Paper chemistry

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Application of CS-CHO-g-PMMA emulsion in paper reinforcement and protection

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Abstract: Paper has a high value of culture, history and scientific research as the cultural carrier of historical inheritance. However, with the passage of time and the change of environment, many paper files are aging and damaged. Therefore, it is of great significance to carry out the protection of paper archives. Chitosan, a natural material, has a good compatibility with paper fibers. In this paper, chitosan (CS) was modified by epoxy cyclohexane (CHO) and methyl methacrylate (MMA) to prepare CS-CHO-g-PMMA emulsion. CS-CHO-g-PMMA was applied to paper protection, and the effects of CS-CHO-g-PMMA on heat aging resistance, reversibility and acid-base resistance were investigated. In order to improve the mechanical strength of paper, CS-CHO-g-PMMA and phosphate ester starch (HPDSP) were blended to determine the optimum ratio. The results showed that the degradation rate of paper sample was slowed down obviously and the coating had certain reversibility. Acid-base resistance experiment showed that CS-CHO-g-PMMA could effectively resisit corrosion of external acid-base to protect the paper. The best combination ratio between CS-CHO-g-PMMA and HPDSP was: m (CS-CHO-g-PMMA): m (HPDSP) = 5:2. Under this compound ratio, the performance indexes of the paper met the requirements, conforming to the "repair as old, keep the original" and other requirements.

Keywords: chitosan; cyclohexene oxide; HPDSP; paper protection; reversibility.

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Introduction

Whether it is the relics handed down from ancient times or unearthed cultural relics, all of them suffer from displacement along with the evolution of history and the replacement of dynasties, and because of its uniqueness and non renewable nature (Liang et al. 2017), the protection of them is particularly important. Especially for the protection of paper-based cultural relics, because the raw material of paper-based cultural relics is plant fiber, its material is very thin and easy to be damaged, so the protection work is more difficult.

Paper has been the most important carrier of cultural information for many centuries, and paper and paper-based precious materials such as books, paintings, archives, etc. undergo deterioration and discoloration over time (Hong et al. 2019). The paper relics because of their slender and delicate material, easily affected of pathological changes by the environmental factors, are hard to be preserved for the cultural relics (Jin 2015). Furthermore, considerable research has shown that dust, insects and mould can damage the mechanical behavior and influence the appearance of paper (Li et al. 2013). Therefore, it is an urgent task to study the methods of paper protection and restoration and do a good job of paper file protection.

In recent years, polymer strengthening method (Princi et al. 2005, Princi et al. 2007, Cocca et al. 2014, Zervos and Alexopoulou 2015) is one of the hot spots in the field of paper file protection. By spraying the material on the surface of paper, the potential damage caused by external bad factors can be restrained or slowed down. However, the aging performance of ordinary polymer is not good, and it can not effectively protect paper documents for a long time. When the synthetic polymer material is used for paper cultural relics protection, the protection effect in the later stage of reinforcement treatment is not ideal and there are many shortcomings. For example, high molecular weight resin has poor wettability to paper fiber, which is easy to form concentration gradient on the surface of paper and inside of paper fiber, resulting in accelerated aging of paper (Li et al. 2013). And the high molecular weight resin is easy to form a film on the surface of the paper, thus changing the texture and appearance of the paper (Mariacristina et al. 2006).

Compared with synthetic polymer materials, natural polymer materials have unique advantages. For example, the biocompatibility (Xu et al. 2007, Hao et al. 2007) of natural polymer materials with paper is good, and the permeability and infiltration to paper fibers are good. Moreover, the natural polymer materials are rich in sources (Xie et al. 2007), non-toxic (Sinha et al. 2004) and renewable (Tang et al. 2016). However, the solubility and aging resistance of natural polymer materials are not satisfactory (Jaafar et al. 2011). It needs to be modified in order to be better used in paper reinforcement and protection.

