Preparation and Surface Sizing Application of Sizing Agent Based on Collagen from Leather Waste

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Collagen extracted from leather waste was modified with maleic anhydride. Then, using ammonium persulfate as an initiator, by pre-modifying collagen reacted with styrene and ethyl acrylate monomers, a vinyl-grafted collagen sizing agent (VGCSA) for paper was prepared. Before the experiment, the performance of VGCSA was tested and VGCSA emulsion was applied to the surface sizing of the corrugated paper. Effects of the amount of VGCSA, the compound proportion of VGCSA, and starch and styrene-acrylic emulsion were studied relative to paper properties. The morphological changes of the paper before and after sizing were characterized by SEM. It was found that the collagen reacted with styrene and ethyl acrylate monomers. Through the grafting of vinyl and collagen, the crystallinity and thermal stability of VGCSA increased. The structure of VGCSA was spherical with a uniform size, and the average particle size was approximately 350 to 400 nm. After being sized, the surface fibers of paper became smooth and orderly. The optimal sizing of VGCSA was 8 g/m^2. The optimal proportion of VGCSA with starch was 4:6, and the optimal proportion of VGCSA with SAE was 2:8. The research indicates that collagen extracted from leather waste could be used as a biomaterial, and environmental and economic benefits could be created as well.

Keywords: Waste leather collagen; Vinyl modification; Paper sizing agent; Applications

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INTRODUCTION

Currently, the demand for sizing agents is rising with the rapid development of the paper industry. Because traditional pulp sizing agents do not always achieve the desired effects, require substantial levels of addition, and easily impact the operations of the paper machine, there is motivation to consider new sizing agents. Thus, the surface sizing process, which sometimes has the advantages of lower demand of sizing agents and a better sizing effect, has received increasing attention. Commonly used synthetic surface sizing agents include copolymers of styrene and maleic anhydride (SMA), copolymers of styrene and acrylic (SAA), copolymers of styrene and acrylate (SAE), water-soluble polyurethane (PUD), alkyl ketene dimer (AKD), and poly-vinyl alcohol (PVA) (Hodgson 1994; Ashori *et al.* 2008; Samyn *et al.* 2010). Biological sizing agents include starch (Moutinho *et al.* 2011), rosin, chitosan, cellulose derivatives (Liu *et al.* 2008; Stanssens *et al.* 2011; Zhang *et al.* 2013), and collagen (Ibrahim *et al.* 2009). These materials can greatly improve the mechanical properties and water resistance of paper. To reduce costs, a mixture of these raw materials has been used for surface sizing. However, in recent years, the cost of biological sizing agents has increased with the increase in food price. Furthermore, most biological sizing agents have a poor hydrophobic sizing effect not only because most of them are water-soluble substances with structures containing hydrophilic groups, but also because the film has difficulty resisting the penetration of the liquid after sizing. Also, the use of synthetic sizing agents is restricted because synthetic sizing agents are expensive. Therefore, it is necessary to accelerate the development of new biological sizing agents by using cheap natural polymer reasonably.

Collagen, a common biological material, has a unique three-dimensional helical, fibrous structure and a large number of active groups, such as amino, carboxyl, amide, *etc*. It can be grafted or cross-linked with a variety of monomers to synthesize new sizing agents. Sommer and Kunz (2012) investigated the dependency of water resistance of collagen films on different processing factors during crosslinking. It was reported that a collagen film without crosslinking was almost completely disintegrated after a 2-h cooking period at 80 °C . It was also reported that a thermally crosslinked film showed a significantly higher resistance to water. Brauer and Termini (1973) aimed to determine the scope of the grafting reaction. In their research, over 30 monomers were grafted to steer hide collagen and collagen films using ceric ammonium nitrate as an initiator. They found that high yields of apparent graft polymer could be obtained with more acrylate and methacrylate esters. They also found that monomers containing such diverse substituents as hydroxy, cyano, chloro, trifluoroethyl, or glycidyl groups might be grafted onto collagen.

Each year, a large amount of leather waste is produced in China, more than 80% of which is composed of collagen. Reasonable use of this collagen will speed up the utilization of solid wastes, and create economic and environmental benefits as well.

