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Oxidized Acetate Starch as a New Surface Sizing Agent

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ABSTRACT

Oxidized acetate starch was synthesized from corn oxidized starch and vinyl acetate. The sizing concentration and degree of substitution of modified starch on surface strength, smoothness and water resistance of the paper have been studied. The results showed that the surface strength, smoothness and other properties of paper sized by oxidized acetate starch is better than that of oxidized starch. When the degree of substitution of modified starch is from 0.04 to 0.14, the properties of paper sized by oxidized acetate starch have been improved more effectively.

Keywords: *oxidized starch; oxidized acetate starch; papermaking; surface sizing agent; surfac estrength;*

1. Introduction

One of the most important properties of printing and writing papers is their resistance to penetration by aqueous liquids. Sizing agents are often added to paper to decrease the rate of liquid penetration into its capillary structures. In general sizing agents are classified as: (1) internal sizing agents which are added to the pulp slurry and (2) surface sizing agents which are applied to the surface of the paper after the paper sheet is formed.[1] Both sizing agents can increase the water-repellency of paper and furthermore, surface sizing agents can reduce the number and size of pores as well as paper roughness, and modify paper surface energy [2].

Today, chemical modifications of the paper surface for improving printing quality are a common practice in papermaking, and as a consequence, there is a large increase in the production of new chemicals that meet specific end-use paper requirements [3] Modified starch has long been used in wet end applications because of its relatively low price and its ability to improve paper strength [4]. The effect of starch on the paper properties was widely studied with respect to wet end starch. The main role of surface size is to promote surface properties, e.g.strengthen the surface and make paper get good printing performance meanwhile; it can improve paper's physical intensity [5]. Traditional, the surface sizing starch used in paper-making industry was mainly the oxidized starch and they once were used widely for surface sizing and coating because the oxidized starch pastes are excellent film formers and strong binders and are resistant to congealing. But the oxidized starch

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solution is easily to permeate and the glue membrane formed in the paper is not well-distributed [6]. The acetate starches are, therefore, coating binders and effective surface sizes because the acetate starch is considered no congealing, lower viscosity and highly resistant to permeability. The acetate starch with low degree of substitution used for surface sizing can improve paper's printing adaptability, wear ability and water resistance ofthe paper. In our work, the objective was to improve the corn oxidized starch by the addition of acetyl groups onto it to get oxidized acetate starch, to study the amount of the surface sizing starch to sheets and to observe the resulting effect of oxidized acetate starch on the properties of the paper sheet.

2. MATERIALS AND EXPERIMENTAL

2.1 Materials

All the chemicals were of reagent and used without further purification. Corn oxidized starch was obtained from Shaanxi Qinyang biologic product Company of China, the viscosity of this starch was 2.8 mPa·s (Brookfield 100 rpm, 95°C) at a concentration of 5%. Vinyl acetate was provided by Shanghai Shanpu Company.

Wood free base paper sheets produced on a fine paper machine without surface sizing and with a basis weight of 52 g/m^2 were used for the study. The properties of the base paper are presented in Table 1.

Table 1 properties of base paper

properties	value
Surface strength, m/s	0
Printing smoothness, s	30.8
MD Folding endurance, time	68
CD folding endurance, time	9
MD tensile index, N·m/g	84.66
CD tensile index, N·m/g	28.56

2.2 Preparation of oxidized acetate starch

In a glass vessel, 50 g corn oxidized starch was slurried in 110 g water with mechanical stirring, and then 10% aqueous sodium hydroxide solution was added to the starch slurry to adjust system pH value to 9.0 with vigorous agitation. After the addition of sodium hydroxide, 4 g vinyl acetate was slowly added. The reaction vessel was closed and the temperature was raised to 30℃ with constant stirring for 60 minutes. The resulting starch suspension was cooled to room temperature and neutralized to pH 7.0 with dilute sulphuric acid. The oxidized acetate starch product was dewatered on a suction filter. The starch filter cake was then reslurried in 3 liters of a 20/80 by volume ethanol/water mixture and filtered (when higher substituted starches were synthesized, they were reslurried in an ethanol/water mixture with a higher amount of alcohol to prevent the gelation which could stop the filtration).This process was repeated until all of the unreacted monomer and salt byproducts were removed. The starch filter cake was crumbled and dried at room temperature to the moisture of 9 to 12%. The dried oxidized acetate starch was then ground in mortar and stored in a plastic bag.

