Water-Soluble Sulfonated Amino-Formaldehyde Resins. V. Effect of Reaction Conditions on Molecular Weight Distribution

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Synopsis

The effect of reaction conditions of sulfonated urea–melamine formaldehyde on molecular weight distribution was studied. It was found that the molecular weight distribution of these materials is influenced by the percent of urea to melamine in the mixture, the concentration of the reaction mixture, the pH and the time of reaction of the low pH condensation step, and, finally, the reaction time during the high pH condensation and rearrangement step. Weight average molecular weights increased as percent melamine to urea, concentration of reaction mixture, the alkalinity of the third step, and the reaction time of the fourth step increased. The weight average molecular weight decreased as the reaction time of the third step decreased. The reaction variables influenced the fraction of the high molecular weight species that, in turn, influenced these materials performance. Finally, it appeared that the final product contained separate sulfonated urea formaldehyde and sulfonated melamine formaldehyde components in addition to sulfonated urea–melamine formaldehyde polycondensates.

INTRODUCTION

Sulfonated amino–formaldehyde resins are water-soluble polycondensates that can be used for a variety of applications. For example, they can be used as concrete additives in the form of superplasticizers.[1–4] Other applications of these versatile polymers are their use to stabilize soil and prevent its erosion by the action of water and wind.[5] Another novel application is their use as drilling mud additives; they can be very effective thinning agents to control the rheological properties of drilling mud.[6] The reaction mechanism of amino groups with formaldehyde is very complex and it becomes more complicated if the amino group is a mixture of urea and melamine. The reason is that, in the presence of urea and melamine, several reaction schemes are possible because urea can be considered a bifunctional molecule, whereas melamine is trifunctional. The reactions of pure melamine with formaldehyde were covered in a previous publication,[1] whereas the reaction of urea and melamine mixture with formaldehyde was the subject of another publication.[7]

The reason that these polymers are very versatile for various applications is that these water-soluble polymers can be prepared with different molecular structures that render them unique properties for that particular application. However, the molecular structure is being strongly affected by the reaction conditions of these polymers. These polymers are prepared in a four-step pro-

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cedure,[8] where the amino group is reacted with formaldehyde in a first step called hydroxymethylation. The second step is sulfonation where the mixture is reacted with sodium metabisulfite followed by a polycondensation step that takes place at low pH. The fourth step is a molecular rearrangement step that takes place at high pH. The four-step procedure uses time, temperature, and pH as main variables. Other variables in the preparation procedure of these polymers include the formaldehyde to amino group ratio, the sulfite to amino group ratio, and concentration of the reactants in the mixture solution.

Therefore, the main objective of this paper is to report on our findings on the effect of the various reaction variables on the molecular weight distribution of a sulfonated urea–melamine formaldehyde resin.

EXPERIMENTAL

Materials

The raw materials used in this study are those described in the first part of this series.[1]: melamine, urea, sodium metabisulfite, paraformaldehyde, sulfuric acid, and sodium hydroxide.

Procedure

Preparation of the SUMF Polycondensates. The method for preparing the sulfonated urea–melamine formaldehyde polycondensation products follows a modified procedure developed by Lahalih and Absi-Halabi.[8] The reaction is conducted on a 1-l scale and involves four steps: hydroxymethylation, sulfonation, low pH condensation, and high pH condensation–rearrangement. The four steps are summarized below for a typical 0.5 mol scale reaction.

Step 1. Paraformaldehyde (51.7 g, 1.72 mol) is dissolved in water (500 mL) in a jacketed reactor flask at 80°C and the pH is adjusted to 10 (NaOH, 6 *N*). After complete dissolution, melamine (37.8 g, 0.3 mol) and urea (12 g, 0.2 mol) are added all at once and the reaction is stirred for 15 min at 80°C.

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

Step 3. The pH is lowered to a range of 3.0–4.5 (H_2SO_4, 3 *N*) and the reaction is stirred at 80°C for 60–120 min.

Step 4. Finally, the mixture pH is raised to 9 and the reaction is continued at the same temperature for 40 min.

In experiments involving the mixtures of melamine and urea, the formaldehyde used in these experiments was calculated so that the aldehyde to amine ratio was held constant whenever the ratio of melamine to urea was varied. Various reaction conditions are presented in Table I.

