PRINTING OF TOUGH HYDROGELS INTO STRUCTURES WITH TITIN-LIKE DOMAINS

Fengbo Zhu[1], Libo Cheng[2], Zhi Jian Wang[3], Zi Liang Wu[3], Jun Yin[2], Jin Qian[1] and Qiang Zheng[3]

[1] Department of Engineering Mechanics, Zhejiang University, Hangzhou 310027, China
[2] School of Mechanical Engineering, Zhejiang University, Hangzhou 310028, China
[3] Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, China

Keywords: Tough hydrogel, 3D printing, Biomimetic structure, Folded domain, Hidden length

ABSTRACT

Three-dimensional (3D) printing has been of recent interest because of its ability to distribute materials into customized shape and geometry, and the progress of tough polyion hydrogels has promoted the application of such materials in load-bearing components. This study combined the material and the "recipe" by mimicking a molecular-level paradigm in titin for the macroscopic gel structures with desired toughness. The strategy of 3D printing relies on the distinct strength of ionic bonding in polyion complex (PIC) hydrogels at different stages of printing. In concentrated saline solution, PIC forms viscous solution, which can be directly extruded out of a nozzle into water, where dialyzing out of salt and counterions results in a fast sol-gel transition to form tough physical PIC gel with intricate structures. The printability of PIC solutions was systematically investigated by adjusting the PIC material formula and printing parameters, where proper viscosity and gelation rate were found to be key factors for successful 3D printing. Inspired by titin, we designed and fabricated structural domains with backbone and sacrificial bonds by tuning the disparate geometries in heterogeneous printing. The fabricated hairpins with such domains exhibit extraordinary extensibility and toughness under loading, because of the consecutive domain unfolding and energy dissipation. These titin-like folded domains with sub-connections have been incorporated into a synthetic spider-web, which shows significantly enhanced extensibility and toughness compared to the counterpart without folded domains. This work may provide a new avenue for the design of artificial materials with desired mechanical properties by sophisticated material distribution within multi-level or heterogeneous structures, which should also extend the applications of tough hydrogels in biomedical devices and artificial tissues.

1 INTRODUCTION

Titin is composed of structured domains that achieve extraordinary toughness by reversible breaking and healing of sacrificial bonds, which dissipate a large amount of energy under loading and thus avoid catastrophic failure. Such stepwise unfolding of molecular-level domains/loops releases the hidden length and relaxes the resultant force, which has been observed and quantified by single-molecule experiments. It remains a challenge to directly correlate such molecule-level structures to the mechanical performance of bulk materials.

Here we employed the concept of sacrificial bond and hidden length in the design of structured materials with desired toughness at macroscopic level. We demonstrate the design of gel structures with relatively weak parts that break ahead of the stronger ones under loading, accompanied by the consecutive release of intentionally buried length that greatly toughens the integrated structures.

2 GENERAL SPECIFICATIONS

These gel constructs with complex structures were fabricated by 3D printing of plasticized PIC solution in deionized water, where fast solidification occurred to form tough physical hydrogels [1, 2]. Heterogeneous 3D printing with multiple nozzles was used to fabricate gel fibers of different diameters, corresponding to the backbone and sacrificial portions of a structure (Fig. 1a).

To demonstrate the concept of heterogeneous breaking, we fabricated and tested a hairpin hydrogel construct with three titin-like domains, where three "sacrificial" thin fibers were embedded in each

domain. During the stretching process, the thin fibers of each domain sequentially break and release a fraction of the total hidden length, concomitant with the drop of force by a small amplitude. When one domain is fully unfolded, a relatively large hidden length is released to the structure, and a large drop of force is observed in the force-extension curve (Fig. 1b).

