

Chemical Investigation of Potassium Methyl Silicate as Deacidification and Strengthening Agent for Preservation of Aged Papers^{*}

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Abstract Potassium methyl silicate (PMS) was investigated as a simple physicochemical modification in aged paper using silane coupling technique. The PMS-based solution was shown to favor penetration in the cellulose fibers on the paper with suitable uptakes being achieved at low concentrations. The studies of the physicochemical properties of the treated paper (mechanical strength and alkalinity) demonstrated that, besides the required deacidification feature and high level of alkali reserves, the immersion treatment by PMS allowed the enhancement of the mechanical intensities of paper arising from the interaction between Si—OH generated in hydrolysis of PMS and C—OH of cellulose on the paper. Adding ethanol into PMS solution could significantly improve mechanical properties of the aged paper treated by the formula apart from modifying the flatness of the paper. Optimized treatment process was achieved by altering the ratio of ethanol to water in PMS-based solutions. Contact angle measurements indicated the occurrence of hydrophobic character of the papers in immersion treatment with PMS-based solutions. The easy availability of the materials and simplicity of the method rendered it convenient for treatment for aged paper documents.

Keywords: Potassium methyl silicate; Paper; Deacidification; Reinforcement; Ageing.

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INTRODUCTION

With the development of digital technology and the internet, digital resources have become a major source of people's access to knowledge and information. Nevertheless, paper literature resources are still the main carriers of information and culture, so our paper-based cultural heritage can be used and consulted for much longer than our own lifetime. These paper-based precious archive materials, manuscripts, prints, newspapers, books, and paintings *etc.* have to be preserved for the future. For paper-based archives, the acidity generated during the natural ageing of paper is the main cause for its discoloration and deterioration. In some cases, the deterioration is so severe, that the stored documents can no longer be consulted, the paper breaks just when touched. These paper-based archives face the risk coming from the acid-induced de-polymerization of cellulose fiber through hydrolysis. Paper is a fairly random network consisting mostly of cellulose fibers, and very small amounts of lignin and hemicelluloses. The structure of the network and the length of the fibers determine the physical and mechanical properties of the paper. The strength of paper depends on the quality of the cellulose fibers used. Paper is easily decomposed and damaged by chemical, physical, and thermal treatments. Actually, the acid-catalyzed hydrolysis is the main chemical route for cellulose de-polymerization^[1]. Several reactive processes

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taking place in the cellulose fibers promoted with the presence of acids would shorten the average chain length of cellulose, resulting in a catastrophic loss of paper strength. Cellulose may be degraded by hydrolysis or oxidation. Under the influence of oxygen or light, lignin may degrade more rapidly than cellulose. Hemicellulose is hydrolyzed more easily than cellulose and lignin. Paper deterioration is a complicated process where internal and external factors can stimulate each other. The internal factors are introduced during the manufacture of the paper, thereby resulted in the presence of acidic compounds, metal ions, and other materials in the paper sheet. The external factors are related to the conditions during storage or use, in which air pollutants play an important role. Among common atmospheric pollutants nitrogen dioxide is one of the most powerful in promoting the oxidative and hydrolytic degradation of cellulosic materials^[2]. These deterioration processes can be slowed down by deacidification treatment. Deacidification, as the name suggests, is a chemical process which involves the neutralization of the acidic materials presented in the surface and interior of the paper, and the sedimentation of alkaline materials (referred to as alkaline reserve) on the surface of the paper to prevent or delay further acidification with natural ageing. Currently, many different methods have been developed in order to remove acidity from paper^[3]. There has been numerous literature reviews focused on the conservation of paper-based archives deacidification^[4]. Considering the amount of paper-based resources stored in the archives and libraries, only manual-deacidification methods cannot be able to protect these materials. Mass treatments in deacidification are commercially available for the archives and libraries in some of countries^[5, 6]. However, mass deacidification for the collections which are severely acidified, or so brittle that they hard to handle is unrealistic. In brief, the main drawback of the various deacidification methods currently in use was that they could not significantly improve the mechanical properties of the treated papers^[7–9]. In addition, some deacidification methods are questionable even for sometimes reducing paper strength and degrading the quality of paper or blurring the ink^[10–12].

Alkoxysilanes have been proposed for the reinforcement of natural fibers^[13–15]. A new chemical process that simultaneously neutralizes the acidic materials, and improves the mechanical properties of the paper through introducing aminoalkylalkoxysilane or diaminealkylalkoxysilane has been produced recently^[16, 17]. In these processes, alkoxysilane type of molecules could form interpenetrated networks with natural fibers, thereby resulted in a clear improvement in the mechanical properties of the paper. *N,N,N*-Tris (triethoxysilylpropyl) melamine was prepared by using polychlorostyrene as a skeleton and grafting with aminosiloxane KH-550 and was recently used to paper treatment^[18]. The results demonstrated that both the pH value and tensile-strength increased significantly after treatment.

