Synthesis and Properties of High-Sulfonated Melamine–Formaldehyde Resin

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SYNOPSIS

High-sulfonated melamine–formaldehyde (HSMF) resins were prepared with 1.0–2.0 of sulfite/melamine (S/M) molar ratio. The factors affecting the preparation and the properties of the resin were studied. Chemical analysis indicated that there are 0.98–1.96 sulfonate groups per unit of the polymeric chain. The viscosity of HSMF resins is lower than that of sulfonated melamine–formaldehyde (SMF) resins, and the HSMF resins are more effective superplasticizers at small dosages of admixture. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Sulfonated melamine–formaldehyde (SMF) resins are playing important roles in construction industry and other fields. In the past two decades, researchers have developed many methods to prepare SMF resins which show good performance in concrete. However, in the syntheses with these methods the sulfite/melamine (S/M) molar ratios were between 0.5–1.2, and no study was reported regarding the preparation of SMF resins with S/M molar ratios above 1.2.[1-6]

To distinguish from the SMF resins synthesized with S/M molar ratios below 1.2, we refer to the resins synthesized with S/M molar ratio above 1.2 as high-sulfonated melamine–formaldehyde (HSMF) resins. Since the sulfonate groups solubilize melamine–formaldehyde (MF) resins, give the resins electronegative charge, and block one or more of the active chain propagation centers, the S/M molar ratio is expected to affect strongly the properties of the resin and the condensation conditions. Therefore, HSMF is different from SMF in preparation and properties.

In this paper, we present and discuss the results obtained from the preparation of HSMF resins and their influence on cement sand mortar when they are used as superplasticizers.

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EXPERIMENTAL

Materials

Melamine obtained from Sichuan Chemical Factory (Chengdu, Sichuan) was used without further purification. Formaldehyde aqueous solution stabilized with methanol was obtained from Guangzhou Solvent Factory (Huangpu, Guangzhou: formaldehyde, 36–37% w/w; methanol, 10–12% w/w). Sodium sulfite and sodium bisulfite (laboratory reagent) was used without further purification.

Preparation Procedure for Resins

The preparation procedure for HSMF resins is divided into four steps: hydroxymethylation, sulfonation, low-pH condensation, and high-pH condensation. Following is an example of the procedure used to prepare the HSMF resin:

Step 1: 150 ml formaldehyde aqueous solution of 37% concentration diluted with 50 ml of water is heated to 55°C. 56.9 g of melamine is added to the formalin solution after the pH of the solution is adjusted to 8.5 with 2.25 ml 1 N NaOH solution. The temperature of the reaction mixture increases automatically while the melamine dissolves, and rises to 59–60°C when the solution becomes clear. The reaction mixture is then heated at 60°C for 10 min.

Step 2: 8.4 g of Na_2SO_3 dissolved in 50 ml of water is added to the solution, causing an increase in pH to 12.0. Then 62.4 g of $NaHSO_3$ is added, causing an increase in temperature of 10–12°C while the sulfite salt is dissolving. The temperature of the solution is raised to 80°C in 15 min and kept at the new temperature for 80 min.

Step 3: The solution is then cooled rapidly to 53°C and 25 ml of 30% (w/w) H_2SO_4 is added, causing a drop in pH to 3.8 and an increase in temperature to 55°C. The solution is kept under these conditions for 60 min.

Step 4: 20 ml of 30% (w/w) NaOH is added to the solution, causing an increase in pH to 6.5. The solution is heated to 85°C in about 20 min and kept at that temperature for 60 min. The reactants are stirred during the whole reaction time. The solution is finally cooled to room temperature, filtered to remove solid particulates, and treated with sodium hydroxide to adjust its pH to 8.5.

The resin prepared according to this procedure has a solid content of approximately 40%.

Testing Resin Effect on Cement Sand Mortar Properties

The testing methods were according to JGJ 56–84 "Water Reducing Admixture Used for Concrete—Quality Requirements and Testing Methods." A control mix design as follows was used: Cement, 1.00; Sand, 2.50; Water, 0.44.

