

Water-Soluble Sulfonated Amino-Formaldehyde Resins. IV. Melamine-Urea Resins: Synthesis and Properties

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Synopsis

The factors affecting the preparation and the properties of sulfonated melamine urea-formaldehyde resins were studied. The resins were synthesized using a four-step procedure previously used in preparing sulfonated melamine formaldehyde resins. The melamine-urea resins required higher hydroxymethylation and condensation temperatures as the percentage of urea increased. The molecular weight distribution of the prepared resins revealed the formation of low molecular weight species in increasing amounts with higher percentages of urea. The effectiveness of the prepared resins as dispersants for concrete mixes was found to be lower than the pure melamine resins; however, it was possible to enhance them by raising the ratio of sulfonated groups in the resins.

INTRODUCTION

In earlier articles in this series,¹⁻³ we presented our results on the preparation or sulfonated melamine formaldehyde (SMF) resins and their applications as dispersants, particularly in the construction industry. We were later able to develop a process, consisting of four steps, that is affected by pH, temperature, time, and molar ratios of reactants that leads to highly stable products.

In a continuation of earlier research, we investigated the effect of replacing portions of the melamine with urea. The objective of these studies is to determine the effect of urea on the reaction conditions and on the properties of the copolymers. The main advantage of the melamine-urea copolymers is the low cost of urea compared with melamine. Due to the introduction of urea, it was anticipated that the reaction conditions for the preparation of optimized sulfonated melamine urea-formaldehyde (SMUF) resins are different than those of SMF resins. This could be attributed to the differences in both the reactivity and structure of urea compared with melamine.^{4,5} Auten and Rainey⁶ and Aignesberger et al.⁷ reported the preparation of SMUF resins; however, no detailed studies were made to assess the factors affecting the preparation.

In this article, we report on the results of our detailed investigation on the effects of pH, temperature, reaction time, and ratio of various reactants on the

properties of SMUF resins. Selected properties of these resins, particularly their effect as dispersants for concrete mixes, are also discussed.

EXPERIMENTAL

Materials

Melamine obtained from the Kuwait Melamine Industries Company was used without further purification. Calculated for $C_3H_6N_6$: C = 28.6%, H = 4.8%, N = 66.7%; found: C = 28.3%, H = 4.7%, N = 67%. Decomposition point: literature, 360°C; found, 370°C. Formaldehyde aqueous solution stabilized with methanol was obtained from BDH (formaldehyde, 37–41 w/w; methanol, 11.0–14.0% w/w) and Riedel-De-Haen AG (formaldehyde, 35% w/v). Paraformaldehyde technical grade from the Kuwait Insulating Material Manufacturing Co. was used without further purification. The concentration of formaldehyde in paraformaldehyde was determined by the Iodometric method. The average concentration was 94.6%. Sodium metabisulfite ($Na_2S_2O_4$) (BDH, laboratory reagent) was used without further purification. Urea obtained from the Petrochemical Industries Co. (Shuaiba, Kuwait) was used without further purification.

Procedure

Laboratory Scale Synthesis of the Resins. The melamine urea-formaldehyde resins were synthesized by a procedure similar to that used for the pure melamine resins.¹ The procedure consists of four steps for 10% urea resins. A special setup was used as described earlier.¹ Paraformaldehyde, 53.14 g (1.68 mol), was mixed with 242 mL of water heated to 55°C and its pH adjusted to 11.3–11.5 with NaOH solution (10*N*). After complete dissolution of paraformaldehyde, 50.0 g of melamine (0.4 mol), 2.65 g of urea (0.44 mol), and 93 mL of water were added. The reaction mixture was heated at 55°C with continuous stirring until it became clear; then 41.89 g (0.22 mol) of sodium metabisulfite ($Na_2S_2O_5$) mixed with 10 mL of water was added. This solution was kept at 55°C for 5 min, then pumped to the second reaction flask, heated to 80°C, and kept at this temperature for 60 min. The solution was then transferred to the third reaction flask and cooled to 55°C, and its pH was lowered to 3.5 by rapid addition of H_2SO_4 (15*N*). The solution was stirred continuously for 60 min; then its pH was raised to 7.0 by adding CaO slurry, and the mixture was transferred to the fourth reaction flask. The reaction mixture was heated to 80°C with continuous stirring and kept at this temperature for 60 min; then it was filtered and cooled to room temperature. The pH of the final solution was adjusted to 8, its solid content was determined by total water evaporation at 60°C, and the concentration was later adjusted to 20% solid content by adding water. The viscosities of the final resin solutions were determined using a HAAKE CV-100 rotational viscometer. The quantities of reagents used with different percentages of urea are presented in Table I.

