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Large Toughening Effect in Biomimetic Geopolymer Composites via Interface Engineered 3D Skeleton

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Abstract

Green and eco-friendly geopolymers with high thermal/acid resistance represent potential candidates for the replacement of traditional Portland cement in construction, as well as many other applications, however, the intrinsic brittleness and low toughness typical of ceramic hinders widespread adoption of this material in various applications. In this work, we fabricated a new type of geopolymer composites by impregnated with interface engineered 3D skeleton resembling the lotus root structure. Highly porous melamine foam was selected as the 3D skeleton and its interior surface was coated with elastomeric PDMS-polyurea block copolymer. Under loading, the interfacial elastomer could deform and absorb large amount of energy

concurrently with crack deflection of melamine foam and delamination of interfaces, thus the toughness was substantially improved as results indicated a transition of fracture behavior from brittle failure mode to a more ductile one. With as low as 2.5 wt. % elastomer, the fracture toughness and work of fracture were increased by 258% and 654%, respectively. Owing to the three-dimensional reinforcement preform, the issue with dispersion of reinforcing fillers is circumvented. The obtained geopolymer composites with enhanced toughness allow for applications requiring high load capacity. This strategy of manufacturing composites through 3D skeleton opens new pathway to improving mechanical performance of various brittle materials and material processing techniques.

Keywords: Bioinspired materials, Geopolymer, Melamine foam, Lotus root, Composite, Interface

Introduction

Geopolymer is a low carbon footprint eco-material that has received increased attention in recent years.¹⁻³ First termed by French scientist Davidovits in 1970s, geopolymers are a class of three dimensional (3D) inorganic polymers which are formed by mixing aluminosilicate materials with strong alkaline solutions.⁴ The main component of amorphous geopolymers are cross-linked AlO_4^- and SiO_4 tetrahedrals with positive charge balance provided by hydrated alkali metal cations.⁵ Several Si and Al rich mineral and industrial waste including metakaolin (MK), blast furnace slags, fly ash and etc. have been used to fabricate geopolymers.⁶ Geopolymers can be easily processed at low temperature, and possess mechanical performance comparable to conventional ceramics and alumina alloy.⁷ Other merits include low density, low greenhouse gas emission during production, high thermal stability, fire and acid resistance.⁸ Owing to its many excellent properties, geopolymers have been considered a promising and environmentally

friendly alternative to replace Portland cement for construction applications.⁹ Geopolymers are currently being investigated in other potential applications such as in fire resistant materials¹⁰, coatings¹¹, radioactive waste container¹² and heavy metal absorbent¹³.

Despite its numerous excellent properties, however, geopolymers suffer intrinsic brittleness and poor fracture resistance to mechanical and environmental loadings similar to conventional concrete and ceramic materials, hindering the realization of its potential in various applications. Much efforts have been devoted to suppress the brittleness and enhance fracture toughness by various strategies such as the use of reinforcing fillers including inorganic fiber¹⁴⁻¹⁵, polymer fiber¹⁶, graphene¹⁷, cotton fabric¹⁸ and etc. Among these fillers, fibers often deliver the best results and is the most widely used. As compared with the fast crack propagation in pure geopolymer, fiber containing geopolymer composites could interrupt, slow down and even terminate the crack development, effectively improving its toughness coefficient. This process is known as crack bridging effect of fibers, and specifically in fiber reinforced geopolymer composites, various mechanisms including microcrack formation, fiber debonding, fiber pull-out and crack deflection, all contributes to increasing toughness and energy absorption during fracture.¹⁴ Other than fibers, inclusion of nanomaterials was also reported to increase the geopolymer toughness through various toughening mechanisms.¹⁹ Nevertheless, the introduction of fillers present several processability issues. Firstly, fiber-filled geopolymer paste are very difficult to process due to its reduced workability.¹⁷ Secondly, the uniform mixing of fibers or other fillers into geopolymer slurry usually involving additional energy intensive processes such as ball milling, mechanical mixing or ultrasound dispersion which greatly increases the embodied energy, diminishing the greenness of the final product. Non-uniform dispersion of fillers would create defects and induce stress concentration, which in turn deteriorate the final

mechanical properties. Furthermore, there are concerns on the toxicity and recyclability related to the use of nanomaterials as fillers.²⁰