In testing the resin, cement and sand were first dry-mixed, then water was added with continuous mixing, and finally the resin solution was added. The whole mixing time was 3 min. The percentage of the solid resin used in the mix was based on cement weight only.

RESULTS AND DISCUSSION

Preparation of HSMF Resins

The preparation of HSMF resins consists of four stages. The chemical change during these four steps are hydroxymethlation, sulfonation, low-pH condensation, and high-pH condensation (Scheme 1). Each step is dependent on pH, temperature, and reaction time.

Hydroxymethylation

Hydroxymethylation is simply an addition reaction between the amino group of melamine and the carbonyl group of formaldehyde at pH value of 8 or above (reaction 1):

$$-NH_2 + HCHO \rightarrow -NHCH_2OH \quad (1)$$

$$M + xF \xrightleftharpoons{pH_1,T_1,t_1} MFx \quad \text{(step 1)}$$

$$MFx + yS \xrightarrow{pH_2,T_2,t_2} MFxSy \quad \text{(step 2)}$$

$$MFxSy \xrightarrow{pH_3,T_3,t_3} P_1(MFxSy) \quad \text{(step 3)}$$

$$P_1(MFxSy) \xrightarrow{pH_4,T_4,t_4} P_2(MFxSy) \quad \text{(step 4)}$$

$$(x = 3.0\text{–}5.0 \quad y = 1.0\text{–}2.0)$$

Scheme 1

A molecule of melamine has six active sites on its chemical structure, and can react with six molecules of formaldehyde to form hexamethylolmelamine. To prepare HSMF resin with more than 1.2 sulfonate groups per unit of the chain, multimethylolmelamine must first be obtained from the reaction of melamine with formaldehyde. On one molecule of multimethylolmelamine, more than 3.2 methylol groups are expected to exist, more than 1.2 of which are suggested to react with sodium bisulfite; others react with the methylol groups on the other unit to form a large molecular condensate. Therefore, the formaldehyde/melamine (F/M) molar ratio must be more than 3.2.

Hydroxymethylation is affected by the factors of pH, temperature, reaction time, and concentration of reactants. It is a long time for complete dissolution of the melamine at low pH and low temperature, while high pH and high temperature result in precipitation of methylolmelamine in a short time. For F/M molar ratio of 3.0–5.0, pH of 8.0–9.0, and temperature of 50–80°C, the reaction time of 15–30 min is better. Little condensation occurs at pH above 8, but it is noted that the pH of the reaction mixture drops during the proceeding of the reaction due to the formation of formylic acid and the reduction of NaOH resulting from the reaction between formaldehyde and NaOH. Therefore, it is necessary to maintain the pH above 8 in case possible premature condensation takes place in the hydroxymethylation stage.

Sulfonation

Sulfonation is initiated by the addition of sodium sulfite and sodium bisulfite, which hydrolyze in water to produce bisulfite ions in the methylolmelamine solution. The sulfonation is the reaction between bisulfite ions and methylolmelamine (reaction 2):

$$-NHCH_2OH + HSO_3^- \rightarrow -NHCH_2SO_3^- + H_2O \quad (2)$$

The mix of two sulfonates favors reaction control and a high reaction degree of sulfonation. Sodium bisulfite is added as the main sulfonate and sodium sulfite as the assistant sulfonate. Hydrolysis of sodium sulfite produces hydroxide ions as well as bisulfite ions, which raise the pH of the solution to 12 (reaction 3).

$$Na_2SO_3 + H_2O \rightarrow 2Na^+ + HSO_3^- + OH^- \quad (3)$$

At the end of hydroxymethylation, the direct addition of sodium bisulfite may cause extensive condensation due to its acid, and using hydroxide to raise pH value easily results in precipitation of methylolmelamine. Sodium sulfite is not the same as hydroxide, because sulfonation starts as soon as it is added.

