Study of the Preparation, Characterization, and Sizing Performance of Modified Collagen Surface Sizing Agent

Xuechuan Wang,[a,*] Xiaoli Hao,[b] Longfang Ren,[a] Taotao Qiang,[a] and Sufeng Zhang [c]

In this work, a surface sizing agent for paper was prepared by the emulsion polymerization method, in which the collagen extracted from leather shavings was modified. The product was characterized using Fourier Transform-Infrared Spectroscopy (FT-IR), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), Energy Dispersive X-ray detector (EDX), and atomic absorption spectrophotometry. Corrugated papers were used as models. The synergy between modified collagen sizing emulsion and two commercial synthetic sizing agents was studied. Finally, the morphology of the papers before and after being treated was observed by Scanning Electron Microscopy (SEM). The results indicated that the sizing agent could be prepared using collagen as a raw material, which not only can alleviate a pollution problem in the leather industry, but also provide a novel alternative sizing agent for the paper industry, providing considerable economic, social, and environmental benefits to both industries.

Keywords: Leather shavings; Collagen; Grafting modification; Sizing performance

*Contact information: a: Institute of Resources and Environment, Shaanxi University of Science and Technology, Xi'an, 710021 China; b: Institute of Chemistry and Chemical Engineering, Shaanxi University of Science and Technology, Xi'an, 710021 China; c: Shaanxi Research Institute of Agricultural Products Processing Technology, Xi'an 710021, Shaanxi, China;***Corresponding author: wxc-mail@163.com*

INTRODUCTION

Surface sizing treatment can have a tremendous impact on the performance of paper. It can also increase the liquid wetting resistance and mechanical strength (Cho and Garnier 2000). There are many kinds of surface sizing agents, such as starch (Moutinho *et al.* 2011), chitosan, poly-vinyl alcohol (PVA) (Ashori *et al.* 2008), styrene butadiene rubber latex (Pelton 2009), copolymers of styrene and maleic anhydride (SMA) (Stanssens *et al.* 2011), copolymers of styrene and acrylate (SAE), and so on. The application of these sizing materials has shown that the performance of the sized paper is also related to the features of the sizing agents, in addition to greatly affecting the base paper structure (Kjellgren *et al.* 2006).

To improve the cost-effectiveness of the surface sizing, on the premise of keeping the paper substrate the same, it is necessary to locate and use reasonably cheap natural polymer products and synthetic polymer additives with outstanding performance. It is also necessary to accelerate the performance improvements of existing products, and to develop novel, excellent sizing formulations in terms of their sizing effect, storage stability, and cost of manufacture.

It is well known that the Chinese leather industry is large and important. In the process of adding value to the leather, the production of a large amount of leather solid wastes is inevitable.

According to incomplete statistics, more than 1.4 million tons of leather solid wastes are produced every year in China. More than 80% of the solid wastes generated during production of leather include collagen (Brown *et al.* 1996; Hernàndez-Balada *et al.* 2009). The gel character of the collagen endows it with excellent adhesive properties, so it can be used as a binder or surface sizing agent. However, the sizing effect of the collagen is not good because of its poor wet fastness (Figueiro *et al.* 2004; Dong and Gu 2002). It was reported by Zhang *et al.* (2011) that a sizing agent based on grafting modification to the gelatin was prepared by soap-free seed emulsion polymerization. In their work, the sizing degree, the bursting strength, and the tensile strength of papers sized by the sizing agent was similar to or even better than that of the similar products, such as the papers sized by Perglutin K532 (surface sizing agent) from BK Giulini Performance Products Co., Ltd. in Germany and the pure starch. In addition, the water resistance was much greater than the base paper. However, animal glue is expensive and it is mainly used to size high-grade paper, so its widespread application is limited.

The paper sizing agent was prepared using the collagen extracted from leather shavings. This approach allows for wastes from the leather industry to be recycled. It also provides a novel raw material and additive for the paper industry. There are therefore good economic and social benefits. Combining the present situation of the leather and paper-making industries, a kind of collagen surface sizing agent was prepared using collagen extracted from leather shavings as a raw material. The collagen was modified by emulsion polymerization, and the sizing efficiency of the product was studied.

EXPERIMENTAL

Reagents

Collagen extracted from the waste leather was provided by Zibo Poly Grace Group. Butyl acrylate (BA), styrene (St), and potassium persulfate (analyzed reagent grade) were provided by Tianjin Kermel Chemical Reagent Co., Ltd. Alkylketene dimer (AKD), styrene, and acrylate copolymer (SAE) were supplied by Hubei Jiayun Chemical Technology Co., Ltd. Corrugated paper was provided by Cailun paper mill in Shaanxi.

