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Fly Ash Polymer Concretes

Lech Czarnecki, Andrzej Garbacz, and Joanna J. Sokołowska

Department of Building Materials Engineering, Faculty of Civil Engineering of Warsaw University of Technology – Al. Armii Ludowej 16, 00-637 Warsaw, Poland. E-mail: <l.czarnecki@il.pw.edu.pl>, <a.garbacz@il.pw.edu.pl>, <j.sokolowska@il.pw.edu.pl>.

ABSTRACT

In the paper the effect of silica microfiller replacement by calcium fly ashes on polymer concrete mechanical properties, as well as binder hardening characteristics were investigated. This approach follows the sustainable development requirements in a building industry. Additionally, replacing components with less expensive equivalents lowers the material cost. Although fly ashes are commonly used in portland cement concrete technology, the calcium fly ashes are difficult to utilize in CC, mainly due to high variation in chemical composition. Investigation was carried out for polyester resin and calcium fly ashes from brown and hard coal combustion, with special attention given to the second one, as fly ash of lignite showed substantial similarities in properties to silica microfiller – quartzite meal. Twenty mixes with different polymer/microfiller, aggregate/polymer and microfiller/aggregate ratios were tested using statistical design of experiment. The obtained results were used for optimization of composition of PC containing calcium fly ash.

INTRODUCTION

FC – polymer concrete, the concrete-like composite where portland cement binder is substituted with an organic resin [Czarnecki 2005] is considered as a high performance material due to its main advantages – high values of mechanical parameters and chemical resistance. Those demanded in civil engineering features cause that the range of application of PC is wide [Fowler 1999, Czarnecki 2007] – e.g. pre-cast elements, such us manholes, sewer pipes, drainage channels, chemically resistant vessels and anti-corrosion protection of various structures that stay in contact with chemically aggressive agents, e.g. industrial floors [Ohama 2004, Czarnecki 2005]. Good mechanical strength, as well as chemical resistance, are obtained in PC thanks to specific properties of high quality components. High material cost of PC is the main drawback against the common use of this composite.

One of the methods of lowering the material cost is replacing components with not so expensive equivalents but the substitution should be still accompanied by fulfilling the material and technical requirements. The equivalents do not need to be raw substances, as recently – in accordance with the precepts of sustainable development – a lot of effort is done to utilize wastes and by-products in civil industry (also in polymer concretes technology [Bignozzi et al. 2004, Choi et al. 2001, Lancellotti 2000]). Such approach is well known from cement concrete technology where a number of various mineral additives is used and one of the commonly used additives is fly ash. However, some kinds of fly ashes are difficult to utilize in cement concrete technology, mainly due to high variation of their chemical composition.

In this paper the effect of silica microfiller replacement by calcium fly ashes on selected polyester concrete mechanical properties (compressive, flexural and tensile strength), as well as binder hardening characteristics were investigated. The range of silica microfiller replacement by calcium fly ash was discussed. The investigation was carried out for two types of calcium fly ashes, the by-products from hard coal and brown coal (lignite) combustion.

CHARACTERISTICS OF APPLIED CALCIUM FLY ASHES

Both calcium fly ashes applied in the polyester concrete in this investigation were the by-products of energetic industry. They were the by-products of coal combustion that took place in Polish power stations. The first fly ash was the by-product of the hard coal combustion in cogeneration placed in Warsaw and the second type was the by-product of the lignite (referred also as brown coal) combustion in power station placed in central Poland.

The granulation of applied microfillers – the calcium fly ashes, as well as the quartzite meal – was tested using the laser granulometer Horiba L300 (Fig.1). .

