Influence of cement substitution by calcareous fly ash on the mechanical properties of polymer-cement composites

Beata Jaworska[1,*], *Paweł* Łukowski[1], and *Jerzy* Jaworski[1]

[1]Warsaw University of Technology, Faculty of Civil Engineering, Al. Armii Ludowej 16, 00-637 Warsaw, Poland

Abstract. The aim of the presented research was to determine the influence of cement substitution with calcareous fly ash on the mechanical properties of polymer-cement composites. Coal combustion products such as calcareous fly ash have been already used in traditional cement composites as a part of cement and considered potential additions for concrete but its introduction into polymer-cement composites is still under preliminary investigation. The morphology of fly ash causes problems with its compatibility with polymer-cement binders but its insertion into those building materials is another way to utilize mineral combustion products that are cumbersome in storage and recycling. The influence of the mineral addition on polymer-cement composites containing 20% of polymer was especially taken into consideration. Mechanical properties of polymer-cement mortars modified with calcareous fly ash were tested after 28 and 90 days of curing. As a part of preliminary study, activity index of mineral addition was determined. Polymer-cement composites containing calcareous fly ash were characterized by higher flexural and tensile strength comparing to standardized mortar, even for the mortars containing 40% of mineral addition. The negative effect of the polymer-cement composites modification with calcareous fly ash was especially observed on the compressive strength of this composites.

1 Introduction

Polymer-cement concretes and mortars are part of the concrete-like composites group in which a polymer modifier is present in addition to the cement binder. The polymer-cement composites production technology is similar to the technology of obtaining conventional cement concrete. The content of the polymer modifier is usually in the range of 10 ÷ 20% by cement mass, but only a small number of polymers are suitable for the modification of cement binder. The presence of a polymer modifier causes the increase of flexural and tensile strength of the composite and the reduction of its permeability [1]. Chemical resistance and freezing/thawing resistance, and – therefore - durability of the material are improved.

* Corresponding author: b.jaworska@il.pw.edu.pl

Polymer-cement composites are used is such areas as repairs and protection of concrete structure [2], production of industrial floors and pavements [3] as well as production of pre-cast elements [4].

The main obstacle to using polymer-cement composites is their high material cost, although lower than the cement less resin composites, due to the smaller amount of the polymer needed to produce them. The need to reduce the material cost while maintaining the material properties leads to a search for new material solutions [1]. One of the methods to reduce the material cost is the replacement of some components with cheaper substitutes, both natural resources and waste materials. Examples of such materials are fly ashes – coal combustion products (CCP).

Whereas siliceous fly ash is commonly used as addition to concretes according to PN-EN 206 [5] and common cement according to PN-EN 197-1 [6], the calcareous fly ash is not such an obvious choice. This lignite combustion product differs from siliceous ashes both in chemical composition and in properties [7, 8]. Most of all, its irregular grains with a porous surface [9] are the reason for the increased water demand of composites containing this ash, thus negatively affecting the workability of the concrete mix, and consequently the properties of the hardened material.

The utilization of mineral wastes, also including coal combustion products, is a part of a sustainable development strategy, according to which, inter alia, it is necessary to minimize the consumption of matter, re-use elements and materials and effectively manage waste.

The purpose of this work was to solve the scientific problem regarding the influence of the presence of coal combustion product – calcareous fly ash – on the mechanical properties of polymer-cement composites.

2 Experimental

2.1 Methodology of the research program

The aim of the presented research was to determine the influence of cement substitution by calcareous fly ash on the mechanical properties of polymer-cement composites. Mixtures were designed with the following assumptions:
- dosage levels of calcareous fly ash: 0÷40% of cement mass,
- constant polymer content: 20% of cement mass,
- constant level of water-cement ratio equal to 0.5.

Polymer-cement mortars were prepared using Portland cement CEM I 42.5R, standard sand fulfilling requirements of PN-EN 196-1 [10], a water dispersion of styrene-acrylic copolymer and calcareous fly ash from one of the Polish power plants. The reference material used in this research was standardized cement mortar according to PN-EN 196-1.