Preparation of the Modified Collagen Surface Sizing Agent

Ten grams of collagen were allowed to swell for a period of time in 100 mL of distilled water. The suspension was heated at a temperature of 45 ^{o}C and stirred constantly until the collagen was completely dissolved as a transparent solution. Then it was filtered through the gauze and the pH of the collagen solution was adjusted to 5. Ten grams of mixed monomers of BA and St were added to the collagen solution, and the mixture was emulsified for 30 min at 75 ^{o}C; 3% potassium persulfate (based on the monomer dosage) was added slowly and allowed to react for 2 h. Finally, the temperature was increased to 85 ^{o}C and the reaction continued for an additional 2 h. A white and faintly blue emulsion was obtained by free radical polymerization (Gantar *et al.* 1987). Figure 1 shows the molecular structure of the modified collagen sizing agent. The nature of the emulsion is shown in Table 1.

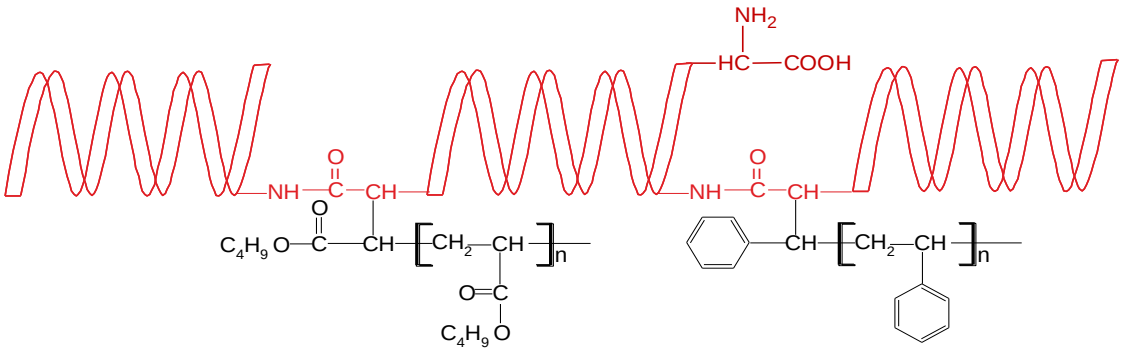


Fig. 1. Molecular structure diagram of the modified collagen sizing agent

Table 1. Nature of the Emulsion

Appearance	Milky liquid with a blue light
Solid content	14.3%
pH	5 to 6
Viscosity	30 mPa·s
Particle size	100 nm
Storage stability	good

Characterization

Fourier Transform-Infrared spectroscopy (FT-IR, VERTE70, Germany) analyses of samples were carried out by using compressed pellets of KBr with collagen and modified collagen powders. All FT-IR spectra were recorded by absorption mode in the wavenumber range of 500 to 4500 cm^{-1}. The morphology and particle size of the modified collagen emulsion were determined by Transmission Electron Microscopy (TEM, H-600, Japan). The sample of modified collagen emulsion was diluted to 1/1000 of the solid content with distilled water. Then a little was subsequently deposited on copper grids and dyed for 5 min with 3%(wt) phosphotungstic acid for TEM observations. X-ray Diffraction (XRD, D/max2200PC, Japan) studies were performed to identify the changing of the crystal form of collagen and modified collagen samples by using Cu K α X-radiation. The patterns were recorded over a range of 2θ from 10 to 60 degrees. An Energy Dispersive X-ray detector (EDX, S4800, Japan) was used to determine elements contained in the collagen and modified collagen. The samples were fixed on the sample table by conductive rubber and then sprayed with metal for 60 s. A polarization Zeeman atomic absorption spectrophotometer (Z-2000, Japan) was used to determine the chromium content of the modified collagen sizing agent.

Surface Sizing Method

Corrugated base paper was used as the base-stock throughout the study. The coating method was used with the Horizontal Roller Type surface sizing by the K303 MULTI coater from RK Print Coat Instruments Ltd. The corrugated base paper was sized by using the modified collagen emulsion and its mixtures with the commercial synthetic sizing agents (AKD and SAE) as the surface sizing agents (Tian *et al.* 2012). The coating weight was controlled by selecting the appropriate coating roll and coating velocity in a K303MULTI coater. Then the sized papers were dried at 105 ^{o}C and equilibrated for 24 h at the temperature of 25 ^{o}C and 65$\pm$20% relative humidity.

Application Performance

The ring crush index and the tensile index of papers before and after being sized were measured using a DC-KY3000A computer measurement and control compression tester from Changjiang papermaking instrument factory in Sichuan and a HH-KZ30/300/500 tensile strength tester from Huahan paper testing instrument equipment Co., Ltd., in Hangzhou. The water resistance performance of paper was represented by the value of water absorbing in 60 s, on the basis of the ISO 5637:1989 standard. The application effect of the surface sizing agent was comprehensively investigated.

