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Biomass Origin Waste as Activators of the Polyurethane Foaming Process

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Abstract: Rigid polyurethane foams (RPUFs) are characterized by their excellent viable properties; thus, these materials can be successfully used as thermal insulation materials. The main problem, the solution of which is partly indicated in this paper, is that the products for the synthesis of RPUFs are produced from petrochemicals. Due to this, the use of natural fillers in the form of waste biomass is introduced for the synthesis of RPUFs. The biodegradable biomass waste used in the RPUF production process plays multiple roles: it becomes an activator of the RPUF foaming process, improves selected properties of RPUF materials and reduces the production costs of insulating materials. The paper presents the results of the foaming process with the use of six different fillers: sunflower husk (SH), rice husk (RH), buckwheat husk (BH), sunflower husk ash (SHA), rice husk ash (RHA) and buckwheat husk ash (BHA). In all cases, composites of rigid polyurethane foam with 10 wt.% of filler were produced. New foams were compared with polyurethane materials without the addition of a modifier. Moreover, the paper presents the results of the fillers' analysis used in the tests and the effects of the fillers' addition as activators of the RPUF foaming process. Promising results were obtained for two of the fillers, BHA and SHA, as activators of the foaming process and confirmed by the volumetric results, where the named samples reached their maximum value in half the time compared to the remaining samples. In addition, the expansion rate for PU_10BHA was a maximum of approximately 11 cm³/s and PU_10SHA was a maximum of approximately 9 cm³/s, whereas the remaining samples showed this parameter at about 3 cm³/s. During the research, the scanning electron microscopy method and infrared camera technique were used.

Keywords: rigid polyurethane foam; foaming process; biomass ash; biomass waste



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1. Introduction

Rigid polyurethane foams (RPUFs) belong to a group of porous materials with a closed-cell structure. Due to their unique properties, such as low density, abrasion resistance and low thermal conductivity, they are widely used as heat or sound isolators. Over 60% of the polymer materials sold in the world are RPUFs. This is because they are an inseparable element of people's everyday life. The most common uses for them include the automotive industry, thermal insulation materials and the packaging industry [1–6]. The synthesis of polyurethane foams is based on the polymerization of hydroxyl groups derived from polyol with isocyanate. The main products for the synthesis of RPUFs, polyol and isocyanate, are produced from crude oil, which is a non-renewable raw material. Recently, a significant crisis has also been observed, which affects the fluctuation in oil prices. In order to limit the possibility of producing polyurethane foams from petrochemical products, intensive research is being conducted regarding the introduction of renewable raw materials into the polyurethane foam system. Therefore, it is crucial to conduct research on the impact of biodegradable raw materials on the process of foam synthesis and their final properties [7]. Biomass waste is currently used in many areas of the waste management sector, e.g., for

the production of biogas or syngas [8,9]. Biomass waste also performs well as fillers in the production of polyurethane materials. In the literature, there are also studies concerning the extraction of natural fibres that could be used as fillers in the future. Suárez et al. described a method of extracting giant reed fibres from stems and leaves [10].

In order to design environmentally friendly polyurethane materials, ongoing research on the possibility of introducing fillers into foams is observed. The literature describes cases of introducing both organic and inorganic fillers into foams [11]. The inorganic fillers include silica and expanded graphite [12–14]. For the purpose of obtaining sustainable materials, organic fillers and industrial waste are more desirable. Among the organic fillers described in the literature that have a positive effect on the final properties, one can distinguish: cellulose nanocrystals, egg shells, nut shells and chitin [15,16]. As regards inorganic fillers, there is ash from coal combustion, which has a positive effect on the mechanical and thermal properties of RPUFs [17–20]. Moreover, after additional modification, the ash also acts as a flame retardant in foams [21]. The advantages of using fillers in the form of biomass solids or biomass ash are primarily the reduction in the use of petrochemicals in the synthesis of RPUFs, the creation of environmentally friendly materials and improvements in the properties of the final foams.

