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Polymeric plasticizers for gypsum-free cement

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Abstract

The influence of water solutions of polyvinyl alcohol, a copolymer of acrylamide/*N*-methylol-acrylamide, and six water-borne polymer dispersions made from vinyl acetate and acrylic comonomers on the hardening of cement paste and on chemical resistance of the obtained concert samples was investigated. The cement paste was obtained by mixing of pure, gypsum-free ground clinker with water, and lower or higher amount of plasticizer. The coils of water-soluble polymers or the particles of dispersions covered only from 7% to 17% of the surface of the cement particles. The plasticizers increased compressive strength by 17% at an age of 28 days and by 23% after treatment by aggressive solutions for 6 months.

Keywords: Cement; Polymers; Plasticizers

1. Introduction

Plasticizers for cement are organic water-soluble compounds such as lignosulfonates, sulfonated melamine, or naphthalene condensates with formaldehyde [1]. The influence on the properties of concert samples, made from gypsum-free cement and several water-soluble polymers and nitrogen-containing epoxy oligomer, is described in [2]. For example 3% of plasticizer B (mixture of tercopolymer acrylamide–methylmethacrylate–vnilsulphonate with oligomer based on phenol and nine units long chain obtained from ethylene oxide) increased the compressive strength of the samples with 106%; the value for plasticizer C (epoxy oligomer based on dihydroxydimethylolethylene urea) is 28%. The plasticizers increased the initial and final time of set. Water-borne dispersions are obtained from hydrophilic group containing monomers [3], and its different particle size dimensions and distribution [4] give a possibility to calculate the extent of cement surface coverage by the polymers. The aim of this research is to compare the influence of two water-soluble polymers and six water-borne dispersions on cement paste properties and on the compressive strength of 3-, 7-, 14-, and 28-day-old samples or samples stored for 6 months in an aggressive solutions and to relate these properties to the chemical structures of the compounds as well as the possibility of their particles to cover the surface of the cement particles.

2. Experimental

The clinker was made in the cement plant Devnja, Bulgaria. It was with mineralogical composition, W%: C_3S—41.8; C_2S—29.6; C_4AF—18.5; C_3A—3.2; saturation coefficient 0.84. The specific surface of its particles determined by the method of Blaine was 2900 cm^2/g. The cement pastes were made by automatic mixing for 5 min of pure ground clinker with solutions or mixtures water-plasticizers. The water content was 25.5% in all cement pastes. The normal consistency and the flow ability of the obtained cement pastes were determined according to Ref. [4]. The plasticizers used were as follows:

No. 1. Water solution of medium viscosity 88% hydrolyzed polyvinyl alcohol (Hoechst, Germany),
No. 2. Water solution of copolymer acryl amide/*N*-methylol acryl amide, 96:4 g/g laboratory made sample,
No. 3. Water-borne dispersion of polyvinyl acetate (DOW Chemicals, USA),

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No. 4. Water-borne dispersion of polyvinyl acetate, made with 7% protective colloid polyvinyl alcohol and surfactants (DAL, Bulgaria),
No. 5. Water-borne dispersion of copolymer vinyl acetate/vinyl ester of verstatic acid/acrylic acid (70:30:0.5) g/g, (DAL, Bulgaria),
No. 6. Water-borne dispersion of copolymer vinyl acetate/acryl amide, 96:4 g/g, laboratory made sample,
No. 7. Water-borne dispersion of copolymer vinyl acetate/*N*-methylol acryl amide, 96:4 g/g, laboratory made sample,
No. 8. Water-borne dispersion of copolymer methyl methacrylate/butyl acrylate/acrylic acid (74:76:2) g/g, laboratory made sample.

The viscosimetric molecular weights averages of water soluble polymers were calculated according method, as described in Ref. [5], and using the data for relative viscosity η_{rel} of their solutions with concentration from 0.1 to 1 g/100 cm^3, obtained by Ostwald viscosimeter at 293 K and pH 7. The values of the constants in Mark–Houwink equation K and α were published in Ref. [6]. From the data for relative viscosity, obtained at 293 K and pH 11–12, the curves $\ln(\eta_{rel})$ versus C were made and the values of C_{cr} were calculated [7]. The particle size of the dispersions was measured using a Philips 400 electron microscope. The maximal flow ability (d, mm) of the cement paste was measured on a standard shaking table. The compressive strength for different time of set of the concrete samples (20:20:20 mm) and after 6 months treatment with aggressive solutions was measured according to Ref. [8]. The aggressive solution was made from 200 g NaCl, 17 g $MgCl_2$, 9 g $CaSO_4$, and 1000 ml distilled water. The treatment was made at room temperature.

