Synthesis and Properties of High-Performance and Good Water-Soluble Melamine–Formaldehyde Resin

LIHONG SU, SHENGRU QIAO, JUN XIAO, XUAN TANG, GUODONG ZHAO, SHENGWANG FU

Department of Chemical Engineering, Northwest Polytechnical University, Postcode 710072, Xi'an, People's Republic of China

Received 2 August 2000; accepted 20 November 2000

ABSTRACT: In this article, high-sulfonated melamine–formaldehyde (HSMF) resins were prepared with a sulfite/melamine (S/M1.5) molar ratio. During the sulfonation process, the reaction temperature and the added velocity of sodium bisulfite affecting the properties of the resin were studied. In the condensation stage, where the pH range is 6.0 and the temperature is about 25°C, the condensation time was prolonged above 24 h. The stability and water solubility of the resin was improved greatly. It is an effective superplasticizer at small dosages of admixture. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 3268–3271, 2001

INTRODUCTION

In the past two decades, researchers have developed many methods to prepare sulfonated melamine–formaldehyde resins. HSMF resins has been the attention of researchers in recent years.[1] In this experiment, we discover that the temperature and added velocity of sodium bisulfite and the sequence of a sulfonation operation can dramatically affect the properties of the HSMF resins.

EXPERIMENTAL

Materials

Melamine obtained from Shaanxi Chemical Factory was used without further purification. Formaldehyde aqueous solution stabilized with methanol was obtained from the Xi'an Chemical Factory (formaldehyde, 36–37% w/w, methanol, 10–12%). Sodium bisulfite (laboratory reagent) was used without further purification.

Preparation Procedure for Resins

The preparation procedure for HSMF resins is divided into three steps: hydroxymethylation, sulfonation, and condensation. The following is an example of the procedure used to prepare the HSMF resin.

Step 1

Seventy-five milliliters of formaldehyde aqueous solution of 37% concentration is heated to 50°C. Thirty grams of melamine is added to the formalin solution after the pH of the solution is adjusted to 9.0 with 1.5 mL 1 *N* NaOH solution. The temperature of the reaction mixture increases automatically while the melamine dissolves, and rises to 60°C when the melamine becomes clear. The mixture should be cooled by circulating cool water to maintain the temperature at 55–60°C.

Step 2

At first, the temperature of the solution is raised to 80°C. Twenty-five grams of $NaHSO_3$ dissolved

Correspondence to: L. Su.

Journal of Applied Polymer Science, Vol. 81, 3268–3271 (2001)

in 60 mL of water are added to the solution using a burette, where the adding velocity is 2 mL per minute. Then the temperature of the solution is kept at 80°C for 80 min. We discover that the operation sequence is very important at this step.

Step 3

Fifteen milliliters of 1 *N* H_2SO_4 is added to the solution, causing a drop in pH to 6.0. The solution is finally cooled to room temperature, and kept at this temperature for 24 h. The reactants are stirred during the whole reaction time. At last, the solution is treated with sodium hydroxide to adjust its pH to 8.5.

The resin prepared according to this procedure has a solid content of approximately 42–45%.

Testing Resin Properties as Superplasticizers

The test method is according to the JGJ standard.

RESULTS AND DISCUSSION

The preparation of HSMF resins includes three stages: hydroxymethlation, sulfonatipn, and condensation. Each step is dependent on pH, temperature, and reaction time.

Hydroxymethylation

Hydroxymethylation is a simple reaction between the amino group of melamine and formaldehyde. Because researchers have done a great deal of work on this previously,[2,3] this article will not discuss this further. In the experiment, there was a pH of 9.0, formaldehyde/melamine (F/M) molar ratio of 3.3, a temperature of 55–60°C, and a reaction time of 30 min.

Sulfonation

Sulfonation is the reaction between sodium bisulfite and methylomelamine. The factors affecting the sulfonation have been studied. The factors include the pH, addition velocity of sodium bisulfite solution, temperature, revolution of the stirrer, reaction time, and the operation sequence of the process. The number of sulfonate groups per unit of the polymeric chain was determined by chemical analysis.

Reaction Time

In the experiment, the sulfonate easily reacts with methylolmelamine, and the reaction degree of sodium bisulfite is determined by its concentration. If its concentration is lower than 1.5%, we consider that the reaction is complete. Reaction time above 40 min is usually proper.

Added Velocity of Sodium Bisulfite (S/M 1.5)

Added velocity of sodium bisulfite can affect the process dramatically. Sodium bisulfite solution (30% w/w) is added as the sulfonate. Hydrolysis of sodium bisulfite produces bisulfite ions and hydroxide ions, which raises the pH of the solution. If the addition velocity of sodium bisulfite is controlled, the pH of the solution and the concentration of sodium bisulfite can be controlled at a proper range. If the pH is lower than 10 or higher than 12.5, the sulfonation leads to poor resins performance.