A commercially available waterproof reagent, potassium methyl silicate (PMS) was used as a hydrophobic sealant for cement protection, and recently has also been used for the fabrication of superhydrophobic cellulose-based materials through a solution-immersion process^[19]. The superhydrophilic cellulose could transform to superhydrophobic with a water contact angle of 157° after immersion treatment by PMS solution. The chemical modification of cellulose fibers received much attention in composite formulations; however, the modification of cellulose in the form of paper with functional groups has not been well explored.

In this work, a facile and green approach consisting in a solution-impregnation process at room temperature and atmospheric pressure for the deacidification of aged papers was developed. Potassium methyl silicate (PMS) was firstly investigated as a new deacidification agent to neutralize the aged acidic papers. Beyond as suitable deacidification agent, PMS solution, together with the chemical surface modification associated with the replacement of some cellulose —OH groups by —O—Si—CH₃ moieties, could significantly improve the mechanical properties and wettability of aged papers. An optimization of the treatment protocol, alkaline reserve and accelerated ageing measurements were carried out to characterize the quality and extent of the poly-silanol in the aged papers. Mechanical measurements (tensile strength and folding endurance) were performed to access the strengthening properties of the treatments. Finally, contact angle measurements were carried out to evaluate the hydrophilic/hydrophobic character of the treated papers.

EXPERIMENTAL

Materials

Potassium methyl silicate aqueous solution (25 wt%) was supplied by Jinan Qimin Chemical Co., Ltd. and was used as received. The naturally aged (1986) mechanical wood-pulp paper was henceforth called MWP. The cold extract (internal) and surface pH values were 5.36 and 4.64, respectively. The paper henceforth called BDP was the sample of the Beijing Daily newspaper (1978), the cold extract surface and surface pH values were 5.86 and 4.65, respectively. The paper henceforth called RP was rice paper, also called Xuan paper. The rice paper was made of sandalwood pulp (> 75%) with trace amount of cotton linters, the cold extract surface and surface pH values were 8.48 and 6.44, respectively. Control papers were not subjected to any treatment. Deionized water was used throughout.

Methods and Characterizations

The PMS aqueous solution (25 wt%) was diluted to certain concentration using deionized water. Subsequently, the paper sample was carefully coated on the fine metal mesh which was immersed in the diluted PMS solution. The immersion process lasted for 1 h at 40 °C. The paper sample (together with the mesh) was then removed from the solution, and dried at room temperature for about 10 h. The detailed experimental diagram is demonstrated in Fig. 1. In order to achieve a satisfactory deacidification, ethanol aqueous solution was used as the dilute medium instead of pure deionized water.

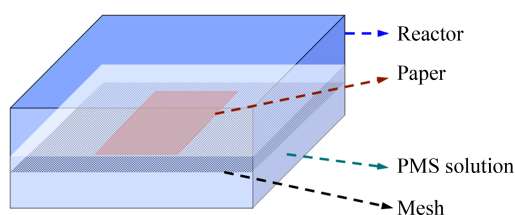


Fig. 1 The experimental diagram for deacidification

The surface pH of the papers was measured by the paper pH Meter (HANNA HI 99171). The cold extract pH (internal pH) of the papers was measured using ISO 6588-1:2012 model with 2 g mass of paper.

ISO brightness (Measurement of diffuse blue reflectance factor) was performed using the instrument BD-1 (Changchun Paper Test Co., Ltd.) according to ISO 2470:1999. The instrument equipped with a filter having an effective wavelength of 457 nm and a width at half-height of 44 nm, the intrinsic reflectance factor measured with a reflectometer having the characteristics described in ISO 2469 and adjusted so that the UV-content of the illumination incident upon the test piece corresponds to that of the CIE illuminant. Each ISO brightness value was an average of 10 measurements.

Folding endurance (FE) (the log of the number of double folds) was determined with a double fold instrument (NZ-135, Hangzhou Qingtong&Boke Automation Technology Co., Ltd.) according to ISO 5626:1993. The applied force was 5 N.

Tensile Strength was determined with a double fold instrument (KZW-300, Changchun Paper Test Co., Ltd.) according to ISO 1924-2:2008.

The mechanical property was measured in the machine direction of the paper of 10 strips taken from the same sample conditioned at 23 °C and 50% RH. Reported values are the average of the 10 measurements (ISO 187-1990).

The alkaline reserve of paper (mol/kg) was assessed according to ISO 10716:1994.

