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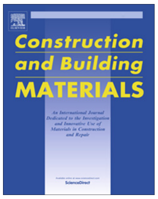

The properties of cement systems superplasticized with methacrylic ester-based polycarboxylates

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HIGHLIGHTS

- Metacrylic ester-based polycarboxylate superplasticizers were synthesized.
- SP action in cement suspensions were tested in terms of rheology.
- Shear-thickening was observed as a rheological behaviour.
- Cement system properties (strength, setting time, fluidity etc.) were determined.
- Copolymers of mPEGMA-co-MAA provided high performances to cement-based materials.

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ABSTRACT

Methacrylic ester-based polycarboxylate superplasticizers of methoxypolyethylene glycol metacrylate-co-methacrylic acid (mPEGMA-co-MAA) with various side-chain density and side-chain length were synthesized, characterized and their impacts on workability, rheology, setting time and mechanical strengths of cement systems were studied. The results showed that, synthesized copolymers change the rheological behaviour of cement suspensions to shear thickening and, SPs with low side chain densities increase fluidity, fluidity retention and strengths of samples higher than their counterparts. Additionally, polycarboxylates retard the hydration of cement and low triethanol-amine dosages can be preferred as an accelerator for cold weather applications or for early mechanical strengths of cement systems.

1. Introduction and objectives

Production of more flowable concrete and development of novel superplasticizers (SPs) which makes it possible are still being researched at the present time. Polycarboxylate (PC)-type superplasticizers began to be produced in the middle of 1980s [1] and their superb dispersion ability and stability in cement paste are the prominent factors for preference [2–4]. Subsequent to the adsorption of polycarboxylates onto cement surface, the flocculated cement particles are highly dispersed by dominantly steric effects. Besides, these polymers are also high-range water reducing admixtures (HRWRAs) providing a flowable mixture with less water amount that strengthens it mechanically.

Understanding the rheological behaviour of concrete is a requirement for mixing, transportation, pumping and moulding in construction site [5]. Besides, the rheological property is a key factor in automation and special material processing, such as 3-D printing with cement-based materials [6]. Depending on the physical and chemical factors like SP type and dosage, w/c ratio, cement type and property and substitution of mineral additives, cement paste behaves non-Newtonian rheologically [5,7–11]. Shear-thickening is a phenomenon in the flow of suspended solids. The concentrated suspensions of nonaggregating solid particles will always show shear-thickening and the actual nature of this behaviour comes from the parameters of the suspended phase, such as phase volume, particle size distribution, particle shape, as well as those of the suspended phase [12]. PC-type superplasticizers enhance shear thickening of cement paste and, many researches focused on this behaviour previously [5,7–9]. Shear-thickening is very important especially in operations carried out at high shear rates (pumping, mixing, etc.) and more energy is required for the flow of the material. For the protection of the system from breaking, this behaviour should be controlled effectively [11].

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Shear thickening is described in literature as "an increase in (apparent) viscosity with increasing shear rate" [13]. There are two different theories which explain shear thickening mechanism: 1) cluster theory, 2) grain inertia theory. The first theory includes the formation of so-called (hydro-) clusters, which are temporary groups of small particles [11,14–18]. These clusters start being formed from a certain shear stress on the critical shear stress. Flow-induced clusters results in an increased dissipation of energy and the viscosity of the system increases [11,18]. The second theory depends on grain inertia, where a part of the shearing force is transmitted through direct momentum transfer between solid particles. Depending on literature it was mentioned that, "grain inertia theory" is not the main cause of shear thickening in self-compacting concrete [11].

The studies of Bender and Wagner including optical dichroism measurements provided further information about the clustering hypothesis [19,20]. For suspensions exhibiting shear-thickening behaviour, two conditions must hold. Firstly, the volume fractions of solids in the suspension must be very high, secondly, the suspension must be nonflocculated. The last requirement consists that the particles be either neutral or repel one another by the effects of electrostatic, steric or entropic interactions [13,21]. Phan et al. mentioned that cement suspensions behave rheologically different due to the shear rate. At low shear rates shear thinning is observed, Newtonian behaviour follows the sequence and shear thickening is the main characteristic at high shear rates [22]. Also, polycarboxylic ether type HRWRA was pointed out as a significant factor on rheology, as the dosage increases viscosity of suspension decreases at a given shear rate. Zhang et al. studied with different types of SPs and showed that cement pastes prepared with PCEs obey shear-thickening [8]. In their study, Cyr et al. [7] also mentioned the same behaviour for superplasticized cement pastes.

