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COMPOSITES THEORY AND PRACTICE

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CEMENT COMPOSITES MODIFIED WITH POLYPROPYLENE FIBRES AND TYPE II ADDITIVES

In the article, three different type II additives (fly ash, silica fume and slag) were used in order to improve the adherence of polypropylene fibres to cement mortar. Estimation of the level of fibre adherence to the cement matrix change was conducted on the basis of mechanical research of the composites, as well as observation of the interfacial transition zone between the fibres and cement paste in scanning electron microscopy. It was shown that the mechanical properties of cement composites modified with polypropylene fibres strongly depend on the type of pozzolanic additive and compactness of the interfacial transition zone between the fibres and cement paste. The obtained values of fracture toughness of the cement composites proved that during the whole research period (180 days), the presence of 0.5 vol.% polypropylene fibres, regardless of the cement matrix applied, improves the fracture toughness of the cement matrix. However, two ranges of reaction between the cement matrix and the fibres were observed; the first up to 56 days of hardening, where the fibrocomposite properties depend, besides the fibre properties, on clinker fine-crystalline phases of cement paste. The second one - after 56 days of bonding, where the composite properties depend mostly on the pozzolanic and hydraulic additives.

Keywords: **cement composites, polypropylene fibres, pozzolanic and hydraulic additives, mechanical properties, scanning electron microscopy SEM**

KOMPOZYTY CEMENTOWE MODYFIKOWANE WŁÓKNAMI POLIPROPYLENOWYMI I DODATKAMI TYPU II

W artykule zastosowano trzy różne dodatki typu II (popiół lotny, pył krzemionkowy i żużel wielkopiecowy) w celu poprawy przyczepności włókien polipropylenowych do zapraw cementowych. Ocenę zmiany stopnia przyczepności włókien do matrycy cementowej prowadzono na podstawie badań mechanicznych kompozytów oraz obserwacji strefy kontaktowej włókno-zaczyn cementowy metodą elektronowej mikroskopii skaningowej. Wykazano, że mechaniczne właściwości kompozytu cementowego modyfikowanego włóknami polipropylenowymi zależą od rodzaju zastosowanego dodatku pucolanowego i zagęszczenia strefy przejściowej pomiędzy włóknami i zaczynem cementowym. Uzyskane wartości odporności na pękanie kompozytów cementowych wykazały, że w całym okresie prowadzonych badań (180 dni) obecność włókien polipropylenowych w ilości 0.5%. obj., niezależnie od zastosowanej matrycy cementowej, wpływa na poprawę odporności na pękanie matrycy cementowej. Ponadto, zaobserwowano dwa zakresy oddziaływania włókien z matrycą cementową, pierwszy do 56 dnia twardnienia, gdzie o właściwościach fibrokompozytu, oprócz własności włókien, decydować będą głównie drobnokrystaliczne fazy klinkierowe zaczynu cementowego, oraz drugi, po 56 dniach wiązania, gdzie o właściwościach kompozytu będą decydowały głównie zastosowane dodatki pucolanowe i hydrauliczne.

Słowa kluczowe: **kompozyty cementowe, włókna polipropylenowe, dodatki pucolanowe i hydrauliczne, właściwości mechaniczne, skaningowa mikroskopia elektronowa SEM**

INTRODUCTION

The intensive development of plastic technology at the end of the last century resulted in great interest in those materials in many areas of life. Plastics also found a wide range of applications in building materials, for example polyurethane and styrene aerated plastics as heat-insulating materials; polyester, epoxy and polyacrylate resins as components of glues, paints, concretes and polymer mortars, as well as components of many composites like polymer-carbon, polymer-metal or polymer-concrete. In cement composites, synthetic fibres received from different organic precursors (like polypropylene, polyethylene, polyamide or acrylonitrile) are also very popular. The application of synthetic fibres, instead of asbestos, glass or steel ones, in cement composites is becoming more popular due to their numerous advantages such as low bulk density, high chemical resistance to acids and alkali, relatively good mechanical properties on the mass unit and constantly decreasing cost of production. Synthetic fibres come as single fibres or as light bunches of several hundred fibrils with different diameters and lengths [1-3]. Due to surface treatment, synthetic fibres are characterised by anti-electrostatic and hydrophilic properties, which result in their good dispersion in the cement matrix. Already a small amount of 0.1÷0.3 vol.% results in the elimination of scratches and contraction cracks occurring in the initial moment of concrete hardening. In greater amounts of above 1 vol.%, synthetic fibres cause an increase in fracture toughness in cement composites [4, 5]; they also raise their mechanical resistance to abrasion and fire resistance [6].

