ISSN Online: https://doi.org/10.35534/asrj.

Advanced Scientific Research Journal – 2025, 1(1): 1–10

Research on the Preparation of Modified Polyacrylic Acid Superabsorbent Resin and Its Potential Application in Fruit Preservation in Combination with Chinese Herbal Medicine Composites

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Abstract: In order to enhance the water absorption capacity and degradation performance of acrylic acid superabsorbent resin (PAA), this paper used 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and naturally degradable macromolecular carboxymethyl cellulose (CMC) as modifiers and adopted the aqueous solution polymerization method to prepare modified polyacrylic acid (PAA) superabsorbent resin. The results showed that when the content of acrylic acid was 21%, and the contents of AMPS, CMC, cross-linking agent and initiator were 20%, 1.8%, 0.02% and 2% of the mass of AA respectively, the water absorption capacity of the prepared PAA superabsorbent resin in deionized water increased from 483 g/g before modification to 875 g/g, and the water absorption capacity in physiological saline was 238 g/g. The degradation rate of the modified PAA in cellulase was 64.8%. It can be seen that the modification with CMC and AMPS can improve the water absorption, salt resistance and degradation performance of PAA resin. Meanwhile, the composite material of modified PAA superabsorbent resin and Chinese herbal medicine powder can prolong the shelf life of fruits and vegetables. The research results can provide a reference for the further research of fruit preservatives and a new idea for the expanded application of superabsorbent resins.

Keywords: Superabsorbent Resin; Salt Resistance; Biodegradation; Fruit Preservation

According to the Analysis Report on China's Fruit Industry in 2020, the fruit production, consumption, and market sales increased from 263 million tons, 269 million tons, and 25 trillion yuan in 2019 to 299 million tons, 303 million tons, and 27.5 trillion yuan in 2025 respectively. It can be seen that the scale of the fruit market is on an upward trend year by year, and 34 million tons need to be imported. However, due to the lack of preservation or improper preservation techniques, the weight loss of fruits and vegetables in China reaches 20% - 40% every year. Therefore, strengthening the research on the preservation of fruits and vegetables is of great significance for the development of China's agricultural economy and the improvement of people's living standards. The storage period of fruits is mainly closely related to temperature and humidity [1]. Usually, fruits adopt low-temperature storage technology, which can inhibit the growth and reproduction of microorganisms and reduce the activity of enzymes required for the respiration of fruits, thus maintaining the quality of post-harvest fruits, delaying cell senescence and fruit decay [2]. However, there is usually a temperature difference between the picking, transportation process and storage, and water droplets are easily formed on the surface of fruits. The main technical problem encountered in the preservation of fruits and vegetables is the dew drops generated in the packaging, which serve as a culture medium for the reproduction of microorganisms and will accelerate the decay of fruits and vegetables. Traditionally, hormonal drugs such as indoleacetic acid and

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indolebutyric acid are commonly used as fruit preservatives; in order to prevent fruits from being infected by pathogenic bacteria, synthetic fungicides such as thiophanate-methyl and carbendazim are often used. It can be seen that the safety and environmental protection of traditional fruit preservation methods need to be improved.

Superabsorbent resins are organic polymer materials with a large number of hydrophilic groups and a three-dimensional network structure. They can absorb several times their own weight of water and have a strong water-locking ability. They can be used as water-retaining agents in agriculture, adsorbents for removing heavy metals in industrial wastewater, core materials for sanitary napkins and diapers, and other applications. However, unmodified acrylic acid superabsorbent resins have disadvantages such as low water absorption capacity, poor salt resistance, and poor degradation performance, which limit their applications. Therefore, they usually need to be modified [3-5]. Xu Jihong et al. studied the grafting of acrylic acid (AA) and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) onto carboxymethyl cellulose (CMC) by microwave radiation method, and the obtained superabsorbent resin had a water absorption ratio of 690 g/g and a physiological saline absorption ratio of 90 g/g [6]. Wu Shuming prepared a superabsorbent resin by graft copolymerization of CMC, and its water absorption ratios in deionized water and physiological saline were 498 g/g and 59 g/g respectively [7]. Li Jie et al. used CMC to graft AA and NVP, and the obtained modified PAA had water absorption ratios in distilled water and physiological saline of 2339 g/g and 110 g/g respectively [8]. Deng Weibo et al. used CMC, AA, and AMPS to prepare a superabsorbent resin, and its water absorption ratio in deionized water was 580 g/g [9]. The modification of acrylic resin with CMC can not only improve its water absorption capacity but also enhance its degradation performance [10].

