Effect of Reactant Ratios on Gel Point of Sulphonated Melamine–Formaldehyde Superplasticizer

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ABSTRACT

The effect of molar ratios of reactants on physical properties of sulphonated melamine-formaldehyde (a superplasticizer) prepared under different reaction conditions is studied. It is found that the more stable products are affected slightly by melamine to formaldehyde (M/F) and melamine to sodium metabisulphite (M/S) molar ratio. In addition, the pH, temperature and time are the main controlling factors for product stability.

Key Words: superplasticizer, sulphonated-amino resins, gel point, condensation, reactant ratios

INTRODUCTION

Superplasticizers are widely used as high-range, water reducing admixtures in concrete [1]. They increase the workability of the mixture enabling the lower water/solid (W/S) ratio to be used. Other factors being equal, the lower W/S ratios lead to higher compressive strength and improved durability [2].

Commercial superplasticizers are mainly based on sulphonated melamine-formaldehyde (SMF); a polymer with high molecular weight and contains polar groups which render it soluble in water. Interaction between superplasticizer and cement during the early stages of hydration is believed to take place through these polar groups [3]. The chemical and thermal stability of almost all water-soluble polymers are limited. This limitation in stability is determined by the free volume, and transport phenomena such as diffusion coefficient and viscosity. The free volume is the only parameter which determines the rate of molecular rearrangements [4].

The stability of SMF can also be limited by molar ratios of melamine to formaldehyde (M/F) and melamine to sodium metabisulphite (M/S). This can be proved by measuring the changes in the viscosity of the polymer solution because any molecular transformation, whether chemical or physical, influences the viscosity of the polymer solution. Therefore, the measurement of the viscosity of the polymeric solution would be an acceptable parameter for determining the stability of this water-soluble polymer [5].

EXPERIMENTAL

Melamine was obtained from Saravid Melamine Industry of Iran and used without further purification. Paraformaldehyde used is a commercial product of Sina Industrial Co. Iran and was employed without further purification. The concentration of formaldehyde in paraformaldehyde was determined by the iodometric method to be 94%. Sodium metabisulphite of laboratory pure grade (Fluka) was also used with no further purification.

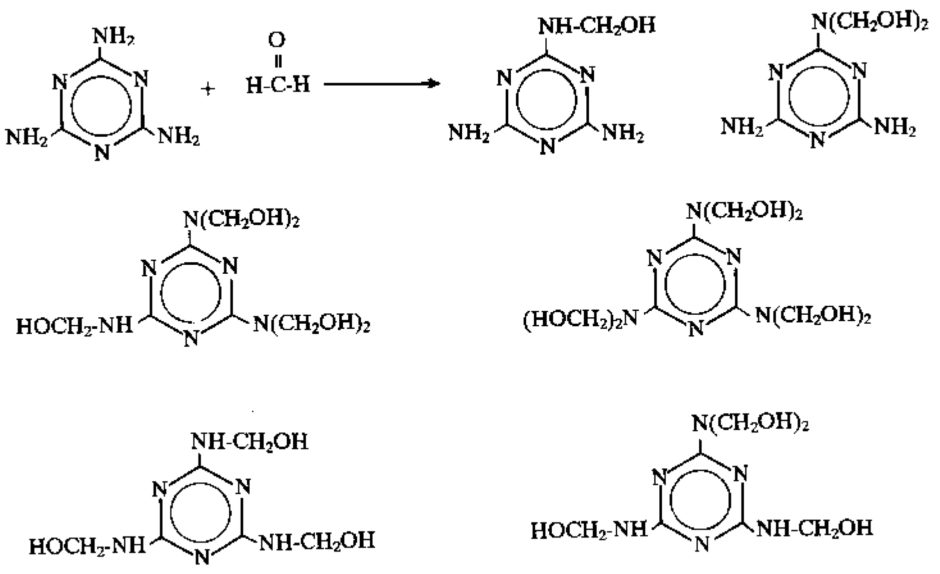
Molecular weights and molecular weight distribution of samples were determined by gel permeation chromatography (GPC) using Waters chromatograph model 150C with UV detector 484. The analysis was carried out by GPC at 25 °C using distilled water as eluant and silica gel (10 ηm) with pore sizes 250–500 Å as separating materials, and viscosity was measured at 25 °C using a Brookfield viscometer model LV1. FTIR spectra were run on a Bruker model IFS 48 and UV spectra were run on a Philips model PU 8800 spectrophotometer.

