Water-Soluble Sulfonated Amino-Formaldehyde Resins. II. Characteristics As Dispersing Agents

S. M. LAHALIH, M. ABSI-HALABI, and K. F. SHUHAIBAR,
Products Department, Petroleum, Petrochemicals and Materials Division, Kuwait Institute for Scientific Research, P.O. Box 24885, 13109-Safat, Kuwait

Synopsis

The use of sulfonated melamine–formaldehyde resins as dispersants with inorganic materials was investigated, and the effect of these dispersants on the rheology of cement pastes was studied. The improvement in compressive strength of sand and mortar was also investigated. Results show that these polyanionic resins are effective dispersing agents when they are mixed with inorganic materials. Significant improvements in the flow and compressive strength of these systems can be realized when small quantities of the water-soluble polymers are added. The effect of reaction conditions on the molecular structure and its effect on performance is discussed.

INTRODUCTION

The preparation procedure of water-soluble sulfonated melamine–formaldehyde polycondensates was reviewed and reported in the first part of this series. Because of their ability to disperse the resins can be used in such applications as mortars, grouts, coatings, and adhesives. These polymers are also referred to as superplasticizers.

Because of their anionic nature, the polymers are thought to be adsorbed on the surface of the particles causing them to be negatively charged and thus to repel each other.[1] This adsorption and dispersion effect results in a matrix of uniform morphology. In addition, because of their lubricity, they tend to enhance the flow of materials by reducing frictional forces between particles.[2] The degree of dispersion and plasticizing efficiency is dependent on their molecular arrangements, which are greatly affected by the reaction conditions and procedure (see the first part of this series).

Little attention has been paid in the literature[3,4] to the use of these polyanionic resins as dispersing agents with inorganic matter (i.e., sand and cement). Even those dealing with this subject made no attempt to study the effect of reaction conditions on the resins' final performance. Therefore, it is the objective of this paper to show that these polyanionic polycondensates can be powerful dispersants for the applications mentioned above. Another objective is to show that the dispersion effect is affected by the extent of reaction and degree of polymerization of these water soluble polymers. The stability of the polymers during storage is greatly affected by the reaction procedure. This will be the subject of another article in this series.

Journal of Applied Polymer Science, Vol. 33, 2997–3004 (1987)

CCC 0021-8995/87/082997-08$04.00

EXPERIMENTAL

Materials

Sulfonated melamine–formaldehyde solutions were prepared as described in the first paper of this series. Sample 2062 has a 20% solid content and a viscosity of 4.42 cP at 20°C with an average molecular weight of 844,000 ($\bar{M}_w$) and an average number molecular weight of 76,400 ($\bar{M}_n$). The formaldehyde to melamine ratio (F/M) is 4 : 1, and the sulfite to melamine ratio (S/M) is 1 : 1. Sample 2072 is similar to sample 2062 except that the F/M ratio is 3 : 1 and its 20% solid content has a viscosity of 3.87 cP when measured at 20°C. The average molecular weight ($\bar{M}_w$) is 644,000 and the average number molecular weight is 74,100. Samples 2062 and 2072 were prepared according to the four-step process discussed in the first part of this series. Sample 2062P was prepared according to a three-step process.[3,5] Its solid content has a viscosity of 5.6 cP when measured at 20°C. The sulfite to melamine ratio is 1 : 1 and the formaldehyde to melamine ratio is 3 : 1. The average molecular weight $\bar{M}_w$ is 682,000 and the average number molecular weight ($\bar{M}_n$) is 81,000. Gatch type sand and portland type I cement was used in this study. Gatch is made up of 90% SiO_2, 4.35% Al_2O_3, 0.6% CaO, 1.33% K_2O, 0.88% Fe_2O_3, 0.21% TiO_2, and 2.55% LOI.

PROCEDURE

Molecular Weight Distribution. Molecular weight analyses were carried out by Mikro Analytisch Pascher, Bonn, West Germany. The analysis was done by GPC at 50°C using distilled water as eluant and silica gel (10 μm) with pore sizes 6–100 μm as separating materials.

