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Two-step gradation of particle size in an inorganic-organic hybrid

Abstract: An inorganic-organic hybrid (IOH) of silica particulates and polyethylene (PE) was investigated, where silica was employed as an analogue to lunar soil. The objective was to search for the optimum materials design strategy for "lunar cements" – infrastructural materials based on locally harvestable resources on the Moon. If the silica particulate size was uniform, the flexure strength of the IOH decreased quite linearly with the PE content. With a two-step size gradation of silica particulates, the flexure strength of the silica-PE IOH could be much improved, higher than that of Portland cements with only 4 wt% of PE. A threshold PE content around 6 wt% existed. Above the threshold, the PE content has only a secondary effect on the IOH flexure strength; below the threshold, the IOH flexure strength decreases abruptly. In order to further enhance the IOH strength and to reduce the binder content, this threshold value must be minimized.

Keywords: inorganic-organic hybrid; locally harvestable resources; lunar cement; size gradation.

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1 Introduction

The invention and application of composite materials has greatly changed almost all the aspects of human life. A composite material usually consists of a continuous matrix and a reinforcement phase. The matrix-to-reinforcement mass ratio is typically around or larger than 1:1, so as to ensure the complete wetting of the reinforcements and the smooth transmission of external loadings and internal stresses [1]. With an appropriate microscopic structure, the benefits of the high strength and stiffness of the reinforcement as well as the high toughness and deformability of the matrix can be combined, compensating for the shortcomings of each other [2]. They are widely utilized as lightweight, strong, and cost-efficient structural materials.

This concept, while not exactly for the same purpose, may be explored to develop infrastructural materials on the Moon [3, 4].

Currently, the scale of human activities on the Moon is very limited. A major reason is the lack of suitable infrastructural materials to construct life-supporting lunar bases and outposts, as well as bulky and massive structural components of research facilities, such as large-scale space telescopes. If all the structural components were carried from the Earth, to build a lunar structure similar to the Low-Orbit International Space Station (ISS), it may take more than 200–400 years, as the distance from the Earth to the Moon is longer than to the ISS by three orders of magnitude [5]. It is desirable that locally harvestable resources, e.g., lunar regolith, can be utilized [6].

Lunar regolith contains most of the components needed for the processing of ordinary Portland cement [7]. However, even if Portland cement could be produced by using massive and energy-consuming facilities and equipment, it needs 30–40 wt% water for the hydration reactions [8]; and even if this could be done, the hardened cement, mainly calcium silicate hydrates (C-S-H), would rapidly decompose in the harsh, vacuum lunar environment, where the daily temperature varies from -200°C to 130°C [9].

Another concept that people have explored is to directly sinter the lunar soil grains together using microwaves, as they contain a large portion of silica [10]. The major technical challenges include the relatively shallow penetration depth of the heating radiation waves and the fragility of the fused glass components.

Recently we initiated an investigation on inorganic-organic hybrid (IOH) lunar infrastructural materials: if lunar soil grains (the inorganic phase) can be strongly bonded together by a small amount of organic phase, the IOH can be used to construct large-scale structures on the Moon. On some planets and planetary satellites where carbon-based small molecules are available [11], the organic phase may even be synthesized locally. For the Moon, the organic binder material should be transported from the Earth, and, therefore, its content in the IOH “lunar cement” must be minimized, ideally below 5%, much lower than the matrix content in a regular composite material.

One possible method to minimize the organic content in an IOH is to optimize the size gradation of the inorganic grains. As the smaller grains fill the free space among the larger ones, the amount of the organic material can be reduced while the overall mechanical properties may be improved. Such a technique has been, for example, commonly employed in concrete processing [12], in which aggregates of different sizes are mixed together to lower the use of the relatively expensive cementitious materials.

Currently, experimental data of the effects of particle size gradation in IOH, especially when the content of the organic phase is close to its lower limit, are still lacking.

2 Materials and methods

In order to focus on the particle size gradation effects, we used silica micro-particulates as an analogue to the actual lunar regolith grains, as they have regular shapes and sizes and represent the major component of lunar soil [10]. The organic phase under investigation was polyethylene (PE), as its rheological behaviors are controllable. Previous studies have examined a few important processing parameters for PE-silica composites [13–15].

