Tunnel elasticity enhancement effect of 3D submicron ceramics (Al_2O_3 , TiO_2 , ZrO_2) fiber on polydimethylsiloxane (PDMS)

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Abstract: Some polymers are flexible, foldable, and wearable. Structural–functional composite is fabricated by adding inorganic fillers with functional properties. Up to date, compared with the polymer matrix, the composite prepared by polymer-inorganic fillers has lower flexibility, higher brittleness, and higher modulus of elasticity. In this paper, three-dimensional (3D) net-shaped submicron $\alpha\text{-Al}_2\text{O}_3$, orthorhombic ZrO_2 , and rutile TiO_2 fiber were fabricated by solution blowing spinning on a large scale. On the contrary, the elastic modulus (E) of the composite prepared by this 3D ceramic fiber was greatly reduced, and the flexibility of the composite was higher than that of the polymer matrix. When the strain was 75%, the E of the 3D net-shaped Al_2O_3 fiber-polydimethylsiloxane (PDMS) composite was 20% lower than that of PDMS. When the strain was 78%, the E of the 3D net-shaped TiO_2 fiber-PDMS and 3D net-shaped ZrO_2 fiber-PDMS composites decreased by 20% and 25%, respectively. This abnormal effect, namely the tunnel elastic enhancement effect, has great practical significance. In all-solid-state lithium-ion batteries, the composite inhibits lithium dendrite growth and the 3D inorganic network contributes to lithium ion transport. It is possible to promote the industrial production of low-cost and large-scale flexible solid-state lithium-ion batteries and it can enhance the energy storage density of energy storage materials. This novel idea also has bright prospects in flexible electronic materials.

Keywords: ceramic fiber; tunnel elasticity enhancement effect; solution blowing spinning

1 Introduction

Flexible composite enables broad application in flexible solid-state batteries [1–3], wearable and implantable electronic devices [4–8], and intelligent soft robots [9,10]. Flexible composite has become one of the research priorities in material science and engineering.

Polymer-inorganic composite can blend the mechanical properties of flexible polymer materials with the functional properties of inorganic materials, such as electrical [1–4,6,9,10], photoelectric [11,12], and electrothermal [13] properties. It is generally believed that the flexibility of the composite prepared from polymer and inorganic materials will decrease overall. Therefore, current research work basically only focuses on polymers, and its flexibility is improved by chemical modification and structural engineering. For example,

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some studies improve the mechanical properties of composite in specific dimensions by changing the geometry of polymer matrix, such as preparing net-shaped flexible films [14–16]; some studies use pre-stressing of the compliant substrate to indirectly improve the flexible behavior [17]; some studies exploit chemical modification of polymers, such as adding conjugated polymers [5,18], adding transition-metal salts to form metal–ligand coordination bond [19,20], thereby improving flexibility.

In this paper, we manufactured three-dimensional (3D) net-shaped submicron α - Al_2O_3 [21], orthorhombic ZrO_2 , and rutile TiO_2 fiber on a large scale by solution blow spinning process [4,22]. Then the flexible composite composed of polydimethylsiloxane (PDMS) matrix and three 3D ceramic fiber fillers ($\sim 0.3\%$) were synthesized directly in an on-step solution-casting method. On the contrary, the elastic modulus (E) of the composite is greatly reduced (i.e., $E_{\text{composite}} < E_{\text{PDMS}} < E_{\text{ceramic}}$), the flexibility is higher than that of the polymer matrix, and this abnormal flexibility remains unchanged in the stress–strain curve after 100 cycles. We first discovered this kind of flexibility anomalous effect of polymer–inorganic composite. In this paper, it is named as 3D tunnel elastic enhancement effect. The discovery of this anomalous effect will open a new way to study the mechanical properties of organic–inorganic composites. We can make use of this anomalous effect to design the elastic materials, and further broaden the field of functional application of organic–inorganic composites. For example, we can increase the amount of functional inorganic materials, and obtain a more flexible composite, achieving dual control of the mechanical and functional properties of the composite. The new design and understanding of the 3D network interface of organic–inorganic materials has also given us an important inspiration: Starting with tradition, but not sticking to it.