After millennia of evolution, organisms have created fascinating and sophisticated hierarchical structures,²¹ and by deciphering and mimicking their structure, materials with exceptional properties could be attainable. *Nelumbo nucifera*, more known as lotus, is an aquatic plant widely distributed throughout Asia. Apart from its aesthetic and highly prized edible value, the uniqueness of its biological structure and features have aroused the interest of academia in recent years. For instance, scientists have fabricated materials with superhydrophobic and superwetting surfaces resembling the structure of lotus leaf.²²⁻²³ Apart from the heavily studied leaf, the root of the lotus plant is also interesting. By imitating its multi-channeled structure, highly porous ceramic scaffold with hollow channels that favors cell delivery, nutrient diffusion and blood vessel formation have been designed for bone regeneration application recently.²⁴ The lotus root is a composite consisting of two main structural element, respectively being the starchy matrix and fibers (made of cellulose, hemicellulose and lignin)²⁵, where the stretchable long fibers are encapsulated in brittle starch. Due to the crack bridging effect of its long fibers, the lotus root remains unseparated even when the starch is fractured (Figure 1a). Inspired by this structure, herein we present a work to fabricate tough geopolymer composites by infiltration of geopolymer into highly porous melamine foam (MF) with interfacial coated elastomeric polydimethylsiloxane-polyurea block copolymer (PDMS-Polyurea, Figure S1) layer that resembles the lotus root construct. MF was chosen because of its extremely high porosity (>99%) which is favorable for surface coating.²⁶ Thermoplastic elastomer PDMS-polyurea block copolymer is solvent dissolvable and possesses high value of toughness, which function as the stretchable fiber in this composite. A simple dip coating process was employed to coat PDMS-

polyurea onto MF skeletal interior surface. Compared with conventional filler encompassed composite system, the dispersion-free 3D macrofiller is greener during manufacturing due to less energy required for homogenizing. Under external loads, the PDMS-polyurea elastomeric interface could be deformed while still linking the fracture surface together and absorbing large amount of energy, which coupled with other energy dissipation mechanisms, effectively disrupt crack propagation, consequently enhancing the toughness and the work of fracture of the geopolymer composite.

Results and Discussion

Figure 1. Fabrication of geopolymer composite as inspired by lotus root structure. (a) Digital image of lotus root showing the fracture surface are connected by fibers. (b) Schematic

illustration of geopolymer and composites fabrication procedure. (c) Surface morphology of uncoated and coated MF with additional EDX mapping of coated MF. (d) FTIR spectra.

The fabrication procedure of geopolymer and its composites was illustrated in Figure 1(b) (all the experimental and characterization details are given in the supplementary materials). Specifically, the polymerization mechanism of geopolymer comprises of three steps: dissolution, polymerization and solidification.²⁷ Firstly, the MK powder (Figure S2) was dissolved through the breakage of Si-O-Si and Al-O-Al bonds under strong alkaline activator to produce free SiO_4 and AlO_4 tetrahedral units which serve as monomers. Subsequently, the liberated aluminate and silicate species are connected alternatively via polycondensation to form amorphous gels. Afterwards, as the geopolymer gel densify, water was expelled out from the network to form solid geopolymer. In this work, neat geopolymer (G_{neat}) was prepared by curing MK/NaOH/sodium silicate slurry at 40 °C for 2h and 60 °C for 24h followed by aging for 6 days. Geopolymer composites containing MF foam (G_{MF}) and PDMS-polyurea coated MF foam ($G_{\text{PDMS@MF}}$) were prepared by impregnating the geopolymer slurry into MF or PDMS@MF respectively before curing. To fabricate composite samples, the press-release cycle was repeated several times on the foams to remove the trapped air and facilitate the infiltration of viscous geopolymer paste into the pores. PDMS-polyurea elastomer was attached onto the surface of MF fiber by simple dip coating method (Figure 1b). Before coating, the neat MF surface was quite smooth and clean (Figure 1c), while in contrast, it is clear that a layer of polymer was deposited onto the surface of MF skeleton after dip coating (Figure 1c). Some microstructured circled shape observed were formed by the self-assembly of block copolymer elastomer during solvent evaporation. The EDX mapping (Figure 1c) shows the existence of Si, indicating the successful coating of PDMS onto MF strands. Surface coating was also confirmed by FTIR (Figure 1d).

