applied sciences

MDPI

Article

Assessment of Sieving as a Mean to Increase Utilization Rate of Biomass Fly Ash in Cement-Based Composites

Jakub Popławski * and Małgorzata Lelusz

Faculty of Civil and Environmental Sciences, Bialystok University of Technology, ul. Wiejska 45e, 15-351 Białystok, Poland

* Correspondence: j.poplawski@pb.edu.pl; Tel.: +48-728-317-778

Featured Application: The aim of this work is to increase the utilization rate of biomass fly ash in cement-based composites through activating fly ash with sieving.

Abstract: Biomass fly ash is a growing challenge for combustion by-product (CBP) management. This research was conducted to investigate the influence of activation by sieving through a 63 µm sieve and a 125 µm sieve on fresh and hardened cement mortar properties. Sieving increased the CaO content by 9.3 percentage points (p.p.) in the oxide composition of the fly ash. The 28-day Strength Activity Indices increased by 24.9 p.p. A 25% replacement rate of cement with fly ash sieved with a 63 µm sieve increased the 2-day compressive strength of mortars by 24% when compared with untreated fly ash. The 90-day compressive strength results of cement mortars with a 15% replacement rate of cement with fly ash sieved with a 63 µm sieve were similar to the control specimen results. The utilization rate of biomass fly ash can be increased to 15% of binder mass without the detrimental effect of the mechanical properties of cement mortar. SEM and TG analyses showed that activated biomass fly ash promoted the growth of the C-S-H phase and ettringite.

Keywords: fly ash; cement mortars; activation; sieving; biomass

Citation: Popławski, J.; Lelusz, M. Assessment of Sieving as a Mean to Increase Utilization Rate of Biomass Fly Ash in Cement-Based Composites. *Appl. Sci.* **2023**, *13*, 1659. https://doi.org/10.3390/app13031659

Academic Editors: Joan Formosa Mitjans and Jessica Giró Paloma

Received: 18 November 2022
Revised: 18 January 2023
Accepted: 20 January 2023
Published: 28 January 2023

1. Introduction

More than 3 billion tons of forest residue and more than 3.1 billion tons of agricultural biomass are used worldwide by the energy sector. Approximately 48 Mt of biomass ash is generated annually from that amount of fuel [1,2]. The share of energy produced from renewable sources in Poland has grown to over 15% of the total energy produced in the country. In 2020, almost 72% of renewable energy was derived from solid biomass combustion [3]. Regarding the current technological and legal obstacles, managing waste obtained from the combustion of biomass is considered to be the most difficult and important issue for the energy sector in Poland [4].

Biomass fly ash can exhibit a wider variance in chemical oxide composition and physical properties than coal fly ash, making it more difficult to manage as an industrial by-product [5,6]. Biomass fly ash is characterized by a high content of calcium and potassium and a lower amount of silica, alumina, and ferric oxides than bituminous fly ash. The average silica content of wood biomass fly ash is about 22%, while the lime content is about 43% [2,6]. Silica and lime are mainly present in woody biomass fly ash as quartz, calcite, and free lime. The presence of amorphous minerals was also detected in this kind of fly ash. The shape of particles of this kind of fly ash is irregular and has a high specific surface. The combustion conditions and technology influence the loss-on-ignition (LOI) value of fly ash and the number of amorphous minerals [2,7].

A considerable variance in the oxide composition, the mineralogical composition, and the physical properties results in much wider differences in the research results on the influence of biomass fly ash on the properties of concrete with its addition. The utilization

of fly ash in the range of 10–30% binder mass (b.m.) has resulted in a small increase in the water absorption of concrete [8]. The cement matrix prevents the leaching of heavy metals from biomass fly ash particles [9,10]. Biomass fly ash can be added as a sand substitute at up to a 30% replacement rate in concrete without reducing compression strength and freeze–thaw resistance [8]. The influence of woody biomass fly ash on mechanical properties can vary widely, which is related to its pozzolanic and hydraulic properties, grain size distribution, and the oxide composition of the additive. A mass replacement of 25% of the binder with fly ash from the combustion of wood biomass may result in a 7-day concrete compressive strength similar to that of the control samples, but from 28 days up to 1 year, modified concrete develops less strength than the control specimens [11]. In another study, up to a 25% replacement rate of biomass fly ash can lead to results similar to the control specimen compressive strength of concrete specimens [12]. Concurrently, the 28-day compressive strength of mortars with up to 20% b.m. of wood biomass fly ash can be 17% higher than that of the control series samples [13]. There is a positive correlation between the amount of reactive lime, reactive alumina with free lime and sulfates, and the compressive strength of mortar, with ettringite as the main hydration product [14]. At 25% b.m. replacement of cement with biomass fly ash in the binder, its effect on freeze–thaw resistance was not observed. Chloride ion migration studies performed as part of the same experiment showed that 25% fly ash replacement rate slightly increases the electric conductivity of the specimen [15].

Currently, the EN 450-1 standard prohibits the use of fly ash that was not collected from the combustion or co-combustion of coal [16,17]. For any potential use in the industry, biomass fly ash could be preprocessed or activated to change certain insufficient properties of that material. The adequate treatment of combustion by-products can increase their usability in other industries and decrease the spaces needed for their landfilling [18].

Sieving, grinding, washing, or drying are potential methods that can modify the properties of fly ash for desirable utilization routes [19]. The chemical activation and modification of the aluminosilicate composition of fly ash–cement systems can be used to increase the efficiency of the fly ash pozzolanic reaction [20]. Washing can be an effective way to remove excess chlorides found in unburnt coal particles of biomass fly ash [21]. The electrodialysis of biomass fly ashes can be used to separate more than 70% of its initial cadmium content [22]. Biomass fly ash can be effectively mineralogically activated by combining it with more active pozzolanic material [14,23]. Although there is considerable knowledge on the treatment of coal fly ash, there is a limited amount of research on the activation and treatment of biomass fly ash for usage in cement binders.

The preprocessing of fly ash is an important part of the utilization process. The sieving of fly ash can modify the selected properties of the material and also potentially separate its parts that are more suitable for different means of utilization. The aim of this research is to assess the influence of sieving on the basic properties of cement mortar: the development of compressive strength, water absorption, and the quality of the microstructure. Sieving enabled an increase in the utilization rate of fly ash up to 15% of binder mass without the detrimental effect of the mechanical properties of cement mortar.

2. Materials and Methods

As a binder material, CEM I 42.5R cement that followed the EN 197-1 standard requirements was utilized. The material conformed to the requirements of the EN 197-1 standard [24]. Biomass fly ash (BFA) was acquired from the local combined heat and power plant, which uses fluidized bed combustion (750 °C) for firing woody material. Chemical oxide compositions of the fly ash are presented in Table 1. The main oxides in fly ash compositions were calcium oxide, potassium oxide, and silica oxide. The minerals detected by the XRD study were quartz, calcite, calcium oxide, portlandite, calcium sulfite hydrate ($CaSO_3 \cdot 0.5H_2O$), iron hydrogen oxide ($Fe_{1.78}H_{0.66}O_3$), calcium silicate hydrate ($Ca_2SiO_4 \cdot 0.5H_2O$), calcium silicate, hematite, arcanite (Figure 1).

Table 1. Chemical oxide composition of biomass fly ash before activation and CEM I 42.5 R cement used in the study.

Oxide	Biomass Fly Ash	CEM I 42.5R
SiO_2	9.6%	17.4%
Al_2O_3	2.4%	4.2%
P_2O_5	0.0%	0.3%
Na_2O	0.0%	0.3%
K_2O	14.7%	0.7%
MgO	0.0%	0.7%
CaO	56.1%	67.9%
MnO	3.1%	0.1%
Fe_2O_3	7.9%	3.6%
CuO	0.0%	0.0%
ZnO	0.5%	0.1%
As_2O_3	0.0%	0.0%
SO_3	4.3%	3.8%
SrO	0.0%	0.2%
TiO_2	0.6%	0.5%
Cl	0.7%	0.2%
BaO	0.1%	0.0%

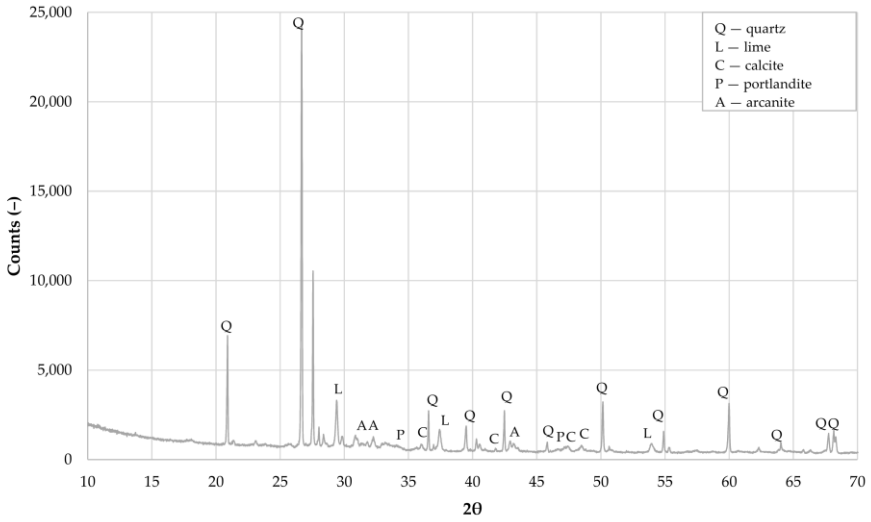


Figure 1. XRD analysis of biomass fly ash used in the study before activation.

