Nanostarch Surface Coating of Lightweight Coated Paper

Qijie Chen,* Xufang Dong, Liling Zhou, Xueming Zheng, Jianhui Wang, and Ping Wang

Nanostarch has a small particle size and large surface area compared with traditional modified starch. In this study, nanostarch was prepared by dual screw extrusion and was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), and X-ray diffraction (XRD). The nanostarch was studied as a coating adhesive in surface coating of lightweight coated paper. The crystallinity of nanostarch granules was decreased by dual screw extrusion, and its average particle size was about 100 nm. The results showed that for the paper coating formula of styrene butadiene latex and an ordinary oxidized coating starch ratio of 9:5, all ordinary oxidized coating starch and part of the styrene butadiene latex can be replaced by nanostarch. When 5 parts of ordinary oxidized coating starch and 4 parts of styrene butadiene latex were replaced by 6.5 parts nanostarch, the water retention property of nanostarch coating was increased by 64.0%, and its viscosity was decreased by 11.0%. The IGT printing surface strength of lightweight coated paper by the nanostarch coating was increased by 11.6%, and the glossiness of coated paper was increased by 7.2%. These results show that nanostarch surface coatings have good prospects for application in papermaking.

Keywords: Nanostarch; Double screw extrusion; Coating; Lightweight coated paper; Styrene butadiene latex

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INTRODUCTION

With the growing shortage of oil resources and increasing awareness of environmental protection, low carbon manufacturing requirements are increasing, and the need for a renewable and environmentally friendly adhesive has aroused widespread concern in the field of pigment coated paper. An adhesive is an important component of the pigment coating formulation, and its role is to enable mutual adhesion among pigment particles or between pigment and coating substrate (Byrne 2002; Sihem et al. 2013; Wei et al. 2013). Surface-coated paper should have sufficient adhesion strength to adapt to the requirements of the high-speed printing. The viscosity, water retention, and rheological properties of the coating are determined by the adhesive. The type and amount of adhesive has a great influence on the optical properties and printability of coated paper (Wang et al. 2011; Hee et al. 2013; Imam et al. 2013). Styrene butadiene latex and ordinary coating starch are used most often as adhesives in paper coatings.

Starch is a polysaccharide that serves as an energy reserve in various plants, and it is one of the most abundant natural polysaccharide raw materials. Starch consists of 20 to 30% linear amyllose and 70 to 80% branched amylopectin (Bloembergen et al. 2008). As
an abundant natural polymer, starch has many attractive properties, which include degradability and biocompatibility. Because starch is a low-cost versatile biopolymer, it has been widely used as the adhesive in papermaking. However, the viscosity and adhesion of starch cannot meet the requirements of advanced coating technology. With the coating speed and the solids content of coating increasing, adding more ordinary coating starch will decrease the shear rheological properties of paint, thus affecting the coating operation performance (Liu and Liu 2001). Biological latex based on starch is a new type of coating adhesive, but with the increase of biological latex substituted styrene butadiene latex, the surface strength of coated paper decreases (Qiu et al. 2011; Ren et al. 2013).

As a typical biodegradable natural polymer, starch is a good candidate for preparation of nanoparticles. By adding starch to a coating formulation in the form of nanoparticles, rather than as solubilized starch molecules, there may be an opportunity to avoid the high viscosity associated with concentration polymer solutions. Presumably the starch nanoparticles would be able to swell and develop adhesive character later in the process, when heat is applied to dry the coating. Recently, Lecorre et al. (2010) reviewed starch nanoparticle preparation, characterization, and applications. Nanostarch or starch nanoparticles have many potential applications in plastic fillers, food additives, drug carriers, coating binders, and adhesives (Antonietti et al. 1994; Wei et al. 2014). Also, nanostarch has great potential for use in the papermaking wet end, surface sizing, and especially in coating as a biodegradable substitute to petroleum-based adhesives (Hee et al. 2015). Nanostarch can be prepared in three different ways, including acid or enzymatic hydrolysis, regeneration, and mechanical treatment (Lecorre et al. 2013). Nanostarch with small particle size and large surface area has many advantages, such as the lower viscosity and strong adhesive ability. Extrusion is an environmentally friendly mechanical method (Wang and Rong 1989). In this work, double screw extrusion technology was adopted to prepare nanostarch, and the nanostarch was characterized with Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray diffraction (XRD). The effect of nanostarch as a coating adhesive on the performance of lightweight coated paper was also studied for guiding its application in the coated paper.

