Cellulosic associative thickeners

L.-M. Zhang[*]

Institute of Polymer Science, Zhongshan University, Guangzhou 510275, People's Republic of China

Accepted 12 July 2000

Abstract

Cellulosic associative thickeners with well-defined hydrophilic and hydrophobic parts are currently of increased interest because of their extensive applications, biodegradability, lack of toxicity, and abundant raw materials. However, such polymeric thickeners are often difficult to prepare and analyze. In this article, their synthesis routes via lateral-group reactions and graft copolymerization, and the methods for determining the content of bound hydrophobe and the feature of hydrophobic microstructure are reviewed briefly. Besides, the solubility characteristic and the viscosity behavior of cellulosic associative thickener in aqueous solutions as well as other properties such as surface activity, adsorption on a hydrophobic substrate, and hydrogel forming are also presented and discussed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Amphiphilic cellulose derivatives; Associative thickeners; Hydrophobic association; Review

1. Introduction

Polymeric associative thickeners are water-soluble polymers containing hydrophobic groups that are capable of non-specific hydrophobic association, similar to surfactants (Ng, Tam & Jenkins, 1999). They can exhibit unusual aqueous solution behavior due to the hydrophobic association (Chang & McCormick, 1993; Shimamura, White & Fellers, 1981; Werbowyj & Gray, 1984). Such polymers have been the subject of considerable research beginning with the classical studies of Strauss and Jackson (1951) and have many potential applications in such diverse fields as surface coatings, personal care, oil field formulation, rheology modification, and colloid stabilization (Irja, 1992; Xu, 1997a,b). Up to now, the majority of these studies have been performed on three distinct classes of associative thickeners: hydrophobically modified polyethylene oxide (PEO) copolymers (Tam, Farmer, Jenkins & Rassett, 1998; Xu, Yekta, Masoumi & Winnik, 1996), hydrophobically modified polyacrylamides (Biggs, Selb & Candau, 1992; Schulz, Kaladas, Maurer, Bock, Pace & Schulz 1987), and hydrophobically modified water-soluble cellulosics (Thuresson, Nysterom, Wang & Lindman, 1995; Zhang, Zhang & Li, 1998).

Cellulosic associative thickeners are a relatively new class of associative polymers and are of great interest due to their wide applications, abundant raw materials, lower cost, and biodegradability. In general, cellulosic associative thickeners may be regarded as water-soluble amphiphilic cellulose derivatives. The hydrophilic–hydrophobic balance (Zheng & Hu, 1995) plays a large role in their practical uses as associative thickeners. Starting with the pioneering work of Landoll (1980) in preparing water-soluble cellulosic surfactants containing large hydrophobic groups in the late 1970s, an intermittent study regarding cellulosic associative thickeners has been done in the past 20 years. This paper presents a brief overview of some advances in the study of the synthesis, characterization and properties of cellulosic associative thickeners.

2. Synthesis

Cellulose in its native form is not soluble in water. It can be rendered water-soluble by chemical reaction of its hydroxyl groups with hydrophilic substituents. In this manner water-soluble cellulose derivatives such as carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), methyl cellulose (MC), and hydroxypropyl cellulose (HPC) are produced (Felcht, 1985). These cellulosic polymers may be further modified by reacting with hydrophobic reagents (Table 1), surfactant macromonomers or water-soluble surface-active monomers (Table 2), resulting in cellulosic associative thickeners. In addition, cellulosic associative thickeners may also be prepared by direct reaction of

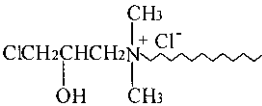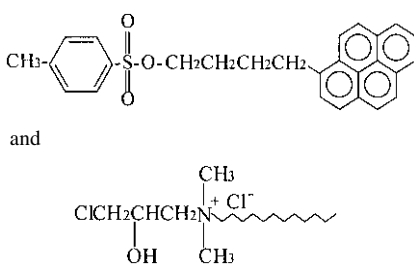* Tel.: +86-20-8403-5181; fax: +86-20-8403-7549.
E-mail address: ceszhlm@zsu.edu.cn (L.-M. Zhang).

Table 1
Preparation of cellulosic associative thickeners via lateral-group reactions

No.	Cellulosic substrate	Hydrophobic reagents	References
1	HEC, MC or HPC	CH_2—CH ~~~~~~ $\quad\diagdown O \diagup$ or X~~~~~~~~ or $\quad$ or $\quad O$ $\qquad | $ $X-C$~~~~~~~ or $O=C=N$~~~~~~~~~ or (succinic anhydride structure) where ~~~~~~ is the alkyl hydrogen chain, X is a halogen	Landoll (1980, 1982a,b, 1985); Hoy and Hoy (1984); Evani (1984); Sau and Landoll (1989); Goodwin et al. (1989); Meadows et al. (1994); Tanaka et al. (1992); Tanaka (1996);
2	HEC	CH_3-(benzene ring)-$\overset{O}{\underset{O}{S}}$-O-$CH_2(CF_2)_nCF_3$ or CH_2—$CHCH_2OCH_2(CF_2)_nCF_3$ $\quad\diagdown O \diagup$ $(n = 2,6)$	Hwang and Hogen-Esch (1992); Zhang et al. (1994);
3	CMC	Br~~~~~~~~~~	Zhang et al. (1997)
4	CMC	NH_2~~~~~~~~	Cohen-Stuart et al. (1998); Merle et al. (1999)
5	HEC	(phenyl with long alkyl chain and glycidyl ether)	Partain (1998)
6	Cellulose	CH_2—$CHCH_2OCH_2CH_2CH_2CH_3$ $\quad\diagdown O \diagup$	Nishimura et al. (1997)
7	HPC	CH_3-(benzene ring)-$\overset{O}{\underset{O}{S}}$-O-$CH_2CH_2CH_2CH_2$-(pyrene) or CH_3-(benzene ring)-$\overset{O}{\underset{O}{S}}$-O-$CH_2$-(fluorene)	Winnik, Winnik and Tazuke (1987a) and Winnik, Winnik, Tazuke and Ober (1987b) ; Winnik (1987, 1989)

Table 1 (*continued*)

No.	Cellulosic substrate	Hydrophobic reagents	References
8	HEC		Brode et al. (1998, 1987, 1995)
9	HEC	and	Winnik et al. (1997)

cellulose with the reactive amphiphilic reagent (Nishimura, Donkai & Miyamoto, 1997).

