Structure Formation and Properties of Composite Building Materials Modified by Organic Additives of Bicomponent Composition

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STRUCTURE FORMATION AND PROPERTIES OF COMPOSITE BUILDING MATERIALS MODIFIED BY ORGANIC ADDITIVES OF BICOMPONENT COMPOSITION

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Abstract. Numerous results of domestic and foreign studies show the effectiveness of complex chemical additives of various functional purposes use for improving the technological and construction-technical properties of cement concrete and cement-cement compositions. The development of bicomponent composition organomineral plasticizing additives with hardening activators provides an extension of effective modifiers range and concrete compositions with enhanced desired properties improvement. The article actualizes the questions of modifying water-soluble organic additives of a bicomponent composition using technical feasibility in the technology of composite building materials and examines the material science and technological aspects of the structure directional formation and properties to obtain cement-containing compositions.

1 Introduction

The use of modern methodological approaches in the study of hydration and hardening processes of modified cement systems makes it possible to control these processes at all stages of composite building materials structural formation and to obtain materials with desired properties. One of the most effective ways to intensify the technology of composite building materials, increase operational properties, reduce cost is to use a complex of chemical additives that allow to regulate structure formation directionally and create highly functional concretes with indicators of manufacturability, strength and durability [1-5].

Technological process management is based on a multilevel analysis of a hardening binder matrix of composite materials (nano-, micro-, meso- and macrolevels) and the study of mutual relations in the logical chain “composition-structure-property-functional ability”. The study of relationships is determined by materials science and technology aspects with the release of controlled parameters that can be predicted, experimentally determined and adjusted in the production process by changing in the right direction.

According to the classification criterion, modern cements are polymer-mineral binders containing, in addition to clinker minerals, gypsum and mineral additives.

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The development of physical and chemical principles and mechanisms for controlling the structure formation of cement matrices as complexly organized material systems determines the establishment of qualitative relationships of acid-base interactions at the phase boundary. Almost all inorganic solids and many organic ones by their chemical nature may be classified as solid acids and bases. The surfaces of many of them may have amphoteric properties. It was experimentally shown that the surfaces of portland cement clinker minerals: silicon oxide SiO_2, aluminum silicate $Al_2O_3 \cdot mSiO_2$, calcium carbonate $CaCO_3$ have these properties.

Polymerizable surface-active substances (surfactants) are used to improve the technological properties of cement compositions, concrete performance indicators, have high surface activity, as well as certain specific properties of hydrophilic-hydrophobic interaction at the phase boundary.

The expansion of chemical additives range - modifiers of plasticizing, structuring action, hardening regulators, complex with the effect of multifunctional action is due to the tasks within the framework of the modern paradigm of methodological aspects of materials science and concrete technology development.

Modern ideas about the processes of cement hydration indicate the need of taking the spatial factor when creating organic additives for cement systems into account, especially in light of the multifaceted nature of its manifestation. The significance of the structural and spatial parameters of the molecules of organic additives is often considered discretely, either as a factor of a plasticizing additive [6–9] or as a factor in the distortion of hydration processes [10–13]. In the light of modern ideas, an organic additive is effective only if its role in hydration processes is reduced. If the plasticization mechanisms are relatively clear and simply controllable, the multifactorial nature of hydration processes is the most difficult aspect of creating a plasticizing additive, where little attention is still paid to the structural and spatial factor of the structure of the organic modifier molecule.

The analysis of the idea of the organic plasticizer additives action mechanism on cement systems aims at studying the effect of the bicomponent composition of the modifier on the nature of hydration processes of cement systems providing the effect of regulating the rheological properties at the initial stages of cement stone hardening and participation in the formation of its structure depending on the functional structure molecules of organic additives.

