

# Preparation of Ultrafine Starch Particle and its Application in Paper Coating

JinGang Liu<sup>1,2</sup>, JiaFu Wang<sup>1,2</sup>, YanFen Du<sup>1,2,\*</sup>, BiSong Wang<sup>1,2</sup>,  
HongCai Li<sup>1,2</sup>, YanQun Su<sup>1,2</sup>, JingHuan Chen<sup>1,2</sup>

1. China National Pulp and Paper Research Institute, Beijing, 100102, China

2. National Engineering Laboratory for Pulp and Paper, Beijing, 100102, China



JinGang Liu, senior engineer;  
E-mail: liujgang@126.com



\*Corresponding author:  
YanFen Du, PhD; research  
interests: theoretical research  
and product development of  
coated paper;  
E-mail: du\_yanfen@126.com.

**Abstract:** Despite its biodegradability, adequate cohesive strength and comparatively low cost, the use of cooked starch as a paper coating binder is limited due to its high viscosity and serious negative impact on the gloss. Starch-based bio-latex with size in the nanometer or sub-micrometer range has been developed recently to overcome these shortcomings. In this study, ultrafine starch particle (UFSP) was prepared by mechanical milling using a DYNO mill in combination with light chemical pretreatment. Model coating colors containing different dosages of UFSP were applied to base paper and the properties of the coated papers were evaluated. The results showed that the UFSP was disc-shaped with a median particle diameter of 167 nm. Water retention capacity of the coating colors was improved considerably with the addition of UFSP, i.e., the water retention value decreased by nearly 40% when styrene-butadiene latex was replaced by UFSP at a dosage of 3 pph (per hundred parts of pigment). The high shear rate viscosities of the coating colors containing no more than 2 pph of USFP were similar to that of the control coating color at shear strain rate higher than  $2000\text{ s}^{-1}$ . The properties and performances of the coated papers were comparable to the control coated paper with single synthesized latex binder. The gloss and the print gloss of paper samples with or without USFP were 59.7% and 58.2%, 79.0% and 78.8%, respectively. Surface strength of paper samples with or without USFP were 0.96 and 0.90 m/s, respectively, while the ink absorptivity values were 34% and 33%. This study demonstrates a promising approach to obtain sub-micrometer sized starch for paper coating.

**Keywords:** ultrafine starch particle; mechanical milling; coating color property; coated paper performance

---

Received: 10 November 2016; accepted: 1 December 2016.

## 1 Introduction

In view of the increased awareness towards environmental protection and reducing carbon footprint, the development of new adhesives based on biological materials and using different modification techniques to replace the traditional petroleum-based polymer latex, has gained much attention in the paper coating industry.

Application of cooked starch in paper coating color is restricted by its high viscosity as well as its negative impact on the gloss. It was reported that cold water-soluble coating starch prepared from pearl starch could be used for surface coating of art paper and the paper so produced was of high quality<sup>[1]</sup>. The cold water-soluble starch can be directly added in the coating color to partially replace the styrene-butadiene (SB) latex and reduce production costs.

The objective of this work is to develop a new kind of starch derivative, namely, ultrafine starch particle (UFSP), by mechanical milling and evaluate its application properties, including its effects on paper coating color and coated paper performance.

## 2 Experimental

### 2.1 Raw materials and equipment

Raw materials include phosphate ester modified starch, cross-linking agent, kaolin clay (with 96 wt% of particles finer than 2  $\mu\text{m}$ ), GCC (with 95 wt% of particles finer than 2  $\mu\text{m}$ ), carboxymethyl cellulose (CMC), SB latex, lubricant, water-resistant agent, defoaming agent, and base paper with a grammage of  $(70 \pm 1) \text{ g/m}^2$ .

Main equipment used in this work include HW60 mixer, HH-SJ constant temperature water bath, ECM-AP05 nanometer milling machine, 2000MU Malvern particle size analyzer, HC-2064 high speed centrifuge, CX41RF optical microscope, GFJ-0.4 high-speed dispersion machine, NDJ-5S low shearing viscometer, high shearing rotational rheometer, AA-GWR gravimetric water retention meter, KRK super calender, GM gloss meter, and paper thickness tester.