How to develop a material that can prevent the formation of dew drops in packaging, has antibacterial properties, can maintain a certain humidity so that fruits will not dehydrate and shrivel, and is environmentally friendly, so that the preservation period of fruits can be greatly extended. Therefore, in this paper, AMPS with strong hydrophilic groups and naturally degradable macromolecular CMC were used as modifiers, and the modified PAA superabsorbent resin was prepared by the aqueous solution polymerization method. The water absorption and water retention abilities of PAA in different metal ion solutions and its degradation performance under the action of cellulase were investigated. Then, the modified PAA was mixed with Chinese herbal medicine powder to prepare fruit preservation materials, and a preliminary exploration of the fruit preservation effect was carried out. The experimental results can provide a new idea and theoretical reference for fruit preservation technology.

1. Experimental Section

1.1. Main Experimental Instruments and Chemicals

High-speed universal pulverizer, model FW-200T, manufactured by Beijing Zhongxing Weiye Instrument Co., Ltd.; Electric variable-speed stirrer with a speed of 3000 r/min, manufactured by Jiangsu Jintan Jincheng Guosheng Experimental Instrument Factory. Acrylic acid, potassium persulfate, sodium hydroxide, sodium chloride (analytical pure), N,N'-methylene bisacrylamide and 2-acrylamido-2-methylpropanesulfonic acid were purchased from Chengdu Kelong Chemical Reagent Factory; Sodium carboxymethyl cellulose (food grade) was provided by Henan Huayue Chemical Products Co., Ltd.

1.2. Preparation and Performance Characterization of Superabsorbent Resin

1.2.1. Preparation of Superabsorbent Resin

Weigh a certain amount of acrylic acid and place it in a three-necked flask. Adjust its neutralization degree with NaOH solution, and then add an appropriate amount of CMC, AMPS and cross-linking agent. Mix and dissolve them thoroughly. After dropping the initiator solution at 60°C for about 1 hour, raise the temperature to 70°C and conduct a constant temperature reaction for 2 hours to obtain a viscous liquid. Then dry it, pulverize it and store it in a desiccator for later use.

1.2.2. Determination of Water Absorption Capacity

Weigh a small amount of resin sample and put it into a dry tea bag, and then place the tea bag into a beaker filled with deionized water and let it stand for 24 hours. After that, weigh it. The liquid absorption ratio is calculated according to formula (1):

$$\text{The liquid absorption ratio} = \frac{m_1}{m_0} \tag{1}$$

where: m1 — the mass of PAA after water absorption; m0 — the mass of PAA before water absorption

1.2.3. Determination of Water Retention Capacity

Place the CMC-modified resin that has been saturated with water absorption under normal temperature, 50°C and 65°C respectively to measure its water retention performance. Weigh the tea bag once every 30 minutes. After five measurements, calculate its water absorption ratio according to formula (1), and then calculate its water retention rate according to formula (2):

$$\text{The water retention rate} = \frac{m_3}{m_4} \times 100\% \tag{2}$$

where: m3 — the mass of PAA at different temperatures; m4 — the mass of PAA saturated with water absorption

1.2.4. Determination of Degradability

Put the AMPS- and CMC-modified superabsorbent resins that have been saturated with water absorption into 0.05% - 0.5% cellulase solutions respectively, and measure the change in the water absorption ratio of the resins every other day. The degradation rate of the superabsorbent resin is calculated according to formula (3):

$$\text{The degradation rate} = \frac{m_5 - m_6}{m_5} \times 100\% \tag{3}$$

where: m5 — the mass of PAA before degradation; m6 — the mass of PAA after degradation

1.2.5. Fruit Preservation Experiment

Mix a certain amount of Chinese herbal medicine powder and modified PAA resin powder, put them into a tea bag, and then put the tea bag together with a bunch of fresh grapes into a plastic food bag and seal it. Place it in a refrigerator at 4°C - 6°C and observe the number of detached grapes. Evaluate the preservation effect on grapes by the detachment rate.

