

Preparation of PVA-GO Composite Hydrogel and Effect of Ionic Coordination on Its Properties

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Abstract: This paper adopts a method combining hybrid self-assembly, cyclic freezing-thawing and annealing treatment to prepare polyvinyl alcohol (PVA) and graphene oxide (GO) composite hydrogel. Then, the PVA-GO composite hydrogels are re-swelled in different ionic solutions (NaCl, MgCl₂, CaCl₂ and AlCl₃) to improve mechanical strength, toughness and wear resistance by the ionic coordination bonds. The microstructure and morphology are characterized by Fourier transforms infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Scanning electron microscopy (SEM), finding that the internal structure is porous three-dimensional network. Mechanical experiments indicate that the composite hydrogel with GO content of 0.05wt% immersed in MgCl₂ solution displays the best mechanical properties overall. Its tensile strength can reach 11.10MPa and the elastic modulus reaches 1.72MPa, which is 175% and 85% higher than the pure PVA, respectively. Sliding friction experiments illustrate that the composite hydrogel immersed in AlCl₃ solution exhibits the lowest friction coefficient, and the higher the valence state of metal cation is, the better the wear reduction effect is. We expect to enrich the development of PVA-GO hydrogels in tissue engineering through synergy of hydrogen bonds and ionic coordination bonds.

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1. Introduction

Cartilage tissue engineering is one of the effective ways to treat joint injury in clinical practice, and scaffold materials as the main content of tissue engineering have been highlighted by researchers. Natural articular cartilage is an anisotropic, heterogeneous, viscoelastic and liquid-filled permeable substance that requires good elasticity, lubrication and wear resistance under physiological load to mitigate the impact and shock of stress. In view of this unique structural and performance characteristics, the scaffold materials that replace cartilage require higher stiffness and similar tissue structure [1-3]. Hydrogel is a three-dimensional network structure formed by cross-linking of hydrophilic polymers, which can enormously mimic the microenvironment of human extracellular matrix (ECM) owing to the high water content and great hydrophilicity. Therefore, hydrogel has been widely used as a matrix material for biomedical and tissue engineering [4-7].

Polyvinyl alcohol (PVA) is considered to be a very promising tissue engineering material for repairing cartilage and meniscus due to its excellent biocompatibility, non-toxicity, and favorable water absorption and lubricity [8-9]. However, the mechanical properties of pure PVA hydrogels are often poor, limiting their application and development. In recent years, researchers have done a lot of research to improve the mechanical strength of hydrogels. It is considered that the introduction of nano-enhancers into hydrogels is an effective way to enhance the mechanical strength [10]. Nano-materials such as silicon dioxide, carbon nanotubes, clay and hydroxyapatite are added to the polymer matrix to improve the final result [6-7, 11-12]. Graphene oxide (GO) is an important derivative of graphene, which not only possesses the original properties of graphene,

such as high mechanical strength and bearing capacity, excellent wear resistance and self-lubricity, but also has high hydrophilicity and reactivity due to some oxygen-containing functional groups (hydroxyl, epoxy, carboxyl, etc.) on the surface or edge of the graphene oxide, and thus has become a hot spot in recent years [13-15].

Yu et al. [16] prepared PVA-GO nanocomposite hydrogels by means of in-situ chemical cross-linking. Compared with pure PVA hydrogels, the specific area increased by 138% and the pore volume increased by 181% which could provide better living space for MIC (microorganism). Zhang et al. [17] prepared PVA-GO composite hydrogel by freezing-thawing method. After adding 0.8% GO, the tensile strength increased by 132% and the compressive strength increased by 36%, furthermore, they were nontoxic to osteoblasts.

Although a great deal of research has been done in this field, the mechanical strength of PVA-GO hydrogels reported is still much lower than expected. Based on the toughening mechanism of hydrogels, increasing the crosslink density is a common method for enhancing mechanical strength. Therefore, PVA-GO hydrogel can be immersed in a salt solution of different valence metal ions to swell, forming dynamic non-covalent ionic coordination between composite matrix and polyvalent metal, thus forming entanglement between molecular chains, further improving the mechanical strength and toughness of hydrogels [18-19].

This paper aims at adding firstly GO nanoparticles to PVA for hybrid self-assembly, conducting preliminary cross-linking through the interaction of covalent bonds and hydrogen bonds, and then executing further cross-linking by freezing-thawing as well as annealing. Subsequently, the ionic coordination is carried out by swelling in salt solution of different valence metal ions. Finally, PVA-GO composite hydrogels with excellent mechanical strength and

biological properties are expected to be prepared through the synergistic reaction of hydrogen bonds and ionic coordination bonds, so as to expand its application in cartilage tissue engineering.

2. Experiment

2.1 Experimental materials

Polyvinyl alcohol (PVA) is obtained from Sinopharm Chemical Reagent Co., Ltd., model number is 20-99, polymerization degree is 2050 ± 70 , and alcoholysis degree is 99.9%. Graphite oxide (GO) with sheet size of 500nm-40 μ m and sheet thickness of 1 nm is purchased from Shenzhen Turing Evolutionary Technology Co., Ltd. Polyethylene glycol (PEG) coming from the Sinopharm Chemical Reagent Co., Ltd, whose average molecular weight is 400g/mol.