The fineness and loss-on-ignition values of the fly ash are presented in Table 2. Both Strength Activity Indices (SAIs) of the biomass fly ash required by EN 450-1 prior to its activation were below 75% for 28-day SAI and 85% for 90-day SAI [17].

Table 2. Physical properties of biomass fly ash used in the study before activation.

Property	Biomass Fly Ash	EN 450-1 Requirements
Fineness	43.1%	≤40% (N category)
Specific surface (Blaine method)	2559 cm^2/g	-
Volume-specific surface (dynamic light scattering)	5738 cm^2/cm^3	-
Loss on ignition	7.8%	≤9% (C category)
Strength Activity Index after 28 days	64.3%	≥75%
Strength Activity Index after 90 days	66.1%	≥85%

Table 3 presents the grain size distribution of initial untreated fly ash. Particles with a diameter above 45 µm were 38.2% of the particle size mix. Standard sand that followed EN 196-1 requirements was used. Tap water was used during mixing.

Table 3. Grain size distribution of biomass fly ash used in the study before activation.

Material	>2.0 mm	2.0–1.0 mm	1.0–0.5 mm	0.50–0.25 mm	0.250–0.125 mm	0.125–0.063 mm	0.063–0.045 mm	0.045–0 mm
Biomass fly ash	0.0	0.0	0.0	0.3	12.0	18.7	7.2	61.8

Three types of biomass fly ash were used: untreated fly ash (FA(B)N), fly ash that was sieved with a 125 µm sieve (FA(B)125), and fly ash that was sieved with a 63 µm sieve (FA(B)63). For the basis of the calculation for the mixes, the EN 196-1 standard mortar mix (450 g of cement, 1350 g of sand, and 225 g of water) was used [25]. Totals of 5%, 15%, or 25% of cement binder in mortars were replaced with fly ash and expressed as an experimental factor: the mass of fly ash to the whole binder mass ratio (fa/b). Based on those assumptions, mix proportions of cement mortars were prepared and are presented in Table 4.

Table 4. Cement mortar mix proportions.

Nr	Series Codes		Biomass Fly Ash			Cement (g)	Sand (g)	Water (g)
	Type of Fly Ash (-)	Amount of Fly Ash (-)	Sieved with 63 µm Sieve (g)	Sieved with 125 µm Sieve (g)	Untreated (g)			
1.	FA(B)63	fa/b = 0.05	22.5	0.0	0.0	427.5	1350	225
2.	FA(B)63	fa/b = 0.15	67.5	0.0	0.0	382.5	1350	225
3.	FA(B)63	fa/b = 0.25	112.5	0.0	0.0	337.5	1350	225
4.	FA(B)125	fa/b = 0.05	0.0	22.5	0.0	427.5	1350	225
5.	FA(B)125	fa/b = 0.15	0.0	67.5	0.0	382.5	1350	225
6.	FA(B)125	fa/b = 0.25	0.0	112.5	0.0	337.5	1350	225
7.	FA(B)N	fa/b = 0.05	0.0	0.0	22.5	427.5	1350	225
8.	FA(B)N	fa/b = 0.15	0.0	0.0	67.5	382.5	1350	225
9.	FA(B)N	fa/b = 0.25	0.0	0.0	112.5	337.5	1350	225
10.		K	0.0	0.0	0.0	450.0	1350	225

For each series, twelve 40 mm × 40 mm × 160 mm mortar specimens were prepared in accordance to EN 196-1 guidance [25]. Specimens were cured in tap water up to the test day. Consistency tests were performed on fresh mortar mixtures according to EN 1015-3 [26]. For each series, mechanical properties tests (compressive and tensile strength tests) were performed after 7, 28, and 90 days of curing. Water absorption and density tests were performed after 28 days of water curing. Each mechanical strength test was performed on three specimens in accordance with EN 196-1 [25] (three specimens were used for the tensile strength test, and six halves obtained after this test were used for the compressive strength test). For water absorption and density tests following PN-85/B-04500 standard instructions, three specimens were used [27]. Thermogravimetric (TG) and scanning electron microscope (SEM) tests were conducted on 28-day mortars. Statistical analyses were performed using Tibco Software Inc. Statistica 13.3 software [28].

3. Results and Discussion

3.1. Characteristics of Activated Fly Ash

Both sieving methods of the fly ash changed the grain size distribution of fly ash (Figure 2). Sieving decreased the maximum dimension of the particles of the material. The smoothness of the slope of the cumulative mass graph for 63 µm shows that sieving through such a small sieve size eliminated clusters of particles.

Sieving decreased the value of EN 450-1 fineness (understood as the amount of residue left on the 45 µm sieve after wet-sieving or air-sieving). In the case of FA(B)63 fly ash, there was a change of 41.6 percentage points (p.p.) from 43.1% for FA(B)N to 1.5% (Table 5). Both sieved types of fly ash were characterized by higher than required by EN 450-1 28-day Strength Activity Index values. A 25 p.p. increase in the 28-day SAI value was observed in fly ash sieved through the 63 µm sieve. With sieving, the specific surface of fly ash increased. A similar influence of sieving was observed in the loss-on-ignition values, indicating that a

substantial amount of unburnt carbon is in the form of particles smaller than 125 µm. After sieving through the 125 µm sieve, about 77% of the initial material was used. After sieving through the 63 µm sieve, around 63% of the untreated fly ash was used. Around 23–37% of initial untreated material would require further utilization as a by-product of activation.

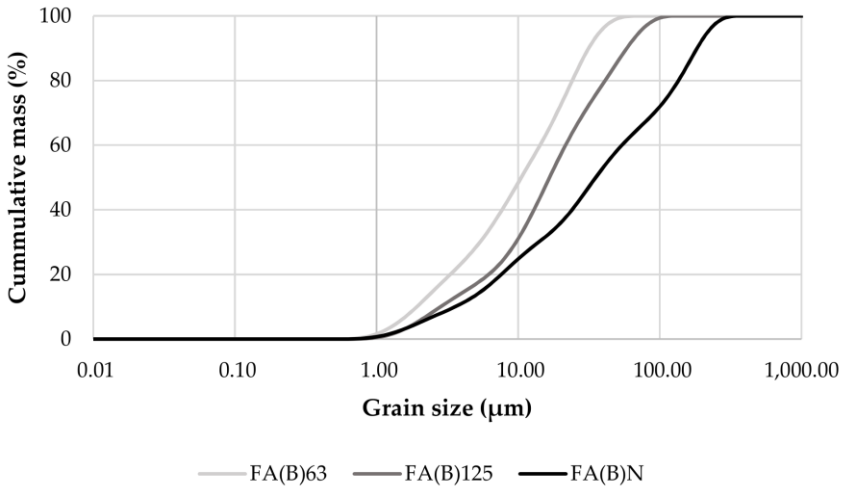


Figure 2. Grain size distribution of fly ash sieved with 63 µm (FA(B)63) or 125 µm (FA(B)125) sieve compared with untreated fly ash (FA(B)N).

Table 5. Physical properties of sieved fly ash (FA(B)63 and FA(B)125) compared with untreated fly ash (FA(B)N).

Property	FA(B)63	FA(B)125	FA(B)N
Fineness	1.5%	16.3%	43.1%
Specific surface (Blaine method)	6281 cm^2/g	3416 cm^2/g	2559 cm^2/g
Volume-specific surface (dynamic light scattering)	12,445 cm^2/cm^3	7573 cm^2/cm^3	5738 cm^2/cm^3
Loss on ignition	18.3%	11.8%	7.8%
Strength Activity Index after 28 days	89.2%	81.1%	64.3%
Strength Activity Index after 90 days	80.4%	79.6%	66.1%

The morphology of the fly ash did not significantly change through activation. SEM photographs, presented in Figure 3, show that activated and untreated fly ash mostly consist of irregularly shaped particles. Sieving successfully separated bigger particles of quartz from entering the mix (Figure 3b). However, it does not completely eliminate irregular black particles of unburnt carbon.

Sieving mainly changed the amount of two crucial oxides, SiO_2 and CaO, in the oxide composition of the activated material (Table 6). Sieving fly ash through 63 µm increased the amount of lime in the oxide composition by 9.3 p.p. and decreased the amount of silica by 6.3 p.p. This suggests that a substantial amount of quartz in the fly ash was present as particles of the upper parts of its grain size distribution, whereas lime is present as smaller particles.

The distribution of lime and silica in the morphological composition of fly ash was studied through an EDS analysis of the material (Table 7). EDS analysis is semi-quantitative, and the figures shown in Table 7 are approximate but enable distinguishing the concentration points of crucial elements. The smallest fluffy-shaped particles mostly consist of CaO (spots 1, 5, 6, and 8 in Figure 4), whereas bigger and more profound particles are rich in SiO_2 (spot 2 in Figure 4). EDS analysis also confirmed the presence of unburned carbon in a form of micro-size particles.