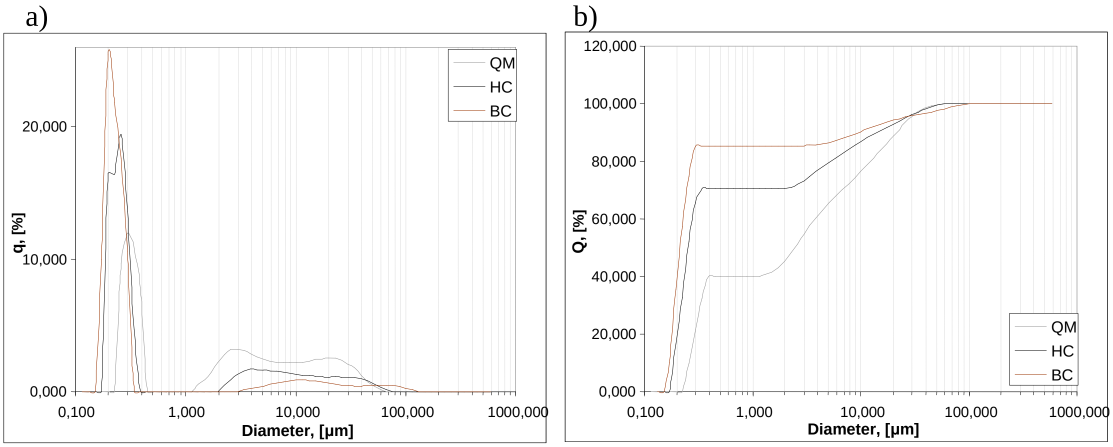

Fig. 1. Grain Size Distribution Curves for Quartzite Meal (QM), Calcium Fly Ash of Hard Coal (HC) and Calcium Fly Ash of Brown Coal (BC): a – Relative Frequency Plot; b – Cumulative Frequency Plot

The results of the tests showed that the considered calcium fly ashes contained more fraction of grain size below 1 μm. The size of the particles of fly ash of hard coal as well as quartzite meal did not exceed 75 μm but the fly ash of brown coal contained fraction 100 μm.

EFFECT OF CALCIUM FLY ASH ON POLYESTER RESIN HARDENING

The mechanical parameters of PC except the quality of the components depend also on the aggregate to resin binder ratio as well as microfiller content [Czarnecki 1982]. The basic aim of the research was to investigate the influence of the calcium fly ashes on the unsaturated polyester resin hardening process. The investigation was carried out for the specimens of polyester resin containing various amounts of calcium fly ashes (microfiller/resin ratio: 0.25, 0.50, 0.75, 1.00) from hard and brown coal in comparison to typical microfiller – quartzite meal. The characteristic of resin setting were determined on the basis of the measurements of changes of temperature, viscosity and conductivity during hardening. The investigation of setting was carried with commercial Gelnorm test system that gives possibility to automatic test of the changes of temperature, viscosity and conductivity, simultaneously.

The obtained results of investigation of polyester resin setting with different content of microfillers. It was noted that in case of quartzite meal (QM) and calcium fly ash from brown coal (BC) the drop of temperature of hardening was more rapid along with increase of gel time, whereas in case of calcium fly ash from hard coal (HC) drop of temperature of hardening was comparable but along with much wider range of variability of gel time (see Fig.2a). Above conclusions are repeated for relation: temperature of hardening – hardening time, as the relation hardening time – gel time characterized by high values of correlation ratio, r (see Fig.2b). It was observed (Fig.3) that the relative content of microfiller has significant influence on setting of resin: the more microfiller the binder contained, the lower the hardening temperature, the longer gel and hardening times and the lower the value of maximal relative conductivity were. Although the applied microfillers presented differences in granulometric composition the silica microfiller – quartzite meal – and calcium fly ash of brown coal showed similar influence on hardening process of polyester resin, while calcium fly ash of hard coal showed different influence. The same relative content of calcium fly ash of hard coal caused greater decrease of temperature of hardening and greater elongation of gel time and hardening time than quartzite meal or calcium fly ash of brown coal. Also in case of fly ash of hard coal the distinct influence on conductivity was observed. When the relative content exceeded value 0.75 the relative conductivity gained only 30%, what corresponded with low workability in comparison to other mixes.