Methods for the accelerated ageing of paper were standardized. The method chosen for this research was based on the ISO 5630-1:1991 method for thermal ageing of paper for 72 h at a temperature of (105 ± 2) °C. The evaluation of durability of the paper and prints after accelerated artificial ageing according to ISO 5630-3:1996. The paper samples were submitted to moist heat ageing at 80 °C and 65% relative humidity for 3 days. Artificial

ageing tests only provided relative results, and thus they were only used for comparing the paper samples with the studied deacidification and strengthening treatments without trying to predict lifetimes.

Fourier transform infrared spectra of the samples were taken using a Perkin-Elmer FTIR spectrometer (model: Spectrum GX) with a DTGS detector. The spectrometer was set to collect 32 scans at a resolution of 4 cm^{-1} in the range of $400\text{--}4000\text{ cm}^{-1}$. The paper sample, which was made in the form of powder, was sandwiched in the KBr pellet.

A scanning electron microscope (HITACHI S-4800) was used to examine the samples. The accelerating voltage was 20 kV. Samples were observed using back-scattered electron imaging providing atomic number contrast to detect the location of specific atoms within the samples. The mappings were done over the same area by energy dispersive X-ray spectrometry (EDS) by means of an Oxford Instruments INCA X-sight (Model: 7593) and Inca Link software. The EDS operating conditions were as follows: accelerating voltage 20 kV, ATW2 window, working distance 180 mm, approximate dead time 120 s. The samples were gold coated before analysis.

The surface hydrophobicity of the papers was evaluated by measuring contact angle of water using a DCAT 21goiometer from Data Physics (Germany) at room temperature with a conventional sessile drop method. A droplet of $5\text{ }\mu\text{L}$ volume of distilled water was applied on the specimens. The shape of each droplet was recorded and analyzed using the SCA 20 software. At least three measurements were taken for each sample.

RESULTS AND DISCUSSION

Reactivity of PMS toward Cellulose Fiber on Aged Paper

Basically, the PMS used was a strong alkaline solution which contained PMS, KOH and water. Once the pH value of the alkaline solution reduced, PMS in the solution could be partly hydrolyzed to form silanols. The silanols underwent polycondensation to form polysilanols. The mixture of monomers, silanols and polysilanols in the solution gradually formed a network containing liquid and solid, and precipitated from the solution^[20]. Cellulose has three hydroxyl groups per anhydroglucose unit^[21]. When a cellulose paper, which was the source of cellulose fibers, contacted with the solution, the silanols and polysilanols could be easily impregnated into the cellulose fibers, and enabled the polysilanol network to be anchored to the fibers by the hydrogen bonding between the polysilanol and hydroxyls on the fibers^[19]. For the cellulose in the form of paper, the rough and porous surface structure made the modification of the cellulose fibers become more complicated. Figure 2 shows the FTIR spectra of the original MWP and the MWP treated with PMS. By contrast, the new peaks at 1273 cm^{-1} and 780 cm^{-1} appeared in the spectrum of the PMS-treated MWP, which were ascribed to the stretching vibrations of Si-CH_3 and Si-C bonds^[19], the weak peak at $\sim 910\text{ cm}^{-1}$ corresponded to the Si-O stretching of the silanols Si-OH groups^[22] (Fig. S1). The typical absorption peak at 1642 cm^{-1} was assigned to the stretching vibration resulting from H-O-H intermolecular linkages^[23]. The peaks at 1433 and 1328 cm^{-1} in the spectra were assigned to symmetric CH_2 bending and wagging^[23]. Compared with original MWP, the broad peak in the $3500\text{--}3000\text{ cm}^{-1}$ range due to the O-H stretch was somewhat reduced in intensity and shifted to a lower wavenumber in the spectrum of the PMS-treated MWP. The peak intensities in the ranges of $1500\text{--}1200\text{ cm}^{-1}$ and 1642 cm^{-1} were found to be enhanced. These results suggested that some of the hydroxyls on the fibers of MWP were replaced by O-Si bonds, which confirmed the interaction of fibers and silanols monomers and chains. The EDS mapping showed Si (green) as well as K (pink) was localized across the paper sheet of MWP (in Fig. 3). The weight percent of silicon and potassium element in MWP increased to 4.43% and 6.03% from 0.56% and 0.22% respectively after being treated by PMS solution. The observation clearly demonstrated the existence of PMS on the cellulosic fibers. Figures 3(a) and 3(b) also demonstrated that there was no apparent change in fiber structure on the paper before and after modification by PMS solution.

