Chemical Characterization of Calcium Aluminate-Phenol Resin Composite

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The chemical characteristics of a calcium aluminate-phenol resin composite with very high flexural strength are discussed. The flexural strength of the composite was found to be 120 to 220 MPa, which is greatly dependent on the fabrication method. The best system of these composites is made of calcium monoaluminate and the resole type of phenol resin. The evidence of possible cement-resin interaction has been found experimentally in roll milling, during heat curing, and in the final product. We discuss the evidence of interaction of phenol moiety and calcium aluminate based on the observations in processing, experimental data of differential scanning calorimetry, electron probe microanalysis, conduction calorimetry, and X-ray diffraction analysis. Based on our findings, we propose a cross-linking mechanism assumed to occur in processing and during curing. ADVANCED CEMENT BASED MATERIALS 1997, 6, 45–52. *© 1997 Elsevier Science Ltd.*

KEY WORDS: Calcium aluminate, Cement-resin interaction, Cross-linking mechanism, Flexural strength, Methylene bridge formation, Phenol resin precursor

In 1992 we introduced a system of very high strength cement paste with water insoluble phenol resin precursor [1–3]. This new composite is made by combining high alumina cement, alcohol soluble phenol resin precursor, and minor amounts of N-methoxymethyl 6-nylon and glycerol under high shear mixing to produce an viscoelastic cement paste through a twin roll mill. This innovation introduced the concept of making a high strength cement paste in which no additional free water is added, but utilizing water generated by the phenol resin precursor during heat curing to hydrate the surface of cement particles. The highest mechanical and durability properties are only achieved by composites made with a resole-type methanol soluble phenol resin precursor and high alumina cement. The strength loss after immersion in water at 20°C and after outdoor exposure for 1 year is only 9% and 6%, respectively, and the elastic modulus remains almost unchanged [4]. Linear expansion and weight increase of high alumina cement-phenol resin composite are 0.12% and 0.82%, respectively, after immersion in water at 20°C.

Among the several mineralogical components in the high alumina cement, those phases with higher Al^{3+} concentration and higher hydraulic activity performed the best. The evidence of possible calcium aluminate-resin interactions has been found experimentally in processing, during curing, and in the final product. This article mainly discusses the calcium aluminate and phenol resin interactions that are responsible for high strength, based on the observations in processing, experimental data of differential scanning calorimetry, electron probe microanalysis, conduction calorimetry, and X-ray diffraction analysis. Based on our latest findings, we propose a cross-linking mechanism assumed to occur in processing and during curing.

Materials

Inorganic Fillers

Two types of commercially available high alumina cements (HACs; Secar 71 and 51), ordinary Portland cement (OPC), calcined alumina, $Al(OH)_3$, $Ga(OH)_3$, CaO, and $Ca(OH)_2$ were used as particulate fillers. The chemical compositions and physical properties of the cements are listed in Table 1.

Organic Components

Methanol soluble resole-type phenol resin precursors have been shown to have the best results among several formaldehyde resins. The nature of the hydroxyl group in the phenol moiety seems to be the leading factor that controls the resultant strength. The resole-type phenol resin precursor used in the present experiments has the following physical and chemical properties: viscosity (25°C) 340 cps, M_w 6319, specific gravity (25°C) 1.09, nonvolatile matter (135°C) 61.3%, gel time (150°C) 3.8

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TABLE 1. Chemical compositions and physical properties of the cements

Type of Cement	Chemical Composition (wt%) Al_2O_3	CaO	SiO_2	TiO_2	Fe_2O_3	MgO	SO_3	Blaine's Specific Surface Area (m^2/g)
Secar 71	70.22	28.30	0.27	0.26	0.15	0.14	0.03	0.4010
Secar 51	53.75	36.52	4.22	2.52	0.74	0.39	0.01	0.4017
OPC	5.30	63.40	21.40	0.26	3.10	1.00	2.0	0.3260

OPC = ordinary Portland cement.

(min), and moisture content <2%. High molecular weight (M_w = 880,000) N-methoxymethyl 6-nylon was incorporated to modify the phenol resin and to develop the rubbery consistency of the phenol resin-cement paste. Glycerol was used as a plasticizer.