Molecular Weight Distribution. Molecular weights and molecular weight distribution of samples were determined using gel permeation chromatography (GPC). Distilled water was used as elution agent at 60°C. Silica gel (grain size

TABLE I
Reaction Conditions for Preparation of Water-Soluble Sulfonated Amino–Formaldehyde Resins[a]

			Step 1			Step 2			Step 3			Step 4				
Sample no.	U/M[b]	F/(M + U)[c]	pH_1	T_1 (°C)	t_1 (min)	pH_2	T_2 (°C)	t_2 (min)	pH_3	T_3 (°C)	t_3 (min)	pH_4	T_4 (°C)	t_4 (min)	Concentration of solids in solution before dilution (%)	Viscosity of 20% solid at 20°C (cP)
01	6/4	3.2	10	80	15	10	80	60	3.0	80	60	9	80	40	20	4.20
02	6/4	3.2	10	80	15	10	80	60	4.0	80	60	9	80	40	20	3.80
03	6/4	3.2	10	80	15	10	80	60	3.0	80	120	9	80	40	20	21.80
04	6/4	3.2	10	80	15	10	80	60	3.5	80	60	9	80	40	30	4.50
05	6/4	3.2	10	80	15	10	80	60	3.5	80	60	9	80	40	40	5.20
06	6/4	3.2	10	80	15	10	80	60	3.5	80	60	9	80	90	40	4.59
07	6/4	3.2	10	80	15	10	80	60	3.5	80	60	9	80	180	40	3.28
08	8/2	3.2	10	80	15	10	80	60	3.0	80	60	9	80	40	20	2.00
09	0/10	4.0	11.35	50	15	11.35	80	60	3.5	50	90	7	80	60	20	4.56
010	0/10	Commercially available product (Melment L-10)													20	4.50

[a] All reactions were carried out with S/(M + U) = 1 [sulfite to (melamine + urea)] ratio.
[b] U/M is urea to melamine ratio.
[c] F/(M + U) is formaldehyde to (melamine + urea) ratio.

10 μm) of pore size 6 and 100 nm was used as separating material. Two steel columns each 250 mm long with inner diameter of 8 mm were used. A differential refractometer was used at 60°C. The injected amount was 250 μL for 0.2% solution and the elution speed was 0.5 mL/min. Dextran blue and glucose were used for calibration. The tests were done by Mikroanalytiches Labor Pascher, Bonn, West Germany.

RESULTS AND DISCUSSION

Due to the complex nature of the reactions of sulfonated urea–melamine formaldehyde, the chemistry of these resins is poorly understood. A large number of isomeric structures can be obtained because of the variety of reaction mechanisms involved. Therefore, to understand the behavior of these resins and to be able to predict their performance, knowledge of their structure is essential. Resin molecular weights and molecular weight distributions are strongly influenced by the preparative conditions. The pertinent reaction variables include the percent of urea to melamine in the final product, the pH, time and temperature of the third and fourth steps of the reaction procedure, and the concentration of the constituents in the final product.

Since GPC traces were calibrated by dextran blue, the molecular weight data is relative rather than absolute. Table II presents apparent weight average molecular weight ($\bar{M}_w$) and the apparent number average molecular weight ($\bar{M}_n$) and the weight distribution for the prepared sulfonated urea–melamine formaldehyde resins (SUMF).

Effect of Urea to Melamine Ratio on Molecular Weight Distribution. For economical considerations, it is always desirable to have more urea replacing melamine in these sulfonated resins since urea is far cheaper than melamine. However, the inclusion of urea should not hamper in any way the properties of the final resin and reduce its efficiency. In this study, urea to melamine ratios ranged from 0 to 4 or the percent of urea ranged from 0 (pure melamine) to 80% based on urea plus melamine in the mixture. The molecular weight distribution is strongly affected by the inclusion of urea. Typical curves are shown in Figure 1 where molecular weight distribution is shown for laboratory-prepared samples of SUMF containing 60% urea (U-6), 80% urea (U-8), and SMF resins containing pure melamine as the amino component. Figure 1 shows that 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 weight species and leads to a decrease in the proportion of high molecular weight species. Also, as the proportion of urea increases, the low molecular weight species shift towards lower molecular weight. This is also clearly seen when one compares weight average molecular weights obtained on samples of SMF (100% M), U-6 (60% U), and U-8 (80% U) (Table II). These results are in agreement with the nature of urea and melamine as monomer precursors in the condensation reaction. Comparing urea and melamine, the former can be considered a bifunctional molecule, whereas the latter is trifunctional. Therefore, an increase in the melamine content should increase the average number of branching points, thus increasing the hydrodynamic