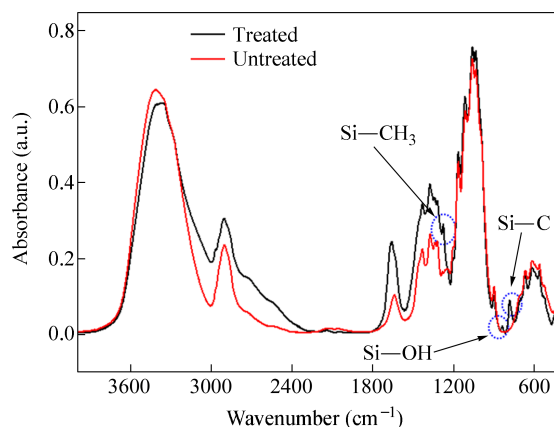


Fig. 2 FTIR spectra of original MWP and PMS-treated MWP

Physicochemical and Mechanical Properties of Paper Treated with PMS Solution

Optimizing the treatment process was necessary to better control the polysilanol uptake in the aged paper. The determination of suitable concentrations of PMS aqueous solutions for a uniform impregnation was a preliminary requirement. At first, the effect of the concentration of the PMS solution was studied. The original PMS aqueous solution (25 wt%) was diluted into different concentrations using deionized water. The paper sheets (MWP) were placed in the testing solution at 40 °C for 1 h. All treatments resulted in an increase in the pH values of the MWP samples after deacidification process. The surface and cold extract pH values of MWP rapidly increased to more than 8.00 from original 4.64 and 5.36, respectively. A little change in pH values occurred over the 0.5 wt% to 5.0 wt% concentration range in the testing solution (Fig. 4). For the ISO brightness of MWP, change in values with a concentration of the solution was almost ignored (Fig. S2). Sufficient ageing resistance for the mechanical behavior of paper samples was required for the storage of archive documents and books. Therefore, this study focused on the issue of determining the tensile strength of the aged paper samples after deacidification. In Fig. 5, the tensile strength of the aged paper as a function of the concentration of the testing solution was represented for each impregnation process.

All the treatments impregnated by PMS solution led to an improvement of mechanical strength compared to untreated MWP, indicating that intra- and inter-fiber bonds of the cellulose fibers were strengthened by the formation of polysilanol network on the paper. The tensile strength of the treated MWP samples increased as the concentration of PMS solution increased until it reached an optimum PMS concentration of 2.3 wt%. The tensile strength obtained at this concentration was 1.95 kN/m. The increase in the PMS concentration improved the tensile strength of the modified fibers on the papers. However, the tensile strength decreased rapidly when the PMS concentration was further elevated after exceeding to 2.3 wt%. In this study, the testing solution with different concentration came from the dilution to the original PMS highly alkaline solution in which PMS was freely soluble. Dilution of the PMS solution reduced the concentration of KOH, and resulted in lowering the pH of the solution. This, in turn, caused the formation of silanols by hydrolysis, which then formed polysilanol by polycondensation. The stability of siliconate solution might be illustrated in Scheme 1. Reducing the pH of the solution shifted the equilibrium to the silanols, and further resulted in greatly enhancing the condensation rate. The —Si—OH groups formed were assembled on the fiber surfaces *via* hydrogen bonds. The hydrogen bonds between polysilanol and hydroxyls on fibers anchored the network system to the spreading fiber surface, and improved the mechanical intensity of fibers on the aged paper samples. Further dilution of the siliconate reduced the condensation rate due to a low concentration of the reactants in the solution, which resulted in an insignificant increase in mechanical strength of fibers in the paper sheet. Therefore, the value of tensile strength reached a maximum at relatively low concentration of PMS solution.