In addition to providing the necessary strength support for the paper fiber, the protective material used for the paper reinforcement cannot introduce additional acid into the paper. The protective material must have good permeability and wettability, and can be wrapped outside the fiber to isolate the corrosive effect of harmful substances on the fiber. Chitosan is the only basic polysaccharide in natural polysaccharides. It contains free amino group and can combine with acid molecules. The main component of paper is natural fiber, which has good compatibility with natural polymer materials. When natural polymer materials are used for paper reinforcement, mutual exclusion of materials can be avoided.

In this paper, a new kind of chitosan derivative is studied. The derivative not only serves the purpose of strengthening and protecting paper, but also satisfies the principle of reversibility of protective materials and the principle of minimum intervention in paper preservation. It is expected to provide a new and economic and effective method for paper preservation and even paper cultural relics protection.

Materials and methods

Materials

Chitosan (viscosity 100–200 mP.s, the degree of deacetylation 95 %) was purchased from Introduction of Jinhu Crust Product CO., LTD (China). Dibutyltin dilaurate (DBTL), acetic acid glacial, methyl methacrylate (MMA), potassium peroxydisulfate (KPS), acetone, absolute alcohol, methyl alcohol (MeOH), N,N-dimethylformamide (DMF), benzene, dimethyl sulfoxide (DMSO), ethyl acetate, methylbenzene, were all purchased from Shanghai Aladdin Biochemical Technology co. LTD. All reagents were all analytical grade and used without further purification. Xuan paper was provided by China Xuan Paper Co., Ltd.

Preparation of CS-CHO-g-PMMA

The CS-CHO-g-PMMA was synthesized by one-pot method: a certain amount of CS (1 g) and 1 wt% dilute acetic acid (100 mL) were weighed and added to the four-port flask equipped with a condenser pipe, and then magnetic agitation was applied at the temperature of 40–50 °C with a stirring speed of 1500 r/min for 30 min. Then 0.06 g DBTL was added and stirred for another 5 min. After that, 5.5 g CHO was slowly added to the system drop by drop when the temperature rose up to 65 °C and a kind of light-yellow and transparent liquid was obtained after 7.5 h of continuous agitation. Next, the system was heated up to 75 °C, and 5 mL KPS-DSP aqueous solution (0.01 g/mL) was added to the reaction system with the protection of nitrogen and stirred for 15 min. After that, 2 g MMA was added and the reaction was terminated after stirring continuously for 4 h.

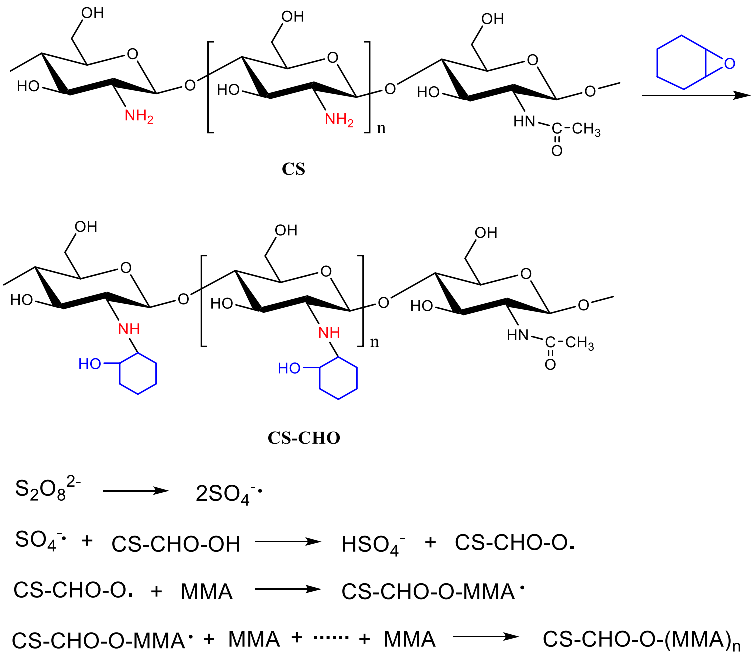
Preparation of paper samples

According to Jin's (Jin et al, 2019) research, we choose Xuan paper as the simulation paper to study the protective effect of the modified chitosan reinforcement solution. Xuan paper (Li et al. 2019) (or rice paper as it is known in the West) is a traditional Chinese handmade paper used by calligraphers and painters, made from the bast fiber of than tree (Pteroceltis tatarinowii Maxim) and rice straw. Firstly, the Xuan paper was cut into the size of 210 mm × 297 mm according to the curtain pattern. Next, two identical pallets were prepared, in which a layer of diluted CS-CHO-g-PMMA solution of different concentrations and the same amount of distilled water as a blank control were spread evenly, respectively. Having been immersed in the solution for 5 min, the paper sample was taken out and placed in an environment with stable temperature and humidity to dry naturally.

