

Preparation, structural characterization, and flocculation ability of amphoteric cellulose



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ABSTRACT

A series of amphoteric celluloses (QACMCs) were prepared from sodium carboxymethyl cellulose (CMC) and 2,3-epoxypropyltrimethylammonium chloride (EPTMAC) with a cationic degree of substitution (DS_{cat}) of 0.24–1.06 and a carboxymethyl degree of substitution (DS_{ani}) of 0.60. The structures of the samples were characterized by FTIR and NMR spectroscopy, which revealed that DS_{cat} depended on the ratio of EPTMAC to CMC in the reaction mixture and that the substituent distribution of the cationic group at the C2, C3, and C6 positions of the QACMCs ranked as follows: C2 > C6 > C3. The QACMCs dissolved over a wide range of pH levels and exhibited flocculation ability against kaolin suspensions. In particular, the samples with high DS_{cat} exhibited excellent flocculation performance. In addition, the flocculation characteristics of the QACMCs depended on the pH of the kaolin suspension.

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1. Introduction

The separation of solid particles from suspensions via the use of flocculating agents is a widely used process in many industries. Studies related to coagulation and flocculation as they apply to the pulp [1], beverage [2], and chemical industries [3] have recently been reported, in addition to investigations into drinking water purification [4,5]. Such treatments usually exploit inorganic salts (coagulation agents) to form aggregates from solid and colloidal materials in wastewater and subsequently use synthetic and charged flocculating agents to further flocculate the aggregates [6]. These flocculating agents increase the size and density of the aggregates and promote the settling rate and dewaterability of suspensions [7,8]. Despite the advantages of synthetic flocculants, the poor biodegradability and adverse impacts on personal health associated with the degradation products of these nonrenewable chemicals have diminished their general appeal [9]. Consequently, there is a growing interest in replacing oil-based flocculants such as polyacrylamide with more sustainable alternatives such as cellulose, chitin, starch, and their derivatives [10,11].

Abbreviations: AGU, anhydroglucose unit; CMC, carboxymethyl cellulose; DOSY, diffusion-ordered spectroscopy; DP, degree of polymerization; DS, substitution degree; DS_{ani} , substitution degree of anionic group; DS_{cat} , substitution degree of cationic group; EPTMAC, 2,3-epoxypropyltrimethylammonium chloride; FTIR, Fourier transform infrared spectroscopy; M_w , weight-average molecular weight; NMR, nuclear magnetic resonance; QA, quaternary ammonium sodium salt.

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Among naturally occurring polysaccharides, cellulose—which is the most abundant natural polymer on earth—has great potential as one of the most environmentally friendly non-food sources in the production of a wide range of eco-friendly products. In addition, the high degree of polymerization (DP) and the number of potential chemical modifications of cellulose also make it an attractive candidate for flocculation purposes [12]. Among numerous cellulose derivatives under investigation, CMC has been identified as a candidate of particular promise. CMC, which is a water-soluble anionic polymer obtained from the reaction of hydroxyl groups at the 2, 3, and 6 positions of the anhydroglucose units (AGUs) of cellulose with chloroacetic acid, is one of the most important cellulose ethers because it is relatively inexpensive, nontoxic, highly biocompatible, and biodegradable [13,14]. Because of these excellent properties, the polymer is now employed in the food, pharmaceutical, and cosmetics industries; in the paint industry as a viscosity modifier, thickener, emulsion stabilizer, and water-retention agent; and in pharmaceutical products such as controlled-release drug delivery carrier matrices [15]. Although CMC has exhibited promising results as a flocculation agent, the general use of anionic flocculation agents is still rare [16]. In addition, the poor solubility of CMC in acidic solutions limits the practical application of the polymer as a flocculation reagent [17].

Amphoteric polysaccharides containing both anionic and cationic groups have recently come into focus as effective flocculation candidates because of their wide range of applicability, which is due to their remarkable solubility across the entire pH range

[18–23]. For example, amphoteric chitosan derivatives containing both anionic carboxymethyl (CM) and cationic quaternary ammonium sodium salt (QA) groups have demonstrated notable improvements in solubility compared with chitosan and have exhibited good flocculation performance [24]. In addition, several polysaccharide-based amphoteric flocculants, including cellulose [25], chitosan [26,27], amylopectin [18], glycogen [28], guar gum [20], starch [29,30], and tamarind kernel polysaccharides [31], have been reported as efficient flocculants for the treatment of industrial wastewater and synthetic effluents. The excellent flocculation performance demonstrated by amphoteric polymers is related to two major mechanisms. The first mechanism is the charge neutralization of suspended particles by amphoteric polymers [32]; suspended particles in water or sludge are usually negatively charged [33], and charge neutralization occurs between the suspended particles and the positively charged groups of the amphoteric polymers. The second major mechanism involves the intermolecular bridging between the anionic group of a polymer and the cationic group of another polymer chain [32]. Through the two mechanisms, suspended solids in water or sludge are aggregated, and the size of the aggregated particles is increased by the amphoteric polymers, resulting in effective particle sedimentation. Because the two major mechanisms are related to charge neutralization between polymer chains, as well as between polymers and suspended particles, the degree of substitution (DS) of both cationic and anionic groups in the polyampholytes, as well as the solution pH of the suspended particles, strongly affects the flocculation performance [34].

