Water-Soluble Sulfonated Phenolic Resins. II. Surface Property and Effectiveness as a Dispersing Agent

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SYNOPSIS

This article presents the surface activity of a synthetic sulfonated phenolic resin (SPR) and evaluates its performance in cement mortars. It is indicated that the prepared SPR has the characteristics of a polymeric surfactant that can decrease the surface tension of water. When resin was added into cement mortars, the resulting materials exhibited better workability, more consolidated structure, and higher compressive strength than the untreated. Therefore, SPR could be used as a water reducing admixture for cementitious materials. In addition, resins with higher sulfonate group content and low molecular weight appear to be more effective. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The water reducing admixture is one of the important ingredients used in concrete. Only a small dosage could significantly improve the workability, mechanical strength, and other properties of cementitious materials.[1] The roles of the chemical admixture are: controlling the amount of free water and the viscosity of fresh concrete for improving the deformation and the segregation behavior[2]; acting as a lubricant or a dispersing agent so that the cement particles are uniformly dispersed and high mechanical strength of the resulting material is obtained[3,4]; interacting with $Ca(OH)_2$, which is one of the hydrated products of cement, to modify the morphology of the resulting material.[5,6]

Most commercial water reducers could be regarded as polymeric surfactants. Lignosulfonates, sulfonated melamine formaldehyde condensates, and sulfonated naphthalene formaldehyde condensates are typical examples.[7] These admixtures, after being adsorbed on cement particles, 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 material system. They also contribute to the decrease in the surface tension of water and to producing lubricating films at particle surfaces.[8,9]

Consequently, the research and development of water reducing agents is important in concrete technology and has received great attention recently. In order to investigate the properties of these admixtures and to develop a new one, a sulfonated phenolic resin (SPR) was prepared and evaluated as a water reducer for cementitious materials in this study. The preparation procedure of this compound was reported in our first article. In this article the surface activity of SPR was determined and its performance in cement mortars was examined and discussed.

EXPERIMENTAL

Preparation of Resins

The resin was prepared from formaldehyde, phenol, and $NaHSO_3$ through a four-step reaction. Details of the preparation procedure can be found in our companion article. Table I lists some synthetic resin samples with different sulfur/carbon (S/C) ratios and solution viscosities. From this table the sulfonate group content of the resin molecule, which is represented by the S/C ratio, was observed to be decreased with the solution viscosity. This is because

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Table I Characteristics of Resins

Resin	S/C Ratio[a]	Viscosity (cP)[b]
S8	0.26	14.9
S15	0.32	2.0
S22	0.28	8.9
S30	0.34	2.4
S34	0.35	2.6
NP100	Not measured	1.6

[a] The S/C ratio of resin was determined by a Leco CS-244 analyzer.

[b] The viscosity of 20 wt % resin solution measured by a Brookfield DV-II viscometer.

sulfonation and condensation of methylolphenols were affected by each other during the preparation steps.[10] Resins with S/C ratio no less than 0.32 were thought to be subjected to sufficient sulfonation.[11] Furthermore, NP100 in Table I is a commercial, sulfonated naphthalene formaldehyde base, high-range water reducer. The performance of various SPRs and NP100 in cement mortars was evaluated and compared later.

Preparation of Mortars

Resin was first dissolved in water to form a 20 wt % solution. Mortar was made by mixing water, type I Portland cement, and river sand with or without addition of resin solution. The water/cement/sand ratio was fixed at 1/3.3/4. In other words, the water/cement ratio is 0.3. The resin/cement ratio ranged from 0 to 2 wt %.

Measurements

Surface Tension

The surface tensions of resin solutions in various concentrations were determined at room temperature with a Face automatic surface tensiometer model CBVP-A3.

Fluidity

Mortars were poured on the flow table. The flow spread diameter was measured after mortars were vibrated 25 times. Greater spread diameter means higher fluidity or better workability.

Calcium Ion Chelating Ability

A standard $0.01M$ calcium ion was prepared. The resin solution was then added in small increments into the standard solution. The equilibrium calcium ion concentrations were measured by a calcium selective electrode (HNU ISE-20-20-00) and a digital pH/mV meter (Hanna HI 8521) following Chang's procedure.[12] From the variation of calcium ion concentration, the calcium ion chelating ability of resin was determined.