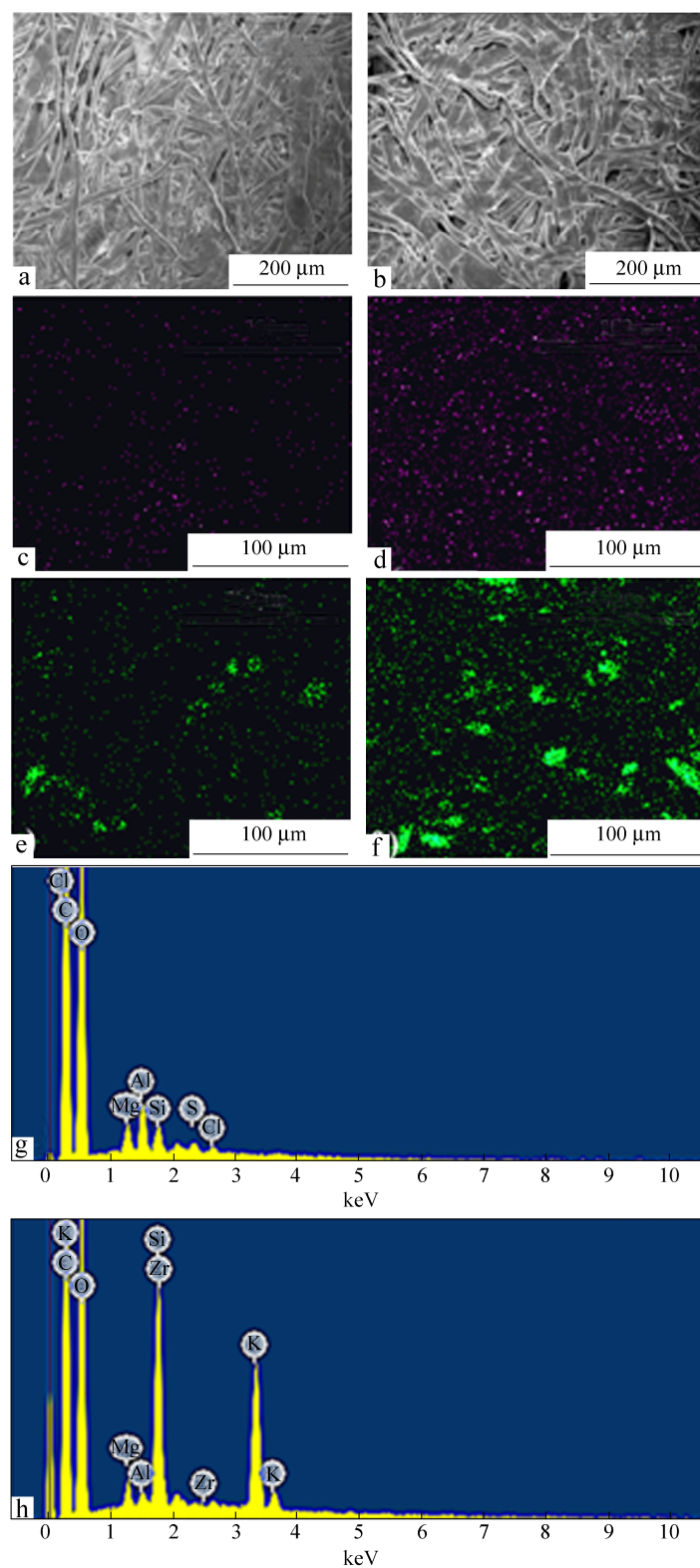


Fig. 3 SEM micrographs of MWP untreated (a) and treated with PMS solution (b); EDS atomic mappings of K (pink), Si (green) in corresponding areas untreated (c), (e) and treated with PMS solution (d), (e); EDS spectra of the surface of MWP untreated (g) and treated with PMS solution (h)

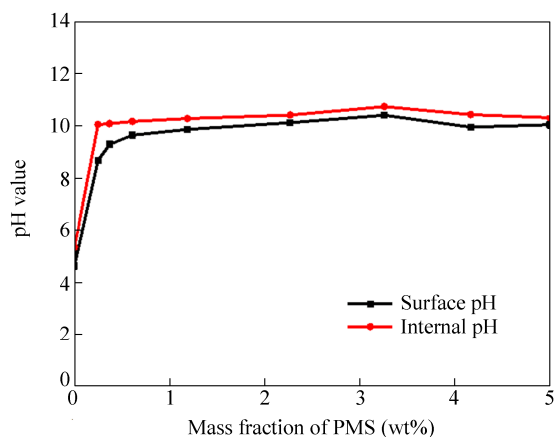


Fig. 4 The pH value versus mass fraction of PMS for MWP

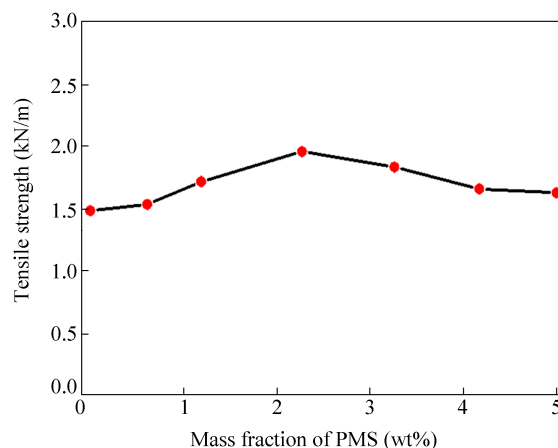
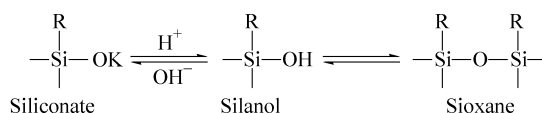


Fig. 5 The tensile strength versus mass fraction of PMS for MWP



Scheme 1

In this work, the testing solution with different concentrations came from the dilution of the original PMS highly alkaline solution in which PMS was freely soluble. The diluted PMS solution was homogeneous. The aged paper directly dried in air at room temperature after being impregnated by uniform PMS solution. In the case of BDP and RP, the measured tension strength, folding endurance and pH value were all smaller than those in one-step immersion if the paper rinsed by purified water after PMS immersion (Table S1).

