Effect of Some Water-Soluble Melamine Formaldehyde-Free Polycondensates on the Rheological Properties of Cement Pastes

Ismail Aiad

Egyptian Petroleum Research Institute, Nasr City 11727, Cairo, Egypt

Received 21 July 2003; accepted 10 March 2005
DOI 10.1002/app.22414
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Water-soluble melamine formaldehyde-free polycondensate products were prepared. The chemical structure of these polymers was confirmed with different spectroscopic techniques. The effects of these polymers on the rheological properties of the cement pastes were investigated. The rheological parameters (shear stress, yield stress, and plastic viscosity) were calculated with the Bingham model. The minislump of superplasticized cement pastes at different interval times (5, 30, 60, 90, and 120 min) was determined. The results showed that the new superplasticizers increased the fluidity and minislump of the cement pastes and reduced the minislump loss of the cement pastes not only at early ages (30 min) but also at later early ages (120 min). © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2212–2218, 2005

Key words: rheology; viscosity

INTRODUCTION

Nowadays concrete is being used for many purposes under different conditions, and ordinary concrete may fail to exhibit the required quality. In such cases, an admixture often is added to make it more suitable for any required application, instead of a special cement being used; it is possible to change some of the properties of the cement in hand by the use of suitable chemical admixtures.

Superplasticizers, like many other types of admixtures, are added to concrete to perform particular functions. Consequently, they are described according to their functional properties. Superplasticizers are classified as high-range water reducers to distinguish them from other categories of less effective chemical admixtures that initially served to reduce the water content of concrete. Superplasticizers have effective dispersing properties on the cement. The dispersing action increases the workability of concrete. The resulting concrete can be placed with little or no compaction, blending, and segregation. Superplasticizers have a distinct ability to give not only much workability to concrete but also a larger water reduction than that possible with normal plasticizers. Superplasticizers are chemical admixtures that can maintain an adequate workability of fresh concrete at a low water/cement ratio for a reasonable period of time without affecting the setting and hardening behavior of the other components of the system.

In chemical terms, superplasticizers are organic polyelectrolytes, which belong to the category of polymeric dispersants by analogy to other types of chemicals (e.g., silicate and phosphate solids in heterogeneous systems as pigments and resins).[1]

Concrete superplasticizers may be considered specialized dispersing admixtures. The term *polyelectrolyte* refers to a substance that contains polyions, which are macromolecules bearing a large number of ionizable groups. To preserve the electroneutrality of a polyelectrolyte substance, the polyion charges must be compensated by counterions, which are typically ions of low molecular weight such as H^+, Na^+, and Ca^{2+}. Polyelectrolytes are usually soluble in polar solvents, such as water; with respect to their protonation equilibrium in aqueous solutions, they can be classified as polyacids, as polybases, or, when both acidic and basic groups are present, as polyampholates.

The most famous superplasticizers are melamine formaldehyde sulfonate (MFS) and naphthalene formaldehyde sulfonate (NFS). Superplasticizers are the main ingredients in high-performance concrete (HPC), which is used in tall structures, bridges, and offshore structures.[2] Because of their industrial importance in concrete technology, the properties of superplasticizers as well as their actions in concrete have been continuously studied and explored,[3,4] and new types of superplasticizers are being evaluated or developed.[5] The most recent one is a polycarboxylate type.[6]

As things stand, there is no way of predicting the rheological behavior of a specific cement and super-

Correspondence to: I. Aiad (yiaiad@yahoo.co.uk).