Formulation and Methods

Formulation

Mix proportions are categorized into two main groups as listed in Table 2. HACs and OPC were proportioned according to a "standard" mix proportion, neglecting slight differences in their specific gravities. The mix proportion called "comparison" is used in this study to compare the properties of cement based composites with non-cement based composites. All non-cement based mixtures [calcined alumina, $Al(OH)_3$, $Ga(OH)_3$, CaO, $Ca(OH)_2$] were proportioned considering differences of specific gravities, i.e., total of particulates in non-cement based mixtures is equal in volume to particulates in "standard" mix proportion.

Processing

The paste containing organic/inorganic compounds was prepared by mixing inorganic compounds, the modified methanol solution of phenol resin precursor, and plasticizer in a kneader-style mixer. The general method of roll milling is nearly equal to the Macro-Defect-Free (MDF) technology, except in its attempt to cool the rolls to minimize rising temperature [5]. When the paste is mixed in the roll, its temperature rises due to the work of the rollers. The viscosity of the paste also rises so that the paste becomes moderately hard. Then the paste is condensed into a thin layer and twined around the faster roller. This sheet is scraped away, folded, and re-rolled several times until it becomes a homogeneous sheet. The resulting mass is allowed to cure at 200°C for 18 hours. If the sheet is further densified by pressing (6 MPa at 80°C) after the calendering, a considerable increment in final strength can be obtained. To ensure the highest strength, it is necessary to elevate the temperature slowly and keep it at 65°C or above for more than 30 minutes under pressure. The heat pressing step can be skipped if necessary, depending on property requirements.

Test Methods

The heat-cured specimens were tested by a three-point bending method from which the strength and the modulus of elasticity of the specimen were calculated. Deflection of the specimens was measured by a displacement transducer, and the span/depth ratio of the three-point bend test was 30 to 40 for strength and elastic modulus tests.

Differential scanning calorimetry (DSC) analyses were made on several powders (HAC, pure calcium monoaluminate, Al_2O_3, SiO_2) and phenol resin combinations to determine their interactions during thermal curing. Each powder was mixed with the phenol resin in a ratio of 0.5, and the paste was vacuum dried at 30°C for 24 hours. The resulting material was ground and pressed into an aluminum crucible. The DSC analysis was carried out on approximately 10 mg of each sample at a heating rate of 10°C/min.

The influence of phenol resin on the normal hydration of HAC and OPC was studied by conduction calorimetry. HAC, HAC-phenol resin composite, OPC, and OPC-phenol resin composite were analyzed. Both HAC-phenol resin composite and OPC-phenol resin composite were ground and sieved to a size < 53 μm,

TABLE 2. Mix proportions

Mix Type	Resin + Methanol + Modifier (parts by weight)	Mix Proportions (parts by weight) Particulates HAC	Al_2O_3	$Al(OH)_3$	Resin	Methanol	Modifier	Plasticizer
Standard	23	100			13.06	8.24	1.70	2.30
Comparison	23		66	40	13.06	8.24	1.70	2.30

TABLE 3. Processing characteristics of several inorganic powders with the addition of phenol resin precursor

Type of Powder	Forming Ability
High alumina	
Secar 71	Good
Secar 51	Good
Ordinary Portland cement	Fair
$Al(OH)_3$	Good
$Ga(OH)_3$	Good
$Ca(OH)_2$	Immediately hardened
Al_2O_3	Did not harden
CaO	Immediately hardened
$Al(OH)_3/Al_2O_3$ (comparison)	Fair

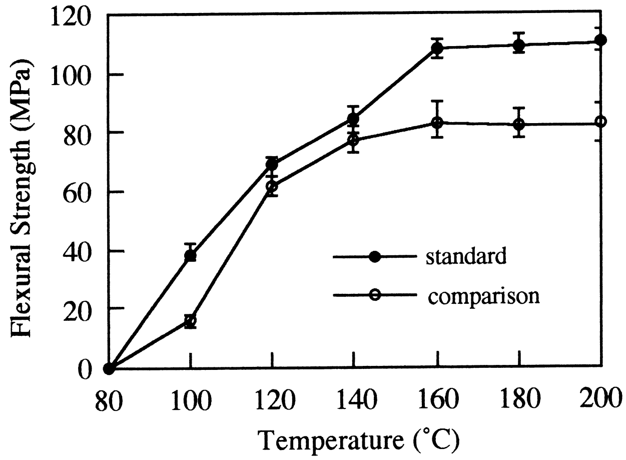


FIGURE 1. Development of flexural strength of the composite during various stages of thermal curing.

and then used in calorimetry. After mixing the powder and water at a ratio of 2.0, the heat evolution curves were recorded at 20°C using a conduction calorimeter.

