

A simplified processing technique of organic–inorganic intercalation/exfoliation nanohybrid

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Abstract

A simplified processing technique of polymer–cement intercalation/exfoliation (PCIE) nanohybrid is investigated. By using a silicate precursor, through a “one-pot” procedure, polyamide 6 based interphase reinforced by exfoliated silicate nanolayers and intercalated nanolayer stacks is produced. The nanointerphase acts as the binder, leading to the high tensile strength. The optimum nanointerphase content is larger than 15%.

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1. Introduction

Developing high-tensile-strength cement based materials has been an active research area for decades, for which using polymer interphases has drawn considerable attention [1,2]. Usually, as the binding phase, which in an ordinary cement is of the major component of either calcium silicate hydrate or calcium aluminate hydrate, is modified or replaced by a polymer interphase, the tensile strength and the fracture toughness can be significantly improved. For instance, the tensile strength of a polymer modified cement is typically around 20–30 MPa, about an order of magnitude higher than that of portland cements [3]. The so-developed materials are often referred to as polymer modified cements, polymer impregnated cements, or polymer cements, depending on the nature of their processing techniques [4].

Recently, based on the progress in polymer intercalation/exfoliation techniques, polymer–cement intercalation/exfoliation (PCIE) nanohybrids were developed [5]. The binding phase in a PCIE nanohybrid has a multiscale structure. At the nanometer level, silicate tactoids were mixed with and intercalated by polymer macromolecules, and a certain portion of nanolayers were exfoliated, acting as reinforcements that improve the stiffness, the strength, the thermal stability, and the gas/liquid transportation properties [6]. At the microscopic level, cement particles were strongly bonded by the polymer–silicate interphase, as depicted in Fig. 1. As a result, the tensile strengths of PCIE nanohybrids were comparable with that of structural steels, and their high-temperature performance [7] and moisture resistance [8] were superior.

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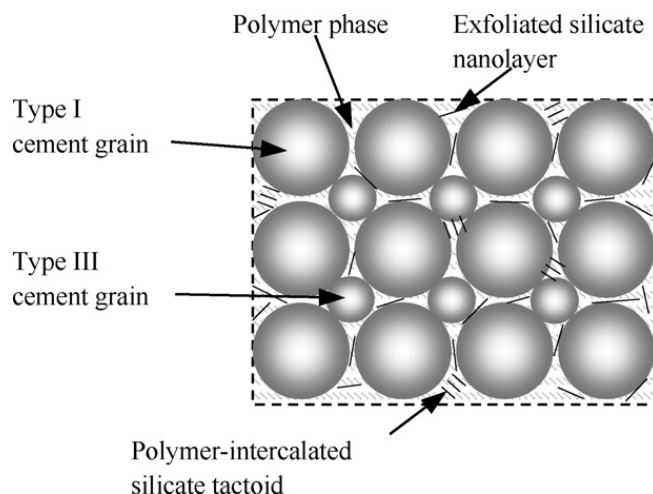


Fig. 1. A Schematic diagram of the PCIE nanohybrid, which consists of types I and III cement phases as well as polyamide 6-silicate nanointerphase. Note that in an actual material, the silicate nanolayers and tactoids are smaller than the cement grains by 3–4 orders of magnitude.

One of the problems of the PCIE nanohybrids is the relatively complicated preparation procedures of the nanointerphase, which was produced by first intercalating monomers in the layer stacks of silicate tactoids, then exfoliating individual nanolayers through in situ polymerization, and finally dispersing all the components [9]. The process consisted of multiple heating, curing, and mixing steps [10]. In the current study, we synthesized and characterized PCIE nanohybrids using a “one-pot” technique. The results showed that the tensile strengths were at the level of 80–100 MPa, similar to that of previously developed materials, which provides a basis for developing PCIE nanohybrids that can be handled and placed in a similar manner as conventional cement–polymer hybrids.

