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Study on Preparation of PVA-Borax Hydrogel Based on Polymer Nanomaterials Technology

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Abstract

Aiming at the current problem that polyvinyl alcohol (PVA) hydrogel is used as a phase change cold storage agent in cooling clothes, there is a problem that it is too hard after freezing. The article adopts a freezing-thawing method and uses Borax as a performance improvement additive. The Borax-PVA composite hydrogel of polymer cellulose nanocrystal. The results show that 5% PVA solution, 2mL propylene glycol, 2mL glycerol, 10% Borax solution. The PVA hydrogel synthesized under these conditions has a phase transition temperature of -6.2 ℃ and a phase transition latent heat as high as 243.6J/g, and after being frozen for 24 hours in a low temperature environment of -15 ℃, the softness is moderate, which is more suitable for cooling clothes.

***Keywords**: Polymer nanomaterials, cellulose nanocrystals, polyvinyl alcohol hydrogel, PVA-Borax hydrogel, borax.*

I. Introduction

Polyvinyl alcohol (PVA) hydrogel has excellent lubrication, shock absorption, wear resistance and good biocompatibility, and can be used to prepare artificial joint cartilage materials. PVA hydrogels can be prepared by physical and chemical cross-linking methods. Generally, increasing the degree of cross-linking can improve its mechanical properties, but it will reduce swelling and limit its application. Therefore, without changing the degree of cross-linking, the addition of inorganic fillers such as hydroxyapatite and bentonite are often used to strengthen PVA hydrogels, but inorganic fillers are not degradable in the human body. Polyvinyl alcohol hydrogel has two preparation methods: chemical crosslinking and physical crosslinking. There are two ways of chemical cross-linking: radiation cross-linking and chemical reagents [1]. Chemical reagent cross-linking refers to the use of chemical cross-linking agents to chemically cross-link the polyvinyl alcohol water molecules to form a gel. At present, because the polyvinyl alcohol gel in the mixture of dimethyl sulfoxide and water has good adhesiveness, water retention and transparency, many people have carried out in-depth research on it, but if polyvinyl alcohol is used When the gel is used in medicine, the gel must not contain toxic dimethyl sulfoxide. Therefore, in this article, we mainly study the preparation of polyvinyl alcohol hydrogel in aqueous solution and discuss its swelling characteristics.

II. Experimental Method

2.1 Raw Materials

PVA: The degree of polymerization is 1750±50, the degree of alcoholises is greater than or equal to 98%, chemically pure, Shanghai Ling Feng Chemical Reagent Co., Ltd., before preparing the solution, place it in a vacuum oven at 80°C for 24 hours to remove water [2]. The purity of borax is ≥99.5%. CNC: Prepared by acid hydrolysis with filter paper (mainly cotton cellulose) in 45°C, w=65% concentrated sulfuric acid for 45 minutes. The acid hydrolysed sample is diluted with 10 times deionized water and centrifuged at 5000r/min. Centrifuge for

10 minutes at rpm to remove a large amount of acid; then place the centrifuged product on a dialysis membrane and immerse it in deionized water for dialysis to neutrality; finally, sonicate the dialyzed sample for 5 minutes to obtain a CNC suspension. The CNC morphology is shown in Figure 1. The diameter of the cotton CNC is 5-20nm and the length is about 200nm.

