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Synergy of CMC and modified chitosan on strength properties of cellulosic fiber network

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ABSTRACT

Previously, the application of modified chitosan (MCN) and carboxymethyl cellulose (CMC) in a dual polymer system showed promising results in increasing the strength of fiber networks. This work evaluates the influence of CMC molecular weight (MW) and of CMC/MCN ratio on the characteristics of formed CMC/MCN complexes in polymer solutions and on the properties of cellulosic fiber networks. The results showed that the application of MCN and the high MW CMC (HCMC) (1:1 charge ratio) enhanced the tensile, burst, and tear indices, but reduced the light scattering coefficient of the fiber network more significantly than that of MCN and the low MW CMC (LCMC). Increasing the ratio of HCMC/MCN marginally affected the tensile index, the burst index, and the light scattering coefficient of the fiber network, even though the ratio significantly affected the characteristics of the CMC/MCN complexes in polymer solutions. The tear index and brightness were improved by increasing the HCMC/MCN ratio. These results were explained based on the retention of HCMC/MCN complexes and the layer-by-layer assembly of HCMC and MCN on the fiber surface.

1. Introduction

The application of polymers has been a successful method to enhance the strength properties of cellulosic fiber networks (Fatehi & Xiao, 2008; Fatehi, Ates, Ward, Ni, & Xiao, 2009a; Lofton, Moore, Hubbe, & Lee, 2005; Reis, Caraschi, Carmona-Riberio, & Petri, 2003). Chitosan has been applied in a variety of areas due to its abundance and comparative cost-effectiveness. It was introduced in the paper industry as a dry strength additive and an antimicrobial agent (Chi, Qin, Zeng, Li, & Wang, 2007; Holappa et al., 2006; Lertsutthiwong, Chandrakrachang, Nazhad, & Stevens, 2002). However, its application in papermaking is limited due to its poor water solubility, particularly under neutral or alkaline environments (Lim & Hudson, 2004). To address this difficulty, chitosan has been modified (Lim & Hudson, 2004; Lu, Song, Cao, Chen, & Yao, 2004), and the modified chitosan has been employed as a retention aid in papermaking (Li, Du, & Xu, 2004).

Carboxymethyl cellulose (CMC) is an anionic polymer that has been introduced in papermaking as a strength agent (Jokinen, Niinimaki, & Ammala, 2006; Watanabe, Gondo, & Kitao, 2004). Since the surface of fibers is also negatively charged, CMC has a limited adsorption on the fiber surface (Jokinen et al., 2006; Watanabe et al., 2004). Modifying CMC to improve its adsorption on fibers has been studied in previous research (Fras-Zemljic, Stenius, Laine, & Stana-Kleinschek, 2006; Fujimoto & Petri, 2001; Wang & Somasundaran, 2005). The adsorption of modified CMC on fibers was enhanced under the acidic condition (Watanabe et al., 2004).

The application of modified chitosan (MCN), which is a highly charged cationic polymer, along with CMC showed promising results in improving the strength of the fiber network (Fatehi, Qian, Kititerakun, Rirksomboon, & Xiao, 2009b). In this system, MCN is introduced in the fiber suspension above its maximum adsorption. By introducing CMC to the suspension, some CMC can be adsorbed on top of MCN that already adsorbed on fibers, which may follow the layer-by-layer assembly concept, while the others can form complexes with unadsorbed MCN (Fatehi et al., 2009b; Lofton et al., 2005). The formation of CMC/MCN complexes and their retention characteristics were investigated in our previous research (Fatehi et al., 2009b). We reported that this system improved the paper strength more effectively than the layer-by-layer assembly of CMC and MCN (Fatehi et al., 2009b). The size of polymers influences the size of complexes in solutions (Reis et al., 2003) and the thickness of the polymer layer coated on the fiber surface, which can impact the final properties of fiber net-

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works (Gärdlund, Forsstrom, Andreasson, & Wagberg, 2005; Gärdlund, Wågberg, & Gernandt, 2003a; Gärdlund, Wågberg, Gernandt, & Dautzenberg, 2003b; Lofton et al., 2005). The first objective of the present study was to investigate the influence of the MW of CMC on the efficiency of CMC/MCN in improving the strength of the fiber network.

It was reported that the tensile strength of the fiber network was more significantly improved by adding the complexes of poly amideamine (PAA) and CMC preformed in one-to-one charge ratio than by adding the complexes preformed in other ratios (Gärdlund et al., 2003a). However, if the MCN and CMC are added separately to the fiber suspension, the ratio of such polymers will affect the formation and retention of the formed complexes, as well as the layer-by-layer assembly of the polymers on fibers. The second objective of the current study was to assess how changes in the ratio of CMC/MCN would affect the strength of the fiber network.

