

Article

The Effect of Ash Silanization on the Selected Properties of Rigid Polyurethane Foam/Coal Fly Ash Composites

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Abstract: According to the assumptions of the European Union, by 2050 it is planned to achieve climate neutrality. For this purpose, a document called the “European Green Deal” was established, which is a set of policies of the European Commission. One of the assumptions is a circular economy that takes into account the use of waste in subsequent production cycles. In order to meet the latest trends in environmentally friendly materials and use of waste in the production of building materials, composites of rigid polyurethane foam with 10 wt.% of waste were produced. Fly ash from coal combustion after modification was used as a filler. Three types of modifications were used: silanization, sieving, and both processes together. The silanization process was carried out for 1 and 2% silane ([3-(2-aminoethylamino)propyl]trimethoxysilane) concentration in relation to the fly ash mass. The sieving was aimed at reaching a fraction with a particle diameter below 75 µm. Six composites with modified fillers were compared and one material containing unchanged fly ash was used as a reference. A comparative analysis was carried out on the basis of surface analysis, thermal stability and physical properties. It turned out that the polyurethane materials modified fly ash silanized with 1% and 2% silane solution proved the best results in performed tests. On the other hand, the polyurethane foam containing sieved ash was characterized by the lowest flammability and the lowest emission of smoke and CO. The use of modified fly ash in technology of polyurethane foams can be a good method of its disposal and can increase the applicability of the composites.

Keywords: fly ash recycling; silanization; polyurethane composites



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1. Introduction

Currently, all over the world there is a trend of creating environmentally friendly polymer materials with a reduced amount of petrochemical products, often replaced with plant substrates or fillers [1]. The majority of fillers have got hydrophilic nature. It causes low adhesion between filler and polymer matrix [2]. The use of fillers may disturb the structure of the material and deteriorate the properties of the material. To increase the compatibility between a modifier and a polymer matrix, modifications of the filler are used. The following methods are used in the literature: alkalization (change of surface topography with roughness) and silanization (introducing functional groups to fillers). After the silanization process, the silane molecule acts as a coupling agent to form a chemical bond between the solid modifier and the polymer matrix [3]. This modification method is successfully used in dental composites [4], bone cement formulations [5], esophageal stents [6]. Silanization has not only been widely used in medicine, but also in engineering.

An example could be a silanized filler in resin composites [7,8], polyurethane foams [9,10] and in epoxy-based laminates [11].

In this work, fly ash from coal combustion was subjected to the silanization process. In the world literature, there are articles whose purpose was to modify the fly ash. Goh et al. [12] added silanized fly ash to the epoxy resin and on the basis of the results of the SEM analysis and strength tests showed that the modification of the additive surface increased the filler-polymer interfaces. Şen et al. [13] showed that the silanized filler did not shorten the curing time of the resin and that the silanization of the fly ash reduced the swelling. What is more silanized fly ash has been used in materials such as poly(vinyl chloride) composites [14] and in geopolymer [15]. In the available literature, no studies on the use of silanized fly ash in the rigid polyurethane foam technology were found. In this paper, the possibilities of filler modification that could improve the properties of the composite were investigated. Due to the necessity to seek for new environmentally neutral flame retardants for polymers, extensive research was carried out on the influence of fly ash on the flammability of the material. There are results available in the literature on unmodified FA in PU foam, but none of them concern flammability.

Rigid polyurethane foams (RPUFs) are a group of closed-cell polymers whose structure is characterized by high cross-linking. RPUFs account for 23% of all polyurethane production in the world [16,17]. RPUFs have good thermal insulation properties, low apparent density and good mechanical properties. Their advantages also include resistance to weather conditions. Due to all these features, RPUFs are often used in everyday life, incl. construction, furniture and vehicles [18–20]. The most important application is in construction, as thermal insulation materials. According to the data, buildings are responsible for over 1/3 of the total energy consumption in the world [21]. Due to this fact, it is crucial to use energy in more efficient way. The demand for RPUFs is constantly growing, which implies that this material is more and more widely researched and described in the literature.

The polyurethane (PU) industry is strongly related to petrochemical products. For this reason, polyurethane foams are considered as less environmentally friendly materials. Additionally, RPUFs are more expensive compared to other thermal insulation materials. Therefore, in the PU industry inorganic and organic fillers are often used [22]. The use of fillers improve the mechanical properties, have an influence on the flammability and other RPUF properties. One of the inorganic fillers described in the literature is silica. This filler improves the mechanical properties and reduces the flammability of RPUFs [23,24]. Another type of filler that reduces flammability and, on the other hand, deteriorates mechanical properties is expanded graphite [25]. In PU foams, in order to strengthen them, inorganic fillers are used carbon fiber, PET, carbon nanotube, nanoclay and talc [26–29]. On the other hand, organic fillers are increasingly described in the literature. One of the limited fillers used in the synthesis of RPUFs are cellulose nanocrystals. This filler improves the mechanical properties, dimensional stability and reduces the absorbability of the obtained composites [30]. Egg shells, walnut shells or chitin extracted from arthropods are other fillers that modify the properties of rigid foams PU. The conducted research has shown that a small addition of this type of fillers has a positive effect on the mechanical properties of the foams [31].

In this article, the effect of modification (silanization and sieving) on fly ash from coal combustion on polyurethane composites was evaluated. The evaluation was based on the research results of thermal, mechanical and flammability properties.

