

## High-temperature tensile properties of a polymer intercalated/exfoliated cement

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### Abstract

A polymer intercalated/exfoliated (PIE) cement is synthesized and its high-temperature tensile performance is characterized. Due to the reinforcing effect of the nanointerphase, the flexure strength of the PIE cement is higher than that of ordinary cements by more than an order of magnitude in a broad temperature range. The temperature at which the optimum mechanical properties are obtained is about 120 °C, and the thermal distortion point is around 180 °C.

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### 1. Introduction

Polymer cement (PC) received increasing attention in the past decade due to their superior mechanical properties, specifically the high tensile strength that is usually around 30 MPa, higher than that of portland cements by an order of magnitude [1,2]. Recently, a novel PC, macro-defect-free (MDF) cement, has been developed [3–5]. By mixing polymers, such as poly(vinyl alcohol) (PVA) or phenol resin, and cement powders, the weak calcium silicate hydrate binders in ordinary cements can be replaced by MDF polymeric interphases, resulting in the tensile strengths comparable with that of structural steels. However, the thermal distortion points of these polymer interphases are often relatively low, and therefore the heat resistance of the MDF cements is poor, causing immense uncertainty in assuring safe performance of these materials. In order to solve this problem, new processing techniques must be developed to reinforce cements with more thermally robust polymeric interphases. One promising method is to enhance the interphase by using silicate nanolayers.

The recent progress in polymer intercalation/exfoliation technique has provided a simple yet efficient way to mix silicate nanolayers and polymer chains at the nanometer level [6]. The basic structural unit of a silicate is tactoid of a layered structure. At appropriate temperature and pressure, monomers can be intercalated into the pre-swelled interlayer and form macromolecules through in situ polymerization, leading to the further expansion of the layer stack and the eventual exfoliation of individual platelets [7]. As a result, polymer-silicate nanocomposites with different degrees of positional and orientational correlations of nanofillers can be obtained. Usually, the diameter of a silicate nanolayer ranges from 100–1000 nm and the thickness is only about 1–2 nm. This technique has been applied to produce advanced engineering plastics based on a variety of polymers including polyamide 6, polypropylene, epoxy resin, etc. These nanocomposites are of high stiffness and strength as well as low permeability, and the heat resistance can be improved considerably [8]. For instance, polyamide 6-silicate nanocomposites have been used as fireproof coatings [9].

In this article, we synthesize a novel polymer intercalated/exfoliated (PIE) cement consisting of a polyamide 6-silicate nanointerphase. Its tensile properties at various temperatures are evaluated through flexure experiment.

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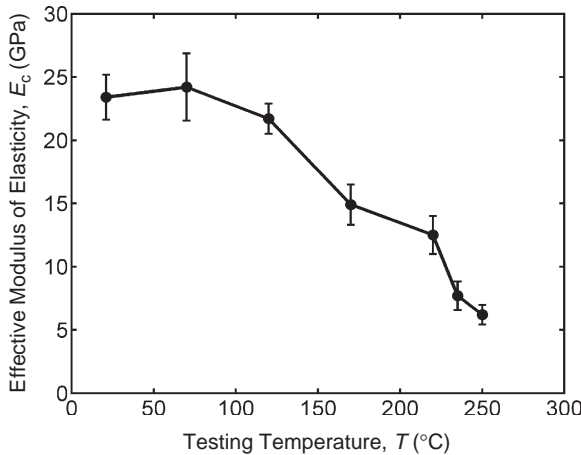


Fig. 1. The thermal softening of the PIE cement.

The testing data show that the thermal distortion point of the PIE cement, which is defined as the temperature at which the flexure strength is reduced by 50%, is quite high.

## 2. Experimental

### 2.1. Sample preparation

The polyamide 6-silicate nanointerphase used in the present study was synthesized through in situ polymerization and provided in pellet form by Dr. M. Kato from The Toyota CRD, Inc. The layered structure of the tactoids was first pre-swelled in water and then expanded by  $\epsilon$ -caprolactam. The details of the processing procedure were discussed in [6]. The silicate content in the nanointerphase was 3.7%, and the nanolayers were partially exfoliated, forming a multiscale reinforcing network [7]. The glass transition temperature is about 160 °C.

