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The material properties of sulphonated phenolic resin reinforced cement mortars

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The material properties of new sulphonated phenolic resin (SP) reinforced cement mortars have been investigated. SP was found to promote the dispersion of cement particles and to interact with $Ca(OH)_2$. As a result, the resulting mortars exhibit better workability, more compact structure and higher compressive strength than plain mortars. The mortar with 1 wt% SP present after 28 days curing exhibits a compressive strength of 66 MPa, which is about 18% higher than that of plain mortar.

1. Introduction

Recently, high performance concrete (HPC) has become very attractive to civil engineers. HPC is defined as a high level construction material and has high performance to compensate the effect of poor structural detailings or construction works [1]. This material could be made by including certain proportions of chemical admixtures such as superplasticizer or minerals such as silica fume or slag in concrete through proper mixing. The water/cement ratio is lowered to the range 0.2–0.4 [2]. As it exhibits superior properties such as workability, mechanical properties and durability over conventional concrete, HPC has been increasingly applied in such constructions as tall buildings, bridges and off-shore structures [3].

Meanwhile, a new inorganic material, called chemically bonded ceramics (CBC), has also been developed. CBC can be prepared by adding chemical aids such as polymer or superplasticizer into cement paste or concrete, then is high-shear mixed and compression moulded with or without vibration [4]. CBC interests material scientists very much not only because its properties are close to structural ceramics but also because it can be fabricated at low temperatures without sintering steps. This new material was thought to be able to replace plastics and metals in a wide variety of applications [5].

As mentioned above, superplasticizer is an important ingredient in making either CBC or HPC. Sulphonated melamine formaldehyde condensate and sulphonated naphthalene formaldehyde condensate are two well-known commercial admixtures [6]. Superplasticizer plays a dual role in cementitious materials. Physically, it controls the amount of free water and the rheology of fresh concrete to improve the deformation and the segregation behaviour [7]. It also acts as a lubricant or a dispersing agent so that the cement particles are uniformly dispersed and high mechanical strength of the resulting material is obtained [8, 9]. Chemically, it can interact with $Ca(OH)_2$ which is one of the hydrated products of cement so as to modify the morphology and to reduce the permeability of concrete [10, 11].

Due to the industrial importance of superplasticizer in cement-based material technology, it is worthwhile to develop new admixtures and explore the related properties. The purpose of this study is to prepare a new admixture which is a water-soluble sulphonated phenolic resin (SP). Phenolic resins were developed early in this century and have maintained a prominent position in the polymer market to the present time. They are used for moulding compounds, adhesives and structure boards due to their good mechanical properties, heat stability and impact resistance [12]. SP is thought to be a potential admixture for cementitious materials. In the following, SP reinforced mortar specimens were made. The properties such as workability, compressive strength and the microstructure of the samples were examined and discussed.

2. Materials and preparation

Materials used in this study were type I Portland cement, SP, river sand (from east Taiwan) and water. SP was prepared from formaldehyde, phenol and $NaHSO_3$ through a four-step reaction. The chemical structure of this resin is shown in Fig. 1. It is noted that the $-CH_2SO_3^-$ group or the methylene bridge ($-CH_2-$) could be at either *ortho* or *para* positions. Details of the preparation procedure and the determination of resin structure have been described elsewhere [13]. Table I lists the characteristics of some resin samples. The sulphonate group content of the resin molecule is represented by the sulphur/carbon (S/C) ratio in this table. Water, cement and sand were in a fixed 1:3.33:4 ratio by weight. That is, the water/ cement ratio is 0.3. The SP/cement ratio ranged from 0 to 2 wt%.

3. Analysis and testing

3.1. Workability

Mortar samples were poured on the flow table. The flow spread diameter was measured after 25 times vibration. Greater spread diameter means higher fluidity or better workability of materials.

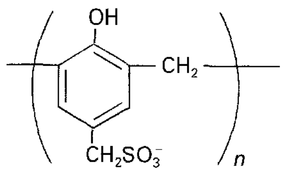

Figure 1 The chemical structure of a sulphonated phenolic resin.

TABLE I The characteristics of resins

Resin	S/C ratio[a]	Viscosity (cp)[b]
S7	0.33	2.12
S10	0.35	2.02
S15	0.34	2.0
S30	0.34	2.4
S34	0.35	2.6

[a] The S/C ratio of resin was determined by a Leco CS-244 analyser.
[b] The viscosity of 20 wt % resin solution, measured by a Brookfield DV-II viscometer.

3.2. Calcium ion chelating ability

A standard 0.01 M calcium ion aqueous solution was prepared. SP was then added in small increments into the standard solution. The equilibrium calcium ion concentrations were measured by a calcium selective electrode (HNU ISE-20-20-00) and a digital pH/mV meter (Hanna HI 8521) following Chang's procedure [14]. From the variation of calcium ion concentration, the calcium ion chelating ability of SP was demonstrated.