2 Experimental

2.1 Synthesis of 3D net-shaped ceramic fiber network

2.1.1 Al_2O_3 fiber network

2 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ powder was added to 1.5 mL glacial acetic acid and magnetically stirred at 60 °C for 2 h until it was completely dissolved to form stable solution A; 1.5 g polyvinyl pyrrolidone (PVP) (mass

average molar mass (M_w) = 1,300,000) was dissolved in a mixed solvent of dimethyl formamide (DMF) and ethanol in a mass ratio of 3:1 and magnetically stirred for 2 h at room temperature to form solution B. Then the solutions A and B were uniformly mixed and magnetically stirred for 5 h at room temperature to obtain a precursor solution. The mixture was loaded into a 10 mL syringe with a specific needle. The solution was injected by syringe pump with a speed of 2 mL/h, under a gas pressure of 200 kPa, naturally stretched by the air flow and solidified to fibers associated with solvent evaporation and then the 3D connected $\text{Al}(\text{NO}_3)_3$ /PVP fiber network (Fig. S1 in the Electronic Supplementary Material (ESM)) was fabricated in the porous collector). The $\text{Al}(\text{NO}_3)_3$ /PVP fiber network was sintered at a rate of 2 °C/min, held at 1100 °C for 2 h, and then cooled down in the furnace to room temperature.

2.1.2 TiO_2 fiber network

Tetrabutyl titanate [$\text{Ti}(\text{OBu})_4$] and PVP with a mass ratio of 2:1 were dissolved in glacial acetic acid and ethanol in a volume ratio of 7:3. The precursor solution was obtained after magnetically stirred for 5 h at room temperature. The experimental parameters of solution blow spinning process were the same as those of Al_2O_3 fiber. The fiber network was sintered at a rate of 2 °C/min, held at 700 °C for 2 h, and then cooled down in the furnace to room temperature.

2.1.3 ZrO_2 fiber network

Zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and PVP with a mass ratio of 2:1 were dissolved in deionized water and ethanol in a volume ratio of 1:1.5. The precursor solution was obtained after magnetically stirred for 5 h at room temperature. The experimental parameters of solution blow spinning process were the same as those of Al_2O_3 fiber. The fiber network was sintered at a rate of 2 °C/min, held at 1200 °C for 2 h, and then cooled down in the furnace to room temperature.

PDMS's main agent and curing agent (10:1 mass ratio) was magnetic stirred for 0.5–1 h to obtain homogeneous fluid. The sintered 3D Al_2O_3 , TiO_2 , and ZrO_2 fiber network were placed in a self-made mold, and an appropriate amount of fluid was added, then standing for 10 min to make the linear polymer enter the abundant pores of the ceramic fiber more uniformly. The mixture was quickly evacuated to the highest vacuum in the vacuum oven at room temperature for

10 h to remove all bubbles in the polymer. Finally, the mixture was heated to 125 °C for 20 min to fully cure the PDMS. As a control experiment, the sintered 3D ceramic fiber network was ground with a mortar to obtain the short rod-shaped ceramic fibers (Fig. S2 in the ESM) having an aspect ratio of 2–5. The solution-casting process was the same as that of 3D ceramic fiber network.

2.2 Material characterization

2.2.1 Ceramic fiber characterization

The field-emission scanning electron microscope (SEM, LEO-1530, Zeiss, Germany) and the transmission electron microscope (TEM, JEOL-2010, Japan) were used to characterize the morphologies of Al_2O_3 , TiO_2 and ZrO_2 , and determine the average diameter of the fibers. The crystal structure was tested by X-ray diffraction (XRD, Rigaku D/max-2500, Japan) with 2θ ranging from 20° to 80° at 40 kV and 200 mA.

