Utilization of Tannery Solid Waste: Dry Strength Additive for Papermaking

by

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Abstract

An approach of utilizing tannery solid waste was developed by using untanned solid waste as raw material to prepare a dry strength additive for papermaking. Cationic derivatives of collagen hydrolysate (C-CHs) were prepared by incorporating (2,3-epoxypropyl) trimethyl ammonium chloride into collagen hydrolysates with different molecular weights. C-CHs were employed in sheet formation for enhancing physical properties of hand-sheets, and the results indicated that C-CHs were useful in tap water and white water to improve the tensile strength and folding endurance of the hand-sheets. This should be due to the fact that C-CHs with cationic moieties are prone to be retained in anionic cellulose fibers, which is beneficial for the formation hydrogen bonds among hydroxyl groups in the cellulose fibers.

Resumen

Una aproximación para utilizar los desperdicios de curtición sólidos fue desarrollado por medio de la utilización de desperdicios sólidos sin curtir para preparar un aditivo para mejorar la resistencia en seco para ser empleado en la fabricación de [pañuelos] de papel. Derivativos catiónicos de hidrolizados colagénicos de varios diferentes pesos moleculares (C-CHs) fueron preparados incorporando (2,3-epoxi propil) cloruro de trimetilamonio al producto no-tejido para así mejorar las propiedades físicas; los resultados indican que los C-CHs fueron útiles tanto en agua de la canilla así como en agua enjabonada para mejorar no solo la resistencia a la tensión así como a la fatiga por repetidos doblados. Esto se debe seguramente por el hecho que los C-CHs con sus grupos catiónicos tienden a ser retenidos por las fibras celulósicas aniónicas, lo cual es beneficial para la formación de enlaces de hidrógeno entre grupos hidroxílicos en las fibras celulósicas.

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Introduction

Because a lack of proper disposal of solid waste will result in environmental pollution as well as a waste of resource, much research in recent years has focused on utilization of tannery solid waste,[1] which usually constitutes approximately 60% of the weight of raw hides.[2] In fact, the tannery solid waste is a valuable resource due to its high content of collagen. Furthermore, it has been shown that the waste can be reused by preparing gelatin,[3] collagen,[4] organic fertilizers[5,6] and filler for leather.[7] However, only a very limited amount of this waste has been disposed of using these techniques. Therefore, it is necessary to develop new methods for the utilization of tannery solid waste.

Collagen and collagen hydrolysate (CH) have many functional groups such as amino, carboxyl and hydroxyl groups along the side chain. These functional groups are prone to form hydrogen bonds with hydroxyl groups of cellulose, which is the major component of paper. It is well known that the dry strength of paper can be enhanced by increasing the number of hydrogen bonds in the cellulose fibers.[8] In addition, gelatin has been applied to the surface of paper as a sizing agent since the late thirteenth century, and can improve the mechanical properties of paper and increase solidity of paper.[9] Therefore, it is reasonable to hypothesize that CH can be used as an additive to enhance hydrogen bonding in the cellulose fibers and improve the dry strength of paper during sheet formation. Moreover, cationic derivative of CH (C-CH) may be a more promising dry strength additive, because cellulose fibers generally have negative charges on their surfaces in paper marking process.[10]

In this study, untanned solid waste was employed as raw material for obtaining CHs with different molecular weights by enzymatic hydrolysis. As a result, novel dry strength additives, C-CHs, were prepared by cationization of CHs. The structure of C-CHs was characterized by Fourier transform infrared (FT-IR) spectroscopy, zetasizer, and measurement of primary amine content. C-CHs were applied in sheet formation to improve physical properties of hand-sheets, and their effectiveness was investigated.

