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Rheological properties of hydrophobically modified carboxymethylcelluloses

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Abstract

This paper describes the rheological properties of two hydrophobically modified carboxymethylcellulose (HMCMC) which differ in their hydrophilic–lipophilic balance (HLB). They were CMC-9C_{12-18} (monografted) and CMC-30C_4-3C_{12-18} (bigrafted), where in cote designation CMC-$x$$C_n$, x is the percentage of alkyl grafted chain and n the number of carbon atoms in the chain.

It is shown that both samples evidence similar behavior although they differ in their HLB. Flow curves show extreme shear thinning behavior that resemble colloidal dispersion behavior, but oscillatory sweep and creep analysis are consistent with a sticky entanglement behavior. It seems that the structure of the pseudo-gel is largely heterogeneous with the presence of very dense zones made up of hydrophobic moieties together with a mainly entangled and sticky network of associated macromolecules.

Keywords: Hydrophobically modified carboxymethylcelluloses; Rheology; HLB; Amphiphilic

1. Introduction

Hydrophobically modified polysaccharides are frequently used as stabilizers, binders, viscosifying or gelling agents. They show specific properties mainly due to their ability to develop intermolecular association through hydrophobic side chains introduced by chemical modification of the precursor (Akiyoshi, Degushi, Morigushi, Yamagushi, & Sunamoto, 1993; Bataille, Huguet, Mocanu, Carpov, & Muller, 1997; Glinel, Huguet, & Muller, 1999; Goodwin, Hughes, Lam, Miles, & Warren, 1989; Landoll, 1982; Landoll & Sau, 1989; Mocanu, Carpov, Chapelle, Merle, & Muller, 1995; Picton, Merle, & Muller, 1996; Sinquin, Hubert, & Dellacherie, 1993). These associations can induce in some cases the formation of a three-dimensional network. For environmental consideration, less polluting and dangerous aqueous fluids have been developed using water-soluble associative polymers based on polysaccharides as thickeners. Hydrophobic associations can be intramolecular and/or intermolecular leading to aggregating structures and/or three-dimensional networks (Shulz & Bock, 1991). Generally above a critical concentration, the hydrophobically modified polysaccharides exhibit apparent viscosities of several orders of magnitude higher than their precursors, because of intermolecular associations of weak energy (Landoll, 1982). These interactions can be easily disrupted under shear then formed again after a short time (Picton & Muller, 1996). The tendency for such systems to undergo associations in the concentrated domain leads to various unusual linear or non-linear rheological behaviors which give rise to many industrial applications. Such systems are frequently thixotropic gels. The gel formation results in a radical change in dynamical and mechanical behavior, that can be monitored by rheological dynamic measurements (Aubry & Moan, 1994; Picton & Muller, 1996).

In a previous study, the elaboration and physico-chemical properties (in dilute and semi-dilute solutions) of carboxymethylcelluloses (CMCs) modified with a few percent (0.9–6%) of grafted hexadecylamine (C_{16}) have been reported (Charpentier et al., 1997). The modification of

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CMC and mainly the step of activation of the carboxylic groups with *N*,*N*′-dicyclohexylcarbodiimide, induced a slight degradation of the polysaccharidic backbone via a β glycosidic bound scissions (Merle, Charpentier, Mocanu, & Chapelle, 1999). Nevertheless, physico-chemical characterization of the hydrophobically modified CMCs has evidenced intramolecular associations and compact aggregates in dilute solution. As expected, above a critical concentration (Ccr), a large increase in viscosity is observed. It has also been found that a critical amount of apolar chains of about 4% is needed to develop viscosity higher than that of the CMC precursor in the studied range of concentration.

Another interesting property of amphiphilic water-soluble polysaccharides concerns the control of interfaces. To develop interfacial properties, it seems preferable to shift the hydrophilic–lipophilic balance (HLB) toward a more lipophilic character with a larger amount of shorter hydrophobic moieties together with a lower amount of long chains to avoid any insolubility of the polymer in aqueous media. The challenge is now to obtain amphiphilic systems, which show interesting interfacial properties together with improved rheology.