In this paper: (1) the complexes formed between MCN and two different MW CMCs were further characterized in water; (2) MCN and CMC were added subsequently to the fiber suspension at different dosages based on the equal charge ratio, and the corresponding properties of fiber networks were systematically analyzed; (3) MCN was added at 2 mg/g on fibers and different dosages of high MW CMC (HCMC) were applied into the fiber suspension and the properties of fiber networks were assessed. The results of this work are directly related to the application of strength additives in dual polymer systems to improve the properties of fiber networks.

2. Experimental

2.1. Materials

Commercial chitosan powder with a MW of 70,000–180,000; glycidyltrimethylammonium chloride (GTMAC), 75% in water; carboxymethyl cellulose sodium salt (CMC), DS = 0.7 with MWs of 90,000 (LCMC) and 250,000 (HCMC); poly diallyldimethylammonium chloride (poly-DADMAC) with a MW of 100,000–200,000 were all purchased from Aldrich Co., and used as received. Potassium polyvinyl sulfate (PVSK) with a MW of 100,000–200,000 (97.7% esterified) was obtained from Wako Pure Chem. Ltd. Japan.

2.2. Pulp preparation

A bleached sulfite pulp sample was kindly supplied from a mill in Eastern Canada. The sulfite pulp is known to have inferior strength properties (Fatehi & Xiao, 2008; Jain & Ni, 2008; Ni et al., 1998; Zheng, Xiao, & Ni, 2006), which was the reason for choosing it for this study. The sample was soaked in water for 24 h and mixed (0.5% consistency) by a laboratory mixer after disintegration in a standard disintegrator for 15,000 revolutions. It was then washed three times with deionised, distilled water and filtered. The filtration was conducted under stirring to remove the fiber fines. The fines content of pulp was measured by a Fiber Quality Analyzer (FQA), (Optest Equipment Inc., ON, Canada). Also, the pulp was kept in a refrigerator at 5 °C for 2 days prior to measuring its moisture content according to TAPPI T 412.

2.3. Chitosan modifications and charge density determination

Deacetylation and synthesis of chitosan were conducted in accordance with the procedure established previously (Fatehi et al., 2009b; Lertsutthiwong et al., 2002; Lim & Hudson, 2004). MCN and CMC powders were dissolved in water (1% wt.). To measure the charge density of the polymers, their solutions were titrated against poly-DADMAC or PVSK, using a particle charge detector, Mütek PCD 03 (Herrsching, Germany). The details of this procedure were demonstrated in the literature (Gärdlund et al., 2003b; Lofton et al., 2005). Three repetitions were conducted to give an average value for each sample.

2.4. Fiber modifications

Pulp fibers were first dispersed in distilled water into a 1 L 3-neck glass flask at a 3% consistency, a pH of 7, and a temperature of 30 °C for 1 h. In the first set of experiments, different dosages of MCN (1% wt.) were added to the fiber suspensions, which was stirred for 2 h at 90 rpm. In the second set of experiments, after 1 h of mixing MCN with pulp, HCMC or LCMC (1% wt.) were added to the suspensions (the CMC/MCN charge ratio was one). In the third set of experiments, the dosage of MCN was kept constant at 2 mg/g on fibers, while the dosage of HCMC was varied so that different HCMC/MCN charge ratios were used. The CMC/MCN fiber suspensions were all stirred for another hour under the above-mentioned mixing conditions. Finally, the pulp fibers were washed thoroughly with distilled water to remove unadsorbed polymers.

2.5. Paper-sheet preparation and properties

Paper-sheets were made from unmodified fibers and fibers modified with the polymers according to TAPPI T 205, and dried at an elevated temperature of 110 °C for 30 min using an electrically heated dryer. They were kept in a conditioning room in accordance with TAPPI T 402 prior to analysis. The light scattering coefficient and brightness of paper-sheets were determined in accordance with TAPPI T 425 and T 452 methods, respectively, employing a Technibrite (Micro TB-1C, New Albany, Indiana, USA) optical tester. The tensile and tear strengths were measured according to TAPPI T 494 and T 414, respectively, using Lorentzen & Wettre (L&W) tensile and tear testers. The burst strength of paper was also measured according to TAPPI T 403, using a Burst-o-Matic, Sweden, burst tester.

2.6. AFM and QELS characterizations

This analysis was carried out in deionised and distilled water instead of fiber suspension. The MCN and CMC solutions (200 ppm) were first filtered using syringe filters, sterile 0.2 μm pore size. Silicon wafers were employed as substrates for polymer deposition for investigating the changes in the surface morphology. Silicon wafers were kept in water, and then MCN and/or CMC were added accordingly. The treated wafers were then air dried, and the roughness of the treated wafers was analyzed using an atomic force microscope, AFM (Nanoscope IIIa, Veeco instruments Inc. CA, USA).

