

# Preparation and Properties Study of PVA/Bamboo Cellulose Composite Membrane

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**Abstract:** *The effect of bamboo fiber content on mechanical properties, moisture permeability and light transmittance of composite membrane was studied. The results show that the tensile strength of the composite film is increased by 30%, and the mechanical properties of PVA film are improved obviously with the addition of bamboo cellulose, which can be used as a good reinforcing material of PVA matrix. Bamboo cellulose composite film is a kind of transparent material because of its high light transmittance.*

**Keywords:** *ambo, PVA, moisture permeability, mechanical property*

## 1. Introduction

With the rapid development of social economy, environmental damage is becoming more and more serious, and people's awareness of environmental protection is gradually strengthened, which makes the development and utilization of degradable plastic products become very important. People invest a lot of energy in the development of degradable plastic products [1]. Nano cellulose materials prepared from natural bamboo cellulose have many special advantages, such as easy modification, regeneration, wide sources, high strength, low price, light weight, degradability and so on. Bamboo cellulose has short growth cycle and strong renewable ability. It is the most important forest resource in China next to wood. The chemical composition of bamboo cellulose is similar to wood, mainly lignin, cellulose and hemicellulose. In order to alleviate the shortage of wood resources and maintain the sustainable and coordinated development of economy and environment, the ecological imbalance caused by the excessive utilization of wood can be alleviated through the research and development of bamboo. Therefore, the preparation of composite membrane with bamboo fiber as raw material is very environmentally friendly and economical [2-9].

Because the toughness of bamboo cellulose based film is not ideal and the brittleness of the material is large, the application of bamboo fiber in the field of food preservation and packaging is limited. Bamboo fiber must be added to other polymer matrix to improve the comprehensive properties of the material. Polyvinyl alcohol in high molecular organic polymers is commonly known as PVA. Its most remarkable feature is that it is water-soluble and has many hydroxyl groups in its molecules. In addition to its obvious stability and gloss, PVA has good film-forming, water solubility, emulsification and degradation, as well as super mechanical strength, tear resistance and organic solvent resistance. These properties are due to the polymerization forms of PVA internal molecules that are different from other molecules. Polyvinyl alcohol (PVA) can be blended with a variety of water-soluble polymers to prepare packaging materials [10-13]. However, the ambient relative humidity has a great impact on the gas barrier of PVA. The gas barrier performance of polyvinyl alcohol film will decrease when the ambient relative humidity increase. Therefore, PVA also needs to be compounded with other materials. Bamboo fiber can be blended with PVA to form a transparent and tough film. Wang Shuqiang [14] prepared the composite membrane by blending the prepared nano cellulose crystal suspension and polyvinyl alcohol solution, the properties of the composite membrane was characterized by XRD and contact angle. XRD results show that pure PVA has a certain degree of crystallinity, and the characteristic crystal structures of NCC and PVA do not affect each other, which further shows that NCC and PVA have good compatibility in a certain range. Contact angle analysis shows that both NCC and PVA have strong

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hydrophilicity, indicating that they produce adsorption through strong hydrogen bond force. This provides us with a successful case.

In this paper, bamboo fiber/polyvinyl alcohol composite membrane was prepared by adding bamboo cellulose to PVA (1788) and glycerol as plasticizer. The composite membrane was tested by scanning electron microscope and XRD. The effect of glycerol content on the mechanical properties of the membrane was studied. Effect of PVA solution concentration on mechanical properties of composite membrane was studied. Effects of bamboo fiber content on mechanical properties, moisture permeability and light transmittance of composite membrane were studied. The results show that the tensile strength of bamboo cellulose composite membrane is increased by 30%, and the addition of bamboo cellulose can significantly improve the mechanical properties of PVA membrane, which can be used as a good reinforcement of PVA matrix. At the same time, bamboo cellulose composite film has high light transmittance and is a material with good transparency [15]. Comparing to other similar reports, all raw materials in our research are safe and non-toxic, the high performance fresh-keeping material active packaging film prepared by us is non-toxic and odorless. It does not produce substances harmful to human body in contact with food, showing good application and development prospects. Composite film was beneficial to prolong the fresh-keeping period of Xinjiang fragrant pear.

