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### ORIGINAL PAPER

### Preparation and application of modified carboxymethyl cellulose Si/polyacrylate protective coating material for paper relics

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There are large numbers of paper cultural relics in China, the country where paper making was invented. However, the paper relics have not been adequately protected so they are at risk of ageing, damage and disappearance. In order to better protect the paper relics, modified carboxymethyl cellulose/Si/polyacrylate protective materials were prepared with acrylicresin and modified carboxymethyl cellulose which has a good affinity with the paper and modified silica, improving the mechanical strength and ability to withstand weathering. The modified CMC/Si/polyacrylate protective material was analysed using infrared spectroscopy, transmission electron microscopy, differential scanning calorimetry and other performance-testing devices. The surface morphology of the paper samples was analysed using scanning electron microscopy. The protective material so prepared was evaluated by subjection to accelerated ageing (dry heat treatment). The results showed the protective material films to have good hydrophobicity, acid/alkali resistance and mechanical strength. When the content of SiO<sub>2</sub> is 6 mass %, the protective material has an excellent comprehensive performance. The results of the ageing test reveal that the prepared material can effectively slow down the ageing rate. The prepared material is suited to the protection of paper cultural relics. (C) 2016 Institute of Chemistry, Slovak Academy of Sciences

Keywords: carboxymethyl cellulose, paper relics, protection, accelerated ageing

### Introduction

With its long history, China has many cultural relics and ancient art, with a rich cultural and historical value which has attracted worldwide attention. Paper cultural relics represent an important part of the cultural heritage, containing an abundance of precious cultural and historical records. However, paper cultural relics have not only survived the vicissitudes of the past, but also now have to withstand erosion from all aspects of modern environmental pollution, oxygen, light, temperature, biological, water and soon, which result in the loss of their value as relics.

The various reasons for damage to paper relics can be classed into internal and external factors. On the one hand, there are factors of paper cultural relics inherent in their own material. In the exhibition hall, most of the paper relics, consisting of hand-made paper of which the main components are cellulose, lignin and hemicelluloses, are readily hydrolysed and oxidised, leading to yellowing of the paper and a reduction in hardness and folding strength. The hydrolysis of cellulose is catalysed by acids which derive from four main sources: the product of photo-oxidation, oxidation, inorganic acid from air, organic acid from biodeterioration, and additives, such as aluminium sulphate (Wang et al., 2013). Different additives possess special features and different impacts on paper but acidic additives cause serious damage to the paper. Acidity from the absorption of atmospheric pollutants, oxidation of lignin and additives from the papermaking process can all act as catalysts in the process of the

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acidic hydrolysis of paper (Area & Cheradame, 2011). Fig. 1 shows the process of cellulose hydrolysis. However, if the pH value of the paper surface is too high, it would undergo alkaline depolymerisation, leading to a decrease in the chain-lengths of the cellulose (Qi et al., 2010). Currently, the protection of paper relics, particularly deacidification, has attracted a great deal of attention.

On the other hand, paper cultural relics are subject to various external factors. Temperature, humidity, harmful gas, dust, light and microbes all affect the preservation of paper cultural relics. Higher temperature and humidity can cause the growth of microorganisms in paper relics, and degradation of the cellulose becomes more severe. Under certain conditions of humidity and temperature, paper may undergo a biodeterioration process due to action of the microorganisms present in the air (Strzelczyk, 2004; Karbowska-Berent et al., 2011). Microorganisms are the cause of serious forms of damage, such as weakening or loosening of paper, books overgrown with fungi and foxing, mainly apparent in loss of structure, surface discoloration and the presence of filamentous fungi and slimy substances (Michaelsen et al., 2006; Gutarowska et al., 2012). Harmful gases dissolved in water, such as  $SO_2$  and  $NO_2$ , their acidity or oxidability, which have adverse consequences on the paper heritage. A luminous beam (especially ultraviolet) have adverse effects on paper, accelerating ageing of paper. The effects of illumination on paper relics are incremental, and when paper is excessively exposed to light the chemical reaction rate is accelerated, causing serious ageing. Fig. 2 depicts paper relics with different degrees of damage.

Recently, ongoing surface protection and consolidation research on paper relics have included physical and especially chemical methods. Accordingly, the conservation and restoration of these items, including the use of special preserving polymers (Totolin & Neamtu, 2011), should be based on fundamental scientific principles: reversibility, inertness, maintenance of the integrity of the objects (aesthetic appearance and compatibility with the substrate). Scientific studies on improving paper strength include silk net lamination, polyester film encapsulation,  $\gamma$ -radiation polymerisation, the parylene process and the graft copolymerisation coating method (Cocca et al., 2006; Princi et al., 2007; Li et al., 2014). All the methods possess advantages and have an important role in preserving paper relics, albeit with inherent disadvantages. Hence, an efficient, harmless and effective method for the conservation of paper relics is urgently needed.

