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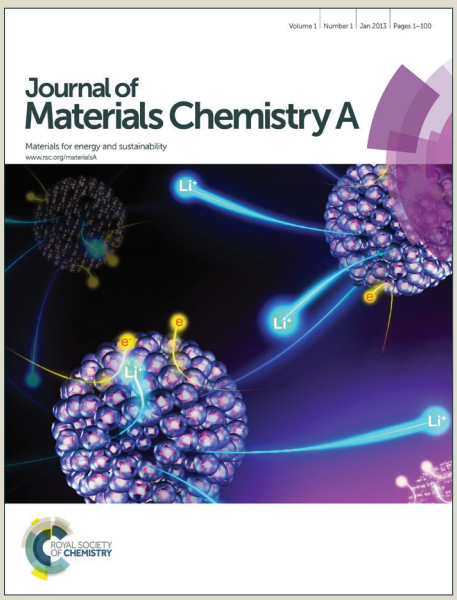

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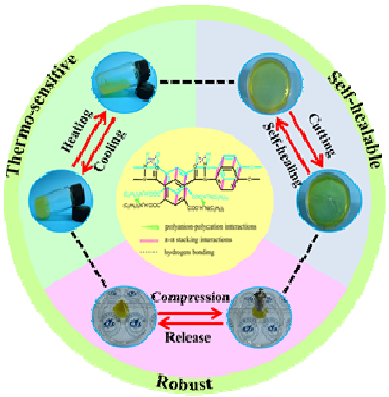
A Novel Self-Healing Poly(amic acid) Ammonium Salt Hydrogel with Temperature-responsivity and High Mechanical Properties

Li Zhang, Juntao Wu, Na Sun, Xiaomin Zhang, and Lei Jiang*



A novel self-healing poly(amic acid) ammonium salt hydrogel with temperature-responsivity is fabricated and the possible self-healing mechanism are proposed.

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A Novel Self-Healing Poly(amic acid) Ammonium Salt Hydrogel with Temperature-responsivity and High Mechanical Properties

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The fabrication of hydrogels with excellent self-healing property and high mechanical strength has become a challenging and fascinating topic. The aim of this study is to fabricate a novel robust PAS hydrogel with self-healing property. The self-healing mechanism and possible interactions between PAS chains of the hydrogel are proposed.

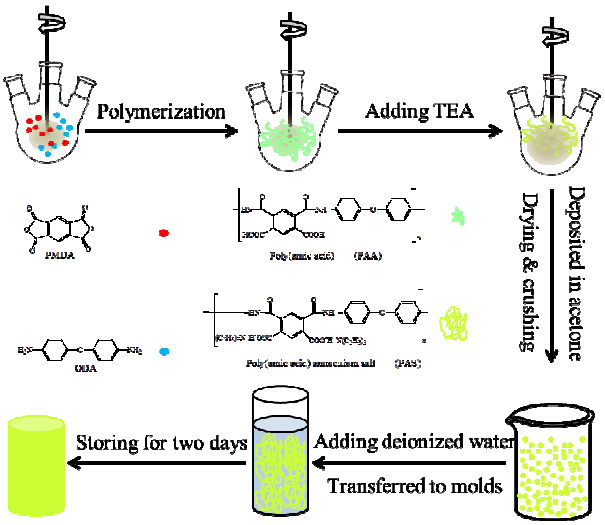
Introduction

Hydrogels, solid-like cross-linked polymer networks holding a large quantity of water, have a wide range of applications in various areas including medical fields, sensors and environmental fields.[1-6] Academic curiosity and practical need has motivated intense efforts to study the self-healing nature of hydrogels.[7-11] However, it remains an extremely challenging task to develop hydrogels combining self-healing and load-bearing property. Basically, the self-healing ability of a hydrogel is antagonist of its mechanical strength. Because of the robust and irreversible natures of the covalent bonds, the networks in chemical cross-linked hydrogels are stable and lack of self-healing property under ambient conditions.[12] In contrast, physically cross-linked hydrogels with non-covalent interactions, such as hydrogen bonding, π–π stacking and polyanion–polycation interactions, are self- healable but mechanical weak,[13] which limit their extensive use for practical applications. Therefore, demand for finding novel physically cross-linked hydrogel that can self-heal with high strength is highly imperative.

Indeed, mechanical property of the hydrogel with a single non-covalent bond is weak, but what if many different non-covalent bonds are working in concert? Integration of multiple non-covalent bonds into a hydrogel system may endow it high mechanical property. Poly(amic acid) ammonium salt (PAS),[14] a precursor of polyimide (PI), possibly combines quadruple hydrogen bonding, π–π stacking and polyanion–polycation interactions between its polymer chains. Inspired by this, herein, we designed and successfully synthesized a novel PAS hydrogel with multiple non-covalent interactions. Although PAS had been reported by a few researchers, [14] to the best of our knowledge, however, there were no reports on the fabrication of PAS hydrogel so far. The as-fabricated PAS hydrogel exhibited high mechanical strength and thermo-sensitivity. In addition, excellent self-healing property is also observed. The combination of high mechanical strength, thermo-sensitivity with self-healing property may guarantee the hydrogel to find uses in a variety of fields.

