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Synthesis of Water-soluble Highly Sulphonated Melamine-formaldehyde Resin as an Effective Superplasticizer in Concrete*

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ABSTRACT

Highly sulphonated melamine-formaldehyde resin (HSMF) is prepared by atmospheric reflux from melamine, formaldehyde, sodium sulphite and meta-bisulphite through a four-step reaction. The sulphite/melamine molar ratio between 1.0–2.0 and the formaldehyde/melamine molar ratio varied between 3.0 and 5.0. The effects of degree of sulphonation and F/M ratio on the fluidity of resin solutions were studied. The F/M ratio is directly and S/M ratio is inversely proportional to viscosity of the resin solution. Because of lower viscosity of HSMF resins than that of SMF resins, it is expected to be more effective superplasticizer in cement sand mortar. The results show that viscosity of the solutions increases with increasing $\bar{M}_w$ of the polymers until a critical molecular weight, beyond which there is a rapid increase in viscosity due to formation of a hexagonal close-packed system.

Key Words: water-soluble, highly sulphonated, melamine-formaldehyde resin, synthesis, concrete, superplasticizer

INTRODUCTION

Superplasticizers are widely used as water reducing admixtures in concrete; they also increase the workability of mixture and lower water requirement of concrete, so that they lubricate the concrete for facile pumping at high level positions and lead to a concrete of higher compressive strength and improved durability [1].

On the basis of theory, a water/cement ratio of about 0.27 is adequate for the hydration of cement, so any water in excess of that amount in concrete for improving the workability will reduce the compressive strength of concrete [2]. It is also well known that decreased water/cement ratios result in cured concrete of improved strength [3, 4].

Slump is also a measure of the workability of concrete. High slump concretes can be placed with less mechanical vibration [3]. For a given slump, concrete can be formulated with less water. In addition,

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for a given water/cement ratio, it is necessary to have greater slump or improved fluidity. The low water/cement ratio and the high slump concrete modifications can be achieved by adding a suitable superplasticizer.

Addition of superplasticizers as chemical additives on cement sand mortar creates electrostatic charges. These negative charges cover the different cement pastes particles so that they repel each other and prevent any agglomeration or precipitation, thereby, causing the concrete to be lubricated and readily pourable.

The suitable superplasticizers are divided into five categories:

- Sodium or calcium lignosulphonate salts.
- Sulphonated and highly sulphonated melamine formaldehyde condensate products (SMF and HSMF).
- Sulphonated naphthalene formaldehyde condensate products (NFS).
- Sulphonated phenol formaldehyde condensate products (SPF) [5].
- Carboxylic acid salts.

Using a superplasticizer affects dispersion, adsorption, morphology and rheological properties of the cement [6]. Advantages of introducing superplasticizer in cement would be as follows:

- A rheological property such as viscosity of the concrete is reduced.
- The agglomerates of cement are dispersed into small particles, so the particles become more uniformly dispersed.
- The interaction of chemical additives with cement pastes decreases the concrete porosity and modifies its morphology.
- The compressive strength of concrete is increased.
- The shrinkage of concrete is decreased.

EXPERIMENTAL

Materials

Melamine was obtained from the Oroumieh Petrochemical Co. and used as received. Formaldehyde aqueous solution 34–35% (w/w) was obtained from Fars Chemical Industries Co. and was used as supplied. Technical grades of sodium sulphite and sodium metabisulphite were also used with no further purification.

Apparatus

The viscosity of solutions was measured using a Brookfield viscometer model LV1 at 25 °C. A Bruker model IFS 48 and Philips model PU 8800 spectrophotometers were used to obtain FT-IR and UV spectra, respectively. Molecular weight and molecular weight distribution of samples were determined by gel permeation chromatography (GPC) using Waters chromatograph model 150C with UV detector 484. The analysis was carried out by GPC using distilled water as eluent and ultrahydrogel with 250–1000 °A pore size as stationary phase at 25 °C.