2.2 Testing procedure

Mechanical properties of polymer-cement composites were tested after 28 and 90 days of curing in mixed wet conditions. For the first day of curing specimens were covered with polyethylene sheets and, after demoulding, immersed for five days in water at 20-22˚C. These are favourable conditions for the hydration of cement binder. After removing specimens from water, until testing, they were held in air-dry conditions at temperature of 20-22˚C and relative humidity of 60±5˚C. The air-dry condition is adequate for the formation of a continuous polymer film. Standardized mortars were stored in wet conditions as recommended in PN-EN 196-1. As a part of preliminary study, the activity index of calcareous fly ash was tested.

2.3 Activity index of mineral addition

The activity index of calcareous fly ash which was used in the research as a substitution of cement in polymer-cement composites was tested according to PN-EN 450-1 [11] and is presented in Table 1, Figure 1.

Table 1. Compressive strength (f_c) and activity index (AI) of specimens after 28 and 90 days of curing (CFA - calcareous fly ash, SM – standardized mortar – reference level).

No.	Specimen	f_{c28}, MPa	AI_{28}, %	f_{c90}, MPa	AI_{90}, %
1	CFA	41.4	**83.0**	49.5	**85.9**
2	SM	49.9	-	57.6	-

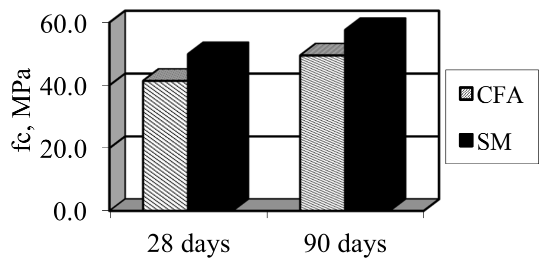

Fig. 1. Compressive strength of specimens after 28 and 90 days of curing (CFA - calcareous fly ash, SM – standardized mortar – reference level).

Calcareous fly ash was characterized by high activity index, reaching a value above 75% after 28 days and above 85% after 90 days of curing the specimens.

2.4 Mechanical properties of polymer-cement composites containing calcareous fly ash

Mechanical properties of polymer-cement composites containing calcareous fly ash were tested after 28 and 90 days of curing. The investigation was carried out for composites modified with 20% content of polymer and up to 40% content of mineral addition (by cement mass). Mechanical properties of these composites were tested in accordance with PN-85/B-04500 [12].

2.4.1 Flexural strength

Cement mortars containing 40.0% of mineral addition were characterized by the smallest flexural strength - 7.5 MPa after 28 days of curing and 8.3 MPa after 90 days of curing (Table 2). The cement substitution by calcareous fly ash in polymer-cement composites did not result in larger differences in the obtained flexural strength results. Polymer-cement composites containing calcareous fly ash were characterized by flexural strength of up to 12.0 MPa. Polymer-cement composites containing 40% of mineral addition were characterized by the smallest flexural strength (9.8 and 10.5 MPa after 28 and 90 days of curing respectively). Cement mortars containing 40% of calcareous fly ash were characterized by 1.3% and 4.6% decrease of flexural strength and polymer-cement composites with 40% of calcareous fly ash were characterized by 17.6% and 14.6% decrease of flexural strength, after 28 and 90 days of curing respectively, comparing to the mortars without fly ash (Table 2, Figure 2).

Table 2. Flexural strength of PCC mortars with different content of calcareous fly ash – after different time of curing (p/c – polymer content by cement mass, m/c – mineral addition by cement mass, SD – standard deviation, CV – variability index)