2.1. Lateral-group reactions

A number of cellulosic associative thickeners have been synthesized via lateral-group reactions of common water-soluble cellulose derivatives with reactive hydrophobes. As seen in Table 1, such water-soluble cellulose derivatives include HEC, HPC, MC, and CMC, and the hydrophobic reagents involve long-chain alkyl epoxide, alkyl halides, acyl halides, isocyanates or anhydrides (Evani, 1984; Goodwin, Hughes, Lam, Miles & Warren, 1989; Hoy & Hoy, 1984; Landoll, 1980, 1982a,b, 1985; Meadows, Williams & Tanaka, 1994; Sau & Landoll, 1989; Tanaka, 1996; Tanaka, Meadows & Williams, 1992; Zhang, Huang & Li, 1997), fluorocarbon tosylate and epoxides (Hwang & Hogen-Esch, 1992; Zhang, Hwang & Hogen-Esch, 1994), alkyl amine (Cohen-Stuart, Fokkink, van der Horst & Lichtenbelt, 1998), glycidyl ether (Nishimura et al., 1997; Partain, 1998), 4-(1-pyrenyl)butyl tosylat and 9-fluorenlmethyl tosylate (Winnik, 1987, 1989; Winnik, Regismond & Goddard, 1997; Winnik et al., 1987a; Winnik et al., 1987b), quaternary halohydrins (Brode, Kawakami, Doncel & Kemnitzer, 1998; Brode, Kreeger, Goddard, Merritt & Braun, 1987; Brode, Kreeger & Salensky, 1995; Winnik et al., 1997). To handle the incompatibility of the hydrophobic regents and the hydrophilic cellulosic polymers, the reactions are usually carried out in slurry media.

Slurry methods are preferred due to lower viscosity of the system, which is favorable for the lateral-group reactions. A typical slurry process involves swelling the raw material cellulose derivative with organic solvent, adding NaOH in H_2O, followed by addition of reactive hydrophobe. For example, Landoll (1982b) prepared three series of non-ionic cellulosic derivatives incorporating long hydrocarbon chains by adding respectively long-chain *n*-alkyl

epoxides (1,2-epoxydecane, 1,2-epoxydodecane, a mixture of 1,2-epoxyeicosane, 1,2-epoxydocosane and 1,2-epoxytetracosane) to HEC, HPC and MC in alkaline slurries. Similarly, Hwang and Hogen-Esch (1992) synthesized fluorocarbon-containing cellulosic associative thickeners by the reaction of the HEC–NaOH slurry with 1,1-dihydroperfluorobutyl or octyl *p*-toluenesulfonate and with 1,1-dihydroperfluorobutyl or octyl glycidyl ether at 50° in various solvents including dioxane (DOX), IPA and triethylamine (TEM). Recently, it has been reported that anionic cellulosic associative thickeners can be prepared by etherification CMC with a long-chain alkyl halide (Zhang et al., 1997) or by amidation of CMC with dodecylamine in alkaline slurries (Cohen-Stuart et al., 1998). In addition, some cationic cellulosic associative thickeners also can be synthesized in alkali-catalyzed slurry systems (Brode et al., 1998, 1987, 1995; Winnik et al., 1997).

Different from the above heterogeneous reactions, Nishimura et al. (1997) synthesized lately a new cellulosic surfactant by a homogeneous etherifying reaction of cellulose power with butyl glycidyl ether (BGE) in a 10% (w/w) LiCl–DMAc solution. For cellulose and BGE as well as their product, LiCl–DMAc is a common solvent system.

2.2. Graft copolymerization

Some cellulosic associative thickeners also have been synthesized by graft copolymerization. In these cases, the surfactant macromonomers with both a hydrophilic head group and a hydrophobic tail, as well as water-soluble (or dispersible) surface-active monomers have been widely used (Table 2).

Among the various methods available for initiating the graft copolymerization, chemical initiation method appears to be relatively simple, and has been exploited by some investigators. For example, Cao, Li and Xu (1997b) have synthesized anionic cellulosic associative thickeners by

Table 2
Preparation of cellulosic associative thickeners via graft copolymerization