2.2 Preparation of PVA-GO composite hydrogels with different mass ratios

First, polyvinyl alcohol particles are added to the deionized water in proportion, and the uniform solution is formed by stirring with glass rods. Then a certain amount of graphene oxide powder is weighed and added to the above solution according to the concentration gradient. After sealing, ultrasonic oscillation is carried out at 30°C for 2-3 hours, and then heated in a water bath at 95°C for 2 hours to allow the solution to be mixed and self-assembled. When the solution is completely dissolved, it is gently taken out and poured into the prepared mold. Later the mold is placed in a low temperature storage box at -20°C, and after freezing for 6 hours, it is thawed at room temperature for 2 hours, which is repeated for 3 times. Subsequently, the sample is immersed in polyethylene glycol solution for 2 hours to remove moisture. Furthermore, the dehydrated sample is annealed in a precision box furnace at 120°C for 1 hour, and then the remaining polyethylene glycol on the surface is washed with deionized water. Finally, the sample is placed in sufficient deionized water for 3-4 days to re-swell, and a PVA-GO composite hydrogel

is obtained. The preparation process is shown in Figure 1.

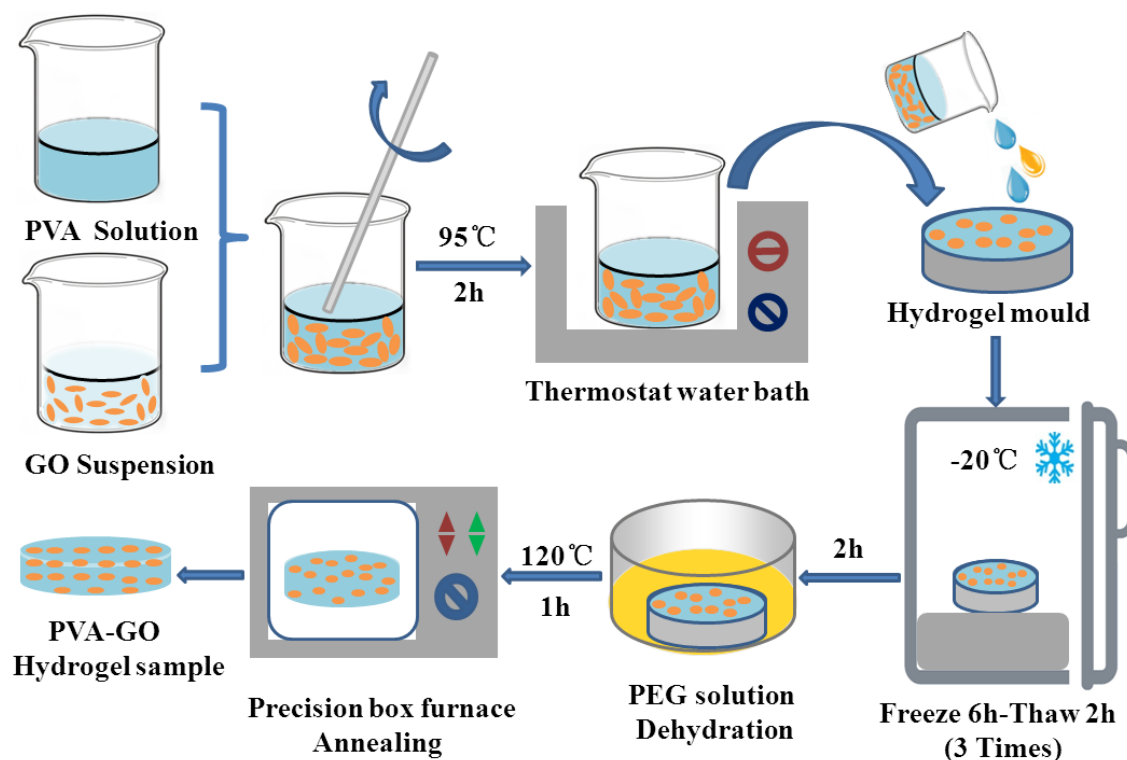


Figure 1. Schematic diagram of preparation process of PVA-GO composite hydrogel

2.3 Characterization of PVA-GO composite hydrogels with different mass ratios

2.3.1 Fourier transforms infrared spectroscopy (FTIR)

In this experiment, the VTRTEX 80V Fourier Transform Infrared Spectrometer of German Bruker Company is adopted, and hydrogel samples are freeze-dried in vacuum for 24 hours before the experiment. The test conditions are: ATR infrared spectroscopy, scanning 32 times, 4 wave number resolutions.

2.3.2 X-ray diffraction (XRD)

In this experiment, the D8 ADVANCE X-ray diffractometer produced by Brook Company of Germany is used, and the voltage is 40kV, the current is 30mA, the target material is Cu, Ka rays, and the scanning speed is 0.2sec/step, sampling interval is 0.019450(step). The samples need to be freeze-dried and ground into powders before testing.

2.3.3 Scanning electron microscopy (SEM)

This experiment adopts Quanta 250 scanning electron microscope produced by FEI Company of America to analyze the micro-morphology of samples. Before the experiment, the samples are freeze-dried in vacuum for 24 hours and then sprayed with gold on the surface.

2.3.4 Tensile properties

In this experiment, the WDW-2 electronic universal testing machine produced by Jinan Hengxu Experimental Machine Technology Co., Ltd. is used. The sample size is 32mm×8mm×4mm, and the sample is stretched at a speed of 5mm/min until broken. Before the experiment, the hydrogel sample should be immersed in the re-swelled solution to keep it fully swelled.

2.3.5 Friction properties

The sliding friction experiment of PVA-GO composite hydrogel immersed in Na^+ 、 Ca^{2+} 、 Mg^{2+} 、 Al^{3+} solution is carried out by UMT-II multi-functional friction and wear tester. The composite hydrogel is fixed on the experimental machine, and the cartilage of bovine with a diameter of 6mm is used as the indenter, the contact load is 10N, the sliding rate is 10mm/s, the sliding distance is 5mm, and the friction time is 0.5h.