Analysis and testing methods

The tensile strength of paper was tested by the computer tensile testing machine according to the national standard GB/T 12914-2008, where the size of paper sample to be tested was 250 mm × 15 mm.

The folding endurance of paper was tested with a folding endurance tester according to the national standard



Scheme 1: The reaction mechanism of CS-CHO-g-PMMA.

GB/T 457-2008, and the size of paper sample to be tested was 140 mm × 15 mm.

The tearing strength of paper was tested with a computerized paper tearing instrument according to the national standard GB/T 455-2002, and the size of paper sample to be tested was 75 mm × 63 mm.

The G75-glossiness of paper was tested using a glossiness tester according to ISO 8254-3:2004, and the size of paper sample to be tested was 100 mm × 100 mm.

The R457-whiteness of paper was tested with a whiteness meter according to ISO 2470-2:2008, and the size of paper sample to be tested was 100 mm × 100 mm.

The dry-heat aging experiment was carried out at 105±2 °C according to ISO 5630-4:198. In this process, the original Xuan paper samples and samples treated with CS-CHO-g-PMMA were exposed to dry heat for 24 h, 48 h and 72 h respectively, and then the changes of mechanical properties (tensile strength, folding endurance, tearing strength) and optical properties (whiteness and glossiness) of aged paper samples were tested.

Reversibility experiment: a kind of organic solvent in which the material for paper reinforcement is soluble while the paper fiber itself is insoluble was selected. After being soaked in the solvent and dried, the weight of sized paper samples was measured every 1 h until the two weight losses before and after the soaking were less than 1 %, and the material can be considered as meeting the reversibility requirements (Del et al. 2019, Xu et al. 2020).

Acid and alkali resistance test: the paper samples were immersed in 0.1 mol/L HCl solution and 0.1 mol/L NaOH solution for 24 h, respectively. And then the acid and alkali resistance of paper samples were evaluated according to the changes of tensile strength, folding endurance and tearing strength before and after the treatment.

Results and discussion

The reaction mechanism of CS-CHO-g-PMMA

The reaction mechanism of CS-CHO-g-PMMA is shown in Scheme 1. Firstly, $-NH_2$ in the CS molecule combines with binds H^+ to protonize and become NH_3^+ in acidic media, and the molecular chain stretches gradually due to the repulsive effect of NH_3^+, making the active amino-group fully exposed outside of the CS molecule chain. By this time, CHO is added and the active amino-group rapidly binds to the active ternary epoxy group in CHO. Thus, CS-CHO is obtained by nucleophilic-cycloopen-addition reaction.

Next, free radical grafting polymerization is carried out in the system of KPS-DSP redox initiator to synthesize the CS-CHO-g-PMMA emulsion. Free radicals are firstly generated by the decomposition of KPS with a high decomposition speed. However, as a result of short life and easily being deactivated of the free radicals, this reaction should be carried out with the protection of nitrogen. Then, the free radical produced by the decomposition of KPS is transferred to the oxygen atom on the hydroxyl group of CS-CHO to form the CS-CHO-O· free radical. In this process, MMA hasn't been added to the system in order to prevent MMA from self-polymerization. When most of free radicals in the system exists in the form of CS-CHO-O·, MMA is added and the active species, CS-CHO-O·, begins to initiate MMA's polymerization. As a result, MMA containing active vinyl is grafted onto the long chain of CS-CHO.

In actual operation, the transparent CS-CHO solution becomes blue after MMA was added for about 5 min. With the passage of time, the blue gradually disappeared, and the white emulsion showing slightly blue was obtained eventually.