Tetraethoxysilane (TEOS) polymerises via hydrolysis to yield siloxane, a silica-based polymer (Barberena-Fernandez et al., 2015), which has heat/ cold resistance, good ventilation. The most common biopolymers employed are cellulose derivatives like sodium carboxymethyl cellulose (CMC), which is considered both environmentally friendly and non-toxic (Orelma et al., 2011; Fan et al., 2012; Yang et al., 2015). On the basis of polyacrylate having a good adhesion and flexibility, silicone materials as well as biopolymers, which have a better affinity with paper fibres, without being mutually exclusive after repair, are added. Some reports on the protection of paper cultural relics involve the use of cellulose and its derivatives, but most of the cellulose is modified and applied directly onto the paper.

In the present work, cellulose was modified with an acrylic monomer and took part in reaction with acrylic monomers. In addition, nano-silica, which has a good weather resistance, abrasion resistance and is biologically inert, was added. The protective material was also found to be reversible, this being an important component of the fundamental scientific principles. A series of modified CMC/Si/polyacrylate (CMC/Si/PA) protective coating materials were prepared using a semi-continuous seed emulsion polymerisation process. The physical properties of the emulsions, such as stability, viscosity, particle size and surface tension, were investigated. The hydrophobicity, acid/alkali resistance and compatibility of the prepared films with the paper were measured. The protective material thus prepared was evaluated by accelerated aging (dry heat treatment) tests.

#### Experimental

Methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MA), tetraethyl orthosilicate (TEOS),  $\gamma$ -methacryloxypropyl trimethoxysilane (KH-570), polyoxyethylene octylphenyl ether (OP-10), hydrochloric acid, ethanol and sodium sulphate were all provided by Sinopharm Chemical Reagent, Shanghai, China. Disodium hydrogen phosphate was supplied by Shanghai Su Yi Chemical Reagent, Shanghai, China. Potassium persulphate (KPS) and carboxymethyl cellulose were purchased from Tianjin Chemical Reagent Factory, China. The DS of CMC chosen was 0.9. Sodium dodecyl sulphate (SDS) was obtained from the Shanghai reagent factory. Ammonia was acquired from Shanghai Pilot Chemical Corporation, China. All reagents were used as received without further purification.

### Samples of paper cultural heritage

In order to better evaluate the effect of the protective material prepared, Chinese art paper which is similar to the material of the paper cultural relics was selected for use as paper samples. In accordance with Chinese Standard GB/T450-2008 (The Chinese National Standards, 2008a), a certain amount of paper samples were used in the test. The paper samples were prepared without protective material. The front sides of the paper were coated with the emulsion and



Fig. 1. Process of cellulose hydrolysis.



Fig. 2. Appearance of different kinds of paper relics, such as manuscript (A), ancient book (B), calligraphy (C) and painting (D).

948



Fig. 3. Synthetic route to CMC-MA.



Fig. 4. Synthetic route to modified silica dispersion.

painted three times. After the emulsion was dry, the emulsion was applied three times on the obverse side of paper. The paper samples with protective material were prepared.

### Preparation of CMC-MA

A certain amount of CMC was added into a fournecked round flask and dissolved in water at 60 °C. Next, KPS was added as a catalyst and stirred for 20 min. A certain amount of methacrylic acid (MA; molar ratio of CMC : MA = 1 : 1) was slowly added drop-wise into the four-necked flask. Finally, the crude product was obtained after 6 h of the reaction. Fig. 3 shows the synthetic route for obtaining CMC-MA.

### Preparation of modified silica dispersion

First, the tetraethyl orthosilicate (TEOS), water, ethanol (at mass ratio of 3:4:4) were added into a three-necked flask, then HCl was added in order to adjust the pH to 4. Magnetic agitation was applied



Modified CMC/Si/PA protective material

Fig. 5. Synthetic route to modified CMC/Si/PA protective material; 1 – PA; 2 – CMC-Si-0; 3 – CMC-Si-1; 4 – CMC-Si-2; 5 – CMC-Si-3; 6 – CMC-Si-4.

at ambient temperature for 2 h. Finally, KH-570 (12 mass % of TEOS) was added and allowed to react for 2 h until the product was obtained. Fig. 4 shows the synthetic route to modified silica dispersion.

