Water-Soluble Sulfonated Melamine–Oxytriazine Resins: Synthesis and Properties as Dispersants*

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Synopsis

Oxytriazine impurities are frequently considered as undesirable compounds in the production of melamine resins. In this study, we have determined the reaction conditions required for preparing water-soluble sulfonated melamine–oxytriazines formaldehyde resins using a four-step process involving cycling of temperature and pH to avoid gelation of the resins. The properties of the prepared resins as dispersants for cement mortars and concrete mixes were examined, and the products were found to be slightly inferior to comparable resins prepared from pure melamine.

INTRODUCTION

Melamine resins have been well known for over half a century. Nevertheless, to their application and the problems encountered during their preparation are still being studied.[1] A major problem in the synthesis of these resins is their sensitivity to the presence of the impurities that are produced during the manufacturing of melamine. These impurities include various compounds such as ammeline, ammelide, and cyanuric acid, which cause wide fluctuations in polycondensation rates. Thus, Zagranichmyi et al.[2] reported that melamine containing as little as 0.1% cyanuric acid or ammeline reacts with formaldehyde three times as fast as does pure melamine. Mlochowski et al.,[3] however, found that these compounds considerably increase polycondensation time. Ammelide also causes this effect.[4] In addition to their effect on kinetics, these compounds usually cause an undesirable color in the resulting resins, particularly in molding resins. No studies have been reported on the effects of higher concentrations of these compounds on the properties of the polycondensation resins.

The object of this study was to determine the reaction conditions required for synthesizing a specific class of resins, namely sulfonated resins, from melamine and oxytriazines. Sulfonated resins were selected because in color is not critical for their use in the construction industry as dispersants, similar to the uses of analogous pure melamine resins.[5]

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EXPERIMENTAL

Materials

Crude melamine containing up to 30% oxyaminotriazines was obtained from Kuwait Melamine Industries Company. The analysis of a typical sample (N, 59.5%; C, 28.3%; H, 4.40%) was compared with that of pure melamine sample (N, 66.6%; C, 28.6%; H, 4.8%). Cyanuric acid (Al-Sane Chemical Co., Kuwait) was used without further purification. The analysis for a typical sample (C, 26.8%; H, 2.4%; N, 31.5%) compared with the calculated one for $C_3N_3O_3H_3$ (C, 27.9%; H, 2.3%; N, 32.5%). Paraformaldehyde laboratory pure grade (Fluka) and sodium metabisulfite ($Na_2S_2O_5$), laboratory pure grade (Fluka) were also used with no further purification.

Procedure

Determination of Oxytriazines. A sample of crude melamine containing various oxytriazines was weighed, treated with excess NaOH solution, and then continuously stirred for 2 h. The mixture was then filtered, and the filtrate neutralized with HCl solution. After aging for 12 h, the filtrate was filtered under vacuum, and the resulting oxytriazine solids were dried in an oven at 105°C and weighed.

Preparation of Resins. To prepare the sulfonated resins, the process involves hydroxymethylation, sulfonation, condensation at low pH and a rearrangement reaction at high pH. A detailed description of a typical experiment is given below.

Exactly 50.34 g paraformaldehyde (94.6% formaldehyde by weight) was mixed with 230 mL water. A basic mixture was produced by adding NaOH solution and heating this at 55°C for 30 min with continuous agitation. Then the pH was adjusted to 12 and an additional 88 mL of water was added. The solution was cooled to 45°C, 50 g melamine–oxytriazines mixture was added and the mixture agitated for a further 15 min. A slurry of 37.7 g sodium metabisulfite and 12 mL water were then added to the reaction solution. The reaction was continued at 80°C for 120 min, and then the temperature was lowered to 45°C and the pH to 3.0 by adding 30 mL H_2SO_4 (14.5*M*). The reaction solution was agitated under these conditions for another 60 min. Then its pH was raised to 7 by adding NaOH solution, and it was heated to 80°C with continuous agitation; it was kept under these final conditions for 60 min. The solution was then diluted to 20% resin content after adjusting its pH to 11. Its viscosity at 20°C is 3.2 cP.