**EXPERIMENTAL**

**Raw Materials**

Clay (70% solid content, 95 grades) and ground calcium carbonate (GCC, 75% solid content, 98 grades) were used as received without further purification. Ordinary oxidized coating starch, styrene butadiene latex (SBL, 50% solid content), carboxymethyl cellulose (CMC), lubricant, and water-resistant agent were used in the coatings. All were provided by the Yueyang Paper Co., Ltd. (Yueyang, China). Nanostarch was prepared in the laboratory by twin-screw extrusion. The coated base paper was also provided by the Yueyang Paper Co., Ltd., and its basis weight was 60 ± 1 g/m².

**Preparation of Corn Nanostarch**

Nanostarch was prepared according to the method described in Chen et al. (2015). Corn starch was premixed with 10% glycerin (to dry corn starch) and 0.2% cetanol (to dry corn starch), adding water until the system moisture content was 26%. It was then mixed in a high-speed homogenizer. The mixture was fed into twin-screw extruder with twelve...
barrels (DS-32, FuMa Engineering Limited Company, Changsha, China), and the screw speed was set to 260 rpm. The crosslinking agent of 2% glyoxal (to dry corn starch) was injected to the extruder from the tenth barrel. The extrudate was dried and smashed to obtain the corn nanostarch.

**FTIR Spectral Analysis**

FTIR spectra of corn nanostarch and corn starch were recorded by a Bruker Vertex 70v vacuum spectrometer (Karlsruhe, Germany) in reflection mode. The range was from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\), and the resolution was 2 cm\(^{-1}\).

**Scanning Electron Microscopy**

The surface morphology of corn nanostarch and corn starch was analyzed using a Jeol scanning electron microscope (JSM-6490LV, Kyoto, Japan). The images were obtained using an accelerating voltage of 10 to 15 kV at an appropriate magnification.

**X-ray Diffraction**

The XRD patterns investigations of corn nanostarch and corn starch were recorded on an X-ray diffractometer (D/MAX2200X, Rigaku Corporation, Tokyo, Japan) with Cu \(\text{ka}\) radiation source energized at 45 kv. Measurements were collected in the 2\(\theta\) range from 10° to 40°. The measurement resolution was 0.02°.

**Preparation of Coating**

Nanostarch was used as the coating adhesive and it substituted for the SBL and ordinary oxidized coating starch in the coating. Different coating formulations are shown in Table 1.

**Table 1. Coating Formulation**

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl( ppm)</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>GCC (ppm)</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>SBL (ppm)</td>
<td>9</td>
<td>9</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>Ordinary oxidized Coating Starch (ppm)</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nanostarch (ppm)</td>
<td>0</td>
<td>2.5</td>
<td>4.5</td>
<td>6.5</td>
</tr>
<tr>
<td>CMC (ppm)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Water-resistant agent (ppm)</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Lubricant agent (ppm)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Solid Content (%)</td>
<td>64</td>
<td>64</td>
<td>64</td>
<td>64</td>
</tr>
</tbody>
</table>

The clay and GCC were mixed and dispersed in a high-speed dispersion machine (GFJ-0.4, Shanghai Coating Chemical Machinery Co. Ltd, Shanghai, China), with a dispersion speed of 2000 rpm and dispersion time of 20 min. After the SBL, starch, and other agents such as CMC, water-resistant agent, lubricant agent were added to the mixture, the dispersion speed and time were adjusted to 1500 rpm and 6 min, respectively. Thus the coating was prepared and its properties was measured.

**Determination of Water Retention Value of Coating**

The water retention value of coatings was determined by a coating water retention
value tester (AA-GWR, Kaltec Scientific Inc., Novi, MI, USA). A lower water retention value indicated a better water retention performance of the coating. For each type of coatings, three measurements were conducted and average value of the three measurements was used as final result.

**Coating Process**

An automatic sheet coating machine (ZAA-2300, Zehntner GmbH Testing Instruments, Sissach, Switzerland) was used to coat the paper. Ten sheets of paper were coated for each type of coating formulation. The coating weight was controlled in 8 to 9 g/m² (single-sided coating) for each sheet; the coated paper was followed by a super calendaring machine (KRK, Kyoraku Co., Ltd, Osaka, Japan) to press and decorate. The calendaring temperature was 70 °C and the line pressure was 4.0 MPa. The positive and negative sides of the coated paper were pressed one time each.

