Modified Natural Polymer Materials for Paper Protection

Xuemei Wang[1], Shanshan Jin, Yingping Qi[2], Hua Li*

[1]Zhengzhou University, Zhengzhou, Henan,450001

[2]Zhengzhou Museum, Zhengzhou, Henan,450000

Abstract

Natural polymer materials, such as cellulose, chitosan, starch, are compatible with paper fiber, which can be used for paper reinforcement. However, due to the poor performance of aging, flexibility, adhesion, it needs to be modified. The progress of the modification of some natural materials in paper artifacts protection is introduced. Research and application of some natural materials in paper artifacts protection is summarized. And the development prospects of paper artifacts protection are also discussed.

Keywords: Natural polymer materials, cellulose, chitosan, starch, modification, paper artifacts protection

Introduction

Synthetic polymer materials are used for the protection of paper artifacts, which is popular research focus of paper heritage conservation in recent years. However, the protective effect of most polymer materials is not satisfactory [1]. What's more, there are many shortcomings in the use of synthetic polymer materials for the protection of paper relics. For example, the resin of high molecular weight is easy to cause a concentration gradient on the surface and inside of cultural relics, with poor permeability and infiltration, which speeding up paper aging; and the resin glue is easy to form film on the surface of paper to make the texture and appearance change. As a result, it is difficult to meet the requirements of "repairing the old and maintaining the original appearance" in the protection of cultural relics.

Compared with the synthetic polymer materials, natural polymer materials have their unique advantages. Natural macromolecule material not only has good compatibility with paper, good permeability and infiltration for paper fiber, but also abundant source, nontoxicity and innocuousness and strong reversibility. However, due to the poor solubility and aging resistance of natural polymer materials, it needs to be modified to apply to the protection of paper relics.

1. Modified cellulose for the protection of paper artifacts

Cellulosic chemical modification mainly depends on the reaction related to cellulose hydroxyl groups [2]- [5]. Since each glucose unit in the cellulose chain has three polar hydroxyl groups, cellulose can undergo a series of reactions involving hydroxyl groups, mainly including esterification, etherification, graft copolymerization and other reaction process, which is called cellulose derivatization. Through etherification and esterification, the properties of cellulose can be significantly changed. Many new products are prepared, such as hydroxyethyl cellulose, cyanoethyl cellulose, cellulose acetate and other products, with transparent, colorless, high-intensity, anti-aging. Cao Yuhong studies the modification of hydroxyethyl cellulose, cellulose acetate butyrate and modifided cellulose can be applied to the protection of paper cultural relics [6]. The results show that the comprehensive

performance of CAB-MCHT grafts is good by comparing the appearance test, tensile strength test, flex resistance test, and aging test data. When its concentration is 2%, the tensile strength of paper samples is increased by 86% and the folding resistance is increased by 78 times, and the tensile strength and folding resistance of the paper samples after the accelerated aging are smaller which is retained after grafting with chitosan. At the same time, better water absorption and air permeability of chitosan was obtained, which not only improves the deficiency of CAB, but also has no obvious effect on the appearance of the paper, according with the principle of"repair the old as the old".

Xu Leilei prepares MEPDM using orthogonal selection test, which is used as raw material to modify CAB [7]. The research results show: CAB-g-MEPDM glue has better comprehensive protection effect. When the glue concentration is 2%, the tensile strength of the paper sample is increased by nearly 90% compared with that of the blank paper sample, and the folding endurance is increased 78 times. After the dry heat aging test, the tensile strength and bending strength loss values of the paper samples are also smaller. According to the comprehensive impact analysis, the sizing does not cause great disturbance to the paper pattern, which accords with the requirements of cultural relic protection "repair the old as the old and keep the original appearance".