Experimental

Materials

The tannery solid waste supplied by a local tannery (Chengdu, China) was generated from shaving pigskin wet-white, where the wet-white was obtained by treating conventionally delimed pelts with sodium sulfate.[11] It is easy to remove sodium sulfate from wet-white by washing and the washed wet-white is very similar to raw skin. An alkaline protease preparation (commercial grade) and a pepsin preparation (biological grade) were employed for the hydrolysis of the tannery solid waste. The alkaline protease (Alcalase® 2.5 L, subtilisin, activity 550,000 U/mL at 60°C and pH 9) was supplied by Novozymes (China) Investment Co. Ltd, and the pepsin extracted from pig stomach (activity 220,000 U/g at 38°C and pH 2) was supplied by Beijing Hongrunbaoshun Technology Co. Ltd. Bamboo bleached kraft pulp (41°SR (Schopper-Riegler degree)), cationic starch and alkenyl succinic anhydride (ASA) were obtained from a local paper mill (Chengdu, China). (2,3-epoxypropyl) trimethyl ammonium chloride (EPTAC) was purchased from Titanchem Co. Ltd. (Shanghai, China). All other chemicals were of analytical grade.

Preparation of CHs with Different Molecular Weights

CH with high molecular weight (CHH), where more than 90% of the fragments were in the molecular weight of about 300 kDa, was prepared by the method described in literature with some modifications.[4] Briefly, the tannery solid waste was washed to remove sodium sulfate, and then 10 g of the waste was suspended in 300 mL of 0.5 mol/L acetic acid solution. Subsequently, 0.2 g of pepsin was added into the suspension, and the enzymatic hydrolysis reaction was performed at 4°C for 48 hours. After reaction, the hydrolysate was centrifuged to remove unhydrolyzed solid waste, and then CHH was salted out by adding 3 mol/L NaCl solution into the filtrate. As a result, CHH was collected after centrifuging and drying. For achieving CH with middle molecular weight (CHM), where more than 60% of the fragments were in the molecular weight range of 50 - 100 kDa, 50 g of the washed waste was first suspended in 500 mL of water. Then, the pH of the suspension was adjusted to 2.0 by using 1 mol/L HCl solution. Incubating the suspension with 0.75 g of pepsin at 38°C for 3 hours subsequently performed the enzymatic hydrolysis reaction. After reaction, the hydrolysate was treated by the same procedures described above, and then CHM was obtained.

CH with low molecular weight (CHL), where more than 80% of the fragments were in the molecular weight range of 3 - 10 kDa, was obtained by hydrolyzing the washed waste with alkaline protease. 100 g of the waste was suspended in 1000 mL of water, and then the pH of the mixture was adjusted to 9.0 using 2 mol/L NaOH solution. Subsequently, the mixture was incubated at 60°C for 30 min. After adding 0.5 mL of alkaline protease into the mixture, the hydrolysis reaction was carried out at 60°C for 3 hours. Then, the reaction was stopped by heating at 90°C for 5 min. After centrifuging, salting out and drying, CHL was obtained.

Cationization of CHs to Obtain C-CHs

Using EPTAC as a cationization agent performed the cationization of CHs, and the preparation process was shown in Fig. 1. In an optimal manner, a certain amount of CH was dissolved in 100 mL of distilled water, and then the pH of the CH solution was adjusted to 10.0 using 2mol/L NaOH solution.

Subsequently, the CH solution was incubated at 60°C for 30 min. Then, a certain amount of EPTAC was added into the CH solution, and the cationization reaction was performed at 60°C for 6 hours. Finally, the reaction was terminated by adjusting the pH to 6.0. After filtering and drying, C-CH was obtained. The amount of CH and EPTAC used in the reaction was varied as listed in Table I.

In order to analyze the degree of cationization of C-CHs, the primary amine content of C-CHs and CHs were measured according to the method established by Sarin *et al*.[12] In addition, the structures of C-CHL and CHL were determined by FT-IR spectroscopy (Nicolet iS10, Thermo Scientific, USA). The isoelectric points (pI) of C-CHL and CHL were estimated by determining their zeta potentials using a zetasizer (Nano ZS90, Malvern, U.K.), and all samples (500 µg/mL) were allowed to equilibrate at 25 °C for 30 min before determination.

