Synthesis and Applied Properties of Carboxymethyl Cornstarch

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ABSTRACT: In this article, carboxymethyl starch (CMS) with a high degree of substitution (0.91) and a high viscosity was synthesized by optimized reaction conditions, and its structure and surface morphology were analyzed by IR spectroscopy and scanning electron microscopy. The results of this application study show that CMS exhibited excellent printing behavior. CMS could substitute for 60% sodium alginate when it was used as a thickening agent in the printing paste of reactive dyes; therefore, the cost was greatly reduced. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3016–3020, 2003

Key words: modification; morphology; viscosity; rheology; dyes/pigments

INTRODUCTION

Sodium alginate is an ideal thickening agent for the printing paste of reactive dyes because of the extent of interaction between them is very small. This is due to the absence of primary hydroxyl groups and to the repulsion of dye anions by the ionized carboxyl groups of the sodium alginate under alkaline conditions. However, as applications for the medical and food industries have increased, so has the price of sodium alginate.[1] Research and development aimed at seeking an alternative has been carried out. Carboxymethyl starch (CMS) has come into the horizon for its excellent behaviors and low cost. CMS is starch ether produced by starch reacting with chloroacetic acid in the presence of sodium hydroxide. It is usually prepared by one of three methods: with water as a medium, a water solvent as a medium, or a solvent as a medium. CMS with a high degree of substitution (DS) is usually obtained by the last method because it tends to form gels in water.[2–6] Many factors influence the etherification reaction, such as the choice of solvent system, the molar ratio of starch/alkali/chloroacetic acid, and the operating parameters of the reaction. In this study, we synthesized a CMS with a high DS (0.91) by optimized reaction conditions obtained through Taguchi design and investigated its properties as a printing thickener for reactive dyes.

EXPERIMENTAL

Materials

Cornstarch (Weifang Shengtai Medicine Co., LTD, Weifang, China), alcohol (Qingdao Jinyu Chemical Co., LTD, Qingdao, China), sodium alginate (Qingdao Jiaonan Bright Moon Seaweed Industrial Co., LTD, Qingdao, China), and reactive red K2BP (C.I. reactive dye 24) (Tianjin Tianshun Chemical Dyestuff Co., LTD, Tianjin, China) were commercial grade. Chloroacetic acid, sodium hydroxide, and acetic acid (supplied by Tianjin Bodi Chemical Co., LTD, Tianjin, China) were chemical pure agents.

Synthesis of carboxymethyl cornstarch (CMS)

Cornstarch (40 g) and alcohol (60 mL) were stirred in 500-mL three-necked flasks for 10 min, and then, gradually an amount of sodium hydroxide powder was added at 35–40°C. After this was stirred for 1 h, a solution of chloroacetic acid (28 g, 100%) in alcohol was added dropwise. Then, some sodium hydroxide powder was again added, and the reaction was allowed to proceed for 3 h at 50–55°C. The products were then cooled, neutralized, filtered, and washed three times with 90% alcohol. The product was dried in an oven at 60°C. The DS of the obtained CMS was determined by the method described in ref. 7. The

TABLE I
The Characterization of Synthesized CMS

Item	Appearance	DS	Content of NaCl	Viscosity (4%, 20°C)
Characterization	White powder	0.91	2%	8500 mPas