Two types of silica particulates of different sizes were investigated, with the diameters of 100 μm and 5 μm, respectively. The 100-μm silica particulates were obtained from Sigma-Aldrich (St. Louis, MO, USA) (Part No. G8893), with the particle size ranged from 50 μm to 106 μm; the 5-μm particulates were obtained from Cospheric (Santa Barbara, CA, USA) (Part No. P2011SL), with the particle size fell in to the range of 3 μm–8 μm. The polyethylene pellets were provided by Shamrock (Newark, NJ, USA) (Part No. Taber Tiger 5512).

A series of IOH samples were prepared with the PE contents of 19 wt%, 14 wt%, 9 wt%, 6 wt%, 4 wt%, and 2 wt%, respectively, so as to analyze the influence of the organic phase content on the IOH strength. The effectiveness of the inorganic particle size gradation was examined by testing two sets of IOH samples: Group A, containing only 100 μm silica particulates; and Group B, containing both 100 μm and 5 μm silica particulates. In Group B samples, the mass ratio of the larger silica particulates to the smaller silica particulates was 765:235. The weight ratio was calculated on the assumption that the particles are close-packed and the smaller particulates are located at the tetrahedral sites among the larger ones.

Silica particulates and PE pellets were weighed and mixed in a ceramic crucible, and heated on a Barnstead Thermolyne-HP131225 hot plate at 300°C for 10 min. As the PE pellets melted, the mixture was thoroughly blended, and placed into a 1″×1/4″×1/4″ aluminum mold. The hot plate was then turned off and the sample was air-cooled on the hot plate.

After solidification, the IOH sample was taken out of the mold and polished to remove surface roughness. Its flexure strength was measured through a three-point bending test on a type 5582 Instron machine, in the displacement control mode with a crosshead speed of 3.0 mm/min. The span length, L, was 19.05 mm. The flexural strength was calculated as $R=(3/2)(P_{max}L/bd^2)$, where P_{max} is the maximum load at which the sample fails, b is the sample width, and d is the sample height.

3 Results and discussion

The processed IOH samples were whitish bars with smooth surfaces, as shown in Figure 1A. Their weight densities were in the range from 1.6 g/cm^3 to 2.2 g/cm^3, depending on the PE content, close to the mass average of the organic and the inorganic phases. In a flexure strength measurement experiment, as depicted in Figure 1B, an IOH sample was freely supported at the both ends by two

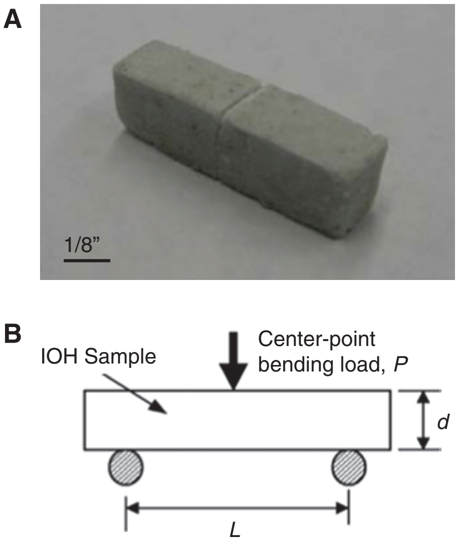

Figure 1 (A) Photo of a tested IOH sample. (B) Schematic of the flexure strength measurement experimental setup.

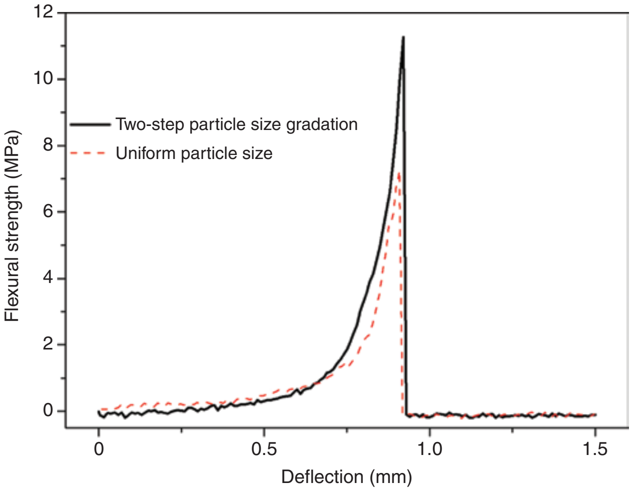

Figure 2 Typical testing curves of Group A and Group B samples.

hardened steel pins, and loaded at the middle point by another steel pin. The span length was much larger than the sample width and height, to avoid possible boundary effects. The loading rate was sufficiently low and could be regarded as quasi-static; further lowering the loading rate would not cause any detectable change in sample performance.