Results and Discussion

Interaction During Processing

The ability to make a sheet through a twin roll mill is highly dependent on the base powder used. All hydraulic cements perform considerably well in the roll milling process regardless of the main mineralogical component contained. Young and Berg [6] concluded that a controlled cross-linking action is needed to develop the rubbery characteristics that are suitable for roll milling. We observed the same tendency. Table 3 lists the processing characteristics of cements, metal oxides, and hydroxides with the addition of phenol resin precursor.

Among all the powders tested, HACs showed good processing characteristics. When OPC is used, roll milling is difficult because of rapid hardening during the milling. Our experiments showed that the cement can be replaced by inert fillers for up to 50% of the volume; higher than 50% negatively influences processing, i.e., sheet making is unsuccesful. However, complete replacement of the cement by group III hydroxides provided good processing characteristics but specimens were of lower strength. The paste consisting of calcined alumina and resin did not combine properly during roll milling.

The paste of calcium oxide and resin underwent a highly exothermic reaction shortly after mixing in the twin roll mill and hardened rapidly; thus, sheet forming became impossible. Calcium hydroxide showed similar features. The different behavior of calcium and aluminum can be explained by their oxidation potentials. Oxidation potentials of calcium and aluminum are +2.87 and +1.66 V, respectively [7]; thus, calcium should have a higher oxidation tendency in the phenol resin system. Moreover, hardened calcium oxide or hydroxide dough can be softened by dipping it in acetic acid; thus, the occurrence of ionic-type interaction (rapid and reversible) is confirmed. It is reasonably expected that such an ionic reaction also occurs between phenol resin and cement phases in the cement to a certain extent; the ionic-type reaction corresponds to the development of a controlled consistency that is essential for making a good sheet. This idea has been confirmed by the different processing characteristics shown by different calcium aluminates, i.e., highly reactive Ca^{2+} ion-rich phases ($C_{12}A_7$) hardened rapidly, whereas the low reactive calcium hexaluminate (CA_6) phases combined poorly during roll milling [8].

Interaction During Heat Curing

Hardening of the phenol resin cement sheet occurs with a polycondensation reaction of phenol resin to form a three-dimensional cross-linked structure between 130°C and 170°C; in this temperature range water is released from the phenol resin. Figure 1 shows the development of flexural strength of the composite during various stages of thermal curing. The flexural strength was measured on the specimens kept at each temperature level for 2 hours and with the temperature elevating at a rate of 20°C/hour. The strength of the standard specimen was compared with a non-cement based composite that was made according to the "comparison" mix proportion. The standard specimen showed a significant strength increment between 140°C and 160°C.

The thermal behavior of phenol resin and several powder/phenol resin mixtures was investigated by DSC. Figure 2 shows the Thermogravimetry (TG) and DSC curves of the phenol resin precursor. The sharp endothermic peak observed at approximately 162°C corresponds to the cross-linking formation that accompanies the release of water molecules. The weight loss observed between 162°C and 200°C reaches 6.59%,

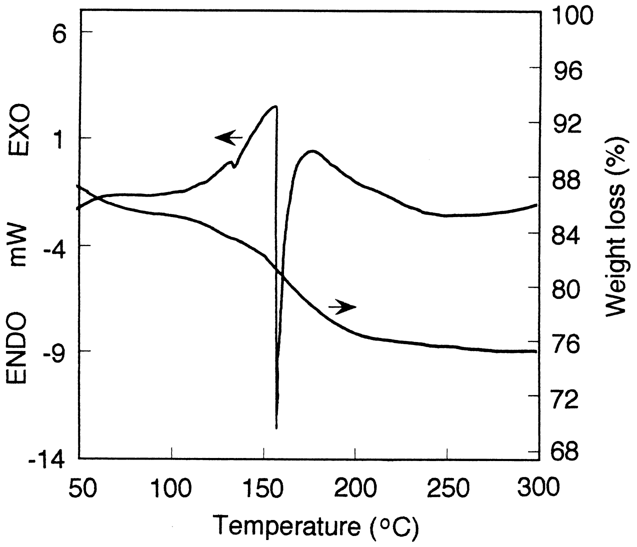


FIGURE 2. DSC and TG curves of the phenol resin precursor.

which approximately corresponds to the amount of water released during hardening.