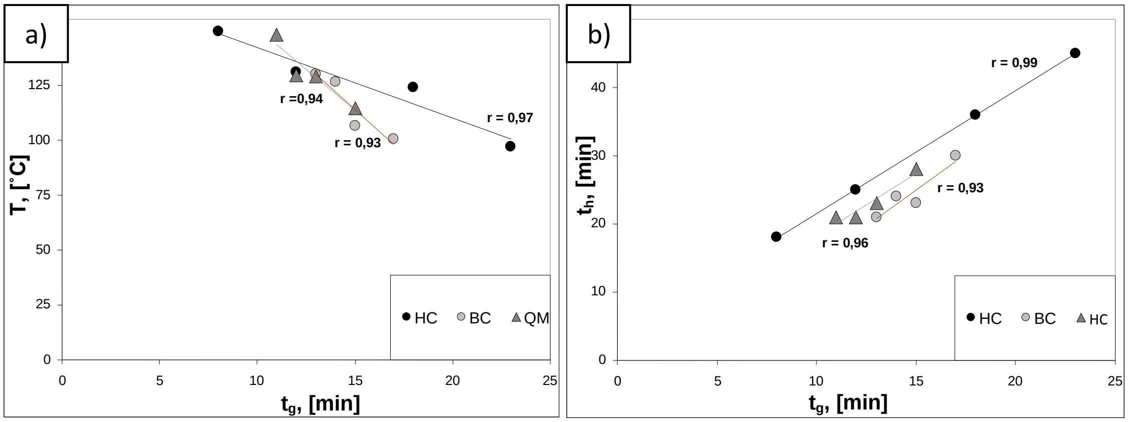

Fig. 2. Summary Plots For Quartzite Meal (QM), Calcium Fly Ash of Hard Coal (HC) and Calcium Fly Ash of Brown Coal (BC): a – Temperature; b – Hardening Time; Both in Function of Gel Time