To investigate the reaction degree of sulfonate, various F/M and S/M molar ratios were adopted to prepare SMF and HSMF resins, and the number of sulfite groups on the chain and the viscosity of the resins were determined. Table I shows the results.

The number of sulfonate groups per unit of the polymeric chain was determined by chemical analysis. The free HSO_3^- and SO_3^- were analyzed by titration with 0.01 N I_2 after the resins had been diluted to 2% solid content. Na_2CO_3 solution was added to release $-HSO_3^-$ from the compound combined by free formaldehyde and $NaHSO_3$. Then the number of $-SO_3^-$ per unit of the chain was calculated. Furthermore, the fact that the diluted solution of the resin was titrated with the titrant of cationic surfactant of cetyltrimethylammonium bromide showed the same results.

The results indicate that the sulfonate, including sodium sulfite and sodium bisulfite, easily reacts with methylolmelamine even if the S/M and F/M ratio vary. The fact that up to 1.96% sulfonate groups have been joined onto the resin chain concludes that HSMF resins have been prepared.

Table I Effect of S/M Ratio on the Number of $-SO_3^-$ per Unit of the Chain and the Viscosity of the Resins[a,b]

No.	F/M	S/M	$-SO_3^-$/M	Viscosity (cp)
1	4.5	1.0	0.984	26.43[c]
2	4.5	1.2	1.175	23.31
3	4.5	1.4	1.374	16.95
4	4.5	1.6	1.576	14.81
5	4.5	1.8	1.763	9.68
6	4.5	2.0	1.959	8.05
7	3.5	1.6	1.569	9.25
8	4.0	1.6	1.558	11.15
9	5.0	1.6	1.575	15.10

[a] Reaction conditions were: pH_1, T_1, t_1 = 8.5, 60°C, 20 min; pH_2, T_2, t_2 = 12.5, 80°C, 80 min; pH_3, T_3, t_3 = 3.3, 55°C, 60 min; pH_4, T_4, t_4 = 6.5, 85°C, 60 min.

[b] Viscosity of the final solution (35% solid content) at 25°C.

[c] t_3 = 12 min; the resin gelate when $t_3 > 20$ min.

The factors affecting the sulfonation have been studied. If the temperature is lower than 60°C, sodium bisulfite cannot dissolve completely over a long time, resulting in gelation during the third step. A reaction time less than 40 min and pH lower than 10.5 also result in gelation. Variation of temperature between 70–100°C, reaction time of 60–120 min, and pH 10.5–13.0 apparently cannot affect the viscosity of the resins. However, the effect of the resins prepared according to various conditions on the concrete is not the same, as will be discussed in the next paper.

Condensation

The condensation is divided into two stages: Low-pH condensation (step 3) and high-pH condensation (step 4). In the low-pH condensation stage, the pH

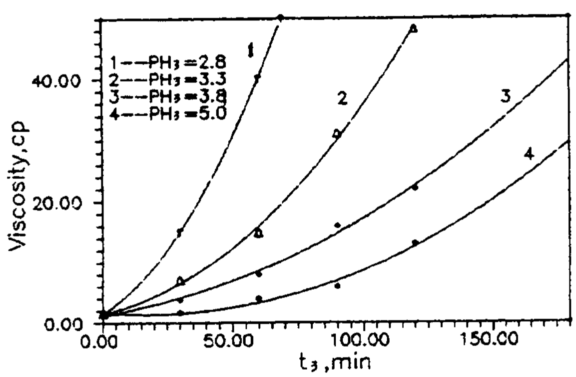

Figure 1 Effect of pH and reaction time of Step 3 on the viscosity of the resins.