2. Materials and Methods

2.1. Characterization of Filler and Its Modification

Fly ash (FA) from the combustion of coal is used as a filler. The fly ash came from a conventional (pulverized) hard coal combustion boiler from power plant in southern Poland. The ash was collected from the electrostatic precipitators. The physical density of the fly ash is 2.15 g/cm³. According to data provided from manufacturer the ash has

category A (taking into account the loss on ignition). The filler particles size are varied from a few to about 500 μm . In this work, fly ash was introduced into polyurethane in an unmodified form and after the silanization and sieving process. Conventional fly ash is characterized by the presence of unburned porous carbon particles which could affect the flammability of the material. Therefore, it was decided to sift the filler on a sieve with a mesh diameter of 75 μm . The fly ash was modified by sieving and silanizing it. In earlier work, the authors investigated the effect of particle size on their chemical composition [32]. It turned out that above the particle diameter of 75–100 μm , the amount of unburned carbon particles increased significantly. Therefore, it was decided to modify the fly ash, which consisted in screening and separating the fraction below 75 μm . The second part of modification was silanization, the main purpose of which was to increase the adhesion of the particles. On the other hand, the chemical composition of fly ash depending on the particle sizes (apart from carbon content) practically does not differ from each other (before and after sieving). Fly ash consists mainly of: SiO_2 (52.3%), Al_2O_3 (27.4%), Fe_2O_3 (7.9%), K_2O (4.1%), CaO (2.9%), TiO_2 (1.4%) and MgO (1.4%) [33,34]. The analyzed fly ash belongs to the group of silicate fly ash due to the large amount of SiO_2 and in accordance with the ASTM C 618 standard, it is classified as an ash of the group F. Figure 1 shows the structure of fly ash and two characteristics types of particles: microspheres and unburned carbon. These elements occur in pulverized fly ash, they are not formed during the combustion of coal in a fluidized bed. The screened residue can be seen in photo d, EDS analysis showed that this fraction contains large amounts of carbon.

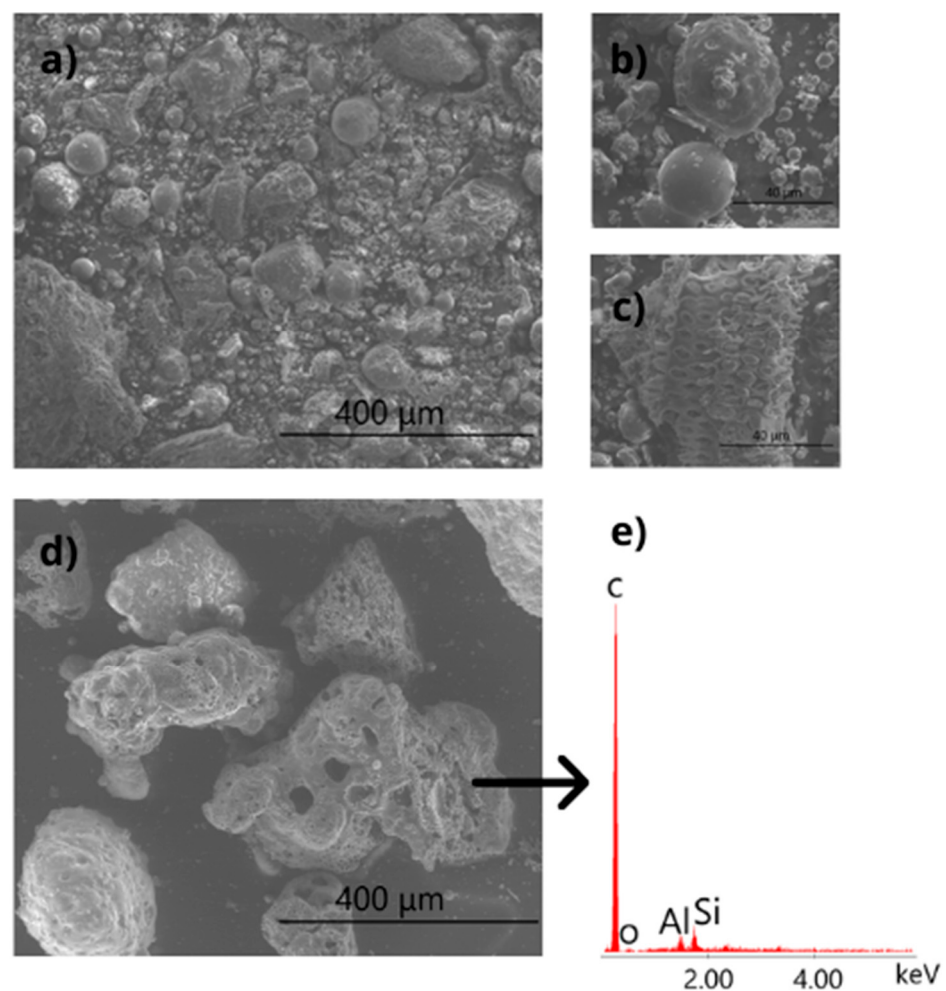


Figure 1. Fly ash microphotography (a), microsphere microphotography (b), unburned carbon microphotography (c), screened residue microphotography (d), EDS spectroscopy of residue (e).

The next step of the content modification is silanization. Figure 2 shows the scheme of silanization process.

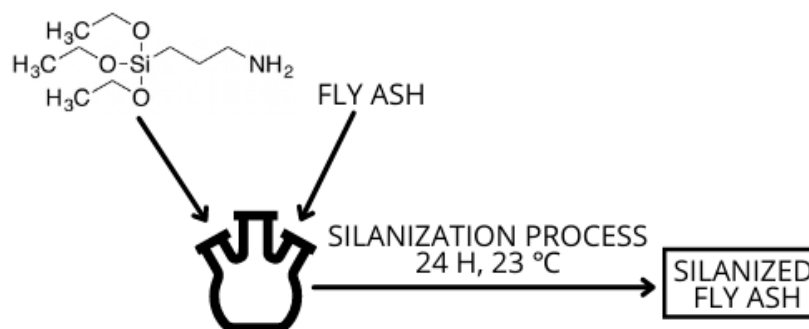


Figure 2. Scheme of silanization process.

