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INVESTIGATION OF THE INFLUENCE OF SOME PLASTICIZERS OF GYPSUM - FREE CEMENT PASTE

C. Bojadjieva and I. Glavchev
Higher Institute of Chemical Technology
Sofia, Bulgaria

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ABSTRACT

The influence of three types of plasticizers on the hardening of gypsum-free cement pastes has been investigated. Cement pastes have been obtained by mixing pure ground clinker with water and plasticizers. The plasticizers were water soluble tercopolymer, mixture of tercopolymer and surface active oligomer and epoxy resin. A small amount of these compounds decreased the normal consistency by 24% and increased the time of set and the compressive strength of the samples in 28 days.

Introduction

The plasticizers are organic water soluble compounds: lignosulphonates, oxycarbonates, saccharoses, condensated aromatic sulphoderivates, sulphonated melamineformaldehyde oligomers (1). These compounds have polar groups, which determine the solubility in water and the absorption of the compounds. We have no information about application of oligomers with epoxy groups or about tercopolymers with different polar groups in their molecules. If there are two or three kinds of polar groups in the macromolecules, the possibility for adsorption of these compounds would be greater. That is the reason why in our experiments we have worked with a new water-soluble epoxy resin, synthesized by the method described in (2), and with tercopolymer or mixture of this copolymer by oligomer.

Usually the plasticizers have been applied in Portland cement pastes and concretes. There is information concerning the application of plasticizers in gypsum-free Portland cements also (3), but only in the presence of alkaline carbonates, bicarbonates or hydroxides like hardening accelerators. The specific surface of the clinker must be from 6000 to 10000 cm^2/g. It would be more effective if the specific surface of the clinker is smaller - about 3000 cm^2/g - and if there are only organic plasticizers in the mixtures (without any accelerators).

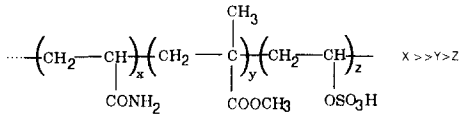
This possibility has been investigated in the work of our team.

Experimental

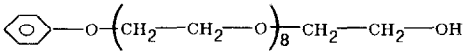
The clinker made in the cement plant "Devnya" was with mineralogical composition, W%: C_3S - 41.8; C_2S - 29.6; C_4AF - 18.5; C_3A - 3.2 and with characteristics: saturation coefficient 0.84, silica ratio

$M_s = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} = 1.89$; alumina ratio $M_A = \frac{Al_2O_3}{Fe_2O_3} = 0.84$. The specific surface derminated by the method of Blaine was 3200 cm^2/g. The optimum in the normal consistency was a decrease of 45%. Normal consistency was measured by the method, described in Bulgarian state standard 72-86. 300 g cement was mixed 5 min. with the water. The cement paste was put in the ring with dimensions: h=40±0,5 mm. d_1= 65±0,5 mm; d_2=75±0,5 mm. The consistency of the cement paste was a normal one, if the plunger of Vicat stopped 5-7 mm from the bottom of the ring. The time of set of the paste of pure clinker was so short that it was impossible to be determined. The plasticizers used in these investigations were:

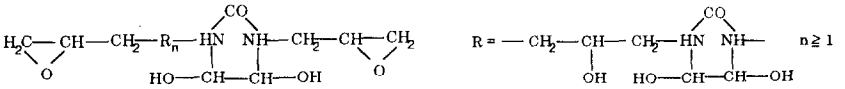
A - tercopolymer of acrylamide methylmethacrylate and vinylsulphonate with molecular weight about 60000;



B - mixture of plasticizer A with oligomer based on phenol and 9 units long chain obtained from ethylene oxide with molecular weight 500;



C - epoxy oligomer based on dihydroxydimethylolethylene urea with molecular weight 600.



Several kinds of cement pastes were made:

1. - mixture of clinker with 5% gypsum;
2. - mixtures of clinker with 0.5 - 3 W% of plasticizer A;
3. - mixtures of clinker, gypsum 5% and 0.5 - 3 W% of plasticizer A;
4. - mixtures of clinker and 0.2 - 3 W% of plasticizer B;
5. - mixtures of clinker, 3 W% plasticizer B and 2.5 - 15 W% $CaCO_3$;
6. - mixtures of clinker and 0.25 - 8 W% of plasticizer C;

The normal consistency, initial set and final set of all these mixtures and the compressive strength of the samples of the mixtures were determined. A method of application of optical system was used to determine the angle of wetting. A drop of water solution of each plasticizer was put on the polished surface of a piece of clinker and the angle was determinated.

Results and Discussion

A survey of different plasticizers for gypsum-free Portland cements was presented in (4). These compounds consist of polar groups: -SO_3H and -OH in lignosulphonates; -CH_2OH and -NH- in urea formaldehyde oligomers; -SO_3H and -CH_2OH in the compounds obtained from naphthalenesulphonate-SO_3H and -CH_2OH in sulphonated phenolformaldehyde oligomer. In the synthesized for this investigation copolymers there are three polar groups: -$CONH_2$, -$COOCH_3$ and -SO_3H. The ratio of these groups may change by the concentration of the monomers in the polymerization mixture. The molecular weights of this copolymer and of all other compounds may be decreased or increased in accordance with the condition of polymerization.

Plasticizer A had little influence on the normal consistency and time of set was little.