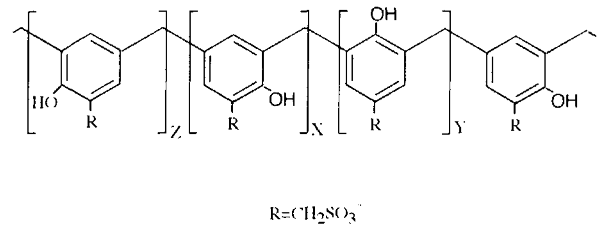

Figure 1 The chemical structure of resin.

Compressive Strength Test

Compressive strengths of mortar specimens of 5 × 5 × 5 cm were determined at the ages of 3, 7, and 28 days using a MTS100 ton testing machine according to ASTM C109-80. Each compressive strength value is an average of three data sets.

Scanning Electronic Microscopic (SEM) Observations

The specimens, after the compressive strength test, were made into samples for SEM examinations by using a Joel JSM-T100.

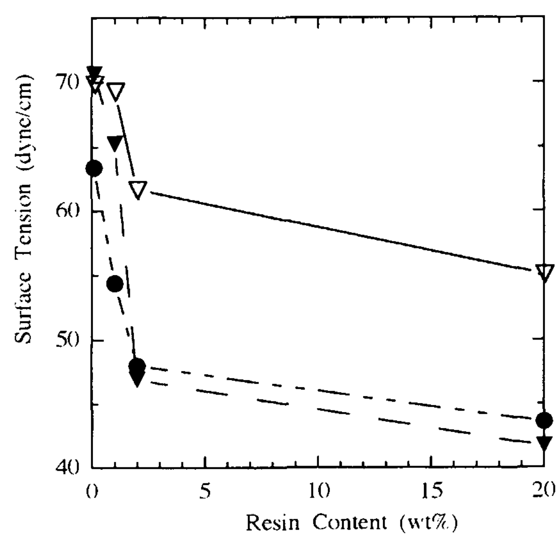

Figure 2 The relationship between the surface tension of aqueous solution and resin content. (●) S15; (▽) S22; (▼) S30.

Table II Relationship Between Fluidity of Mortars and Resin Content

Resin Content[a] (wt %)	S1	S8	S30	S34	NP100
0.0	11 ± 0.5	11 ± 0.5	11 ± 0.5	11 ± 0.5	11 ± 0.5
0.5	12 ± 0.5	12 ± 0.5	14 ± 0.5	13.5 ± 0.5	14.5 ± 0.5
1.0	13 ± 0.5	12.5 ± 0.5	16 ± 0.5	16 ± 0.5	19.5 ± 0.5
2.0	14 ± 0.5	13.5 ± 0.5	17.5 ± 0.5	17 ± 0.5	21 ± 0.5

[a] Resin content = resin/cement.

Differential Scanning Calorimeter (DSC) Measurements

A Seiko DSC 5200 was applied for indicating the amount of $Ca(OH)_2$ in mortars from the endothermal peak at about 470°C.[13] The heating rate was 10°C/min.

RESULTS AND DISCUSSION

Surface Tension of Resin Solutions

The chemical structure of a prepared resin is shown in Figure 1. The resin is a polyelectrolyte that contains an anionic sulfonate group in the repeating unit. Therefore, it should be capable of decreasing the surface tension of water and acting as a dispersant.[14] Figure 2 shows the relationship between the surface tension of aqueous solutions and resin content. The surface tension is indeed reduced with the amount of resin in the solution. Lower values were noted for resins (S15, S30) with higher sulfonate group content.

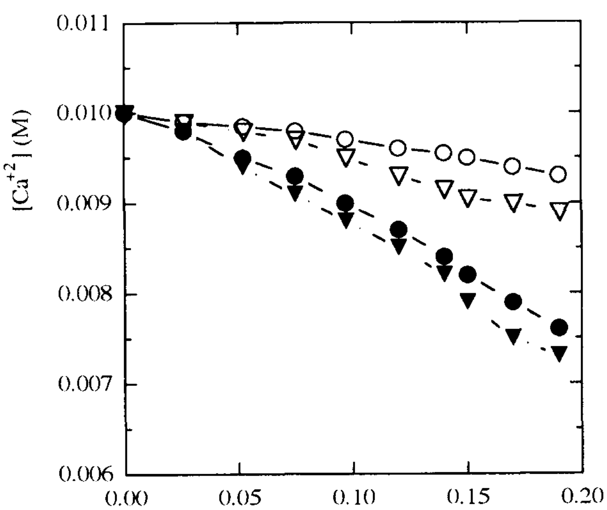

Figure 3 The relationship between the equilibrium calcium ion concentration and resin content (○) S8; (●) S15; (▽) S22; (▼) S34.

