

Preparation of Self-Healing Acrylic Copolymer Composite Coatings for Application in Protection of Paper Cultural Relics

Jicheng Xu^{1,2} Tao Zhang^{0,3} Yan Jiang,² Dongya Yang^{0,3} Fengxian Qiu^{0,3} Qian Chen,³ Zongping Yu⁴

¹School of the Materials Science & Engineering, Jiangsu University, Zhenjiang, 212013, China

²Zhenjiang Key Laboratory of Functional Chemistry, Institute of Medicine & Chemical Engineering, Zhenjiang College, Zhenjiang, 212028, China

³Institute of Green Chemistry and Chemical Technology, School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212013, China

⁴Suzhou Mingda Macromolecule Science and Technology Co., Ltd., Suzhou, 215234, China

Due to the limitation of storage condition, paper cultural relics are constantly subject to human damage and natural aging, requiring rescue protection. In this study, a series of nanocellulose/calcium carbonate microcapsule/fluorineacrylamide styrene/acrylic copolymer composite protection materials were prepared and used as an efficient selfhealing composite coating for paper cultural relics protection. CaCO₃ microcapsules were prepared by interfacial reaction method and doped into the polymer materials to obtain the self-healing composite coating. The properties of composite protection materials were studied via the self-healing experiment, dry heat accelerated aging test. and reversible experiment. The effects of composite protection materials on simulate paper cultural relics were analyzed. The results show that when the amount of hollow calcium carbonate microcapsules was 0.500 g, the composite protection materials had good comprehensive performances. The prepared materials work positive influence on the conservation of simulate paper cultural relics that could be one of the potential materials for application in protection of paper cultural relics. POLYM. ENG. SCI., 00:000-000, 2019. © 2019 Society of Plastics Engineers

INTRODUCTION

Cultural relics are unique historical products that have immeasurable significance for studying ancient humanities and economy [1]. As one of the main carriers of traditions, civilization, art and ways of behaving, paper plays a vital role in the dissemination and transmission of information [2]. Paper cultural relics can show science and technology in the history of a country and are one of the important symbols of education and culture. As the carrier of human civilization, paper cultural relics are not only the

Published online in Wiley Online Library (wileyonlinelibrary.com). © 2019 Society of Plastics Engineers crystallization of ancient art culture, but also a non-renewable cultural resource [3].

The main components of paper are cellulose, hemicellulose, lignin, and hemi-lignin, which are easily hydrolyzed and oxidized, resulting in paper crepe, chalking, and aging [4, 5]. Paper deterioration mainly manifests as a decrease in mechanical properties caused by acid hydrolysis and yellowing caused by oxidation of cellulose [6]. There are many paper cultural relics in the world, which are invaded by light, heat, and microorganisms, and then will gradually be destroyed or even disappeared. The work of paper cultural relics protection is imperative, and new composite protective materials are urgently needed for development and research. It is important that the composite protective materials should not change the physical, chemical, and optical appearance of the paper cultural relics including gloss or color saturation. Furthermore, composite protective materials should be "reversible" [7].

Acrylic resin can block oxygen, water vapor, and acid gas, has low surface tension, good permeability and film-forming properties, heat resistance and corrosion resistance [8, 9]. The -COOH group in acrylic acid and the -NH₂ group in acrylamide can form stable hydrogen bonds with cellulose, so the acrylic resin can be used as a protective surface coating for wood and paper [9–11]. Nanocellulose and paper cellulose have the same composition and special affinity. Adding cellulose to the protective material can improve the compatibility with the substrate.

It is well known that the formation process of hydrophobic surface can be formed by rough surface and low surface energy [12, 13]. Based on this principle, various techniques have been developed by exploiting the hydrophobic based on the surface synergistic effect of surface roughness and low surface energy [14, 15]. The material has low surface energy and high roughness to improve oil and water resistance [16]. Fluorine-containing polyacrylate polymers have many excellent properties such as heat resistance, aging resistance, solvent resistance, weather resistance, low dielectric constant, and low surface free energy due to the strong electronegativity of fluorine atoms [17, 18]. The introduction of inorganic particles into the polymer can improve the hydrophobicity, mechanical properties and thermal stability of the composite material. Calcium carbonate (CaCO₃) is a commonly compatible inorganic material that is durable, biocompatible, and biodegradable [19-21]. It has a high porosity and specific surface area and is doped into an organic polymer to improve surface roughness. In addition, the hollow structure calcium carbonate microcapsules can be prepared by interfacial reaction, and the composite protective materials are wrapped to form