No.	Cellulosic substrate	Vinyl monomers	References
1	CMC	$CH_2=CH-C(=O)-(CH_2CH_2O)_{\overline{n}}CH_2(CH_2)_{10}CH_3$ ($n = 3,9,20$)	Cao et al. (1997a)
2	CMC	$CH_2=CH-C(=O)-(CH_2CH_2O)_{\overline{n}}\langle C_6H_4 \rangle-C_9H_{19}$ (n=9) ($n = 9$)	Cao et al. (1997b)
3	HPCMC	$CH_2=CH-C(=O)-(CH_2CH_2O)_{\overline{n}}CH_2(CH_2)_{10}CH_3$ (n=9) ($n = 9$)	Cao et al. (1997c)
4	CMC	$CH_2=CH-C(=O)-(CH_2CH_2O)_{\overline{n}}CH_2(CH_2)_{10}CH_3$ (n=9) ($n = 9$) and $CH_2=CH-\langle C_6H_5 \rangle$	Cao et al. (1997a)
5	HEC	$CH_2=CH-C(=O)-(CH_2CH_2O)_{\overline{n}}\langle C_6H_4 \rangle-C_9H_{19}$ ($n = 9$) and $CH_2=CHCOCH_3$ with CH_3 and O	Sun et al. (1997)
6	CMC	$CH_2=CHCOCH_2CH_2N^+(CH_3)_2$ Br$^-$ (alkyl) and $CH_2=CH$, $C=O$, NH_2	Zhang et al. (1999a,b)
7	HEC	$CH_2=C(CH_3)-C(=O)-O-CH_2-CH_2-N^+(CH_3)_2-CH_2-N$(pyrrolidinone) and $CH_2=CHCOCH_2CH_2N^+(CH_3)_2$ Br$^-$ (alkyl)	Shih and Paramus (1991); Chuang et al. (1989)

grafting the surfactant macromonomer dodecylpoly-oxyethylene acrylate onto CMC or hydroxypropyl carboxymethyl cellulose (HPCMC) using ceric ion-initiated solution polymerization technique. Zhang, Zhang and Li (1999b) have synthesized amphoteric cellulosic associative thickeners by grafting acrylamide and the surface-active monomer methacryloxyethyl-dimethyloctylammonium bromide onto CMC in an aqueous solution using potassium persulfate/tetramethylethylenediamine initiating system. However, simply dispersing these vinyl monomers in the aqueous phase with water-soluble cellulose derivatives may lead to a heterogeneous product with low hydrophobe incorporation.

In order to overcome the phase incompatibility between water-soluble cellulosic substrate and hydrophobic vinyl monomer, mutual solvents (e.g. alcohol) and solvent mixture (e.g. acetone/water) have been used in the grafting copolymerization (Zhang et al., 1998; Shih & Paramus, 1991). However, this method also has some limitations and may result in low molecular weight products because of the chain transfer of organic solvent.

A better method for grafting surfactant macromonomers onto water-soluble cellulose derivatives may involve novel ultrasonic irradiation (Xu, 1995). In comparison with the above chemical initiation method, this initiation method can lead to the introduction of more surfactant macromono-mers (higher grafting extent). It has been reported (Cao, Li & Xu, 1997a,b; Sun, Duan, Huang, Zhang & Chen, 1997) that some macromonomers such as dodecylpoly(etheroxy) acrylates ($R_{12}EO_nA$, where $n = 3, 7, 9, 20$) and nonylphe-nylpolyoxyethylene acrylates of variable poly(etheroxy) chain length can be grafted onto CMC, HPCMC or HEC, forming the cellulosic associative thickener with improved properties.

3. Characterization

3.1. Hydrophobe incorporation

Evidence for the hydrophobe incorporation and the deter-mination for the hydrophobe content are the most principal concerns in the characterization of cellulosic associative thickeners. As a result of the pronounced intermolecular hydrophobic interaction, the proof for the incorporation of hydrophobic reagent, surfactant macromonomer or surface-active monomer is easy to observe in the solution properties (e.g. viscosity, solubility and rheology) of water-soluble cellulosic surfactants (Landoll, 1982b; Zhang et al., 1999b). It is also possible to develop inferential relation-ships between levels of hydrophobic monomer or reagent charged to the reaction system and the final solution proper-ties of the cellulosic thickeners (Hwang & Hogen-Esch, 1992). However, detailed analytical data on the incorpora-tion of hydrophobic monomer or reagent, especially for simple alkyl hydrophobes has proven difficult to obtain.

Among the characterization methods used, the degrada-tion/gas chromatography (GC), nuclear magnetic resonance (NMR) and ultraviolet (UV) spectroscopy are three main techniques.

Degradation/GC has been successfully adopted by Sau and Landoll (1989) to determine the level of bound alkyl groups of non-ionic hydrophobically modified cellulosic polymers from non-ionic cellulose ethers (HEC, MC and HPC) and long-chain *n*-alkyl epoxides. The procedure involves exhaustive cleavage of the cellulosic thickener by aqueous hydroiodic acid followed by GC analysis of iodoalkane formed.

NMR determinations are not sensitive enough to detect low levels of hydrophobe (i.e. 1–2%). For fluorocarbon-containing cellulosic associative thickeners, however, ^{19}F NMR has been proven to be effective (Hwang & Hogen-Esch, 1992; Zhang et al., 1994). To carry out the ^{19}F NMR analysis, Hwang and Hogen-Esch (1992) prepared aqueous solutions of fluorocarbon-containing cellulosic thickeners from HEC and fluorocarbon tosylates or epoxides by using sodium triflate (CF_3SO_3Na) as internal standard and $CFCl_3$ (dissolved in $CDCl_3$) as external reference. From the ratio of the peak area [$NaSO_3CF_3$ at -80.8 ppm and $-(CF_2)_nCF_3$ at -82.8 ppm], the weight percent of fluorine in the polymer was calculated and thus the molar ratio of fluorocarbon hydrophobe over anhydroglucose unit (AGU) of the cellulosic associative thickeners.

UV is a probe that is sensitive enough to measure low levels of hydrophobes, provided that there is a UV active chromophore in cellulosic associative thickeners. By using such a UV method, the incorporation levels of nonylphe-noxypoly(etheroxy) acrylates and nonylphenylpolyoxyethy-lene acrylates into CMC or HPCMC backbones have been determined (Cao et al., 1997a,b).