## 2. Materials and methods

### 2.1. Chemicals

Polyvinyl alcohol 1788, Shanghai Chenqi Chemical Technology Co., Ltd; Glycerol (analytical pure), Sinopharm group; Absolute ethanol (analytical purity), Changsha Xingning Chemical Technology Co., Ltd; Bamboo cellulose, Self prepared;

### 2.2. Preparation of composite membrane

#### 2.2.1. Preparation of PVA control membrane

3g PVA (1788) was added into 50 mL water, stir it with magnetic force at 60°C until it is completely dissolved. 2 mL glycerol was added into PVA aqueous solution, the temperature was kept at 60°C for 30 min, we put mixed solution into glass Petri dish and dry it in 80°C vacuum drying oven to form a film. Finally, the film sample is cooled at room temperature and placed in a self sealing bag for storage.

#### 2.2.2. Preparation of PVA/bamboo fiber film

A certain amount of 20% bamboo fiber solution, 3g polyvinyl alcohol and 2mL glycerol were mixed together, fix the volume to 50 mL with distilled water, fully stir for 60min at 80°C, cast the glass Petri dish, dry at constant temperature at 80°C for 3h, the film sample is cooled at room temperature for 1h, and then uncover the film.

### 2.3. Performance test and characterization of composite membrane

#### 2.3.1. Section morphology analysis (SEM)

The PVA single film and PVA/bamboo fiber film were observed and studied by field emission scanning electron microscope of Japan Electronics Corporation. The samples before observation were treated by gold spraying, and each sample was observed with  $\times 5000$  and  $\times 10000$  magnification. The test site is Xiangtan University.

#### 2.3.2. XRD test

German Bruker d8advanceda Vinci X-ray automatic diffractometer was used to test sample in 2 $\theta$  continuous scanning in the range of 5-80°. The testing place is the higher research center of Central South University.

### 2.3.3. Tensile property test

According to the national standard GB/T 1040.3-2006, the tensile strength and break extension rate of PVA single film and PVA/bamboo fiber film were measured by polymer universal mechanical testing machine.

### 2.3.4. Moisture permeability test

Take a 100 mm×100 mm sample, conduct temperature and humidity pretreatment on the sample according to GB10739, and measure it with a moisture permeability tester.

### 2.3.5. Preservation Test of Xinjiang fragrant pear with composite membrane

Fresh Xinjiang fragrant pears were divided into two groups. Group 1 was packed with bamboo fiber packaging film and placed at room temperature. Group 1 was placed at room temperature without any treatment. The decay of Xinjiang fragrant pears was observed every day and photographed and recorded after 15 days.

## 3. Results and discussions

### 3.1. Study on properties of pure PVA membrane

#### 3.1.1. Effect of glycerol content on mechanical properties of pure PVA membrane

Adding plasticizer glycerol into the film matrix can enhance the flexibility of the film. Glycerol is often used as plasticizer to change the mechanical properties of PVA films. In order to investigate the influence of glycerol content on the properties of PVA film, 0%, 5%, 10%, 15%, 20% and 25% glycerol of polyvinyl alcohol were added to PVA polymer matrix solution. Figure 1 is the change diagram of the effect of glycerol addition on the mechanical properties of PVA film. It can be seen from Figure 1 that with the increase of glycerol content in PVA, the change law of tensile strength of PVA film is that it first increases slightly and then decreases, and the tensile strength reaches the maximum value of 18Mpa when the glycerol concentration is 10%. The reason for the improvement of the mechanical properties of the composite membrane is that the addition of glycerol can enhance the mobility of PVA molecules and change the aggregation state of PVA molecules. However, if too much glycerol is added, the PVA molecules will not be closely arranged, the flexibility will be enhanced, the compactness of the film will be reduced, and then the tensile strength of the film will be reduced.