# $\label{eq:preparation} Preparation \ of \ modified \ CMC/Si/PA \ protective \ material$

The modified CMC/Si/PA protective material emulsion was prepared by means of semi-continuous seeded emulsion polymerisation and pre-emulsification technology. First step: distilled water, OP-10 and SDS mixture (mass ratio of OP-10 : SDS = 2:1) were added into a four-necked round flask and stirred until dissolved. At 50 °C, MMA, BA and CMC-MA were added and subjected to rapid stirring; the preemulsification proceeded for 1 h. The protective material emulsion without CMC-MA and  $SiO_2$  was expressed as PA. Second step: a certain amount of the modified silica dispersion, OP-10 and SDS mixture was transferred into another four-necked flask and stirred for 1 h at 50 °C. Next, a buffer solution  $(Na_2HPO_4)$  and one-third of the initiating agent (KPS) were added. When the temperature attained 80°C, one-ninth of the pre-emulsification was added to the flask. When the blue phase appeared, one-third of KPS was added. Simultaneously, the rest of the pre-emulsification was slowly added drop-wise (over 2 h). At the end of the drop-wise procedure, the remainder of the KPS was added to the flask. The temperature was increased to 90 °C and maintained for

4 h. The liquid mixture was stirred and allowed to cool at ambient temperature. Finally,  $NH_3 \cdot H_2O$  was used to adjust the pH to7–8. Altering the contents of SiO<sub>2</sub> (0 mass %, 2 mass %, 4 mass %, 6 mass % and 8 mass % based on total monomers), a series of modified CMC/Si/PA protective coating materials were prepared and denoted as CMC-Si-0, CMC-Si-1, CMC-Si-2, CMC-Si-3 and CMC-Si-4, respectively. The synthetic route for the modified CMC/Si/PA protective material is shown in Fig. 5 and the basic components of the modified CMC/Si/PA materials are listed in Table 1.

The films were prepared by coating cleaned poly (tetrafluoroethylene) plates with the emulsions and allowing them to dry at ambient temperature then all the films were placed in sealed bags for further use.

#### Characterisation

In order to observe the storage stability of the modified CMC/Si/PA materials, all the emulsions were stored in sealed containers for more than one month at ambient temperature. Because the lime water was added to the ancient paper and calcium bisulphite was used to be as a papermaking additive in modern times, the paper need to determine the stability for  $Ca^{2+}$ . A  $CaCl_2$  solution (5 mass %) was added to the test tube, in which all the kinds of emulsions were added, respectively, and allowed to stand at ambient temperature for 48 h. In order to determine the stability of the freeze-thawing procedure, an appropriate amount of

950

Somple	РА	CMC-Si-0	CMC-Si-1	CMC-Si-2	CMC-Si-3	CMC-Si-4
Sample				g		
		P	reparation of CMC	-MA		
CMC	0	2.42	2.42	2.42	2.42	2.42
MA	0.86	0.86	0.86	0.86	0.86	0.86
KPS	0	0.1622	0.1622	0.1622	0.1622	0.1622
	First	step of preparation	n of modified CMC	/Si/PA protective 1	naterial	
MMA	10	10	10	10	10	10
BA	12.8	12.8	12.8	12.8	12.8	12.8
OP-10	0.488	0.538	0.549	0.559	0.570	0.581
SDS	0.244	0.269	0.274	0.280	0.285	0.291
	Second	d step of preparatio	on of modified CM	C/Si/PA protective	material	
$SiO_2$	0	0	0.52	1.04	1.56	2.09
OP-10	0.163	0.179	0.183	0.186	0.190	0.194
SDS	0.081	0.090	0.091	0.093	0.095	0.097
$Na_2HPO_4$	0.130	0.143	0.146	0.149	0.152	0.155
KPS	0.146	0.161	0.165	0.168	0.171	0.174

Table 1. Basic composition of modified CMC/Si/PA materials

the emulsion was frozen at  $-20 \,^{\circ}$ C for 18 h and allowed to stand at ambient temperature for 6 h. The test of the heat-resisting property was as follows: the samples were kept in the oven at 60  $^{\circ}$ C for 72 h. All the results were obtained by observing whether stratification or precipitation occurred.

The viscosity of the emulsion was measured using a numerical viscometer (NDJ-9S, Shanghai Precision and Scientific Instrument, Shanghai, China). The particle size of the modified CMC/Si/PA protective coating material was measured using a laser particle size analyser (BIC-9010, Brookhaven Instrument, Holtsville, NY, USA). The surface tension of the emulsion was tested using a surface/interfacial tension tester (DCAT11, Dataphysics, Germany). All measurements were carried out five times, and the average value was calculated.

