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Improvement of Mechanical Strength, Thermal Stability, Swelling, Moisture Content of Triple Network Hydrogels by Carbon Nanotubes

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Improvement of Mechanical Strength, Thermal Stability, Swelling, Moisture Content of Triple Network Hydrogels by Carbon Nanotubes

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Abstract. In this study, we prepared a novel carbon nanotubes reinforced three network hydrogels composed of carbon nanotubes, polyacrylic acid(PAA), agar and polyvinyl alcohol(PVA), consisting of an agar gel as the first physical network, a PAA-Fe³⁺ gel as the second physical network and a polyvinyl alcohol as the third physical network. The surface modification of MWCNTs was carried out by oxyfluorination to introduce the functional groups on the hydrophobic MWCNTs. Agar/PAA-Fe³⁺/PVA/MWCNTs hydrogels with high tensile and compression strength(σ_f of 1.5 Mpa, ϵ_f of 14.24 mm/mm) and (σ_f of 1.69 Mpa, the deformation of 80%), thermal stability, low-swelling, high moisture content properties were successfully prepared by a simple three-step method. The addition of carbon nanotubes has significantly improved the thermal stability of the gels, its thermogravimetric curve drops obviously until 387°C. Under the joint action of hydrogen bonding and ion coordination interaction, the gel achieves a perfect balance of swelling and moisture content. The research provide a new method to improve mechanical, swelling, thermal stability, moisture content ability by adjusting the compositions and interactions in the gels.

1. Introduction

Polymer hydrogels as soft-wet materials with a large amount of water can maintain a certain shape which was used in various fields, including photo-chemistry [1], tissue engineering [2-4], sensors [5], super absorbent resin [6-7]. However, Hydrogels have a fatal flaw, its network structure cannot effectively dissipate energy, and resulting in poor mechanical properties cannot meet the practical application. At present, experts and scholars at home and abroad change the network structure, network combination and introduction of nano materials in order to improve the mechanical properties, such as nanocomposite [8-10], ionically cross-linked hydrogels [11-13], double network hydrogels [14-15], hydrogen bonding or dipole-dipole enhanced hydrogels [16-19] and triple network hydrogels [20].

Triple network hydrogels (TN gels) have exhibited their greatly mechanical and low-swelling properties as a result of their special network structures [21]. When stress is applied to the triple network hydrogels, the first, fragile, agar network acts as sacrificial bonds to consume energy and to protect the second and third networks. Through freezing/thawing procedure generating PVA crystalline network, the physically cross-linked PAA-Fe³⁺ network was used to bear high stress and support large deformation. Although the mechanical properties of the triple-network hydrogels have been significantly improved, it can be applied under the action of slight stress, not for those applications involving heavy loading. In addition, as a soft-wet material with an inherent flaw cannot maintain its network structure and moisture content at higher temperature. Thus we present a new three-step



method to simultaneously improve the mechanical, swelling, moisture content and thermal stability properties by introducing carbon nanotubes and Fe³⁺ ions into gel networks.

2. Experimental Section

2.1. Materials

Polyvinyl alcohol particle (PVA, Molecular weight=1750±50, hydrolysis>99%) and N, N-methylene diacrylamide (MBA) were purchased from Sinopharm Chemical. Agar (high gel strength of 1000-1200g/cm² and melting point of 85-90°C). Ammonium persulfate (APS) and FeN₃O₉•9H₂O were purchased from Aladdin Shanghai Co. Ltd. Acrylic acid (AA) was kindly provided by Damao Tianjing Co. Ltd. Carbon nanotubes was purchased from Dekedaojin Beijing Co. Ltd. Deionized water was used in all polymerization reactions. All chemicals and solvents purchased were of the higher available purity.