In the present research, the collagen extracted from leather waste was used as a raw material. It was first pre-modified with maleic anhydride. Next, it was initiated by ammonium persulfate, pre-modified through the reaction between collagen and styrene and ethyl acrylate monomers, and a vinyl-grafted collagen sizing agent (VGCSA) for papers was prepared. Corrugated paper used as packing material must exhibit good physical strength as well as liquid water or moist air resistance, which is typically achieved by sizing treatment during paper manufacture (Dong *et al*. 2014). The VGCSA was applied as a surface sizing additive to corrugated paper in this work. The impact of the amount of VGCSA, the compound proportion of VGCSA and starch, and styrene-acrylic emulsion on the paper’s properties were studied, respectively.

EXPERIMENTAL

Materials

The collagen powder extracted from the waste leather was provided by Hebei Zhongpi Dongming Environmental Science and Technology Co., Ltd., (China). Maleic anhydride was purchased from Tianjin Fengchuan Chemical Reagent Co., Ltd. Styrene (St), ethyl acrylate (EA), and ammonium persulfate (analyzed reagent grade) were obtained from Tianjin Kermel Chemical Reagent Co., Ltd. Acrylate copolymer (SAE) was obtained from Hubei Jiayun Chemical Technology Co., Ltd. Corrugated paper was obtained from the Cailun paper mill in Shaanxi.

Preparation of VGCSA Emulsion

Fifteen grams of collagen were allowed to swell for 30 min in 150 mL of distilled water. The suspension was stirred constantly until the collagen was completely dissolved into a transparent solution. The solution was placed in a 500-mL four-neck flask armed with a reflux condenser, a mechanical stirrer, a thermometer, and a constant pressure drop funnel. Then the pH of the collagen solution was adjusted to 8, and the reflux condenser was opened. Three grams of maleic anhydride were allowed to swell in 30 mL distilled water, and the maleic anhydride solution was added to the collagen solution. The reaction mixture was agitated at 75 °C for 2 h at a pH of 8 to 9. Then the pH of the mixture was adjusted to 5, 10 g of mixed monomers of EA and St were added to the flask, and the mixture was emulsified for 30 min. The initiator was added slowly over a period of 3 h into the flask from a constant pressure drop funnel. The reaction was continued for an additional 30 min, after which the VGCSA emulsion was obtained. The mechanism of the reaction is shown in Fig. 1.

