Water-Soluble Sulfonated Phenolic Resins. I. Synthesis

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SYNOPSIS

A new water-soluble sulfonated phenolic resin as a water reducer in concrete was prepared in this study. It was synthesized from formaldehyde, phenol, and NaHSO₃ through a four-step reaction procedure. The structure of resin was determined through analyses of IR and NMR spectra. The influence of reaction conditions on the properties of synthesized products was also examined and discussed. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Water-soluble sulfonated resins have been applied in many areas such as the paint industry and dye manufacturing.[1,2] Another important area of applications is in construction engineering. The resins are called water-reducing admixtures. Lignosulfonate is one of the typical examples of the resins used in the concrete industry for more than 30 years. It could reduce by 8–10% the amount of water to obtain a concrete of a given workability. It is known that strength of concrete is inversely proportional to the water/cement ratio.[3] Therefore, concrete treated with water reducers will exhibit higher strength than the untreated. Recently a new category of admixtures has appeared. These admixtures, called superplasticizers (SPs) or high-range water reducers, have the ability to reduce the amount of water up to 30% while maintaining workability. Sulfonated melamine formaldehyde condensate and sulfonated naphthalene formaldehyde condensate are two well-established commercial SPs[4,5] As SPs offer considerable advantages in producing concrete with high workability at much lower water/cement ratio and developing much higher strength, the SP reinforced cementitious materials have been applied increasingly in the construction of high level structures such as high-rise buildings, bridges, and off-shore structures.[6]

Due to their industrial importance in concrete technology, the properties of admixtures as well as their actions on concrete have been continuously studied and explored.[6,7] And new types of admixtures are being evaluated or developed.[8] This work focuses on the latter aspect; that is, a new water-soluble resin, namely, sulfonated phenolic resin (SPR), was prepared and evaluated as a water reducer for cementitious materials. Phenolic resins have been developed for more than 75 years. They are used for moldings and many other applications due to their good electrical properties, high heat resistance, and excellent mechanical properties.[1] It is thought that SPR is a potential admixture for cementitious materials. The preparation of SPR is described in this article. The structure of synthesized resin was determined by IR and NMR spectra. The amount of sulfonate groups and the molecular weight are two key parameters determining how effective the resin is that is used as a water reducer in concrete. Therefore, the influence of reaction conditions on the sulfur/carbon ratio of SPRs and the viscosity of aqueous SPR solutions is discussed. The surface activity of SPR and its performance in cement mortars will be reported in the companion article.

EXPERIMENTAL

Preparation of Resins

Phenol, formaldehyde, and NaHSO₃ were used as reactants and NaOH as a catalyst. The mole ratio of phenol/formaldehyde/NaHSO₃ was fixed at 1/
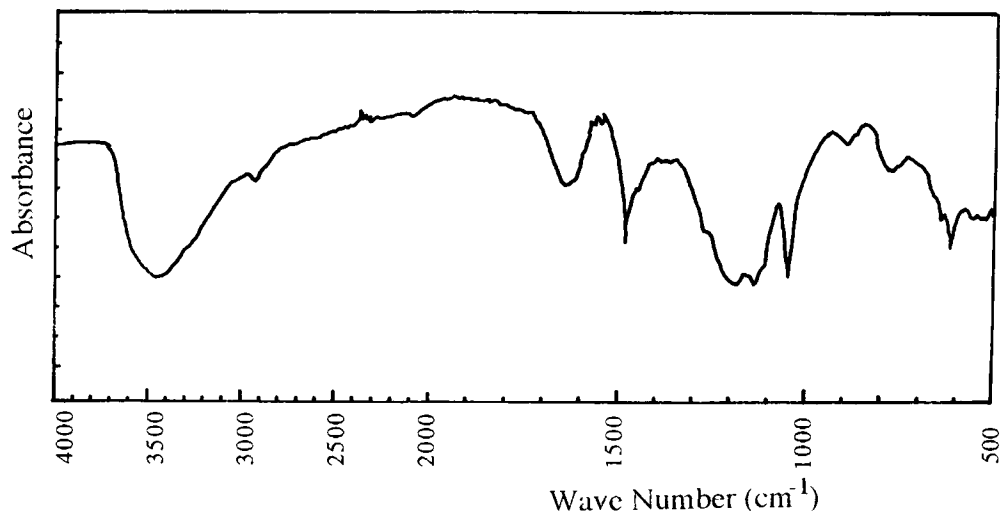
Figure 1   The IR spectrum of sulfonated phenolic resin.

2/1. SPRs were prepared from the above materials through addition, sulfonation, condensation, and rearrangement reactions. The procedure of each reaction step is described in the following sections.

