literature, there are studies on the use of currant pomace in flexible polyurethane foams [22]. The authors observed that the discussed additive increased the foam growth time and the reduction of the temperature of the foaming process. The density of the material also increased. The pomace additionally accelerated the degradation of the rigid polyurethane segments and slowed down the degradation of the soft segments. No information has been found in the literature on the use of currant waste in rigid polyurethane. The experiment described in the article may expand the use of currant pomace not only in the food industry, but also in the material technology and have a positive effect on the properties and price of rigid polyurethane foams. Additionally, the addition of blackcurrant pomace to the PU foams may create a new method of utilizing this type of waste. This waste constitutes 20-35% of the weight of the processed raw material [23].

II. MATERIALS AND METHODS

A. Preparation of the filler and rigid polyurethane foams

This article uses blackcurrant pomace as a filler for RPUF. Before introducing it into the foams, it was processed by drying it to a constant mass at the temperature of 105℃ and then, using a laboratory mill, the expeller was crushed to a powder form.

In order to analyze the filler used, the content of the elements (carbon, hydrogen, nitrogen) was examined, and is presented in Table 1.

Table 1. Elemental analysis of blackcurrant pomace

	C [%]	H [%]	N [%]
Blackcurrant pomace	49.20	6.94	2.26

The carbon content of blackcurrant pomace is over 49%, hydrogen is almost 7%, and nitrogen is just over 2%. These values do not differ from the chemical composition of agricultural and forest biomass. Blackcurrant pomace also contains a large amount of lignin, cellulose and hemicellulose.

Polyurethane foams were produced using the one-step method. A polyol masterbatch was mixed with an isocyanate to form a reference foam (PU_0), while a 10% foam (PU_10) with blackcurrant expeller was produced by introducing expeller into the polyol masterbatch and then adding the isocyanate. All ingredients were mixed with a mechanical agitator at a constant speed of 2000 rpm. RPUF were prepared using the two-component commercial system EKOPRODUR PM4032 (PCC Group, Poland).

The process of preparing the filler and foams is presented below (Figure 1).

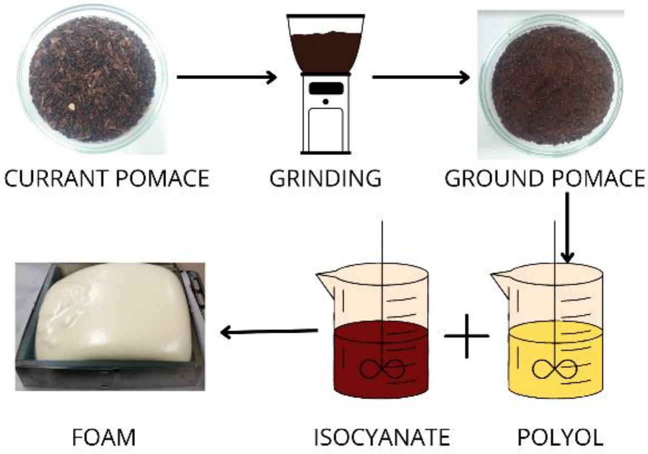

Figure 1. Scheme of preparation of the filler and RPUF

Polyurethane foam is produced by the intensive mixing of two main components: isocyanate and petroleum-derived polyol. During their mixing, additives such as catalysts and stabilizers are also added, which can create different properties of the polyurethane [24].

B. Methods

The microstructure of the obtained polyurethane composites was determined at a magnification of 6x using an optical microscope (Vision Engineering SX 45).

The apparent density of the material was tested on the basis of the EN ISO 845:2009 standard.

The water absorption of the foams was determined in accordance with the ASTM D570-98 standard by determining their starting weight, then after 5 minutes, 3 hours and 24 hours of a water bath.

The dimensional stability of polyurethane materials was determined in accordance with the PN-92/C89083 standard by testing the length change before the aging process, after 20 h and 40 h of the aging process, which was carried out at the temperature of 150℃.

The analysis of carbon, hydrogen, nitrogen and oxygen elements was carried out for the obtained materials in order to assess the aging process through the action of UV light and water spray as well as the actual weather conditions.

