

PREPARATION OF DIALDEHYDE CHITOSAN/CROSSLINKED AMINO STARCH AND ITS EFFECT ON PAPER STRENGTH

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The dialdehyde chitosan/crosslinked amino starch (DCS/CAS) composite was prepared by the reaction of DCS and CAS. The structure of DCS/CAS and the effects of DCS/CAS on paper strength were investigated. It was demonstrated by FTIR and UV-Vis spectral analyses that DCS was partly grafted onto the main chain of CAS, leading to a Schiff base. The thermal property of DCS/CAS was analysed by TG and DSC, and the thermal decomposition temperature of 200 °C can meet the requirements of the papermaking industry. In addition, the strength of paper sheets can be greatly increased by adding the DCS/CAS composite to pulp, compared with adding DCS or CAS. Specifically, the tensile index and burst index of paper sheets can be increased by 31% and 35%, respectively, if the reaction occurs at a pH value of 6 and a temperature of 70 °C.

Keywords: dialdehyde chitosan, crosslinked amino starch, Schiff base, paper sheet, paper strength

INTRODUCTION

Chitosan is a non-toxic, harmless and environmentally friendly natural alkaline polymer. With its excellent biodegradability, biocompatibility and film-forming properties, chitosan has been widely used in the papermaking industry, for example, in wastewater treatment, barrier coating and antibacterial applications.¹⁻⁴ In addition, due to irreversible electrostatic adsorption between positively charged chitosan and negatively charged fibre in water, chitosan was reported as a strengthening agent.⁵⁻⁸ However, compared to other paper additives, chitosan has poor solubility in water, which has greatly limited its research and application. Therefore, the modification of chitosan and the development of composites of chitosan and other additives are the current trends in the papermaking industry.

Periodate oxidation is a common way to oxidize polysaccharides. It is known that periodate

oxidation cleaves the C2-C3 bond of chitosan to introduce dialdehyde groups, while the glycosidic bond is broken, leading to a lower polymerization degree. The product called dialdehyde chitosan (DCS) was prepared by Lv *et al.*⁹ and Wang *et al.*,¹⁰ using the experimental method of Vold.¹¹ DCS provides better solubility than unmodified chitosan.^{11,12} Furthermore, the introduced dialdehyde groups can react with amino groups to obtain a Schiff base. He *et al.*¹³ modified cotton fabrics with a DCS solution containing ethylenediamine. The results showed that the formation of a Schiff base between the aldehyde groups of DCS and the amino groups of ethylenediamine contributed to the formation of a hydrogel, and then the mechanical properties of cotton fabric were increased. Jia *et al.*¹⁴ synthesized a water-soluble chitosan derivative with low biological toxicity by the grafting

reaction of DCS and the diamine compound. In addition, DCS can also react with spermine,¹⁵ polyethyleneimine¹⁶⁻¹⁹ and thionine²⁰ to form a Schiff base.

Starch has become one of the most commonly used additives in paper pulp as it improves the mechanical properties of paper sheets and enhances their surface properties.²¹⁻²⁵ Amino starch (AS) is a starch derivative formed by introducing an amino group to the structure of starch. The use of AS as a new polymeric additive for fixed facilitated transport of carbon dioxide through an asymmetric polyethersulfone (PES) membrane has been reported previously.²⁶ AS modified with biogenic amine has been also investigated for collecting microalgae.²⁷ In addition, crosslinked amino starch (CAS) was prepared by crosslinking with epichlorohydrin (ECH), followed by the reaction of crosslinked starch and ethylenediamine.²⁸ Owing to its high molecular weight and good thermal stability, CAS has been widely used for the absorption of metal ions and dyes. Furthermore, CAS with its structure of reactive amino groups could greatly improve the physical bond between the fibres by electrostatic adsorption and then increase paper strength.^{29,30}

In recent years, many researches on developing composites of chitosan and starch have reported that such a product would strengthen the paper sheet,⁵ protect the paper surface^{23,31} and improve its mechanical properties.^{32,33} Several studies were focused on the composite of dialdehyde starch and chitosan, for applications in different fields.³⁴⁻³⁷ However, related research on a composite of DCS and CAS has not been reported.