A disadvantage of synthetic fibres is their low adherence to the cement matrix caused by their low developed specific surface. To improve their adherence to the cement slurry, we can modify the surface of synthetic fibres or we can chemically modify the content of the cement paste by type II additives. In this work, three different type II components were used (fly ash, silica fume and slag) in order to improve the adherence of polypropylene fibres to cement mortar. Estimation of the level of fibre adherence to the cement matrix change was conducted on the basis of mechanical research on composites, as well as observation of the interfacial transition zone between the fibres and cement paste in scanning electron microscopy.

EXPERIMENTAL PROCEDURE

The cement matrix consisted of cement mortar: 450 g of CEM I 42.5 R, 180 ml of water, 1350 g of aggregate 0/2 mm (KWARCMIX, Tomaszów Mazowiecki), 1.5% fluidizing admixture of polycarboxyl ethers. As reinforcement of the cement mortars, polypropylene fibre with a diameter of 60 x 180 μm and length of 12 mm, in the amount of 0.5 vol.% was used. In order to condense the microstructure of the cement mortar, three types of additives were used: silica fume (SILIMIC, Huta Łaziska), fly ash from fluidized beds (FLUBET) in the amount of 10 wt.% of the cement mass, and slag in the form of metallurgical cement CEM III A 42.5 L/N with the amount of slag exceeding 50 wt.%. The contents of the individual matrices are presented in Table 1.

TABLE 1. **Composition of particular cement mortars**
TABELA 1. **Skład poszczególnych matryc cementowych**

	Mortar 1	Mortar 2	Mortar 3	Mortar 4
Cement [g]	450 (CEM I)	405 (CEM I)	405 (CEM I)	450 (CEM III)
Water [cm^3]	180	180	180	180
Sand [g]	1350	1350	1350	1350
Additive [%]	-	45 (SILIMIC)	45 (FLUBET)	-
Admixture [% m. c.]	1.5	1.5	1.5	1.5
PP fibres [vol. %]	0.5	0.5	0.5	0.5

Defining the right consistency of cement paste and examining the initial bonding of the cement with reference to the applied type II admixtures was conducted according to the procedure included in norm PN-EN 196-1.

As the measure of plasticity of mortar, the value of reflow of the cement mortar sample under dynamic shock was taken, given as an arithmetic mean of two measurements. This test was conducted on the reflow table according to the procedure in the PN-EN 1015-3 norm. Research on the bending strength was conducted on beams 4×4×16 cm with a three-point bending technique with the use of an INSTRON press with a maximum pressure of 300 N. During the test, a stress-deflection curve was registered, on the basis of which the following mechanical parameters of the mortars were defined: maximum bending stress, maximum bending strength, maximum deflection, destruction energy by maximum deflection and maximum bending stress. Mechanical tests were conducted after 2, 7, 28, 56, 90 and 180 days of hardening of the cement mortars. Each test was based on 6 samples. As a measure of fracture toughness of the cement composites, sample destruction energy expressed in J, with the maximum deflection was applied. The contact area between the polypropylene fibre and cement paste modified with type II additives was examined with a scanning electron microscope type EVO40 from Carl Zeiss.

RESULTS AND DISCUSSION

Influence of type of additive on cement paste properties

Table 2 presents the results of the research on the required amount of water to achieve the normative consistency and the beginning of bonding for particular cement matrices with the examined additives. The analysis of these results proved that the presence of pozzolanic and hydraulic additives clearly increases water demand. The highest water demand was discovered in the cement with silica fumes, whereas the lowest one was found in the one containing slag.

