Structural Effect of Prepared and Commercial Superplasticizers on Performance of Cement Pastes

I. Aiad, A. A. Hafiz

Petrochemical Department, Egyptian Petroleum Research Institute, 2 Ahmed El-Zomer Street, Nasser City, Cairo 11727, Egypt

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ABSTRACT: The sodium salt of melamine-phenol formaldehyde sulfonate (MPhFS), melamine formaldehyde sulfonate (MFS), and phenol formaldehyde sulfonate (PhFS) were prepared according to a four-step reaction procedure. The four steps of the reaction are hydroxymethylation, sulfonation, low pH condensation, and high pH rearrangement. Fourier transform IR and differential scanning calorimetry spectra were used to determine the structure of the synthesized resins. The effects of MFS, PhFS, MPhFS, and commercial superplasticizers on the rheological properties of cement pastes were investigated using a rotating coaxial viscometer. It was found that the prepared resins enhanced the rheological properties of cement pastes more than commercial ones. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 482–487, 2003

Key words: melamine; phenol; sulfonation; condensation; rheology

INTRODUCTION

Water-soluble resins called superplasticizers (SPs) have been applied in many areas such as the paint industry and dye manufacturing.[1,2] Other important areas of application are in construction engineering as water reducers. These SPs reduce standard consistency water by about 30% while maintaining the workability of cement concrete or increasing its workability at a constant water/cement ratio. It is well known that the strength of concrete is inversely proportional to the water/cement ratio.[3]

The most famous SPs are melamine formaldehyde sulfonate (MFS) and naphthalene formaldehyde sulfonate (NFS). SPs are the main ingredient in high performance concrete (HPC), which is used in tall structures or bridges and offshore structures.[4] Because of their industrial importance in concrete technology, the properties of the SPs and their action on concrete have been continuously studied and explored,[5,6] and new types of SPs are being evaluated or developed.[7] The most recent one is a polycarboxylate type.[8]

Typical examples of polymeric surfactants are MFS, NFS, and lignin sulfonate.[9] These admixtures adsorb on cement particles and exert an electrostatic repulsion. This results in the dissociation of the cement agglomerates into primary particles with a significant decrease in the viscosity of the materials system. This also contributes to the decrease in the surface tension of water and produces lubricating films at the cement particle surfaces.[6,10] In chemical terms, SPs are organic polyelectrolytes, which belong to the category of polymeric dispersants.[11] Organic admixtures are also polymeric surfactants with hydrophobic groups and/or polar functional groups. The nature of hydrophilic and hydrophobic groups should ensure minimum surfactancy to avoid foaming and air entrainment by the admixture.

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[12–15] can attest to this importance. In addition, 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. The rheology of concrete is known to be affected by the cement paste content, which contributes to the gap between the aggregates. It is also known that SPs play an important role in the flow behavior of concrete or cement pastes.

This study sought to prepare concrete admixtures of MFS, phenol formaldehyde sulfonate (PhFS), and melamine-PhFS (MPhFS). We also wanted to confirm the structure of prepared materials and evaluate the rheological properties of cement pastes admixed with the prepared or commercial SPs.

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

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TABLE I
Chemical Oxide Composition

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

EXPERIMENTAL

Materials

Cement

A freshly produced sample of ordinary Portland cement (OPC) was supplied by Helwan Portland Cement Company. Table I shows the chemical composition of the OPC and phase composition. The Blain surface area was ≈3054 cm^2/g. The phase composition was calculated from Bogue's equation as follows: C_3S = 50%, C_2S = 23%, C_3A = 8.6%; C_4AF = 10.4%.

Commercial SPs

Melment L10 (Mt) is a commercial SP, and its chemical composition is MFS. It was supplied by Modern Building Materials Co. as white solid material and used as a 35% solution. The NFS is a commercial SP, and its chemical composition is as the sodium salt of NFS. It was supplied by Modern Building Materials Co. as a solid brown material and used as a 35% solution.