In this work, a DCS/CAS composite, with the structure of a Schiff base, has been obtained by graft copolymerization between DCS and CAS. The crosslinked composite with dual characteristics of DCS and CAS could improve the mechanical properties of paper.

EXPERIMENTAL

Materials and equipment

Needle-leaf bleached kraft pulp (NBKP) with a beating degree of 58 °SR was used as raw material to make paper sheets. The pulp, as well as corn starch with a viscosity of 13 mPa·s (1 wt%, 25 °C), chitosan (deacetylation degree of 84%, Mw = 200 kDa), sodium periodate, ethylenediamine (EDA), epichlorohydrin (ECH) and other reagents, were purchased from

Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

A PFI Beater (PL11), a Handsheet Former (ZQJ1-B-II), and the analysis equipment were from Xianyang Taist Equipment Co., Ltd. Also, a thermogravimetric (TG) analyzer (TA Q600, Waters, USA), a differential scanning calorimeter (DSC, Q200, Waters, USA), a Fourier transform infrared spectrometer (FTIR; Is10, Nicolet, USA), an elemental analyzer (Elementar VARIOEL III, Germany) and a UV-visible absorption spectrometer (Cary 100, Varian, USA) were used to investigate the properties and performance of the DCS/CAS composite.

Experimental method

Preparation of DCS/CAS

Preparation method of DCS: chitosan was dissolved in an acetic acid aqueous solution with a pH of 3 under stirring for 5 h to achieve a uniform solution. An aqueous solution of sodium periodate was slowly added to it ($n(\text{IO}_4^-)/n(\text{chitosan}) = 1/1$) at 4 °C under nitrogen atmosphere and in the dark. The reaction was terminated after 24 h by adding ethylene glycol (10 ml), then followed by precipitation with ethanol, dialysis (MWCO of 3,000) and freeze-drying.¹¹

Preparation method of CAS: corn starch and ECH were magnetically stirred in a dilute alkaline solution for 12 h, the crosslinked starch was oxidized by a NaIO_4 solution for 4 h with a pH value of 3 at 40 °C. Oxidized starch (OS) was obtained after washing and vacuum drying at 70 °C. Then, EDA was added to the OS with a molar ratio of $n(\text{EDA})/n(\text{OS}) = 3/1$ in a 70% ethanol aqueous solution. The reaction solution with a pH value of 6 was magnetically stirred for 2 h at 40 °C, then the product was washed, dried and ground to obtain the CAS.

Preparation method of DCS/CAS: DCS/CAS was prepared by adding CAS to the DCS solution with a molar ratio of $n(\text{DCS})/n(\text{CAS}) = 1/1$ at 70 °C for 4 h. The obtained blue solution was precipitated by ethanol and lyophilized to get the DCS/CAS composite. The synthesis route of DCS/CAS is shown in Figure 1.

Test methods of DCS/CAS

The C, N and H content of DCS, CAS and DCS/CAS was measured by an elemental analyzer after the samples were freeze-dried for 24 h.

FT-IR spectra of the samples were taken by the KBr pellet technique in the scanning range of 400-4000 cm^{-1} .

The samples were dissolved in acetic acid of pH 6 and filtrated by a G3 sand core funnel. The UV-Vis absorbance spectra of the supernatant liquor were investigated at room temperature in the wavelength range of 210-360 nm.

The thermal stability of the samples was

investigated by TG analysis: the samples were heated from 40 °C to 500 °C with a heating rate of 30 °C/min. For the DSC tests, the samples were equilibrated at 25

°C, and heated to 400 °C with a heating rate of 10 °C/min.