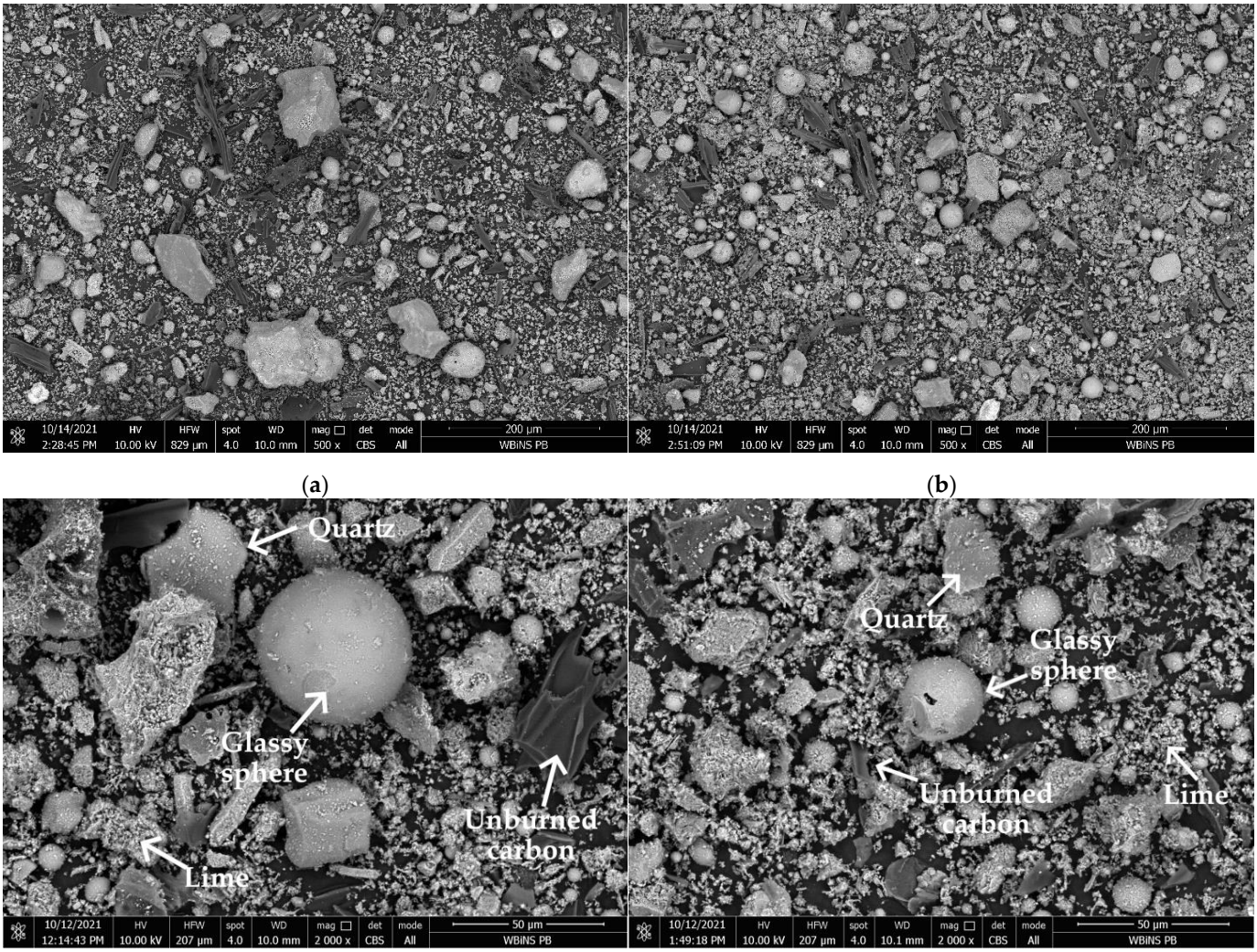


Figure 3. SEM photographs of fly ash (**a**) untreated (FA(B)N) (500× magnification), (**b**) sieved with 63 µm (FA(B)63) (500× magnification), (**c**) untreated (FA(B)N) (2000× magnification), and (**d**) sieved with 63 µm (FA(B)63) (2000× magnification).

Table 6. Chemical oxide composition of sieved biomass fly ash.

Oxide	FA(B)63	FA(B)125	FA(B)N
SiO_2	3.3%	5.9%	9.6%
Al_2O_3	0.0%	0.0%	2.4%
P_2O_5	0.0%	0.0%	0.0%
K_2O	14.6%	14.7%	14.7%
CaO	65.4%	61.7%	56.1%
MnO	3.6%	3.4%	3.1%
Fe_2O_3	7.4%	8.5%	7.9%
CuO	0.1%	0.1%	0.0%
ZnO	0.6%	0.6%	0.5%
As_2O_3	0.0%	0.0%	0.0%
SO_3	4.3%	4.2%	4.3%
TiO_2	0.4%	0.6%	0.6%
Cl	0.0%	0.0%	0.7%
BaO	0.3%	0.3%	0.1%

Table 7. Chemical elements detected in EDS spots of fly ash sieved with 63 μm (by weight %).

Element	Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Spot 6	Spot 7	Spot 8
C	10.8	-	15.5	20.6	-	-	29.1	19.8
O	52.9	44.9	42.0	35.9	38.4	38.0	39.5	45.1
Na	-	-	1.6	-	5.2	-	-	-
Mg	1.8	-	6.4		10.3	8.5	6.0	3.4
Al	0.8	-	1.3	11.5	-	2.2	0.9	-
Si	1.1	55.1	3.3	12.3	2.0	4.4	2.1	1.7
Cl	-	-	-	-	-	-	-	1.5
P	-	-	4.9	-	13.0	6.3	3.6	-
K	1.6	-	1.6	17.1	10.4	1.4	1.9	1.8
Ca	31.0	-	23.4	2.6	20.7	34.8	16.9	26.7
Mn	-	-	-	-	-	2.7	-	-
Fe	-	-	-	-	-	1.7	-	-

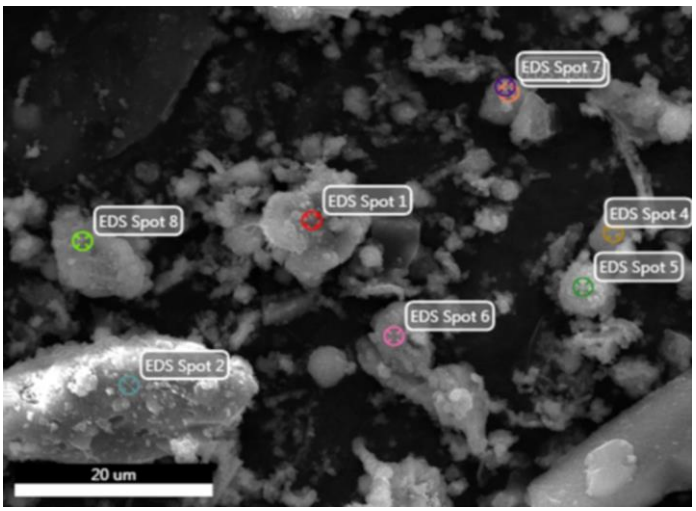


Figure 4. EDS spot distribution in an SEM photograph of fly ash sieved with 63 μm.

As shown in Tables 5 and 6, sieving influenced both the chemical composition and physical properties of the investigated wood biomass fly ash. FA(B)63 and FA(B)125 fly ash had higher amounts of CaO and smaller amounts of SiO_2 than untreated FA(B)N fly ash. CaO was observed in the form of lime and portlandite (Figure 1). These minerals, together with arcanite, were mostly responsible for the hydraulic reactivity of biomass fly ash [29]. Sieving separated SiO_2, which was mostly in the form of non-reactive quartz and increased the amount of reactive calcium-based minerals (Table 6). Lime and alkalis from biomass fly ash can function in the mix as a reservoir of alkalinity that can accelerate the dissolution of minerals from cement and other additives into the solution of fresh mortar mix, thus, quickening the initial stages of hydration reactions [30,31].

Fineness and loss on ignition are the two most often required properties in international standards for fly ash [32]. They are the best predictor for the quality of siliceous fly ash [33–35]. In the case of FA(B)63 fly ash, fineness decreased from 43.1% to 1.5%. Sieving improved the grain size distribution of biomass fly ash. Sheng et al. [36] observed that biomass fly ash is capable of broadening the particle size distribution of cement by increasing the number of particles smaller than 45 μm and by that can increase the self-cementitious strength of fly ash [36]. The relationship between fineness, wide particle size distribution, and self-hardening properties has also been highlighted by Ohenoja et al. [37]. Both FA(B)63 fly ash and FA(B)125 fly ash are mainly composed of particles in this range of 1–100 μm. Especially, FA(B)63 fly ash had a much smoother particle size distribution than untreated FA(B)N fly ash (Figure 2), which indicates that the grain size composition of that

fly ash had fewer clusters. The modification of the particle size distribution influenced the early compressive strength of cement mortars.

Sieving increased the observed loss-on-ignition values of activated fly ash. These results might indicate that a substantial amount of unburnt carbon is in form of particles smaller than 125 µm and might need to be removed by other means of activation to further enhance the properties of fly ash in the context of its utilization in concrete production. The amount of unburned carbon and the increase in the specific surface can explain the difference in which FA(B)63 fly ash influenced the fresh consistency of cement mortar.

It is important to note that loss-on-ignition measurements cannot give a precise estimate of unburned carbon in other types of fly ash than siliceous fly ash [38]. The results may overestimate the amount of organic carbon due to the fact that ignition loss of mass is also due to reactions such as the calcination of carbonates, the dehydration of portlandite, the removal of physically bound water, and the oxidation of sulfur and iron minerals [39]. Most of these compounds were detected by XRD studies of the fly ash (Figure 1).