The brittleness of the obtained foams was analyzed according to the ASTM C 421-08 standard.

The compressive strength of the foam was determined in accordance with EN ISO 14125:198. In the test, the value of the given relative deformation was equal to 10%.

Flammability parameters were tested, such as: limit oxygen index (LOI) based on the PN-EN ISO 4589-2: 2006 standard, the UL 94V foam flammability test in accordance with the PN-EN 60695-11-10: 1999 standard and reaction to fire by determination of the grass calorific value (ISO 1716: 2018). Flammability tests were also carried out on a cone calorimeter, determining the characteristic parameters (average heat release rate (HRR), maximum heat release rate (PHRR), effective heat of combustion (EHC), time to ignition (TTI), percentage mass loss (PML)).

III. RESULTS

A. Physical properties of PU foams

The water absorption of the foam is summarized in Table 2. Based on the analysis of the results, it can be concluded that the water absorption increases most rapidly in the first minutes of immersion. The absorbency value increases with the passage of time. In both cases, the foam soaks up water, however, for PU_10 foam, the increase in water absorption is significantly lower.

Table 2. Water absorption of rigid polyurethane foams

Sample	Water absorption [%]		
	5 min	3h	24h
PU_0	14.48	24.68	36.14
PU_10	12.63	15.32	34.55

The reduction in absorbency is most likely due to the cellulose in the filler, which disperses inside and over the edges of the cells, thus blocking the foam from absorbing moisture [15]. The changes in dimensions and mass of samples after 20 and 40 h of conditioning at 150 ° C are shown in Table 3.

Table 3. Dimensional stability and weight loss of rigid polyurethane foams

Sample	Dimensional stability		Loss in mass	
	(Δl, 20h, 150°C) [%]	(Δl, 40h, 150°C) [%]	(Δm, 20h, 150°C) [%]	(Δm, 40h, 150°C) [%]
PU_0	3.86	4.18	9.23	9.23
PU_10	1.33	1.79	11.36	11.36

Basically three times lower values of linear stability were obtained for the PU_10 sample as compared to the reference foam. This ratio was maintained after both 20 and 40 hours. The improved dimensional stability for cellulose-containing foams was also confirmed by M. Szpiłyk et al. [25]. The weight loss stabilized and remained unchanged after 40 h. The difference between the samples amounts to approx. 2% due to the moisture contained in the filler, which evaporated during the conditioning.

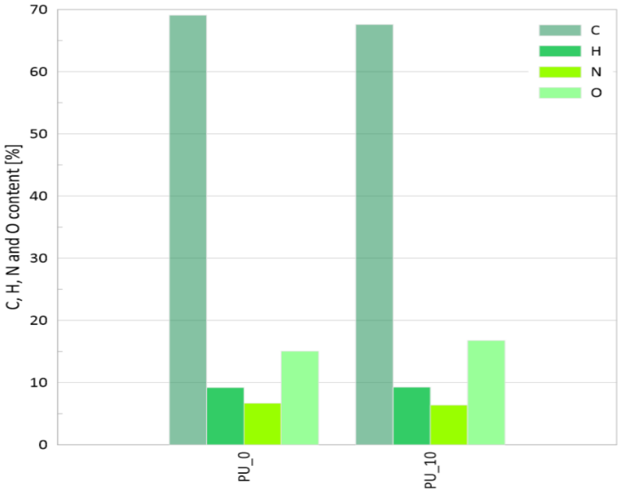

Figure 2 Elemental analysis of C, H, N and O of rigid polyurethane foams

Figure 2 shows the elemental analysis of basic foams. Compared to both foams, PU_0 has a higher carbon content and a lower oxygen content compared to PU-10. The other two elements, that is N and H, in both of the foams are at a comparable level.

Figure 3 shows the elemental analysis after an artificially created aging process. The foams were treated with UV light and water spray. Comparing with Figure 1, it can be seen that in both samples the carbon content remained at the same level, the hydrogen content in PU_0 decreased and the nitrogen and oxygen content increased slightly. At the same time, in the case of PU_10, the hydrogen content increased, the nitrogen content decreased, and the oxygen content decreased compared to the unmodified foam.

