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An Organic-Inorganic Nanohybrid Based on Lunar Soil Simulant**

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One of the long term goals of sending human beings to the Moon and the Mars is to stay there, for which temporary outposts and permanent bases must be constructed.[1] Due to the tight constraint of space transportation capacity, it is highly desirable that the outposts and bases can be built by using locally harvestable resources, such as lunar soils. For instance, it is, theoretically, possible that as lunar soils of different chemical compositions are appropriately mixed together, through complicated heating and curing procedures "lunar cements", materials that can react with water or other liquid agents to form load-bearing components, can be obtained.[2–4] However, to achieve this, massive and energy-consuming "cement plants" must be built on the Moon, before the "lunar cements" are available. Even if this could be done, the "lunar cements", as any other ordinary cementitious materials, are of low flexure strengths. Their long-term reliability, especially in the vacuum or high/low-temperature environments, is also problematic. Moreover, the availability of water or reactive chemicals necessary for the cementing process is quite limited.

In view of these issues, over the years a few alternative techniques such as direct sintering of lunar soils,[5] water-free sulfur cements,[6] applications of lunar/planetary lava,[7,8] and in-situ fabrication of glass or metals/alloys [9,10] have been proposed. The main issues related to these techniques include the lack of systematic testing data, the relatively high energy consumption, the relatively poor material properties, and/or the limited availability of resources. Therefore, they are still far from being directly useful for space construction.

Recently, in a study on high-flexure-strength infrastructural materials, Qiao et al.[11–13] developed polymer intercalation/exfoliation (PIE) cements. In a PIE cement, the binder is not formed through hydration. Rather, a small amount of polymer interphase reinforced by exfoliated silicate nanolayers and intercalated silicate layer stacks is employed to hold the inorganic particles together, forming a multiscale organic-inorganic structure. Due to the barrier effect of the nanolayers, the permeability of the PIE cement is low, resulting in the superior air/water-proofness. The flexure strength can be more than 100 MPa, larger than that of many aluminum alloys. The thermal stability is also superior.

It is envisioned that, if the PIE technique can be extended to lunar soils; that is, if lunar soil grains can be strongly bonded by the nanointerphase, space infrastructural materials of high strength, low permeability, and high survivability can be developed. To produce these materials at the lunar surface, only the organic nanointerphases need to be prepared on and transported from the Earth, and the inorganic components can be harvested locally. The processing procedure is water free and quite straightforward, having great potential in building large-scale structures on the Moon as well as other planets or planetary satellites.

Experimental

In the current study, JSC-1 lunar soil simulant was employed as a close analog to lunar soils. It was developed at The Johnson Space Center based on the analysis of Apollo lunar soil samples,[14] taking into consideration the major chemical and physical properties such as the chemical composition, the grain size, the inter-particle friction and cohesion, etc. According to the work by McKay et al.,[15] the JSC-1 simulant contained 47.7 % of silica, 10.4 % of CaO, 9.0 % of MgO, 7.3 % of FeO, 3.4 % of Fe_2O_3, 1.6 % of TiO_2, 0.8 % of K_2O, as well as small amounts of MnO, Cr_2O_3, and P_2O_5. Its grains contained glass, plagioclase, and olivine phases, with the size in the range of 10–100 μm.

The nanointerphase was prepared through a simplified "one-pot" procedure.[16,17] At room temperature, ε-caprolactam, aminocaproic acid, montmorillonite, and deionized water were uniformly mixed together, with the weight ratio of 814:105:14:1000. A trace amount of phosphoric acid was added as the accelerator. The montmorillonite was obtained from The Kunimine Industries and was used as the silicate precursor. The mixture was thermal-treated in a Lindberg tube furnace in nitrogen environment at 260 °C for 6 hrs, so that the ά-caprolactam molecules could intercalate into the montmorillonite tactoids and form polyamide 6 macromolecules through in situ polymerization,[18] leading to the expansion of the layer stacks, the delamination of individual nanolayers, and the eventual formation of the nanointerphase. The nanointerphase was then cooled down to room temperature in the furnace, ground into pellets with the size of about 0.5 mm, thoroughly washed by warm water, and finally dried in air at 110 °C for 24 hrs. It was characterized using a Bruker AX8 X-ray diffractometer, and the result is shown in Figure 1.