TABLE 2. **Composition and physical parameters of cement mortars**
TABELA 2. **Skład i parametry fizyczne zapraw cementowych**

Type of binder	Amount of cement [g]	Amount of additive [g]	Amount of water [cm^3]	Initial setting time [min]	Workability without fibres [cm]	Workability with fibres [cm]
CEM I	500	-	144.5	162.5	14.2	10.4
CEM I + SF	450	50	171.0	137.5	11.2	11.7
CEM I + FA	450	50	167.5	197.5	11.2	10.4
CEM III	500	-	166.5	172.5	13.2	11.8

Comparison of the initial setting times for the cements with the studied additives proved that the presence of fly ashes in the cement paste clearly delays the beginning of cement bonding; and in the case of the slag additive, the beginning of bonding was slightly delayed in comparison to the cement paste from pure clinker cement. Accelerated bonding was observed in the cement pastes modified with silica fumes, where in all the cases the bonding time of the cement was compatible with the marginal normative conditions for a given cement class, and equalled over 75 minutes [7].

Influence of polypropylene fibres and type II additives on rheological properties of fresh mortars

After the tests on mortar workability, the results of which are presented in Table 2, it was noticed that the additives of pozzolanic materials - silica fume, fly ashes and slag - decrease the workability of the mortar samples. The cement mortars that had 10 wt.% fly ash and silica fume, showed less tendency to reflow, thus their workability was lower than that of the cement mortar sample without additives. The difference value of reflow decreased in this case by 20%, which is related to the greater water demand of those materials. A similar tendency was observed in the case of mortars with slag, where the workability was limited by almost 10%.

In mortars with the addition of 0.5 vol.% polypropylene fibres, their presence caused an additional decrease in workability of all the mortars; the greatest in the mortar from pure clinker cement. The conducted research showed a positive influence of all the additives, especially of slag, on the rheological properties of the mortars with added fibres. The presence of pozzolanic additives, as well as of slag, resulted in improvement of mortar workability in comparison with mortar from pure clinker cement.

Mechanical properties of polypropylene - cement composites

Figure 1 presents the typical characteristics of the behaviour of pure cement composites (CEM I) and cement composites modified with polypropylene fibres (CEM I + PPF) under bending stress after 2 days of hardening. Regardless of the used cement matrix, after reaching the maximum bending stress, the samples without fibres show a rapid decrease in force, which is characteristic for cracking the brittle cement matrix. In the case of the composites with the 0.5 vol.% additive of polypropylene fibres, when the maximum bending stress was reached, the force slightly decreased and then increased again, which was related to transferring the load by the fibres. Figure 2 presents the comparison of exemplary stress-deflection curves obtained for cement matrices modified with additives and polypropylene fibres after 2, 56 and 180 days of hardening; they show essential moments of behaviour of the tested cement fibrocomposites.

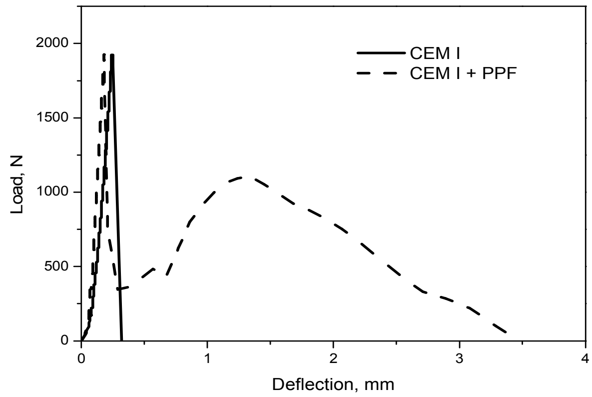


Fig. 1. Typical characteristics of behaviour of cement composites with and without PP fibres

Rys. 1. Charakterystyki zniszczenia kompozytu cementowego z i bez włókien PP

Analysis of the stress-deflection curves has proven that the maximum bending stress of the cement composite increased with time and the greatest fracture toughness was obtained on cement matrices made of CEM I with SF and FA on the 56th day of hardening, whereas the matrices of CEM I and CEM III, on the 28th and 180th day of hardening, respectively.

The effectiveness of fibres in terms of transferring the load, as well as their cooperation with the cement matrix, is shown in the values of the fracture toughness, which are presented as the energy of fibrocomposite destruction (Fig. 3). The value of the fracture toughness of the composite consists of the following parameters: fibre tensile strength, its elasticity, fibre surface characteristics, their adherence to the cement matrix and the maximum tension of the fibrocomposite. The values presented in Figure 3, which show the fracture toughness of the cement composites modified with type II additives and polypropylene fibres, prove that throughout the whole period of testing (180 days), the presence of polypropylene fibres, regardless of the cement matrix used, improves the fracture toughness of the cement matrix.