For preparations of sulfonated melamine urea-formaldehyde polycondensates containing higher percentages of urea, a modified four-step procedure

TABLE I
Mass and Number of Moles of Reagents Used to Prepare Sulfonated Urea-Melamine
Formaldehyde Condensates

	Molar percentage of urea in mix							
	10%		20%		30%		40%	
	g	mol	g	mol	g	mol	g	mol
Paraformaldehyde (94.6%)	53.14	1.68	56.62	1.79	61.12	1.92	67.11	2.12
Melamine	50.00	0.40	50.00	0.40	50.00	0.40	40.00	0.40
Urea	2.65	0.044	5.95	0.10	10.2	0.17	15.90	0.27
Melamine + Urea	0.00	0.44	0.00	0.50	00.0	0.57	00.00	0.67
Water								
(a) With formalin	242.00	0.00	258.00	0.00	279.0	0.00	306.00	0.00
(b) With melamine	93.00	0.00	100.00	0.00	105.00	0.00	116.00	0.00
(c) With sulfite	10.00	0.00	15.00	0.00	25.00	0.00	35.00	0.00
Sodium meta bisulfite	41.89	0.22	47.12	0.25	53.80	0.28	62.83	0.33

was employed involving higher temperatures. The four steps are summarized for a typical 0.5 mol scale reaction.

Step 1. Paraformaldehyde [51.7 g (1.63 mol)] was dissolved in water (500 mL) in a jacketed reactor flask at 80°C and at pH 10. After complete dissolution, 37.8 g of melamine (0.3 mol) and 12.0 g of urea (0.2 mol) were added all at once and the reaction was stirred for 15 min at 80°C.

Step 2. To the solution obtained in step 1, 38 g of sodium metabisulfite (0.25 mol) was added, and the pH was readjusted to 10. The reaction was continued at 80°C for 60 min.

Step 3. The pH of the solution was lowered to 3.5 by adding 3N H₂SO₄ solution and the reaction was stirred at 80°C for 60 min.

Step 4. The mixture pH was raised to 9 by adding 6N NaOH and the reaction was continued at 80°C for 40 min. After cooling, the solution was readjusted to 20% solid content.

Molecular Weight Distribution. Molecular weight analyses of an SMF resin and selected SMUF resins were carried out by Mikro-analytisch Labor Pascher, Bonn, West Germany. The analyses were done by gel permeation chromatography (GPC) at 50°C using distilled water as eluant and silica gel (10 μm) with pore sizes 6–100 μm as separating material.

Testing Resin Effect on Concrete Properties

To test the properties of SMUF resins as concrete superplasticizers, a control mix design as follows was used:

Cement	Water	Sand	Aggregate
1.00	0.53	1.79	3.43

The mix had a compressive strength (28 days) of 350 kg/cm² and a slump of 30 mm. In testing the resins, cement, sand, and the aggregates were first

dry-mixed, then water was added with continuous mixing, and, finally, the resin solution was slowly added. The percentage of resin solution used in the mix was based on cement weight only.

The Slump Test. The slump of concrete (plain and treated with resin) was determined according to ASTM C143.

The Compressive Strength Test. This test determined the compressive strength of concrete mixes using 15 cm cubes. The concrete cubes were cast and kept under high humidity conditions for 24 h. The cubes were removed from the molds after 24 h and kept in water at a temperature of $23 \pm 2^\circ\text{C}$ until their test age (3, 7, and 28 days was reached).

RESULTS AND DISCUSSION

Preparation Conditions Affecting SMUF Resin Properties

Effect of Formaldehyde/(Urea + Melamine) Ratio (F/M + U). The molar ratio of formaldehyde to total amine was studied because of its importance in sulfonated melamine formaldehyde (SMF) resins.¹ In previous work involving SMF resins, stable water-soluble products were obtained at $F/M = 4$ in which the molar ratio of aldehyde groups to amino groups was 1.33. For sulfonated melamine urea-formaldehyde (SMUF) polycondensation products, the $F/(M + U)$ ratio was varied while maintaining a constant aldehyde/amine ratio when the ratio of urea to melamine (U/M) was varied. This was done to avoid the introduction of another variable when the ratio of urea to melamine in the prepared resins was changed. The aldehyde to amine ratio was varied between 3.0 and 5.0 for preparations of SMUF resins containing different proportions of urea and melamine and prepared under similar experimental conditions. The viscosity of the final product solutions diluted to 20% solid content was found to increase as the $F/(M + U)$ increased and as the proportion of melamine in the reaction mixture increased (Table II). Ratios of aldehyde/amine lower than unity always resulted in insoluble products during the low pH condensation step, whereas for aldehyde/amine ratios greater than $5/3$, the reaction product condensed to a white precipitate during the first step of the four-step synthetic procedure. Table II shows that the viscosity of solutions increased with an increasing $F/(M + U)$ ratio for all reactions containing equal proportions of melamine to urea. This can be attributed to higher rates of condensation reactions in resins containing more *N*-methylol functional groups. Linear and crosslinked chains of melamine and urea 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 either 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 should increase the degree of polymerization and branching in all cases.