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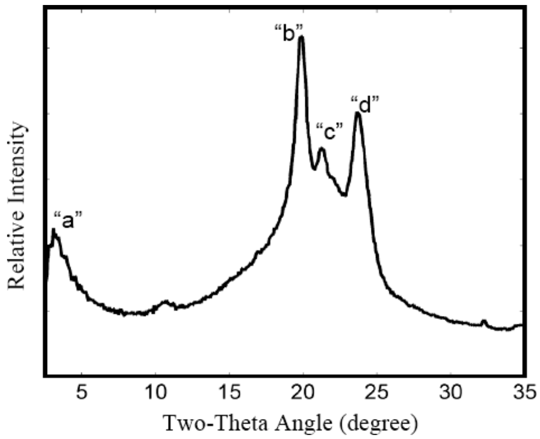

Fig. 1 The x-ray diffraction result of the nanointerphase.

In order to develop load-carrying materials, the nanointerphase was pre-heated in a brabender at 220 °C until it was softened, followed by the addition of lunar soil simulant. The nanointerphase content was 15 %. The temperature was then raised to 270 °C, and the simulant and the nanointerphase were mixed at 120 rpm to reach uniform dispersion and then at 10 rpm to minimize defect density. The resultant material, which will be referred to as simulant-based PIE (SBP) lunar cement in the following discussion, was taken out of the chamber immediately after the mixing procedure was finished, and cooled down to room temperature in air.

To evaluate flexure properties, the SBP lunar cement was hot pressed into smooth sheets with the thickness of 3.2 mm by using a type 3912 Carver hydraulic compression molding machine. The pressure was set to 27.5 MPa and the temperature was 270 °C. Flexure specimens, with the width of 10.2 mm and the length of about 24.2 mm, were cut from the sheets using a fresh razor blade. The flexure experiment was performed in a three-point bending setup using a type 5569 Instron machine. The loading rate was 1 mm/min. Altogether 5 samples were tested. The average flexure strength $Y=(3/2)\ PL/bt_0^2$ was measured to be 74.1 MPa, and the standard deviation was 6.7 MPa, where P is the maximum center-point loading, L is the support distance, b is the sample width, and t_0 is the sample thickness. The fracture surfaces were observed in a FEI Quanta 200 environmental scanning electron microscope (see Fig. 2).

Discussions

At the microscopic scale, the material consists of close-packed simulant grains and continuous nanointerphase, as shown in Figure 2. The nanointerphase can be regarded as polymeric membranes in between the simulant grains, bonding them together. The membrane thickness, t, is at the level of a few µm. Note that t is dominated by the nanointerphase content, c. If the nanointerphase content is high, the simulant-nanointerphase mixture is quite flowable at an elevated temperature, and thus the mixing procedure is easy to control. However, in order to reduce the amount of components that need to be prepared on the Earth, for a lunar cement c must be minimized. According to the characterization results of PIE cements,[11–13,17] as c is lower than 8 %, the interphase is insufficient to wet all the inorganic particles. The un-wetted particles would form macrodefects of loosely packed grain clusters, which leads to a significant decrease in flexure strength. Furthermore, due to the changes in rheological properties,[19] a larger inorganic content usually results in a higher energy requirement for heating and mixing, which must be carefully taken into consideration as the power supply for lunar base/outpost construction is limited. It is also important to keep a leeway for the relatively un-investigated space environments; that is, for safety purpose, the nanointerphase content should be higher than the theoretical "optimum" value. In the current study, c is set to 15 %. Under this condition, the handling and placing of softened simulant-nanointerphase mixture are straightforward, and the flexure strength is more than one order of magnitude higher that that of ordinary portland cements, which is quite satisfactory for construction applications even for adverse conditions.