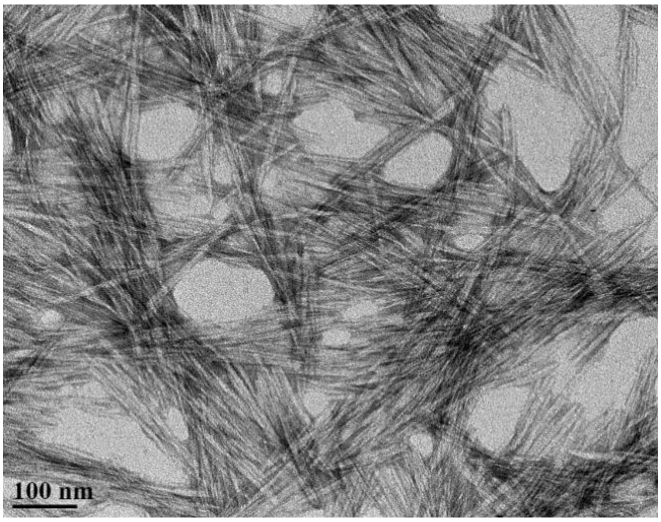

Figure 1 : TEM photo of cellulose nanocrystals

2.2. Technical Route

Weigh a PVA sample with a certain mass and a degree of polymerization of 1750±50, and use distilled water as a solvent to prepare PVA aqueous solutions with different concentrations. Place the prepared PVA aqueous solution in a ground-necked flask, use a constant temperature water bath heater to heat up to 90 ℃, stir and heat, after the PVA is completely dissolved, stand at 60 ℃ for 30 minutes to keep the air bubbles in the solution, and then pour Stainless steel mild. According to m(Borax)/m(PVA) = 0.5%, 1.0%, 2.0%, 3.0%, 4.0%, add a certain amount of CNC suspension to W = 10% PVA aqueous solution Add an appropriate amount of deionized water to control W(PVA)=7% in the final mixing system, and then ultrasonically disperse the PVA-BORAX mixture for 5 minutes to promote the dispersion of CNC in the PVA solution [3]. Pour the solution into a glass mild, put it in the refrigerator, and prepare PVA-BORAX hydrogel through 5 freeze-thaw cycles at -35°C and room temperature, where the freezing time is 20h and the thawing time is 4h. Based on the experimental purpose of this article, on the basis of previous experiments, first fix other synthesis conditions: add 2 mL of propylene glycol and different volumes of glycerine to 50 mL of 6% polyvinyl alcohol solution, stir well and add 15 mL of 10% borax solution.

2.3. Performance Test

2.3.1 Thermal Stability Test

The thermal stability of the freeze-dried hydrogel samples was analysed by the TG209F1 thermogravimetric analyser. Place about 3.0 mg of the sample to be tested in an open aluminium pan, set the gas flow rate to 20 mL/min in a nitrogen atmosphere, and increase the temperature of the sample at a constant rate in the range of 50 to 700°C, at a rate of 10°C/min. Record the change curve of thermal weight loss.

2.3.2 Dynamic Rheology Test

The prepared hydrogel was cut into a disc with a diameter of 25 mm and a thickness of 2 mm with a cutter, and its rheological properties were measured on an ARES-RFS rotary rheometer. A parallel plate measuring system with a diameter of 25mm is selected for testing at 25°C. First, test the strain sweep curve of the hydrogel at 6.28 Hz, and then scan the gel at a dynamic frequency (0.1-100 Hz) in the strain linear region.

2.3.3 Mechanical Performance Test

We use a material universal testing machine (model: INSTRON3367) to test the mechanical properties of PVA hydrogels. The strain rate of the test material is 10 mm/min.

2.3.4 Test of Swelling Performance of Hydrogel

Put the prepared polyvinyl alcohol hydrogel sample into an oven to dry until constant weight, and weigh. Then, put the dry glue in distilled water or saline, and weigh the wet gel after the swelling is balanced. The swelling rate is calculated as follows:

$$SR = \left(M_w - M_s\right) / M_s \tag{1}$$

M_w represents the mass of wet gel after swelling equilibrium; M_s represents the mass of dry gel.

III. Experimental Results

3.1. Softness Experiment of Polyvinyl Alcohol Hydrogel After Freezing

Test the softness after freezing for different times. The results are shown in Table 1. From the experimental results, it can be seen that when more than 2mL of glycerol is added, after 24 hours of freezing, the softness of the polyvinyl alcohol hydrogel is significantly improved.

Table 1: Comparison of softness of polyvinyl alcohol hydrogel after different freezing times

Glycerine volume (mL)	0	1	2	3	4
12 hours	Harder	hard	Softer	soft	soft
24 hours	hard	hard	Harder	Softer	soft

Through the above experiments, it can be seen that in order to ensure the softness of the polyvinyl alcohol hydrogel after being frozen for 24 hours, it is necessary to add more than 1 mL of glycerine. The following discussion will ensure the softness of the polyvinyl alcohol hydrogel while studying the polyvinyl alcohol solution, Experiments on the effecvf nbct of the addition of propylene glycol, borax and other single factors on the phase change latent heat and phase change temperature, combined with orthogonal experiments, to find the best preparation conditions.

3.2. Experiments On the Factors Affecting the Amount of Borax Added

We selected 50mL of 6% polyvinyl alcohol solution, 2mL of propylene glycol, and 2mL of glycerine to study the effect of the amount of borax added on the latent heat of phase transition and the temperature of phase transition. The phase change temperature does not change much [4]. However, the latent heat of phase change generally rises first and then decreases, which is the largest when the concentration of borax solution is 8%.