Modification can be carried out both in the process of resin synthesis, and by combining with various hydroxyl-containing compounds, polyhydric phenols, amines, aldehydes. In this case, it seems possible to widely vary the composition and properties of the obtained oligomers [14,15]

The multifunctional additive - acetone-formaldehyde resin ACF-75 - is the target product of chemical production (2228-006-48090685-2002 Specification with amendment 1), obtained by condensation of acetone and formaldehyde in an alkaline medium, it is low toxic, difficult to burn, can be stored without changing the composition and properties until 2 years and is intended as an effective additive for multifunctional purposes, combining the properties of plasticization, air entrainment and acceleration of concrete hardening.

2 Methods

At the initial stage of the study the tasks of analyzing the chemical additives in hardening systems use effectiveness based on Portland cement and substantiating the composition of the bicomponent composition consisting of ACF and urea-formaldehyde resin (Standard specifications for ACF resin 14231-88) were solved.

The introduction of UFR into the composition of the ACF resin leads to a smooth increase in viscosity over time, compared with the initial acetone-formaldehyde resin, which is explained by the formation of intermediate products due to the available reactive groups in both the ACF resin and UFR [16].

The use of binary compositions from ACF and UFR resins allows to control more efficiently the curing process in both alkaline and acidic media, as well as improving the physicomechanical properties of the resulting bicomponent binder, in contrast to the use of a single-component composition. During the curing of the mixture in the presence of alkali, the mechanism of aldol and croton condensation is observed, which is typical for the curing of ACP resins; upon curing with acid hardeners, bridging –CH_2– and –CH_2 – O – CH_2– ether bonds are formed, which leads to crosslinking of the oligomers of the resins as a result of the interaction amino groups of PCF with methylol groups of ACF resins and methylol groups of UFR and ACF resins.

It was established [16, 17] that interpolymer complexes (Fig. 1) are formed in a mixture of UFR and ACF resins (UACF) due to the interaction of chemically and structurally complementary macromolecules (Fig. 1), contributing to the stability of the curing of polymer compositions and the possibility of their shelf life increasing.

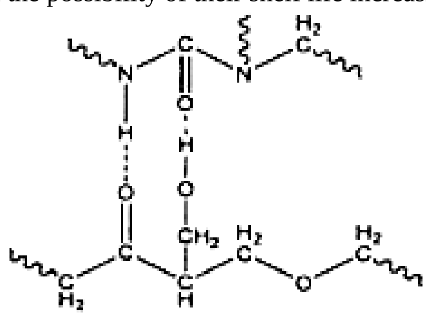

Fig. 1. The structure of the interpolymer UACF complex

3 Results and Discussion

The method of IR spectroscopy was applied to ACF, UFR resin and their mixture (1:1 mass.h). The IR spectra of ACF, UFR and their mixtures are presented in the figures (Fig. 2-4).

