



WASTE MINERAL POWDERS AS A COMPONENTS OF POLYMER-CEMENT COMPOSITES

B. JAWORSKA¹, J. J. SOKOŁOWSKA², P. ŁUKOWSKI³, J. JAWORSKI⁴

The introduction of the sustainable development elements in the construction industry leads to finding new ways of using waste minerals that are difficult in storage and recycling. Coal combustion products have been already introduced into building materials as a part of cement or concrete but they have been thought insufficiently compatible with the polymer-cement binders [7]. The paper presents results of the mechanical properties of polymer-cement composites containing two types of mineral additives: waste perlite powder that is generated during the perlite expanding process, and calcium fly ash which is the byproduct of burning coal in conventional furnaces. Mechanical tests of polymer-cement composites modified with wastes were carried out after 28 and 90 days of curing. As a part of preliminary study specific surface area and particle size distribution of mineral wastes were determined.

Keywords: polymer-cement composites (PCC), waste perlite powder, calcium fly ash, sustainable development

1. INTRODUCTION

The worldwide development of building industry is associated with concrete production, where the greenhouse gas emission is unavoidable. However, the implementation of the sustainable development strategy principles [3] leads to a low-carbon economy introduction. It is possible,

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thanks to the use of energy industry combustion by products to reduce greenhouse gas emission associated with cement and concrete production. The continual demand for electricity leads to an increased consumption of coal and thus to production of large amounts of combustion byproducts such as calcium fly ash [4]. Storing of wastes in landfills can be cumbersome for the environment, and since fly ashes have proved to be a valuable resource from the sustainable development point of view, their application in building materials is completely justified. However, unfavorable morphology of wastes [5] may cause difficulties when it comes to application in polymer-cement composites. Another difficult to store and recycle waste material is perlite powder, the byproduct formed during the expanded perlite production process. The expanded perlite has found many applications and thus a large amount of byproduct is produced. Besides the construction applications, one of many expanded perlite use is e.g. horticulture [2]. However, when it comes to building materials engineering, its ability to absorb water is a disadvantage, because it means increased water demand. Despite these problems, increased production of industrial waste leads to seeking of new material solutions and new ways of waste disposal.

2. EXPERIMENTAL

2.1. SCOPE OF THE RESEARCH PROGRAM

The research program was designed to assess the impact of waste mineral powders content on the mechanical properties of polymer-cement composites. Mixtures were designed with the following assumptions:

- dosage levels of waste powders: 5%, 10%, 15%, 20%, 25% of cement mass,
- constant polymer content: 20% of cement mass,
- constant level of water-cement ratio of 0.5.

Modified polymer-cement mortars were prepared using Portland cement CEM I 42.5, standard sand fulfilling requirements of PN-EN 196-1 [8], an aqueous dispersion of styrene-acrylic copolymer, calcium fly ash from one of the Polish power plants and waste perlite powder from expanded perlite factory. The reference material used in this investigation was standard cement mortar.

2.2. TEST PROCEDURE

Polymer-cement composites were tested after 28 and 90 days of curing in mixed wet conditions. During the first day specimens were tightly covered with polyethylene sheets and, after disbandment, immersed for five days in water at 20-22°C, then, until testing, held in air-dry conditions (temperature of 20-22°C, relative humidity of 60±5°C) to provide adequate conditions for the hydration of cement binder as well as the formation of a continuous polymer film. Standard mortars were stored in wet conditions as recommended in PN-EN 196-1. As a part of preliminary study, the specific surface area and particles size distribution of mineral wastes were tested using laser analyzer.

