Biocompatible Swelling Textile Structure Reinforced Hydrogels with High Toughness and Stiffness

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Abstract. In the present work, a toughness hydrogel was manufactured by introducing kapok/PET assembly into single network of polyacrylamide hydrogels. The textile reinforced hydrogels (TRH) exhibits apparently higher young modulus than PAAM hydrogel. The normal strength of TRH was six-times higher than that of PAAM hydrogel when it was compressed at 40%. In addition, the swelling ability of TRH in x-y planar direction was largely suppressed, with only a 6.25% increase in the edge length. It was significantly lower than the swelling ability of PAAM hydrogel, which was high to 62.5%. While in the z direction, the swelling ability of TRH was much improved if compared with that of PAAM hydrogel, indicating the anisotropy in swelling properties of TRH. Besides, although the solution absorption ability of TRH was clearly decreased because of the suppress of kapok/PET assembly, the TRH and PAAM hydrogel depicted approximately the same swelling behaviour in the initial 8 hours of absorption from totally dry state.

1. Introduction

Hydrogels, as an inspiring soft material, have received lots of research attention, due to their three-dimensional (3D) polymeric networks containing large amounts of water. Currently, hydrogels are extensively employed in soft robot, drug delivery, healthcare, tissue engineering, and so on, because of their remarkable swelling ability. Meaningfully, hydrogels can swell and deswell according to various external stimuli like temperature, light, pH, and ionic concentration. However, the poor mechanical properties resulting from large swelling greatly limit their potential application in biomedical area and soft robot.

In last decade, various approaches including double-network (DN) hydrogels [1,2], slide-ring hydrogels [3], nanocomposite hydrogels [4], triblock copolymer hydrogels [5], hydrophobic modified hydrogels [6], tetra-PEG gels [7], and macromolecular microsphere composite (MMC) hydrogels [8], have been developed and studied to improve mechanical properties of hydrogels. Although these approaches, especially DN hydrogels, can effectively promote mechanical properties of hydrogels, the swelling nature still results in mechanical fracture by introducing water into polymeric network, which impede their application in different areas. As well known, swelling relies on the viscoelastic properties of hydrogels [9]. Briefly, introduction of solvent molecules into hydrogels results in an extension of polymeric network in the rubbery phase, leading to a dimensional expansion of hydrogels and lots of mechanical fractures in swelling hydrogels [10].

In 2014, Sakai and his co-workers published their amazing work about “nonswellable” hydrogels on Science, which give a new perspective to design hydrogel network. By combining hydrophilic and thermo-responsive polymers, the “nonswellable” hydrogels could retain its original dimensions and
mechanical properties under physiological conditions [7]. However, the polymeric network in these “nonswellable” hydrogels required complicated process, leading to high cost and these “nonswellable” hydrogels were able to be “nonswellable” at unique temperature because of its molecular design. DN hydrogels have been widely and systematically studied to achieve improved hydrogels with superior toughness and stiffness by introducing first sacrificial network, because of its simple manufacturing process and designability by varying cross-linker and polymeric network. However, swelling is still one of drawbacks to limit their applications. In our previous work, we introduced touch calcium alginate network and graphene oxide to suppress swelling ability of hydrogels to retain their mechanical properties [1, 9]. Although tough hydrogels were achieved at their swelling state compared to single network polyacrylamide hydrogels, the swelling nature still weakened the mechanical properties of tough hydrogels. Therefore, a novel method to modify swelling property of hydrogels is urgent.

Kapok fibre, which mainly consists of cellulose, lignin and polysaccharide, was a natural cellulosic fibre extracted from the seedpod of kapok tree [11]. It possesses a cylindrical hollow lumen throughout the longitudinal direction with two ends closed, indicating an airbag structure of kapok fibre. Its porosity was reported to be high up to 90%, which differentiate the kapok fibre from other natural fibres [12, 13]. In this manuscript, kapok/PET assembly manufactured by air forming machine was introduced into single network polyacrylamide hydrogels for reinforcing the overall structure. The structural, swelling and mechanical properties of textile reinforced hydrogels (TRH) have been well characterized. The compressive toughness and strength of TRH were greatly improved due to presence of fabric structure. In addition, the swelling ability in x-y planar direction was largely suppressed with negligible hydrogel expansion. While the z-directional swelling ability was improved. The anisotropy in swelling properties of hydrogels may gift tough hydrogels potential application in building materials.

2. Experimental Section

2.1. Materials

Acrylamide (AAm), N,N’-methylenebis(acrylamide) (MBAA), calcium chloride (CaCl₂), sodium alginate (SA) and ammonium persulfate (APS) were purchased from Sigma Aldrich. The kapok/PET assembly was purchased from GOODTURN INDUSTRIAL INC, with the blend ratio of kapok/PET at 60/40.

