Preparation and Properties of Polyethylene Glycol Modified Nanocellulose/Polyvinyl Alcohol Composite Gel

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Abstract. The traditional polyvinyl alcohol (PVA) gel has low mechanical properties and poor stability, which greatly limits its application in the fields of bioengineering and packaging engineering. Polyethylene glycol (PEG) has been used as porogen and the cellulose nanofiber (CNF)/PVA porous composite gel were prepared by freezing thawing in this study. The changes in physicochemical properties, microstructure and swelling properties of composite gels with different formulations were studied. The results indicated that the CNFs-PEG/PVA gel had a uniform inter-perforated hole structure and good mechanical properties with PEG incorporated. When the mass ratio of CNFs:PVA was 1:10, the average pore size of the formed composite gel was the smallest and the porosity was the largest, and its performance in all aspects was the most excellent. At the same time, the swelling degree can reach 1010, which was greatly improved compared with pure PVA hydrogel. The porous aerogel with high swelling and good mechanical properties prepared in this paper has great potential in the fields of heat and sound insulation and adsorption.

Keywords: Nanocellulose · Polyethylene glycol · Polyvinyl alcohol · Composite gel · Porous

1 Introduction

Environmental protection has always been the goal of all countries in the world, and new types of environmentally friendly materials have also attracted more and more scholars' attention. In recent years, polymer hydrogels have been widely used in fields such as biomedicine and electronic sensing. Many researchers have begun to focus on industrial applications such as wastewater treatment, oil-water separation, and the food industry [1]. Polyvinyl alcohol-based hydrogel has good water solubility, low toxicity and excellent biocompatibility and biodegradability. It is widely used in the food industry,

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biomedicine, chemical industry and other fields, and it has great development potential [2].

Nanocellulose is mainly obtained from plant materials such as cotton, wheat straw, trees, etc. It is a renewable material with abundant reserves [3]. Introducing nanocellulose into the hydrogel matrix can not only improve its mechanical properties but also achieve functionalization. The hydroxyl groups on the PVA molecular chain can combine with the hydroxyl groups on the nanocellulose molecular chain to form hydrogen bonds [4], The formed composite gel not only maintains the functional properties of nanocellulose itself but also incorporates the thermal stability, rigidity and dimensional stability of nanofibers, which significantly improves the physical-mechanical properties and thermal stability of hydrogels [5].

In recent years, many researchers have devoted themselves to the study of composite gels. For example, carbon nanotubes [6], nanofibrillated cellulose [7], chitosan [8], etc. are added as reinforcement phases to the gel system. Polyethylene glycol has good biocompatibility, and its addition to the gel system can significantly improve its mechanical properties. At present, some scholars have prepared CNFs-PEG/PVA composite gel with PEG and CNFs as the reinforcement phase [9]. On this basis, we used PEG and CNFs as the reinforcing phase, to prepared composite gels of different formulas of polyvinyl alcohol and nanocellulose, explored the effect of different mass ratios of PVA and nanofibers on the properties of polyvinyl alcohol composite gel. At the same time, porous aerogels were prepared by freeze-drying, and the various properties of aerogels were explored and analyzed to develop their potential as environmentally friendly materials for thermal insulation, thermal insulation, sound insulation, and impurity adsorption [10].

2 Materials and Methods

2.1 Materials

Polyvinyl alcohol, degree of polymerization 1750 $\pm$ 50, degree of alcoholysis greater than 98%; polyethylene glycol, 4000, analytically pure, all purchased from Sinopharm Group Co., Ltd.; nanocellulose purchased from Guilin Qihong Co., Ltd.; deionized water.

2.2 Preparation of CNFs-PEG/PVA Composite Gel

The PVA aqueous solution with a mass fraction of 3% were prepared by add 3 g of polyvinyl alcohol into 97 g of deionized water with stirring and heating for 2 h under a constant temperature water bath at 95 °C until the polyvinyl alcohol was completely dissolved [11]. PEG 4000 with a mass fraction of 3.0wt% were dissoived in PVA solution, nanocellulose suspensions with different ratios (the mass ratio of CNF to PVA is 1:20, 1:15, 1:10) was added to the mixed solution and the mixed solution should be kept still for a period of time to removed the bubbles. The resulting mixture was poured into the template for 5 freeze-thaw cycles (frozen at −18 °C for 18 h and thawed at 25 °C for 4 h), The resulting hydrogels were purified by immersing in deionized water to extract the pore forming agent and the unreacted materials to obtain a porous hydrogel with stable performance [12]. Finally, the soaked hydrogel was placed in the cold trap of the freeze-drying box (LGJ-10M) and frozen it for 24 h. After completely freezing, it was removed from the cold trap and be put in a vacuum drying room to vacuum dried for 4 days to obtain the aerogel. PVA, CNFs-PVA, PEG/PVA hydrogels and their aerogels were prepared according to the above steps. The distribution of each group is shown in Table 1.