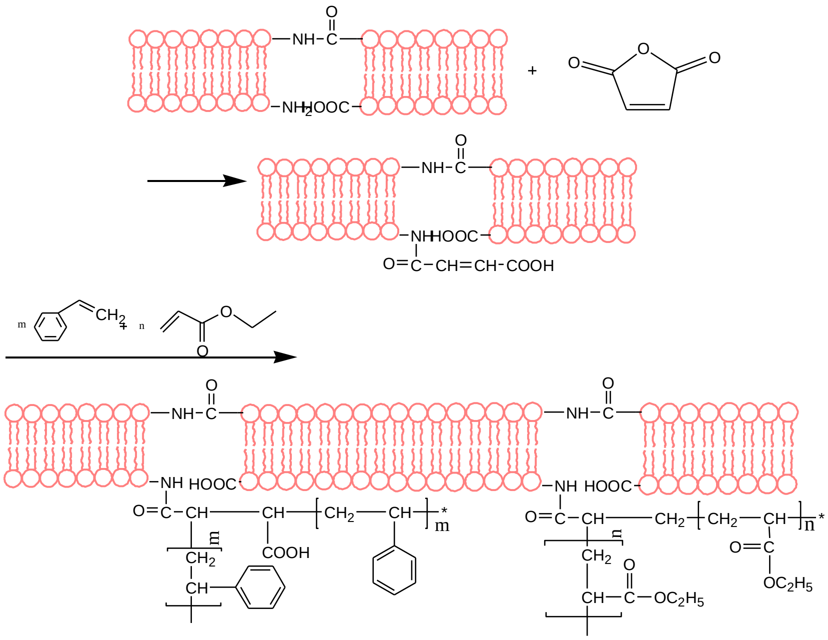

Fig. 1. Scheme for the reactive mechanism

Characterization

The VGCSA emulsion was repeatedly washed by anhydrous ethanol, then was precipitated, filtered, and dried by vacuum to obtain the crude product. The crude product was then extracted in the Soxhlet apparatus for 24 h with acetone as the extraction agent. The crude product was dried by vacuum to obtain the single product. Fourier Transform-Infrared Spectroscopy (FT-IR, VECTOR-22, Germany) analysis of the samples was carried out using compressed pellets of KBr with collagen and VGCSA samples. The wave number ranged from 500 to 4500 cm^{-1}. X-ray Diffraction (XRD, D/max2200PC, Japan) studies were performed to identify the changing of the crystal form of collagen and VGCSA samples using CU K α X-radiation. The patterns were recorded over a range of 2θ from 10 to 60 degrees. Thermogravimetric analysis (TGA, Q500, USA) was used to analyze the thermal stability of the collagen and VGCSA samples. The heating rate was 5 °C/min, the range of temperature was from room temperature to 800 °C, and the flow of nitrogen gas was 60 mL/min. The VGCSA emulsion obtained was diluted to 1/1000 of the solid content with distilled water, and then was deposited on the copper grids. Then, the morphology and particle size of the VGCSA emulsion were determined by transmission electron microscopy (TEM; FEI Tecnai G2 F20 S-TWIN, USA).

Surface Sizing Method

The process of surface sizing for papers in industry was used for the surface sizing process in this work. Corrugated base paper was used as the base-stock, cut from pristine papers to a size of approximately 16 cm × 20 cm. The coating method was used with the horizontal roller type surface sizing using the K303 MULTI coater from PK Print Coat Instruments Ltd., England. The amount of sizing was controlled by choosing appropriate coating bars and coating speed. Then the sized papers were dried at 105 °C and equilibrated for 24 h at a temperature of 25 °C and 65 ± 20% relative humidity. In this work, the VGCSA emulsion obtained was used for surface sizing of the corrugating medium. Firstly, the optimum sizing amount of VGCSA emulsion was investigated. The sizing amounts were 0, 2, 4, 6, 8, and 10 g/m^2. Secondly, the optimum mixed proportions of VGCSA emulsion with commercial styrene acrylic emulsion and starch emulsion were studied, respectively. The ratios about the mass were both 10:0. 8:2, 6:4, 4:6, 2:8, and 0:10.

Properties of the Surface-Sized Sheets

The tensile strength index and the ring crush index of papers before and after sizing were determined according to GB/T 12914-2008 (2008) and GB/T 2679.8-1995 (1995). The absorbency based on GB/T 1540-2002 and the Cobb$_{60}$ test (GB/T 1540-2002, 2002) was used to measure the water absorption. Then the papers before and after sizing were cut into small pieces, fixed on the sample stage using a conductive adhesive, and sprayed with gold for 60 s with an electricity of 8 to 10 mA in vacuum. Finally, the transverse and vertical section of the paper fibers were characterized by scanning election microscopy (SEM, S4800, Japan).

RESULTS AND DISCUSSION

Characterization of VGCSA Emulsion

FT-IR Analysis of collagen and VGCSA

Curves (a) and (b) in Fig. 2 show the FT-IR spectra of collagen and VGCSA. The absorption peak at 1637 cm^{-1} corresponds to the amide C$=$O bond stretching in the peptide bond (amide I). The absorption peak at 1491 cm^{-1} indicates the amide-II bond stretching, amide III (1386 cm^{-1}) (Li *et al*. 2015). Curve (b) in Fig. 2 indicates that after modification, the amide I, II, and III peaks were slightly shifted to lower wave numbers. It was similar to the contents reported in the literature (Chen *et al*. 2012). This was caused by the change of connection order, or conformation, in the main chains of collagen and its branches after modification. Evidently, the environment around the amide bond was changed, resulting in movement of the infrared absorption peaks. The peak at 1726 cm^{-1} can be attributed to the C$=$O bond stretching from the saturated aliphatic, indicating that the EA was grafted onto the collagen. The peaks at 1491 and 1135 cm^{-1}, respectively, were attributed to the saturated C-H and C-C(C$=$O)-O absorption peaks of the saturated aliphatic. The peaks at 763 and 700 cm^{-1} were the absorption peaks of 5 H from the benzene ring. All of these observations revealed the fact that the vinyl monomers were grafted onto the collagen.