Effectiveness of C-CHs in Sheet Formation

C-CHs were used for improving the mechanical properties of hand-sheets during sheet formation. CH or C-CH aqueous solution was added to 6 L of 0.5 g/L bleached kraft pulp solution, where the dry weight of CH or C-CH was 2% of pulp dry weight. After dewatering, hand-sheets were pressed at 0.4 MPa for 7 min and then dried at 90°C for 20 min using a plate dryer. As a result, the hand-sheets having a gram weight of 90 g/m^2 was obtained. In addition, hand-sheets without strength additive introduced were used as control. Two types of water including tap water and a simulated white water were employed for papermaking. The term "white water" is defined as the aqueous solution that drains from sheet formation, and the white water is rich in anionic trash.[13] The simulated white water was obtained according to the following approach. 0.6 g of aluminum sulfate and 0.06g of ASA were mixed in 6 L of 10 g/L pulp solution. After up former ("up former" means that the pulp is initially formed into hand-sheets), the mixture was filtered, and subsequently the filtrate was collected and used as simulated white water. The tensile strength and folding endurance of the hand-sheets were determined by standard methods.[14, 15] The morphology of the hand-sheets was observed using a field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan) and element analysis was performed using X-ray photoelectron spectroscopy (XPS, ESCALAB200, VG Scientific, U.K.).

TABLE I
Reaction conditions of cationzition of CHs.

Products	Amount of CH (g)	Amount of EPTAC (g)
C-CHH	0.5	1
C-CHM	10	3
C-CHL	10	3

RESULTS AND DISCUSSION

Characteristics of C-CHs

The purpose of this study was to utilize the tannery solid waste by preparing dry strength additives used in paper marking. Because positively charged dry strength additives should be more beneficial to interact with negatively charged cellulose fiber in paper marking process, CHs obtained from untanned solid waste were first cationized by using a high-activity cationic monomer, EPTAC.

In order to determine whether the cationization of CHs is effectively performed, primary amine contents of CHs and C-CHs were determined due to the fact that the cationization should mainly take place at the primary amine groups of CHs[16] The degree of cationization of C-CHs was further analyzed with the degree of substitution calculated as:

$$\text{degree of substitution} = \frac{\text{-NH}_2\text{ content of CH} - \text{-NH}_2\text{ content of C-CH}}{\text{-NH}_2\text{ content of CH}}$$

According to Table II, it is evident that the increase of the extent of collagen hydrolysis exhibits positive effect on the degree of substitution of C-CH as well as the content of primary amine groups of CH. C-CHs, especially C-CHM and C-CHL, possess high degrees of substitution accompanied by low contents of primary amine groups. This fact suggests that the primary amine groups of CHs are prone to react with the epoxy group of EPTAC. The FT-IR spectra of C-CHL and CHL can be seen in Fig. 2. The band at 1478 cm^{-1} assignable

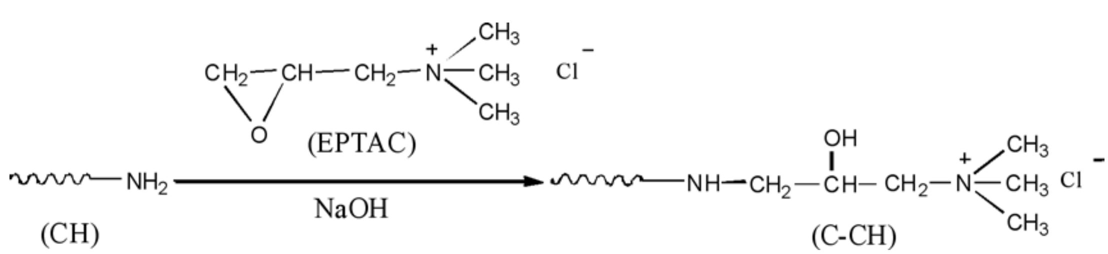

Figure 1. Cationzition of collagen hydrolysate.

to methyl groups of quaternary ammonium can be observed in C-CHL, while there is no absorption band around 1478 cm^{-1} in the spectrum of CHL,[17] indicating that EPTAC was incorporated into CHL after cationization reaction.

