Water-Soluble Sulfonated Phenolic Resins. III. Effects of Degree of Sulfonation and Molecular Weight on Concrete Workability

KUNG-CHUNG HSU,[1] SHENG-DA CHEN,[1] NAN SU[2]

[1] Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan 116, Republic of China

[2] Department of Construction Engineering, National Yunlin University of Science and Technology, Yunlin, Taiwan, 640, Republic of China

Received 12 March 1999; accepted 3 June 1999

ABSTRACT: The effects of the degree of sulfonation (DS) and molecular weight (MW) of sulfonated phenolic resins (SPF) on the flow properties of cementitious materials were investigated. SPF resin was prepared from phenol, formaldehyde, and sodium bisulfite through a four-step reaction. It was found that an increase in either DS or MW would enhance the dispersion effects in the system. The results indicate that the fluidity of cement pastes and the workability of concrete increased with higher DS until the resin was fully sulfonated. For resins with sufficient sulfonation, the performance of cementitious materials would increase with increasing MW. Apparently, resins with MW of about 3×10^4 are most effective in promoting concrete properties in terms of workability and compressive strength. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1762–1766, 2000

Key words: sulfonated phenolic resin; degree of sulfonation; molecular weight; workability

INTRODUCTION

Water-soluble polymers have been applied in many areas such as mineral processing, water treatment, or coatings.[1,2] Another important area of application is in the construction industry.[3] Only a small amount of the polymer, known as a high-range water reducer or a superplasticizer, can significantly improve the workability, mechanical strength, and other properties of concrete. The roles of this chemical admixture are to (1) reduce the rheological properties of fresh concrete without segregation or bleeding; (2) act as a lubricant or a dispersing agent so that solid particles become more uniformly dispersed; (3) interact with cement or hydrated products to modify the morphology of material; and (4) make hardened concrete stronger or more durable.[4–6]

Lignosulfonates, sulfonated melamine formaldehyde condensates, and sulfonated naphthalene formaldehyde condensates are three typical superplasticizers used commercially. These admixtures, after being adsorbed on cement particles, create electrostatic repulsions and overcome attractive forces. This results in the dissociation of the cement agglomerates into primary particles with a significant decrease in the viscosity of the material system.[7] In addition, the polymers would decrease the surface tension of water, produce lubricating films at particle surfaces, or alter the courses of cement hydration.[5]

It is clear that the degree of sulfonation (DS) and molecular weight (MW) are two important properties of admixtures governing the flow prop-

Correspondence to: K.-C. Hsu.
Contract grant sponsor: National Science Council of the Republic of China; contract grant number: NSC-86-2211-E-003-001.

Journal of Applied Polymer Science, Vol. 76, 1762–1766 (2000)

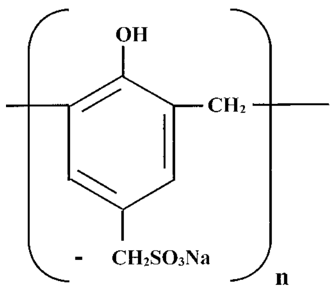

Figure 1 The chemical structure of SPF resin.

erties of cementitious materials.[8,9] Regarding the latter factor, Anderson et al.[7] reported that admixtures with higher MW gave greater negative zeta potential, and would, therefore, have a better dispersing capability. Basile et al.[10] found that the fluidifying effect for cement pastes could be increased by reducing the content of the monomer and increasing the MW of the condensates. Moukwa et al.[9] indicated that there were optimal degrees of polymerization for best performance in concrete in terms of water reduction, air entrainment, setting time, and compressive strength. Although the effect of DS is of equal importance, this factor has rarely been studied. Nevertheless, it has been mentioned that the number of sulfonated groups per naphthalene ring of sulfonated naphthalene formaldehyde condensates should be close to 1.[11]

Previously, we have developed a water-soluble sulfonated phenolic resin (SPF) as a chemical additive for concrete.[12] For this article, SPF samples with different DS or MW were prepared. These samples were added into cement pastes and concrete. The viscosity of these cement pastes was measured, and the workability of the resulting concrete was evaluated. Thus, the effects of DS and MW of SPF resin on the dispersion effects could be examined.