2.2. Fabric Reinforced Polyacrylamide Gels

Figure 1 shows the flow chart for preparation of TRH. The AAm, MBAA and APS were stirred to achieve a homogeneous solution. The concentration of AAm is 120 mg/ml, and the weight of MBAA and APS was 0.0025 and 0.03 times that of AAm, respectively. After that, the kapok/PET assembly was immersed into the AAm solution to soak at the maximum load. Then the soaked assembly was placed into a closed Teflon mold, the rest AAm solution was injected to fill the mold. The mold was heated in an oven at 80 °C for 3 hours. This sample was labelled as kapok/PET assembly reinforced polyacrylamide hydrogels (TRH). PAAM single network (SN) hydrogels were prepared like previous work [9].

![Figure 1. TRH preparation flow chart.](image)

2.3. Compressive Test

An Universal material testing machine (XS(082)-10T) was used to measure cylindrical gel samples and
compressive velocity was 1mm/min. And the compressive strain $\varepsilon$ is defined as

$$\varepsilon = \frac{h}{h_0}$$

(1)

where $h$ is the height during deformation and $h_0$ is the initial height of gels sample. The normal compressive stress $\sigma_{\text{normal}}$ is defined

$$\sigma_{\text{normal}} = \frac{F}{A_0}$$

(2)

where $F$ is the applied load and $A_0$ is the original top surface area of hydrogel sample.

2.4. Swelling Measurements of Hydrogel

The swelling ratio (SR) was defined as

$$SR = \frac{W_s - W_o}{W_o} \times 100\%$$

(3)

where $W_s$ and $W_o$ represent the weight of hydrogel after swelling in DI water in different time period and the weight of hydrogel before swelling, respectively. The ESD is calculated from the equation:

$$ESD = \frac{W_e - W_d}{W_d}$$

(4)

where $W_e$ represents the weight of the dried hydrogels and $W_d$ means the weight of hydrogels at swelling equilibrium state.

3. Result and Discussion

3.1. Swelling Properties of Hydrogels

To study the swelling behavior as well as effect of kapok fibers on the structure, the results of TRH and PAAM hydrogel including size change and ESD were performed. The size variations in x-y planar and z directions were separately plotted as a function of time in figures 2a and 2b.

![Figure 2](image-url)

Figure 2. (a) Length of gels varies with swelling time, (b) Thickness of gels varies with swelling time, (c) Geometric change of TRH and PAAM, (d) Swelling degree of hydrogels (as prepared) with time.
As can be seen in figure 2a, the horizontal size of PAAM hydrogel obviously changed after being soaked in water solution, and the typical swelling procedure can be divided into two stages, in which the horizontal size firstly increased in a rapid rate and then became gentle. The original horizontal size of the PAAM hydrogel was 4.05 cm before the experiment, which rapidly rose to 4.80 cm after 2 hour of water soaking. It continuously increased to 5.0 cm, 5.25 cm, 5.55 cm and 5.75 cm after being immersed in water solution for 4, 8, 16 and 24 hours. This is because the when the PAAM hydrogel was immersed in water solution, the water molecules attached on the gel surface and then invaded into the inside structure, thus leading to an expansion of polymeric network in the rubbery phase.

After 24 hours was taken, the PAAM hydrogel swelled in a relatively slower rate if compared with that before 24 hours, with the average slop of the curve low to 0.00625 cm/h. At the end of the swelling experiment, the PAAM hydrogel still kept swelling, with the horizontal size reached the maximum value 6.65 cm, which was 64.2% longer than that in original state. Besides, the PAAM hydrogel became very soft after being treated with long-term swelling, and it was easy to be broken even subjected to quit small stress and deformation resulting from hand holding. The is due to the fact that hydrogels were reported to be an arbitrary dispersion of crosslinking on a lattice which was constructed by the interchain contact points. The small polymeric clusters turned into larger ones after absorbing water in solvent, and the new regions with low concentration created during the absorbing process lead to mechanical failure.

While for TRH, an apparently different swelling behavior with PAAM hydrogel could be observed in figure 2a. The swelling ability in x-y planar directions was largely suppressed with negligible hydrogel expansion, with the maximum elongation below 0.45 cm after 168 hours soaking in water. As can be seen in the figure 2a, the horizontal size of the TRH extended to 4.10 cm after 8 hours, and then it gradually increased to 4.30 cm in another 112-hours duration. Then the swelling progressed into the second stage, where a constant value was achieved for the horizontal size of TRH in the rest of the experiment.

This could be explained by the introduction of kapok/PET assembly into the TRH, which formed a stable and tough network besides the single network of polyacrylamide hydrogels. When the TRH was swollen in DI water, the solvent invaded into the space between polymeric networks via osmotic pressure, leading to enlarged capacities among covalent crosslinked and ionic crosslinked points. However, less water was allowed to leak into the gel structure, because of more crosslinked points in the double-network TRH. Therefore, the swelling ability of TRH in x-y planar directions was largely suppressed with negligible hydrogel expansion.