The AFM images were scanned in a Multimode in air using commercial silicon contact tips (NP-S20, Veeco Instruments). Approximately 50 spots on the samples were scanned (scan size 10 μm) and the root mean square roughness (Rq) was obtained, as listed in Table 1. The root mean square roughness is defined by the following equation:

$$\mathrm{Rq} = \sqrt{\frac{\sum_{i=1}^{N}(Z_i - Z_{ave})^2}{N}} \tag{1}$$

where Rq is the root mean square roughness within the given area, Z_i is the current height value, Z_{ave} is the average height, and N is the number of spots. A similar method was employed by Gärdlund et al. (2003a) to study the surface variation of silicon wafers upon the retention of polymer complexes.

The quasi-elastic light scattering (QELS) analysis was conducted for the supernatants of the polymer mixtures. In the first set of experiments, the hydrodynamic sizes of polymers were identified

Table 1
Average hydrodynamic size of CMC/MCN (1:1 charge ratio) in deionised and distilled water (concentration = 200 ppm).

	Hydrodynamic size (nm)	Wafer roughness (nm)	Charge density (meq/g)
Blank	–	2 ± 1	–
MCN	30 ± 2	3 ± 0.5	+6.5 ± 0.2
LCMC	25 ± 3	2.5 ± 0.7	−6.2 ± 0.1
HCMC	30 ± 2	3.2 ± 1	−6.4 ± 0.2
LCMC/MCN	168 ± 8	32 ± 4	–
HCMC/MCN	243 ± 9	46 ± 5	–

before and after mixing of the polymers with the same charge ratio, while the total concentration was kept at 200 ppm. In the second set of experiments, the hydrodynamic sizes of polymers and the zeta potential of the solutions (salt free) were measured at different charge ratios of the HCMC/MCN, while the concentration was kept at 200 ppm. The data was obtained at 25 °C with a Zeta-Plus Brookhaven (Holtsville, NY, USA) with the software of 90plus/BI-MASS. The scattering angle and operating wavelength were 90° and 658 nm, respectively. Analysis was conducted automatically to yield the mean diffusion coefficient. Then, from the Stokes–Einstein equation, the apparent hydrodynamic sizes of the polymers and formed complex were assessed. This method has been widely applied for the determination of the size of polymers and complexes in water solution (Buchhammer, Mende, & Oelmann, 2003; De Luca & Richards, 2003; Demarger-Andre & Domond, 1993, 1994; Yusa, Kamachi, & Morishima, 2000). The zeta potential was calculated by measuring the electrophoretic mobility, using Smoluchwski's approximation by a ZetaPlus Zeta potential analyzer (Brookhevan, Holtsville, NY, USA) (Onesippe & Lagerge, 2008; Reis et al., 2003).

2.7. SEM analysis

The samples were collected from the paper-sheets made from unmodified fibers or fibers modified with various dosages of the CMC/MCN mixture (1:1 charge ratio), while the dosage of MCN was 10 mg/g. The samples were dried and coated with carbon and gold to obtain high-resolution images. The images were then taken by a scanning electron microscope, SEM (JEOL, JSM-6400, Japan).

3. Results and discussion

3.1. Characterization of CMC/MCN complex

The hydrodynamic sizes of the polymers and their mixtures are listed in Table 1. It was found that the hydrodynamic size of the HCMC was larger than that of the LCMC. Therefore, the complexes derived from the HCMC/MCN system were larger than those derived from the mixture of the LCMC/MCN. The deposition of HCMC/MCN complexes on silicon wafers changed the surface morphology, and hence the surface roughness, which was reported in an earlier work (Fatehi et al., 2009b). The changes in the surface morphology of silicon wafers as a result of various polymer depositions are listed in Table 1. The adsorption of MCN marginally changed the surface roughness of the silicon wafers (3 ± 0.5), whereas the LCMC/MCN complexes considerably increased their surface roughness (32 ± 4). The increase was more significant for the silicon wafers that the HCMC/MCN complexes retained on them (46 ± 5). Therefore, one can conclude that a greater change in the surface morphology can be obtained upon depositing the complexes formed from larger polymers. This phenomenon might be due to the larger size of the complexes and/or the greater retention of them.