EXPERIMENTAL

Preparations of SPF Resins

The SPF resin was prepared from formaldehyde, phenol, and sodium bisulfite through a four-step reaction. Details of the preparation procedure can be found in our previous article.[12] In this study, resins with different DS or MW were obtained through controlling reaction conditions. Figure 1 shows the chemical structure of SPF resin.

Preparations of Cementitious Materials

Resin was first dissolved in water to form a 20 wt % solution. Cement pastes were made by mixing water and type I Portland cement with or without addition of resin solution. The water/cement (W/C) ratio was 0.30; and the resin/cement (SP/C) ratio ranged from 0 to 4 wt %. Concrete was made by mixing water, type I Portland cement, river sand, and gravel with or without addition of resin solution. Mixing of concrete was made following ASTM C13. The W/C ratio was 0.30; the cement/sand/gravel ratio was fixed at 1/1.13/1.36; and the SP/C ratio ranged from 0 to 4 wt %.

Viscosity Measurements

The viscosity of either resin solutions or cement pastes was measured by a Brookfield DV-II viscometer.

Sulfur/Carbon (S/C) Ratio Measurements

The S/C ratio of resin was measured by a Leco CS-244 analyzer. S/C represents DS or the number of sulfonate groups in the corresponding resin molecules.

Gel Permeation Chromatography (GPC) Measurements

MW of SPF resin was determined from GPC measurements that were carried out with a Jasco liquid chromatography equipped with two coupled columns Shodex OHpak KB802.5 and KB804, a pump (Jasco PU-980), and a UV detector (Jasco UV-970) at a wave length of 254 nm. The samples were analyzed using a 0.1-M KCl/methanol (80/20) aqueous solution as eluant, at a flow rate of 1 mL/min. Monodispersed polystyrene sulfonates of different MW (1600–4000–6500–16,000) were used as calibration standards.

Workability Test

The workability of concrete was indicated by the slump value from a slump test according to ASTM C143. The apparatus for this test consists primarily of a hollow mold in the form of a frustrum of a cone with the base 20 cm in diameter, the top 10 cm in diameter, and the height 30 cm. The mold is filled with concrete in three layers of equal volume; each layer is rodded 25 times with a steel rod. The mold is then lifted away vertically, and the slump is measured by determining the difference between the height of the mold and the height of the concrete over the original center of the base of the specimen.

Compressive Strength Test

Concrete specimens of 10 $\varphi \times 20$ cm were prepared, cured, and tested at the ages of 3, 7, and 28 days according to ASTM C39.

Table I Characteristics of Resins

Resin	#1	#2	#3	#4	#5
S/C	0.36	0.38	0.33	0.32	0.30
MW, (g/mol)[a]	13,300	12,800	13,200	12,600	13,100

[a] MW is number-average molecular weight.

RESULTS AND DISCUSSION

Effect of Degree of Sulfonation of Resin

Table I lists the S/C ratio and MW of series 1 samples. It shows that the MW of each sample is close to 1.3×10^4, and the S/C values range from 0.3 to 0.38. Figure 2 shows the effect of S/C of resin on the viscosity of aqueous solutions containing 20 wt % solid resin. As S/C increases, the solution viscosity decreases first, and then approaches a constant value when S/C is greater than 0.34. Resin with a higher S/C value indicates that it has greater DS, and contains more sulfonate groups, and would be easier to disperse and dissolve in the solution. Therefore, the solution would become less viscous. When the S/C value is higher than 0.34, the polymer is thought to be fully sulfonated, and the solution viscosity reaches a minimum, and is independent of S/C thereafter. Resin containing a sulfonate group in each structure unit (see Fig. 1), is regarded as being sufficiently sulfonated in preparation, and its theoretical S/C value is 0.33. The observed value (0.34) from Figure 2 is slightly higher than the theoretical one, because there would be more than one sulfonate groups on the chain ends of polymer molecules.