Resins based on melamine/cyanuric acid mixtures were prepared in a similar manner to that described above. The main modification, which prevents gelation at early stages of the preparation, was to heat the reaction solution prior to adding sodium metabisulfite.

Cement mortars were prepared using standard mixers with ordinary Portland cement (Type I) and sand with (ASTM C-109) standard specifications.

Equipment

The heating and cooling cycles and the duration of the reaction at each step of the preparation of sulfonated resins are critical for successful production of the water-soluble ones. To ensure reproducibility of results and to prevent the gelation of the resin, four jacketed flasks thermostated at the desired temperature by circulating baths were set up.[6] Reaction solutions were transferred between flasks using efficient peristaltic pumps to rapidly cool or heat the solutions and to control the reaction conditions. The solution's pH was continuously monitored and adjusted to the desired reaction conditions using standard pH meters with combination glass electrodes. Viscosities were measured with a Haake Rotation Viscometer, Model CV 100, with a ME-30 sensor. Consistency was measured by a Vicat needle apparatus manufactured by Soiltest Inc., according to ASTM C-187 different needle size. Compressive strength was measured by an Instron Universal Testing Machine, Model 1195.

RESULTS AND DISCUSSION

The preparation and the properties of melamine–formaldehyde polycondensation resins are affected strongly by the presence of other amino groups or compounds, such as the oxytriazines that form during the manufacturing of melamine under reduced ammonia pressure (Fig. 1). The effect of these byproducts on the polymerization reactions of melamine with aldehydes can be attributed to their acidity, and to the mesomeric forms that exist in solution under the polycondensation reaction conditions. Ammeline, which is the main byproduct, has a phenolic hydroxyl group; consequently, the dissociation constant for the protonic hydrogen on that group is larger than those of the amine groups. This increased dissociation constant results in a lower pH for the reaction rate. Furthermore, both the reactivity of the oxytriazines towards formaldehyde and the condensation reaction that follows are affected significantly by the phenolic groups and the effect of these groups on the basicity of the amino groups, and the ring nitrogen. In addition, the prevalent mesomeric forms vary between various oxytriazines and depend on the number of hydroxyl groups in the ring. Thus, melamine is predominantly in the aromatic amine form, while cyanuric acid was found in the solid state to exist

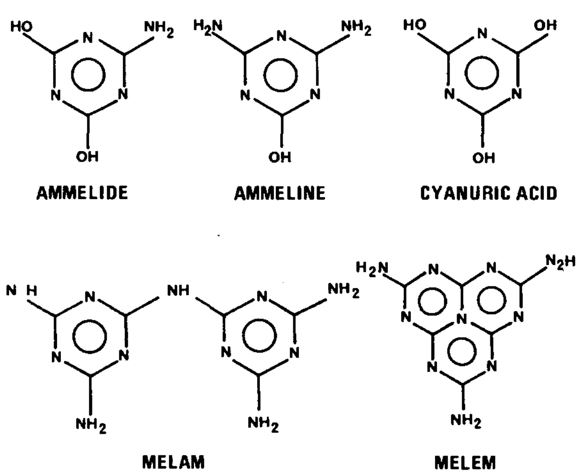


Fig. 1. The most important oxytriazines formed during melamine manufacturing.

in the triketo form only.[7] For example, formaldehyde (HCHO) condenses with ammelide at a ring NH group, whereas with ammeline it reacts with the NH_2 groups.[8] Similarly, Kucharski and Rokszewski[9] observed that HCHO reacts only with the ring NH groups of cyanuric acid.

Because of these effects, production of melamine-based resins requires pure melamine as a starting material. Impure melamine is, therefore, generally disposed of as waste or occasionally treated to recover pure melamine. In this study, we have successfully prepared a number of melamine–oxytriazine resin solutions in which part of the melamine is replaced by either 30% mixture of oxytriazine or up to 50% pure cyanuric acid. The resins are sulfonated amino–formaldehyde condensates that can have a wide variety of applications as dispersants in the cement, concrete, paper, oil drilling, and solid processing industries.