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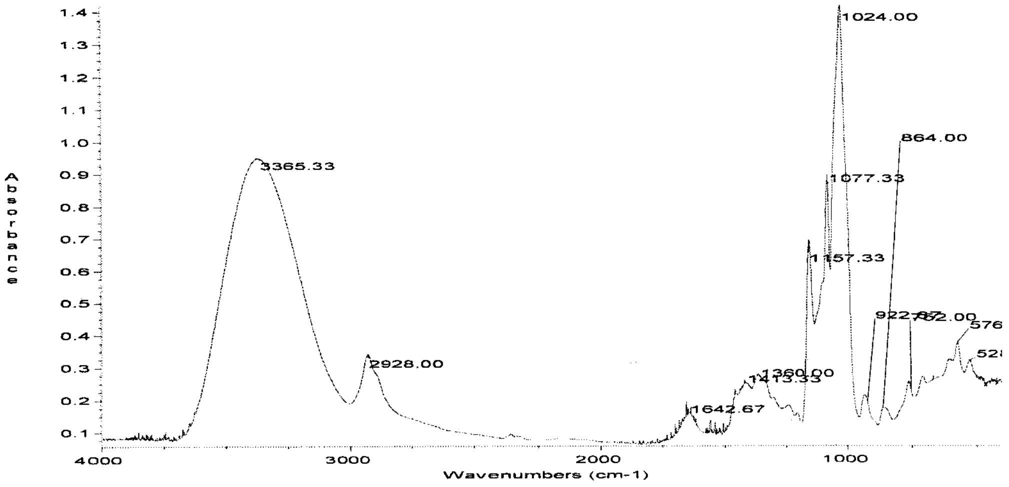

Figure 1 IR spectrum of cornstarch.

content of sodium chloride left in the product was measured by the method described in ref. 8.

IR analysis and scanning electron microscopy (SEM)

The IR spectra of cornstarch and CMS were recorded with a Nicolet 550-II IR spectrophotometer (Thermo Nicolet, USA). The surface morphologies of cornstarch and CMS were investigated with a JSM-848 scanning electron microscope (JEOL USA Inc.).

Viscosity

Viscosity was measured by NDJ-1 viscometer (Shanghai Balance Instruments Factory, Shanghai, China) with a No. 4 spindle at a speed of 6 rpm at 20°C.

pH value

The pH value was measured with a PHS-3C acidimeter (Shanghai Rex Instruments Factory, Shanghai, China).

Printing properties

The printing properties of the printing paste, including water-holding ability, dye-fixation ability, and interaction between the printing paste and reactive dye, were determined as per ref. 9. The recipe of printing paste was as follows: 1.5 g of reactive red K2BP, 2.5 g of urea, 0.5 g of resist salt, 1.0 g of sodium carbonate, 25 g of original paste, and 19.5 g of water for a total of 50 g.

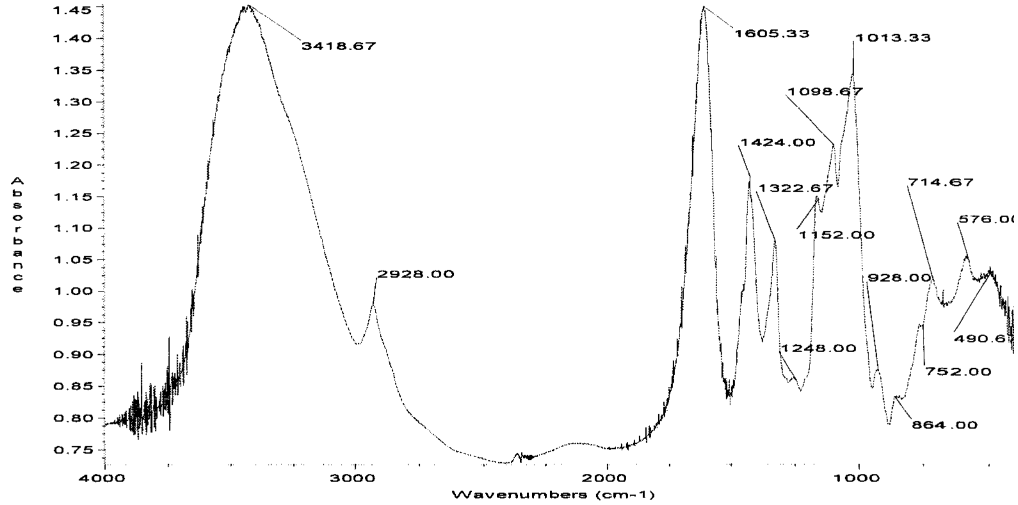

Figure 2 IR spectrum of CMS.