This means that synthetic fibres used in the amount of 0.5 vol.% are not only anti-contraction agents but they also transfer the load by increasing the carrying capacity of the cement composite. Moreover, the data presented in Figure 3 explicitly show two types of effects of the fibres on the cement matrix, the first one up to the 56th day of hardening, where, apart from the presence of fibres, the properties of the fibrocomposites are basically determined by fine-crystalline phases of cement paste; the second one refers to the period after the 56th day of hardening, where the properties of the fibrocomposites are mainly determined by the used pozzolanic and hydraulic additives.

Analysis of the fracture toughness of the cement composites has proven that in the initial state of the cement bonding period, up to the 7th day, fine--crystalline products of the clinker phase hydration are the most significant in terms of the impact of polypropylene fibres on the cement matrix.

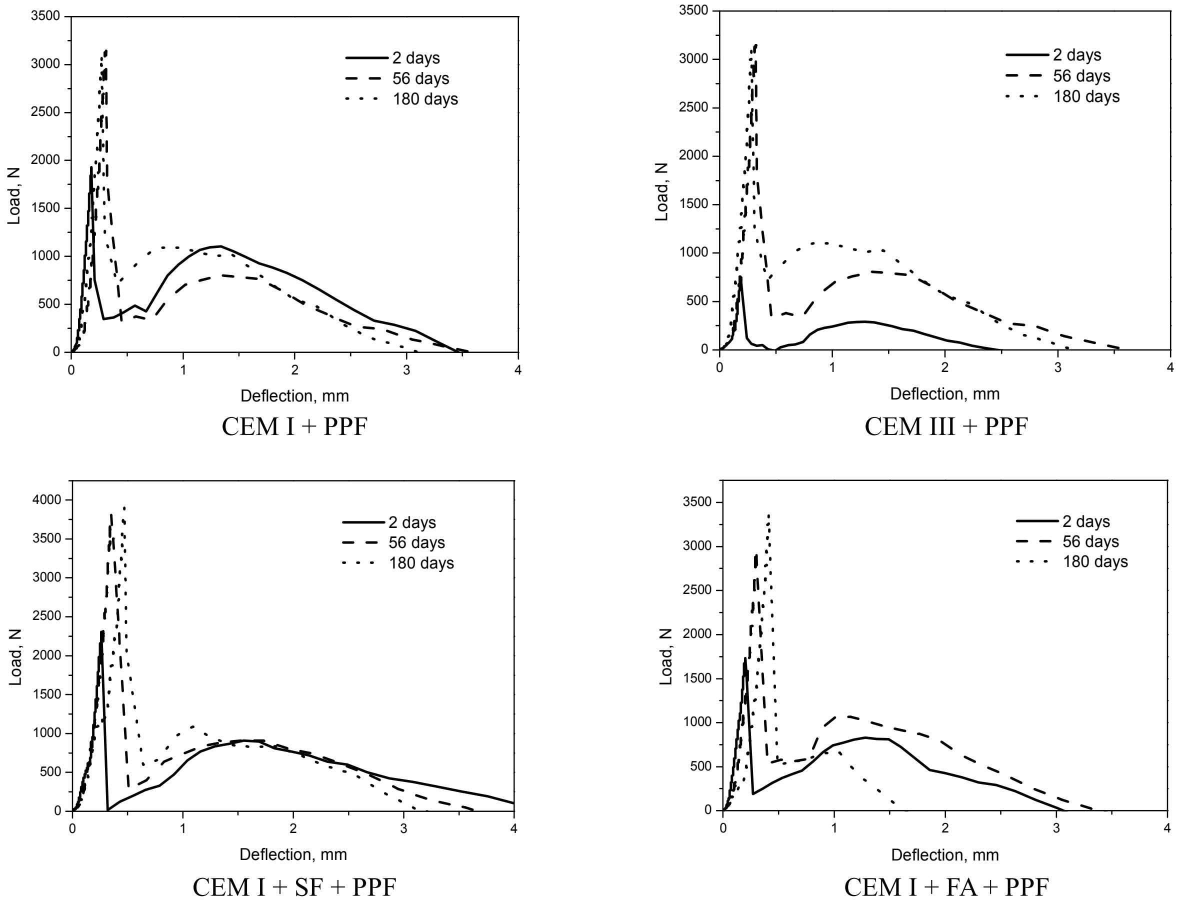
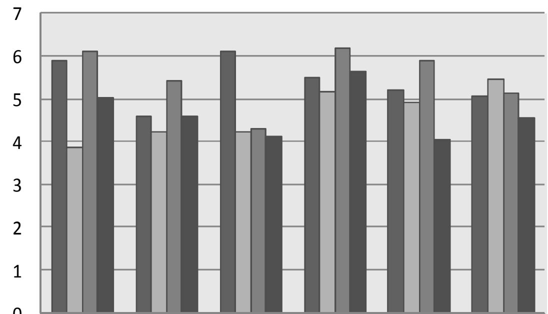