The architecture of spider-webs has been proven to provide excellent mechanical performance under different loading conditions with an efficient distribution of materials. To further demonstrate the potential application of our biomimetically designed structure, we fabricated a spider-web-like construct by incorporating multiple folded domains to the radial threads [3]. Our goal is to explore the opportunity of further enhancing the toughness of spider webs and other network structures by including macroscopic folded domains. The structures of printed webs with and without folded domains are shown in Fig. 1c; three folded domains with two sacrificial thin fibers in each domain are placed within each of the eight radial threads, which sustain the main part of applied load and dominate the energy absorption. The tensile behaviors and force-displacement curves of the webs with and without folded domains have been shown in Fig. 1c, when the force was applied at the web center and pulled perpendicular to the web plane. With the incorporation of folded domains, an evident drop of loading force appeared at a displacement of ~260 mm because of the breakage of radial threads, which was twice that of the normal web, indicating that the catastrophic failure was effectively delayed by the incorporation of folded domains. Moreover, at the initial stage of stretching, the tensile curve of the normal web was smooth, similar to that of straight gel fibers. However, in the presence of folded domains, the tensile curve showed subtle sawtooth peaks at the initial loading phase, indicating the breakage events of weak gel fibers within the folded domains. As the result, the release of programmed hidden length and sub-connections gave rise to twice of the extensibility and toughness in the normal web. It is easy to envision that the mechanical performance of the weblike structures can be further enhanced by employing more sophisticated distribution of constrained and folded domains in macroscopic-level topological design.

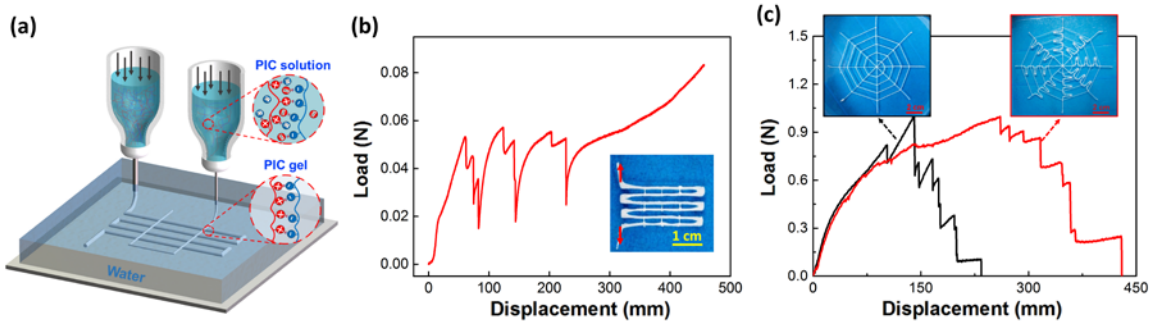

Figure 1: (a) A customized 3D printing system with multiple syringes on the basis of sol-gel transition of plasticized PIC solutions. (b) Tensile behavior of a hairpin gel structure with three folded domains, where three “sacrificial” thin fibers were embedded in each domain. The inset presents the morphology of the printed hairpin gel structure for the tensile test. (c) Force-displacement curves of the printed networks mimicking spider-webs with and without titin-like domains.

9 CONCLUSIONS

In conclusion, we have demonstrated the design of biomimetic gel structures with folded domains that release hidden length in response to force at macroscopic scale. Via 3D printing with multiple nozzles, heterogeneous gel structures with relatively weak fibers that constrain and enforce the folded structure were fabricated and tested. Under pulling, the weak portion sacrificially breaks to postpone the failure of the main structure. The force-displacement curves of these printed structures exhibit a sawtooth pattern, resembling the forcible response of titin despite of the vastly different scales. The programmed release of hidden length from stacking domains has effectively improved the extensibility and toughness of the gel structures. Such strategy was used in designing a spiderweb-like gel structure with folded domains, which showed remarkably enhanced toughness compared to that of a normal

web. This work may provide a new avenue for the design of artificial materials with desired mechanical properties by sophisticated material distribution within multilevel or heterogeneous structures.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (51403184, 11672268, 11402056, and 11621062), and Zhejiang Provincial Natural Science Foundation of China (LR16A020001).

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