To prepare the desired resin solutions, a four-step synthetic procedure is used (Fig. 2). The procedure is analogous to a procedure developed for pure melamine resins[6] except that the reaction conditions are different. The type of chemical reactions that take place during the synthesis are similar to those of pure melamine resins. However, since the present mixture consists of many components, the number of reactions and equilibria involved are considerably larger and more complex, particularly during the hydroxymethylation and sulfonation steps. We will, therefore, analyze these two steps in more detail.

Hydroxymethylation. The general reaction that takes place during this step is a nucleophilic attack by a basic group on the carbonyl group of

$$X + aF \underset{t_1}{\overset{T_1 \;\; pH_1}{\rightleftharpoons}} XF_a \quad \text{(Step 1 = Hydroxymethylation)}$$

$$XF_a + S \xrightarrow[t_2]{T_2 \;\; pH_2} XF_aS \quad \text{(Step 2 = Sulfonation)}$$

$$XF_aS \xrightarrow[t_3]{T_3 \;\; pH_3} P_1(XF_aS) \quad \text{(Step 3 = Low pH Condensation)}$$

$$P_1(XF_aS) \xrightarrow[t_4]{T_4 \;\; pH_4} P_2(XF_aS) \quad \text{(Step 4 = High pH Rearrangement.}$$

Where:

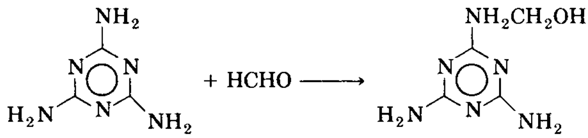
X	= Effluent solids
F	= Formaldehyde
S	= Sulfite group
XF_aS	= Sulfonated formaldehyde-waste solid monomers
$P_1(XF_aS)$	= Low-pH condensation intermediate
$P_2(XF_aS)$	= Final product
T_i	= Temperature of corresponding step
pH_i	= pH of corresponding step
t_i	= Reaction time of corresponding step

Fig. 2. The four-step synthetic procedure for preparing resin solutions.

formaldehyde [reaction (1)]:

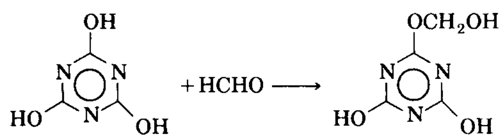
$$-\underset{|}{B}H + HCHO \longrightarrow -\underset{|}{B}CH_2OH \qquad (1)$$

For a compound containing more than one type of basic group, the group involved in the addition reaction with formaldehyde depends on the relative basicities and the steric requirements of the groups. Thus, for *s*-triazine compounds with amino groups such as melamine, the preferred reaction sites are the amino groups [reaction (2)] as opposed to the ring nitrogen groups:

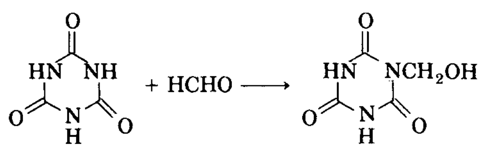


(2)

On the other hand, for *s*-triazine compounds with no amino groups, such as cyanuric acid, which contains hydroxyl groups, two types of reactions are possible [reactions (3) and (4)]. Detailed studies of these reactions showed that reaction (4) is the preferred one. Under appropriate conditions of pH and temperature, however, we may anticipate competition by reaction (3) to be important to the overall reaction:



(3)



(4)

In addition to the competition among various sites within the same molecule, intermolecular competition for formaldehyde among components of the triazine mixture may be important. This is caused by the differences in the basic properties of the molecules, which are affected by changes in the reaction conditions (e.g., pH and temperature).

Sulfonation. The reactions that can take place during this step are

$$-NCH_2OH + HSO_3^- \longrightarrow -NCH_2SO_3^- + H_2O \qquad (5)$$

$$-OCH_2OH + HSO_3^- \longrightarrow -OCH_2SO_3^- + H_2O \qquad (6)$$

$$HCHO + HSO_3^- \longrightarrow -HOCH_2SO_3^- \qquad (7)$$

The hydroxymethylated groups shown in reactions (5) and (6) are the expected products of addition reactions such as those shown in reactions (2), (3), and (4). The sulfonation step is actually a complicated series of equilibria involving the hydroxymethylated products of the components of the melamine-oxytriazine mixture.