Step 1: Addition Reaction

This step is the formation of methylol-substituted phenols from phenol and formaldehyde. The reaction scheme is shown below:
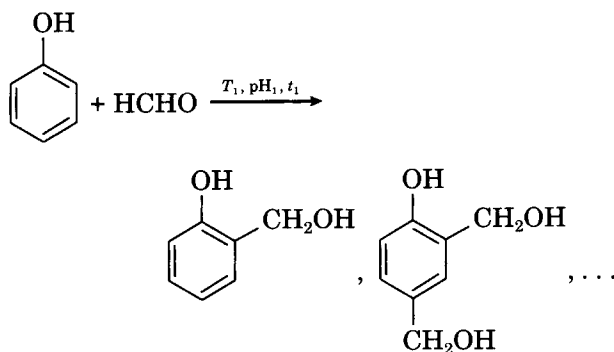

Either mono-, di-, or trimethylolphenols were possibly formed, depending on the reactant concentration and reaction conditions. The substituted groups are expected to be in either the *ortho* or *para* position of phenol.[9]

Step 2: Sulfonation Reaction

This step is the sulfonation of methylolphenols to produce water-soluble sulfonated methylolphenols. As the sulfonation went on, the methylol groups in methylolphenols were gradually replaced by the

$-CH_2SO_3^-$ groups. The reaction scheme is shown below:

$$-CH_2OH + HSO_3^- \xrightarrow{T_2,pH_2,t_2} -CH_2SO_3^- + H_2O$$
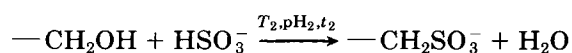
Step 3: Condensation Reaction

The polymerization of water-soluble sulfonated methylolphenols was conducted in this step in obtaining resins with high molecular weight. The resin structure with dimethyl ether bridges was produced from the following condensation of the remaining methylol groups in the molecules:
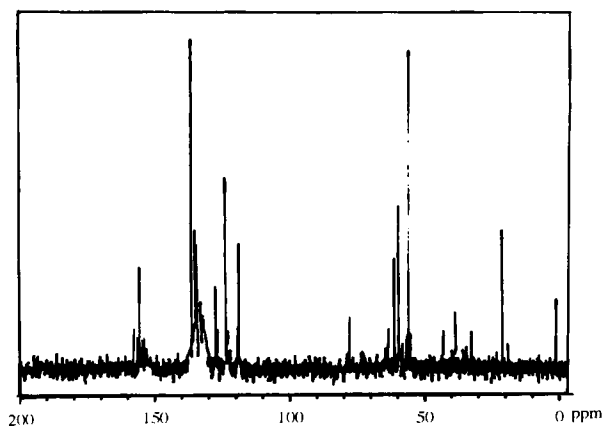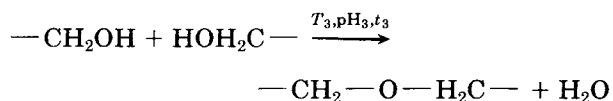
$$-CH_2OH + HOH_2C- \xrightarrow{T_3,pH_3,t_3}$$

$$-CH_2-O-H_2C- + H_2O$$

Figure 2   The ^{13}C-NMR spectrum of sulfonated phenolic resin via a four-step reaction.
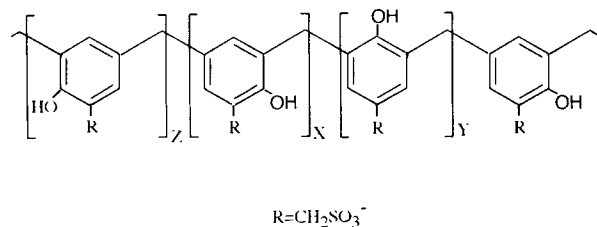
R=CH₂SO₃⁻

Figure 3   The structure of a sulfonated phenolic resin.

Step 4: Rearrangement Reaction

The resins from the previous step were produced under acidic conditions. They are not stable in a basic environment. This step is to rearrange the resin structure so that a more stable structure with methylene bridges was obtained,[10] as is shown below:

$$-CH_2-O-H_2C- \xrightarrow{T_4, pH_4, t_4} -CH_2- + H_2O$$
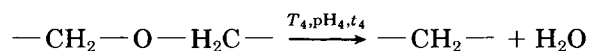
Phenol, 19 g, and 37% formaldehyde solution, 33 g, were added into a stirred reactor with reflux. The reaction mixture was heated at 80°C for 20 min after its pH was raised to 11 by adding 85 mL 2N NaOH solution. Next, 21 g NaHSO₃ in 20 mL of water was added and the mixture was kept at the same temperature and pH value for 60 min. In the third step, the mixture was cooled down and its pH was adjusted to 4 by adding 5 mL 18N H₂SO₄ solution. Reaction was carried out at 50°C for 90 min. Finally, the mixture was neutralized by the addition of 0.5 g Ca(OH)₂ and further reacted at 90°C, pH value of 7, for 60 min. Then the reacted mixture was filtered
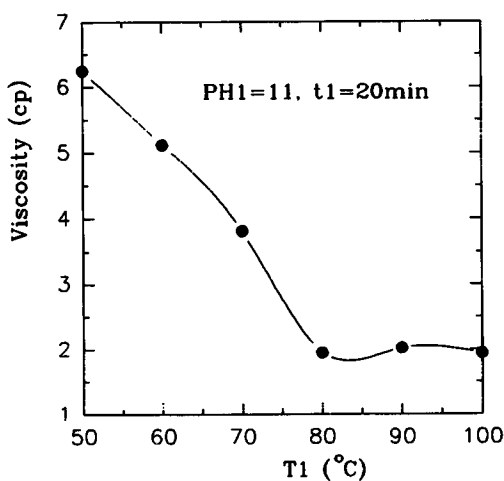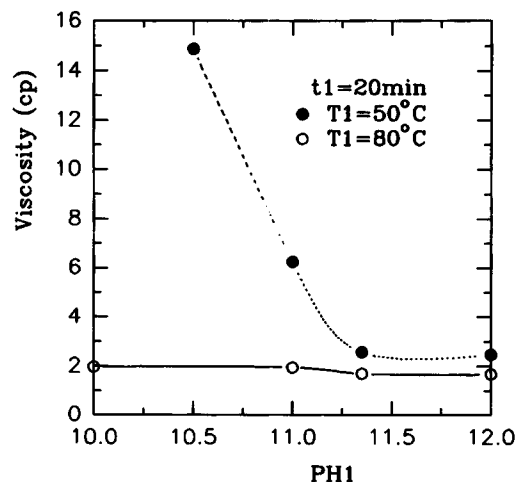