The FT-IR spectra of the samples were obtained using an FT-IR spectrometer (AVATAR360, Madison, Nicolet). A minimum of 32 scans was signal-averaged with a resolution of 2 cm<sup>-1</sup> in the 4000–400 cm<sup>-1</sup> range. The KBr wafer-coating method was used for pre-treatments. The morphology was investigated using a TEM (Tecnai12, Philips Company, Eindhoven, The Netherlands) microscope at an accelerating voltage of 120 kV.

The hardness of the films was measured using a KYLX-A sclerometer (Jiangdu Kaiyuan Test Machine, China). The contact angles of water on the surface of the coating films were measured on a commercial CAM200 optical system (KSV Instruments, Finland) using the sessile drop method. The measurements were carried out three times and the temperature and relative humidity were  $(23 \pm 2)^{\circ}$ C and  $(50 \pm 3)$  %, respectively. The FT-IR spectra of the films were obtained using a spectrometer (iS50, Nicolet, Massachusetts, USA) with the scanning air as the background. Without pre-treatment, the films could be measured directly. A scanning electron microscope S-4800 (Hitachi, Tokyo, Japan) was used to characterise the surface and the morphology of paper both bare and coated with the protective material. Differential scanning calorimetry (DSC) of the coating films was performed using a Netzsch instrument (204 F 1, Netzsch, Seligenstadt, Germany).

The swelling degree (%, water) of the films was measured as follows: the films were cut to pieces of 3 cm × 3 cm and placed in deionised water, 3.0 mass % NaOH, 3.0 mass % H<sub>2</sub>SO<sub>4</sub>, respectively, at 25 °C after weighing. They were removed after 24 h, filter paper was used to wipe the water on the surface of films and they were weighed again. The degree of swelling,  $\omega$  in mass %, was calculated using the following Eq. (1), where  $m_1$ ,  $m_2$  are the mass of the films prior to and after being placed in the water (or 3.0 mass % NaOH, 3.0 mass % H<sub>2</sub>SO<sub>4</sub>), respectively. The measurements were carried out three times for each sample, and the average value was calculated. The standard deviation was calculated using the following Eq. (2), where  $\bar{X}$  is the average value; and n is the number of iterations:

$$\omega = 100 \frac{m_2 - m_1}{m_1} \tag{1}$$

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (X_i - \bar{X})^2}$$
(2)

The smaller the standard deviation is, the lower the deviation from the average value is.

Table 2. Physical properties of modified CMC/Si/PA emulsions

Sample	PA	CMC-Si-0	CMC-Si-1	CMC-Si-2	CMC-Si-3	CMC-Si-4
$SiO_2/mass \%$	0	0	2	4	6	8
Appearance	Translucency, blue	Milkiness, blue				
Storage stability $> 6$ month	Stable	Stable	Stable	Stable	Stable	Precipitate
$Ca^{2+}$ stability	Stable	Stable	Stable	Stable	Stable	Stable
Freeze-thawing stability	Stable	Stable	Stable	Stable	Stable	Stable
High temperature stability	Stable	Stable	Stable	Stable	Stable	Stable
Viscosity/(mPa s)	$16 \pm 1$	$18 \pm 1$	$20 \pm 1$	$20 \pm 1$	$21 \pm 1$	$24 \pm 2$
Particle size/nm	$59.3\pm0.3$	$86.2\pm0.4$	$98.4\pm0.2$	$98.7\pm0.3$	$109.1\pm0.3$	$141.2\pm0.5$

### Property and characterisation of paper samples

In order to compare the impact of the protective materials on the thickness of the paper, the thickness of the paper samples was measured using a micrometer. The measurements were carried out five times for each sample, and the average value was calculated. To directly observe the appearance of the paper samples, the surface and cross-section of the paper samples were investigated using a scanning electron microscope (S-4800, Hitachi, Tokyo, Japan).

## Accelerated ageing (dry heat treatment) of paper samples

In accordance with Chinese standard GB/T 464-2008 (The Chinese National Standards, 2008b), the blank paper pattern (A) and the paper pattern coated with a protective material (B) were suspended in a thermostatic oven and heated at  $(105 \pm 2)$  °C for  $(72 \pm 1)$  h. By comparing the samples prior to and after aging, the retention rate of tensile strength and the weight loss were calculated.