3.3. Differential scanning calorimeter (DSC) measurements

A Seiko DSC 5200 was used for indicating the amount of $Ca(OH)_2$ in mortars from the endothermal peak (of about 470 °C) of the samples [15]. The heating rate was 10 °C min^{-1}.

3.4. Compressive strength test

Mortar specimens of $5 \times 5 \times 5$ cm were prepared, cured and their compressive strengths were determined at the ages of 3, 7 and 28 days using a MTS 101 t testing machine.

3.5. Scanning electron microscopic (SEM) observations

The specimens, after the compressive strength test, were prepared for SEM examinations using a Jeol JSM-T100.

3.6. Determination of pore size distribution

Pore size of different mortar samples cured for 28 days were determined at different pressures by mercury intrusion method using a Micrometrics Autopore II 9220 porosimeter.

4. Results and discussion

4.1. Workability of mortars

Promoting the workability of cementitious materials with low water/cement ratio is one major role offered by chemical admixtures. In this study, the workability of mortar samples were evaluated using a flow spread test. Higher flow diameter value indicates greater fluidity or better workability of materials. The effectiveness of SP on the workability of mortars could be judged from the measured diameter. Fig. 2 gives the test results. The plain mortar exhibits the worst fluidity, which implies the existence of a strong attractive force or frictional force among the cement particles. Addition of SP into mortars were found from Fig. 2 to have a significant increase in fluidity. Furthermore, the more resin added, the better fluidity obtained. There is a little difference in diameter value for different resins. This result indicates that SP would be a good dispersion agent. The increase of workability can be attributed to the chemical structure of resin which would lower the surface tension, reduce the frictional force and enhance the dispersion of the cement particles [8].

4.2. Interactions between SP and calcium ions

Since SP contains sulphonate groups, it should have the capability to interact with $Ca(OH)_2$ which is one of the hydrated products of cement [11]. Consequently, the morphology or microstructure of the resulting mortar would be altered and the mechanical property or other properties of the material would also be affected [10, 11]. The interactions between SP and calcium ions could be demonstrated by the change of the equilibrium calcium ion concentration in an aqueous solution when adding SP into the system. A decrease of concentration value implies some interactions occurred between resin and calcium ions. Fig. 3 shows the influence of SP on the equilibrium calcium ion concentration. It is shown that SP could

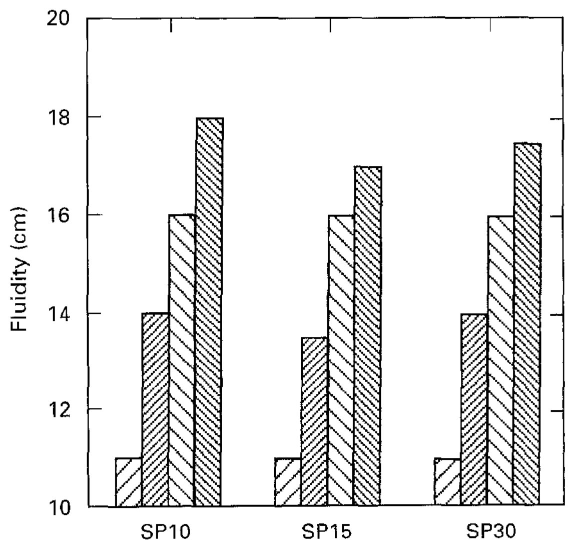

Figure 2 The effect of SP on the workability of mortars. 0, 0.5, 1, and 2.0 wt%.

indeed interact with calcium ions. The equilibrium calcium ion concentration apparently decreases with SP content as a response to the gradual increase of interactions between resin and calcium ions.

Fig. 4 is the effect of 1 wt% resin on the relative amount of $Ca(OH)_2$ in mortars after 28 days curing. The amount of $Ca(OH)_2$ in mortars was evaluated from the endothermal peak at about 470 °C of the samples using DSC measurements [15]. The endothermal peak of plain mortar (OPC) was chosen as a basis and its $Ca(OH)_2$ content was set to be 100%. The amount of $Ca(OH)_2$ of the treated samples was calculated from the relative ratio of their endothermal peaks to that of OPC. It is clear from Fig. 4 that the $Ca(OH)_2$ content of OPC is the highest. When resins were added into mortars, the lime contents are more or less decreased. This result, besides the possible physical factors, gives another indication of the interactions between SP and hydrated products of cement.

