Wet Strength and Antibacterial Performance of Cellulosic Paper Induced by Maleic Anhydride-Acylated Chitosan

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Paper sheets were dipped in maleic anhydride-acylated chitosan (MAAC) to enhance their wet strength and antibacterial performance. The wet strength of paper sheets treated with MAAC or chitosan solutions and cured at 90 and 170 °C was investigated. *Escherichia coli* was used to evaluate the antibacterial performance of the treated paper sheets. The antibacterial performance was determined by measuring the absorbance at 610 nm based on the turbidity of the bacterial suspension on the surface of the treated paper sheets. The MAAC performed better than chitosan in improving wet strength, especially in the case of permanent wet strength. Paper sheets treated with MAAC under certain conditions resulted in 23 to 33% improvements in the permanent wet strength. As a result of the surface treatment, a reduction of at least 80% in *E. coli* growth was observed. The MAAC was more efficient in inhibiting the growth of *E. coli* than chitosan.

Keywords: Maleic anhydride-acylated chitosan (MAAC); Wet strength; Antibacterial properties

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INTRODUCTION

Cellulosic paper, a material widely used in daily life and numerous industries, has physical properties that can be improved such that it can be used for more functions. Wet strength is a necessary property for paper products such as household paper, food wrapping paper, and some specialty papers (Saito and Isogai 2007). The antibacterial performance of paper products such as household paper is also important for some applications. Various wet strength additives can be used to improve the wet strength of paper products. Although the use of polyamideamine-epichlorohydrin resin (PAE) releases absorbable organic halogens (AOX), it is still dominant over other wet strength agents (Obokata and Isogai 2007). The antibacterial properties of paper have attracted the interest of many researchers and there are many reports in this field (Ghule *et al.* 2006; Tang *et al.* 2009; Tankhiwale and Bajpai 2009; Hu *et al.* 2010; Imani *et al.* 2011; Nassar and Youssef 2012; Wang *et al.* 2013; Youssef *et al.* 2012, 2013). Papermaking chemicals with synergistic wet strength and antibacterial properties have recently been discovered. A new polymer containing a guanidine group was synthesized by Qian *et al.* (2008), and the composite resulting from the interactions of this polymer with carboxymethyl cellulose has been used to improve the wet strength and antibacterial properties of cellulosic paper (Qian *et al.* 2008). Sun *et al.* (2010) reported chitosan-guanidine

complexes with synergistic effects on the wet strength and antibacterial properties of paper. However, only temporary wet strength was mentioned in these studies.

In a previous study maleic anhydride-acylated chitosan (MAAC) was synthesized and used to improve the wet strength of paper *via* addition to the papermaking stock prior to sheet formation (Chen *et al.* 2013). Chitosan is a natural strength additive used in papermaking that can inhibit the growth of some microorganisms (Lindström *et al.* 2005; Vallapa *et al.* 2011; Zhang *et al.* 2013). In this work, the wet strength (both temporary and permanent) and antibacterial properties of paper treated with MAAC were studied.

EXPERIMENTAL

Materials

Maleic anhydride-acylated chitosan with a degree of substitution of 63.3% (based on elemental analysis) was synthesized according to a previously published work (Chen *et al.* 2013). *Escherichia coli* (*E. coli*) was purchased from the Qingdao Hope Bio-Technology Co., Ltd. Nutrient broth (10 g of peptone, 3 g of beef extract, and 3 g of NaCl; pH 7.2 to 7.4) and nutrient agar culture media (10 g of peptone, 5 g of beef extract, 5 g of NaCl, and 14 g of agar; pH 7.4) were purchased from the Beijing Aoboxing Bio-Technology Co., Ltd. (China). Unbleached larch kraft pulp with a brightness of 24 to 26% ISO used to create the paper sheets was prepared in the lab and beaten to 25 to 27 °SR using a laboratory Hollander beater.

Methods

Paper sheet preparation and treatment

Paper sheets were prepared using a handsheet former (TD10-200, China) with a target grammage of 70 g/m^2. These paper sheets were dipped in the MAAC solution for 60 s and were then pressed to remove the surplus solution, ultimately reaching a wet pick-up of around 110% by mass. Then, the treated paper sheets were dried and cured in a speed dryer (SD24D, Labtech Instruments Inc., Canada) for 5 min at 90 or 170 °C. The solutions tested were 0.5% (v/v) aqueous acetic acid, 1% (w/w) chitosan in 0.5% (v/v) aqueous acetic acid, and 1% (w/w) MAAC in 0.5% (v/v) aqueous acetic acid.

Evaluation of dry and wet tensile strength

The dry and wet tensile strengths of the paper sheets were evaluated in accordance with the corresponding TAPPI standard test methods (T456 om-03 2005; T494 om-88 2006). The sample strips used for wet tensile strength measurement were dipped in distilled water for 1 min (corresponding to their temporary wet strength), 2 h, and 24 h (corresponding to their permanent wet strength) and were subjected to tensile strength measurement immediately afterward. The wet strength was determined in terms of the W/D ratio. The W/D ratio is the ratio of the wet tensile strength of treated paper sheets to the dry tensile strength of the control sample. Ten strips were measured for each paper sheet sample to obtain an average dry or wet strength.