Cement system is under the effects of Van der Waals attraction and hydrodynamic forces. High hydrodynamic forces between the spherical particles cause shear-thickening, these forces are more dominant than the repulsion forces (Brownian, electrostatic or steric) and made up clusters in the sheared region [11,23–25]. The dynamics of suspensions is explained by Stokes' law as a function of Peclet number (Pe). Feys et al. mentioned that Pe is a dimensionless shear rate and Brownian viscosity tends to decrease with the increment of Pe [11,15]. In the same study, Brownian viscosity was determined to increase with $Pe > 10^3$ and was shown that shear-thickening is a hydrodynamic phenomenon. One of the aim of this research is to evaluate the effects of PC-type SPs' molecular structure, SP dosage and w/c on rheological flow curves of cement pastes. Therefore, novel polycarboxylate SPs with different side-chain density and side-chain length were synthesized and, the shear-thickening behaviour of the superplasticized cement pastes were investigated with Herschel-Bulkley model. Besides, determining the fluidity and fluidity retention of pastes and understanding the additional effects of synthesized SPs on cement systems (like setting time, mechanical strength etc.) are the other aims of the study.

2. Experimental

2.1. Materials

Methacrylic acid-MAA (Aldrich) and methoxy polyethyleneglycol methacrylate-mPEGMA (Aldrich) were used in synthesis of superplasticizers. The chain transfer agent sodium allylsulfonate-SAS and the initiator ammonium persulfate-APS were obtained from Aldrich and Merck respectively. CEM I 42.5 R Portland cement (OPC) was used in the experiments, the properties of cement were defined in Table 1. Cement mortars were prepared with CEN Standard Sand [26], sand particle size distribution was shown in Table 2.

Table 1
The chemical and physical properties of Portland cement (CEM I 42.5 R).

Composition	wt.%	Physical properties
C_3S	61.34	Density (g/cm^3)
C_2S	10.66	3.14
C_3A	5.60	Blaine fineness (cm^2/g)
C_4AF	10.25	3480
SiO_2	20.26	Initial setting time (min.)
Al_2O_3	4.27	150
Fe_2O_3	3.37	Final setting time (min.)
CaO	63.05	195
MgO	1.53	
SO_3	3.01	
Na_2O	0.10	
K_2O	0.59	
Ignition loss	2.85	

2.2. Superplasticizer synthesis

The polymers were synthesized from macromonomer (mPEGMA- M_n: 500, 950 g/mol) and MAA through free-radical polymerization. The macromonomer and monomer were dissolved in distilled water, and chain tranfer agent SAS was added to the system. Then pH was set at 8 with NaOH solution. Under reflux at 75 °C, polymerization reaction was completed in 4 h with N_2 purging. All polymers can be used in cement without further purification. The chemical structure of synthesized polymers is shown in Fig. 1. Table 3 points out the molar compositions of synthesized polycarboxylates.

2.3. Characterization of SPs

Superplasticizers were characterized by means of FTIR and Gel Permeation Chromatography-GPC. The obtained samples from the synthesis of the PC-polymers contain fractions of polymer, oligomer and unreacted monomers. Therefore, polymers were precipitated from their solutions and washed with ethanol. The chemical structures of the dried polymers were characterized by a FTIR (Perkin Elmer Spectrum 400 FT-Mid IR ATR unit) instrument. Molecular weights of SPs were determined by using Ultrahydrogel 250 and 500 Columns made by Waters and a refractive index detector (Agilent 1260 Infinity). 0.15 M phosphate buffer (pH 7.2) was fed as an eluent at a flow rate of 0.7 mL/min. Polyethylene oxide and polyethylene glycol (average molecular weight: 1870–594,000) were used for calibration.

2.4. Test methods

2.4.1. The rheological behaviour of superplasticized cement paste

The rheological tests of cement pastes were achieved by Anton Paar MCR 52 rheometer equipped with Building Material Cell (BMC

Table 2
Particle size distribution of the CEN reference sand (1350 ± 5 g) according to TS EN 196-1.

Square mesh size (mm)	Cumulative sieve residue (%)	Result
2.00	0	0
1.60	7 ± 5	7.24
1.00	33 ± 5	32.53
0.50	67 ± 5	66.01
0.16	87 ± 5	86.45
0.08	99 ± 1	99.37
Moisture content%	<0.2	0.10