2. Experimental

In order to achieve a high degree of intercalation and exfoliation, a montmorillonite precursor was employed, as discussed by Kojima et al. [11]. Initially, 814 g of Alfa Aesar A19374 ϵ -caprolactam, 105 g of Alfa Aesar A14719 aminocaproic acid, 38 g of Kunimine K01274 montmorillonite, 45 nmol of J.T. Baker Y11A06 phosphoric acid, and 1000 cm³ of de-ionized water were mixed together for 2 h using an IKA mixer. The mixture was put in a glass container and thermally treated in a Lindberg furnace in nitrogen environment at 260 °C for 6 h, followed by furnace cooling. During this process, the ϵ -caprolactam molecules intercalated into the montmorillonite tactoids and formed polyamide 6 chains, accompanied by the expansion of layer stacks and the eventual delamination of nanolayers [11]. The product was then ground in a Weima Eurodrive RF62DM grinder for 5 min, thoroughly washed by warm water, dried in a VWR 1330GM oven at 110 °C for 24 h, and thus became the nanointerphase. It was characterized in a 40 mA to 40 kW Bruker AX8 X-ray diffractometer with Cu K α_1 radiation. The result is shown in Fig. 2.

The synthesized nanointerphase, which was in pellet form with the grain size around 0.5 mm, was softened in a C.W. Brabender Multi Corder DR2072 mixer at 220 °C for 30 min. Then, the temperature was raised to 270 °C and cement powders were added. The cement phase, which had been pre-heated at 200 °C, contained three parts of type-I portland cement and one part of type-III portland cement. The nanointerphase content was in the range of 10–30% by weight. The cements and the nanointerphase were first mixed at 120 rpm for 10 min, and then the mixing rate was gradually reduced to 10 rpm and maintained at this level for 10 min. The two-staged mixing procedure was repeated for four to six times until the components were uniformly dispersed, forming the PCIE nanohybrid.

In order to perform tensile tests, the PCIE nanohybrid was compression molded into flat sheets using a type 3912 Carver hydraulic compression molding machine at 270 °C under 27.5 MPa. The sheet thickness was about 0.5 mm. Two Teflon loading plates were used so as to minimize the friction force. Then, rectangle tensile samples were cut from the sheets, with the dimension about 10 mm $\times$ 2 mm. Altogether, five groups of samples were investigated, with the nanointerphase contents of 10%, 15%, 20%, 25%, and 30%, respectively. For each group, four to six specimens were analyzed. The measured tensile strengths are shown in Fig. 3. After the tensile experiment, the fracture surfaces were examined in a FEI Quanta 200 environmental electron scanning microscope. Fig. 4 shows the typical fractography.

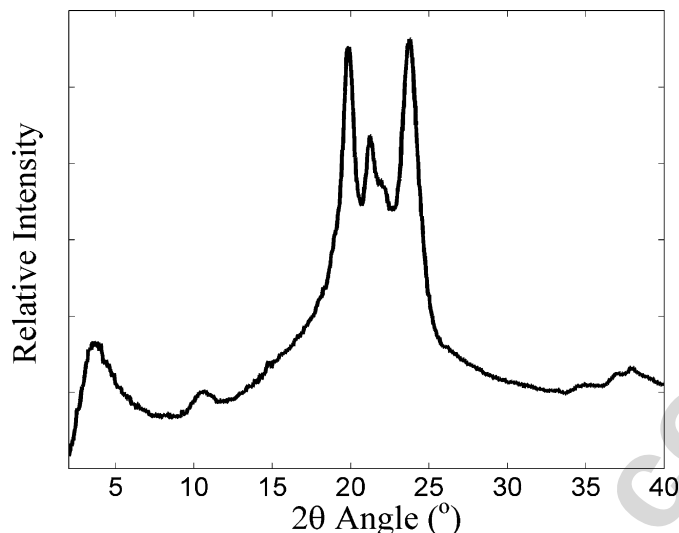


Fig. 2. The X-ray diffraction result of the nanointerphase.