Cellulose acetate butyrate (CAB), which is transparent and colorless, not only has excellent hydrophobicity, solubility, flexibility, wear resistance, anti-pollution ability and weather resistance but also has certain air permeability. Chitosan, which is a derivative of chitin deacetylation, is a kind of natural material, with highly absorbent, breathable, mold-resistant and antibacterial. The molecular structure of chitosan contains free active amino and hydroxyl groups, therefore, they can be carried out cross-linking, acid sulfonation, carboxymethylation, alkylation, nitration, redox and complexing reaction. Cao Yuhong *et al*. study the graft copolymerization of cellulose acetate butyrate and chitosan[8], which is applied to the surface of the paper with a proper amount of crosslinking agent. In this paper, the test and analysis of anti - tensile strength, anti - drying heat accelerated aging and glossiness are carried out respectively. The results show: after the glue protection, the paper maintains the original texture, gloss and color; tensile strength and folding resistance are significantly improved. It is proved that the protective glue which is mainly composed of cellulose - chitosan grafting products has obvious protective effect on paper cultural relics.

Microcrystalline cellulose (MCC), as an important derivative of cellulose, is widely used in medicine, food, cosmetics, chemical industry and other fields. The source of MCC is abundant. It has the advantages of biodegradability, low cost, reproducibility and good mechanical properties. MCC is modified by silane coupling agent to obtain better dispersion and hydrophobicity because of the poor dispersion of the polar surface of MCC in nonpolar solvents. Chen Qian uses modified MCC, modified nano-TiO2 and organic fluorine to jointly modify the styrene-acrylic emulsion to prepare a series of microcrystalline cellulose-titania-fluoro-styrene-acrylic copolymer composites [9]. After analyzing the properties of the emulsion and membrane, the composite material has good dispersibility, homogenization and stability. Its viscosity is between 16m Pa·s and 29m Pa·s, and the surface tension is small, which can penetrate into the paper and fully protect the paper fiber. The membrane has good water resistance (water absorption is as low as 7.3%), hydrophobic and oil-repellent, which can prevent paper artifacts from being contaminated by water and oil. After the simulation and dry-heat aging experiments, the results show that the composite material can effectively slow down the aging rate and can effectively protect the paper artifacts for a long time, and the reversible experiment can remove the protective material in time when it is not used.

2. Modified chitosan for the protection of paper artifacts

Chitosan molecules are linear polymers, with good film formation and sufficient adhesive strength to fibers that can bridge brittle fibers. The molecular chain has many positive charge centers and hydrogen bond centers, which are easy to combine with the negative charge on the fiber to form ionic bonds, and can form hydrogen bonds on the non-ionic surface of the fiber to improve the strength of the paper. Its chemical structure is similar to cellulose, and has good adsorption and compatibility and affinity with fiber. Besides, it is non-toxic and pollution-free, with anti-mildew, antibacterial and other functions. Based on the above features, chitosan is used to reinforce the protection of paper artifacts.

Chitosan is the deacetylation product of the second largest natural polymer chitin. Its amino and hydroxyl groups have strong chemical activity, which can carry out various chemical modifications, such as hydroxy alkylation, alkylation, acylation, etc. And cyanoethylation of chitosan has also greatly expanded its use. Lu Shan *et al.* performe cyanoethylation modification of chitosan and use cyanoethylated chitosan for the protection of paper cultural relics [10]. Not only the original gloss, texture and color of the paper samples were maintained, but also the folding endurance was improved 5.5 times and the tensile strength was increased by 67%. This result breaks broad prospects for the cultural relics protected by natural polymers .

Paper cultural relics reinforcement protection materials, in addition to providing certain strength of paper fibers, must not bring extra acid to the paper and must have good penetration and wetting properties, which can be wrapped on the outside of the fiber to cut off the contact between harmful substances and fibers. Sun Zhenqian *et al.* adopt a heterogeneous polymeric method to prepare the chitosan water-soluble derivative—Hydroxypropyl Chitosan (HPCS)—by grafting the modified chitosan with propylene oxide, which applied to reinforce paper artifacts [11]. The hydroxypropyl chitosan obtained by the test has good water solubility. After treated with hydroxypropyl chitosan, the tensile strength of the paper is increased by 30% to 85%, and the folding endurance that is increased by 20% to 37%. Among them, when the mass fraction of hydroxypropyl chitosan is 20%, the tensile strength and folding resistance increased greatly. After the protection, the appearance of the paper pattern was basically unchanged, following the principle of "repairing the old as the old ". Hydroxypropyl chitosan has advantages such as good compatibility with paper fibers, reinforcement and no damage to the paper.