Effect of CS-CHO-g-PMMA on the mechanical properties of paper

The CS-CHO-g-PMMA emulsions diluted to different concentrations were coated on the surface of the paper samples, and then their mechanical properties (tensile strength, folding endurance and tearing strength) were tested. The test results are shown in Figure 1. The mechanical properties of the paper samples increase first and then gradually decrease with the increasing concentration of emulsions. The reasons are as follows: the emulsion with a low concentration has good fluidity and can fully fill in the gaps of the paper fibers, leading to the strengthening of the paper through thickening fibers; when the concentration is too high, the fluidity of the emulsion is poor, and it cannot penetrate well into the inside of the fibers, and it is more likely to remain on the surface of the paper, resulting in the uneven thickness of the paper. Such a paper was more likely to be damaged when impacted by external forces, so the paper strength becomes poor. Therefore, it is very important to choose a suitable dilution concentration when latex is applied. It can be seen from Figure 1 that when the emulsion concentration is 50 %, the mechanical properties of paper pattern are better, the tensile strength is increased by 69 %, the folding endurance is increased by 558 %, and the tear strength is increased by 15 %.

Effect of CS-CHO-g-PMMA on the optical properties of paper

The CS-CHO-g-PMMA emulsions diluted to different concentrations were coated on the surface of paper samples, and then their optical properties (G75-glossiness and R457-whiteness) were tested, as shown in Figure 2. With the increase of CS-CHO-g-PMMA emulsion concentration, the G75-whiteness of paper sample is basically unchanged, but its R457-glossiness decreases gradually. The reasons may be: when the concentration is high, the fluidity of the emulsion is less than that of diluted solutions. It is easy to form uneven film on the surface of the paper, which makes the smoothness of the paper worse, thus the glossiness is reduced.

Considering the influence of emulsion concentration on the mechanical properties (tensile strength, folding endurance and tearing strength) and optical properties (G75-glossiness and R457-whiteness) of the paper samples,

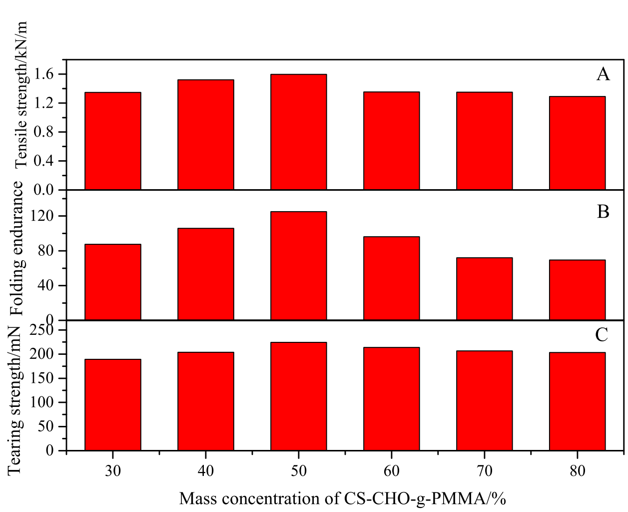


Figure 1: Effect of the concentrations of CS-CHO-g-PMMA on the tensile strength (A), folding endurance (B), and tearing strength (C) of paper.

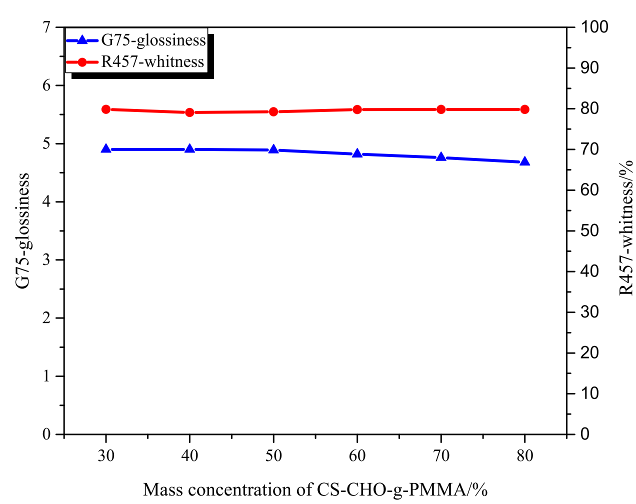


Figure 2: Effect of the concentrations of CS-CHO-g-PMMA on the glossiness and whiteness of paper.