2.3. SPECIFIC SURFACE AREA AND PARTICLES SIZE DISTRIBUTION

Specific surface area, relative frequency and cumulative frequency of mineral waste powders grains size distribution were tested by Horriba L300 laser analyzer (using the Laser Scattering Method [1]). Parameters of measurement were as follows: index of refraction - 1.16-0.00i, circulation pump speed of 7.0, duration of the ultrasounds emission – 1 min. Tested materials were dispersed in a sodium polimetaphosphate water solution. Cumulative frequency plots of size distribution curves for two tested waste mineral powders are presented in Fig. 1. For each waste powder, three samples were subsequently tested. The obtained results were compared with data obtained for metakaolin, one of the most effective mineral additives for concrete. Waste perlite powder particle diameters did not exceed 100 µm, as it was in the case of calcium fly ash. All of the mineral additives contained particles smaller than 4 µm (Fig. 1) and similar content of particles smaller than 45 µm (for perlite powder – 97%, calcium fly ash – 89% and metakaolin – 99%). Only the calcium fly ash contains particles bigger than 67 µm. Average size of perlite powder particle was about 19 µm whereas for fly ash it was nearly 25 µm - larger than in the case of metakaolin (Table 1). Waste perlite powders particles are of similar average diameter to metakaolin but of nearly 5 times smaller specific surface area. Those differences in diameter and specific surface area cause various curves shape. Both waste mineral powders having a small average particle diameter may act as filler, which fills voids between particles of cement. However, increased porosity of waste perlite powder particles [6] results in an increased water demand and deterioration of mix consistency. And in case of calcium fly ash on the deterioration of the mix workability may affect particles higher than 45 µm.

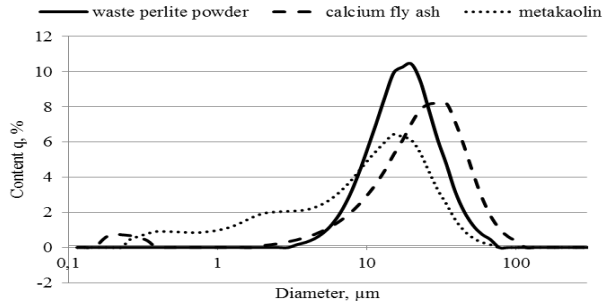


Fig. 1. Grain size distribution curves for tested mineral additives (relative distribution)

Table 1. Specific surface area and particle average diameters of mineral additives

No	Mineral additive	Specific surface area, cm^2/cm^3	Average diameter, μm
1	waste perlite powder	4237	18.69
2	calcium fly ash	13677	24.91
3	metakaolin	21052	11.94

2.4. MECHANICAL PROPERTIES OF MODIFIED POLYMER-CEMENT COMPOSITES

Flexural and compressive strength of polymer-cement composites modified with mineral wastes were tested after 28 and 90 days of curing. The investigation was carried out for composites modified with 20% content of polymer and 5% to 25% content of waste minerals (of cement mass). Flexural and compressive strength tests were performed in accordance with PN-EN 196-1 using testing machine INSTRON 567.

2.4.1. FLEXURAL STRENGTH OF MODIFIED POLYMER-CEMENT COMPOSITES

Flexural strength results of polymer-cement composites after 28 days of curing are presented in Fig. 2. First loss of strength occurs after adding of 5% of wastes. For composites containing calcium fly ash, increasing the amount up to 15% resulted in a further strength reduction. In the case of composites modified with waste perlite powder first loss of strength of up to 10% content of additive and another one after adding of 25% of waste. Compared to unmodified polymer cement-composites, flexural strength of composites with 25% content of waste minerals decreased by 17% and 33% for calcium fly ash and waste perlite powder, respectively. Flexural strength change for composites modified with up to 20% content of those waste mineral powders is similar.

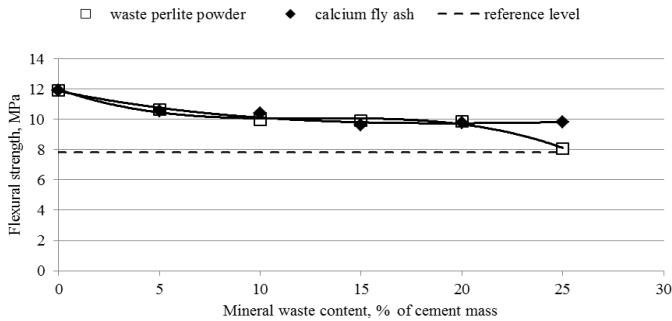


Fig. 2. Flexural strength for polymer-cement composites with 20% polymer content in function of waste mineral powder content (after 28 days of curing) compared to the standard cement mortar (no mineral waste) – reference level

Flexural strength results of polymer-cement composites after 90 days of curing are presented in Fig. 3. The contents of mineral wastes had a similar effect on the samples tested after long period of curing. First deterioration of composite's properties was observed after adding 5% of wastes, and then up to 20% content of powders resulted in similar flexural strength changes. Increasing calcium fly ash content up to 25% did not have an effect on further strength deterioration as much as it was observed for polymer-cement composites containing waste perlite powder. Compared to unmodified polymer cement-composites, flexural strength of composites with 25% content of waste minerals decreased by 8% and 29% for calcium fly ash and waste perlite powder, respectively.