4.3. Compressive strength of mortars

The compressive strength of mortar samples treated with different SPs cured for 3, 7 and 28 days was examined. A typical result is shown in Fig. 5 in which SP15 was the added admixture. The compressive strength generally increases with time. Because of the dispersion effect provided by resin, mortars treated with SP15 exhibit higher compressive strength than the untreated mortars [8, 9]. It seems that the material containing 1 wt% resin shows the best effect. Fig. 6 compares the compressive strength of mortars treated with different resins in 1 wt % addition after 28 days. Apparently, mortars with SP34 exhibit the highest value in compressive strength. The value is 66 MPa, which is about 18% higher than that of plain mortar (56.1 MPa).

4.4. Microstructure of mortars

To demonstrate the morphological changes of the material due to the addition of admixtures, SEM photographs of mortars with or without SP present after 28 days were taken. For the untreated mortar, the hydrated cement products were not uniformly

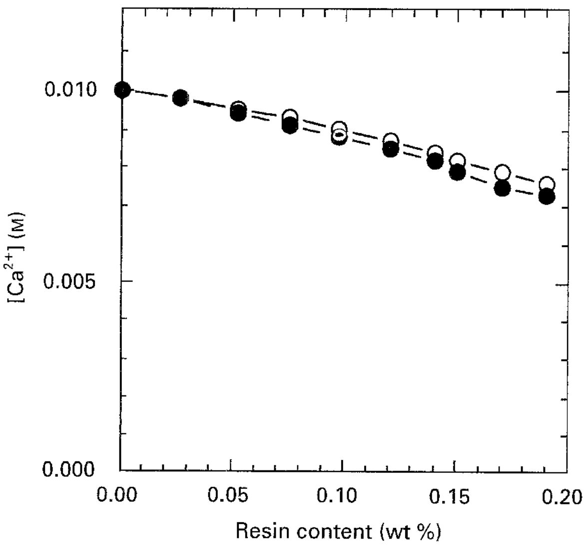

Figure 3 The effect of SP on the equilibrium calcium ion concentration. ○ S15, ● S34.

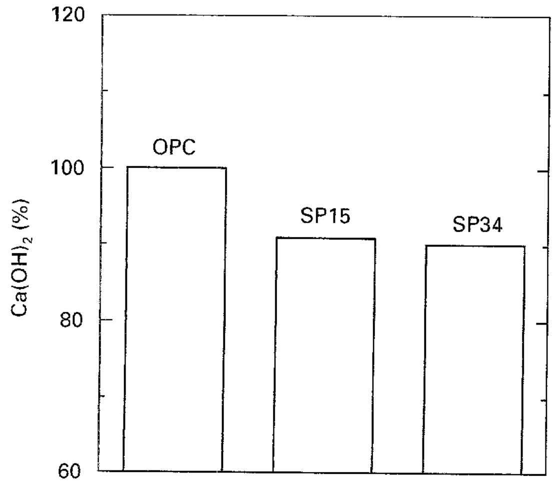

Figure 4 The effect of SP on the relative amount of $Ca(OH)_2$ in mortars after 28 days.

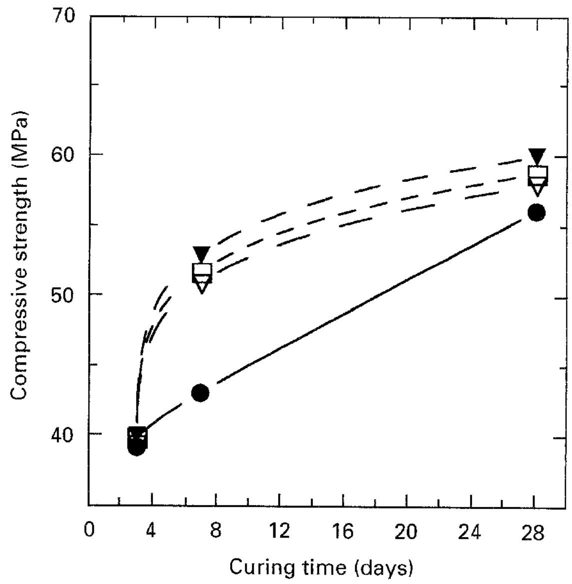

Figure 5 The effect of SP15 on the compressive strength of mortars after 28 days. ● OPC; ▽ 0.5% SP15; ▼ 1.0% SP15; □ 2.0% SP15.

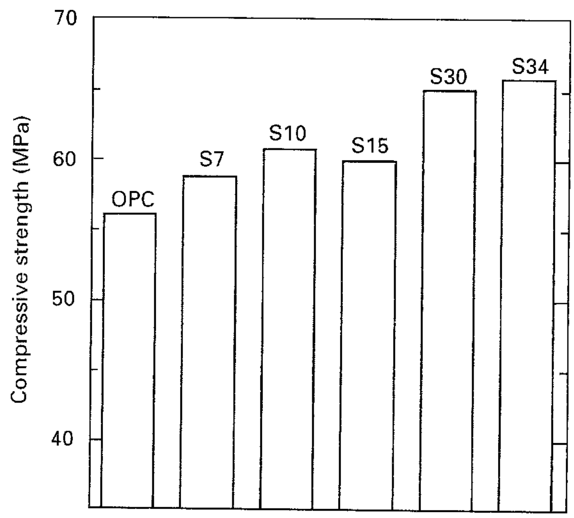

Figure 6 The compressive strength of mortars with or without 1 wt % resins present after 28 days.

distributed and the microstructure appeared to be porous, as is shown in Fig. 7. By adding SP34 to the mortar, the hydrated cement products were found from Fig. 8 to become more uniformly distributed and more consolidated.