This alteration of filler was made by toluene method according to [35] in room temperature (23 °C) and for 24 h. The silanization was performed for various silane concentrations. The weight of silane in filler is 1% (1SFA) and 2% (2SFA) of the weight of fly ash. Additionally fillers were sieved before silanization to obtain two more fillers (1SPFA, 2SPFA).

For all fillers elemental analysis of carbon, nitrogen and hydrogen was performed using LECO CHN628 device. The analysis of particle size of fillers was performed used the methods of laser light diffraction and the Mastersizer 2000S apparatus (Malvern Instruments Ltd., Malvern, UK). The particle size distribution of fillers is shown in Figure 3. It can be seen that the screened fly ash (PFA) and screened and silanized fly ash (1SPFA, 2SPFA) have a particle diameter below 100 µm, therefore it contains much less unburned carbon particles (approx. 6–7%), which is confirmed by elemental analysis. On the other hand, non-sieved (FA) and non-sieved and silanized fly ash (1SFA, 2SFA) has a lot of particles with a diameter of several hundred µm, which is related to the higher content of unburned carbon (approx. 9–10%). The specific surface area (SSA) of samples was determined using the multipoint BET adsorption method (ASAP 2010, Micromeritics Instrument Corporation, Norcross, GA, USA). Explanation of filler symbols and analysis results are presented in the Table 1.

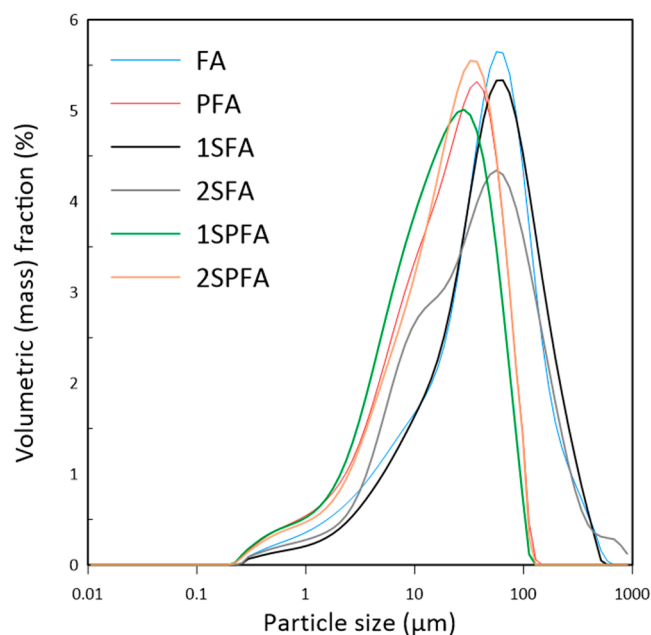


Figure 3. Particle size distribution of fillers.

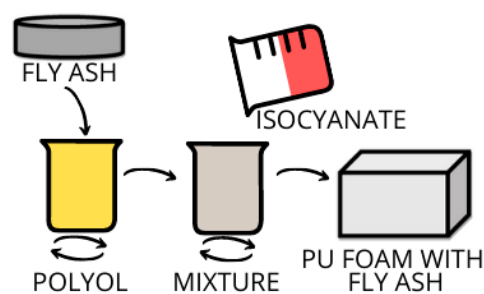
Table 1. Elemental analysis of C, H, N and SSA of fillers.

Filler	Description	C (%)	H (%)	N (%)	SSA (m ² /g)
FA	unmodified fly ash	9.46	0.00	0.19	5.47
PFA	sifted fly ash	6.93	0.02	0.17	3.23
1SFA	fly ash silanized with 1% silane solution	9.95	0.15	0.30	2.24
2SFA	fly ash silanized with 2% silane solution	10.47	0.19	0.49	0.95
1SPFA	sifted fly ash silanized with 1% silane solution	6.52	0.08	0.27	1.09
2SPFA	sifted fly ash silanized with 2% silane solution	6.42	0.04	0.21	2.21

The sieved fillers, i.e., PFA, 1SPFA, 2SPFA were characterized by the smallest amount of carbon, about 30% less unburned carbon particles compared to the FA filler. The raw fly ash (not sieved and unsilanized) is characterized by the highest value of the SSA, which amounts to over 5 m²/g. The other values do not create any dependence, therefore the research should be extended in terms of the mechanism of SSA formation.

2.2. Preparation of Modified Polyurethane Foams

The main components of polyurethane rigid foam are additives (10 wt.% of fly ash, modified fly ash), polyol system with blowing agent, fire retardants, catalyst (component A). The last element of the material is isocyanate prepolymer (component B). Polyurethane foams were prepared using the two-component commercial system EKOPRODUR PM4032 (PCC Group, Brzeg Dolny, Poland). Components were mixed at a ratio of 100:110 by weight (according to product characteristic). Firstly the polyol was mixed with the fly ash until the homogeneous mixture was obtained, after that the isocyanate was poured into the mixture and it was mixed together by mechanical agitator for 8 s at 1200 rpm. The well mixed polyurethane-fly ash mixture was poured into square mold. The composites were left in the forms for 24 h. After this time, the foams were removed from the mold and prepared for tests. The production process of polyurethane composite modified with fly ash is presented in the Figure 4.

**Figure 4.** Schematic presentation of the production of polyurethane composites.

2.3. Methods

The foaming process. The foaming process was analyzed by determining characteristic times: cream time—the time from mixing components A and B to the beginning of the increase in the volume of the resulting mixture, rise time—the time after which it is achieved there is a maximum increase in RPUFs, tack free time—time after which a non-sticky layer form on the RPUFs surface.

Microstructure. The RPUFs microstructure was observed with the scanning electronic microscope (SEM; Nova NanoSEM 200; FEI Company, Hillsboro, OR, USA). Samples of dimensions 50 × 50 × 50 mm³ were sputtered with gold and analyzed at an acceleration of 10 kV.

