Paper chemistry

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A transparent polyurethane based on nanosilica in reinforcing papers

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Abstract: Paper has been the most significant carrier of written information for many centuries. To prolong the life expectancy of papers, the polyurethane based on nanosilica was used to strengthen the paper fibers in this work. The relation between the mass concentration of polyurethane based on nanosilica and the specific properties of papers (e. g., folding endurance, tensile strength, tearing strength, whiteness and glossiness) were investigated. In addition, the effect of polyurethane based on nanosilica on the acid/alkali resistance and ageing resistance were studied. The results showed that polyurethane based on nanosilica could significantly improve the mechanical properties and ageing resistance of papers.

Keywords: nanosilica; paper protection; polyurethane.

Introduction

Paper as the most important carrier of information has been used for nearly 2000 years. It is estimated that libraries and archives worldwide currently store approximately 2.5 million km of works on paper (Vohrer et al. 2001, Camargos et al. 2017). But over time, papers influenced by internal and external environment conditions such as climate, pollution, biological agents, and mechanical stresses (Bégin et al. 1999, Conio 2001, Larsson and Wågberg 2008, Afsharpour and Imani 2017). It results the loss of mechanical strength of paper is mainly due to the acid-catalyzed depolymerization of cellulose of paper fiber. In order to slow down these degradation processes, a suif treatment needs to be specifically designed for the reinforcement and protection of paper.

Many countries have developed measures to prevent further aging of paper cultural relics, such as mounting methods, low temperature dewarming techniques (Melo et al. 2019), plasma deacidification methods (Li et al. 2014b), and electrospinning techniques (Li et al. 2014a). However, these above methods often suffer from the disadvantages, such as high cost, poor mechanical properties and hydrophobicity, which limiting the scope of its application.

In recent years, polymer coating protection technology is to apply high-quality coating on the surface of paper to form a protective film (Piovesan et al. 2014, Jin et al. 2019, Xu et al. 2020). Developing simple and environmentally friendly processes to prepare organic polymeric compounds is received increasing attention (Stuart et al. 2010, Ye et al. 2015). Acrylic resin (paraloid B72) is the most commonly used material (Cocca et al. 2004, Favaro et al. 2007). Chen prepared modified carboxymethyl cellulose/Si/polyacrylate protective materials, which have good hydrophobicity, acid/alkali resistance and mechanical strength (Chen et al. 2016). Qiao et al. had studied the reinforcement of paper by poly(methyl methacrylate-co-butyl acrylate-co-styrene), and results showed some of the mechanical properties of the treated paper were significantly improved (Qiao et al. 2017). All the materials possess advantages and have an important role in preserving paper, albeit with inherent disadvantages. Hence, an efficient, harmless and effective method for the conservation of paper relics is urgently needed.

Nanomaterials have been frequently applied to conservation of cultural relics due to their particular characteristics in recent years (Allen et al. 2002, Giorgi et al. 2002, Bonini et al. 2007). Strengthening fragile paper with nanosilica which is non-toxic and tasteless should be a good option. It is transparent when it is dispersed uniformly in solution because of the particle size of it is small, so it will not affect the color and appearance of paper when it is used in paper reinforcement.

To the best of our knowledge, there is currently no report on the use of polyurethane based on nanosilica to strengthen paper. In the present work, we synthesized

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polyurethane by nanosilica and hexamethylene diisocyanate (HDI) trimer applied to protection of paper. In this way, the mechanical properties of paper were improved significantly.

Materials and methods

Materials

Nanosilica, Ditin butyl dilaurate, Ethyl acetate were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All these chemicals were of analytical grade and used without further purification. HDI trimer was industrial grade and was purchased from Bayer (Germany). Xuan paper was produced from pulped bark fibres of blue sadalwood mixed with a rice straw (Oryza sativa) that grows in silica-rich land and purchased from Xuan Paper Company Group (Anhui, China).

Tensile strength Tester, PN-TT300, Folding endurance Tester, PN-NZ135, Glossiness Meter, PN-GM, Brightness Tester, PN-48B, are all from Hangzhou Pinghong Technology Co., Ltd.

Synthesis of polyurethane

Nanosilica was placed in a vacuum drying oven for 10–24 hours to remove moisture. (HDI) trimer and dried nanosilica were added to ethyl acetate and 1 % dibutyltindilaurate was added based on the total weight of reactants. In the reaction, the content of isocyanate (-NCO) was determined at regular intervals, and the reaction was terminated when the content of isocyanate (-NCO) reached 10 %.