### 2.2 Preparation and characterization of UFSP

Crosslinking of starch<sup>[2-3]</sup>: phosphate ester modified starch was added to water to form a dispersion with a solid content of 40%, after which 3 wt% (based on the dry starch weight) anhydrous sodium carbonate and 5 wt% (based on the dry starch weight) crosslinking agent were added. The dispersion was mechanically stirred at 50°C in a constant temperature water bath to form a homogeneous emulsion. The pH value of the emulsion was adjusted to about 11.2 with 3% NaOH solution and the emulsion was continuously stirred for 6 h at 50°C. Cross-linked samples were obtained after neutralizing, rinsing with water, and air drying.

Milling of starch: the cross-linked starch samples were diluted with distilled water to a solid content of 10.0%~12.0%, and milled for different time periods using a nanometer milling machine. The milling beads were made of  $\text{ZrO}_2$  with an average diameter of about 0.4 mm. Starch particles were broken into smaller sized debris under intense collision and friction. Temperature was monitored during the milling process and maintained below 40°C. The size and shape changes of the starch particles during the milling process were measured using Malvern particle size analyzer and optical microscope. The target diameter of the UFSP was set to below 0.2  $\mu\text{m}$  (close to that of the polymer latex).

Morphology analysis of UFSP: the UFSP samples were diluted with water and dropped on a glass slide, and then were imaged with an optical microscope.

### 2.3 Preparation and testing of coating colors

Coating color formulations are listed in Table 1. Kaolin clay was pre-dispersed in water with 69% solid content, and 0.3 pph (per hundred parts of pigment) commercial dispersant was added. CMC was dissolved to form an 8 wt% solution in water. Model coating colors were prepared by mixing kaolin clay dispersion, GCC suspension, additives, and water. UFSP was added to the pigment mixture and stirred for 10 min before other additives such as CMC and SB latex were added. The coating colors were filtered with a 325 mesh sieve before use.

Table 1 Formulation of the coating colors

| Samples        | Kaolin<br>clay/pph | GCC<br>/pph | CMC<br>/pph | UFSP<br>/pph | SB latex<br>/pph | Solid<br>content/% |
|----------------|--------------------|-------------|-------------|--------------|------------------|--------------------|
| 1 <sup>#</sup> | 20                 | 80          | 0.4         | 0            | 12               | 60.5               |
| 2 <sup>#</sup> | 20                 | 80          | 0.4         | 1            | 11               | 60.5               |
| 3 <sup>#</sup> | 20                 | 80          | 0.4         | 2            | 10               | 60.5               |
| 4 <sup>#</sup> | 20                 | 80          | 0.4         | 3            | 9                | 60.5               |

\*Other additives were added at normal dosage.

The low shear viscosity of the coating color was measured at a speed of 60 r/min at 21 °C using a viscometer. The test parameters for water retention capacity were 120 s, 25 °C and 0.5 MPa. The high shear viscosity of the coating color was determined using a parallel plate unit with a diameter of 40 mm at 25 °C. The gap between the parallel plate and the sample holder was kept at 200  $\mu\text{m}$  and the shear rate range was 1~50 000  $\text{s}^{-1}$ . The water retention capacity was measured using an AA-GWR gravimetric water retention meter. This measurement is based on pressure filtration and involves the gravimetric determination of the dewatered water phase. A 4 mL of coating color was inserted into the cylindrical vessel above a polycarbonate membrane and an absorbent blotter paper. The cylinder was closed and coating color sample was held under an overpressure of 50 kPa. The pressure was released after 120 s, during which dewatering through the membrane occurred. The blotter paper was weighed before and after the measurement. The weight difference was multiplied by 1250  $\text{m}^{-2}$  (inverse of the cylinder cross-sectional area). It is clear that the greater the weight difference is, the poorer the water retention capacity is.

#### 2.4 Preparation and performance testing of the coated paper

The coating color was applied on the base paper using a wire wound rod and dried in a hot air oven at 105 °C for 2 min. The line pressure of the super calendar was set at 40 N/cm and the temperature was set at 50 °C. The coat weight was controlled to be about 16  $\text{g}/\text{m}^2$ .

