STUDIA UBB CHEMIA, LIX, 1, 2014 (p. 159-170)
(RECOMMENDED CITATION)

ORGANIC POLYMER-MODIFIED CEMENT CONCERET

MARIN AMĂREANU[a], LARISA MELIŢĂ[a,*]

ABSTRACT. The present paper presents the research results about the organic and inorganic additions influence, in different percentages in the lab-processed cement concretes, on their mechanical strengths. The cement CEM I 52.5 was used as mineral binder, an epoxy resin was used as polymer and silica fume (SF) as addition. Experiments were performed regarding on availability of the complex binder (organic-inorganic) - water system, in order to assess its ability to develop resistant strengthened structures. These are exemplified by the compression and tensile strengths of obtained concretes, by the developed forces (F) in avulsion tests of the concrete reinforcement, as well as the organic solvent extractions (toluene and ethanol) of polymer from the strengthened cement matrix. It was highlighted the positive role of additions in preparation of those concretes.

Keywords: *concrete, polymers, hydraulically active additives, mechanical* strengths

INTRODUCTION

The flexural and tensile strengths of the cement stone is five times and ten times, respectively, smaller than the compression strength; the deformation extent under load is limited, while it becomes brittle when it breaks. When the applied load increases a largely elastic deformation takes place, followed by a sudden break [1].

When metal components are used for reinforcement, the elastic properties of the construction elements are improved. However, the mechanical performances of the reinforced concrete it's only about 10% of the tensile strength of the metal reinforcement, because the theoretical, intrinsic strength of the cement stone cannot be reached in practice due to its important high porosity.

[a] *Technical University of Civil Engineering of Bucharest, Bdul. Lacul Tei nr: 122-124, Sector 2, cod 020396, Bucharest, Romania, * larisamelita@gmail.com*

The porosity of the cement stone can be reduced by diminishing the water/binder ratio (W/B) when super-plasticizers are used, and by addition of water soluble polymers which can form stable colloidal aqueous emulsions; thus, the pores are filled with polymers and the latter have a plasticizing effect which allows lowering of W/B ratio.

Polymer-modified concrete cements are obtained if, during preparation, a macro-molecular component is added; thereby turning them into a type of concrete with modified properties in comparison to common concretes [2-4]. The **cement** is the predominant component of the complex binder system of cement - organic polymer. **The organic binder**, in small amounts, helps to improve the adhesion between cement stone and aggregate and also between the cement particles [1]. The polymer-modified concrete cements have significantly improved mechanical properties, such as the tensile and bending strength and are more compact, as well as more chemically stable [5-13].

The specialty literature [1, 6] mentions the vinyl poly-acetate, hydroxymethyl-propyl cellulose, polyacrylamide and the epoxy resin as being the polymers used for obtaining cement concrete types. The polymer may account for up to 20% of the complex binder. When choosing the inorganic binder-polymer system attention must be paid to the degree of compatibility between the components, by correlating their properties and the way in which they influence each other during hardening.

For example, the viscosity of the polymer dispersions influences the diffusion processes taking place during the hydration – hydrolysis of the Portland or aluminous cement [1]. In the case of epoxy resins, the presence of a basic environment resulting from hydration – hydrolysis can ensure the monomer cross-binding, thus rendering unnecessary the use of a special hardening component (amines) and thereby simplifying the concrete processing technology. Moreover, using the epoxy resin – cement mixture, the maximal mechanical properties obtained for the polymer/cement ratio are significantly lower than when a binder is added: approximately 0.1 as compared to 0.5 [14].

In this paper the experimental research, performed on organic polymer-modified cement concrete, obtained with river siliceous aggregates mixed with epoxy resin and silica fume are presented. Thus, the dosage effects of resin with / without hardener and silica fume respectively are analyzed, on the physical-mechanical properties of the polymer cement concrete obtained. The effect of calcium ions from the cement on the reinforce resin has been shown through the extraction tests of the epoxy resin from concrete.