In addition, the distribution of aliphatic long-chain amines on the anhydroglucose ring of the cellulosic associative thickeners from hydrophobically modified carboxymethylcellulose series has been recently investi-gated by Merle, Charpentier, Mocanu and Chapelle (1999). It has been found that ^1H NMR spectroscopy of modified cellulosics hydrolyzed to very short units is parti-cularly useful to show the distribution pattern of the hydro-phobic long chains in the cellulosic associative thickeners and the knowledge of this distribution is important in understanding structure–property relationships.

3.2. Hydrophobic microstructure

A challenge in the study of cellulosic associative thick-eners is the characterization of hydrophobic microstructure in aqueous solutions. Exploring microstructural features can add value to the efforts in preparation and property control of cellulosic associative thickeners. For this purpose, fluor-escence studies of pyrene-labeled hydroxypropyl cellulose (HPC-Py) have been performed by Winnik (1987, 1989), Winnik et al. (1997), Winnik et al. (1987a) and Winnik,

Winnik et al. (1987b). The evidence for intermolecular aggregation was presented in terms of the degree of excimer fluorescence to that of monomer fluorescence. The ratio of the fluorescence intensity of excimer relative to monomer fluorescence (I_E/I_M) may be used as an indicator of polymer–polymer interaction. By measuring I_E/I_M as a function of HPC-Py concentration, methanol content in methanol/water mixtures, as well as temperature, the modes of hydrophobic associations between the pyrenyl groups, the nature of the hydrophobic aggregates as well as the association mechanism have been determined. By utilizing fluorescence label technique, the hydrophobic microstructure of commercial Quatrisoft LM 200, a cationic cellulosic associative thickener, has been characterized recently also (Winnik et al., 1997). Besides, the micellar behavior of CMC-based associative thickeners incorporating surfactant macromonomers has been investigated using dynamic laser scattering (DLS) and scanning electronic microscope (SEM) (Cao & Li, 1999a,b; Cao, Li & Xu, 1997c).

4. Solution properties

4.1. Solubility

Solubility characteristics of cellulosic associative thickeners are influenced largely by their chemical architecture and composition, especially by the hydrophobe content and type. The higher the hydrophobe content and the longer the hydrophobic chain, the greater the extent of aggregation and the less soluble is the cellulosic thickener in water. As observed with conventional surfactants (Zheng & Hu, 1995), a critical chain length of about 6–8 carbons is required for the onset of aggregation; but when the carbon length approaches 10–18, there is a drastic decrease in solubility. For example (Landoll, 1982a), hydrophobically modified HEC with hydrophobe levels of up to 3.4 wt% n-C_{12} have been found to be soluble. As the hydrophobe chain length increases to n-C_{14}, the amount of hydrophobe must be decreased to 2.91 wt% in order to maintain solubility. Similar phenomena have been found also for hydrophobically modified HPC and hydrophobically modified MC (Landoll, 1982a,b) as well as fluorocarbon-containing cellulosic thickeners (Zhang et al., 1994). Generally, the critical micelle concentration of cellulosic thickeners depends on the architecture of the molecule, relative amount of hydrophilic to hydrophobic functionality, chain length and structure of the hydrophobe, as well as physicochemical parameters such as temperature, pH, ionic strength of the water, etc. It is anticipated that these variables will also influence the solubility of cellulosic associative thickeners.

The effects of salts, polymer concentration and small molecule surfactants on the solubility of cellulosic surfactants have been investigated (Cao & Li, 1999a,b; Cao, Li & Xu, 1997c,d; Nishimura et al., 1997). With increasing salinity, the hydrophobic chains are forced into closer proximity to the point where the subtle balance between hydrophobic associative forces and hydrophilic hydration forces breaks down, resulting in the decrease of the solubility. Increasing the concentration of cellulosic associative thickeners causes the system to pass from a dilute to semi-dilute to gel phase. The solubility of cellulosic surfactants in solutions of small molecule surfactants should increase because small molecule surfactants themselves aggregate above their critical micelle concentrations and provide hydrophobic regions in the micellar structure.

4.2. Viscosity

4.2.1. Dependence of viscosity on content and structure of bound hydrophobe

The viscosity property of cellulosic associative thickeners in aqueous solution is strongly influenced by the intra- and intermolecular aggregation. The aggregation level depends largely on the content and structure of the bound hydrophobe.

As in the case of the fluorocarbon-containing cellulosic associative thickeners derived from HEC and the modifier 1,1-dihydroperfluorooctyl glycidyl ether (PFOGE) (Hwang & Hogen-Esch, 1992; Zhang et al., 1994), the results of the Brookfield viscometric measurements at a shear rate of 0.4 s^{-1} and 25°C show that there is a substantial viscosity enhancement at a modifier level of between 2 and 4 mol% (with respect to AGU). The viscosity in 2.0 wt% solution is increased more than 200% compared to the unmodified HEC. Significantly, as the PFOGE modifier is increased to 4 and 5%, the Brookfield viscosity of the product is decreased to about the value of the unmodified HEC. Starting with very low mole fractions of perflurocarbon groups, the hydrophobic association is largely intermolecular to form network-like structures and this increases as the mole fraction of perflurocarbon groups increases, resulting in an increase of the apparent hydrodynamic size and thus of the viscosity. However, at higher perflurocarbon content, the intramolecular hydrophobic association of the perfluro-carbons becomes more prevalent and this tends to compete with intermolecular association, which causes a collapse of the polymer coils resulting in lower viscosity. Similar changes have been observed by Landoll (1982a) for analogous hydrocarbon-containing HEC-based associative thickeners. Besides, the cellulosic associative thickeners containing fluorocarbon moieties have stronger viscosification efficiency than the corresponding hydrocarbon analogs due to greater hydrophobic character (Zhang et al., 1994).