Experimental

Preparation of PAS hydrogel



Scheme 1. Schematic diagram for the synthesis of the PAS hydrogel.

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† Electronic Supplementary Information (ESI) available: compression of PAS hydrogel. See DOI: 10.1039/c000000x/

PAS hydrogel was prepared according to scheme 1. 2.4g 4,4'–oxidianiline (ODA) and 45.144g dimethylacetamide (DMAc) were added into a 100 mL three-neck round-bottom flask fitted with a mechanical stirrer. Once the ODA had dissolved completely, equivalent molar quantity (2.616g) of Pyromellitic dianhydride (PMDA) was added, and the mixture was stirred for 4 h. After making PAA solution, 2.424g of triethylamine (TEA) (the PAA/TEA molar ratio was 1:2) was added into PAA solution at room temperature and the mixture was stirred for 2 hours. Then, the resultant solution was poured into acetone. After washing, drying in vacuum, and crushing, light yellow PAS powder was obtained. 17g deionized water was added to 3g PAS powder, the resultant suspension was stirred for several hours till homogeneous solution was formed. Afterward, the samples were transferred to cylindrical molds and stored at 5°C for two days. Finally, the samples were removed from the molds, and PAS hydrogels were obtained.

Characterization

Scanning electron micrographs (SEMs) were recorded on a Quanta 250 FEG scanning electron microscope. The xerogel for the measurement was prepared by freezing the hydrogel in a laboratory freezer, approximately -18°C, and dried in a Christ freeze-dryer. The compressive tests of the PAS hydrogels were performed by using an Instron 5843 testing machine, equipped with a 1000-N load cell, at a constant crosshead speed of 7.8 mm/min.

Results and discussion

Herein, water-swellable PAS was designed and synthesised, and a novel PAS hydrogel with a water content of 85% was prepared successfully via a facile and applicable method. In order to characterize its micro morphology, the PAS hydrogel was freeze-dried to obtain xerogel. A 1.7cm^3 PAS xerogel is light enough to stand stably on the top of a flower like dog's tail (Figure 1a). As shown by scanning electron microscopy (SEM) image of the freeze-dried PAS hydrogel in Figure 1b, the three-dimensional network structure of PAS xerogel composed of macropores with the diameter in the range of tens of micrometers.

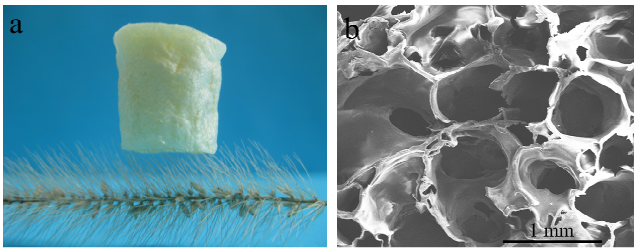

Figure 1. Macroscopic and microscopic structures of the freeze-dried PAS hydrogel. (a) A 1.7cm^3 monolith standing on a flower like dog's tail; (b) SEM image of the xerogel obtained from the PAS hydrogel.

Regardless of its porous attribute and high water content, the PAS hydrogel exhibits high mechanical properties, as shown in Figure 2. The PAS hydrogel is mechanically very tough and a 4.211g hydrogel can withstand up to 50g weight without any crack and can recover its original cone shape after release of the compression (Figure 2a). Compression measurements were carried out to characterize the mechanical properties of PAS hydrogels quantitatively. During the loading processes, The linear-elastic regime at strains <20% records the elastic bending of cell wall, and the non-linear regime at strains of 20–50% has an increased slope (Figure 2b), where the deformation is still recoverable because of the elastic buckling of the cell walls. Hysteresis loops appear due to dissipation of mechanical energy, and negligible and overlapped hysteresis loops in all the five loading cycles are showed, indicating a typical rubber elastic behavior.[15] The stress keeps above zero until ε =0 (Figure 2c) suggesting the hydrogel can rapidly and completely recover to its original volume,[16] which is consistent with the observation in movie (Movie S1). The robust mechanical properties of the PAS hydrogels can be attributed to their unique interconnected 3D network, as illustrated in Figure 1.