RESULTS AND DISCUSSION

Characterization of the Modified Collagen Sizing Agent

FT-IR analysis

As revealed in the FT-IR spectra (Fig. 2), the absorption peaks in unmodified collagen (curve a) are assigned to amide (1643 cm^{-1}), amide II (1535 cm^{-1}), and amide III (1446 cm^{-1}). Generally, the spectral pattern obtained for collagen extracted from the scrap leather was close to those of collagens from other tanned leather (Velez-Pages and Martin-Martinez 2005). The modified collagen by the vinyl monomers (curve b) exhibited similar peaks with unmodified collagen, but it was found that after modification, the amide I, II, and III peaks were slightly shifted to higher wavenumbers. The shifting of these peaks to higher wavenumbers is associated with a change in the chemical environment of amide bonds and is in a very good agreement with the data reported in the literature (Safandowska and Pietrucha 2013). The peak at 2958 cm^{-1} is attributed to CH_2 stretching vibration. The peaks at 1730 cm^{-1} and 1255 to 1161 cm^{-1} are respectively attributed to C=O and C-C(C=O)-O absorption peaks from the saturated aliphatic. The peaks at 760 and 700 cm^{-1} are the characteristic absorption peaks of 5H from the benzene ring. All of these observations supported the finding that the vinyl polymers had reacted with the collagen molecular chain by the graft copolymerization reaction.

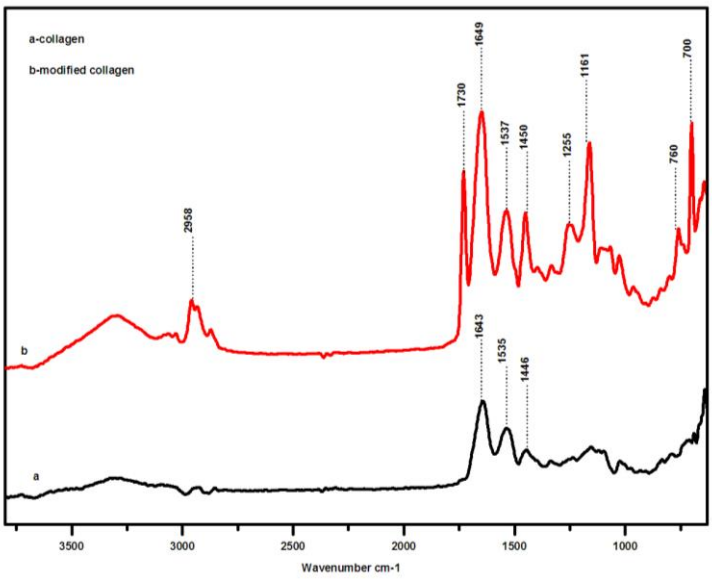
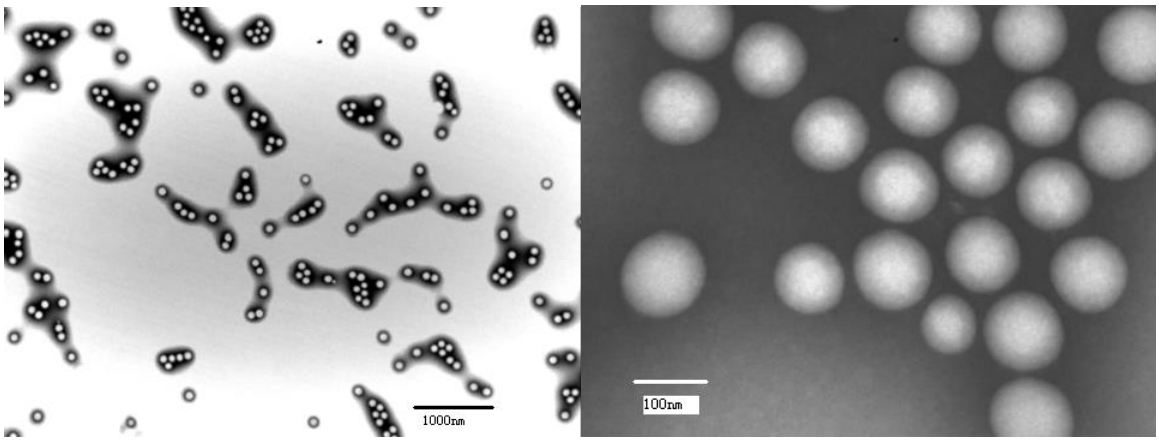


Fig. 2. FT-IR spectra of the collagen and modified collagen sizing agent

TEM analysis

Figure 3 parts (a) and (b) show TEM images of the modified collagen emulsion under different magnification. It is clearly observable that the polymer particles were finely dispersed in the distilled water and their particle size was fairly uniform. Figure 3(b) shows that the latex particles of the modified collagen were spherical in nature with a size around 100 nm.



(a) 20000× (b) 200000×

Fig. 3. TEM images of the modified collagen sizing agent emulsion

Analysis of X-ray diffraction data

As shown in Fig.4, the collagen (curve a) extracted from the scrap leather exhibited XRD patterns similar to that of pure collagen (Cucos *et al.* 2011). The main diffraction peaks appeared very distinctly at 2θ values of 23, 24, and 25.5 degrees. The presence of the characteristic diffraction peaks of Cr at 2θ values from 30 to 40 degrees directly confirms the presence of a small amount of chrome in the collagen.