Figure 5   The effect of pH value in step 1 on the viscosity of resin solution. (T_2 = 80°C, pH₂ = 11, t_2 = 60 min; T_3 = 50°C, pH₃ = 4, t_3 = 90 min; T_4 = 90°C, pH₄ = 7, t_4 = 60 min).

to remove calcium sulfate or other solid particles and a resin solution of yellowish brown color was finally obtained. The solid content in the solution was about 20%. In other words, the product yield was approximately 50%.

Identification of Prepared Resins

SPRs were obtained from the reaction mixture following the above four-step reaction procedure through filtration and drying. These resins were further purified in an alcohol/water solution three times, dried, and ground into powder before struc-
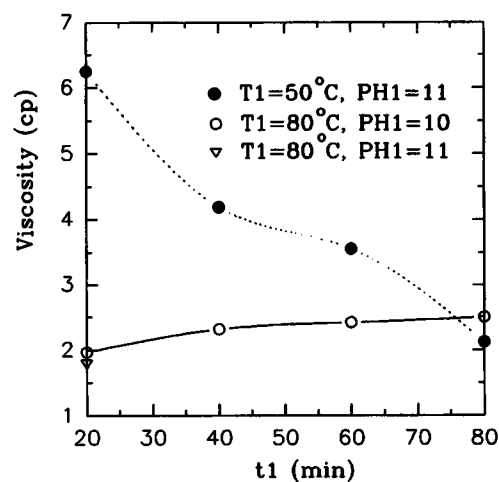

Figure 4   The effect of temperature in step 1 on the viscosity of resin solution. (T_2 = 80°C, pH₂ = 11, t_2 = 60 min; T_3 = 50°C, pH₃ = 4, t_3 = 90 min; T_4 = 90°C, pH₄ = 7, t_4 = 60 min).

Figure 6   The effect of time in step 1 on the viscosity of resin solution. (T_2 = 80°C, pH₂ = 11, t_2 = 60 min; T_3 = 50°C, pH₃ = 4, t_3 = 90 min; T_4 = 90°C, pH₄ = 7, t_4 = 60 min).

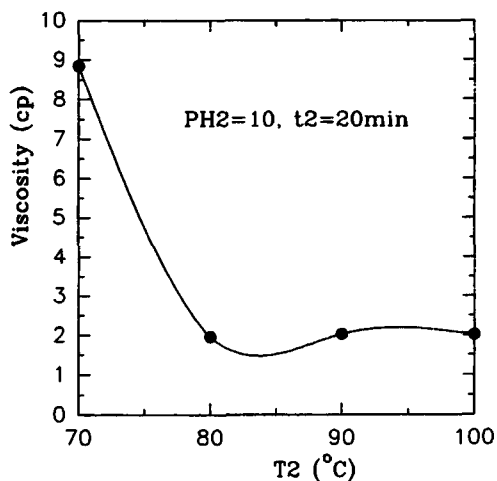**Figure 7** The effect of temperature in step 2 on the viscosity of resin solution. (T_1 = 80°C, pH_1 = 10, t_1 = 20 min; T_3 = 50°C, pH_3 = 4, t_3 = 90 min; T_4 = 90°C, pH_4 = 7, t_4 = 60 min).

ture determination or other uses. A Jasco IR-700 spectrometer and a Joel EX-400 NMR spectrometer were applied for the identification of resins.
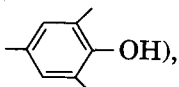
Viscosity and Sulfur/Carbon (S/C) Ratio Measurements

The viscosity of resin solutions was measured by a Brookfield DV-II viscometer. A Leco CS-244 analyzer was used for determining the S/C ratio of SPRs. Thus, the sulfonation groups in the resin molecule could be estimated.
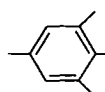
RESULTS AND DISCUSSION