50 % dilution concentration is selected as the appropriate concentration of paper sizing agent.

Accelerated aging test

The paper samples were treated with CS-CHO-g-PMMA emulsion with a mass concentration of 50 % and dried at room temperature. Then, the dry-heat aging tests were carried out at 105±2 °C to explore the effect of aging time on the mechanical properties of paper samples. The results are shown in Figure 3. According to the report (Li et al. 2014, Area 2011), the paper aged by dry heat at 105±2 °C for 3 days is equivalent to that of being stored at room temperature for 25 years.

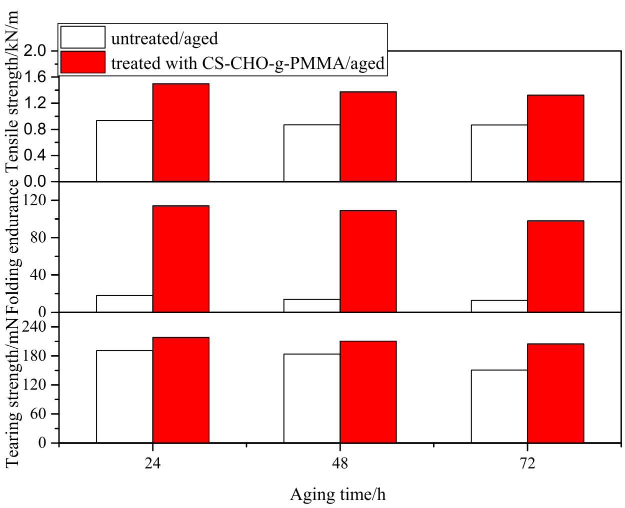


Figure 3: Effect of the aging time on the mechanical properties of paper.

It can be seen from Figure 3 that the mechanical properties of the blank paper sample are significantly reduced after the aging treatments of 24 h, 48 h and 72 h, while the G75-glossiness and R457-whiteness are basically unchanged. The decline of its mechanical properties can be attributed to the fact that dry-heat aging destroys the bond strength between the paper fibers, causing the fibers prone to fracture, and the paper sample's ability to resist the impact of external forces becomes poor.

Compared with the blank paper, the tensile strength, folding endurance and tearing resistance of coated paper increased by 53 %, 654 % and 36 % respectively after aging for 72 h, indicating that the paper had a certain aging resistance after coating with CS-CHO-g-PMMA. The reason may be that CS-CHO-g-PMMA can closely combine with paper fiber, which could not only improve the strength of paper sample, but also delay the degradation of paper fibers.

Table 1: Effect of the aging time on the optical properties of paper.

Aging time/h	24	48	72
G75-glossiness (untreated paper)	5.04	5.02	4.90
G75-glossiness (treated paper)	4.96	4.95	4.96
R457-Whiteness (untreated paper)/%	66.62	66.36	66.06
R457-Whiteness (treated paper)/%	68.72	68.84	68.53

The effect of aging time on the optical properties of paper sample is shown in Table 1. After aging, the G75-glossiness of coated paper is basically unchanged, but the R457-whiteness is increased. This may be because MMA, as a paper polish, can effectively improve the optical properties of paper after being introduced into the long chain of CS molecules. The aging of paper is due to the oxidation of hydroxyl group in the molecular structure of cellulose to carbonyl or carboxyl group, which leads to the yellowing of paper and the decrease of whiteness. However, the whiteness of the paper treated with CS-CHO-g-PMMA can still maintain a high level after aging for 72 h, indicating the paper treated with CS-CHO-g-PMMA has a certain aging resistance.

Reversibility experiment

The solubility of CS-CHO-g-PMMA in organic solvents was tested, and the results were shown in Table 2. According to Table 2, CS-CHO-g-PMMA is insoluble in other organic solvents, but soluble in DMF. Therefore, DMF was used as the solvent to conduct reversibility of aged paper samples after sizing. The weight of paper sample was measured every 1 h and the results were listed in Table 3.