Figure 2 shows typical testing curves of Group A and Group B IOH samples, both demonstrating similar characteristics as that of Portland cements: as the concentrated bending force was relatively low, the deflection increased nearly linearly; as the bending force reached a critical level, catastrophic failure happened rapidly.

Figure 3 shows a typical fracture surface. In all the samples the silica particulates were strongly bonded in the PE matrix and no microcracks were detected, suggesting that the organic and inorganic components wet with each other well. Both the larger and the smaller particulates distributed nearly uniformly, without evident aggregation.

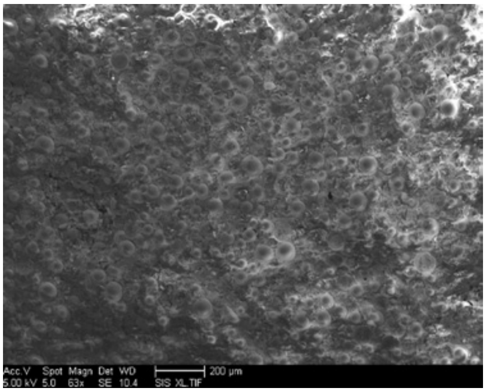

Figure 3 A SEM image of the fracture surface of an IOH sample with a two-step silica particulate size gradation. The PE content is 14 wt%. It can be seen that the silica particulates are well bonded in the PE matrix.

Table 1 Testing results of Group A IOH samples.

PE content (wt%)	Average flexural strength (MPa)	Standard deviation (MPa)
100	13.8	0.65
19	7.4	1.02
14	7.3	1.74
9	5.4	1.38
4	3.0	0.25

The measurement results of the flexure strength, *R*, are shown in Tables 1 and 2 and Figure 4. Flexure strength reflects the resistance of the material to tensile loadings, representing the performance of structural beams. Typical flexure strengths of Portland cement is 5–6 MPa [16]. Typical tensile strength of PE is 10–20 MPa [17], and the flexural strength is usually about 2 times higher than the tensile strength.

Table 2 Testing results of Group B IOH samples.

PE content (wt%)	Average flexural strength (MPa)	Standard deviation (MPa)
100	13.8	0.65
14	12.5	2.31
9	11.3	3.39
6	12.9	2.29
4	7.0	1.75
2	2.4	0.63

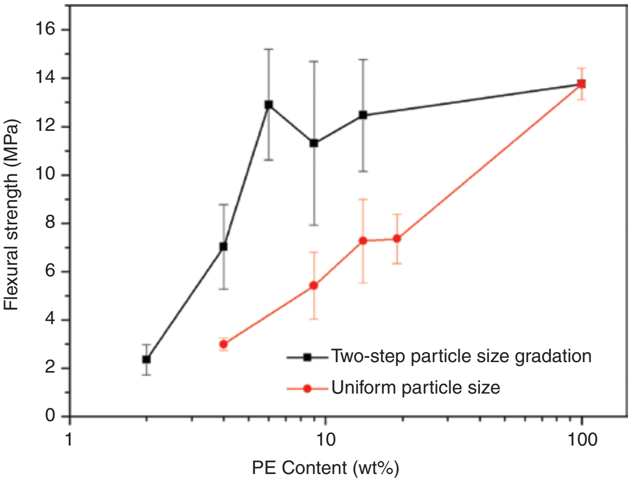

Figure 4 The flexure strength, *R*, as a function of the PE content, *C*.

Without the addition of silica particulates, the samples were made of neat PE, and their testing results defined the reference. For Group A samples, when the PE content is around 19 wt%, the flexure strength decreases to about 50% of reference value. At such a PE content level, PE was insufficient to fill all the gaps among the silica particulates, causing defects inside the material. Therefore, as the PE content, C, is lowered, the overall structural performance was reduced. The R-C relationship was linear. When C=4 wt%, R is around 3 MPa, lower than but still comparable with the flexure strength of Portland cements. When only 2 wt% of PE was added in the system, the IOH sample was structurally unstable, and the flexure strength measurement experiment could not be conducted.

For Group B samples, when the PE content decreased from 100 wt% to 6 wt%, the flexure strength was only slightly reduced. The R-C relation was relatively linear in this range of PE content, whereas the descending rate of flexure strength was much slower than that of Group A samples. When the PE content is 20 wt%, the flexure strength of the IOH sample was 90% of that of the reference neat PE; when the PE content was 6 wt%, the average flexure strength of the IOH was around 93% of that of neat PE. With the data scatter being taken accounted for, there is little statistically meaningful change in flexure strength. Clearly, with the two-step size gradation of silica particulates, the gaps among the larger silica particulates that would otherwise become defects were filled by the smaller ones, significantly increasing the structural integrity of the IOH. With only 6 wt% of PE, 94 wt% of silica was able to be bonded together, without much decrease in resistance to the external loading.