Effect of S/(M + U) Ratio. Since the sulfonate group plays a major role in solubilizing amino-formaldehyde resins both by its ionic character and its ability to block bridging sites, namely, the *N*-methylol groups, it is expected to strongly influence the properties of the prepared resins. The molar ratio of

TABLE II
Effect^a of F/(M + U) Ratio on the Viscosity^b of the Final Solution
for Different M/U Ratios

M/U	Aldehyde/Amine	F/(M + U)	Viscosity (cP)
100% M	5/3	5.00	74.0
8/2	5/3	4.67	20.6
6/4	5/3	4.34	28.6
4/6	5/3	4.00	7.3
2/8	5/3	3.67	3.2
100% U	5/3	3.34	2.8
100% M	4/3	4.00	15.3
8/2	4/3	3.73	11.1
6/4	4/3	3.45	6.2
4/6	4/3	3.20	2.6
2/8	4/3	2.93	2.5
100% U	4/3	2.66	1.6
100% M	3/3	3.00	5.1
8/2	3/3	2.80	3.8
6/4	3/3	2.60	2.8
4/6	3/3	2.40	2.1
2/8	3/3	2.20	2.0
100% U	3/3	2.00	1.6

^a Reaction conditions are: pH₁, T₁, t₁ = 10, 80°C, 15 min; pH₂, T₂, t₂ = 10, 80°C, 60 min; pH₃, T₃, t₃ = 3.5, 80°C, 60 min; pH₄, T₄, t₄ = 9, 80°C, 40 min.

^b Viscosity of the final solution (20% solid content) at 20°C.

sodium metabisulfite to urea-melamine was varied between 0.3 and 0.5, i.e., sulfite/urea-melamine ratios of 0.6-1.0. At a S/(M + U) ratio lower than 0.8, the resins tend to gel at a rapid rate and precipitate out of solution. As expected, lowering the degree of sulfonation led to increased viscosity of the final product solutions (Table III). Lowering the S/(M + U) ratio decreased the concentration of sulfonated monomers produced in the second step of the synthesis and resulted in a lower degree of sulfonation of the oligomers produced during the first step of the synthesis. As a result, these species were expected to undergo further condensation reactions more rapidly when the pH of the solution was lowered in the third step, thus leading to more viscous products. In another comparative study, the effect of different degrees of sulfonation was studied for two ratios of S/(M + U) (0.8 and 1.0) on preparations containing urea and melamine in a proportion of 60:40. Figure 1 shows that more viscous final products are obtained for lower S/(M + U) ratios. However, an important interrelationship is observed between formaldehyde and sulfite concentrations in the production of water-soluble resins. In Figure 1, at the lower degree of sulfonation where S/(M + U) = 0.8, the viscosity of the final solution decreases with a decreasing F/(M + U) ratio until gelation takes place at much lower F/(M + U) ratios. The added formaldehyde, by providing methylol groups in the initial stages of the reaction, should also provide sites for sulfonation to take place in the later stages of the synthesis. If the methylol groups are not sufficient, the solubilizing effect of the sulfonate ($-\text{SO}_3^-$) groups are kept at a minimum and gelation occurs.

TABLE III
Effect^a of S/(M + U) Ratio on the Viscosity^b of the Final Solution
at a Constant Aldehyde/Amine Ratio of 3/3

U/M	S/(M + U)	Viscosity (cP)
100% M	1.0	5.1
100% M	0.8	137.0
100% M	0.6	∞ (gel)
2/8	1.0	3.8
2/8	0.8	6.2
2/8	0.6	∞ (gel)
4/6	1.0	2.8
4/6	0.8	7.1
4/6	0.6	∞ (gel)
6/4	1.0	2.1
6/4	0.8	∞ (gel)
6/4	0.6	∞ (gel)
8/2	1.0	2.0
8/2	0.8	4.1
8/2	0.6	∞ (gel)
100% U	1.0	1.7
100% U	0.7	1.7
100% U	0.3	1.8

^aReaction conditions are: pH₁, T₁, t₁ = 10, 80°C, 15 min; pH₂, T₂, t₂ = 10, 80°C, 60 min; pH₃, T₃, t₃ = 3.5, 80°C, 60 min; pH₄, T₄, t₄ = 9, 80°C, 40 min.

^bViscosity of final solution (20% solid content) at 25°C.