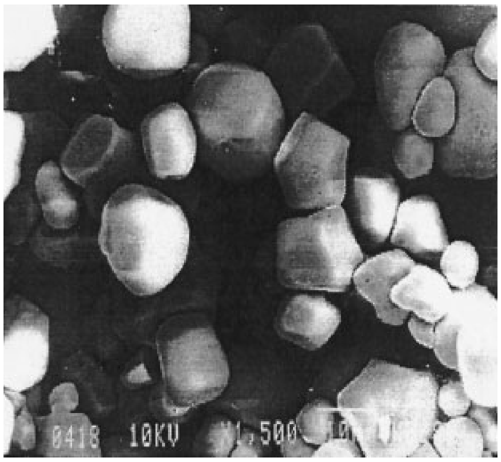

Figure 3 SEM picture of cornstarch.

RESULTS AND DISCUSSION

Characterization of the synthesized CMS

The characterization of synthesized CMS is shown in Table I.

As shown in Table I, the synthesized CMS had a high DS, a high viscosity at low concentration, and a low content of NaCl.

Structure and surface morphology analysis of the product

The IR spectra of cornstarch and CMS are shown in Figures 1 and 2. The SEM pictures of cornstarch and CMS are shown in Figures 3 and 4.

As shown in Figures 1 and 2, CMS had new and strong characteristic absorption peaks of carboxyl at 1605.33, 1424.00, and 1322.67 cm^{-1} compared with corn starch. This indicates that the carboxyl group was introduced into the cornstarch molecule.

As shown in Figure 3, the granules of cornstarch were of different sizes, and the surfaces of the starch granules were very smooth, just like many cobbles. As shown in Figure 4, the CMS still maintained a granular shape, but the surface of CMS was very rough and scraggly. This means that the carboxymethyl reaction not only took place on the surface of the starch granules but also inside them.

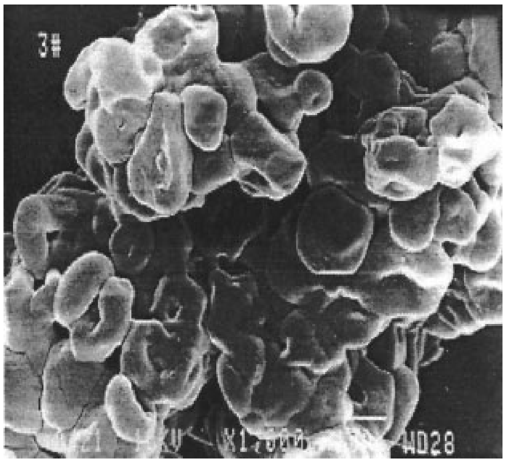

Figure 4 SEM picture of CMS.

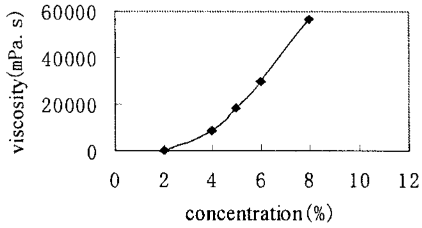

Figure 5 Viscosity of CMS at different concentrations.

Effect of concentration on viscosity

Viscous properties are very important for printing paste because these affect the amount of paste applied and the spread of the paste on the surface. The thickening agent should provide a high enough viscosity to carry the colorant, control the spread of liquid by capillary action along the spaces of fibers, and help the dyes transfer to the fibers during fixation. Figure 5 shows the viscosity of the synthesized CMS at different concentrations. Figure 6 shows the curve of the viscosity of sodium alginate versus the concentration.

According to Figures 5 and 6, the synthesized CMS had a high viscosity at lower concentrations, which is suitable for printing paste. The curve of the viscosity of CMS was less steep than that of sodium alginate, which indicated that the viscosity of CMS did not significantly vary in certain concentration ranges.

Effect of pH on viscosity

To lessen the change of the concentration of the paste during pH adjustment, concentrated hydrochloric acid and saturated aqueous sodium hydroxide were used to adjust the pH value of 1% CMS paste and 1% sodium alginate paste, respectively. The influence of pH on the viscosity is shown in Figure 7.