Structure of Prepared Resins

The IR and ^{13}C-NMR spectra of a typical prepared resin are shown in Figures 1 and 2, respectively. The IR spectrum displayed bands at 3486 (O — H), 1478 (C — H, aromatic), 1185, 1044 (S — O), and 612 cm^{-1} (S — O).[11] The ^{13}C-NMR spectrum of the resin sample gave signals at 153.8–158 ppm (phenoxy car-

bon connecting to hydroxyl group, ![structure]—OH),

118–136.6 ppm (aromatic carbons except for the one connecting to the hydroxyl group, ![structure]—OH), 30.9, 37.1, 41.6 ppm (2,2', 2,4', and
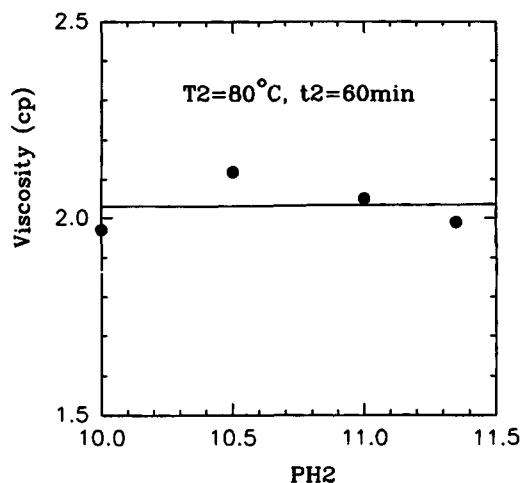
4,4' bridging methylene carbons, —CH$_2$—). All

Figure 8 The effect of pH value in step 2 on the viscosity of resin solution. (T_1 = 80°C, pH_1 = 10, t_1 = 20 min; T_3 = 50°C, pH_3 = 4, t_3 = 90 min; T_4 = 90°C, pH_4 = 7, t_4 = 60 min).

these signals and their corresponding structure units are referred to the ^{13}C-NMR spectra of phenolic resins.[12] In additions, new signals at 54.7, 58.4, and 60.1 ppm were observed in Figure 2. No information is currently available on the characterization of sulfonated phenolic resins by ^{13}C-NMR analysis. The signals do not belong to aromatic sulfonates (e.g.,

![structure]—SO$_3^-$), whose chemical shifts should be

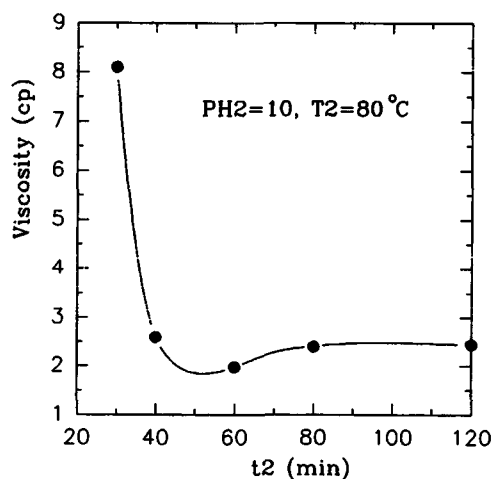at 140–150 ppm.[13] They were believed to be the sulfonate group —CH$_2$SO$_3^-$, because Pasch et al. confirmed the signals of —NHCH$_2$SO$_3^-$ groups

Figure 9 The effect of time in step 2 on the viscosity of resin solution. (T_1 = 80°C, pH_1 = 10, t_1 = 20 min; T_3 = 50°C, pH_3 = 4, t_3 = 90 min; T_4 = 90°C, pH_4 = 7, t_4 = 60 min).
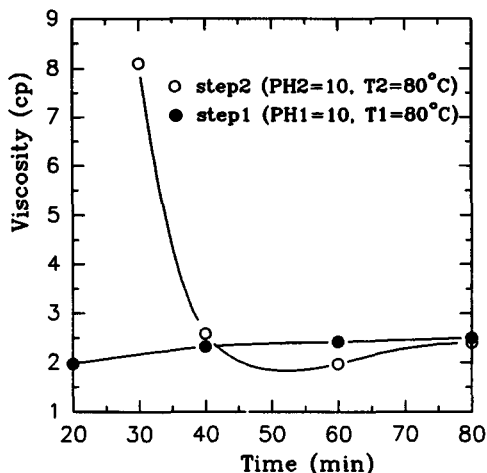
Figure 10   The comparison of time effect on the viscosity of resin solution between step 1 and step 2. (T_3 = 50°C, pH_3 = 4, t_3 = 90 min; T_4 = 90°C, pH_4 = 7, t_4 = 60 min).

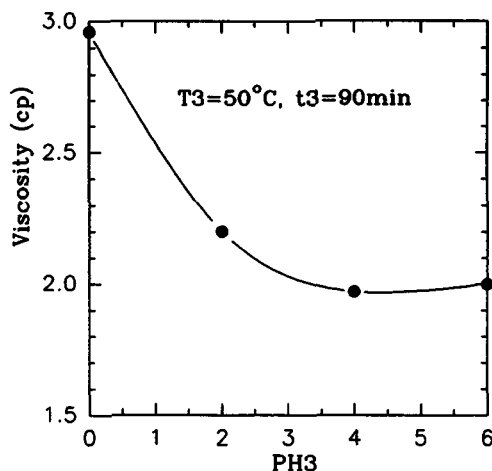**Figure 12**   The effect of pH value in step 3 on the viscosity of resin solution. (T_1 = 80°C, pH_1 = 10, t_1 = 20 min; T_2 = 80°C, pH_2 = 11, t_2 = 60 min; T_4 = 90°C, pH_4 = 7, t_4 = 60 min).

occurred at 50.8, 60.7, and 62.5 ppm in their investigations of the chemical structure of sulfonated amino-formaldehyde resins using ^{13}C-NMR.[14] Figure 3 presents the chemical structure of the resin following the analysis of the IR and NMR spectra in Figure 2. The true structure of sulfonated phenolic resins would be highly branched because phenol has three active sites for reactions. The $X/Y/Z$ ratio of the structure unit in Figure 3 is 1/1.4/1, that was evaluated from the signal intensities at 30.9, 37.1, and 41.6 ppm from Figure 2. The $X/Y/Z$ ratio will obviously be different for different resin sample.