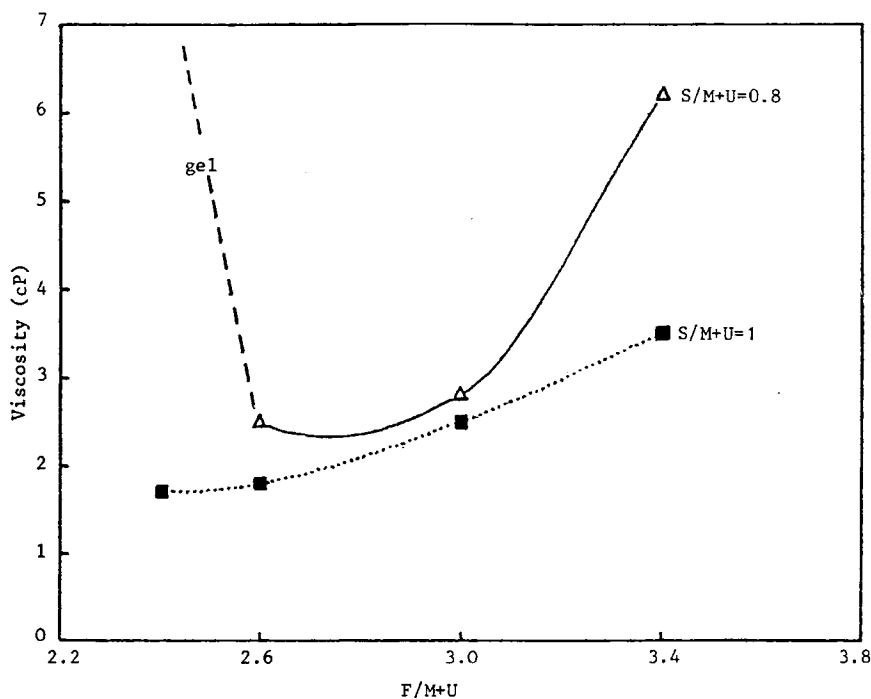


Fig. 1. Effect of F/M + U ratio on the viscosity of final solutions of SMUF resins containing 60% urea. Viscosity (20% solid content) at 25°C. Gelation occurs at F/M + U < 2.6 for S/M + U = 0.8.

TABLE IV
Effect of the First and Third Step Temperature and Time on the Viscosity
of the Final Resin Solutions Containing 20% Urea

T_1, T_3 (°C)	t_3 (min)	Viscosity (cP) at 20% solids at 20°C
45	90	2.7
55	90	3.0
70	90	4.0
75	90	5.5
55	20	2.7
55	120	3.5

Effect of Low pH Condensation Conditions. The temperature of the reaction solution during the first and third steps was varied between 45 and 75°C. The viscosity of the final solution after dilution to 20% solid content at 20°C increased from 2.7 cP to 5.50 cP (Table IV) for a formulation containing 20% urea. The duration of the reaction at the third step was also varied at 55°C (Table IV) for the same formulation (20% urea). An increase in the viscosity of the final solution was observed for longer condensation periods consistent with an expected increase in the molecular weight of the formed resins.

The effect of pH during the third step was investigated on two closely related formulations containing 60 and 70% urea. The study was conducted for two durations (60 and 120 min) during the low pH condensation step. The results presented in Table V indicate that pH during the condensation step plays an important role in the preparation and the properties of sulfonated melamine urea-formaldehyde resins. At lower pH values, more viscous products are obtained, and, in cases where condensation reactions are allowed to proceed for long periods at low pH values, gelled products are obtained.

TABLE V
Effect^a of pH_3 and t_3 on the Viscosity^b of the Final Solutions
for Resins Containing 60% and 70% Urea

U/M	pH_3	Viscosity (cP)	
		$t_3 = 60$ min	$t_3 = 120$ min
6/4	3.0	53.5	∞ (gel)
6/4	3.5	18.3	19.3
6/4	4.0	3.3	3.6
6/4	4.5	2.0	3.5
7/3	3.0	3.4	8.0
7/3	3.5	2.0	1.9
7/3	4.0	2.0	2.0
7/3	4.5	1.9	2.1

^a Reaction conditions are: $\text{pH}_1, T_1, t_1 = 10, 80^\circ\text{C}, 15$ min; $\text{pH}_2, T_2, t_2 = 10, 80^\circ\text{C}, 60$ min; $T_3 = 80^\circ\text{C}$; $\text{pH}_4, T_4, t_4 = 9.0, 80^\circ\text{C}, 40$ min; aldehyde/amine = 5/3; S/(M + U) = 1.

^b Viscosity of final solution (20% solid content) at 25°C.