Thermal analysis. Thermogravimetric (TG) analysis of the obtained materials was performed on a Discovery TGA 550 (TA Instruments, New Castle, DE, USA) to evalu-

ate the thermal properties of the obtained RPUFs. The thermal behavior of a samples (ca. 10 mg) was analyzed in platinum pans under nitrogen atmosphere (20 mL/min) and in the temperature range 20–700 °C at a heating rate of 10 °C min^{−1}.

Density. The density for RPUFs was determined in accordance with the standard EN ISO 845:2009. The sample used for the tests had a volume of 100 cm³.

Friability. Friability was determined during an experiment carried out according to the ASTM C421-08 standard. Twelve cubic cubes of foam were weighted. Then they were rotated with the oak cubes in an oak box for 10 min at speed 60 r/min. After the process, the foam samples were reweighted.

Dimensional stability. The dimensional stability for RPUF at 70 °C was determined after 48 h. The measurement was carried out in accordance with the ASTM D2126-09 standard. The change in length was calculated.

Water absorption. Water absorption was calculated according to ASTM D570-98 standard. The samples were immersed in distilled water and their weight was determined after 48 h.

Limited Oxygen Index. The limitation of the oxygen index (LOI) was the test was measured according to ISO 4589-2: 2017. The samples used for the test were 150 × 10 × 10 mm³.

Heat release intensity. The average heat release rate (HRR), maximum heat release rate (PHRR), effective heat of combustion (EHC), time to ignition (TTI), percent mass loss (PML) of the tested sample were determined on the conical calorimeter. The test was measured according to ISO 5660:2015. The samples used for the test were 30 × 100 × 100 mm³.

Flammability. Flammability tests were carried out using the UL 94V. A vertical burning test was performed. For the test, samples with dimensions of 125 × 13 × 13 mm³ were used. The sample was placed in a holder and a burner was located underneath it.

Reaction to fire. Reaction to fire tests of the samples were also carried out by determining the gross calorific value (LECO AC500 isoperibolic calorimeter). The measurement was performed in accordance with the ISO 1716:2018 standard. A sample with a mass of 80 mg placed in a calorimetric bomb was completely burnt in an atmosphere of oxygen under pressure.

3. Results and Discussion

3.1. Foaming Characteristics of Polyurethane Composites

The impact of fillers and their modification on foaming kinetics of composites was assessed by foaming parameters such as cream time, rise time and tack-free time. The obtained samples and characteristic times can be found in the Table 2.

Table 2. Foaming parameters of polyurethane composites.

Foam Code	Cream Time (s)	Rise Time (s)	Tack Free Time (s)
PU_FA	45	236	350
PU_PFA	51	251	330
PU_1SFA	42	281	310
PU_2SFA	45	284	310
PU_1SPFA	49	266	305
PU_2SPFA	50	259	300

Based on the analysis of the results presented in the Table 2, it was found that the modification of the filler affects the kinetics of foam forming. The screened fly ash filler increased the forming time of the foams. This is due to its higher density, which affects the viscosity of the polyol-fly ash mixture. As a result it has a significant impact on foam behavior and increases reaction time [36,37]. For composites containing silanized fillers (1SFA and 2SFA), the rise time is higher compared to others. It is caused by the reaction of the hydroxyl groups present in the filling material after the silanization process, which

react quickly with isocyanate groups and influence the correct stoichiometry of the material synthesis [38].

3.2. Properties of Polyurethane Composites

Apparent density is an important parameter that affects the mechanical properties of the RPUFs.

The apparent density presented in Table 3 for PU_FA with unmodified filler was 38.4 [kg·m⁻³]. The modification of the filler by silanization resulted in a reduction of the apparent density of the foams. This is due to the fact that the filler's silanization process improves its compatibility with the polyurethane matrix. Foams with a higher cross-link density are created. For this reason, the apparent density value for foams with silanized filler decreases [38]. The modification of the filler by sieving and its subsequent silanization had the opposite effect. The PU_PFA, PU_1SPFA and PU_2SPFA foams have a higher apparent density value than the reference foam. Typical RPUFs should have an apparent density in the range of 28–60 [kg·m⁻³] [39]. The obtained foams have density within the recommended range.

Table 3. Results of apparent density, dimensional stability and water absorption of RPUFs.

Sample	Apparent Density (kg·m ⁻³)	Dimensional Stability (Δl, 48 h, 70 °C) (%)	Loss in Mass (Δm, 48 h, 70 °C) (%)	Water Absorption (48 h, 21 °C) (%)
PU_FA	38.4	1.20	0.45	48.68
PU_PFA	39.8	0.40	0.55	76.16
PU_1SFA	37.3	1.40	0.43	45.45
PU_2SFA	37.8	0.70	0.41	45.29
PU_1SPFA	39.8	0.40	0.50	77.92
PU_2SPFA	40.8	0.45	0.54	76.23

The change of linear dimensions (Δl) and weight loss (Δm) of the analyzed RPUFs after conditioning at 70 °C for 48 h is presented in Table 4. Based on the results of accelerated aging tests for the obtained RPUFs with modified fillers, it was observed that the weight loss was in the range of 0.41–0.55%. The PU_2SFA sample had the lowest weight loss. Additionally, the change in linear dimensions did not exceed 1.40%. The PU_PFA and PU_1SPFA samples are the most thermally stable. In general, it can be seen that the results obtained are random and there is no logical cycling in them. However, the described foams comply with the provisions of the building code, which indicate that polyurethane materials subjected to the increased temperature cannot show changes in linear dimensions greater than 3% [22,40].

Table 4. Characteristics of thermal degradation of the PU composites.