In addition to the above-mentioned chitosan modification, some people have successfully developed a kind of multifunctional protective glue solution on the basis of modification. For example, Qiu jianhui *et al.* study a kind of multifunctional protective gluesolution, which consists of modified fluorine resin, modified chitosan, oligomeric materials and nano-materials [12]. The whiteness, thickness, bending strength and tensile strength were tested, as well as differential thermal, infrared, ultraviolet, scanning electron microscopy were analyzed respectively, which were used in practice. The experimental analysis and application results show that the adhesive solution can preserve the original color and texture of paper relics. And it has many kinds of protection functions such as fiber thickening, powder consolidation, brittle fracture strengthening, anti-mildew and antibacterial.

Duan Dacheng studies the interaction of bacterial cellulose and chitosan to reinforce paper artifacts [13]. Experiments use different concentrations of chitosan and bacterial cellulose to treat paper samples, and the effects of different combinations of concentrations on the paper's indexes are measured. The results show that

the combination of 1.0% chitosan and 1.0% bacterial cellulose is the optimal result, compared with blank paper, which can significantly increase paper pull strength and paper tear. At the same time, there is no obvious effect on the gloss and whiteness of the paper.

A patent invented by Wang Junlong *et al.* relating to the preparation of a chitosan-calcium hydroxide composite material [14]. In the materials, chitosan has good compatibility with paper, which will not damage paper relics, and it has good permeability and wettability to paper fibers. Calcium hydroxide can absorb carbon dioxide from the air to generate calcium carbonate, which can effectively prevent air interact with paper, making the paper have good aging performance and not affecting the paper texture. Such a new kind of paper cultural relic reinforced material has good application prospect.

3. Modified starch for the protection of paper artifacts

Starch has been widely used in the paper industry, but it has not been reported in the protection of paper cultural relics. Natural starch is a water-soluble polymeric material, with certain adhesion, film formation and other properties, which is applied to some paper adhesive. However, this feature is very limited, especially not suitable for the harsh requirements of paper cultural relics protection. Therefore, the modified starch grafting is usually prepared to strengthen the protection of paper cultural relics [15].

Xu Leilei prepared starch grafted butyl acrylate/trifluoroethyl methacrylate (ST-g-BA/TFEMA) to reinforce and protect paper artifacts [16]. ST-g-BA / TFEMA glue has obvious influence on the mechanical strength of paper samples. Compared with blank paper samples, the tensile strength of the treated paper increases by nearly 1 times, and the folding endurance increases by 5 times. In particular, the resistance to dry heat accelerated aging of the treated paper samples is excellent.

Starch and its derivatives have the advantages of abundant resources, low price, chemical modification and biodegradation. The original starch slurry has a rigid ring structure of macromolecular chains and polar hydroxyl groups. Cyanoethyl starch can be prepared by introducing cyanoethyl groups into its macromolecules. Moreover, according to the substitution degree, cyanoethyl starch is widely used in paper making and textile industry, and can also be used as adhesives or fillers.

Fei Guiqiang *et al.* use cassava starch and acrylonitrile as raw materials to prepare cyanoethyl starchin alkaline medium, and use acrylamide to graft cyanoethyl starch to prepare a reactive reinforcing agent [17]. The experimental results show that the ring pressure and tensile strength of the paper are increase by 37.8% and 42.1%respectively, when the amount of the agent is about 0.4%. Zhuo-ni wang and guang-hua zhang respectively use cyanoethylated starch and acetyl oxide cyanoethylated starch (that is, the multivariate composite modified starch) to surface sizing of paper, both of which improve paper folding degree, smooth degree and tensile strength [18]- [19]. Nie Wangyan *et al.* oxidize the corn starch to make its molecular weight moderate and introduce larger carboxyl groups. Then it is cyanoethylated to introduce cyanoethyl, which significantly reduce the gelation due to hydrogen bonding between molecular chains. The results show that the modified products have the characteristics of strong initial adhesion, good storage stability and fast drying speed, which are more suitable for paper adhesion [20].