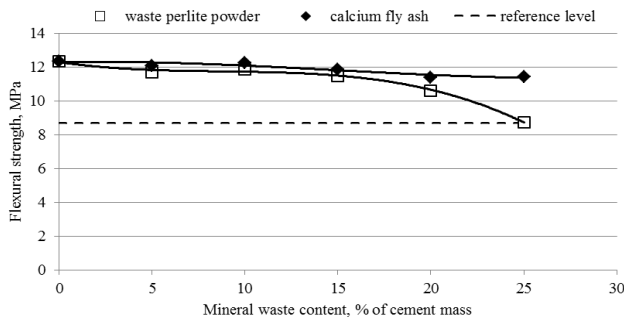


Fig. 3. Flexural strength for polymer-cement composites with 20% polymer content in function of waste mineral powder content (after 90 days of curing) compared to the standard cement mortar (no mineral waste) – reference level

Flexural strength of tested composites after 28 days of curing is within the range 8.0-10.7 MPa and 9.8-10.6 MPa for composites with waste perlite powder and calcium fly ash, respectively, and after 90 days of curing is 8.6-11.7 MPa and 11.4-12.1 MPa. For standard cement mortar it is 7.8 MPa after 28 days and 8.7 MPa after 90 days. It means that all of the 28-days tested modified polymer-cement composites has better flexural strength, compared to cement binder, and after 90 days, only mortar with 25% waste perlite powder was slightly weaker. Relations shown in Fig. 2 and Fig. 3 can be approximated by polynomials of the third degree (second degree in the case of composites with calcium fly ash after 28 days curing). Solution of linear equations allows determining the inflection point of the graph and thus estimating the optimum value of wastes at which the change in the strength of the composite is made. Approximation results are shown in Table 2.

Table 2. Estimation of optimal mineral waste content in polymer-cement composite – impact on flexural strength

Additive	Curing day	Approximating function	Coefficient of determination, R ²	Optimum content, %	Calculated flexural strength, MPa
calcium fly ash	28	$f_b = 0.0059 \text{ m/c}^2 - 0.2258 \text{ m/c} + 11.82$	0.95	19.1	9.7
	90	$f_b = 0.0001 \text{ m/c}^3 - 0.0055 \text{ m/c}^2 + 0.0231 \text{ m/c} + 12.281$	0.89	18.3	11.5
waste perlite powder	28	$f_b = -0.001 \text{ m/c}^3 + 0.0384 \text{ m/c}^2 - 0.4737 \text{ m/c} + 11.991$	0.98	12.8	10.1
	90	$f_b = -0.0006 \text{ m/c}^3 + 0.017 \text{ m/c}^2 - 0.1621 \text{ m/c} + 12.298$	0.99	9.4	11.8

2.4.2. COMPRESSIVE STRENGTH OF MODIFIED POLYMER-CEMENT COMPOSITES

Compressive strength results of polymer-cement composites after 28 days of curing are presented in Fig. 4. First loss of strength occurs after addition of 5% of wastes. For composites containing calcium fly ash increasing the amount of up to 15% and then up to 25% resulted in further slight strength reductions. In the case of composites modified with waste perlite powder first loss of strength is up to 5% content of additive and another one after addition of 15% of waste. Compared to unmodified polymer cement-composites, compressive strength of composites with 25% content of waste minerals decreased by 20% and 41% for calcium fly ash and waste perlite powder, respectively.

