

# Moisture and drying resistance of a nanointerphase reinforced cement

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Received 15 May 2005; received in revised form 9 December 2005; accepted 22 January 2006

Available online 15 May 2006

## Abstract

The moisture and drying resistance of a novel cement based nanocomposite, polymer intercalated/exfoliated (PIE) cement, is analyzed. The effects of the post-processing treatment procedure and the nanofiller content are discussed. The experimental results indicate that the flexure strength of the PIE cement is higher than that of ordinary Portland cements by more than an order of magnitude, and is quite insensitive to the humidity level.

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*Keywords:* Polymer modified; Silicate; Nanointerphase; Moisture resistance

## 1. Introduction

In order to enhance the load-bearing properties of cementitious materials, polymer cements (PC) have received increasing attention for several decades [1]. Even with the increase in material cost, due to the large improvement of mechanical properties, particularly the tensile strength and the fracture toughness, the cost-performance balance of a PC can be superior. For instance, by adding poly(vinyl alcohol) (PVA) in a calcium aluminate cement (CAC) to form a macro-defect-free (MDF) cement, the flexure strength can be increased to the level of that of structural steels [2]. However, currently, the PVA–CAC MDF cement still cannot be widely applied in the industry. One of the hurdles to be overcome is the poor moisture resistance caused by the relatively high solubility of PVA in water [3].

In a recent experimental study [4–6], it was noticed that the reinforcing effect of polymers can be further improved by silicate nanofillers, leading to the development of polymer intercalated/exfoliated (PIE) cements. In a PIE cement, the cement particles are strongly bonded together by a polymer–silicate nanointerphase consisting of a polymer matrix and dispersed silicate nanolayers, as depicted in

Fig. 1. The silicate nanolayers were exfoliated from tactoids that are of layered structures [7]. In addition to the mechanical properties, the moisture resistance can also be enhanced significantly by the nanofillers [8]. With their high tensile strengths as well as the advanced moisture/drying resistance that will be reported in this article, the PIE cements have great potential for precast components, repair procedures, etc.

## 2. Experimental

Dispersing silicate nanolayers in polyamide 6 has been an active research area for a decade. As silicate tactoids are immersed in water, the layer stacks can expand and the interlayer ions can be displaced by polymer chains or monomers, which causes further increase in interlayer distance. Eventually, when the interlayer distance is raised from about 1 nm to 10–20 nm, individual nanolayers could be delaminated [7]. Two nanointerphases, with the nanofiller contents of 1.7 wt% (group 1) and 3.7 wt% (group 2) respectively, were investigated. According to an X-ray diffraction analysis [5], the silicate nanolayers are partially exfoliated. The details of the morphology have been discussed in [9].

To minimize the influence of thermal history, the nanointerphase was first dried in a type 285A Isotemp vacuum oven at 110 °C for 24 h. The weight loss after the drying

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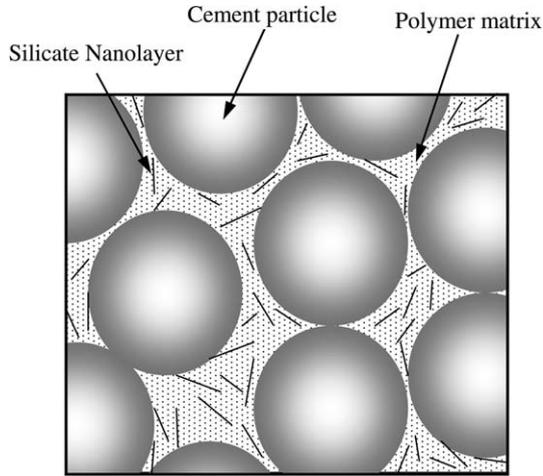


Fig. 1. A schematic diagram of the polymer intercalated/exfoliated (PIE) cement. The cement particles are bonded together by the polymer matrix enhanced by nanofillers (silicate nanolayers). The cement particle size is in the range of 10–100 μm. The thickness and the width of a silicate nanolayer are typically 1–10 nm and 100–500 nm, respectively.