Low pH Condensation. This step results in the formation of solid condensation products when the reaction is allowed to continue for relatively long periods. The exact reaction taking place is not known, but the reaction conditions suggest that ether-linkage type products are formed:

$$2\,NHCH_2OH \longrightarrow -NHCH_2OCH_2NH - + H_2O \quad (8)$$

This type of condensation is favored at low temperatures with pH 2–5. Temperature and pH must be used to control the extent of condensation.

High pH Rearrangement. This is necessary to stop the condensation reactions in step 3 and prevent the gelation of the resins, if water-soluble resins are desired. The reactions taking place in step 4 are not well understood. The conditions are, however, appropriate for methylene-linkage type condensation [reaction (9)]. It appears that some of the condensation linkages formed during the previous step break up or rearrange as evidenced by the sharp reduction in viscosity which occurs immediately following the addition of base. This step seems to be essential at this stage to improve the stability of the condensates toward further crosslinking:

$$\sim NHCH_2OH + \sim NH_2 \longrightarrow \sim NHCH_2NH + H_2O \quad (9)$$

Effects of Reaction Conditions on Products. From the condensation chemistry of melamine and urea, it is well known that the synthesis of condensation resins, and in properties, depend on pH, temperature, duration of each step of the synthesis procedure and the nature of the reactants. In this study of sulfonated melamine–oxytriazine formaldehyde resins, we investigated the effect of time of the sulfonation and the low pH condensation steps (steps 2 and 3), and the effect of temperature in the hydroxymethylation and low pH condensation steps (steps 1 and 3) on the viscosities of the final product. We also investigated the effects of the formaldehyde/melamine–oxytriazines ratio and the presence of high percentages of cyanuric acid.

The results indicate generally that, to have water-soluble resins, sulfonation (step 2) must be conducted at pH 11.5 or higher. Solid products form if the pH is lower than 11.5 or if the sulfonation reaction time is less than 60 min. The sulfonation step was examined further by preparing the resins at sulfite to melamine–oxytriazines molar ratios of 0.8–1.1. At ratios lower than 1.0, the tendency of the resins to precipitate as insoluble solids is very high. Thus, it appears that the effect of the sulfonate group is similar to that observed for pure melamine resins, namely, to block one of the polymerizable sites of the methylol derivatives of melamine or oxytriazines, and to solubilize the resulting condensation resins as a result of the hydrophilic properties of the sulfonate group.

Selected resin preparation conditions are listed in Table I. Generally, the viscosity of the resulting resin is not affected by the reaction time of steps 2 and 4 (resins 1–5). This is to be expected as no condensation reaction can occur in these two steps of the preparation procedure. The largest difference observed between the synthesis of the present resins and those of pure melamine (resins 10 and 12) is in the pH of steps 1 and 2 and the conditions of step 3. With pure melamine resins, at pH higher than 11.5, the prepared resin

TABLE I
Effect of Reaction Conditions on the Viscosity of the Resin Solution[a]

Sample	Resin no.	T_1 (°C)	t_2 (min)	T_3 (°C)	t_3 (min)	t_4 (min)	Viscosity[b] (cP)
5022	1	45	90	45	10	60	2.64
8005	2	45	90	45	30	60	3.44
5023	3	45	120	45	10	60	2.80
8001(1)	4	45	120	45	30	60	3.10
5032	5	45	120	45	30	120	3.05
5033	6	45	120	45	30	180	3.03
8001	7	45	120	45	60	60	3.20
8003	8	45	120	55	60	60	3.30
8004	9	55	120	55	75	60	3.58
8006	10	55	120	70	150	60	5.60
	11	80	120	80	120	60	Solid resin
	12[c]	50	60	50	110	60	5.40
	13[d]	45	50	40	10	60	4.15

[a]All resins except those indicated are prepared from melamine-oxytriazine mixture (Fig. 2). The remaining reaction conditions as shown in Figure 2 are: $pH_1 = pH_2 = 12.0$, $t_1 = 15$ min, $T_2 = T_4 = 80$°C, $pH_3 = 3.0$, and $pH_4 = 7.0$.

[b]Viscosity measurements were conducted at 20°C on the resin solution after dilution to 20% solid content.