The surface strength and optical properties of the coated paper such as density, gloss, ink absorbency, printing surface strength, print gloss, and printing surface roughness were measured according to the

corresponding international standard testing procedures.

### 3 Results and discussion

#### 3.1 Morphology and size of UFSP

Fig.1 shows the particle size variation of starch as a function of milling time. It could be seen that the size of the starch particles reduced rapidly from 15.978  $\mu\text{m}$  to 0.339  $\mu\text{m}$  in the first hour of milling, and thereafter decreased slowly. It was presumed that large starch particles could easily collide with the milling beads during the initial milling stage, and most of the starch particles were subjected to shear force. However, at later stages of milling, the starch particles were too small to have effective collisions with the milling beads, making milling difficult. Therefore, a long milling time and high energy input were necessary to obtain starch with smaller particle size. The median particle diameter of the UFSP was 0.167  $\mu\text{m}$ , close to nanoscale. Fig.2 shows the particle size distribution curve of starch after milling for 2 h. As can be seen, the particle size distribution is mainly in the size range 0.1~0.3  $\mu\text{m}$ , and about 50% (by volume) of the particles are smaller than 0.2  $\mu\text{m}$ .

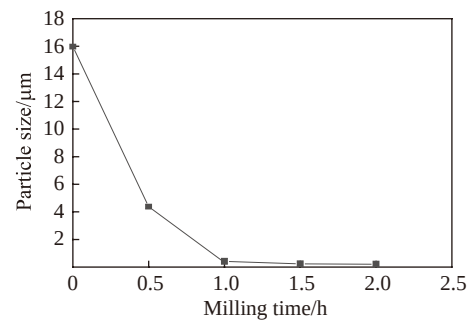


Fig. 1 Effect of milling time on starch particle size

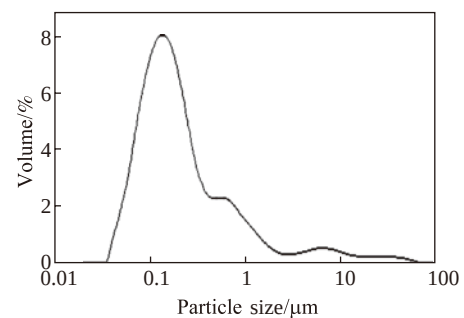


Fig. 2 Particle size distribution of starch milling for 2 h

Fig.3 shows the change in the morphology of the cross-linked starch particle during milling. It can be

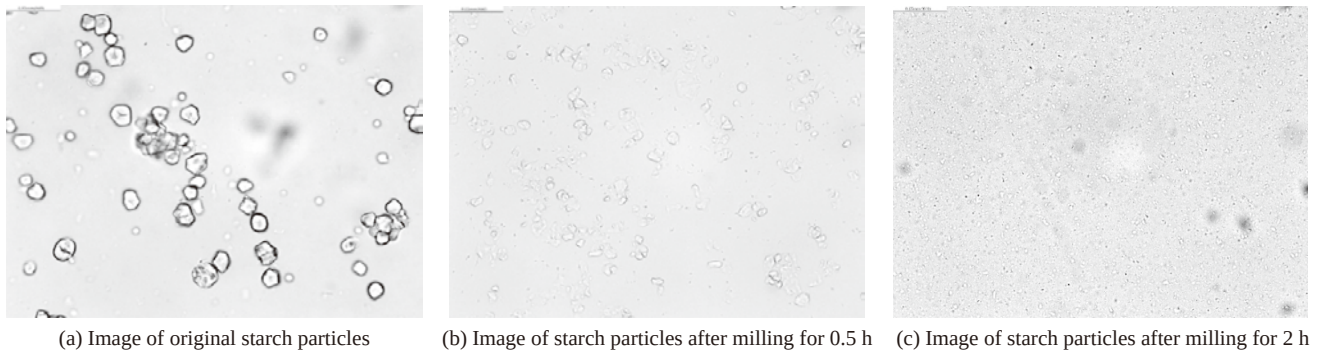


Fig. 3 Images of starch particles

seen that the original starch particle has a relatively large diameter and is spherical in shape. After milling for 0.5 h, the starch particle was broken, and a large number of fragments with irregular shape could be observed in the optical microscopy image. With continued milling, nearly all the large starch particles were crushed into nano-sized one, as shown in Fig.3(c), suggesting that almost all the crystalline region in starch was broken during the milling and a large quantity of molecular chain in the non-crystalline region were cut off.