treatment was about 0.3%. Then, through a two-stage mixing process, cement particles were combined with the nano-interphase in a KMB-100 Brabender to form the PIE cement. In the first stage, which took 5 min, the mixing rate was set to 120 rpm. In the second stage, which took 10 min, the mixing rate was decreased to 10 rpm so as to achieve the uniform dispersion of the cement particles and minimize the entrapped air content. In both stages, the temperature was maintained at 275 °C. Before being added in the Brabender, the cement was preheated at 260 °C. The cement phase consisted of three parts of type-I Portland cement and one part of type-III Portland cement. The cement to nanointerphase ratio was 5 in weight. The PIE cement was compressed into 12.7 × 3.2 × 3.2 mm flexure testing specimens using a type 3912 Carver hydraulic compression molding machine at 270 °C under 5 MPa, and air cooled with the stainless steel mold. The mold was detachable so that the specimen surfaces were smooth. Note that the samples were relatively small compared with ASTM standard specimens. There could be a considerable size effect, and therefore the data measured in the current study are primarily for self-comparison purpose.

Both groups of PIE cement samples were then treated under six different conditions: (1) oven drying (OD), in which the samples were heated at 110 °C in a type 285A Isotemp vacuum oven for 12 h; (2) vacuum drying (VD), in which the samples were kept in vacuum in a Lindberg environmental tube furnace for 24 h at room temperature; (3) 50% relative humidity (RH) treatment (RH50), in which the samples were kept in an environmental chamber with 50% RH for seven days at room temperature; (4) 100% RH treatment (RH100), in which the samples were saturated in 100% RH environment for seven days at room temperature; (5) water saturation treatment (WS), in which the samples were immersed in cold water for seven days; and (6) boiled water treatment (BW), in which the samples

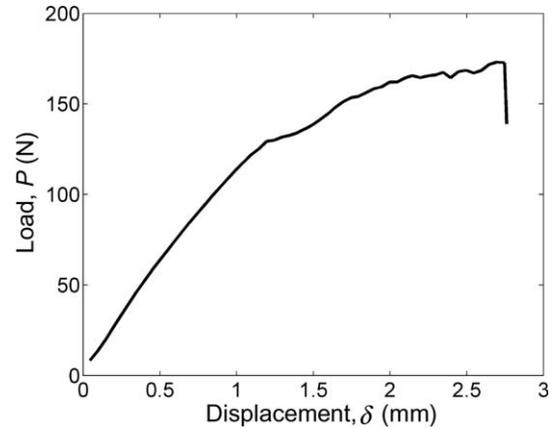


Fig. 2. A typical load–displacement curve of RH100-treated group-1 PIE cement.

were first immersed in cold water for seven days and then kept in boiled water for 0.5 h prior to and during the flexure experiment. For each group and each post-processing treatment condition, 3 PIE cement samples were prepared.

The samples were tested through center-point bending experiment. Fig. 2 shows a typical load–displacement curve. The load was applied by a type 5569 Instron machine. The crosshead speed was 1.0 mm/min, and the span distance was 11.2 mm. Based on the measured maximum load,  $P_m$ , the modulus of rupture was calculated as

$$R = (3/2)(P_m L/bd^2), \tag{1}$$

where  $L$ ,  $b$  and  $d$  are the sample length, thickness, and height, respectively. The total fracture work was calculated as

$$W = \int_0^{\delta_{max}} P d\delta, \tag{2}$$

where  $P$  and  $\delta$  are the center-point load and deflection, respectively, and  $\delta_{max}$  is the ultimate deflection. The average values of  $R$  and  $W$  are given in Tables 1 and 2,

Table 1

The influence of post-processing treatment process on the modulus of rupture of the PIE cement (MPa)

Silicate content	Post-processing treatment condition					
	OD	VD	RH50	RH100	WS	BW
1.7 wt%	102	98	106	112	108	103
3.7 wt%	116	110	119	114	107	110

Table 2

The influence of post-processing treatment process on the fracture work of the PIE cement (kJ)

Silicate content	Post-processing treatment condition					
	OD	VD	RH50	RH100	WS	BW
1.7 wt%	0.32	0.34	0.33	0.33	0.29	0.32
3.7 wt%	0.41	0.38	0.40	0.38	0.36	0.35

respectively. The standard deviation is about 11% of the average value for  $R$  and 8% for  $W$ .