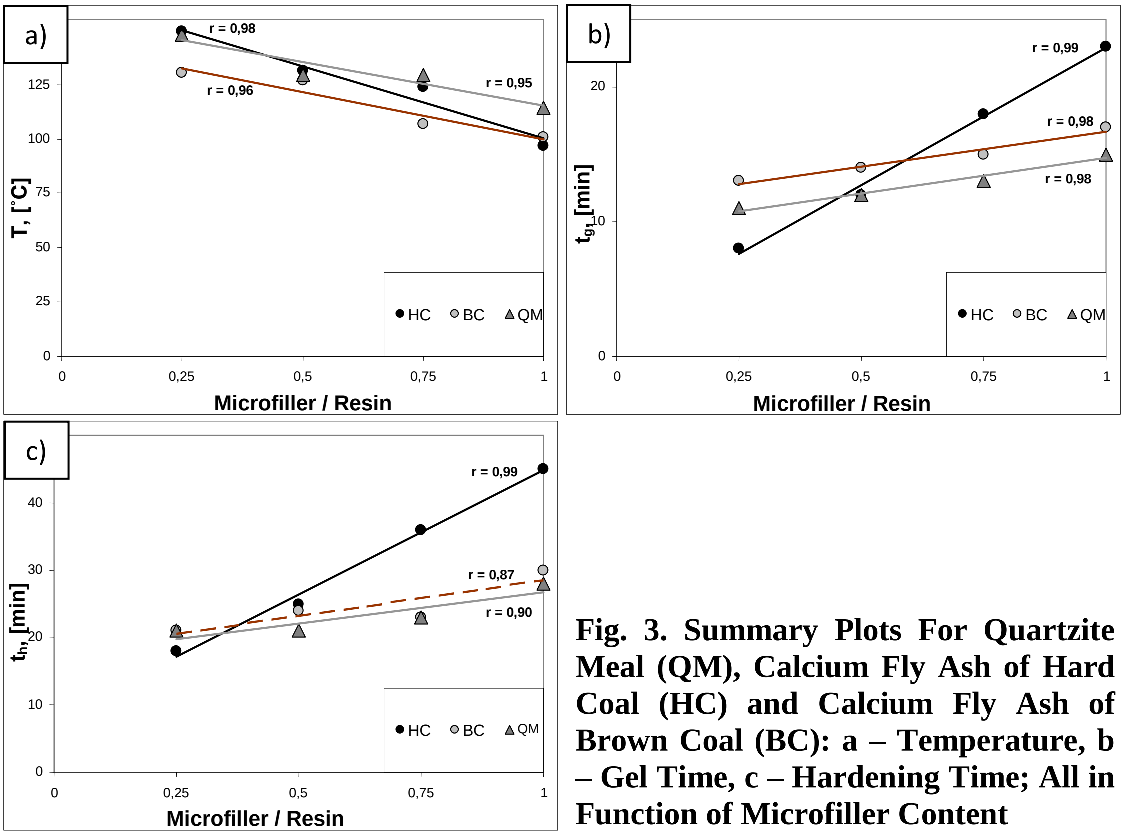

Fig. 3. Summary Plots For Quartzite Meal (QM), Calcium Fly Ash of Hard Coal (HC) and Calcium Fly Ash of Brown Coal (BC): a – Temperature, b – Gel Time, c – Hardening Time; All in Function of Microfiller Content

MATERIAL MODEL OF THE FLY ASH POLYMER CONCRETE

Material model assumption

The material model is defined in the form of the quadratic regression functions, in which the amounts of the particular components are the input variables, and the technical properties are the output variables [Czarnecki et al. 1999]:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 + a_{12}X_{12} + a_{13}X_{12} + a_{23}X_{23} \qquad (1)$$

where Y is a value of selected technical property; a_0 , ..., a_{ij} are the regression coefficients; X_1 , ..., X_{ij} are the coded material variables; $X_{ij} = X_i \cdot X_j$ – mix variables.

Material variables (the real values) are transformed into coded values according to the formula (2) which enables to use the statistic plan of experiment.

$$x_{real} = x_{cod} \cdot ½ \cdot \Delta x + x_0 \qquad (2)$$

where x_{cod} is a coded variable, x_{real} is a real variable, x_0 is a center value of range of parameter variability and Δx is range. The variables range is a area of experiment for particular property. For a coded variable the range is <-1; 1>.

Material model of fly ash

The preliminary tests of compressive and flexural strength for three types of polyester mortars - containing different microfillers: quartzite meal, calcium fly ash of brown coal and calcium fly ash of hard coal showed no significant differences in tested mechanical properties (Fig.4).

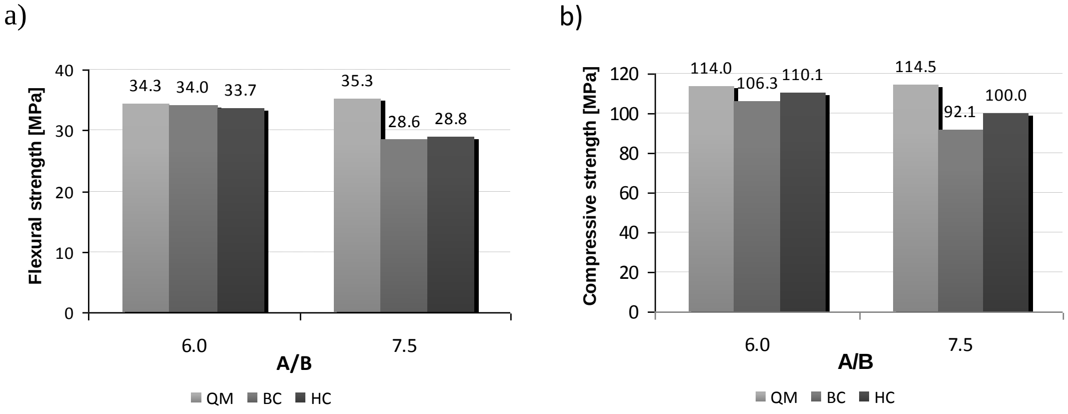

Fig. 4. Mechanical Parameters of Polyester Mortars Containing Quartzite Meal (QM), Calcium Fly Ash of Hard Coal (HC) and Calcium Fly Ash of Brown Coal (BC) in Function of A/B: a – Flexural Strength; b – Compressive Strength