Viscosity of Resin Solution

The molecular weight or chain length of resins is usually controlled in a certain range to achieve the best performance in concrete.[4,5] In this study, the resin solutions with 20 wt % solid content were prepared, as the solid contents in most commercial admixtures are about 20–40 wt %. The viscosity of resin solutions was measured and used as an indication of the molecular weight of prepared resin. In the following the influence of the reaction conditions of each step on the viscosity of resin solution is discussed.
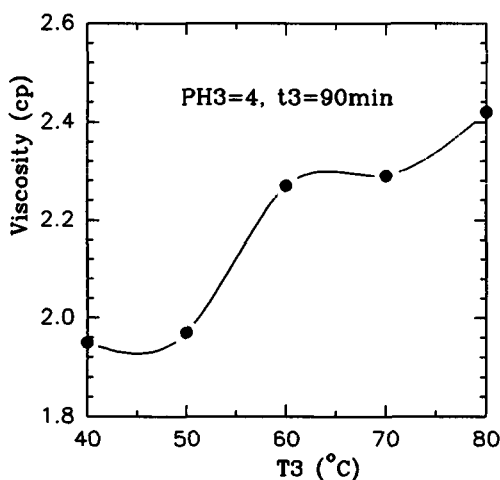

Figure 11   The effect of temperature in step 3 on the viscosity of resin solution. (T_1 = 80°C, pH_1 = 10, t_1 = 20 min; T_2 = 80°C, pH_2 = 11, t_2 = 60 min; T_4 = 90°C, pH_4 = 7, t_4 = 60 min).

Figure 13   The effect of time in step 3 on the viscosity of resin solution. (T_1 = 80°C, pH_1 = 10, t_1 = 20 min; T_2 = 80°C, pH_2 = 11, t_2 = 60 min; T_4 = 90°C, pH_4 = 7, t_4 = 60 min).

Figure 14 The effect of pH value in step 4 on the viscosity of resin solution. (T_1 = 80°C, pH_1 = 10, t_1 = 20 min; T_2 = 80°C, pH_2 = 11, t_2 = 60 min; T_3 = 50°C, pH_3 = 4, t_3 = 90 min).
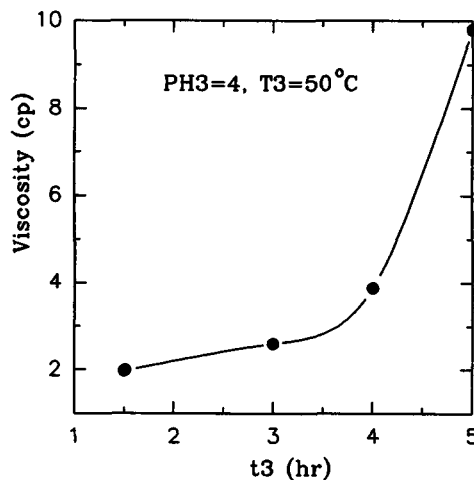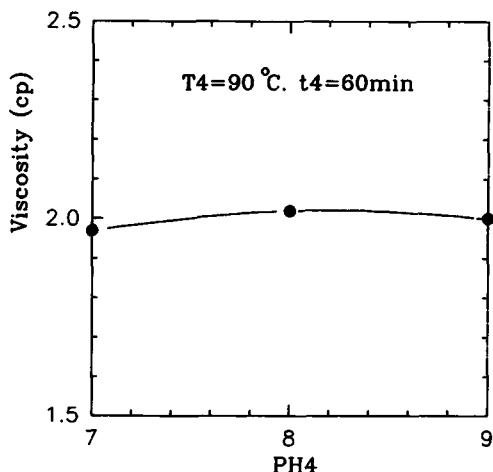

Figure 16 The effect of time in step 4 on the viscosity of resin solution. (T_1 = 80°C, pH_1 = 10, t_1 = 20 min; T_2 = 80°C, pH_2 = 11, t_2 = 60 min; T_3 = 50°C, pH_3 = 4, t_3 = 90 min).