Figure 3 shows the DSC thermograms of the mixtures of inorganic powders (HAC, pure calcium monoaluminate [CA], Al_2O_3, SiO_2) with the phenol resin precursor.

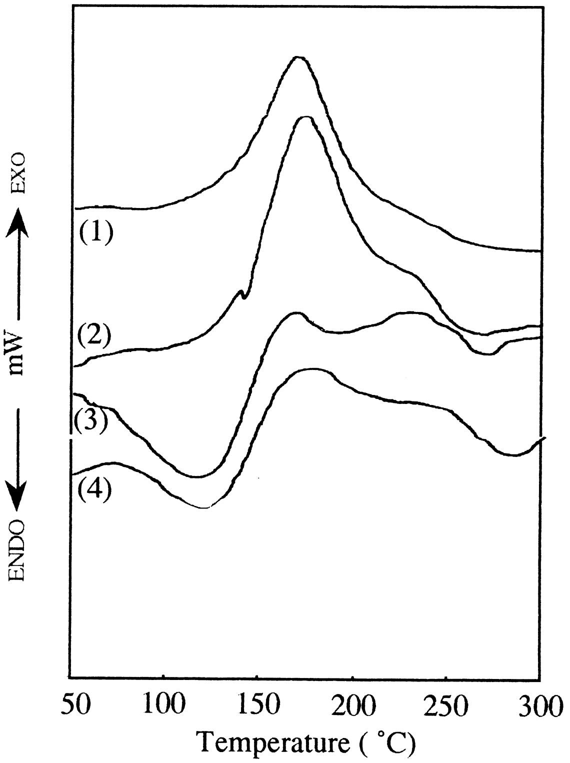


FIGURE 3. DSC thermograms of the mixtures of inorganic powders with phenol resin precursor. (1) HAC + phenol resin; (2) CA + phenol resin; (3) Al_2O_3 + phenol resin; (4) SiO_2 + phenol resin.

In the case of HAC/phenol resin (curve 1), the endothermic peak of the phenol resin disappeared and a new broad exothermic peak appeared at approximately 171°C. Curve 2 of pure calcium monoaluminate (CA)/ phenol resin is essentially the same as curve 1 and indicates that CA appears to be responsible for possible interactions. In contrast, neither peak is observed for inert fillers (curves 3 and 4). The difference between cement and inert fillers seems to depend on the stabilization in each system due to a chemical cross-linking reaction between cement and resin, or utilization of water in making hydration products.

Strength Dependence on Base Powder

Table 4 lists the flexural strengths and bending modulus results of specimens made of several inorganic powders. Mechanical properties are heavily dependent on the method of processing. Two processing routes were followed: calendering/heat curing (route 1) and calendering/heat press/heat curing (route 2).

Among the inorganic powders tested, composites containing Secar 51 exhibited the highest flexural strengths. The modest strength differences exhibited by composites fabricated from Secar 51 and Secar 71 are attributed primarily to differences in their phase composition. Secar 71 has a higher amount of CA_2 relative to the more reactive CA phase, as compared to Secar 51 [9]. Therefore, we believe this further demonstrates the importance of good hydraulic activity during heat curing. The "comparison" formulation with non-cement powders shows moderate strength when processed by route 1; however, further strength improvement by heat pressing was not possible.

