Nano-SiO₂ Used with Cationic Polymer to Improve the Strength of Sack Paper

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As a green and sustainable packaging material, industrial sack paper has gained increased attention in recent years due to the public’s heightened environmental awareness. Practical applications for industrial packaging sack paper demands that the paper possess high physical strength properties. In this study, silicon dioxide (SiO₂) nanoparticles in conjunction with poly(diallyldimethylammonium chloride) (PDADMAC) were applied to improve the physical strength of sack paper. The results showed that the physical strength properties of the sack paper increased with the addition of the SiO₂ nanoparticles and PDADMAC, while the air permeability of the paper also remained high. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) were used to characterize the sack paper with the SiO₂ nanoparticle filler.

Keywords: Sack paper; SiO₂ nanoparticles; Strength properties; Air permeability; Poly(diallyldimethylammonium chloride)

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INTRODUCTION

In recent years, the global demand for packaging materials has increased dramatically due to strong economic activities worldwide. It is estimated that the global packaging market may reach approximately 1,000 billion USD in 2023 (Smithers 2019). In recent years, the concept of green packaging has received increasing attention due to heightened environmental concerns and more stringent governmental regulations. This has created a general interest in cellulosic paper products as green alternatives to non-biodegradable products such as plastics (Dai et al. 2020; Qin et al. 2021). The global market of green packaging is expected to reach 237.8 billion USD by 2024 (Grand View Research 2020). Paper-based packaging is one of the most important green packaging products (Singh et al. 2020). Cellulose paper-based packaging products possess great features, including sustainability, recyclability, and biodegradability (He et al. 2019). These features position paper to potentially replace plastic packaging products in many applications. Transparent cellulosic paper can even be made for specific applications (Guan et al. 2020).

As a common paper-based packaging product, industrial packaging sack paper is mainly used for packaging bulk industrial products, such as cement, chemical fertilizer, and building materials. It is essential that sack paper have superior strength properties and excellent air permeability (Gurnagul et al. 2005). Especially, the tensile energy absorption (TEA), which is defined as the integral of the tensile force and sheet elongation up to the
point of sheet breakage, with its index unit expressed as J/g, can give sack paper the ability of resisting impact stress (Shallhorn and Gurnagul 2010). To meet these requirements, additives such as polyamine and starch are applied in the production of sack paper (Wang et al. 2015).

Silicon dioxide (SiO$_2$) nanoparticles, which are traditionally called colloidal silica, are environmentally friendly nanomaterials. Rich silanol groups (Si-OH) on the surface of the SiO$_2$ nanoparticles impart excellent hydrophilicity and dispersibility in water. Silicon dioxide nanoparticles have commercial applications in the plastic (Sun et al. 2006), coating (Dastmalchian et al. 2012), rubber (Song et al. 2014), and tackifier (Pang et al. 2013) industries. Due to their small size, large specific surface area, and good thermal resistance, SiO$_2$ nanoparticles can improve the strength, aging resistance, and flame retardation properties of various substrates. Silicon dioxide nanoparticles can also be applied as strength additives in the preparation of cellulose fiber-based composites (Kulpinski 2005; Pinto et al. 2008). Compared to other nanoparticles, SiO$_2$ nanoparticles are inexpensive, are easy to process, and have overall strong performance (Song and Zheng 2013).

In the paper mill systems, the colloidal silica is usually combined with high molecular mass cationic polymers as wet-end chemical programs, which have been successfully applied to promote the drainage of pulp slurries and retention of fine particles during the formation of paper (Hubbe 2005). Sometimes the dry strength of paper can also be improved, especially when cationic starch is used (Gill 1991; On and Thorn 1995). When the microparticle system is utilized, the cationic polymers are usually first added and the colloidal silica is subsequently added after strongly dispersing polymer-induced fiber flocs. Although it is less harmful to formation uniformity of paper sheets, the fiber flocs will form due to the introduction of colloidal silica (Swerin et al. 1992). A study has proposed that the lower-mass cationic polymer combined with microparticles was employed to avoid the overflocculation of stock (Jokinen and Palonen 1986). The charge may dominate the interactions between a highly charged cationic polymer and colloidal silica. For example, different results were obtained in one study when the pH was raised to reduce the effective charge density of the cationic polymer (Lindquist and Stratton 1976).