Fluidity of Mortars

One major function of water reducing admixtures is to maintain the workability of cementitious materials with low water/cement ratio.[7] Table II lists the fluidity of mortars with or without resin present. The fluidity is indicated by the flow spread diameter of the material. Higher diameter value means greater fluidity or better workability. The mortar without resin present exhibits the worst fluidity, which implies the existence of a strong attractive force or frictional force among the cement particles. Addition of resin into mortar would reduce the frictional force and promote the dispersion of the cement particles.[3] Thus, higher fluidity is achieved. The fluidity was further found from Table II to be increased with resin concentration. And resins (S30, S34) having higher S/C ratios are more effective in promoting the fluidity of the resulting materials.

In Table II mortars treated with NP100 show the greatest fluidity that is relevant to the excellent dis-

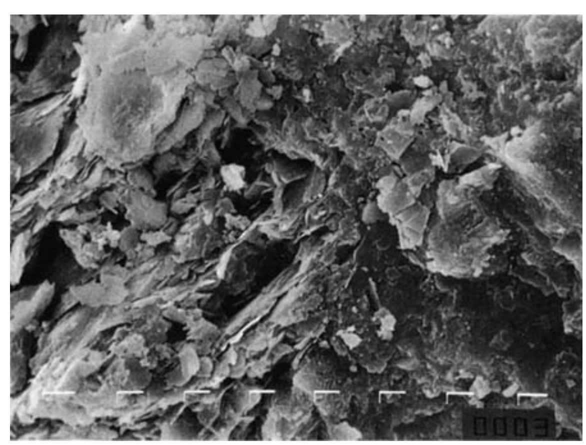

Figure 4 SEM photograph of mortar without resin present (× 1500).

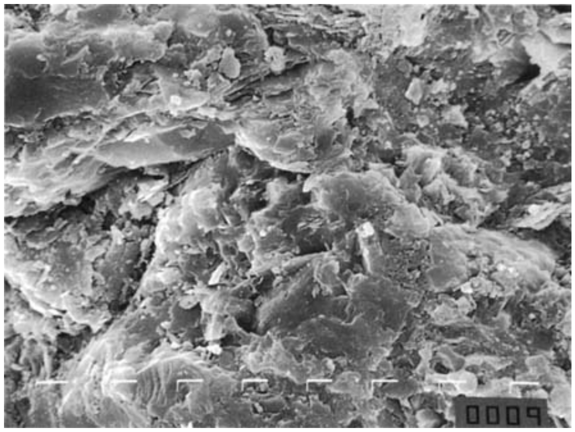

Figure 5 SEM photograph of mortar with S34 resin present (× 1500).

persing property of this admixture. SPRs are less effective in promoting the fluidity of mortars than NP100. The fluidifying effects of water reducers are reported to be related to the different amount of the monomer and the low molecular weight fraction.[15] Moreover, resins with high molecular weight (degree of polymerization above 1000) show low water reduction due to the occurrence of the flocculent interaction.[16] It is shown in Table I that the viscosity of SPR solutions is higher than that of the NP100 solution. This implies that SPRs contain a lesser amount of low molecular weight fraction and their molecular weights are higher than NP100. Therefore, SPRs are less effective than NP100. Nevertheless, the fluidity of mortar was improved significantly with the presence of SPR resin.

Interactions Between Resin and Calcium Ions

Because the resin contains sulfonate groups, it would have some interaction with $Ca(OH)_2$, which is one of the hydrated products of cement. As a result, the morphology or microstructure of the resulting mortar would be altered and the mechanical property or other properties of the material would also be affected.[6] The interactions between resin and calcium ions were studied by utilizing a calcium selective electrode to measure the equilibrium calcium ion concentration of various resin solutions.[12] A decrease of concentration value indicates interactions occurred between the resin and calcium ions. Lower value means stronger or more interaction in the system. Figure 3 shows that the equilibrium calcium ion concentration decreases with resin content. In addition, the resin (S15, S34) with higher S/C ratio appeared to interact with calcium ions more strongly.