Preparation of Highly Sulphonated Melamine Formaldehyde Resin

The following procedure is an example to illustrate the HSMF resin preparation: The HSMF resin is prepared by a four-step procedure [7].

Step 1

Formaldehyde aqueous solution (2.25 mol) of 34–35% (w/w) concentration diluted with 50 mL of water is heated to 55 °C. Melamine (0.45 mol) is added to reaction vessel after pH of the solution is adjusted to 8.5 with 1N sodium hydroxide solution. The temperature of the reaction mixture rises to 60 °C when solution becomes clear and it is then heated at 60 °C for 15 min.

Step 2

Sodium sulphite (0.066 mol) and sodium metabisulphite (0.36 mol) are added to reaction mixture. The pH increased between 12 and 13. The temperature is raised to 80 °C and kept for 80 min.

Step 3

The solution is cooled rapidly to 55 °C and pH is adjusted between 3.0 and 5.0 by addition of 30% (w/w) sulphuric acid. The solution is kept under these conditions for 60 min.

Step 4
To stop the reaction, slurry of calcium oxide in water is added to reaction mixture, causing an increase in pH to 6.0–7.0 and then heated to 85 °C and kept at that temperature for 60 min. The reactants are stirred during the whole reaction time. The solution is cooled to 20 °C, filtered and its pH adjusted to 8.0–9.0 with sodium hydroxide solution. The solid content of resin is determined by drying in an oven for 2 h at 60 °C.

RESULTS AND DISCUSSION

The reaction routes for production of the HSMF resin are divided into four steps: hydroxymethylation, sulphonation, low-pH and high-pH condensation.

Hydroxymethylation
The general addition reaction that takes place during this step is a nucleophilic attack of melamine on the carbonyl functional group of formaldehyde in alkaline media, which produces the different methylolmelamines. Different factors including, pH, temperature, reaction time and concentration of reactants affect this step (Chemical eqn 1).

$$-NH_2 + HCHO \longrightarrow -NHCH_2OH \qquad (1)$$

The molar ratio of formaldehyde to melamine is varied from 3.0–5.0.

Sulphonation
These sulphonated amino resins were produced by sulphonation of different methylolmelamines using a mixture of sodium sulphite and sodium metabisulphite. Firstly the sulphonating agents are hydrolyzed in water to produce bisulphite and hydroxide ions as follows (Chemical eqns 2 and 3):

$$Na_2SO_3 + H_2O \longrightarrow 2Na^+ + OH^- + HSO_3^- \qquad (2)$$

$$Na_2S_2O_5 + H_2O \longrightarrow 2Na^+ + 2HSO_3^- \qquad (3)$$

The presence of hydroxide ions raises the pH of the solution to 12–13 and then the bisulphite ions sulphonate the methylolmelamines in alkaline media (Chemical eqn 4).

$$-NHCH_2OH + HSO_3^- \longrightarrow -NHCH_2SO_3^- + H_2O \qquad (4)$$

This stage, involves the addition of a sulphonating agent to reaction medium containing the initial melamine-formaldehyde condensate. The sodium sulphite and sodium metabisulphite are the preferred sulphonating agents and their amounts are such that the ratio of sulphite ions to melamine is varied from 1.0 to 2.0. Among factors affecting the sulphonation step, pH, reaction time and temperature are of importance.

Low-pH Condensation
This stage is begun following completion of the sulphonation step by lowering the temperature of the reaction mass to about 50 °C. Lowering the pH of the reaction mixture between 3.0–5.0 by dilute sulphuric acid leads to resin condensation. During this type of condensation, ether-linkage type products are formed.

These products undergo further condensation reactions more rapidly with time or reduced pH of the solution, thus leading to more viscous solutions and high molecular weight in such an extent that gelation may occur (Chemical eqn 5).

$$-NHCH_2OH + -NHCH_2OH \longrightarrow$$

$$-NH-CH_2-O-CH_2-NH- + H_2O \qquad (5)$$

High-pH Condensation
This final stage involves stabilization of the resin solutions. To prevent gelation of the resin and reaching high molecular weights, it is necessary to stop the reaction in low pH condensation step. Therefore, pH of the reaction mixture is adjusted at 6–7 by adding calcium oxide slurry, which results in formation of calcium sulphate as precipitate.