The variation in the average hydrodynamic size of the CMC/MCN complex versus the ratio of CMC/MCN in deionized and distilled water was shown in Fig. 1. The maximum hydrodynamic size was achieved at the charge ratio of one, regardless of the MW of CMC. This is in agreement with the claims in the literature that the maximum hydrodynamic size was obtained for the polymers mixed with the charge ratio of one (Buchhammer et al., 2003; Loftan et al., 2005; Reis et al., 2003). If the charge ratio is not one, not all of the polymers induce complexes and some remain as free polymers in the solutions, resulting in a lower average hydrodynamic size.

Fig. 2 shows the zeta potential of CMC/MCN complexes. As expected, if the ratio of CMC/MCN was one, the zeta potential of the solution was close to zero, which indicated that by mixing such polymers with the same charge ratio, the formed complexes would be neutralized, which facilitated their retention. These results also show that mixing polymers with different ratios can produce complexes with variously charged surfaces (Gärdlund et al., 2003b; Reis et al., 2003).

3.2. Deposition of CMC/MCN on fibers

Since the surface area of fines is larger than that of fibers, upon adding MCN or CMCs, the polymer prefers to adsorb on fines than on fibers. In the literature, to eliminate the influence of fines on the adsorption analysis of polymers on pulp fibers, pulp fibers were washed under stirring (Fatehi & Xiao, 2008; Shirazi, Van de Ven, & Gargier, 2003). Our results showed that the fines content dropped from 24% (wt.) to 2.5% (wt.) via following this method. Although the washing procedure could not remove all the fines, it significantly decreased the impact of fines in our analysis. In our previous work, we reported that, due to the relatively large MW and charge density of MCN, its maximum adsorption on fibers was limited to 0.8 mg/g on fibers (Fatehi et al., 2009b). Therefore, at a dosage of higher than 0.8 mg/g, some part of MCN remains unadsorbed in the fiber suspension. By adding CMC to the fiber

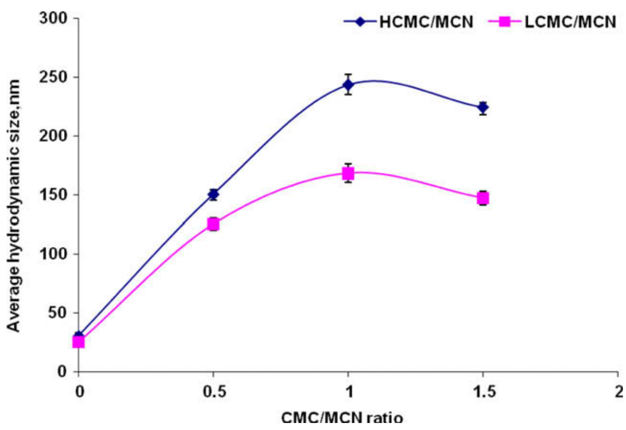

Fig. 1. Hydrodynamic size of the CMC/MCN complex formed by mixing different ratios of CMC/MCN.

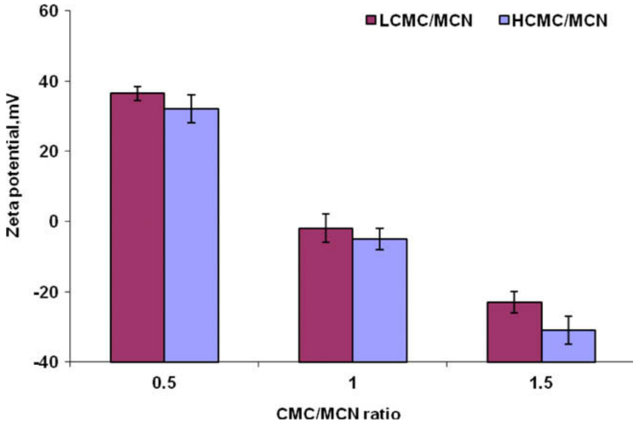

Fig. 2. Zeta potential of the CMC/MCN complex formed by mixing different ratios of CMC/MCN.

suspension that contains unadsorbed MCN, some CMC forms complexes with the unadsorbed MCN, while other CMC adsorbs (as the second layer) on top of the fiber surface, which already had MCN on it (as the first layer). In this way, more polymers are retained, thus improving the strength of fiber networks. Fig. 3 shows the surface of unmodified fibers (left) and modified fibers with HCMC/MCN (right). Evidently, the deposition of the HCMC/MCN complexes altered the surface morphology, which will influence the chemistry of fibers and thus the properties of the fiber networks. Similar results were obtained upon applying MCN followed by the addition of LCMC on fibers.

3.3. Influence of the MW of CMC on paper properties

Fig. 4 shows the tensile and burst indices of the networks made from the fibers modified with various dosages of MCN or CMC/MCN polymers (1:1 charge ratio).