Evaluation of antibacterial performance

The antibacterial properties of treated paper sheets were evaluated by their inhibition of *E. coli* growth. One porous, porcelain ball containing seed *E. coli* was cultivated in nutrient broth and incubated overnight at 37 °C. While the bacteria grew in

the logarithmic phase (18 h), the bacterial suspension with an approximate concentration of 1 x 10^8 colony forming units per milliliter (CFU/mL) was diluted 10-fold by 0.87% physiological saline to a concentration of 1 x 10^2 CFU/mL. Then, 0.5 mL of diluted bacterial suspension was uniformly spread over the nutrient agar culture media in Petri dishes. Paper sheets cut to the diameter of the Petri dishes were carefully placed on the nutrient agar culture media. These Petri dishes were inverted and incubated at 37 °C for 36 h. The bacterial suspension on the paper sheets was harvested and diluted with physiological saline to a certain concentration at which the absorbance of the bacterial suspension of control sample at 610 nm by a spectrophotometer (TU-1901, Beijing Purkinje General Instrument Co., Ltd., China) was 0.4 to 0.6. The antibacterial properties of the paper sheets were determined by measuring the absorbance at 610 nm based on the turbidity of the bacterial suspension. All glassware and samples were sterilized with UV irradiation for 60 min before experiments were carried out. Each sample was evaluated in triplicate, and the means were reported for all experiments.

RESULTS AND DISCUSSION

Wet Strength of Cellulosic Paper Treated with Maleic Anhydride-Acylated Chitosan

Table 1 shows a comparison of dry and wet strength indices between the treated paper sheets and the control samples. The wet strengths of the control sample and the paper sheets treated with 0.5% (v/v) aqueous acetic acid were too low to measure, and there was no obvious improvement in the dry strength after the paper sheets were treated. The paper sheets treated with both chitosan and MAAC had higher dry and wet strength than the control samples. In comparison with chitosan, the paper sheets treated with MAAC had better temporary and permanent wet strength. MAAC-treated sheets had less wet strength loss than chitosan-treated sheets when the duration of immersion in water increased. Higher treatment temperatures improved the wet strength of the paper sheets treated by chitosan and MAAC. One likely explanation is that a higher temperature is needed to facilitate the etherification reaction between the carboxylic groups of MAAC and the hydroxyl groups of cellulose fibers (Zakaria 2004). Similarly, higher temperatures allowed Schiff bases to form between the primary amino groups of the chitosan and the aldehyde groups of the cellulose fibers (Lindström *et al*. 2005).

Table 1. Dry and Wet Strength Indices of Control and Treated Paper-Sheets

Sample	Dry Tensile Index (kN·m/g)	Wet Tensile Index (kN·m/g)			Wet Strength (%)		
		1 min	2 h	24 h	1 min	2 h	24 h
Control	59.80	---	---	---	---	---	---
A1	61.93	---	---	---	---	---	---
A2	59.96	---	---	---	---	---	---
C1	78.39	13.23	8.17	4.82	22	14	8
C2	89.75	16.46	13.82	9.05	28	23	15
M1	76.43	16.32	15.40	13.60	27	26	23
M2	85.83	20.58	19.87	19.69	34	33	33

Note: A1 and A2 were treated with 0.5% (v/v) aqueous acetic acid and were dried at 90 and 170 °C, respectively; C1 and C2 were treated with 1% (w/w) chitosan in 0.5% (v/v) aqueous acetic acid and were dried at 90 and 170 °C, respectively; M1 and M2 were treated with 1% (w/w) MAAC in 0.5% (v/v) aqueous acetic acid and were dried at 90 and 170 °C, respectively

Antibacterial Performance of Paper Sheets Treated with Maleic Anhydride-Acylated Chitosan

As shown in Fig. 1, in comparison with the control samples, the bacterial suspension on the paper sheets treated with acetic acid, chitosan, or MAAC decreased even by observation with the naked eye, especially in the case of the sheet treated with MAAC. To quantitatively evaluate the growth of *E. coli* on the surface of the paper sheets, the bacterial suspensions on the paper sheets were harvested and diluted before their absorbance at 610 nm was measured.

The results of these measurements are shown in Fig. 2, and they agree with the observations made from Fig. 1. The growth of *E. coli* on the paper sheets treated with acetic acid and chitosan declined by about half compared to that of the control samples. However, chitosan did not exhibit noticeably better antibacterial properties than acetic acid. This was likely a result of unpredictable experimental error or because chitosan stimulated bacterial growth at this treatment concentration. The growth of *E. coli* on the paper sheets treated with MAAC declined by more than 80% compared to that of the control samples.