2. Results and Discussion

2.1. Influence of the Mass Fraction of Monomer AA on the Water Absorption Ratio of PAA

Figure 1 shows the influence of the amount of monomer AA on the water absorption ratio of PAA. It can be seen from the figure that when the amount of AA increases to 21%, the water absorption ratio of PAA increases to 342 g/g, and when the amount of AA increases to 29%, the water absorption ratio of PAA decreases to 222 g/g. When the concentration of acrylic acid is very low, the molecular weight of the formed polyacrylic acid is small. Moreover, when the amount of the cross-linking agent NMBA is fixed, the distance between the formed cross-linking points is short, and it is not easy to expand during water absorption and swelling, resulting in a very low water absorption ratio of the resin. When the amount of AA is gradually increased, the molecular weight of the polymer gradually increases, the distance between the cross-linking points gradually increases, the number of effective three-dimensional network structures increases, and the water absorption rate of the PAA resin gradually increases. When the amount of AA is 21%, the molecular weight of the polymer is moderate, the distance between the cross-linking points is the most appropriate, the number of effective three-dimensional network structures is the largest, and the water absorption ratio of PAA reaches the maximum (342 g/g). However, when the amount of acrylic acid is too high, the molecular weight of the PAA superabsorbent resin is large, the distance between the cross-linking points is too long, and the three-dimensional network structure becomes loose, resulting in a decrease in the water absorption ratio of PAA [11]. Meanwhile, when the concentration of monomer AA is too high, the viscosity of the system is large, which easily leads to the occurrence of explosive polymerization. Therefore, in this experiment, a monomer mass fraction of 21% is relatively reasonable.

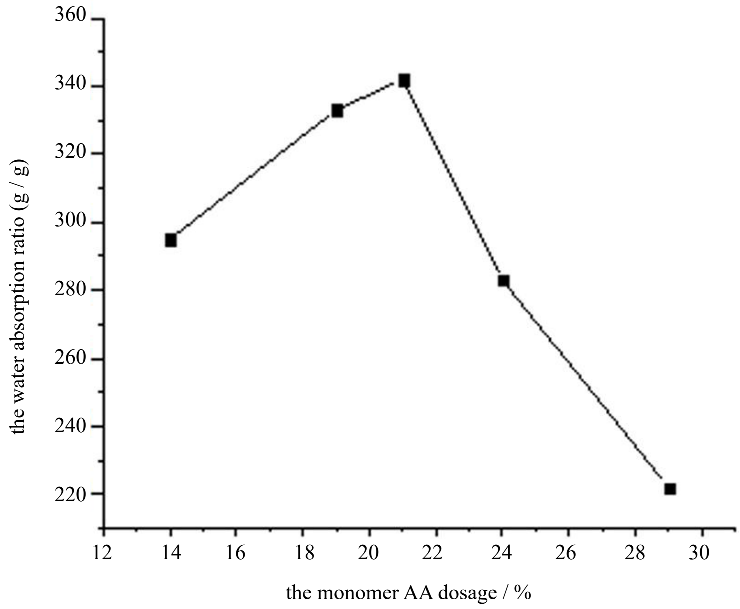


Figure 1. Influence of monomer AA dosage on water absorption rate of PAA

2.2. Influence of the Degree of Neutralization on the Water Absorption Ratio of PAA

Figure 2 shows the influence of the degree of neutralization on the water absorption ratio of PAA. It can be seen from this figure that when the degree of neutralization increases to 66%, the water absorption ratio of PAA increases to 440 g/g, and when the degree of neutralization increases to 74%, the water absorption ratio of PAA decreases to 380 g/g. When the degree of neutralization is low, with the increase in the degree of neutralization, the content of carboxylate ions (-COO-) in the PAA superabsorbent resin will increase, the electrostatic repulsion will increase, which is beneficial to the spatial expansion of the three-dimensional network structure of PAA, increasing the osmotic pressure of the solution inside and outside the product and increasing the water absorption ratio of PAA. When the degree of neutralization is 66%, the most effective three-dimensional network structure is formed, and the water absorption ratio of PAA reaches the maximum (440 g/g).