When the PE content was below 6 wt%, the R-C relation became highly nonlinear: the flexure strength began to decrease abruptly as the PE content was further lowered. Nevertheless, with 4 wt% PE, the flexure strength was around 7 MPa, or about 50% that of neat PE. This was still better than Portland cements. When C=2 wt%, the flexure strength was nearly 17% of that of neat PE; when C=1 wt%, the IOH sample became structurally unstable and no flexure strength could be measured. It can be seen that a threshold of PE content, C_0 existed, below which the matrix was no longer able to cover all the surfaces of silica particulates, leading to a high density of silica-PE interface defects; consequently, the IOH strength decreased to zero as C changes in a relatively narrow range. Above C_0, the PE content had only a secondary effect on the flexure strength. For the silica-PE system under investigation, the value of C_0 was around 6 wt%.

4 Conclusion

To summarize, we processed and characterized silica-PE IOH, as an analogue to “lunar cement” made of lunar soil grains. If the silica particle size is uniform, the flexural strength of IOH decreases with the PE content quite linearly. With a two-step size gradation of silica particulates, the strength-composition relation is highly nonlinear: There exists a threshold PE content, C_0, around 6 wt%. Above C_0, The flexure strength of IOH is insensitive to the PE content; as the PE content reduces from 100% to 6%, the flexure strength decreases by <10%. Below C_0, however, the flexure strength rapidly decreases with the PE content, indicating an abrupt increase in the silica-PE interface defect density. That is, as the PE content (C) is below C_0, the IOH is no longer structurally robust. Thus, in order to optimize the strength of IOH and, at the same time, to minimize the use of organic binder phase, the strategy should be neither improving the silica-PE bonding strength in the range of $C>C_0$; nor slowing down the strength reduction in the range of $C<C_0$; but minimizing the value of C_0 itself. Possible approaches include using better particle size gradation curves and adjusting particle shapes, which will be important topics for our future study.

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References

[1] Chawla KK. *Composite Materials: Science and Engineering*, Springer: New York, 2012.

[2] Christensen RM, *Mechanics of Composite Materials*, Dover Publications: Moneola, New York, 2005.

[3] Qiao Y, Chen J, Han A. *Adv. Eng. Mater.* 2007, 9, 325–327.

[4] Qiao Y, Chen J, Han A, Deliwala JK. *Mater. Res. Bull.* 2007, 42, 1332–1336.

[5] Seedhouse E. *Lunar Outpost: The Challenges of Establishing a Human Settlement on the Moon*, Springer-Praxis: New York, 2008.

[6] Casanova I, Aulesa V. In *Proceedings of Space 2000: The Seventh International Conference*, Johnson SW, Chua KM, Galloway RG, Richter PI, Eds., ASCE: Reston, Virginia, 2000, pp. 271–350.
[7] Ruess F, Kuhlmann U, Benaroya H. In *Earth and Space 2004*, Malla RB, Maji A, Eds., ASCE: Reston, Virginia, 2004.
[8] Taylor HFW. *Cement Chemistry*, Thomas Telford Publications: London, UK, 1997.
[9] Kelly TJ, *Moon Lander*, Smithsonian Books: Washington, 2001.
[10] Read PL, Lewis SR. *The Martian Climate Revisited: Atmosphere and Envrionment of a Desert Planet*, Springer: New York, 2004.
[11] Morris RV, Score R, Dardano C, Heiken G. *Handbook of Lunar Soils*, NASA Report No. JSC 19069, Planetary Materials Branch, NASA, 1983.
[12] Gan MSJ. *Cement and Concrete*, Chapman & Hall: London, 1997.
[13] Lai S, Hsiou Y. *Polym. Eng. Sci.* Wiley, 2010.
[14] Tajima K, Ogawa G, Aida T. *J. Polym. Sci. A: Polym. Chem.* 2000, 38, 4821–4825.
[15] Sertchook H, Avnir D. *J. Am. Chem. Soc.* 2007, 129, 98–108.
[16] Mehta P, Monteiro PJM. *Concrete: Microstructure, Properties, and Materials*, McGraw-Hill: New York, USA, 2006.
[17] Mark JE. *Polymer Data Handbook*, Oxford University Press: New York, 2009.