RESULTS AND DISCUSSION

Experimental results

The obtained results, following the physical and mechanical tests, are presented in tables 1 to 3.

Assessment of results

Compression strength

Figure 1 shows the variation of the compression strengths for concrete types B1, BH1, BH2 and B3 depending on the introduced amount of modified concrete B3, against to the concrete B1, with the resulting values.

An increase of the compression strength values was noted following the improvement of the blank concrete composition if during the process an amount of modified concrete B3 was added; this was placed starting with the basic layer of cubic test specimens, in the amount of 33.33% (for BH1 concrete), 66.66% (for BH2 concrete) and 100% (for B3 concrete) respectively.

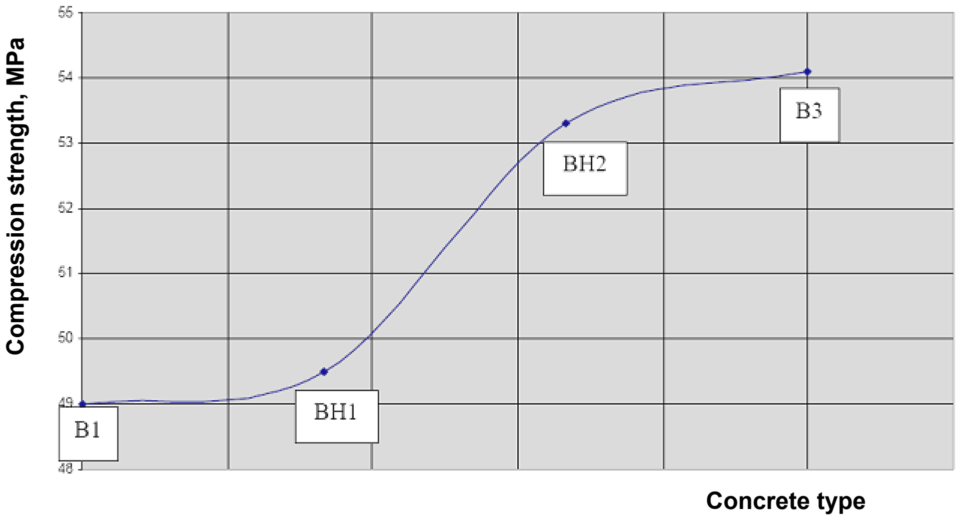

Figure 1. Variation of the compression strengths for concrete types B1, BH1, BH2 and B3 depending by the amount of SF, resin and hardener in the mixture; B1 – blank concrete; BH1 – concrete with 33.33% mixture corresponding to B3, in the cube basis layer, and 66.67% blank concrete B1; BH2 – concrete with 66.66% mixture corresponding to B3 in the cube basis layer, and 33.34% blank concrete B1; B3 – concrete with resin, hardener and ultrafine silica (100%).

Table 1. The concretes compression strength at 28 days

Type of concrete	f_c (MPa)
Blank concrete (B1)	49.0
Concrete with resin and hardener (B2)	48.8
Concrete with resin, hardener and SF (B3)	54.1
Concrete with resin (B2')	35.6
Concrete with resin and SF (B3')	36.7
Concrete with 1/3 resin, hardener and SF (BH1)	49.5
Concrete with 2/3 resin, hardener and SF (BH2)	53.3

It can be noted in table 1 that B2 modified concrete does not differ, as value, from the point of view of the compression strength from the concrete B1. Concrete types B2' and B3' do not reach the compression strength values of the blank concrete, as they are used in significantly smaller amounts, because the presence of the resin without hardener hinder carrying on the polycondensation-crystallization phase of the cement hydrocompounds; this phase completes the resistance structure of the concrete [15].

Flexural tensile strength

Figure 2 shows the variation of the flexural tensile strength values for concrete types B1, BH1, BH2 and B3, depending on the amount of modified concrete, in comparison to the blank concrete B1, with the resulting values.