One of the mechanisms of MAAC's antibacterial properties could be that the secondary amine group on the MAAC molecule is more electropositive than the primary amine group of chitosan. Because the cell membrane of *E. coli* is electronegative, MAAC could penetrate into the cell membrane of *E. coli* easily. Moreover, MAAC could chelate metal ions within the cell, such as Ca^{2+} and Mg^{2+}, which act as catalytic agents during the *E. coli* metabolism process more efficiently than chitosan due to the additional carboxyl groups on the MAAC molecule.

The paper sheets treated with acetic acid, chitosan, or MAAC which were dried at 90 °C had better antibacterial properties than sheets dried at 170 °C. The Schiff base and etherification reactions could proceed more easily under higher curing temperatures, so when the curing temperature was increased, the paper sheets treated with chitosan and MAAC had slightly worse antibacterial properties.

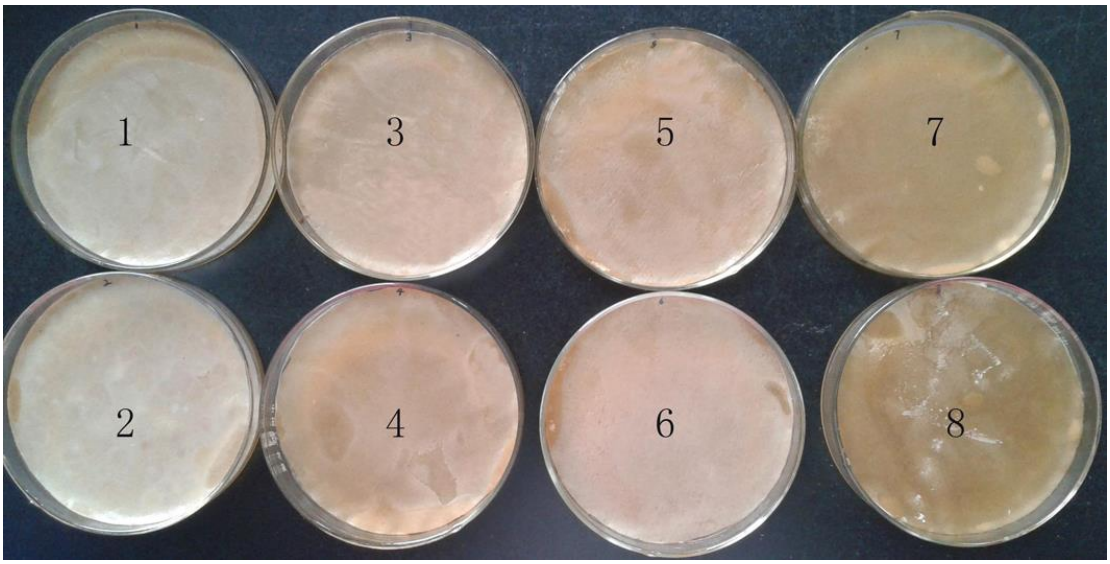

Fig. 1. Photograph of *E. coli* growth on the surfaces of paper sheets after incubation for 36 h at 37 °C.

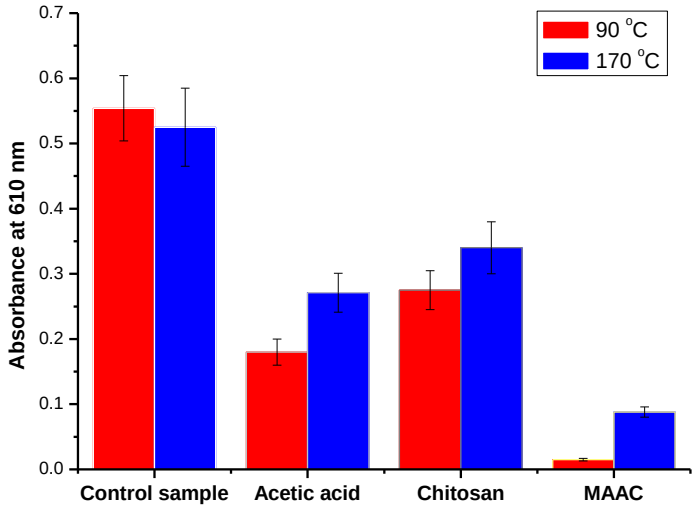

Fig. 2. Absorbance at 610 nm for the bacterial suspensions on the paper sheets after incubation for 36 h at 37 °C. Note: Petri dishes 1 to 8 represent Control Sample 1, Control Sample 2, A1, A2, C1, C2, M1, and M2, respectively.

CONCLUSIONS

1. Compared to the paper treated with chitosan, paper treated with MAAC performed better in terms of both its temporary and permanent wet strengths. The MAAC had a smaller loss of wet strength than chitosan as the duration of immersion in water increased. Higher curing temperatures were favorable and improved the wet strength of the paper sheets treated with both chitosan and MAAC.
2. The MAAC effectively inhibited the growth of *E. coli* on the surface of treated paper sheets. The growth of *E. coli* on paper sheets treated with MAAC declined by more than 80% compared to that of the control samples. The MAAC exhibited better antibacterial properties than chitosan.

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