No.	p/c, %	m/c, %	Flexural strength, MPa					
			28 days			90 days		
			Average value	SD	CV, %	Average value	SD	CV, %
1	0.0	0.0	7.6	0.3	3.8	8.7	0.4	4.6
2	0.0	5.0	8.6	0.8	8.7	9.2	0.2	2.7
3	0.0	10.0	8.1	0.8	9.9	8.6	0.2	2.9
4	0.0	15.0	7.7	06	8.2	8.4	0.2	2.9
5	0.0	20.0	8.0	0.1	0.8	8.8	0.3	3.7
6	0.0	25.0	7.6	0.4	5.6	8.5	0.2	2.8
7	0.0	30.0	7.5	0.4	5.6	8.5	0.0	0.0
8	0.0	40.0	7.5	0.5	6.2	8.3	0.4	4.2
9	20.0	0.0	11.9	0.1	0.7	12.3	0.9	7.4
10	20.0	5.0	10.6	0.1	1.1	12.1	0.1	0.9
11	20.0	10.0	10.4	0.3	3.1	12.2	0.0	0.0
12	20.0	15.0	9.6	0.1	1.3	11.9	0.3	2.5
13	20.0	20.0	9.8	0.3	3.2	11.4	0.3	2.9
14	20.0	25.0	9.8	0.1	0.9	11.4	0.4	3.2
15	20.0	30.0	9.9	0.2	1.6	10.9	0.1	1.1
16	20.0	40.0	9.8	0.0	0.0	10.5	0.1	0.6

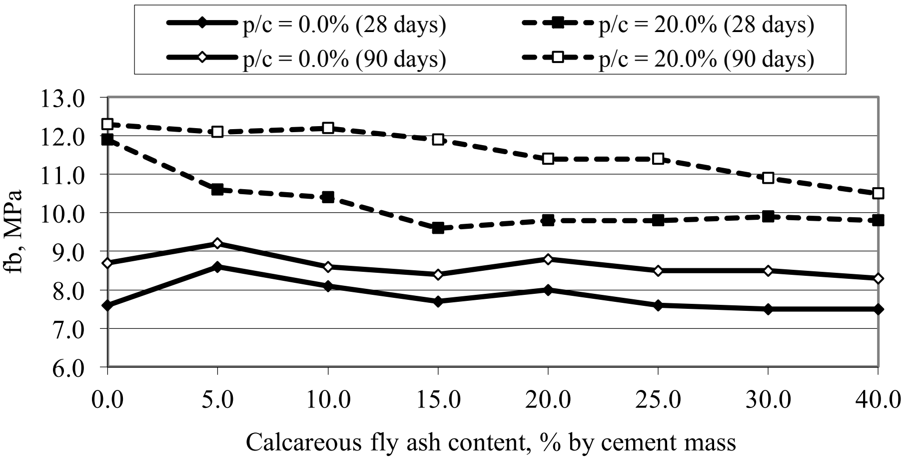

Fig. 2. Flexural strength of polymer-cement composites containing different content of calcareous fly ash after different time of curing.

2.4.2 Tensile strength

Cement mortars containing 40.0% of mineral addition were characterized by the smallest tensile strength (3.1 MPa). The cement substitution by calcareous fly ash in polymer-cement composites did not result in larger differences in the obtained tensile strength results. Polymer-cement composites containing calcareous fly ash were characterized by tensile strength of up to 6.0 MPa. Polymer-cement composites modified with 40% of calcareous fly ash were characterized by 11.1% and 15.8% decrease of tensile strength, after 28 and 90 days of curing respectively (Table 3, Figure 3).

Table 3. Tensile strength of PCC mortars with different content of calcareous fly ash – after different time of curing (p/c – polymer content by cement mass, m/c – mineral addition by cement mass, SD – standard deviation, CV – variability index).