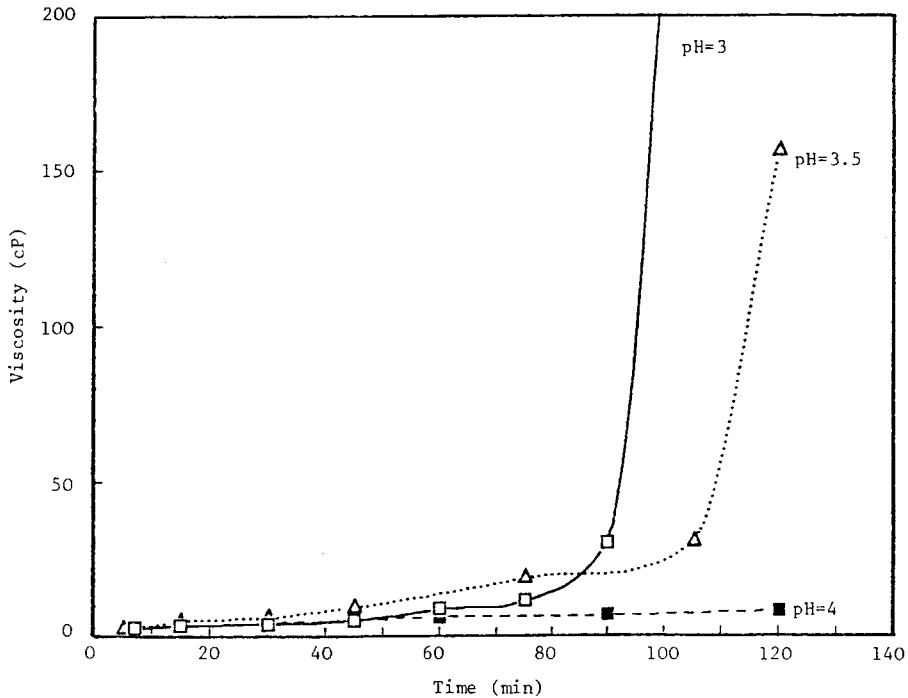


Fig. 2. Variation of viscosity during low pH condensation reaction at different pH_3 values (60% urea). Viscosity, 20% solid content at 25°C . Viscosity at $\text{pH}_3 = 3$ was 1050 cP at 25°C after 120 min of reaction.

The pH of the third step was also found to affect the behavior of the reactions during the condensation step. The viscosities of solutions were monitored during the low pH condensation step by withdrawing samples at different intervals, cooling them immediately to 20°C , and recording their viscosities. Figure 2 shows the changes in viscosity observed during low pH condensation at different pH values for a resin preparation containing a mixture of melamine and urea in a ratio of 40:60. The viscosity increased gradually during the early stages of the condensation and, after this initial period, an exponential increase was observed with the sharpest increase observed at a lower pH value. During the first hour of the condensation, smaller oligomers condensed to form polymers of intermediate size. On the other hand, as the pH of the solution is lowered, these species condense further to form larger polymer molecules during the second hour of the condensation until gelation if the reaction was allowed to continue.

Effect of Urea Molar Percentage on the Preparation and Properties of SMUF Resins. Increasing the percentage of urea in the melamine mix while maintaining all other reaction conditions constant causes a gradual decrease in the viscosity of the final product solution. This is evident from Tables II, III, and V. The lower viscosities in urea-rich mixtures are due to differences between the chemistry of melamine formaldehyde and urea formaldehyde resins.⁸

- The three $-\text{NH}_2$ groups in melamine provide more possibilities for crosslinking, thus giving more complex 3-dimensional structures.