During this type of condensation, high pH rearrangements are taken place and methylene-linkage type products are formed and the resin is stabilized (Chemical eqn 6) [8].

$$R\text{–}NHCH_2OH + H_2N\text{–}R \longrightarrow$$

$$R\text{–}NH\text{–}CH_2\text{–}NH\text{–}R + H_2O \qquad (6)$$

Among factors affecting the low-pH and high-pH condensation steps, an exact pH of the medium, reaction time and temperature are of importance.

This final resin solution is added to a concrete mixture in an amount ranging from 0–4.0 % based on the weight of the cement. This increases the slump of the paste and decreases the amount of water needed for the paste, and also improves the mechanical properties of concrete [2].

Many of the known sulphonated amino resins exhibit superplasticizing properties. But since these resin solutions contain sulphate ions as impurities, they can alter the hydration reaction of cement; hence they have undesirable effects on mechanical properties of concrete. HSMF resin was produced according to the procedure described and finally it was purified to remove sulphate ions [9].

Various methods have been used to identify the highly sulphonated amino resins. The ultraviolet spectra of HSMF resins were measured at 190–400 nm wavelength region and distilled water was used as diluent. The HSMF produces an absorption peak at 200–220 nm, which is a characteristic of HSMF resins (Figure 1) [10]. Resin infrared spectra were studied in KBr pellet form in the region 500–4000 cm^{-1}. The characteristic IR absorption bands of HSMF are as follows: a broad band at 3414 cm^{-1} is attributed to N–H and O–H groups; at 2953 cm^{-1} for stretching vibration of C–H groups. Four absorption bands at 766, 812, 1375 and 1560 cm^{-1} are related to melamine ring and $R\text{–}NH_2\text{–}CH_2\text{–}$ group. The broad band at 1182 cm^{-1} is related to stretching vibration of S=O and C–S of $R\text{–}SO_3^-$ group and the band at 1043 cm^{-1} is due to ether linkage group (Figure 2).

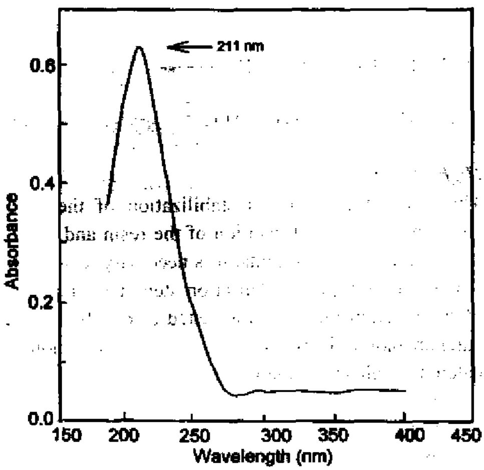

Figure 1. Ultraviolet spectrum of HSMF resin.

Table 1. The characteristics of resins.

Sample No.	$\overline{M}_w$	Viscosity (cp)	S/M	F/M
1	244006	32.8	1	5
2	225569	18.5	1.2	5
3	207159	11	1.4	5
4	191886	10.8	1.6	5
5	182310	10	1.8	5
6	176363	9.5	2	5

In the prepared samples (data in Table 1), at constant F/M molar ratio and varied S/M molar ratios between 1.0–2.0, weight average molecular weight ($\overline{M}_w$) and viscosity of the HSMF resins were measured. It should be noted that in all measurements the volume fraction (ϕ) of solutions is constant and equals to ϕ=0.4. The results show that viscosity of the resin solutions as well as $\overline{M}_w$ would decrease with increasing the S/M molar ratios. This is because by increasing the S/M molar ratio, the electrostatic forces in the resin become appreciable. At higher S/M molar ratios, the number of ionized sites on the polymer