Correspondence to: T. Zhang; e-mail: zhangtaochem@163.com or F. Qiu; e-mail: fxqiu@ujs.edu.cn

Contract grant sponsor: Zhenjiang College Scientific Research Team; contract grant number: ZJCKYTD2017023. contract grant sponsor: Society Development Fund of Zhenjiang; contract grant numbers: FZ2017070; SH2018009. contract grant sponsor: Jiangsu Planned Projects for Postdoctoral Research Funds; contract grant number: 1701067C. contract grant sponsor: 333 High-Level Personnel Training Project of Jiangsu Province; contract grant number: BRA2016142. contract grant sponsor: National Natural Science Foundation of China; contract grant number: 21706100. contract grant sponsor: Natural Science Foundation of Jiangsu Province; contract grant number: BK20161362. DOI 10.1002/pen.25282

 $CaCO_3$ self-healing microcapsules [22]. With crack emerging of the coating film, the $CaCO_3$ microcapsules will break and release the interior healing agents to repair the crack [23, 24]. Selfhealing coatings have shown remarkable development over the recent number of years and demonstrated great promise in extending the service life, reducing maintenance costs, thereby improving the durability of conventional coatings [25]. Therefore, it is of great practical significance to develop a self-healing protection material to improve the performance of traditional polymer coating for paper cultural relics protection.

In this work, composite protection materials (CPM) were prepared by using hollow CaCO₃ microcapsules (HCM), modified nanocellulose, OP-10, SDS, MMA, BA, AA, St, AM, and DFMA as main raw materials. The physical properties including particle size, viscosity, and surface tension of the CPM emulsions were studied. The thermal stability, solvent-resistance, mechanical properties, and self-healing of the CPM films were also investigated. The effects of composite protection materials on simulated paper cultural relics were analyzed by thickness test, dry heat accelerated aging test, and reversible experiment.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA), styrene (St), acrylamide (AM), sodium dodecyl sulphate (SDS), polyoxyethylene octylphenyl ether (OP-10), disodium hydrogen phosphate (Na₂HPO₄), potassium persulphate (KPS), γ -aminopropyltriethoxysilane (KH-550), polyoxyethylenesorbitan monooleate (Tween 80), (Z)-sorbitan mono-9-octadecenoate (Span 80), sodium carbonate (Na₂CO₃), calcium chloride (CaCl₂), methyl alcohol (CH₃OH), sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), ethanol (CH₃CH₂OH), ammonium hydroxide (NH₃·H₂O), diethyl ether, and paraffin liquid were all provided by Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Microcrystalline cellulose (MCC) was purchased from Tianjin Chemical Reagent Factory, Tianjin, China. Dodecafluoroheptyl methacrylate (DFMA) was purchased from Harbin Xuejia Fluorine-Silicon Chemical Co., Ltd., Heilongjiang, China. All reagents were used as received without further purification.

Preparation of Modified Nanocellulose

Twenty grams of MCC was dissolved into the 400 mL H_2SO_4 solution (35 wt.%) and stirred for 1.5 h at 40 °C. Then deionized water was added to stop the acid hydrolysis reaction. After centrifugal separation (8,000 rpm, 10 min), washing to neutral and lyophilization (-50 °C, 24 h), the nanocellulose (NC) was prepared successfully.

Fifteen grams of NC and 1 g of KH-550 were added into a three-neck flask equipped with 200 mL 95% ethanol solution, stirring continuedly at 80 °C. After 1 h, the solution was filtered, washed, and dried. The modified nanocellulose (MNC) was successfully prepared.

Preparation of Polymeric Emulsion

1. OP-10, SDS, and deionized water were added into a fournecked round-bottomed flask and stirred until dissolved to prepare compound emulsifier. Na_2HPO_4 was dissolved in deionized water to obtain buffer solution. KPS was dissolved in deionized water to obtain initiator solution.