No.	p/c, %	m/c, %	Tensile strength, MPa					
			28 days			90 days		
			Average value	SD	CV, %	Average value	SD	CV, %
1	0.0	0.0	3.1	0.3	8.0	3.2	0.2	6.3
2	0.0	5.0	4.2	0.2	4.8	4.6	0.3	6.5
3	0.0	10.0	4.1	0.1	2.4	4.9	0.2	3.1
4	0.0	15.0	3.9	0.3	8.1	4.6	0.1	1.5
5	0.0	20.0	3.6	0.0	0.0	4.4	0.1	1.3
6	0.0	25.0	3.5	0.1	2.4	4.3	0.0	0.0
7	0.0	30.0	3.5	0.3	8.6	4.0	0.1	2.5
8	0.0	40.0	3.1	0.1	1.9	4.1	0.1	2.4
9	20.0	0.0	5.4	0.3	4.6	5.7	0.2	3.5
10	20.0	5.0	5.6	0.4	7.1	6.1	0.0	0.0
11	20.0	10.0	5.1	0.1	1.1	5.9	0.1	1.7
12	20.0	15.0	5.1	0.0	0.0	5.6	0.1	1.1
13	20.0	20.0	5.2	0.2	3.8	5.4	0.1	1.9
14	20.0	25.0	5.2	0.1	3.3	5.2	0.1	1.0
15	20.0	30.0	5.4	0.2	3.7	5.1	0.1	2.0
16	20.0	40.0	4.8	0.1	1.2	4.8	0.1	1.2

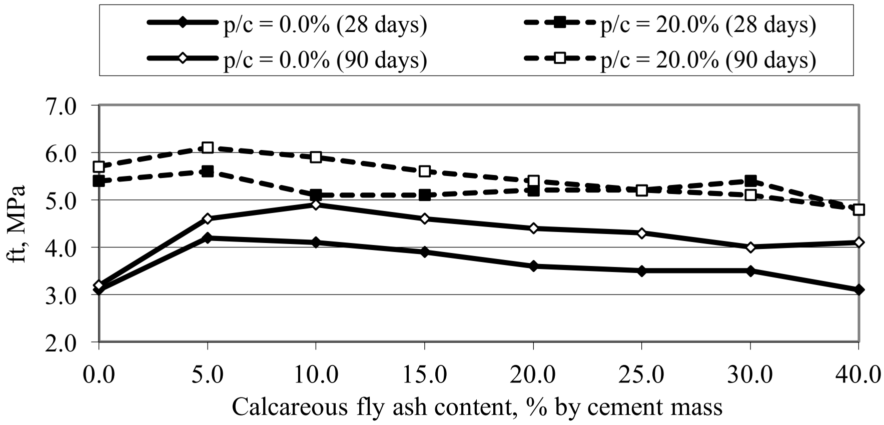

Fig. 3. Tensile strength of polymer-cement composites containing different content of calcareous fly ash after different time of curing.

2.4.3 Compressive strength

Polymer-cement composites containing calcareous fly ash were characterized by compressive strength of up to 46.0 MPa. Polymer-cement composites containing 40.0% of mineral addition were characterized by the smallest compressive strength (30.4 MPa) even comparing to cement mortar modified with the same amount of fly ash. Polymer-cement composites modified with 40% of calcareous fly ash were characterized by 29.0% and 25.7% decrease of compressive strength, after 28 and 90 days of curing respectively (Table 4, Figure 4).

Table 4. Compressive strength of PCC mortars with different content of calcareous fly ash – after different time of curing (p/c – polymer content by cement mass, m/c – mineral addition by cement mass, SD – standard deviation, CV – variability index).

No.	p/c, %	m/c, %	Compressive strength, MPa					
			28 days			90 days		
			Average value	SD	CV, %	Average value	SD	CV, %
1	0.0	0.0	48.3	1.4	2.9	59.6	1.4	2.4
2	0.0	5.0	50.6	0.7	1.4	59.2	1.8	3.1
3	0.0	10.0	46.7	0.3	0.7	55.1	1.1	2.0
4	0.0	15.0	42.3	1.0	2.4	53.6	1.3	2.3
5	0.0	20.0	41.7	1.3	3.1	52.2	0.7	1.4
6	0.0	25.0	38.7	1.6	4.0	49.7	1.8	3.5
7	0.0	30.0	35.2	0.6	1.7	48.1	2.4	5.0
8	0.0	40.0	31.7	1.4	4.3	40.2	0.7	1.6
9	20.0	0.0	42.8	0.4	1.0	47.1	0.7	1.4
10	20.0	5.0	39.5	1.4	3.6	46.2	0.8	1.7
11	20.0	10.0	39.4	0.9	2.2	44.8	1.3	2.9
12	20.0	15.0	37.6	1.4	3.8	43.4	0.8	1.8
13	20.0	20.0	37.0	0.7	1.9	43.4	0.2	0.5
14	20.0	25.0	35.1	0.6	1.6	40.2	0.9	2.3
15	20.0	30.0	31.6	0.6	1.8	37.2	0.3	0.8
16	20.0	40.0	30.4	0.4	1.2	35.0	0.5	1.5