Preparation of Sulphonated Melamine–Formaldehyde

Preparation of sulphonated melamine–formaldehyde resin varies considerably with the reaction conditions, and molar ratio of reactants. Thus, it is possible, by varying these conditions, to obtain resins with a wide range in properties. Following is an example of the procedure used to prepare sulphonated melamine-formaldehyde resin [6,7].

Paraformaldehyde of 100 g was mixed with 400 mL water. A basic mixture was produced by adding NaOH solution and heating at 60 °C for 20 minutes with continuous agitation. Then the pH was adjusted to 12 and an additional 120 mL of water was added. The solution was cooled to 50 °C, and 100 g melamine was added and the mixture was agitated for a further 20 minutes. Finally a slurry of 50 g sodium metabisulphite and 25 mL water were added to the reaction solution.

The reaction was allowed to continue at



Scheme I

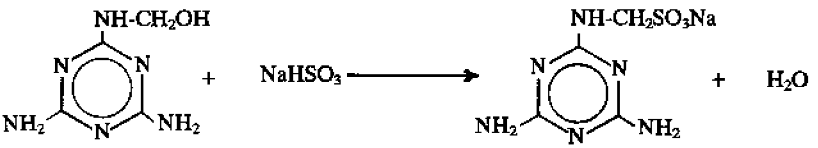
85 °C for 150 minutes and then the temperature was lowered to 60 °C and the pH was adjusted to 3.0 by adding 34 mL H_2SO_4 (14.5 M).

The reaction mixture was agitated under these conditions for another 120 minutes. Then the pH of the solution was raised to 8 by adding adequate NaOH solution. It was heated to 85 °C with continuous agitation, and kept under these conditions for 60 minutes. The solution was then diluted to 20% resin content after adjusting its pH to 8.5–9.

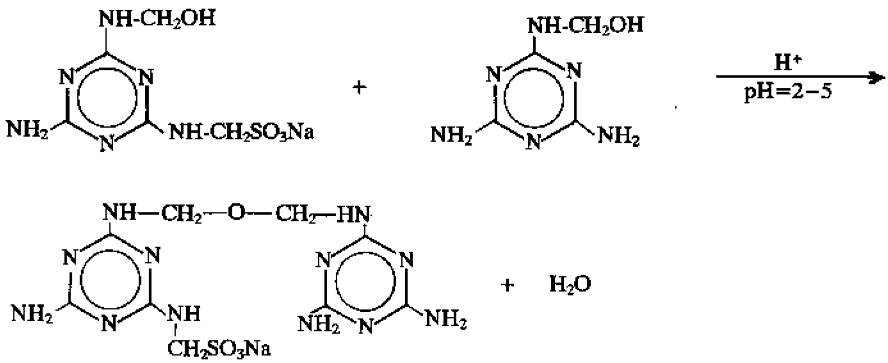
RESULTS AND DISCUSSION

The reaction routes for production of sulphonated resins by a four-step procedure are as follows:

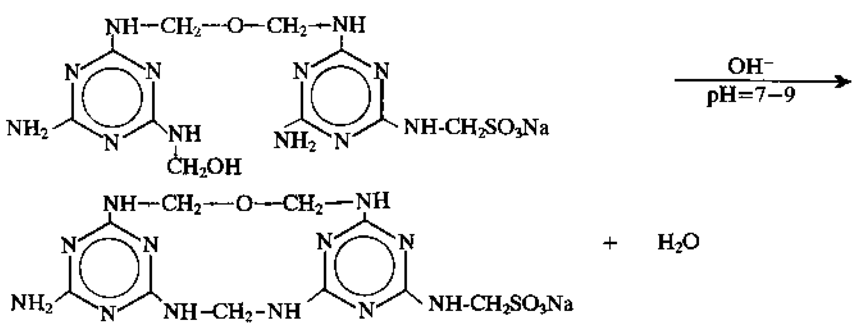
-The general reaction that takes place during the first step is a nucleophilic attack by melamine on the carbonyl group of formaldehyde which



Scheme II



Scheme III



Scheme IV

results in methylol melamine derivatives such as mono, di, tri, tetra, penta and hexamethylol melamine (Scheme I).

-In the next step sodium metabisulphite added is hydrolyzed in water to sodium bisulphite.