Surprisingly, the z directional swelling ability of TRH was significantly improved if compared to that of PAAM hydrogel, as indicated by the deformation in figure 2b. In the initial 4 hours, the PAAM hydrogel and TRH shown similar swelling performance, with a 25% expansion in the z direction. Afterwards, the TRH kept continues rapidly swelling to 14 mm within 24 hours, during which the thickness of PAAM hydrogel gradually increased to 11.1 mm. The two kinds of gels both achieved stable state in z direction at about 48 hours, with the thickness of TRH and PAAM hydrogel separately enhanced to 15mm and 12.2 mm. The reason for the anisotropic swelling properties of TRH was that the reinforced kapok/PET assembly, which were blended with ES, was prepared by air forming machine. The application of air-forming way was favorable for kapok/PET assembly to form uniform and randomly arranged fibrous structure with minimum fiber damage. The layer-by-layer structure introduced by air forming made the kapok/PET assembly possessed steady size in the x-y planar direction, but easy to be deformed in the z direction. The PAAM hydrogel was a kind of homogenous and isotropic material that can deform equivalent in all direction when absorbing water. While the introduction of kapok/PET assembly in TRH suppress the expansion in x-y planar directions and thereby, resulting in a larger deformation in the z direction compared with the PAAM hydrogel.

Although the TRH shows larger deformation in the z direction, the SR and ESD value of TRH still lower than that of PAAM hydrogel due to the strict suppress in the z direction. As shown in figure 2d, the PAAM hydrogel could absorb 219% water of its original weight at equilibrium, while that of TRH was only 126%. The apparently lower SR of TRH indicating that although it exhibited larger deformation in the thickness, the overall swelling and water absorption ability were restrained due to
the negligible horizontal expansion. Besides, the TRH exhibited constantly lower absorbing rate than PAAM hydrogel throughout the whole experiment.

For both TRH and PAAM hydrogel, the water absorbing rates in SR curve were separately high to 0.114 g/h and 0.249 g/h at the initial stage, and then decreased to 0 after long-time soaking. This is due to the fact that the hydrophilic group in the gels could form hydrogen bond with water molecule, resulting in elongation of the polymer chain. This would further expand the volume of gels and afford a high osmotic pressure to introduce water into the gels. Moreover, the enlarged gels allowed more water molecule to contact with the surface and hence, accelerate the absorbing and swelling behavior. When the polymer chain continuously elongated and approached to its limitation, the water absorbing rate decreased and the swelling finally progressed into a balance state.

For the equilibrium swelling degree (ESD), which represents the water absorbing ability of gels from totally dry state without any water, the TRH and PAAM hydrogel after drying depicted approximately the same swelling behavior in the initial 8 hours, with the SR rose to 709% and 722%, as shown in figure 3a. Afterwards, the PAAM hydrogel shown a higher value than that of TRH in the rest of the experiment due to the anisotropic properties of TRH.

![Figure 3](image)

**Figure 3.** (a) Swelling degree of (dry) with time, (b) equilibrium swelling degree of hydrogels.

### 3.2. Mechanical Properties of Hydrogels

The compression tests were systematically conducted to demonstrated the different compressive strength and toughness of TRH and PAAM hydrogel. The compression results presented in figure 4a clearly indicated that the TRH exhibited superior compression properties than PAAM hydrogel. The normal strength of TRH and PAAM hydrogel at 10% strain were 0.02MPa and 0.004MPa, respectively. When the strain increased to 40%, the value for TRH enhanced to 0.13MPa, while that of PAAM hydrogel were only 0.03MPa. Besides, the TRH depicted a five-times higher young modulus than PAAM hydrogel. This phenomenon was regarded to be caused by the kapok/PET assembly, which reinforced the overall structure of TRH and consumes dissipation energy, resulting in a tougher gel compared to the PAAM hydrogel. The TRH was crashed when the strain rose to 45%. While the PAAM hydrogel presented a smooth curve when the strain increased from 0% to 60%, indicting an undamaged structure after compression. This is because when the gels subjected to compression, the thickness was greatly decreased, with an expansion tendency in the x-y planar directions, since the gel was a kind of incompressible material. However, the kapok/PET assembly in TRH exert a strict constraint and suppress the expansion in this direction. When the expansibility exceeded the limitation from kapok/PET assembly, the TRH was broken. While the PAAM hydrogel can sustain severe deformation and recover to the original structure due to its excellent elasticity. Furthermore, comparing figures 4a and 4b the gels subjected to compression test right after preparation generally shown higher normal strength (about 3 times) than the one after balanced swelling at the same strain percentage. This can be explained by the fact that in the balanced swelling gels, the absorbed water permeated into the inner space and elongated the polymer chain, which could reduce the crosslinks and weaken the mechanical properties.
4. Conclusions
A toughness hydrogel reinforced by kapok/PET assembly was manufactured in the present work. The structural, swelling and mechanical properties of textile reinforced hydrogels (TRH) was carefully characterized. Comparing with the PAAM single network hydrogels, TRH shows apparently higher compressive toughness and strength, with the normal strength six times higher that of PAAM hydrogels when it was compressed at 40%. Furthermore, the swelling ability of TRH in x-y planar direction was largely suppressed, with negligible hydrogel expansion. While in the z direction, the swelling ability of TRH was much improved and it was 3mm thicker than that of PAAM hydrogels. The anisotropy in swelling properties of hydrogels may gift tough hydrogels potential application in building materials.

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