Electron Probe Microanalysis

Samples of high alumina cement-phenol resin composite made according to the "standard" mix proportion and processing route 1 were investigated using an electron probe microanalyzer. Thin sections of composite were prepared by grinding and polishing for microanalysis. Special precautions were taken to prevent cement hydration during grinding and polishing. A wave dispersive spectrometer in the electron microscope was used to quantify calcium and aluminum contents. Figure 4 shows a backscattered electron microscopic image of a cement grain surrounded by the polymer matrix and an overlaid graph of the aluminum/calcium (A/C) ratio versus distance from the interface. A/C ratios were measured along the line of analysis at the distances indicated by bold circles. The A/C ratio of the center of the particle is 1.5 and decreases as it approaches the interface, where the ratio was found to be 1.36. In addition, calcium and aluminum were found in the polymer matrix.

TABLE 4. Flexural strengths and bending moduli of specimens made with different inorganic powders

Type of Powder	Calendering/Heat Curing (route 1)		Calendering/Heat Press/Heat Curing (route 2)	
	Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)
Secar 51	134	29.57	198	39.08
Secar 71	123	30.34	167	34.85
OPC	74	25.10	86	27.19
$Al(OH)_3$	76	18.36	97	25.43
$Ga(OH)_3$	73	18.05	—	—
$Al(OH)_3/Al_2O_3$ (comparison)	88	28.10	Heat press is ineffective	

— Data not obtained.

Majumdar and Edmonds [10] have suggested for the HAC/poly vinyl alcohol (PVA) system that the polymer (PVA) forms complexes more readily with aluminum than with calcium ions, which results in the removal of aluminum ions from the grain surfaces and the formation of a calcium-rich perimeter. Moreover, according to their suggestion, the calcium-rich hydration shells around CA and CA_2 grains suggest that the hydration involves first the removal of aluminum ions from the grain surfaces, followed later by the calcium ions. Thus, we prefer to suggest that the aluminum-poor perimeter found by Electron Probe Micro Analysis (EPMA) is due to the hydration that occurred by utilizing water released from the resin during the methylene bridge formation reaction.

Conduction Calorimetry and X-Ray Diffraction

Figure 5 shows the integral heat evolution curves obtained by hydrating the HAC, HAC-phenol resin composite, OPC, and OPC-phenol resin composite. The HAC curve shows a sharp increase of heat evolution at about 15 hours, thus indicating the heat of hydration. The presence of phenol resin in HAC results in the lack of such a sharp increase; however, the amount of heat evolved increases gradually with time. In the OPC-phenol resin composite, the amount of heat evolved was the same as OPC at up to 12 hours of hydration; between 12 to 43 hours the heat evolution increment lagged behind that of OPC. After 85 hours of reaction the OPC-phenol resin composite produced more heat than plain OPC paste.

The hydration behavior of both HAC and OPC with and without phenol resin was also investigated by X-ray diffraction. Samples were ground and sieved as described above. HAC, HAC-resin composite, OPC, and OPC-resin composite powders were then packed into the filter bags and stored in water at 20°C. Samples were taken out at prescribed time intervals, immersed in acetone, and tested in an X-ray diffractometer. Figure

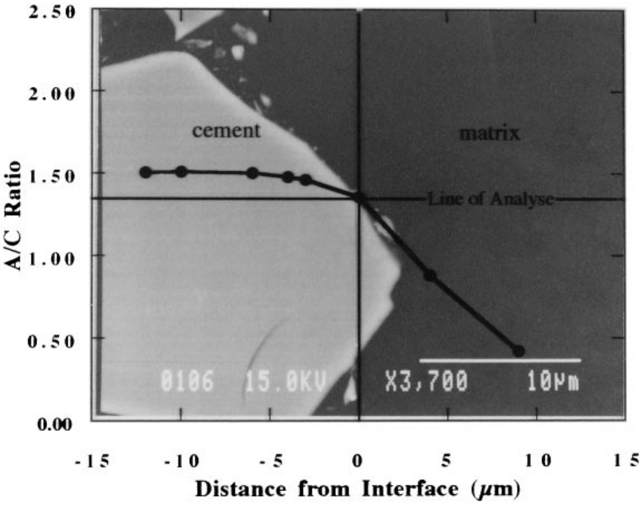


FIGURE 4. Backscattered electron microscopic image of a CA grain surrounded by the polymer matrix and an overlaid graph of the A/C ratio versus the distance from the interface.