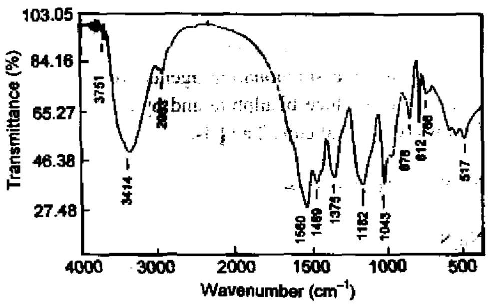

Figure 2. Infrared spectrum of HSMF resin.

increases, the electrostatic forces tend to straighten the polymer chains and increase the distance between neighboring chains. As a result, the viscosity as well as the $\overline{M}_w$ will decrease.

A plot of viscosity vs. $\overline{M}_w$ (data in Table1) indicates that viscosity of the solutions increases with increasing $\overline{M}_w$ of polymers (Figure 3), until a critical molecular weight ($\overline{M}_c$) beyond which there is a rapid increase in viscosity. As seen in the figure there is a critical molecular weight (210,000 g/mol) at which the viscosity is abruptly changed. The results indicate that to improve concrete properties in terms of fluidity of the cement paste, it is better that the $\overline{M}_w$ to be lower than 210,000 g/mol.

Since the polymeric chains on both sides of $\overline{M}_c$ point are too long, therefore a sharp increase in viscosity is probably attributed to the organized particles into a hexagonal close-packed network [11]. The point at which, the particles are big enough to go into a hexagonal close-packed system, $\overline{M}_c$, would thus lead to a rapid increase in viscosity. In this network, the fluidity of solvent is restricted. The number of total particles is constant, but the double layer parameter is increased with increasing the $\overline{M}_w$, thus leading to a rapid increase in viscosity.

Figure 4 shows the effect of F/M molar ratios

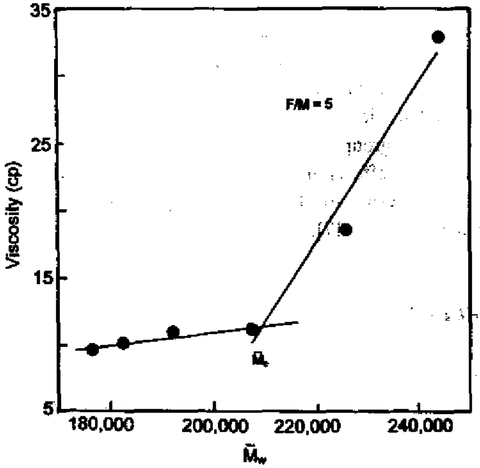

Figure 3. Variation of $\overline{M}_w$ with various viscosity (cp) at constant F/M molar ratio and varied S/M molar ratios.

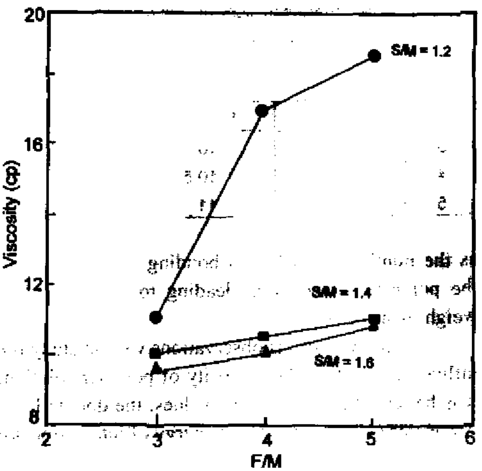

Figure 4. Variation of viscosity with various F/M molar ratios at constant S/M.

on viscosity of the resin solutions (40 % solid content) at 25 °C, at constant S/M molar ratio (data in Table 2). Viscosity of the resin solutions was found to increase with increasing F/M ratio for all reactions at similar conditions [12,13]. This can be attributed to higher rates of condensation reactions in resins containing more *N*-methylol functional groups [1], therefore, the presence of *N*-methylol groups should increase the degree of polymerization and branching in all cases.