Figure 3 shows the effect of the S/C value of SPF resin on the viscosity of cement pastes (W/C = 0.30). In general, along with increasing S/C value, the paste viscosity decreases first, and then levels off. It is reported[13] that cement particles would contain some positive charges on the surface during the hydration period, which favors the adsorption of polymer with more sulfonated groups on solid particles. The cement thereby becomes more negatively charged, which leads to stronger electrostatic repulsion among cement particles.[7] This causes the observed plasticizing effects, and the cement pastes would become less viscous. The reduction in viscosity is responsible for improving fluidity of the resulting cementitious materials. At constant S/C, the paste viscosity decreases with resin concentration initially, reaches a minimum, and increases subsequently. The viscosity of pastes with 2% polymer appeared to be the lowest. Normally, pastes with chemical admixtures can be regarded as concentrated suspensions. According to Farris' model,[14] the viscosity of pastes depends on the viscosity of polymer solutions and the volume fraction of solid particles. When polymer concentrations increase, the solutions and the resulting pastes are expected to be more viscous. However, the added polymer, as a dispersing agent, can disperse cement particles,

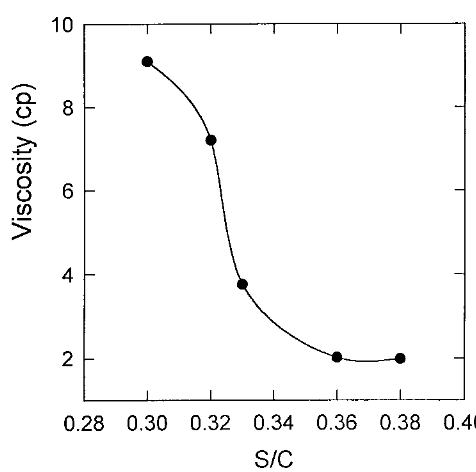

Figure 2 The effect of S/C on the viscosity of resin solution.

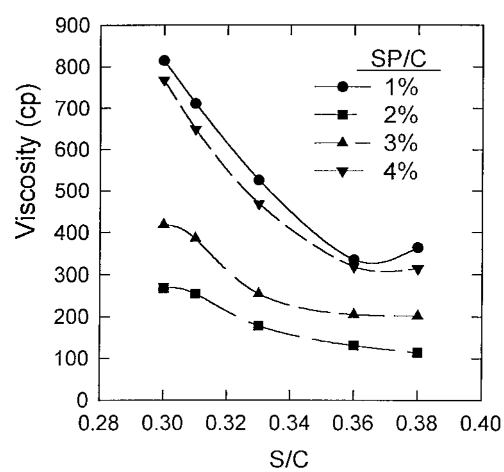

Figure 3 The effect of S/C on the viscosity of cement pastes.

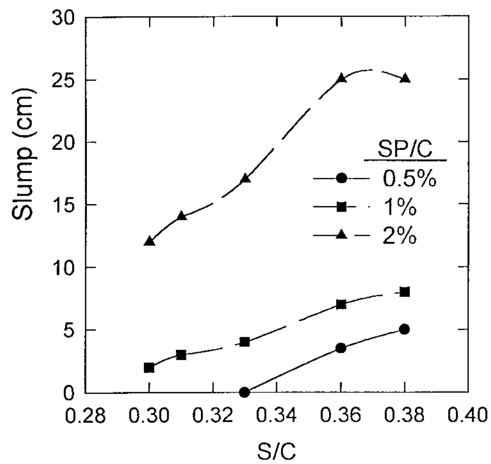

Figure 4 The effect of S/C on the slump of concrete.