In the present work, the combination of poly(diallyldimethylammonium chloride) (PDADMAC) and SiO$_2$ nanoparticles were mainly used to increase the strength properties of handsheets. The mixture solution of PDADMAC and SiO$_2$ nanoparticles was first prepared and then added into the pulp slurry together. The extra PDADMAC was further applied after the addition of mixture of PDADMAC and SiO$_2$ nanoparticles. Considering the negative charge of SiO$_2$ nanoparticles and pulp fibers, this operation scheme may overcome the low retention of SiO$_2$ nanoparticles in the handsheets when the molecular weight of cationic polymers is lower. Also, the fiber flocculation might be weakened and thus improve the formation uniformity. The mechanical properties, the air permeability, the formation uniformity, the chemical composition, and the surface morphology of the resulting handsheets were investigated in detail.

**EXPERIMENTAL**

**Materials**

The commercial unbleached softwood kraft pulp without any additives, which had been refined for producing sack paper, was provided by an enterprise in the Fujian province of China. The beating degree and zeta potential of the pulp were 17 °SR and -57.85 mV,
respectively. The PDADMAC solution in water (Aladdin, Shanghai, China) had a viscosity of 1054 cP at the concentration of 20 wt%, and its charge density was 16.44 meq/g. The SiO\(_2\) nanoparticles (Solid, Aladdin) which was provided in sol form had an average particle diameter of 40 nm.

**Method**

Different mixtures with various mass ratios of SiO\(_2\) nanoparticles to PDADMAC solids were prepared. The 0.05 g PDADMAC solution (conc. 20 wt%) was first diluted into concentration of 0.02 wt% solution in 50 mL water. Different amounts of SiO\(_2\) nanoparticles were then added into the PDADMAC solutions (conc. 0.02wt%) for obtaining mixture suspensions with different SiO\(_2\) nanoparticle to PDADMAC mass ratios. The pH of the SiO\(_2\) nanoparticle and PDADMAC mixture was adjusted to 10 with the addition of diluted NaOH solution (conc.1.0 wt%). The solution was stirred at 400 rpm for 20 min, after which it was ready for the subsequent use. The zeta potentials of mixtures of PDADMAC and nano-SiO\(_2\) with different mass ratios were determined using a particle size analyzer (Malvern nano-ZS90, Malvern, U.K.). To prepare the handsheets related to the effect of PDADMAC alone (Fig. 1), the unbleached kraft pulp was first fully deflaked to a concentration of 0.4%. Then, a pre-determined amount of PDADMAC (conc. 0.02 wt%) was added into the pulp suspension and thoroughly mixed for 30 s to prepare the pulp slurry for handsheets making. The control sample was prepared without any additives.

To prepare the handsheets related to the effect of the SiO\(_2\) nanoparticles and PDADMAC (Fig. 2), the mixture solutions above prepared with different SiO\(_2\) nanoparticle to PDADMAC mass ratios were added to the well dispersed 0.4 wt% pulp slurry. The PDADMAC dosage was fixed to 0.4% based on the oven-dry weight of the pulp through fixing the added amount of mixture solutions. The pulp slurry was then mixed for 30 s. Subsequently, another portion of PDADMAC was added at a dosage of approximately 0.16% and the slurry was mixed for another 60 s. The control sample was prepared with the addition of PDADMAC alone at the optimum dosage (Fig. 1).

The handsheets were prepared according to the Technical Association of the Pulp and Paper Industry (TAPPI) standard T205 (2002) with a Frank-PTI handsheet former (Birkenau, Germany) at a basis weight of 80 g/m\(^2\).

**Test Standards**

The tensile and tearing strength properties were determined according to the TAPPI standard T220 (2001). The air permeability measurement was conducted according to the Schopper method of the Chinese standard GB/T 458 (2008). The uniformity index was evaluated using the method of CCD image with a uniformity tester (Autoform-II, South China University of Technology, China). The Zeta potential of pulp was determined using a zeta potential instrument (SZP-10, BTG company, Sweden). The handsheets, which were manufactured at the optimum dosage of additives in terms of the physical strength properties, and control samples were used for the subsequent analysis. The paper surface morphology was examined via scanning electron microscopy (SEM) (Nova Nano 230; FEI Company, Hillsboro, OR, USA). The chemical groups on the cellulose fibers were determined via attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) using a Bruker VERTEX 80 spectrometer (Saarbrücken, Germany). The X-ray photoelectron spectroscopy (XPS) analysis was carried out using a K-Alpha spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA) to evaluate the chemical modifications.
RESULTS AND DISCUSSION