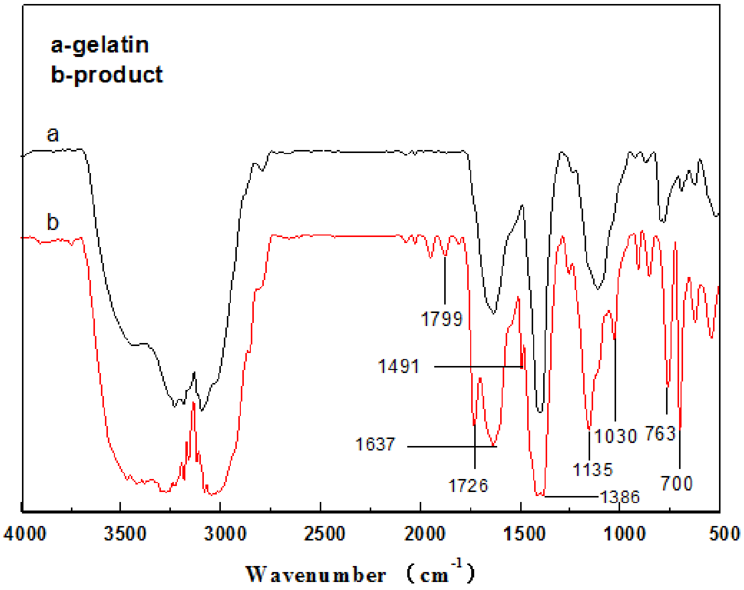

Fig. 2. FT-IR spectra of the collagen and VGCSA

XRD analysis of collagen and VGCSA

Curves (a) and (b) in Fig. 3 show the XRD spectra of the collagen and VGCSA. The position of the collagen diffraction spectra before and after grafting were similar, and the main diffraction peaks (curve a) appeared very distinctly at 2θ values of 22, 23, and 24 degrees. This indicates the active groups –COOH, -NH_2 and –OH on the collagen molecular chains formed hydrogen bonds within the molecular chains or between molecular chains (Cucos *et al*. 2011).

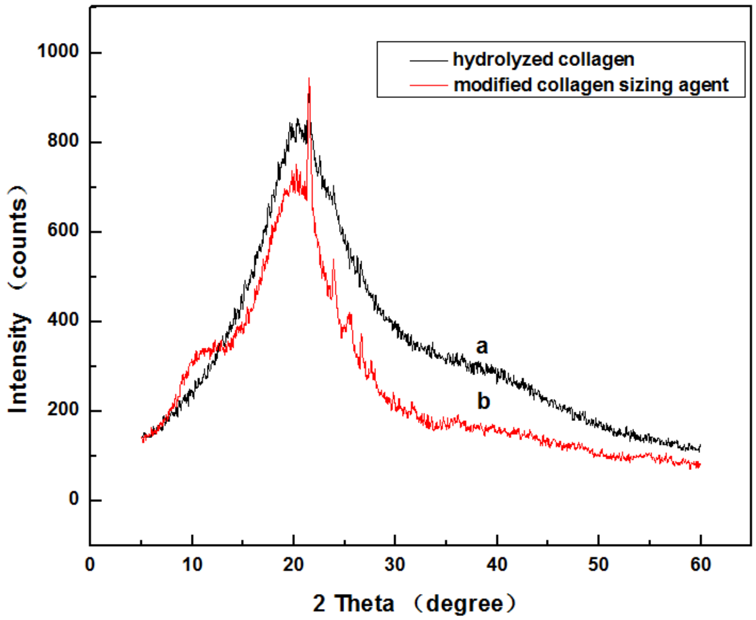

Fig. 3. XRD spectra of the collagen and VGCSA

The diffraction peaks of VGCSA at 2θ values of 24, 25, and 27 degrees were enhanced. It appears that modified collagen has a larger proportion of crystalline material than of the starting collagen, suggesting that grafted polymeric chains formed from styrene and ethyl acrylate have more crystalline areas than collagen (Zhang *et al*. 2014). In addition, this shows that after modification, the chains of collagen were coupled with each other due to the grafting of vinyl monomers. In addition, the side chains of collagen were elongated, and the collagen molecules became neat rather than chaotic. The size of the grain grew larger, so the crystallization trend was increased.

TG analysis of collagen and VGCSA

The thermal degradation behaviors of collagen as well as VGCSA were investigated by TG, and the occurrence of efficient graft modification was also confirmed based on the TG results. Curve (a) in Fig. 4 shows that the thermal degradation of virgin collagen mainly involved three stages. For the first step, in the temperature range of 20 to 100 °C, the absorbed and bound water was lost. While the second stage started at 100 °C and continued up to 220 °C, the weight loss was relatively slower. This was because the nitrogen, oxygen, sulfur, hydrogen and other elements escaped off from the peptide bond and formed small volatile molecules (Zhang *et al*. 2014). During the third step in the temperature range of 200 to 500 °C, the weight loss was relatively higher. This indicates the original organic macromolecules were gradually “carbonized” at higher temperature.