The hydrophilic nature of cellulose made it sensitive to water. As a disadvantage of wet-chemical processes, the solution impregnation might cause distortions of the paper structure or shrinkage of the paper and dissolution of the printing ink. As the testing solution came into contacting with paper surface, the rough and porous surface structure of paper further enhanced spreading of the aqueous solution by capillary action between the cellulose fibers. The wetting and spreading were dependent on the capillarity which was the ability of a liquid to be drawn into porous materials due to inter-molecular interactions between the liquid and the surrounding micro-structure. Ethanol reduced the viscosity and surface tension of an aqueous solution, and also changed the solubility parameters and polarity of the solution^[24], which in turn facilitated the infiltration of PMS into narrow gaps between the fibers of the paper. In this study, the effects of ethanol on the pH value and mechanical properties of the aged paper sheets treated by PMS solution were analyzed. The results in Fig. 6 and Fig. S3 demonstrated that ethanol had no apparent effect on the pH value of the paper impregnated. In order to prove that the treatment provided multifunctional protection to the aged papers, mechanical properties of different kinds of aged paper treated with PMS solutions were measured. Generally, tensile strength related to the fiber structure itself on the paper, and the folding endurance was proportional to the intrinsic strength of the fiber^[25]. The increase in the tensile strength might be related to the enhanced stiffness and decreased ductility of the paper sheets^[26]. Folding endurance was a judgment index for deformation capacity and plasticity of the paper^[27]. Folding endurance was regarded as the most sensitive indicator of paper breakage upon ageing. Tensile strength and folding endurance characterized the mechanical properties of the aged paper in different ways. Figure 7 shows that the tensile strength basically increases with an increase in the ratio of ethanol to water. The fold endurance of the treated BDP samples increased as the ratio of ethanol to water increased until it reached an optimum in the ratio of water to ethanol of 80:20, and the fold endurance started to decrease with further increase in the ratio of ethanol to water. In the case of treated RP, the fold endurance leveled out when the ratio of water to ethanol was greater

than 60:40 (in Fig. S4). In short, the balance between the tension strength and folding endurance could be maintained when the ratio of water to ethanol was in the range of 40:60 to 60:40. These different behaviors might have a relation with the paper composition as well as with the morphology of the papers. The explanation proposed for this phenomenon was related to the formation of the cross-linked particles inside the paper web. With the hydrolysis reaction proceeding, monolayer coverage of the paper due to self-assembly or horizontal polymerization was not generally favored. Instead, vertical polycondensation of hydrolyzed silane occurred^[28, 29]. The expected schematic outcome of chemical structure under the treatment by PMS solution is illustrated in Fig. 8.

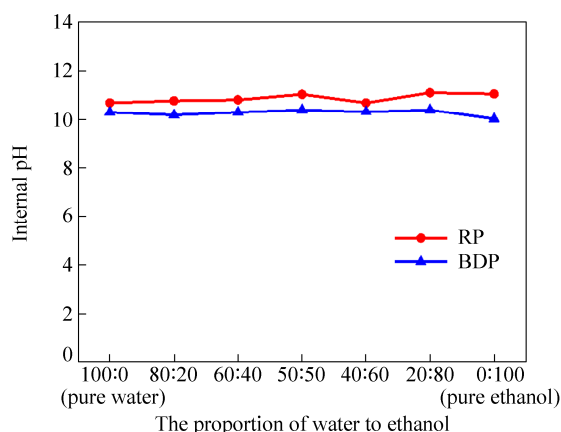


Fig. 6 The internal pH as a function of the proportion of ethanol to water for RP and BDP

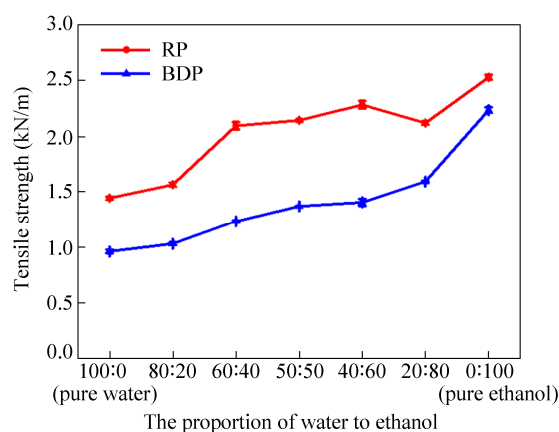


Fig. 7 The tensile strength as a function of the proportion of ethanol to water for RP and BDP