TABLE II
Molecular Weight Distribution of Selected SUMF Resins

Sample no.	Designation	Apparent wt average molecular weight ($\bar{M}_w$)	Apparent no. average molecular weight ($\bar{M}_n$)	Polydispersity ($\bar{M}_w/\bar{M}_n$)	Remarks
01	SUMF (U-6)[a]	267,000	16,000	16.7	Reference U-6 sample
02	SUMF (U-6)	591,000	25,200	23.5	Same as 01 pH_3 = 4.0
03	SUMF (U-6)	161,000	18,100	8.9	Same as 01, t_3 = 120 min
04	SUMF (U-6)	590,000	46,1000	12.8	Same as 02, concn = 30%, pH_3 = 3.5
05	SUMF (U-6)	665,000	39,700	16.8	Same as 05, concn = 40%, pH_3 = 3.5
06	SUMF (U-6)	775,000	51,100	15.2	Same as 05, t_4 = 90 min
07	SUMF (U-6)	855,000	58,800	14.5	Same as 05, t_4 = 180 min
08	SUMF (U-8)[b]	184,000	18,500	10.00	20% melamine, reaction conditions same as 01
09	SMF (100% M)[c]	1,130,000	70,700	16.0	100% melamine, reaction conditions same as 01
010	SMF (100% M)	1,020,000	136,000	7.5	Commercial Melment L-10

[a] SUMF (U-6) means sulfonated urea–melamine formaldehyde with urea 60% and melamine 40%.
[b] SUMF (U-8) means sulfonated urea–melamine formaldehyde with urea 80% and melamine 20%.
[c] SMF (100% M) means sulfonated melamine formaldehyde with 100% melamine.

volume. This is manifested in the gel permeation chromatographic analysis as resins with higher molecular weight. Although the obtained results show no indications of urea–melamine random copolymers, the UV absorbance of the eluted fractions suggest that the amount of melamine in the high molecular weight fraction is higher than that in the low molecular weight fractions. Thus, it is possible that the prepared SUMF are mostly mixtures of SUF and SMF resins with only a small proportion of random SUMF resins.

Effect of Solution Concentration on Molecular Weight Distribution. Depending on the final application, the sulfonated amino–formaldehyde resins are usually employed at low concentrations ranging from 5 to 20% solid content. However, it is more economical if these resins are prepared at higher concentrations and then diluted to the desired values. In this study, solution concentrations ranging from 20 to 40% were prepared and the effect of this on the molecular weight distribution was determined.

The effect of preparation concentration is seen in Figure 2. The three SUMF resin samples shown in Figure 2 were prepared under the same reaction conditions, but at three different concentrations of 20, 30, and 40%. Increasing the

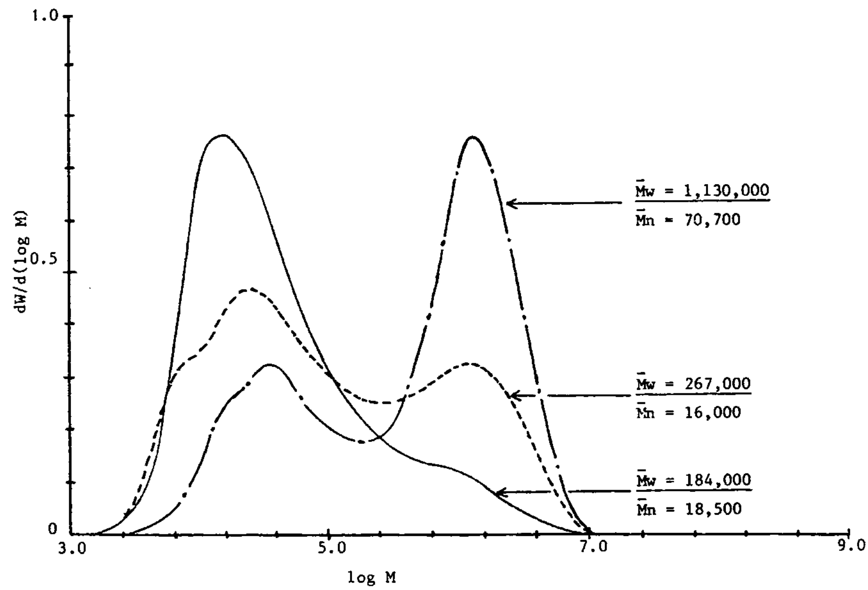

Fig. 1. Effect of urea on the molecular weight distribution of resin U-8 (——) (sample 8), resin U-6 (- - -) (sample 1), and SMF resin (- • - • -) (sample 9).