Sample	T _{1%} (°C)	T _{5%} (°C)	T _{10%} (°C)	T _{50%} (°C)	T _{DTGmax} (°C)	Residue at 600 °C (%)
PU_FA	250	276	290	378	305	32.0
PU_PFA	250	277	291	382	308	32.9
PU_1SFA	251	277	291	379	306	31.7
PU_2SFA	248	274	288	372	303	29.6
PU_1SPFA	250	277	291	386	308	33.0
PU_2SPFA	251	278	292	388	307	32.7

In porous materials water absorption is related to the number of closed and open cells in their structure [41]. Table 3 presents the results of water absorption for the RPUF with modified fillers. Foams with silanized filler-PU_1SFA and PU_2SFA are characterized by low water absorption. This is due to the fact that PU_1SFA and PU_2SFA have a more uniform structure and a larger number of cells with smaller diameter. Such cells cannot store large amounts of water [42]. On the contrary, the modification of the filler by sieving causes an increase in water absorption by about 30%. Connection between apparent density and water absorption is presented in the Figure 5. The foams with a higher apparent density were characterized by significantly higher water absorption parameters.

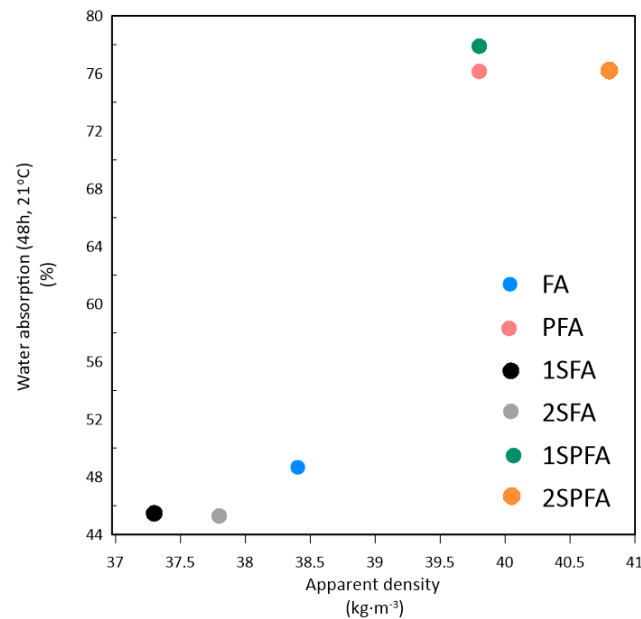


Figure 5. Dependence between apparent density and water absorption of samples.

The friability results for polyurethane foams with modified fillers are depicted in Figure 6.

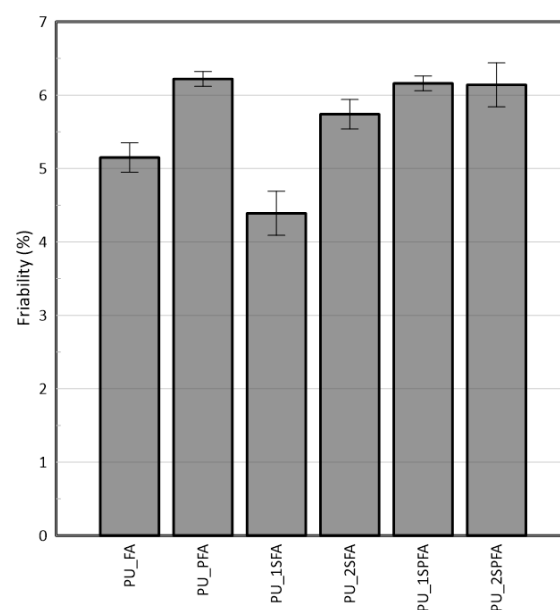


Figure 6. Dependence of the brittleness of polyurethane composites on the type of filler used.

The brittleness of the tested foams was in the range of 4.39–6.22%. The PU_1SFA sample showed the lowest weight loss in the friability test, which indicates a positive effect of FA silanization on the properties of foams. As we mentioned earlier, the mechanical properties, including friability, are closely related to the shape of cells in the foam structure and its apparent density [43]. PU_1SFA analysis indicated that it has the lowest apparent density value among the analyzed materials. The positive effect of introducing the filler into the RPUF was also observed by Barczewski et al. [44]. In contrast, modification of the filler by sieving and silanization increased the friability of the foams.

3.3. Microstructure Analysis of Polyurethane Composites

The influence of filler modification on the porous microstructure of RPUFs was carried out using scanning electron microscopy (SEM). Exemplary images of the morphology of the analyzed materials are presented in the Figure 7.

The morphology of the foam with unmodified filler (PU_FA) depicted in Figure 7a shows that the size and distribution of the cells are heterogeneous. Closed cells were characteristic for the foam structure.