Treatment of paper

Both sides of paper samples were immersed in the polyurethane liquid (polyurethane dispersions in ethyl acetate solution) for 2~5 min, and then they were collected with tweezers and left in suspension in dry air at room temperature for 24 h. For comparison, the papers were also immersed in ethyl acetate and nanosilica dispersed in ethyl acetate under the same conditions.

Measurement of -NCO content

The content of -NCO was determined by dibutylamine–hydrochloric acid method (Zhang and Cao 2016). The principle of the reaction is that -NCO in the polymer reacts with dibutylamine to obtain a new compound urea, and then the standard solution of HCl is used to titrate the unreacted dipositrine in the system. The method of operation is as follows:

$$\mathrm{NCO}\,\% = \frac{(v_2 - v_1) \times C \times 42.02}{m \times 1000} \times 100\,\%$$

where v_1 represent the volume of the HCl standard solution required for the titration blank test, ml; v_2 represent the volume of HCl standard solution consumed by the sample, ml; c represent the concentration of HCl standard solution, mol/L; m represent sample quality, g.

Analysis and testing methods

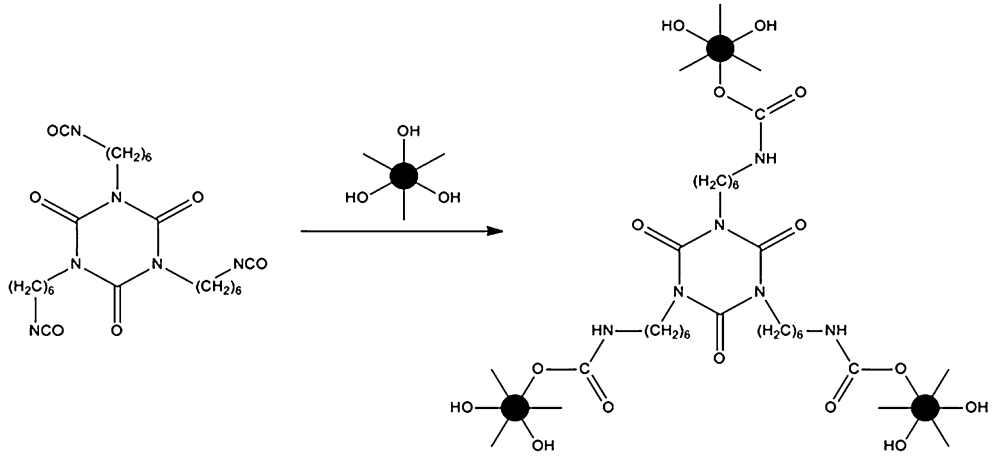
The tensile strength of paper was measured according to the Chinese National Standard GB/T12914-2008 (ISO 12914-2: 1994, MOD) by PN-TT300 at a speed of 20 mm per minute. The paper samples were 1.5 cm in width and 24.0 cm in length. The folding endurance of paper was measured by PN-NZ135 double fold instrument, with a force of 9.8 N according to the Chinese National Standard GB/T 457-2008 (ISO 5626: 1993, MOD). The test specimens' width was 1.5 cm and length was 15.0 cm and the applied force was 4.91 N. The tearing strength of paper samples (5.0 cm in width and 6.5 cm in length) was determined according to Chinese standard GB/T 455-2002 (eqv ISO 1974: 1990) by PN-TT1000. All the measurement use machine direction of papers.

The gloss of paper was measured by a PN-GM Glossmeter with 75° geometries according to the Chinese National Standard GB/T 8941-2013 (ISO 8254-1-2009, MOD). The brightness of paper was measured according to Chinese standard GB/T 7974-2002 (ISO 2470: 1999, MOD) by a brightness tester (PN-48B). The configuration adopted was in reflectance mode (spectral range 457 nm in 10 nm steps), and the brightness was represented with R457 in this paper.

Results and discussion

The reaction mechanism

The polyurethane was synthesized by low molecular weight HDI trimer and nanosilica, and applied to protection of paper. The reaction mechanism is shown in Scheme 1. As seen from Scheme 1, isocyanate group in HDI trimer show high reactive ability with hydroxyl groups of



Scheme 1: Reaction mechanism.

nanosilica under the dibutyltindilaurate as catalyst. Carbamate bonds also can replaced the hydrogen bonds in the fibers, enhance the bonding force in the paper fiber.