Microstructure of Mortars

To demonstrate the morphological changes of the material due to the addition of resin, SEM photographs were taken of various mortars after 28 days curing. Figure 4 shows that the hydrated cement products of the untreated mortar were not uniformly distributed. Some large white spots corresponding to $Ca(OH)_2$ crystals were observed. By treating with S34 resin, the resulting mortar becomes more consolidated (Fig. 5) as a result of the dispersion effect and the lubrication action of resin.[5] $Ca(OH)_2$ crystals are smaller and more uniformly dispersed. This is due to the retarding action of resin on the cement hydration[15] and the interaction between resin and calcium ions.[5,6] The amount of $Ca(OH)_2$ in 1 wt % S34 treated mortar after 28 days curing, from DSC measurements, is about 90% of that of the untreated.

In contrast, Figure 6 shows the SEM photograph of mortar with the addition of S8 resin. As S8 contains less S/C ratio and has molecular weight higher than S34, it becomes less effective in densifying the material and the microstructure was observed to be similar to that of the untreated. The amount of $Ca(OH)_2$ in 1 wt % S8 treated mortar after 28 days curing is about 93% of that of 1 wt % S34 treated mortar. Because S8 has less interaction with calcium ions than S34, it is clear that the decrease of the $Ca(OH)_2$ amount in the resulting material results from its stronger retarding action on cement hydration.

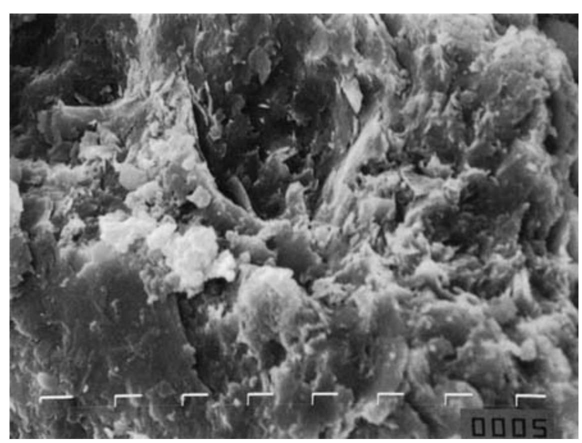

Figure 6 SEM photograph of mortar with S8 resin present (× 1500).

Table III Compressive Strength of Mortars Treated with 1 wt % of Various Resins after 28 Days Curing

Resin	S8	S15	S22	S30	S34	NP100
Compressive strength (MPa)	53 ± 2	60 ± 2	54 ± 2	65 ± 2	66 ± 2	70 ± 2

The compressive strength of untreated mortar is 56 ± 2 MPa.

Compressive Strength of Mortars

Table III lists the compressive strength of mortars treated with various resins after 28 days curing. Mortars treated with resins have generally higher compressive strength than the untreated. As discussed earlier, higher strength is due to better dispersion of cement particles, some interactions with calcium ions, and better compaction of the structure when resin was included in the material.[4,5] Especially for those resins having higher S/C ratio, the improvement in strength is more significant. The strength of 1 wt % S34 treated mortar after 28 days curing is 66 MPa, which is about 18% higher than that of the untreated. Furthermore, this value is close to that of 1 wt % NP100 treated mortar (70 MPa). On the other hand, in resins with low S/C ratio (< 0.32), the improvement is insignificant and the strength of the resulting mortars is even worse than that of the untreated. This shows that SPR could be used as a dispersing agent if the degree of sulfonation is controlled carefully during synthesis.

CONCLUSIONS

The prepared sulfonated phenolic resin has the potential to be used as a water reducing admixture. It could decrease the surface tension of water and be used as a dispersion agent in cementitious materials. Addition of resin in mortars was found to improve the workability, densify the structure, and increase the compressive strength of the resulting materials. The resins with higher sulfonate group content and lower molecular weight appear to perform more effectively.

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