The tensile strength testing for all the paper samples was carried out on a tensile tester (KY-8000A, Jiangdu Kaiyuan Test Machine, Jiangdu, China) at ambient temperature at a speed of 100 mm min<sup>-1</sup>. All the measurements were expressed as an average of ten times. The paper samples were 100 mm long and 15 mm wide. The retention rate (u) was calculated by Eq. (3), where  $Y_1$  and  $Y_2$  are the tensile strength results of the paper samples without accelerated ageing and with accelerated ageing, respectively. The mass of the sample without accelerated ageing was recorded as  $m_1$ , and the mass of sample with accelerated ageing was recorded as  $m_2$ . The weight loss  $(\Delta m)$  was calculated according to Eq. (4). Measurements were carried out three times for each sample, and the average value was calculated:

$$u = 100 \frac{Y_2}{Y_1}$$
(3)

$$\Delta m = 100 \frac{m_1 - m_2}{m_1} \tag{4}$$

### **Results and discussion**

## Physical properties of modified CMC/Si/PA emulsion

The physical properties of the modified CMC/Si/ PA protective material are listed in Table 2. It is apparent that the pure acrylic emulsion was translucent and blue. After the addition of modified CMC and SiO<sub>2</sub>, the emulsion became milky and slightly blue. After the 6 months' storage, the emulsions, with the exception of CMC-Si-4, exhibited only a small amount of precipitation, showing the emulsions to possess good storage stability. Under natural light, the films and paper samples with protective materials did not exhibit any significant changes, which indicate their good photostability. Moreover, the modified CMC/Si/PA protective material exhibited good stability, including the stability of Ca<sup>2+</sup>, the stability in freeze-thawing, etc.

In addition, the viscosity is in accord with the permeability of the protective material. The ability to penetrate the paper requires the material to have low viscosity. Table 2 shows the viscosity range of 0.016 Pa s to 0.024 Pa s, meeting the requirements of the paper heritage. The particle size of the protective material is also displayed. The particle size of pure polyacrylate is 59.3 nm; after adding CMC, which is a polymer, the particle size changed substantially, then with the content of  $SiO_2$  increasing, the particle size increased slightly. The addition of  $SiO_2$  can reduce the formation of cracks and improve the UV resistance, although it also increases the possibility of agglomeration of the emulsion so the  $SiO_2$  content needs to be optimised. Irrespective of that, the modified CMC/Si/PA protective material exhibited excellent physical properties.

In order to study the effect of modified CMC and  $SiO_2$  on the surface tension of the emulsion, the surface tension (SFT) was investigated, with the results shown in Fig. 6. It is clear that the surface tension of the CMC/Si/PA emulsion is lower than that of the PA emulsion. With the content of SiO<sub>2</sub> increasing, the surface tension continued to decrease, and the surface tension decreased to (32.459  $\pm$  0.027) mN m<sup>-1</sup>. This was mainly because the modified CMC and SiO<sub>2</sub> had

Sample  $\mathbf{PA}$ CMC-Si-0 CMC-Si-1 CMC-Si-2 CMC-Si-3 CMC-Si-4 Hardness number  $84.57 \pm 0.07$  $85.05\,\pm\,0.05$  $86.72\,\pm\,0.06$  $87.18\,\pm\,0.04$  $88.14 \pm 0.04$  $88.86\,\pm\,0.08$ Swelling degree<sup>a</sup>/%  $12.18 \pm 0.09$  $16.82 \pm 0.06$  $13.70\,\pm\,0.05$  $11.18 \pm 0.06$  $10.14 \pm 0.07$  $12.01 \pm 0.09$ Swelling degree<sup>b</sup>/% $12.02 \pm 0.08$  $14.31 \pm 0.07$  $10.35 \pm 0.05$  $8.60\,\pm\,0.05$  $7.32 \pm 0.04$  $8.88 \pm 0.06$ Swelling degree<sup>c</sup>/%  $14.22 \pm 0.11$  $17.62\,\pm\,0.12$  $14.57 \pm 0.09$  $11.55 \pm 0.09$  $10.34\,\pm\,0.08$  $12.46 \pm 0.08$ Contact angle/°  $55.12 \pm 0.04$  $41.75 \pm 0.05$  $57.42 \pm 0.06$  $62.63 \pm 0.07$  $67.48 \pm 0.08$  $68.67 \pm 0.07$ 

Table 3. Some properties of modified CMC/Si/PA films

a) 3.0 % NaOH solution; b) 3.0 %  $H_2SO_4$  solution; c) water.



Fig. 6. Surface tension of materials. PA (A); CMC-Si-0 (B); CMC-Si-1 (C); CMC-Si-2 (D); CMC-Si-3 (E); CMC-Si-4 (F).

a lower surface free energy and the wettability could be improved. The smaller the surface tension of the emulsion is, the better the flowability is; and the better the adhesion to the surface of the paper is.