Effect of polyurethane liquid on the mechanical property of paper

The mechanical properties of paper samples coated by different concentrations of polyurethane were studied and results are presented in Figure 1.

It can be seen that the polyurethane significantly enhanced the value of tensile property (tensile strength and elongation). From Figure 1(a), the tensile strength of the paper coated by polyurethane liquid grows gradually with the increase of mass concentration. Specifically, the tensile strength of coated paper reached a maximum when the polyurethane content was increase above 10 %. This phenomenon is considered to be the result of some negative factors caused by the increase of polyurethane content, such as the poor dispersibility, the enlargement of particle size, the decease of mutual interaction and so on.

Elongation is also regarded as another important tensile strength of paper. The effects of the mass concentrations on the elongation are shown in Figure 1(b). With the increase of mass concentration of polyurethane, the elongation shows the same increasing trend as tensile strength. It is due to the fact that carbamate bonds replaced the hydrogen bonds in the fibers, enhance the bonding force in the paper fiber. However, when the paper coated by a higher concentration of polyurethane, the appearance such as glossiness and brightness, compared with the uncoated paper, could change significantly.

The folding endurance of papers coated by different concentrations of polyurethane is depicted in Figure 1(c). It can be observed that the folding endurance of coated paper is higher than those of blank paper samples, which means that the fibers of coated paper are more capable of keeping the original flexibility, compared with the blank paper samples, during the process of folding. As shown in Figure 1(c), the folding endurance of paper first increased and then decreased with the increase of mass concentration. When the mass concentration of polyurethane is 10 %, the folding endurance of coated paper is approximately 67 times higher than that of uncoated paper. Subsequently, the folding resistance began to decrease with the mass concentration continued to increase. This phenomenon is probably considered to be the result that the folding endurance, to some extent, is associated with the thickness of the paper. The increased thickness of paper could result rigidity, which was found in a previous research (Souguir et al. 2011). When the mass concentration is higher, the paper will uptake more polyurethane, and the thickness of paper will increase, shown in Table 1, so the folding endurance of paper will decrease.

G75 represent the various glossiness of paper, which was measured at 75°. Brightness of R457 represent the papers refection ability of the light around 457 nm.

Tearing strength of paper is mechanical rupture process initiated and propagated at a high stress concentration causing a cut. The effects of mass concentration on the tearing strength are shown in Figure 1(d). With the increase of mass concentration, the tearing strength first increase and then decrease. Specifically, the tearing strength of paper, reached a maximum when the mass concentra-