It is well known that the pH at which the zeta-potential is zero is referred to as the isoelectric point, pI.[18] Hence, the pI values of C-CHL and CHL were estimated by measuring their zeta potentials. The zeta potential of C-CHL solution and CHL solution at different pH values is shown in Fig. 3. It is obvious that the pI of C-CHL is about 10.3, much higher than that of CHL (about 5.2), which indicates that cationic moieties are successfully introduced into CHL after cationization reaction.

Effectiveness of C-CHs in Sheet Formation

In paper making processes, dry strength property of paper is generally improved by performing mechanical processes or by adding dry strength additives.[19] Thus, C-CHs with different molecular weights were used as dry strength additives in this study, and their effectiveness was evaluated by analyzing folding endurance and tensile strength of hand-sheets. In general, it is necessary for strength additives to have an excellent ability to form hydrogen bonds with cellulose fibers and good retention in anionic cellulose fibers.[20]

TABLE II
Content of primary amine groups and degree of substitution.

Samples	H	M	L
$-NH_2$ content of CH (mmol/100 g)	25	30	120
$-NH_2$ content of C-CH (mmol/100 g)	13	2	26
degree of substitution	0.48	0.93	0.78

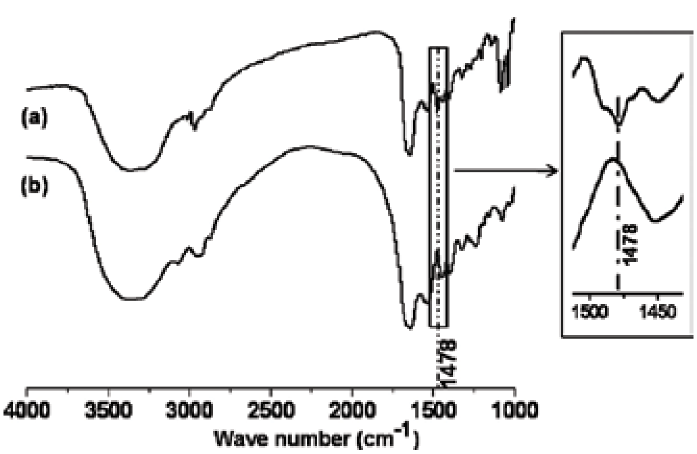

Figure 2. FT-IR spectra of C-CHL (a) and CHL (b).

The physical properties of hand-sheets are shown in Figure 4. It can be seen that there is only little improvement in tensile strength and folding endurance by adding CHs as dry strength additives, especially CHH with high molecular weight. However, the physical properties of hand-sheets are effectively improved by using C-CHs, which indicates that the cationization of CHs is very useful to enhance the physical properties of hand-sheets. This is mainly due to the fact that cationic moieties introduced into CHs can promote the adsorption of C-CHs onto anionic cellulose fibers, which is beneficial to form a sufficient number of hydrogen bonds among hydroxyl groups in the cellulose fibers.[10, 21]

Moreover, the surfaces of hand-sheets treated with CHL and C-CHL were analyzed by XPS. The N(1s) XPS spectra of samples are shown in Fig. 5, and the fitting of the N(1s) peaks was performed. The N(1s) peak of the hand-sheet treated with CHL is composed of the only component labeled N1 at 399.8 eV, while that of the hand-sheet treated with C-CHL is composed of two components labeled N1 at 399.8 eV and N2 at 401.0 eV, where N1 at 399.8 eV and N2 at 401.0 eV should be attributed to nitrogen bonded in the peptide bond of collagen[22] and quaternary ammonium groups,[23] respectively. These results also demonstrated that quaternary ammonium groups were successfully grafted onto CHL. The relative percentages of elements (atomic percent, at %) present at the sample surface were also determined by using XPS, and the data are given in Table III. A small amount of nitrogen as well as abundant oxygen and carbon was detected. Since collagen is a nitrogen-rich compound, nitrogen concentration can be considered as an initial indication of retention of CH/C-CH in hand-sheets. The nitrogen concentrations of hand-sheets treated with CHL and C-CHL were both higher than the control, and that treated with C-CHL was highest. This confirms that the introduction of cationic moieties into CHs causes better retention of C-CHs in cellulose fibers.