concentrations from 20 to 40% leads to an increase in the weight average molecular weight. The number average molecular weight was found to increase when the concentration increased from 20% ($\bar{M}_n$ = 16,000) to 30% ($\bar{M}_n$ = 46,000), but then decreased slightly ($\bar{M}_n$ = 39,700) when the concentration was further increased to 40%. The increase in the weight average molecular weight is anticipated on the basis that the order of dependance of the rate of condensation polymerization reactions is higher than unity with respect to the reactants. Also, according to Flory,[9] weight average molecular weights are sensitive to the presence of larger species, whereas the number average molecular weight is sensitive to the proportion by weight of smaller molecules. At 40% concentration, the increased concentration tends to condense the low molecular weight species leading to a higher proportion of larger molecular weight species. Thus, the weight average molecular weight ($\bar{M}_w$) increases at the expense of the number average molecular weight ($\bar{M}_n$). Figure 2 also shows that as the concentration increases the fraction of the high molecular weight species increases.

Effect of Reaction Conditions. The effect of reaction conditions on the performance of these resins as dispersants was studied in detail. Some of the results on sulfonated melamine formaldehyde performance were reported previously.[2] It was found from those studies that the reaction conditions of the third step (low pH condensation step) and the fourth step (high pH condensation or rearrangement step) are most influential on the final properties of these resins. More specifically, the pH, temperature, and time of reaction of the third and fourth step were found to influence the final performance as well as the stability of these products. In this study, the third step, alkalinity (pH_3) and time (t_3) and the fourth step time (t_4) were studied. Since time and tem-

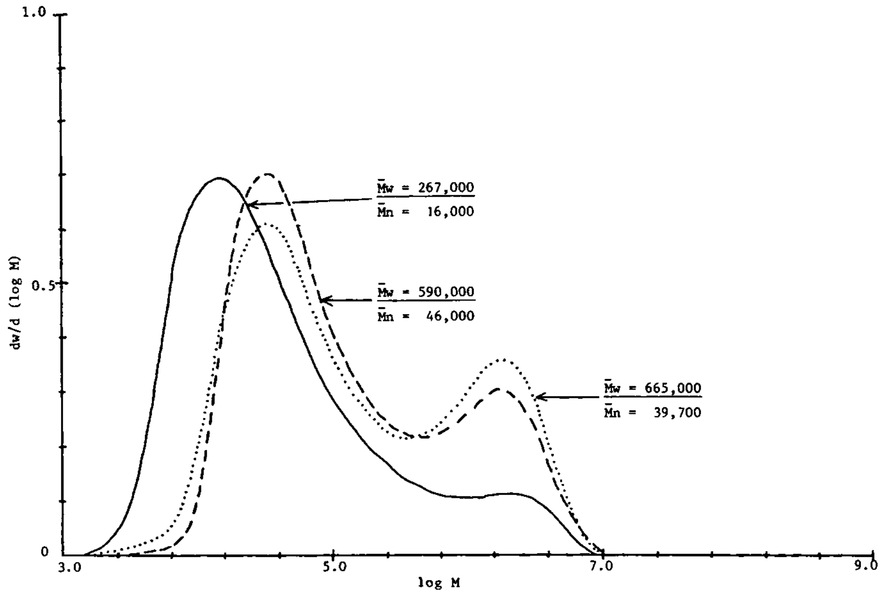

Fig. 2. Effect of solution concentration on the molecular weight distribution of SUMF (U-6) resins prepared at 20% (——) (sample 1), 30% (- - -) (sample 4), and 40% (-----) (sample 5).

perature are equivalent in chemical reactions, the temperature of both steps was kept constant.