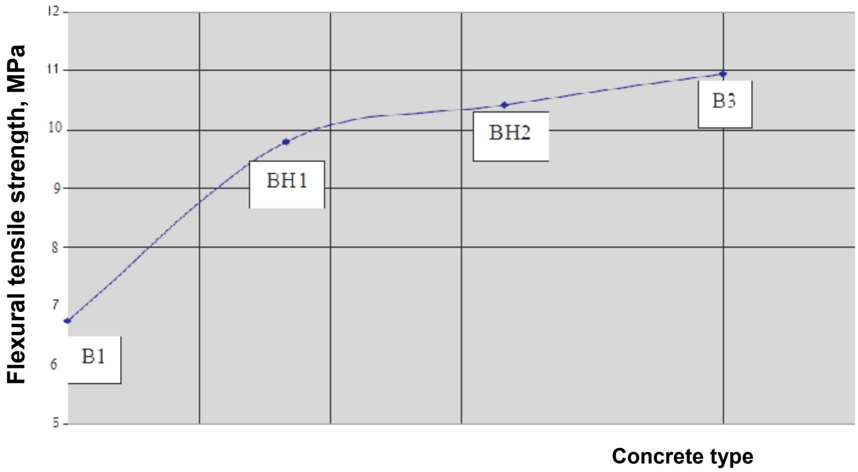

Figure 2. Variation of the flexural tensile strength values for concrete types B1, BH1, BH2 and B3 depending by the amount of SF, resin and hardener in the mixture; B1 – blank concrete; BH1 – concrete with 33.33s% mixture corresponding to B3, in the stretch load layer, and 66.67% blank concrete B1; BH2 – concrete with 66.66% mixture corresponding to B3 in the stretch load layer, and 33.34% blank concrete B1; B3 – concrete with resin, hardener and ultrafine silica (100%).

The flexural tensile strength tests also resulted in an enhancement of concrete values if the blank concrete was improved by adding the corresponding mixture of concrete composition B3, placed starting with the basic layer (the layer submitted to the tensile strength) of prismatic samples, in amounts of 33.34% (BH1), 66.67% (BH2) and 100% (B3) respectively.

Table 2. The concretes flexural tensile strength at 28 days

Type of concrete	$f_{tî}$ (MPa)
Blank concrete (B1)	6.75
Concrete with resin and hardener (B2)	8.55
Concrete with resin, hardener and SF (B3)	10.95
Concrete with resin (B2')	6.98
Concrete with resin and SF (B3')	7.65
Concrete with 1/3 resin, hardener and SF (BH1)	9.79
Concrete with 2/3 resin, hardener and SF (BH2)	10.41

It can be noted, in table 2 that all the other systems under focus, having a polymer-modified structure, account for an obvious enhancement of the flexural tensile strength values in comparison with the blank cement (including the concrete types improved only by adding resin, without hardener).

It is important to underline that all these polymer-modified concrete types showed a ductile break under stress, unlike the blank concrete which became brittle.

Tables 1 and 2 also account for the decisive role played by the SF in modifying the physical and mechanical properties of concrete types under focus, a fact which is also proven by the higher values of the mechanical strengths of concrete types having SF in their composition, in comparison to those which do not (the concrete with resin without hardener with lesser compression strength make exception).

Table 2 also shows the role of the epoxy resin on the flexural tensile strength values, but also the fact that, even if the resin is added without a hardener, it favours a slight increase of the flexural tensile strength of the resin-modified concrete. The resulting concrete types are ductile, unlike the blank concrete, evidenced also in the reference [4].

The importance of the mineral adding (SF) and of the organic polymer (epoxy resin) is therefore confirmed, both of them having a significant role in enhancing the mechanical strength values.

This can be explained by the fact that the mixture of the inorganic binder with the polymer emulsion determines two concurring effects resulting in a higher density of the system: a dispersion effect of the inorganic binder particles – with the advantage of a more uniform texture – and a lubricating effect which allows for reducing the distance between solid particles to a minimum, thus favouring rapid coagulation. All these effects have a positive influence on the strength structure.