The present paper concerns two industrial hydrophobically modified carboxymethylcelluloses (HMCMC) that differ by the amount and the length of apolar grafted moieties. The first polymer consists of 9% of mixed C_{12} from C_{18} chains and its behavior is expected to be quite similar to that of previous studied HMCMC. The monografted polymer was designed to obtain good rheological properties. The second polymer consists of a bi-grafted CMC with a lower extent of C_{12}–C_{18} chains but with a large amount of C_4 short chains. The bi-grafted HMCMC is expected to present properties at interfaces better than that of the mono-grafted HMCMC. The aim of this work is to compare and discuss the rheological behavior of both polymers.

2. Experimental part

2.1. Chemical

Hydrophobically modified carboxymethylcelluloses (CMCs) were elaborated by Akzo Nobel company (Netherlands) (Van der Host, Batelaan, & Reuvers, 1994). Two polymers were studied:

(i) a monografted CMC which contains 9% of $C_{12\text{–}18}$ (CMC-9$C_{12\text{–}18}$)
(ii) a bigrafted CMC which contains 30% of C_4 and 3% of $C_{12\text{–}18}$ (CMC-30C_4-3$C_{12\text{–}18}$)

After modification, both samples have nearly the same degree of substitution ($DS_{COOH}\sim 0.50$). This characteristic is important because it permits the HLB of both polymers to be compared only on the basis of the lipophilic contribution.

2.2. Preparation of the solutions

The purified polymer powders were dispersed directly in pure milli-Q water, at their natural pH ~ 6.5–7. The dilute solutions were filtered finally through 0.45 μm filter (Millipore). The concentrations were determined by the dry extract method. The sodium chloride was added after the dissolution and the solutions were equilibrated during one night at 4 °C before measurements. For the more concentrated range (above 15 $g\,L^{-1}$), the polymer solution was dispersed under mechanical agitation (100 rpm), directly in the appropriate solvent (water or NaCl solutions), then stored for one night at 4 °C. For every solutions, 0.1% NaN_3 was systematically added to prevent any bacterial degradation.

2.3. Light scattering measurements

Low Angle Laser Light Scattering (LALLS) measurements have been conducted using the Chromatix KMX-6 (Milton Roy) fitted with a He–Ne laser ($\lambda = 633$ nm), at a low angle of 4.88°. Solutions were passed through a 0.45 μm Millex filter upstream of the measurement cell to remove dust and other large particles. More details about this technique have been reported previously (Picton et al., 1996).

2.4. Rheological measurements

The viscosity of dilute solutions was measured under controlled temperature with a low-shear 30 Contraves apparatus between 10^{-2} and 10^{2} s^{-1}. Rheological measurements were performed using a controlled stress rheometer (Carri Med CSL 100) with a Peltier temperature control device at 25 °C, in steady and oscillatory shear with cone-plate geometry (diameter 4 cm, angle 2°, gap 55 μm) for viscoelastic solutions and with double gap geometry for viscous solutions. All measurements were performed with a solvent trap to prevent any evaporation. The linearity of the viscoelastic properties was checked for all solutions before measurements of the storage (G') and loss (G'') moduli.

3. Results and discussion

3.1. Dilute solution characterization

HMCMC samples have been analyzed by both viscometry and light scattering in the dilute range and the results are compiled in the Table 1. As HMCMC samples came from industry, we did not have the original precursor. Nevertheless, for comparison, we have chosen to report data of another industrial CMC (Charpentier et al., 1997),

Table 1
Dilute physico-chemical characteristics of CMC and both HMCMCs in 0.1 M NaCl at 25 °C