As seen, MCN marginally improved the strength of the fiber network in the single MCN polymer system, which was due to the limited adsorption of MCN on fibers (0.8 mg/g) (Fatehi et al., 2009b). However, the dual polymer system made from MCN and CMC was much more effective than the single polymer system in improving the strength, and its effectiveness was more pronounced at a higher polymer dosage. Interestingly, the high MW CMC in the HCMC/MCN system was more effective than the low MW CMC in the LCMC/MCN system in improving the strength of the fiber networks. It is well known that the size of polymers is a key factor influencing the strength of the fiber networks. In fact, the larger the polymer, the greater the improvement in the strength of paper-sheets (Fatehi & Xiao, 2008; Pelton, 2004). The larger complexes can bridge the fibers more efficiently. Therefore, they can develop more contact areas between fibers, thus improving the fiber bonding more efficiently (Fig. 4).

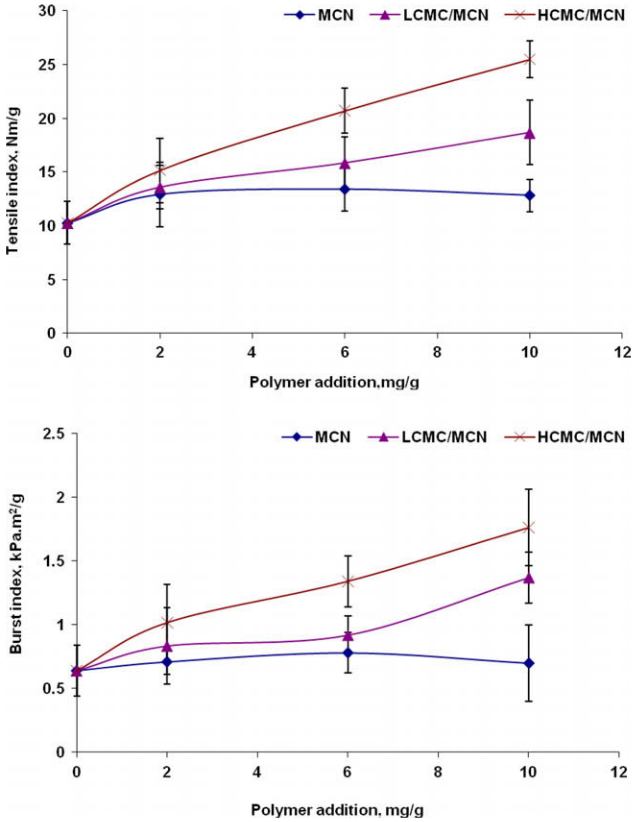

Fig. 4. Tensile and burst indices of the networks made from fibers modified with various dosages of MCN or CMC/MCN complexes (1:1 charge ratio).

Fig. 5 shows the tear index of the networks made from the fibers modified with the MCN or CMC/MCN polymers (1:1 charge ratio) versus the polymer dosage. Obviously, the CMC/MCN dual polymer system, especially the HCMC/MCN one, improved the tear index of papers significantly, even at only 2 mg/g polymer charge. This is in contrast to the addition of MCN alone, since it only marginally improved the tear index at a 2 mg/g addition. Upon adsorbing poly-

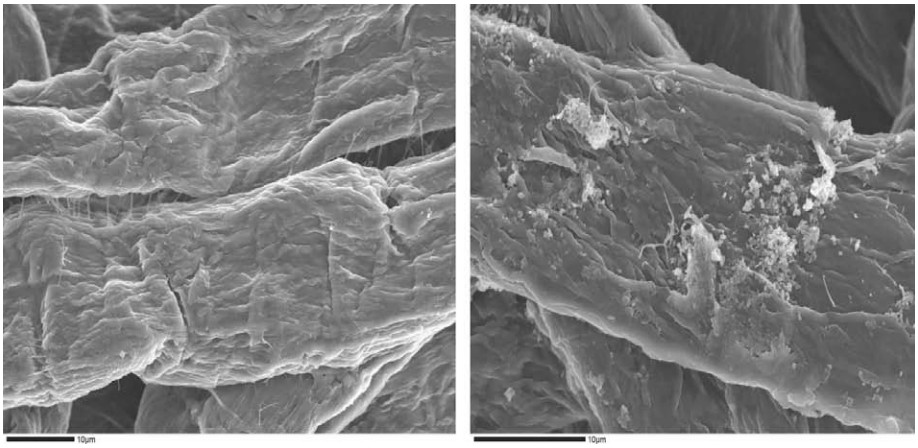

Fig. 3. Surface morphologies of unmodified fibers (left) and fibers modified with HCMC/MCN complexes (right) (10 mg/g of MCN, HCMC/MCN charge ratio = 1).