The hardening structure is processed along several stages [14, 16] as follows:

- immediately after mixing the components, the non-hydrated cement particles, the polymer and aggregate particles are surrounded by water and small air bubbles formed during mixing. In the first stage of the interaction process, gelling water particles are formed. At the same time, the polymer particles migrate towards the cement grains and set on them;

- in a more advanced stage, these processes develop and high density, continuous layers of polymer are set on the surface of solid particles (cement covered with water components, or aggregate particles). Finally a continuous binding matrix is formed by water components covered with polymer membranes, which include the remaining non-hydrated cement grains, aggregate particles and small air bubbles. The organic continuous binder matrix influences the nucleation and crystal forming processes, but also their morphology.

The tests focusing on polymer extraction from the hardened polymer - cement matrix showed that the polymer sets on the surface of an anhydride grain or on a cement-hydrated grain, through a series of chemical bonds, with the Ca^{2+} ions. The amount of extracted polymer was significantly smaller than the initially introduced amount (with 22%, mass percent, as follows: from 100 g of binder matrix with 3 g of polymer initial content, has been extracted, in used solvent, 2.34 g of polymer) which shows that part of the polymer was set on insoluble components, as a result of chain reticulation through bivalent Ca^{2+} basic ions. It can be deduced that the presence of Ca^{2+} basic ions determines polymer reticulation, as confirmed by test results presented by other authors [17].

Due to the fact that the polymer binds the calcium ions from the surface of anhydrous or hydrated cement grains, a continuous binding matrix that tightly links these particles is formed; as a result the mechanic strength values are enhanced.

Apart from these chemical interactions, the presence of polymers in the inorganic binder-water system also leads to significant physical effects.

Physical interaction is emphasized by the surface active character of the polymer, resulting from HO^- clusters' adsorption on the surface of anhydrous or hydrated particles, thereby modifying the pace of physical and chemical processes taking place in the system, such as the hydration of anhydrous particles or changes undergone by hydrous components. The presence of adsorbed layers on the particle surface changes the conditions for the formation of new components; it also influences the contact between newly formed layers and their structure [15].

In case of systems with a high interaction rate (with a high content of C_3A) where strong internal stresses usually take place, the presence of polymers reduces such negative phenomena; due to its elastic properties the polymer absorbs the internal structure stresses and partially leisure the process, with the help of sub-microscopic contacts formed between the hydrous component particles. The lubricating and dispersion processes favour the primary close congealing, thus enhancing mechanical strengths [17, 18].

Avulsion test

The criterion for assessing the level of adherence of the binding matrix to the reinforcement is given by the result of avulsion tests performed on the concrete-embedded rods.

For the concrete types used in the experiment the resulting strength values are presented in table 3.

Table 3. The forces values after applying the avulsion load and break-up characteristic of concrete

Type of concrete	Force F, (daN)	Break-up characteristics
Blank concrete (B1)	4100	Bar breaks
Concrete with resin and hardener (B2)	4000	Concrete fails
Concrete with resin, hardener and SF (B3)	4300	Bar breaks
Concrete with resin (B2’)	3400	Concrete fails (easy slip)
Concrete with resin and SF (B3’)	3700	Concrete fails

A higher value of force can be noted for the avulsion test performed on concrete with SF, resin and hardener but, the same like in blank concrete case, the metallic rod embedded was broken. A high value of the force was obtained for the concrete type modified with an amount of resin and hardener; in this case the concrete broken.

When preparing the concrete, the use of resin (combined or not with SF) does not increase the avulsion force. It can be noted the decisive role, in concrete preparation, of the hardener with epoxy resin in their structural strength development.

CONCLUSIONS

The present paper points out the role of SF and of the organic polymer (epoxy resin with a binder) in the hardening of the concrete types under focus, through an enhancement of mechanical strength values. The continuous binder matrix made by the hydrocompounds, covered with polymer membranes which include the un-hydrated cement remains, the aggregate particles and the bubbles, influence the nucleation process and crystal growth so that, positively influencing the hardening [15].Thus, a densification of the system takes place due to the two combined effects: an effect of dispersion involving the inorganic binder particles, leading to the formation of a more uniform texture, and a lubrication effect allowing the convergence of solid particles to a minimum distance, thus favouring close range coagulation; both effects have a positive influence on the formation of a strong structure.