### 3.2 Effect of UFSP on the properties of coating colors

The water retention values of coating colors are given in Fig.4. It was observed that water retention values decreased considerably with the addition of UFSP, and this decrease was proportional to the dosage of UFSP. For example, the control coating color (1<sup>#</sup> coating color) had the maximum water retention value of about 149 g/m<sup>2</sup>, i.e., the water retention capacity was the worst. The 2<sup>#</sup> coating color (1 pph UFSP was added to replace 1 pph SB latex) had a water retention value of 130 g/m<sup>2</sup>. The 4<sup>#</sup> coating color (3 pph UFSP was added to replace an equal amount of SB latex) had a water

retention value of 87 g/m<sup>2</sup>, and the water retention value decreased by nearly 40%. Therefore, the addition of UFSP improves the water retention of coating color.

The water retention capacity reflects the ability of coating color to maintain water when it is exposed to the base paper<sup>[4-6]</sup>. This property is influenced by the network structure formed by the coating components and the viscosity of the water phase. The UFSP in the coating color could undergo total swelling due to the presence of abundant exposed hydroxyl group on its surface that adsorbs water molecule and contribute to improving the water retention capacity.

Fig.5 illustrates the low shear viscosity of the coating colors with different dosages of UFSP. From Fig.5, it is seen that the low shear viscosity and rheological property of the 2<sup>#</sup> and 3<sup>#</sup> coating colors are similar to those of the 1<sup>#</sup> coating color. However, the coating color viscosity increased dramatically when 3 pph of SB latex was replaced by an equal amount of UFSP. This may be due to the abundant hydroxyl group on the starch particle surface and its strongly hydrophilic property originating from the low cross-

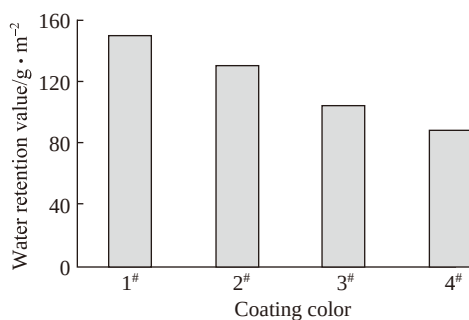


Fig. 4 Water retention values of coating colors containing different dosages of UFSP

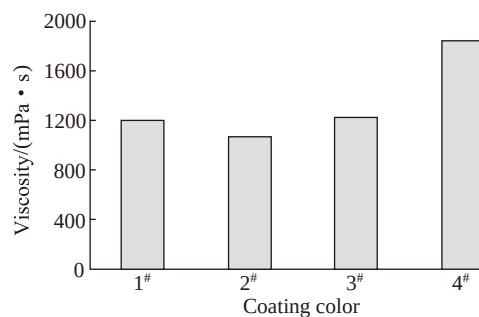


Fig. 5 Low shear viscosity of coating colors containing different dosages of UFSP

linking degree of the starch during the pretreatment of the raw material.

The viscosity-shear strain rate curves of the coating colors are illustrated in Fig.6. All the coating colors showed a reduction in viscosity with increase in the shear rate, especially in the range from  $1 \text{ s}^{-1}$  to  $100 \text{ s}^{-1}$ , indicating that the coating color had shear-thinning characteristic; however, at higher shear rate, all the samples had similar viscosities at the same shear rate<sup>[7-9]</sup>. High shear viscosity increased with the increase of UFSP dosage. The coating color with 1 pph UFSP (2<sup>#</sup>) had a relatively lower viscosity than the control coating color (1<sup>#</sup>). Coating color with 2 pph UFSP (3<sup>#</sup>) exhibited nearly the same rheology as the control coating color, while coating color with 3 pph UFSP (4<sup>#</sup>) displayed the highest viscosity in the whole range of shear rate used during testing. Consequently, the coating colors retained good rheological behavior when the dosage of UFSP used for replacement was not more than 2 pph.