Considering the above results as well as the hardening process characteristics it was decided to investigate the effect of replacement the quartzite microfiller with calcium fly ash from hard coal. The basis for the determination of the material model of fly ash polymer concrete were the results of the laboratory tests carried out using statistical design (Box compositional design) of the experiment [Clifton et al. 1995]. An unsaturated polyester resin was used as a binder. Aggregate consisted of standard sand and natural gravel; microfiller was the mix of quartzite meal and calcium fly ash from hard coal combustion. The material variables were: aggregate/binder ratio (X_1, g/g), binder/microfiller ratio (X_2, g/g) and calcium fly ash/microfiller ratio (X_3, g/g). The considered properties were: flexural strength (f_b, MPa), tensile strength (f_t, MPa), compressive strength (f_c, MPa) and density (d, kg/m^3). Using the data from the tests (Tab.1) the material model of polyester concrete containing calcium fly ash was defined (Tab.2). Examples of graphic representation of the defined material model of polyester PC are presented in Fig. 5.

The correlation ratios (R) higher than 0.95 and the determination ratios (R^2) higher than 0.90. indicate that the model is close to the empiric data from laboratory tests and that the variability of PC property is strongly dependent on variability of the input variables.

ADVANCED MATERIAL MODEL – OVERALL DESIRABILITY

As polymer concrete is a composite material where various demands need to be fulfilled simultaneously it should be evaluated according to various criteria at the same time. To make such estimation possible the overall desirability function, developed by Harrington (1965) was used. Three sets of evaluation criteria (wages and sufficient ranges) have been chosen

(Tab.3) and the it was evaluated whether material can be applied in the particular situations. In all variants physical property – density is considered and its wage is always 0,10. Density was considered as it is demanded that produced polymer concrete were possibly light. When considering mechanical parameters only flexural and compressive strength were considered, as the tensile strength is correlated with flexural strength. In the first variant both mechanical properties were equivalent – their wages were equal (0.45).

Table 1. Results of Tests for Polyester Concrete with Calcium Fly Ash of Hard Coal

No.	Material variables			Technical property			
	A/B	B/M	Ash/M	Density, kg/m^3	Flexural strength, MPa	Tensile strength, MPa	Compress. strength, MPa
1	-0.58	-0.58	-0.58	2167	22.2	8.4	114.5
2	0.58	-0.58	-0.58	2187	20.7	10.8	102.4
3	-0.58	0.58	-0.58	2193	19.6	7.5	105.0
4	-0.58	-0.58	0.58	1746	1.7	1.7	10.7
5	0.58	0.58	-0.58	2278	20.7	10.6	113.8
6	0.58	-0.58	0.58	1854	1.9	0.6	8.6
7	-0.58	0.58	0.58	2062	17.5	7.4	70.9
8	0.58	0.58	0.58	2028	8.2	4.7	23.3
9	-0.97	0.00	0.00	2074	20.6	11.1	115.1
10	0.97	0.00	0.00	2121	11.6	7.2	40.8
11	0.00	-0.97	0.00	1961	3.2	2.8	16.4
12	0.00	0.97	0.00	2203	20.8	11.1	110.5
13	0.00	0.00	-0.97	2243	20.8	9.9	112.7
14	0.00	0.00	0.97	1791	2.0	0.5	8.2
15	0.00	0.00	0.00	2154	21.0	10.1	102.3
16	0.00	0.00	0.00	2161	18.0	7.8	96.1
17	0.00	0.00	0.00	2192	21.9	10.2	104.0
18	0.00	0.00	0.00	2150	19.3	10.7	85.7
19	0.00	0.00	0.00	2174	19.6	9.9	100.7
20	0.00	0.00	0.00	2160	18.6	8.0	88.2

Table 2. Material Model of Polyester Fly Ash Polymer Concrete

Regression coefficient	Model according to property		
	Flexural strength	Tensile strength	Compress. strength
A_0	19.68	9.47	96.03
A_1	-3.11	-0.61	-22.48
A_2	6.21	2.86	29.70
A_3	-10.82	-4.90	-63.03
A_{11}	-2.98	-0.62	-17.15
A_{22}	-7.34	-2.96	-32.56
A_{33}	-7.98	-4.82	-35.75
A_{12}	-2.56	-0.33	-9.14
A_{13}	-3.23	-3.46	-17.24
A_{23}	9.18	4.05	27.13
Correlation	0.97	0.96	0.95