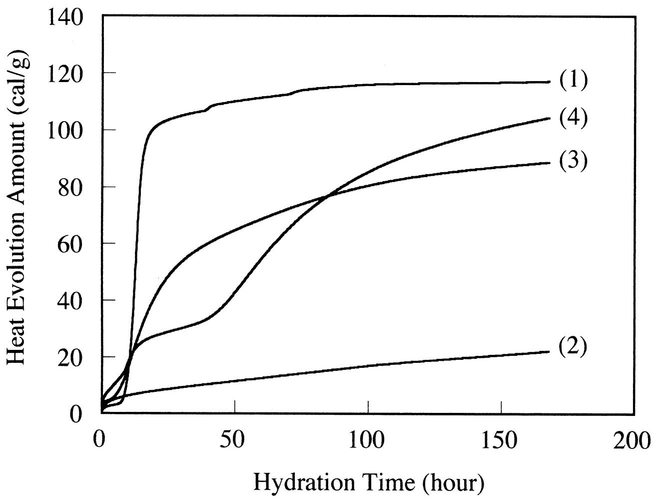
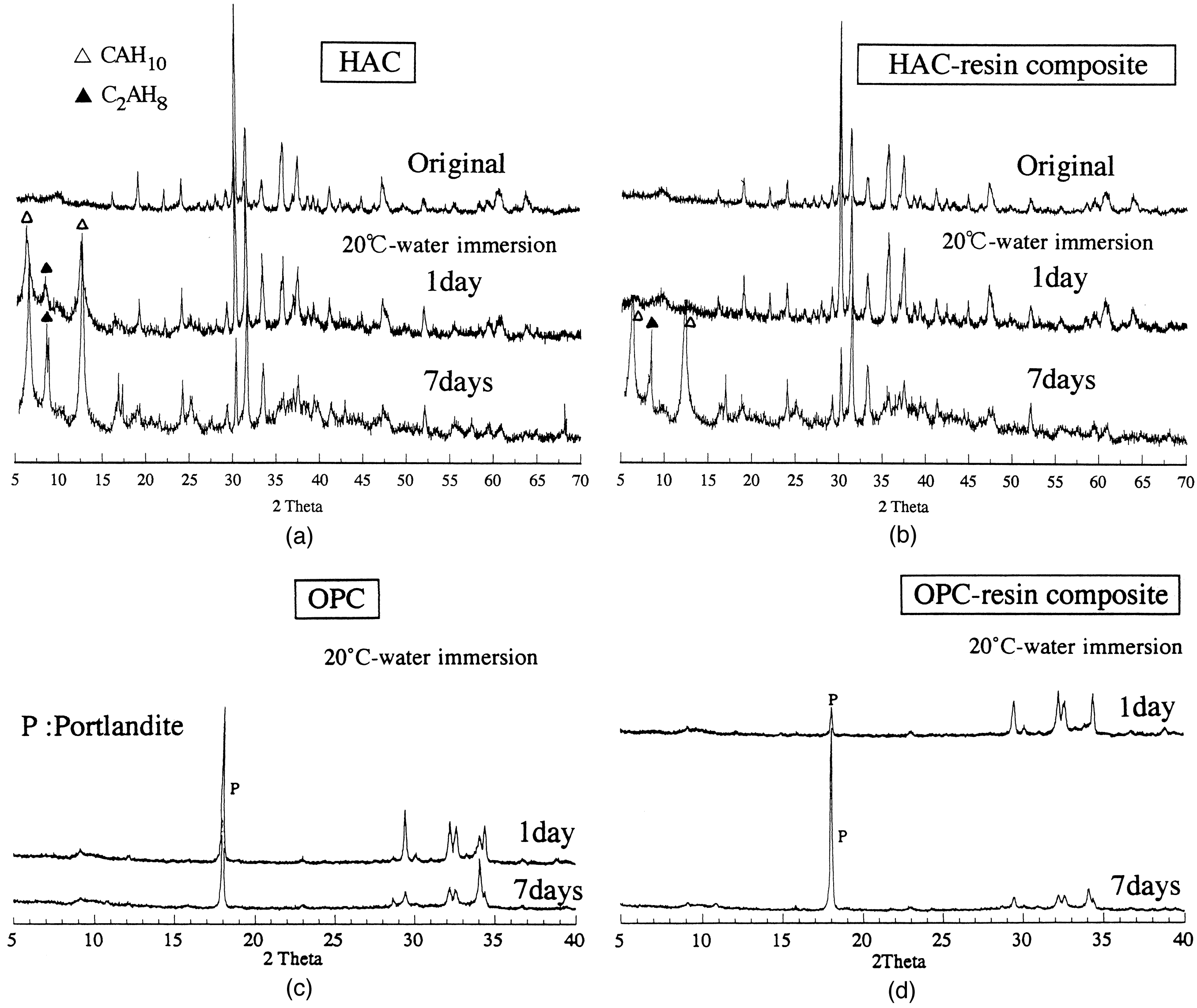