Compressive strength results of polymer-cement composites after 90 days of curing are presented in Fig. 5. The contents of mineral wastes had a similar effect on the samples tested after long period of curing. First deterioration of composites properties was observed after addition of 5% of wastes, and then after 15% content of powders compressive strength change was similar. Increasing calcium fly ash content up to 25% resulted in a further slight strength reduction. More significant strength deterioration was observed for polymer-cement composites containing waste perlite powder. Compared to unmodified polymer cement-composites, compressive strength of composites containing 25% of waste minerals decreased by 15% and 34% for calcium fly ash and waste perlite powder, respectively.

Compressive strength of tested composites after 28 days of curing is in range 26.5-37.4 MPa and 35.1-39.5 MPa for composites with waste perlite powder and calcium fly ash, respectively, and after 90 days of curing is 30.9-42.5 MPa and 40.2-46.2 MPa. For standard cement mortar it is 48.3 MPa after 28 days and 57.6 MPa after 90 days. None of the tested modified polymer-cement composites had better compressive strength, compared to cement binder. This is due to worse mechanical properties of polymer itself rather than the impact of wastes.

Statistical analysis of impact of wastes on the compressive strength of composites shows that this relationship can be approximated by a third order polynomial (Table 3).

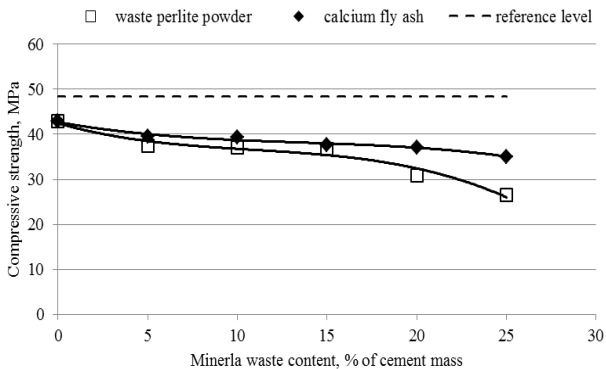


Fig. 4. Compressive strength for polymer-cement composites with 20% polymer content in function of waste mineral powder content (after 28 days of curing) compared to the standard cement mortar (no mineral waste) – reference level

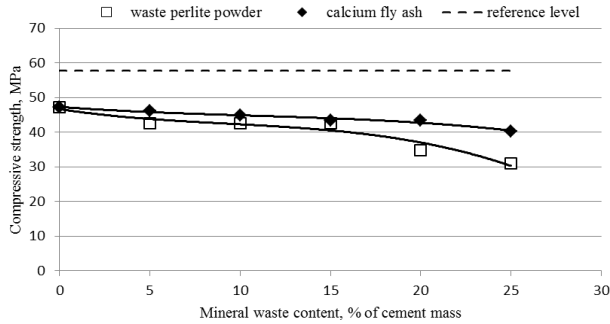


Fig. 5. Compressive strength for polymer-cement composites with 20% polymer content in function of waste mineral powder (after 90 days of curing) compared to the standard cement mortar (no mineral waste) – reference level

Table 3. Estimation of optimal mineral waste content in polymer-cement composite – impact on compressive strength

Additive	Curing day	Approximating function	Coefficient of determination, R^2	Optimum content, %	Calculated compressive strength, MPa
calcium fly ash	28	$f_c = -0.001 \text{ m/c}^3 + 0.0424 \text{ m/c}^2 - 0.7181 \text{ m/c} + 42.681$	0.98	14.1	38.2
	90	$f_c = -0.0007 \text{ m/c}^3 + 0.0216 \text{ m/c}^2 - 0.3903 \text{ m/c} + 47.27$	0.96	10.2	44.8
waste perlite powder	28	$f_c = -0.0025 \text{ m/c}^3 + 0.0827 \text{ m/c}^2 - 1.1436 \text{ m/c} + 42.438$	0.96	11.0	36.5
	90	$f_c = -0.002 \text{ m/c}^3 + 0.0565 \text{ m/c}^2 - 0.8003 \text{ m/c} + 46.625$	0.93	9.4	42.4

In the case of mineral wastes impact on compressive strength of polymer-cement composites the optimum content is in range 10.2-14.1% for calcium fly ash and 9.4-11.0% for waste perlite powder.