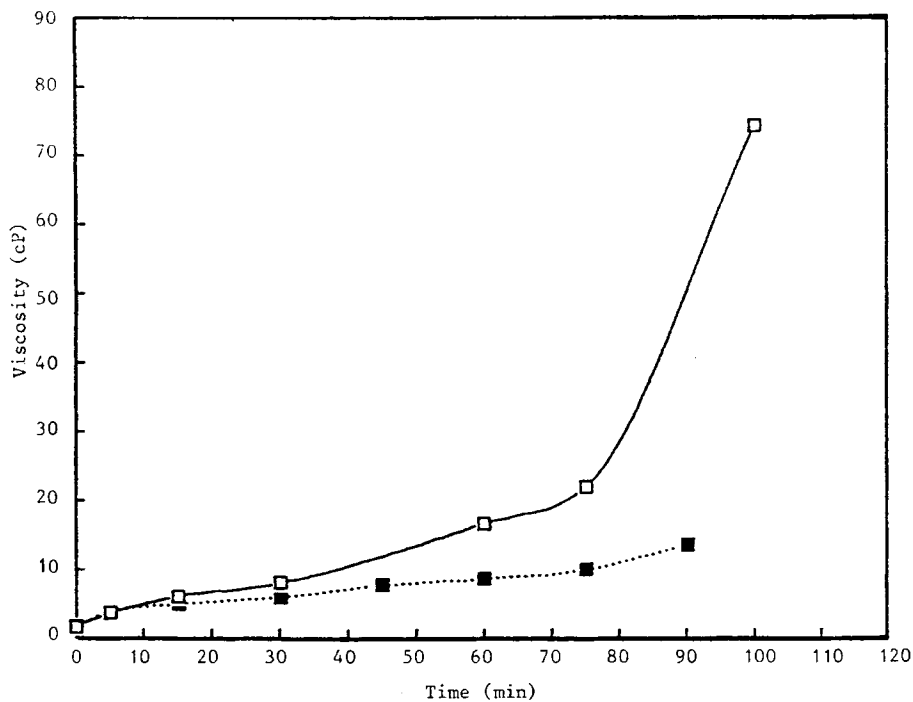


Fig. 3. Variation of viscosity during low pH condensation reaction at different U/M ratios (···) 70% urea; pH₃ = 3.1. (—) 20% urea; pH₃ = 4.1 Viscosity (20% solid content) at 25°C.

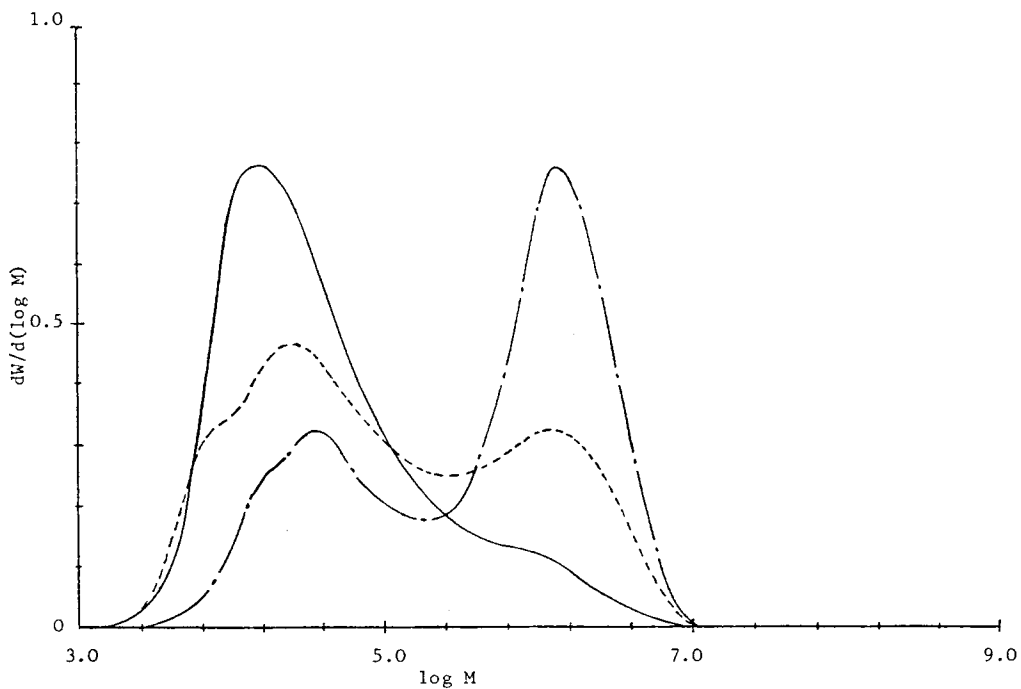


Fig. 4. Effect of urea percentage on the molecular weight distribution in prepared SMUF resins: (···) 0% urea; (---) 60% urea; (—) 80% urea.

TABLE VI
Apparent Average Molecular Weight (\bar{M}_w) Distribution of Sulfonated Amino Formaldehyde Resins at Different Urea Percentages

Urea percentage	Viscosity at 25°C (cP) of 20% solids	Apparent weight average molecular weight (\bar{M}_w)	Apparent number average molecular weight (\bar{M}_n)	Polydispersity (\bar{M}_w/\bar{M}_n)
0	4.5	1,130,000	70,700	15.98
60	2.1	591,000	25,200	23.45
80	2.0	184,000	18,500	10.05