Rheological Behavior of Cement Slurries. The shear stress–shear rate relationship was measured with a Haake Rotoviscometer with MD500 measuring head and MVIIP sensor for neat cement paste and cement paste treated with different percentages of the prepared resins. All mixes had a water–cement ratio of 0.35 and were tested under the same conditions, i.e., time of mixing 3 min and time of testing 2 min at room temperature.

Compressive Strength Measurements. For compressive strength testing of sand, cylindrical specimens of 5 cm diameter were prepared. To prepare a plain specimen (control), 20 g of water was mixed with 200 g of sand till a homogeneous wet sample was obtained. Then the wet sand was cast in a 5 cm cylindrical mold and compacted by the Instron compressive machine. The compaction load was 2000 kg. The specimen was taken out of the mold and dried in an oven at 70°C. For the treated specimen, 20 mL of the sulfonated melamine–formaldehyde solution with a 10% solid concentration was used instead of water; then the same procedure was followed. To test the dried specimens for compressive strength, the Instron machine was used to crush the specimen at a rate of 1 mm/min. For testing the compressive strength of mortar, a mortar consisting of sand, cement, and water was prepared in proportions of 2.75 : 1.0 : 0.485. Cubical samples of 5 cm were molded and kept in water for curing according to ASTM C109 standard. After the samples were cured, they were tested according to the procedure described above.

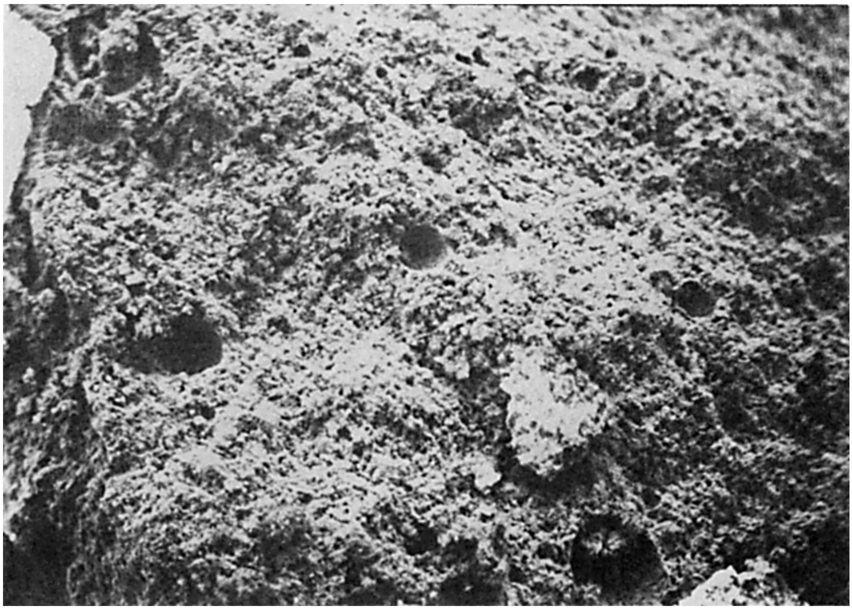

Fig. 1. SEM of ordinary portland cement agglomerates with no additive present.

Scanning Electron Microscope (SEM). Samples of cement pastes were prepared according to this procedure, and SEM pictures were taken after hydration was completed.

RESULTS

Action Mode of Water-Soluble Dispersants

Scanning electron microscope (SEM) pictures show that untreated cement paste particles agglomerate (Fig. 1) whereas these particles are uniformly distributed when the cement was treated with sulfonated melamine–formaldehyde solutions (Fig 2). This uniform distribution of particles is a result of the adsorption of these additives on the surface of the particles. It is proposed that these polymers form a very thin layer encapsulating the inorganic particles. Because of the anionic nature of the polymers, the negative charges generated on the surface of the particles causes them to repel one another, resulting in a uniform morphology of the inorganic matrix. This uniformity is thought to be responsible for the improved mechanical properties of systems under the same testing conditions. In addition, some studies[2] show that, although no significant changes in the surface tension occur, internal lubrication improves significantly. The improvement in internal lubrication make these polymers flow improvers.