- 2. The MMA, BA, AA, St, AM, DFMA, and two-thirds of above compound emulsifier were added into a four-necked round-bottomed flask and stirred for 1 h at 50 °C to obtain shell pre-emulsion.
- 3. MNC and the remaining one-third of above compound emulsifier were added into a four-necked round-bottomed flask and stirred continuously for 1 h at 50 °C to obtain core preemulsion.
- 4. The above buffer solution, one-third of initiator solution, and one-ninth of shell pre-emulsion were added into a four-necked round-bottomed flask, reacted at 80 °C with stirring for 1 h. When the mixture became bluish, another one-third of initiator solution and the rest of shell pre-emulsion were dropwise added within 2 h. At the end of the dropwise procedure, the remainder of the initiator solution was added to the flask kept stirring for 4 h at 90 °C. Then, the emulsion was cooled to room temperature and pH value was adjusted to about 7 with NH₃·H₂O to obtain the polymeric emulsion.

Preparation of CaCO₃ Microcapsule

The CaCO₃ microcapsules were effectively obtained by the interfacial reaction method using both carbonate salts such as Na₂CO₃ in the inner water phase and calcium salts such as CaCl₂ in the outer water phase [26, 27]. Ten milliliters of paraffin liquid, Span 80 solution (0.217 g of Span 80 dissolved in 10 g of deionized water) and Tween 80 solution (0.217 g of Tween 80 dissolved in 10 g of deionized water) and 200 g of deionized water were stirring 30 min in a three-neck flask. Then the CaCl₂ solution (5.55 g of CaCl₂ dissolved in 100 g of deionized water) was added into the mixture and stirred for 1 h. And the Na₂CO₃ solution (5.30 g of Na₂CO₃ dissolved in 100 g of deionized water) was added drop by drop reacting 4 h. After filtering, washing, and lyophilization (-50°C, 24 h), the CaCO₃ microcapsules with paraffin were gained.

The CaCO₃ microcapsules with paraffin were immersed in diethyl ether for 24 h, then filtering, washing, and lyophilization, the hollow CaCO₃ microcapsules (HCM) were obtained due to the CaCO₃ microcapsules had the higher porosity. The CaCO₃ microcapsules with polymeric emulsion (CMPE) were prepared by added the HCM into the prepared polymeric emulsion, steeping for 24 h. The synthetic route of the CaCO₃ microcapsules is given in Fig. 1.

Preparation of Composite Protection Materials

The different amounts of HCM were added into the polymeric emulsion then ultrasonic dispersing (40 KHz, 35 W) 20 min and allowed to stand for 24 h. According to the different contents of HCM, a series of composite protection materials (CPM) were expressed as CPM-1, CPM-2, CPM-3, CPM-4, CPM-5, and CPM-6, respectively. The synthetic route of composite protection materials is shown in Fig. 2, and the basic recipes are listed in Table 1.

The prepared CPM emulsions were poured into the clean poly(tetrafluoroethylene) plates and dried at room temperature. Then the CPM films were obtained and put into sealed bags for further study.

Simulate Paper Cultural Relics

The simulate paper cultural relics samples were Xuan paper of Hongxing brand, purchased from China Xuan Paper Co., Ltd.,



FIG. 1. The synthetic route of CaCO3 microcapsule. [Color figure can be viewed at wileyonlinelibrary.com]



FIG. 2. The synthetic route of composite protection materials. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1. The basic co	omponents o	f the composite	protection	materials.
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Sample	CPM-1	CPM-2	CPM-3	CPM-4	CPM-5	CPM-6
HCM (g)	0	0.125	0.250	0.375	0.500	0.625
MNC (g)	0	1.25	1.25	1.25	1.25	1.25
DFMA (g)	4.90	4.90	4.90	4.90	4.90	4.90
MMA (g)	5.16	5.16	5.16	5.16	5.16	5.16
BA (g)	10.18	10.18	10.18	10.18	10.18	10.18
AA (g)	0.39	0.39	0.39	0.39	0.39	0.39
St (g)	2.88	2.88	2.88	2.88	2.88	2.88
AM (g)	0.19	0.19	0.19	0.19	0.19	0.19
SDS (g)	0.27	0.34	0.34	0.34	0.34	0.34
OP-10 (g)	0.54	0.68	0.68	0.68	0.68	0.68
Na_2HPO_4 (g)	0.11	0.13	0.13	0.13	0.13	0.13
KPS (g)	0.12	0.15	0.15	0.15	0.15	0.15

Beijing, China. The characters were written onto the Xuan paper with ink to ensure the consistency of simulate sample with the paper cultural relics and easy to observe sample changes. The Xuan papers were sampled and prepared according to GB/T 450–2008 (Chinese national standard) for conducting further research.