To whom correspondence should be addressed. E-mail: lihua@zzu.edu.cn Fax: 0086-371-63886154. Present address: School of Chemical and Energy Engineering, Zhengzhou University, No.100 Science Road85, Zhengzhou, Henan, China, 450001

4. Conclusion

The main strength support of paper artifacts is natural fiber, which has good compatibility and affinity with natural polymer materials. The use of natural polymer materials, as the main material of glue liquid, can avoid the mutual exclusion of materials during the process of reinforcement and protection. At the same time, Natural polymer materials are more sustainable because they are derived from natural renewable resources such as plants and animals.

5. References

1. Wang R, Li Y H, Huang S P, et al. On application and Requirements of Organic Polymer Materials in Cultural Relics Preservation[J]. Protection of human cultural heritage, 2011(00):20-25.

2. Zhang Z. Research progress in cellulose modification[J]. Chemical Industry & Engineering Progress, 2010, 29(08):1493-1501.

3. An H Y, Yang J Z, Guo C S. Research progress in cellulose modification[J]. Journal of chengdu textile college, 2016, 33(03):160-163.

4. Luo C, Wang H, Chen Y. Progress in modification of cellulose and application[J]. Chemical Industry & Engineering Progress, 2015, 80(04):416-428.

5. Liu C, Tan Z, Li H M, et al. Research Progress in Cellulose Extraction, Modification and Application[J]. Materials Science Forum, 2016, 852:1194-1200.

6. Cao Y. Research on Application of Multifunctional Protective Glue of Paper Cultural Relics[D]. Nanjing University of Aeronautics and Astronautics, 2008.

7. Xu L. Experimental Study on Protection of Paper Cultural Relics by Modified Natural Materials[D]. Nanjing University of Aeronautics and Astronautics, 2011

8. Cao Y, Qiu J H, Zhu z, et al. Study on the Conservation of Paper Based Historic Relics by Cellulose-chitosan Graft Product. China Pulp & Paper, 2008, 27(03):32-35.

9. Chen Q. Preparation of cellulose derivative modified polyacrylate composite and its application in paper cultural relic protection[D]. Jiangsu University, 2017.

10. Lu S, Qiu J H, Zhao Q, et al. Study on the conservation of paper historic relic by cyanoethylated-chitosan[J]. Sciences of Conservation and Archaeology, 2006, 18(03):1-4.

11. Sun Z, Qiu J H, Xu F Y, et al. Study on the Conservation of Paper Relic by O- (Hydroxyl Isopropyl)Chitosan[J]. Chemistry&Bioengineering, 2005, 22(01):39-41.

12. Qiu J, Lu S, Peng C, et al. Glue for Reinforcing Protecting Paper Historic Relics[J]. Journal of Nanjing University of Aeronautics and Astronautics, 2006, 38(01):126-130.

13. Duan D. Study on the Application of Bacterial Cellulose and Chitosan in the reinforcement and Anti-mildew

Protection of Paper Cultural Relics[D]. Liaoning University, 2017.

14. Wang J, Lv H, Ding Y Z, et al. Chitosan-Calcium Hydroxide Composite Material and Its Preparation and Application as Paper Reinforcing Agent[P]. Gansu:CN104727186A, 2015-06-24.

15. Xiao Y, Cai Y, Liu M, et al. Application of Modified Starch in Pulp and Paper Industry[J]. Paper Science & Technology, 2015, 34(01):61-65.

16. Xu L. Experimental Study on Protection of Paper Cultural Relics by Modified Natural Materials[D]. Nanjing University of Aeronautics and Astronautics, 2011.

17. Fei G, Shen Y D, Wang H, et al. Preparation and application of acrylamide grafted cyanoethyl starch as paper dry strengthening agent[J]. China Pulp & Paper Industry, 2010, 31(14):37-40.

18. Wang Z, Zhang G H, Zhun J. Preparation of Cyanoethyl Starch and its Application in Surface Sizing[J]. China Pulp & Paper Industry, 2006, 25(04):9-11.

19. Zhang G, Wang Z N, Li H. Preparation and Application of Oxidized Acetyl Cyanoethylated Starch as Surface Sizing Agent[J]. China Pulp & Paper Industry, 2007, 26(06):19-22.

20. Nie W, Zhou Y F. Study on the oxidic cyanoethylated corn starch adhesive[J]. Journal of Anhui University Natural Science Edition, 2006(05):74-77.