2.4 Re-swelling and ionic coordination of PVA-GO composite hydrogels in different ionic solutions

Based on the PVA-GO composite hydrogel with graphene oxide content of 0.05wt%, the composite hydrogels are mainly immersed in four kinds of chloride solution containing 5% Na^+ 、 Ca^{2+} 、 Mg^{2+} 、 Al^{3+} respectively to further investigate the effect of these four ions on the properties of composite hydrogels during re-swelling. Herein, an appropriate amount of dilute hydrochloric acid

solution is added to prevent precipitation/hydrolysis of $MgCl_2$ solution and $AlCl_3$ solution at room temperature. The mechanism of re-swelling in different ionic solutions is shown in Figure 2.

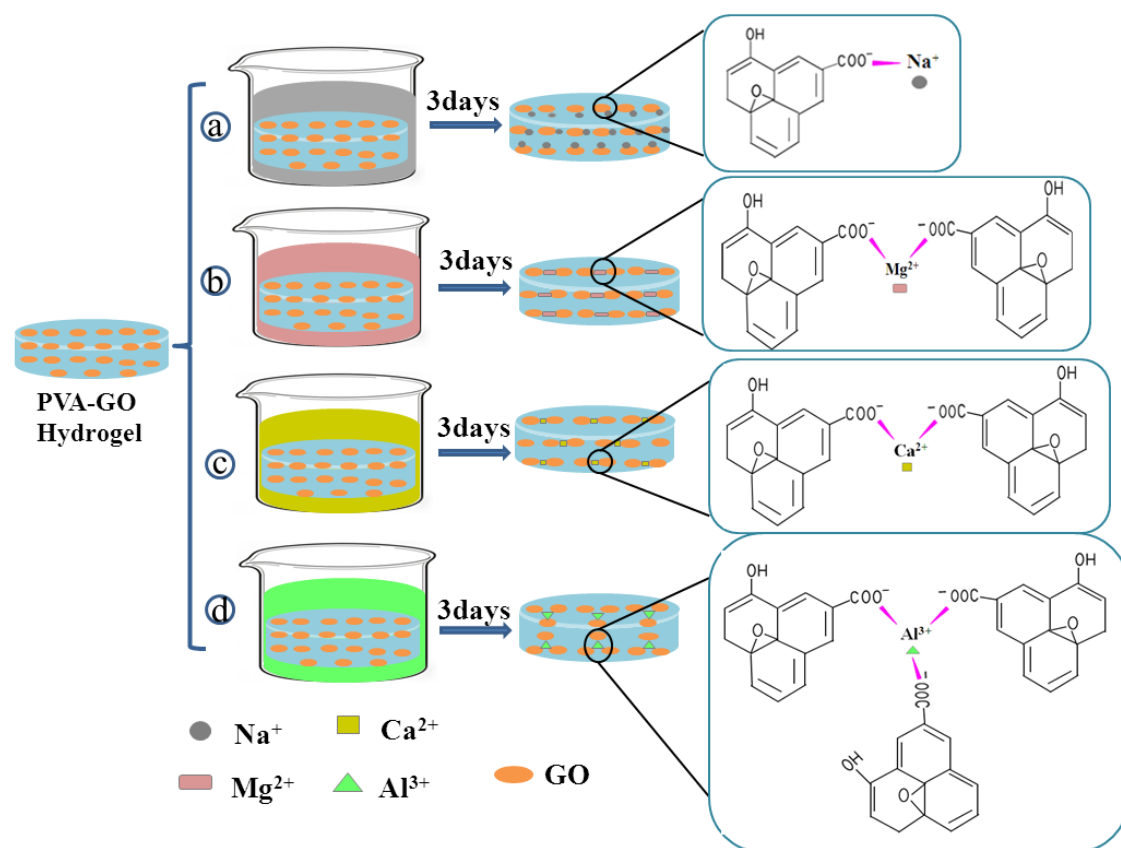


Figure 2. Re-swelling mechanism of PVA-GO composite hydrogels immersed in different ionic solutions.

(a) NaCl solution (b) $MgCl_2$ solution (c) $CaCl_2$ solution (d) $AlCl_3$ solution

3. Results and discussion

3.1 Characterization of PVA-GO composite hydrogels with different mass ratios

3.1.1 FTIR analysis

Figure 3 shows the Fourier transform infrared spectrum of PVA-GO composite hydrogels with different mass ratios. It can be seen from that the peak appeared at 1084cm^{-1} is due to stretching vibration of the $-CO-$ group; the absorption peak at 1338cm^{-1} is caused by the asymmetric bending vibration of the $-CH_2-$ group, and that at 1453cm^{-1} is because of the symmetric bending vibration of the $-CH_2-$ group. In addition, there exists a wider stretching

vibration peak of the -OH group at 3288cm^{-1} , and a vibrational peak formed by free -OH groups at 3621cm^{-1} . In the pure PVA hydrogel, the stretching vibration peak of the -OH group at 3288cm^{-1} is a broad absorption peak with large intensity, but there is almost no peak at 3621cm^{-1} , which can be attributed to the physical crosslinking reaction between hydrogen bonds formed during the freezing and thawing.

