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A NEW CLASS OF HIGH STRENGTH, WATER AND HEAT RESISTANT POLYMER - CEMENT COMPOSITE SOLIDIFIED BY AN ESSENTIALLY ANHYDROUS PHENOL RESIN PRECURSOR

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ABSTRACT

Cement clinker is a hard substance as strong as ceramics. However, hydrated cement products have poor mechanical properties in bending and tension because of lower bonding strength between cement particles. Flexural properties of hydrated cement products may be enhanced by minimizing porosity in cement region and adhering cement particles by high flexural polymeric materials. This article reveals an innovation of a high flexural cement based material which was solidified by phenol resin precursor. The material has a flexural strength between 120MPa and 220MPa, that is greatly dependent on the fabrication system, and has considerable stability to moisture and heat.

Introduction

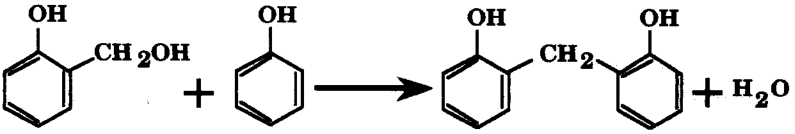
Cement clinker is a material which is produced by grinding and mixing clay and lime bearing minerals and then burning the mixture to about 1400°C in a rotary kiln. This cement clinker is a firm material that can be crushed only in a ball mill. Cement itself has adhesive and cohesive properties as well as the property of setting and hardening under water by virtue of a chemical reaction. According to classical theories of hardening or gaining strength of cement, strength probably arises from two types of cohesive bonds. The first type is the physical attraction between solid surfaces which is usually referred to as van der Waals forces and the second type is the chemical bond. The latter is much stronger than van der Waals forces but the chemical bonds cover only a small fraction of the boundary of the gel particles (1). Because of these weaker adhesive and cohesive properties, resulting hydration products have lower mechanical properties in bending and tension than original cement clinkers.

The separate cement particles cannot withstand loads that occur in service, if they do not adhere together as a rigid solid body. The adhesion between particles should be sufficiently strong to resist disruptive forces on the body (2). If the van der Waals force dominating bonds at the traditional cement hydration products could be converted into ionic or covalent bonds that are some hundred times tougher than van der Waals bonding, the products might become much stronger.

Generally considered, all cement based materials rely on the hardening of cement by added water; the strength of hardened cement paste increases as the water-cement ratio is reduced because of the decreasing of residual porosity. Even though many attempts, such as the use of high range water reducers, have been made to reduce the amount of water, there is a practical limit if the mixture is to remain workable (3). The residual porosity in the paste is either bubbles of entrapped air or spaces left after the excess water has been removed. The potential strength of cement paste at theoretical density have never been approached because considerable porosity always remains after complete hydration of the cement.

In 1992, we started the research aimed towards high flexural strength by adding hydrophobic phenol resin precursor through essentially water-free cement paste. The key points of this innovation are to (i) adhere cement particles by strong bonding technique, (ii) decrease stress concentrated defects from the body, and (iii) exempt from adding water and acquire hydration by eliminated water from the phenol resin precursor during heat curing. This precursor acts as both processing aid and the hydration resource. To reduce the porosity, cement paste was mixed and calendered through the twin roll mill. As a result we succeeded in establishing the composition and the process which afforded a new class of high flexural strength cement based material (phenol resin-cement composite) with remarkably enhanced moisture and thermal stabilities (4,5).

To the material we innovated, it is not necessary to add any water because a slight amount of water (1 to 1.2 weight percent of cement), that is expelled out from the precursor during thermal curing, is utilized for solidifying the cement. The polymerization reaction during thermal curing as follows:



Experimental

The cement paste was prepared by mixing high alumina cement (HAC), methanol solution of phenol resin precursor (specific gravity ; 1.06, viscosity ; 250cps, nonvolatile content ; 58.0%) and other additives in a kneader style mixer. The mix proportion and chemical composition of HAC are given in Tables 1 and 2, respectively. By adding a small amount of modifier, such as alcohol-soluble polyamide, the rheology of the resin-cement paste is much improved and flexural strength of hardened polymer-cement composite is greatly enhanced.

TABLE 1
Typical Mix Proportion of Phenol Resin-Cement Composite

Material	Parts by weight
High alumina cement	100.0
Phenol resin precursor (methanol soluble resole)	12.3
Methanol	8.9
Modifier	1.8
Plasticizer	2.3

TABLE 2
Chemical Composition (wt %) of High Alumina Cement
(according to data provided by supplier)

Al_2O_3	CaO	SiO_2	Fe_2O_3	TiO_2	Total
54.3	37.0	4.5	1.5	2.6	99.9

Blaine specific surface area ; 4750 cm^2/g

General method of processing is nearly equal to the MDF technology (6), except its attempt to cool the rolls to minimize the temperature rising (7). When the paste was further mixed in the roll, the viscosity rises and the paste becomes semi hard which may be due to the evaporation of methanol and mechano-chemical reaction. Then the paste was condensed into a thin layer and twined around the faster roller. This sheet was scraped away, folded and re-rolled several times until it became a homogeneous sheet. The resulting mass was allowed to cure at 200°C for 18h. The temperature was increased up to 200°C through 12 hours.