**Coated Paper Properties Testing**

The coated paper was kept in the constant temperature at 23 °C and 50% relative humidity for 24 h. The optical properties, printing performance, and strength properties of the coated paper were measured according to the relevant national standards of China. For each performance of coated paper, ten measurements were taken and average value of the ten measurements was used as final result.

**RESULTS AND DISCUSSION**

**FTIR Spectral Analysis**

The FT-IR spectra of corn starch and corn nanostarch are presented in Fig. 1. The spectra of both samples were very similar, indicating that the molecular base structure and group of nanostarch prepared by twin-screw extrusion did not change. However, some characteristic adsorption peaks of nanostarch were enhanced, such as the broad peak at 3150 cm⁻¹ and at 1011 cm⁻¹.

**Fig. 1.** FT-IR spectra of starch
The broad peak at 3150 cm$^{-1}$ was due to the $\text{–OH}$ stretching vibration, and the peak at 1011 cm$^{-1}$ was due to $\text{–C-O}$ stretching vibration and $\text{–C-OH}$ bending vibration (Du et al. 2011). Corn nanostarch prepared by twin-screw extrusion is rich in specific surface area and had more hydroxyl groups than the corn starch, which made the $\text{-OH}$ absorption peak of nanostarch stronger.

**SEM Analysis**

The SEM photos of corn starch, plasticized starch (no crosslinking agent), and the corn nanostarch are presented in Fig. 2. The average particle size of corn starch was around 15 µm, and the particles were rather big and nonuniform in shape. However, the plasticized starch without adding the crosslinking agent was completely melted by extrusion, and it did not form the starch particle (Fig. 2b). Figure 2c shows the SEM of nanostarch prepared by extrusion, plastication, and crosslinking step. Its average particle size was about 100 nm, which is much smaller than that of corn starch and which is close to the particle of carboxyl styrene butadiene latex. Moreover, nanostarch granules were complete and smooth. During extrusion, starches are subjected to high temperature and high shear force. Essentially, starch gelatinization, melting and fragmentation occur. The starch nanoparticles prepared by reactive extrusion were also considered as “regenerated starch” nanoparticles because of the crosslinking step (Le Corre et al. 2010). It also has been shown that at the same extrusion temperature, the size of starch particles extrude with crosslinker is much smaller (Song et al. 2011). This result confirmed that nanoscale starch was successfully prepared by the twin-screw extrusion and the crosslinking agent was very important for the preparation of nanostarch.

![SEM photos of (a) corn starch, (b) plasticized starch (no crosslinking agent), and (c) nanostarch](image)

**XRD Analysis**

The XRD patterns of corn starch and corn nanostarch are presented in Fig. 3. Corn starch granules had A-type crystallinity and showed strong diffraction peaks at 15°, 17°, 18°, and 23°, as previously reported (Sívoli et al. 2009; Song et al. 2011). However, the peaks of nanostarch at 15°, 17°, and 23° totally disappeared, and there was only a small peak at 18°, which suggested that the crystalline region of the granule was broken down and crystallinity decreased. During the extrusion process, the combination of heat and shear force caused a destruction in both the crystallinity and amorphous region of starch. The degree of crystallinity of starch particles decreases with the reduction of particle size during high-pressure homogenization treatment (Liu et al. 2009).
Effect of Adding Method of Nanostarch on the Properties of Coating

Ordinary oxidized coating starch needs to be gelatinized before it is used to prepare coating, and the concentration of gelatinization usually cannot exceed 30%, which means that starch will bring a considerable amount of water to the coating. Powdery nanostarch is easily soluble in cold water and it can be directly dispersed with pigment together without gelatinization, which is good for preparing the coating. Table 2 shows the properties of sample coating formulation C with different adding methods of nanostarch addition.