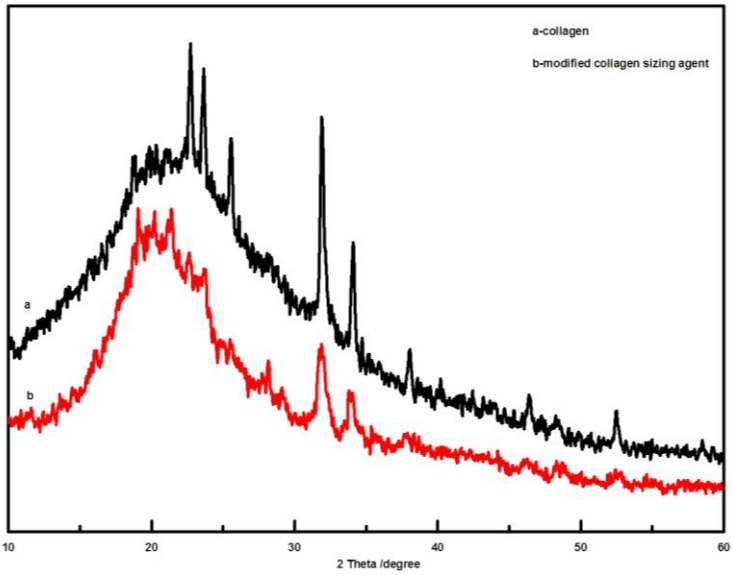
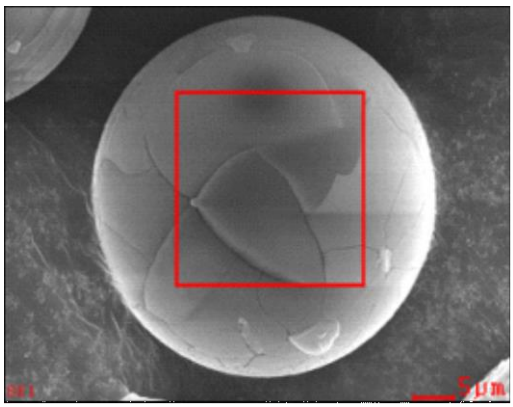


Fig. 4. XRD patterns of the collagen and modified collagen sizing agent

The collagen modified by the vinyl monomers (curve b) exhibited a similar position of these diffraction peaks with unmodified collagen (curve a). But all peak intensities generally showed a slight decline, and the diffraction peaks at 46 degree and 53 degree disappeared after modification. It was demonstrated that the graft copolymerization reaction between the vinyl monomers and collagen took place mainly in the amorphous region of collagen and the compatibility between them was very good. The formation of the longer side chain reduced the molecular ordering due to the vinyl polymers grafted on the collagen chain. So the crystallization trend of the modified collagen was reduced. The graft reaction among collagen, BA, and St was thus confirmed.

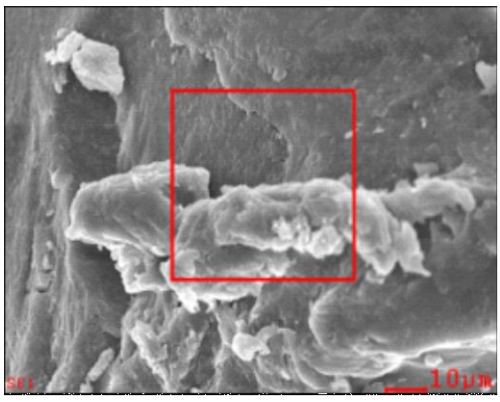
Analysis of EDX and the content of chromium

Figures 5 and 6 show respectively the EDX analysis results for the collagen and modified collagen. It can be seen that the elements contained in the collagen and modified collagen were the same. This was because there were only C, H, and O in the grafting vinyl monomers. Other elements were all from amino acids in collagen. In addition, the removal of chromium from collagen extracted from leather shavings was incomplete, so there were traces of chromium in the collagen and modified collagen. This was consistent with the testing results of XRD. The measured result for the chromium content using the polarization Zeeman atomic absorption spectrophotometer was 0.0265%. This amount of chromium would not affect the collagen's application. Also, this amount of chromium in the product would still meet the requirements of environmental safety, such as the EU directives 94/62/EC (Cornelis *et al.* 2000).



Element	Wt%	At%
CK	41.09	50.04
NK	17.14	17.90
OK	26.28	24.03
NaK	06.99	04.45
BrL	00.43	00.08
PK	02.51	01.19
SK	03.71	01.69
ClK	01.31	00.54
IL	00.40	00.05
CrK	00.14	00.04
Matrix	Correction	ZAF

Fig. 5. EDX of the collagen



Element	Wt%	At%
CK	50.04	59.25
NK	14.10	14.32
OK	21.15	18.80
NaK	06.14	03.80
PK	02.75	01.26
SK	05.68	02.52
ClK	00.08	00.03
IL	00.00	00.00
CrK	00.05	00.01
Matrix	Correction	ZAF