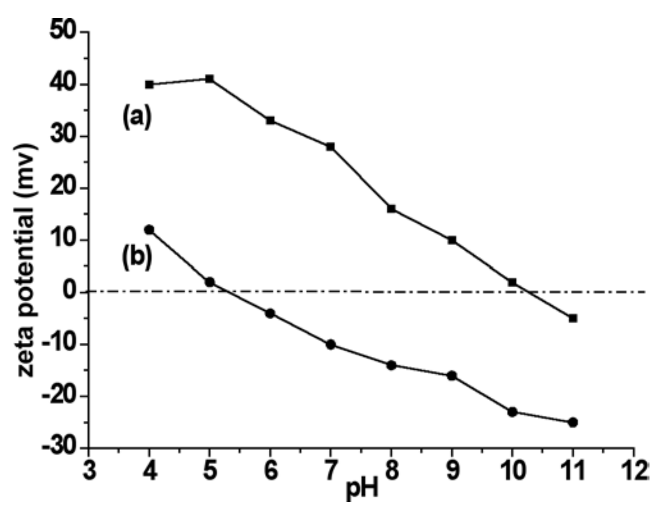

Figure 3. Zeta potential of C-CHL (a) and CHL (b) solutions at different pH values.

In addition, C-CHM is the most effective additive among C-CHs, which increases the tensile strength of hand-sheet from 3.68 kN/m to 4.10 kN/m (Fig. 4(a)). This may be due to the fact that C-CHM has a more appropriate size than C-CHH or C-CHL to form hydrogen bonds in the cellulose fibers. However, the folding endurance of hand-sheets increased with the decrease of molecular weights of C-CHs (Fig. 4(b)). It is well known that gelatin membranes are fragile, but their friability can be reduced by decreasing the molecular weight of gelatin.[24] Therefore, it is reasonable to infer that C-CHs with relatively low molecular weight are effective in increasing the folding endurance of hand-sheets. These facts suggest that proper molecular weight of C-CHs is essential to the improvement of both the tensile strength and folding endurance of hand-sheets.

The surface morphology of hand-sheets was observed by FESEM, as shown in Fig. 6. It can be seen that the surface of the hand-sheet treated with C-CHM is much smoother than that treated with no additive (control), because the space among cellulose fibers was filled by C-CHM. This fact suggested that C-CHs were well retained in cellulose fibers, which is helpful to make cellulose fibers conglutinate together and results in the improvement of physical properties of hand-sheets.[20]

Due to economic and environmental considerations, white water, which is the aqueous solution that drains from sheet formation, is normally recycled in pulp and paper plant. So it is required for a strength additive to be used effectively in white water system. In this section, the effectiveness of enhancing physical properties of hand-sheets by using C-CHs in the simulated white water system was investigated. The tensile strength and folding endurance of hand-sheets treated in white water and tap water are illustrated in Fig. 7. Comparing the physical properties of the controls in white water system and tap water system, it is evident that the white water greatly reduces the strength of hand-sheets, which should be due to its accumulation of anionic trash.[13] However, after adding C-CHs in sheet formation, the physical properties of hand-sheets prepared from white water were significantly improved, and also higher than those in tap water system. These may be explained by the facts that C-CHs can act as an anionic trash catcher and that they are useful to retain some