The strong signal of PDMS in FTIR spectra indicates that the MF strands were basically fully covered by this elastomer, which also formed some film-like structure that covered parts of MF (Figure S3). There is otherwise no obvious macroscopic difference in appearance between the pure geopolymer and composite samples (Figure S4). The density of composite samples was found to be lower than that of pure geopolymer (1.67 g/cm^3). The decrease of G_{MF} (1.66 g/cm^3) was very slight as MF is highly porous foam with porosity over 99%. The density decrease of $G_{\text{PDMS@MF}}$ was found to be much larger, however, at $\sim 9.6\%$ to 1.51 g/cm^3 , which was due to the voids formed during fabrication. The voids were induced due to the formation of some closed cells during the dip coating process. XRD patterns showed similar and typical broad amorphous hump of geopolymer for G_{neat} , G_{MF} and $G_{\text{PDMS@MF}}$ with marginal difference (Figure S5), indicating the introduction of MF and PDMS has little influence on phase composition of geopolymer matrix, while the observed several sharp peaks are ascribed to the presence of quartz in raw metakaolin.

The toughness of geopolymer and its corresponding composites were determined by single-edge notched three point bending test (SENB). Compared with G_{neat} , the toughness of G_{MF} increased by 33%, from 0.36 to $0.48 \text{ MPa}\cdot\text{m}^{0.5}$ (Figure 2a). The toughening effect was partly contributed by the breakage of MF strands. It is well known that in fiber reinforced system, fibers will be pulled out if the fiber shorter than critical fiber length, and rupture if exceeds critical fiber length.²⁸ Considering the fact that MF strands are interconnected within the foam and can be assumed to be indefinitely long, thus they would break rather than being pulled out under force. It should be noted that while the skeletal strands of MF is a rigid and brittle material, the spongy properties of MF foam is due to the open cell structure and small dimension of each strands, rather than the softness of melamine resin. More clues on the toughening mechanism in G_{MF} can

be found in morphology of fractured surface as evidenced by SEM images. The neat geopolymer surface was observed to be smooth and featureless (Figure 2d), indicative of the brittle fracture mode whereby small loads can induce fast crack development resulting in clean fracture surfaces. For G_{MF} , the ruptured MF strands protruded out the fracture surface (Figure 2e). Evidence of crack deflection, which will create more new surface during fracture and absorb more energy, were observed in regions surrounding MF strands (Figure 2f, indicated by arrow). Thus, it can be inferred that MF foam could impede the crack propagation by virtue of MF strands rupture, as well as crack deflection.

Figure 2. Toughening mechanism in geopolymer composites. Fracture toughness (a), load-deflection curves, from left to right: G_{neat} , G_{MF} and $G_{\text{PDMS@MF}}$ (b) and work of fracture (c); fracture surface image of neat geopolymer G_{neat} (d), G_{MF} (e, f) and $G_{\text{PDMS@MF}}$ (g, h, i); digital image of geopolymer composite under load showing elastomer fibrils bridge across the fracture

surfaces (j); digital image showing that sample $G_{PDMS@MF}$ could survive the striking without fragmented into pieces (k).

Even higher toughness improvement was observed for $G_{PDMS@MF}$, whereby the fracture toughness increased by 254 % to $0.93 \text{ MPa}\cdot\text{m}^{0.5}$, as compared to neat geopolymer, which is an impressive increment considering the low loading content of elastomer (2.5 wt. %). The enhancement in toughness is proportional to the PDMS-polyurea content from 0 to 2.5 wt. % (Figure S6), with 0.4 wt. % and 0.9 wt. % bringing corresponding increment ~67 % and ~119% in toughness respectively. Even after factoring into consideration the effect from MF, the normalized toughness increment due to PDMA-polyurea contribution are 34% and 86 %, respectively. This toughening effect is higher compared to geopolymer composites filled with other fibrous materials, such as glass fiber²⁹, cotton fabric¹⁸, carbon fiber felt³⁰, and comparable to nanoscaled graphene-toughened geopolymer composites¹⁷, yet with a much lower cost of reinforcement materials and simpler fabrication. At higher loading level of 5.4 wt. %, a slight reduction in toughness was observed probably due to more voids formed; nevertheless, the toughness value remains higher than that of neat geopolymer (0.82 versus $0.36 \text{ MPa}\cdot\text{m}^{0.5}$).