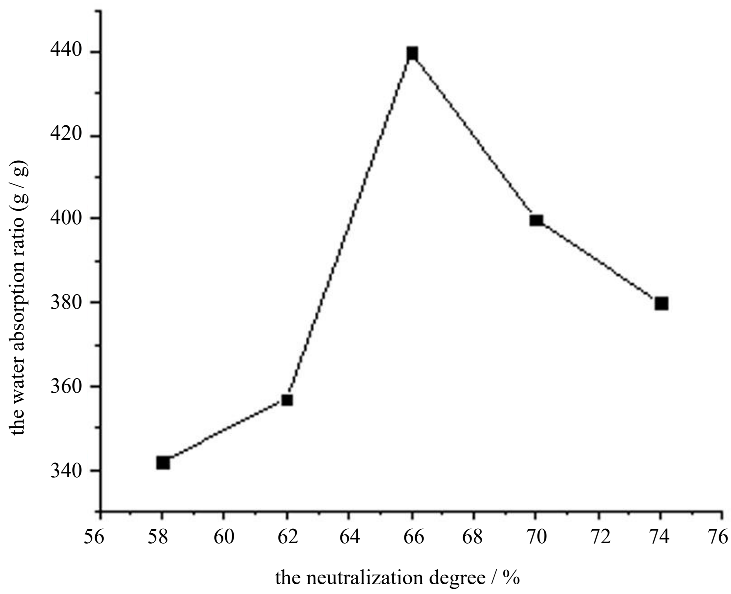


Figure 2. Influence of neutralization degree on water absorption rate of PAA

When the degree of neutralization is greater than 66% and continues to increase, the number of carboxylate ions increases, the electrostatic repulsion of the molecular chains increases, which is not conducive to the formation of an effective three-dimensional network structure, and finally leads to a decline in the water absorption performance of the superabsorbent resin [11]. Therefore, in this experiment, a degree of neutralization of 66% is relatively reasonable.

2.3. Influence of the Amount of NMBA on the Water Absorption Ratio of PAA

Figure 3 shows the influence of the amount of NMBA on the water absorption ratio of PAA. It can be seen from the figure that when the amount of NMBA increases to 0.03%, the water absorption ratio of PAA increases to 483 g/g, and when the amount of NMBA continues to increase to 0.14%, the water absorption ratio of PAA decreases to 230 g/g. When the amount of NMBA is less than 0.03%, the formed cross-linking points are few and the distance is long, the number of effective three-dimensional network structures is small and relatively loose, resulting in a very low water absorption ratio of PAA [11]. With the increase in the amount of the cross-linking agent, the cross-linking density in the high-molecular polymer gradually increases, and the water absorption ratio of PAA gradually increases. When the amount of NMBA is 0.03% of the mass of AA, the length of the cross-linking points is moderate, the number of formed effective network structures is the largest, and the water absorption ratio of PAA reaches the maximum (483 g/g). When the amount of NMBA is greater than 0.03% and continues to increase, the cross-linking density in the polymer gradually increases, the three-dimensional network structure gradually becomes tight, the water absorption and swelling properties gradually weaken, resulting in a gradual decrease in the water absorption ratio of PAA [12]. Therefore, an amount of NMBA of 0.03% of the mass of monomer AA is relatively reasonable.