Step 1 Reaction

Methylolphenols are the compounds produced from the addition reaction of reactants in this step. The influence of reaction temperature (T_1) on the viscosity of resin solution is shown in Figure 4. The solution viscosity is decreased with T_1 at pH_1 = 11 and reaction time (t_1) = 20 min. When T_1 is equal to 80°C or higher, there is not much variation in the solution viscosity. At T_1 < 80°C the addition goes on slowly and the formation of methylolphenols appeared to be incomplete after 20 min reaction. They were formed continuously in the next step because both steps 1 and 2 had similar reaction conditions.
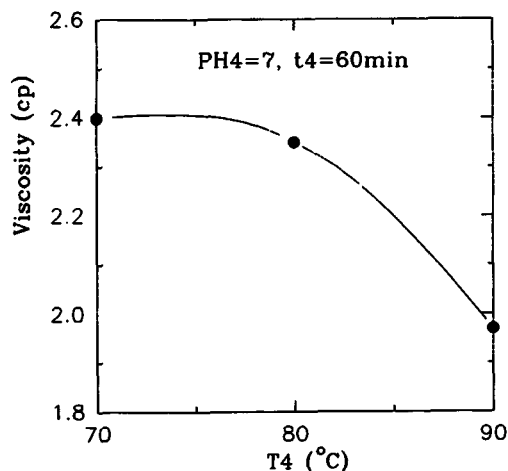
This leads the sulfonation in step 2 to being incomplete. The incomplete sulfonation would then result in accelerating the condensation in step 3.[15] Consequently, the solution viscosity of the final resin is higher. As temperature goes up, the reaction rate increases. When temperature is at or above 80°C, 20 min seems to be long enough and most reactants converted into methylolphenols. Thus, the solution with low viscosity was observed in Figure 4. It is noted that the temperature is controlled within 80–100°C to produce methylolphenols in industrial production of phenolic resins.[9]

Figure 15 The effect of temperature in step 4 on the viscosity of resin solution. (T_1 = 80°C, pH_1 = 10, t_1 = 20 min; T_2 = 80°C, pH_2 = 11, t_2 = 60 min; T_3 = 50°C, pH_3 = 4, t_3 = 90 min).
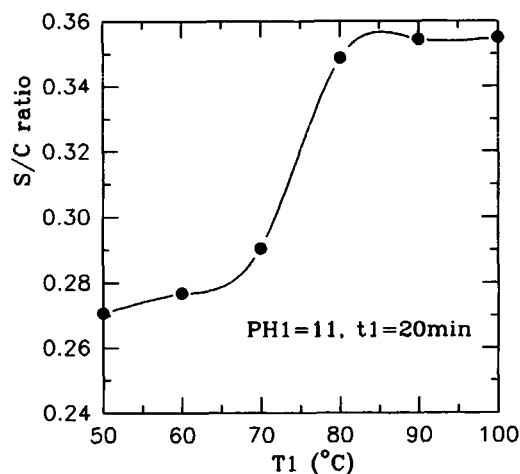

Figure 17 The effect of temperature in step 1 on the S/C ratio of resin. (T_2 = 80°C, pH_2 = 11, t_2 = 60 min; T_3 = 50°C, pH_3 = 4, t_3 = 90 min; T_4 = 90°C, pH_4 = 7, t_4 = 60 min).
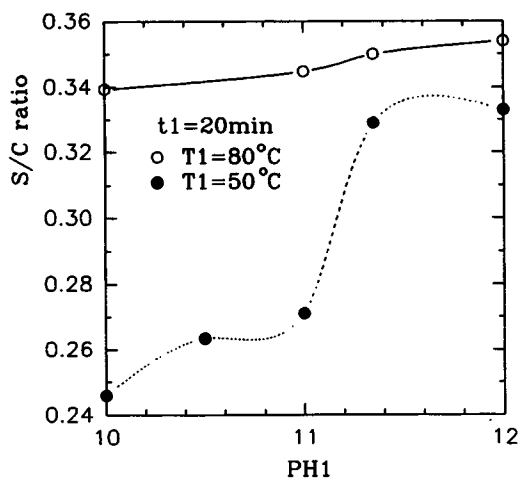
Figure 18 The effect of pH value in step 1 on the S/C ratio of resin. ($T_2 = 80°C$, $pH_2 = 11$, $t_2 = 60$ min; $T_3 = 50°C$, $pH_3 = 4$, $t_3 = 90$ min; $T_4 = 90°C$, $pH_4 = 7$, $t_4 = 60$ min).

Figure 20 The effect of temperature in step 2 on the viscosity of resin solution. ($T_1 = 80°C$, $pH_1 = 10$, $t_1 = 20$ min; $T_3 = 50°C$, $pH_3 = 4$, $t_3 = 90$ min; $T_4 = 90°C$, $pH_4 = 7$, $t_4 = 60$ min).

Figures 5 and 6 shows the effect of pH_1 and t_1 on the viscosity of the resin solution, respectively, at different temperatures. At $T_1 = 50°C$, the solution viscosity is decreased with either pH_1 or t_1. Higher pH value or longer reaction time would promote the addition and produce more converted methylol-phenols. This leads the sulfonation in the next step to be more efficient. As a result, lower solution viscosity was obtained. In contrast, all resin solutions exhibited low viscosity for T_1 of 80°C. This indicates that the addition was sufficient in this situation and was not much affected by either pH value or reaction time.