### 3. Discussion

For both groups of materials and for all the post-processing treatment conditions,  $R$  and  $W$  of PIE cements are higher than that of ordinary Portland cement based materials with water/cement ratios around 0.4 by more than one order of magnitude. By comparing the data of group 1 and group 2 samples, for which the only significant difference is the content of silicate nanolayers,  $c$ , it can be seen that in the range of  $c$  under consideration, the addition of nanofillers has a beneficial effect on the flexure strength and the fracture toughness. In Table 1, in almost all the cases, the moduli of rupture of group 2 samples are higher than that of group 1 samples by 8–20%. In Table 2, for all the post-processing treatment conditions, the fracture work increases by 5–20% as  $c$  rises from 1.7 wt% to 3.7 wt%. This is in agreement with the experimental result of polymer–nanoclay composites that, with either fully exfoliated or partly intercalated silicate nanolayers, the mechanical properties can be improved considerably, the reasons of which are still under investigation [7]. It probably can be attributed to the high aspect ratios of nanofillers, the crystallization of polymer chains near the nanofiller surfaces, and the difficulty in craze formation and growth [8–10]. If no nanofillers were used, the material would be reduced to an ordinary polymer cement and the strength would be much lower [1].

When the post-processing treatment condition changes from one extreme case (OD) to the other (BW), the variations in  $R$  and  $W$  are quite small. When  $c = 1.7$  wt%, the maximum flexure strength is obtained as the samples are cured in 100% RH; and when  $c = 3.7$  wt%, the best condition is 50% RH. A dryer or a more humid condition might cause a decrease in  $R$ . When the PIE cement is overdried, the loss of water of the nanointerphase would result in microdamages due to local shrinkage and/or partial relaxation of secondary groups. Drying of cement particles also has a weakening effect. As the material is saturated with water, residual swelling stresses can be significant, especially at the cement–nanointerphase interfaces. However, since the silicate nanolayers can lower the permeability and confine the motions of the polyamide 6 macromolecules, these effects are only secondary.

The influence of post-processing treatment condition on the fracture resistance of PIE cement, on the other hand, does not have a well-defined pattern, as shown in Table 2. The difference of the fracture works is less than 10%, within the uncertainty range of the measurement, and looks quite random as the humidity varies. Therefore, it can be stated that the post-processing treatment procedure does not have a measurable influence on  $W$ . This can be attributed to that  $W$  is determined not only by the strength, but also by the extensibility. As the material becomes weaker, the deformability can increase, especially when

the plastic deformation mechanisms of the nanointerphase such as crazing, shearing banding, and microvoiding are promoted. As a result, the integral of Eq. (2) is nearly constant.

### 4. Concluding remarks

In conclusion, by using a silicate nanolayer-enhanced and polymer-based interphase, the flexure strength of cement based materials can be increased significantly. It is clear that more detailed materials characterization, e.g. long-term stability, cyclic hygral, thermal loading, and statistical analyses, is necessary before the properties of the PIE cements can be fully understood. Nevertheless, the experimental results show that the mechanical properties of this material are insensitive to the post-processing treatment conditions. The drying and moisture resistances, under the experimental condition of the current study, are superior.

### Acknowledgements

This study is supported by The National Science Foundation under Grant No. CMS-0408276. We are grateful to Mr. D. McVane and Mr. S. Xing for the help with the experiments. Special thanks are also due to Dr. M. Kato in Toyota CRD, Inc., for providing the polyamide 6-silicate nanocomposite pellets.

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