Prepared SPs

MFS and PhFS were prepared according to a four-step method.[16,17] The polymers were formed through hydroxymethylation of melamine or phenol by formaldehyde, yielding trimethylol melamine or phenol; sulfonation of one methylol group of the product by sodium bisulfite, giving sulfonated methylol melamine or phenol; low pH condensation; and high pH rearrangement, yielding MFS or PhFS.

The MPhFS was prepared in the same manner in which the sulfonated methylol melamine and sulfonated methylol phenol underwent low pH condensation and high pH rearrangement with the same vessel and conditions, according to the following reactions:

$$M + xF \xrightarrow{T_1,\ pH_1,\ t_1} MF_x \tag{1}$$

$$MF_x + S \xrightarrow{T_2,\ pH_2,\ t_2} MF_xS \tag{2}$$

$$MF_xS + PhF_xS \xrightarrow{T_3,\ pH_3,\ t_3} P_1(MPhF_xS) \tag{3}$$

$$P_1(MPhF_xS) \xrightarrow{T_4,\ pH_4,\ t_4} P_2(MPhF_xS) \tag{4}$$

where M is melamine, Ph is phenol, F is formaldehyde, S is the sulfite group, MF_x is trimethylol melamine, MF_xS is sulfonated melamine formaldehyde, P_1 $(MPhF_xS)$ is a low pH condensation intermediate resin, P_2 $(MPhF_xS)$ is the sulfonated MPhF condensate, T_i is the temperature of the corresponding step, pH_i is the pH of the corresponding step, t_i is the reaction time of the corresponding step, and $x = 3$.

The products have the following solid contents: 24% MFS, 29% PhFS, and 27% MPhFS. The MFS and PhFS were also mixed in a 1/1 ratio (hereafter MFS/PhFS), and the solid content was 26.3%.

Techniques

Rheological measurements

Different mixes of SPs and cement were prepared at a constant water/cement ratio (0.30). The SP dosage ranged from 0 to 2 mass %. The mixes were stirred with a spatula at about 120 rpm for 3 min; after a 1-min rest, the mixture was stirred for 1 min at 120 rpm. Exactly 17 mL of this mix was transported to a Rheotest cell; the ratio of the radii of the measuring tube to the measuring cylinder (R/r) was 1.24. The test begins exactly 6.5 min after the contact of the cement and water, including the stirring time. The shear rate was 0.3–146 s-1.

Analysis of synthesized copolymer

Fourier transform IR (FTIR) and differential scanning calorimetry (DSC) spectroscopic analyses were performed to investigate the structure of our prepared MPhFS. The structure confirmation of MFS and PhFS were provided in our previous article.[13]

FTIR spectroscopy

The structure of the synthesized SPs was confirmed by FTIR spectrophotometric analysis with ATI Mattson Genesis™ equipment.

DSC analysis

The DSC analysis was performed in the Thermal Laboratory at the Building Research Center. A Shimadzu DSC-50 detector was used at a rate of 5°C/min with a holder temperature of 400°C.

RESULTS AND DISCUSSION

Confirmation of prepared SPs

FTIR spectra

According to preparation methodology, the general process is the reaction of formaldehyde with the NH_2 of melamine or the CH groups of phenol, which form trimethylol groups. One of them is sulfonated by sodium bisulfite, forming a sulfonated compound; and the methylol groups were condensated, forming an ether linkage (CH_2—O—CH_2). The FTIR spectrum of the copolymer (MPhFS) shows the characteristic bands from OH stretching that are due to the terminal methylol group, which coincides with those obtained from the absorption of NH stretching (3434–3397 cm^{-1}), which appear at lower frequencies than the free hydroxyl or amino group. The main band characterizing the condensation process is the ether linkage, which appear at (1043 cm^{-1}). The other bands show S═O stretching at 1362 cm^{-1}, an S—O group at 615 cm^{-1}, and C═C and C═N aromatic groups at 2365 and 1557 cm^{-1}, respectively.