It is possible to further decrease the nanointerphase content without lowering the flexure strength by appropriately control the size gradation of simulant grains. For instance, by using gap gradation protocols, the interphase content can be reduced by nearly 50 %.[20] If more accurate continuous gradation protocols are used, c can be even smaller.[21] However, as most of concrete structures on the Earth, the developed lunar cements can be employed as the binding phase for aggregates, such as lunar rocks or coarse lunar soil grains, to form "lunar concretes". In a concrete material, the cement binder content is often around 20 %,[22] which, for the SBP lunar cement developed in the current study, results in a low nanointerphase content of 3 %. That is, to produce 100 parts of space construction materials, only 3 parts of nanointerphase need to be transported from the Earth. Further lowering c would lead to only marginal benefits.

At the nanometer scale, the nanointerphase can be regarded as a polyamide 6 matrix nanocomposite, with the reinforcements of both intercalated silicate tactoids and exfoliated silicate nanolayers. As shown in Figure 1, the nanointerphase is characterized by the x-ray diffraction peaks at the

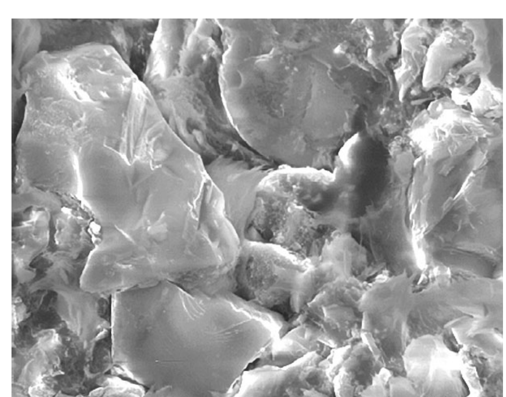

Fig. 2 ESEM microscopy of the simulant-based PIE lunar cement.

two-theta angles of 4.3 ° ("a"), 20.5 ° ("b"), 21.5 ° ("c"), and 24° ("d"). Peaks "b–d" reflect the semi-crystalline structure of polyamide 6, among which "b" and "d" are for α phase and "c" is for γ phase. In α phase, chain slippage is relatively difficult due to the contoured configuration of monoclinic unit cells. In γ phase, amide groups are twisted from methylene group planes. Their initiation and growth are mainly determined by the cooling condition and the degree of exfoliation of silicate nanolayers, which is reflected by peak "a". A high peak "a" indicates a high degree of intercalation, and if all the silicate tactoids are delaminated, this peak would entirely disappear.[18] In the current material, the full exfoliated is not achieved, which can actually be beneficial since the multiscale reinforcement mechanism improves strength and toughness simultaneously.[23] The exfoliated nanolayers promote the formation of γ phase and lower the chain mobility; the intercalated tactoids can act as either craze initiation sites or stoppers, bridge stretched fibrils, and increase energy dissipation.[24,25] Therefore, the mechanical properties of the nanointerphase is much better than that of the neat polyamide 6. These effects are further enhanced as the nanointerphase is compressed into membranes in between the simulant grains. As the characteristic length becomes smaller, the chain alignment is more pronounced, and crazing and shear banding are depressed. As a result, the strength rises. Moreover, the thermal stability and the air/water-proofness can also be significantly improved.[11–13] The simulant grains also hinder the fracture process by promoting crack bifurcation, causing jerky fracture surfaces, as shown in Figure 2, somewhat similar to the role of the inorganic phase in a nacre.[26]

Concluding Remarks

Clearly, the experimental study discussed above provides only a proof-of-concept result. More detailed study needs to be carried out to identify the optimum processing parameters and post-processing treatment conditions. Furthermore, the nature of simulant-nanointerphase interaction, the key factors dominating the bonding strength, and the roles of silicate nanolayers and matrix morphology in each stage of material deformation must be adequately understood. Nevertheless, through the current study it has been validated that the PIE technique can be extended to JSC-1 lunar soil simulant so as to produce strong infrastructural materials. The flexure strength of the developed material is higher than that of ordinary portland cement by more than an order of magnitude. This technique is of great potential in utilizing resources available on the lunar surface for the construction of outposts and bases. It may also be extended to martian soils as well as dusts and rocks on other planets or planetary satellites.

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