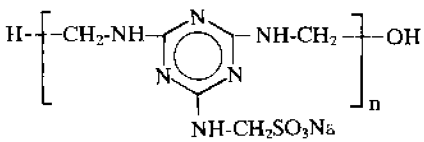
$$Na_2S_2O_5 + H_2O \longrightarrow 2NaHSO_3$$

Then by reaction of sodium bisulphite with methylol melamines, the sulphonated resins are produced (Scheme II).

-The reaction taking place is of a low pH condensation during which ether-linkage type products are formed (Scheme III).

-It is necessary to stop the condensation reactions in the former step and prevent the gelation of the resin, so the reaction that takes place is of a high pH rearrangement in which methylene-linkage type condensation products are formed (Scheme IV).

The final sulphonated resin is formulated as:



Various methods have been used to identify and quantify sulphonated melamine-formaldehyde. The ultraviolet spectra of sulphonated melamine-formaldehyde were measured at 200–400 nm wavelength limit.

The SMF concentration was kept constant and distilled water was used as diluent. The SMF produces an absorption peak at 200–220 nm characteristic of a sulphonated melamine-formaldehyde (Figure 1).

Resin infrared spectra were studied in KBr pellet form in the region between 600–4000 cm^{-1}. The characteristic IR absorption bands of SMF are as follows:

-A broad band at 3420 cm^{-1} attributed to N-H and O-H groups; at 2981 cm^{-1} for stretching vibration of C-H groups. Three absorption bands at 774, 819 and 1575 cm^{-1} are related to triazine ring. The broad band at 1200 cm^{-1} is related to stretching vibration of S=O and C–S of RSO_3^- group, and the band at 1054 cm^{-1} due to ether linkage (C–O–C) group (Figure 2).

The molecular weight and molecular weight distributions of selected samples of prepared resins were determined using gel permeation chromatography (GPC). The apparent weight-average molecular weight, M_w was about 400,000, the apparent number-average molecular weight, M_n was about 340,000 and the polydispersity was 1.190.

The molar ratio of melamine to formaldehyde was studied because of its importance in SMF resins. For SMF polycondensation products, the F/M ratio was varied between 3.18 and 6.00 under similar experimental conditions.

The viscosity of the final product solutions diluted to 20% solid content, was found to increase as the F/M increased. Ratios of F/M greater than 5 during the low pH always resulted a white precipitate. Figure 3 shows that the viscosity of solutions, 20% solid content at 25 °C, increased with an increasing F/M ratio for all reactions at the same experimental conditions. This can be attributed to higher rates of condensation reactions in resins containing more N-methylol functional groups [2]. Linear and crosslinked chains of melamine-

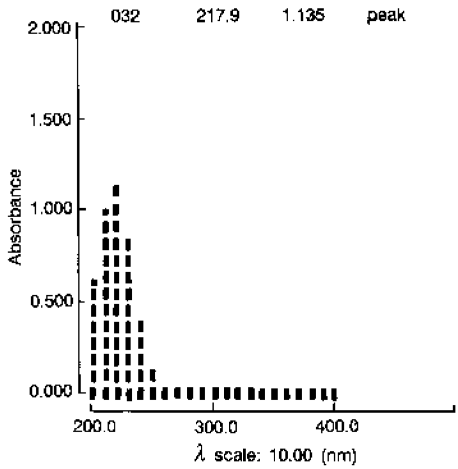


Figure 1. UV spectrum of SMF.