FIGURE 5. Integral heat evolution curves for HAC (1), HAC-resin composite (2), OPC (3), and OPC-phenol resin composite (4).



(a) (b) (c) (d)

FIGURE 6. The X-ray profiles of (a) HAC, (b) HAC-resin composite, (c) OPC, and (d) OPC-resin composite.

6 shows the X-ray profiles of HAC, HAC-resin composite, OPC, and OPC-resin composites.

As shown in Figure 6, there is no difference between the original HAC and HAC-resin composite powder. Within 1 day of immersion in water, HAC produced hydration products such as CAH_{10} and C_2AH_8, but the HAC-resin composite powder did not show any hydration products. On the other hand, after 7 days of immersion in water, both samples prominently showed formation of the same hydration products, CAH_{10} and C_2AH_8. In contrast, within 1 day of immersion in water OPC-resin composite powder produced hydration products such as Portlandite. Peak intensities showed the availability of a large amount of unhydrated cement in the OPC-resin composite. An interesting result is that, in the seventh day of hydration, peaks related to unhydrated cement almost disappeared in the OPC-resin composite, but some still appeared in OPC. This agrees satisfactorily with the results of conduction calorimetry, which gave a higher heat evolution amount after 85 hours of hydration compared with OPC.

The results of conduction calorimetry and X-ray diffraction show that the phenol resin alters the usual hydration behavior of cement to some extent. Moreover, the presence of phenol resin considerably inhibits the formation of crystalline calcium aluminate hydrates.

Cross-Linking Reactions

Calcium-rich calcium aluminates, CaO, and $Ca(OH)_2$ showed high reactivity with phenol resin during roll milling; calcined alumina showed poor combining during roll milling. This indicates that the Ca^{2+} ion is the reactive component during roll milling whereas Al^{3+} ions control the excessive stiffness of the high alumina