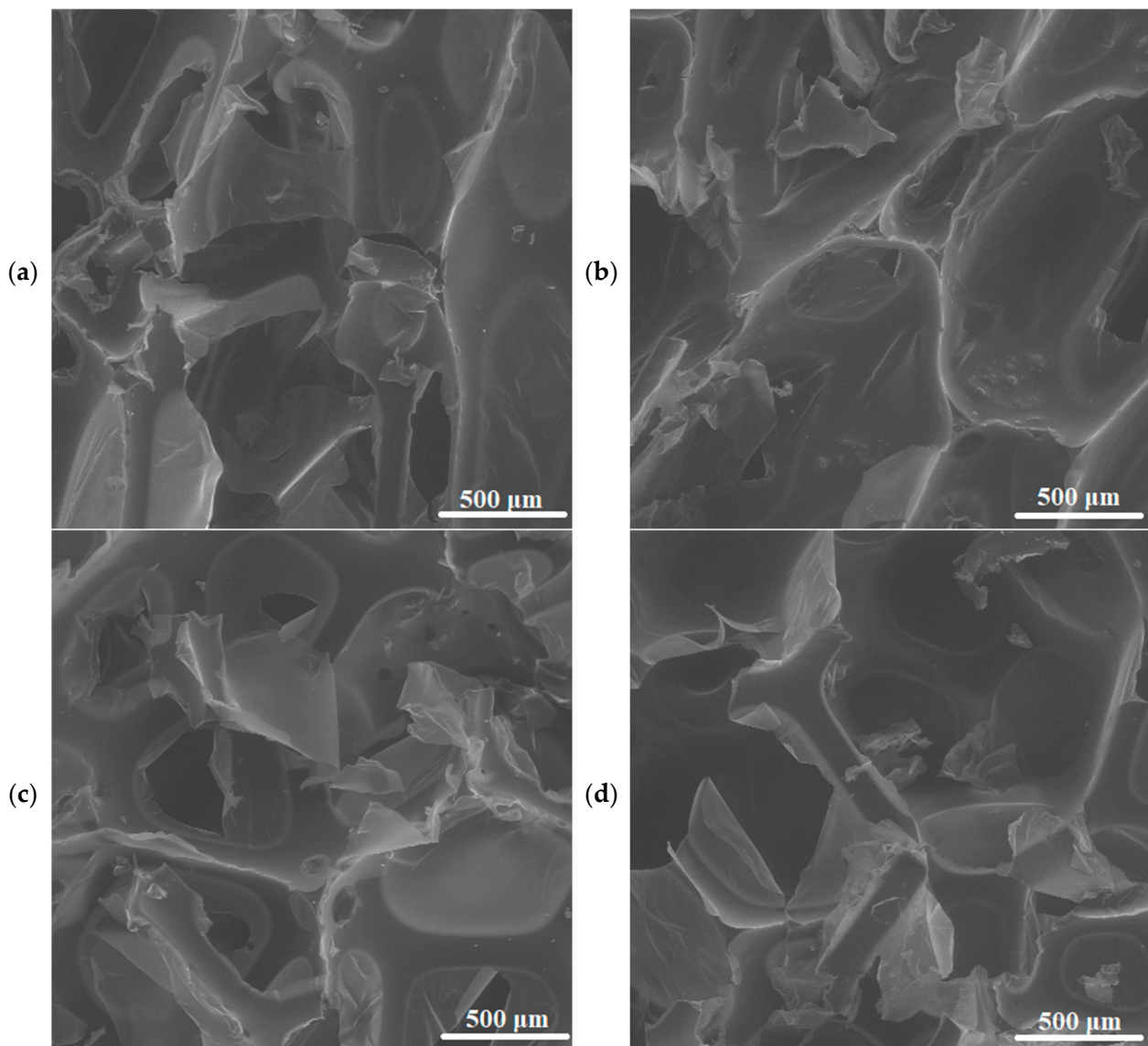


Figure 7. Cont.

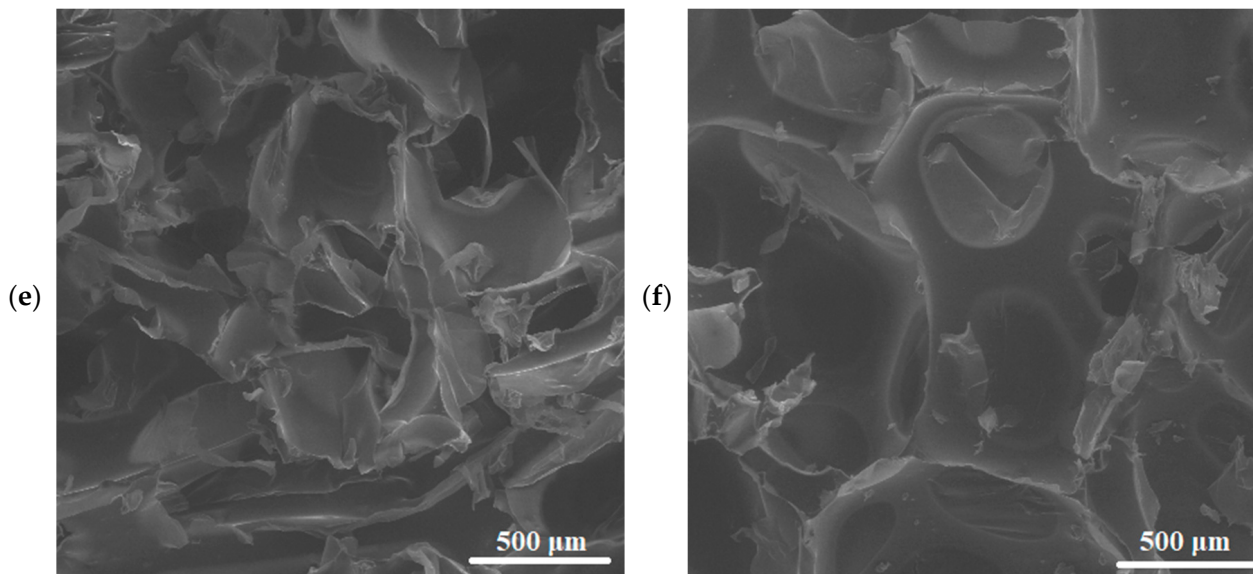


Figure 7. SEM images of the PU_FA (a), PU_PFA (b), PU_1SFA (c), PU_2SFA (d), PU_1SPFA (e), PU_2SPFA (f).

Modification of the filler by sieving has a positive effect on the morphology of RPUFs as the size and distribution of cells are more homogeneous (Figure 7b) compared to the reference foam (Figure 7a). Additionally, modification of the filler by silanization reduces the size of the cells. The analysis of PU_1SPFA and PU_2SPFA morphology showed a greater number of damaged cells.

The morphology of the silanized FA modified RPUFs is shown in Figure 7c,d. The introduction of this type of filler causes the structure to become uniform and the thickness of the cells' walls is reduced. The filler silanization process reflects in more spherical shape of the cells [45]. In the case of PU_2SFA, a greater number of open cells is associated with a reduced adhesion between the polymer matrix and the surface of the filler [29].