From the above, methylolphenols could be sufficiently formed in this step under the conditions of
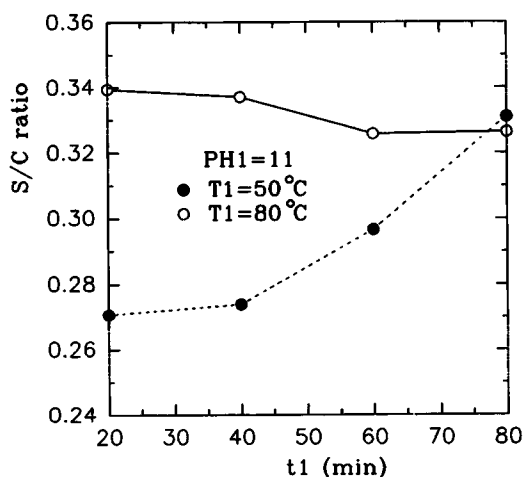
$T_1 = 80-100°C$, $pH_1 = 10-11$, and $t_1 = 20$ min. If the temperature is below 80°C, higher pH value or longer reaction time would help to complete the addition.

Step 2 Reaction

Figure 7 demonstrates the relationship between the viscosity of resin solution and the sulfonation temperature (T_2). The solution viscosity at $T_2 = 80°C$ was about 8.9 cp, which was higher than those at $T_2 = 80-100°C$. It is implied that the sulfonation would be incomplete at lower temperature due to slower

Figure 19 The effect of time in step 1 on the S/C ratio of resin. ($T_2 = 80°C$, $pH_2 = 11$, $t_2 = 60$ min; $T_3 = 50°C$, $pH_3 = 4$, $t_3 = 90$ min; $T_4 = 90°C$, $pH_4 = 7$, $t_4 = 60$ min).

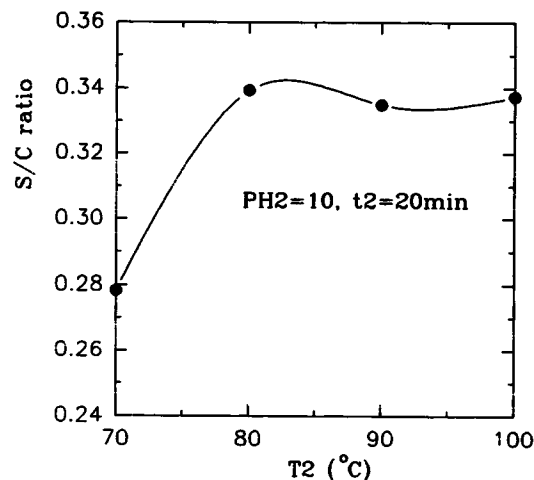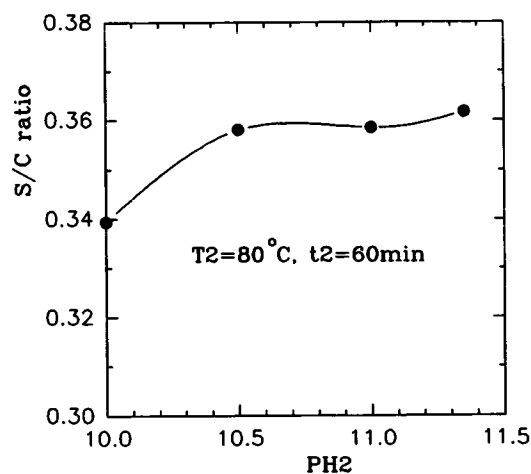**Figure 21** The effect of pH value in step 2 on the viscosity of resin solution. ($T_1 = 80°C$, $pH_1 = 10$, $t_1 = 20$ min; $T_3 = 50°C$, $pH_3 = 4$, $t_3 = 90$ min; $T_4 = 90°C$, $pH_4 = 7$, $t_4 = 60$ min).

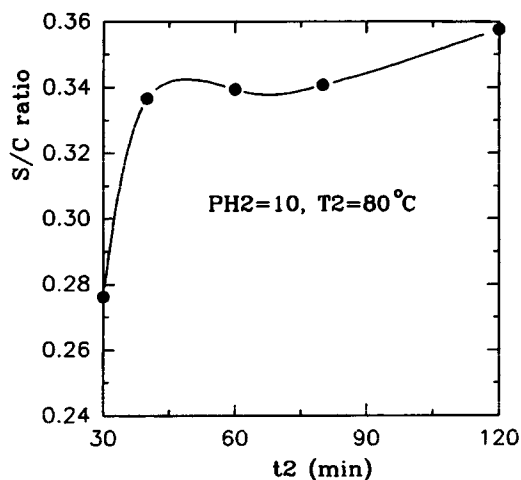**Figure 22**   The effect of time in step 2 on the S/C ratio of resin. ($T_1 = 80°C$, $pH_1 = 10$, $t_1 = 20$ min; $T_3 = 50°C$, $pH_3 = 4$, $t_3 = 90$ min; $T_4 = 90°C$, $pH_4 = 7$, $t_4 = 60$ min).

reaction rate. Again, the incomplete sulfonation would cause the condensation in the subsequent step to be accelerated and more viscous solution was obtained.[15] If the temperature was lowered to 60°C, even insoluble resin products or precipitates occurred. For T_2 ranging from 80 to 100°C, the degree of sulfonation would be sufficient and all solution viscosities were below 2.5 cP and close to each other. The influence of pH value on the viscosity of resin solution is shown in Figure 8. At $T_2 = 80°C$ and $t_2 = 60$ min, the pH effect is minimal. Figure 9 illustrates the effect of reaction time on the viscosity of resin solution. At short reaction time, more viscous solution was obtained. If t_2 was below 30 min, insoluble resins were indeed produced. As time increased, the solution viscosity decreased as a response to higher degree of sulfonation. When $t_2 > 60$ min, the solution viscosity would be slightly increased with time due to some premature condensation.