3. Results and discussion

Fig. 2 shows clearly that the layer stack of the montmorillonite tactoids is disrupted, since the characteristic peaks of montmorillonite at 7.1° and 9.2° cannot be detected. The layer stack expands, leading to the formation of the peak at 4.3° , corresponding to a basal distance of $20.6 \text{ \AA}$ that can be attributed to the presence of a complex of silicate and intercalated polyamide 6 oligomer [6]. This peak is relatively weak, indicating that the expanded layer stacks are partly exfoliated. That is, the nanointerphase is reinforced by both the intercalated layer stacks and the exfoliated nanolayers. The multiscale reinforcement is beneficial to increasing both the tensile strength and the fracture toughness [12–14]. The peaks at 20.5° and 24° indicate the α phase of the semi-crystalline polyamide 6, and the peak at 21.5° indicates the γ phase. It can be seen that in the nanointerphase the α phase is more pronounced, which should be related to the slow furnace cooling process.

As a PCIE nanohybrid is produced, the amount of nanointerphase must be sufficient so that the cement phases are well wetted. As shown in Fig. 3, when the nanointerphase content, c , is only 10%, the cement grains are poorly bonded (also see Fig. 4a), and therefore the tensile strength, Y , is quite low, where Y is defined as $F_m/(w_0 t_0)$, with F_m being the peak load reached in the tensile experiment and w_0 and t_0 are the initial width and thickness of the sample, respectively. As c increases to larger than 15%, the nanointerphase becomes continuous, as shown in Fig. 4(b). Hence, it is

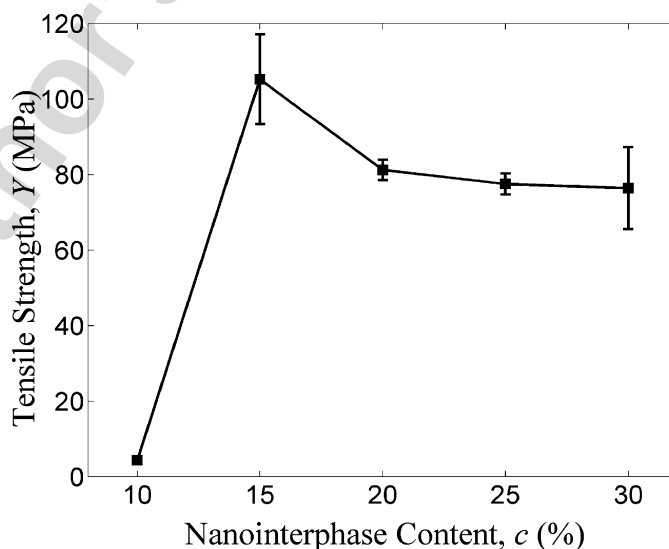


Fig. 3. The tensile strength as a function of the nanointerphase content.