3.4. Thermal Properties of Polyurethane Composites

The thermal stability of RPUFs was determined by TG method. Table 4 shows the characteristic temperatures, i.e., with a 5% and 50% weight loss of the tested sample and the char residue after thermal treatment. Polyurethane composites containing modified fillers are less thermally stable than the reference foam (PU_FA). The PU_FA degradation process starts at 194 °C, while for foams with silanized filler it is already at 186 °C, and for foams with sieved and then silanized ash it is already at 191 °C. Filled modified foam, on the other hand, has a lower maximum weight loss than the reference foam, with the exception of PU_2SFA. Partial deterioration of thermal properties may be related to the uneven distribution of the filler in the polymer matrix [1]. The TG analysis showed that foams containing the modified fillers have a higher residue after analysis than PU_FA. Only PU_2SFA had less residual. The faster process of PU_2SFA foam degradation may be influenced by the higher content of open cells (Figure 7d).

As can be seen from the TGA results (Table 4 and Figure 8) incorporation of flay ash-based additives does not change the thermal stability of the polyurethane matrix. The first mass loss is related to the evaporation of moisture and unreacted volatile substances and unreacted isocyanate monomers that remained in the materials [46]. Thermal decomposition of all investigated composites starts above 250 °C. The maximum degradation rate and the selected percentage of mass loss occur at similar temperatures for all PUR composites. As can be seen from DTG curves, degradation process in analyzed materials takes place in two overlapping stages at ca. 250–500 °C. In the first stage, the hard segments of the RPUFs structure are degraded, which is related to the breaking of urethane bonds. In the second

stage, degradation of the polyol-based soft segments of the RPUFs structure occurs and leads to formation of some kinds of aliphatic ethers or alcohols [46].

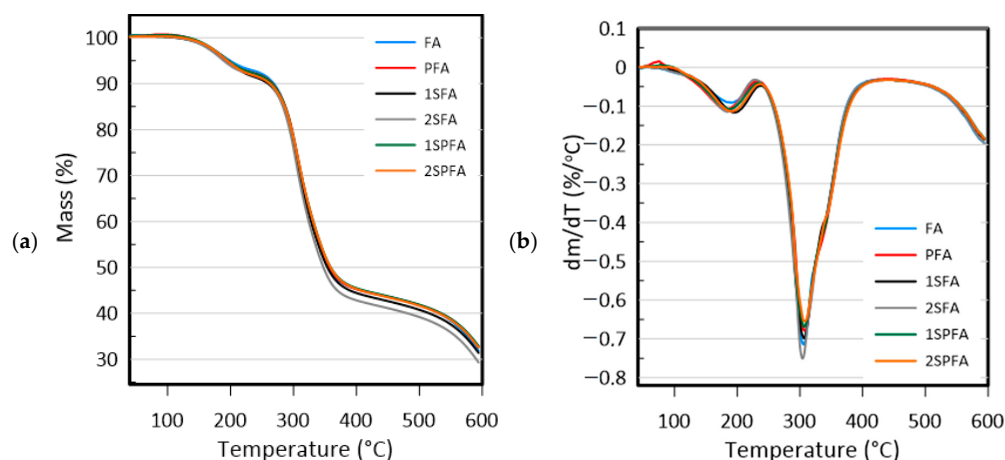


Figure 8. TG (a) and DTG (b) curves of PUR composites.

3.5. Flammability

The effect of filler modification on the gross calorific value of polyurethane composites was determined using a calorimetric bomb is summarized in Table 5.

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

Sample	Gross Calorific Value (MJ·kg ^{−1})	LOI (%)	UL94
PU_FA	24.4	22.0	N.R.
PU_PFA	23.5	21.8	N.R.
PU_1SFA	23.2	21.8	N.R.
PU_2SFA	23.5	21.9	N.R.
PU_1SPFA	23.7	22.0	N.R.
PU_2SPFA	23.7	22.0	N.R.

The obtained results showed that the modifier treatment influenced the value of the gross calorific value of polyurethane composites. The highest value is shown by the foam that contains unmodified fly ash (24.4 MJ·kg^{−1}). The same value was characteristic for the rigid polyurethane foam containing 10% fly ash addition in other published studies [47]. Nonetheless, the lowest value (23.2 MJ·kg^{−1}) was obtained for sample PU_1SFA. The decrease in the heat of combustion value in the case of PU_FA and PU_1SFA is 5%. This means that, for the same amount of filler in the foam, it is possible to further reduce the heat of combustion by modifying the filler. Sieving also decreased the combustion heat value. Moreover, the Table 5 summarizes the results of LOI and vertical tests performed in accordance with the UL94 standard. The oxygen index values for all samples oscillate around 22%. Meanwhile, all samples have no rating (N.R.) in vertical burning tests. It means that 10% addition of unmodified and modified fly ash is not sufficient to retard the flame. In the literature, no UL94 and LOI results were found for rigid polyurethane foams containing fly ash.