DSC technique

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

The prepared copolymer MPhFS shows different peaks. The first is the glass-transition temperature (T_g) at 54.90°C (−48.81 J/g), the second is the crystallization temperature (T_c) at 310°C (15.05 J/g), and the third is the melting temperature (T_m) at 320.81°C (−30.40 J/g). These are different from MFS/PhFS, which shows a T_g peak at 72.96°C (−138.8 J/g); three T_c peaks at 192°C (52.5 J/g), 277°C (15.6 J/g), and 300.36°C (13.9 J/g); and a T_m at 319°C (−42.19 J/g).

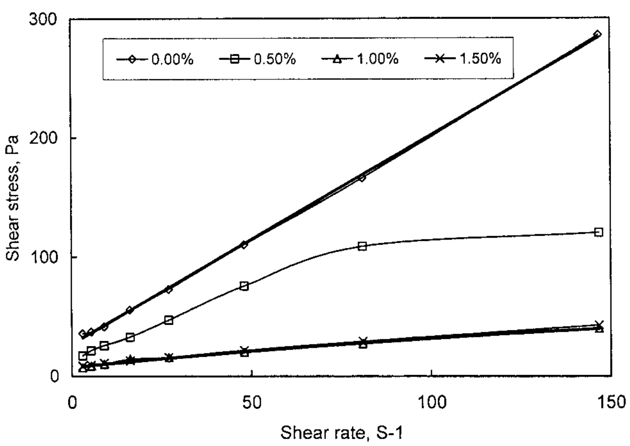

Figure 1 The shear stress to shear rate relationship of cement pastes admixed with different dosages of MFS.

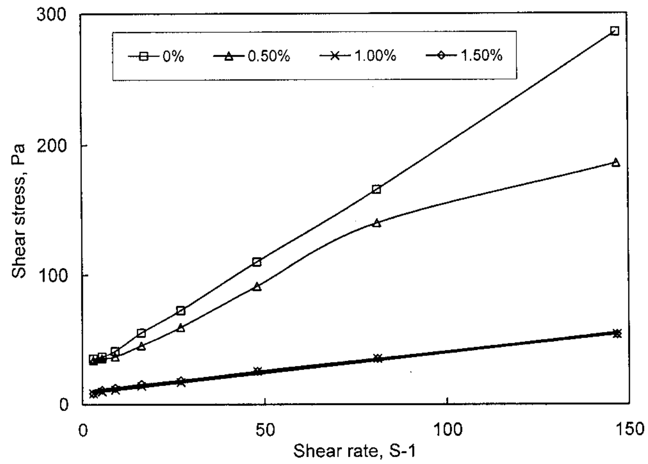

Figure 2 The shear stress to shear rate relationship of cement pastes admixed with different dosages of Mt.

Rheological measurements

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

There are different models for the flow behavior of cement pastes. The most suitable ones are the Bingham flow model or the Hershel–Bulkley flow model [yield power low, eq. (6)], depending on different factors, for example, cement nature, water/cement ratio, and type and dosage of the SP.

$$\tau = \tau_0 + \mu\gamma \tag{5}$$

$$\tau = \tau_0 + k\gamma^n \tag{6}$$

where τ is the shear stress (Pa), τ_0 is the yield stress (Pa), υ 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 is the relationship of the shear stress or apparent viscosity versus the shear rate. In this study the more suitable model is the Bingham flow model because the Hershel–Bulkley flow model give us negative yield stress values in some cases.