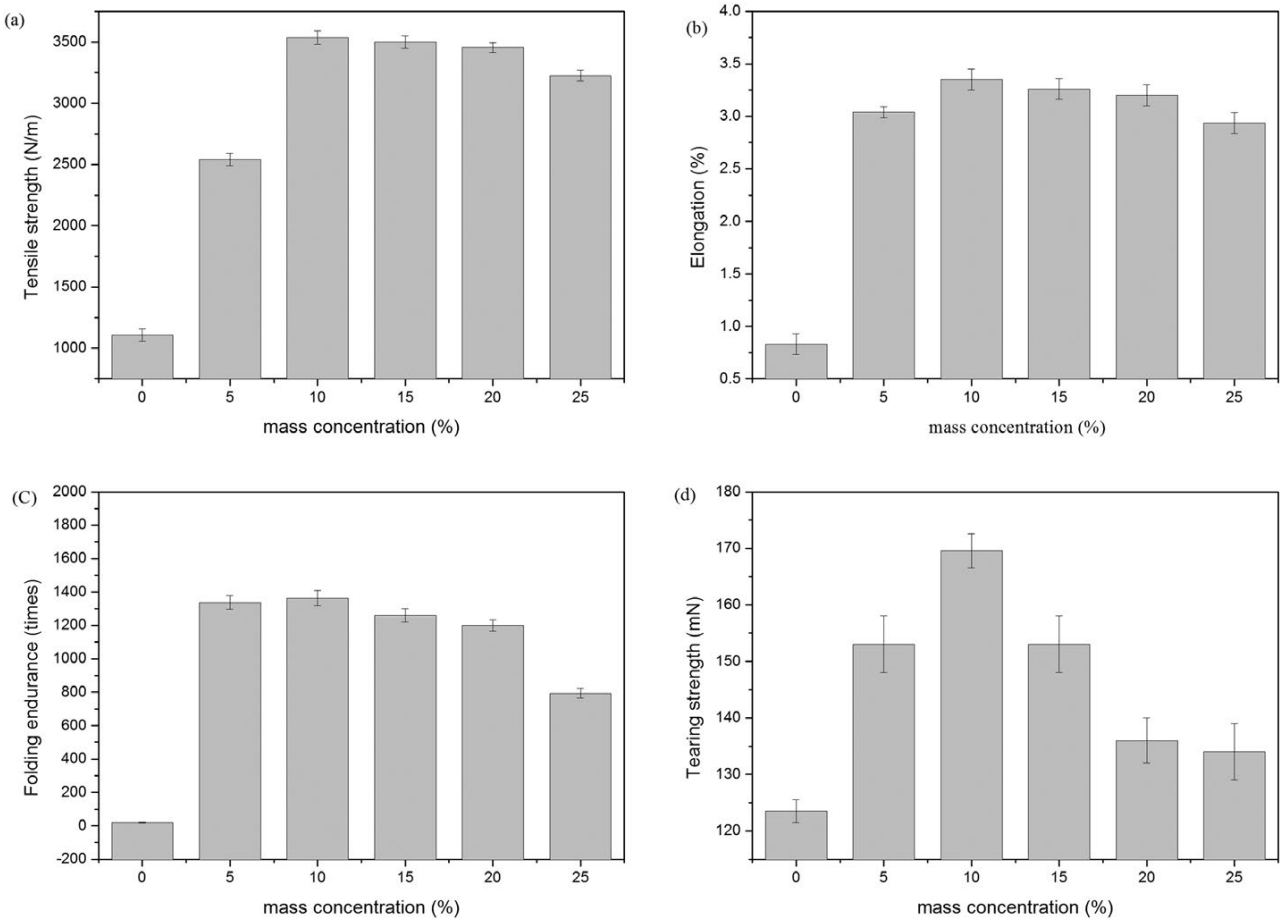


Figure 1: The mechanical properties of papers coated by different concentrations of polyurethane.

tion was 10 %. It indicates that polyurethane may have the ability to link the broken fibers.

To test the influence of polyurethane liquid on the appearance of the paper, we further determined the glossiness, brightness and thickness of the paper. The results were shown in Table 1.

These data reveal that the paper coated by polyurethane shows a tiny decrease in brightness with the increase of mass concentration of polyurethane. The reason may be that the polyurethane has not the ability to reflect the light as fibers. However, when paper coated by 10 % mass concentration of polyurethane, the decrease of brightness is just less than 3 % (compared with the blank paper samples). It cannot be distinguished by the naked eye, and the gap meets the requirement of paper preservation, so the variation of brightness of the coated paper can be reasonably ignored.

Glossiness is associated with the capacity of a surface to reflect lights. With the increase of polyurethane mass concentration from o to 25 %, the glossiness gradually decreases. The reason is that the paper will adsorb a small amount of polyurethane and part of the polyurethane can be embedded into the gap between fibers, while part of the polyurethane would just stay on the surface of the paper, so the surface flatness degree may decrease to some extent, leading to the decline of reflecting capacity of the paper.

Consequently, taking all factors (e. g., tensile property, folding endurance, tearing strength, brightness and glossiness) into consideration, the best mass concentration of polyurethane is 10 %.

In order to further understand the effect of polyurethane on paper, four paper samples were prepared. As we can see from the Figure 2, compared with uncoated paper, the mechanical properties of the paper coated with ethyl acetate were decreased, while the paper sample coated with nanosilica was slightly increased. The significant changes of mechanical properties of papers coated with polyurethane liquid. It can be concluded that the main function of the reinforcement liquid is the synthesized polyurethane, independent of the solvent.

Table 1: Brightness, glossiness of the papers coated by different paper samples.