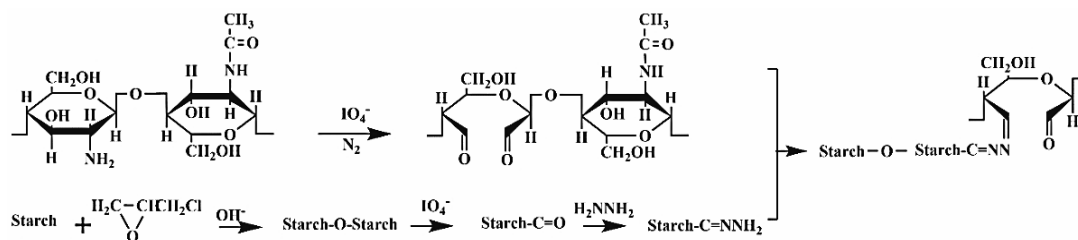


Figure 1: Synthesis route of DCS/CAS

Table 1
Elemental analysis

	N (%)	C (%)	H (%)
CAS	0.222	39.71	7.311
DCS	4.581	33.05	6.217
DCS/CAS	2.337	37.20	6.827

Mechanical properties of paper sheets

The effects of molar ratio, reaction temperature and reaction time of DCS/CAS on the mechanical properties of paper sheets were studied. A paper substrate was prepared with a basis weight of 60 g/m² according to ISO 5269-1-79. The dosage of additive was 1% (to oven-dry pulp). The tensile index and burst index of the paper were measured according to TAPPI T494 and TAPPI T403.

RESULTS AND DISCUSSION

Elemental analysis

The C, N and H content of CAS, DCS and DCS/CAS is shown in Table 1. The substitution degree of CAS was calculated to be 2.56% by the formula:

$$DS = \frac{162 \cdot N\%}{1400 - M \cdot N\%} \quad (1)$$

where N% is the nitrogen content of AS and M is the molecular weight of substituent groups.³⁸

The oxidation degree of DCS was calculated to be 14.76% according to the formula:

$$\frac{N}{C} = \frac{F_A + (1 - F_A) \cdot (1 - F_{ox})}{2F_A + 6} \quad (2)$$

where F_A is the acetyl group content of chitosan (16%) and F_{ox} is the oxidation degree of DCS.¹¹

FTIR analysis

The FTIR spectra of DCS, DCS/CAS and CAS

are shown in Figure 2. In the spectrum of DCS, a broad peak is observed at 3380 cm⁻¹, which can be attributed to the stretching vibration of C-H and N-H. A double peak appears at 2880 cm⁻¹ and 2930 cm⁻¹ – it may be caused by the Fermi resonance of ν C-H and δ C-H, which is considered as the characteristic absorption of aldehyde groups.⁹ Moreover, a strong peak of stretching vibration at 1630 cm⁻¹ is attributed to carbonyl groups and indicates the formation of DCS with more aldehyde groups after the oxidation of chitosan.

In the spectrum of CAS, the associate absorption peak at 3350 cm⁻¹ is assigned to C-H and N-H, and a very sharp peak at 1730 cm⁻¹ belongs to the absorption peak of C=O and C=N. In addition, CAS presents double absorption peaks of aldehyde groups at 2940 cm⁻¹ and 2860 cm⁻¹, due to the process of periodate oxidation.

Similarly with the spectra of DCS and CAS, in that of DCS/CAS, there is an absorption peak at 3430 cm⁻¹. However, unlike them, here only a single peak appears at 2920 cm⁻¹, belonging to the stretching vibration of -CH₃, and the characteristic absorption peak of aldehyde groups disappears. Furthermore, the peak at 1630 cm⁻¹ caused by C=O and C=N is reduced significantly. These differences indicate that the aldehyde groups of DCS reacted with the amino groups of CAS to generate a Schiff base.