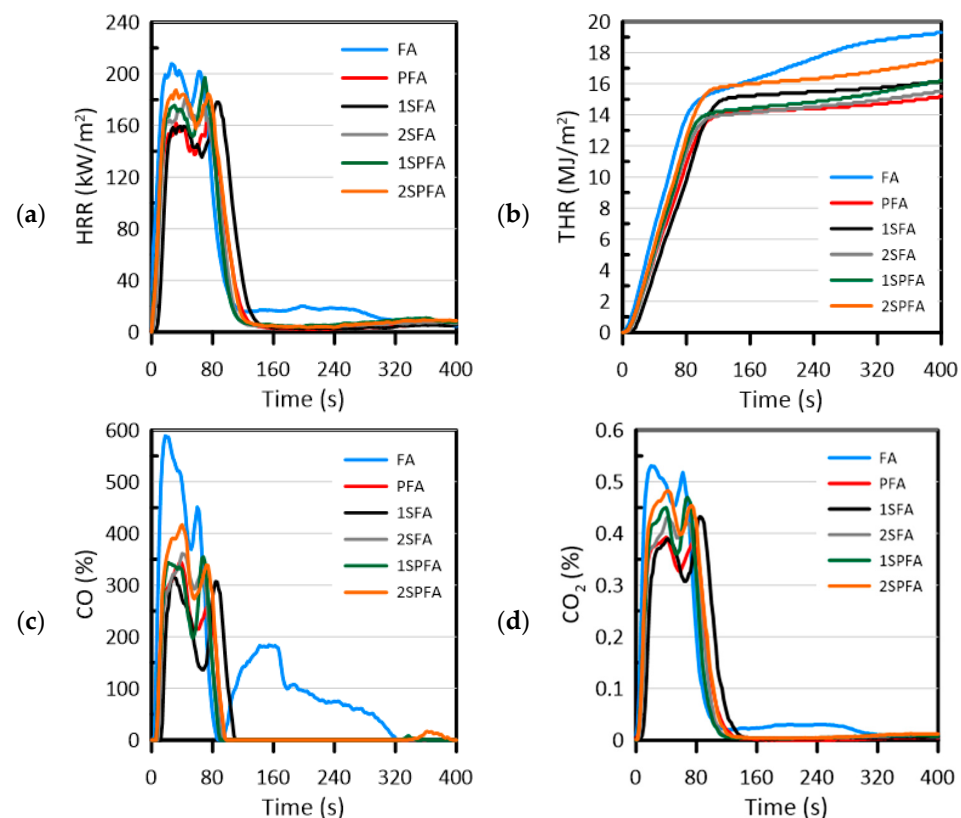
The cone calorimeter tests were carried out to assess the flammability and smoke production. The measuring instrument is effective in assessing the flame retardance of materials as it reflects the fire under real conditions [47]. The Table 6 presents the results of the time to ignition (TTI), effective heat of combustion (AEHC), maximum heat release rate (pHRR), time to pHRR (T-pHRR), fire growth rate (FIGRA), maximum average rate of heat emission (MARHE) and total smoke release (TSR).

Table 6. Cone calorimeter results of polyurethane composites.

Sample	TTI (s)	AEHC (MJ/kg)	pHRR (kW/m ²)	T-pHRR (s)	FIGRA (kW/m ² s)	MARHE (kW/m ²)	TSR (m ² /m ²)
PU_FA	2	28.1	207.8	26	7.99	177.16	679.9
PU_PFA	6	18.1	164.1	32	5.13	136.52	579.5
PU_1SFA	6	19.3	178.2	86	2.07	131.35	571.2
PU_2SFA	6	19.0	180.9	44	4.11	144.95	555.9
PU_1SPFA	4	20.6	197.2	70	2.82	151.63	544.5
PU_2SPFA	4	21.8	187.6	32	5.86	157.24	552.2

The shortest TTI time was obtained for PU_FA. The highest ignition delay (4 s. in relation to PU_FA) was achieved for PU_PFA and PU_1SFA samples. The highest values of AEHC and pHRR were found for the foam with unmodified FA and the lowest for foam with sieved fly ash. Sifting out of fly ash of the unburned carbon fraction and reducing the filler particles allowed to reduce the maximum HRR by 21%. Silanization of the modifier allowed to reduce pHRR by 13% in relation to the PU_FA. FIGRA is important index for heat risk assessment. It is defined as the ratio of the maximum HRR (p-HRR) value to the time the peak occurred (T-pHRR) [48]. Due to the FIGRA parameter, PU_FA was characterized by the greatest heat risk. A similar dependence of the results was observed for the MARHE parameter. The TSR decreased with each modification of the foam filler. The best value was obtained for the foam with the filler subjected to both modifications: sieved and silanized (PU_1SPFA).

The Figure 9 shows the charts of heat release rate (HRR), total heat release (THR), CO emission, CO₂ emission.

**Figure 9.** Charts of HRR (a), THR (b), CO (c), CO₂ (d).

The HRR plots of PU composites have the largest peak with a maximum value of approx. 208 kW/m² (Table 6). The lowest peak of the HRR curves was obtained for PU_PFA. On the basis of the analysis of the curves, it was observed that after 160 s to about 300 s, the foam containing unmodified ash continued to emit heat of about 20 kW/m². In the case of the HRR curves, the highest value for the TSR curves was obtained for PU_FA and then PU_2SPFA. The lowest value of the curve (maximum approx. 14 MJ/m²) was determined for the PU_PFA plot. The highest emissions of CO and CO₂ were also obtained for the foam containing unmodified fly ash.

4. Conclusions

In the study, three modifications of the filler (fly ash) were performed: silanization, sieving, silanization and sieving, and the influence of the filler on the properties of polyurethane composites was investigated. The reference foam was a foam containing unmodified coal fly ash.

The foams containing sieving fly ash (PU_PFA, PU_1SPFA, PU_2SPFA) were characterized by higher apparent density, water absorption and friability compared to the other samples. Despite the low values of the above parameters, they were characterized by reduced flammability, the lowest flammability values were obtained for the PU_PFA sample. As a result, the authors proved that a simple modification, which is sieving, reduces the amount of heat released and the emission of CO and CO₂ during combustion of polyurethane material.

Samples containing silanized fillers were characterized by the lowest apparent densities and water absorption. The lowest brittleness values of the material were obtained for the PU_1SFA sample. PU_1SFA foam also showed good flammability properties, however, they were still worse than PU_PFA.

The use of fly ash in technology of PUR foam is a great solution that reduces the amount of petrochemical products in the production of polyurethane materials and is a good method of waste disposal. The modifications presented in the article may improve the properties of the fly ash-polyurethane composite, however, before starting the adjustment process, the material properties to be improved should be selected and the appropriate modification method adjusted.

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