Fig. 6. EDX of the modified collagen sizing agent

Application Tests

The sizing performance of different mixtures

Figure 7 shows the change in the ring crush index for papers sized by the different mixtures. When the paper was sized with the mixture of AKD and the modified collagen sizing agent, the ring crush index was less than that of paper sized by the modified collagen sizing agent alone. The molecular weight of AKD is smaller than that of the modified collagen, and there were differences between the molecular structure and properties of AKD and the modified collagen sizing agent, so the compatibility between them was poor and the stability of the mixing emulsion was reduced. As a result, there was no synergism between AKD and the modified collagen sizing agent, and there was also a negative influence on the sizing effect. However, the molecular structure of SAE was similar to that of the modified collagen sizing agent. The synergy between SAE and the modified collagen sizing agent was prominent. Therefore, the ring crush index of the sized paper increased with an increase in the ratio of SAE to the modified collagen sizing agent. When m(SAE): m(modified collagen sizing agent) was 5:10, the ring crush index was 6.859 N·m/g, which was 1.87 times more than that of paper sized only by the modified collagen sizing agent.

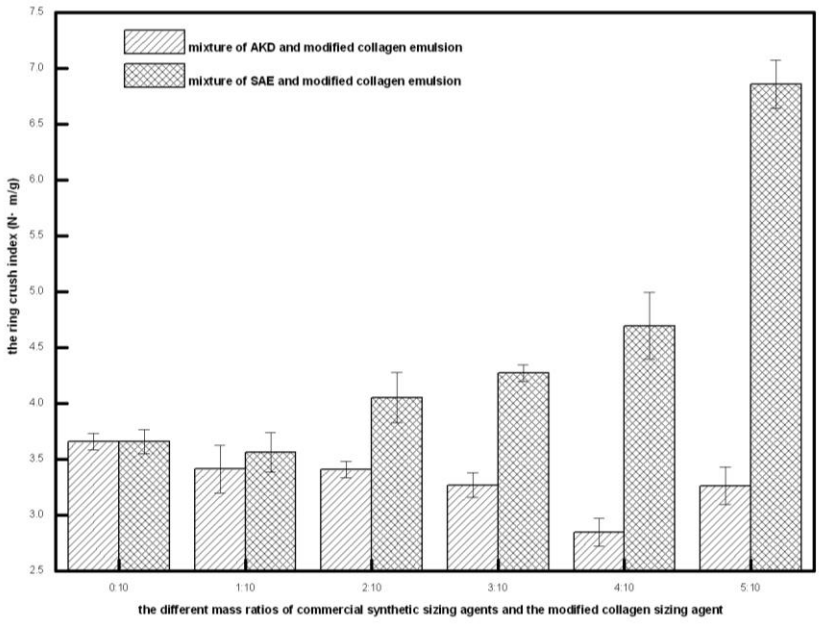


Fig. 7. The change of the ring crush index for paper sized by different mixtures

As shown in Fig. 8, the tensile index of paper sized with the mixture of AKD and the modified collagen sizing agent was less than that of paper sized with the modified collagen sizing agent alone. However, the tensile index of the sized paper increased with an increase in the ratio of SAE to the modified collagen sizing agent. When the ratio of m(SAE): m(modified collagen sizing agent) was 5:10, the tensile index was 4.131 kN/m, which was 1.42 times more than that of paper sized by the modified collagen sizing agent alone.