The paper samples without coating protective material were denoted as Paper-A. Paper-A (1) samples were some parts of Paper-A samples after dry heat accelerated aging experiment. According to GB/T 20777–2006 (Chinese national standard), the obverse and reverse sides of some parts of Paper-A samples were coated CPM emulsion by wire rod coater (RDS #12, RD Specialties Inc, New York) and then clamped and hung to dry at room temperature. The paper samples prepared above were denoted as the Paper-B. Paper-B (1) samples were some parts of Paper-B samples after dry heat accelerated aging experiment. Paper-B (2) samples were some parts of Paper-C samples were some parts of Paper-B samples after the dry heat aging test and the measurement of reversibility. The numbering diagram of paper samples is shown in Fig. 3.

The Properties of CPM Emulsions

The CPM emulsions were stored in sealed containers for more than 3 months at ambient temperature to observe the storage stability.

The CPM emulsions were placed at -20 °C for 12 h and then were moved to 25 °C for 12 h as a cycle repeated five times. The freeze thawing stability of all samples were evaluated by observing whether the sample was precipitated.



FIG. 3. The numbering diagram of paper samples.

The CPM emulsions were placed into vacuum drying oven at $60 \,^{\circ}$ C for 72 h. The manipulations were performed five times. The temperature stability could be evaluated by observing the appearance changes of CPM emulsions.

Numerical viscometer (NDJ-9S, Shanghai Precision and Scientific Instrument Co., Ltd., Shanghai, China) was used to test the viscosity of CPM emulsions. The particle diameter was measured twice average by a laser particle size analyzer (BI-9000, Brookhaven Instrument, Holtsville, New York, USA). Surface tension of CPM emulsion was tested by surface/interfacial tension tester (DCAT 11, Dataphysics Company, Germany).

The Properties of CPM Films

FT-IR spectrum of CPM films were tested by FT-IR spectrometer (AVATAR 360, Madison, Nicolet) from 4,000–400 cm⁻¹ ranges. The hardness was performed on a sclerometer (KYLX-A, Jiangdu Kaiyuan, China). Tensile strength test and elongation at break testing for the test specimens were performed on a tensile tester (KY-8000A, Jiangdu Kaiyuan, China) at room temperature. The contact angle measurement of the CPM films was carried out on a commercial video-based contact angle measuring device (KSV Instruments Ltd., Finland). Thermal stability of films was test by Netzsch instrument (STA 449 C, Netzsch, Seligenstadt, Germany). It was performance at a heating rate of 10 °C/min and under N₂ atmosphere, and heating range was from room temperature to 800 °C.

The CPM films were tailored to a specific shape $(2 \text{ cm} \times 2 \text{ cm})$ and immersed in test liquid (deionized water and 5.0 wt% NaOH solution) at ambient temperature after being weighted. Then, the films were wiped with a piece of filter paper to remove the test liquid on the film surface after 24 h and then weighted again. The water absorption (or swelling degree), ω %, was calculated with the following Eq. (1).

$$\omega = \frac{m_2 - m_1}{m_1} \times 100\%$$
 (1)

where m_1 is the mass of the film before being put into the liquid, m_2 is the mass of the film after being put into the liquid, respectively.