The Wages and Sufficient Ranges of Properties for 3 Considered Variants

Property	Variant I	Variant II	Variant III	Sufficient range
Flexural strength, MPa	0.45	0.20	0.70	20 ÷ 30
Compressive strength, MPa	0.45	0.70	0.20	85 ÷ 95
Density, kg/m^3	0.10	0.10	0.10	6 ÷ 12

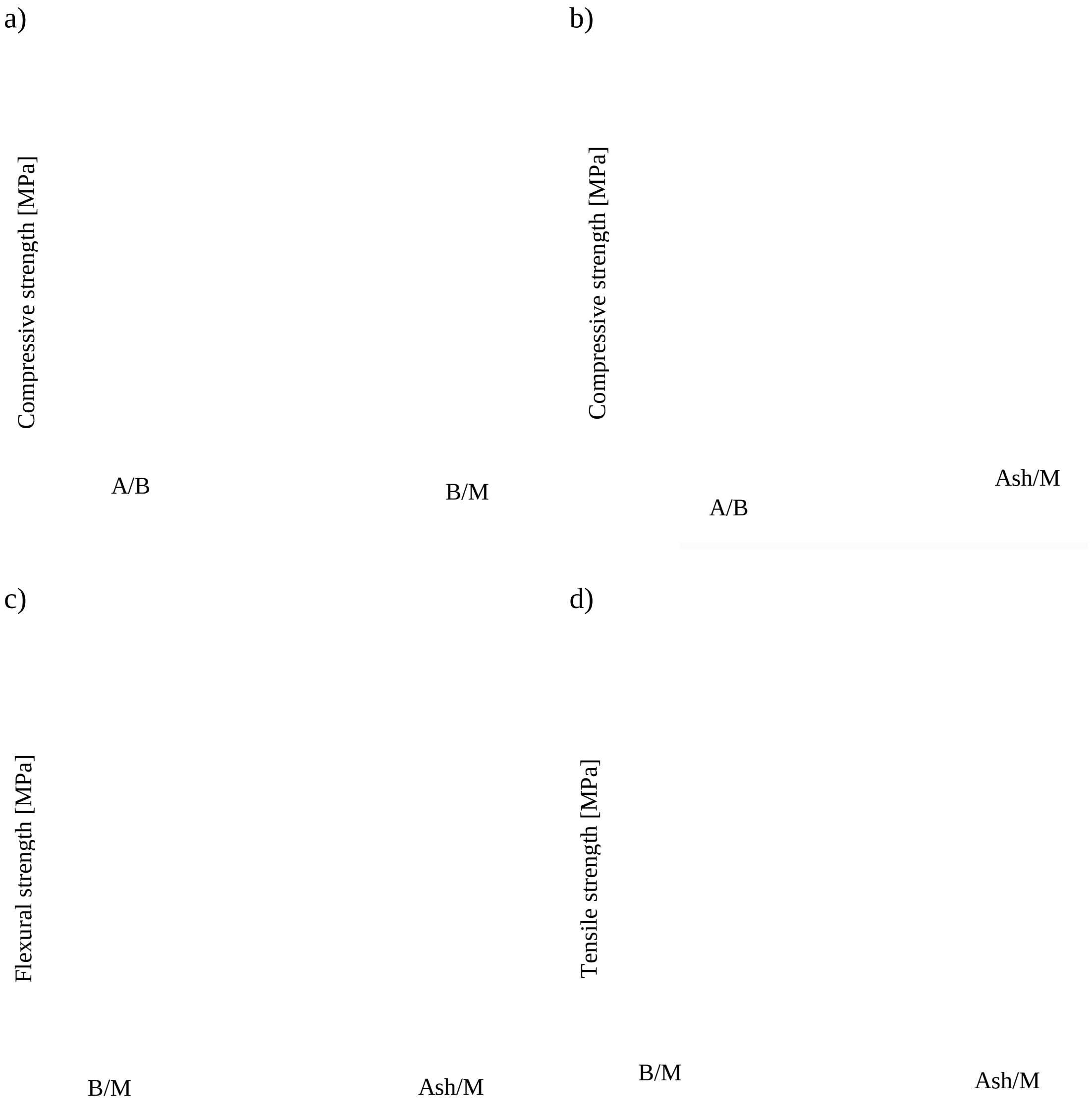

Fig. 5. Graphical Representation of the Material Model: a – Compressive Strength in Function of A/B and B/M; b – Compressive Strength in Function of Variables A/B and Ash/M; c – Flexural Strength; d – Tensile Strength; Both in Function of B/M and Ash/M

In the second variant wage of compressive strength was higher (0.70) than wage of flexural strength (0.20) and in the third variant it was opposite. All variants concerned polymer concrete as a material of pre-cast elements that work under compressive loads. In the third case it was assumed that the elements were also exposed to bending loads.

On the base of given above wages and sufficient ranges (see Table 3) overall desirability for all polymer concretes designed and tested according to used statistical design was calculated (Table 4). Taking into account that satisfactory level of overall desirability is 0.37 [Czarnecki et all. 1999] the great majority of the PC compositions containing up to 50% of calcium fly ash were evaluated as useful towards demanded criteria (bolded values). Using the values of overall desirability for the particular concretes for each variant the regression functions which describe the relations between the overall desirability and the material parameters were evaluated. These functions were treated as an advanced material model. The regression functions were described by the second degree polynomials – compare equation (1) – and the values of the regression coefficients are presented in Table 5. Graphical representation of advanced material model is presented on Fig. 6.

RESULTS AND DISCUSSIONS