2.2. Preparation of TN Hydrogels

The triple-network hydrogel composed of Carbon nanotubes, PAA, agar and PVA was prepared by a simple three-step method of polymerization, cooling, and freezing/unfreezing. Firstly, PVA, PAA and agar were de-oxygen with nitrogen and dissolved in deionized water at 95°C. The mixture system was cooled to -4°C to form agar gel. APS, MBA, Carbon nanotubes and FeN₃O₉•9H₂O were added into the mixture system. The resulting solution was injected into a cylindrical mold (diameter=5mm, length=7.5cm or diameter=9mm, length=5.5cm) and the reaction mixture was kept at 60°C for 6h to accomplish the free radical polymerization reaction to form PAA gel. After that, hydrogels were removed from the molds to deionized water. Then, the resultant mixture was cooled to room temperature and kept at -4°C. At last, for forming PVA gel, the samples frozen at -20°C for 6h and unfrozen at room temperature for 2h. The freezing/unfreezing process was performed three times. The eventual samples were named Agar/PAA/PVA TN hydrogel, Agar/PAA-Fe³⁺/PVA TN hydrogel, Agar/PAA-Fe³⁺/PVA/MWCNTs TN hydrogel.

2.3. Characterization

The FTIR spectra of various hydrogels were taken using an E55+FRA106 FTIR spectrophotometer in the range of 3900-600 cm⁻¹. XRD measurements for various samples were carried out by the diffractometry (Kevex-Sigma, NRAM, USA) in the range 10-90° at ambient temperature. TG measurement for very samples were conducted by the thermal gravimetric analyzer (STA 449F5, NETZSCH, Germany) increasing 10°C /min under argon protection in the range 25~490°C. The tensile tests of the all samples (round of 5mm) were carried out using a universal tensile tester equipped with a 100N load cell with a crosshead speed of 10 mm•min⁻¹. For compression test of the all samples (round of 9mm) were measured by Universal Testing Machine with a 3000N load cell at compression speeds of 0.5 mm•min⁻¹.

2.4. Swelling and Moisture Content Tests

Swelling ratio (SR) and moisture content (MC) of gels were determined by weight method. The swelling ratio and moisture content were calculated using Equation (1) and Equation (2):

$$S_R = \left(\frac{W_{se} - W_0}{W_0} \right) \times 100\% \quad (1)$$

$$M_c = W_0 - W_1 \quad (2)$$

W₀ is the weight of the sample gel before swelling, w_{se} is the weight of the wet gel after sufficient swelling, W₁ is the weight of the dry gel after drying in the 40°C oven.