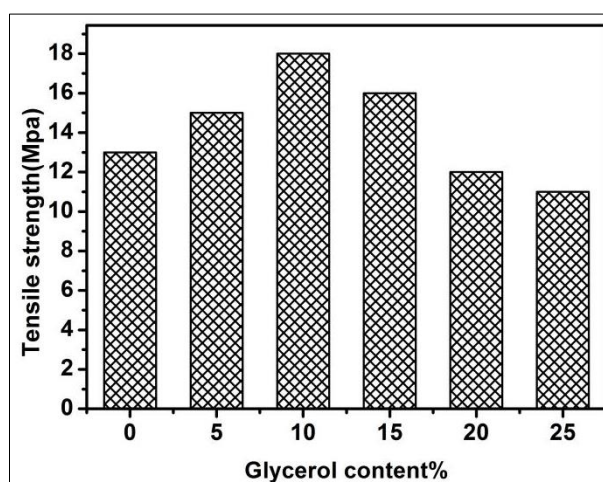


Figure 1. Effect of glycerinecontent on mechanical property of film

#### 3.1.2. Effect of PVA solution concentration on properties of composite membrane

The concentration of polyvinyl alcohol solution plays an important role in the properties of PVA films. In the process of preparing PVA films, it also has an important impact on the properties of materials. When the concentration of solution is too high, the resulting film is too thick and uneven. The

viscosity of the solution is large, which may lead to the gel state. When the solution concentration is too low, the solution viscosity is small. Due to too much water in the system, the film thickness is low and the comprehensive performance is poor. In order to explore the effect of polyvinyl alcohol solution concentration on the properties of PVA film, we set the polyvinyl alcohol solution concentration as 4%, 6%, 8%, 10% and 12% of the mass of aqueous solution respectively, and obtained the best PVA solution concentration for film preparation.

Figure 2 shows the variation of tensile strength of PVA film with PVA solution concentration. It can be seen from Figure 2 that the tensile strength of PVA film first increases and then decreases with the increase of PVA solution concentration. When the PVA concentration is small, the film is thin, and the deformation and continuity of PVA film are easy to be damaged. In the tensile process, the tensile strength and break extension rate of the film are reduced. When the PVA concentration is large, the film is thicker. Due to the increase of the viscosity of the mixture, the mechanical properties of the film can be increased, but the mechanical properties of the film will be reduced if the viscosity is too high. Based on the above analysis, the comprehensive performance of PVA membrane is the best when the concentration of PVA solution is 8%.