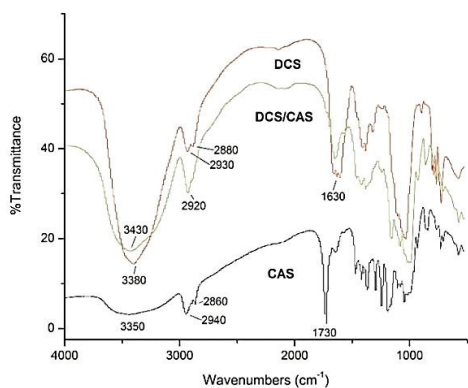


Figure 2: FTIR spectra of DCS, CAS and DCS/CAS

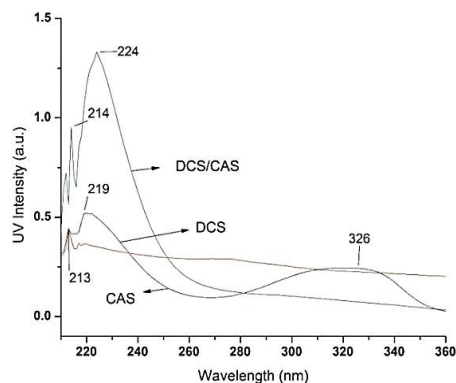


Figure 3: UV-Vis spectra of DCS, CAS and DCS/CAS

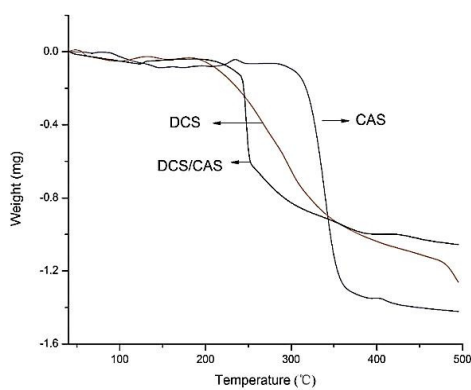


Figure 4: TGA curves of DCS, CAS and DCS/CAS

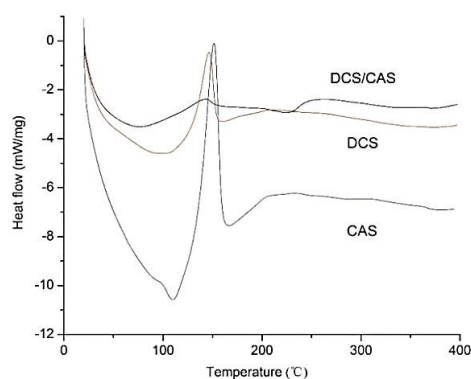


Figure 5: DSC curves of DCS, CAS and DCS/CAS

UV-Vis spectroscopy

The colour of the DCS/CAS solution gradually changed from colourless to blue purple after adding CAS to the DCS solution. However, it turned to pale purple and finally became colourless again with the increase in temperature. After freeze-drying, the product of DCS/CAS was blue purple, and this was caused by the formation of a Schiff base between the dialdehyde groups of DCS and the amino groups of CAS, the azoic compound provided with the colouring property was finally obtained. In addition, the colour of the solution and product could be changed with the increase in temperature because of the low stability of the azoic structure.

The absorbance curves of the three polymers were tested and the results are shown in Figure 3. It can be observed that the peak at 326 nm corresponds to the carbonyl group of DCS. Compared to DCS and CAS, in the case of DCS/CAS, the peak at 224 nm was strengthened and the red-shift of the maximum absorption wavelength indicated the presence of a K-band due to the two conjugated unsaturated bonds of

$C=N-N=C$. Therefore, the results demonstrated that a reaction occurred between DCS and CAS, which partly generated the azoic structure.