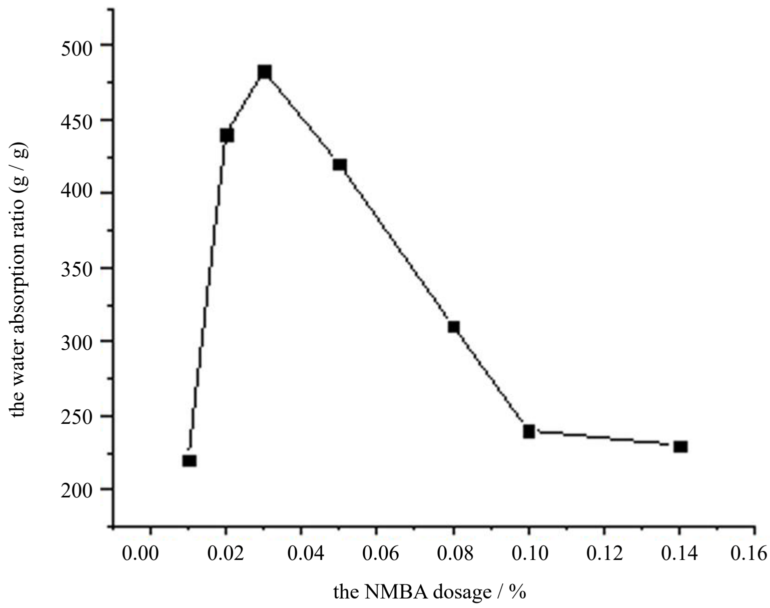


Figure 3. **Influence of NMBA dosage on water absorption rate of PAA**

2.4. Influence of the Amount of Initiator KPS on the Water Absorption Ratio of PAA

Figure 4 shows the influence of the initiator on the water absorption ratio of PAA. As shown in the figure, when the amount of KPS increases to 2%, the water absorption ratio of PAA increases to 483 g/g, and when the amount increases to 4%, the water absorption ratio of PAA decreases to 150 g/g. When the amount is small, the molecular weight of the generated PAA is large, the distance between the formed cross-linking points is long, and the structure is relatively loose, resulting in a very low water absorption ratio. When the amount of KPS is gradually increased, the distance between the cross-linking points is gradually shortened, the number of effective cross-linked network structures is gradually increased, and the water absorption ratio is gradually increased. When the amount of KPS is 2%, the water absorption ratio of PAA reaches the maximum (483 g/g). However, when the amount of KPS is too large, the molecular weight of the polymer gradually decreases, the distance between the cross-linking points is too short, the network structure is dense, and the resin is not easy to expand during water absorption, resulting in a decrease in the water absorption ability of PAA [13]. Therefore, an amount of KPS of 2% is relatively reasonable.

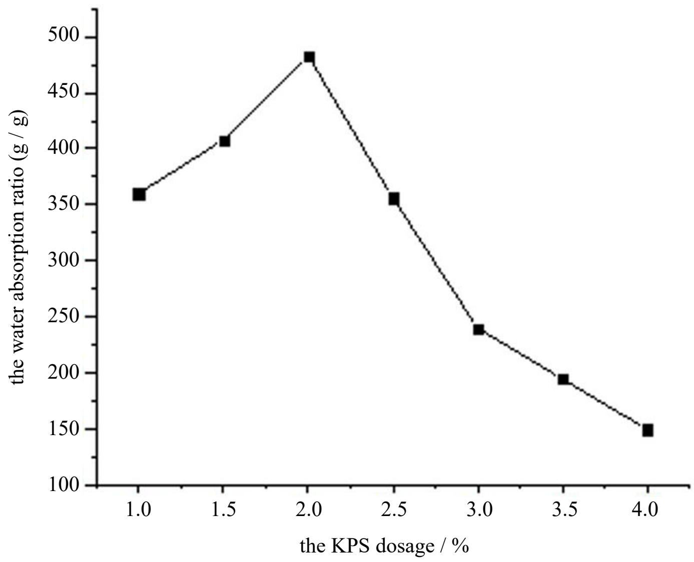


Figure 4. **Influence of KPS dosage on water absorption rate of PAA**

2.5. Influence of the Amount of Modifier CMC on the Water Absorption Ratio of PAA

Figure 5 shows the influence of the amount of modifier CMC on the water absorption ratio of PAA. It can be seen from the figure that when the amount of CMC increases to 1.8%, the water absorption ratio of PAA increases to 733 g/g, and when the amount of CMC continues to increase to 2.3%, the water absorption ratio of PAA decreases to 150 g/g. When a small amount of CMC is added, the amount of generated graft polymer is small, and the number of effective network structures is also small. Meanwhile, since the water absorption ratio of CMC itself (70 g/g) is low, when the amount of CMC is low, the water absorption ratio of CMC-modified PAA (300 g/g) is lower than that of unmodified PAA (483 g/g), but it is still higher than the water absorption ratio of CMC. With the increase in the amount of CMC, the number of effective network structures of CMC-modified PAA increases, resulting in an increase in the water absorption ratio. When the amount of CMC is 1.8%, the water absorption ratio of PAA reaches the maximum (733 g/g). However, when the amount of CMC continues to increase, the viscosity of the polymerization system will also continuously increase, which is not conducive to the formation of an effective three-dimensional cross-linked network spatial structure for CMC graft modification, causing a sharp decrease in the water absorption ratio [14]. Therefore, an amount of CMC of 1.8% of the mass of AA is relatively reasonable.