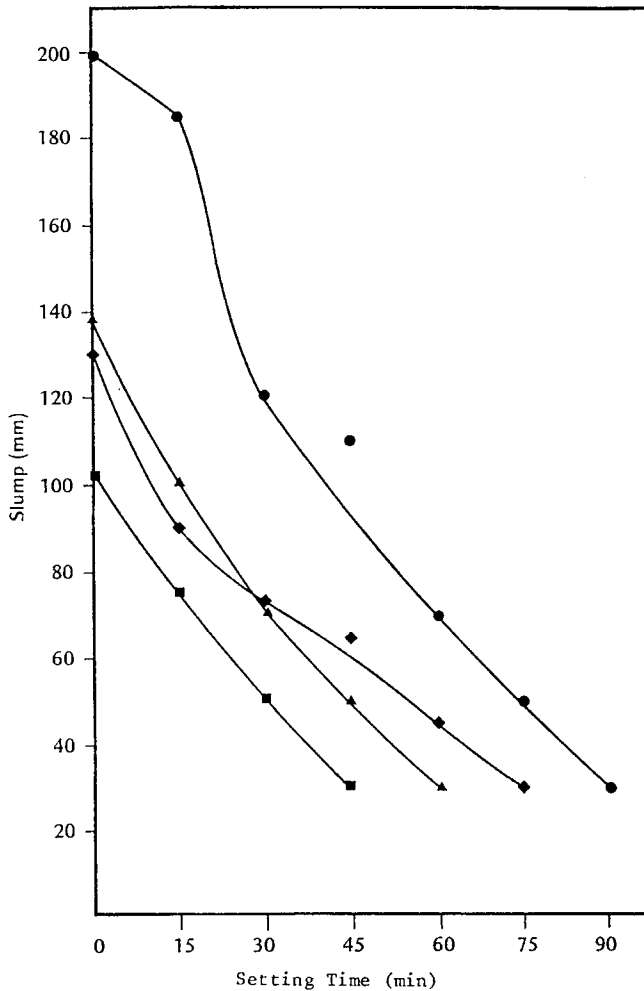


Fig. 5. Variation of slump with time for SMUF resins: (●) Aldehyde/amine = 3, 100% melamine; (▲) Aldehyde/amine = 4, 100% melamine; (◆) Aldehyde/amine = 4, 40% urea, $T_1, T_2, T_3 = 80^\circ\text{C}$; (■) Aldehyde/amine = 4, 40% urea, $T_1, T_2, T_3 = 75^\circ\text{C}$.

- The —NH_2 groups in melamine behave more like amide groups than the —NH_2 groups in urea, they are highly reactive, and methylene bridges are readily formed even under basic conditions.
- The methylolmelamines are more resistant to dissociation into formaldehyde and melamine than their urea counterparts.

The differences observed in the behavior of formulations containing varying ratios of urea to melamine were also observed during the condensation (low pH) step of the synthesis. Figure 3 shows the behavior of the viscosity of resin solutions during the condensation step for mixtures of urea and melamine in ratios of 2:8 and 7:3. Due to the depressed reactivity of the formulation containing 70% urea, the condensation step was conducted at a lower, more reactive pH value of 3.1 compared with a pH value of 4.1 for the formulation containing 20% urea. In spite of this, the formulation containing 20% urea showed a much faster increase in viscosity compared with the formulation containing 70% urea. Again, this is attributed to a lower possibility of crosslinking or formulation of 5-dimensional networks in urea-rich formulations.

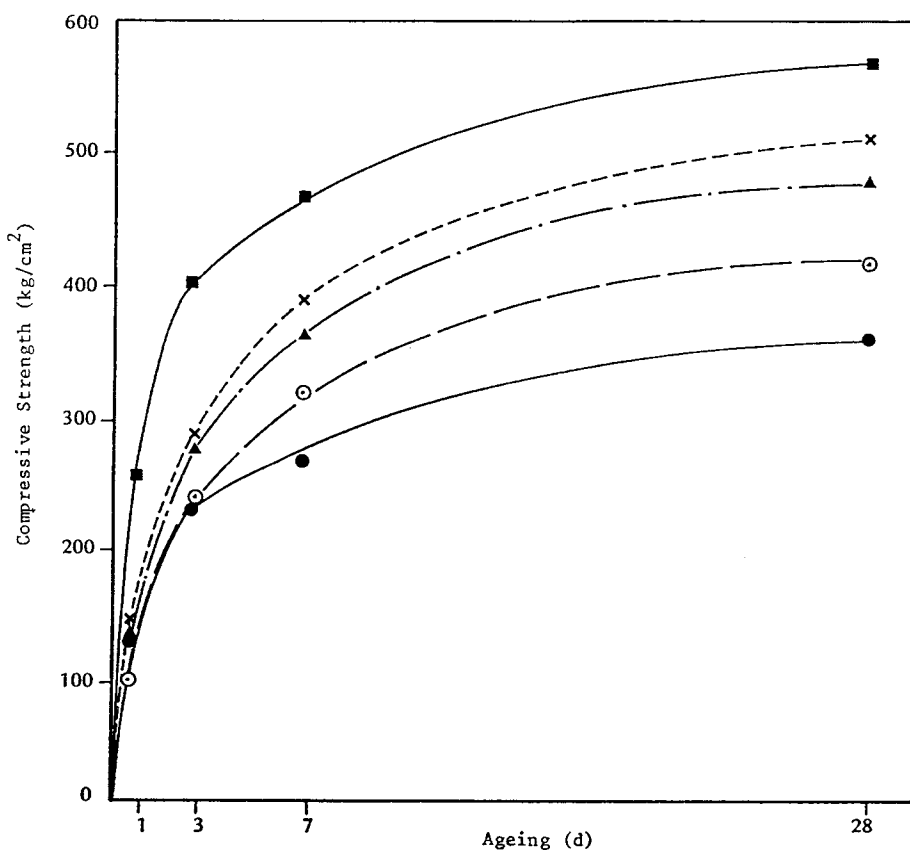


Fig. 6. Effect of urea percentage on the compressive strength of concrete treated with SMUF admixtures: (—■—) 100% M; (—×—) 10% U; (—▲—) 20% U; (—○—) 30% U; (—●—) plain concrete.