3. Results and Discussion

3.1. FTIR and XRD Analysis

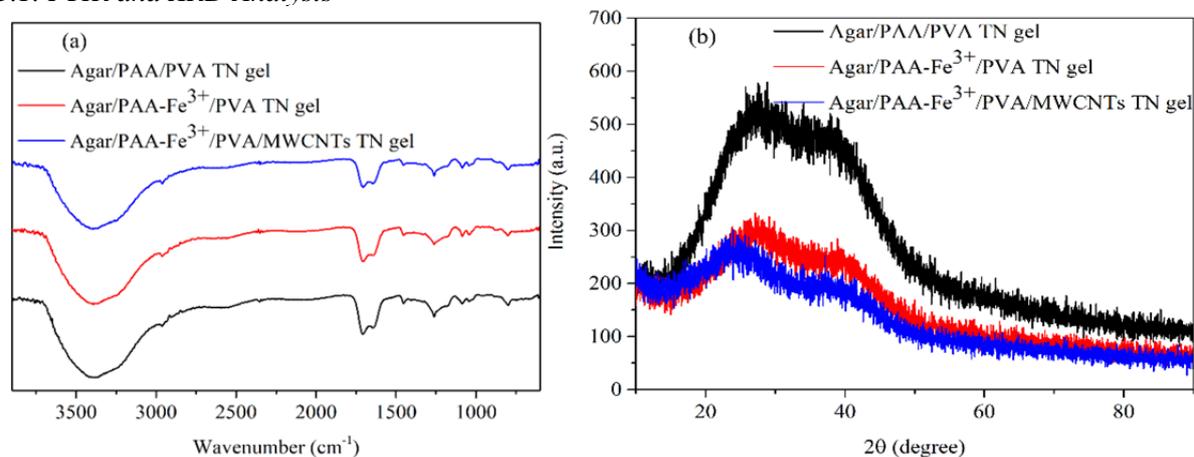


Figure 1. (a) FTIR analysis (b) X-ray diffraction analysis

This observation shows no difference between these three TN gels, which have the same absorption peak and graphical trend. The above description shows that the acidified carbon nanotubes are coated with Agar/PAA-Fe³⁺/PVA to form composite TN gels. In the spectrum of the Agar/PAA-Fe³⁺/PVA/MWCNTs sample, the broad and strong peak for the stretching vibration of -OH and C-OH around 3400 cm⁻¹ is present and sensitive to the hydrogen bonding. The weak broad peaks at near 1710 cm⁻¹ are due to the presence of the C=O stretching, which suggested hydrogen bonding interactions between both polymers [22]. The absorption peak around 1450 cm⁻¹ was caused by bending vibration of C-O-H bond of carboxyl functional group. The absorption peaks appear around 1260 cm⁻¹ and 1130 cm⁻¹ for the N-H groups and stretching vibration of C-N groups from MBA [21]. XRD was used to detect the crystallinity change of polymers, which is associated with mechanical properties for gels. Wang et al. have used XRD to study the crystallinity change of gels. They found that the 2θ at 23.1° was the XRD pattern of the agar and the diffraction peaks of the PVA could be found at 19.5° and 41.1° [23]. From the figure 1b, we found that the peak intensity of Agar/PAA-Fe³⁺/PVA and Agar/PAA-Fe³⁺/PVA/MWCNTs TN gel greatly reduced, which may be attributed to the increase of PVA crystallinity resulting from the assemble of polymer chains [24]. It can be concluded that the addition of Fe³⁺ and carbon nanotubes into gel networks enlarged the crystalline region [25].