After being dried in an Isotemp 285A vacuum oven at 110 °C for 24 h, the nanointerphase were mixed with 76.5 wt.% of type I portland cement and 23.5 wt.% of type III portland cement in an KMB-100 Brabender at 275 °C. The mixing process contained two stages: (1) rapid mixing at 120 rpm for 5 min, followed by (2) slow mixing at 10 rpm for 10 min. The uniform dispersion of cement was achieved in stage 1, and in stage 2 the air content was minimized. The nanointerphase/cement ratio was 1/5 in weight. The nanointerphase reinforced cement was then hot pressed into flexure samples in a Carver 3912 hydraulic compression molding machine at 270 °C under 5 MPa. The length, width, and height of the samples were 12.7, 3.2, and 3.2 mm, respectively.

### 2.2. Flexure experiment

The flexure properties of the PIE cement were measured by using a type 5569 Instron machine, following the procedure defined by ASTM C293. The span length,  $L$ ,

was 11.5 mm. The crosshead speed was set to 1 mm/min. The flexure experiment was performed at seven different temperatures in the range of 21 to 250 °C. At each temperature 3–4 samples were tested.

The stiffness of the PIE cement was characterized by the effective chord modulus of elasticity similar with that specified in ASTM C469

$$E_c = \frac{L^3}{4bd^3} \frac{P_2 - P_1}{\delta_2 - \delta_1} \quad (1)$$

where  $b$  and  $d$  are the sample width and height, respectively;  $P_2 = 0.4 \cdot P_{ul}$ , with  $P_{ul}$  being the ultimate center-point load;  $\delta_2$  is the center-point deflection corresponding to  $P_2$ ;  $\delta_1 = 8.33 \times 10^{-6} \cdot L$ ; and  $P_1$  is the corresponding load. The flexure strength was measured by the modulus of rupture

$$R = \frac{3}{2} \frac{P_{ul} L}{bd^2} \quad (2)$$

and the toughness was measured by the total fracture work

$$W = \int_0^{\delta_f} P d\delta \quad (3)$$

where  $P$  and  $\delta$  are the center-point load and deflection, respectively, and  $\delta_f$  is the ultimate deflection at which the final failure occurs. The experimental results of  $E_c$ ,  $R$ , and  $W$  are shown in Figs. 1–3 as functions of the temperature,  $T$ , respectively.

## 3. Results and discussion

The glass transition of the polyamide 6-silicate nanointerphase is dependent on a variety of factors including the silicate content, the degree of intercalation and exfoliation, the molecular weight, and the thermal treatment history [10,11]. Through Fig. 1, it can be seen clearly that, even at a temperature much higher than 70 °C, which is the glass transition temperature of neat polyamide 6, the effective chord modulus of elasticity is still quite high. As the

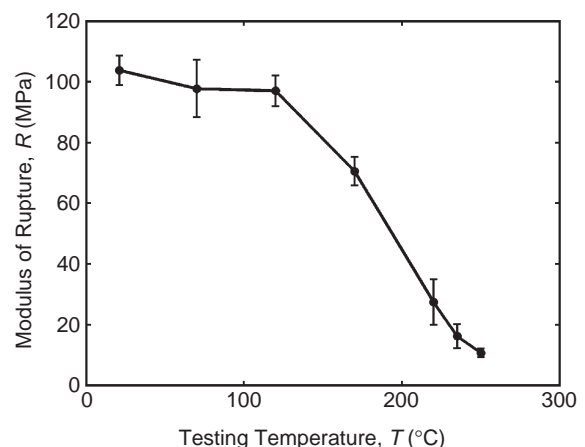


Fig. 2. The flexure strength as a function of the temperature.