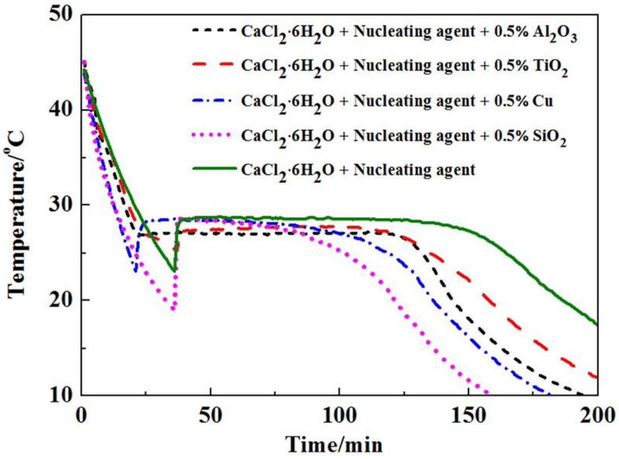

Figure 2: The effect of different borax additions on the latent heat of phase change and the temperature of phase change

3.3. Mechanical Properties

Figure 3 shows the tensile performance test results of PVA-BORAX hydrogel. It can be seen from Figure 3 that the addition of CNC can significantly increase the tensile strength, tensile modulus and elongation at break of PVA hydrogels. On the other hand, when m(Borax)/m(PVA)=1.0%, the tensile strength is 0.34MPa, which is 60% higher than the tensile strength of pure PVA hydrogel (0.21MPa). The tensile modulus and elongation at break both have their maximum valuesat m(Borax)/m(PVA) = 1.0%, and the tensile modulus increased from 0.21 MPa to 0.44 MPa, an increase of 110%; The elongation increased from 104% to 174%, an increase of 70%. This is mainly because CNC is easy to disperse in water. In the PVA-BORAX mixed solution, CNC can be dispersed very uniformly. After freezing-thawing to form a gel, CNC maintains a uniform dispersion state among PVAs. According to the percolation theory, if the rod-shaped material can be uniformly dispersed in the system, its critical overlap concentration is about (D/L)2, where D and L are the diameter and length of the rod-shaped filler, respectively. The aspect ratio of the cotton CNC is 10-20. When m(Borax)/m(PVA)≥1%, the CNCs start to contact each other and form a physical network. Therefore, the CNC plays a part of the physical cross-linking in the PVA. The role of. In the initial stage of stretching, the CNC restricts the movement of the PVA molecular chain and increases the tensile modulus; as the gel continues to stretch, the PVA molecules are stretched, the physical cross-linking points are destroyed, and energy is absorbed, which manifests as tensile strength [5]. With the increase in elongation at break. The CNC is evenly dispersed in the system, so that the stretching process will not cause stress concentration due to CNC aggregation and premature failure. Therefore, the elongation at break has also been improved.

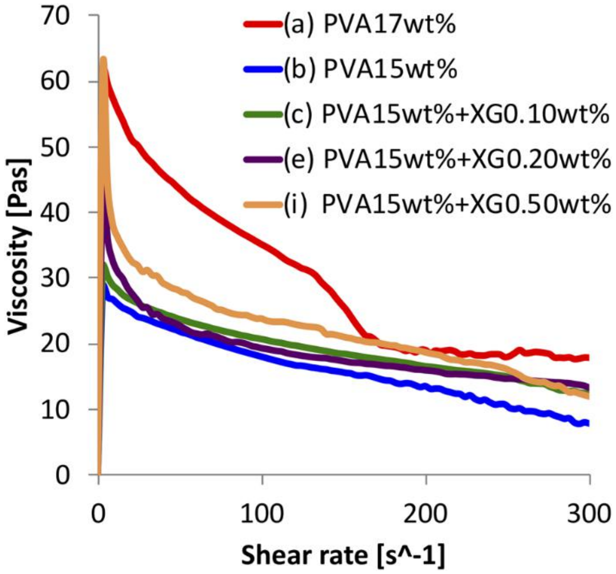

Figure 3: Mechanical properties of PVA hydrogel

3.4. Swelling Characteristics of Gel

Figure 4 shows the swelling ratio of 5% PVA hydrogel in physiological saline and distilled water over time after one freeze-thaw cycle. It can be seen from the figure that the time required for PVA hydrogel to reach swelling equilibrium in distilled water is less than the time required for it to reach swelling equilibrium in physiological saline. That is, when the solvent used for preparing PVA gel is the same as the swelling medium, the PVA gel reaches the swelling equilibrium in a short time.