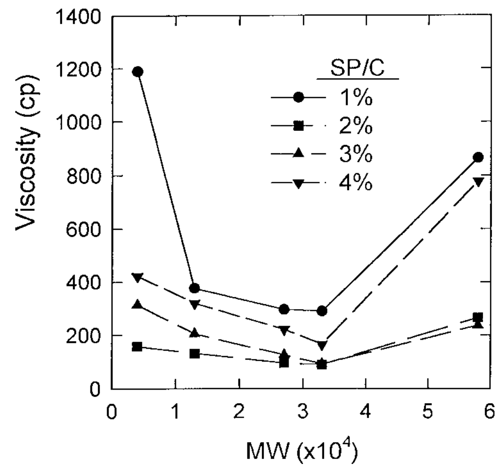

Figure 5 The effect of MW on the viscosity of cement pastes.

cause plasticizing effects, and therefore, decrease the paste viscosity. The concentration of SPF to produce pastes with minimum viscosity was found to be about 2%; this corresponds to the situation that the cement surfaces are saturated with adsorbed polymer. When polymer concentration is greater than 2%, the increased amount of SPF could not enhance the dispersion effects further. On the contrary, the dispersion effects may be decreased because the repulsion force among cement particles is decreased as the double layer becomes compressed in solution with higher ionic strength. Moreover, the occurrence of some bridging phenomena among cement particles or polymer entanglements is possible in a more concentrated solution.[9] Therefore, the resulting paste becomes more viscous.

Figure 4 shows the effect of S/C of SPF on the workability of concrete with W/C equal to 0.30. It is clear that the slump of concrete increases with either S/C or dosage. When S/C is greater than 0.36, the added SPF is completely sulfonated, and the resulting concrete exhibits the highest slump value. This is consistent with the previous results.

Effect of Molecular Weight of Resin

From the above results, it is clear that SPF resin with sufficient sulfonation is more effective in dispersing solid particles or increasing the workability of concrete. In the following, series 2 SPF samples were prepared and used. All these samples were fully sulfonated, i.e., their S/C values are greater than 0.34, but their MWs are different. Figure 5 shows the effect of MW on the viscosity of cement pastes (W/C = 0.30). As expected, the paste viscosity decreases with increasing MW of polymer. The observed lower paste viscosity for the higher degree of polymerization is attributed to greater negative charges on the cement surface, and therefore, stronger electrostatic repulsions generated among solid particles.[7] The optimum MW for the admixture, in achieving the best plasticizing effects, is about 3×10^4. For SPF resin with MW above the optimum value, the paste viscosity begins to increase because of the occurrence of the flocculent interactions.[9] Apparently, cement paste with 2% resin exhibits a minimum viscosity.

Figure 6 shows the effect of MW of SPF resin on the slump of concrete with W/C = 0.30. There is no flow for concrete without the presence of admixtures at such a low W/C ratio. Addition of SPF resin would reduce the frictional force and promote the dispersion of solid particles. There-

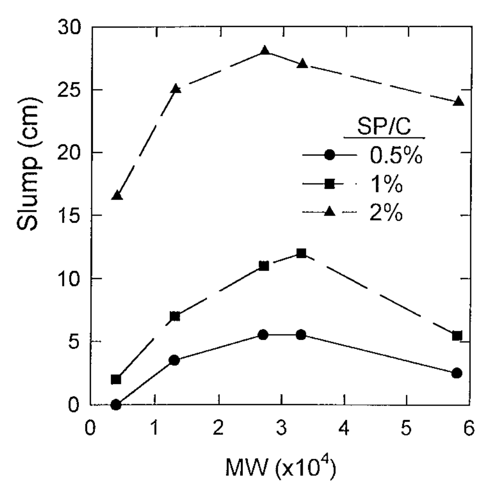

Figure 6 The effect of MW on the slump of concrete.