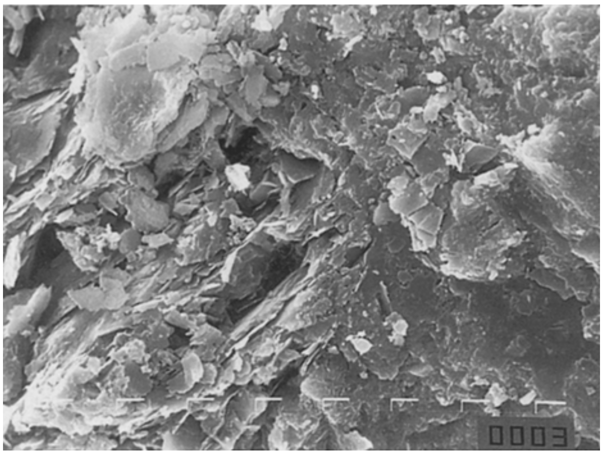

Figure 7 SEM photograph of plain mortar after 28 days (× 1500).

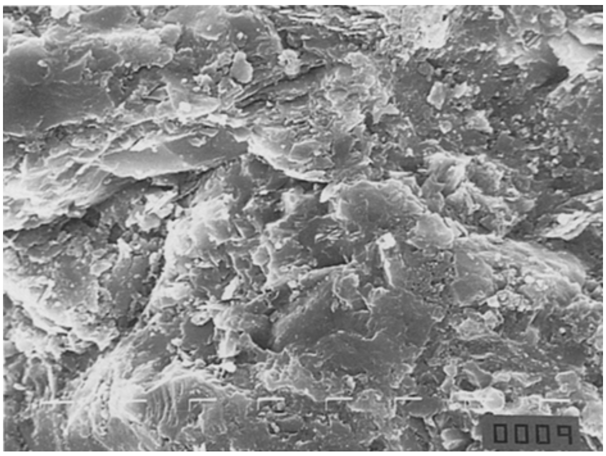

Figure 8 SEM photograph of mortar with 1 wt % SP34 present after 28 days (× 1500).

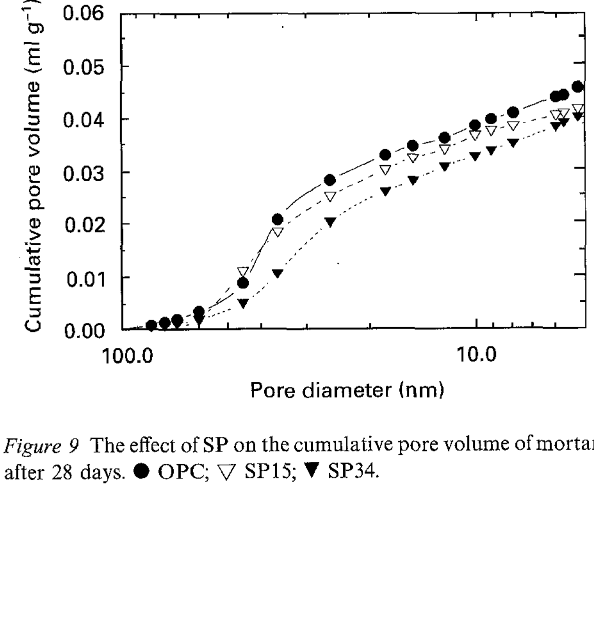

Figure 9 The effect of SP on the cumulative pore volume of mortars after 28 days. ● OPC; ▽ SP15; ▼ SP34.

Apart from the previous SEM observations, the pore size distribution of mortar samples was determined by a mercury intrusion method. Fig. 9 shows that the cumulative pore volume of the mortar treated with either S15 or S34 after 28 days curing is indeed smaller than that of the untreated.

5. Conclusions

The material properties of new sulphonated phenolic resin reinforced mortars were tested and examined. SP was found to be a good dispersion agent which would enhance the dispersion of cement particles and let the hydration reaction be carried out more uniformly. This resin also has some interactions with the hydrated products. As a result, a significant improvement in workability, morphology and compressive strength was observed for the resulting materials. The proper resin content in mortars is about 1 wt %. The strength of mortar with 1 wt % SP34 after 28 days curing is 66 MPa, which is about 18% higher than that of plain mortar.

Acknowledgements

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