2.2.2 Characterization and mechanical testing of composite

The same SEM and TEM were used to characterize the micro-morphologies and fracture morphologies after

mechanical properties test of PDMS, PDMS-3D ceramic fiber composites, and PDMS-short rod-shaped ceramic fiber composites. The above polymer and composites were tested using the Fourier transform infrared spectroscope (FTIR, Nicolet 6700, USA) and the dynamic thermomechanical analyzer (DMA, TA Q800, USA).

The compressive, cyclic compressive, and shear tests of the above materials were performed by an electronic universal testing machine (SHIMADZU AGS-X5kN). Among them, the loading speed in the compression test was 3 mm/min, and the loading speed in the shear tests was 10 mm/min.

3 Results and discussion

Figures 1(a)–1(c) are the SEM images of 3D net-shaped Al_2O_3 , TiO_2 , and ZrO_2 fibers with average diameter of ~650, ~300, and ~300 nm, respectively. Compared with TEM images (Figs. 1(d)–1(i) and Fig. S3 in the ESM), they can be found that all three fibers are formed by crystalline particles tightly connected. Among them, the crystal particles of Al_2O_3 are relatively small, and the diffraction ring shown in Fig. S3(b) in the ESM can be observed; the crystal particles of ZrO_2 are relatively

Fig. 1 Micromorphologies of 3D net-shaped ceramic fibers: (a) SEM image of 3D Al_2O_3 fiber, (b) SEM image of 3D TiO_2 fiber, (c) SEM image of 3D ZrO_2 fiber, (d, g) TEM images of 3D Al_2O_3 fiber, (e, h) TEM images of 3D TiO_2 fiber, and (f, i) TEM images of 3D ZrO_2 fiber.

large, and the thin region in the TEM image (Fig. S3(f) in the ESM) can be converted into regular diffraction lattices after Fourier transform. The XRD test results (Fig. S4 in the ESM) show that the crystalline structures are α - Al_2O_3 , rutile TiO_2 , and orthorhombic ZrO_2 , respectively, which are also matched with the lattice fringes in Figs. 1(g)–1(i), where Al_2O_3 is hexagonal, and TiO_2 and ZrO_2 are quadrilateral.

Figures 2(b), 2(c), and Figs. S5(d)–S5(f) in the ESM show the cross-sectional SEM images of PDMS_3dAl, PDMS_3dTl, and PDMS_3dZr composites (PDMS_3dAl, PDMS_3dTl, and PDMS_3dZr are the abbreviation of 3D net-shaped Al_2O_3 –PDMS composite, 3D net-shaped TiO_2 –PDMS composite, and 3D net-shaped ZrO_2 –PDMS composite, respectively). Among them, the volume content of 3D net-shaped Al_2O_3 fibers in PDMS_3dAl1, PDMS_3dAl2, and PDMS_3dAl3 are 0.3%, 0.1%, and 0.5%, respectively, in which the content of ceramic fibers is extremely small. Figure 2(a) and Figs. S5(a)–S5(c) in the ESM are of TEM photographs PDMS_3dAl, in which the amorphous part is PDMS, and the dark part with clear lattice fringes is Al_2O_3 . It can be seen that the polymer is in close contact with the surface of the ceramic.

FTIR spectra of PDMS, PDMS_3dAl, PDMS_3dTl, PDMS_3dZr, PDMS_rAl, PDMS_rTi, and PDMS_rZr composites (PDMS_rAl, PDMS_rTi, and PDMS_rZr are the abbreviation of short rod-shaped Al_2O_3 –PDMS composite, short rod-shaped TiO_2 –PDMS composite, and short rod-shaped ZrO_2 –PDMS composite, respectively). Among them, the volume content of short rod-shaped Al_2O_3 fibers in PDMS_rAl1, PDMS_rAl2, PDMS_rAl3 are 0.3%, 0.1%, and 0.5%, respectively; the volume content of short rod-shaped TiO_2 and ZrO_2 fibers are