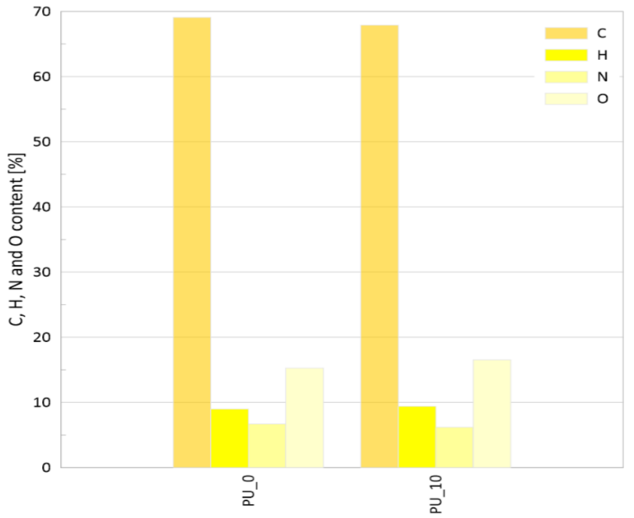

Figure 3 Elemental analysis of C, H, N and O of rigid polyurethane foams subjected to water spray and UV light

Figure 4 shows the results of the analysis for foams exposed to natural weather conditions. PU_0 has a lower carbon content, a higher hydrogen, nitrogen and oxygen content. In PU_10, the carbon content remains constant, the hydrogen and nitrogen content increases, but the oxygen content drops significantly from 16.77% for unmodified foam to 14.57% for the foam placed under the action of atmospheric conditions. Generally, foam modified with blackcurrant expeller filler is more resistant to artificial and real atmospheric conditions than PU_0. This is confirmed by the fact that such pomaces act as antioxidant substances.

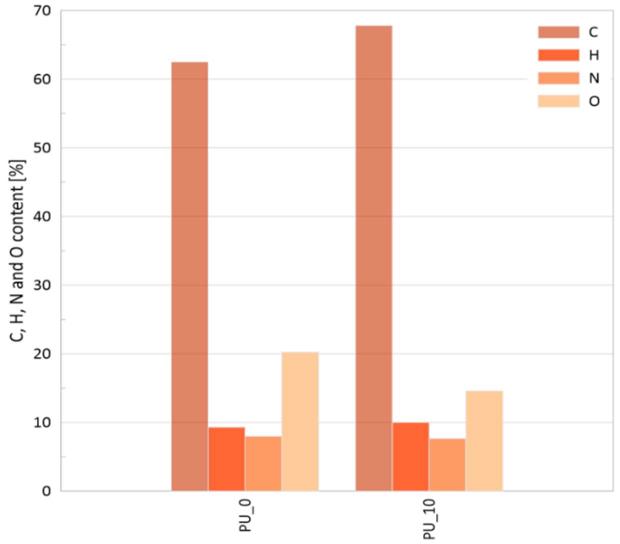

Figure 4 Elemental analysis of C, H, N and O of rigid polyurethane foams exposed to real atmospheric conditions

Such analyzes are very important from the point of using RPUF as insulating materials. In the literature, one of the main causes of aging of polyurethane insulations is the phenomenon of gas diffusion. As a result of oxygen and nitrogen entering the foam structure, cellular gases such as carbon dioxide and cyclopentane are forced out, which results in an increase in heat conduction coefficient [26].

B. The structure of PU foams

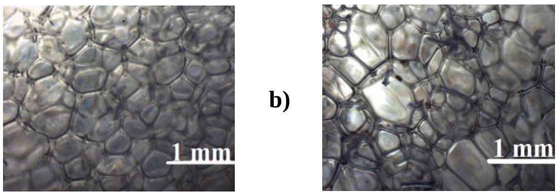

Figure 5. Structure of rigid polyurethane foams: a)PU_0, b)PU_10

The cellular structure of rigid polyurethane foam has a considerable impact on the mechanical properties. The photos from the optical microscope are summarized in Figure 2. PU_0 foam cells are characterized by similar dimensions, there is no large fluctuation in the values of the diameters. In the case of PU_10 foam, the morphology is more diversified, the cells are elongated and do not resemble spheres as for the reference foam. The presence of such a cell shape is related to the high reactivity of the polyurethane system. As a result, the currant pomace intensified the process of cell nucleation. This thesis is confirmed by examples from the literature in which the cellulosic filler caused the growth of the cells of the polyurethane composite [27], [28].