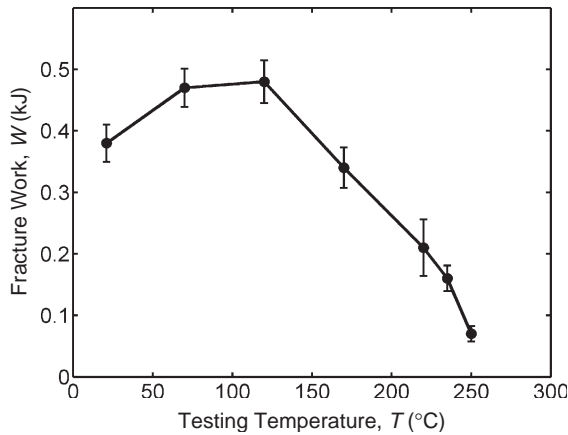


Fig. 3. The fracture work as a function of the temperature.

temperature increases, the softening starts to take place at about 120 °C, which should be attributed to the relaxation of secondary bonds in the polymer phase. At 170 °C, there is a plateau region, followed by the accelerated softening when the temperature exceeds 220 °C, probably due to the softening of the cement–nanointerphase interface. Eventually, when  $T$  reaches about 270 °C, as observed in the compression molding process, the nanointerphase is fully melt and the stiffness decreases to zero. The stiffness of the cement phase is about 30 GPa [12], and that of the nanointerphase is around 5 GPa [6]. At a low temperature,  $E_c$  is relatively high and therefore the PIE cement should be regarded as a Maxwell-model-type composite. As the temperature is higher than 220 °C,  $E_c$  is lowered rapidly as  $T$  rises. Since the softening of the nanointerphase is much more pronounced compared with that of the cement phase, the PIE cement should be discussed in a Voigt-model-type framework.

The temperature dependence of the flexure strength, as shown in Fig. 2, is somewhat similar with that of the stiffness. At a relatively low temperature, the modulus of rupture is about 100–110 MPa. According to the literature data, without the addition of the nanolayers, the flexure strength of a neat polyamide based cement composite is only around 30–50 MPa [13]. The superior strength of the PIE cement should be attributed to the reinforcing effect of the nanointerphase. When  $T$  is below 180 °C,  $R$  is higher than one half of the maximum value. When  $T > 120$  °C,  $R$  decreases as  $T$  rises with a nearly constant rate. As  $T$  reaches 250 °C, the flexure strength of the PIE cement is still about two times larger than that of ordinary portland cement. However, the performance of the material at this temperature is no longer reliable since when  $T$  increases to 270 °C, with the melting of the nanointerphase, the effective strength would vanish. It is clear that the  $R$ – $T$  relationship is governed by the behaviors of the polymer phase. The decrease in tensile strength can be related to the thermally aided local rupture that triggers crazing, shear banding, and/or microvoiding. Since the silicate nanolayers can reduce the mobility of polymer chains, the thermal effect on the nanointerphase is suppressed and thus the thermal distortion point is much higher than that of polyamide 6.

The thermal effect on the fracture work, on the other hand, is more complicated. As indicated by Eq. (3), the fracture work is determined by both the strength and the deformability. As temperature rises, the strength, as discussed above, would decrease, while the deformability can increase, leading to a higher value of

$\delta_f$ , primarily due to the increase in ductility of the nanointerphase. According to Fig. 3, when the temperature is relatively low, the fracture work increases with  $T$ , that is, increasing temperature is of a beneficial effect on the toughness of PIE cement, primarily because, while the strength decreases slightly, the deformability becomes considerably larger. When the temperature is higher than 120 °C, increasing  $T$  would lead to a decrease in  $W$ , indicating that the softening effect is dominant.

#### 4. Conclusion

The polymer intercalated/exfoliated cement is synthesized by reinforcing portland cement by a polyamide 6-silicate nanointerphase. The nanointerphase results in significant increases in flexure strength and fracture toughness in the temperature range of 20–250 °C. The following conclusions are drawn:

- (1) The silicate nanolayers in the nanointerphase lead to a considerable enhancement of high-temperature performance of the PIE cement.
- (2) Softening of the PIE cement is negligible when the temperature is lower than 120 °C.
- (3) The flexure strength of the PIE cement is insensitive to the temperature when  $T < 120$  °C, and is still much higher than that of ordinary cements when  $T = 250$  °C. The thermal distortion point is around 180 °C.
- (4) When the temperature is relatively low, the fracture toughness of the PIE cement increases with  $T$ . The maximum fracture work is obtained at about 120 °C.

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