Effect of the PDADMAC alone on the Physical Properties of the Handsheet

Poly(diallyldimethylammonium chloride) is a typical cationic polymer that is used in the wet-end of the papermaking process. The effect of the PDADMAC by itself on the physical strength of the handsheets is shown in Fig. 1. Compared with the control handsheet whose tearing index was 17.8 mN·m²/g, the addition of PDADMAC had a negligible effect on the tearing strength of the handsheets. However, the addition of the PDADMAC appeared to increase the tensile strength and the TEA index values when it was dosed below 0.4%. The tensile index and TEA index could be increased from 56 N·m/g and 1.3 J/g to 66.1 N·m/g and 1.65 J/g, respectively, at the dosage of 0.2% (o.d. pulp) PDADMAC compared to control sample without any additives. A report has found that the cationic polymer can be beneficial for the strength of both virgin paper and recycled paper although the dosage of PDADMAC addition to a kraft pulp suspension is small (Zhang et al. 2002). There are several explanations for this behavior. The tearing strength of handsheets is mainly affected by the fiber length, as the inter-fiber bonding has a minimal effect. However, inter-fiber bonding has a significant effect on the tensile strength of sheets formed with fixed pulp fiber, and the TEA can be influenced by both the tensile force and sheet elongation. In the current study, the effect of sheet elongation could be ignored due to the handsheet formation on a laboratory circular former. Thus, the addition of PDADMAC is expected to have positive effects on the inter-fiber bonding. Previous studies showed that the addition of PDADMAC can increase the tensile strength of different pulps (Montplaisir et al. 2006; Xie and Qian 2009). Such a positive effect was also observed in a literature, except that an additional negative effect was found that the recycled paper made after the original handsheets were resuspended in water and formed into another new handsheets had very low strength (Zhang et al. 2002).

Fig. 1. The effect of the PDADMAC dosage on the physical strength properties of handsheets
Effect of the SiO$_2$ Nanoparticles and the PDADMAC on the Physical Properties of the Handsheets

As shown in Fig. 2, the addition of the mixtures of SiO$_2$ nanoparticles and PDADMAC increased the physical strength of the handsheets. The tearing index, the tensile index, and the TEA index all reached their maximum values when the SiO$_2$ nanoparticle dosage was 0.5%, which indicated that the addition of SiO$_2$ nanoparticles, in sequence with PDADMAC addition, can reinforce the bonding strength of cellulose fibers. The results can also be supported from the data in Table 1. However, when the SiO$_2$ nanoparticle dosage exceeded 0.5%, the strength index values began to decrease. It is proposed that the possible aggregation of the SiO$_2$ nanoparticles led to the decrease of strength indexes due to the increased content of SiO$_2$ nanoparticles.

![Graphs showing the effect of SiO$_2$ nanoparticle dosage on tensile, tearing, and TEA index values](image)

**Fig. 2.** The effect of the SiO$_2$ nanoparticle dosage on the a) tensile index, b) tearing index, and c) TEA index values of the handsheets at 0.56% (o.d. pulp) dosage of PDADMAC

The increased zeta potential of the mixtures of PDADMAC and nano-SiO$_2$ due to the increased mass ratio of SiO$_2$ nanoparticles might cause the lower retention of SiO$_2$ nanoparticles, and this led to the decrease of strength properties of handsheets. Wu *et al.* (2005) reported similar results. Song and Zheng (2013) also found that the addition of SiO$_2$ nanoparticles to microcrystalline cellulose (MCC) film could increase the tensile strength of the cellulose composite film.
Table 1. Physical Properties of Handsheets Manufactured under Optimum Dosage of Additives

<table>
<thead>
<tr>
<th>Sample</th>
<th>Physical Strength</th>
<th>Uniformity Index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tearing Index (mN·m²/g)</td>
<td>Tensile Index (N·m/g)</td>
</tr>
<tr>
<td>No additives</td>
<td>17.8</td>
<td>56</td>
</tr>
<tr>
<td>0.2% dosage of PDADMAC alone</td>
<td>16.36</td>
<td>66.1</td>
</tr>
<tr>
<td>0.5% dosage of SiO₂ nanoparticles and 0.56% dosage of PDADMAC</td>
<td>19</td>
<td>78.91</td>
</tr>
</tbody>
</table>

The air permeability of the handsheets was also determined. The air permeability of the handsheets with the SiO₂ nanoparticles and PDADMAC was slightly lower (11.3 μm/Pa·s) than the air permeability of the handsheets with the PDADMAC alone (12.6 μm/Pa·s). The decreased air permeability was mainly attributed to the better sheet formation with the addition of PDADMAC and nano-SiO₂ than that with addition of PDADMAC alone. The uniformity index of handsheets under the addition of PDADMAC and nano-SiO₂ was increased from 9.0 to 13.0 compared to that of addition of PDADMAC alone. Also, some of the polyelectrolyte complex that is formed with SiO₂ nanoparticles might fill the micropores among fibers as fillers and thus decreased the air permeability. However, the 11.3 μm/Pa·s air permeability value was still higher than that of the Chinese standard GB/T 458 (2008), which was 5.0 μm/Pa·s.