As shown in Figure 1, it is clear that the addition of MFS to the OPC pastes decreases the obtained shear stress values up to 1%; the maximum shear stress values were 286, 120, 40, and 43 Pa for MFS dosages of

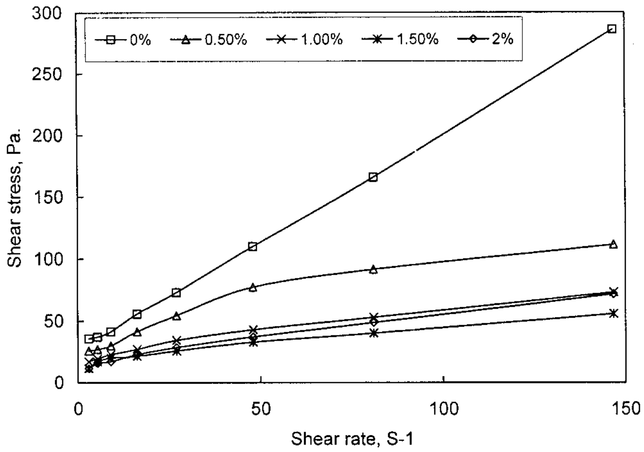

Figure 3 The shear stress to shear rate relationship of cement pastes admixed with different dosages of PhFS.

0.0, 0.5, 1.0, and 1.5 mass % cement, respectively. The apparent viscosity values were 1.95, 0.82, 0.27, and 0.29 Pa s. The cement pastes containing 0.5% MFS exhibit similar flow behavior with lower shear stress and apparent viscosity values compared to those of the neat cement pastes. The increase in the dosage of MFS leads to a shift of the flow curves to lower shear stress and apparent viscosity values. This indicates that MFS adsorbed on the cement particles surfaces and prevented the formation of flocculated structures, which is due to the increased negative charge on these particles that causes the electrical repulsive forces between them to increase, yielding cement pastes with higher fluidity. As the dosage of MFS is increased, the surface potential of the cement grains increases and leads to more disperse actions; consequently, the shear stress or apparent viscosity decreases (fluidity increases).

Figure 2 shows the shear stress values of cement paste admixed with Mt. Compared to the results in Figure 1, Mt has a lower fluidity effect than MFS. The

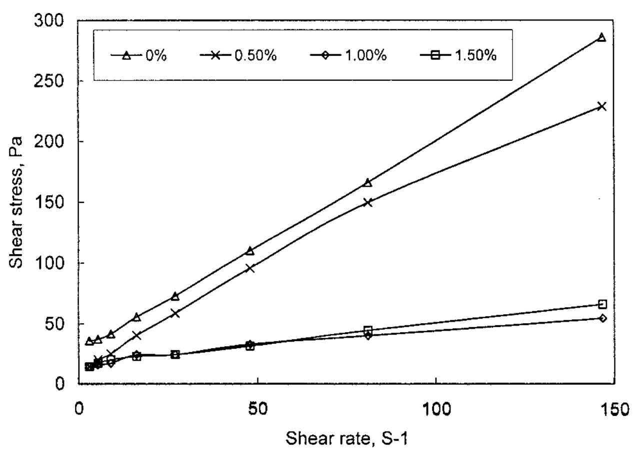

Figure 4 The shear stress to shear rate relationship of cement pastes admixed with different dosages of MPhFS.

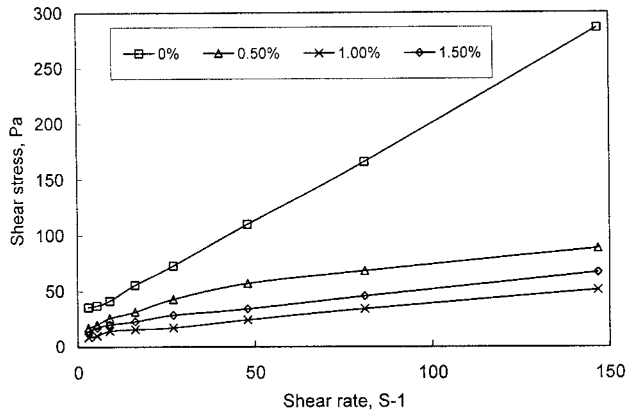

Figure 5 The shear stress to shear rate relationship of cement pastes admixed with different dosages of MFS/PhFS.

maximum shear stress values were 186, 54, and 54 Pa and the apparent viscosity values were 1.27, 0.37, and 0.37 Pa S for Mt dosages of 0.50, 1.0, and 1.5 mass % cement, respectively. This may be due to the fact that MFS is freshly used or to impurities in Mt.