### Properties of modified CMC/Si/PA films

Table 3 shows some properties of the modified CMC/Si/PA films, revealing the hardness of the modified CMC/Si/PA films to be greater than that of pure PA film. Moreover, with the content of SiO<sub>2</sub> increasing, the hardness of the film increased. This is attributed to modified CMC possessing good flexibility and the rigid SiO<sub>2</sub> can cross link the structure between the organic and inorganic phases by a chemical bond. Consequently, the modified CMC/Si/PA films possess good flexibility and mechanical strength.

The degree of swelling (mass % of water) and acid/alkali resistance are important parameters for paper heritage. Therefore, the degree of swelling of the CMC/SiO<sub>2</sub> films and the acid/alkali resistance were investigated. Because of the high degree of hygroscopicity of CMC in comparison with the pure PA films, the degree of swelling of CMC-Si-0 can attain 3.4 mass %. This is mainly because a small amount of SiO<sub>2</sub> has good hydrophobicity. However, there is lots of SiO<sub>2</sub> flocculate in the emulsion, the hydrophobicity



Fig. 7. FT-IR spectra of CMC (a) and CMC-MA (b).

would be poor. The degree of swelling firstly decreases, and then increases. The introduction of  $SiO_2$  can enhance the water resistance of the sealing material.

From Table 3, when compared with PA, it can be seen that the contact angle decreases from  $55.1^{\circ}$  to  $68.7^{\circ}$  when the content of the modified silica dispersion changes from 0 mass % to 8 mass %. This indicates that the addition of modified CMC could reduce the water resistance of the films due to the hydrophilic character of CMC. However, the addition of SiO<sub>2</sub> can result in a reduction in the degree of swelling. The hydrolysis of Si—O—R generated the Si—O—Si bond, which can provide a lower degree of swelling in the films (Guo et al., 2005; Liu et al., 2008). Therefore, the introduction of SiO<sub>2</sub> can enhance the hydrophobicity of the films, while the result of the acid/alkali resistance is similar to the hydrophobicity.

### FT-IR analysis

The FT-IR spectra of CMC and CMC-MA are shown in Fig. 7. As can be seen from Fig. 7a, absorption peaks are observed at 1612 cm<sup>-1</sup> and 1425 cm<sup>-1</sup>, which are the characteristic absorption peaks of C=O. The stretching vibration peak of C=O-C is at 1120 cm<sup>-1</sup> and the characteristic absorption peak of  $\beta$ -(1,4)-two glycosides is at 1058 cm<sup>-1</sup>, respectively. The characteristic absorption peak at 2915 cm<sup>-1</sup> is observed and attributed to a long chain of methylene.



Fig. 8. FT-IR spectra of  $SiO_2$  (a), KH-570 (b) and KH-570 modified  $SiO_2$  (c).



Fig. 9. FT-IR spectra of PA (a), CMC-Si-0 (b) and CMC-Si-3 (c).

A strong absorption band at around  $3435 \text{ cm}^{-1}$  is the stretching vibration of hydrogen bonding which is affected by the hydroxyl of the cellulose ring. In Fig. 7b, the stretching vibration of hydrogen bonding is observed at  $3394 \text{ cm}^{-1}$ . Moreover, it can be seen that some of the inactive hydroxyl groups in the cellulose did not participate in the reaction, which can form more hydrogen bonds with the paper fibres, enhancing the compatibility of the protective material. There is stretching vibration of C=C at 1639 cm<sup>-1</sup>, and the rocking vibration of =CH<sub>2</sub> is at 836 cm<sup>-1</sup>, indicating that MA modified CMC successfully.

The FT-IR spectra of SiO<sub>2</sub>, KH-570, KH-570 modified SiO<sub>2</sub> are shown in Fig. 8. A strong absorption band at around 1000–1100 cm<sup>-1</sup> can be observed, corresponding to the Si—O—Si asymmetric stretching vibration (Su et al., 2010). In Fig. 8b, stretching vibrations of C=O and C=C at 1720 cm<sup>-1</sup> and 1637 cm<sup>-1</sup> may be observed, respectively. The rocking vibration at 902 cm<sup>-1</sup> is attributed to =CH<sub>2</sub>. In Fig. 8c, there



Fig. 10. FT-IR spectra of PA (a), CMC-Si-0 (b) and CMC-Si-3 (c) films.

are stretching vibrations of C=O at 1695 cm<sup>-1</sup> and C=C at 1645 cm<sup>-1</sup>, indicating that KH-570 modified SiO<sub>2</sub> successfully.