3. CONCLUSION

The research results proved that selected industrial wastes – calcium fly ash and waste perlite powder affect the mechanical properties of polymer-cement composites. Both additives had negative impact on the flexural and compressive strength of the polymer-cement composite, however this impact is not very significant. In the worst case, the substitution of 25% of cement mass by waste perlite powder caused 33% decrease of flexural strength and 41% decrease of

compressive strength of 28-days-old composites. Less deterioration was observed in the case of specimens with calcium fly ash (respectively: 17% and 20%) which may be due to better morphology of fly ash, compared to waste perlite powder. Polymer-cement composites modified with waste powders have lower values of compressive strength, but higher (or similar) values of flexural strength, as compared to the standard cement mortar. Statistical analysis of preliminary studies on the effects of waste on selected mechanical properties of polymer-cement composites showed that in the case of waste perlite powder the optimum content is 9.4% of the cement mass. When it comes to calcium fly ash, the optimum content is in the range of 10-14% of the cement mass. Studies have proved the possibility of use both mineral wastes as components of polymer-cement mortars.

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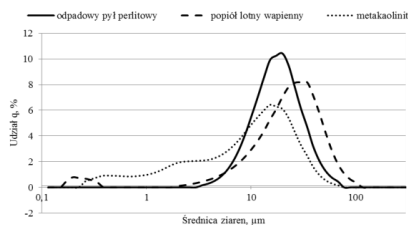
Tab. 3. Oszacowanie optymalnej zawartości odpadów mineralnych w kompozytach polimerowo-cementowych – wpływ na wytrzymałość na ściskanie

ODPADOWE PYŁY MINERALNE JAKO SKŁADNIKI KOMPOZYTÓW POLIMEROWO-CEMENTOWYCH

Słowa kluczowe: kompozyty polimerowo-cementowe, odpadowy pył perlitowy, popiół lotny wapienny, zrównoważony rozwój

STRESZCZENIE:

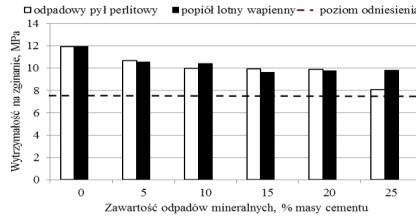
Przedmiotem badań było określenie wpływu zawartości odpadowych pyłów mineralnych na wybrane właściwości mechaniczne kompozytów polimerowo-cementowych. Szukanie nowych sposobów na zagospodarowanie odpadów mineralnych stanowi element strategii zrównoważonego rozwoju w budownictwie. Wprowadzenie odpadów przemysłowych do materiałów budowlanych pozwala zmniejszyć emisję gazów cieplarnianych wydzielających się podczas produkcji cementu czy betonu. Jako przedmiot badań przyjęto polimerowo-cementowe zaprawy, zawierające kopolimer styrenowo-akrylowy, modyfikowane odpadowym pyłem perlitowym (uboczny produkt procesu ekspansji perlitu), oraz produktem ubocznym spalania węgla brunatnego, popiołem lotnym wapiennym. Zawartość odpadowych pyłów mineralnych zmieniała się w przedziale 5-25% masy cementu. Badano wytrzymałość na zginanie i ściskanie zapraw po 28 i 90 dniach dojrzewania próbek w warunkach mieszanych, wodno-powietrznych. Zastosowano taki sposób przechowywania próbek, aby zapewnić odpowiednie warunki dla hydratacji cementu (warunki mokre), przy jednoczesnych odpowiednich warunkach do uformowania ciągłej błony polimerowej (warunki suche). Zbadano również powierzchnię właściwą i uziarnienie wybranych dodatków mineralnych. Wyniki badań granulometrycznych dla popiołu lotnego wapiennego oraz odpadowego pyłu perlitowego porównano z wynikami dla metakaolinitu, jednego z najefektywniejszych dodatków mineralnych do betonu. Analiza granulometryczna wykazała, że największymi rozmiarami ziaren charakteryzował się popiół lotny wapienny, który jako jedyny posiadał ziarna przekraczające 67 μm . Odpadowy pył perlitowy charakteryzowały ziarna o średnim rozmiarze zbliżonym do rozmiaru ziaren metakaolinitu, ale ich powierzchnia właściwa była prawie 5 razy mniejsza. Wszystkie badane dodatki mineralne posiadały ziarna o średnicy z przedziału 4 μm ÷ 45 μm (Rys. 1), przez co spełniają rolę mikrowypełniacza pustych przestrzeni między ziarnami cementu, jednak zwiększona porowatość odpadowego pyłu perlitowego, czy występowanie ziaren popiołu lotnego wapiennego o rozmiarach większych od 45 μm , wpływają na pogorszenie urabialności mieszanek polimerowo-cementowych.