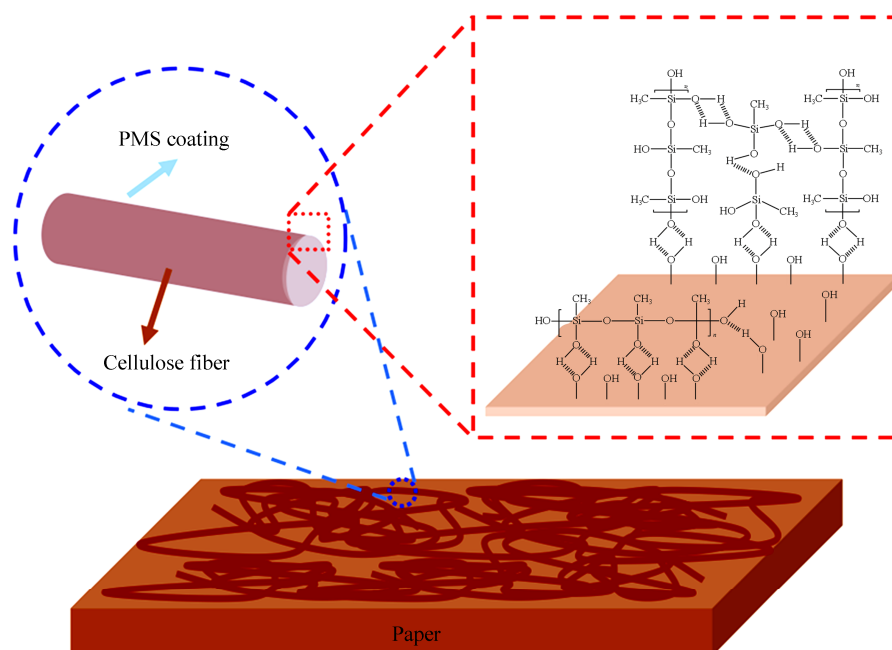


Fig. 8 Illustration of cellulose fibers on paper modified by silane coupling process in the presence of potassium methyl silicate (PMS)

Bringing a sufficient alkaline residues to the paper after deacidification was a significant feature of the multifunctional treatment developed. Alkaline reserve would play important role during the future long ageing

process. Table 1 shows that the values for the alkaline reserve of the different papers treated by PMS solutions were all greater than the required values for permanence (ISO standard 9706:1994). The results suggested that the paper containing low amount of lignin, for example RP, showed comparatively larger alkaline reserve than those with large amounts of lignin (MMP and BDP) because the lignin might buffer part of the alkalinity initially introduced^[16].

Table 1. Alkaline reserve of the different papers (MWP, RP and BDP) after the treatments

	MWP	RP	BDP
Alkaline reserve (mol/kg)	0.816	1.487	1.065

Ageing behavior was an important aspect of the appraisal of deacidification. In the work, two kinds' artificial ageing methods were used to evaluate the PMS deacidification. The aged papers treated by PMS solutions seemed to present fair resistance to the hydrolytic-driven types of ageing. The BDP and RP samples showed different decreases in pH values and tensile strengths after accelerated ageing of three days according to ISO 5630-1:1991. The results in Table 2 showed that the incorporation of silanol in the cellulose web significantly improved the tensile strength before as well as after accelerating ageing. In the present work, the tensile strength of the treated BDP after accelerating ageing was better than that of the untreated paper sheets, which meant that the presence of a macromolecular silanol network superimposed to the cellulosic fibers favored overcoming the degradation of the papers. In the aging process, the covalent bonding between cellulose and PMS because of heating might slow down the decrease in tensile strength^[14, 30]. For the non-acidic paper RP, the tensile strength of treated paper through accelerating ageing decreased to the value which was less than that in untreated paper samples, although the tensile strength of the RP samples treated by PMS solution improved significantly comparing to original paper. The FE data in Table 2 indicated a better deformation capacity and better plasticity of the paper after treatment by immersion although the FE after accelerated ageing decreased compared to untreated paper. These results suggested that the improvement of the mechanical properties in paper likely related to the initial acidity of the papers. The BDP was an acidic paper sample from naturally aged newspapers, the cold extract and surface pH values were 5.86 and 4.65, respectively. As the BDP sheets were impregnated in PMS solution, the micro-environmental acidity on the immediately fiber surface of the paper sheet would facilitate the formation of silanols by hydrolysis of PMS, which easily created dense cross-linking network on the fibers of the papers and resulted in the significant increase in tensile strength of the paper samples. However, in the case of the non-acidic paper RP, the weaker hydrolysis of PMS because of the neutral surface pH value led to the lower amount of the silanol condensation, and eventually resulted in the smaller increase in tensile strength. The moist heat treatment at 80 °C and 65% relative humidity on control samples and PMS-treated samples was performed. As could be observed in Table S2, after 3 days accelerated ageing, the samples pretreated by PMS showed greater reduction in mechanical properties than the control samples. Nevertheless, the final tensile strength and folding endurance for PMS-treated samples were better than those of the control samples.