The FT-IR spectra of PA (a), CMC-Si-0 (b) and CMC-Si-3 (c) are shown in Fig. 9. The FT-IR spectra of CMC-Si-3 and CMC-Si-0 display the characteristic absorption peaks at 2958 cm<sup>-1</sup> and 2872 cm<sup>-1</sup> C—H (methylene). The band at 1735 cm<sup>-1</sup> is attributed to the stretching vibration of C=O. The characteristic absorption peaks of  $-CH_2$ — are at 1457 cm<sup>-1</sup> and 1393 cm<sup>-1</sup>, respectively. When PA is compared with CMC-Si-0, there is a stretching vibration peak of the hydroxyl at around 3200–3600 cm<sup>-1</sup>, due to the introduction of CMC. When PA is compared with CMC-Si-3, the characteristic absorption peak at 1000–1400 cm<sup>-1</sup> becomes wider, and the characteristic absorption peak of Si—O is at around 1000–800 cm<sup>-1</sup> because of the introduction of SiO<sub>2</sub>.

The FT-IR spectra of PA, CMC-Si-0 and CMC-Si-3 films are shown in Fig. 10. Compared with Fig. 10b, there is no obvious change because the functional groups of MA-CMC, such as C==O, C=OC, are similar to those of PA. In Fig. 10c, the absorption peaks at around 900–800  $\text{cm}^{-1}$  are higher than those shown in Figs. 10a and 10b, displaying the characteristic absorption of the Si-O-Si bond. When Figs. 9b and 9c are compared with Figs. 10b and 10c, the stretching vibration peak of the hydroxyl at around  $3200-3600 \text{ cm}^{-1}$  is smaller. Because of the water absorption of CMC, the CMC in emulsion associates a large number of hydroxyl groups, while there is not a lot of water or hydroxyl in the film. The above analysis demonstrates that the modified CMC/Si/PA material was successfully prepared.

### TEM analysis

The TEM images of CMC-Si-1 and CMC-Si-3 are shown in Fig. 11. The particles are shown to be spher-



Fig. 11. TEM images of CMC-Si-1 (A) and CMC-Si-3 (B).



Fig. 12. DSC curves of CMC-Si-0 (a), CMC-Si-1 (b) and CMC-Si-3 (c).

ical in shape and uniform in distribution. This result indicates that the protective material thus prepared could produce across-linked structure. This is mainly attributed to the existence of a large amount of SiO<sub>2</sub> and the inter actions between the particles being strong (Hashemi-Nasab & Mirabedini, 2013). It is recognized that the SiO<sub>2</sub> particles have a higher surface area and surface-free energy, so the TEOS hydrolyses and gels easily but the KH-570 was grafted onto the SiO<sub>2</sub> surface, which greatly reduced the agglomeration of SiO<sub>2</sub> particles. Hence SiO<sub>2</sub> is found to exhibit good dispersity and only a small number of the SiO<sub>2</sub> particles have a tendency to aggregate.

### DSC analysis

The DSC curves of CMC-Si-0, CMC-Si-1 and

CMC-Si-3 are shown in Fig. 12. It is evident that the glass transition temperature of the hard segment occurs at 30-50 °C and is the only one, manifesting that the composition of the films is uniform and compatible. All of the peaks are at almost 370 °C, indicating that the films have a good thermal stability because the PA films have a higher concentration of double bonds and a higher concentration of cross-linking. Also, the temperature increased with the increase in the content of SiO<sub>2</sub>, meaning that SiO<sub>2</sub> can enhance the thermal stability of the films. Due to the high thermal stability of the SiO<sub>2</sub> particles, these play an important role in limiting the molecular mobility of polymer molecular chains (He et al., 2010).

## Simulated application of modified CMC/Si/PA protective material for paper samples

### Analysis of paper samples

From the above analysis and discussion, taking into consideration the comprehensive performances of the protective material, CMC-Si-3 was selected as the reinforcement material in the subsequent tests. The appearance of a paper sample coated with CMC-Si-3 protective material is shown in Fig. 13. It can be seen that the protective material films are colourless and transparent. This result indicates that the material thus prepared could meet the requirements for the protection of paper cultural relics.

The series of paper samples which were not coated with a protective material were denoted as A. The series of paper samples coated with a protective material were denoted as B. The thickness was measured and the results are listed in Table 4, showing that the difference in thickness is 0.0072 mm. This shows the



Fig. 13. Appearance of paper sample A (A) without protective material and paper sample B (B) coated with CMC-Si-3 protective material.