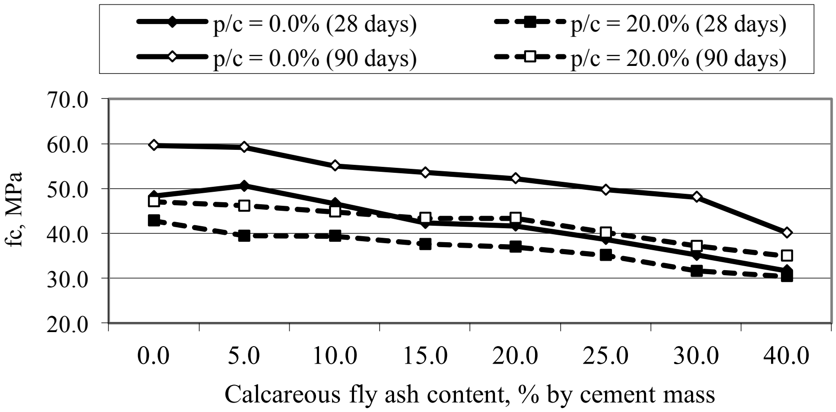

Fig. 4. Compressive strength of polymer-cement composites containing different content of calcareous fly ash after different time of curing.

3 Conclusions

Adding calcareous fly ash to the polymer-cement composites had more influence on the flexural strength of this composites than on the flexural strength of cement mortars. Polymer-cement composites containing 40% of mineral addition were characterized by almost 18% and 15% (after 28 and 90 days of curing respectively) lower flexural strength comparing to polymer-cement composites without ash. Despite this, their flexural strength was higher by about 20% than the flexural strength of standardized cement mortar.

Also, when taking into consideration the influence of cement substitution with calcareous fly ash on the tensile strength of these composites, it can be seen that the addition up to 40% of coal combustion product caused its reduction, but still all the polymer-cement composites were characterized by higher tensile strength comparing to cement mortars.

The biggest influence of calcareous fly ash content was observed for compressive strength. Polymer-cement composites modified with 40% of calcareous fly ash were characterized by 29.0% and 25.7% decrease of compressive strength. Despite this, the decrease was smaller than in the case of cement mortars, where substitution of cement with 40% of calcareous fly ash resulted in 34.4% and 32.6% decrease in compressive strength, after 28 and 90 days of curing respectively.

The studies presented in this paper showed that it is possible to use calcareous fly ash (even in large quantities, up to 40% of cement mass) in polymer-cement composites. The obtained composites were characterized by similar or slightly worse (decrease in strength ≤ 30%) mechanical properties comparing to polymer-cement composites without fly ash.

References

1. D.W. Fowler, Cem.Con.Com. **21**, 449-452 (1999)
2. F. Giustozzi, Con. Buil. Mat. **111**, 502-512 (2016)
3. D. Jeongyun, S. Yangseob, Cem. Con. Res. **33**, 1497-1505 (2003)
4. L. Czarnecki, P. Łukowski, Cem. Wap. Bet. **5**, 243-258 (2010)
5. PN-EN 206+A1 (2016-12)

6. PN-EN 197-1 (2012)
7. J. Małolepszy, *MATBUD'2011*, 17- 48 (2011)
8. B. Jaworska, J.J. Sokołowska, P. Łukowski, J. Jaworski, ACE, **LXI, 4** (2015)
9. Z. Giergiczny, *Role of high calcium and low calcium fly ashes in shaping properties of construction binders and cement materials* (Kraków*,* 2006)
10. PN-EN 196-1 (2006)
11. PN-EN 450-1 (2012)
12. PN-85/B-04500 (1985)