After heat curing, the sheet of phenol resin-cement composite was cut into strips, 25mm wide and 120mm long, on a water-cooled diamond saw. The specimens were tested in a three point flexure with a span of 80mm (40 times of thickness) at a crosshead speed of 2mm/min as described in Japanese Industrial Standard K 6911 (Testing Methods for Thermosetting Plastics). Compressive strength was measured by piling up the 2mm thick specimens according to same standards and tensile strength as described in JIS K 7113 (Testing Method for Tensile Properties of Plastics). Beside to mechanical properties thermal expansion, thermal conductivity and DC resistivity also were measured.

Results and Discussion

Properties

The flexural strength of the composite was higher than 120MPa. If the sheets are further densified under heat pressing (6MPa at 80 °C) before heat curing, flexural strength was improved to higher than 200MPa. This achievement of strength may be due to the reduction of porosity. Bending modules of elasticity lie in the range between 32GPa and 45GPa which depends on fabrication system. The other properties are given in Table 3.

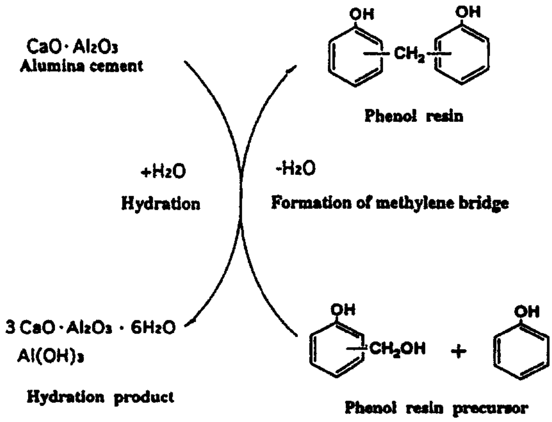
TABLE 3
Properties of Phenol Resin-Cement Composite

Properties	Values
Flexural strength	120 - 220 MPa
Bending modules of elasticity	32 - 45 GPa
Compressive strength	300 MPa
Tensile strength	54 - 100 MPa
Specific gravity	2.2
Weight increase (3 months in water)	0.71 %
Thermal expansion (20-300 °C)	17.8×10^{-6} °C^{-1}
Thermal Conductivity	0.8 W/(m·K)
DC resistivity	10^{13} - 10^{14} Ω·cm

The pore size distribution of non-heat pressed specimens was measured by mercury intrusion porosimetry. The pore volume increases significantly in the diameters smaller than 0.01μm and in the diameters larger than 10μm. The percentage of total pore volume was only 2.05. Such an extremely low porosity in the composite is presumed to be due to the effect of methanol which evaporates much easier than water during the high shear mixing.

Mechanism of Hardening

It is presumed that a slight amount of water is sufficient to proceed with the hydration of cement particles in the surface if it is evenly distributed in the whole cement region. The high shear mixing of the cement and phenol resin precursor leads to wrap the cement particles by the phenol resin, supplying water to the cement surface during the heat curing. A one of the possible mechanisms of the cement solidification is shown below:



At the same time the phenol resin precursor itself serves to fulfil all the necessities that is required to bind the isolated cement particles into a solid flexible mass. Therefore, in addition to the role as a hydration resource, the resin doubtlessly acts as a processing aid and a flexible filler between cement particles. Beside to these effects, the phenol resin seems to form some chemical bonding with cement particles.

However, we were unable to find sufficient evidence to conclude hardening mechanism by X-ray diffraction, FT-NMR Spectrometry and EPMA microanalyzing. Further studies are underway to clarify the hardening mechanism.

The Role of High Alumina Cement

In order to understand the significance of high alumina cement on strength and other properties of some other cements, such as ordinary portland cement, ultra rapid hardening cement and blast furnace slag cement, have been investigated. Their chemical compositions, physical properties and flexural strengths of resulting composites are given in Table 4. There was no detrimental influence on processing

TABLE 4
Chemical Composition (wt%) of Other Cements

Type of cement	Chemical composition (%)				Blaine fineness (cm^2/g)	Flexural strength (MPa)
	Al_2O_3	CaO	SiO_2	Fe_2O_3		
Ordinary portland	5.3	64.4	22.0	3.0	3370	70.0
Blast-furnace slag	8.6	54.4	24.8	2.2	3910	72.0
Ultra rapid hardening	11.4	59.1	13.8	1.5	5600	81.0

ability but considerable decline in strength. The flexural strength of non heat pressed specimens were approximately between 70MPa to 80MPa. The strength results indicate that an increase of the Al_2O_3 content (i.e. increase of the calcium aluminate) tends to increase the strength of the composite. This can be due to the rapid hydration capability of calcium aluminate rich cements which efficiently utilize the liberated water molecules during heat curing. However in contrast to the highly water-resistant property of the composite with the high alumina cement, the strength of these cement composites dropped seriously, particularly in the first week.