	DS_{COOH}	M_w (g mol^{-1})	A_2 (mL mol g^{-2})	[η] (mL g^{-1})	k'	C^* (g L^{-1})
CMC (not the precursor)	0.85	3×10^5	4.0×10^{-3}	650	0.4	5.4
CMC-30C_4-3$C_{12–18}$	0.52	4.9×10^{6}	-1.9×10^{-3}	280	2.1	2.5
CMC-9$C_{12–18}$	0.47	4.8×10^{6}	-5.4×10^{-3}	280	3.1	1.4

All measurements have been made in 0.1 M NaCl solution after filtration on 0.45 μm filter.

expected to be close to the precursor of the HMCMC studied here. It appears that HMCMC exhibits very high weight average molar masses (M_w) of about 5×10^6 g mol^{-1} which is larger than the M_w of a native CMC. This result clearly indicates the existence of aggregating structures. One can notice that scattered light of very large particles (aggregates) is largely enhanced at low angle (LALLS). This precision indicates that the M_w at low angles represents an average value, which should be largely affected even by a small amount of very large aggregates. The second Virial coefficient (A_2), obtained by LALLS in 0.1 M NaCl, is negative for both HMCMC while A_2 is largely positive in the case of CMC. This result, that has been commented on for neutral amphiphilic cellulosic derivatives (Picton & Muller, 1996), evidences unfavorable interactions between amphiphilic samples and aqueous solvent. This result which indicates an increase of polymer–polymer interactions is consistent with the above mentioned aggregate formation. In spite of its high M_w, intrinsic viscosities of HMCMC are largely lower than that of CMC. To explain this apparent contradiction, we can involve the very high association tendency of amphiphilic HMCMC that induce very compact aggregates. This result is fully confirmed by the HMCMC's values of the Huggins constants which are much higher than expected if only strictly repulsive intermolecular interactions prevail as for CMC. It should be noticed that when strong aggregation occurs, the intrinsic viscosity does not reflect the hydrodynamic volume of isolated macromolecules.

The transition between dilute and semi-dilute solution can be studied with the Utracki and Simha (1963) representation which is the bi-logarithmic plot of the zero-shear specific viscosity ($\eta_{sp}=(\eta-\eta_0)/\eta_0$ with η_0 the solvent viscosity) as a function of polymer concentration. Such representation (an example of which is shown Fig. 1 for the CMC) permits the determination of the C^* which corresponds to the observed break in the plot. The larger the intrinsic viscosity, the lower the critical overlapping concentration C^*. The behavior of HMCMC does not agree with a classical entangled water-soluble polymer behavior. It appears that HMCMC exhibits a very low 'C^*' as compared to a classical CMC even with lower intrinsic viscosities. It can be argued that for associative polymers, the increase of viscosity when the concentration increases, is not only due to close packing but also to specific association between coil and/or aggregates. In summary, it does not seem appropriate to describe the critical concentration of hydrophobically modified as an overlapping concentration. For this reason we have replaced C^* by Ccr to describe the behavior of HMCMC. A similar behavior have been evidenced with hydrophobically modified carboxymethyl pullulane (Simon, Dugast, Le Cerf, Picton, & Muller, 2003)

3.2. The rheological behavior of the mono-grafted HMCMC

3.2.1. Dynamic analysis

The Oscillatory shear behavior of the mono-grafted (CMC-9$C_{12–18}$) has been studied at 25 °C in pure water in a concentration range between 9 and 21 g L^{-1}. For reasons of clarity, we have chosen to report the results concerning only 9 and 21 g L^{-1} (Fig. 2). For both concentrations, the storage modulus (G') is larger than the loss modulus (G''). This indicates that the behavior is mainly elastic. Logically, the elastic contribution appears larger when the polymer concentration is increased. However, there is less than one decade between both moduli (even for the higher concentration) and the storage modulus (G') remains slightly frequency dependent. These last observations do not fully agree with the strict definition of a gel. It seems that the rheological behavior of mono-grafted HMCMC is more relevant of a pseudo-gel or a 'gel-like' behavior. In such system, one can consider that the dynamic of polymer