The Operational Sequence of Sulfnation

It is worth emphasizing that the operational sequence is important for the process. It must raise the temperature above 70°C first, then add sodium bisulfite solution, or else it always produces an unstable solution, resulting in gelation during the third step and poor water soluble resins. High temperature is the benefit to the rapid sulfonation reaction; it prevents the pH from being too high in part of the solution. At the high temperature (above 70°C) and proper pH 11–12, it favors the resin, forming a linear polymer chain and causing good water solubility.

Temperature (Reaction Conditions S/M 1.5, Stirrer 600 r/min)

If the temperature is lower than 60°C, the reaction velocity is very slow, resulting in a quick gelation during the third step. When the temperature is 80°C or above, it results in a more stable solution. The condensation velocity can be controlled effectively.

Revolution of Stirrer (Temperature 80°C, S/M 1.5, Time 60 min, Addition Velocity of Sodium Bisulfite 5 mL/min)

If the revolution of the stirrer is lower than 300 r/min, the reaction degree of sulfonate is not complete in 60 min. Variation of the revolution of the stirrer between 300–900 r/min apparently cannot

Table I Effect of the Factors Affecting the Sulfonation

Sample Code	(1)	(2)	(3)	(4)	(5)	(6)
Added velocity (sodium bisulfite)	1 mL/min	5 mL/min	5 mL/min	5 mL/min	5 mL/min	20 mL/min
Temperature °C	80	60	80	80	90	80
After sodium bisulfite added pH	9.5–10	11–12	11–12	11–12	11–12	13.5
Reaction complete time (>98%)	100 min	120 min	60 min	45 min	60 min	45 min
Condensation time (pH 6.0)	>100 hours	20 min	24 hours	24 hours	24 hours	15 min
Viscosity (45% solid content, 25°C)	9.6 cp	24.0 cp	14.9 cp	14.3 cp	15.4 cp	25.6 cp
Water solubility	Very good	poor	Very good	good	good	poor
Ratio of water reduction (1.0% dosage)	6%	8%	28%	24%	22%	12%

affect the process; 600 r/min is a proper number for the reaction.

The number of sulfonate groups per unit of the polymeric chain was determined by chemical analysis.[1] In Table I, sample code (3),(4),(5) showed that 1.405–1.476% sulfonate groups have been joined onto the resin chain in the repetitive experiment.

Condensation

S/M 1.5, pH 11–12, temperature 80°C, reaction time 60 min, revolution of stirrer 600 r/min); according to these parameters, sulfonation can produce a stable solution. When H_2SO_4 (1 N) is added, the pH of the solution drops to 6.0, and the resins form at a very slow rate. It needs more than 24 h to attain the viscosity requirement of resin. This considerable change is attributed to the addition velocity of sodium bisulfite. In the condensation, variation of the temperature between 25–70°C and the pH 4.5–6.5 cannot obviously affect the forming rate. The resins have a good water solubility and proper viscosity (shown in Table I). However, if the pH is above 8.0, the viscosity of the solution is low due to the bond cleavage in the polymer backbone.[4]

As superplasticizers, high-sulfonated melamine–formaldehyde resins require proper viscosity and good water solubility. Proper viscosity shows that the molecular weight of the resin is high enough to enable the resin to perform effectively in concrete. Good water solubility is necessary for the superplasticizers. The resin that is produced under the optimum [Table I, (3) sample] can attain a water reduction average above 22% and does not cause the evident change of compressive strength in concrete (Table II).

CONCLUSIONS

The factors that affect sulfonation and condensation of high-sulfonated melamine–formaldehyde production were studied. It is found that the addition velocity of sodium bisulfite and the sequence of sulfonation operation can dramatically affect the process. Proper viscosity and good water-soluble HSMF resins have been prepared under optimum condensation. The optimum sulfon-

Table II Relative Compressive Strength (Compared with the Plain Sample, Which Is 100) Prepared with the Different Reaction Conditions

Sample Code	(1)	(3)	(4)	(6)
Relative compressive strength	105	167	158	129

Sample code according to Table I (1.0% dosage, hydration time = 7 days).

ation (S/M1.5) are: temperature 80°C, the pH 11–12 (controlled by the added velocity of sodium bisulfite), reaction time 60 min, and revolution of stirrer 600 r/min. The operational sequence of sulfonation must raise the temperature above 70°C, then add the sulfonate. The optimum of condensation are: temperature 25–50°C, pH 6.0, and reaction time above 24 h. The prolonged reaction time is far more than other reports. The prepared HSMF resins have good water solubility and high performance as superplasticizers.

REFERENCES

1. Yunchao, H.; Fansen, Z.; Hu, Y. J Appl Polym Sci 1995, 56, 1523.
2. Lahalih, S.; Absi-Halai, M. U.S. Pat. 4,667,,159, (1987).
3. Hovakeemian, G.; Absi-Halabi, M.; Lahalih, S. M.; Al-Khaled, T. J Appl Polym Sci 1989, 38, 727.
4. Absi-Halabi, M.; Lahalih, S. M.; Al-Khaled, T. A. J Appl Polym Sci 1987, 33, 2975.