3. Results and discussion

The plasticizers, described in [1,2], contained $-OH$, $-SO_3H$, $-CONH_2$, $-OCOCH_3$, and other hydrophilic groups. In this investigation, a comparison is made between two water solutions of the polymer with $-OH$, $-CONH_2$, and $-CO-NHCH_2OH$ groups and several water-borne dispersions consisting hydrophilic groups. The influence of the plasticizers on the maximum flow ability (d, mm) of the cement paste and on the compressive strength of the concrete samples for different ages and after a 6-month treatment with an aggressive solution is presented in Table 1.

Table 1
Influence of the plasticizers

Plasticizers		d (mm)	Compressive strength (mPa) after days of set and treatment				
No.	%		3	7	14	28	6 months treatment
–	–	78.7	35.7	50.2	73.5	74.8	58.75
1	0.05	95.5	25.8	54.0	58.2	82.5	63.25
2	0.10	66.9	29.0	59.0	58.0	72.8	–
3	0.10	82.5	43.3	63.8	76.3	84.3	–
4	0.05	85.5	37.0	53.4	84.2	86.7	55.5
5	0.10	104.2	40.3	65.3	79.3	72.5	57.5
6	0.05	101.6	31.0	57.3	61.8	84.6	61.0
7	0.05	101.25	35.2	57.6	76.6	87.2	72.25
8	0.10	103.05	27.6	62.5	81.8	85.2	–

Table 2
Influence of the type of plasticizer on S and S_P

Plasticizer	Surface	
	S (cm$^2 \times 10^{-4}$)	S_p (%)
No. 3 DOW Latex	2.1	7.24
No. 4 Polyvinyl acetate	4.23	14.59
No. 7 Poly(vinyl acetate/acryl amide)	4.74	16.34
No. 8 Poly(methyl methacrylate/butyl acrylate/acrylic acid)	4.93	17

The most active plasticizer is No. 7 water-borne dispersion, obtained in the presence of protective colloid polyvinyl alcohol and surfactants. The active groups in this plasticizer are $-OH$, $-OCOCH_3$, and $-CONH_2$.

The solution of polyvinyl alcohol (plasticizer No. 1) is better than plasticizer No. 2. The possibility of the $-OH$ groups to form hydrogen bonds is higher than the $-CONH_2$ groups in plasticizer No. 2. In the IR spectrum of polyvinyl alcohol has two absorbencies for H-bond formation: at 360 and 185 cm^{-1}. The hydrogen bonds in polymer solutions increased its values of refractive index increment. The values of the refractive index increment of the water solution of polyvinyl alcohol is 0.170 and of polyacrylamide is 0.163 [9]. The dates confirm the different hydrogen bonds formation in these polymer solutions. The H-bond formation determined the shape of polymer coils. The dimensions of end-to-end distance in the polymer coils were calculated by the equation published in Ref. [6]:

$$(h^2)^{1/2} = 2.84 \times 10^{-8}(M_{vis}/C_{cr})^{1/3},$$

where M_{vis} is the viscosimetric molecular weight average, Daltons, C_{cr} is the critical concentration, g/100 cm^3.The values of $(h^2)^{1/2}$ for the solution of polyvinyl alcohol is 2.34×10^{-6} cm and for copolymer acryl amide/*N*-methylol acryl amide is 1.79×10^{-6} cm. With the equation $D_{equ} = 1.08(M_{vis}[\eta])^{1/3}$ published in Ref. [10], where D_{equ} is diameter of the coils and $[\eta]$ is the viscosity number, calculated was the surface S (cm^3) covered with monolayer of polymer coils. These calculations were made by several assumptions: monolayer adsorption; 100% adsorption of polymer; spherical particles; no change in polymer coil dimensions upon adsorption; and any agglomeration of particles of water-borne dispersions. On the base of the surface of cement particles, $S_o = 290{,}000$ cm^2/100 g were obtained the part S_p, covered with polymer monolayer, $S_p(\%) = S/S_o \times 100$: 12% for polyvinyl alcohol and 7.9% for copolymer acryl amide/*N*-methylol acryl amide. It is evident that the increasing of H-bond formation, end-to-end distance $(h^2)^{1/2}$, coil diameter D_{equ}, and surface covered with polymer monolayer S_p lead to bigger values of maximal flow ability d (mm) of the cement paste and of compressive strength (mPa) of the concrete samples (Table 1). On the basis of electronic microscopy data, the dimensions of particles of water-borne dispersions, their size, and distribution by size were determined. The particles have spherical shape. Their surface in monolayer S (cm^2) and the parts of cement particles S_p covered with polymer were calculated (Table 2).

It is evident that only a part of the surface of the cement particles can be covered by monolayer of polymer particles. The surface energy of the peaks and edges of cement particles is higher and maybe the polymer particles covered them and limit water transport.

The plasticizer increased the compressive strength of the obtained concrete samples and their stability against an aggressive solution. The most stable are the concrete samples, which were obtained by plasticizer No. 7. The surfaces S_p are biggest for plasticizers Nos. 7 and 8, but the first consists most polar groups.

The results show that it is possible to calculate the concrete surface covered by particles or molecules of polymers and to compare the activity of the plasticizers by these values.

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