Figure 7 shows that the viscosity of CMS achieved a maximum and almost remained constant in the pH

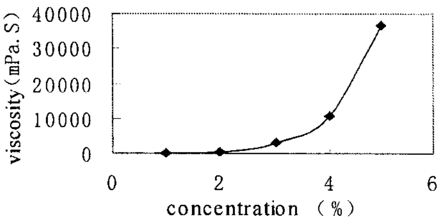

Figure 6 Viscosity of sodium alginate at different concentrations.

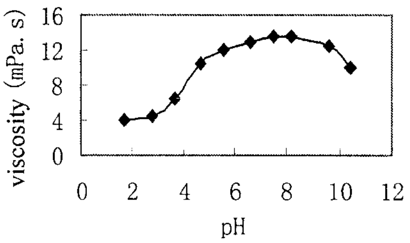

Figure 7 Effect of pH on the viscosity of 1% CMS.

range 5–11, which is appropriate for the printing paste of reactive dyes. In contrast, the viscosity of 1% sodium alginate remained stable from pH 7 to 10, and gels formed above pH 11 and below pH 6.

Effect of calcium ions on viscosity

Figure 8 shows the influence of calcium chloride on the viscosity of 4% CMS solution. With the addition of calcium chloride, the viscosity declined sharply. Gels were formed by complex with calcium ions when the content of calcium chloride added up to 1.5%. Sodium alginate was more sensitive than CMS. A small amount of calcium chloride (0.2%) caused the solution of 4% sodium alginate to precipitate.

Rheological properties

Rheological behavior is essential for a printing paste because it determines the quality of the printing. We could estimate the rheological properties from the relationship between the viscosity and shear stress or from the printing viscosity index (PVI) level. PVI is defined as the ratio of viscosity to different shear rates (usually 10/1).[10] Most PVI values of printing paste thickeners tend to be in the range 0–1. A fluid with PVI = 1 is a Newtonian liquid, whose viscosity is independent of shear stress. The smaller PVI level is, the greater is the influence of the shear stress on viscosity. Table II displays the effect of shear rate on the viscosities of CMS and sodium alginate.

As shown in Table II, sodium alginate had a higher PVI (0.684) than CMS (0.282). This indicated that the viscosity of sodium alginate did not change greatly as the latter did when the shear stress increased or decreased. The rheological behavior of CMS displayed typical shear-thinning behavior, with a significantly reduction in apparent viscosity as the shear increased. This change was reversible; the viscosity increased immediately as shear was reduced.

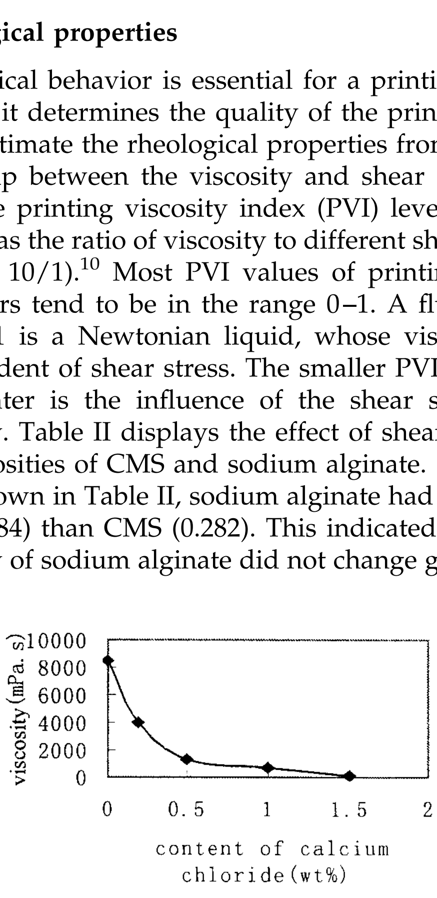

Figure 8 Effect of calcium chloride on the viscosity of 4% CMS.