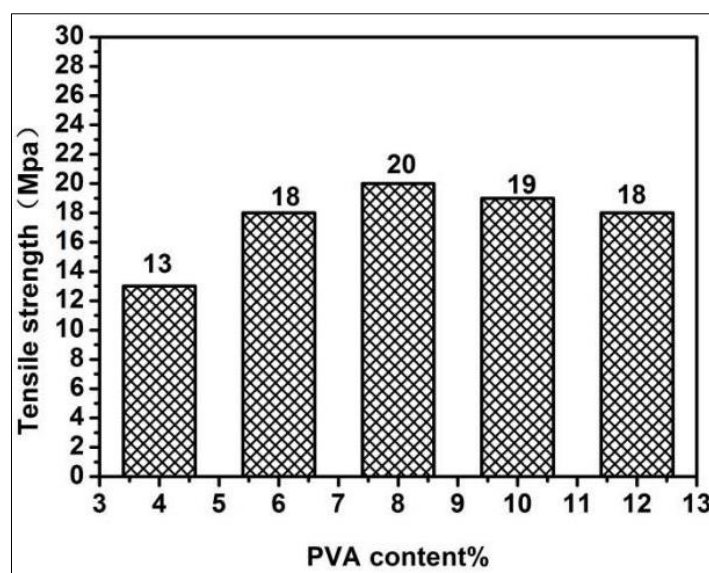
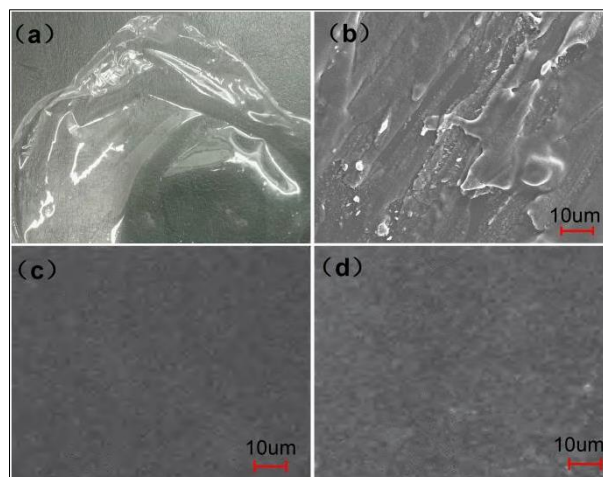


Figure 2. Effect of PVA content on mechanical property of film

### 3.2. Effect of bamboo fiber content on properties of composite membrane

#### 3.2.1. Effect of bamboo fiber on film morphology

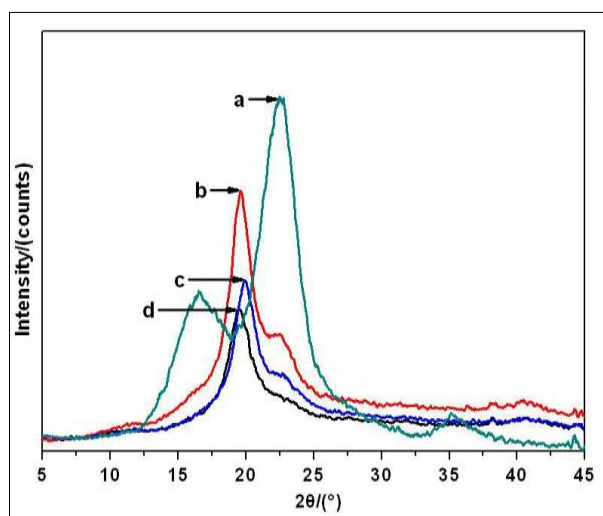
Figure 3 is the physical picture of PVA/bamboo cellulose composite film. It can be seen that the transparency of the composite film is very good. It can be clearly seen from Figure 3c and d that the scanning electron microscope of pure PVA film has no obvious prominent particles, and the surface is smooth and flat. However, prominent fine particles gradually appear on the surface of the composite film, with the increase of bamboo cellulose. This is because the viscosity of the solution gradually increases. With the increase of the content of bamboo cellulose, the worse the fluidity of the solution. With the increase of the viscosity, there will be agglomeration after coating, as can be seen from Figure 3b.



**Figure 3.** Physical picture and scanning electron microscopy of composite films (a) Composite films (b) SEM of composite films (c, d) SEM of PVA films