2.3 Determination of degree of substitution [7]

The sample of oxidized acetate starch (5.0000 g) was slurried in distilled water 50 g in the iodine flask, then adding 3 drops of phenolphthalein indicator, the slurry was titrated with the solution of 0.1000 mol/L sodium hydroxide until little red appeared. And then the titrated slurry was saponify with the solution of 25 mL 0.5000 mol/L sodium hydroxide. In the end, the saponified slurry was again titrated by the solution of 0.5000 mol/L hydrochloric acid until the red of the slurry disappeared, i. e. titrate terminal point. The volume of 0.5000 mol/LHCl consumed for this stage was noted as V1.

The oxidized starch was determined in the same

way as the oxidized acetate starch above. The volume of 0.5000 mol/L hydrochloric acid solution consumed for titrating was noted as V2.

The content of acetyl (ω) of oxidized acetate starch was calculated as following:

$$\omega(\%) = \frac{(V_2 - V_1)c \times 0.043}{m} \times 100\%$$

where

V_2 = volume of oxidizing the starch and consuming the hydrochloric acid, mL

V_1 = thevolumeofconsumingthehydrochloricacid,mL

C = concentration of the hydrochloric acid solution, mol/L

m = quantity of sample, g.

Then degree of substitution (DS) was calculated as:

$$DS = \frac{162 \times \omega}{4300 - 42 \times \omega}$$

where

ω = acetyl content

162 = the relative molecule mass of each glucose unit of starch.

2.4 Surface Sizing of the Sheets

The surface size was applied with a laboratory bar coater (K-Control Coater Model 101, RK Print-Coat Instruments Ltd., UK). All surface-sized sheets were dryed and calendered in a soft nip laboratory calendar (line load 42.9 kN/m, roll temperature 105℃,) before further analysis

2.5 Measurements

Surface strength, front print, breaking length, and folding endurance were measured according to American Tappi Test Methods T475 “Surface Strength of Paper and Paperboard,” T479 “Front Print of Paper and Paperboard,” T404 “Breaking Length of Paper,” T423 “Folding Endurance of Paper and Paperboard,” respectively.

2.6 Characterization

FTIR Measurements Chemical bonding information on carbonyl, hydroxyl, and other functional groups were obtained by use of Fourier infrared spectroscopy (FTIR, VECTOR-22, Brook Company). Each spectrum was collected after 32 scans at a resolution of 1cm^{-1}.

SEM Measurements The morphological of the aggregates of the starch were studied by KYKY1000B scanning electron microscope (SEM) of Beijing, China.SEMwasalsousedtoobservethechangeofthepapersurface after surface sizing.

X-ray diffraction measurements X-ray diffraction experiments were performed for the starch dried naturally in room temperature by D/max 2000pc X-ray diffractomer. The X-ray source was Ni-filtered Cu Kα radiation (40kV, 100mA). Starch samples were scanned from 10 to 55°2θ at a scanning rate of 5°2θ /min.

3 RESULTS AND DISCUSSION

3.1 Characterization of oxidized acetate starch structure

To determine whether an acetate group was introduced into the oxidized starch, we used FTIR to characterize the starch. Figure 1 shows IR spectrogram of oxidized acetate starch and oxidized starch. The absorption regions observed around 3500 cm^{-1} was due to the

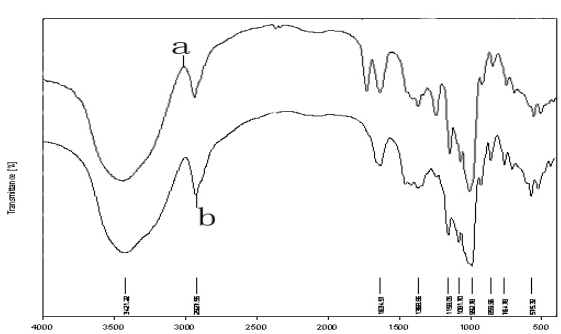


Fig 1. 1FT-IRspectraofoxidized starch (a) and oxidized starch acetate (b)

stretching modes of -OH, and the peak at 1735 cm^{-1}reflects the bending modes of carbonyl. Compare curve a with b, we can see that the absorption region at 1376 cm^{-1} and 1252 cm^{-1} were the characteristic peaks of acetic ester.