C. Mechanical properties of PU foams

Table 4. Apparent density and mechanical properties of rigid polyurethane foams

Sample	Apparent density [kg·m^{-3}]	Brittleness [%]	Compressive strength [MPa]	Young's modulus [MPa]
PU_0	36.09	16.98	0.04	6.70
PU_10	33.82	11.63	0.07	8.96

The literature shows that the apparent density of polyurethane foams is related to the mechanical properties. It is an important parameter therefore it has been determined that a typical RPUF should have a density in the range of 28-60 [kg·m^{-3}] [29]. PU_0 had an apparent density of about 36 [kg·m^{-3}], while the apparent density of PU_10 was almost 34 [kg·m^{-3}]. Both values fall within the defined range (Table 4). The literature also describes cases where the introduction of the filler resulted in a reduction of the apparent density in relation to the reference foam [30].

From the strength tests performed, a positive effect of this type of filler on the mechanical properties of RPUF can be observed. The maximum compressive strength increases (Table 4). The stress-strain diagram shows that the strength improved almost twice after introducing the filler at a load of 10%. From the presented graph, you can see three stages of degradation during compression [31].

Table 4 also shows the results of the brittleness testing of the foams obtained. They show that blackcurrant pomace has a positive effect on brittleness because it reduces it. The brittleness results are correlated with the apparent density of foams [32]. Other researchers received similar conclusions that introducing the filler to a specific concentration has a positive effect on the mechanical properties of polyurethane foams [33].

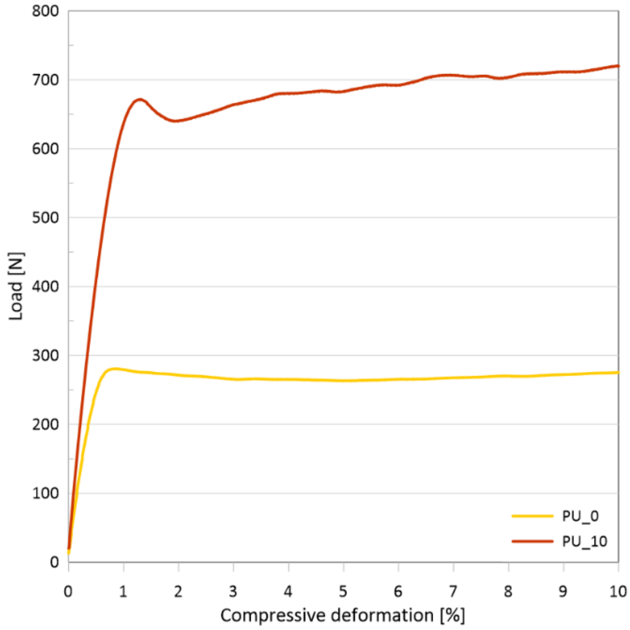

Figure 5. Compressive deformation of rigid polyurethane foams

D. Flammability of PU foams

The flammability of polyurethane foams is an important aspect because they are used as thermal insulation materials, so they should have a specific flammability class. Additionally, as RPUF burns down, many toxic gases are released into the atmosphere [34].

For the analyzed materials, the LOI was determined (Table 5), which for PU_0 was 21.4%, and for PU_10 - 20.7%, which is unfavorable in terms of planarity, because it means that the foam with a filler requires less amount of oxide to maintain the flame. Also, in the reaction to fire test, it was found that introducing the filler into the foam increases the heat value.