Effect of Third Step Acidity (pH_3) and Reaction Time (t_3) on Molecular Weight Distribution. The effect of reaction pH during the low pH condensation step on the molecular weight distribution is shown in Figure 3. Although the rate of condensation is known to increase with decreasing pH,[10] our findings from the gel permeation chromatographic analysis show that increasing pH_3 from 3.0 to 4.0 led to an increase in $\bar{M}_w$ from 267,000 to 591,000. There are two types of linkages that take place in this type of reaction, namely, ether linkages and methylene linkages. With part of the condensation reactions taking place during the low pH condensation as ether crosslinks, it is postulated that extremely low value pH leads to the hydrolysis of this type of crosslink and prevents the formation of fractions with high molecular weight. Further evidence of hydrolytic influence of very low pH_3 values comes from the GPC data of experiments where t_3 was increased from 60 to 120 min at pH_3 = 3.0. The weight average molecular weight was found to decrease from 267,000 (t_3 = 60 min) to 161,000 (t_3 = 120 min) as shown in Figure 4.

Figure 3 shows that as the pH of the third step increases from 3 to 4, the fraction of the high molecular weight species also increases while the fraction of the low molecular weight species decreases. Another observation is that there are two humps existing on the curve of Figure 3 that suggest that the final product might contain separate entities of sulfonated urea products and sulfonated melamine products. The first hump represents the sulfonated urea species whereas the second hump occurring at higher molecular weight represents the sulfonated melamine products. On the other hand, Figure 4 shows

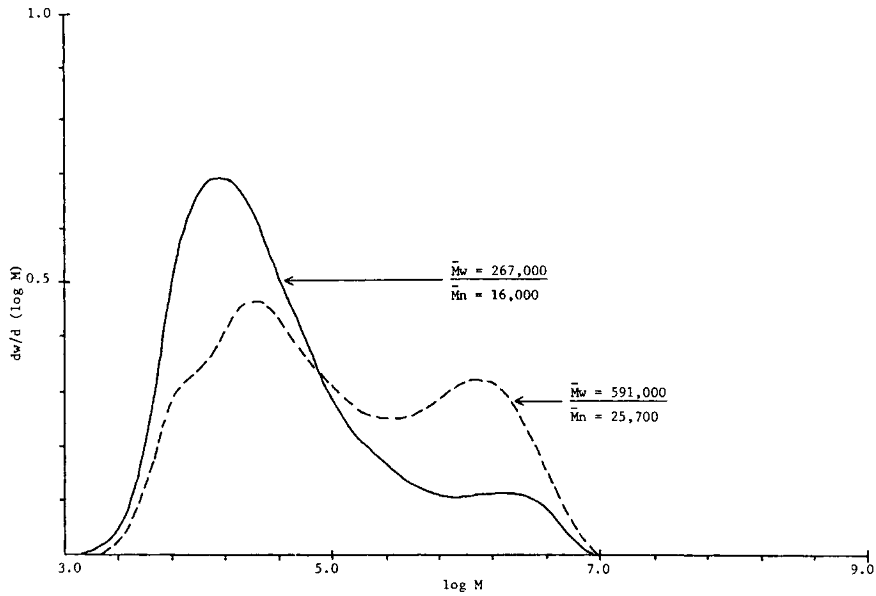

Fig. 3. Effect of third step acidity on the molecular weight distribution of SUMF (U-6) resins prepared at $pH_3 = 3.0$ (——) (sample 1) and $pH_3 = 4.0$ (- - -) (sample 2).

that, as the reaction time of the third step increases, the final product contains a lower fraction of the high molecular weight species and the distribution gets narrower. The weight average molecular weight decreases as the time of reaction of the low pH condensation step increases suggesting that hydrolysis of the ether linkages takes place.

Effect of Fourth Step Reaction Time (t_4) on Molecular Weight Distribution. The effect of reaction time during the high condensation step (t_4) on the molecular weight distribution was also studied. The conditions of the fourth step were found to strongly influence the stability of resin solutions to ageing. It was found that increasing the time during the fourth step led to more stable products as evidenced by the changes in the compressive strength changes during ageing (Table III). The stability test was conducted by storing the various prepared resins at 60°C for 2 weeks. Sand was then treated with these resins before and after they were aged. The results in Table III show that when these resins are prepared at higher concentration, they become less stable. However, stability is improved significantly when the reaction time in the fourth step, t_4, is increased from 40 to 180 min as is evident from the percentage drop in compressive strength of the treated sand from 25.8 to 12.9% respectively. Figure 5 shows the molecular weight distribution of U-6 (60% urea) samples prepared at different reaction times during the fourth step. It can be seen that longer reaction periods lead to an increase in the high molecular weight fractions. When t_4 was increased from 40 to 90 and then to 180 min, $\bar{M}_w$ increased from 267,000 to 775,000 and then to 855,000, respectively. Although it is known that lower pH values favor further condensation, the rate of condensation during step 4 at $pH_4 = 9.0$ is still appreciable enough to afford higher molecular weight