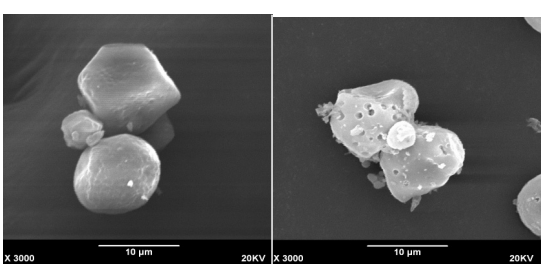
3.2 SEM image of the starch

In order to observe morphology of the aggregates of the starch, starch samples were analyzed by scanning electron microscope. Figure 2b shows SEM image for oxidized acetate starch. For comparison, oxidized starch was also observed by SEM in the study (Fig.2a).

Comparing the figures, we can see that the shape of oxidized starch was relatively regulate, the surface has only a bit hair line crack. However, the phenomenon on the oxidized acetate starch was on the contrary, its regulation was relatively bad, the particle surface has many obvious broken eyelets, and it has sheet particles. The reason was that esterification made the starch particle size small and increased the number of the starch particles. It was evident that the morphology of the aggregates of oxidized starch and oxidized acetate starch were completely different, and the process of esterification occurred not only on the surface of starch, but also inside the starch.

3.3 X-ray diffraction

X-ray diffraction patterns of oxidized acetate starch and oxidized starch were shown in Fig.3. As is known to all, natural corn starch is a typical A-type



(a) (b)

Fig. 2 SEM image of (a) oxidized starch and (b) oxidized acetate starch.

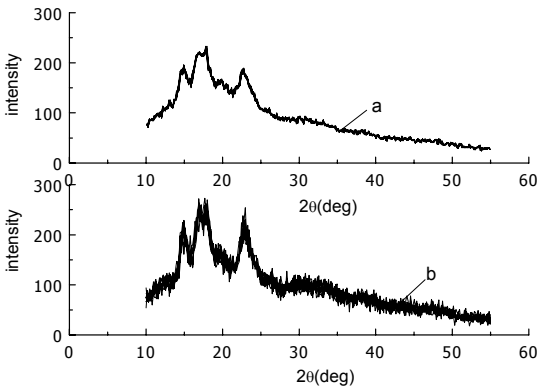


Fig.3 Measured X-ray intensity curves of (a) oxidized acetate starch and (b) oxidized starch

pattern, with typical peaks at 2q of 15.00°, 17.06°, 17.90°, 22.82° and so on. Here oxidized acetate starch and oxidized starch showed A-type pattern, with diffraction peaks at around 2q of 15°、17° and 22°. Curves a and Curves a b were consist of pinnacle diffraction character and dispersion diffraction character, which showed that oxidized starch and oxidized acetate starch were consist of crystallization field and amorphous region. The shape and width of diffraction profile were determined by mass fraction and size of crystal. Comparing curves a and b, we can see that after esterification, diffraction peak intensities decreased and peak width increased (Fig.3), crystalline type and location of characteristic diffraction peak hardly have any change. That is because esterification happened mainly in amorphism.

3.4 Effects of modified starch solution concentration on paper properties

The common use of sizing agent solution concentration was 3~6% [5]. We made one set of paper sheets using oxidized acetate starch, and another set of paper sheets using oxidized starch for comparison. Figures 4-9 show the effects of oxidized acetate starch on paper physical properties. Table 2 shows effects of oxidized starch on paper properties. Fig.4 illustrates the dependency of paper surface strength on different

Tab.2. Effects of oxidized starch on paper properties

paper properties	Sizing agent solution content, %	
	3	6
Surface strength, m/s	0.37	0.51
Front smoothness, s	31.2	37.6
CD folding endurance, time	9	12
MD folding endurance, time	89	104
CD tensile index, N· m/g	30.6	34.68
MD tensile index, N· m/g	70.38	75.48