Mass concentration (%)	0	5	10	15	20	25
R457-brightness (%)	80.9±0.1	79.4±0.1	78.0±0.1	77.9±0.1	72.6±0.1	69.9±0.1
G75-glossiness (Gu)	4.9±0.1	5.0±0.1	4.8±0.1	4.9±0.1	4.6±0.1	4.5±0.1
Thickness/mm	0.088	0.089	0.090	0.090	0.093	0.095

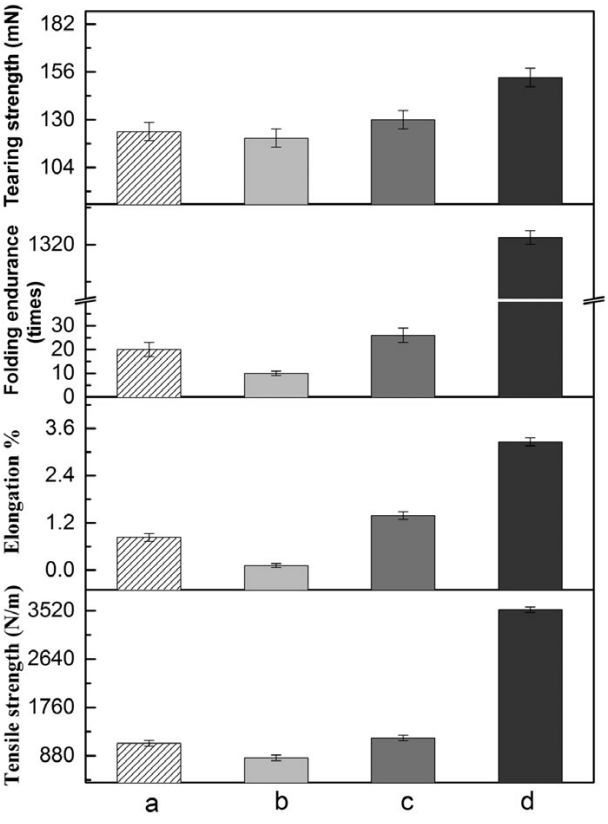


Figure 2: Mechanical properties of the paper sample by different treatments. a. Uncoated paper; b. coated by ethyl acetic; c. coated by 10% mass concentration nanosilica liquid; d. coated by 10% mass concentration polyurethane liquid.

Accelerated aging test

As we know, when considering the use of new materials for conservation of paper, it is important to understand the probable long-term effects of treatment. So accelerated ageing tests was designed to find materials, which can be safe for long-term use and would not cause degradation of coated papers.

All of the paper samples were aged thermally. The accelerated thermal aging tests were performed in a closed system at 105 °C for 72 h. Before and after aging, the samples were kept at 22 °C, 50 % RH in a desiccator. The degradation of mechanical properties of papers during aging had been measured by tensile properties, folding endurance and tearing strength tests and results were shown in Figure 3.

It can be seen from Figure 3 that the tensile strength of sample a decreased gradually with time, while that of sample b increased first and then decreased slightly. Two days aging, the tensile strength of sample b increased obviously, this is because the reaction between isocyanate group and paper fiber or the polymerization of HDI trimer was further enhanced with the temperature increasing. After 2 days, the tensile strength of sample d decreased slightly, but the decreasing trend was not obvious. This indicates that the tensile strength of the reinforced paper can still be maintained within a stable range after the aging of the paper, and the reinforcement liquid can effectively prevent the decrease of the tensile strength of the paper. During the aging process, the loss of paper strength occurred as a consequence of degradation processes. As shown in sample a, the uncoated paper was less thermally stable, and obviously showed a higher loss of paper strength, the loss ratio of tensile strength is 30.4 %. The paper coated by polyurethane liquid showed a higher resistance before aging because of improved fiber–fiber bonding, the loss ratio of tensile strength is 14.3 %. The value of the tensile strength of coated samples with polyurethane liquid showed little decrease compared with the sample a. This result was intended the interfering of polyurethane materials on the fiber–fiber bonding.

The elongation of sample a decreased with the aging time. But the elongation of sample b increased in the 2 days of aging progress, and then decreased. The same trend was found for the tearing strength of aged samples. This is due to the fact that the high temperature makes the reinforcing liquid better combined with the paper, but the continuous high temperature will break the fiber shape, and eventually the elongation will decrease. Even so, the elongation of sample b is still far greater than that of sample a.