RHEOLOGY OF CEMENT PASTES

Samples of ordinary portland cement (OPC) pastes were prepared according to the procedure described above. It is obvious from Figure 3 that significant

Fig. 2. SEM of ordinary portland cement with SMF dispersant present, showing uniform morphology with no agglomeration.

reductions in paste viscosity are obtained when these polyanionic resins are added. The reduction in viscosity is responsible for improving the flowability of these systems. It is interesting to note that, although the viscosity of the untreated cement paste is strongly dependent on the shear stress and shear rate with no noticeable plastic yield, it becomes less independent as the dose increases. In fact, the behavior of the viscosity becomes Newtonian after a certain dose is added, but it was strongly non-Newtonian before polymers

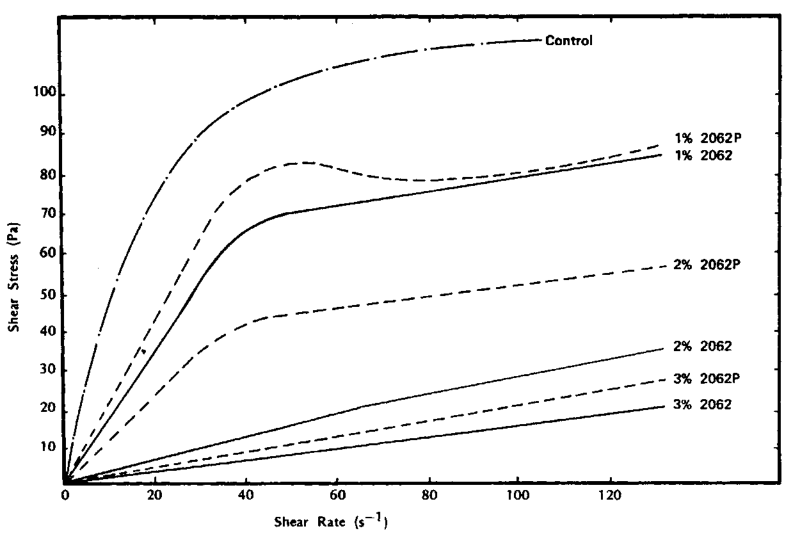

Fig. 3. Rheology of cement paste containing various percentages of admixtures.

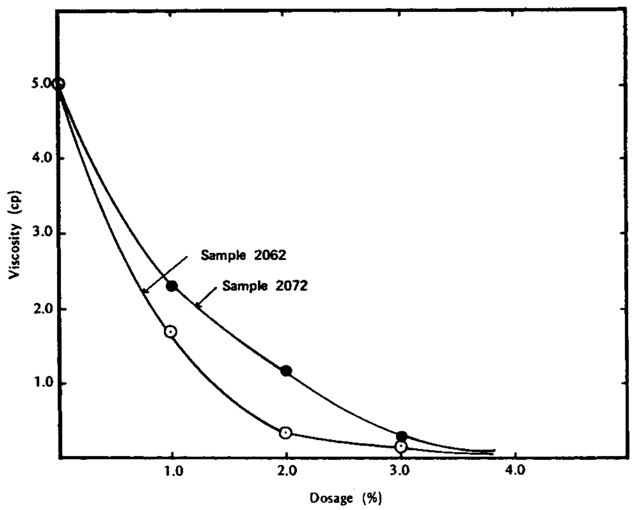

Fig. 4. Viscosity of cement paste vs. percentage of polymer additive, based on weight of cement at low shear rates of two samples prepared at different formaldehyde to melamine ratios.

were added. The same trend is observed for the cement paste yield. Figure 4 indicates that there is an optimum dose for maximum fluidity of the mix, and any additional dosage would increase the flow slightly but at higher cost.