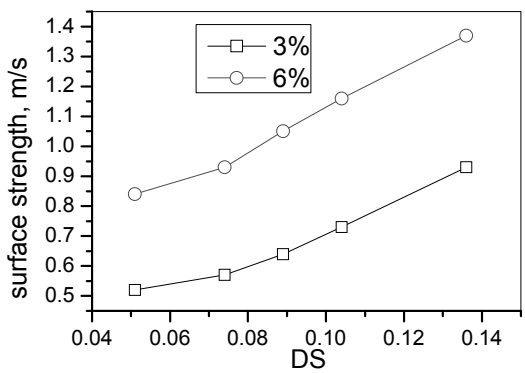


Fig.4. Effect of sizing concentration and degree of substitution of oxidized acetate starch on surface strength

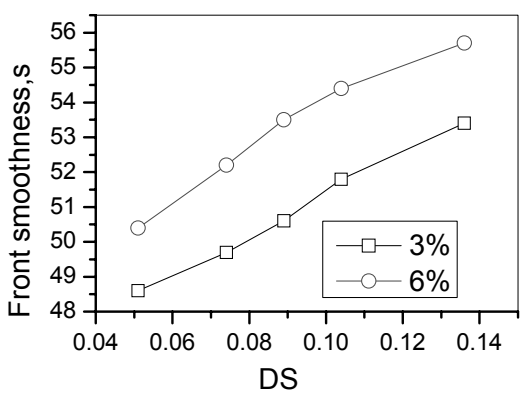


Fig.5. Effect of sizing concentration and degree of substitution of oxidized acetate starch on front smoothness

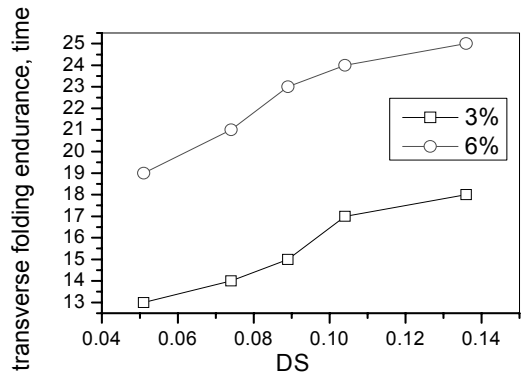


Fig.6. Effect of sizing concentration and degree of substitution of oxidized acetate starch on CD folding endurance

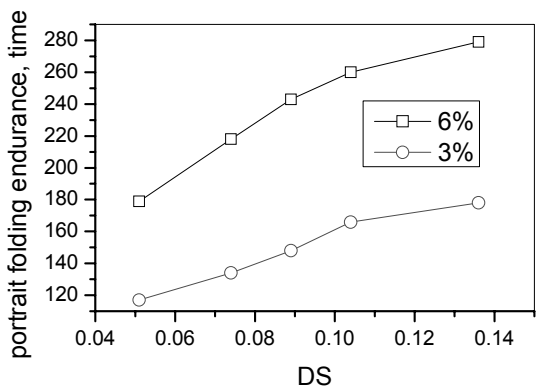


Fig.7. Effect of sizing concentration and degree of substitution of oxidized acetate starch on MD folding endurance

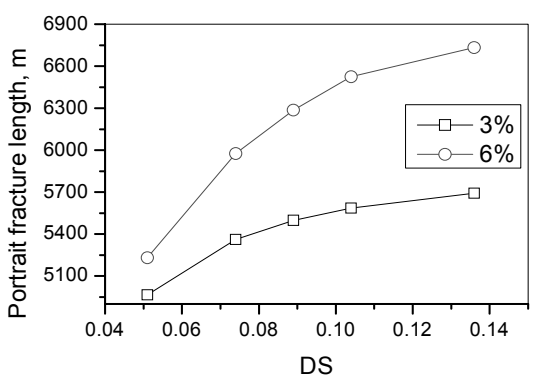


Fig.8. Effect of sizing concentration and degree of substitution of oxidized acetate starch on MD breaking strength