This paper focuses on three types of agricultural biomass waste: sunflower husk (SH), rice husk (RH), buckwheat husk (BH) and their ashes. Sunflower, as one of the aforementioned types of agriculture biomass, is widely cultivated for oil production due to its low soil requirements and drought resistance. During this process, sunflower husk waste is generated, which consists of c.a. 45–50% of the seed weight [22,23]. However, only part of this waste is combusted because the sunflower husk is rich in vitamins and fibre; thus, it can be successfully used as animal fodder. On the other hand, as regards rice husk, which is another natural agricultural bio-waste generated during the production of rice, an approximate 23% of this waste is produced from the total weight of the rice seed. Rice husk is also thermally utilized; therefore, proper ash management is required [24,25]. In the case of buckwheat, this is currently cultivated in Europe and Asia in high quantities as food for humans and animals. The husk waste is stored or thermally recycled [26]. Concluding, the use of the abovementioned fillers and their ashes for the production of RPUFs in this study is justified. Polyurethane foams are produced as a result of two exothermic reactions. The first is the polymerization reaction between a polyol and an isocyanate, resulting in the formation of urethane bonds [27]. The second reaction, which will be explored in greater detail in this paper, is the blowing reaction between isocyanate and water. In the results, the hard urea and CO₂ segments, which are responsible for the foam growth [28], are formed in the RPUFs. The reactions related to the expansion process, i.e., the gelling and blowing, are exothermic; their heat of reaction is -125.5 kJ/mol for the blowing and -93.9 kJ/mol for the gelling [29,30]. The foaming process is one of the most important steps in the production of RPUFs. The cellular structure of the resulting composites is closely related to the method of foaming, as it affects the thermo-mechanical properties [31]. The studies presented in the literature indicate that the use of fillers has a positive effect not only on the final properties, but also on the foaming process, as well as causing a chemical equilibrium between the reactions [32–34]. Cimavilla-Román et al. [28] investigated the influence of silica aerogel particles on the foaming process. As a result, they observed a delay in expansion and an increase in cell nucleation. Moreover, the addition of this type of filler decreases the temperature of the reaction [28]. Kurańska et al. investigated the effect of the addition of bio-polyol produced from rapeseed oil on the foaming process during the synthesis of rigid polyurethane foams. They discovered that this type of additive reduces the dielectric polarization, which directly slows down the foaming and gelling reactions of RPUFs [31].

The current study examined the effects of biomass origin fillers as activators on the RPUF foaming process via physical and chemical analyses and by the application of the following techniques: scanning electron microscopy and infrared camera.

2. Materials and Methods

Six different fillers of biomass origin were used in the research—three types of husk resulting from agricultural waste: sunflower husk (SH), rice husk (RH) and buckwheat husk (BH). The other three fillers were ashes from the abovementioned agricultural waste. Prior to using the husks in polyurethane technology, these were properly pre-treated: dried at 105 °C for 24 h (until a constant mass is obtained) to evaporate the moisture, and then ground in a laboratory mill (IKA MultiDrive Control, Staufen, Germany). The ash was determined and produced from the process of biomass heating in a muffle furnace in an air atmosphere at a temperature of 550 °C for 4 h (according to ISO 18122:2015 “Solid biofuels—Determination from ash content”). The process was repeated for each type of biomass and the samples were labelled as SHA (sunflower husk ash), RHA (rice husk ash) and BHA (buckwheat husk). The images of the fillers are presented in Figure 1.

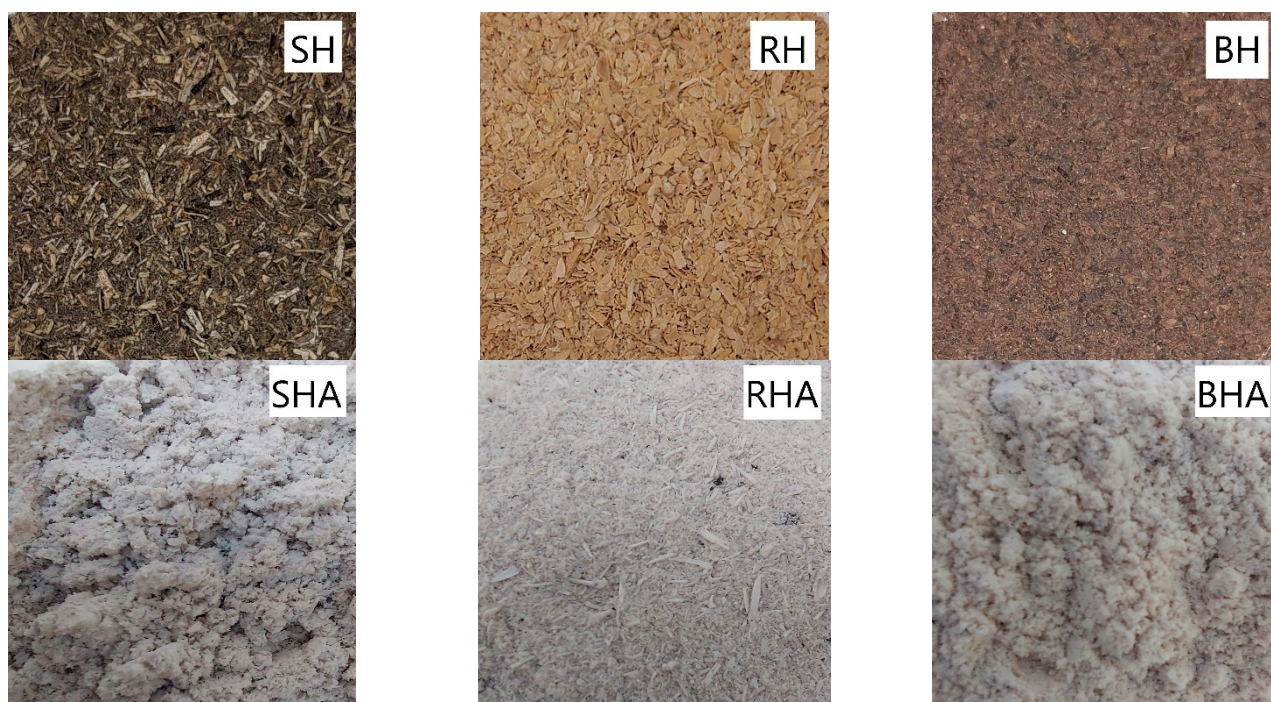


Figure 1. Macroscopic images of the biomass fillers (SH, RH, and BH) and biomass ash fillers (SHA, RHA and BHA).