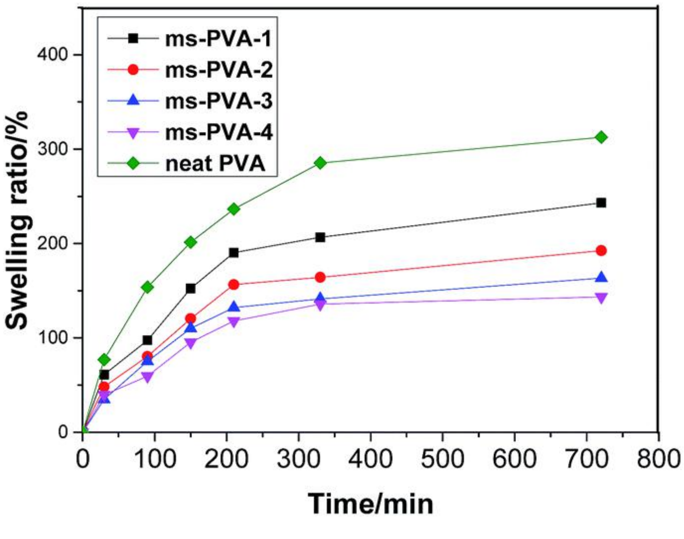

Figure 4: Swelling characteristic curve of PVA hydrogel

The triangle in Figure 4 represents the theoretical value calculated from the swelling kinetic equation. It can be seen from the figure that the theoretical value is quite close to the experimental value. The swelling rate constants of the hydrogel in distilled water and physiological saline were calculated to be 0.019 and 0.0097, respectively. That is, when the solvent and swelling medium of the PVA gel are the same, the swelling rate constant of the PVA gel is larger [6]. This is consistent with the conclusion that it takes less time for PVA gel to reach swelling equilibrium when the solvent is the same as the swelling medium.

3.5. Thermal Performance

Figure 5 shows the thermal weight loss curve of PVA-BORAX xerogel. The pure PVA gel has a three-stage thermal weight loss change. The vicinity of 240°C corresponds to the removal reaction of PVA-OH, and the 410-500°C and 500-600°C mainly correspond to the rupture and degradation of the PVA main chain. Below 500°C, the addition of CNC reduces the thermal weight loss temperature of PVA and slightly reduces the thermal stability of PVA gel; while above 500°C, CNC slightly improves the thermal stability of PVA. When it reaches 700°C, The PVA-BORAX composite still has 8% residual content, while pure PVA has only 2% residual content.

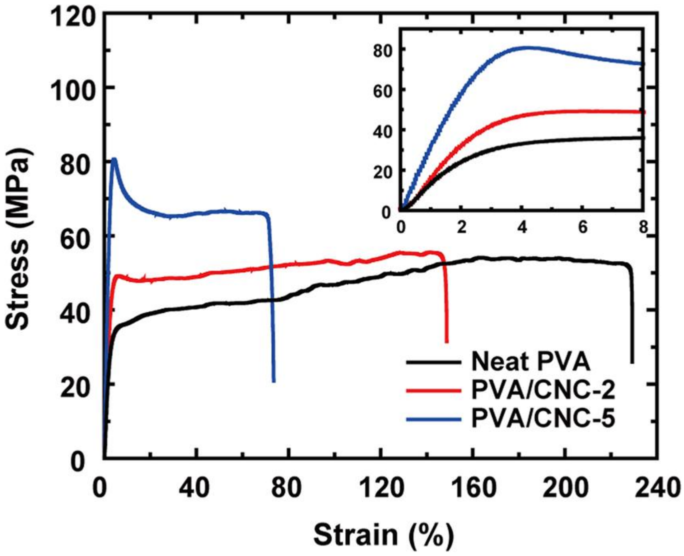

Figure 5: PVA-BORAX thermal stability curve

IV. Conclusion

The PVA-BORAX hydrogel was prepared by freeze-thaw method. CNC can effectively enhance the mechanical properties of PVA hydrogel. When m(Borax)/m(PVA) = 1.0%, PVA-BORAX hydrogel the tensile strength, tensile modulus and elongation at break of PVA gel are increased by 60%, 110% and 70% respectively than that of pure PVA gel. The addition of CNC shortens the time for the PVA hydrogel to reach swelling equilibrium and increases the swelling degree. With the increase of CNC mass fraction, the pore size of PVA gel becomes smaller.

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