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COMPARATIVE EFFECTIVENESS OF POLYCARBOXYLATE SUPERPLASTICIZERS ON CEMENT-SAND PASTE USING BELARUSIAN-MADE CEMENTS

ABSTRACT

Polycarboxylate superplasticizers based on methacrylic acid and methoxylated polyethylene glycol with a molecular weight of 1000 were synthesized by the method of co-administration of monomers in the mixture. The suitability of using the resulting mixture of monomers for the synthesis of polycarboxylates, by the method of radical polymerization, is shown. The influence of the obtaine superplasticizers on the spreadability of cement-sand paste based on cement of 3 Belarusian manufacturers (OJSC «Krasnoselskstroymaterialy»–OJSC «Belarusian Cement Plant»–OJSC «Krichevcementnoshifer») was ivestigated. It was found that the effectiveness of plasticizing additives based on polycarboxylates depends significantly on their molecular weight and tricalcium aluminate content in cement. It has been established that for cement with a lower content of tricalcium aluminate C_3A, the greatest efficiency is achieved for samples with medium mean sizes of macromolecules providing an optimal ratio of the rate of adsorption to the content in the aqueous phase. For cement with a high C_3A content, a low molecular weight sample, which is adsorbed in the C_3A phase, is more effective. Testing the properties of chemical additives was carried out at the Department of Chemical Technology of binders Belarusian State Technological University. The effectiveness of the plasticizing action of *the synthesized samples of these chemical additives was carried out on a cement-sand mixture in the ratio of 1 to 3, using for this purpose the cement grade CEM I 42.5N.*

Keywords: tricalcium aluminate, molecular weight, methacrylic acid, copolymer, spreadability, intrinsic viscosity.

INTRODUCTION

The consumption of cement per capita in Belarus is about 475 kg. By this indicator, Belarus is ahead of most of the neighboring countries The choice of the most effective modeling supplement will allow, in addition to an increase in the specific cement surface of the Blain from 300–320 m^2/kg to 350–400 m^2/kg, to reduce the real cement consumption in prefabricated concrete production plants from 350 kg per 1 m^3 of concrete to the average European level of 180 kg Cement for 1 m^3 [1].

Currently, three state enterprises are engaged in cement production in Belarus: OJSC«Krasnoselskstroymaterialy»–OJSC «Belarusian Cement Plant»–OJSC «Krichevcementnoshifer». Despite the fact that these eterprises were modernized at the same time, they have different raw materials base and, accordingly, different mineralogical composition of cements. To assess the effectiveness of synthesized polycarboxylates, a comparative analysis of the spreadability of the cement cement-sand paste using cement of these three manufacturers was made [1].

At the present stage, the methods of synthesis of additives modifying the rheological properties of mineral suspensions are developing very intensively [2–4]. One of the most widely used examples of such additives are copolymers based on acrylic and methacrylic acid, modified with polyethylene glycols, PCE polycarboxylates. Despite the fact that such additives are already widely used in the construction industry, there are some of moments limiting their use, before all their sensitivity to the mineralogical composition of cement. The solution to this problem may be a further modification of the polymers based of acrylic monomers [4–6], as well as in the case of a particular applied problem, the synthesis of polycarboxylate suits to cement of a specific manufacturer, which this work is devoted.

1. EXPERIMENTAL

All superplasticizers were synthesized by radical copolymerization of blend methacrylic acid and methoxy terminated poly(ethylene oxide) methacrylate. Methacrylic acid (MAA) as well as the initiator sodium persulfate was obtained from the Evonic company. The methoxy terminated poly(ethylene oxide) were supplied by Zavod sintanolov LLC NORCHEM (Russian Federation). Hydroquinone, p-toluenesulfonic acid necessary for synthesis poly(ethylene oxide) methacrylate and sodium persulfate was obtained from Aldrich.

1.1. Cement

Cement SEM I 42.5N cement containing 97% clinker and 3% gypsum produced by these cement plants of Belarus was used for the preparation of cement-sand mortars. All quality indicators of cement complied with the standard EN197–1. The sand corresponded to GOST 8736–2014. The content of the grains passing through the sieve 014 in the sand did not exceed 10%. The amount of clay and dusty fractions is not more than 3%. To shut the cement-sand mortar, water was used in accordance with GOST 23732–79 «Water for concretes and mortars».

The exact mineralogical composition of cements is not given due to the ban on disclosure of this information by factories by producers.

1.2. Definition of spreadability

The spreading of the cement-sand mixture was determined with the help of a cylinder placed on a horizontal sheet of glass. After filling with a solution, the cylinder is sharply raised. At the same time, a circle of cement-sand mortar forms on the glass. The spreading value was estimated from the diameter of a circle measured in two directions. For each type of plasticizer, 3 experiments were performed, according to which the mean value was calculated.