TABLE I
Chemical Oxide Composition (wt %)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
21.05	5.45	3.42	63.41	2.09	2.39	0.18	0.09	1.90

LOI, loss of ignition.

plasticizer at low water/cement ratios simply from their specification sheets. Some initial rheological work with grouts and pastes is necessary. The rheological behavior of cement pastes as a function of the time and superplasticizer dosage provides relevant information on key properties, such as the slump and slump loss, which can be transferred to fresh concrete.[7]

The rheological or flow properties of concrete are important for the construction industry because concrete is usually put into place in its plastic form. The large body of literature existing on concrete rheology can attest to this importance.[8–11] Also, many factors such as ease of placement, consolidation, durability, and strength depend on the flow properties. Generally, the flow behavior of concrete approximates that of a Bingham fluid. Therefore, at least two parameters, the yield stress and plastic viscosity, are necessary to characterize the flow. It is known that the rheology of concrete is affected by the cement paste content, which contributes to reducing the gap between the aggregates. Also, superplasticizers play an important role in the flow behavior of concrete or cement pastes.

In this study, two new water-soluble melamine formaldehyde-free polycondensate superplasticizers were prepared, and their effect on the fluidity of cement pastes was evaluated in comparison with the traditional one.

EXPERIMENTAL

Materials

Cement

A freshly produced sample of ordinary Portland cement (OPC) was supplied by Helwan Portland Cement Co. (Cairo, Egypt). Table I shows the chemical composition of the OPC. The Blaine surface area was 3054 cm^2/g, and the cement phase composition was 50% C_3S, 23% C_2S, 8.6% C_3A, and 10.4% C_4AF for OPC.

Commercial superplasticizers

Melment L10 (Mt) is a commercial superplasticizer; its chemical composition is melamine formaldehyde sulfonate. It was supplied by Modern Building Materials Co. (Cairo, Egypt) as a white, solid material and was used as a 35% solution.

Prepared superplasticizers

Melamine formaldehyde-free sulfonate (MF-FS) and melamine urea formaldehyde-free sulfonate (MUF-FS) were prepared through the polycondensation of melamine or urea/melamine (0.5) with glyoxylic acid at pH 3–4 and 50–60°C; they underwent further condensation with sulfanilic acid at pH 5 and 50°C until their final viscosities of 5.5 and 2.5 cSt (20 wt % solution at 20°C), respectively. The pH of the reaction mixtures was adjusted to 10, and the reaction mixtures were cooled to 25°C. The solid concentrations were 40.5 and 38.5% for MF-FS and MUF-FS, respectively.

Analysis of the synthesized copolymer

Elemental analysis, Fourier transform infrared (FTIR), and differential scanning calorimetry (DSC) spectroscopic techniques were used to investigate the structures of the prepared samples of MF-FS and MUF-FS (Table II).

FTIR spectrophotometry

The structure of the synthesized superplasticizers was confirmed via FTIR (ATI Mattson) and FTIR spectrophotometry analysis.

DSC

The DSC analysis was performed at the Thermal Laboratory of the Building Research Center. The detector

TABLE II
Elemental Analysis of the MF-FS and MUF-FS Polymers

	C (%)		H (%)		N (%)		S (%)	
Polymer	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
MF-FS	31.70	28.80	2.03	4.69	25.85	20.49	4.55	4.81
MUF-FS	30.77	28.30	2.04	4.84	24.66	19.47	3.76	3.30

TABLE III
FTIR Characteristic Bands of the Prepared Polymers

	OH and NH^-	COO^-	S=O	C—N	S—O
MF-FS	3364.7	1603.1	1398.6	1034.2	702.9
MUF-FS	3388–3159	1615.1	1396.6	1032.8	701.8

type was a Shimadzu DSC-50; the rate was 5°C/min, the holder temperature was 400°C, and the holder time was 0 min.

Experimental techniques

Rheological measurements

Different mixes of superplasticizers and cement were prepared at a constant water/cement ratio (0.30). The superplasticizer dosage ranged from 0 to 1%. The mixes were stirred with a spatula (ca. 120 rpm) for 3 min, and this was followed by a 1-min rest and another one at the previous speed. Exactly 17 mL of this mix was transported to a Rheotest cell (Germany); the ratio of the radii of the measuring tube and measuring cylinder was 1.24. The test began exactly after 6.5 min from the contact of cement and water, including the stirring time. The shear rate ranged from 0.3 to 146 s^{-1}.