Other than the toughening contribution from MF in $G_{PDMS@MF}$, the PDMS-polyurea coating on MF strands delivers a multi-faceted approach to increment of toughness. From Figure 2h, the coated PDMS-polyurea on MF was observed to have been peeled off from the geopolymer matrix under stress. The microstructure of PDMS-polyurea was clearly imprinted in geopolymer which indicated a high level of adhesion between them, however no carbon element residue was observed on geopolymer surface from EDX analysis of the fracture surface (not shown here). Thus, while it is unlikely that chemical reaction occurred between PDMS-polyurea and geopolymer, the highly conformal coating and its subsequent delamination would add value to

the overall composite toughness. The elastomer was also observed to be delaminated from MF during fracture, but the presence of residue on the MF strand surface (Figure 2i) indicate strong interaction between MF and PDMS-polyurea leading to good adhesion. The adhesive force might originates from the hydrogen bonding/polar interaction between the hard polyurea segments of copolymer PDMS-polyurea which is chemically compatible with melamine moieties. Bunches of fibrils was observed near the crack tip, which was determined to be highly deformed PDMS-polyurea, bringing reminiscences to the case of linkage fibers in fractured lotus root (Figure 2j). These fibrils were also captured by optical microscopy (Figure S7). Under high flexural loads, PDMS-polyurea interfacial coating undergoes elastomeric deformation between repeated cycles of crack initiation and termination, displaying the high elasticity and toughness of elastomer layer and absorbing large amount of energy in process, which disrupted crack propagation and contribute to overall fracture toughness. The toughening mechanism of PDMS@MF in geopolymer composite is compiled and schematically depicted in Figure 3.

Figure 3. Schematic illustration showing the toughening mechanism of geopolymer composite through interface engineered 3D skeleton.

The load-deflection curves are plotted and shown in Figure 2b to better visualize the data interpretation of the toughness increment mechanism. The area under the load-deflection curve is referred to as the work of fracture. Generally for ductile materials, this value is contributed by the combined energies involved in crack initiation and crack propagation, while for brittle materials almost all the energy is spent on crack initiation with very little energy attributed to crack propagation. For G_{neat} , the load reduced to zero sharply as soon as the load reaches the maximum value as the sample broke into two separate pieces, indicating very little energy was consumed for crack propagation which is a typical brittle failure mode. This fracture behavior is similar to geopolymers based on other sources and traditional cement.^{16, 29} In contrast, the post-crack behavior of G_{MF} and $G_{\text{PDMS@MF}}$ was obviously improved, thus resulting in enhanced ductility. After reaching the peak value the load did not reduced to zero immediately but instead decreased gradually with a long tail that is suggestive of a large and continuous energy consumption by crack propagation, as in the case for $G_{\text{PDMS@MF}}$, which highlighted the durable load capacity of PMDS elastomer. The observed fracture behavior changed distinctly, from a sudden, catastrophic fracture representative of neat geopolymers to a plastic-like, gradual deformation and slow crack propagation. (Supplementary Video S1 & S2). As a result of various energy dissipation mechanism during crack propagation, the work of fracture was largely improved in geopolymer composites, and the work of fracture of G_{MF} and $G_{\text{PDMS@MF}}$ increased by 197% and 654%, respectively (Figure 2c) when compared to neat geopolymer. Contributed by the bridging of PDMS-polyurea, the $G_{\text{PDMS@MF}}$ could survive striking by hammer even though multiple cracks are observed, similar to fiber connected broken lotus root (Figure 2k), while by contrast the neat geopolymer broke into small pieces. This phenomenon could be possibly explored for improving the anti-spalling of construction materials.

In summary, we have prepared MK based geopolymer composites by slurry infiltration into PDMS-polyurea interfacial coated MF inspired by the lotus root structure. The porous MF based 3D skeleton was surface coated with PDMS via a fuss-free facile dip coating method. Considering the fact that geopolymer itself is a thermoset 3D network, a 3-phase organic-inorganic hybrid interpenetrating network was formed. This interlocking structure facilitates load transfer between geopolymer matrix to the reinforcing MF and PDMS-polyurea. During fracture, PDMS-polyurea was heavily stretched and was able to dissipate large amount of energy in the process. With the introduction of PDMS@MF, the toughness of geopolymer was substantially improved by the synergistic mechanisms of elastomer elongation, MF strands breakage, crack deflection and delamination. Filler dispersion was avoided in this approach which highlight its lower energy consumption during composite fabrication. Compared with various fibers, MF and elastomer are relatively inexpensive commodity materials which enable mass production and economic sustainability. The concept in this work can be translated to toughen other intrinsic brittle systems, such as conventional ordinary Portland cement and thermoset polymeric materials including epoxies, polyimide and etc. Besides the PDMS-polyurea elastomer used in this work, many other thermoplastic soluble polymer, inorganic particles or other functional building blocks that can be attached to the MF surface could be employed for the development composites with tailorable properties. Besides, many other types of 3D foams with porous structures are also worth further investigation.

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The introduction of PDMS coated melamine foam mimicking the lotus root structure largely enhanced the toughness and work of fracture of geopolymer.