2.1. Fillers' Characteristics

The particle size distribution of fillers was performed with the light laser diffraction method using a Mastersizer 2000S device (Malvern Instruments Ltd., Malvern, UK). Due to the unimodal distribution, it was assumed that the volume fraction in % is the same as the mass fraction in %. The observation of the structure was studied using the scanning electron microscope JEOL JSM5410 (JEOL, Peabody, MA, USA). The LECO CHN628 (LECO Corporation, St Joseph, MI, USA) device was used to determine the content of basic elements (carbon, hydrogen and nitrogen) present in the biomass.

2.2. Preparation of Rigid Polyurethane Foam Samples and Characterization of the Foaming Process

The EKOPRODUR PM4032 (PCC Group, Brzeg Dolny, Poland) polyurethane system was employed to investigate the influence of fillers on the foaming process. The product consists of two components. Component A is a straw-coloured polyol premix, and component B is a bruising blend of aromatic polyisocyanates. The system is dedicated to the production of foam using a one-step method. Initially, an appropriate amount of filler was added to the polyol premix and mixed until a homogeneous mixture was obtained. Component B was added successively and mixed for approximately 8 s (until exotherm)

with a mechanical stirrer at 1200 rpm. Then, the operation was repeated for each additive. The polyurethane composites prepared in this way were subjected to further foaming process analyses.

Initially, the characteristic times were obtained, which allowed for the evaluation of the influence of the filler on the polyurethane foaming process. Cream time is the time from mixing polyol with isocyanate to the initiation of the increase in the volume of the mixture (start of the chemical reactions). Rise time is the time after which a maximum increase in foam appears and the tack-free time is the time after which a non-sticky layer forms on the foam surface.

2.3. Temperature and Volume Measurements

The temperature distribution of the polyurethane mixture over time was measured during the foam growth. The measurement was carried out using thermocouples located in the core of the plastic cup. K-type sheathed thermocouples with a diameter of 1 mm were used to measure the temperature. In accordance with the PN-EN 60584/IEC 584 standard, the first accuracy class thermocouples were in the range of ± 1.5 °C. Measurements were recorded at a frequency of 10 Hz. Then, the thermocouples were mounted on a wooden rod at different distances from the bottom of the cup: 0.2 cm (TC1), 1 cm (TC2), 5 cm (TC3), and 9 cm (TC4).

Due to the exothermic nature of the process, the expansion kinetics were determined using the infrared radiation (IR) technique in accordance with the methodology presented in [30]. The measurement of foam volume during its growth was carried out on the basis of thermovision images. Additionally, the thermographs were scaled based on the height of the cup (125 mm). Then, a contour of the thermal image was carried out to create a binary mask in order to measure the area of the foam (Figure 2). The volume of the sample and rate of expansion were determined using the following expressions:

$$V = \frac{\pi A^2}{4} \frac{1}{h} \quad (1)$$

$$v = \frac{dV}{dt} \quad (2)$$

where V is the sample volume, A is the area of the binarized mask, h is the height, v is the expansion rate, and t is the time. The examination was performed using the FLIR A615 camera with a frequency of 25 fps. The device is equipped with a standard 25° lens and has a high NETD thermal sensitivity of <0.05 °C in $+30$ °C and an infrared resolution of 640×480 pixels. The measurement was determined at a distance of 70 cm from the rising foam at an emissivity of 0.92; the ambient temperature was 20 °C.

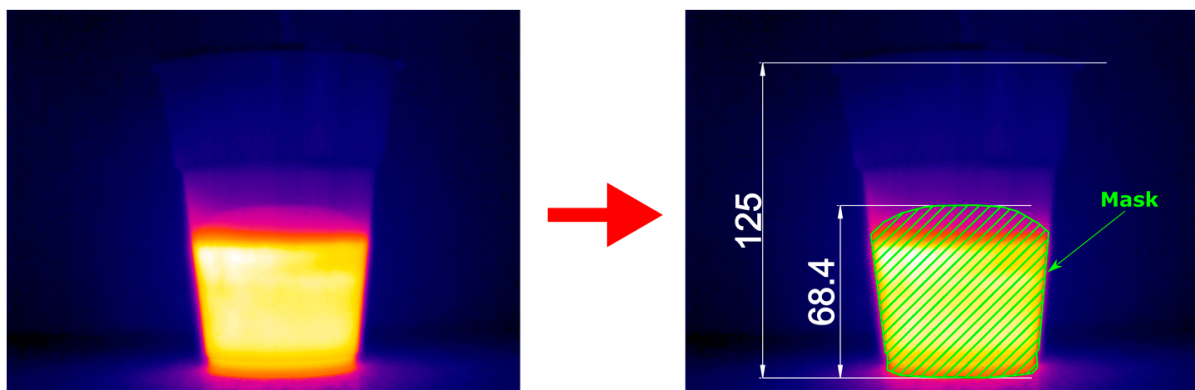


Figure 2. Scheme of the foam area based on the thermal image.