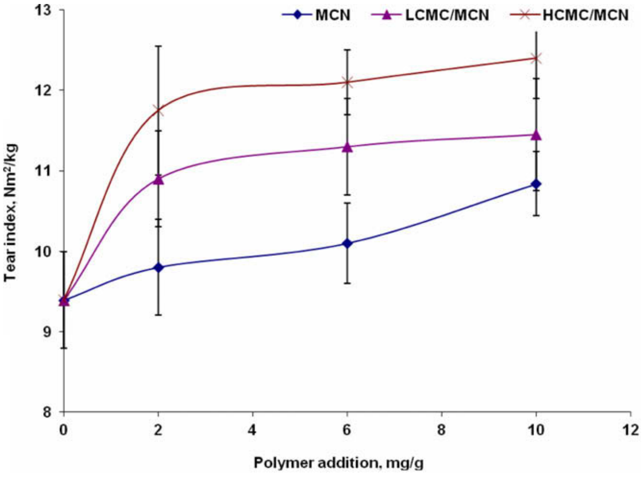

Fig. 5. Tear index of the networks made from the fibers modified with various dosages of MCN or CMC/MCN polymers (1:1 charge ratio).

mers on fibers, the surface morphology and chemistry of fibers are changed, which will affect the fiber–fiber friction as well as the fiber wall and bonding strengths. It was reported that the increase in the fiber wall strength and in the fiber–fiber friction increased the tear index of fiber networks (Askling & Wagberg, 1998; Fatehi & Xiao, 2008; Seth, 1990). The fiber wall strength might have been increased by adsorbing polymers on fibers or by diffusing them into the fiber pores. However, the effect of fiber bonding strength on the tear index is complicated (Nazhad, 2004; Seth, 1990): (1) in the case of a network with a strong fiber bonding, the tear index is decreased by increasing the fiber bonding; (2) in the case of a network with a weak fiber bonding, the tear index is increased by increasing the fiber bonding. The trend in Fig. 5 is likely due to a balance between the decrease in the tear index, as a result of a significant increase in the fiber bonding, and the increase in the tear index, as the results of the increases in the fiber–fiber friction and in the fiber wall strength via polymer adsorption.

Fig. 6 shows the light scattering coefficient of the networks made from the fibers modified with MCN or CMC/MCN polymers (at a 1:1 charge ratio) versus the polymer dosage. The light scattering coefficients declined slightly upon applying MCN alone. In contrast, a profound decline in the light scattering coefficient was observed for the HCMC/MCN system. Based on the strong increase in the tensile index (Fig. 4) and the decrease in the light scattering coefficient (Fig. 6), one can conclude that the bonding of the fiber network was improved significantly by applying the CMC/MCN dual polymer system.

Fig. 7 shows the brightness of the networks made from the fibers modified with MCN or CMC/MCN polymers (1:1 charge ratio) versus the polymer dosage. The brightness of the networks made from the fibers modified with MCN dropped by 3–4% ISO upon applying 2–10 mg/g of MCN, which is caused by the yellowish color of MCN (Fatehi et al., 2009b). However, the CMC/MCN system had only a modest decrease in the brightness. In this case, the high brightness of CMC could compensate for the decrease in the brightness caused by the MCN application.

3.4. Influence of HCMC/MCN charge ratio

Since the HCMC/MCN system was more effective than the LCMC/MCN system in improving the strength of fiber networks, the effect of the charge ratio analysis was only conducted by applying various dosages of HCMC in the fiber suspension that contained 2 mg/g of MCN. Fig. 8 shows the tensile and burst indices of the networks made from the modified fibers versus the charge ratio of HCMC/MCN. The retention of complexes is favorable if the charge ratio of oppositely charged polymers in the dual polymer system is close to one (Fatehi et al., 2009b; Gärdlund et al., 2003b; Lofton et al., 2005; Reis et al., 2003). The strength of fiber networks should be improved the most by applying the polymers with the same charge ratio. This hypothesis is valid if the polymers are premixed and the formed complex is added to fiber suspensions. In addition to the strength improvement from the complex deposition, the layer-by-layer assembly of HCMC/MCN polymers can increase the strength of the fiber network in the current polymer/fiber system (Fatehi et al., 2009b). Such a layer-by-layer assembly can occur at any ratio. At the ratio of 0.5, the adsorbed HCMC on fibers (as the second layer) probably facilitated the deposition of unadsorbed MCN from the system on fibers via the layer-by-layer assembly (bridging concept), while at the ratio of 1.5, the adsorbed MCN on fibers (as the first layer) probably facilitated the deposition of more HCMC from the system on fibers. Therefore, at the ratio of 0.5 or 1.5, the layer-by-layer assembly perhaps played a greater role in fiber bonding improvement, whereas at the ratio of one, the complex deposition did. Therefore, a combination of layer-by-layer assembly and complex deposition was responsible for the observed plateau for tensile and burst indices at a HCMC/MCN of 0.5 and beyond in Fig. 8.