Table 2. Effect of Method of Nanostarch Addition on the Coating Properties

<table>
<thead>
<tr>
<th>Method of Nanostarch Addition</th>
<th>pH</th>
<th>Solid Content (%)</th>
<th>Low Shear Viscosity (mPa.S)</th>
<th>Water Retention Value (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry powder without gelatinization</td>
<td>8.18</td>
<td>64.1%</td>
<td>910</td>
<td>28.8</td>
</tr>
<tr>
<td>With gelatinization</td>
<td>8.17</td>
<td>64.1%</td>
<td>915</td>
<td>30.1</td>
</tr>
</tbody>
</table>

As shown in Table 2, the two methods of adding nanostarch had little effect on the properties of the coating. When the nanostarch was used as dry powder or gelatinization after cooking separately, the low shear viscosity and water retention value of coating were almost the same. Thus, the powdered nanostarch can be directly dispersed with the pigment and produce similar effects compared with the nanostarch used as gelatinization after cooking. In the actual production of coating, high solids content and low viscosity of the coating are needed to reduce the energy consumption and improve the performance of coated paper (Ren et al. 2013).

In actual application, nanostarch can be added as a dry powder without the gelatinization process, which can reduce energy consumption, save the dissolution time, and reduce storage space. Experiments also showed that the mixture dispersion effect of
nanostarch and pigment was good when the dispersion velocity was 2000 rpm and the dispersion time was 8 min.

Effect of Nanostarch on the Low Shear Viscosity of Coating

The effect of nanostarch on the low shear viscosity of coatings is presented in Fig. 4. Nanostarch had a great influence on the viscosity of the coating. Replacing 5 parts of ordinary oxidized coating starch with 2.5 parts nanostarch, the viscosity of coating sample B was decreased by 61.1% compared with coating sample A. When 5 parts of ordinary oxidized coating starch and 2 parts of styrene butadiene latex were replaced by 4.5 parts nanostarch, the viscosity of coating sample C was decreased by 36.8%. When 5 parts of ordinary oxidized coating starch and 4 parts of styrene butadiene latex were replaced by 6.5 parts nanostarch, the viscosity of coating sample D was decreased by 11.0%. Nanostarch in cold water can fully absorb water and swell. It made the coating viscosity decrease compared with ordinary oxidized coating starch because nanostarch in water still kept the swelling of the granular. Nanostarch can effectively reduce the low shear viscosity of coating, which is very favorable to increase the coating concentration and to prepare the high solid content coating.

Fig. 4. Effect of nanostarch on the low shear viscosity of coating

Effect of Nanostarch on Water Retention Value of Coating

Figure 5 shows that the water retention value of coating was decreased gradually with increased nanostarch. A lower water retention value indicates better water retention of the coating (Qiu et al. 2011). In coating sample B, 2.5 parts of nanostarch replaced 5 parts ordinary oxidized coating starch. The water retention performance was near the same as coating sample A, which showed that the nanostarch had excellent water retention ability. The water retention property of one part of nanostarch may be almost equivalent to that of two parts of the ordinary oxidized coating starch. In coating samples C and D, the water retention property increased with the increasing dosage of nanostarch. Coating sample C increased by 39.4%, and coating sample D increased by 64.0%. A better water retention performance of coating was associated with a better operating performance of the coating process, and it was easier to obtain a uniform coating structure for the coated paper.
Effects of nanostarch which substituted the ordinary oxidized coating starch and styrene butadiene latex on paper properties of lightweight coated paper are shown in Table 3. The coated paper of coating sample A, B, C, and D have almost the same basis weight and coating weight. Table 3 shows that they have almost the same density and whiteness. However, the opaqueness of coated paper of nanostarch showed a slight increasing trend. The printing surface roughness reflects the planeness of coating structure at the microscopic level. The printing surface roughness of coated paper decreased a little when nanostarch was used as coating adhesive, and the paper of coating sample D was decreased by 6.5% compared with the coating sample A. Nanostarch has better rheological characteristics than ordinary oxidized coating starch, and the flexibility is better during the pressing and drying process of coated paper. Thus, the printing surface roughness of paper coated with nanostarch was better.