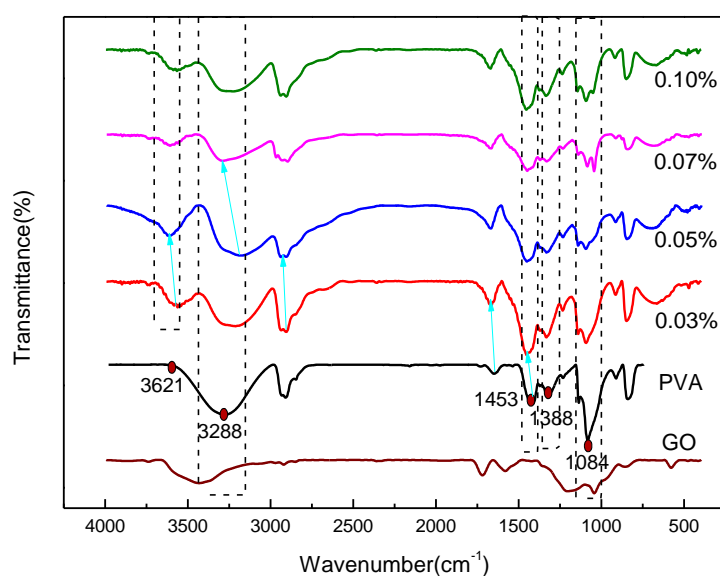


Figure3. FTIR spectra of PVA-GO composite hydrogel with different mass ratios

Comparing the infrared spectra of PVA-GO composite hydrogels with the pure PVA hydrogel, it can be found that some characteristic peaks tend to move toward the high frequency region overall with the addition of GO, and the wider stretching vibration peak of the -OH group at 3288cm^{-1} decreases, while there are new vibration peaks generated by free -OH groups at 3621cm^{-1} [16]. This reveals that the addition of GO not only breaks the hydrogen bond formed by PVA itself, but also promotes the esterification and dehydration reaction between the -COOH group of GO molecules and the -OH group of the PVA molecules, resulting in the formation of free -OH groups. In addition, the peak intensity of the -CH₂- group at 1338cm^{-1} and 1453cm^{-1} are basically increased after the addition of GO, while that of the -CO- group at 1084cm^{-1} is decreased,

demonstrating that the addition of GO weakens the stability of the -CO- group, so the free -OH groups are formed after destruction.

3.1.2 XRD analysis

Figure 4 presents the X-ray diffraction patterns of PVA-GO composite hydrogels with different mass ratios. It can be seen from the figure that the diffraction peaks with the highest intensity are at 19.73° , which is the characteristic peak of the PVA material. After the addition of GO, the diffraction peaks with small intensity are formed at 4.91° and 14.29° , which is the characteristic peak of the GO material. The diffraction peak at 14.29° is broader, illustrating that GO crystallizes to a certain extent, but the diffraction peak with highest intensity is still at 19.73° , showing that the main crystalline phase is still the crystallization of PVA. However, compared with the pure PVA hydrogel, the peak intensity is significantly reduced and the width is increased. This may be due to the esterification between hydroxyl-carboxyl groups of PVA and GO, resulting in crystallization, or the addition of GO increases layered structure inside the hydrogel, and the internal surface energy is increased significantly, inhibiting the crystallization of PVA itself.

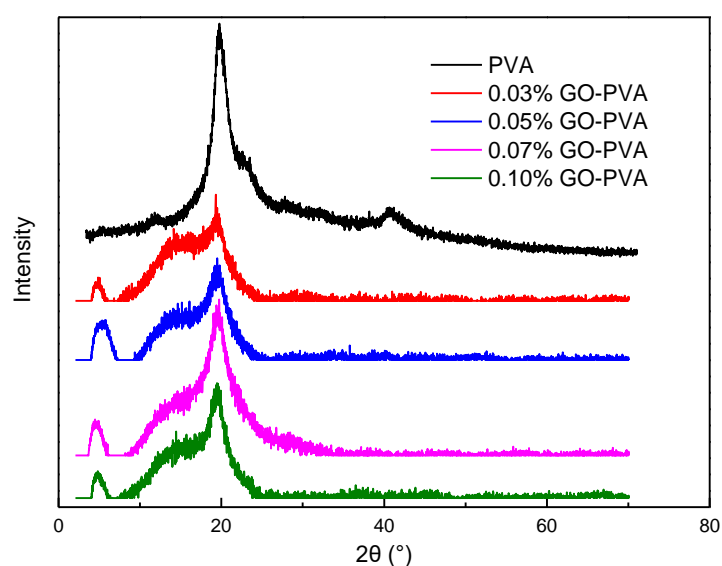
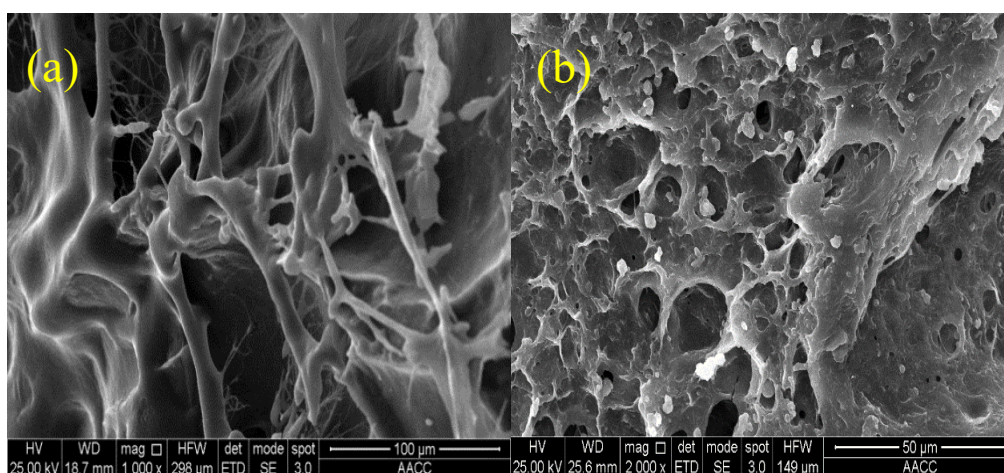


Figure4. XRD patterns of PVA-GO composite hydrogel with different mass ratios

By comparing the X-ray diffraction patterns of composite hydrogels with different concentrations of GO, it can be found that the composite hydrogels with 0.03% and 0.05% GO display the lowest crystallization degree, significantly inhibiting the crystallization of PVA itself. But for the composite hydrogel with 0.07% and 0.10% GO, the crystallinity is increased. This may be due to the agglomeration of dispersed lamellar graphene in the hydrogel with the increase of GO content, which hinders the interaction between PVA and GO, thereby no longer inhibiting the crystallization of PVA itself.