The folding endurance of sample b decreased with the aging time. When the aging time is 2 days, the rate of decreased slowly. This trend is same as the tearing strength. Besides, when the aging time is 3 days, the decrease ratio

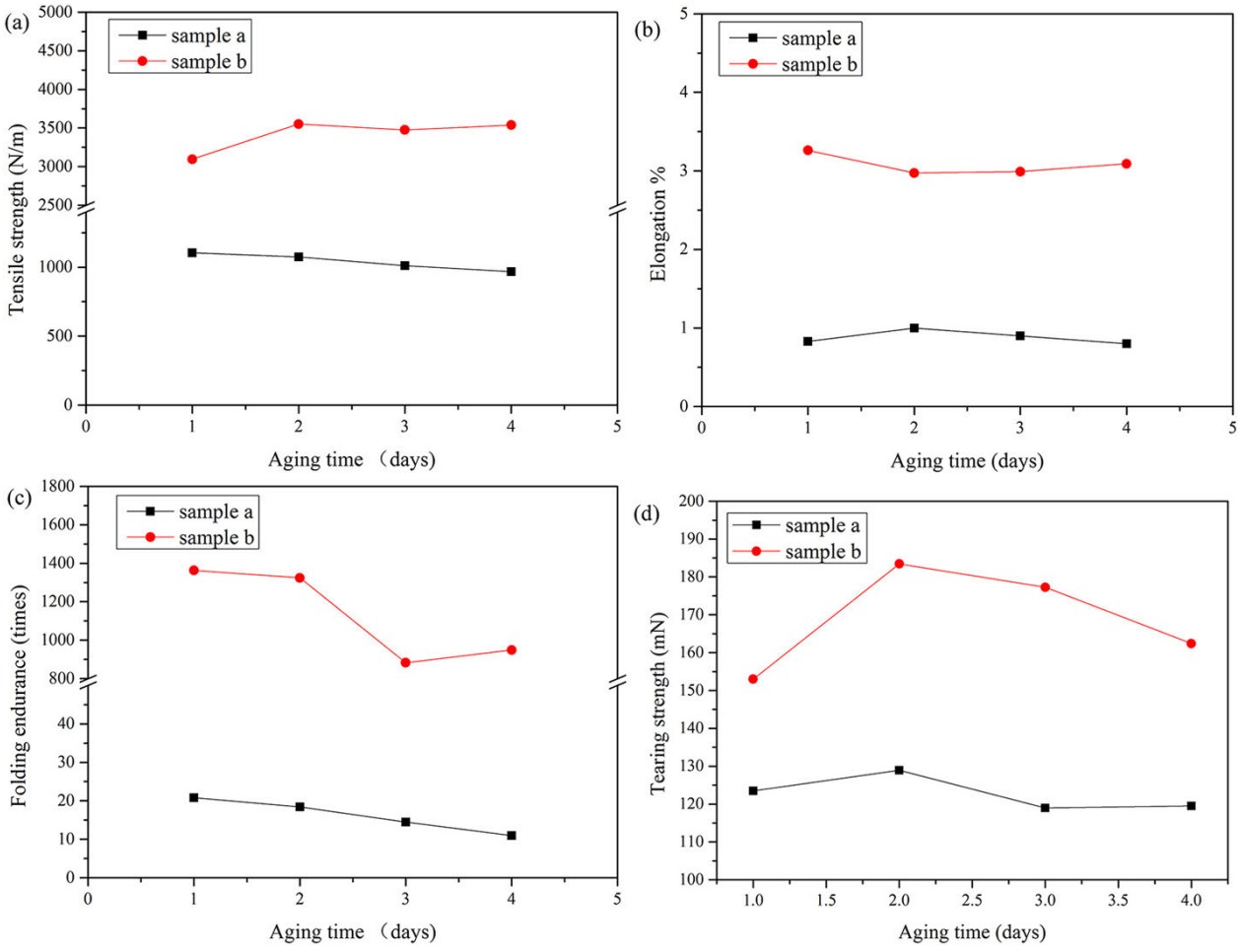


Figure 3: The mechanical properties of paper samples with aging time. a. Uncoated paper; b. coated by 10% mass concentration polyurethane liquid.

Table 2: Brightness, gloss of the paper during the aging time.

Aging time (h)		0	24	48	72
Uncoated paper	R457-brightness (%)	80.9±0.1	79.2±0.1	78.6±0.1	77.3±0.1
Coated paper		78.0±0.1	77.9±0.1	77.5±0.1	76.3±0.1
Uncoated paper	G75-gloss	4.9±0.1	4.9±0.1	4.8±0.1	4.6±0.1
Coated paper		4.8±0.1	4.8±0.1	4.7±0.1	4.6±0.1

of folding endurance reached the maximum, and when aging time is 4 days, the folding resistance increased slightly. However, the folding endurance of reinforced paper is much more than that of uncoated paper. This is attributed to low-molecular-weight polyurethanes penetrated easily into the fibers, fully wetted the paper, protected effectively the fiber structure of paper, prevented the fiber breakage, increased the mechanical properties of the paper and aging resistance. At the later stage of dry heat aging, the reinforcement liquid may be damaged in the thermal environment, resulting in fiber exposure and accelerated fracture.