The shear stress–shear rate curves of two samples prepared under different conditions are shown in Figure 3, which shows that the reaction procedure chosen does affect the final performance of these polymers. The only difference between these samples is that sample 2062 was prepared with a formaldehyde/melamine ratio of 4:1 and sample 2062P was prepared with formaldehyde/melamine ratio 3:1. Figure 4 shows the viscosity of the cement pastes as a function of the dose added. It can be seen that sample 2062 is more efficient in reducing the viscosity of the paste. It was observed during the preparation of cement paste samples that, when polymeric materials were added to adjust sample consistency, the amount of water used can be reduced significantly. For example, to get a mix with a consistency similar to a cement paste prepared without the polymers, a 3% dose of resins reduce the amount of water used by 30%. This significant reduction in the amount of water along with the dispersion ability of the polyanionic polymers are the principal ways in which the properties of the inorganic systems are improved.

COMPRESSIVE STRENGTH OF MORTAR AND SAND

The compressive strength of mortar and sand treated with water-soluble sulfonated melamine–formaldehyde resins was evaluated (Table I). It is obvious that the improvement in compressive strength is significant when the inorganics are treated with these powerful dispersants. We believe that the significant improvement in compressive strength when these polymers are added is a result of their ability to disperse the charged inorganic particles, resulting in a homogeneous morphology. This homogeneous morphology of the matrix is free of agglomerates that could act as a stress concentration point, thus weakening the structure of the matrix. In addition, the uniform homoge-

TABLE I
Compressive Strength of Sandy Soil and Mortar When Treated with Water-Soluble Sulfonated Melamine–Formaldehyde Resins

Material	Dose of resin (%)	Average compressive strength (kg/cm^2)[a]
Mortar		
(control)	0.0	323.0
(Treated with sample 2062)	3[b]	427.5
(Treated with sample 2062P)	3[b]	400.0
Sand		
(control)	0.0	4.74
(Treated with sample 2062)	1.0[c]	13.38

[a]After 28 days of aging at room temperature.
[b]3% resin based on weight of cement.
[c]1% resin based on weight of sand.

neous morphology can be obtained by adding small quantities of the polymers. The significant reduction in the amount of water needed to impart internal mobility and achieve the same morphology increases the compressive strength of these materials significantly.

DISCUSSION

When synthesizing water-soluble sulfonated melamine–formaldehyde polycondensates, we found that a four-step reaction procedure was necessary to get a product with optimum properties. In each step, the pH, time, and reaction temperature were variables to be optimized. Other variables were the formaldehyde to melamine ratio and the sulfite to melamine ratio. Details of the preparation study were discussed in the first part of this series. The effect of these polymers on the rheology and mechanical properties of some inorganic matter has been presented in this part. It was shown that these polymers can be effective dispersants as exemplified by the improvement in rheological properties of cement pastes and the compressive strength of mortar and sand. It was also shown that reaction conditions influence the final performance of these polyanionic resins.

It is well known that reaction conditions in any polymer synthesis influence the molecular structure of the synthesized polymer[6] and that the final molecular structure of any polymer has a great impact on its performance.[7] The same holds true for this group of water-soluble polymers. Although the literature presents preparation procedures in two steps[8] or three steps,[3-5] the first part of this series describes a four-step process developed in our laboratory. The final performance of resins prepared by the four-step process when used with inorganic systems was very significantly better. This significant difference, we believe, may be attributed to the molecular weight and molecular weight distribution of the polymers.

When they are used as dispersing agents, the fraction of the low molecular weight segments and the fraction of the high molecular weight segments play