Effect of SiO₂ Nanoparticles and PDADMAC on the Zeta Potentials of Pulp Samples

It can be seen in Table 2 that the zeta potentials of mixtures of PDADMAC and SiO₂ nanoparticles changed from positive values to negative values with the increasing mass ratio of nano-SiO₂, and this might induce the lower retention of SiO₂ nanoparticles on handsheets. The similar trend for zeta potential of pulp was also found in Table 3 with the increasing dosage of nano-SiO₂. When the mixture of PDADMAC and nano-SiO₂ alone was added under the present condition of fixing dosage of PDADMAC to be 0.4% (o.d. pulp), all the zeta potential values were far below zero with the increase of nano-SiO₂ dosage. As in many microparticle systems, the optimum effectiveness was found at or near the point of charge neutralization in papermaking furnish (Miyanishi and Shigeru 1997; Honig et al. 1999; Hubbe 2005). Therefore, the extra 0.16% dosage of PDADMAC was further added after the addition of mixture of PDADMAC and nano-SiO₂. The zeta potential of pulp was decreased in absolute value after the extra addition of PDADMAC. The zeta potential of pulp was -2.7 mV near the charge neutralization point when the dosage of nano-SiO₂ was 0.5% and extra 0.16% dosage of PDADMAC was added. The physical strength and uniformity index of handsheets also reached the maximum under the aforesaid condition in which the mixture of PDADMAC (0.4% dosage) and nano-SiO₂ (0.5% dosage) was first added, then the extra 0.16% dosage of PDADMAC was in sequence added.
Table 2. Zeta Potentials of Mixtures of PDADMAC and Nano-SiO$_2$ Particles

<table>
<thead>
<tr>
<th>The mass ratio of PDADMAC and nano-SiO$_2$</th>
<th>1:5</th>
<th>2:5</th>
<th>3:5</th>
<th>4:5</th>
<th>5:5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeta potential of mixture (mV)</td>
<td>-31.9</td>
<td>-25.9</td>
<td>-12.6</td>
<td>-2.85</td>
<td>13.2</td>
</tr>
</tbody>
</table>

Table 3. Zeta Potentials of Pulp Samples with Different Addition of Wet-end Chemical Additives

<table>
<thead>
<tr>
<th>Dosage of nano-SiO$_2$ (%)</th>
<th>0.4</th>
<th>0.5</th>
<th>0.67</th>
<th>1.0</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeta potential of pulp (mV) (without extra addition of PDADMAC)</td>
<td>-6.7</td>
<td>-15.8</td>
<td>-22.8</td>
<td>-30.6</td>
<td>-54.9</td>
</tr>
<tr>
<td>Zeta potential of pulp slurry (mV) (with extra 0.16% addition of PDADMAC)</td>
<td>4.8</td>
<td>-2.7</td>
<td>-3.9</td>
<td>-7.5</td>
<td>-25.7</td>
</tr>
</tbody>
</table>

**ATR-FTIR Analysis of the Handsheet Components**

Infrared spectroscopy can be used to characterize the molecular structure of different compounds based on the characteristic peaks of different functional groups. In the ATR-FTIR spectra, shown in Fig. 3, the peaks at 3328 and 2892 cm$^{-1}$ were attributed to the Si–OH, –OH and –CH$_3$, –CH$_2$ stretching vibrations, respectively. The new peak at 1673 cm$^{-1}$ was attributed to the –OH bending vibration of the SiO$_2$ nanoparticles (Kong et al. 2020). The peaks of 1521, 1462, and 1038 cm$^{-1}$ in the handsheet samples with the SiO$_2$ nanoparticles and PDADMAC were the characteristic bonds of the C–C of the PDADMAC, the Si–O of the SiO$_2$ nanoparticles, and the C–N of the PDADMAC stretching vibrations, respectively (Huang et al. 2020). The ATR-FTIR results confirmed that the SiO$_2$ nanoparticles were effectively retained in the handsheets.