From Figure 3, it is evident that the dry heat aging treatment affected the mechanical properties of papers. As shown in sample a, the uncoated paper was less thermally stable and obviously showed a higher loss of paper mechanical. Tests of artificially aged papers that were coated with polyurethane liquid showed the best resistance to mechanical properties compared with uncoated papers because of the structure of the polyurethane

materials. Results clearly showed that polyurethane successfully prevented the papers from cellulose degradation.

The gloss and brightness of papers during aging were shown in Table 2. As shown in Table 2, the gloss and brightness of papers decrease with the increase of aging time. But they has slightly decrease in coated paper.

The FTIR spectra of coated papers compared with the uncoated one after accelerated aging was shown in Figure 4. It is clearly shown that polyurethane coating can successfully prevent paper from cellulose degradation. The carbonyl compounds produced by cellulose degradation greatly enhanced the 1695 cm^{-1}. Therefore, band at 1695 cm^{-1} are assigned to C=O vibrations and proved the degradation of uncoated paper under aging condition. These bands in coated paper with polyurethane are so weak. This observation showed that the paper coated by polyurethane has good aging resistance.

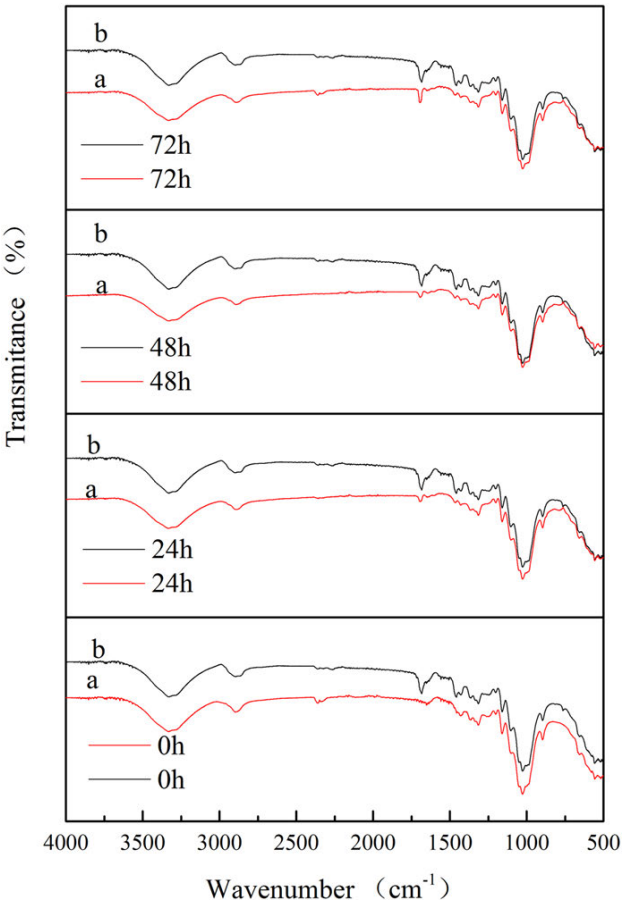


Figure 4: The FTIR spectra of paper samples during aging. a. Uncoated paper; b. coated with 10% polyurethane reinforcement liquid.

To determine how well paper works prevent the damaging effects of chemical materials, a selection of papers were exposed to HCl (pH=4) and NaOH (pH=12) aqueous solution for 72 h. Additionally, degradation of properties of papers with chemical aging has been measured by tensile strength and folding endurance. The results were presented in Table 3. The paper's ability coated with polyurethane based on nanosilica to resist acid and alkali attack is greatly improved. That may due to the protective layer formed on the surface of the fiber by polyurethane could effectively prevent the dissociation of H^+ and OH^- roots to the fiber, as shown in SEM analysis.