4.2.2. Dependence of viscosity on concentration, shear and temperature

Some studies have been done on the viscosity–concentration relationships for cellulosic associative thickeners (Hwang & Hogen-Esch, 1992; Landoll, 1982b; Zhang, Zhang & Li, 1999a,b). At concentrations lower than a

critical value, C_p^c, the modified cellulosics behave similarly to the precursor cellulose derivatives. When the concentration exceeds C_p^c, the solution viscosity increases sharply and, for some samples, gelation may occur at sufficiently high polymer concentrations. The drastic viscosity increase beyond C_p^c can be ascribed to the interchain association through the formation of hydrophobic microdomains. The critical polymer concentration and the sharpness of the viscosity curve beyond C_p^c depend on the degree of hydrophobic modification.

Some examples of the influence of shear rate on the viscosity of cellulosic associative thickeners have appeared in the literature (Merle et al., 1999). A typical pseudoplastic behavior is observed with most of these polymers. The sharp decrease of viscosity with increasing shear is most likely due to the shear-induced disruption of the relatively weak hydrophobic interactions. Of special interest is the fact that when the shear was removed the viscosity of the solutions recovered completely. This result indicates that the formation of the hydrophobic aggregates is reversible.

The effect of temperature on the viscosity of cellulosic associative thickeners has been also investigated (Zhang et al., 1999a,b). For a graft copolymer of CMC with acrylamide and methacryloxyethyldimethyloctyl ammonium bromide, there is a viscosity increase from 20 to 60°C, followed by a decrease between 60 and 80°C. The viscosity increase observed upon heating is consistent with an entropy driven increase in hydrophobic bonding and the viscosity decrease may result from the changes in the hydration of the hydrophobic groups and/or in the structure of water itself.

4.2.3. Dependence of viscosity on addition of various additives

Various additives have different effects on the viscosity property of cellulosic associative thickeners. As reported, the addition of NaCl often leads to an effective thickening, which results from the enhancement of interchain hydrophobic aggregation (Cao & Li, 1999b; Cao et al., 1997c; Hwang & Hogen-Esch, 1992; Zhang, Zhang & Li, 1999a,b, 2000). Consistent with the postulated hydrophobic association in aqueous media, the addition of organic solvents causes a decrease in the viscosity (Cao & Li, 1999b).

Effects of surfactants on the viscosity of cellulosic associative thickeners have been a subject of intense research (Panmai, Prud'homme, Peiffer, Jockusch & Turro, 1998; Stainer, 1985; Tanaka et al., 1992; Thuresson et al., 1995; Winnik et al., 1997; Winnik et al., 1987a; Zhang et al., 2000). When a free surfactant is added to a solution of hydrophobically modified cellulosic polymer, the hydrophobic association is affected so that the solution viscosity changes significantly. In general, the intermolecular association of cellulosic associative thickeners may be strengthened by the added surfactant under suitable conditions. The surfactant molecules aggregate along with the hydrophobic chains of cellulosic associative thickeners to form the clusters resemble mixed micelles.

Recently, it has been reported (Gruber & Konish, 1997) that the combination of a hydrophobically modified, water-soluble cationic ether (HPC bearing *N,N*-dimethyl-*N*-dodecylammonium moiety) with amylose (a linear polysaccharide isolated from potato starch) dissolved together in water at high temperature and carefully cooled afford increased solution viscosity over either polymer acting alone. The mode of viscosity enhancement has been attributed to the formation of a cross-linked network created when this cellulosic associative thickener forms a non-covalent, helical clathrate with the amylose.

5. Other properties

5.1. Surface activity

The amphiphilic nature of cellulosic associative thickeners is expected to induce a decrease in water surface tension and oil/water interfacial tension. Such surface activity is of practical importance to their applications. Sun et al. (1997) reported that hydrophobically modified HEC incorporating the surfactant macromonomer nonylphenylpolyoxyethylene acrylate can lower the surface tension from 72.0 to 29.8 mN/m (1.0 wt%) and the oil/water interfacial tension from 30.0 to 1.66 mN/m (0.5 wt%). Cao et al. (1997a) found that 0.5 wt% hydrophobically modified CMC containing the surfactant macromonomer dodecylpolyoxyethylene acrylate has the surface tension of 29.3 mN/m and the oil/water interfacial tension of 2.062 mN/m. Landoll (1982b) studied the behavior of interfacial tension (water/toluene) versus concentration of the non-ionic associative thickener derived from C_{20}-modified HEC and observed that the interfacial tension decreases from 19.7 to 8.5 mN/m when the concentration increases from 0 to 1.8 wt%. For comb-shaped, amphiphilic *O*-(2-hydroxy-3-butoxypropyl) cellulose (Nishimura et al., 1997), it was found that this cellulosic derivative having a degree of substitution of 0.6 shows the surface activity with critical micelle concentration in the order of 0.8 g/l and surface tension of 31.5 mN/m.

The factors affecting the surface activity of cellulosic associative thickeners have been also investigated (Cao et al., 1997b; Sun et al., 1997). For the cellulosic thickeners studied, the surface and interfacial tensions depend on the polymer concentration, the species and content of the hydrophobe, chemical architecture and the external factors such as temperature and time.

5.2. Adsorption behavior

Due to the existence of hydrophobic groups, cellulosic associative thickeners have an adsorption ability on many hydrophobic substrates, which makes them have potential applications as stabilizers of aqueous dispersions, emulsion and foams (Stainer & Gelman, 1989).