Figure 3 shows the effect of PhFS on the rheological properties of cement pastes. It is clear that the addition of prepared PhFS to cement pastes decreases its shear stress. As the PhFS dosage is increased, the obtained shear stress decreases. The maximum shear stress values were 286, 111.5, 72.9, 55.7, and 71.5 Pa and the apparent viscosity values were 1.95, 0.76, 0.50, 0.38, and 0.49 Pa S for PhFS dosages of 0.0, 0.5, 1.0, 1.5, and 2.0 mass % cement, respectively.

Figures 4 and 5 show the effect of the addition of the copolymer (MPhFS) and blends (MFS/PhFS = 1) of MFS and PhFS on the shear stress values of OPC pastes. It is clear that the shear stress values decrease when increasing the MPhFS or MFS/PhFS. The maximum shear stress values were 229, 54, and 65 Pa for MPhFS and 89, 52, and 67 Pa for MFS/PhFS for doses of 0.5, 1.0, and 1.5 mass % cement.

As shown in Figure 6, as the commercial NFS dosage increased in the cement pastes, the maximum shear stress values of it decreased. The obtained shear stress values were 286, 86, 51, and 49 Pa for NFS dosages of 0.0, 0.5, 1.0, and 1.5 mass % cement, respectively. It is clear that the viscosity of the system was not increased up to a dosage of 1.5% NFS.

Saturated dosage of SPs

One of the key points in the design of an HPC mix is the determination of the optimum dosage of the SPs. 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 (cmc) in surfactant theory.[19] In this theory the SP molecules act as a polymeric surfactant that has hydrophilic (HSO_3^-) and hydrophobic (the rest of mol-

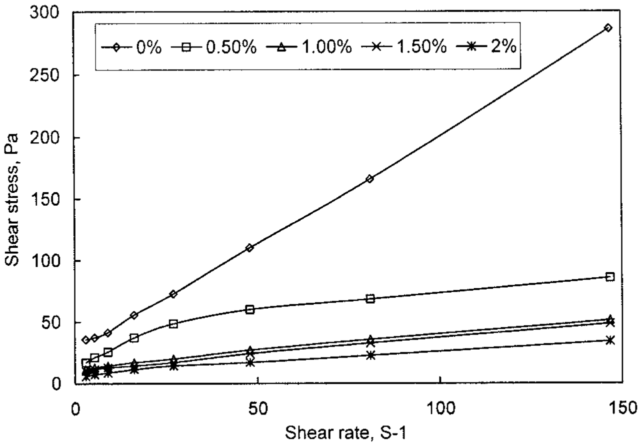

Figure 6 The shear stress to shear rate relationship of cement pastes admixed with different dosages of NFS.

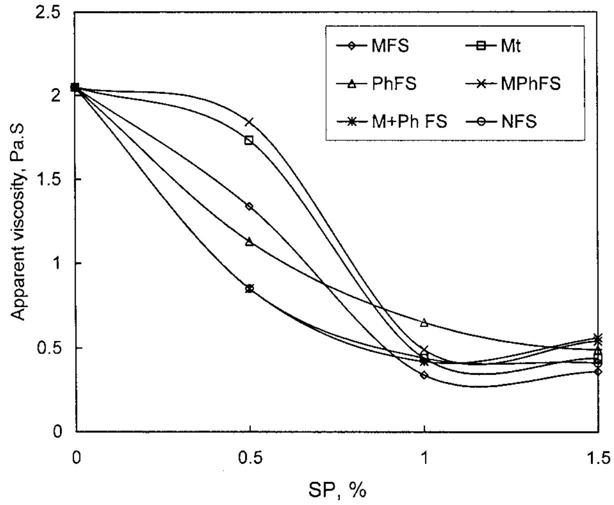

Figure 7 The apparent viscosity of different superplasticizers at different dosages.