Table 1 Formula of each composite hydrogel sample

Sample	PVA (wt%)	PEG (wt%)	CNF:PVA (mass ratio)
PVA	3.0	0	0
CNFs-PVA	3.0	0	1:20
PEG/PVA	3.0	3.0	0
CNFs-PEG/PVA	3.0	3.0	1:20
CNFs-PEG/PVA	3.0	3.0	1:15
CNFs-PEG/PVA	3.0	3.0	1:10

2.3 Performance Testing and Characterization

The difference in appearance of hydrogels prepared with four different ratios of polyvinyl alcohol and nanocellulose were Observed. Fourier infrared spectrometer (FIR Nicolet iS5) was used to test the freeze-dried samples, scanning 32 times in the range of 400–4000cm^{-1}. The cross-sectional morphology were observed and analyzed by a scanning electron microscope (SEM Japan Electronics JSM-IT300). ImageJ software (US National Institutes of Health) was used to analyzed the pore size and pore area on the cross-sectional SEM photos of the aerogel. The porosity was the percentage of the pore area in the total area, and the pore diameter and porosity were averaged [13]. A certain amount of dry gel were put into the deionized water at room temperature, stood still for 24 h to swollen and balanced, then the gel were took out and absorbed the surface moisture with filter paper and weighed it. The swelling degree of the hydrogel were calculated, the swelling degree was as follows Calculation.

$$S = \frac{W_1 - W_0}{W_0} \times 100\% \tag{1}$$

W_0 is the mass of the dried hydrogel and W_1 is the mass after swelling.

3 Results and Discussion

3.1 Effect of Cellulose Solution Concentration on The Physical and Chemical Properties of Hydrogel

It can be seen from Table 2. Pure polyvinyl alcohol (PVA) was inelastic, soft and shapeless after forming a gel. After adding nanocellulose, the physical properties of the gel were greatly improved, and the gel texture becomes hard and bouncy. In addition, the greater the mass fraction of nanocellulose, the better its physical properties. This is because pure polyvinyl alcohol only forms hydrogen bonds through chemical bonding, which is unstable. After the addition of nanofibers, the fibers and polyvinyl alcohol and polyethylene glycol work together through chemical and physical cross-linking to make the molecules intertwined together to form a network interpenetrating structure. Through the above experimental comparison, we can preliminarily conclude that when the mass ratio of nanocellulose: polyvinyl alcohol was 1:10, the shape and mechanical properties of the obtained hydrogel were better.

Table 2 Effect of different cellulose content on physical and chemical properties of hydrogel

CNF: PVA (mass ratio)	Shrinkage performance	Texture	Cutting difficulty	Flatness of cutting fracture
0	Large shrinkage	Soft, inelastic	Not easy	Uneven
1:20	Slight shrinkage	Harder, no elasticity	Relatively easy	Slightly uneven
1:15	Small shrinkage	Hard, high elasticity	Easy	Smooth
1:10	Does not shrink	Hard, high elasticity	Easy	Smooth

3.2 Infrared Spectroscopy

FTIR spectroscopy is one of the commonly used detection methods to analyze the chemical structure of the gel [14]. Figure 1 is the infrared spectrum of pure CNFs, PEG and composite gel. Curve 1 is the infrared spectrum of PEG, in which 1096 cm^{-1} is the characteristic peak of C–O stretching of PEG. Curve 2 is the infrared spectrum of pure CNFs, of which 1021 cm^{-1} and 896 cm^{-1} correspond to the C–O bond vibration of nanocellulose and the anomeric carbon of β-D-glucopyranosyl of cellulose, respectively. Curve 3 is the infrared spectrum of the CNFs-PEG/PVA composite gel. It can be seen that there is no carbon-oxygen stretching vibration peak of PEG, indicating that PEG does not participate in the cross-linking molding process of the gel and has been completely replaced in the deionized water replacement process. At the same time, the composite gel also found a new vibration peak at 1056 cm^{-1}. This is due to the combination of CNFs and PVA to form a hydrogen bond, which caused the C–O vibration of CNFs to blue shift [15].