3.1.3 SEM analysis

It can be seen from Figure 5(a) that the natural cartilage possesses a porous three-dimensional network structure with dense and uniform pores, and the pore size is about 5 μ m, which is beneficial to the excellent permeability and mechanical properties of the natural cartilage. When subjected to stress, the liquid phase is extruded to protect the scaffold, thus reducing the impact of movement.



(a) Natural cartilage 1000 \times

(b) PVA-GO composite hydrogel 500 \times

Figure5. SEM images of natural cartilage and PVA-GO composite hydrogel

From Figure 5(b), we can see that the PVA-GO composite hydrogel exhibits a loose porous three-dimensional network structure with an average pore diameter of 10-20 μ m, making the

PVA-GO composite hydrogel expected to be an ideal artificial joint repair material.

3.1.4 Tensile properties analysis

Figure 6 shows the stress-strain curves of PVA-GO samples with different mass ratios (0%, 0.03%, 0.05%, 0.07%, and 0.10%). It can be seen from the figure that the tensile stress is nonlinear with strain, indicating that the PVA-GO composite hydrogel is a typical viscoelastic material. Under the same stress condition, the strain of 0.05% composite hydrogel is the smallest, and that of 0.07% composite hydrogel is relatively larger. According to the stress-strain curve, Table 1 can be obtained as follows.

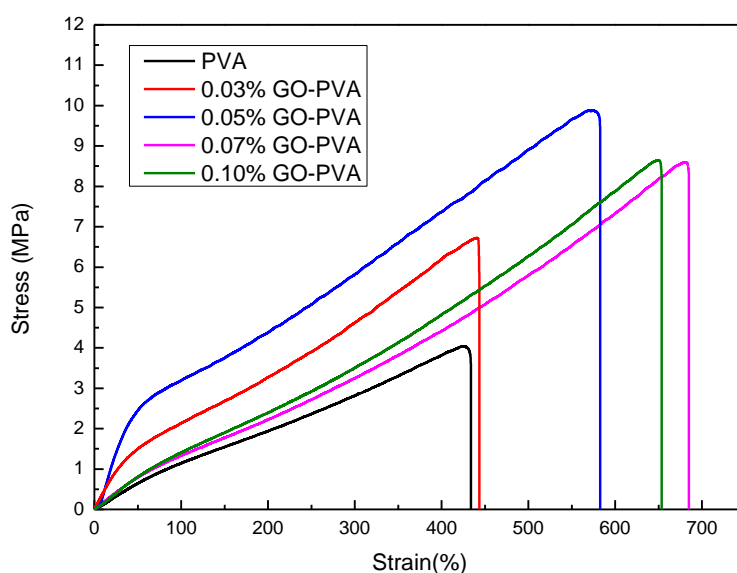


Figure6. Stress-strain curves of PVA-GO composite hydrogel with different mass ratios

It can be seen from Table1 that the tensile strength, maximum elongation and elastic modulus of the composite hydrogel increase first and then decrease overall with the increase of GO content. When the GO content is more than 0.05%, the tensile strength and elastic modulus of the composite hydrogels decrease first and then increase. This may be due to the fact that when the GO content is 0.05%, the chain-type PVA molecules and the lamellar-layer GO molecules are intertwined into a stable network structure due to hydrogen bonding, achieving stronger tensile

strength and elastic modulus; when 0.07% GO was added, because the PVA content is fixed, the slightly excessive lamellar-layer GO molecules are dispersed in the composite hydrogel matrix, reducing the tensile strength and elastic modulus; While when 0.10% GO was added, a large number of lamellar-layer GO molecules produce hydrogen bonding forces between layers, and although the force is not strong, the tensile strength and modulus are improved compared with that of 0.07% GO content. Herein, the composite hydrogel with 0.05% displays the best tensile strength and elastic modulus, and that with 0.07% exhibits the greatest elongation. Considering from the overall, the comprehensive performance of PVA-GO composite hydrogel with 0.05% GO is identified to be the best (“the best” is judged by comprehensively considering the three factors of tensile strength, elastic modulus and elongation, but the tensile strength is the main determination), whose tensile strength reaches 9.88MPa, the maximum elongation is 582.56%, and the elastic modulus is 1.70MPa. In comparison, the performance of pure PVA is significantly worse, the tensile strength is only 4.04MPa, the maximum elongation is 433.68%, and the elastic modulus is 0.93MPa.

Table1. Uniaxial tensile properties of PVA-GO composite hydrogel with different mass ratios

Number	GO content (wt%)	Tensile strength (MPa)	Maximum elongation (%)	Elastic modulus (MPa)
1	0	4.04	433.68	0.93
2	0.03%	6.72	443.41	1.52
3	0.05%	9.88	582.56	1.70
4	0.07%	8.60	684.77	1.26
5	0.1%	8.65	653.51	1.32

This indicates that the addition of GO has greatly improved the properties of original hydrogels, mainly due to the existence of a large number of crystalline regions in the composite

hydrogels, including the crystallization induced by hydrogen bonds formed between -OH and -OH in the intramolecular or intermolecular of PVA; the crystallization induced by hydrogen bonds formed between -OH and -OH or -OH and -COOH in the intramolecular or intermolecular of GO; and the crystallization induced by hydrogen bonds formed between -OH and -COOH in PVA molecules and GO molecules. The ordered entanglement of polymer chains in the crystallization region and the reinforcing phase of the graphene oxide can increase the tensile strength and elongation of hydrogels. Therefore, the addition of a certain amount of GO can improve the mechanical properties of the PVA hydrogel.