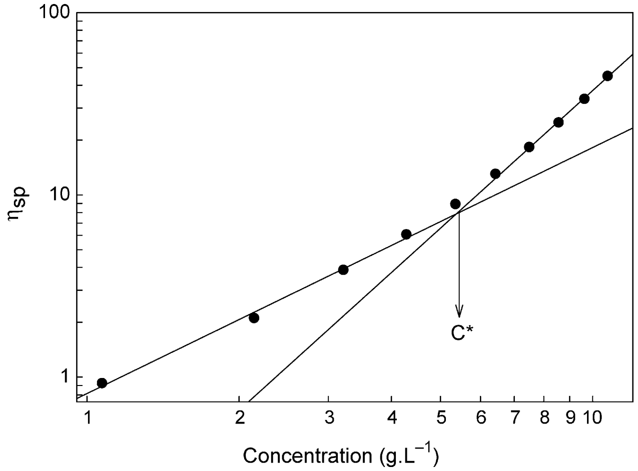

Fig. 1. Example of critical concentration (Ccr) determination by plotting the bilogarithmic representation of zero-shear specific viscosity as a function of concentration for CMC in 0.1 M NaCl at 25 °C.

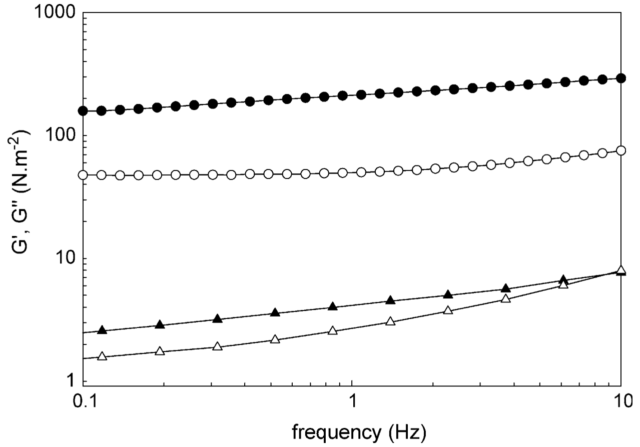

Fig. 2. Mechanical spectra for mono-grafted CMC (CMC-9C_{12-18}) in pure water (25 °C) at 9 g L^{-1} (triangles) and 21 g L^{-1} (circles). G', full symbols and G'', open symbols.

chains is strongly reduced in the range of observed times. This might be explained by the existence of rapid forming and reversible hydrophobic associations that behave like mobile stickers which largely decrease the mobility of entangled chain (Aubry & Moan, 1994; Leibler, Rubinstein, & Colby, 1991). To support this view, we have analyzed the creep behavior of CMC-9C_{12-18} for various temperatures (15, 25 and 40 °C). The results are reported in the Fig. 3. When the temperature is increased, the visco-elastic response progresses from a main elastic behavior (15 °C) to a main viscous one (40 °C). This result clearly shows that the system cannot be described by strongly and physically cross-linked chains according to gel definition but is rather characterized by sticky entangled chains for which the relaxation appears largely function of Brownian motion.

3.2.2. Flow measurements

The flow behavior of the monografted HMCMC has been measured in pure water for both concentrations (i.e. 9 and 21 g L^{-1}). Fig. 4 shows the plots of the apparent viscosity as a function of stress (a) and the plots of shear rates as a function of stress (b). On this last plot (Fig. 4b) have been reported both increasing and decreasing stress sweeps in order to evaluate a possible thixotropy.