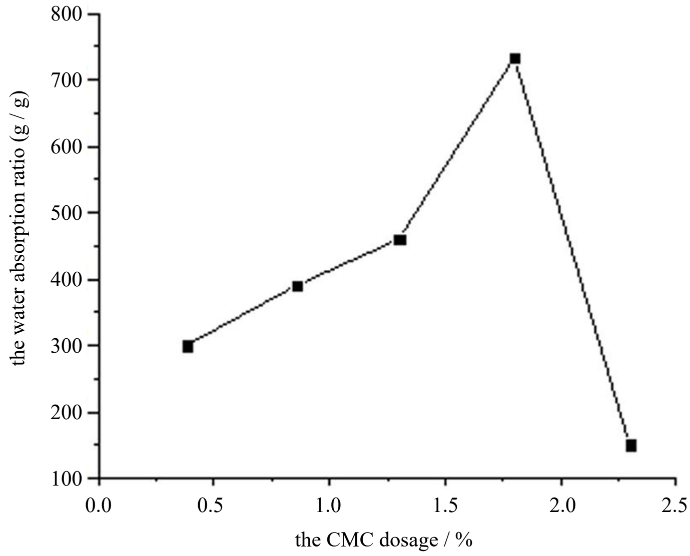


Figure 5. **Influence of CMC dosage on water absorption rate of PAA**

2.6. Influence of the Amount of AMPS-Modified CMC/AA on the Water Absorption Ratio of PAA

Figure 6 shows the influence of AMPS modification on the water absorption ratio of PAA.

It can be seen from the figure that when the amount of AMPS increases to 20%, the water absorption ratio of PAA increases to 875 g/g, and when the amount of AMPS continues to increase to 30%, the water absorption ratio of PAA decreases to 314 g/g. After adding CMC for modification, the polymerization system has already become viscous, and the formed three-dimensional network block structure is already relatively appropriate. When AMPS is added again to introduce sulfonic acid groups, it may lead to an increase in the collision frequency of the groups. Considering the influence of the synergistic effect, the three-dimensional network structure becomes compressed and tight, and the swelling property during water absorption weakens. Therefore, when CMC/NVP are used for co-modification, the optimal amount of AMPS is 20% of the mass of acrylic acid, which is relatively appropriate.