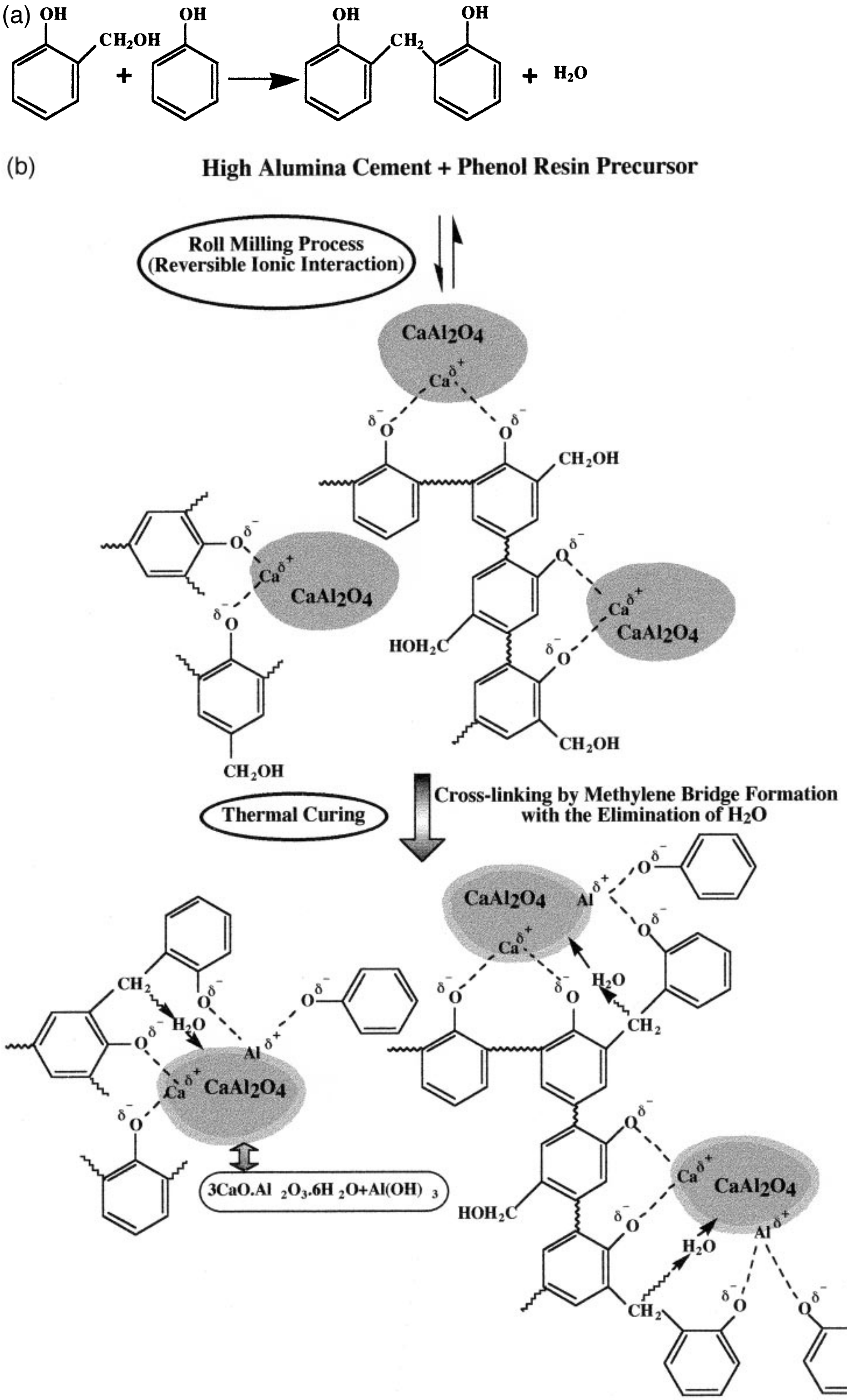


FIGURE 7. (a) Polymerization reaction of the phenol resin precursor. (b) Proposed cross-linking scheme for phenol resin-high alumina cement composite.

cement and phenol resin system during roll milling. The higher strength was shown by Al^{3+} ion-rich calcium aluminate cements, and the lower strength of calcium silicate based OPC indicates that the presence of Al^{3+} ions is essential for active heat curing. On the basis of these observations, we envisage that the phenol resin precursor cross-links with the Ca^{2+} ions of cement through an ionic cross-linking reaction during roll milling and then with Al^{3+} ions through a chemical cross-linking reaction during heat curing. This concept is shown schematically in Figure 7.

Conclusions

This work studied the affinity of phenol resin to high alumina cement from a chemical point of view. The effects of Ca^{2+} and Al^{3+} ions during the main steps of processing were evaluated. The hardened composite was analyzed in terms of the interference of phenol resin in the normal hydration of cement.

Roll milling studies of the phenol resin precursor and different inorganic powders revealed that the chemical nature of the inorganic phase is responsible for the paste and sheet forming ability. It appears that the oxidation tendency of the metallic species plays an important role during roll milling. The higher flexural strengths exhibited by composites fabricated from high alumina cement are attributed to the presence of alumina-rich, active mineralogical phases with good hydraulic reactivity. This result was enhanced by the DSC analysis, which showed a broad exothermic peak in mixtures of calcium aluminate and phenol resin. EPMA analysis indicated an aluminum-poor perimeter in CA grains that is probably due to the hydration that occurred by utilizing water released from the phenol resin during the methylene bridge formation reaction. Conduction calorimetry and X-ray diffraction data revealed that the phenol resin considerably inhibits the formation of crystalline calcium aluminate hydrates.

It is clear from these results that high alumina cement and resole-type phenol resin precursor interact during processing, beginning from the twin roll milling up to the final product, to make it a stronger material. We propose a mechanism in which the phenol resin forms complexes with Ca^{2+} ions through an ionic cross-linking reaction during roll milling and then with Al^{3+} ions through a chemical cross-linking reaction during heat curing.

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