Sample	CPM-1	CPM-2	CPM-3	CPM-4	CPM-5	CPM-6
Appearance	Milky	Milky	Milky	Milky	Milky	Milky
Storage stability (>3 months)	Stable	Stable	Stable	Stable	Stable	Precipitate
Freeze-thawing stability	Stable	Stable	Stable	Stable	Stable	Precipitate
High-temperature stability	Stable	Stable	Stable	Stable	Stable	Precipitate
Particle size (nm)	48.1 ± 0.3	49.7 ± 0.2	51.3 ± 0.2	53.0 ± 0.2	54.7 ± 0.1	57.2 ± 0.5
Viscosity (mPa·s)	16.4 ± 0.3	17.2 ± 0.4	19.2 ± 0.4	21.4 ± 0.2	24.2 ± 0.2	25.8 ± 0.3
Surface tension $(mN \cdot m^{-1})$	38.752 ± 0.03	37.253 ± 0.02	36.591 ± 0.03	35.820 ± 0.02	34.981 ± 0.01	34.784 ± 0.06

The Self-Healing Properties of the CPM Films

In order to test the self-healing, the CPM films were numbered and slashed by art knife. The films were pressed tightly with a 500 g weight on a flat table along the break and placed it for 24 h. The appearances of CPM films were observed by visual observation and recorded by photos.

The Thickness of Paper Samples

The thickness of paper samples was carried out with micrometer caliper (Mitutoyo 342–251, Mitutoyo Institute of Metrology, Tokyo, Japan). The operations were done five times for each sample, and the average of value was calculated.

Dry Heat Accelerated Aging Test of Samples

Dry heat accelerated aging test of samples was acted in strict accordance with the standard of GB/T 464–2008 (Chinese national standard). All samples were hanged in a thermostatic oven which was well ventilated and drying, heated to 105 ± 2 °C for 72 h. All measurements were carried out in triplicate.

Tensile strength testing of the samples was carried out on a tensile tester (KY-8000A, Jiangdu Kaiyuan Test Machine, Jiangdu Kaiyuan, China) at a speed of 20 mm/min. The samples were cut into 20 mm long and 4 mm wide. The measurement was repeated five times to obtain the average value. The retention rate of tensile strength (Δu) and the mass loss (Δm) of samples were obtained to compare the results before or after aging.

The retention rate of tensile strength ($\triangle u$) was calculated according to Eq. (2):

$$\Delta u = \frac{Y_2}{Y_1} \times 100\% \tag{2}$$

where Y_1 and Y_2 are results of paper samples before and after dry heat accelerated aging test, respectively.

The mass loss rata ($\triangle m$) was calculated with the Eq. (3):

 $\Delta m = \frac{m_3 - m_4}{m_3} \times 100\%$ (3)

where m_3 and m_4 are the mass of paper samples before and after dry heat accelerated aging test, respectively.

The Reversible Experiment Analysis

The paper samples with protective material were immersed in methyl alcohol for 1 h at room temperature. Then the samples were naturally dried and weighted. Measurements were repeated until the weight loss of paper samples was less than 1%.

RESULTS AND DISCUSSIONS

The Properties of CPM Emulsions

The physical properties of the prepared CPM emulsions are shown in Table 2. As shown in Table 2, the appearances of CPM emulsions were milky. All of CPM emulsions had good storage stability, freeze-thawing stability, and high temperature stability except CPM-6. This was due to the excessive HCM was added in the CPM-6, resulting in the incompatibility between the HCM and the polymeric emulsion [28].

As the content of calcium carbonate microcapsules increased, the viscosity and the average particle size of the emulsion increased, and the surface tension decreased. This could be due to the increasing of HCM content which leaded to increase in the friction between the emulsion molecules and formed more branch chains. [29] The permeability of the emulsion was related to its surface tension. The smaller the surface tension of the emulsion, the stronger the wetting effect on the solid surface and the better protective effect to the paper fibers.

The Properties of CPM Films

The physical properties of CPM films are given in Table 3. The hardness and tensile strength of CPM films increased with the HCM content increased, showing that the addition of HCM

Sample	CPM-1	CPM-2	CPM-3	CPM-4	CPM-5	CPM-6
Hardness (shore A)	87.7 ± 0.2	90.1 ± 0.5	91.5 ± 0.4	92.9 ± 0.3	94.3 ± 0.2	94.8 ± 0.6
Tensile strength (MPa)	2.34 ± 0.04	4.13 ± 0.03	4.58 ± 0.06	5.21 ± 0.02	5.36 ± 0.05	5.86 ± 0.02
Swelling degree (%, 5.0% NaOH)	16.4 ± 0.2	13.2 ± 0.5	12.8 ± 0.1	12.1 ± 0.4	11.6 ± 0.2	11.4 ± 0.4
Swelling degree (%, deionized water) Contact angle (°)	$\begin{array}{c} 17.9 \pm 0.3 \\ 67.7 \pm 2.2 \end{array}$	$\begin{array}{c} 12.7 \pm 0.3 \\ 78.9 \pm 3.5 \end{array}$	$\begin{array}{c} 12.0 \pm 0.2 \\ 85.7 \pm 4.3 \end{array}$	$\begin{array}{c} 11.4 \pm 0.5 \\ 93.3 \pm 3.9 \end{array}$	$\begin{array}{c} 10.6 \pm 0.2 \\ 98.5 \pm 4.2 \end{array}$	$\begin{array}{c} 10.1 \pm 0.7 \\ 103.1 \pm 5.4 \end{array}$