Meadows et al. (1994) reported the adsorption properties of a commercially available cellulosic associative thickener

containing about 1 mol% C_{12}–C_{18} alkyl side chains (HMHEC), prepared from the hydrophobic modification of HEC, on the polystyrene latex both in the presence and absence of various competitive adsorbate species. Under the same conditions, the adsorption amount of HMHEC is 2–3 times greater than that of unmodified HEC. This may be attributed in part to a reduction in the affinity of the cellulosic thickener for the solvent and an increase in its affinity for the latex surface due to the presence of the hydrophobic chains. Meanwhile, the enhanced adsorption is accommodated by HMHEC adopting a more extended configuration than HEC. In the presence of other anionic or non-ionic surfactants, the plateau adsorption values of HMHEC are reduced significantly, suggesting the possible involvement of the HMHEC hydrophobic chains in the attachment to the surface of the latex particles. Similar studies were carried out by Cohen-Stuart et al. (1998) for the adsorption of the cellulosic associative thickener with 1.2% dodecyl groups (HMCMC), prepared from hydrophobic modification of CMC, on spin-coated polystyrene films. It was found that the adsorption of HMCMC depends on the hydrophobic interaction between the dodecyl groups and the hydrophobic polystyrene surface. Upon addition of salt, the adsorbed amount increases at all pH values studied. However, increasing the charge density on the chain by increasing the pH does not lead to a monotonic decrease of the adsorption. Instead, after an initial decrease in the pH range 4–6, the adsorption tends to increase for pH > 6.

5.3. Gel formation

Besides the above-mentioned properties, certain cellulosic associative thickeners also have the ability to form stiff, water-swollen hydrogels under suitable conditions. For example, hydrophobically modified HEC (HMHEC) can form hydrogels when solubilized in the solutions containing SDS below the critical micelle concentration (cmc) of the surfactant (Dualeh & Steiner, 1990a,b, 1991; Tanaka et al., 1992). Such hydrogels may also be made by solubilizing high concentrations of HMHEC in mixtures of ethanol and water and allowing the excess polymer to precipitate out in gel form (Varelas, Dualeh & Steiner, 1994). Furthermore, these gels may be either charged or non-ionic, depending on the structure of the starting cellulosic polymer and the composition of the solution from which the gels form (Varelas & Steiner, 1992).

6. Summary

As a relatively new class of associative polymers, cellulosic associative thickeners with well-defined hydrophilic and hydrophobic parts are gaining increasing academic and industrial concern. With increasingly stringent environmental regulations, their attractiveness is expected to rise in the future. However, such polymeric thickeners are usually difficult to prepare and characterize. This article reviews briefly the synthesis routes, which involve mainly the hydrophobic modifications of the precursor water-soluble cellulose derivatives by lateral-group reactions and graft copolymerization, and the methods for determining the amount of hydrophobe incorporated via the degradation/ GC, NMR and UV as well as the feature of hydrophobic microstructure. Meanwhile, the solubility characteristic and the viscosity behavior of cellulosic associative thickener in aqueous solutions as well as other properties such as surface activity, adsorption on a hydrophobic substrate, and hydrogel forming have been also presented and discussed.

Acknowledgements

References

Biggs, S., Selb, J., & Candau, F. (1992). Effect of surfactant on the solution properties of hydrophobically modified polyacrylamides. *Langmuir*, *8*, 838–847.

Brode, G. L., Kreeger, R. L., Goddard, E. D., Merritt, F. M., & Braun, D. B. (1987). Hydrophobe substituted, water-soluble cationic polysaccharides. US Patent, 4,663,159.

Brode, G. L., Kreeger, R. L., & Salensky, G. A. (1995). Double substituted cationic cellulose ethers. US Patent, 5,407,919.

Brode, G. L., Kawakami, J. H., Doncel, G., & Kemnitzer, J. E. (1998). Hydrophobe modified cationic polysaccharides (HCPs) for topical microbicide delivery. *Polymer Preprints*, *39* (2), 206.

Cao, Y., & Li, H. L. (1999a). Micellar conformation in aqueous solution of carboxymethyl cellulose-based polymeric surfactants. In: *Preprints of China Symposium on Polymer Science* (p. a-442).

Cao, Y., & Li, H. L. (1999b). Influence of salt, alcohol, alkali on micellar conformation of carboxymethyl cellulose-based polymeric surfactants in aqueous solution. In: *Preprints of China Symposium on Polymer Science* (p. a-444).

Cao, Y., Li, H. L., & Xu, X. (1997a). A study of ultrasonic copolymerization of polymer surfactants based on carboxymethyl cellulose. *Chemical Journal of China University*, *18* (6), 985–989.

Cao, Y., Li, H. L., & Xu, X. (1997b). Studies on structure and surface activity of carboxymethyl cellulose-based polymer surfactants. *Oilfield Chemistry*, *14* (3), 257–260.

Cao, Y., Li, H. L., & Xu, X. (1997c). Studies on molecular morphology of carboxymethyl cellulose-based polymeric surfactants in solution. *Polymeric Materials Science and Engineering*, *13* (3), 106–110.

Cao, Y., Li, H. L., & Xu, X. (1997d). Studies on micellar behavior of carboxymethyl cellulose-based polymer surfactants. *Oilfield Chemistry*, *14* (4), 361–364.

Chang, Y., & McCormick, C. L. (1993). Water-soluble copolymers. 49. Effect of the distribution of the hydrophobic cationic monomer dimethyldodecyl(2-acrylamidoethyl)ammonium bromide on the solution behavior of associating acrylamide copolymers. *Macromolecules*, *26*, 6121–6126.

Chuang, J. C., Cottrell, I. W., & Johnson, S. C. (1989). Heterocyclic containing cellulosic graft polymers. US Patent, 4,831,097.