### 3.2.2. XRD analysis of PVA / bamboo cellulose composite membrane

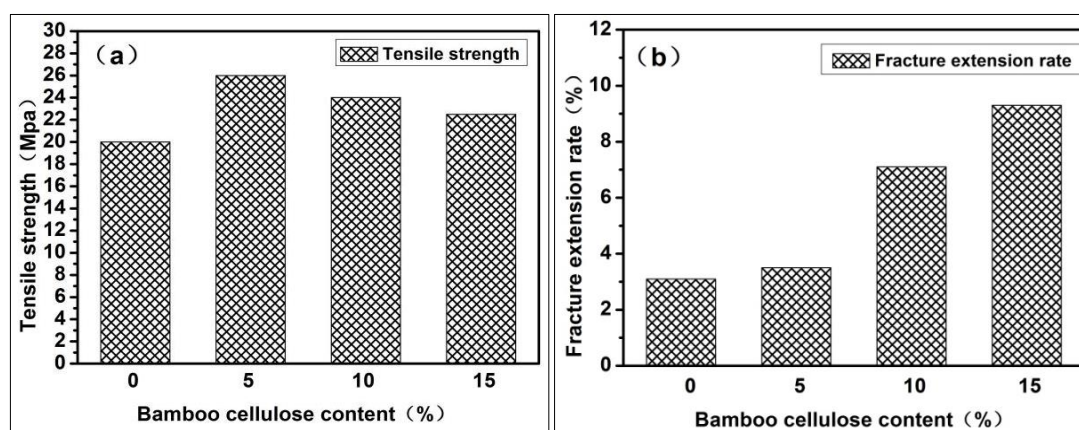
Figure 4 is the XRD pattern of pure PVA, pure bamboo cellulose and PVA/bamboo cellulose composite membrane. It can be seen from Figure 4 that in  $2\theta$  the XRD spectrum of pure PVA film at  $19.4^\circ$  has an absorption peak. The source of this absorption peak is that pure PVA has a certain crystallinity, the volume on polyvinyl alcohol molecule is small and the polarity is strong, and the hydroxyl groups are easy to arrange into a highly ordered lattice structure. Pure bamboo cellulose has strong absorption peaks at  $16^\circ$  and  $22.5^\circ$ , so PVA/bamboo cellulose composite membrane in  $2\theta$  also has an absorption peak at  $22.5^\circ$  with increase of bamboo cellulose, where the peak belongs to the 002 crystal surface of cellulose crystal. The peak intensity increases gradually here with the increase of the addition amount of bamboo cellulose. Therefore, the strength of curve b in the figure is significantly higher than that of curve c, indicating that bamboo cellulose can exist well in PVA and will not affect the crystal structure of bamboo cellulose. However, the bamboo cellulose absorption peak near  $16^\circ$  of the crystal plane originally belonging to the cellulose crystal does not appear obviously in the PVA/bamboo cellulose composite membrane diagram, mainly because the bamboo cellulose content is small and the peak itself is small.



**Figure 4.** The XRD analysis curves of composite film with different bamboo cellulose. a, b, c and d represent pure bamboo cellulose, 15 percent bamboo cellulose, 5 percent bamboo cellulose and pure PVA respectively