TABLE 3. The properties of CPM films.

had a significant positive effect on the hardness and tensile strength of CPM films. The results showed the prepared composite protection materials had good mechanical strength.

The water and alkali resistance of materials were beneficial to paper relics protection. The swelling degree (deionized water and NaOH solution) could reflect the water and alkali resistance of the composite protection materials. Compared the swelling degree of CPM-1 and CPM-2 film, the sharp decline of swelling degree was found because of the introduction of HCM. As the HCM content continued to increase, the cross-linking ability of the polymeric materials were continuously improved, resulting in further increased in water resistance and alkali resistance of the films.

As shown in Table 3, the range of contact angle was from 67.7° to 103.1° . With the content of the HCM increased, the contact angle of the CPM films gradually increased, illustrating that the addition of HCM could improve water resistance.

FT-IR Analysis

FT-IR spectra of MCC, NC, KH-550, and MNC are given in Fig. 4. It could be found the FI-IR curves of MCC and NC were similar, indicating the acid decomposition had no effect on main functional groups of cellulose. From the FT-IR spectrum of KH-550, it could be found that the peaks around $3,400-3,300 \text{ cm}^{-1}$ were assigned to the stretching vibration peaks of $-NH_2$ groups. The flexural vibration peak of $-NH_2$ groups was found at 1582 cm^{-1} . The peaks around $1,168-1,069 \text{ cm}^{-1}$ belong to the absorption peaks of Si–O bond. From the FT-IR spectrum of MNC, stretching vibration overlap peaks of $-NH_2$ and -OH groups located at around $3,600-3,100 \text{ cm}^{-1}$. The flexural vibration peaks of Si–O groups and C–O groups located at around $1,200-900 \text{ cm}^{-1}$, and the peak area increased. These above results suggested that the MNC was prepared successfully.

The FT-IR spectra of HCM, polymeric emulsion, CMPE, and CPM-5 are shown in Fig. 5. In Fig. 5, it could be found that the

MCC

NC



FIG. 4. FT-IR spectra of MCC, NC, KH-550, and MNC. [Color figure can be viewed at wileyonlinelibrary.com]



FIG. 5. FT-IR spectra of HCM, polymeric emulsion, CMPE, and CPM-5. [Color figure can be viewed at wileyonlinelibrary.com]

peaks at 876, 745, and 712 cm⁻¹ both belong to the characteristic peaks of CaCO₃ in HCM and CMPE. The strong absorption peak was found at 1732 cm⁻¹, which was assigned to stretching vibration peak of C=O groups. The peaks around 3,000–2,800 cm⁻¹ were assigned to the absorption peaks of saturated C-H bonds. Compared FT-IR spectra of HCM, polymeric emulsion, and CMPE, the stretching vibration peak of saturated C—H bonds (3000–2,800 cm⁻¹) and C=O bonds (1,737 cm⁻¹) were found in polymeric emulsion and CMPE, and the characteristic peaks of CaCO₃ were contained in HCM and CMPE. The above results indicated that the CaCO₃ microcapsule contained a capsule core (polymer emulsion) and a capsule wall (calcium carbonate) were prepared.



FIG. 6. TG curves of CPM-1 and CPM-5 films. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 4. The specific parameters of thermal properties.