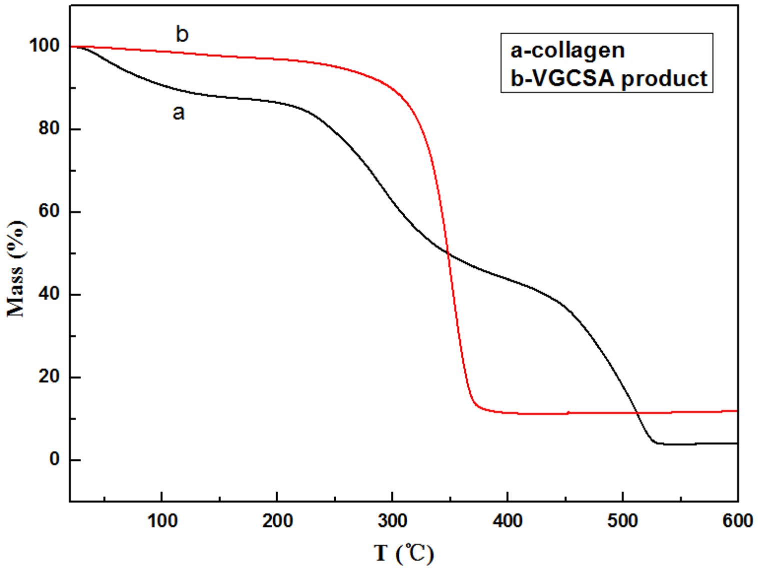

Fig. 4. TG spectrogram of the collagen and VGCSA

Above 520 °C, the weight loss was stable, and the total weight loss rate of collagen was about 95.73%. While the mass loss of VGCSA sample appeared above 300 °C, a sharp mass loss appeared between 300 and 360 °C. This was caused by the introduction of hydrophobic monomers, and there were very few water molecules within the polymer molecules, so no water loss process existed. In addition, the collagen was denaturalized after modified by EA and St, so the pyrolysis stage mainly occurred in 300~360°C, due to the thermal decomposition of grafted chains. Above 360 °C, the weight loss was stable, and the total weight loss rate of VGCSA was about 88.01%. It can be seen from the diagram that the remaining weight of modified collagen was slightly higher than that of unmodified collagen, indicating that the styrene and ethyl acrylate were grafted onto the collagen molecular chain, and the thermal stability increased. And above 500 °C, the difference value of the remaining weight was consistent. All of these indicated that the graft reaction among collagen, EA, and St was confirmed.

TEM analysis of collagen and VGCSA

The TEM patterns of VGCSA emulsion under different magnifications are presented in Fig. 5. It can be seen in Fig. 5(a) that the VGCSA emulsion particles were distributed in the distilled water uniformly and were spherical. Figure 5(b) shows that the surface of the VGCSA emulsion particles was smooth, and obviously, the surface structure appeared to be core-shell. The dispersion of VGCSA emulsion was high and the particle size was fairly uniform, with a size of approximately 350 to 400 nm.