[c]Pure melamine resin. The remaining reaction conditions are $pH_1 = pH_2 = 11.3$, $t_1 = 15$ min, $T_2 = T_4 = 80$°C, $pH_3 = 3.5$, and $pH_4 = 7.0$.

[d]Resin prepared with 20% cyanuric acid. The remaining reaction conditions are $pH_1 = 10.5$, $pH_2 = 12$, $t_1 = 20$ min, $T_2 = T_4 = 80$°C, and $pH_3 = 3.0$.

solutions become dark yellow in color during step 1, presumably as a result of a reaction which affected our control of the remaining steps and prevented us from synthesizing resin with the desired viscosity range of 4–6 cP. In contrast, the condensation resins with oxytriazine must be prepared at a pH higher than 11.5 as discussed above. Generally, for oxyaminotriazine, temperatures up to 70°C and reaction time up to 150 min are required in step 3 to achieve a viscosity of 5.60 cP while the melamine resin required milder conditions with temperatures of around 50°C and time of 110 min to achieve the same degree of condensation. This indicates that the reactivity of the oxytriazines toward condensation is less than that of pure melamine. This should also be anticipated since the more basic amino groups are being replaced by hydroxy groups in the oxytriazine compounds.

A number of experiments were also conducted, using melamine/cyanuric acid mixtures ranging between 10 and 50%, to assess the possibility of preparing water-soluble sulfonated resins containing high percentages of oxytriazines, of which cyanuric acid is the least reactive toward formaldehyde. We were able to conclude from these experiments that such resins could be prepared if appropriate reaction procedures are followed. Thus, an adjustment of the pH to 12.0 and the temperature to 80°C for the sulfonation step prior to the addition of sodium metabisulfite is essential for preparing water-soluble resins.

The resulting resin solutions are clear with a very faint yellow coloration. The thermal stability of the solutions was tested by monitoring the viscosity

TABLE II
Effect of Some Prepared Admixtures on Percentage of Water Reduction and Setting Times of Cement Paste

Resin sample no.	Resin to cement (%)	Water reduction (%)	Setting time Initial	Setting time Final
Neat	0	0	3.00	4.00
7	1	6.52	2.75	3.00
	3	19.56	3.75	3.00
	5	28.26	5.75	6.00
8	1	6.52	3.00	3.25
	3	19.56	3.25	4.00
	5	28.26	5.50	5.75
10	1	6.52	3.75	4.25
	3	19.56	4.25	4.25
	5	30.40	6.50	7.25
12	1	4.35	3.25	3.00
	3	21.74	4.00	4.25
	5	30.43	4.75	5.00

as a function of time. Under ambient temperature, viscosity of the solution remained practically constant for a period of approximately 6 months. Similarly, at 60°C, no change in viscosity was observed for up to two weeks.

Properties of Prepared Resins as Dispersants

One of the most important applications of pure-melamine-based sulfonated resins is their use as dispersants in cement.[5] Thus, it seems appropriate to investigate the use of the novel melamine–oxyaminotriazine resins for similar applications to assess their properties in comparison with those of pure melamine.

Table II shows the results of the effect of the prepared resins on the percentage of water reduction required to maintain the same consistency, and on the settling time of cement pastes, using different doses of resin solutions. The results for pure melamine-based product (resin 12) are also listed for comparison. The incorporation of oxytriazines did not affect adversely the properties of the resins. Table III shows the compressive strength of cement

TABLE III
Effect of Some Prepared Resins on the Compressive Strength of Mortar Mixes.

Resin sample no.	Water reduction (%)	Compressive strength (kg/cm^2) 1 (days)	3	7	28
Neat	—	100.0	173.7	217.4	323.0
7	13.4	114.6	212.6	263.9	416.0
8	13.4	105.6	211.6	278.0	336.4
10	13.4	120.5	181.7	239.2	236.9
12 (pure melamine-based)	13.4	171.9	254.5	288.4	412.7

mortars prepared with various prepared resins, pure-melamine-based resin, and neat mortar containing no resin. These results also confirm the possibility of utilizing these resins as dispersants and the fact that their effectiveness is comparable with that of pure melamine resins.

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