3.2. Fresh Consistency Results

The change in the amount of fly ash in the binder mass did not affect the consistency results when untreated fly ash or fly ash sieved through 125 µm were used in the mix (Figure 5). An interaction of the two studied factors was observed in the case of fly ash sieved with the 63 µm sieve. With the increase in the amount of fly ash sieved with the 63 µm sieve, the consistency significantly decreased from 135.8 mm to 112.5 mm. The mean consistency of the control specimens was 140.8 mm.

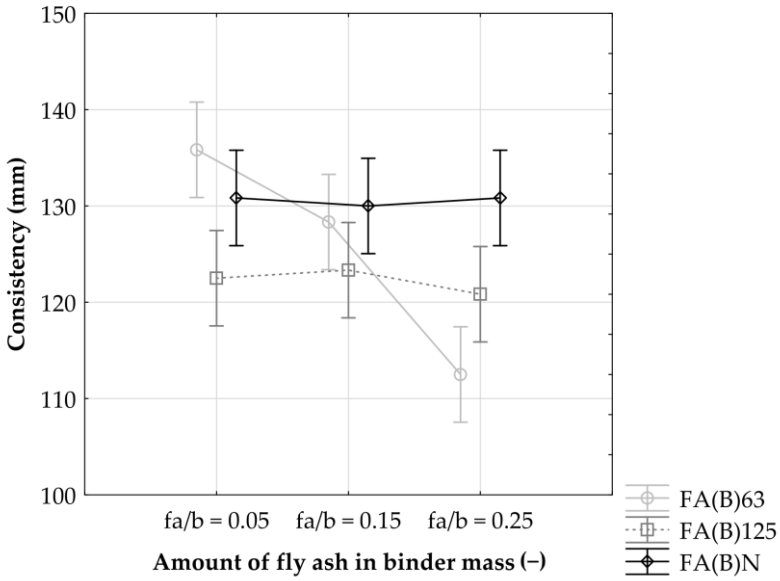


Figure 5. Fresh consistency test results of mortars with addition of sieved fly ash FA(B)63 and FA(B)125 compared with the results of mortars with untreated fly ash FA(B)N (ANOVA 95% CI in the whiskers).

All specimens with the addition of fly ash had consistency results smaller than the control specimens. When comparing specimens with a 5% amount of fly ash in the binder, the value of consistency was significantly higher in specimens with the addition of FA(B)63 fly ash than with the addition of FA(B)125 fly ash, which might be explained by the elimination of the biggest particles of silica visible in the SEM photographs in Figure 3, which resulted in the increased water demand of the material. Consequently, the observed impact of FA(B)63 fly ash on the consistency results can be explained by the increase in the specific surface of fly ash. The influence of particle size distribution on consistency is in line with the results of the study of particle size distribution on the water demand of biomass fly ash and tests conducted on commercial screed mortars [37,40]. The practical

implications for the future use of activated fly ash can be given from the achieved results. Sieving through a 125 µm sieve might not require additional consistency control with the correction of water content in the mix or the use of a plasticizer.

3.3. Tensile Strength Results

Activation of fly ash impacted the 2-day tensile strength results (Figure 6a). With an increase in fly ash in the binder mass ratio, the specimens with the addition of untreated fly ash showed a decrease in the tensile strength results. Sieving fly ash through the 125 µm or 63 µm sieve enabled utilizing up to 25% b.m. of fly ash without a statistically significant detrimental effect on early tensile strength. The mean result of control specimens after 2 days of curing was 4.8 MPa. With the curing time, the effect of fly ash activation on tensile strength results decreased. The change in the amount of fly ash predominantly explained the variance in the tensile strength of the modified cement mortar after 90 days of curing (Figure 6b). The mean result of control specimens after 90 days of curing was 8.3 MPa.

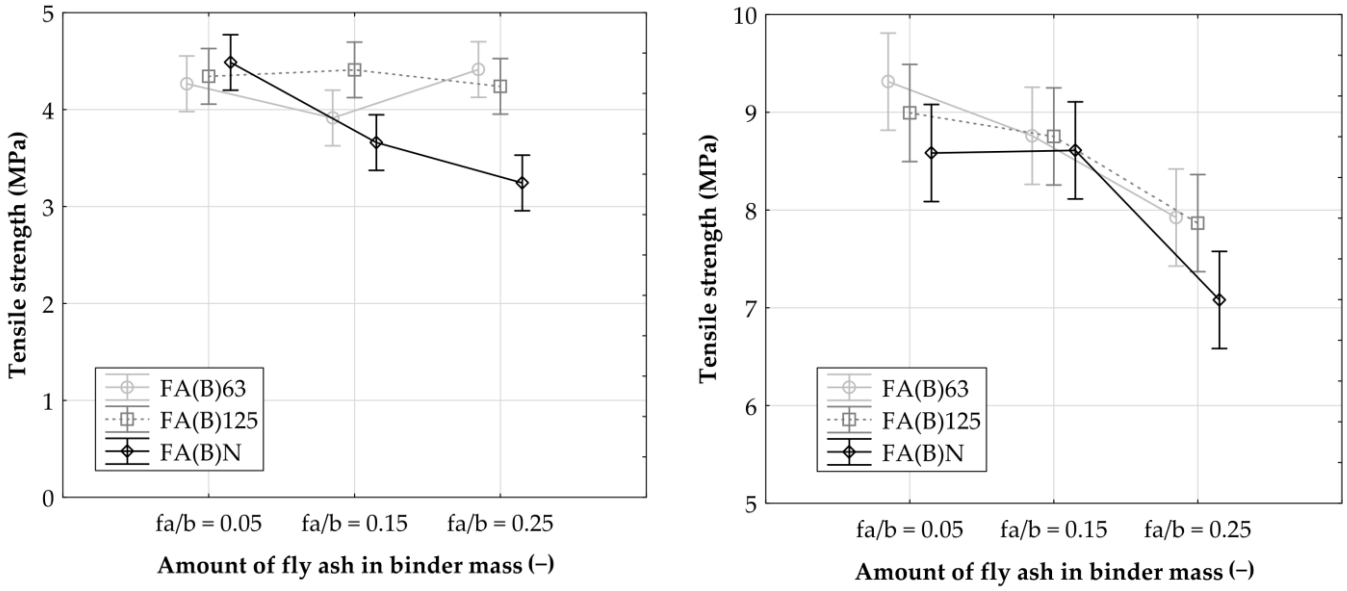


Figure 6. The (**a**) 2-day and (**b**) 90-day tensile strength test results of mortars with the addition of sieved fly ash (FA(B)63 or FA(B)125) compared with the results of mortars with untreated fly ash (FA(B)N) (ANOVA 95% CI in the whiskers).

With the increase in the curing time of the specimens, the impact of the activation method decreased. Sieving had a more profound influence on early hydration. The changes in the specific surface and content of lime in sieved fly ash followed the changes in the mechanical properties of mortars. Sieving enabled an increase in the utilization rate of fly ash to 25% of binder mass without statistically significant detrimental effects on early and late tensile strength.

3.4. Compressive Strength Results

As in the case of tensile strength, the most profound influence of activated fly ash was observed in the early compressive strength results (Figure 7a). With an increase in fly ash, the binder mass specimens with untreated fly ash showed a decrease in the 2-day compressive strength results. The activation of fly ash by sieving with the 125 or 63 µm sieve enabled utilizing up to 25% of fly ash in the binder without a negative influence on the 2-day compressive strength results. With the 90-day results, no detrimental effect was observed with the addition of up to 15% of either FA(B)125 or FA(B)63 fly ash (Figure 7b).

The control specimen result for the 2-day compressive test was 22.8 MPa, and for the 90-day compressive strength test, it was 59.3 MPa.

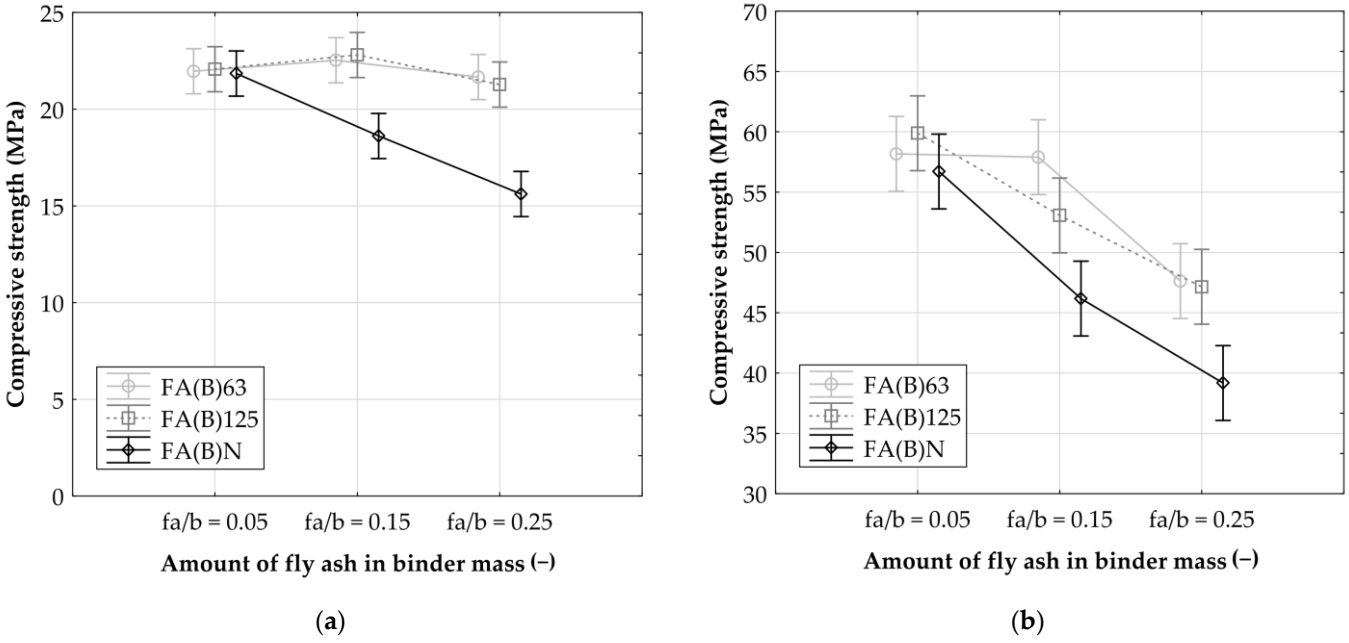


Figure 7. The (**a**) 2-day and (**b**) 90-day compressive strength test results of mortars with the addition of sieved fly ash (FA(B)63 or FA(B)125) compared with the results of mortars with untreated fly ash (FA(B)N) (ANOVA 95% CI in the whiskers).