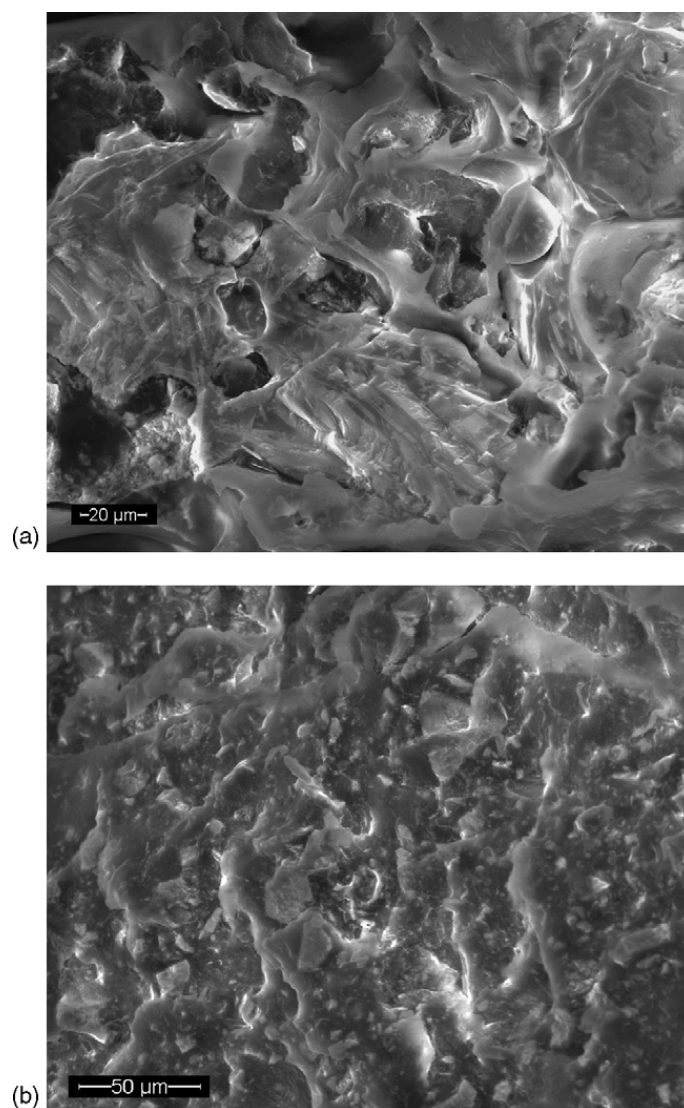


Fig. 4. SEM microscopy of PCIE nanohybrids with the nanointerphase contents of (a) 10% and (b) 20%.

load-carrying and the tensile strength greatly increases to nearly 100 MPa, close to that of the previously developed nanohybrids [5]. This value is 1–2 orders of magnitude higher than the tensile strengths of ordinary portland cements, lower than but comparable with that of structural steels.

As the nanointerphase content further increases, however, the tensile strength slightly decreases. As c reaches 20%, the tensile strength is reduced by about 25% from the maximum value. The tensile strength continues to decrease as c rises; while when c is larger than 20%, its influence becomes much less pronounced, indicating that the material behavior is saturated. This should be attributed to the post-processing treatments of the nanointerphase. As c is relatively small, the cement phases are nearly close-packed. The nanointerphase exists in membrane form in between the cement grains. The cement–polymer interaction promotes lamellae formation, raising the crystallinity, which is somewhat equivalent to increasing the effective cooling rate [12,14]. Under this condition, the strength of the nanointerphase is quite high, so does the strength of the entire nanohybrid. As the nanointerphase content rises, the cement grains are no longer close-packed, and the volume fraction of the cement–polymer interface zone is lowered. Thus, the tensile strength is dominated by the bulk nanointerphase, which causes the decrease in Y . This effect is secondary as the nanointerphase content is much larger than the critical value of the close-packed structure.

Note that for the PCIE nanohybrids based on nanointerphases of higher degrees of exfoliation, the critical nanointerphase content at which the maximum tensile strength is reached is around 8–11% [5], slightly lower than the value of the current study. This should be associated with the two-staged mixing procedure, which is affected by the rheological properties of the nanointerphase. As the intercalation, in situ polymerization, and exfoliation processes are

simplified in the “one-pot” procedure, the degree of exfoliation decreases, and thus the effective viscosity becomes higher [15]; that is, the uniform distribution of cement phases becomes more difficult, and consequently with the same nanointerphase content it is more likely that major defects, such as unwetted grain clusters, can exist, demanding a larger c to form a macro-defect-free structure.

4. Concluding remarks

To summarize, a simplified processing procedure of PCIE nanohybrid is developed. By employing the “one-pot” technique to disrupt the nanolayer stacks of a montmorillonite precursor, the nanointerphase can be prepared quite conveniently. Through two-staged mixing, PCIE nanohybrids of high tensile strengths are synthesized. The nanointerphase content must be higher than 15% so that the binder is continuous and load-carrying. This value is larger than that of the materials developed previously, which can be attributed to the change in rheological properties. As the nanointerphase content becomes larger, the tensile strength decreases slightly, due to the morphology variation.

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