### 3.2.3. Effect of bamboo fiber content on mechanical properties of membrane

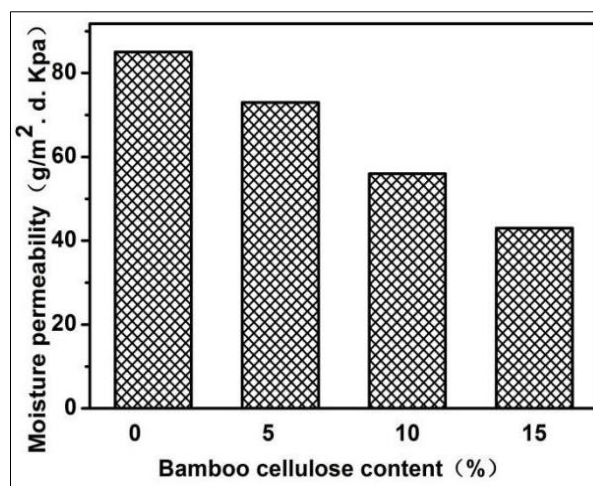
The analysis results of mechanical properties of PVA/bamboo cellulose reinforced composite membrane are shown in Figure 5. It can be seen from Figure 5 that when the content of bamboo cellulose is 5%, the tensile strength of the composite film is the largest, reaching about 26 Mpa. The reason is that the surfaces of bamboo fiber and PVA contain a large number of active groups, and the bonding effect of bamboo fiber and PVA is good. In the process of drawing, bamboo fiber, as a reinforcement, bears part of the external force, resulting in the improvement of the tensile strength of the film. When the bamboo cellulose content was 10% and 15%, the tensile strength of the composite membrane was 24 MPa, and 22.5 MPa, respectively. The results show that the tensile strength of the composite membrane is increased by 30%. Due to the addition of bamboo cellulose, the tensile strength of the composite membrane is increased due to the formation of uniform stress distribution and less stress concentration area, which is due to the formation of close crystal network structure between bamboo cellulose and PVA molecules. With the increase of concentration, the decrease of tensile properties of the composite membrane may be caused by agglomeration, that is, the excessive bamboo cellulose is unevenly dispersed in the composite membrane matrix. The better the flexibility and elasticity is, the greater break extension rate is. Figure 5 shows that the break extension rate of pure PVA film is 3.1%, the break extension rate of composite film with bamboo cellulose content of 5% and 10% is 3.5% and 7.1% respectively, and the break extension rate of composite film with bamboo cellulose content of 15% reaches 9.3%. The results show that the break extension rate of composite film formed by adding bamboo fiber with 15% concentration increases by 66.7%. It is not difficult to see that the mechanical properties of PVA film are obviously improved. With the addition of bamboo cellulose, it can be used as a good reinforcement of PVA matrix.



**Figure 5.** Effect of bamboo cellulose content on mechanical property of film (a) tensile strength (b) fracture extension rate

### 3.2.4. Effect of bamboo fiber content on moisture permeability of membrane

Due to the addition of bamboo cellulose, the moisture permeability of the composite membrane decreased significantly. The specific analysis results are shown in Figure 6, and the minimum value is 43 g m<sup>2</sup>. d. Kpa. The moisture permeability of single PVA membrane was 85 g m<sup>2</sup>.d. Kpa. When the bamboo cellulose concentration was 5% and 15%, the moisture permeability of composite membrane was 73 g/m<sup>2</sup>. d. Kpa and 43 g/m<sup>2</sup>. d. Kpa. The moisture permeability of the composite membrane was 49.4% higher than that of single PVA. When the concentration of bamboo cellulose was 15%, the barrier performance of the composite membrane to water vapor was significantly and effectively enhanced. This may be due to the uniform distribution of bamboo cellulose in PVA matrix. The strong crystalline structure can form a network reinforcing structure, increase the density of hydrogen bond in the membrane, limit the movement of PVA molecules, and weaken the hydrophilicity of PVA molecules, which can effectively hinder the diffusion and transmission of water vapor molecules.

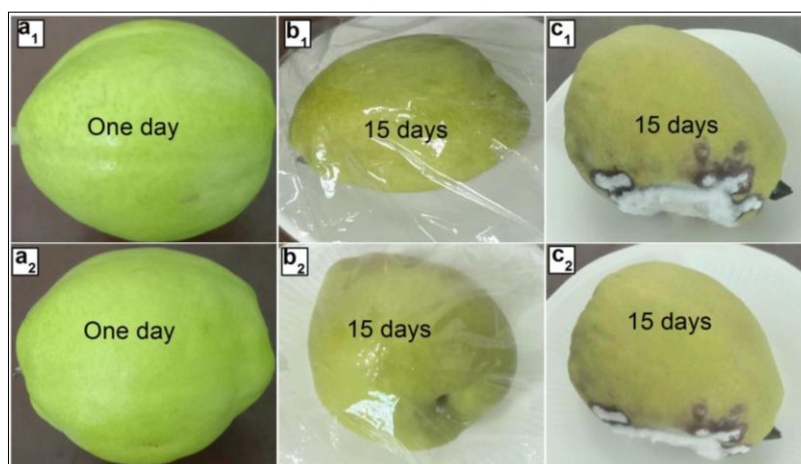


**Figure 6.** Effect of bamboo cellulose content on moisture permeability of film

### 3.3. Fresh preservation effect of fragrant pear with composite film

Decay rate is the most intuitive index to evaluate the freshness of fragrant pear. We packed Xinjiang fragrant pears with composite film and placed them at room temperature. At the same time.