3.2. Thermos-gravimetric Analysis and Swelling Tests

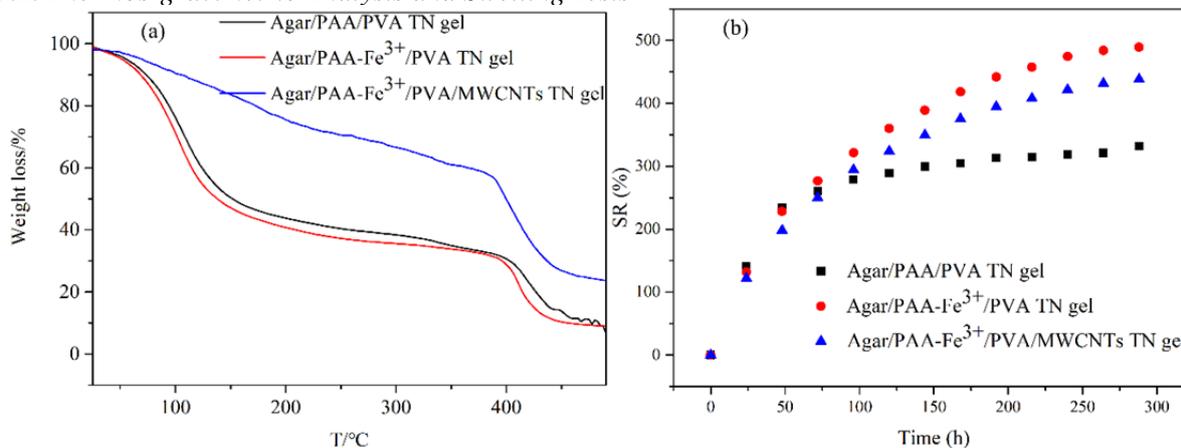


Figure 2. (a) Thermos-gravimetric analysis (b) swelling tests

From the figure 2a, we can intuitively find that the introduction of acidified carbon nanotubes into the triple network hydrogels increasing the crosslink density of gel chains improves the thermal stability of the hydrogel. The interaction between the carbon nanotubes and polymer chains is the key factor for improving the thermal stability. However, the synergistic coordination bond between Fe^{3+} and $-\text{COO}^-$ act as the negative factor to reduce the thermal stability. It could be concluded that carbon nanotubes have the effect of improving thermal stability, and the synergistic coordination of metal ions has the effect of reducing thermal stability. We also examined the swelling tests of these TN gels. From the results we found that the Agar/PAA- Fe^{3+} /PVA TN gels had a large swelling rate than other gels with the rates (362%) and (489%). When we add Fe^{3+} ions into the second network to heighten the stability of the gels, at the same time the network structure of the gels have changed slightly. Chen et al. have used SEM to study the effects of swelling on the ion coordination structure of Agar/PAMAAC- Fe^{3+} DN gels. They found that Agar/PAMAAC- Fe^{3+} DN gels exhibited unique contrasting network structures with the co-existence of both large and small pores [26]. When put the Agar/PAA- Fe^{3+} /PVA TN gels into water, the pores could absorb amount of water. Hydrogen bonding between carbon nanotubes and gel chains can effectively increase the crosslink density of hydrogels and reduce its swelling rate.

3.3. Mechanical Properties

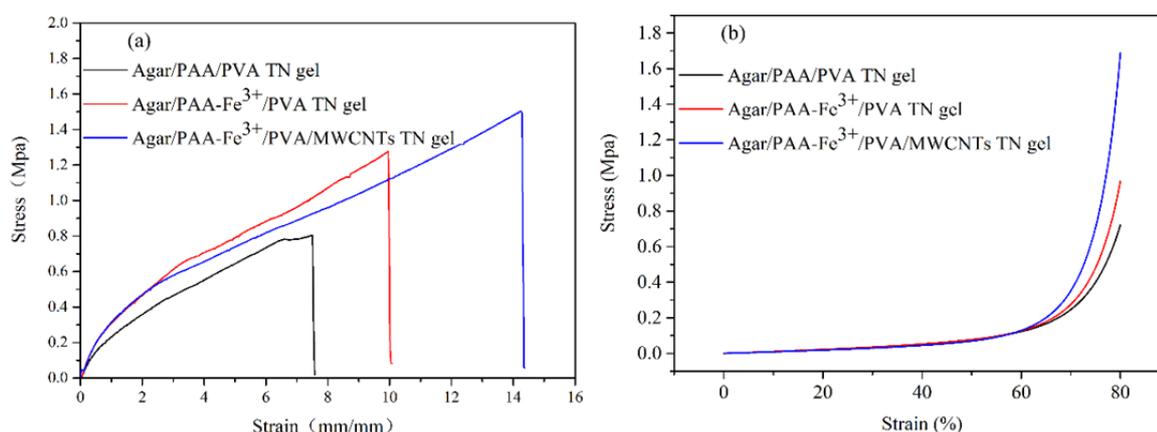


Figure 3. (a) Tensile stress-strain (b) compression stress-strain (Experimental conditions: AA weight of 4g, agar, PVA and $\text{FeN}_3\text{O}_9 \cdot 9\text{H}_2\text{O}$ of 1.5 wt%, MBA of 0.06 wt%, APS of 0.1 wt% and MWCNTs of 0.01 wt%.)

As shown in figure 3a, the tensile properties of Agar/PAA- Fe^{3+} /PVA TN gels and Agar/PAA- Fe^{3+} /PVA/MWCNTs TN gels were significantly changed. The results showed that the fracture stress (σ_f) of Agar/PAA- Fe^{3+} /PVA greatly increased from 0.807 to 1.276 Mpa as the formation of coordination interactions between Fe^{3+} and carboxyl acid. When Fe^{3+} ions and carbon nanotubes were introduced, a coordination interaction with the carboxyl group is respectively performed and the crosslink density of the gel chains is enhanced. Agar/PAA- Fe^{3+} /PVA/MWCNTs have increased its σ_f to 1.509Mpa, ϵ_f to 14.26 mm/mm. It was found that Agar/PAA- Fe^{3+} /PVA/MWCNTs TN gels was the best of Agar/PAA/PVA TN gels and Agar/PAA- Fe^{3+} /PVA TN gels. Figure 3b showed the results of the compression tests. The Agar/PAA- Fe^{3+} /PVA/MWCNTs TN gels was superior to those of both the Agar/PAA- Fe^{3+} /PVA TN gels and Agar/PAA/PVA TN gels with compression stress of 0.97 Mpa and 0.71 Mpa. For the Agar/PAA- Fe^{3+} /PVA/MWCNTs TN gels, which show high compressive strength (1.68 Mpa). The results indicated that the introduction of Fe^{3+} and carbon nanotubes into the gel networks can effectively improve the mechanical properties.