The dynamics of the increase in the compressive strength for specimens with a 15% amount of FA(B)63 fly ash in the binder mass was similar to the compressive strength increase in the control specimens (Figure 8). The difference between the 90-day strength of mortars with the addition of 15% b.m. of FA(B)125 and 15% of FA(B)63 was not statistically significant (Figure 7b). Despite not meeting the 90-day SAI criteria (Table 5), substantial strength growth was observed at 28 days and 90 days of hydration for both types of sieved fly ash.

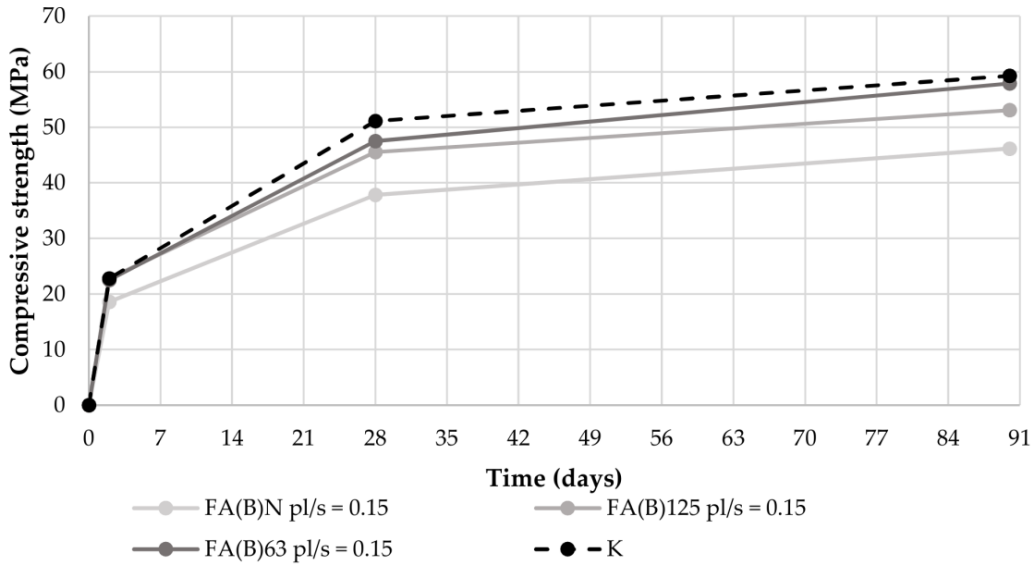


Figure 8. Strength development of mortars with 15% addition of sieved fly ash (FA(B)63 or FA(B)125) compared with the results of mortars with 15% addition of untreated fly ash (FA(B)N).

The development of compressive strength of cement mortars modified with activated fly ash observed in the study can help formulate practical conclusions: the addition of up to 15% b.m. of fly ash sieved through either a 63 µm or 125 µm sieve can give similar mechanical properties to control specimens (Figure 8). However, despite the higher compressive strength results, sieving biomass fly ash through a 63 µm sieve must be economically justified because less than three-quarters of the initial material is utilized. The oversized residue would require further management in different class composites or different industries. Considering the above, the utilization of a 125 µm sieve might be enough for the potential technological installation activating biomass fly ash. Considering the variance in the chemical composition of fly ash, the utilization rate of both FA(B)63 and FA(B)125 fly ash can be increased further by combining it with active pozzolanic material [14,23,41].

3.5. Water Absorption and Bulk Density Results

Both the water absorption results and the bulk density results were affected by the amount of fly ash in the binder without any clear influence of activation itself. Water absorption increased by about 0.5 p.p. when the amount of fly ash in the binder increased from 5% to 25% (Table 8). The bulk density of cement mortar decreased by about 0.1 g/cm^3 on average when the amount of addition changed from 5% to 25% in the mortar mix.

Table 8. Water absorption and bulk density of cement mortars with the addition of sieved fly ash (FA(B)63 and FA(B)125) compared with untreated fly ash (FA(B)N).

Nr	Series Codes		Water Absorption (%)	Bulk Density (g/cm^3)
	Type of Fly Ash (-)	Amount of Fly Ash (-)		
1.	FA(B)63	fa/b = 0.05	8.3	2.10
2.	FA(B)63	fa/b = 0.15	8.8	2.07
3.	FA(B)63	fa/b = 0.25	9.2	2.03
4.	FA(B)125	fa/b = 0.05	8.4	2.09
5.	FA(B)125	fa/b = 0.15	8.6	2.08
6.	FA(B)125	fa/b = 0.25	8.9	2.06
7.	FA(B)N	fa/b = 0.05	8.5	2.06
8.	FA(B)N	fa/b = 0.15	8.6	2.07
9.	FA(B)N	fa/b = 0.25	9.1	2.01
10.	K		8.7	2.02

The slight increase in the water absorption results is in line with the research conducted by Gabrijel et al. [42]. The research team noticed a slight increase in open porosity and capillary absorption of specimens with some tested biomasses of fly ash. They associated the differences in the results with the difference in the particle size distribution of fly ash.

3.6. SEM and TG Analysis

TG-DTG analyses occurred in four sections [43]. The first section occurs from room temperature to around 105 °C, when the loss of free water occurs [43]. The dehydration of C–S–H gels and ettringite took place within the range from 105 to 200 °C [43–45]. The third section of the curve is the weight loss occurring due to thermal degradation around 400–550 °C [43–46]. This section corresponds to the decomposition of portlandite that was created during hydration reactions [43–45]. The fourth section corresponds to the decomposition of calcium carbonate at 550–740 °C [43–45].

Qualitatively, mortars that had different types of sieved fly ash in their composition did not differ from each other—similar DTG peaks were observed as in the control specimen. Some changes in the DTG curves were observed in the scope of 20–200 °C, which were consistent with the addition of 15% (Figure 9) and 25% (Figure 10) of FA(B)63 fly ash. In specimens with fly ash sieved through the 63 µm sieve, the peak at around 125 °C was around 12 p.p. bigger than for specimens with the respective amount of FA(B)N fly ash.

The difference indicates a higher amount of C-S-H gel phase and ettringite in specimens with sieved fly ash.

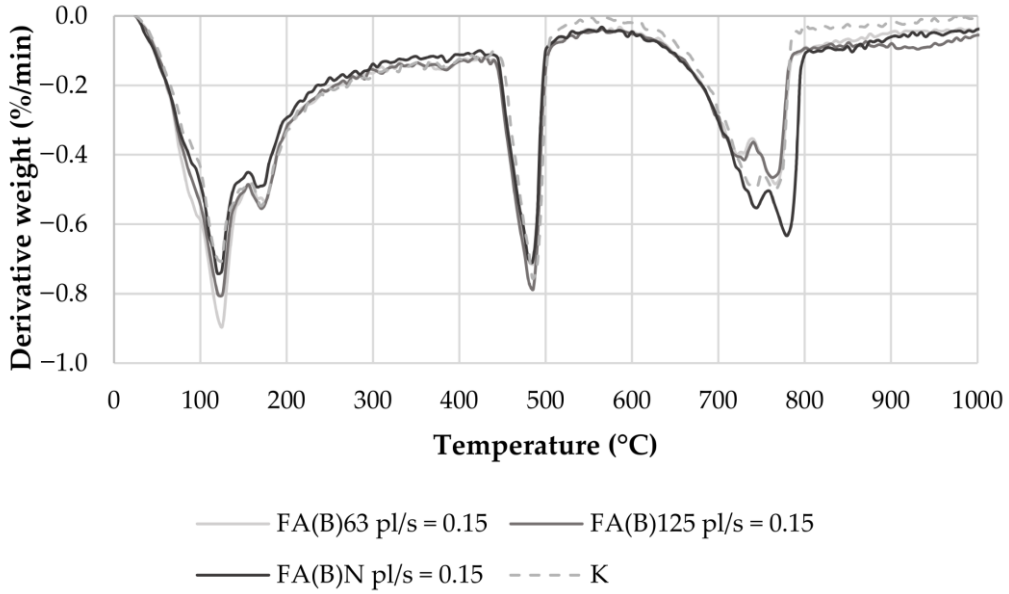


Figure 9. Derivative thermogravimetric (DTG) curves of mortars with a 15% addition of sieved fly ash (FA(B)63 or FA(B)125) compared with the results of mortars with a 15% addition of untreated fly ash (FA(B)N).