By including the organic polymer in the binding matrix structure of the concrete the number of structural macro-flaws decreases and the adherence coefficient of the binding matrix-aggregate increases, thereby offering a potential explanation for strength enhancement [1]. At the same time, the organic polymer, through the above-mentioned effects, can improve the viability of these concrete types, making them safer in various aggressive environments; concrete types with a ductile behaviour during breaking are obtained and evidenced during the mechanical strengths.

Through the original methods of concrete moulding (combining, in various ratio, a standard concrete with an improved composition concrete – set on the stretched side of the hardened mixture, between the two concretes, during their tensile strength) have been obtained better results of its mechanical strengths.

The strengths enhancement in case of the concrete types obtained with a complex binder type: cement-polymer or cement-polymer-SF, against to the blank concrete, corroborated with the reduced energy consumption during compaction (due to the use of fluidizing additives) result in an enhanced concrete viability and construction lifespan, important technical and economic advantages.

The high performance concrete types obtained through experiments can be improved in view of producing high durability concrete (specific for road concretes). They can also be used for bridges, with the following advantages:

- increased bridge span; by using high strength concrete an electro-chemical cell, thereby enlarging the central opening of the bridge and allowing for more passage space under the bridge;
- a reduced number of beams for a given span;
- beams could be lower, thus permitting a higher opening;
- the use of SF determines a lowering of the heat produced during cement hydration, thus reducing the risk of cracks.

EXPERIMENTAL SECTION

Materials and reagents

The organic polymer-modified concrete components are: the mineral binder, the organic binder (polymer), the mixing water, the aggregates and, in certain cases, the additions.

The used mineral binder is cement CEM I 52.5 (Carpatcement) having the physical and chemical characteristics presented in table 4, while the polymer is an epoxy resin (Policolor S.A. Bucharest) with next characteristics: the molecular weight M = 370, the dynamic viscosity, at 25^0C, 10 Pa·s, the epoxy equivalent of 0.51 equiv./100 g and 15% max volatile substances. The used hardener, 30% by the resin, is polyamidoamine type.

Table 4. Physical and chemical characteristics of cement CEM I 52.5

CEM I 52.5	*Chemical composition* (%)										
	CaO	SiO_2	SO_3	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	R_{ins}^x	LOI^{xx}	Free CaO
	63.72	20.13	3.09	4.49	3.28	2.35	0.30	0.91	0.20	2.11	0.90
	Mineralogical composition (%)										
	C_3S			C_2S			C_3A			C_4AF	
	67.18			11.768			6.355			9.97	
	Physical characteristics										
	Specific surface (cm^2/g)			*Stability* (mm)			*Setting time* (minutes)				
							initial			final	
	4198			0.0			165			230	
	Mechanical characteristics										
	Compression strength at 2 days (MPa)						*Compresion strength at 28 days* (MPa)				
	36.8						57.8				

x) *insoluble residuum*; xx) *loss on ignition*

The existing research and data in the field have suggested the potentially decisive role of hydraulically active additions (silica fume-SF) and macro-molecular components on the hardening behaviour, as well as on the properties of cements processed with these complex systems. Starting from this premise, the research results for various types of concrete are synthetically presented in table 5.

The utilized aggregates, in the concretes preparation, are river siliceous aggregates with continuous granularity (0-16 mm) and the required amount is also presented in table 5. The granularity limit in which were chosen the granularity curves are presented in table 6.