3. Results

3.1. Fillers' Characteristics

The microstructure of the biomass (SH, RH, and BH) and biomass ash (SHA, RHA, and BHA) fillers was examined using scanning electron microscopy (SEM). The results of this study are shown in Figure 3.

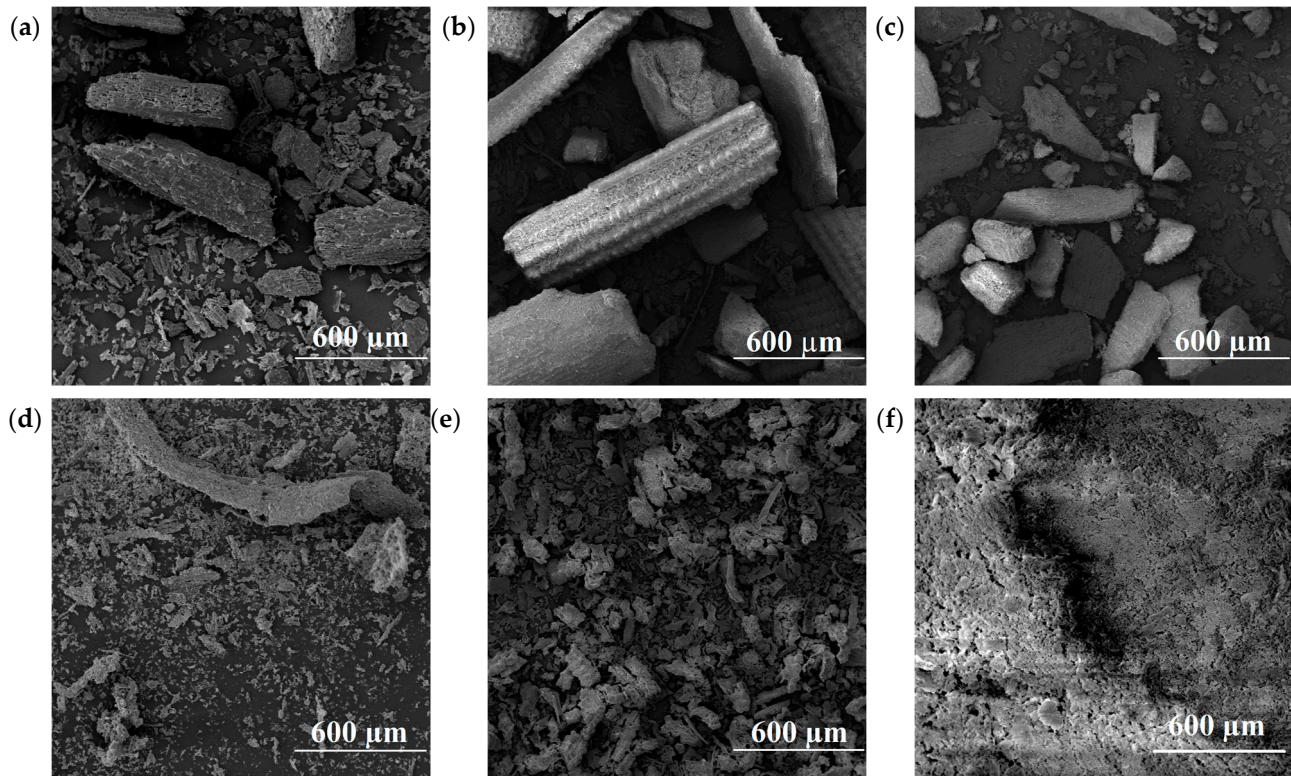


Figure 3. Structure of SH (a), RH (b), BH (c), SHA (d), RHA (e) and BHA (f).

Figure 3a–c depicts the microstructure of ground husks. In all types of fillers, particles presenting an irregular shape and rough surface predominate. Concerning SH and RH, short fibres with a slightly more developed surface can be observed. BH, in contrast, is a typical particle-shaped filler, while the other two have a higher aspect ratio. Similar observations for sunflower husks were produced by other researchers [35], whereas ash fillers with a higher aspect ratio may result in better processing properties [36].