Effect of Urea Percentage on Molecular Weight Distribution. The influence that urea has on the molecular weight distribution of species formed in the preparation of SMUF resins containing varying molar ratios of urea is shown in Figure 4. Gel permeation chromatographic (GPC) analysis was conducted on selected preparations of SMUF resins prepared under the same conditions. The resins consist of a wide distribution of species concentrated in two regions. The incorporation of increasing amounts of urea in the resin increases the proportion of the low molecular species and leads to a decrease in the proportion of high molecular weight species. As the proportion of urea increases, the low molecular weight species also shift towards lower molecular weight. This is shown in Table VI that summarizes the results of molecular weight distributions.

Properties of SMUF Resins as Concrete Superplasticizers

Sulfonated melamine formaldehyde (SMF) resins were reported to be excellent dispersants of inorganic oxides.² In the construction industry, SMF resins have been widely used as concrete superplasticizers. The partial substitution of melamine by urea is expected to lead to resins that are effective superplasticizer at lower cost than pure melamine resins. Therefore, we investigated the properties of a number of the prepared SMUF resins.

Figure 5 shows the variation of slump of concrete mix prepared using 1% of the superplasticizer by the weight of cement. SMUF resins are less effective

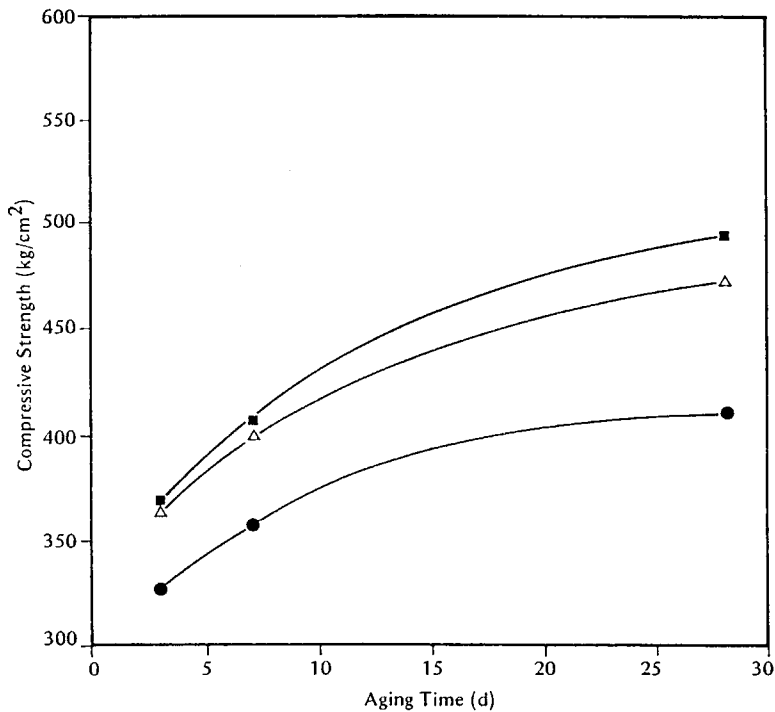


Fig. 7. Compressive strength buildup for SMUF resins (40% urea) with varying degrees of sulfonation: S/M + U: (●) 0.8; (△) 1.0; (■) 1.2.

workability improvers than SMF resins. The same observation was made with regard to the effect of the resins on concrete compressive strength (Fig. 6). SMUF resins are effective in improving the strength of concrete, but, as the urea percentage increases, this effectiveness is substantially reduced. To enhance the effectiveness of the SMUF resins, the ratio of sulfonate groups to melamine was varied between 0.8 and 1.2 for resins containing 40% urea. The results indicate that compressive strength increases progressively with S/M ratio (Fig. 7).

The properties of SMUF as concrete superplasticizers are attributed to the action of the sulfonate groups on the polymeric chains of the resin. The chains encompass the inorganic particulates imparting them with negative charges that cause the particles to repel, thus lowering interparticle friction. This improves the flowability of concrete mixes before setting and causes the particles to be more closely packed, hence improving the compressive strength.² The effect of the sulfonate group is evident from the S/M study that showed that, at higher S/M ratios, the resins are more effective.

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