 Table 4. Thickness of paper samples

Paper sample	Thickness/mm			Average/mm		
A B Thickness difference	$0.074 \\ 0.081 \\ 0.007$	0.075 0.083 0.008	$0.074 \\ 0.082 \\ 0.008$	$0.076 \\ 0.082 \\ 0.006$	$0.074 \\ 0.081 \\ 0.007$	$0.0746 \\ 0.0818 \\ 0.0072$

impact of the protective material on the paper cultural relics to be almost negligible, conforming to the requirements for cultural relics' protection.

### SEM analysis of paper samples

The SEM surface and cross-section images of the original paper (A and C) and the paper after coating CMC-Si-3 (B and D) are shown in Fig. 14. It is evident that the emulsion exhibits good penetrability, having a good protective effect on the fibre of the paper sample. After coating with the protective material, the surface of the paper samples was smooth, and the protective films could be generated, which had no effect on the thickness of the paper samples.

#### Reversibility of protective materials

Because of the importance of the paper relics, reversibility is an important component of the fundamental scientific principles. An accidental discovery in the course of the experiments revealed that acetone could dissolve the protective material so prepared. On the basis of this finding, paper samples coated with protective materials were soaked in acetone in a sealed container for 1 h. The acetone was then replaced several times until the acetone was transparent and not turbid. The high volatility of acetone is perhaps responsible for damage to the paper. Accordingly, the paper sample including a little acetone was covered with a fresh protective film with some small holes in the film so as to reduce the volatilization rate of the acetone. Finally, the paper with the protective materials removed was very similar to the paper samples without protective materials. The appearance of the paper samples is shown in Fig. 15.

The average thickness of the paper sample with the protective materials removed is 0.0719 mm. The average value of the tensile strength is 343.48 N m<sup>-1</sup>. The SEM surface image of the paper sample with the protective material removed is shown in Fig. 16. It can be seen that the cellulose of paper was not damaged by the protective material thus prepared. It may be concluded from these results, that the protective materials thus prepared afford a good reversibility.

### Analysis of accelerated ageing (dry heat treatment)

Although in comparison with other relics, paper relics are more susceptible to ageing and damage, the ageing process is still slow. Accordingly, in order to obtain results within a limited time, the dry heat accelerated ageing test was performed, as a standard for evaluating this protective material. First, the average value of tensile strength for sample A was  $357.75 \text{ N m}^{-1}$ , while the value for sample B that was significantly different from the value of sample A was

956



Fig. 14. SEM surface and cross-section images of original paper (A and C) and paper after coating with CMC-Si-3 (B and D).



Fig. 15. Appearances of paper without protective material (A), paper with coated protective material (B) and paper with protective material removed (C).

1102.17 N m<sup>-1</sup>. Then, after a dry heat accelerated ageing test, the mass loss rate and the retention rate of tensile strength are listed in Table 5.

In the first 24 h, the mass loss of sample A and the tensile strength decreased, while the mass loss of sample B decreased further but the tensile strength did not decrease. This phenomenon is mainly due to the fact that, in the first 24 h, moisture was lost from samples A and B, while sample B contained more water. After 48 h, another sample was extracted to weigh and test. The weight and tensile strength of sample

A reduced significantly, while the weight and tensile strength of sample B reduced only slowly. After heat ageing for 72 h, the ageing of sample A was more serious than for sample B which remained in a good condition. This was possibly because, at this temperature, the cellulose, hemicelluloses and lignin elements of unprotected paper samples will suffer degradation or decomposition from the paper system, whereas for sample B, being protected, the reduction in quality is mainly caused by the loss of water. The above results of the accelerated ageing tests show that the modified

Sample	Mass loss/%			Retention rate of tensile strength/ $\%$		
	24 h	48 h	72 h	24 h	48 h	72 h
А	7.08	10.27	15.89	90.98	86.14	80.77
В	9.11	10.09	11.36	96.71	93.09	88.69

Table 5. Results of accelerated ageing of paper samples



Fig. 16. SEM surface image of paper sample with protective material removed.

CMC/Si/PA protective material played a positive role in protecting paper cultural relics.

#### Conclusions

A series of protective materials which protect paper relics were prepared by a semi-continuous seed emulsion polymerisation process. The emulsion exhibited good stability, lower viscosity and smaller particle size, and surface tension. Moreover, the protective material films showed good acid/alkali resistance and good compatibility with the paper. The dry heat accelerated ageing tests showed that the protective material could reduce the rate of ageing. In addition, the reversing experiment revealed that the protective material was reversible. Especially after the ageing experiment, the paper samples with the protective materials removed were found to be very similar to the paper. Taking the above advantages into consideration, the modified CMC/Si/PA protective material was found to have a positive effect in protecting paper relics, and is in valuable from the aspect of protection of the cultural heritage.

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