ecules) parts. When dissolved in water, it migrates to the interface of the water–air because the repulsion of the hydrophobic parts and the water molecules reduces its surface tension. As the concentration of SP increases, its migration increases and the surface tension of the water decreases up to a saturated point in which a monolayer of surfactants is formed. Thus, no further migration occurs and there is no further reduction in the surface tension of water. The SP molecules still in the bulk of the water solution form micelles; at this point the concentration of SP in the solution is termed cmc. This concentration depends on the nature of the hydrophil and lyophil parts. The same thing occurs if the cement and water molecules come in contact. The SP molecules migrate to the cement–water interface, reducing the interfacial tension between them, up to monolayer adsorbed on the cement particles, and form the maximum negative charge on the cement particle surface, giving the maximum fluidity of cement paste. Beyond this concentration, the viscosity of the solution (the paste) increases.

As shown in Figure 7, as the SP dosage is increased, the apparent viscosity values sharply decrease up to a saturated point (cmc). The saturated point (SP dosage) values were 1.15, 1.15, 1.10, 1.50, 1.2, and 1.20 mass % cement for MFS, Mt, MPhFS, PhFS, MFS/PhFS, and NFS, respectively. These values depend on the hydrophil–lyophil balance. Therefore, MFS and Mt have the same value because they have same structure, which shifts to a lower value for the copolymer MPhFS and to higher value (1.5) for PhFS. The optimum dosage for these SPs is in order MPhFS < MFS = Mt < NFS < MFS/PhFS < PhFS.

Effect of SPs on Bingham parameters

The Bingham parameters (τ_0 and μ) were calculated from fitting the flow data in Figures 1–6 to the

TABLE II
Plastic Viscosity and Yield Stress Values of Prepared and Commercial Superplasticizers

MFS Dose	τ_0	μ	R^2	PhFS Dose	τ_0	μ	R^2
0.00	27.1	1.75	0.9994	0.50	25.35[a]	0.9	0.9579
0.50	23.4	0.77	0.8972	1.00	20.25	0.38	0.9712
1.00	8.6	0.22	0.9835	1.50	16.16	0.28	0.9641
1.50	8.77	0.24	0.9946	2.00	14.72	0.40	0.9820
MPhFS				NFS			
0.50	15.4	1.51	0.9917	0.50	26.18	0.46	0.8762
1.00	16.39	0.27	0.9652	1.00	12.14	0.28	0.9926
1.50	15.52	0.34	0.9943	1.50	10.19	0.27	0.9963
Mt				MFS/PhFS			
0.50	26.1[a]	1.38	0.9949	0.50	23.20	0.49	0.9299
1.00	8.78	0.32	0.9958	1.00	9.80	0.29	0.9907
1.50	9.88	0.31	0.9949	1.50	16.39	0.35	0.9901

[a] Calculated from the low shear rate.

Bingham model. The values of τ_0 and μ of different dosages for different SPs are presented in Table II.

As shown in Table II, as the SP dosage increases, the initial yield stress of the cement pastes is strongly reduced but never vanishes completely with any type of SP. In addition, the plastic viscosity values were reduced by SP dosages up to 1%. In a practical sense, the plastic viscosity and yield stress values together give information on the workability of cement paste. It is also clear that the MFS SP has lower plastic viscosity and yield stress than that of Mt, NFS, and MPhFS. This means that it has a higher workability affect on the cement pastes. This may be attributable to the purity of its chemical composition.

CONCLUSIONS

The following conclusions can be drawn from the current work:

1. The prepared MFS SP has a greater affect on the rheological properties of cement pastes than other prepared and commercial SPs.
2. The prepared MFS has higher a rheological affect than the commercial SPs.
3. For each SP there is one saturated dosage that depends only on its chemical structure.

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