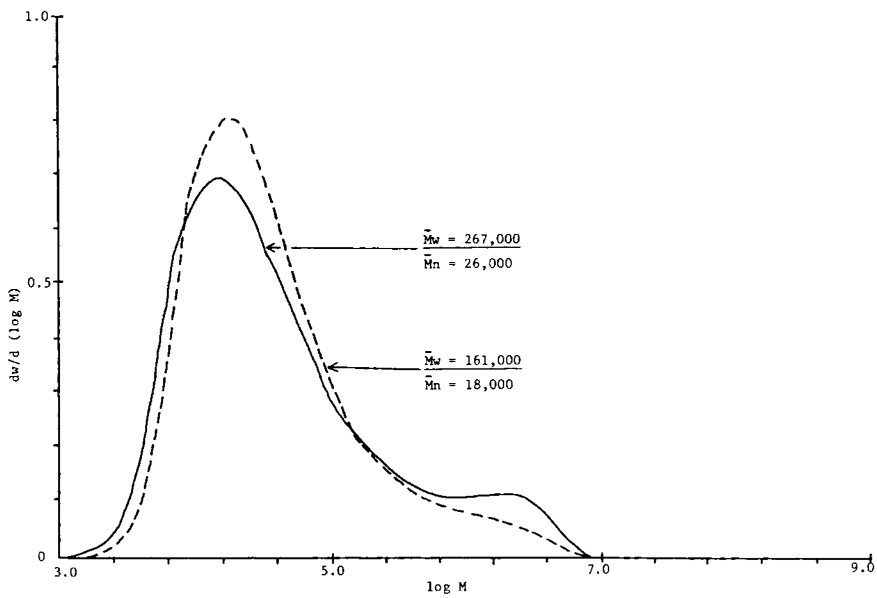

Fig. 4. Effect of third step reaction time on the molecular weight distribution of SUMF (U-6) resins prepared at t_3 = 60 min (——) (sample 1) and t_3 = 120 min (- - -) (sample 3).

species as end products of the preparation. It is also postulated that the increased stability of the resultant solutions prepared with longer t_4 durations is a product of the presence of these higher molecular weight fractions that resist further reactions at extended periods of aging. The shape of Figure 5 also suggests the existence of two separate polycondensates based on urea and melamine. The fraction of high molecular weights represent sulfonated melamine formaldehyde and the fraction of low molecular weights represents sulfonated urea formaldehyde polycondensates.

TABLE III
Effect of Accelerated Aging[a] on the Compressive Strength[b] Development of Sandy Soil Treated with Some SUMF Samples

			Compressive strength of treated sand (kg/cm^2)		
Sample no.	Concentration of resin (%)	t_4 (min)	Before aging	After aging	% Change
04	30	40	23.2	17.9	22.6
05	40	40	24.9	18.6	25.8
06	40	90	22.9	18.9	17.8
07	40	180	21.9	19.0	12.9

[a] Accelerated aging of resin solution was at 60°C for 14 days.
[b] Compressive strength of treated sandy soil for a dose of 1.0% (weight of solid resin to weight of sandy soil).