Table 5. Gross calorific value, LOI values, UL-94 vertical burning behaviors of rigid polyurethane foams

Sample	LOI [%]	Gross calorific value (MJ*kg^{-1})	UL94 V
PU_0	21.4	25.98	N.R
PU_10	20.7	26.02	N.R

The obtained results from the cone calorimeter show that PU_0 ignites faster compared to PU_10 (Table 6). In the context of the possibility of using polyurethane foams as thermal insulation materials, the HRR and PHRR parameters are very important. The first parameter was smaller for PU_10, while in the case of maximum heat release it was the other way round. Generally, the construction law stipulates that the RPUF should have a maximum PHRR of 300 [kW/m^2] [35], [36].

Table 6. Cone calorimeter results of rigid polyurethane foams

Sample	TTI [s]	EHC [MJ/kg]	HRR [kW/m^2]	PHRR [kW/m^2]	PML [%]
PU_0	4	7.98	63.88	77.70	85.7
PU_10	6	9.63	57.80	79.11	80.8

IV. Conclusions

The paper presents the results of research on a polyurethane foam and a polyurethane composite containing 10% of blackcurrant pomace. The addition of a filler has many benefits in reducing the amount of petrochemicals in the foam, reducing production costs and improving some properties. The currant pomace acts as a blockage in the foam and hinders water absorption and increases the dimensional stability of the sample. Compared to the reference sample, the stability is three times higher after both 20 and 40 hours. Additionally, the simulations of the insulation aging process confirm the antioxidant effect of blackcurrant pomace. The foam modified with this filler degraded less as shown by the elements analysis. Moreover, the discussed filler intensified the process of nucleation of bubbles during foam growth. In the case of the reference foam, the foam structure consisted of spherical cells similar in size. In PU_10 foam, the bubbles are elongated and their diameters are more diversified. The filler lowers the apparent density of the foam, which is closely related to the mechanical parameters. The foams containing the filler also showed almost twice the compressive strength, but also lower brittleness, which confirms the positive effect of the filler on the mechanical properties. The differences in the gross calorific value and the LOI index between the samples are similar. The addition of the filler extended the ignition time of the foam and reduced the amount of average heat released.

V. ACKNOWLEDGMENTS

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VI. REFERENCES

[1] A. M. Binyaseen, "Improving thermal performance of existing uninsulated R.C. domes through passive cooling measures using polyurethane foam in double skin layer in hot climate.," *Case Studies in Construction Materials*, vol. 16, p. e00866, Jun. 2022, doi: 10.1016/J.CSCM.2021.E00866.

[2] M. Krarti, "Advanced Building Energy Efficiency Systems," *Optimal Design and Retrofit of Energy Efficient Buildings, Communities, and Urban Centers*, pp. 45–115, Jan. 2018, doi: 10.1016/B978-0-12-849869-9.00002-8.

[3] S. Członka, M. F. Bertino, K. Strzelec, A. Strąkowska, and M. Masłowski, "Rigid polyurethane foams reinforced with solid waste generated in leather industry," *Polymer Testing*, vol. 69, 2018, doi: 10.1016/j.polymertesting.2018.05.013.

[4] D. Xu, K. Yu, and K. Qian, "Thermal degradation study of rigid polyurethane foams containing tris(1-chloro-2-propyl)phosphate and modified aramid fiber," *Polymer Testing*, vol. 67, pp. 159–168, May 2018, doi: 10.1016/J.POLYMERTESTING.2018.01.034.

[5] A. A. Mahmoud, E. A. A. Nasr, and A. A. H. Maamoun, "The Influence of Polyurethane Foam on the Insulation Characteristics of Mortar Pastes," *Journal of Minerals and Materials Characterization and Engineering*, vol. 05, no. 02, 2017, doi: 10.4236/jmmce.2017.52005.

[6] A. Strakowska, S. Członka, and K. Strzelec, "POSS compounds as modifiers for rigid polyurethane foams (Composites)," *Polymers (Basel)*, vol. 11, no. 7, 2019, doi: 10.3390/polym11071092.

[7] S. Członka, A. Strąkowska, K. Strzelec, A. Kairytė, and S. Vaitkus, "Composites of rigid polyurethane foams and silica powder filler enhanced with ionic liquid," *Polymer Testing*, vol. 75, pp. 12–25, May 2019, doi: 10.1016/j.polymertesting.2019.01.021.