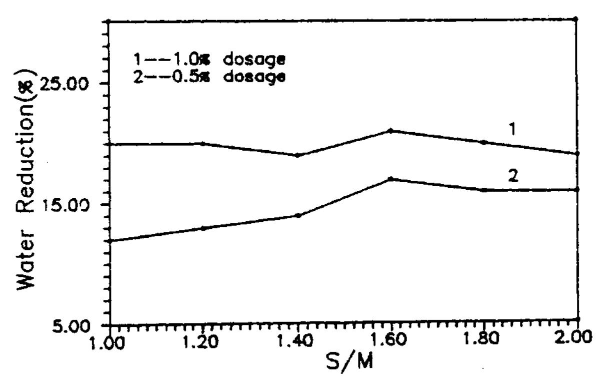

Figure 2 Variation of water reduction of superplasticizers prepared with various S/M molar ratios.

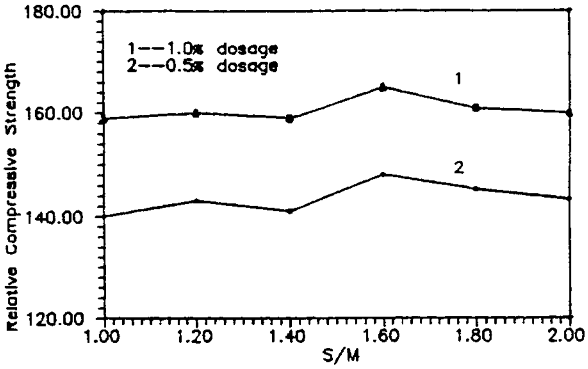

Figure 3 Relative compressive strength (compared with the plain sample, which is 100) of cement sand mortar admixed with superplasticizers. (Hydration time = 7 days.)

range is 2–5 and temperature is 50–60°C. This favors the resin forming at a rapid rate. In the high-pH condensation stage, where pH range is 6–7 and temperature is about 80°C, the resin forms at a slow rate. The combination of two stages favors the control of the reaction and the stability of the resin. However, if the pH of step 4 is above 8, the viscosity of the solution decreases due to the bond cleavage in the polymer backbone,[5] resulting in the molecular weight of the resin not being high enough to enable the resin to perform effectively in concrete.

From the results of Table I, we can see that the higher the S/M ratio, the lower the viscosity of the resin. At low S/M ratios, the resin tends to gelate during condensation at a rapid rate, due to the large number of methylol groups on the sulfonated monomer. At high S/M ratios, sulfite blocks the active chain propagation centers, and the large volume of $-SO_3^-$ groups affects the activity of the methylol group on the same nitrogen atom, resulting in limited polycondensation and low viscosity of the resin solution.

The condensation is also affected by the factors of pH, temperature, and reaction time. Figure 1 shows the effects of the pH and the reaction time of step 3 on the viscosity of the resin.

Properties of HSMF Resins as Superplasticizers

SMF resins were reported to be excellent dispersants of cement particles, and they have been widely used as concrete superplasticizers in the construction industry. The properties of SMF resin as concrete superplasticizers are attributed to the action of the sulfonate groups on the polymeric chains. As the number of the sulfonate groups on the polymeric chain increases, the HSMF resins are expected to be more effective superplasticizers.

Figure 2 shows the variation of the water reduction of superplasticizers prepared with various S/M molar ratios. Figure 3 shows the relative compressive strength of cement sand mortar admixed with the superplasticizers.

When the S/M molar ratio is below 1.6, the water reduction increases with the increase of S/M at 0.5% dosage, while it remains almost the same at 1.0% dosage. When S/M is above 1.6, water reduction tends to drop. The variation of compressive strength is not evident as that of water reduction.

CONCLUSIONS

HSMF resins have been prepared under suitable reaction conditions. It is found that the sulfite reacts easily with methylolmelamine. When the S/M molar ratio is between 1.0–2.0, the property of water reduction of HSMF resins is much better than that of SMF resin at small dosage of admixture, while they are almost the same at large dosage of admixture. The compressive strength of cement mortar prepared with HSMF resins is not evidently different from that with SMF resins.

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