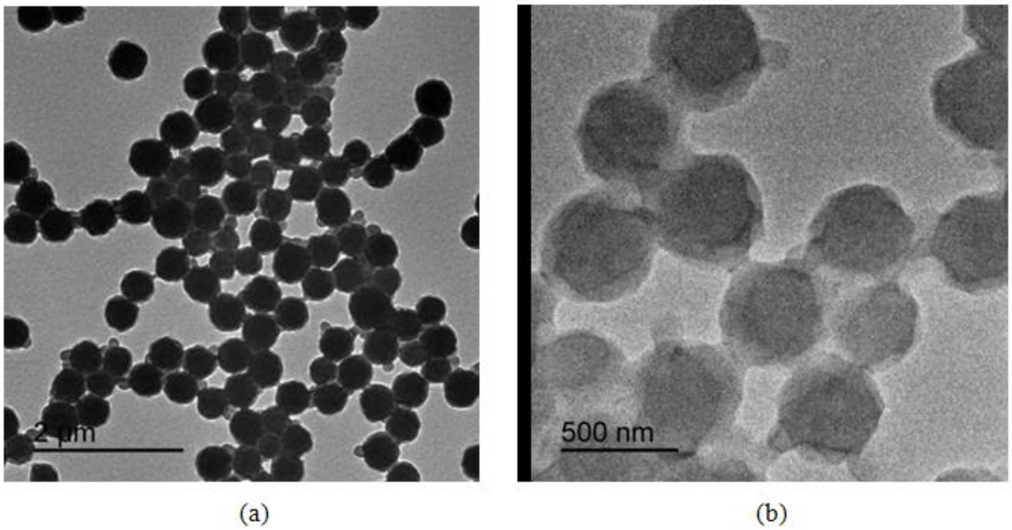

Fig. 5. TEM images of the VGCSA emulsion

The Sizing Properties of VGCSA Emulsion

SEM images of paper fiber before and after being surface-sized

Figures 6 (a) and (b) show the cross-section SEM images of corrugated base paper before and after being sized. It can be seen from Fig. 6(a) that the cross-section fibers of unsized paper appeared disordered and loose, while the cross-section fibers of sized paper (Fig. 6(b)) appeared ordered and tight, indicating that VGCSA emulsion infiltrated into the paper fibers and combined closely with the paper through physical and chemical action, thereafter enhancing the mechanical properties of the paper.

Figures 6 (c) and (d) show the surface SEM images of paper before and after being sized. Figure 6(c) shows the SEM image of unsized paper. It can be observed that there existed a large amount of space in the base paper, and the paper was loose and coarse. Figure 6(d) shows the graph of VGCSA emulsion-sized paper. It can be seen that the paper became smooth and tight and the gap became noticeably smaller, revealing that a protective film of VGCSA emulsion had been formed on the surface of the paper, which is closely integrated with the paper itself. As a result, it could increase the water resistance and mechanical properties of paper to some extent.

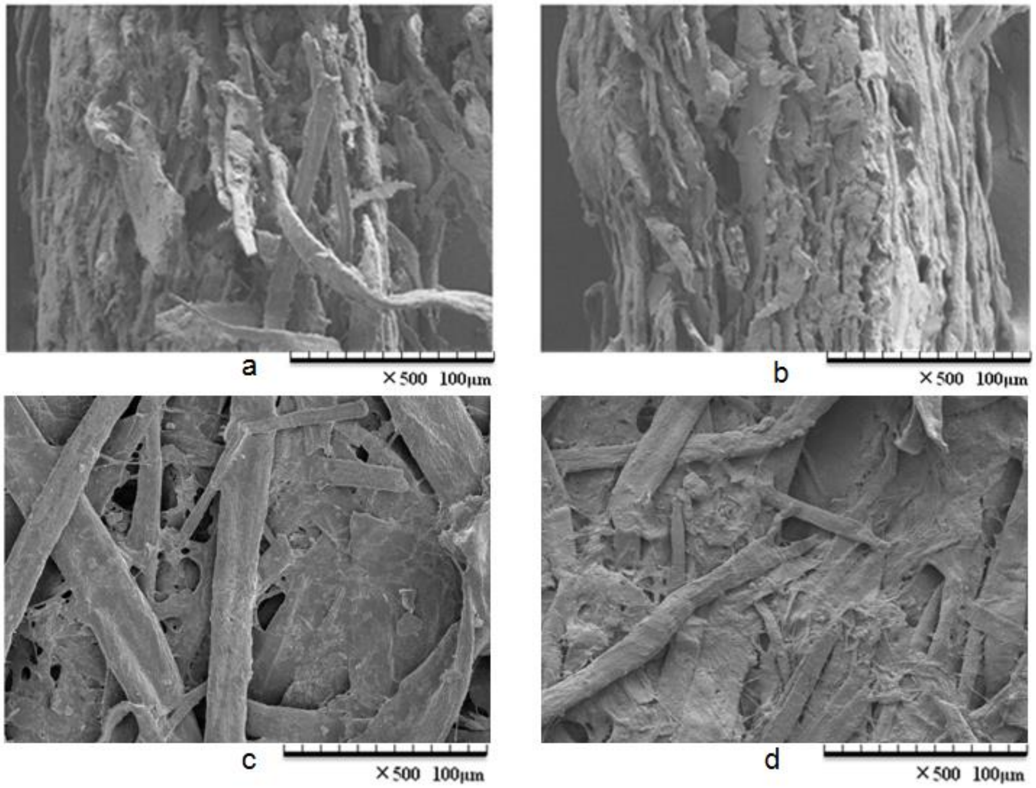

Fig. 6. Cross-section and surface SEM images of corrugated base paper before and after being sized

The analysis of sizing principle

The principle of surface sizing is a molecular phenomenon. When the sizing agent was coated on the surface of the paper, part of the emulsion with small molecules was filled into the voids of the paper fibers. As a result, the fibers were closely linked and the mechanical strength and water resistance of the paper were enhanced. Another part of the emulsion was retained on the surface of the paper and the molecules were redistributed after being heated.