Table 3. Effect of Nanostarch on the Properties of Lightweight Coated Paper

<table>
<thead>
<tr>
<th>Paper Properties</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis weight (g/m²)</td>
<td>68.4</td>
<td>68.2</td>
<td>68.1</td>
<td>68.1</td>
</tr>
<tr>
<td>Coating weight (g/m²)</td>
<td>8.1</td>
<td>8.3</td>
<td>8.1</td>
<td>8.2</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.92</td>
<td>0.93</td>
<td>0.92</td>
<td>0.92</td>
</tr>
<tr>
<td>Whiteness (%ISO)</td>
<td>81.7</td>
<td>81.8</td>
<td>81.8</td>
<td>81.6</td>
</tr>
<tr>
<td>Opaqueness (%)</td>
<td>92.8</td>
<td>93.6</td>
<td>93.4</td>
<td>93.5</td>
</tr>
<tr>
<td>Printing surface roughness (μm)</td>
<td>2.47</td>
<td>2.48</td>
<td>2.43</td>
<td>2.31</td>
</tr>
<tr>
<td>Printing ink absorption (%)</td>
<td>28.1</td>
<td>29.9</td>
<td>30.4</td>
<td>32.1</td>
</tr>
<tr>
<td>Surface glossiness (%)</td>
<td>23.5</td>
<td>24.1</td>
<td>24.8</td>
<td>25.2</td>
</tr>
<tr>
<td>Printing surface strength (m/s)</td>
<td>0.69</td>
<td>0.71</td>
<td>0.75</td>
<td>0.77</td>
</tr>
</tbody>
</table>

Printing ink adsorption ability is one of the important physical properties of coated paper (Wang et al. 2013). It directly affects the quality of printed products. As shown in Table 3, printing ink absorption of the coated paper that used nanostarch coating was better than the ordinary oxidized coating starch. This may result from the more open pore
structure after coating with nanostarch. The surface glossiness is a relatively significant property of the coated paper, which could be influenced by the properties of pigments, category, and dosage of binders (Prasad et al. 2010). Usually, the glossiness of coated paper is decreased when adding the ordinary oxidized coating starch compared to the all-latex-system. However, nanostarch can increase the glossiness of coated paper, and the glossiness of coated paper used coating sample D was improved by 7.2%.

Printing surface strength is an important property of lightweight coated paper, and the coating surface strength depends on the category and dosage of binders. Nanostarch substituting the ordinary oxidized coating starch and styrene butadiene latex can enhance the paper surface strength. The coated paper surface strength was increased by 11.6% for coating sample D of 6.5 shares of nanostarch substituting 5 shares of oxidized coating starch and 4 shares of styrene butadiene latex. The results showed that the binding strength of nanostarch was superior to the ordinary oxidized coating starch (2 times of the ordinary oxidized coating starch can reach the same level of nanostarch) and was close to the styrene-butadiene latex with the 1:1 ratio.

As shown in Table 3, when 2.5 shares of nanostarch replaced 5 shares of ordinary oxidized coating starch, the coated paper properties all could reach the coating sample A, and some properties were even better. When nanostarch further replaced the styrene butadiene latex the coated paper properties all were superior to coating sample B. Therefore, one share of nanostarch could replace two shares of ordinary oxidized coating starch until completely substituted. One share of nanostarch could replace one share of the styrene butadiene latex, and it could replace about 50% styrene butadiene latex in coating when applied in lightweight coated paper. It could ameliorate the coated paper properties and nanostarch used as a coating adhesive has good prospects in papermaking.

CONCLUSIONS

1. The nanostarch was successfully prepared by twin-screw extrusion. The particle size of nanostarch was about 100 nm, and it had a smooth surface. The FTIR spectra of corn starch and corn nanostarch were very similar, and no new absorption peaks arose for the corn nanostarch. The XRD patterns of corn starch and corn nanostarch were different. The peaks of corn nanostarch at 15°, 17°, and 23° totally disappeared, and only a small peak at 18° was present. The crystalline region of nanostarch deteriorated, and its crystallinity was decreased.

2. The corn nanostarch can be dispersed with pigment together in dry powder form and it is good for the preparation of high solids content coating. The water retention capacity of nanostarch coating is better, and its adhesive strength is significantly better than the ordinary oxidized coating starch.

3. When 5 shares of ordinary oxidized coating starch and 4 shares of styrene butadiene latex were replaced by 6.5 shares nanostarch, the water retention capacity of nanostarch coating was increased by 64.0%, viscosity of the coating formulation was decreased by 11.0%, the IGT printing surface strength of lightweight coated paper by nanostarch coating was increased by 11.6%, and the glossiness of coated paper was increased by 7.2%. The nanostarch used as a coating adhesive have good prospects for application in papermaking.
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