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# Flexural strength of polyamide 6 intercalated/exfoliated cements

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# Abstract

Polyamide 6 intercalated/exfoliated (PIE) cements are fabricated and characterized. With the reinforcing nanointerphase, the flexure strength of a PIE cement is higher than that of ordinary cements by an order of magnitude. The optimum nanointerphase content is around 10 wt.%. This technique has great potential in developing advanced precast and repair technologies. © 2005 Elsevier B.V. All rights reserved.

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#### 1. Introduction

It has long been noticed that cementitious materials, which are of low tensile strengths often around 5 MPa, can be reinforced by polymers. Polymer reinforced cements are usually classified as polymer modified cements (PMC), polymer impregnated cements (PIC), and polymer cements (PC) [1–3]. The PMC are fabricated by mixing polymeric materials and cements prior to hydration reactions (e.g. [4,5]), and the PIC are obtained by adding polymers or monomers after active hydration reactions have ceased [6]. In PC, on the other hand, the ordinary calcium silicate hydrate (C-S-H) binders are replaced by polymer interphases [6-8]. For instance, with the addition of a relatively small amount of vinyl polymers or epoxy/polyester resins, the flexure strength can be enhanced significantly, primarily due to the increase in interparticle bonding strength as well as the decrease in water/cement ratio [9-12].

However, although the strength and extensibility of polymer reinforced cements can be improved, the polymer phases themselves often become the "weakest link", imposing tremendous challenges in applying these materials in engineering practices. In a calcium aluminate cement (CAC)–poly(vinyl alcohol) (PVA) macro-defect-free (MDF) composite, for example, because PVA is sensitive to temperature and soluble in water, the heat/moisture resistances of the interphase are poor [13,14]. One of promising methods to solve this problem is to use more durable and stable polymers, such as polyamide, enhanced by nanofillers, such as silicate nanolayers.

The basic unit of bulk silicate is tactoid, which consists of about 100 layers, with the interlayer distance,  $d_0$ , around 1 nm. Each layer contains several sheets of SiO<sub>4</sub> tetrahedral filled by Al<sup>3+</sup> or Mg<sup>2+</sup> [15]. This layer stack can expand in polar solutions such as water, and the ions in the interlayer can be displaced by monomers or polymers under appropriate conditions [16], as depicted in Fig. 1. As the polymer chains intercalate into the interlayer,  $d_0$  can be further increased, and when it exceeds about 10–20 nm, the silicate nanolayers are exfoliated. As a result, a polymer–silicate nanocomposite that is of superior stiffness and strength can be synthesized [17,18].

In this article, the polymer intercalation/exfoliation technique is employed to synthesize polymer intercalated/exfoliated (PIE) cements, which has important relevance to enhancing precast and maintenance procedures. Experimental results have shown that the flexure strength of the PIE cement is higher than that of ordinary cements by at least an order of magnitude.

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Fig. 1. A schematic diagram of the polymer intercalation/exfoliation process: (a) a tactoid surrounded by monomers; (b) the intercalated monomers; (c) the nanolayers exfoliated by polymer chains. The polymer chains are formed through in situ polymerization.

# 2. Experimental

# 2.1. Fabrication of polymer intercalated/exfoliated cement

One of promising polymers that can be used to reinforce cements is polyamide 6, for which the intercalation/exfoliation technique has been well established [18,19]. Neat polyamide 6 is a semicrystalline polymer with the crystallinity usually in the range of 20-50%. The repeat unit is  $\varepsilon$ -caprolactam [20]. It is of excellent strength and environmental resistance. Since the initial interlayer distance of a silicate is smaller than the polyamide 6 chains, in situ polymerization method was applied to interrupt the layered structure of tactoids. The details of the procedure were documented in [21]. The polyamide 6-silicate nanointerphase studied in the current research was provided by Dr. M. Kato in The Toyota CRD, Inc. The content of the silicate nanolayers was 3.7 wt.%. According to X-ray diffraction analysis, the silicate nanolayers were partially exfoliated, as will be discussed shortly.

The as-received nanointerphase was in pellet form. After being dried in a type 285 A Isotemp vacuum oven at 110 °C for 24 h, the pellets were melt and mixed with portland cement in a KMB-100 Brabender at 275 °C. The cement phase consisted of 80 vol.% of type-I portland cement and 20 vol.% of type-III portland cement. The mixing was operated at 120 rpm for 5 min and then at 10 rpm for 10 min. The content of the cement was in the range of 70–95 wt.%. The cement–nanointerphase mixture was then hot pressed in a type 3912 Carver hydraulic compression molding machine at 260 °C under 2.5 MPa, and finally cut into 12.7 mm × 3.2 mm × 2.6 mm flexure testing samples and air cooled.

### 2.2. Wide-angle X-ray diffraction scanning (WXDS)

In order to analyze the degree of exfoliation of the silicate nanolayers, the nanointerphase was scanned by a 40 mA-40 kW Bruker AX8 diffractometer with Cu K $\alpha_1$  radiation. The nanointerphase was first hot pressed into a 0.2 mm thick film. After air cooling, the film was mechanically polished to less than 100  $\mu$ m thick and rinsed in methanol. The



Fig. 2. The WXDS result of the nanointerphase.

scan speed was  $1^{\circ}$  min<sup>-1</sup>. The result is shown in Fig. 2. Note that the scanning sample did not contain any cement phase.