Furthermore, our experiments showed that calcined alumina substitution affected both the processing and the strength (8). In increasing the content of alumina viscoelastic behavior of the paste gradually changed to result in decreasing the ability to process. An increase of alumina substitution more than HAC:Al_2O_3 ratio of 50:50 by volume resulted in a great loss of the rubbery consistency of the paste and the finished sheet. As the ratio of Al_2O_3 to HAC was increased up to 80:20, the strength decreased in more than 10%, although total porosity of the structure decreased. Forming of the sheets by wholly Al_2O_3 based paste appeared to be impossible, but mixing with $Al(OH)_3$ improved the processing ability in some extent but strength decreased in more than 20%, although total porosity and maximum pore size of the microstructure decreased (8). From these observations it is implicit that a certain extent of mechano-chemical reaction takes place between high alumina cement and phenol resin during their high shear mixing.

Stability to Water and Heat

No significant reduction of original strength is seen even after the immersion in water at room temperature for three months (Fig.1). Linear expansion and weight

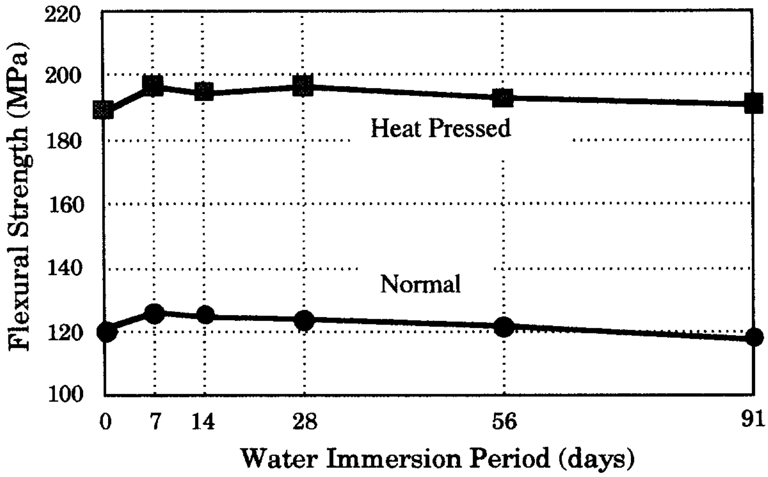


FIG. 1. Effect of immersion in water on the flexural strengths of phenol resin-cement composites

increase of phenol resin-HAC composite is 0.08% and 0.71%, respectively under the same immersion condition. The stability of the composite under the high temperature was also studied. The cut strips were heated at various temperatures in an oven for 6h. Weight losses of cured phenol resin and the composite upon heating were monitored by thermogravimetric analysis (TGA) separately as described by Poon et al. (9). The strength loss and weight loss by heating are graphically presented in Fig.2. The strength is kept even up to 250 °C and begins to decrease above 250°C. The observed losses in strength and weight of hardened composite rather accurately reflect the thermal deterioration of phenol resin above 300°C.

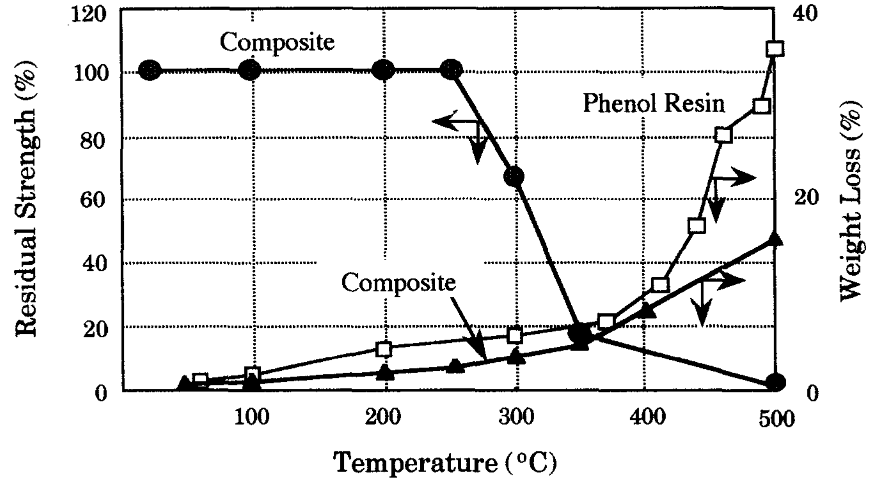


FIG. 2. Flexural strength loss and weight losses vs. temperature

Conclusions

It is concluded that reduction of porosity and chemical interaction between cement and polymer effect the strength achievement of phenol resin-cement composite. Remarkably high performance in water is explained by the hydrophobic nature of the polymeric constituent and stable bonding system between high alumina cement and resin. Use of methanol contributes to improve dispersion of the precursor throughout the cement paste and to evaporate easily during high shear mixing, and simultaneously to give voidless microstructure in the resulting material. Cements are more resistant to higher temperatures and to harsh environments than polymers. However, among ordinary synthetic resins, crosslinked phenol resin is rather resistant to the high temperatures and to the moisture. It should be empathized that present composite is designed to display a combination of the possible best characteristics of each component material. The observed properties would make this composite an unique material which places itself between metals and plastics.

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