Cohen-Stuart, M. A., Fokkink, R. G., van der Horst, P. M., & Lichtenbelt, J. W. Th. (1998). The adsorption of hydrophobically modified carboxymethylcellulose on a hydrophobic solid: effects of pH and ionic strength. *Colloid and Polymer Science*, 276, 335–341.

Dualeh, A. J., & Steiner, C. A. (1990a). Hydrophobic microphase formation in surfactant solutions containing an amphiphilic graft copolymer. *Macromolecules*, 23, 251–255.

Dualeh, A. J., & Steiner, C. A. (1990b). Bulk and microscopic properties of surfactant-bridged hydrogels made from an amphiphilic graft copolymer. *Macromolecules*, 24, 112–116.

Evani, S. (1984). Water-dispersible hydrophobic thickening agent. US Patent, 4, 432, 881.

Felcht, U. H. (1985). Cellulose ethers — synthesis, application and analytical aspects. In J. F. Kennedy, G. O. Phillips, D. J. Wedlock & P. A. Williams, *Cellulose and its derivatives: chemistry, biochemistry and applications* (pp. 273–284). New York: Wiley.

Goodwin, J. W., Hughes, R. W., Lam, C. K., Miles, J. A., & Warren, B. C. H. (1989). The rheological properties of a hydrophobically modified cellulose. In J. E. Glass, *Polymers in aqueous media: performance through association, Advances in chemistry series no. 223* (pp. 365–378). Washington, DC: American Chemical Society.

Gruber, J. V., & Konish, P. N. (1997). Aqueous viscosity enhancement through helical inclusion complex cross-linking of a hydrophobically-modified, water-soluble, cationic cellulose ether by amylose. *Macromolecules*, 30, 5361–5366.

Hoy, K. L., & Hoy, R. C. (1984). Polymers with hydrophobe bunches. US Patent, 4,426,485.

Hwang, F. S., & Hogen-Esch, T. E. (1992). Fluorocarbon-modified water-soluble cellulose derivatives. *Macromolecules*, 26, 3156–3160.

Irja, P. (1992). *Polymeric surfactants*, New York: Marcel-Dekker.

Landoll, L. M. (1980). Modified nonionic cellulose ethers. US Patent, 4, 228,277.

Landoll, L. M. (1982a). Use of hydrophobically modified water-soluble polymers in suspension polymerization. US Patent, 4, 352, 916.

Landoll, L. M. (1982b). Nonionic polymer surfactants. *Journal of Polymer Science. Polymer Chemistry Edition*, 20, 443–455.

Landoll, L. M. (1985). Hydrophobically modified polymers. US Patent, 4, 529, 523.

Meadows, J., Williams, P. A., & Tanaka, R. (1994). Adsorption properties of hydrophobically associating water-soluble polymers. *Macromolecular Reports A*, 31 (Suppls.6/7), 777–785.

Merle, L., Charpentier, D., Mocanu, G., & Chapelle, S. (1999). Comparison of the distribution of associative carboxymethylcellulose derivatives. *European Polymer Journal*, 35, 1–7.

Ng, W. K., Tam, K. C., & Jenkins, R. D. (1999). Evaluation of intrinsic viscosity measurements of hydrophobically modified polyelectrolyte solutions. *European Polymer Journal*, 35, 1245.

Nishimura, H., Donkai, N., & Miyamoto, T. (1997). Preparation and properties of a new type of comb-shaped, amphiphilic cellulose derivative. *Cellulose*, 4, 89–98.

Panmai, S., Prud'homme, R. K., Peiffer, D. G., Jockusch, S., & Turro, J. N. (1998). Rheology of solutions of hydrophobically modified polymers with spherical and rod-like surfactant micelles. *Proceedings of the American Chemical Society Division of Polymeric Materials: Science and Engineering*, 79, 419–420.

Partain, E. M. (1998). The synthesis of hydrophobe-modified hydroxyethyl cellulose polymers using 3-*n*-pentadecenyl phenyl glycidyl ether. *Polymer Preprints*, 39 (2), 82–83.

Sau, A. C., & Landoll, L. M. (1989). Synthesis and solution properties of hydrophobically modified hydroxyethyl cellulose. In J. E. Glass, *Polymers in aqueous media: performance through association, Advances in Chemistry Series No. 223* (pp. 343–364). Washington, DC: American Chemical Society.

Schulz, D. N., Kaladas, J. J., Maurer, J. J., Bock, J., Pace, S. J., & Schulz, W. W. (1987). Copolymers of acrylamide and surfactant macromonomers: synthesis and solution properties. *Polymer*, 28, 2110–2115.

Shih, J. S., & Paramus, N. J. (1991). Heterocyclic quaternized nitrogen-containing cellulosic graft polymers. US Patent, 5,037,930.

Shimamura, K., White, J. L., & Fellers, J. F. (1981). Hydroxypropylcellulose, a thermotropic liquid crystal: characteristic and structure development in continuous, extrusion and melt spinning. *Journal of Applied Polymer Science*, 26, 2165.

Stainer, C. A. (1985). Interactions of hydrophobically modified hydroxyethyl cellulose with amphoteric surfactants. *Polymer Preprints*, 26, 224.

Stainer, C. A., & Gelman, R. A. (1989). New cellulosic surfactants. In H. Inagaki & G. O. Phillips, *Cellulosics utilization: research and rewards in cellulosics* (pp. 132–140). London/New York: Elsevier.

Strauss, U. P., & Jackson, E. G. (1951). Polysoap I. Viscosity and solubilization studies on an *n*-dodecyl bromide addition compound of poly-2-vinylpyridine. *Journal of Polymer Science*, 6, 649–659.