Table 5. Types of concrete taken into account

Characteristic \ *Concrete notation*	B1	B2	B3	B2'	B3'
Class	C 50/60	C 50/60	C 50/60	C 50/60	C 50/60
Consistency	T2	T2	T2	T2	T2
Cement type	CEM I 52.5	CEM I 52.5	CEM I 52.5	CEM I 52.5	CEM I 52.5
Aggregate type and, quantity (kg) for 1m^3 concrete	(0-16) 1730.8	(0-16) 1606.9	(0-16) 1545.56	(0-16) 1606.9	(0-16) 1545.56
Water/ cement ratio	0.4	0.4	0.4	0.4	0.4
Water quantity (L) for 1m^3 concrete	185	185	185	185	185
Cement quantity (kg) for 1m^3 concrete	462.5	462.5	462.5	462.5	462.5
Resin quantity (kg) for 1m^3 concrete	-	48.6	48.6	69.4	69.4
Hardener quantity (kg) for 1m^3 concrete	-	20.8	20.8	-	-
SF quantity (kg) for 1m^3 concrete	-	-	46.2	-	46.2

Table 6. Limit of granulate areas for aggregates (0-16) and the granularity used

Sieve diameter (mm)		0.5	1	2	4	8	16
Passages (%)	*Min.*	8	12	21	36	60	100
	Max.	20	32	42	56	76	100
	Used	18	25	33	45	70	100

Table 7 shows the chemical composition of the used addition: the silica fume (SF).

Table 7. Chemical characteristics of SF

Component	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	MnO	LOI	*Reactive silica*
U.M. (%)	84.1	8.0	0.8	1.0	0.8	-	-	-	3.9	82.37

The amount of aggregates on various types needed for each type of resulting concrete is presented in table 8.

Table 8. Amount of aggregate sorts for each type of concrete

Sort	B1 (kg)	B2 (kg)	B3 (kg)	B2' (kg)	B3' (kg)
(0-1)	432.7	401.8	386.67	401.8	386.67
(1-2)	138.5	128.5	123.33	128.5	123.33
(2-4)	207.7	192.8	185.56	192.8	185.56
(4-8)	432.7	401.8	386.67	401.8	386.67
(8-16)	519.2	482	463.33	482	463.33

The used reinforcement on avulsion test of concrete reinforcement is PC 52 concrete-steel with 12 mm diameter.

Experimental methods

Experimental studies was performed on the above mentioned systems, with reference to the behaviour of the complex binder-water system, as well as to its ability to develop strong hardening structures which can be verified by determining their strength. In order to achieve the proposed objectives, when concretes were prepared the macro-molecular component accounted for 15% (gravimetric percentage) of the cement amount and the SF addition was 10% (gravimetric percentage) toward the cement amount. The water/ cement ratio (W/B) for all types of the obtained cement remained constant and equal to 0.4; the vibration compaction was the procedure used in this case. The experiments have been carried out on the concrete types presented in table 5.

To highlight the influence of the polymer on the stretched part of the samples, used to tensile strength, two other concrete specimens, marked BH1 and BH2 were also prepared by combining BH3 concrete with B1 concrete, in the following proportions:

- 1/3 of the concrete amount required to fill a mould (prism or cube), to be poured at the mould basis, is represented by B3 and the rest being B1;
- 2/3 of the concrete amount required to fill a mould (prism or cube), to be poured at the mould basis, is represented by B3 and the rest being B1.

The levels of compression strength were determined on cubes with a 15 cm side, while the flexural and tensile strength levels on prisms of a 10x10x55 cm size, by applying a concentrated force in the middle of the prism opening being used.

Five of the resulting concrete types (B1, B2, B3, B2' and B3') – cubes with a 15 cm side – were submitted to a reinforcement avulsion test, using a 12 mm diameter embedded rod mounted during casting (on the principle of the chemical anchor).

In order to check the polymer setting, using Ca^{2+} ions, a number of tests were aimed at extracting the polymer from the hardened cement and polymer matrix. For this purpose, the composite cement stone was broken into small pieces and placed in organic solvents (toluene, ethanol) in which the polymer itself was soluble. After drying, the test pointed out the mass loss of the sample immersed in organic solvents.

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