Fig. 9 shows the tear index of the networks made from the modified fibers versus the different ratios of HCMC/MCN. The tear index was gradually enhanced by increasing the ratio. By changing the HCMC/MCN ratio, the amount of complex deposition or layer-by-

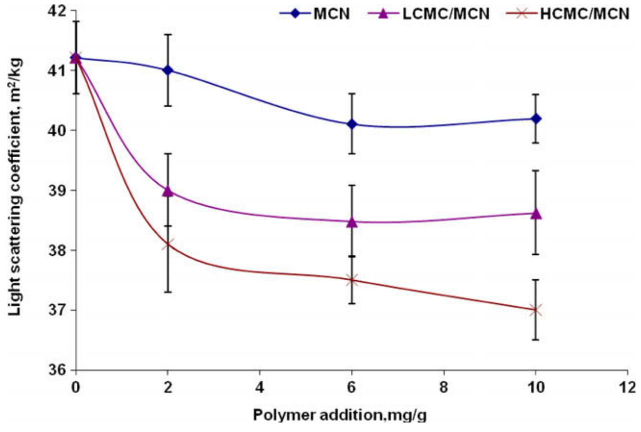

Fig. 6. Light scattering coefficient of the networks made from the fibers modified with various dosages of MCN or CMC/MCN polymers (1:1 charge ratio).

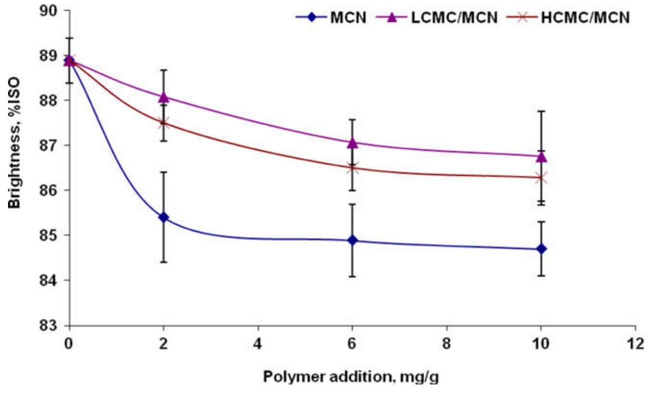

Fig. 7. Brightness of the networks made from the fibers modified with various dosages of MCN or CMC/MCN polymers (1:1 charge ratio).

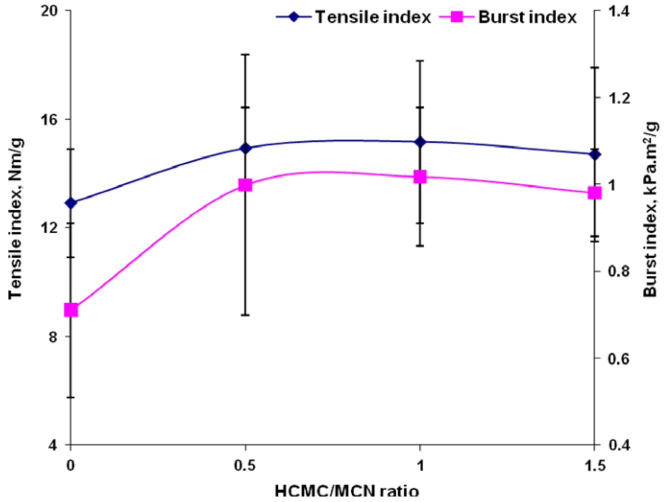

Fig. 8. Tensile and burst indices of the fiber networks versus the HCMC/MCN ratio (MCN dosage = 2 mg/g).

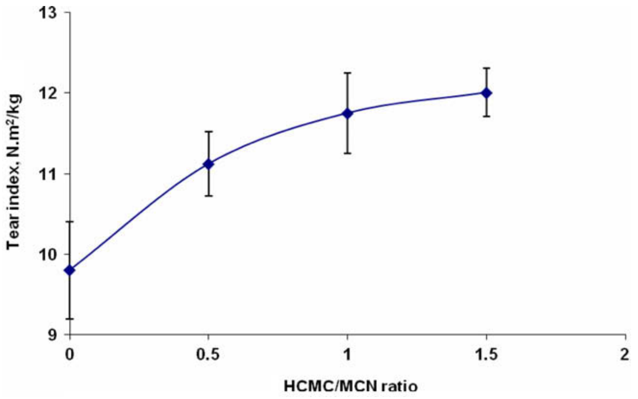

Fig. 9. Tear index of the fiber networks versus the HCMC/MCN ratio (MCN dosage = 2 mg/g).

layer assembly varied, which perhaps resulted in a different surface modification and surface roughness. By increasing the ratio, more HCMC could probably diffuse into the fiber pores, thus increasing the fiber wall strength. Such changes in the surface morphology and/or the fiber wall strength were likely responsible for the increase in the tear index.