Xinjiang fragrant pears were placed at room temperature without treatment. Figure 7 is the picture of fresh-keeping effect of fragrant pear. After 15 days, it was found that Xinjiang fragrant pears packed with composite film basically did not rot, no mold growth, and the epidermis became relatively dry. Without treatment, Xinjiang fragrant pear rotted seriously and a large number of molds grew. There was significant difference between Xinjiang fragrant pear packaged with composite film and Xinjiang fragrant pear placed at room temperature without treatment. Picture of fresh-keeping effect of fragrant pear (Figure 7) show that composite film was beneficial to prolong the fresh-keeping period of Xinjiang fragrant pear.



**Figure 7.** Picture of fresh-keeping effect of fragrant pear (a1, a2) fresh fragrant pear, (b1, b2) fragrant pear treated with PVA/bamboo cellulose membrane for 15 days, (c1, c2) fragrant pear store at room temperature for 15 days

## 4. Conclusions

The reinforced composite membrane was prepared with PVA and bamboo cellulose as raw material. The effects of bamboo cellulose on the properties of the composite membrane were investigated by analyzing the light transmittance, moisture permeability and mechanical properties. The following conclusions can be obtained through the research:



Firstly, pure PVA membrane was prepared. The effects of glycerol content on the mechanical properties of PVA membrane was studied. The results showed that the comprehensive properties of PVA membrane were the best when the glycerol content was 20%. The effects of PVA solution concentration on the mechanical properties of PVA membrane was studied. The results showed that the comprehensive properties of PVA membrane were the best when the concentration of PVA solution was 8%.

XRD results show that pure bamboo cellulose has strong absorption peaks at 16° and 22.5°, but the absorption is weakened in bamboo cellulose/polyvinyl alcohol composite membrane, indicating that bamboo cellulose is well dispersed in PVA matrix.

With the increase of bamboo cellulose concentration in PVA/bamboo cellulose reinforced composite membrane, the surface of the composite membrane becomes rough gradually. The moisture permeability of the composite membrane with 15% bamboo cellulose concentration is increased by 49.4%, the tensile strength of the composite membrane with 5% bamboo cellulose is increased by 30%, and the fracture elongation of the composite membrane is increased by 66% at 15%.

Conclusion with future scope and limitations: Green packaging refers to the appropriate packaging that can be recycled or degraded in nature, and does not cause public hazards to human body and environment in the whole life cycle of products. The high performance fresh-keeping material active packaging film prepared by us is non-toxic and odorless. It does not produce substances harmful to human body in contact with food, showing good application and development prospects. It can better delay the corruption of fruits and vegetables, reduce the deterioration rate, maintain high vitamin C and total sugar content, prolong the fresh-keeping period of fruits and vegetables, prolong the shelf life of products, and ensure their nutritional quality. It is the key to large-scale industrialized production of fruits and vegetables. High performance fresh-keeping materials can also be used for the storage and preservation of meat products and aquatic products. However, the material has no antibacterial property. The next step is to realize the antibacterial function of the packaging film. Select nano materials with antibacterial and bacteriostatic properties, such as nano Ag, nano TiO<sub>2</sub> or nano ZnO, so as to strengthen the ability of fresh-keeping packaging materials to control microorganisms and improve the fresh-keeping effect.