Minislump

As indicated by its name, this method consists of carrying out a slump test on a small amount of cement paste. The cement paste is poured into a stainless steel cone with the same geometry as Abram's cone for regular slump tests, but with reduced dimensions (60 mm high). The minicone is removed, and the diameter of the spread of the cement paste is measured.

RESULTS AND DISCUSSION

Confirmation of the prepared superplasticizers

FTIR spectra

According to the preparation methodology, the general process was the reaction of the aldehyde group of glyoxylic acid with NH_2 of the melamine or urea-forming methylol groups; the methylol groups were condensates with sodium sulfanilate. The FTIR spectra of the copolymers MF-FS and MUF-FS showed the characteristic bands illustrated in Table III.

DSC

DSC is a thermal analytical technique in which the difference in the amounts of heat absorbed by a polymer sample and a standard is measured by the power consumed as the temperature increases.

The prepared copolymer MF-FS showed different peaks: the first was the glass-transition temperature (T_g) at 82.29°C (−191.87 J/g), the second was crystal temperature (T_C) at 233.83°C (−8.11 J/g), and the third was the melting temperature (T_m) at 332.02°C, (−67.79 J/g). MUF-FS showed different peaks shifted to higher temperatures because of the presence of the urea molecule. The T_g peak was at 98.69°C (−318.11 J/g), the T_C peak was at 247.68°C, (18.82 J/g), and T_m was at 337.6°C (−84.14 J/g).

Rheological measurements

The flow curves of different OPC pastes admixed with different dosages of prepared and commercial superplasticizers were determined.

There are different models for the flow behavior of cement pastes. The more suitable one is the Bingham flow model [eq. (1)] or the Hershel–Bulkley flow model [yield power law; eq. (2)]; the suitability depends on different factors, such as the nature of the cement, the water/cement ratio, and the type and dosage of the superplasticizer:

$$\tau = \tau_0 + \mu\gamma \qquad (1)$$

$$\tau = \tau_0 + k\gamma^n \qquad (2)$$

where τ is the shear stress (Pa), τ_0 is the yield stress (Pa), μ and k are the plastic viscosity (Pa S), and γ is the shear rate (S^{-1}). The exponent n characterizes the behavior of the cement pastes: shear thinning for $n < 1$ and shear thickening for $n > 1$. In addition to these models, there are the relationships of the shear stress or apparent viscosity and the shear rate. In this study, the more suitable model was the Bingham flow model because the Hershel–Bulkley flow model in some cases produced negative yield stress values.

Relationship of the shear stress and shear rate

As shown in Figure 1, the addition of MF-FS to the OPC pastes reduced the obtained shear stress values up to 0.5%. The maximum shear stress values were 263, 231, 84, 90, and 91 Pa for MF-FS dosages of 0.0, 0.25, 0.5, 0.75, and 1.0 cement mass %, respectively. The cement pastes containing 0.25% MF-FS exhibited a similar flow behavior with lower shear stress than that of the neat cement pastes. The increase in the dosage of MF-FS led to the flow curves shifting to lower shear stress. This indicated that MF-FS, adsorbed on the