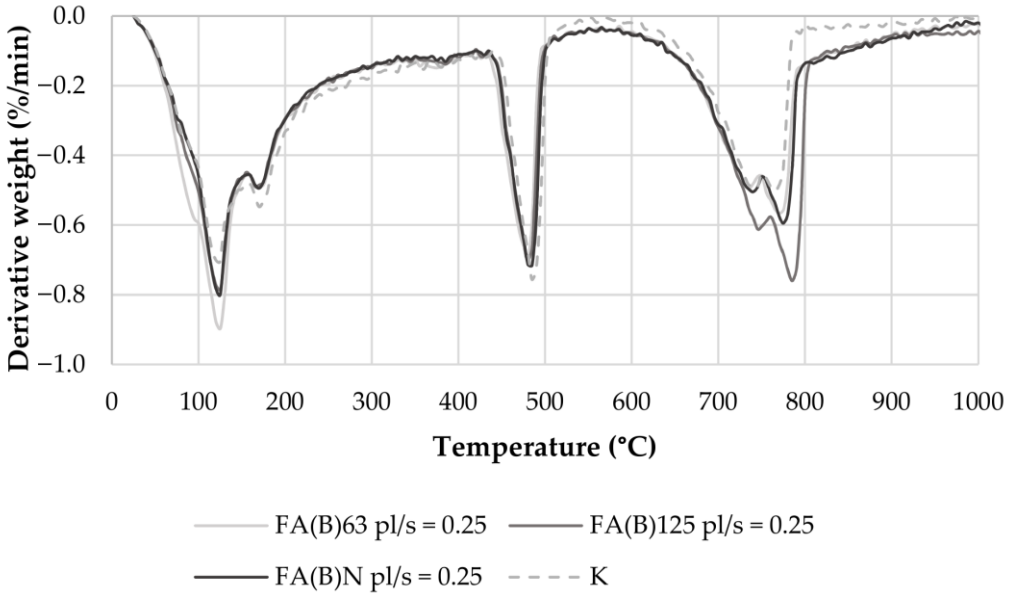


Figure 10. Derivative thermogravimetric (DTG) curves of mortars with a 25% addition of sieved fly ash (FA(B)63 or FA(B)125) compared with the results of mortars with a 25% addition of untreated fly ash (FA(B)N).

When they were analyzed separately, no clear influence of sieved fly ash on the third (450–500 °C) and fourth (550–800 °C) sections of the DTG curves was observed (Figure 11). However, the sum of portlandite and carbonate phases tends to be higher with sieved fly ash than in the control specimens.

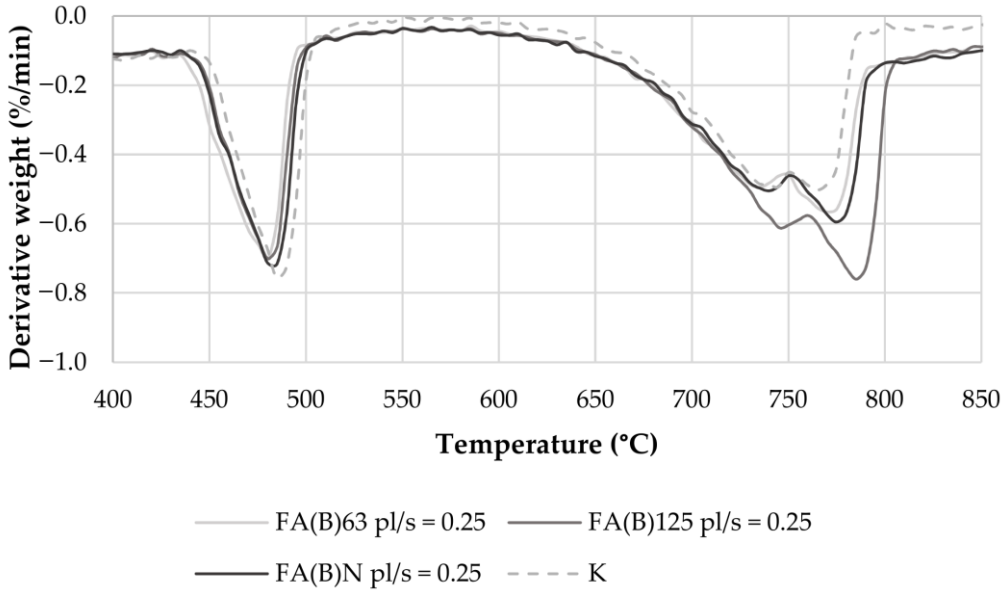
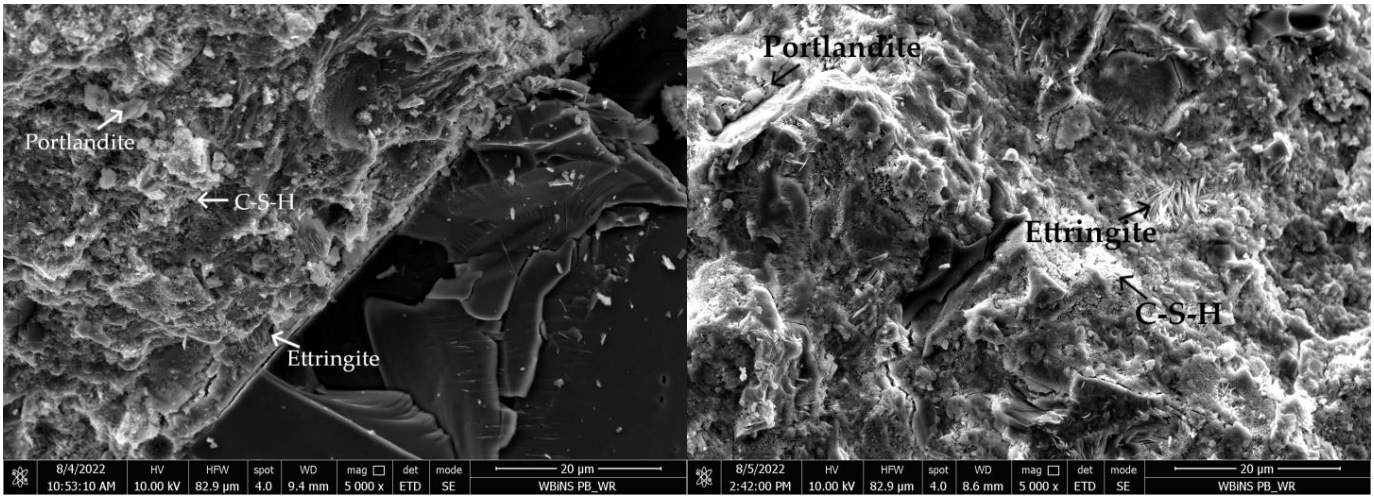


Figure 11. Derivative thermogravimetric (DTG) curves of mortars with a 25% addition of sieved fly ash (FA(B)63 or FA(B)125) compared with the results of mortars with a 25% addition of untreated fly ash (FA(B)N).

SEM analysis confirmed the conclusions from the TG/DTG research. In terms of quality, the microstructure of cement paste was similar between series with the addition of fly ash. The characteristic structures of the C-S-H gel, ettringite crystals, and portlandite crystals were observed in all specimens with the addition of biomass fly ash. Nonetheless, specimens with the addition of FA(B)63 fly ash had a noticeably smaller number of portlandite crystals and a denser structure of C-S-H gel (Figure 12a) than the specimens with the addition of untreated FA(B)N fly ash (Figure 12b). The difference in the $Ca(OH)_2$ content in the cement matrix could be associated with the higher hydration rate and formation of the C-S-H gel in those specimens.

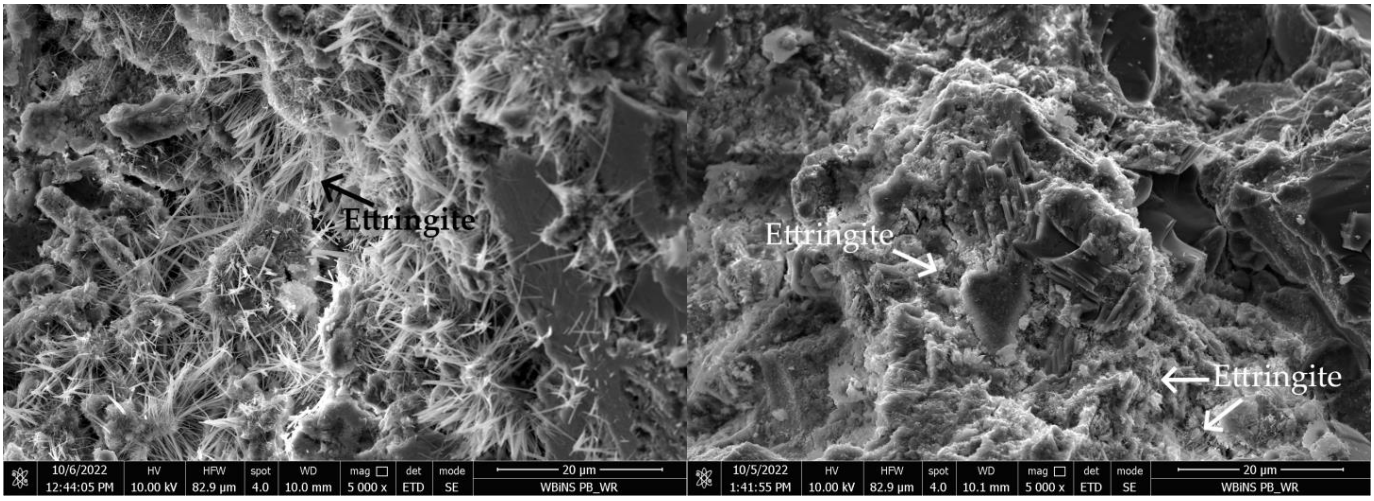


(**a**) (**b**)

Figure 12. SEM photographs of cement mortar with a 25% addition of (**a**) fly ash sieved with 63 µm sieve (FA(B)63) and (**b**) untreated fly ash (FA(B)N).