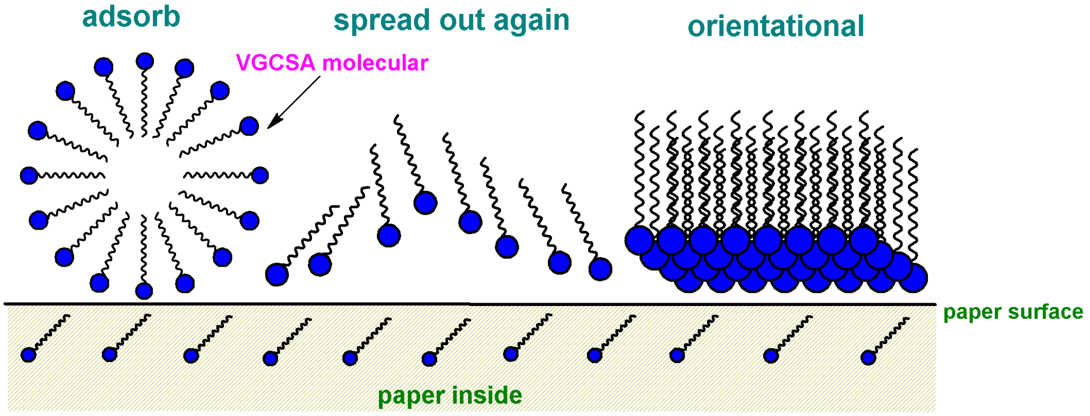

Fig. 7. Sizing mechanism of the sizing agent

The sizing agent covers the paper cellulose and forms a continuous film, with the hydrophilic tail facing the fiber and the hydrophobic tail facing outwards, subsequently creating a water-repellent paper surface (Guo *et al.* 2014). After the VGCSA emulsion was sized on the surface of the paper, the -COOH, $-NH_2$, and -OH hydrophilic groups of the molecular structure of the collagen main chain was combined with paper fibers through hydrogen bonding and electrostatic attraction, and the benzene, ester, and alkyl hydrophobic groups were arranged on the surface of the paper. This increased both the physical mechanical strength and the water resistance of the paper.

The effect of different VGCSA emulsion coating weights

VGCSA emulsion was sized on the surface of the corrugated base papers at sizing amounts of 0, 2, 4, 6, 8, and 10 g/m^2. Then, the tensile index, ring crush index, and 60 s water absorption value ($Cobb_{60}$) of the sized papers were measured. The results are shown in Fig. 8.

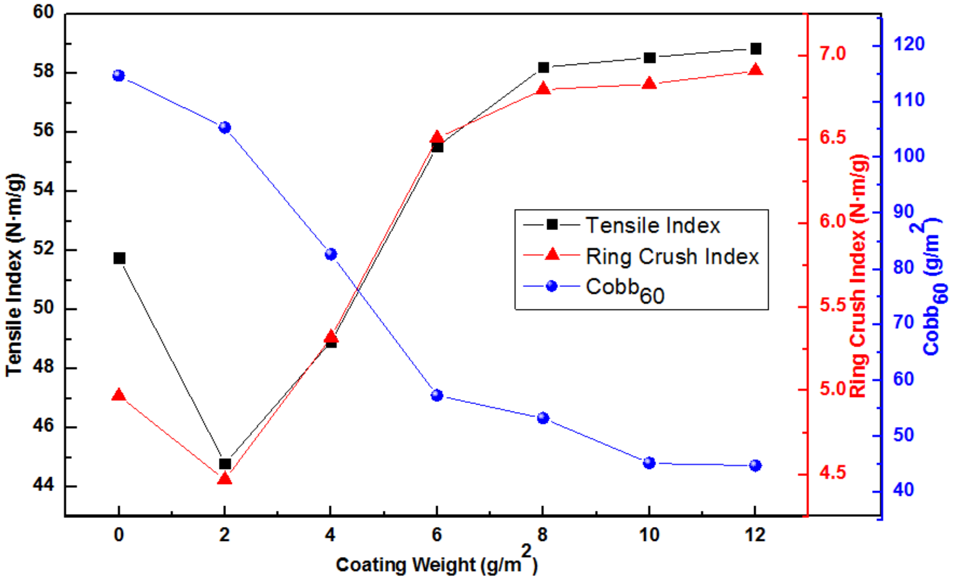

Fig. 8. Mechanical properties of paper sized with various coating weights of VGCSA emulsion