The first part of the paper, where the influence of calcium fly ashes on polyester resin setting process was evaluated, showed that although the applied microfillers presented differences in granulometric composition, the typical PC microfiller – quartzite meal and calcium fly ash of brown coal showed similar influence on hardening process – similar character of changes: rapid drop of temperature of hardening along with increase of gel time. The calcium fly ash of hard coal showed different influence: the drop of temperature of hardening was comparable but in much wider range of variability of gel time, which correspond with relation: hardening temperature – hardening time (as hardening time and gel time are strongly correlated). Moreover, the analysis of tests results showed that exceeding value of 0.75 of relative content of calcium fly ash of hard coal caused decrease of relative conductivity to 30% what meant that such mix had very low workability in comparison to other mixes.

In the second part of the paper there was presented the material models (basic and advanced) of polyester concrete containing calcium fly ash of hard coal which make possible to determine relations between the ingredients and the mechanical parameters of PC and evaluate how the particular content of calcium fly ash influence on the mechanical strength.

The analysis of the basic material model, as well as overall desirability function, indicated that the calcium fly ash content in the microfiller due to compressive strength should not exceed 50% – this value appears to be proper limit for the relatively high use of utilized calcium fly ash, satisfactory values of compressive strength and relatively good workability, which gets worse with an increase in the quantity of calcium fly ash in the microfiller. Analysis of data from the bending and tensile tests confirmed the above findings: content of the calcium fly ash should not exceed 50%. Higher content caused significant decrease of the workability and in consequence improper compaction of the mix. As a result the mechanical properties decreased and the results scatter increased – the differences reached up to 80% in value for samples of the fly ash content of between 79.5 and 98.5%. However the 50% calcium fly ash content in is quite a high content and certainly confirms the validity of studies using calcium fly ashes in polymer concretes as microfillers. The influence of calcium fly ash presence on density of concretes was not very strong.