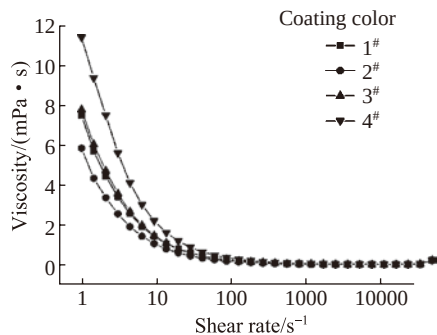


Fig. 6 High shear viscosity of coating colors containing different dosages of UFSP

### 3.3 Effect of UFSP on the coated paper performance

Fig.7 shows the gloss of paper coated with different coating colors. It could be seen that the coated paper gloss decreased gradually with the addition of UFSP. The control coated paper had the highest gloss of 59.7%, while the gloss of the coated papers containing 1 pph, 2 pph and 3 pph of UFSP decreased to 58.2%, 57.5% and 55.8%, respectively. It is widely regarded that the shrinkage of the water-soluble starch binder during drying process leads to rougher coating surface, which can lower the values of critical optical properties

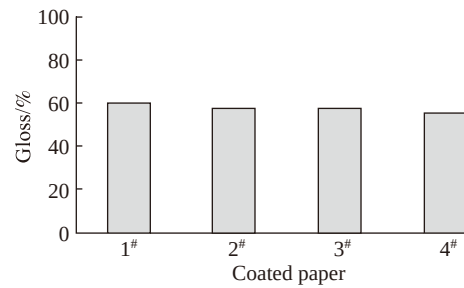


Fig. 7 Coated paper gloss

such as gloss. The UFSP has a much smaller shrinkage than traditional cooked starch during coating drying due to its submicron particle size and relatively high cross-linking degree. However, the hydrophilic hydroxyl groups on the surface can lose combined water molecule during drying and shrink from their aqueous swollen state. This may slightly reduce the coated paper gloss.

The print gloss of the coated papers is illustrated in Fig.8. Compared with the control sample, the print gloss did not change significantly with the addition of 1 pph or 2 pph UFSP, and the values were in the range of 78%~79%. However, the print gloss showed a marked reduction when 3 pph of SB latex in the coating color was substituted with UFSP, suggesting that a large dosage of UFSP had a negative effect on the paper print gloss. Print gloss is affected by factors such as paper gloss and smoothness, i.e., a high paper gloss can improve the surface reflectivity of the ink film, leading to a high print gloss. For coated papers with UFSP less than 2 pph, the print gloss values were nearly equal to those of the control coated paper, and remained high.

Fig.9 illustrates the printing surface strength of the coated papers. It is acknowledged that coating surface strength is mainly determined by the type of adhesive and its dosage. The petroleum-based latex's binding

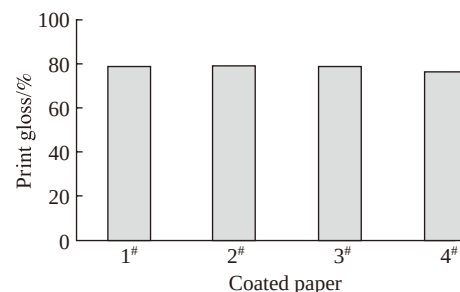


Fig. 8 Print gloss of coated paper

strength is usually higher than traditional starch for the same dosage<sup>[10-11]</sup>. As can be seen in Fig.9, coated paper with 1 pph or 2 pph UFSP showed a marginal decrease in printing surface strength compared to that of (0.96 m/s) the control coated paper. It was presumed that UFSP had better binding ability in coating color than cooked starch due to the large specific surface area of the nano-sized or submicron-sized particles after mechanical milling; however, the intrinsic binding force of UFSP was weaker than that of SB latex.