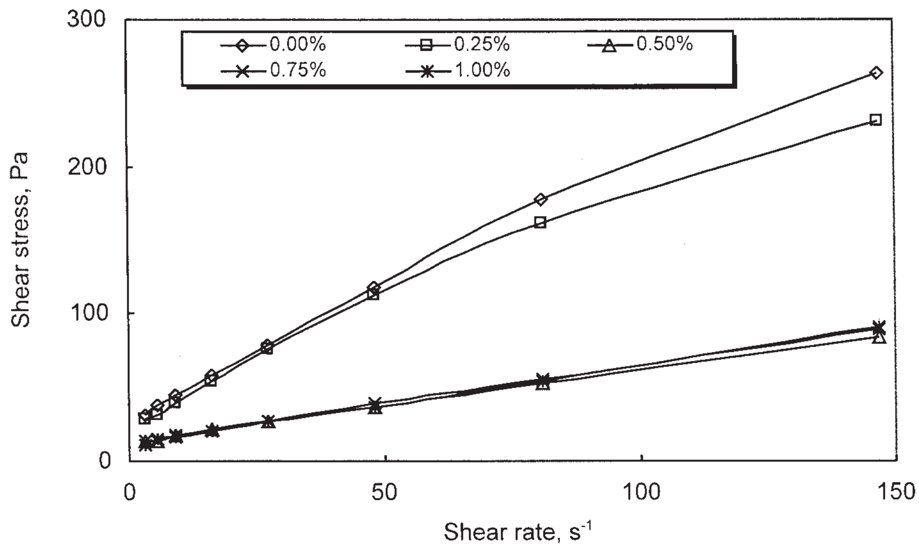

Figure 1 Shear stresses of cement pastes admixed with different dosages of MF-FS.

surfaces of the cement particles, prevented the formation of flocculated structures because of the steric hindrance of the adsorbed molecules and the increasing negative charges on the cement particles; as a result of the increasing negative charges, the electrical repulsive forces between them increased, and this caused the higher fluidity of the cement pastes. As the dosage of MF-FS increased, the surface potential of cement grains and the steric hindrance increased; this led to more disperse actions, and consequently, the shear stress values decreased (the fluidity increased).

Figure 2 shows the effect of MUF-FS on the rheological properties of cement pastes. The addition of the prepared MUF-FS to the cement pastes decreased the shear stress; as the MUF-FS dosage increased, the obtained shear stress decreased. The maximum shear stress values were 263, 170, 137, 122, and 154 Pa for MUF-FS dosages of 0.0, 0.25, 0.5, 0.75, and 1.0 cement mass %, respectively.

Figure 3 shows the shear stress values of cement paste admixed with Mt. According to a comparison with the results in Figures 1 and 2, Mt had a lower fluidity effect than MF-FS. The maximum shear stress values were 231, 147, 130, and 115 Pa for Mt dosages of 0.25, 0.50, 0.75, and 1.0 cement mass %, respectively.

Effect of superplasticizers on the bingham parameters

The Bingham parameters (τ_0 and μ) were calculated by the fitting of the flow data in Figures 1–3 to the Bingham model. The values of τ_0 and μ for different

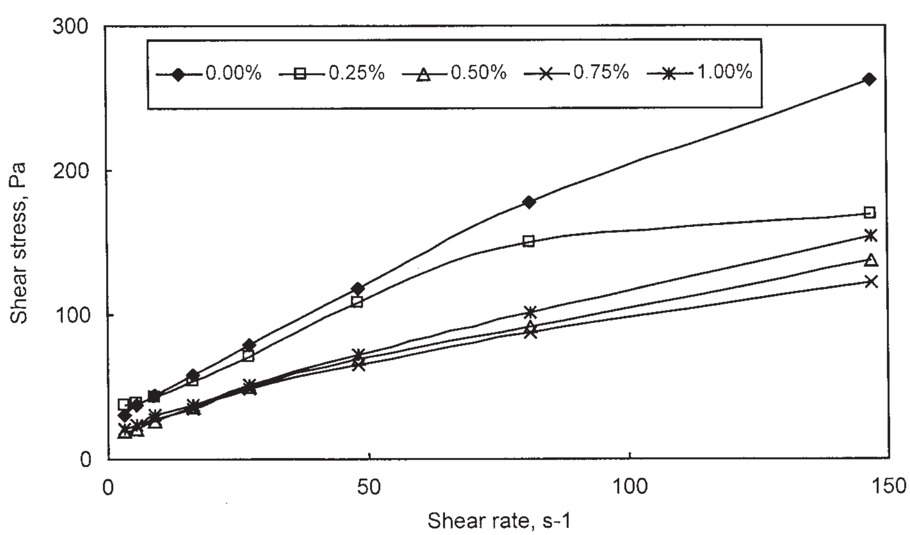

Figure 2 Shear stresses of cement pastes admixed with different dosages of MUF-FS.