3.3 Micro-morphology Analysis

The SEM image of composite gels of different formulations are presented in Fig. 2. The surface of pure PVA gel (Fig. 2a) is relatively smooth and has no obvious pore

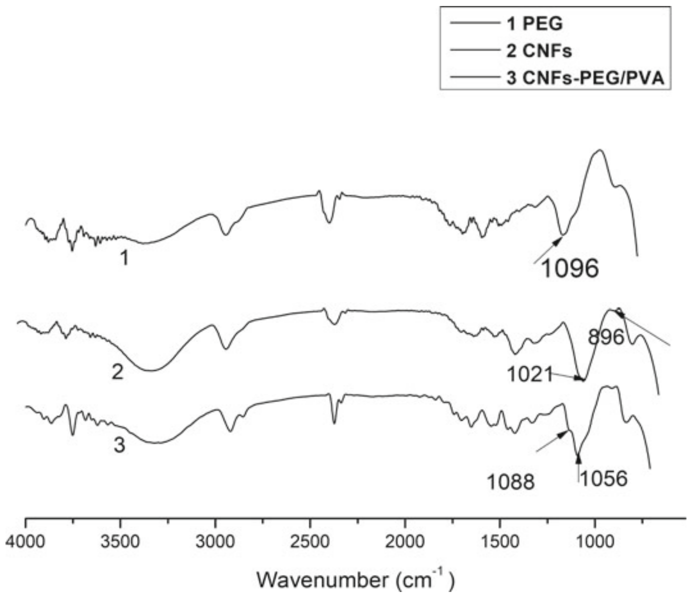

Fig. 1 Infrared spectroscopy of PEG, CNFs, and their composite hydrogels

structure, while the composite gel with nanocellulose (Fig. 2b) has a rough surface and obvious pore structures, but the size distribution is uneven. The PEG/PVA composite gel (Fig. 2c) has a three-dimensional network structure, and the pore size is relatively uniform. When PVA, CNFs and PEG are combined, the hydrogel (Fig. 2d) has a regular pore structure and the pore size is uniform. As the proportion of nanocellulose increases, the pore diameter of the hydrogel gradually decreases, which shows that the increase in cellulose makes the structure of the gel more compact and the binding density is greater, which can greatly improve the gel The mechanical properties and the reduction of holes are also more conducive to the material playing a greater advantage in heat resistance and sound insulation.

3.4 Porosity and Pore Size Testing

Table 3 lists the pore size and porosity of composite hydrogels with different formulations. The pore structure of pure PVA gel is not obvious, and the relevant pore size test is not performed in this experiment. It can be seen from the table that the pore size distribution of CNFs/PVA is wider, the average pore size is the largest, and the porosity is the lowest. When PEG, CNF, and PVA are combined, the greater the mass ratio of CNFs to PVA, the higher the porosity, the smaller the average pore size. This indicates that the three composites form a three-dimensional network interpenetrating structure with good pore size uniformity. The performance of the composite gel formed when the mass ratio of nanocellulose: polyvinyl alcohol is 1:10 is the best.

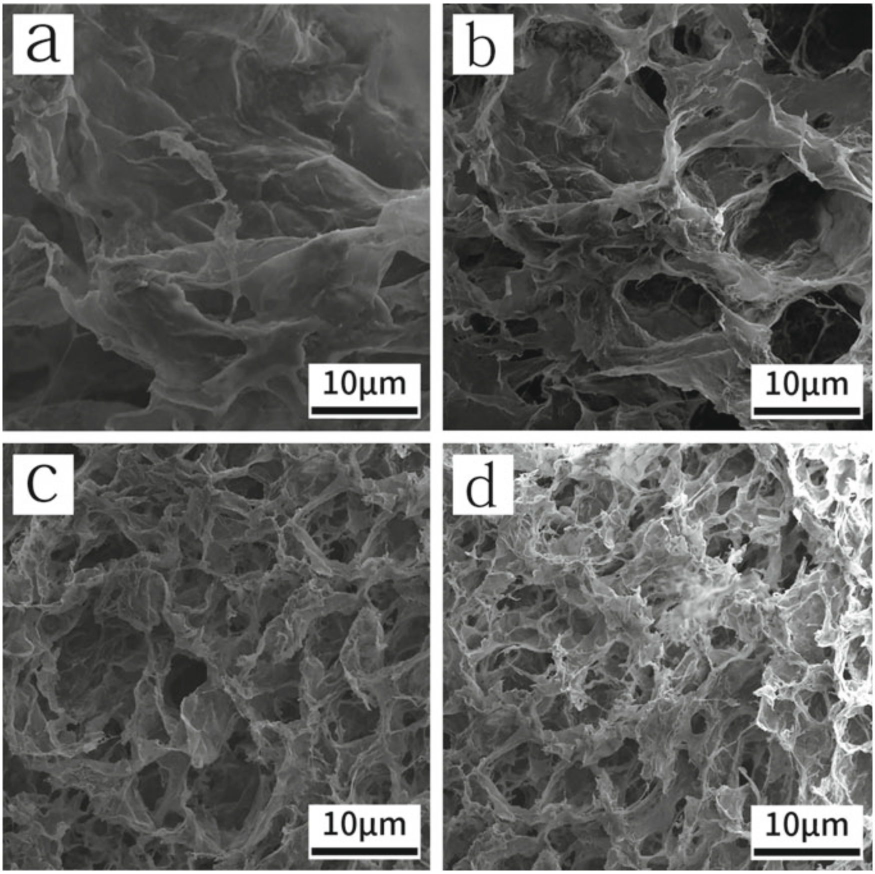

Fig. 2 SEM images of hydrogel samples: **a** PVA, **b** CNF/PVA, **c** PEG/PVA, **d** CNFs-PEG/PVA