Table 2: Solubility test of CS-CHO-g-PMMA.

Solvent	MeOH	ethyl acetate	acetone	benzene	methylbenzene	DMF	DMSO
Solubility	×	×	×	×	×	√	×

×represents insoluble in organic solvent.
√represents soluble in organic solvent.

Table 3: Weight change of the coated paper treated with DMF.

Soaking time of coated paper /h	1	2	3	4	5	6
Weight after soaking /g	2.90	2.86	2.80	2.75	2.71	2.70

The weight of blank paper is 2.7 g, and that of coated paper treated with CS-CHO-g-PMMA is 2.94 g. The weight change of coated paper after DMF treatment is shown in Table 3. It can be seen from Table 3 that with the increase of soaking time of coated paper in DMF, the weight of the paper sample decreases gradually. When the paper sample is soaked for 6 hours, the weight loss rate is 0.37 % < 1 %, and the strength of the paper sample after reversible test is 0.865 kN/m, which is not much different from the strength of the blank paper 0.866 kN/m, so the coating material is considered to be reversible.

Handwriting ink experiment

In order to evaluate the effect of CS-CHO-g-PMMA emulsion, the changes of handwriting and ink of Xuan paper before and after treatment with CS-CHO-g-PMMA were studied. The ink change of paper sample is shown in Figure 4. Comparing the two paper sample, we can draw the conclusion that CS-CHO-g-PMMA has basically no effect on handwriting ink, and the color and luster of paper remain unchanged. The handwriting of paper sample is clear and the ink does not diffuse.

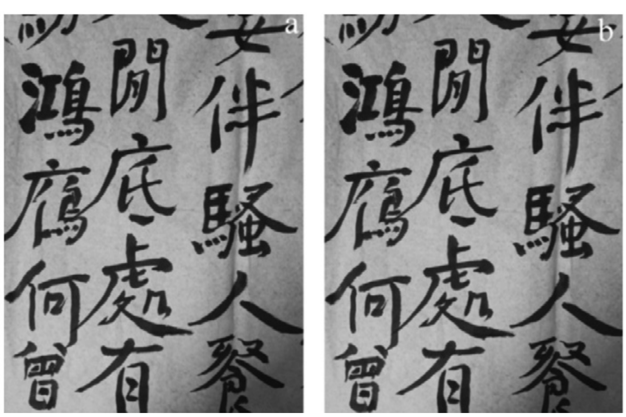


Figure 4: Handwriting ink pattern before and after sizing (pattern a before sizing and pattern b after sizing).

Acid and alkali resistance test

The paper samples treated with 50 % CS-CHO-g-PMMA are called coated paper, of which the results of acid and alkali resistance test are shown in Table 4. It can be seen from Table 4 that after the coated paper is immersed in 0.1 mol/L hydrochloric acid solution, its tensile strength, folding endurance and tearing strength decreases by 20.22 %, 16.8 % and 8.21 %, respectively. After being in immersed in 0.1 mol/L sodium hydroxide solution, the three parameters mentioned above reduces by 22.17 %, 24 % and 7.5 % in sequence. Nevertheless, the mechanical properties of paper sample are still higher than those of untreated paper. This may be due to the fact that CS-CHO-g-PMMA emulsion can effectively resist the corrosion of external acid and alkali to protect the paper.

Table 4: Acid and alkali resistance test results of coated paper.

Paper sample processing	Tensile strength /kN/m	Folding endurance /times	Tearing strength /mN
Untreated paper	0.945	19	194.6
Coated paper	1.597	125	224.32
Acid resistance test	1.274	104	205.9
Alkali resistance test	1.243	95	208.5

Compounding with phosphate starch and performance test

Phosphate starch exists in the form of sodium salt and is negatively charged in aqueous solution due to Na^+ ionization. It belongs to derivative of anionic starch, whose molecular structure determines its lower gelatinization temperature, higher viscosity and transparency, longer paste filament, and good dispersibility and anti-aging ability. Additionally, phosphate starch itself can be used as a strengthening agent for paperboard and a surface sizing agent for printing paper. It has obvious effect on improving the strength and elongation of paper. Hence, in order to further improve the mechanical strength of CS-CHO-g-PMMA and make the strength of the paper samples maintain at a higher level after sizing, phosphate starch (HPDSP) and CS-CHO-g-PMMA were selected to be used in combination.