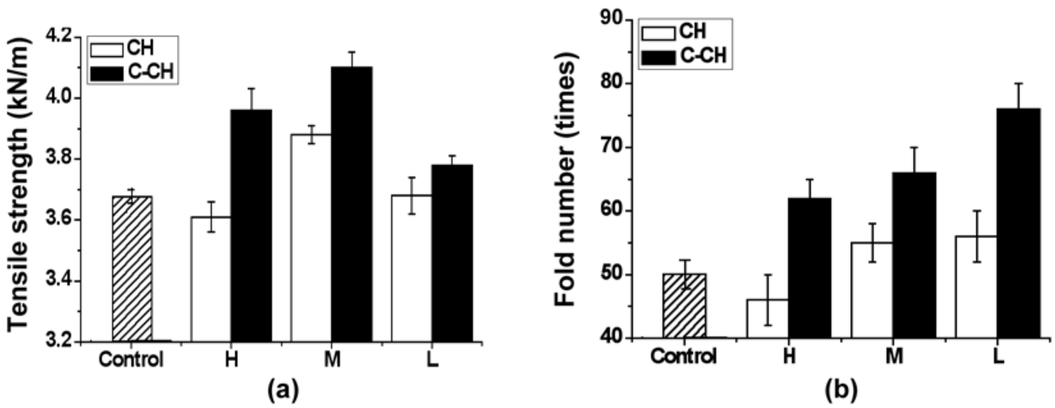

Figure 4. Tensile strength (a) and folding endurance (b) of hand-sheets.

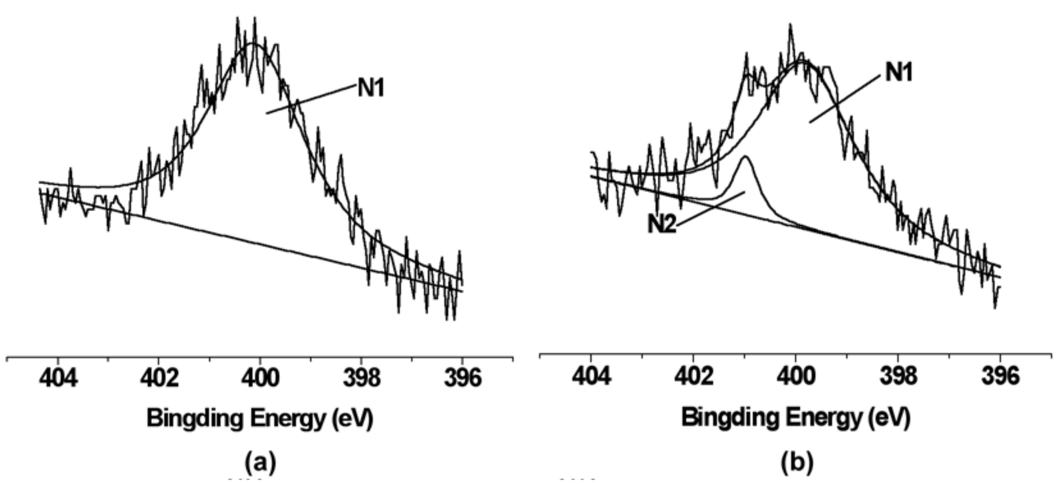

Figure 5. N(1s) XPS spectra of hand-sheets treated with CHL (a) and C-CHL (b).

TABLE III
Relative percentages of elements at sample surface determined by XPS.

Hand-sheets	C (at %)	O (at %)	N (at %)
Control	59.88	39.38	0.74
CHL	58.99	40.1	0.91
C-CHL	61.69	37.19	1.12

fine cellulose fibers from white water during sheet formation.[25,26] It should be noted that this ability of C-CHs in white water is also related with their molecular weights, which is consistent with that in tap water.

In addition, comparing experimental results indicated that the physical properties of C-CH treated hand-sheets are not better than those of cationic starch treated hand-sheets. Indeed, the molecular weight, the degree of cationization and the functional groups forming hydrogen bonds with hydroxyl groups of cellulose, are important factors influencing the effectiveness of C-CHs as strength additive. Therefore, the effectiveness of C-CHs should be improved by further optimizations of these factors. We will continue to optimize the factors in future to improve the effectiveness of C-CHs as strength additive.