both 0.3%) were shown in Fig. S6(a) in the ESM. These main peak position and intensity at 2962, 2900, 1260, 1075, 1020, and 750–800 cm^{-1} are completely consistent with the characteristic absorption peaks of the $-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-$, $\text{Si}(\text{CH}_3)_3$, $\text{Si}(\text{CH}_3)_2$, $\text{Si}-\text{CH}_3$, and $\text{Si}-\text{OH}$ groups of PDMS [23], respectively. It can be considered that the main components are all PDMS. The results of DMA test on PDMS, PDMS_3dAl, PDMS_3dTl, PDMS_3dZr, PDMS_rAl, PDMS_rTi, and PDMS_rZr composites are presented in Figs. S6(b)–S6(i) in the ESM. The glass transition temperature is between -116.4 and -117 $^\circ\text{C}$, indicating that the structure of the polymer chain is not significantly changed.

Figure 3 shows the compressive stress–strain curve of PDMS and composite. Since the hardness, strength, and elongation, etc. of PDMS are affected by the curing process, the data in Fig. 3 was obtained after samples standing in air for 3 days with the same heat curing process. Different from the traditional concept, the E of the composite material is greatly reduced (i.e., $E_{\text{composite}} < E_{\text{PDMS}} < E_{\text{ceramic}}$), and the flexibility is higher than that of the polymer matrix after adding 3D net-shaped submicron Al_2O_3 , ZrO_2 , and TiO_2 fibers.

Figures 3(a) and 3(b) show that after adding 3D net-shaped Al_2O_3 fibers, the E of the composite is about 20% lower than that of PDMS at 75% strain. Similar test results were found when 3D net-shaped TiO_2 and ZrO_2 fibers were added—when the strain is 78%, the E is reduced by 20% and 25%, respectively. After the 3D net-shaped ceramic fibers were added, the E of the composite is significantly reduced, and the fracture strain is relatively improved. On the contrary, when the 3D net-shaped ceramic fibers were ground into short rod-shaped ceramic fibers with a mortar and used as fillers to prepare composite with PDMS, the E and strength of the composite have been improved to different extents. This is consistent with experimental research, engineering applications, and traditional concepts.

Figure S7(b) in the ESM is the results of the compressive stress–strain test of PDMS and PDMS_3dAl composites after standing at atmosphere for 180 days. Obviously, the experimental phenomenon that the reduction of the E of the composite still existed after the sample was left at atmosphere for half a year. In this test, three samples were compressed to the same maximum stress without destroying the sample. The same sample was allowed to stand at atmosphere for another 360 days (540 days in total), and then compressed

Fig. 2 Cross-sectional morphologies of 3D net-shaped fibers-PDMS composites: (a) TEM image of PDMS_3dAl composite, (b) SEM image of PDMS_3dAl composite, (c) SEM image of PDMS_3dTl composite, and (d) SEM image of PDMS_3dZr composite.

to the same maximum stress without fracture. The same experimental phenomenon as shown in Fig. 3(d) was observed.

As shown in Fig. 3(c), the PDMS_3dAl composite was compressed 100 times at a strain of 0%–40% (about 1/2 of the fracture strain) to obtain a stress–strain cycle curve. From the cyclic stress–strain experiment, the stress–strain cycle curve basically coincides with

the first cycle (Fig. S7(a) in the ESM), and the statistical result shows that the error is less than 0.1%. The stress–strain origin has almost no displacement, and no strain hysteresis or stress relaxation occurs [19].

Figure 4(g) shows the shear stress–strain curves of PDMS and composite, which are similar to the compressive stress–strain curves. The E of the composite is significantly lower than that of PDMS.

Fig. 3 Mechanical properties: (a) Compressive stress–strain curves of PDMS, PDMS_3dAl, and PDMS_rAl composites, (b) compressive stress–strain curves of PDMS, PDMS_3dTi, PDMS_rTi, PDMS_3dZr, and PDMS_rZr composites, (c) stress–strain cycle curves of PDMS_3dAl composite, and (d) compressive stress–strain test of PDMS and PDMS_3dAl composites after standing at atmosphere for 540 days.