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## References

1. LIU, Y. Q., JIANG, Y. S., LIU, Y., CHEN, Y.H., WANG, Y., ZHANG, R., LIU, Y. W., Research progress of PVA/natural polymer composite, *Plastics industry*, 48, 2020, 15-20.
2. LI, F., SONG, W. S., WANG, B. Y., LIU, X. M., Research progress of degradable composite materials based on polyvinyl alcohol, *Modern Animal Husbandry*, 2(1), 2018, 35-39.
3. TANG, H. L., XIONG, H. G., GUAN, X. M., Preparaffon of Liqaid Mulching Fnm wim Bamboo Fiber Substrate for Sand Prevention and Control, *Journal of Anhui Agri Sci*, 38(35), 2010, 20426-20428
4. LIU, H. Z., QIU, L. Q., GUAN, H. M., Preparation and properties of bamboo fiber hydrophilic membrane, *Chinese Polymer Bulletin*, 5, 2020, 39-47.
5. CHEN, H. Y., SONG, S., LI, Q. Q., YUAN, Y. L., Preparation and properties of bamboo cellulose reinforced composite membrane, *Journal of China Agricultural University*, 24(12), 2019, 121-127.
6. ZUO, Y. F., LI, W. H., LI, P., ZHAO, X., LI, X. G., WU, Y. Q., Plasticization of bamboo fiber/poly-lactic acid degradable composite, *Journal of Forestry Engineering*, 3(1), 2018, 77-82.
7. DING, T. T., LI, Q., JIN, Z. F., GE, Z. W., LU, W. M., Preparation and properties of bamboo nano powder/carboxymethyl cellulose composite film, *Journal of Forestry Engineering*, 2(5), 2017, 90-94





8. LI, Q. Y., XUE, Z. H., ZHAO, J. Q., AO, C. H., JIA, X. W., XIA, T., WANG, Q. H., DENG, X. Y., ZHANG, W., LU, C. H., Mass production of high thermal conductive boron nitride/nanofibrillated cellulose composite membranes, *Chemical Engineering Journal*, 383, 2020, 123101-123110.
9. ZHU, S. D., WU, Y. X., CHEN, Q., Dissolution of cellulose with ionic liquids and its application: a mini-review, *Green Chem*, 8, 2006, 325-327.
10. KHORAMABADI, H. N., AREFIAN, M., HOJJATI, M., TAJZAD, I., MOKHTARZADE, A., MAZHAR, M., JAMAVARI, A., A review of Polyvinyl alcohol/Carboxymethyl cellulose (PVA/CMC) composites for various applications, *Compounds*, 2(3), 2006, 69.
11. MENAZEA, A. A., ISMAIL, A. M., AWWAD, N. S., IBRAHIUM, H. A., Physical characterization and antibacterial activity of PVA/Chitosan matrix doped by selenium nanoparticles prepared via one-pot laser ablation route, *Journal of Materials Research and Technology*, 9, 2020, 9598-9606.
12. SONG, K. L., ZHU, W. M., LI, X. Y., YU, Z. C., A novel mechanical robust, self-healing and shape memory hydrogel based on PVA reinforced by cellulose nanocrystal, *Materials Letters*, 260, 2020, 126884-126893.
13. ZHOU, P., LUO, Y. Y., LV, Z., SUN, X. W., TIAN, Y. Q., ZHANG, X. X., Melt-processed poly (vinyl alcohol)/corn starch/nanocellulose composites with improved mechanical properties, *International Journal of Biological Macromolecules*, 183, 2021, 1903-1910.
14. NAN, B., YIN, L. P., WANG, S. Q., HUANG, C. J., LI, Y. J., The effect of natural light and ultraviolet lamp radiation on bamboo surface discoloration, *Advanced Materials Research*, 312, 2014.
15. ADAMU, M., REZAURRAHMAN, M. HAMDAN, S. KHUSAIRY BIN BAKRI, M., ASYADI BIN MD YUSOF, F., Impact of polyvinyl alcohol/acrylonitrile on bamboo nanocomposite and optimization of mechanical performance by response surface methodology, *Construction and Building Materials*, 258, 2020, 119693-119702

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