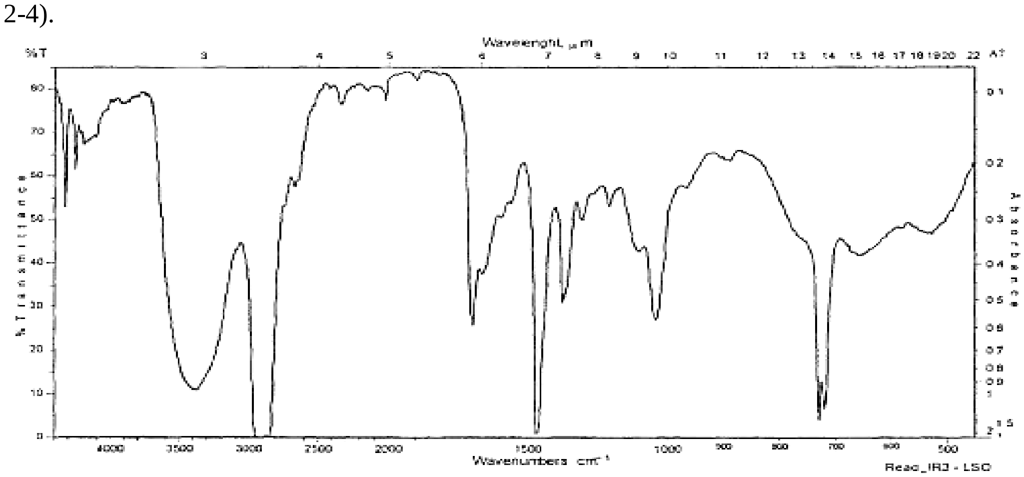

Fig. 2. IR spectroscopy of ACF resin

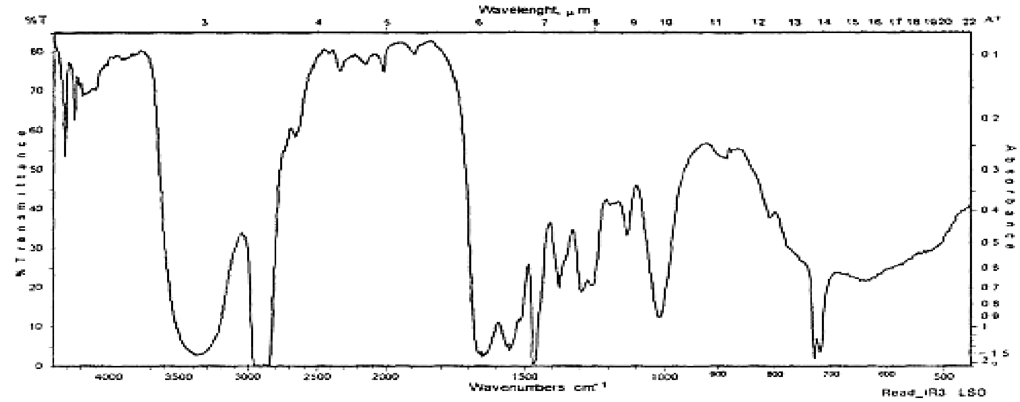

Fig. 3. IR spectroscopy of UFR

In the IR spectrum of the binary PACP composition a characteristic absorption band is observed in the area of 3000-3600 cm-1, that indicates the formation of an interpolymer complex of ACF with UFR with the participation of newly formed intermolecular hydrogen bonds.

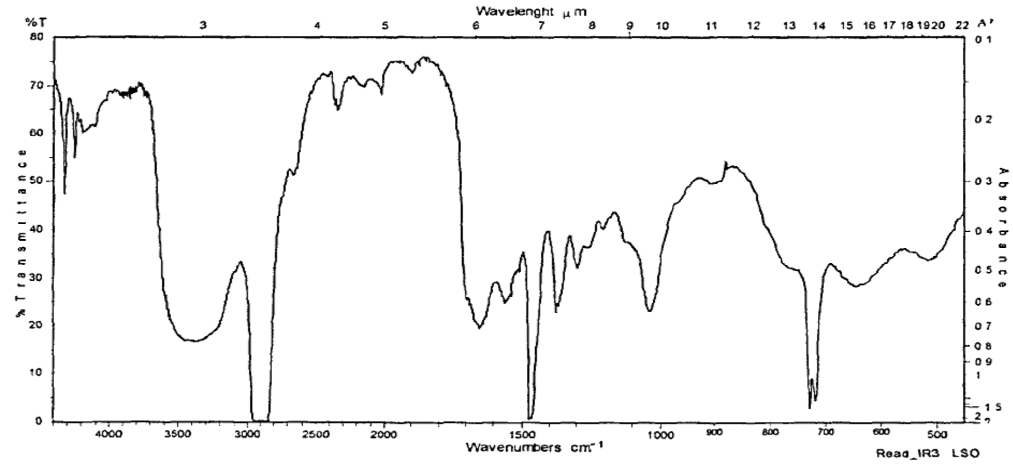

Fig. 4. IR spectroscopy of ACF and UFR resins mixture

Interpretation of the characteristic absorption bands of the IR spectra of ACP, UFR and UACF is presented in Table 1, where there is the appearance of new intermolecular hydrogen bonds.