Sun, Y. X., Duan, W., Huang, S. L., Zhang, W., & Chen, K. Q. (1997). Studies on ultrasonic synthesis of hydroxyethyl cellulose-based polymeric surfactants. *Oilfield Chemistry*, 14 (3), 280–282.

Tam, K. C., Farmer, M. L., Jenkins, R. D., & Rassett, D. R. (1998). Rheological properties of hydrophobically modified alkali-soluble polymers — effects of ethylene-oxide chain length. *Journal of Polymer Science. Part B: Polymer Physics*, 36, 2275.

Tanaka, R. (1996). Characterization of hydrophobically associating water-soluble cellulose derivatives and related natural polymers. In: *Preprints of International Symposium on Cellulose and Lignocellulosics* (pp. 72–73).

Tanaka, R., Meadows, J., & Williams, P. A. (1992). Interaction of hydrophobically-modified hydroxyethylcellulose with various added surfactants. *Macromolecules*, 25, 1304–1310.

Thuresson, K., Nysterom, B., Wang, G., & Lindman, B. (1995). Effect of surfactant on structural and thermodynamic properties of aqueous solutions of hydrophobically modified ethyl(hydroxyethyl)cellulose. *Langmuir*, 11, 3730–3736.

Varelas, C. G., Dualeh, A. J., & Steiner, C. A. (1994). Microdomain composition in two-phase hydrogels. In P. Dubin, J. Bock, R. M. Davies, D. N. Schulz & C. Thies, *Macromolecular Complexes in Chemistry and Biology* (pp. 67–69). Berlin: Springer.

Varelas, C. G., & Steiner, C. A. (1992). Bulk and microscopic properties of copolymer networks in mixed aqueous solvents. *Journal of Polymer Science. Part B: Polymer Physics*, 30, 1233–1238.

Werbowyj, R. S., & Gray, D. G. (1984). Optical properties of (hydroxy-propyl)cellulose liquid crystals: cholesteric pitch and polymer concentration. *Macromolecules*, 17, 1512–1520.

Winnik, F. M. (1987). Effect of temperature on aqueous solutions of pyrene-labeled (hydroxypropyl)cellulose. *Macromolecules*, 20, 2745–2750.

Winnik, F. M. (1989). Association of hydrophobic polymers in water: fluorescence studies with labeled (hydroxypropyl)cellulose. *Macromolecules*, 22, 734–742.

Winnik, F. M., Regismond, S. T. A., & Goddard, E. D. (1997). Interactions of an anionic surfactant with a fluorescent-dye-labeled hydrophobically-modified cationic cellulose ether. *Langmuir*, 13, 111–114.

Winnik, F. M., Winnik, M. A., & Tazuke, S. (1987a). Interaction of hydropropyl-cellulose with aqueous surfactants: fluorescence probe studies and look at pyrene-labeled polymer. *Journal of Physics Chemistry*, 91, 594.

Winnik, F. M., Winnik, M. A., Tazuke, S., & Ober, C. K. (1987b). Synthesis and characterization of pyrene-labeled (hydroxypropyl)cellulose and its fluorescence in solution. *Macromolecules*, 20, 38–44.

Xu, B., Yekta, A., Masoumi, Z., & Winnik, M. A. (1996). The functionality of associative polymer networks: the association behavior of hydrophobically modified urethane-ethoxylate (HEUR) associative polymers in aqueous solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 112, 239.

Xu, J. (1997a). Molecular design of polymer surfactants. *Chinese Polymer Bulletin*, (2), 90–121.

Xu, J. (1997b). Recent advances in polymeric surfactants. *Oilfield Chemistry*, *14*, 290–294.

Xu, X. (1995). Application of new techniques in science and engineering of polymeric materials. In *Preprints of China Symposium on Polymer Science* (pp. 6–9).

Zhang, J., Zhang, L. M., & Li, Z. M. (1998). Synthesis and characterization of hydrophobically modified water-soluble amphoteric cellulose derivatives. In: *Preprints of 4th China Symposium on Cellulose Science* (pp. 44–45).

Zhang, J., Zhang, L. M., & Li, Z. M. (1999a). Properties of hydrophobically associating water-soluble cellulosic thickeners. *Chinese Journal of Applied Chemistry*, *16* (6), 71–73.

Zhang, J., Zhang, L. M., & Li, Z. M. (1999b). Synthesis and properties of hydrophobically modified water-soluble cellulosic graft copolymers. *Journal of Cellulose Science and Technology*, *7* (2), 9–15.

Zhang, J., Zhang, L. M., & Li, Z. M. (2000). Synthesis and aqueous solution properties of hydrophobically modified graft copolymer of sodium carboxymethylcellulose with acrylamide and dimethylmethacryloxyethyloctylammonium bromide. *Journal of Applied Polymer Science*, *78*, 537–542.

Zhang, L. M., Huang, S. J., Li, Z. M. (1997). A new hydrophobically-modified water-soluble cellulose derivative. In: *Preprints of 7th International Symposium on Fine Chemical and Functional Polymers* (pp. 225–226).

Zhang, L. M., Huang, S. J., & Li, Z. M. (1998). Hydrophobized water-soluble cellulose derivatives. *Journal of Cellulose Science and Technology*, *6* (1), 1–8.

Zhang, Y. X., Hwang, F. S., & Hogen-Esch, T. E. (1994). Fluorocarbon-modified water-soluble polymers. In P. Dubin, J. Bock, R. M. Davies, D. N. Schulz & C. Thies, *Macromolecular complexes in chemistry and biology* (pp. 95–116). Berlin/Heidelberg: Springer.

Zheng, Z., & Hu, J. H. (1995). *Physical and chemical principles of surfactants*, Guangzhou: Press of South China University of Technology (pp. 1–10).