Biomass ash is in the form of particles of several microns. In addition, ash clusters can be distinguished, which indicate the occurrence of the sintering process. The sintering phenomenon is typical during the formation of ashes. In addition, no spherical particles were found in contrast to their presence in coal ash as observed by other researchers [37]. The chemical composition of fillers including carbon (C), hydrogen (H) and nitrogen (N) contents are summarized in Table 1. It also includes the specific surface area (SSA_{BET}) measured using the Brunau–Emmet–Teller (BET) method, and the ash content.

Table 1. Chemical composition and specific surface area of the fillers.

Filler	Description	C, %	H, %	N, %	SSA_{BET} , m ² /g	Ash Content, %
SH	Sunflower husk	48.75	5.67	0.82	0.39	3.36
RH	Rice husk	40.82	5.20	0.50	0.51	1.53
BH	Buckwheat husk	47.96	5.67	0.62	0.28	14.25
SHA	Sunflower husk ash	5.68	0.76	0.11	4.13	-
RHA	Rice husk ash	1.35	0.40	0.15	3.91	-
BHA	Buckwheat husk ash	7.09	0.89	0.14	6.57	-

The analysis of C, H and N contents shows that these elements, in sunflower husk and buckwheat husk, are at a similar level. Rice husk showed lower contents of carbon, nitrogen and hydrogen. When comparing ashes to raw biomass, the carbon content is significantly reduced by approximately 40%, and other elements are also present in lower amounts. The content of the analyzed elements is at a comparable level to results produced by other studies in the literature [38]. The organic fillers are rich in cellulose. In addition, the biomass also contains lignin and hemicellulose. For instance, sunflower husk contains 48% cellulose and c.a. 17% lignin [22], rice husk contains c.a. 49–79% cellulose, 10–24% hemicellulose and 3–8% lignin [39]. In contrast, buckwheat husk contains c.a. 40% of cellulose and hemicellulose, and 9% of lignin [40].

The SSA_{BET} value for all biomass fillers is up to approximately $0.5 \text{ m}^2/\text{g}$. The specific surface area value for ashes is within the range of approximately $4\text{--}7 \text{ m}^2/\text{g}$. The obtained results are similar to the data available in the literature [41,42].

The BHA filler is characterized by the highest value of the SSA_{BET} ($6.57 \text{ m}^2/\text{g}$), while BH has the lowest value ($0.28 \text{ m}^2/\text{g}$).

Regarding ash content in agriculture biomass waste, it was determined that the highest ash content is found for RH at 14.25%.

The particle size distribution of all filler samples was carried out in the research and is depicted in Figure 4.

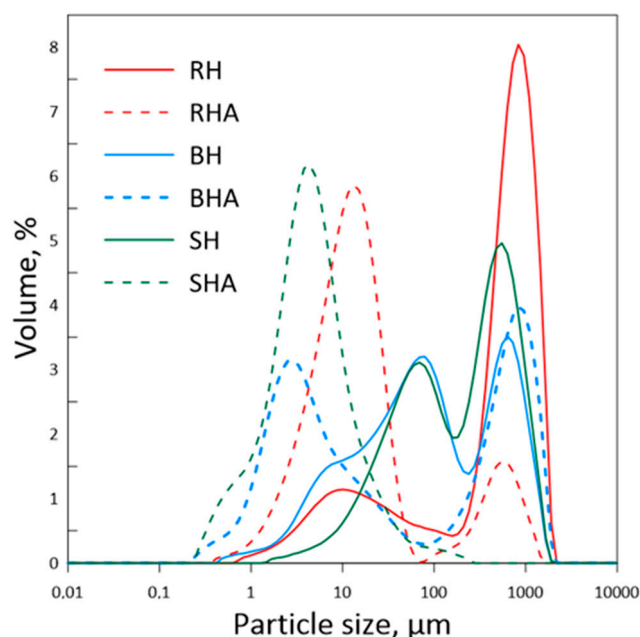


Figure 4. Particle size distribution of the fillers.

Particle size distributions are very similar for all fillers, ranging from 0.02 to $1900 \mu\text{m}$. In the case of biomass fillers, particles larger than $100 \mu\text{m}$ but smaller than $1500 \mu\text{m}$ were found. For biomass ash, particles up to $100 \mu\text{m}$ predominate. In the graph above, it can also be seen that the amount of particles above $1000 \mu\text{m}$ in BHA is significantly higher than for the other two types of ash. BHA has a different structure compared to SHA and RHA (Figure 3f). The structure of this ash is compact and has no loose fractions. Therefore, this type of filler was chosen to be subjected to further research.