TABLE II
Effect of Shear Rate on Viscosity (20°C, mPas)

	Shear rate (rpm)				
	60	30	12	6	PVI level
Sodium alginate (4%)	6500	7440	8570	10500	0.684
CMS (4%)	2400	3600	6000	8500	0.282

The shear-thinning behavior of CMS is helpful for screen printing. A printing paste should have a high viscosity to remain still before printing, and its viscosity should decrease sharply to let it transfer into the fibers through the printing mesh at the moment of press increase. Afterward, its viscosity should recover to a high value in case the paste flows.

Storage stability

We sealed the beaker with 4% CMS paste and stored it at room temperature to examine its viscosity stability. Table III shows the change in viscosity versus time in days. The results indicated that the viscosity of CMS did not vary greatly, which met the requirements of storage.

Printing properties

The water-holding ability, dye-fixation ability, and the extent of interaction with reactive dyes of synthesized CMS, sodium alginate, and their mixtures were compared and investigated. The water-holding ability of a original printing paste is a very important property in printing. If an original paste has a good water-holding ability, a fine flower pattern will be obtained; if not, this will lead to bleeding. Water-holding and dye-fixation abilities are shown in Table IV. The reaction extents between the original pastes and the reactive red dye K2BR were also examined by silica-gel thin-layer chromatography with flowing-phase *n*-butanol/pyridine/water (1/1/1). If the thickening agents did not react with the dyes, the original dot in thin-layer plate was colorless; otherwise, the original dot was colored. The results are shown in Table V.

TABLE III
Storage Stability of 4% CMS Paste

	Days			
	0	2	14	21
Viscosity (mPa.s)	8500	8500	7900	7500

TABLE IV
Dye Fixation Ability and Water Holding Ability of Original Pastes

Original pastes	Printed flower pattern	Dye fixation (%)	Water holding ability (cm)
5% sodium alginate paste	Sharp, no bleeding	67.2	0.5
5% mixed paste (A/B = 4/1)	Sharp, no bleeding	74.5	0.6
5% mixed paste (A/B = 3/2)	Sharp, no bleeding	69.8	0.6
5% mixed paste (A/B = 2/3)	Sharp, no bleeding	64.0	0.8
8% CMS paste	Sharp, no bleeding	67.3	4.8

A = sodium alginate; B = CMS.

TABLE V
Extent of Paste Interaction with Reactive Dyes

	Paste				
	Sodium alginate (5%)	A/B = 4/1 (5%)	A/B = 3/2 (5%)	A/B = 2/3 (5%)	CMS (8%)
Color of original dot	Colorless	Colorless	Colorless	Colorless	Colorless

A = sodium alginate; B = CMS.

According to Table IV, 8% CMS paste and 5% sodium alginate paste gave good results, with sharp printed patterns and similar fixation abilities. The original paste containing mixed thickeners with 20, 40, and 60% CMS replacement of sodium alginate also exhibited good behavior with sharp printed patterns and higher dye fixations. Except for 8% CMS paste, all of the mixed pastes had good water-holding abilities similar to 5% sodium alginate. As mentioned previously, the shear-thinning behavior of CMS makes it easily transfer into the fibers through mesh; this may be the reason that the dye fixation was increased with the mixed pastes. According to Table V, CMS and sodium alginate did not react with reactive dyes.

CONCLUSIONS

CMS with a high DS was synthesized, and its structure and surface morphology were analyzed by IR spectroscopy and SEM. The IR spectra showed that the starch carboxymethylation reaction really took place, and SEM pictures showed that the carboxymethyl reaction not only took place on the surface of starch granules but also inside them.

The synthesized CMS exhibited a high viscosity at low concentration, which remained constant in the pH range 5–11, and also exhibited shear-thinning rheological behavior. The properties of CMS were suitable for a printing paste of reactive dyes.

The printing paste with 8% CMS gave a sharp printed pattern and a high dye fixation; the pastes with CMS replacing sodium alginate (60% at most) also displayed good results with sharp patterns and higher dye-fixations and water-holding abilities. The synthesized CMS did not react with reactive dyes when it was used as thickening agent for reactive dye printing paste.

The synthesized CMS was environmentally friendly and low cost, so the printing costs were greatly reduced when CMS was substituted for sodium alginate in reactive dye printing.

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