Thermal stability

The TG and DSC analysis curves of DCS, CAS and DCS/CAS are shown in Figures 4 and 5, respectively. As regards the TG curve of CAS in Figure 4, it shows a slight weight loss at 100-200 °C, which corresponds to the evaporation of adsorbed and bound water, as well as a significant weight loss at 300 °C, which corresponds to the degradation of CAS. In the TG curve of DCS, the weight loss at 200 °C is due to the degradation of oxidized chitosan. In contrast with the behaviours of DCS and CAS, the DCS/CAS composite presents a thermal decomposition temperature of 230 °C, which is between those of CAS and DCS. In addition, the rate of weight loss of DCS/CAS was relatively slow.

As shown in Figure 5, the DSC curve of CAS presents an endothermic peak at 100 °C, which is higher than glass transition temperature and can be attributed to the crystalline-amorphous transition

of starch. Moreover, another endothermic peak, at 170 °C, is caused by breaking of the molecular chains of CAS and the formation of a large amount of volatile substances. The two endothermic peaks of DCS at 100 °C and 155 °C are caused by moisture loss and thermal decomposition of DCS. Compared with the behaviours of CAS and DCS, in the curve of DCS/CAS, the heat flow of the double endothermic peak, a melting peak at 80 °C and another peak at 230 °C resulting from rapid thermal degradation, decreases and indicates that DCS/CAS was relatively stable.

Due to the heating rate of 30 °C/min for TGA and 10 °C/min for DSC, the thermal degradation temperature of TGA had a slight delay, the results being consistent with those of the DSC analysis. Therefore, the degradation temperature of the DCS/CAS composite was 170-230 °C, which can satisfy the requirements of its application as paper strengthening agent.

Effects of DCS/CAS reaction conditions on paper strength

Effect of molar ratio of DCS and CAS on paper strength

As shown in Figure 6, in comparison with the tensile index and burst index values (31.7 N*m/g, 1.7 kPa*m²/g) of the basic paper (without addition of strengthening agent), the corresponding values for the DCS/CAS strengthened sample increased with the increase in the amount of added DCS as follows: the tensile index increased significantly

from 38 N*m/g to 43.7 N*m/g, and the burst index – from 1.8 kPa*m²/g to 2.3 kPa*m²/g. This indicates that DCS is a strengthening agent that can effectively improve mechanical properties. After grafting copolymerization of DCS and CAS, the interactions and the bridging ability between the fibres of the paper sheet increased, resulting from more branched chains to form a cross-linked networking structure. Furthermore, the electrostatic adsorption between DCS, CAS and the fibres led to improving the strength of the paper sheet. The DCS contained a large amount of amino groups, because the oxidation degree of DCS was only 14.76%, so that the electrostatic force of DCS played a significant role, and the strength of the paper sheet attained its maximum value when the molar ratio of DCS and CAS was 10. Therefore, the experiment was finally optimized at n (DCS)/n (CAS) = 5/5, when the tensile index and burst index values obtained were of 42.5 N*m/g and 2.1 kPa*m²/g, respectively.

Effect of reaction temperature on paper strength

The effect of reaction temperature of DCS and CAS on the tensile index and burst index of the paper sheet is illustrated in Figure 7. It may be observed that the tensile index and burst index first increased and then declined with a rising temperature from 50 °C to 90 °C. This may due to the gradual formation of the Schiff base, enhancing the crosslinking between fibres and DCS/CAS with the increase in temperature.

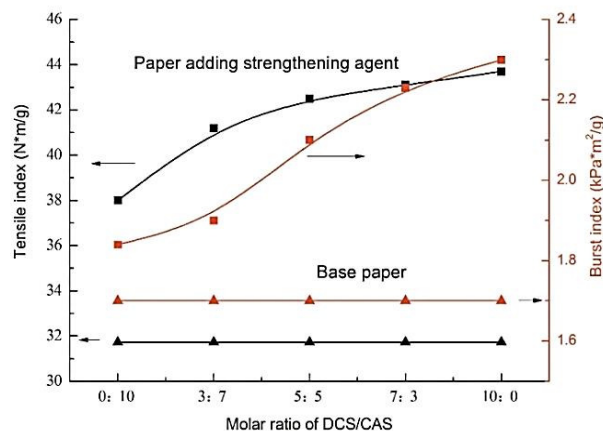


Figure 6: Effect of molar ratio of DCS and CAS on paper strength (70 °C, pH 6)