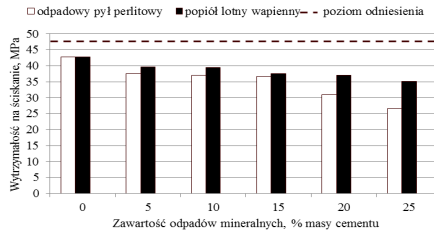
Rys. 1. Krzywe granulometryczne badanych dodatków mineralnych

Wartości wytrzymałości na zginanie kompozytów polimerowo-cementowych modyfikowanych odpadami mineralnymi zarówno po 28 dniach dojrzewania, jak i po 90 dniach, przyjmowały wyższe wartości od zaprawy normowej, niemniej zaobserwowano obniżenie wytrzymałości kompozytów już po dodaniu 5% odpadów. Dalsze zwiększanie zawartości odpadowych pyłów mineralnych nie wpłynęło znacząco na wytrzymałość na zginanie kompozytów polimerowo-cementowych. Wyjątek stanowi 25% (względem masy cementu) zawartość odpadowego pyłu perlitowego, która

spowodowała obniżenie wytrzymałości na zginanie zawierających ten odpad kompozytów, osiągając tym samym wartości zbliżone do wytrzymałości na zginanie zaprawy normowej (Rys. 2). W przypadku wytrzymałości na ściskanie, wszystkie modyfikowane odpadami kompozyty polimerowo-cementowe przyjmowały niższe wartości wytrzymałości w porównaniu do zaprawy normowej. Większy wpływ na wytrzymałość na ściskanie zaobserwowano dla kompozytów modyfikowanych odpadowym pyłem perlitowym (Rys. 3).



Rys. 2. Wytrzymałość na zginanie kompozytów polimerowo-cementowych, zawierających 20% polimeru, modyfikowanych mineralnymi pyłami odpadowymi po 28 dniach dojrzewania (porównane z zaprawą normową niemodyfikowaną odpadami mineralnymi – poziom odniesienia)



Rys. 3. Wytrzymałość na ściskanie kompozytów polimerowo-cementowych, zawierających 20% polimeru, modyfikowanych mineralnymi pyłami odpadowymi po 28 dniach dojrzewania (porównane z zaprawą normową niemodyfikowaną odpadami mineralnymi – poziom odniesienia)

W najgorszym przypadku, zastąpienie 25% cementu odpadowym pyłem perlitowym spowodowało 33% spadek wytrzymałości na zginanie i 41% spadek wytrzymałości na ściskanie kompozytów badanych po 28 dniach. Mniejsze pogorszenie odnotowano w przypadku kompozytów zawierających popiół lotny wapienny (odpowiednio 17% i 20%), co może być spowodowane lepszą morfologią popiołów lotnych, w porównaniu do odpadowego pyłu perlitowego. Zaprojektowane kompozyty, zawierające do 25% odpadów mineralnych, charakteryzowały się niższymi wartościami wytrzymałości na ściskanie, ale za to większymi (lub zbliżonymi - 25% odpadowego pyłu perlitowego) wartościami wytrzymałości na zginanie, w porównaniu do zaprawy normowej. Analiza statystyczna przeprowadzonych badań pozwoliła na określenie optymalnej ilości odpadowego pyłu perlitowego, oraz przedziału zawartości dla popiołu lotnego wapiennego. Na podstawie uzyskanych wyników stwierdzono, że możliwe jest racjonalne zastosowanie odpadowego pyłu perlitowego i popiołu lotnego wapiennego, jako składników budowlanych kompozytów polimerowo-cementowych.