Sample	T _{5%} (°C)	$T_{10\%}(^\circ C)$	T _{50%} (°C)	T _{90%} (°C)	T _{d max} (°C)
CPM-1	285.10	336.23	387.20	412.25	391.2
CPM-5	341.01	372.22	397.10	432.04	747.1

The CPM films after numbered



FIG. 7. The self-healing photos of the CPM series of films. [Color figure can be viewed at wileyonlinelibrary.com]

TG Analysis

The thermal properties of the CPM-1 and CPM-5 films were evaluated by the TGA. The TG curves are shown in Fig. 6 and the specific parameters of thermal properties are given in Table 4. With the increased of the HCM content, the thermal decomposition temperature of the film increased, indicated HCM could effectively improve the heat resistance of the film. And in data analysis, when weight loss was 50%, the temperature of CPM-5 was 397.10 °C, and the temperature of CPM-1 was 387.20 °C. The remaining mass of CPM-1 and CPM-5 was 1.59 and 5.83%, respectively. In addition, T_{d max} data are listed in Table 4, showing that the temperature increased from 391.2 to 747.1 °C. Compared with pure CPM-1, the results indicated that CPM-5 film achieved a higher thermal stability, which was mainly due to the

strong force between $CaCO_3$ microcapsule and polymeric emulsion.

The Measurement of Self-Healing Experiment

The property of self-healing is visually observed in Fig. 7. Marks 1 to 6 on the films correspond to CPM-1 to CPM-6, respectively. There was no self-healing effect in the CPM-1 film due to the absence of CaCO₃ microcapsules, so the incision did not change. The incisions of the CPM-2 and CPM-3 film became smaller, while the incisions of CPM-4, CPM-5, and CPM-6 almost completely renovated. This was mainly because the emulsion contained in CaCO₃ microcapsule was released after being scratched, and a new film was formed after curing, so that the incision could be repaired. Therefore, the CPM films containing CaCO₃ microcapsule had better self-healing properties, and as the CaCO₃ microcapsule content increased, the self-healing effect increased.

Effect of Protective Materials on the Appearance of Simulated Paper Cultural Relics

Based on the above analysis, the CPM-5 emulsion was selected as the protective material in the following tests under the consideration of the comprehensive performances. The appearances of different processed paper samples are shown in Fig. 8. Compared Fig. 8A,B, after coated the CPM-5 protective material, there was no significant change in the paper sample appearance, indicating that the CPM-5 material had a high transparency and glossiness. After dry heat aging test and reversible experiment, paper and characters were not blurred and faded, and the appearance of the paper sample hardly changed in Fig. 8B,C. The results showed that the dry heat accelerated aging test and reversible experiment had no effect on the paper samples, and the protective material met the requirements of paper cultural relics protection.

Effect of Protective Materials on the Thickness of Simulated Paper Cultural Relics

The measurement results and average value of the paper sample thickness are shown in Table 5. The average thickness of the Paper-B sample was 0.0816 mm because of the composite protection material, which was 11.48% thicker than the Paper-A. This was primarily determined by the coating process and the amount of CaCO₃ micro-capsules in the composite protection materials. The average thickness of the Paper-C was 0.6 um thinner than that of the Paper-A, which was about 99.18% of the average thickness of the Paper-A,



FIG. 8. The photographs of paper samples naked (A), paper samples covered with CPM-5 (B) and paper samples after dry heat aging test and reversible experiment (C). [Color figure can be viewed at wileyonlinelibrary.com]

Sample	Thickness (mr	Thickness (mm)					
Paper-A	0.073	0.074	0.072	0.074	0.073	0.0732	
Paper-B	0.082	0.083	0.080	0.082	0.081	0.0816	
Paper-C	0.072	0.073	0.072	0.074	0.072	0.0726	

TABLE 6. The mass loss rate (Δm), tensile strength, and tensile strength retention rate (*u*) of paper samples.

Samples	Δm (%)	Tensile strength $(N \cdot m^{-1})$	u (%)
Paper-A	13.29	358.01 ± 4	79.74
Paper-A (1)		285.48 ± 2	
Paper-B	2.36	2068.33 ± 5	92.85
Paper-B (1)		1950.44 ± 3	
Paper-B (2)	/	350.18 ± 2	99.29
Paper-C		347.70 ± 7	

indicating that the dry heat accelerated aging test and reversible experiment caused 0.82% damage to the thickness of paper sample. The results showed that the protective materials could increase slightly the thickness of the paper sample, but had little effect on the thickness of the paper after reversible experiment.