In this study—as shown in Fig. 1—we synthesized amphoteric celluloses (QACMCs) containing both cationic QA and anionic CM groups from the reaction of CMC with EPTMAC in aqueous solution and evaluated the flocculation performance of the products. As described above, colloidal particles in water are usually negatively charged; we therefore expected that the balance between DS_{cat} and DS_{ani} in the structure of the QACMC would be one of the major factors controlling the flocculation performance. In this work, a series of QACMCs with various DS_{cat} values were prepared from CMC with a DS_{ani} of 0.60, and their flocculant ability toward a kaolin suspension was evaluated. In addition, because the solution pH

strongly affects the ionic charges of the CM groups in the QACMCs, the effect of solution pH on the flocculation performance was also investigated.

2. Experimental

2.1. Materials

CMC was kindly supplied from Dai-ichi Kogyo Seiyaku Co. (Japan). EPTMAC was purchased from Sigma–Aldrich (USA). Kaolin (colloidal particle size 6 μm) was purchased from Kanto Chemicals Co. (Japan). All other chemicals were purchased from Kanto Chemicals (Japan), were of reagent grade, and were used as received.

2.2. Synthesis of QACMC

A series of five QACMCs **1–5** were prepared by the reaction of CMC with EPTMAC. A typical procedure for preparing QACMC was performed as follows: CMC (1.0 g, 4.6 mmol) was completely dissolved in 1.5 M NaOH (25 mL) at 4 °C with constant agitation. To the solution, EPTMAC (1.4 g, 9.2 mmol) was slowly added over a period of 20 min. The reaction mixture was placed in a hot water bath at 60 °C, and the mixture was stirred for 24 h. After cooling to room temperature, the reaction mixture was poured into acetone (100 mL). The precipitate was filtered using a glass filter and then washed three times with a 1:1 mixture of acetone/water (200 mL) to reach neutral pH and to remove unreacted EPTMAC; the precipitate was then dried in a vacuum oven at 60 °C for 24 h. The resultant solid particles were cut and screened through a 40-mesh sieve using a PLC-2 M plastic cutting mill (Osaka Chemical Co., Japan) to obtain a white, granular product (sample **1**). Using a similar method, the QACMCs **2–5** were prepared; the amounts of CMC and EPTMAC used for the preparation of these polymers are listed in Table 1. All samples were stored in a vacuum desiccator prior to use.

2.3. Structural characterization

2.3.1. FTIR spectroscopy

FTIR spectra were measured using a PerkinElmer Spectrum Two spectrometer (PerkinElmer Inc., US). FTIR spectra were recorded after grinding a sample into a powder and mixing it well with KBr powder; the powder mixture was compressed into a transparent disk (3 mm of diameter) using a PerkinElmer table press die set and scanned from 4000 to 500 cm^{-1} using an average of 32 scans, with a resolution of 1 cm^{-1} .

2.3.2. NMR spectroscopy

All NMR data were recorded on a Bruker Avance III spectrometer (Bruker BioSpin GmbH, Germany) operating at 500.13 MHz for ^1H and 125.13 MHz for ^{13}C . The spectrometer was equipped with

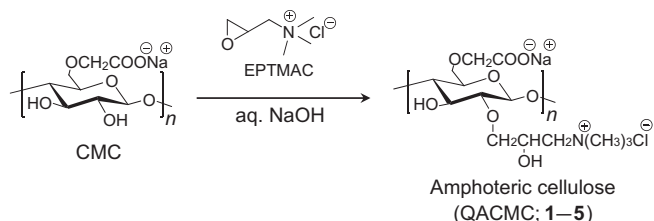


Fig. 1. Synthesis of amphoteric cellulose (QACMC) via etherification of CMC with EPTMAC.

Table 1
Amounts of CMC and EPTMAC used in polymer synthesis, polymer yields, and structural data of the QACMCs **1–5** and related parameters of the CMC starting material.

Samples	Initial additive amounts		DS_{ani}^b	DS_{cat}^b	$M_{\text{wAGU}}^c/\text{g mol}^{-1}$	$D^d/10^{-11} \text{ m}^2 \text{ s}^{-1}$	Yields ^e
	CMC (AGU) ^a	EPTMAC					
1	1.0 g (4.6 mmol)	1.4 g (9.3 mmol)	0.60	0.24	252	2.06	1.13 g (97%)
2	1.0 g (4.6 mmol)	3.5 g (23 mmol)	0.60	0.44	283	1.96	1.24 g (95%)
3	1.0 g (4.6 mmol)	4.9 g (32 mmol)	0.60	0.63	311	1.88	1.32 g (92%)
4	1.0 g (4.6 mmol)	7.0 g (46 mmol)	0.60	0.84	343	1.81	1.45 g (91%)
5	1.0 g (4.6 mmol)	10.5 g (69 mmol)	0.60	1.06	377	1.71	1.53 g (88%)
CMC			0.60	0	216	1.81	

^a Molar quantities of CMC anhydroglucose units (AGUs) added to the reaction mixture.

^b DS of CM (anionic) and QA (cationic) groups of the obtained QACMC.

^c Average molecular weight of the QACMC monomer.

^d Diffusion coefficient for each QACMC as determined by ^1H DOSY experiments performed at 300 K.

^e Yield (%) of each QACMC was determined by the following equation: Yield (%) = [(Yields/g)/($M_{\text{wAGU}}/\text{g mol}^{-1}$)]/4.6 mmol $\times 10^5$.

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