3.2 Effect of ionic coordination on the properties of PVA-GO composite hydrogels

3.2.1 FTIR analysis

Figure.7 shows infrared spectra of PVA-GO composite hydrogels with 0.05% GO content immersed in 5% NaCl solution、MgCl₂ solution、CaCl₂ solution and AlCl₃ solution during re-swelling. It can be seen from the figure that for the composite hydrogel immersed in NaCl solution, the broad stretching vibration peak of -OH group at 3288cm⁻¹ and the free -OH group at 3621cm⁻¹ are linked together, and the tensile vibration peak intensity of the -C=O- group at 1710cm⁻¹ is weakened. This indicates that the ionic coordination bond formed by the complexation reaction between the -COOH group of GO molecules and Na⁺ inhibits the esterification and dehydration between PVA and GO, thus reducing the number of -C=O- group and free -OH group.

For the composite hydrogels immersed in MgCl₂ solution, the stretching vibration peak of -OH group at 3288cm⁻¹ moves to low frequency, and the stretching vibration peak of -C=O- group at 1710cm⁻¹ increases, showing that the introduction of Mg²⁺ promotes the formation of hydrogen bonds and ionic coordinate bonds. For the composite hydrogel immersed in CaCl₂ solution, the

vibration peak intensity of the free -OH group at 3621cm^{-1} increases, and the tensile vibration double absorption peak intensity of the -CH₂- group at 2923cm^{-1} and 2852cm^{-1} decreases. Also, the intensity of the stretching vibration peak of the -CO- group at 1084cm^{-1} is weakened, indicating that the introduction of Ca²⁺ destroyed the stable structure of the C-H bond and the C-O bond in the PVA molecule, thereby increasing the number of free -OH groups. The curve of the composite hydrogel immersed in AlCl₃ solution is basically consistent with that immersed in CaCl₂ solution, indicating that Al³⁺ also exerts a certain influence on the internal structure of PVA molecules.

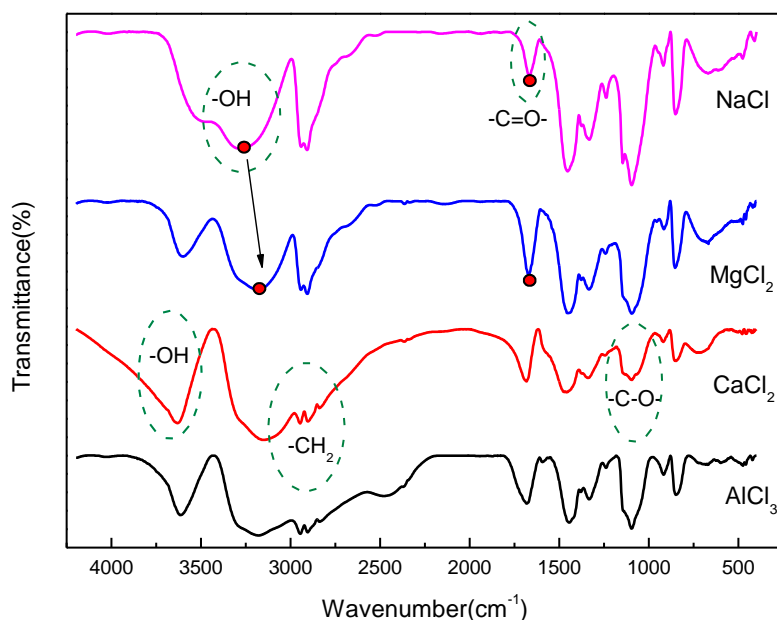


Figure7. Infrared spectrum of PVA-GO composite hydrogel swelled in different ionic solutions

3.2.2 XRD analysis

Figure8 is the X-ray diffraction spectrum of PVA-GO composite hydrogels with 0.05% GO content immersed in different ionic solutions. It can be seen from the figure that the composite hydrogel immersed in NaCl solution possesses the highest diffraction peak intensity at 2θ of 19.73° , which indicates that Na⁺ can promote the crystallization of PVA itself more than Ca²⁺, Mg²⁺ and Al³⁺. For the composite hydrogels immersed in MgCl₂ solution, there exists a broad

tympanic peak near 2θ of 14.29° , and the intensity of the diffraction peak increases at 2θ of 4.91° , indicating that Mg^{2+} not only promote the crystallization of GO itself, but also promote the crystallization of PVA and GO, which may be due to the complexation reaction between Mg^{2+} and $-COOH$ of GO molecules, resulting in a large number of ionic coordination bonds. The X-ray diffraction pattern of the composite hydrogel immersed in $CaCl_2$ solution is basically the same as that of $MgCl_2$, but there is no broad tympanic peaks formed near 2θ of 14.29° , showing that the promotion effect of Ca^{2+} on the crystallization of PVA and GO is correspondingly weakened, probably due to the ionic radius of Ca^{2+} is larger than that of Mg^{2+} , and the number of Ca^{2+} is reduced in the immersion solution of the same concentration, so the number of ionic coordinate bonds formed between Ca^{2+} and $-COOH$ is reduced. The diffraction peaks of the composite hydrogel immersed in $AlCl_3$ solution disappear at 2θ of 14.29° , demonstrating that the addition of Al^{3+} inhibits the crystallization of PVA and GO. It may be due to the increase of the valence state of Al^{3+} ions, needing more $-COOH$ groups to form a coordination bond, leading to the formation of overlapping or agglomeration of GO molecules, thus affecting the crystallization.