Table 4. Overall Desirability for All Tested Fly Ash PC for 3 Considered Variants

No	Material variables			Overall desirability		
	X_1 (A/B) coded (real)	X_2 (B/M) coded (real)	X_3 (Ash/M) coded (real)	Variant I	Variant II	Variant III
1	-0.58 (6.050)	-0.58 (0.442)	-0.58 (0.210)	**0.81**	**0.90**	**0.66**
2	0.58 (8.950)	-0.58 (0.442)	-0.58 (0.210)	**0.68**	**0.78**	**0.56**
3	-0.58 (6.050)	0.58 (0.558)	-0.58 (0.210)	**0.70**	**0.81**	**0.55**
4	-0.58 (6.050)	-0.58 (0.442)	0.58 (0.790)	0.00	0.00	0.00
5	0.58 (8.950)	0.58 (0.558)	-0.58 (0.210)	**0.80**	**0.90**	**0.64**
6	0.58 (8.950)	-0.58 (0.442)	0.58 (0.790)	0.00	0.00	0.00
7	-0.58 (6.050)	0.58 (0.558)	0.58 (0.790)	0.14	0.07	0.23
8	0.58 (8.950)	0.58 (0.558)	0.58 (0.790)	0.00	0.00	0.00
9	-0.97 (5.075)	0.00 (0.500)	0.00 (0.500)	**0.79**	**0.90**	**0.62**
10	0.97 (9.925)	0.00 (0.500)	0.00 (0.500)	0.00	0.00	0.02
11	0.00 (7.500)	-0.97 (0.403)	0.00 (0.500)	0.00	0.00	0.00
12	0.00 (7.500)	0.97 (0.597)	0.00 (0.500)	**0.77**	**0.87**	**0.61**
13	0.00 (7.500)	0.00 (0.500)	-0.97 (0.015)	**0.79**	**0.80**	**0.63**
14	0.00 (7.500)	0.00 (0.500)	0.97 (0.985)	0.00	0.00	0.00
15	0.00 (7.500)	0.00 (0.500)	0.00 (0.500)	**0.68**	**0.77**	**0.56**
16	0.00 (7.500)	0.00 (0.500)	0.00 (0.500	**0.56**	**0.66**	**0.45**
17	0.00 (7.500)	0.00 (0.500)	0.00 (0.500)	**0.71**	**0.80**	**0.60**
18	0.00 (7.500)	0.00 (0.500)	0.00 (0.500)	**0.41**	**0.43**	**0.40**
19	0.00 (7.500)	0.00 (0.500)	0.00 (0.500)	**0.66**	**0.75**	**0.52**
20	0.00 (7.500)	0.00 (0.500)	0.00 (0.500)	**0.46**	**0.49**	**0.40**

Table 5. Advanced Material Model of Fly Ash Polymer Concrete – Overall Desirability in Function of the Properties Values

Regression coefficient	Values of regression coefficient for overall desirability regression function		
	Variant I	Variant II	Variant III
A_0	0.58	0.65	0.49
A_1	-0.19	-0.20	-0.16
A_2	0.18	0.20	0.16
A_3	-0.53	-0.61	-0.41
A_{11}	-0.18	-0.21	-0.16
A_{22}	-0.20	-0.22	-0.17
A_{33}	-0.18	-0.21	-0.16
A_{12}	0.03	0.05	-0.01
A_{13}	-0.04	-0.02	-0.08
A_{23}	0.05	0.02	0.10
Correlation	0.89	0.885	0.91

a)

Overall desirability

Ash/M

A/B

Overall desirability

B/M

Ash/M

b)

Overall desirability

Ash/M

A/B

Overall desirability

B/M

Ash/M

c)

Overall desirability

Ash/M

A/B

Overall desirability

B/M

Ash/M

Fig. 6. Graphical Representation of Overall Desirability Function vs. Material Variables: A/B and Ash/M (left) and B/M and Ash/M (right): a- Variant I; b – Variant II; c – Variant III.

CONCLUSIONS

The following conclusions can be formulated from the investigation presented in the paper:

- The analysis of tests results has shown, that replacing typical microfiller with calcium fly ash from coal combustion in polymer concrete mix is possible but in limited range – up to 50% due significant decrease of mix workability.
- The mechanical properties (flexural, tensile, compressive strength) of polymer concrete containing more than 50% calcium fly ash in microfiller decrease significantly.
- Calcium fly ash of hard coal causes extending gel and hardening time of polyester resin in comparison to quartzite meal and calcium fly ash of brown coal.
- Calcium fly ash of brown coal shows similar influence on hardening process as quartzite meal, the typical PC microfiller.

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