[8] G. Bo *et al.*, "Synthesis and characterization of flame-retardant rigid polyurethane foams derived from gutter oil biodiesel," *European Polymer Journal*, vol. 147, Mar. 2021, doi: 10.1016/j.eurpolymj.2021.110329.

[9] L. Qian, L. Li, Y. Chen, B. Xu, and Y. Qiu, "Quickly self-extinguishing flame retardant behavior of rigid polyurethane foams linked with phosphaphenanthrene groups," *Composites Part B: Engineering*, vol. 175, Oct. 2019, doi: 10.1016/j.compositesb.2019.107186.

[10] S. Członka, M. F. Bertino, and K. Strzelec, "Rigid polyurethane foams reinforced with industrial potato protein," *Polymer Testing*, vol. 68, pp. 135–145, Jul. 2018, doi: 10.1016/j.polymertesting.2018.04.006.

[11] W. Xi, L. Qian, Z. Huang, Y. Cao, and L. Li, "Continuous flame-retardant actions of two phosphate esters with expandable graphite in rigid polyurethane foams," *Polymer Degradation and Stability*, vol. 130, pp. 97–102, Aug. 2016, doi: 10.1016/j.polymdegradstab.2016.06.003.

[12] M. Kurańska, A. Prociak, S. Michałowski, and K. Zawadzińska, "The influence of blowing agents type on foaming process and properties of rigid polyurethane foams," *Polimery/Polymers*, vol. 63, no. 10, 2018, doi: 10.14314/polimery.2018.10.2.

[13] M. Khaleel, U. Soykan, and S. Çetin, "Influences of turkey feather fiber loading on significant characteristics of rigid polyurethane foam: Thermal degradation, heat insulation, acoustic performance, air permeability and cellular structure," *Construction and Building Materials*, vol. 308, 2021, doi: 10.1016/j.conbuildmat.2021.125014.

[14] S. Członka, N. Sienkiewicz, A. Strąkowska, and K. Strzelec, "Keratin feathers as a filler for rigid polyurethane foams on the basis of soybean oil polyol," *Polymer Testing*, 2018, doi: 10.1016/j.polymertesting.2018.09.032.

[15] M. Leszczyńska *et al.*, "Vegetable fillers and rapeseed oil-based polyol as natural raw materials for the production of rigid polyurethane foams," *Materials*, vol. 14, no. 7, 2021, doi: 10.3390/ma14071772.

[16] Md. T. Islam *et al.*, "Effect of Coconut Shell Powder as Filler on the Mechanical Properties of Coir-polyester Composites," *Chemical and Materials Engineering*, vol. 5, no. 4, 2017, doi: 10.13189/cme.2017.050401.

[17] S. Członka, A. Strąkowska, and A. Kairytė, "Effect of walnut shells and silanized walnut shells on the mechanical and thermal properties of rigid polyurethane foams," *Polymer Testing*, vol. 87, 2020, doi: 10.1016/j.polymertesting.2020.106534.

[18] M. Leszczyńska, J. Ryszkowska, and L. Szczepkowski, "Rigid polyurethane foam composites with nut shells," in *Polimery/Polymers*, 2020, vol. 65, no. 10, pp. 728–737. doi: 10.14314/polimery.2020.10.8.

[19] B. Zygmunt-Kowalska, K. Pielichowska, P. Trestka, M. Ziąbka, and M. Kuźnia, "The Effect of Ash Silanization on the Selected Properties of Rigid Polyurethane Foam/Coal Fly Ash Composites," *Energies (Basel)*, vol. 15, no. 6, 2022, doi: 10.3390/en15062014.

[20] M. Kuźnia *et al.*, "Fluidized bed combustion fly ash as filler in composite polyurethane materials," *Waste Management*, 2019, doi: 10.1016/j.wasman.2019.05.012.

[21] A. Michalska, A. Wojdyło, G. P. Łysiak, K. Lech, and A. Figiel, "Functional relationships between phytochemicals and drying conditions during the processing of blackcurrant pomace into powders," *Advanced Powder Technology*, vol. 28, no. 5, 2017, doi: 10.1016/j.apt.2017.03.002.