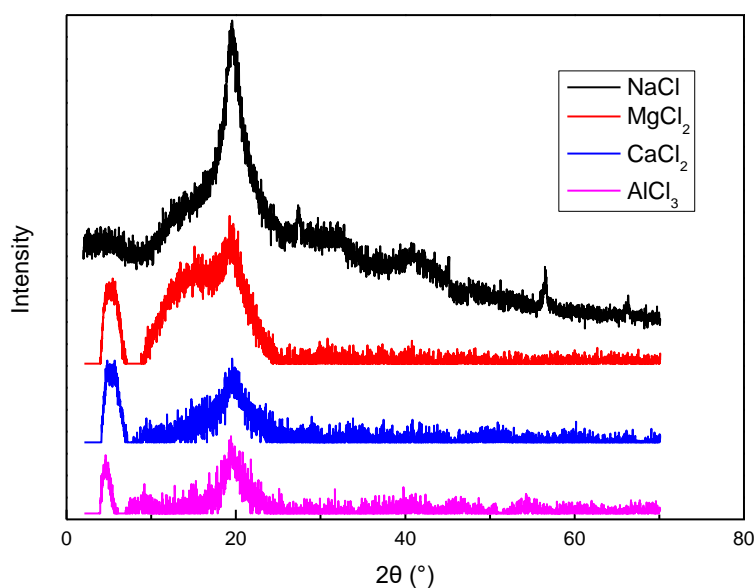


Figure8. XRD patterns of PVA-GO composite hydrogels swelled in different ionic solutions

3.2.3 Uniaxial tension of PVA-GO composite hydrogel immersed in different ionic solutions

Figure 9 shows the stress-strain curves of PVA-GO composite hydrogels with 0.05% GO content immersed in different ionic solutions. It can be seen that for the same stress, the strain of composite hydrogel immersed in Mg^{2+} solution is similar to that of Na^+ solution, and the strain of composite hydrogel immersed in Ca^{2+} and Al^{3+} solution is close.

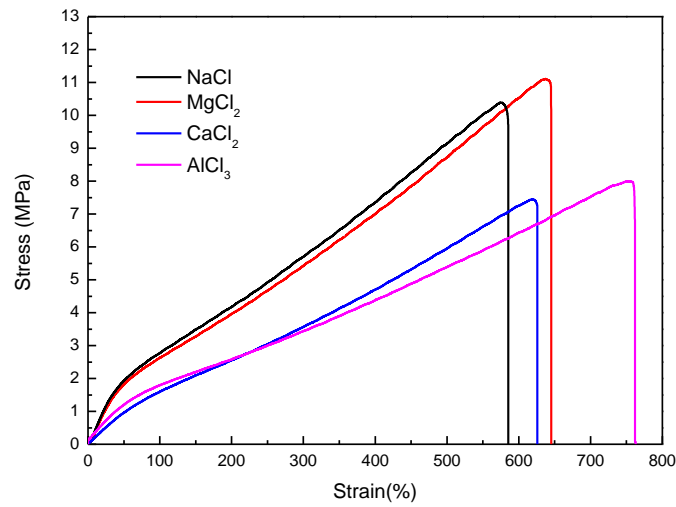


Figure9. Stress-strain curves of PVA-GO composite hydrogel swelled in different ionic solutions

Table2. Uniaxial tensile properties parameters of PVA-GO composite hydrogel swelled in different ionic solutions

Number	Re-swelling solution	Tensile strength (MPa)	Maximum elongation (%)	Elastic modulus (MPa)
1	5wt%-NaCl	10.38	585.43	1.77
2	5wt%-MgCl ₂	11.10	645.21	1.72
3	5wt%-CaCl ₂	7.43	625.98	1.18
4	5wt%-AlCl ₃	7.99	762.79	1.05

Seen from Table 2, the tensile strength and elastic modulus of the composite hydrogel immersed in Mg^{2+} solution are the maximum value of 11.10MPa and the second largest value of 1.72MPa, respectively. The elongation of composite hydrogels immersed in Al^{3+} solution is the

greatest, reaching 762.79%. Overall, the composite hydrogels immersed in Mg^{2+} solution possess the best performance. This is mainly because Mg^{2+} promotes the crystallization of PVA and GO during the immersion process of the composite hydrogel.

3.2.4 Stress relaxation of PVA-GO composite hydrogel immersed in $MgCl_2$ solution

In this experiment, the PVA-GO composite hydrogel immersed in $MgCl_2$ solution is used as a sample to study the stress relaxation phenomenon. The tensile rate is 10 mm/min, the first loading to elongation of 50%, static 0.5h; the second loading to elongation of 50%, static 0.5h; the third loading to elongation of 50%, static 0.5h; the fourth loading to elongation of 50%, static 0.5h; the fifth loading to elongation of 100%, static 0.5h. The stress-time curve of the PVA-GO composite hydrogel obtained by processing the experimental data is shown in Figure 10.