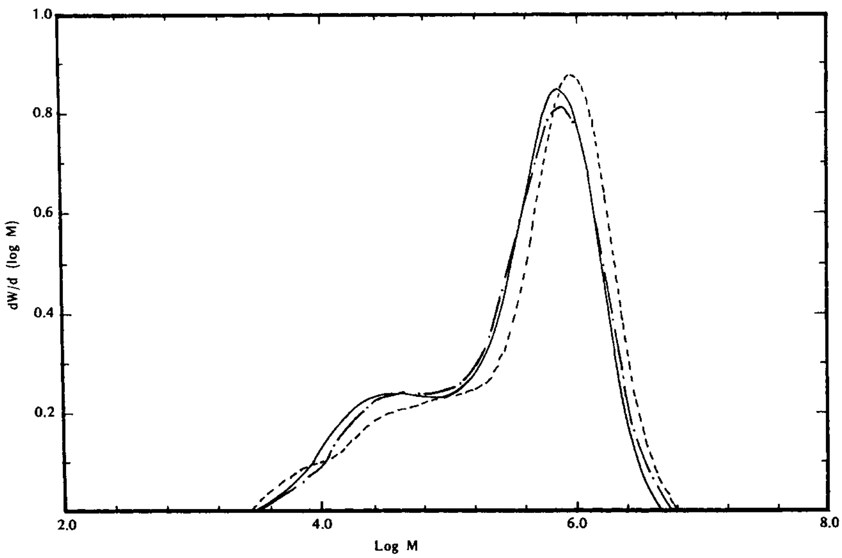

Fig. 5. Molecular weight distribution of resins 2062 (---), 2072 (—), and 2062P (-··-).

a significant role. This becomes clear in Figure 5 which shows the molecular weight distribution of sample 2062 (prepared according to the four-step procedure adopted by us) and sample 2062P (prepared according to the three-step procedure outlined in the literature[5]). Sample 2072 was prepared according to the four-step process except that the formaldehyde to melamine ratio was 3 : 1 instead of 4 : 1 as in the case of sample 2062. There were significant differences between these samples with regard to their effectiveness as water-soluble dispersants (Figs. 3 and 4, Table I). It can be seen from Figure 5 that sample 2062 has the broadest molecular weight distribution followed by 2072 and 2062P (the polydispersity of samples 2062, 2072 and 2062P are 11.05, 8.69, and 8.42, respectively). Moreover, the fraction of the low molecular weight species and the fraction of the high molecular weight species are highest for sample 2062 followed by 2072 and 2062P. Therefore, if one considers the mode of action of dispersion of these polyanionic resins when they are added to inorganic materials and examines the molecular arrangements induced by the different reaction procedures, it becomes apparent that, to produce an optimum dispersant agent with these polymers, the reaction conditions must be examined very closely. In the third part of this series we shall see the effect of the reaction conditions on the stability of these resins upon aging.

Finally, it should be pointed out that the function of these polymers when they are added to inorganic materials ceases after the system has been hydrated. Because of their inertness, further reaction or interference with the inorganic systems is not expected. Therefore, their long-term effect on the systems is negligible. The long term behavior of the treated inorganic systems is controlled by the early arrangement of the matrix morphology that is affected by the addition of these powerful dispersants at the early stages of hydration.

This research has been supported in part by a grant from the Kuwait Foundation for the Advancement of Sciences (KFAS) under Grant No. 84-12-02 and the Kuwait Melamine Industries Company. This is Publication No. KISR 2090, Kuwait Institute for Scientific Research, Kuwait.

References

1. *Superplasticizing Admixtures in Concrete*, report of a Joint Working Party of the Cement Admixtures Association and the Cement and Concrete Association, Cement and Concrete Association, London, 1976.
2. M. R. Rixom, *Chemical Admixtures for Concrete*, Halsted, Wiley, New York, 1978.
3. R. W. Auten and J. L. Riney. U.S. Pat. 2,407,599 (1946).
4. A. Aignesberger, H. Michand, and U. Kriele, Ger. Offen, 2,217,929 (1973).
5. A. Aignesberger, P. Bornmann, H. G. Resenbaur, and H. Theissig, U.S. Pat. 3,985,696 (1976).
6. B. Vollmert, *Polymer Chemistry*, Springer-Verlag, New York, 1973.
7. J. D. Ferry, *Viscoelastic Properties of Polymers*, 2nd ed., Wiley, New York, 1970.
8. G. E. Sheldrick, U.S. Pat. 4,444,945 (1984).

Received September 9, 1986
Accepted November 3, 1986