Analysis of Dry Heat Accelerated Aging Test and Reversible Experiment

The aging resistance of the material could be evaluated by the mass loss rate of the sample before and after the dry heat accelerated aging test. The reversibility of the composite protection materials could be evaluated by the tensile strength retention rate [30]. The mass loss rate (Δm), tensile strength, and tensile strength retention rate (Δu) of the paper samples are listed in Table 6.

Based on the results in Table 6, the mass loss rate (Δm) of the Paper-A was 13.29% after dry heat accelerated aging test, which was almost 5.6 times than that of Paper-B. The mass loss rate of paper samples might be caused by the decomposition of the cellulose, hemicellulose, and lignin in the paper samples during the dry heat accelerated aging test. The mass loss rate of Paper-B was only 2.36%, indicating that CPM-5 protective coating could prevent cellulose decomposition, thus protecting the paper from damage.

The average tensile strength of Paper-A and Paper-B was 358.01 and $2068.33 \text{ N} \cdot \text{m}^{-1}$, respectively. The result showed that

the protective material could increase the tensile strength of the paper sample. The tensile strength retention rate increased from 79.74% to 92.85% after the dry heat accelerated test, indicating that the prepared CPM-5 protective material had a positive role to reduce the dry heat aging damage of the paper sample.

The tensile strengths of Paper-A, Paper-B (2), and Paper-C were 358.01, 350.18, and 347.70 N·m⁻¹, respectively. After the reversible experiment, the tensile strength retention of the paper sample was 99.29%, indicating that the reversible experiment had almost no damage to the paper sample. This was mainly due to the damage of the sample transferred to the surface coating by dry heat accelerated aging, so that the influence on the base paper was small, and the tensile retention rate was increased.

SEM Analysis

The SEM images of Paper-A, Paper-A (1), and Paper-C are shown in Fig. 9. As shown in Fig. 9, the fibers in Paper-A were clearly visible and there were many filamentous joints between the fibers. In Paper-A (1), there were some cracks and flaking on the paper fibers, and most of the fine joints between the fibers were disappeared. In Paper-C, the filamentous between the fibers were reduced, but the fibers became thick and the surface was smooth, and no peeling was observed. This was mainly due to the cellulose contained in the protective material could increase the toughness of the fibers in the paper sample, and the protective material released from the CaCO3 microcapsules could further protect and repair the fibers in paper sample. The SEM analysis results shown that the CPM-5 protective materials could effectively alleviate the damage caused by dry heat accelerated aging test, and it also shown that the reversible experiment had less damage to the paper fibers.

CONCLUSIONS

A series of protective materials were prepared using the method of pre-emulsification and semi-continuous seed emulsion polymerization. The prepared polymer protective material had small particle size, low surface tension, small viscosity, and good stability. As the content of $CaCO_3$ microcapsules increased, the



FIG. 9. SEM images of paper-A (A), paper-A (1) (B) and paper-C (C).

particle size and viscosity of the CPM emulsion increased, and the surface tension decreased; the hardness and tensile strength of the CPM films increased, and the swelling degree in water and NaOH solution decreased. The CPM films could increase the thickness and tensile strength of the paper sample, and there were no significant change in sample appearance. When the CPM film was broken, the inner CaCO₃ microcapsules could release the protective materials and repair the membrane itself. The dry heat accelerated aging test, reversible experiment and SEM analysis showed that the prepared material could protect the paper sample from the damage caused by high temperature and had good antiaging properties and better self-healing property.

The prepared materials had self-healing and anti-aging properties, met the principles of "repair the old as old" for cultural relic protection, and could be applied to the field of paper cultural relics protection.

ACKNOWLEDGMENT

This project was supported by Natural Science Foundation of Jiangsu Province (BK20161362), National Natural Science Foundation of China (21706100), 333 High-Level Personnel Training Project of Jiangsu Province (BRA2016142), Jiangsu Planned Projects for Postdoctoral Research Funds (1701067C), Qing Lan Project of Jiangsu Province (2018-2021), "169 Project" of Zhenjiang City (2016-2020), Society Development Fund of Zhenjiang (SH2018009 and FZ2017070) and Zhenjiang College Scientific Research Team (ZJCKYTD2017023).

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