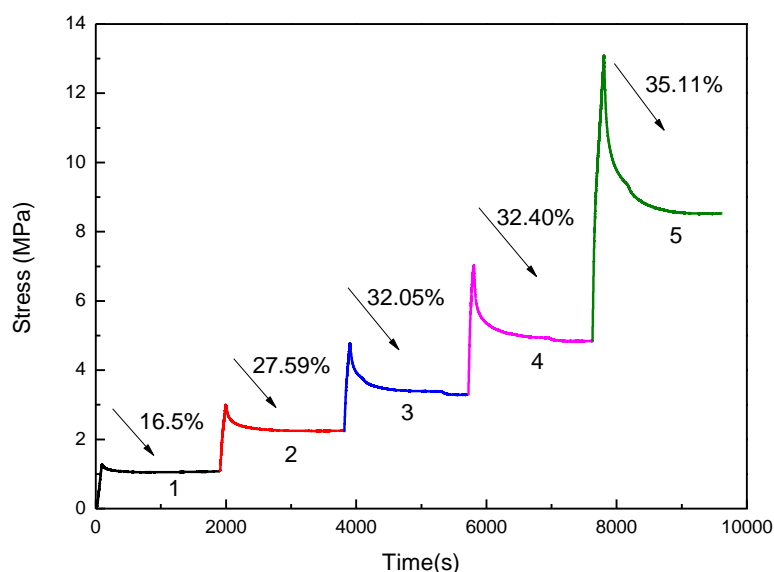


Figure 10. Stress relaxation curves of PVA-GO composite hydrogel swelled in $MgCl_2$ solution

As can be seen from Figure 10, the stress attenuation is a continuous smooth curve, which is divided into two stages: fast relaxation and slow relaxation, and finally tends to be stable. With the increasing of tensile numbers, the stress produced by the tensile increases obviously and the amount of stress relaxation also increases. In addition, comparing the tensile results of 1th-4th, it can be found that as the stress increases, the stress relaxation rate also gradually increases, and

finally remains at a fixed value of about 32%. Comparing 4th with 5th, it is found that when the elongation increases, the stress relaxation rate also increases significantly.

3.2.5 Sliding friction experiment analysis of PVA-GO composite hydrogels immersed in different ionic solutions

Figure 11 shows the friction coefficients of PVA-GO composite hydrogels immersed in different ionic solutions. It can be seen that the friction coefficients is basically between 0.08-0.18, exhibiting a certain improvement compared with that of the pure PVA. This is because the uncrystallized GO particles dispersing in the hydrogel with a lamellar structure, playing a lubricating role between the bovine cartilage and the PVA in the friction progress [20].

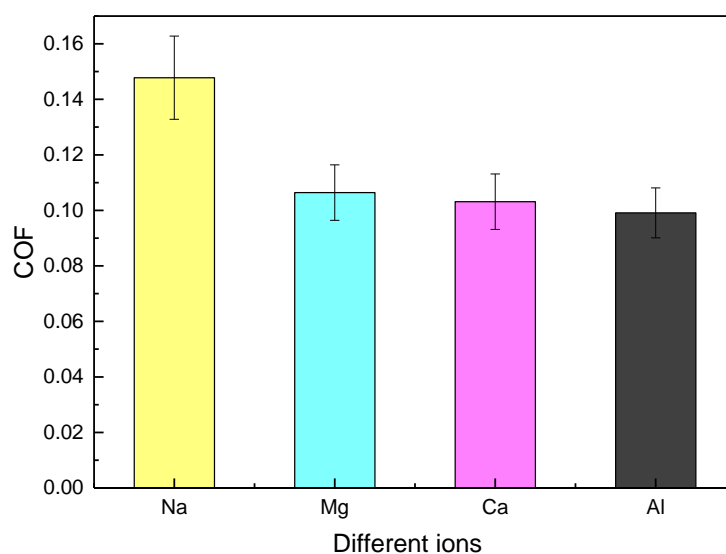


Figure11. Friction coefficient of PVA-GO composite hydrogel swelled in different ionic solutions

The friction coefficient of the composite hydrogel immersed in Na^+ solution is the highest, reaching 0.148; that immersed in Mg^{2+} 、 Ca^{2+} solution is basically the same in middle position, 0.108. And that immersed in Al^{3+} solution is lowest, only 0.103. It can be concluded that the friction coefficients of PVA-GO composite hydrogel decrease with the increase of the valence state of metal cations in the immersed ionic solution, and the friction coefficient between the +1

valent metal cations Na^+ and the +2 valent metal cations Mg^{2+} 、 Ca^{2+} is obviously different, reducing by 37.04%. This may be due to the fact that the addition of Na^+ promotes a large amount of crystallization of GO, resulting in less uncrystallized GO content in the hydrogel matrix, and thus the lubricating effect is poor. However, the addition of Al^{3+} cannot actively promote the crystallization of GO molecules. The content of uncrystallized GO in the hydrogel matrix is large, so the friction coefficient can be reduced and the lubrication effect can be improved.

4. Conclusions

In summary, this paper adopted PVA and GO as raw materials, by means of mixed self-assembly, cyclic freezing-thawing and annealing treatment to prepare PVA-GO nanocomposite hydrogels with different mass ratios. Through the analysis of FTIR, XRD, SEM and tensile properties, it was found that the composite hydrogels with GO content of 0.05wt% exhibit best comprehensive performance. On this basis, the composite hydrogels with 0.05wt% GO were immersed in different metal ionic solutions (NaCl , MgCl_2 , CaCl_2 and AlCl_3) for re-swelling, and the microstructure of the swollen hydrogel was analyzed by FTIR and XRD, confirming that the existence of hydrogen bonds and ionic coordination bonds. The SEM micro-morphology analysis showed that the internal structure with loose and porous three-dimensional network. The mechanical properties test indicated that the composite hydrogels immersed in MgCl_2 solution possess the best mechanical strength, and the tensile strength can reach 11.10MPa, the elastic modulus reaching 1.72MPa. Finally, the sliding friction experiment demonstrated that the composite hydrogels immersed in AlCl_3 solution display the lowest friction coefficient, and the higher the valence state of metal cations is, the lower the friction coefficient is.

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