Table 3 SEM pictures of compound gels with different formulations

Sample	PEG/PVA	CNFs/PVA	CNFs-PEG/PVA (1:20)	CNFs-PEG/PVA (1:15)	CNFs-PEG/PVA (1:10)
Distributi-on range (μm)	1.26–2.79	1.02–3.72	1.12–2.79	1.24–2.52	1.26–2.32
Average pore size (μm)	1.88 ± 0.38	2.07 ± 0.77	1.9 ± 0.41	1.87 ± 0.32	1.76 ± 0.26
Porosity (%)	61.5 ± 3.2	51.4 ± 6.2	67.6 ± 3.5	69.4 ± 4.6	71.2 ± 5.3

3.5 Swelling Analysis

The swelling behaviors of various formulations hydrogels were shown in Fig. 3. It can be seen that after adding CNFs to PVA, the swelling degree of CNFs/PVA composite hydrogel increased from 590% of pure PVA gel to 740%. This is because CNFs themselves are a kind of porous material, and the internal porous structure has a certain water absorption and water retention capacity. After adding the porogen PEG to the PVA hydrogel, the swelling degree of the PEG/PVA hydrogel is increased to 910%, it could be explained that the addition of PEG greatly increases the number of pores inside the gel, provides more storage space for water molecules, and significantly improves its swelling degree.

When CNFs, PEG and PVA are combined to form a gel, the swelling degree is further improved, as the mass ratio of CNFs to PVA increases, the swelling degree still increases to a certain extent, but the growth is not obvious, and with the increase of nanofiber. The increase of swelling degree will decrease. This indicating that nanocellulose occupies more space in the cross-linked network, thereby reducing the storage space of water molecules. The pore size, quantity, and pore rate of the hydrogel could affect its swelling degree. When nanocellulose continues to increase, it will be restricted by the hydrogen bond network of CNF and PVA after reaching a certain swelling rate, resulting in further strengthening of molecular chain entanglement. The expansion rate slows down and the swelling degree decreases. Compared with the composite hydrogel made by Li et al. [15], its swelling degree is further improved.

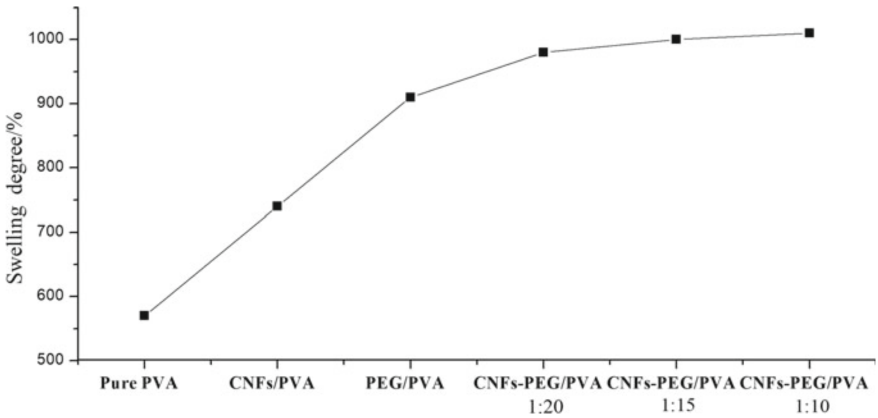

Fig. 3 Swelling degree of hydrogels of various formulas

4 Conclusion

The results of this study indicated that the polyvinyl alcohol can obtain better mechanical strength with nanocellulose incorporated and made the porous structure of the gel more dense. The CNFs-PEG/PVA composite gel had a uniform three-dimensional network porous structure. The addition of PEG can made the pore structure of the gel more uniform and greatly improved the gel swelling performance. When the mass ratio of nanocellulose to polyvinyl alcohol was 1:10, the performance of the composite hydrogel were the best. At this time, the average pore size of the composite gel was the smallest and the porosity was the highest [(71.2 ± 5.3)%]. The swelling degree was improved by 42% compared with pure PVA hydrogel. The insights gained from this kind of composite gel with high swelling degree of porous structure may be of assistance to industrial oil-water separation, wastewater treatment and other functional engineering fields.

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