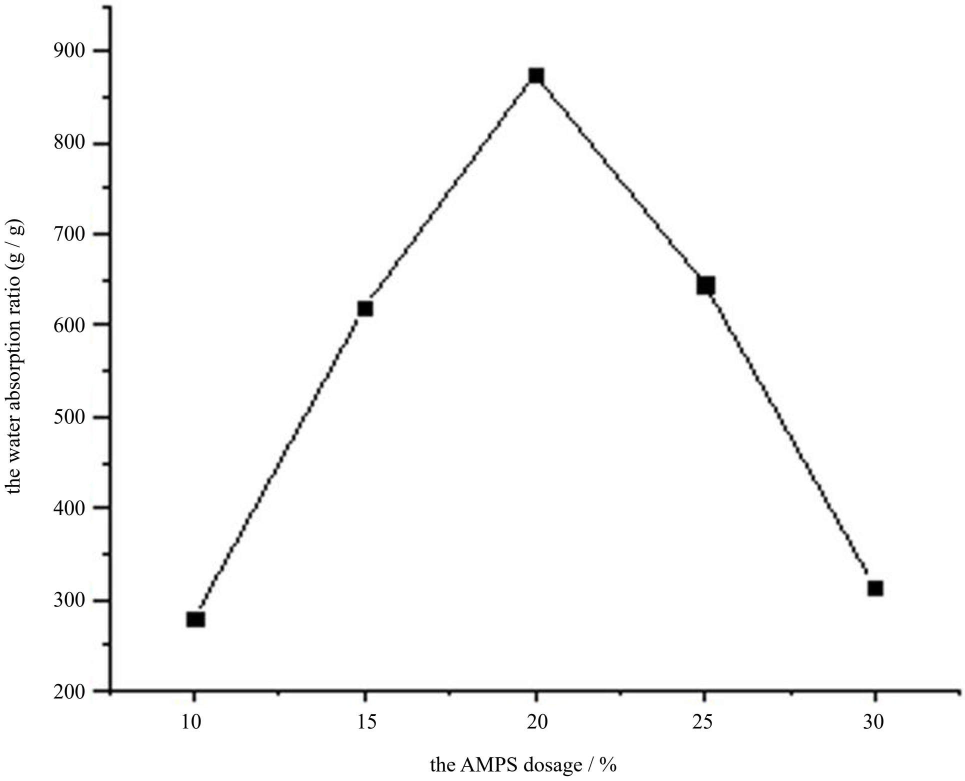
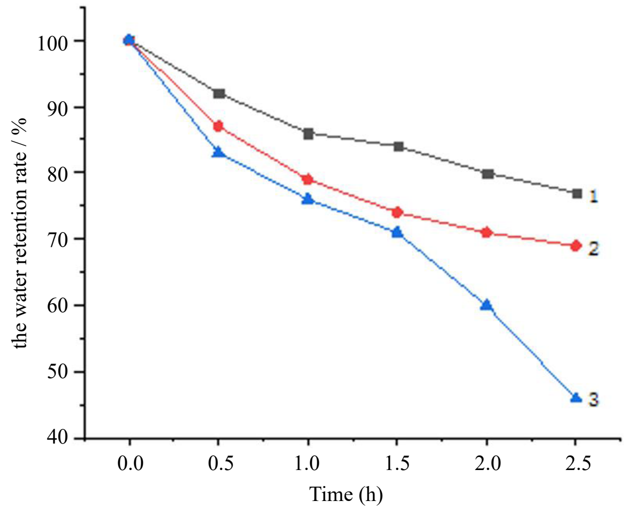


Figure 6. **Effect of AMPS modified CMC/AA dosage on water absorption rate of PAA**

2.7. Determination of the Water Retention Rate of PAA

Figure 7 shows the water retention performance of modified PAA. It can be seen from the figure that the water retention performance of modified PAA weakens with the increase in time. When the temperature is different, the water retention performance is also different and weakens with the increase in temperature. When the room temperature is 20°C, after 2.5 hours, the water absorption ratio of the superabsorbent resin becomes 567 g/g, and the water retention rate is 77%. While at 65°C, after 2.5 hours, the water absorption ratio of the superabsorbent resin is 340 g/g, and the water retention rate is 46% [15]. It can be seen that the influence of temperature on the water retention ability of the superabsorbent resin is quite obvious. Temperature will affect the stability of hydrogen bonds. The higher the temperature is, the fewer the number of hydrogen bonds will be, the weaker the water-locking ability will be, and the lower the water retention ability will be. Therefore, the lower the temperature is, the better the water retention performance of the superabsorbent resin will be.



(water retention rate at 1-20°C, water retention rate at 2-50°C, and water retention rate at 3-65°C)

Figure 7. **Effect of temperature on water retention performance of CMC-modified PAA**

2.8. Determination of the Repeated Water Absorption Performance of PAA

Figure 8 shows the research on the reusable performance of PAA. It can be seen from the figure that the water absorption ratio of PAA generally shows a downward trend with the increase in drying time. However, after the first drying, the water absorption ratio has a significant increase, reaching 1200 g/g. This is because when the resin absorbs water for the first time, due to the action of osmotic pressure, sodium ions in the resin permeate into the water, resulting in an increase in the concentration of sodium ions in deionized water, which will reduce the water absorption ratio and water absorption rate of the resin. In the subsequent drying and water absorption processes, the water absorption ratio of PAA generally shows a downward trend. After drying 4 times, the water absorption ratio of PAA can still reach 735 g/g, and the repeated water absorption rate is 84%, indicating that it can be reused.