The variations of $\overline{M}_w$ are studied at varied S/M molar ratios between 1.0–2.0 and constant F/M ratio. The results show that $\overline{M}_w$ of the resin solutions would decrease with increasing S/M ratios and vice versa (Figure 5). To illustrate the important relationship between S/M molar ratio and molecular weight, several resins were prepared according to the above process. All were prepared under similar conditions, at constant F/M ratio and different S/M ratios. As the degree of sulphonation increases, the negative charges of the anionic groups on the polymeric chains increase, thereby causing the chains to slide on each other more easily. On the other hand, the sulphonation of *N*-methylol groups would decrease the free functional hydroxy group on the triazine ring as well

Table 2. The characteristics of resins with values of viscosities related to constant S/M ratio.

F/M	Viscosity (cp)		
	S/M=1.2	S/M=1.4	S/M=1.6
3	11	10	9.5
4	17	10.5	10
5	18.5	11	10.8

as the number of hydrogen bonding that involves in the polymer system, thus leading to low molecular weight resin solutions.

From the various observations we can study the influence of pH on the viscosity of polymer solution. It is believed that at high pH values, the double layer parameter (1/k) and potential energy of interaction are reduced, thus giving an aggregation due to double layer compression [11]. In this case, the particles fall into a deep energy minimum and come into close contact; hence the number of total particles would decrease due to attraction, thus leading to a decrease in viscosity.

At low pH values, the double layer parameter (1/k) and potential energy of interaction are increased and hence the effect of electric field of particles expands. Therefore, a gelation occurs due to a long-range interaction of particles. In this case, the extent of overlap of particles would increase with increasing the particle size, thus leading to an increase in viscosity.

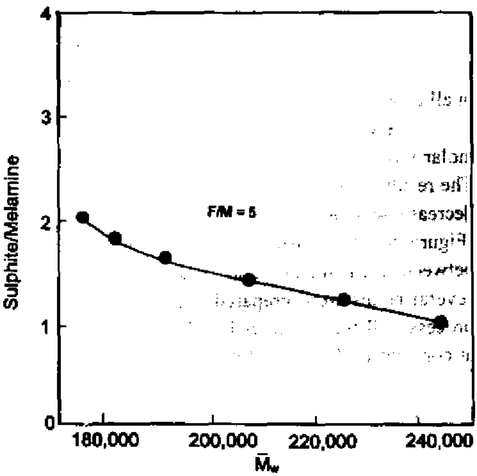

Figure 5. Variation of $\bar{M}_w$ with various S/M molar ratios at constant F/M.

CONCLUSION

Highly sulphonated melamine-formaldehyde resin was prepared according to a four-step procedure. The UV and IR spectra of this resin were analyzed and the variation of $\overline{M}_w$ with various viscosities at constant F/M ratio and varied S/M ratios is studied. The results show that viscosity of the solutions increases with increasing $\overline{M}_w$ of the polymers until a critical molecular weight, $\overline{M}_c$, beyond which there is a rapid increase in viscosity due to formation of a hexagonal close-packed system. The effects of different degrees of sulphonation and formaldehyde to melamine molar ratios of a number of resins are studied at S/M molar ratios between 1.0 and 2.0. The results show that the higher the F/M ratio, the higher the viscosity of the final solution and the higher the weight average molecular weight of the resin would be. Increased S/M ratio, results in lower viscosity of the final solution and weight average molecular weight of the resin. Therefore, S/M molar ratio is inversely proportional to viscosity of the solution and F/M molar ratio is directly proportional to viscosity of the solution. On the other hand, as the number of sulphonated groups per unit of the polymeric chains increases, the solubilizing effect of these groups increases and would enhance the dispersing effects of the resin. So it is expected that the HSMF resin to be a more effective concrete superplasticizer [7].

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