The results in Figs. 8 and 9 indicated that increasing the amount of HCMC in the dual polymer system of HCMC/MCN is effective to achieve simultaneous enhancements in tensile, burst, and tear indices.

Fig. 10 shows the variation in the light scattering coefficient of the networks made from the fibers modified with different ratios of HCMC/MCN. The light scattering coefficient decreased until the HCMC/MCN charge ratio reached one. This behavior is attributed to the increase in the fiber bonding, which was supported by the increase in the tensile strength (Fig. 8). At other HCMC/MCN charge ratios, smaller charged complexes were formed (see Figs. 1 and 2), which were less effective in developing the inter-fiber bonds among the fiber networks.

Fig. 11 shows the brightness of the networks made from the fibers modified with HCMC/MCN versus the HCMC/MCN ratio. The brightness was enhanced by increasing the charge ratio, which is owing to the retention of more HCMC on fibers. The retention of HCMC via both the formed complexes and the layer-by-layer assembly is responsible for the increase in the brightness.

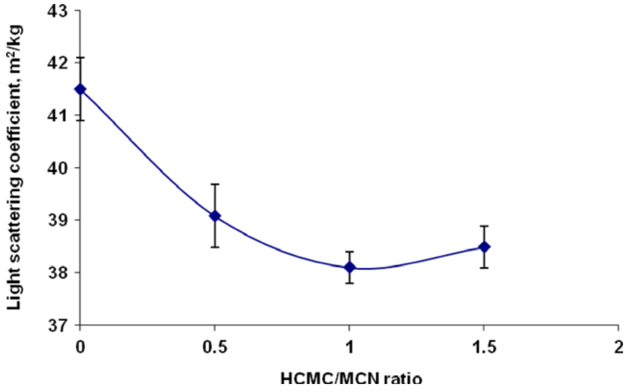

Fig. 10. Light scattering coefficients of the fiber networks versus the HCMC/MCN ratio (MC dosage = 2 mg/g).

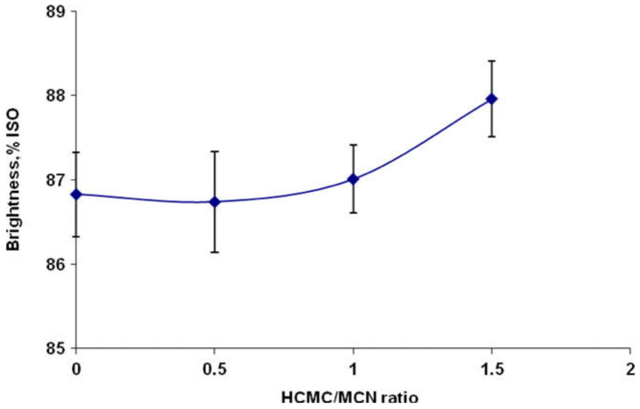

Fig. 11. Brightness of the fiber networks versus the HCMC/MCN ratio (MCN dosage = 2 mg/g).

4. Conclusions

At the CMC/MCN charge ratio of one, the hydrodynamic size of HCMC/MCN complexes was larger than that of LCMC/MCN complexes in deionised and distilled water. The formed HCMC/MCN complexes increased the surface roughness of silicon wafers more than the formed LCMC/MCN complexes did. At a charge ratio of one, the HCMC/MCN complexes had the largest hydrodynamic size with almost neutral charge density. MCN alone marginally increased the strength properties of the fiber networks, while decreasing the brightness significantly. By increasing the dosage of CMC/MCN in the fiber suspension (1:1 charge ratio), the tensile, burst, and tear indices were all increased. Such increases were more pronounced for the HCMC/MCN system than for the LCMC/MCN system. The application of CMC/MCN, especially that of the HCMC/MCN, resulted in a considerable decrease in the light scattering coefficient and a considerable brightness improvement compared with the application of MCN alone. By varying the charge ratio of HCMC/MCN, the tensile, burst, and tear indices, as well as the brightness, were increased, while the light scattering coefficient decreased. These positive results were due to the retention of HCMC/MCN complexes and the layer-by-layer assembly of polymers on fibers.

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