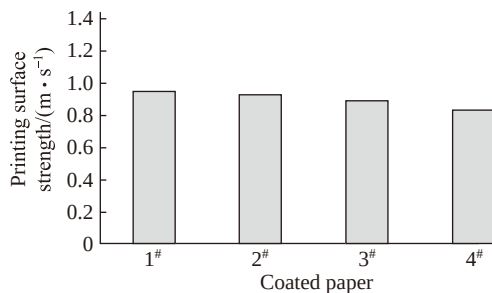


Fig. 9 Printing surface strength of coated paper

The ink absorbency values of the various coated papers are shown in Fig.10. Coated paper with 1 pph or 2 pph of UFSP had the same ink absorbency of 33%, which was only 1% lower than that of the control coated paper. With increasing UFSP addition, ink absorbency values decreased gradually indicating that UFSP had only a slight effect on the ink absorbency of coated papers.

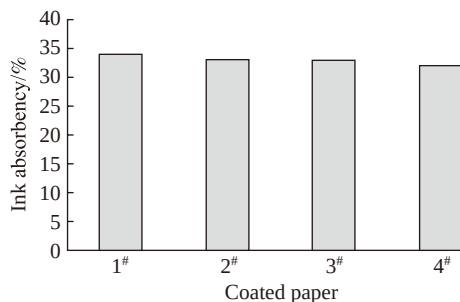


Fig. 10 Ink absorbency of coated paper

#### 4 Conclusions

Ultrafine starch particle (UFSP) was prepared by mechanical milling combined with light chemical pretreatment and utilized in coating color. The median diameter of the UFSP was 167 nm. The addition of UFSP to coating color could improve the water retention

capacity considerably, e.g., by improving nearly 40% if 3 pph styrene-butadiene latex was substituted by UFSP. Coating colors with no more than 2 pph UFSP showed similar rheological properties to the control coating color. Coated paper properties such as gloss, print gloss, surface strength, and ink absorbency were comparable to those of the control coated paper when the amount of UFSP substituted was less than 2 pph. An intense cross-linking of starch before and during the mechanical milling process is recommended to improve the performance of UFSP in paper coating.

#### Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Grant No. 51403239).

#### References

- [1] Wang B S, Liu J G, Hu Y, et al. Application of cold water soluble starch in the top coating of art paper[J]. Paper and Paper Making, 2013, 32(9): 50-54.
- [2] Zhang Y S. Manual for the production and applications of modified starch[M]. Beijing: China Light Industry Press, 1999.
- [3] Zhang B S, Xu L H, Gao D W, et al. The non-crystallization characteristics of high cross-linked corn starch[J]. Journal of Wuxi University of Light Industry, 2001, 20(3): 233-237.
- [4] Lehtinen E. Paper dye coating and surface sizing[M]. Beijing: China Light Industry Press, 2005.
- [5] Liu J G, Peng J J, Wang B S, et al. Water retention performance of CMC coating[J]. Shanghai Paper Making, 2002, 33(2): 35-39.
- [6] Sandas S E, Salminen P J, Eklund D E. Measuring the water retention of coating color[J]. TAPPI, 1989, 72(12): 207.
- [7] Klass C P. New nanoparticle latex offers natural advantage[J]. Paper 360°, 2007(1): 30-31.
- [8] Du Y F, Liu J G, Wang B S, et al. Study of the rheological properties of starch based biological latex for paper coating[J]. Paper and Paper Making, 2015, 34(1): 40-44.
- [9] Shin J Y, Jones N, Lee D I, et al. Rheological properties of starch latex dispersions and starch latex-containing coating colors[C]//TAPPI Paper Conference. New Orleans, USA, 2012.
- [10] Zhang H. Introduction of the relationship between glossiness of coated paper and quality of the print[J]. Printing Quality and Standardization, 2008(9): 67-69.
- [11] Wang X Q, Zhou X F. Replacing parts of the latex with starch on the properties of coated paper[J]. Journal of Nanjing Forestry University, 2011, 35(1): 79-82. PBM