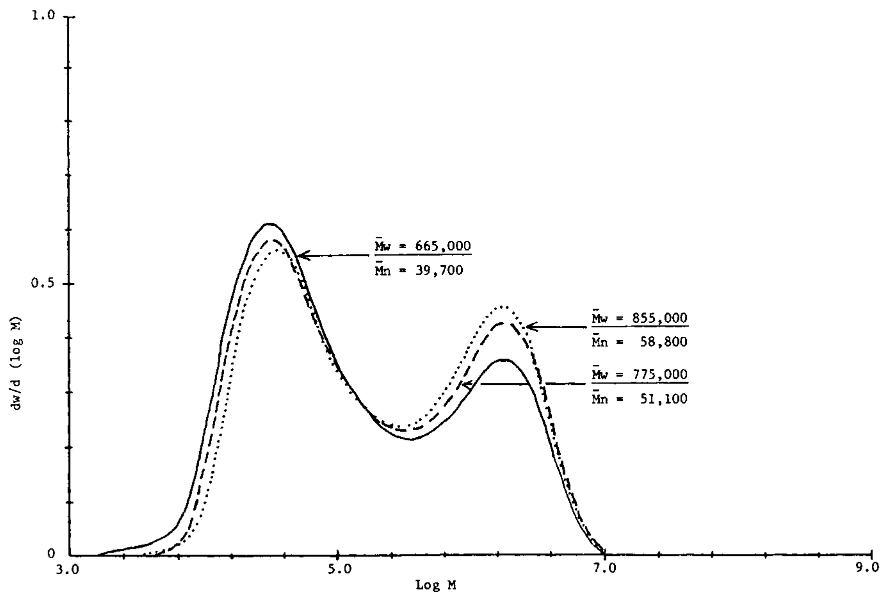

Fig. 5. Effect of fourth step reaction condition on the molecular weight distribution of SUMF (U-6) resins prepared at t_4 = 40 min (——) (sample 5), t_4 = 90 min (- - -) (sample 6), and t_4 = 180 min (sample 7).

Effect of Reaction Variables on the Performance of These Resins as Soil Stabilizers. The effect of the main reaction variables of step 3 and step 4 (i.e., pH_3, t_3, and t_4) and the effect of reaction solution concentration on the molecular weight distribution of these resins was discussed above. The resins are effective dispersants and they were applied to sandy soil to improve its mechanical properties. More specifically a 1% (weight of solid resin to weight of treated soil) of these resins were mixed with sandy soil and specimens of the treated sand were molded, cured and tested for compressive strength according to a standard procedure outlined before.[5] The results are shown in Table IV. The data shows that the third step acidity (pH_3) and time (t_3) have very little effect on compressive strength of treated sand as evidenced from samples 1, 2, and 3. However, the increase in the weight average molecular weight of these resin by increasing pH_3 or decreasing t_3 increases slightly the compressive strength of treated sand. The effect of reaction time in the fourth step (t_4) on the compressive strength of treated sand is much more pronounced as evidenced from examples 5, 6, and 7. As t_4 increases, $\bar{M}_w$ increases and thus the fraction of the molecular weight species resulting in a lower compressive strength value of treated sand. Similarly as the concentration of the prepared resins increase from 20 to 40%, $\bar{M}_w$ also increases but the compressive strength of the treated sand increases as evidenced from samples 1, 4, and 5. These results are consistent if one examines the molecular weight distribution or the polydispersity of these resins. Table II shows that as the concentration of resin solutions increases from 20 to 40% polydispersity increases from 8.9 to 16.8 and so does the compressive strength of the treated sand which increases from

TABLE IV
Effect of Main Reaction Variables on the Performance of These Resins as Soil Stabilizers

	Reaction conditions				
	Step 3		Step 4	Concentration of prepared resins	Compressive[a] strength of treated sand
Sample	pH_3	t_3	t_4	(%)	(kg/cm^2)
Control	—	—	—	—	4.74
01	3.0	60	40	20	17.00
02	4.0	60	40	20	17.50
03	3.0	120	40	20	16.90
04	3.5	60	40	30	23.20
05	3.5	60	40	40	24.90
06	3.5	60	90	40	22.90
07	3.5	60	180	40	21.90

[a] Compressive strength of treated sandy soil for a dose of 1.0% (weight of solid resin to weight of sandy soil).

16.9 to 24.9 kg/cm^2, respectively. On the other hand, as the reaction time (t_4) increases from 40 to 180 min, the polydispersity decreases from 16.8 to 14.5 and so does the compressive strength of the treated sand which decreases from 24.9 to 21.9 kg/cm^2, respectively. Therefore, the compressive strength of the treated sand gets improved as the molecular weight distribution gets broader. The broad distribution of these resins might be responsible in providing the appropriate proportions of the low and high molecular weight species that are responsible for rendering these resins effective dispersing abilities.

CONCLUSION

It can be concluded from this study that reaction conditions of sulfonated urea–melamine formaldehyde resins have a great influence on their molecular weight distribution. The sulfonation of urea and melamine formaldehyde appears to result in a mixture of sulfonated urea formaldehyde and sulfonated melamine formaldehyde. The final performance of these materials seems to be governed by the fraction of the high molecular weight species that is being affected by the reaction conditions. The third step pH and time as well as a fourth step time of reaction and the percent of urea to melamine along with their concentration in solution have a great influence on the weight average molecular weight and molecular weight distribution of these resins and their performance as dispersing agents.

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