[22] M. Auguścik-Królikowska *et al.*, "Composites of open-cell viscoelastic foams with blackcurrant pomace," *Materials*, vol. 14, no. 4, pp. 1–22, 2021, doi: 10.3390/ma14040934.

[23] L. Kawecka and S. Galus, "Wytłoki owocowe – charakterystyka i możliwości zagospodarowania".

[24] N. v. Gama, A. Ferreira, and A. Barros-Timmons, "Polyurethane foams: Past, present, and future," *Materials*, vol. 11, no. 10. MDPI AG, Sep. 27, 2018. doi: 10.3390/ma11101841.

[25] M. Szpiłyk, R. Lubczak, and J. Lubczak, "The biodegradable cellulose-derived polyol and polyurethane

foam," *Polymer Testing*, vol. 100, p. 107250, Aug. 2021, doi: 10.1016/J.POLYMERTESTING.2021.107250.

[26] Ewa Kręcielewska and Damien Mendard, "Współczynnik przewodzenia ciepła izolacji," *Ciepłownictwo*, vol. 11, pp. 14–20, 2014.

[27] K. Uram *et al.*, "Polyurethane composite foams synthesized using bio-polyols and cellulose filler," *Materials*, vol. 14, no. 13, 2021, doi: 10.3390/ma14133474.

[28] X. Zhou, M. M. Sain, and K. Oksman, "Semi-rigid biopolyurethane foams based on palm-oil polyol and reinforced with cellulose nanocrystals," *Composites Part A: Applied Science and Manufacturing*, vol. 83, pp. 56–62, Apr. 2016, doi: 10.1016/j.compositesa.2015.06.008.

[29] R. J. Prociak A., Rokicki G., *Materiały poliuretanowe*. PWN, 2016.

[30] M. Leszczyńska *et al.*, "Vegetable fillers and rapeseed oil-based polyol as natural raw materials for the production of rigid polyurethane foams," *Materials*, vol. 14, no. 7, Apr. 2021, doi: 10.3390/ma14071772.

[31] N. Sienkiewicz, S. Członka, A. Kairyte, and S. Vaitkus, "Curcumin as a natural compound in the synthesis of rigid polyurethane foams with enhanced mechanical, antibacterial and anti-ageing properties," *Polymer Testing*, vol. 79, Oct. 2019, doi:10.1016/j.polymertesting.2019.106046.

[32] F. Saint-Michel, L. Chazeau, J. Y. Cavaillé, and E. Chabert, "Mechanical properties of high density polyurethane foams: I. Effect of the density," *Composites Science and Technology*, vol. 66, no. 15, pp. 2700–2708, Dec. 2006, doi: 10.1016/j.compscitech.2006.03.009.

[33] M. Barczewski *et al.*, "Rigid polyurethane foams modified with thermoset polyester-glass fiber composite waste," *Polymer Testing*, vol. 81, Jan. 2020, doi: 10.1016/j.polymertesting.2019.106190.

[34] D. K. Chattopadhyay and D. C. Webster, "Thermal stability and flame retardancy of polyurethanes," *Progress in Polymer Science (Oxford)*, vol. 34, no. 10. pp. 1068–1133, Oct. 2009. doi: 10.1016/j.progpolymsci.2009.06.002.

[35] S. Członka, A. Strąkowska, K. Strzelec, A. Kairytė, and A. Kremensas, "Melamine, silica, and ionic liquid as a novel flame retardant for rigid polyurethane foams with enhanced flame retardancy and mechanical properties," *Polymer Testing*, vol. 87, Jul. 2020, doi: 10.1016/j.polymertesting.2020.106511.

[36] L. Qian, F. Feng, and S. Tang, "Bi-phase flame-retardant effect of hexa-phenoxy-cyclotriphosphazene on rigid polyurethane foams containing expandable graphite," *Polymer (Guildf)*, vol. 55, no. 1, pp. 95–101, Jan. 2014, doi: 10.1016/j.polymer.2013.12.015.