Fig. 4 SEM images of the surface after compression fracture: (a) pure PDMS, (b) PDMS_3dAl composite, (c) PDMS_3dTi composite, and (d) PDMS_3dZr composite. (e) Photographs of PDMS and PDMS_3dAl composites. (f) Schematic of 3D net-shaped fibers in matrix. (g) Shear stress–strain curves of PDMS, PDMS_3dAl, PDMS_3dTi, and PDMS_3dZr composites.

The above flexibility anomalous effect of the inorganic-polymer composite will be explained by the 3D tunnel elasticity enhancement effect, which is an interface lubrication effect between the 3D net-shaped ceramic fibers and the polymer. As shown in Figs. 3(a) and 3(b), the E and shear modulus of the three 3D net-shaped ceramic fiber-PDMS composites are significantly lower than those of PDMS, while the experimental phenomenon was not found in the short rod-shaped ceramic fiber-PDMS composite. When subjected to an external force, the shear force between the ceramic fibers and the PDMS matrix is continuously present at the interface of the 3D net-shaped tunnel, and the shear resistant stress at the interface is less than the shear resistant stress of the PDMS matrix. The weakened interface shear stress is dispersed by the 3D net-shaped tunnel. At the same strain, the stress on the polymer matrix is reduced, and the E is also reduced, thereby improving the flexibility of the composite. When short rod-shaped ceramic fibers are added, the interfacial shear stress cannot be continuously conducted at the fiber interface. The stress is confined to the closed region formed by the polymer segment and the short rod-shaped fiber. This in turn forms a local pinning effect, increasing the shear stress and E .

Figures 4(a)–4(d) are SEM images of the fracture surface of PDMS, PDMS_3dAl, PDMS_3dTi, and PDMS_3dZr composites after compression fracture. The micromorphology of the PDMS matrix in the three composites after fracture is the same as that of pure PDMS. After the three composites are broken, the 3D ceramic fibers will break, but the continuity of the tunnel formed by the fibers will not change. After compression fracture, no ceramic fibers are obliquely inserted into the PDMS matrix (Figs. 4(b)–4(d) and Fig. S7 in the ESM). Although the entire fiber in Figs. 4(b)–4(d) and Fig. S7 in the ESM is broken, it is still located in the tunnel formed by 3D net-shaped ceramic fibers. In the compression cycle experiment (Fig. 3(c)), the stress–strain curve basically coincides with the first cycle, and there is no strain hysteresis, stress relaxation, stress increase, or the E change. The repeatability of the 3D tunnel elasticity enhancement effect is confirmed again.

In summary, in the submicron fiber-polymer composite, the criterion (sufficient condition) for the 3D tunnel elasticity reinforcement effect is:

1) The filler in the composite is a 3D net-shaped fiber (Fig. 4(f)).

2) Under the same deformation condition, shear resistant stress of composite synthesized from fibers and matrix is found to be lower than pure matrix (i.e., $\tau' < \tau$, τ' is the shear resistant stress of composite and τ is the shear resistant stress of pure matrix).

4 Conclusions

In this study, the flexibility anomalous effect was found—the E of the composite was found to be lower than that of the polymer matrix. We have quantitatively analyzed this experimental phenomenon through the 3D tunnel elastic enhancement theory. It is found that there is an interfacial lubrication effect between the 3D net-shaped ceramic fiber and the polymer, and the weakened interfacial shear stress is uniformly dispersed by the 3D net-shaped tunnel. When the strain is constant, the stress on the polymer matrix is reduced, and the E is reduced, thereby improving the flexibility of the material. The 3D tunnel elastic enhancement effect and its criterion proposed in this paper have theoretically explored the anomalous mechanical effects of ceramic fiber-polymer composite in the micro/nano field.

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Electronic Supplementary Material

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