Conclusions

As dry strength additives, cationic derivatives of collagen hydrolysate (C-CHs) are effective in enhancing physical properties of hand-sheets for white water system as well as tap water system, which suggests that C-CHs may have practical applications for paper making. The cationization of collagen hydrolysates (CHs) with proper molecular weight is necessary for the utilization of tannery solid waste as strength additives, and it is important for the strength additive to form hydrogen bonds with cellulose fibers and to be retained in anionic cellulose fibers. Preparation of dry strength additives based on untanned solid waste may be a potential technology for reusing tannery solid waste. However, the safety risk of these papers using C-CHs as strength additives should be fully evaluated before used in food industry.

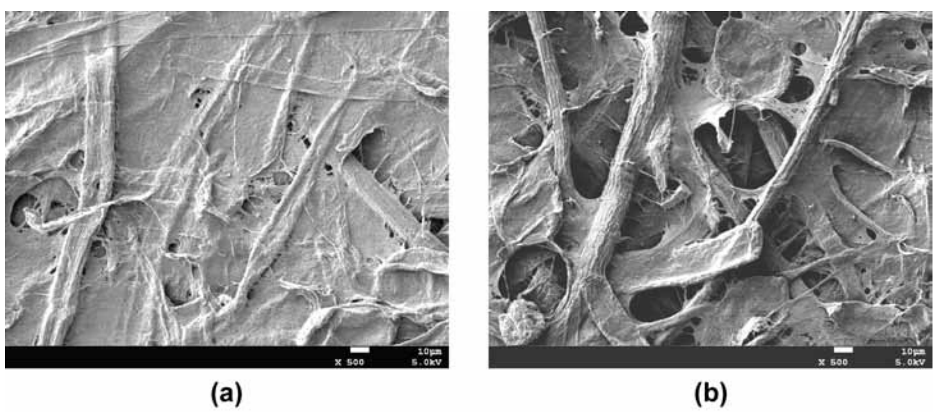

Figure 6. Surfaces of hand-sheets observed by FESEM at a magnification of 500: (a) treating with C-CHM; (b) control.

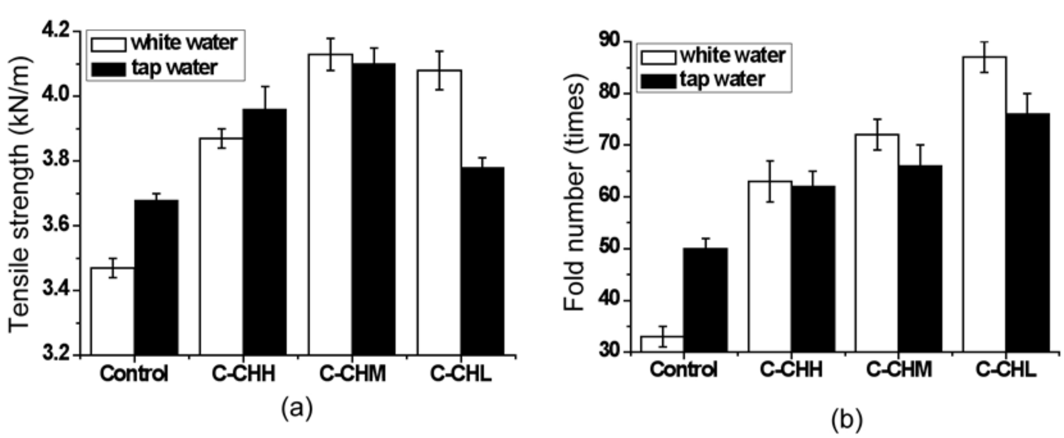

Figure 7. Tensile strength (a) and folding endurance (b) of hand-sheets treated in white water system and tap water system.

Acknowledgements

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