Fig. 2. Comparison of exemplary load-deflection curves obtained for cement matrices modified with additives and PP fibres after 2, 56 and 180 days of hardening

Rys. 2. Porównanie przykładowych krzywych obciążenie-ugięcie otrzymanych dla matryc cementowych modyfikowanych dodatkami i włóknami PP po 2, 56 i 180 dniach wiązania



	2 days	7 days	28 days	56 days	90 days	180 days
CEM I	5,9	4,59	6,11	5,49	5,2	5,04
CEM III	3,87	4,24	4,23	5,16	4,91	5,44
CEM I + SF	6,1	5,41	4,31	6,16	5,89	5,14
CEM I + FA	5,02	4,6	4,12	5,65	4,05	4,53

Fig. 3. Relation between flexural toughness and time of hardening for considered cement composites

Rys. 3. Zależność pomiędzy odpornością na pękanie a czasem twardnienia dla badanych kompozytów cementowych

In this period, the best values of fracture toughness of the composite were obtained for mortar made of pure clinker cement. Additional increases in the fracture toughness of the composites after 2 and 7 days of bonding were obtained for the cement matrix modified with a 10 wt.% additive of silica fumes, however, this tendency is observed only during the first 7 days of bonding; on the 28th day the best parameters of the composite were obtained for the cement mortar without any additives. Since the granulation of the silica fume is below 0.045 mm, which is far more grained than the cement granulation, the presence of silica fumes in the cement paste influences the density of the cement paste microstructure in the initial period; this results in better adhesion of the polypropylene fibres to the cement matrix.

Moreover, silica fumes, which consist of more than 90% silicon dioxide, probably account for the crystallization nucleus for the clinker phases, they improve the cement mortar in terms of mechanical parameters [8, 9]. This effect cannot be seen in the cement matrix with the additive of fly ashes and with the additive of the slag exceeding 50%. Activation of the pozzolanic additives is observed only after 56 days of hardening of the cement composite. Both mortars with silica fume and mortars with fly ashes obtain the best values of fracture toughness in that period but the best results were observed for the cement matrix with the additive of silica fume. The increase in the mechanical parameters of the fibrocomposites in the later period of hardening is the result of the pozzolanic reaction between calcium hydroxide, which is one of the products of cement hydration, and silicon dioxide, which is the main ingredient of both additives. The reaction results in creating the hydrated calcium silicate, i.e. CSH phase, which is characterised by far more grained crystallites, causing the concentration of the cement paste microstructure and thus, improvement in adhesion to polypropylene fibres [10, 11].

In the case of the cement matrix made of the slag cement, the whole period of research showed gradual increase in both the maximum bending tension and the fibrocomposite fracture toughness; up to the 90th day of hardening. The obtained results were lower than the results obtained for other cement matrices. The best results concerning fracture toughness, better than the parameters of other cement matrices, were obtained only after 180 days of hardening. The admixture of the slag exceeding 50% in the cement matrix (CEM III) influences a very slow increase in the cement composite strength in the initial stage of bonding. The microstructure of the cement paste in that period is very porous; after some time, its density grows due to the latent hydraulic properties of the slag, which results in the increase in paste adhesion to the fibres and eventually, increases the fracture toughness of the fibrocomposite after 180 days of hardening [12].