Noticeably, the microstructure of ettringite crystals was different between specimens with FA(B)63 and FA(B)N fly ash. Specimens with FA(B)N fly ash were characteristic of a

very light structure of ettringite with very long-needle-shaped minerals (Figure 13a). In specimens with FA(B)63 fly ash, the microstructure of ettringite was different, with dense areas of short minerals (Figures 13b and 14).



(**a**) (**b**)

Figure 13. SEM photographs showing the ettringite structure of cement mortar with a 25% addition of (**a**) untreated fly ash (FA(B)N) and (**b**) fly ash sieved with 63 µm sieve (FA(B)63).

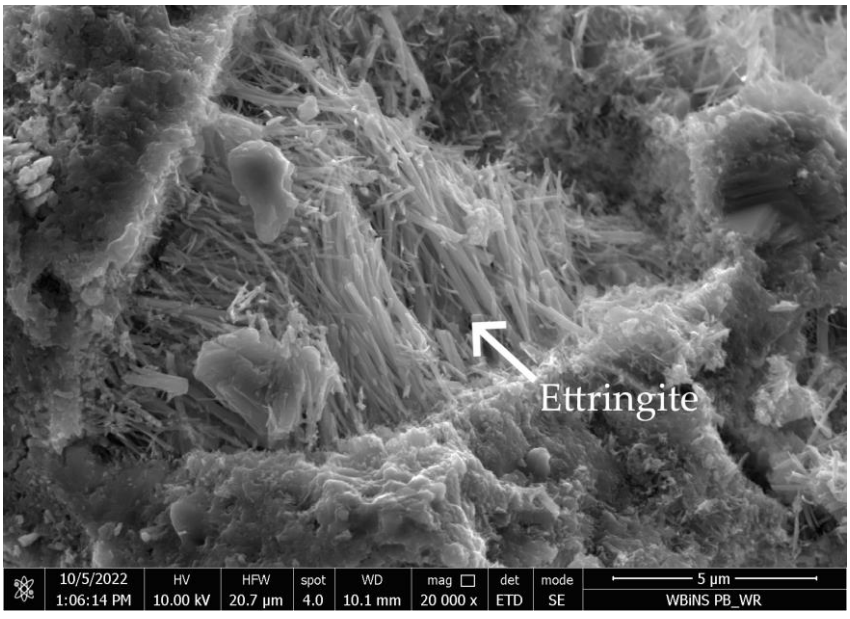


Figure 14. A close-up SEM photograph showing the ettringite structure of cement mortar with a 25% addition of fly ash sieved with 63 µm sieve (FA(B)63).

Sheng et al. [36] observed that the self-hardening properties of fly ash produced by co-firing coal in a fluidized bed combustion boiler are mostly associated with the CaO content, SO_3 content, and fine particle size distribution of fly ash. Those properties can be beneficial for the early generation of the C-S-H phase and AFt. The minerals detected through the XRD study are in line with those detected by other research teams that also highlighted the hydraulic potential of fly ash. Ohenoja et al. [29] emphasized the role of early ettringite formation in the development of early compressive strength in this kind of cement composite. The dense structures of small ettringite crystals were detected in FA(B)63 specimens, which were not observed in FA(B)N specimens (Figure 13). The

ettringite formations detected in specimens with untreated fly ash were loose in structure with much longer crystals. As can be observed in the DTG results (Figure 10), FA(B)63 fly ash prompted the creation of a denser cement matrix, which contributed to the early compressive results. These observations are also in line with the influence of sieving on the Strength Activity Indices (Table 5).

4. Conclusions

The conducted research showed that sieving changed the properties of biomass fly ash. Those changes influenced the properties of cement mortar with the addition of activated materials and enabled the use of more fly ash in the binder composition without detrimental effects on mechanical properties:

1. Sieving increased the amount of CaO and decreased the SiO_2 content in the oxide composition of fly ash. In the case of fly ash sieved with a 63 μm sieve, the amount of lime increased by 9.3 p.p. compared with untreated fly ash. SEM/EDS analyses showed that most CaO is in the form of small particles.
2. Sieving through a 125 μm sieve reduced the amount of used initial material to 77%, while sieving through a 63 μm sieve left for usage around 63% of the untreated fly ash.
3. Sieving substantially increased the specific surface of fly ash. In the case of fly ash sieved with a 63 μm sieve, the increase was twofold, and in the case of fly ash sieved with a 125 μm sieve, the increase was 31.9%. The grain size distribution of fly ash sieved with a 63 μm sieve was smoother, which increased the packing effect of the additive.
4. The 90-day Strength Activity Index of both activated fly ash did not achieve the 85% threshold. Nonetheless, the 28-day and 90-day Strength Activity Indices of both activated biomass fly ashes increased by 15–20 p.p.
5. The consistency of fresh mortar decreased when sieved fly ash was used in the cement mortar mix. However, contrary to untreated fly ash and fly ash sieved through a 125 μm sieve, only fly ash activated through sieving with a 63 μm sieve decreased consistency values with the increase in the amount of additive in the mix.
6. The utilization of sieved fly ash in the cement mortar mix increased the early tensile and compressive strength of the hardened material. The 25% b.m. additive of activated fly ash resulted in similar mechanical properties as those of the control specimens. The 2-day compressive and tensile strength results of untreated fly ash were about 35% smaller than those of the control specimens.
7. The 90-day compressive strength results of specimens with 15% b.m. of activated fly ash were similar to those of the control specimens. Only 5% b.m. of untreated fly ash could be used without a detrimental effect on the late compressive strength of cement mortar.
8. Water absorption and bulk density were only slightly and not explicitly affected by the size of the sieve used during activation.
9. TG analyses showed an increase in the amount of C-S-H and ettringite phases for mortars with a 15% and 25% b.m. addition of fly ash sieved with a 63 μm sieve, which could explain its influence on the increase in the early and late mechanical properties of cement mortar.

Activation through the sieving of biomass fly ash enabled an increase in the utilization rate of the additive from 5% of binder mass to 15% without a detrimental effect on the mechanical properties of cement mortar. The results of the consistency tests show that biomass fly ash, as with any other concrete additive, requires checking before its usage in a concrete mix. The high alkali content in fly ash requires an additional checking of alkali–silica reactivity, and the high content of lime requires an additional checking of soundness.

Author Contributions: Conceptualization, J.P. and M.L.; methodology, J.P. and M.L.; software, J.P.; validation, M.L.; formal analysis, J.P.; investigation, J.P.; resources, M.L.; data curation, J.P.; writing—original draft preparation, J.P.; writing—review and editing, M.L.; visualization, J.P.; supervision, M.L.; project administration, J.P.; funding acquisition, M.L. All authors have read and agreed to the published version of the manuscript.

Funding: The study was performed as part of a research project conducted at the Bialystok University of Technology and was funded by the Polish Ministry of Education and Science.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