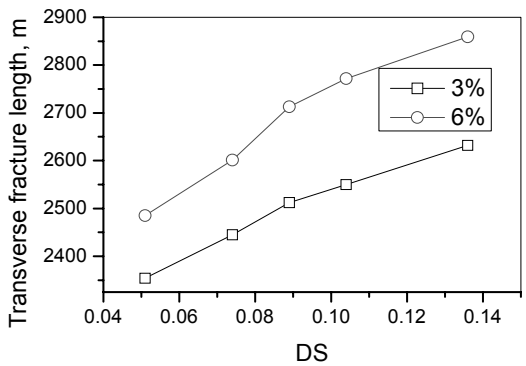
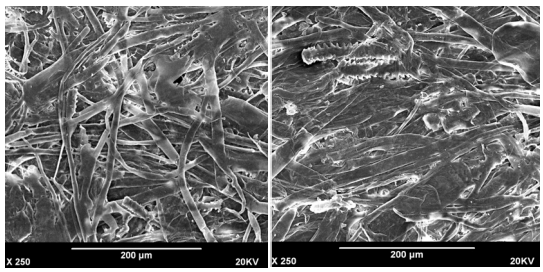


Fig.9. Effect of sizing concentration and degree of substitution of oxidized acetate starch on CD breaking length

degree of substitution of oxidized acetate starch. Surface strength of paper sizing was expressed by broom-finish velocity. We can see that surface strength is improved by surface sizing. Oxidized acetate starch improved better than oxidized starch, with 3% or 6% oxidized acetate solution at DS 0.051, they both had better surface strength than oxidized starch. Surface strength was improved with the increase of starch degree of substitution, and improved the content of surface sizing solution and DS of oxidized acetate starch were of good advantage to paper surface strength. Fig.5 shows the effect of sizing agent content and degree of substitution of modified starch on surface smoothness of the paper. As oxidized acetate starch has better film forming property than oxidized starch, sizing agent formed a continuous film on paper surface after surface sizing, which is good to improve paper smoothness. So oxidized acetate starch is superior to oxidized starch in improving paper smoothness. Figure 6-9 show effects of modified starch on folding endurance and breaking length. As sizing agent filtered in the paper, the combination of fiber increased, so the folding endurance and breaking length of paper were improved. The main reason was that through surface sizing, the sizing agent was filtered in the paper and the strength of was improved.



(a) (b)

Fig.10 Surface image for the paper surface sized with (a) oxidized starch and (b) oxidized acetate starch.

3.5 SEM observation of surface sizing sheets

In order to observe the change of the paper with different starches after surface sizing, we obtained SEM image to investigate the paper samples. Figure 10a and 10b show the image for the paper sized with oxidized starch and oxidized acetate starch, respectively. From comparing, we can see that the paper surface fiber interphase become more ambiguity after surface sizing with oxidized acetate starch, and the smoothness of paper surface was improved, this maybe was that the film formed on the fiber surface of oxidized acetate starch was better than oxidized starch.

4. CONCLUSION

This work describes a simple, efficient method of preparing oxidized acetate starch. The paper sized by oxidized acetate starch is better than that of oxidized starch in properties of the Surface strength, smoothness and others. When the degree of substitution of modified starch is from 0.04 to 0.14, the properties of paper sized by oxidized acetate starch have been improved more effectively. Oxidized acetate starch can combine with fiber easily, so it has better surface sizing effect than oxidized starch.

References

1. Yasuyukl Ishida, Hajime Ohtani, and Shin Tsuge etc., Styrene Copolymer Sizing Agents in Paper by Pyrolysis Gas Chromatography, Anal. Chem. 66(9):1444-1447(1994).
2. Koskela, J P.; Hormi, O. E. O., Improving the print-ability of paper with long-chain quaternaries, Appita J. 56 (4): 296 -300 (2003).
3. Isabel M. T. Moutinho, Paulo J. T. Ferreira, and Margarida L. Figueiredo., Impact of Surface Sizing on Inkjet Printing Quality, Ind. Eng. Chem. Res.46(19): 6183-6188 (2007).
4. Brouwer, Piet H.,Anionic Wet-end Starch: A Wealth of Possibilities to Improve Paper Quality and/or Reduce Paper Costs , Tappi Technology J.267-292(2003).
5. Lee, Hak Lae., Surface sizing with cationic starch: Its effect on paper quality and papermaking process, Tappi Journal, 1(1)34-40(2002).
6. Bramel, G. F. (1986): “Modified starches for surface sizing and coating of paper”, Tappi, J 54-56(1986).
7. Dill, Dale R, (1985): “Surface sizing utility through understanding”, TAPPI Notes, J15-20(1985)