![Fig. 3. The ATR-FTIR spectra of the handsheets with 0.2% PDADMAC alone and with the mixture of SiO$_2$ nanoparticles and PDADMAC (0.5% dosage of SiO$_2$ nanoparticles and 2.8% dosage of PDADMAC)](image-url)
The XPS Analysis of the Handsheets

Results of XPS analysis, revealing the surface chemical compositions of the handsheet samples (the dosage of PDADMAC and SiO₂ nanoparticles was 2% and 0.5%, respectively) are shown in Table 1 and Fig. 4. The spectrum of the control handsheet sample only showed O1s and C1s peaks, near 533 eV and 286 eV, respectively. When the SiO₂ nanoparticles and PDADMAC were added to the handsheets, the silicon and nitrogen element peaks appeared with bonding energies of 103 and 400 eV, respectively. The elemental composition of the handsheets (Table 4) show that the atomic ratio of N and Si was 0.96% and 0.61%, respectively. These results support the conclusion that the PDADMAC and SiO₂ nanoparticles were successfully retained in the handsheets.

Table 4. Elemental Composition of the Handsheets

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Composition (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>0.2% dosage of PDADMAC alone</td>
<td>66.51</td>
</tr>
</tbody>
</table>
| 0.5% dosage of SiO₂ nanoparticles and 0.56% dosage of PDADMAC | 66.99  | 31.44  | 0.96  | 0.61

Fig. 4. The XPS spectra of the sack paper with a, b) PDADMAC alone and c, d) SiO₂ nanoparticles and PDADMAC
The high resolution C1s spectra of the handsheet samples are shown in Figs. 4b and 4d. The elemental peaks that appeared at the bonding energies of 287.7, 286.6, and 285.1 eV were mainly attributed to the bands of O–C–O, C–O, and C–H/C–C, respectively. The bonding energy of C–O is usually higher than that of C–H/C–C for cellulose, which can be verified by the results in Fig. 4b for the handsheet samples with just PDADMAC. The bonding energy results of the C–H/C–C in the handsheets with the SiO2 nanoparticles and PDADMAC (Fig. 4d) was higher than that of the handsheets with PDADMAC alone (Fig. 4b). The carbon element in the PDADMAC is mainly presented as C–C and C–H bonds.

**Morphological Features of the Sack Paper**

The retention of the SiO2 nanoparticles and the PDADMAC in the handsheets was also confirmed by the results from the SEM analysis (Fig. 5). The presence of the SiO2 nanoparticles and the PDADMAC (Fig. 5b) improved the inter-fiber bonding better than the addition of PDADMAC alone in the control samples. In addition, the fiber surface was relatively clean in the control sample. Generally, the SiO2 nanoparticle and PDADMAC sample (Fig. 5b) illustrated tighter fiber bonding properties than the control sample (Fig. 5a).

The particles that appear white in the SEM micrograph in Fig. 5b can be referred to the SiO2 nanoparticles. This indicates that the electrostatic interactions of the cationic PDADMAC, the anionic SiO2 nanoparticles, and the anionic fibers were effective in retaining the SiO2 nanoparticles material. The addition of the SiO2 nanoparticles in conjunction with the PDADMAC improved the inter-fiber bonding and consequently increased the paper strength properties (Fig. 2).

**CONCLUSIONS**

1. SiO2 nanoparticles were applied in combination with poly(diallyldimethylammonium chloride) (PDADMAC) to increase the strength properties of handsheets that were made from bleached softwood kraft pulp. Compared with addition of PDADMAC alone, the addition of SiO2 nanoparticles and PDADMAC increased the tensile index, the tearing index, and the TEA index from 66.1 N·m/g, 16.36 mN·m²/g, and 1.65 J/g to 78.91 N·m/g, 19.0 mN·m²/g, and 1.96 J/g, respectively. The improved strength properties illustrated the beneficial impact of the addition of the combination of SiO2 nanoparticles.
nanoparticles and PDADMAC.

2. The analytical results of the attenuated total reflectance – Fourier transform infrared (ATR-FTIR) spectrometry and X-ray photoelectron spectrometry (XPS) analyses confirmed that the SiO$_2$ nanoparticles were effectively retained. The scanning electron microscopy (SEM) images further verified that the presence of the SiO$_2$ nanoparticles and PDADMAC improved the fibers bonds.

3. The air permeability of the sack paper decreased slightly with the addition of the SiO$_2$ nanoparticles and PDADMAC. However, the measured air permeability value (11.3 μm/Pa·s) was still much higher than that specified by the Chinese national standard.

REFERENCES CITED