3.2. Polyurethane Foaming Process

RPUFs are three-dimensional structures that consist of cells separated by thin walls. The foam formation process consists of several stages, namely nucleation, growth, and stabilization of cells in the reacting medium. The first step after mixing the reagents, e.g., polyol and isocyanate as well as filler, is the process of cell nucleation. This process is

crucial because the other properties of RPUFs depend on the type of cells (open or closed) and their sizes. The cell nucleation process can be altered by introducing modifiers, e.g., fillers, which act as heteronuclei. The heteronucleation process leads to the formation of a greater number of gas bubbles, which results in a homogenization of the structure and the formation of cells with a smaller diameter. In other studies, the effect of introducing a filler in the form of crushed blackcurrant pomace on the process of heteronucleation and modification of the structure of foams was observed [43]. In the next step of the foaming process, the bubble nuclei increase in volume, which is caused by the formation of CO₂, the increase in temperature, and the reduction in the distance between the bubbles. Therefore, the specific times, e.g., cream, rise and tack-free times, are crucial parameters used to assess the nucleation and rate of foam growth. Table 2 lists the times for each sample.

Table 2. Foaming parameters of polyurethane composites.

Foam	Description	Cream Time, s	Rise Time, s	Tack-Free Time, s
PU_0	Foam without fillers	8.37	170	932
PU_10SH	Foam with 10% SH	8.46	164	799
PU_10RH	Foam with 10% RH	8.83	180	695
PU_10BH	Foam with 10% BH	8.60	178	863
PU_10SHA	Foam with 10% SHA	8.63	51	14
PU_10RHA	Foam with 10% RHA	8.98	196	573
PU_10BHA	Foam with 10% BHA	8.42	55	28

According to the data available in the literature [44,45], the addition of a filler extends the cream and rise times, which was confirmed by this investigation. For all samples, except PU_10BHA and PU_10SHA, the above times were higher or close to the parameters obtained for PU_0 (reference foam). All types of fillers accelerated the polyurethane synthesis process. However, the tack-free times obtained for each sample with the modifier were lower than for PU_0. This can be explained by the better accumulation of heat in the polyol with fillers than in the polyol without any additives. As a result, and according to the Arrhenius equation of kinetics reaction, the foaming and crosslinking reactions proceed faster [46]. Regarding PU_10SHA and PU_10BHA foams, cream time and rise time are lower than for the other samples. The tack-free times are over thirty times lower than in the case of PU_0. Analysis of the fillers indicated that SHA and BHA are characterized by the highest SSA_{BET} values as well as uniform particle size distribution, resulting in a positive effect on the insulating properties of the polyol. In the most recent literature, no information has been found on the impact of such high reactivity of sunflower and buckwheat husk ash on the polyurethane system. Accordingly, in this work, a number of further analyses were performed to determine the impact of these fillers on the foaming process in order to fulfil this knowledge gap.

In order to assess the influence of selected fillers on the foaming process, the temperature characteristics were determined. Figure 5a shows the temperature distribution for the analyzed composites recorded by TC2 (1 cm from the bottom of the cup) placed in the axis of the sample. Figure 5b presents the distribution of temperature recorded by TC3 (5 cm from the bottom of the cup). In Figure 5a, it can be seen that the highest temperature was measured for PU_10BHA and PU_10SHA. For unmodified foam (PU_0), the maximum temperature recorded by TC2 was 77.2 °C, while for PU_10BHA, it was 83.0 °C, and for PU_10SHA, 80.4 °C. The TC3 temperature distributions differed slightly. The temperature for PU_10BHA and PU_10SHA was no longer in the highest range because the formation reaction of the urethane bonds in the two discussed foams proceeds faster than in the other cases. This is also confirmed by the volume and expansion rate of all samples depicted in Figure 5e,f. The highest temperatures recorded by TC3 were for PU_10SH (91.3 °C) and PU_10RH (88.0 °C). In Figure 5a,b it can be seen that not all organic fillers activate the foaming process. Similar observations were also reported in Barczewski et al.'s work, where they studied the influence of vermiculite on the foaming process of RPUFs [47].