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

References

1. Belviso, C. State-of-the-Art Applications of Fly Ash from Coal and Biomass: A Focus on Zeolite Synthesis Processes and Issues. *Prog. Energy Combust. Sci.* **2018**, *65*, 109–135. [CrossRef]
2. Vassilev, S.V.; Baxter, D.; Andersen, L.K.; Vassileva, C.G. An Overview of the Composition and Application of Biomass Ash. Part 1. Phase-Mineral and Chemical Composition and Classification. *Fuel* **2013**, *105*, 40–76. [CrossRef]
3. Statistics Poland. *Energy 2022*; Statistics Poland: Warsaw, Poland, 2022.
4. Uliasz-Bocheńczyk, A.; Bąk, P. Management of Waste from Energy Production—Waste Combustion in Poland. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *427*, 012019. [CrossRef]
5. Vassilev, S.V.; Baxter, D.; Andersen, L.K.; Vassileva, C.G. An Overview of the Composition and Application of Biomass Ash: Part 2. Potential Utilisation, Technological and Ecological Advantages and Challenges. *Fuel* **2013**, *105*, 19–39. [CrossRef]
6. Uliasz-Bocheńczyk, A.; Mokrzycki, E. The Elemental Composition of Biomass Ashes as a Preliminary Assessment of the Recovery Potential. *Gospod. Surowcami Miner. Miner. Resour. Manag.* **2018**, *34*, 115–132. [CrossRef]
7. Azam, M.; Setoodeh Jahromy, S.; Raza, W.; Wesenauer, F.; Schwendtner, K.; Winter, F. Comparison of the Characteristics of Fly Ash Generated from Bio and Municipal Waste: Fluidized Bed Incinerators. *Materials* **2019**, *12*, 2664. [CrossRef] [PubMed]
8. Jura, J.; Ulewicz, M. Assessment of the Possibility of Using Fly Ash from Biomass Combustion for Concrete. *Materials* **2021**, *14*, 6708. [CrossRef] [PubMed]
9. Carević, I.; Štirmer, N.; Trkmić, M.; Kostanić Jurić, K. Leaching Characteristics of Wood Biomass Fly Ash Cement Composites. *Appl. Sci.* **2020**, *10*, 8704. [CrossRef]
10. Berra, M.; Mangialardi, T.; Paolini, A.E. Reuse of Woody Biomass Fly Ash in Cement-Based Materials. *Constr. Build. Mater.* **2015**, *76*, 286–296. [CrossRef]
11. Wang, S.; Miller, A.; Llamazos, E.; Fonseca, F.; Baxter, L. Biomass Fly Ash in Concrete: Mixture Proportioning and Mechanical Properties. *Fuel* **2008**, *87*, 365–371. [CrossRef]
12. Nagrockienė, D.; Daugėla, A. Investigation into the Properties of Concrete Modified with Biomass Combustion Fly Ash. *Constr. Build. Mater.* **2018**, *174*, 369–375. [CrossRef]
13. Barathan, S.; Gobinath, B. Evaluation of Wood Ash as a Partial Replacement To Cement. *Int. J. Sci. Eng. Technol. Res.* **2013**, *2*, 2009–2013.
14. Baričević, A.; Carević, I.; Bajto, J.Š.; Štirmer, N.; Bezinović, M.; Kristović, K. Potential of Using Wood Biomass Ash in Low-Strength Composites. *Materials* **2021**, *14*, 1250. [CrossRef] [PubMed]
15. Wang, S.; Llamazos, E.; Baxter, L.; Fonseca, F. Durability of Biomass Fly Ash Concrete: Freezing and Thawing and Rapid Chloride Permeability Tests. *Fuel* **2008**, *87*, 359–364. [CrossRef]
16. Giergiczny, Z. Fly Ash and Slag. *Cem. Concr. Res.* **2019**, *124*, 105826. [CrossRef]
17. *EN 450-1:2012*; Fly Ash for Concrete—Part 1: Definition, Specifications and Conformity Criteria. CEN: Brussels, Belgium, 2012.
18. Vilakazi, A.Q.; Ndlovu, S.; Chipise, L.; Shemi, A. The Recycling of Coal Fly Ash: A Review on Sustainable Developments and Economic Considerations. *Sustainability* **2022**, *14*, 1958. [CrossRef]
19. da Costa, T.P.; Quinteiro, P.; Tarelho, L.A.C.; Arroja, L.; Dias, A.C. Environmental Assessment of Valorisation Alternatives for Woody Biomass Ash in Construction Materials. *Resour. Conserv. Recycl.* **2019**, *148*, 67–79. [CrossRef]
20. Wilińska, I.; Pacewska, B. Influence of Selected Activating Methods on Hydration Processes of Mixtures Containing High and Very High Amount of Fly Ash: A Review. *J. Anal. Calorim.* **2018**, *133*, 823–843. [CrossRef]
21. Doudart de la Grée, G.C.H.; Florea, M.V.A.; Keulen, A.; Brouwers, H.J.H. Contaminated Biomass Fly Ashes - Characterization and Treatment Optimization for Reuse as Building Materials. *Waste Manag.* **2016**, *49*, 96–109. [CrossRef]
22. Pedersen, A.J. Characterization and Electrodialytic Treatment of Wood Combustion Fly Ash for the Removal of Cadmium. *Biomass Bioenergy* **2003**, *25*, 447–458. [CrossRef]
23. Popławski, J.; Lelusz, M. Influence of Mechanical and Mineralogical Activation of Biomass Fly Ash on the Compressive Strength Development of Cement Mortars. *Materials* **2021**, *14*, 6654. [CrossRef] [PubMed]

24. *EN 197-1:2011*; Cement—Part 1: Composition, Specifications and Conformity Criteria for Common Cements. CEN: Brussels, Belgium, 2011.
25. *EN 196-1:2016*; Methods of Testing Cement—Part 1: Determination of Strength. CEN: Brussels, Belgium, 2016.
26. *EN 1015-3:1999*; Methods of Test for Mortar for Masonry—Part 3: Determination of Consistence of Fresh Mortar (by Flow Table). CEN: Brussels, Belgium, 1999.
27. *PN-B-04500:1985*; Zaprawy Budowlane—Badania Cech Fizycznych i Wytrzymałościowych. PKN: Warsaw, Poland, 1985.
28. Tibco Software Inc. *Statistica 2017*; Tibco Software Inc.: Palo Alto, CA, USA, 2017.
29. Ohenoja, K.; Tanskanen, P.; Wigren, V.; Kinnunen, P.; Körkkö, M.; Peltosaari, O.; Österbacka, J.; Illikainen, M. Self-Hardening of Fly Ashes from a Bubbling Fluidized Bed Combustion of Peat, Forest Industry Residuals, and Wastes. *Fuel* **2016**, *165*, 440–446. [CrossRef]
30. Teixeira, E.; Camões, A.; Branco, F.; Matos, J. Effect of Biomass Fly Ash on Fresh and Hardened Properties of High Volume Fly Ash Mortars. *Crystals* **2021**, *11*, 233. [CrossRef]
31. Teixeira, E.R.; Mateus, R.; Camões, A.; Branco, F.G. Quality and Durability Properties and Life-Cycle Assessment of High Volume Biomass Fly Ash Mortar. *Constr. Build. Mater.* **2019**, *197*, 195–207. [CrossRef]
32. Jin, S.; Zhao, Z.; Jiang, S.; Sun, J.; Pan, H.; Jiang, L. Comparison and Summary of Relevant Standards for Comprehensive Utilization of Fly Ash at Home and Abroad. *IOP Conf. Ser. Earth Environ. Sci.* **2021**, *621*, 012006. [CrossRef]
33. Kurdowski, W. *Cement and Concrete Chemistry*; Springer Netherlands: Dordrecht, The Netherlands, 2014; ISBN 978-94-007-7944-0.
34. Chen, H.-J.; Shih, N.-H.; Wu, C.-H.; Lin, S.-K. Effects of the Loss on Ignition of Fly Ash on the Properties of High-Volume Fly Ash Concrete. *Sustainability* **2019**, *11*, 2704. [CrossRef]
35. Sanjuán, M.Á.; Argiz, C. Fineness of Coal Fly Ash for Use in Cement and Concrete. *Fuels* **2021**, *2*, 471–486. [CrossRef]
36. Sheng, G.; Li, Q.; Zhai, J.; Li, F. Self-Cementitious Properties of Fly Ashes from CFBC Boilers Co-Firing Coal and High-Sulphur Petroleum Coke. *Cem. Concr. Res.* **2007**, *37*, 871–876. [CrossRef]
37. Ohenoja, K.; Tanskanen, P.; Peltosaari, O.; Wigren, V.; Österbacka, J.; Illikainen, M. Effect of Particle Size Distribution on the Self-Hardening Property of Biomass-Peat Fly Ash from a Bubbling Fluidized Bed Combustion. *Fuel Process. Technol.* **2016**, *148*, 60–66. [CrossRef]
38. Brown, R.; Dykstra, J. Systematic Errors in the Use of Loss-on-Ignition to Measure Unburned Carbon in Fly Ash. *Fuel* **1995**, *74*, 570–574. [CrossRef]
39. Mohebbi, M. Reliability of Loss on Ignition (LOI) Test for Determining the Unburned Carbon Content in Fly Ash. In Proceedings of the Conference: 2015 World of Coal Ash, Nashville, TN, USA, 5–7 May 2015.
40. Capela, M.N.; Tobaldi, D.M.; Tarelho, L.A.C.; Seabra, M.P.; Labrincha, J.A. Development of a Commercial Screed Mortar with Low OPC Content by Incorporation of Biomass Fly Ash. *Appl. Sci.* **2021**, *11*, 9630. [CrossRef]
41. Popławski, J. Influence of Biomass Fly Ash Blended with Bituminous Coal Fly Ash on the Properties of Concrete. *Constr. Optim. Energy Potential* **2020**, *9*, 89–96. [CrossRef]
42. Gabrijel, I.; Jelčić Rukavina, M.; Štirmer, N. Influence of Wood Fly Ash on Concrete Properties through Filling Effect Mechanism. *Materials* **2021**, *14*, 7164. [CrossRef]
43. Tsivilis, S.; Kakali, G.; Chaniotakis, E.; Souvaridou, A. A Study on the Hydration of Portland Limestone Cement by Means of TG. *J. Anal. Calorim.* **1998**, *52*, 863–870. [CrossRef]
44. Singh, L.P.; Goel, A.; Bhattachharyya, S.K.; Ahalawat, S.; Sharma, U.; Mishra, G. Effect of Morphology and Dispersibility of Silica Nanoparticles on the Mechanical Behaviour of Cement Mortar. *Int. J. Concr. Struct. Mater.* **2015**, *9*, 207–217. [CrossRef]
45. Kang, H.; Kang, S.; Lee, B. Strength and Water-Repelling Properties of Cement Mortar Mixed with Water Repellents. *Materials* **2021**, *14*, 5407. [CrossRef] [PubMed]
46. Zhang, Z.; Du, J.; Shi, M. Quantitative Analysis of the Calcium Hydroxide Content of EVA-Modified Cement Paste Based on TG-DSC in a Dual Atmosphere. *Materials* **2022**, *15*, 2660. [CrossRef] [PubMed]