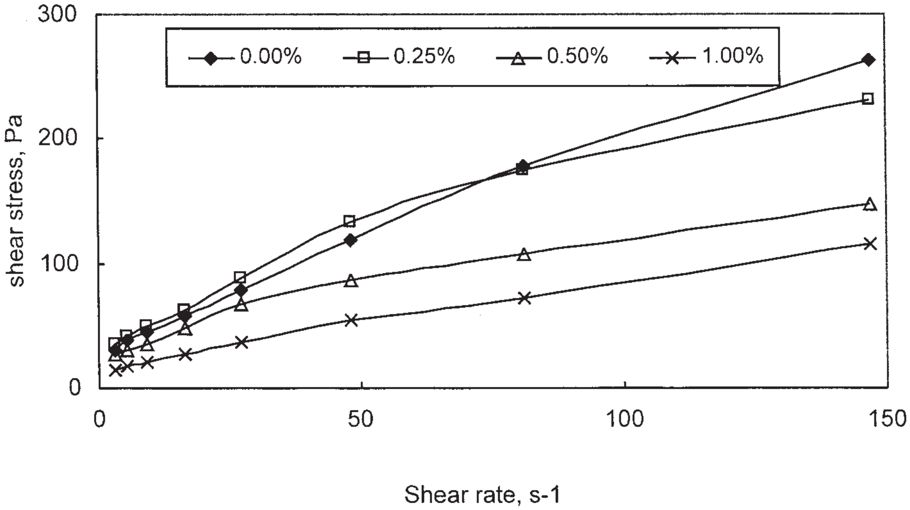

Figure 3 Shear stresses of cement pastes admixed with different dosages of MFS.

dosages of different superplasticizers are presented in Table IV.

As shown in Table IV, as the superplasticizer dosage increased, the initial yield stress of the cement paste strongly decreased but never vanished completely with any type of superplasticizer. Also, the plastic viscosity values were reduced by the superplasticizer dosage. The plastic viscosity and yield stress values together practically give us almost all information on the workability of cement pastes. Also, the MF-FS superplasticizer had lower plastic viscosity and yield stress values than MUF-FS and Mt; this meant that it had a higher workability effect on the cement pastes. This may be due to its chemical composition.

Saturated dosage of superplasticizers

One of the key points in the design of concrete or, more specifically, an HPC mix is the determination of the optimum dosage of the superplasticizers. The saturation dosage appears to correspond to the maximum degree of dispersion of the cement particles. This point is known as the critical micelle concentration in surfactant theory:[12] in this theory, the superplasticizer molecule acts as a polymeric surfactant, which has a hydrophilic part (HSO_3^{-1} and COO^{-1}) and a hydrophobic part (the rest of the molecules). When dissolved in water, it migrates to the water/air interface because of the repulsion of the hydrophobic parts and water molecules reducing its surface tension; as the concentration of the superplasticizer increases, its migration increases, and the surface tension of the water decreases up to a saturated point at which the monolayer of the surfactants form. Therefore, no further migration occurs, and there is no more reduction of the surface tension of water. The superplasticizer molecules still in the bulk of the water solution are forming micelles; at this point, the concentration of the superplasticizer in the solution is named the critical micelle concentration. This concentration depends on the nature of the hydrophilic and lipophilic parts. The same thing occurs if the cement and water molecules come into contact: the superplasticizer molecules migrate to the cement/water interface, reducing the interfacial tension between them, up to the monolayer adsorbed on the cement particles, forming the maximum negative charges on the cement particle surface, giving the maximum fluidity of the cement paste; beyond this concentration, as the concentration of the superplasticizer increases, the viscosity of the solution (the paste) increases.