Table 1. Analysis of the IR spectra of ACF, UFR and UACF

ACF		UFR		UACF		Interaction mechanism model
ν, см$^{-1}$	I, %	ν, см$^{-1}$	I, %	ν, см$^{-1}$	I, %	
				3446	83	**NH**...**OC** intermolecular **OH**...**OC** intermolecular
3388	89	3358	97	3366	83	**OH**
1698	75			1700 (плечо)	75	**— C —** ‖ **O**
1664	62	1650	97	1652	80	**C = C**
		1556	95	1558	75	**— CO — NH —, —NH**
1038	73	1016	87	1038	77	**C—O** in **C—O—C**

The binary UACP composition regardless of the type of curing catalyst has a reduced brittleness, that is mainly explained by the curing of one of the resins, while the other is distributed inside the resulting polymer network, which reduces the crosslink density and the samples retain an elastic-plastic state.

An experimental evaluation of the bicomponent UACF modifier was carried out in the manufacture of reinforced concrete structures with concrete class B30 on Portland cement Type I (GU) 32.5, which meets the requirements [18,19]. In this work, the calculation of concrete composition using a complex binary additive UACF, ACF and hardening accelerator Na_2SO_4 - technical sodium sulfate (Standard specifications for Na_2SO_4 6318-77) was based on the regression dependences of the amount of additives on the properties of the concrete mixture influence (table 2).

Table 2. Properties of cement concrete with a modifying additive

Concrete class in compression	Concrete composition kg/m^3					Conditions	Workability, mm	Concrete requirement
	cement	sand	stone	water	ACF add			
Heavy concrete: 1. B 30 PC Type I(GU) 32.5 (without add.)	470	650	1208	260	-	nat. cond.	10-40	F-100; W2; Stiff plastic
2. B30 PC 400 (with ACF + Na_2SO_4)	435	625	1260	235	0,65	nat. cond.	50-75	F-150; W4; Stiff plastic
3. B30 PC Type I(GU) 32.5 (with ACF + UFR 70/30%)	435	625	1260	235	0,65	nat. cond.	80-110	F-200; W4; Plastic

4 Conclusions

The results of an experimental assessment of concrete mixtures technological properties indicate a sufficiently high manufacturability of a bicomponent additive. Evaluation of workability indicates an improvement in this indicator.

The main criteria in assessing the effectiveness of modified concrete use and their competitiveness should be considered: improving product quality, including durability; cost reduction; saving energy and raw materials. The analysis was carried out on the basis of calculations data on of the factory planned costing of products:

1) increasing the mobility of the concrete mixture reduces the cost and time for molding when using UACF additives (15 ... 20%);

2) the duration of the preparation of concrete mix is reduced by 1.2 ... 1.5 times;

3) achieved a reduction in binder consumption by 7-8%;

4) overhead costs are reduced to 7%;

5) the service life of vibration equipment and devices is increased by 1.2 ... 1.3 times due to improved vibration formability of concrete mixtures;

6) prerequisites for increasing the durability of structures are created.

Thus, the possibility of controlling the technological characteristics of cement compositions due to the good water-reducing ability of the bicomponent polymer composition is shown. The experience of using water-soluble polymer additives in the technology of building materials, as well as an analysis of their structure-forming role, makes it possible to ascertain the real possibility of controlling technological processes for producing perfect composite building materials with multifunctional organic additives.