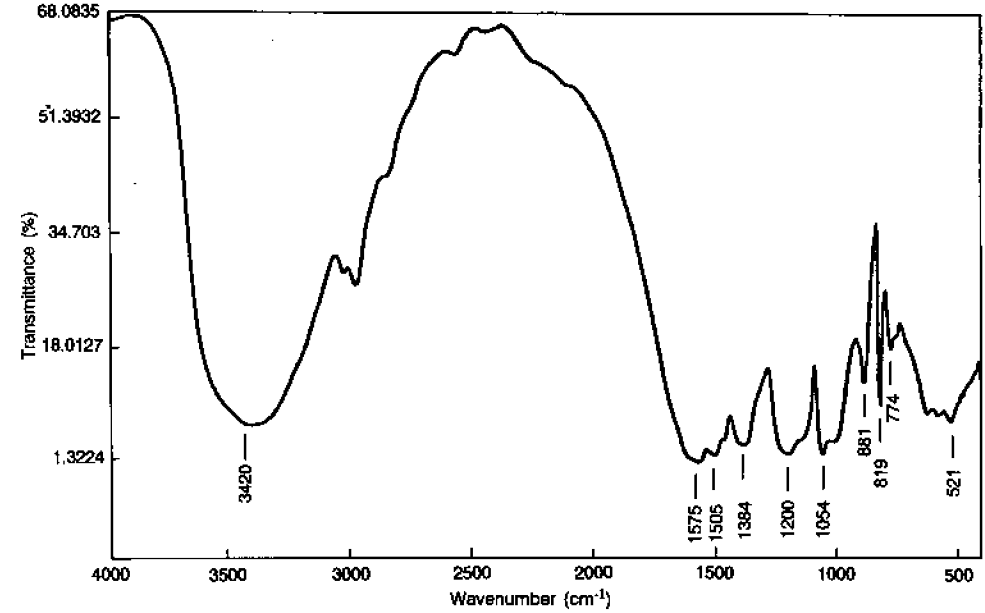


Figure 2. FTIR spectrum of SMF.

formaldehyde are always formed by condensation reactions involving the N-methylol groups. In the formation of N,N-dimethylene bridges, an N-methylol group and an amino group are involved. In the formation of ether linkages, two N-methylol groups are involved; and in the formation of methylene bridges by the elimination of water and formaldehyde, two N-methylol groups are involved. Therefore, the presence of N-methylol groups

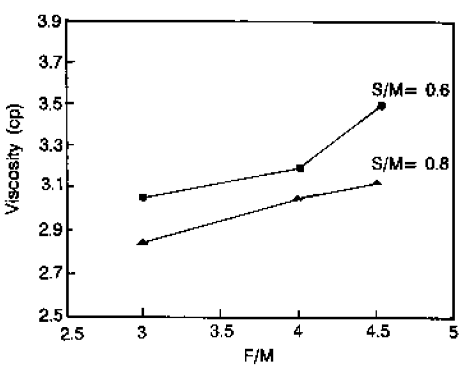


Figure 3. Effect of F/M ratio on the viscosity of final solutions of SMF resin.

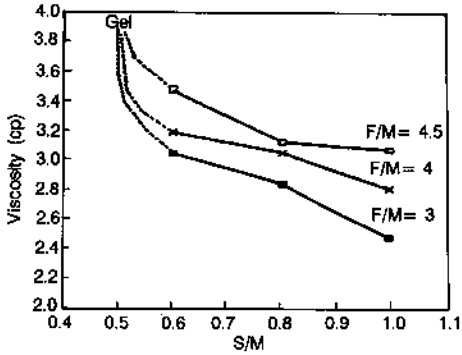


Figure 4. Effect of S/M ratio on the viscosity of SMF solution.

-Dotted curves are estimated from experimental data.

should increase the degree of polymerization and branching in all cases.

Since the sulphonated groups play a major role in solubilizing melamine-formaldehyde resins, both by ionic character and their ability to block bridging sites, namely, the N-methylol groups, they are expected to strongly influence the properties of the prepared resins [9,10].

The molar ratio of sodium metabisulphite to melamine was varied between 0.5 and 1.2. At S/M ratio lower than 0.5, the resins tend to gel at a rapid rate and precipitate out of solution. As shown in Figure 4, lowering the degree of sulphonation resulted in increased viscosity of the final product solutions.

Lowering the S/M ratio reduces the concentration of sulphonated monomers and thus decreases the degree of sulphonation of the produced oligomers. As a result, these species were expected to undergo further condensation reactions more rapidly when the pH of the solution was lowered, thus leading to more viscous products.

CONCLUSION

The effect of different degrees of sulphonation is studied at several ratios of S/M (0.6−1.2). Results show that final products obtained for lower S/M ratios are more viscous. At lower degree of sulphonation, where (S/M)=0.6, the viscosity of the final solution decreases with a decreasing F/M ratio until gelation takes place at much higher F/M ratios (Figure 4). However, an important relationship is observed between formaldehyde and sulphite concentration in the production of water-soluble resins [10], in other words, the added formaldehyde, by providing methylol groups in the initial stages of the reaction, should also provide sites for sulphonation to take place in the later stages of the synthesis. If sodium metabisulphite or the methylol groups are not sufficient, the solubilizing effect of the sulphonate groups is kept at a minimum level and gelation occurs.

ACKNOWLEDGEMENT

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