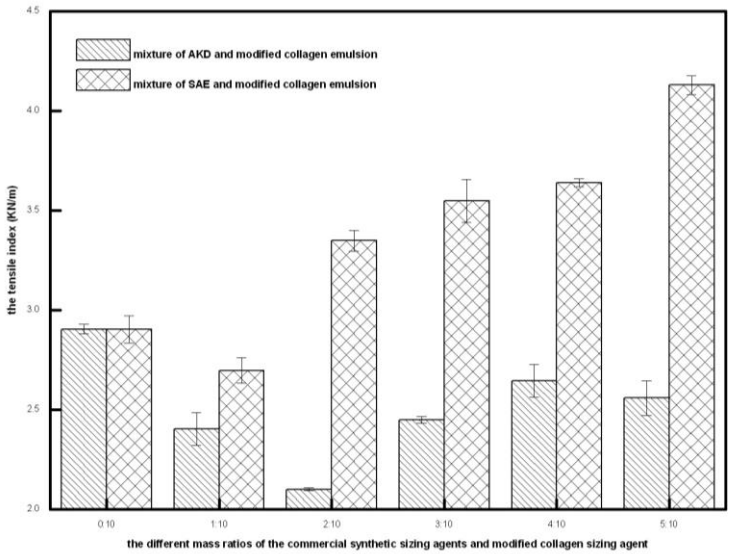


Fig. 8. The change of the tensile index for paper sized by different mixtures

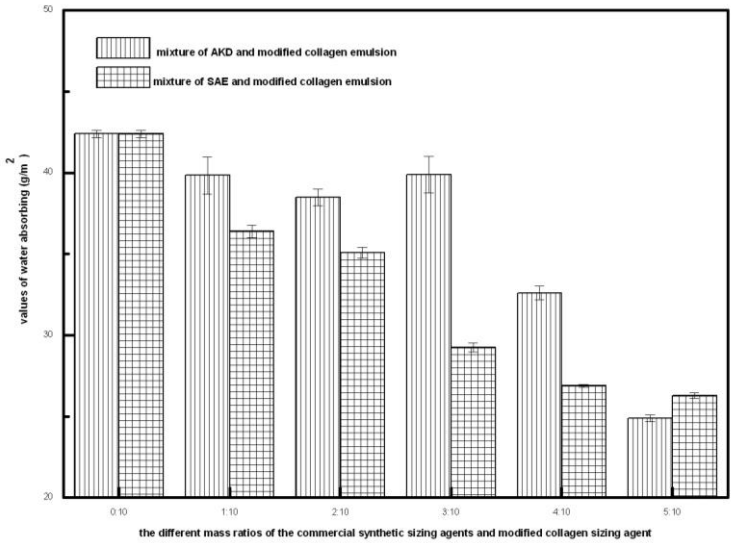


Fig. 9. The change of value of water absorbing in 60s of paper sized by different mixtures

Figure 9 shows the change in the value of water absorbing in 60 s of paper sized by different mixtures. The smaller the value of water absorbing, the stronger was the water resistance. As shown in Figure 9, the water resistance performance of the paper was improved with an increase in the ratio of AKD to the modified collagen sizing agent. The water resistance performance of the paper was also enhanced with an increase in the ratio of SAE to the modified collagen sizing agent, and the efficiency was greater than that with AKD. The synergy between SAE and the modified collagen sizing agent was thus more prominent. AKD, with its long-chain alkane, and SAE, with its benzene ring, both have strong hydrophobicity. When they were mixed with the modified collagen sizing agent, the water-resistance performance of the sized paper was significantly enhanced.

Comparison with other products

The results showed that the synergism of SAE with the modified collagen sizing agent was beneficial, and the sizing efficiency could be greatly enhanced. Therefore, the performance of paper sized by the mixture of SAE and the modified collagen sizing agent was compared with that from the Cailun paper mill in Shaanxi and the other findings from the literature. The coating weights were both 8 g/m^2, consistent with the industrial dosage.

Table 2. Comparison of the Performance of Different Sized Papers

Samples	Ring crush index (N·m/g)	Tensile index (kN/m)	Value of water absorbing (g/m^2)
Blank	4.77	1.29	159.0
Collagen Solution	6.55	1.40	66.7
Modified Collagen Sizing Agent	7.11	2.38	56.0
Modified Collagen with Starch	7.93	2.89	55.0
Factory sizing (Commercial SAE with Starch)	7.91	2.39	56.0
Commercial SAE with Modified Collagen	9.09	3.47	37.0
Cationic Acrylic with Starch(Wang et al.2009)	6.57	-	35.9
AKD Internal sizing(Wang et al.2009)	1.99	-	82.7
Commercial SAE 8906(Hu et al.2011)	-	2.597	30.6
Commercial surface sizing agent AKD (Hu et al. 2011)	-	2.471	50.9

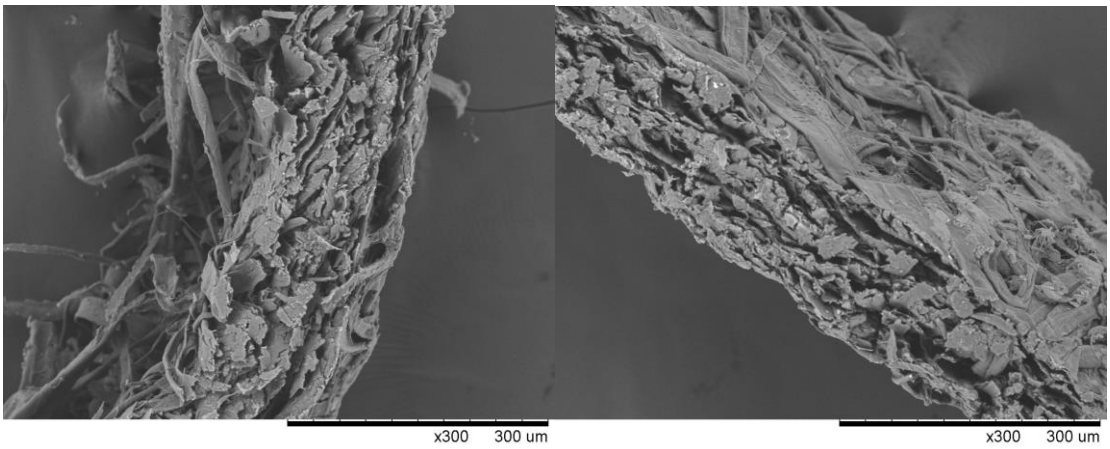
*The smaller the value of water absorbing for papers is, the better their water resistant performance is. "-" is vacancy