References

1. I.N. Akhverdov, *Teoreticheskie osnovy betonovedeniya*. – M.: Vysshaya shkola, (1991)
2. Yu.M. Bazhenov, *Tekhnologiya betona* (Moscow, ACB, 2007)
3. V.V. Babkov, Fiziko-mekhanicheskie aspekty optimizatsii struktury tsementnykh betonov. Avtoreferat diss. dokt. tekhn. nauk. (Leningrad, 1990)
4. Yu.G. Ivashchenko, Strukturoobrazovanie, svoystva i tekhnologiya modifitsirovannykh furanovykh kompozitov. Avtoreferat diss. dokt. tekhn. nauk, (Saratov, 1998)
5. Gay M. Admixtures for High Performance Concrete. Proc. of Intern. Cong. «Durability of High Performance Concrete». (Freiburg, 2004)
6. A.A. Slyusar', Reologicheskie svoystva i agregativnaya ustoychivost' vodnykh mineral'nykh suspenziy s modifikatorami na osnove oksifenolfurfurol'nykh oligomerov: dis. …d-r. tekh.nauk.: 02.00.11. (Belgorod, 2009)
7. N.A. Shapovalov, V.A. Lomachenko, A.A. Slyusar', Vliyanie stroeniya oligomerov na plastifitsiruyushchuyu sposobnost' // Novye tekhnologicheskie resheniya i ekonomicheskie problemy v proizvodstve betonov, drugikh materialov i izdeliy: sb. tr. (Belgorod, Bel-GTASM, 1996)
8. E.A. Shoshin, Yu.G. Ivashchenko, N.N. Vologina, Plastifitsiruyushchaya sposobnost' organicheskikh soedineniy v zavisimosti ot ikh stroeniya // Sovremennye problemy stroitel'nogo materialovedeniya: materialy VIII-kh akademicheskikh chteniy RAASN, (Ivanovo, 2003)
9. V.R. Falikman, M.G. Bulgakova, A.I.Voak, L.A. Savidova, Zavisimost' svoystv betona s superplastifikatorom S-3 ot stepeni polikondensatsii polimetilenpolinaftalinsul'fonatov // Betony s effektivnymi modifitsiruyushchimi dobavkami: sbor.nauch.tr. [pod red. F.M. Ivanova, V.G. Batrakova]. (M.,NIIZhB Gosstroya SSSR, 1985)
10. Batrakov V.G. *Modifitsirovannye betony. Teoriya i praktika*. Izd. 2-e. – (M.,1998)

11. V.S. Ramachandran, R.F. Fel'dman, M.Kollepardi, *Dobavki v beton: Spravochnoe posobie*. (M.: Stroyizdat, 1998)
12. F.L. Glekel', *Fiziko-khimicheskie osnovy primeneniya dobavok k mineral'nym vyazhushchim*. (Tashkent, Izd-vo «Fan», 1974)
13. Yu.S. Cherkinskiy, *Polimertsementnyy beton. Novye stroitel'nye materialy*. (M., Gosstroyizdat, 1960)
14. Yu.G. Ivashchenko, R.T. Mameshov, K.K. Mukhambetkaliev, Glinosoderzhashchie stroitel'nye kompozity na osnove khimicheski aktivirovannogo syr'ya i organicheskikh svyazuyushchikh // Vestnik Dagestanskogo gosudarstvennogo tekhnicheskogo universiteta. Tekhnicheskie nauki. – 2018. t. 45. – № **3**. pp. 185-193.
15. N.I. Borodkina, E.A. Vakhtangova i dr. Poluchenie, primenenie i modifitsirovanie atsetonformal'degidnykh smol // Plasticheskie massy. – 1971. – №**4**. – pp. 16-17.
16. A.K. Sakhapova, Atsetono- i karbamidoformal'degidnye smoly v kachestve tamponazhnykh materialov dlya remontno-izolyatsionnykh rabot v skvazhinakh: avtoreferat dis. kand. tekhn. nauk: 05.17.06. (Kazanskiy gosudarstvennyy tekhnologicheskiy universitet, Kazan', 2006)
17. O.N. Kuznetsova, V.P. Arkhireev, Napravlennoe regulirovanie svoystv termoreaktivnykh smol i materialov na ikh osnove // Vestnik Kazanskogo gosudarstvennogo tekhnologicheskogo universiteta. – 2008. №**5**. – S 90-94.
18. ASTM C150-07 : Standard Specification for Portland Cement.
19. EN 197-1 : Composition, specifications and conformity for common cements