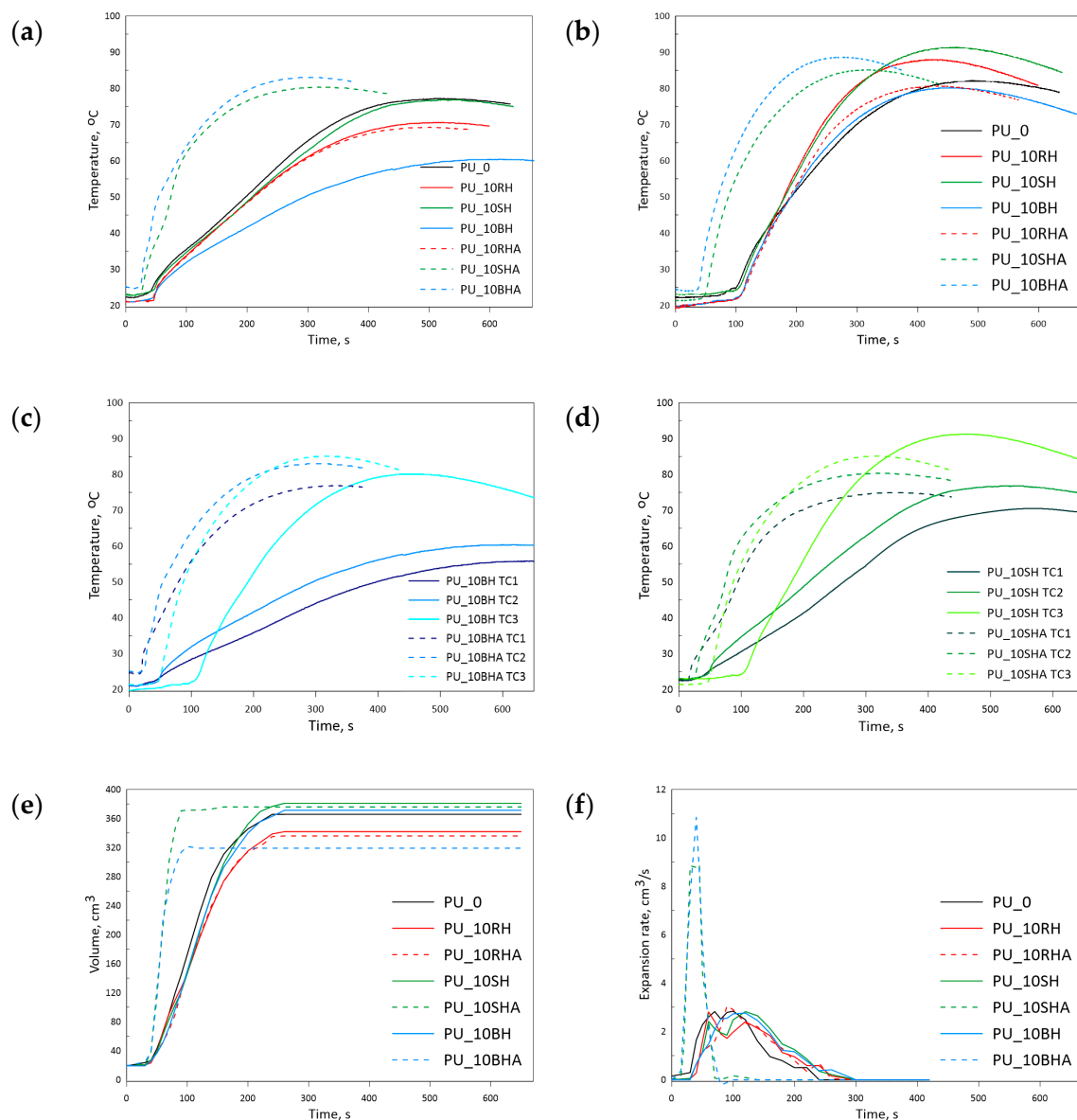


Figure 5. Temperature recorded by TC2 (a) and TC3 (b) for all samples; temperature recorded by TC1, TC2 and TC3 for BH and BHA (c) and for SH and SHA (d) samples; determined volume for all samples (e); and expansion rate for all samples (f).

In order to compare different fillers, the temperatures of TC1, TC2 and TC3 were presented for the BH and BHA samples (Figure 5c), and for the SH and SHA samples (Figure 5d). The graphs depict a much greater influence on the temperature of the foaming process of composites with biomass ash fillers than when using biomass as fillers. The maximum temperature for the SH foam was lower by 3.5 °C compared to the foam containing SHA. Regarding BH and BHA foams, the maximum temperature was lower by 22.6 °C, respectively. The RH peak was lower by 1.7 °C compared to the RHA foaming temperature. The greatest difference between biomass and biomass ash in the foaming temperature process was observed for buckwheat husk foams.

Based on the images from the infrared camera, the expansion volume was measured (Figure 5e). Figure 6 shows selected thermograms for all samples. PU_0 had a volume of about 350 cm³. A similar volume value was also obtained for PU_10BH, PU_10SH and PU_10SHA. In contrast, a lower value of volume, approximately 320 cm³, was observed for PU_10BHA, PU_10RH and PU_10RHA. It was concluded that the PU_10SHA and PU_10BHA samples had reached their final volume faster than the other samples. Moreover,

the final volume of the sample depends on the amount of foaming agents, which was also reported by other researchers [30,48].