Table 2 shows the performance comparison of different sized papers. Compared with the blank paper, the ring crush index, the tensile index and the water resistance performance of papers sized by collagen solution were all improved. There was still some difference in properties compared with papers sized by the modified collagen sizing agent, which was nearly the same as the factory sized papers (SAE with starch). The tensile index was superior to that of the commercial SAE 8906 and commercial surface sizing agent AKD, due to mixing the modified collagen sizing agent with the starch. After the modified collagen sizing agent mixed with SAE, the ring crush index and tensile index were much better than those of the others. The ring crush index and tensile index were respectively 1.9 and 2.7 times greater than that of the base paper. But its water resistant performance was a little worse than that of the cationic acrylic with starch and commercial SAE 8906, being far more than the factory-sized paper. It is suggested that the modified collagen sizing agent could be used to replace the starch or the other synthetic sizing agent, showing potential for industrial application.

SEM Analysis of Paper Before and After Being Sized

Figure 10 shows the morphology of fibers in cross-section of the paper. The fibers of the base paper were loose and disordered, while the fibers of the sized paper were tight and smooth. These showed that the sizing emulsion permeated into the paper fibers and

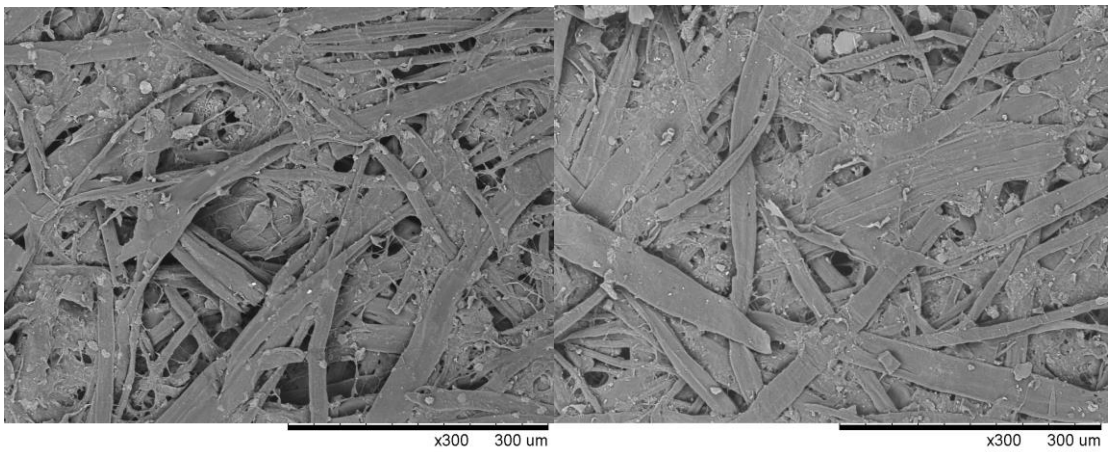
interacted with the paper fibers by physical and chemical effects, which strengthened the binding force and bond energy among the fibers, thus enhancing the physical strength of the paper.



(a) (b)

Fig. 10. SEM cross-section images paper before and after being sized

Figure 11 shows the morphology of the fibers in the surface of the paper. It can be seen that the surface of unsized papers was rather crude and unpolished, whereas the surface of sized papers looks very smooth and glossy in the micrograph. It was reflected from the side face that the emulsions may have filled the fiber interspaces and formed a layer of continuous film after drying on the surface of the paper, subsequently rendering the paper surface smooth and glossy (Guo *et al.* 2013).



(a) (b)

Fig. 11. SEM surface images of paper before and after being sized

CONCLUSIONS

1. Unmodified and modified collagen were characterized by FT-IR, TEM, XRD, EDX, and atomic absorption spectrophotometry. The results showed that the reaction among the collagen, BA, and St had taken place, and the latex particles of the modified collagen emulsion were spherical in nature with size around 100 nm. The crystal form was altered slightly after modification. There were some common elements from the collagen in the

product, in addition to traces of chromium, but these would not affect the application of the sizing agent.

2. The results of the application test showed that the synergy between SAE and the modified collagen sizing agent was prominent, and the ring crush index and tensile index of papers sized by their mixture was much better than that of the other products. The water resistance property was slightly inferior to that reported in the other literature. It is suggested that the modified collagen sizing agent could be used to replace the starch or the other synthetic sizing agent, showing potential for industrial application.

3. SEM images of papers before and after being sized demonstrated that the sizing agent emulsion permeated into the paper fibers and interacted with the paper fibers by physical and chemical effects. At the same time, it filled the fiber interspaces and formed a layer of continuous film after drying on the surface of the paper, subsequently rendering the paper surface smooth and glossy.

ACKNOWLEDGMENTS

The authors are grateful for the support of the National High Technology Research and Development Plan Project, Grant. No. 2011AA06A108, the Key Scientific Research Group of Shaanxi province, Grant. No. 2013KCT-08, the Scientific Research Group of Shaanxi University of Science and Technology, Grant No. TD12-04, and the Graduate Innovation Fund of Shaanxi University of Science and Technology.