As shown in Figure 4, as the superplasticizer dosage increased, the shear stress values sharply decreased up to the saturated point (the critical micelle concentration). The saturated point (superplasticizer dosage) values were 0.575 and 0.725 cement mass % for MF-FS and MUF-FS, respectively. The Mt superplasticizer

TABLE IV
Plastic Viscosity (μ) and Yield Stress (τ_0) Values of Superplasticized Cement Pastes

	τ_0	μ	R^2
MF-FS (%)			
0.00	32.5	1.63	0.99
0.25	31.0	1.40	0.98
0.50	12.6	0.49	0.99
0.75	12.1	0.53	0.99
1.00	10.9	0.54	0.99
MUF-FS (%)			
0.25	41.7	1.00	0.91
0.50	21.99	0.82	0.98
0.75	23.77	0.71	0.97
1.00	22.56	0.92	0.99
Mt (%)			
0.25	43.56	1.40	0.96
0.50	33.73	0.83	0.95
0.75	23.70	0.76	0.98
1.00	15.46	0.69	0.99

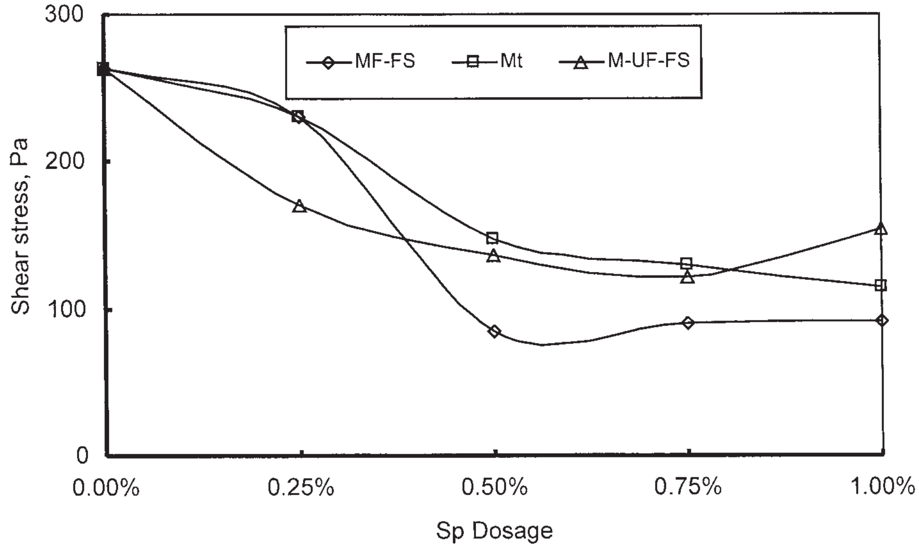

Figure 4 Maximum shear stresses of different superplasticized cement pastes (Sp = superplasticizer).

did not have any saturated point up to a dose of 1%. In our previous study, the saturated point of the Mt superplasticizer was 1.15 cement mass %.[13] These values depended on the hydrophilic/lipophilic balance, which shifted to a higher value for copolymer MUF-FS and Mt; this was due to the nature of its chemical structure.

Minislump

Figure 5 shows the variation of the minislump of the cement pastes prepared with 0.75% superplasticizers and a water/cement ratio of 0.40 with hydration times of 5, 30, 60, 90, and 120 min. As shown in Figure 5, the minislump of the prepared formaldehyde-free superplasticizers was higher than that of the conventional one (Mt). This means that the prepared polymers were more effective as workability improvers than the traditional one, not only at an early age (5 min) but also at a later early age (120 min) of hydration. It is also clear that the MUF-FS resin was less effective than MF-FS at the initial time (5–30 min); this was due to the lower sulfonate/(melamine + urea) ratio, which reduced the negative charges on the cement particles and caused lower particle repulsion, thus lowering the cement paste fluidity. When the minislump of MUF-FS became higher than that of MF-FS, this was due to the presence of urea in the superplasticizer molecule,