Appearance of papers

The SEM surface of paper samples were shown in Figure 5. SEM of the uncoated paper sample was closely packed cellulose fibers with an interwoven network with no deformation. As seen in Figure 5(b), the loose mesh structure was still partially maintained between the fibers, allowing the inherent texture of the paper to be preserved. Also, there is a layer of high molecular connection between the fibers, which connects the broken fibers and increases the overall strength of the paper sample. In addition, due to the low molecular weight of HDI trimer, it can penetrate into the inside of the paper fiber and thicken the fiber.

Figure 6 shows the appearance of a calligraphy work before and after treating with polyurethane liquid. It is clear that the polyurethane material is completely trans-

Table 3: Mechanical property of paper samples.

Samples	Tensile strength (N/m)		Folding endurance (times)	
	Uncoated paper	Coated paper	Uncoated paper	Coated paper
Initial value	1005	2715	23	884
After treated by HCl	673	2288	10	798
Loss ratio %	30.0 %	15.7 %	56.5 %	9.7 %
After treated by NaOH	725	2536	3	689
Loss ratio %	27.8 %	6.6 %	86.9 %	22 %

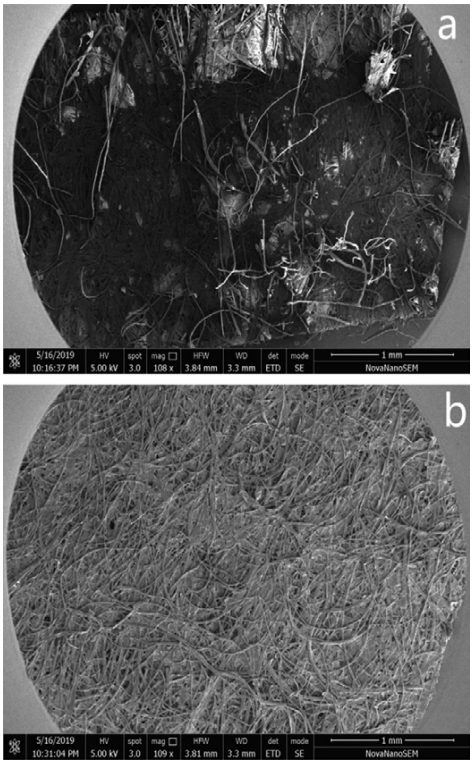


Figure 5: SEM of paper samples. a. Uncoated paper; b. coated with 10% mass concentration polyurethane liquid.

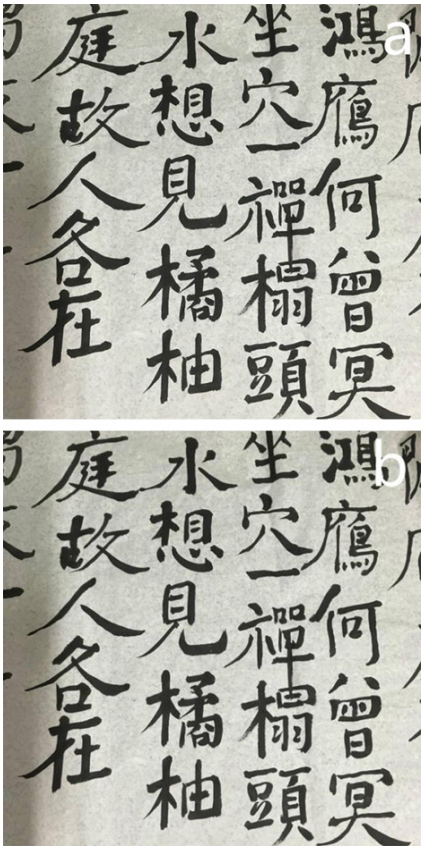


Figure 6: Image of a calligraphy works. a. Uncoated calligraphy work; b. coarted with 10% polyurethane liquid.

parent and no changes in color, hue, or gloss can be observed after coating.

Conclusion

The polyurethane was synthesized by nanosilica and hexamethylene diisocyanate trimer. In this study, we successfully strengthened papers by polyurethane liquid. After the treatment, the mechanical properties of the papers improved significantly, while the appearance of the paper changed slightly. At the same time, the antiaging property of the papers was greatly improved. This study is a great innovation in the field of paper cultural relics protection. Nevertheless, we must emphasize that there may be complex interactions between polyurethane and different papers, pigments, inks, and paper fillers. It is very necessary to further improve and evaluate this method. Obviously, at this stage this method should not be used in the practical conservation.

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