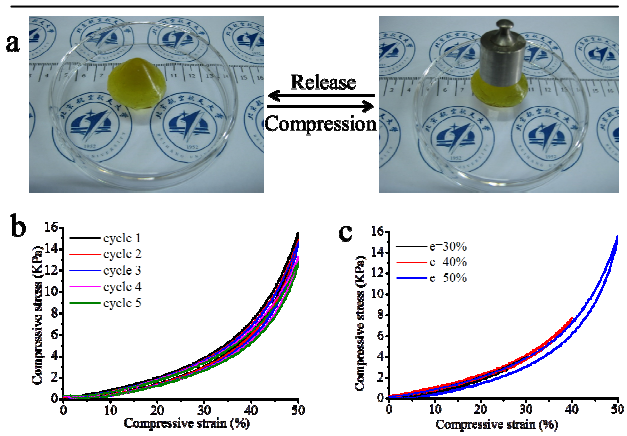

Figure 2. Mechanical properties of PAS hydrogels. (a) The reversible compression–release process of PAS hydrogel; (b) cyclic compressive stress–strain curves of the hydrogel; and (c) compressive stress–strain curves of the hydrogel at different set strains of 30, 40, and 50%.

In addition to high mechanical properties, the hydrogel is temperature sensitive. It dissolves when the temperature increases to 55°C, gels when cooling to room-temperature, and re-dissolves on heating (Figure 3a). The process can be recycled for many times. The possible interactions between PAS chains of PAS hydrogels are hydrogen bonding, π–π stacking interactions and polyanion–polycation interactions (Figure 3b). Thus, mechanism account for the thermo-sensitivity of the PAS hydrogel as follows: the thermal reversibility process of the hydrogel network is initiated by partial dissociation of the abovementioned non-covalent interactions as the temperature rises. On cooling, these three non-covalent interactions are progressively re-established, so regenerating the physical properties of the pristine hydrogel.[17-22]

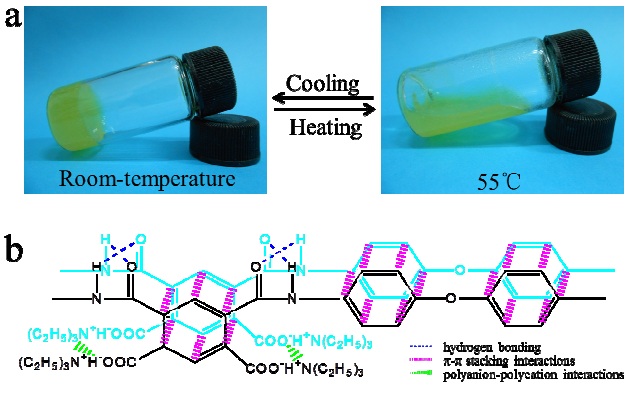

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Figure 3. The reversible gel–sol transition of PAS hydrogel (a); possible interactions between PAS chains of PAS hydrogels (b).

The thermo-sensitive hydrogel can re-establish when cooling to room temperature after heating, should it re-establish at room-temperature after fracture, demonstrating self-healing property? As is expected, the as-prepared free-standing PAS hydrogel self-heals immediately after it was broken (Figure 4a). A column-shaped hydrogel was cut into three segments with a razor, and then the three segments were put together with a gentle press. It was found that the three parts merged into a continuous hydrogel immediately. Thus, for a crack in a hydrogel to heal under room-temperature, macromolecules at the two broken interfaces diffuse into each other and interpenetrate and finally re-entangle with neighbouring chains, thereby knitting the two portions of the hydrogel together (Figure 4b).[23-25] However, the relatively large mobility of the molecules is only one of the necessities for a hydrogel to possess a self-healing property. For example, another necessity is that the strength of the hydrogel must be strong enough to self-support itself.[25] Therefore, the self-healing property of PAS hydrogel originates from its relatively large mobility of the molecules and high mechanical properties.

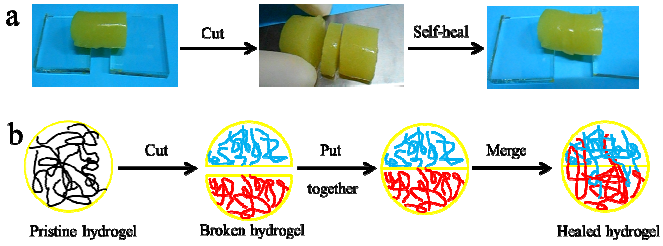

Figure 4. Self-healing process: the as-prepared free-standing PAS hydrogel was cut with a razor into three small blocks and the blocks could adhere to each other in less than 10s by pushing the freshly formed surfaces gently to contact together (a); schematic representation of thermoplastic healing via reptation and reentanglement of the polymer chains across a fracture interface (b).

Conclusions

In summary, a novel thermo-sensitive PAS hydrogel is designed and synthesized. It can be moulded into shape-persistent, free-standing soft matter owing to its high mechanical strength, and rapidly self-heal when damaged. The combination of self-healing property, high mechanical strength with thermo-sensitive may guarantee the hydrogel to find uses in a variety of fields.

Acknowledgements

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