Table 2. The variations of the RP and BDP samples after 3 days of accelerated ageing (ISO 5630-1:1991)

		Untreated	Treated	After artificial ageing (untreated)	After artificial ageing (treated)
RP	Surface pH	6.44	10.87	5.81	9.92
	Internal pH	8.48	11.05	8.36	10.26
	Tensile strength (kN/m)	1.730 ± 0.022	2.143 ± 0.011	1.515 ± 0.020	1.590 ± 0.021
	Folding endurance (FE)	0.745 ± 0.018	0.802 ± 0.074	0.509 ± 0.022	0.633 ± 0.046
BDP	Surface pH	4.65	10.10	4.34	9.79
	Internal pH	5.86	10.40	5.76	10.27
	Tensile strength (kN/m)	0.954 ± 0.021	1.371 ± 0.056	0.947 ± 0.022	1.361 ± 0.024
	Folding endurance (FE)	0.519 ± 0.026	0.594 ± 0.084	0.259 ± 0.026	0.317 ± 0.016

The wettability of the aged papers treated with PMS solution was evaluated by measuring the changes in contact angles. Contact angle is defined geometrically as the angle formed by a liquid, gas and solid intersect. Higher contact angle means hydrophobicity and lower contact angle means higher hydrophilicity. The cellulose is intrinsically hydrophilic and hygroscopic, but the formation of a more-hydrophobic polymer film on the surfaces of the fibers may alter their wettability by increasing hydrophobicity. The optical images of water droplets on the surfaces of the control RP and the RP treated by PMS solution are shown in Figs. 9(a) and 9(b). It could be noticed that in the case of the control RP, the contact angle could not be measured as water droplets were instantly spread and absorbed rapidly on the surface of the RP, making it difficult to obtain an accurate reading of the contact angle values, which were normally lower than 10° (Fig. 9c). However, the droplets on RP samples in the case of being treated by PMS solution were almost spherical in shape and did not spread. The specimens had good water repellent properties where they had contact angles above 130° (Fig. 9d). Wettability alteration on the surface of RP would attract great interests due to its potential applications. Self-cleaning surfaces of the papers were among the most frequently suggested applications. In addition, hydrophobic surface on the fibers could effectively resist the deterioration from acidic or alkaline hydrolysis, and reduce bacterial growth^[31], making these papers being preserved for a longer time. For the MWP and BDP paper samples, the contact angle increased in different degrees after treatment by PMS solutions (Figs. S5 and S6). More importantly, the as-prepared RP and BDP were optically transparent and the visibility of the paper sheets was not disturbed after deacidification in PMS solution.

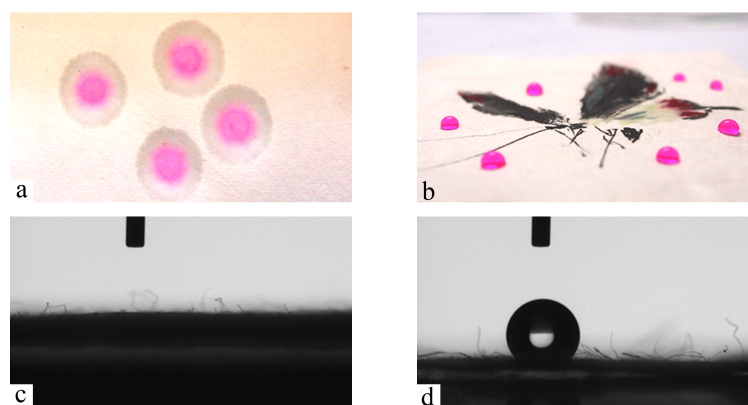


Fig. 9 The image of water droplets on the surface of the original RP (a), and image of water droplets on the surface of the modified RP by PMS solution (b), the contact angle of water droplet on the original RP ($< 10^\circ$) (c), the treated RP (130.9°) (d)

CONCLUSIONS

We have demonstrated the successful one-step modification of aged paper with potassium methyl silicate solution using silane coupling technique. The purpose of this research was to achieve the formation of copolymer network in seriously degraded paper. The experimental results clearly showed that after the deacidification treatment by PMS solution, besides alkaline buffer deposition, the paper strengthening and significant resistance to ageing were improved for the treated papers. This finding would be very promising because the PMS was known to be economically cost and the process was easy to perform, which gave good results in paper preservation. The reagents, including the by-products which could participate in improving alkaline reserve in the treatment process, were environment-friendly. All these features will be favorable for the long-term preservation of aged paper documents, and meet the green concept of heritage conservation. For the wet-chemical processes, the swelling of paper and dissolution of the printing ink were the sensitive issues. The further evaluations in treatment with PMS for different kinds of papers are needed even though in this particular case no swelling occurred for the paper samples used in the work.

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