3.4. Moisture Content Tests

From the figure 4, we could get that the Agar/PAA- Fe^{3+} /PVA/MWCNTs TN gels and Agar/PAA- Fe^{3+} /PVA TN gels were little weaker in moisture content than Agar/PAA/PVA TN gels. The hydrogen bonding and ion coordination interaction play important roles in moisture content, which be used to

effectively prevent moisture loss. So the moisture content of Agar/PAA-Fe³⁺/PVA/MWCNTs TN gels was similar with the Agar/PAA/PVA TN gels and Agar/PAA-Fe³⁺/PVA TN gels.

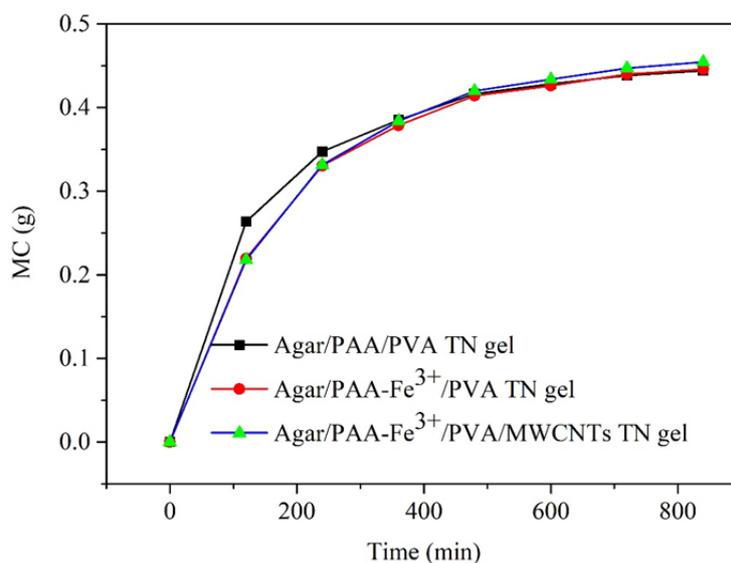


Figure 4. Moisture content measurement

4. Conclusion

In summary, the Agar/PAA-Fe³⁺/PVA/MWCNTs TN gels were synthesized by a simple three step method, and the effect of carbon nanotubes and ions coordination interaction concentrates on tensile properties, compression properties, swelling, thermal stability, moisture content of the gels by amount of tests. It was found that the fracture stress, fracture strain and compression stress of TN gels increased significantly as Fe³⁺ ions and carbon nanotubes introduced into gel networks. In this work, we proposed a new design strategy of Agar/PAA-Fe³⁺/PVA/MWCNTs TN gels to form high coordination interaction and hydrogen bonding, which could reach high mechanical properties. The best tensile properties and compression properties of TN gels in this study were σ_f of 1.5 Mpa, ϵ_f of 14.24 mm/mm and σ_c of 1.69 Mpa, the deformation of 80%. Our study further indicates that combination of carbon nanotubes in the networks is an effective method to prepare high strength and tough hydrogels. The swelling, mechanical strength, thermal stability, and moisture content properties of hydrogels could control by adjusting the content of Fe³⁺ and carbon nanotubes. We believe this work will provide a new way how to prepare high mechanical strength, thermal stability, low-swelling and high moisture content TN gels.

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