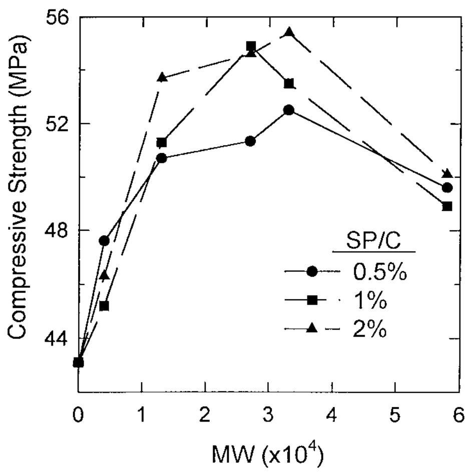

Figure 7 The effect of MW on the compressive strength of concrete.

fore, the fluidity of the resulting materials was improved. In general, the slump of the concrete was found to be greater with increasing the concentration or MW of the polymer, as seen in Figure 6. Polymers with MW of about 3×10^4 give concrete the greatest fluidity. At a 2% dosage, except for low MW polymer, the slump values of all concrete are greater than 25 cm, which is one of the criteria of high-performance concrete defined in Taiwan.[15]

Figure 7 shows the effect of MW of SPF resin on the compressive strength of concrete cured for 28 days. The trend in this figure appears to be similar to that in Figure 6, i.e., the compressive strength also rises with increasing concentration or MW of SPF resin. The maximum value also occurs at an MW of about 3×10^4. The improvement in properties such as workability and compressive strength can be attributed to the dispersion effect of SPF resin in the concrete. The effect of polymer on workability seems to be more significant than that on compressive strength.

From the results mentioned above, the effect of DS of resin on concrete workability appears to be similar to that of resin MW. In other words, an increase in either DS or MW would produce the dispersion effects, and therefore, improve the fluidity of concrete. Furthermore, it is worth mentioning that the former is, in fact, more influential than the latter, because it was found in another study on mortars that the fluidity and the compressive strength of materials decreased with MW if resins were under incomplete sulfonation.[16]

CONCLUSIONS

Both DS and MW of SPF resin affect the performance of cementitious materials. The fluidity of cement pastes or the slump of concrete is decreased with higher S/C values until the resin was sulfonated sufficiently. For those SPFs with sufficient sulfonation, the performance of cementitious materials increases with the degree of polymerization. Furthermore, resins with MW of about 3×10^4 gave the best concrete properties in terms of workability and compressive strength.

The authors are grateful for the support of this work by the National Science Council of the Republic of China (Contract # NSC-86-2211-E-003-001).

REFERENCES

1. Molyneux, P. Water-Soluble Synthetic Polymers: Properties and Behavior; CRC Press: Boca Raton, FL, 1984.
2. Piirma, I. Polymeric Surfactants; Marcel Dekker: New York, 1992.
3. Hwang, C. L., Ed. Proceedings of R&D and Promotion of High Performance Concrete, Taipei, Taiwan, ROC, 1997.
4. Aitcin, P. C.; Jolicoeur, C.; MacGregor, J. G. Concrete Int 1994, 16, 45.
5. Rixom, M. R.; Mailvaganam, N. P. Chemical Admixtures for Concrete; E & FN SPON: New York, 1986, 2nd ed.
6. Gagne, R.; Boisvert, A.; Pegeon, M. ACI Mater J 1996, 93, 111.
7. Anderson, P. J.; Roy, D. M.; Gaidis, J. M. Cement Concrete Res 1988, 18, 980.
8. Lahalih, S. M.; Absi-Halabi, M.; Shuhaibar, K. F. J Appl Polym Sci 1987, 33, 2997.
9. Moukwa, M.; Youn, D.; Hassanali, M. Cement Concrete Res 1993, 23, 122.
10. Basile, F.; Biagini, S.; Ferrari, G.; Collepardi, M. ACI Special Pub SP119–11, 209, 1989.
11. Aitcin, P. C. High-Performance Concrete; E & FN SPON: New York, 1998.
12. Hsu, K. C.; Lee, Y. F. J Appl Polym Sci 1995, 57, 1501.
13. Ghosh, S. N., Ed. Advances in Cement Technology; Pergamon Press: New York, 1983.
14. Farris, J. Trans Soc Rheol 1968, 12, 281.
15. Chern, J. C.; Hwang, C. L.; Tsai, T. H. Concrete Int 1995, 15, 71.
16. Lee, Y. F.; Chen, S. D.; Hsu, K. C. Supplementary papers of Fifth CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, 97, 1997.