The plasticizer B is more effective: the decrease of the normal consistency was 25% in the presence of 1% of these compounds. The influence of the concentration of the plasticizer B on time of set is given in Fig. 1: the optimal concentration is 0.5%.

There is information that it is possible to increase the influence of the plasticizers in the presence of fine-grained $CaCO_3$ (5). The results from the investigation of the system clinker-3% plasticizer B - $CaCO_3$ -H_2O are given in Fig. 2. The maximum of the curve indicates the complexity of the influence of $CaCO_3$. The pieces of insoluble $CaCO_3$ absorbed some amount of the plasticizers. This is the probable reason for the increase of time of set. If the amount of $CaCO_3$ rises, a reaction with C_3A resulting in formation of $3CaO.Al_2O_3.CaCO_3.11H_2O$ is possible. Also the time of set decreases.

The influence of plasticizer C is presented in Fig. 3. The normal consistency decreases 24% in gypsum-free Portland cement paste with 3.5% plasticizer. The probable reason for the smaller effect is the molecular weight of this compound - only 600.

The compressive strength of the samples made from several mixtures is given in Table 1. It is evident that the compressive strength of the sample made from mixtures with plasticizer B is about two times higher, and the results indicate that CaCO3 does not increase the influence of the plasticizers.

The difference in the compressive strength was confirmed by the experiments for determining the angle of wetting. It is well known that the angle of wetting determines the surface qualities and the adsorption of the solutions on solid materials. The results are presented in Table 2.

TABLE 1

N	Additive, %	Compressive strength, MPa			
		3 days	7 days	14 days	28 days
1.	Gypsum, 5%	14.6	23.6	24.6	26.5
2.	Plast. A, 0.5%	4.0	9.8	20.8	21.3
3.	Plast. B, 3%	3.3	5.8	24.0	54.5
4.	Plast. B 3%, 10% $CaCO_3$	0.8	0.8	23.0	33.8
5.	Plast. C, 7.5%	0.6	0.8	0.8	6.6

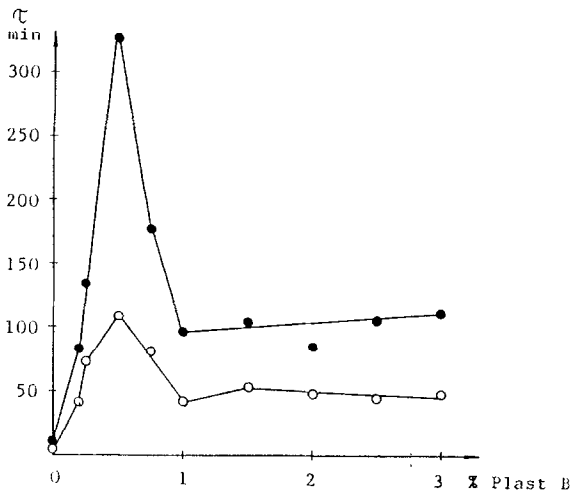


FIG. 1.
Influence of the quantity of the plasticizer B on time of set

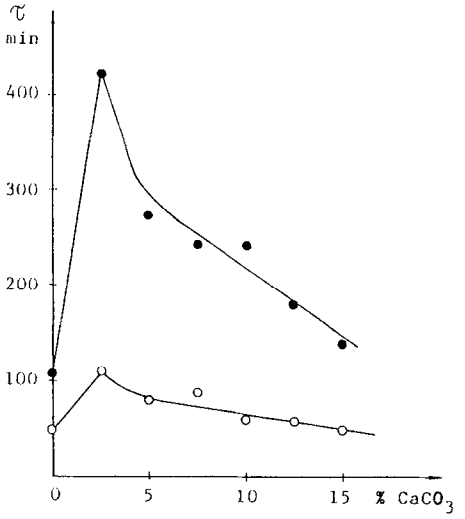


FIG. 2.
Influence of the quantity of $CaCO_3$ on the time of set (with 3% plasticizer B)

o - initial set; • - final set

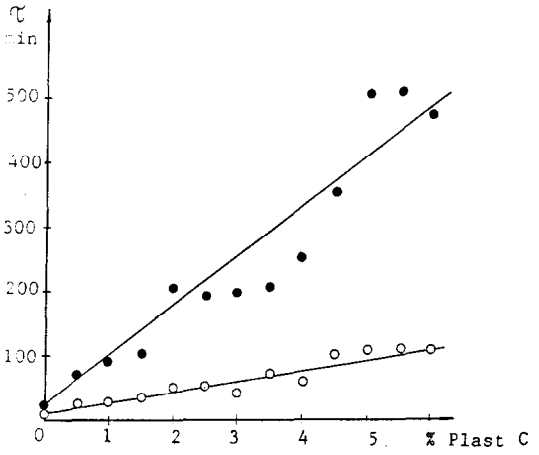


FIG. 3.
Influence of the quantity of plasticizer C on the time of set
o - initial set; • - final set

TABLE 2

N	System clinker-plasticizer	Angle of wetting, ^{o}
1.	A	30
2.	B	15
3.	C	60

If the results from Table 1 and 2 are compared it is obvious that the system with the smallest angle of wetting will be the one, whose samples have the highest compressive strength.

To sum up, we could recommend making gypsum-free Portland cement pastes only with plasticizer B. This way the addition of alkali carbonate would not be needed and the sufficient degree of grinding could be only 3000 cm^2/g.

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