REFERENCES CITED

Ashori, A., Raverty, W. D., Vanderhoek, N., and Ward, J. V. (2008). "Surface topography of kenaf (*Hibiscus cannabinus*) sized papers," *Bioresour. Technol*. 99(2), 404-410.

Brown, E. M., Taylor, M. M., and Marmer, W. N. (1996). "Production and potential uses of co-products from solid tannery waste," *JALCA* 91(10), 270-276.

Cho, B. U., and Garnier, G. (2000). "Effect of the paper structure and composition on the surface sizing pick-up," *TAPPI J.* 83(12), 60-62.

Cornelis, R., Camara, C., Ebdon, L., Pitts, L., Sperling, M., Morabito, R., Donard, O. F. X., Crews, H., Larsen, E. H., Neidhart, B., Ariese, F., Rosenberg, E., Berrouiguet, O., Morrison, G. M., Cordier, G., Adams, F., Dero, B., Marshall, J., Stojanik, B., Ekvall, A., and Quevauviller, Ph. (2000). "The EU network on trace element speciation in full swing," *Anal. Chem.* 19(2+3), 210-214.

Cucos, A., Budrugeac P., Miu L., Mitrea, S., and Sbarcea, G. (2011). "Dynamic mechanical analysis (DMA) of new and historical parchments and leathers: Correlations with DSC and XRD," *Thermochimica Acta* 516(1-2), 19-28.

Dong, Q. Z., and Gu, L. X. (2002). "Synthesis of AN-g-casein copolymer in concentrated aqueous solution of sodium thiocyanate and AN-g-casein fiber's structure and property," *Europ. Polym. J.* 38(3), 511-519.

Figueiro, S. D., Goes, J. C., Moreira, R. A., and Sombra, A. S. B. (2004). "On the physico-chemical and dielectric properties of glutaraldehyde crosslinked galactomannan-collagen films," *Carbohydr. Polym.* 56(3), 313-320.

Guo Y. H., Guo J. J., Li S. C., Li, X., Wang, G. S., and Huang, Z. (2013). "Properties and paper sizing application of waterborne polyurethane emulsions synthesized with TDI and IPDI," *Colloids and Surfaces A: Physicochem. Eng. Aspects.* 427(20), 53-61.

Hernàndez-Balada, E., Taylor, M. M., Phillips, J. G., Marmer, W. N., and Brown, E. M. (2009). "Properties of biopolymers produced by transglutaminase treatment of whey protein isolate and gelatin," *Bioresour. Technol.* 100(14), 3638-3643.

Hu, H. R., and Xu, J. F. (2011). "Modification of styrene acrylate emulsion (SAE) and its application in paper surface sizing," *China Pulp & Paper* 130(12), 11-16.

Kjellgren, H., Gällstedt, M., Engström, G., and Järnström, L. (2006). "Barrier and surface properties of chitosan-coated greaseproof paper," *Carbohydr. Polym.* 65(4), 453-460.

Moutinho, I. M. T., Ferreira, P. J. T., and Figueiredo, F. M. L. (2011). "Paper surface chemistry as a tool to improve inkjet printing quality," *BioResources* 6(4), 4259-4270.

Pelton, R. (2009). "Bioactive paper provides a low-cost platform for diagnostics," *Trac-Trends Anal. Chem*. 28(8), 925-942.

Safandowska, M., and Pietrucha, K. (2013). "Effect of fish collagen modification on its thermal and rheological properties," *International Journal of Biological Macromolecules* 53, 32-37.

Gantar, A., Sebenik, A., Kavcic, M., and Osredkar, U. (1987). "Study of grafting ethylene oxide onto gelatin by one-and hetero two-dimensional ^{13}C N.M.R. spectroscopy," *Polymer* 28(8), 1403-1406.

Stanssens, D., Den Abbeele, H. V., Vonck, L., Schoukens, G., Deconinck, M., and Samyn, P. (2011). "Creating water-repellent and super-hydrophobic cellulose substrates by deposition of organic nanoparticles," *Mater. Lett.* 65(12), 1781-1784.

Tian, C. J., Li, B. P., and Li, R. (2012). "R & D and application of cationic compound surface sizing agent of vegetable gum polymer and AKD emulsion," *Paper Chemicals* 24(4), 24-27.

Velez-Pages, T., and Martin-Martinez, J. M. (2005). "Application of one- component primer to avoid the roughening of leather and increase its adhesion to polyurethane adhesive," *International Journal of Adhesion & Adhesives* 25(4), 320-328.

Wang, F., Chen, G., and Fang, Z. Q. (2009). "Study on synergistic effect of surface sizing starch and synthesized surface sizing agent," *Paper Science & Technology* 128(6), 56-60.

Zhang, G. H., Liu, L. J., and Wang, F. (2011). "Study on preparing gelatin graft copolymer emulsion as sizing agent," *China Adhesives* 20(4), 26-30.

Article submitted: September 14, 2013; Peer review completed: November 19, 2013; Revised version received and accepted: January 18, 2014; Published: January 22, 2014.