1.3. Synthesis of PCEs

To study the spreadability of the cement-sand paste, samples of polycarboxylate superplasticizers of various molecular weights based on methacrylic acid (MA) and metoxypolyethylene glycol (MPEG1000) by radical polymerization were synthesized. The preparation of this product involves several steps: synthesis of methacrylic acid ester and methoxypolyethylene glycol (MAMPEG1000); neutralization of methacrylic acid to obtain sodium methacrylate; Radical copolymerization of a certain amount of sodium methacrylate and methacrylic acid ester with MPEG. In this paper, a method is proposed for using for the synthesis of PBEs a mixture of monomers MA MAMPEG1000 obtained by the esterification reaction of MA. This method makes it possible to shift the equilibrium of the MA esterification reaction, and also to somewhat simplify the scheme for the synthesis of polycarboxylate (Figure 1).

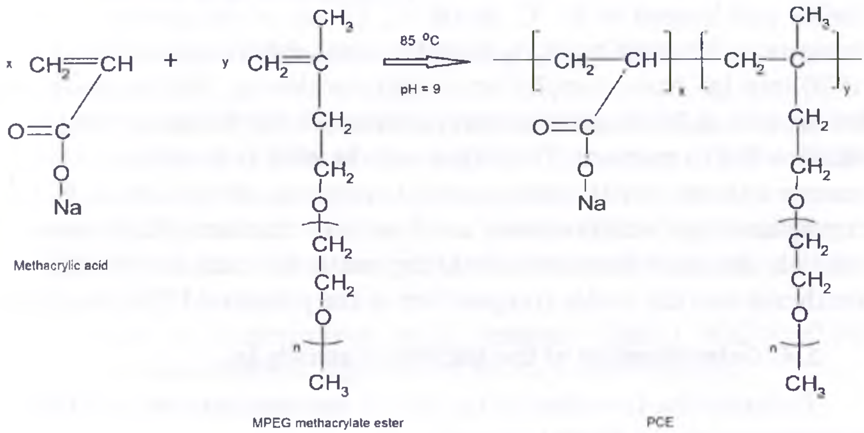

Figure 1. Synthesis of the polycarboxylates

In the first stage of the synthesis, MA was esterified with methoxylated polyethylene glycol with a molecular weight of 1000 (MPEG 1000), for this 500-mL five-neck round-bottom flask was charged with 100 g methacrylic acid, 166 g MPEG 1000, 1 g Hydroquinone and 2.7 g p-toluenesulfonic acid. After completion of all components dosing, stirring continued for 3 hour min at 150 °C. The water evolved during the esterification was condensed with a reflux condenser and collected in a Dean-Stark nozzle. In the initial mixture, the ratio of MA to MAMPEG1000 was 7: 1.The resulting product was a dark brown liquid consisting of a mixture of MA and MAMPEG1000 in a ratio of 6 to 1.

The preparation of PCE followed the general reaction scheme exhibited in Fig.1. In a typical synthesis, a 500-mL five-neck round-bottom flask was charged with 90 mL of distilled (DI) water, stirred at 200 rpm, and purged with nitrogen for 20 min. The required quantity of monomer mixture was preliminarily neutralized with the equimolar amount of solid NaOH. After NaOH had been dissolved mixture were charged into the flask. During the addition of all raw materials (Table 2), nitrogen purging was continued and a total of 187.5 mL of DI water was used in small portions to rinse the containers holding the monomers and thus ensuring complete transfer into the reaction flask. The mixture was adjusted to a pH of 9.7 using a 30 wt.% aqueous NaOH and heated to 65 °C. At 65 °C, 15 mL of an aqueous solution containing 2.5 g of $Na_2S_2O_8$ initiator was added over a total period of 30 min by. After completion of initiator dosing, stirring continued for 30 min at 70 °C and for another hour at 90 °C before the liquids were cooled to ambient. The PCE solutions were yellowish or brownish viscous solutions with solids contents between 30 and 35 wt.%. The superplasticizer solution was used without further purification. In Table 1, the exact amounts of starting materials used for the different syntheses and the molar composition of the prepared PCEs are shown.

1.4. Determination of the intrinsic viscosity [η].

To determine the effect of the size of macromolecules, synthesized 5 samples with a different viscosity.

Table 1

Raw materials and quantities used in the synthesis

Copolymer	Molar ratio MA and a MAMPEG1000	Amounts of raw materials			[η]
		MA+ MAMPEG1000	$Na_2S_2O_8$	H_2O	
PCE1	6:1	50	0.5	100	0.91
PCE2	6:1	50	1	100	0.40
PCE3	6:1	50	1.5	100	0.27
PCE4	6:1	50	2	100	0.21
PCE5	6:1	50	3	100	0.12

A 0.3 g/dl copolymer solution was prepared in a 3M aqueous NaCl solution. Determination of the outflow time of the copolymer solution was carried out in a Ostwald capillary viscometer with a capillary diameter of 0.56 mm at a temperature of 25 °C. 10 ml of the copolymer solution were poured into the viscosimeter extension, thermostatted for at least 10 minutes at this temperature, and the time for the solution to flow out through the capillary was determined by stopping the time of passage of the solution between the marks of the viscometer.