The specific operation is as follows: 1 g HPDSP was added to 100 mL deionized water, and transparent gelatinized starch solution was obtained after gelatinizing at 75 °C for 1 hour. Then, it was diluted to 5 %, and mixed with 50 % CS-CHO-g-MMA according to different mass ratios. Next, paper samples were treated with the mixture and placed at room temperature to dry naturally. After that, the mechanical and optical properties of the paper samples were tested.

Table 5: Mechanical properties test of paper.

Mass ratio of CS-CHO-g-PMMA to HPDSP	Tensile strength (kN/m)	Folding endurance (times)	Tearing strength (mN)
0:0 (Untreated paper)	0.945	19	194.6
5:0 (without HPDSP)	1.597	125	224.32
5:1	1.912	263	314.6
5:2	2.312	578	565.9
5:3	2.461	786	576.2
5:4	2.648	1005	586.5

Mechanical properties test of paper

The test results of mechanical properties of the paper sample treated with composite reinforcement fluid are shown in Table 5. When HPDSP is not included in the reinforcement fluid, the paper's tensile strength is 1.597 kN/m, folding endurance is 125, and tearing strength is 224.32 mN. After the addition of HPDSP, the mechanical properties of the paper sample are obviously improved with the amount of HPDSP increasing. This may be attributed to the fact that the strength and toughness of HPDSP gelatinizing solution are better, and the mechanical properties of paper samples increase significantly after the compound strengthening solution is applied.

Optical properties test of paper

After paper sample was treated with composite reinforcement solution, the optical properties of the paper sample were tested. The results are shown in Table 6. With the amount of HPDSP solution increasing, the R457-whiteness of paper sample basically remains unchanged, but its G75-glossiness gradually decreases. This may be due to the fact that when the HPDSP solution is added in a large amount, the viscosity of composite reinforcement solution is large and fluidity is poor. After drying, the surface of paper sample is obviously wrinkled and uneven, and the smoothness of paper sample becomes poor, so G75-glossiness decreases.

Table 6: Optical properties test of paper.

Mass ratio of CS-CHO-g-PMMA to HPDSP	G75-glossiness	R457-Whiteness/%
0:0 (Untreated paper)	4.90	80.70
5:0 (without HPDSP)	4.96	80.24
5:1	4.96	80.32
5:2	4.95	80.30
5:3	4.80	80.28
5:4	4.50	80.24

Considering the changes of mechanical and optical properties of paper, the mass ratio of the composite reinforcement fluid is determined to be 5:2, under which the mechanical properties of paper sample are significantly enhanced and the optical properties are basically unchanged.

Conclusion

CS-CHO-g-PMMA emulsion was synthesized by one-pot method and applied to the paper sample, and its mechanical properties were tested. The test results showed that when the mass concentration of CS-CHO-g-PMMA was 50 %, the tensile strength, folding endurance and tearing strength of the paper were increased by 69 %, 558 % and 15 %, respectively. After aging for 72 hours, the tensile strength, folding endurance and tearing strength of paper sample increased by 53 %, 654 % and 36 %, respectively, indicating that the paper has certain aging resistance. The reversibility experiment showed that CS-CHO-g-PMMA had a certain reversibility, and the acid and alkali resistance experiment showed that CS-CHO-g-PMMA can effectively resist the corrosion of external acid and alkali to protect the paper. In order to further improve the mechanical properties of the emulsion, HPDSP was mixed with CS-CHO-g-PMMA. It was found that the mechanical strength of the paper was significantly enhanced when the mass ratio of HPDSP to CS-CHO-g-PMMA is 5:2, which played a role of reinforcement and protection, and satisfied the guiding principle of "repairing the old as the old and keeping the original appearance".

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