It can be seen from Fig. 8 that the mechanical properties of the sized paper were less than the base paper when the sizing weight was lower than 6 g/m^2. This was because when the coating weight was small, the glue solution would become infiltrated into the paper through soaking effect during the sizing process for papers. Due to the low content of adhesive solution and the high content of water, so the bonding strength between the fibers was reduced when the water entered into the paper fibers. As a result, the mechanical properties of the sized paper were reduced. While when the sizing weight was above 6 g/m^2, the sizing effect significantly greater than the soaking effect, and the tensile index, ring crush index, and water resistance increased along with increasing coating weight. When the sizing weight was 8 g/m^2, the increase became lower. When the optimal coating weight was raised to 8 g/m^2, the tensile index, ring crush index, and water resistance of the sized papers were 12.46%, 36.82%, and 53.61% higher than those of the base paper, respectively.

The effect of VGCSA emulsion respectively mixed with SAE and starch with different ratios

VGCSA emulsion was compounded with styrene acrylic emulsion and starch, respectively. The compound ratios of mass of both were 10:0, 8:2, 6:4, 4:6, 2:8, and 0:10. Then the mixtures were sized on the corrugated base paper. The results are shown in Table 1.

Table 1. Mechanical Properties of Paper Sized with VGCSA Emulsion Respectively Mixed with SAE and Starch at Various Ratios

Proportion	Tensile Index (N•m/g)		Ring Crush Index (N•m/g)		$Cobb_{60}$ (g/m^2)	
Classification	VGCSA:SAE	VGCSA:starch	VGCSA:SAE	VGCSA:starch	VGCSA:SAE	VGCSA:starch
10:0	56.15	56.15	6.7	6.7	57.33	57.33
8:2	58.04	57.75	6.39	6.49	38.67	73.33
6:4	58.45	57.7	6.45	6.78	34.67	74.67
4:6	59.25	57.53	6.7	6.85	33.33	77.33
2:8	59.53	56.96	7.01	7.23	28	109.33
0:10	56.53	55.24	6.78	7.49	27.89	114.67

As can be seen in Table 1, VGCSA emulsion combined with SAE emulsion was applied to the corrugated base paper. The tensile index, ring crush index, and water resistance of the sized papers increased with increasing proportions of SAE in the mixtures. When the mass ratio of VGCSA and SAE was 2:8, the tensile index and ring crush index reached their maximum strength performance of the paper. This indicates that the physical properties of the paper can be increased when VGCSA emulsion is tightly combined with paper fiber under physical and chemical reactions, significantly enhancing the tensile index of the sized paper.

Additionally, the structures of VGCSA and SAE were similar. There were more hydrophobic groups in SAE, which made it easier for VGCSA to increase the water resistance of the paper after treatment with SAE. The optimal formula of VGCSA and starch was 4:6, and the synergistic effect was slightly lower than the synergistic effect of VGCSA and SAE.

With increasing proportions of starch in the mixtures, the tensile index and water resistance of the sized paper decreased, but the ring crush index increased. The reason is that the hydrogen bonding between hydroxyl from the free glucose of starch and cellulose molecules on the surface of the paper fibers had been formed, enhancing the adhesion strength inside the paper fibers. Therefore, it is easier to enhance the ring crush strength of the sized paper. However, the starch molecule is made up of annular glucose with three hydroxyls, so the molecular weight is higher and the viscosity is thicker. It is different for the starch chain to move with the strong hydrogen bond, so it is easily trapped in the film of emulsion, resulting in the decreased water resistance of the film.

CONCLUSIONS

1. FT-IR characterization showed that the vinyl monomers were grafted onto the collagen, and XRD and TG characterization showed that the graft copolymerization of vinyl monomers onto collagen increased its crystallinity and thermal stability.
2. TEM images demonstrated that VGCSA emulsion particles, appearing to be spherical, were uniformly distributed in the distilled water. The surface of the VGCSA emulsion particles was smooth, and the surface structure presented an obvious core-shell with a size of approximately 350 to 400 nm.
3. SEM images of papers before and after sizing demonstrated that the fibers of the sized paper became tight, smooth, and ordered.
4. VGCSA emulsion was applied to the surface sizing of the corrugated paper. The optimal coating weight of VGCSA was 8 g/m^2, and the tensile index, ring crush index, and water resistance of the sized papers were 12.46%, 36.82%, and 53.61% higher than those of the base paper, respectively. VGCSA emulsion was sized on papers mixed with starch and SAE, respectively. The optimal proportion of VGCSA with starch was 4:6 and the optimal proportion of VGCSA with SAE was 2:8.

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