The results in step 2 are apparently similar to those in step 1. In fact, both steps belong to the substitution nucleophilic bimolecular (S_N2) reaction,[16] so they can be carried out under similar conditions. However, a subtle difference was present when making a comparison of these two reactions, as is indicated in Figure 10. Under the same pH value and controlled temperature, the required time was about 40 min to accomplish sulfonation, which is much longer than that to accomplish addition. The difference can be accounted for by two factors. First, the phenolate ion was the nucleophile in step 1 that is stronger in basicity and more powerful in attacking the substrate than the sulfite ion in step

2.[16] Second, the rate constant in step 1 is greater than that in step 2.[17] Therefore, the addition reaction requires less time to be complete than the sulfonation reaction.

Step 3 Reaction

The temperature (T_3) effect on the viscosity of resin solution is shown in Figure 11. Increasing temperature would fasten the condensation reaction and produced higher solution viscosity. However, the temperature in this step is suggested to be controlled at lower value in avoiding the accelerating buildup of the solution viscosity as the reaction continues.[15] Both pH value and reaction time have a similar effect as temperature, as is indicated from the results in Figures 12 and 13. In other words, the solution viscosity increases with decreasing pH value or increasing time.

Step 4 Reaction

The effect of reaction conditions on the viscosity of resin solution is illustrated in Figures 14–16. The influence of pH value on the solution viscosity was observed from Figure 14 to be insignificant. Increasing either temperature or time would enhance the rearrangement of resin structure. Accordingly, a slight decrease of the solution viscosity was found in Figures 15 and 16.

S/C Ratio of Resins

Knowing the degree of sulfonation in resin molecules is necessary because it affects the surface activity of resins and the effectiveness for being used as a water reducer in cementitious materials. In this study, the degree of sulfonation in resin molecules was indicated by the measured S/C ratio of each resin sample. Figures 17–22 show the effect of reaction conditions in either step 1 or 2 on the S/C ratio of SPRs. The response of the S/C ratio to reaction conditions was similar for these two steps because both steps went on with similar S_N2 reactions. The S/C ratio of resin was generally increased with temperature, pH value, and reaction time as an indication that either addition in step 1 and/or sulfonation in step 2 became more sufficient. For temperature less than 80°C, a great change in the S/C ratio was observed in Figures 17, 18, or 20. As temperature reached 80°C or higher, the change in the S/C ratio of resin seemed to be insignificant. One exception, as is shown in Figure 19, is that the S/C ratio was slightly decreased with time for T_1

= 80°C and pH$_1$ = 11. This phenomenon was believed to be the occurrence of some condensation. In other words, some dimer, trimer, or higher multimers were formed from methylolphenols and increased with time under such reaction conditions. The reaction conditions in steps 3 and 4 do not affect the S/C ratio very much and was confirmed by the experimental results.

The results on the S/C ratio of resins are consistent with those on the viscosity of resin solutions. The trend of the S/C ratio in Figures 17–22 was just opposite to that of the solution viscosity in Figures 4–9 in changing with reaction conditions. The solution viscosity apparently decreases as the S/C ratio increases. This infers that sulfonation and condensation are affected by each other.[17] Finally, the S/C ratios of most resins produced in this study are within 0.32–0.36. The calculated S/C ratio of resin based on the chemical structure illustrated in Figure 3 is 0.333. These values are close to each other. It indicates that most synthesized resins were undertaken with sufficient sulfonation.

As a water reducer in concrete, water-soluble resin must have good dispersant properties determined by its sulfonate group content and its molecular weight.[18] In the synthesis of SPR, products with high S/C ratios usually result in low solution viscosities because sulfonation and condensation affect each other. It appears that those resins with sufficient sulfonation would be more effective for applications in concrete, as will be discussed more in our companion article.

CONCLUSIONS

A new sulfonated phenolic resin that will be used as a water reducing agent in concrete was synthesized through a four-step reaction. The chemical structure of resin was determined by IR and NMR spectra. The properties of resin were also determined. To obtain resins with suitable properties (i.e., low viscosity and high degree of sulfonation) for applications in concrete, the addition and sulfonation reactions should be controlled under strong base conditions with pH = 10, temperature 80–100°C, reaction time of 20 and 60 min, separately. The condensation reaction was about 1.5 h under a weak acid state with pH = 4–5, and temperature of 50°C. The rearrangement reaction was maintained at a temperature of 90–100°C and pH of 7–9 for 1 h. Furthermore, the higher the S/C ratio the resin possesses, the lower the viscosity of its aqueous solution is. By controlling the reaction conditions carefully, the S/C ratios of most produced resins are about 0.32–0.36, which approaches the limit of sulfonation.

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