The representation of examined composites after 180 days of hardening with consideration of the edge between the cement paste - polypropylene fibres is presented in Figure 4. The SEM analysis proved that the presence of type II additives influences the microstructure of the thcement paste. It is particularly visible in the case of the cement matrix modified with silica fume. In Figure 4c, a porous fine-crystalline CSH phase is visible around the polypropylene fibre that is very well adherent to the surface of the fibre. Similar representation of the microstructure around the fibre was achieved for the matrix from slag cement (Fig. 4b). In this period the matrix was characterised by the best mechanical parameters among all the examined composites. The cement matrices from pure clinker cement and those modified with fly ashes have a more compact structure, which causes the fibres to slide off the cement paste more easily. Thus their adherence is worse, as well as their fracture toughness.

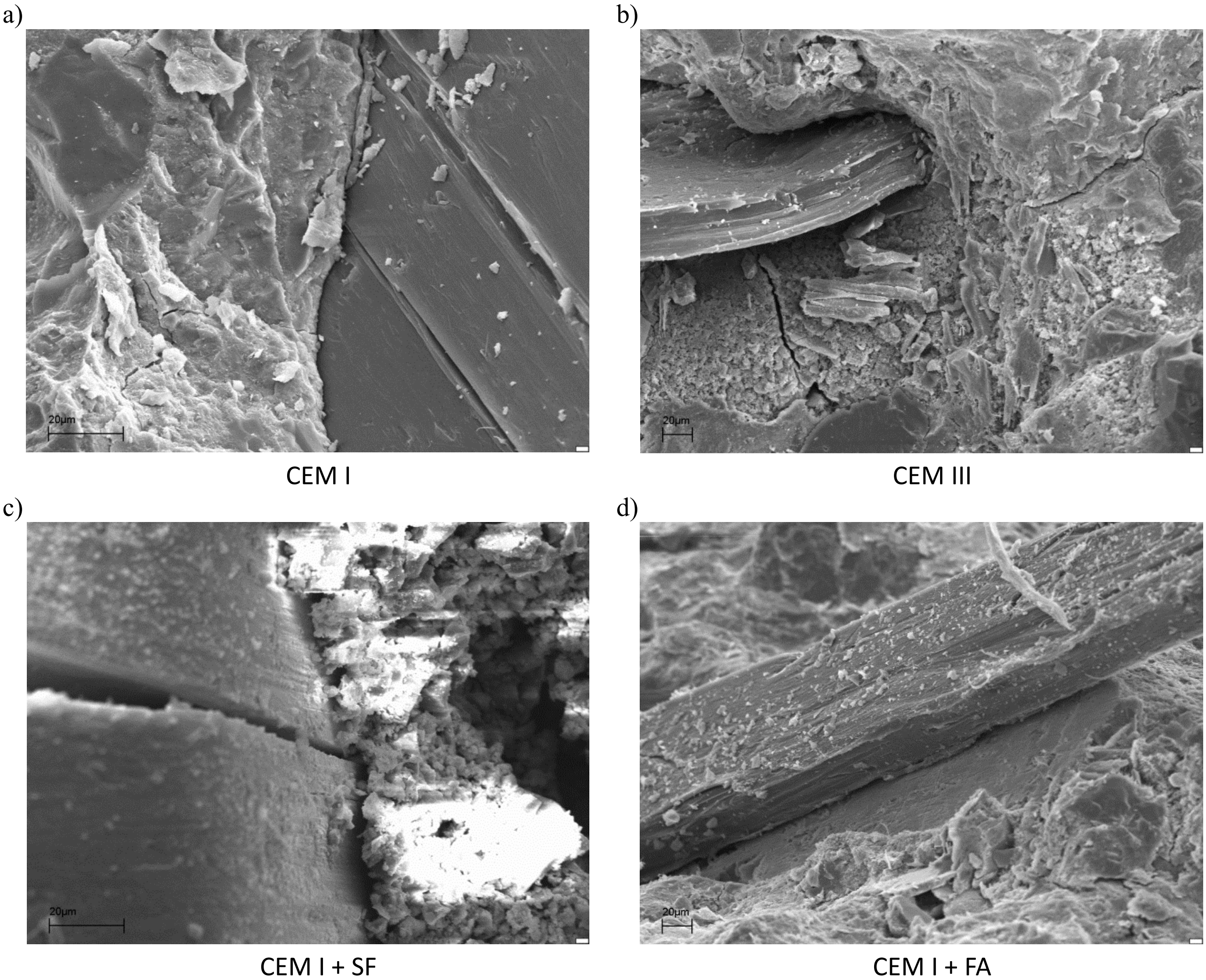


Fig. 4. SEM spectra for investigated cement - PP composites

Rys. 4. Obrazy SEM dla badanych kompozytów cementowo-polipropylenowych

CONCLUSIONS

The research examined the influence of type II additives on the properties of cement composites modified with polypropylene fibres. On the basis of the research the following conclusions can be made:

1. The obtained values of fracture toughness of cement composites modified with type II additives and polypropylene fibres proved that during the whole research period (180 days), the presence of 0.5 vol.% polypropylene fibres, regardless of the cement matrix applied, improves the fracture toughness of the cement matrix. Moreover, two ranges of reaction between the cement matrix and the fibres were observed; the first up to 56 days of hardening, where the fibrocomposite properties depend, besides the fibre properties, on the clinker fine-crystalline phases of the cement paste. The second one - after 56 days of bonding, where the composite properties depend mostly on the pozzolanic and hydraulic additives.
2. The presence of the silica fume in the cement paste, due to their granulation below 0.045 mm - much lower than that of cement, in the initial period influences the concentration of the cement paste microstructure (the so-called filling effect), which results in better adhesion of the polypropylene fibres to the cement matrix. Activation of the pozzolanic additives took place after 56 days of hardening of the cement composite. Mortars with silica fume, as well as those with fly ashes, achieved in that period the best values of fracture toughness, and the highest results were registered for the cement matrix with admixtures of silica fumes.
3. In the case of the matrix from slag cement, in the whole research period a gradual increase in maximum bending stress, as well as fracture toughness of the fibrocomposite was observed; the achieved results up to 90 days of hardening were lower than the results for the other cement matrices. The best fracture toughness, better than the parameters of the other cement matrices, was achieved after 180 days of hardening.
4. The research of the composites modified with type II additives proved that in the first 6 months, the best mechanical parameters (fracture toughness) were achieved for the matrix with the silica fumes, whereas at the end of the research period, the best parameters were achieved in the mortars with the additive of slag.

REFERENCES

[1] Bentur A., Mindess S., Fibre Reinforced Cementitious Composites, Taylor & Francis, London and New York 2007.

[2] Zheng Z., Feldman D., Synthetic fibre-reinforced concrete, Prog. Polym. Sci. 1995, 20, 185-210.

[3] Zollo R.F., Fiber-reinforced concrete: an overview after 30 years of development, Cem. Concr. Comp. 1997, 19, 107--122.

[4] Ślosarczyk A., Jasiczak J., Alternative ways of reinforcing cement composites, Composites Theory and Practice 2012, 4, 266-267.

[5] Ślosarczyk A., The influence of non-metallic and metallic fibres on the mechanical properties of cement mortars, Brittle Matrix Composites 10, Proceedings of the 10 International Symposium, Cambridge-Warsaw 2012, 167-176.

[6] Li M., Wu Z., Sun W., Qian C., Experimental study and mechanism analysis of restraining spalling of high strength concrete with polypropylene micro-fibers, Cement Wapno Beton 2011, 3, 129-138.

[7] Malhotra V.M., Ramachandran V. S., Feldman R. F., Aïtcin P.-C., Condensed Silica Fume in Concrete, CRS Press, Florida 1987.

[8] Korpa A., Kowald T., Trettin R., Hydration behavior, structure and morphology of hydration phases in advanced cement-based systems containing micro and nanoscale pozzolanic additives, Cement and Concrete Research 2008, 38, 955-962.

[9] Nelson J.A., Young J.F., Addition of colloidal silicas and silicates to Portland cement pastes, Cement and Concrete Research 1977, 7, 277-282.

[10] Cyr M., Lawrence F., Ringot E., Mineral admixtures in mortars. Quantification of the physical effects of inert materials on short-term hydration, Cement and Concrete Research 2005, 35, 719-730.

[11] Cyr M., Lawrence F., Ringot E., Efficiency of mineral admixtures in mortars: Quantification of the physical and chemical effects of fine admixtures in relation with compressive strength, Cement and Concrete Research 2006, 36, 264-277.

[12] Li G., Zhao X., Properties of concrete incorporating fly ash and ground granulated blast furnace slag, Cement and Concrete Composites 2003, 25, 293-299.