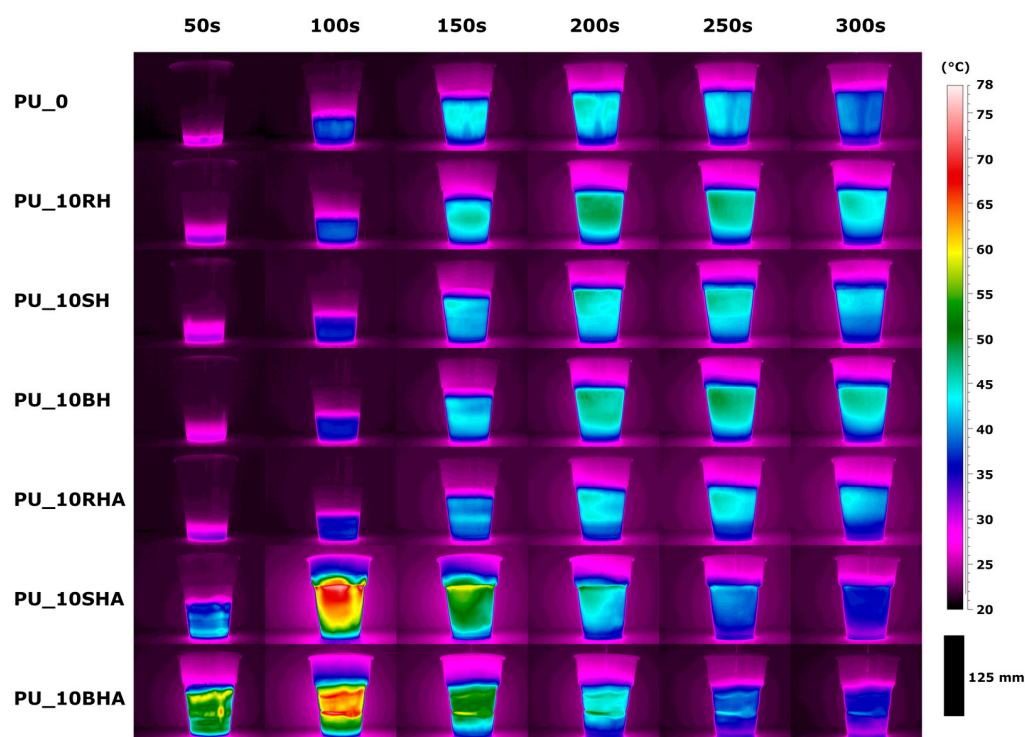


Figure 6. Photographs of all samples during the RPUFs' synthesis at selected times.

One of the most important parameters applied in order to understand the kinematics of the foaming process is the rate of expansion. The results of the expansion rate for the analyzed samples are shown in Figure 5f, which confirm the significant influence of two fillers (SHA and BHA) on the foaming reaction. The fillers accelerate the expansion reaction in the initial time (up to 100 s) by approximately three times compared to the others. Then, after 100 s, the foaming reaction slows down, while for other fillers, it stops after about 300 s. The expansion rates for polyurethane with sunflower and buckwheat ashes are approximately three times higher than for the other samples. This is probably because SHA and BHA have compounds that act as blowing agents. This observation will be confirmed in further studies. Santiago-Calvo et al. reported a similar observation, whereby increasing the addition of blowing agents accelerates the rate of expansion [30]. Other authors have also reported that the final volume and expansion of a given material is affected by the amount of blowing agent [48].

As mentioned earlier, due to the nature of the reaction between the polyol and isocyanine, in which the exothermic foaming reaction takes place, it was possible to examine the reaction with a thermal imaging camera using infrared radiation [30]. In order to compare the results, the same temperature scale was set for all samples. Figure 6 depicts images from the IR method for the following periods of foam growth: 50, 100, 150, 200, 250 and 300 s.

Based on the images presented in Figure 6, it is possible to observe how various fillers affected the foaming process. Considering the foaming process of PU_0 started after 50 s, this moment (50 s) was used as a starting point for the foaming process comparison. The highest temperature and growth rate can be observed for PU_10BHA and PU_10SHA, respectively. In addition, the foams with biomass fillers (PU_10 RH, PU_10SH and PU_10BH) retain heat for much longer; thus, after 300 s, the recorded temperature is higher than for PU_0. It was confirmed that the SHA and BHA fillers had the greatest influence on the exothermic foaming reaction [49].

4. Conclusions

The effects of biomass origin waste as activators on the RPUF composites foaming process were studied. Firstly, the chemical and physical properties of biomass and biomass ash fillers were determined. Consequently, elemental analysis showed that biomass had a high carbon content, c.a. 50%, while biomass ash fillers contained up to 7%. The nitrogen content in all samples did not exceed 1%. Rice husk (RH) biomass was characterized by the highest content of large particles (700–1500 μm) in comparison to other biomass fillers. Biomass had ten times lower SSA_{BET} values in relation to biomass ash, e.g., 6.57 m^2/g for buckwheat husk ash (BHA). The scanning electron microscopy identified a more homogenous morphological structure of biomass ash than in the case of biomass.

Secondly, the foam synthesis process was activated by the addition of biomass origin fillers. The foaming characteristic times, including cream, rise and tack-free, were measured. The addition of a filler extended the cream time in comparison to foam without filler addition (PU_0). The tack-free times of samples with modifier were lower than for PU_0 due to heat accumulation in the composites. Observations from the infrared camera confirmed the significant influence of two fillers (SHA and BHA) through their volume growth and expansion rate during the foaming process. Furthermore, the higher temperature of the foaming process accelerated polyurethane foam growth.

Concluding, it was found that the addition of biomass ash caused a high reactivity in the polyurethane foaming process. Therefore, further analyses of this phenomenon mechanism are required.

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