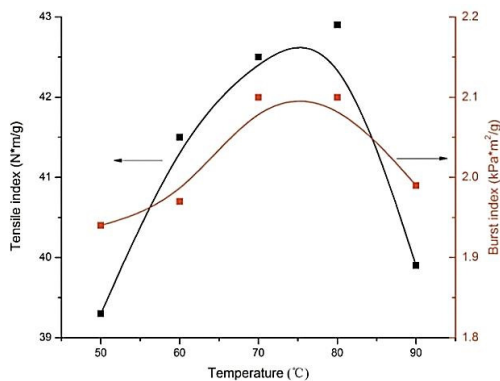


Figure 7: Effect of reaction temperature on paper strength ((n(DCS): n(CAS) = 5:5, pH 6)

However, the Schiff base was unstable in water and the C=N bond was destroyed, while the colour of the solution turned from deep purple to colourless when the temperature reached 90 °C. In addition, the high temperature led to hydrolysis and to cleavage of the 1,4-glucosidic bond in DCS, so paper strength was significantly decreased. In conclusion, the optimum reaction temperature was considered that of 70 °C, which allowed reached good levels of tensile index and burst index of the paper sheet.

Effect of pH value on paper strength

Though the water solubility of DCS was higher than that of chitosan, DCS can be completely dissolved only under weak acidic conditions. Therefore, the effect of the pH value from 3 to 7 on paper strength was investigated in the experiment. As shown in Figure 8, due to generally higher stability of a Schiff base under neutral and alkaline conditions than under acidic conditions, the DCS/CAS can hardly generate a Schiff base structure at pH value of 3. Hence, the increase in tensile index and burst index resulted from electrostatic interaction of the residual amino group in DCS and CAS. However, a certain amount of Schiff base was produced, and DCS could disperse in the solution with the gradual increase in the pH value. Higher tensile index and burst index values of the paper sheet were obtained due to the synergistic effects of electrostatic interaction and the crosslinking between fibres and DCS/CAS. At a pH value of 7, the low solubility of DCS/CAS led to an inhomogeneous solution, and undissolved DCS and CAS were lost along with whitewater, resulting in a decreased effect of the strengthening

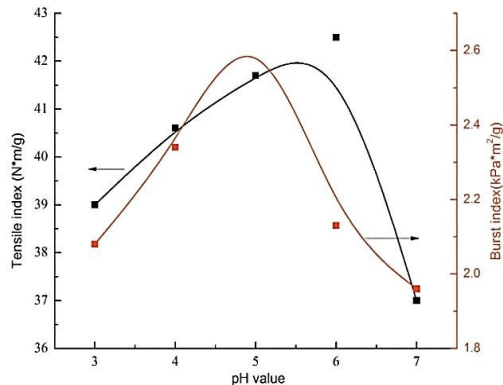


Figure 8: Effect of pH value on paper strength ((n(DCS): n(CAS) = 5:5, 70 °C)

agent. Therefore, the variation of pH had a significant effect on the tensile index and burst index, and the pH value of 6 was considered as optimum.

CONCLUSION

The crosslinked DCS/CAS composite presented an azo structure and a colouring property. In addition, due to the better thermal stability and lower price of DCS/CAS, compared with those of DCS, the obtained composite material has a great potential to find broad application. As a strengthening agent, DCS/CAS has a good effect on paper strength. To achieve the best values of the tensile index and burst index, the following reaction conditions were found to be optimum: a molar ratio of DCS and CAS of 1:1, a reaction temperature of 70 °C, and a pH value of 6.

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