#### 2.3. Flexure experiment

The PIE cement samples were characterized by centerpoint bending experiment using an Instron 5569 machine in displacement control mode (see Fig. 3). The crosshead speed was set to 1.0 mm/min. The span length, *L*, was 11.2 mm. Four groups of samples were investigated, with the nanointerphase contents, *c*, being 7.6 wt.% (group 1), 10.7 wt.% (group 2), 13.5 wt.% (group 3), and 15.2 wt.% (group 4), respectively. The measured modulus of rupture, which is defined as  $R = (3/2)(P_{\text{max}}L/bd^2)$ , is shown in Fig. 4, where  $P_{\text{max}}$  is the maximum load, *b* the sample width, and *d* is the sample height.

#### 2.4. Scanning electron microscopy

After the flexure tests, the fracture surfaces of PIE cement samples were studied through scanning electron microscopy so as to examine the failure mechanisms. The samples were first coated by silver in an Emitech K575X turbo sputter coater, and then observed in a Hitachi S2150 SEM. Fig. 5 shows the fracture surface of a group 3 sample.



Fig. 3. A schematic diagram of the flexure experiment.



Fig. 4. The modulus of rupture as a function of the nanointerphase content.



Fig. 5. SEM fractography of a PIE cement: (a) a crack in the nanointerphase and (b) a crack in a cement particle.

#### 3. Results and discussion

Usually, there are two crystalline forms of polyamide 6:  $\alpha$  form and  $\gamma$  form. The peak reflection angles of  $\alpha$  form are 20.5° and 24°, and that of  $\gamma$  form is around 21.5°. Fig. 2 shows that, in the polyamide 6-silicate nanointerphase,  $\gamma$ form, which is characterized by parallel chains with twisted amide groups, is dominant. This is in consistent with the result of a previous study that the chain mobility can be reduced considerably by the nanofillers [22]. The WXDS results of polyamide 6 composites of various silicate contents have been documented in [23]. The relatively weak intensity peaks at about 11° and 1.5°, which respectively correspond to the interlayer distances of about 1 nm and 10 nm [18], indicate that the silicate nanolayers were partially exfoliated [16]. Under this condition, some of the tactoids are unintercalated, some are intercalated, and the rest of them are exfoliated, forming a three-dimensional multiscale filler network. The intercalated tactoids and the exfoliated silicate nanolayers can greatly improve the stiffness and the strength along all the

directions, and the unintercalated tactoids, which are actually sub-micrometer scale microparticles, can interact with crazes and shear bands and thus affect fracture properties.

If there were no nanointerphase in the testing samples, they actually become ordinary portland cements. It is well known that, although the compressive strength of a portland cement can be higher than 80 MPa, the flexure strength can seldom exceed 10 MPa, even with a low water/cement ratio [11]. As a result, cementitious materials cannot be applied in tensileload-bearing structures. The low tensile strength is caused by that, while the C–S–H particles can interlock with each other under compressive stresses, they would fail to carry large tensile loadings. Fig. 4 shows that with the reinforcing nanointerphase, the modulus of rupture of the PIE cement is significantly improved by more than an order of magnitude. If the nanointerphase content is relatively low, perfect bonding among cement particles is difficult. The defects include the large voids formed from air bubbles in polymer phase and the nonwetted cement particles. The size and the amount of air bubbles can be reduced by optimizing the two-stage mixing procedure; however, the surfaces of cement powders can be fully wetted by the nanointerphase only when c is sufficiently high. If the nanointerphase content is too high, on the other hand, the cement particles are no longer closepacked and the tensile strength of the material is determined by the "weakest link" among the strengths of cement particles, nanointerphase, and cement-nanointerphase interface. Since the strength of cement particles ranges from 100 to 150 MPa, and that of nanointerphase is around 90-100 MPa [22], R primarily depends on the behavior of the nanointerphase. As the interparticle distance increases, the degree of constraint of polymer chains is lowered and therefore the crystallinity would decrease [23], leading to a lower strength. In the extreme case, where the cement content is nearly zero, the flexure strength of the PIE cement would converge to that of the polyamide 6-silicate nanocomposite.

According to the testing data shown in Fig. 4, the optimum nanointerphase content is about 10-12 wt.%, at which the nanointerphase is just enough to fill the space between the close packed cement particles. This optimum range is somewhat independent of the silicate nanolayer content, c [24]. In the fracture surfaces of PIE cements, both nanointerphase cracking and particle cracking can be observed, as shown in Fig. 5, demonstrating that, while the average strength of cement particles is higher than that of nanointerphase, the failure of cement particles cannot be avoided, probably due to the strength distribution and/or the stress concentration. Note that few cement–nanointerphase interfaces are exposed in the fracture surfaces, suggesting that the interface is stronger than both of the cement and the nanointerphase.

# 4. Conclusions

In this article, the synthesis and characterization of PIE cement, which was fabricated by replacing the C–S–H binder

by a polyamide 6-silicate nanointerphase, was discussed. The following conclusions were drawn:

- (1) The tensile strength of PIE cement can be higher than 100 MPa.
- (2) The optimum nanointerphase content is around 10–12 wt.%.
- (3) The final failure of the PIE cement is caused by the cracking in both of the nanointerphase and the cement particles.
- (4) The cement–nanointerphase interface failure is negligible.

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