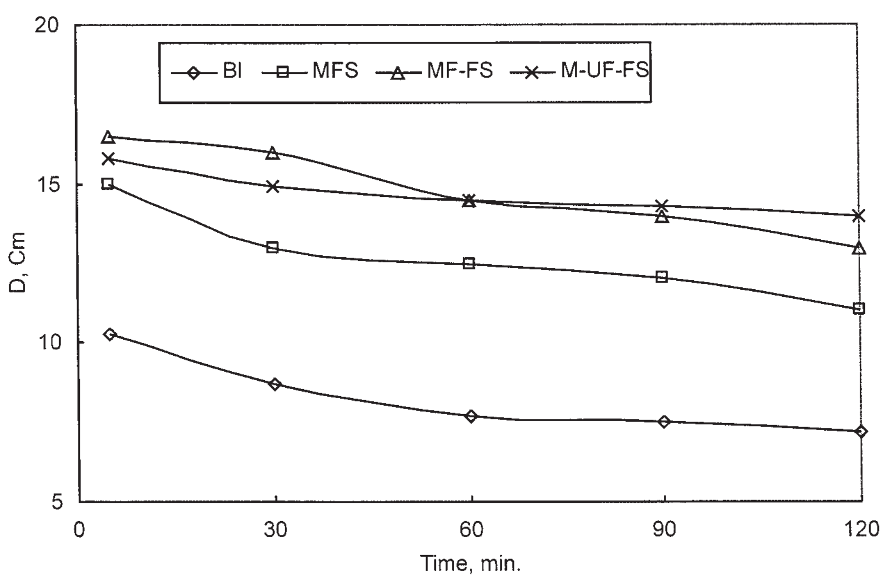

Figure 5 Minislump of superplasticized cement pastes at different hydration times.

which was different in its chemistry from melamine. The slump losses with time for the cement pastes were 27, 21, and 11% for the Mt, MF-FS, and MUF-FS superplasticizers, respectively.

CONCLUSIONS

The following conclusions can be drawn from the results:

1. The prepared formaldehyde-free polycondensate was more effective as a fluidity improver for cement pastes than the prepared conventional superplasticizer.
2. The minislump loss of cement pastes prepared with formaldehyde-free polymer was lower than that of cement pastes admixed with the traditional one.
3. The MUF-FS polymer was more effective than the MF-FS polymer as a minislump loss reducer at the later early ages.

References

1. Conley, R. F. Practical Dispersion: A Guide to Understanding and Formulating Slurries; VCH: New York, 1996.
2. Aitcin, P. C.; Miao, B. In Proceedings of the Second Seminar on High Performance Concrete, Taipei, Taiwan, 1992; Chern, J. C., Ed.; 1992; p 91.
3. Seminar on High Performance Concrete, Proceedings of the 2nd Conference, Taipei, Taiwan, 1992; Chern, J. C., Ed.; 1992.
4. Malhotra, V. M. ACI Spec Publ 1989, 119-1, 1.
5. Ramachandran, V. S.; Feldman, R. F.; Beaudoin, J. J. Concrete Science; Heyden & Son: London, 1981.
6. Yamada, K.; Takahashi, T.; Hanehara, S.; Matsuhisa, M. Cem Concr Res 2000, 30, 197.
7. Jiang, S.; Kim, B.-G.; Aitcin, P.-C. Cem Concr Res 1999, 29, 71.
8. Bartos, P. Fresh Concrete: Properties and Tests; Elsevier: Amsterdam, 1992.
9. Banfill, P. F. G. Rheology of Fresh Cement and Concrete; E&FN Spon: London, 1991.
10. Properties of Fresh Concrete, Proceedings of the Collection RILEM; Wierig, H. J., Ed.; Chapman & Hall: London, 1990.
11. (a) Tattersall, G. H. The Workability of Concrete: A Viewpoint Publication; PCA: 1976; (b) Porter, M. R. Handbook of Surfactants; Blackie: Glasgow, 1994.
12. Porter, M. R. Handbook of Surfactants; Blackie: Glasgow, 1994.
13. Aiad, I.; Hafiz, A. A. J Appl Polym Sci 2003, 90, 482.