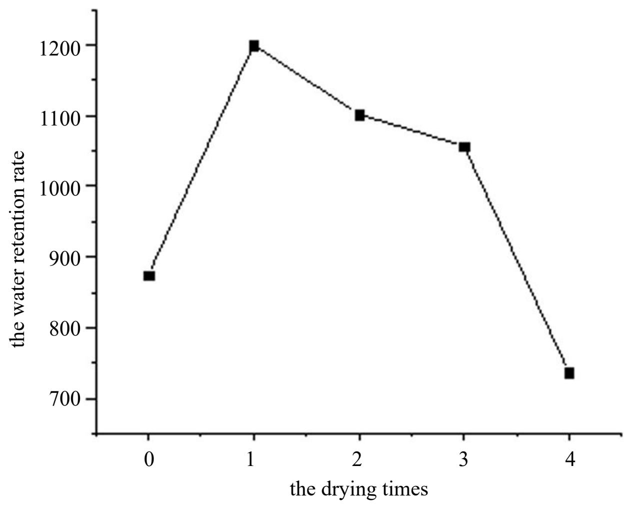
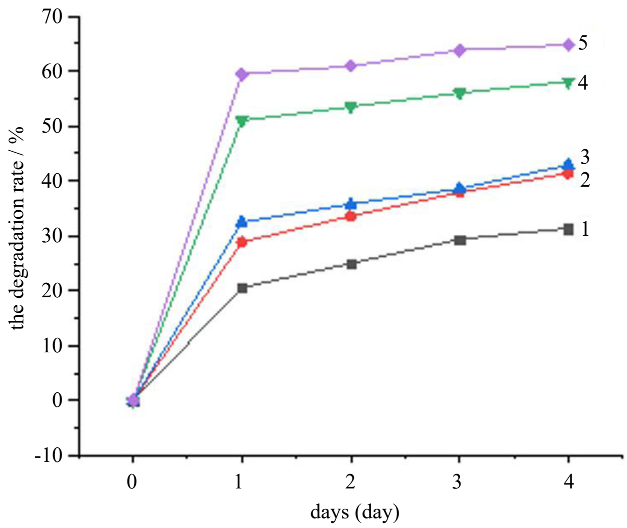


Figure 8. **Influence of drying times on repeated water absorption performance of PAA**

2.9. Determination of the Degradation Performance of Modified PAA

Figure 9 examines the degradation performance of CMC-modified PAA in 0.05% - 0.5% cellulase. The degradation rate of PAA in 0.05% cellulase is relatively slow, and the degradation rate after 4 days is 31.43%. However, with the increase in the concentration of cellulase, the degradation rate of modified PAA gradually accelerates, and the degradation rate in 0.5% cellulase is 64.8%, indicating that CMC modification can improve the degradation ability of PAA.



(1-0.05% cellulase, 2-0.1% cellulase, 3-0.2% cellulase, 4-0.3% cellulase, 5-0.5% cellulase)

Figure 9. **Effect of cellulase concentration on degradation performance of PAA**

2.10. Influence of Modified PAA and Chinese Herbal Medicine Powder on Fruit Preservation

In the control group, the detachment rate of grapes was 35%, and there were water droplets in the bag, and the water mist on the surface of grapes was quite obvious. However, when the composite preservative composed of Chinese herbal medicine and modified PAA superabsorbent resin was added, the detachment rate of grapes was only about 9%, and there were no water droplets on the surface of the bag or on the grapes, and the quality was good.

3. Conclusions

(1) The water absorption rate of CMC- and AMPS-modified PAA in deionized water increased from more than 480 times before modification to about 900 times after modification, and it had good water retention performance. It can be seen that the modification with CMC and AMPS can improve the water absorption and water retention abilities of acrylic resin.

(2) After the modified PAA superabsorbent resin was dried and reused five times, the water absorption ratio of the resin could still remain at about 730 g/g, indicating that the resin had good reusability.

(3) The degradation rate of CMC-modified PAA superabsorbent resin in cellulase could reach 64.8%, showing that the resin had degradable performance and thus was an environmentally friendly material.

(4) The composite material of modified PAA superabsorbent resin and Chinese herbal medicine powder can prevent the formation of water droplets during the low-temperature storage of fruits and inhibit the reproduction of bacteria, thus playing a role in fruit preservation.

It can be seen that the composite material of modified PAA superabsorbent resin and Chinese herbal medicine has water absorption, water-locking and antibacterial properties and can be used as a fruit preservative to reduce fruit losses.

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