2. RESULTS AND DISCUSSION

Determination of the plasticizing effect of additives on a cement-sand paste.

Investigation of the plasticizing properties of additives was carried out at a dosage of 0.45% of the mass of the cement. CEM I 42.5N cements of the above-mentioned cement plants of Belarus were used for research. The cement-sand mixture had the following composition: cement 50 g, sand 150 g, water 43 g. The results of the tests are presented in Tables 2–4.

A series of experiments with cement CEM I 42,5N OJSC «Krichevcementnoshifer». The results are shown in Table 2.

Table 2

Spreadability of cement-sand paste on cement CEM I 42,5N OJSC «Krichevcementnoshifer». C_3A (tricalcium aluminate content) = 4.5%

Sample	Intrinsic viscosity [η]	Spread, mm
Without PCE	–	50
PCE1	0,91	94
PCE2	0,4	115
PCE3	0,27	127
PCE4	0,21	114
PCE5	0,12	103

From the data presented in Table 2 it follows that the dependence of the spreadability of the cement paste on the size of the macromolecule of the polycarboxylate obtained has an extreme dependence. This is probably due to the relatively low molecular weight polycarboxylate providing a less steric repulsion, and the high molecular weight sample has a high affinity not only to the C_3S but also to the C_3A phase, as a result of adsorption its content in the aqueous phase is small [7]. The obtained data correlate with studies using separate fractions of one synthesized polycarboxylate [8]. Optimum spreading of the cement paste provided a PCE3 sample with an intrinsic viscosity of 0.27.

The results of the cement-sand paste spreading using cement of the similar brand produced by JSC «Belarusian Cement Plant» showed a similar result: a slightly smaller amount of aluminate tricalcium in this cement was manifested in an increase in the swinging for almost all. The samples for optimal PCE3 were 132 mm.

A series of experiments with cement CEM I 42,5N OJSC «Belarusian Cement Plant». The results are shown in Table 3.

Table 3

Spreadability of cement-sand paste on cement CEM I 42.5N OJSC «Belarusian Cement Plant». C_3A (tricalcium aluminate content) = 4.0%

Sample	Intrinsic viscosity [η]	Spread, mm
Without PCE	-	50
PCE1	0,91	118
PCE2	0,4	123
PCE3	0,27	132
PCE4	0,21	120
PCE5	0,12	104

Cement of OJSC «Krasnoselskstroimaterialy» production has the same brand as used early cements however tricalcium aluminate content in it is much higher and is 8.1%. A series of experiments with cement CEM I 42,5N OJSC «Krasnoselskstroimaterialy». The results are shown in Table 3.

Table 4

Spreadability of a cement-sand paste on CEM I cement 42.5N OJSC «Krasnoselskstroimaterialy». C_3A (tricalcium aluminate content) = 8.1%

Sample	Intrinsic viscosity[η]	Spread, mm
Without PCE	–	50
PCE1	0,91	85
PCE2	0,4	94
PCE3	0,27	104
PCE4	0,21	103
PCE5	0,12	107

In the case of cement with a high content of tricalcium aluminate, the addition of PCE5 with the lowest molecular weight proved to be the best, because of the relatively lower adsorption capacity, which allowed these macromolecules to be available in the aqueous phase for dispersing the cement grains.

Polycarboxylates with higher molecular weight have strong adsorption on the mineral particles. Similar results concerning molecular weight were reported by other authors for PC and other type of superplasticizers such as sulfonated acetone-formaldehyde condensate and lignosulfonates. Consequently, if a high proportion of PCs is adsorbed and consumed by C_3A, there could be less admixture available in aqueous phase for dispersing the cement grains by adsorption onto their surface [9].

CONCLUSIONS

1. The methoxylated methacrylic acid derivative was synthesized, with a 7 fold excess of acid, in order to shift the equilibrium of the esterification reaction towards the products, as well as to prepare a mixture for the subsequent polymerization of methacrylic acid and its ether in a ratio of 6:1.
2. The suitability of using the resulting mixture of monomers for the synthesis of polycarboxylates, by the method of radical polymerization, is shown. To determine the influence of the size

of macromolecules, 5 samples were obtained, with a viscosity ranging from 0.12 to 0.91.

3. The effect of macromolecule size on the plasticizing ability of additives for cement-sand paste on the basis of cement of 3 Belarusian plants was determined. It has been established that for cement with a lower content of tricalcium aluminate C_3A (4.0–4.2%), the greatest efficiency is achieved for samples with medium mean sizes of macromolecules $[\eta] = 0.27$ providing an optimal ratio of the rate of adsorption to the content in the aqueous phase. For cement with a high C_3A content (8.5%), a low molecular weight sample $[\eta] = 0.12$, which is adsorbed in the C_3A phase, is more effective.

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