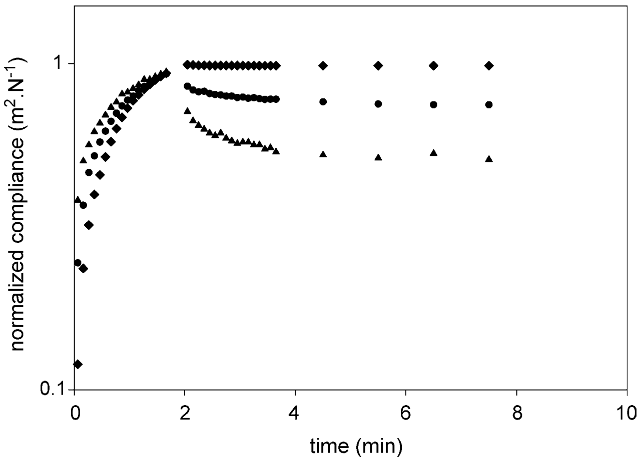

Fig. 3. Creep curves for mono-grafted CMC (CMC-9C_{12-18}) in pure water at 16 g L^{-1} as a function of temperature (▲, 15 °C; ●, 25 °C; ◆, 40 °C)

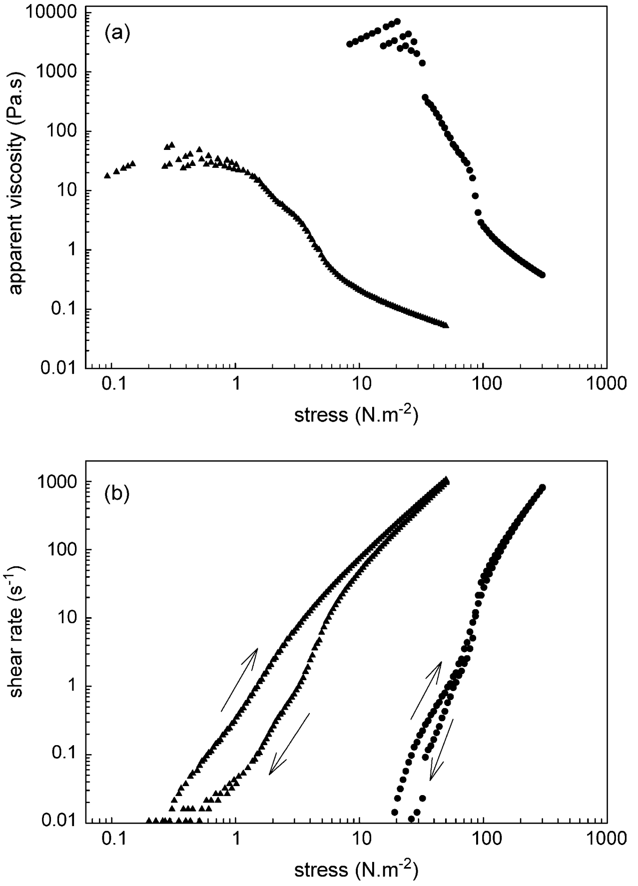

Fig. 4. Apparent viscosity (a) and shear rates (b) as a function of stress for mono-grafted CMC (CMC-9C_{12-18}) in pure water (25 °C) at 9 g L^{-1} (▲) and 21 g L^{-1} (●). For (b), increasing and decreasing sweeps of stress are identified by up and down arrows, respectively.

The low shear rate viscosity drastically increases as the concentration increases and the results show a strong shear thinning behavior which is more pronounced for the higher concentration. No artifacts of measurements (Magnin & Piau, 1990), as fracture or expulsion of the sample from the geometry has been observed during the analysis and the reproducibility of this phenomenon has been verified. The decrease in viscosity is drastic and occurs in a narrow range of stress values. This extreme rheological behavior appears quite similar to the behavior of dispersions (Goodwin & Hugues, 1997). In the same way, Fig. 4(b) should be characteristic of yield stress fluids with a thixotropy behavior that decreases for higher concentration. The restoration of the zero shear viscosity is faster for higher concentrations. This can be explained by the specific concentration of hydrophobic moieties in the bulk which logically increases with the polymer concentration. Consequently, it can be expected that both hydrophobic association probabilities and kinetic are increased with polymer concentration. The type of shear thinning behavior may be characteristic of a weak gel or a 'pseudo-gel' structure of a concentrated colloidal dispersion as mentioned by Ross-Murphy (1995).

Taken as a whole, the results are surprising as they are characteristic of both sticky entangled chains and colloidal dispersions. It can be assumed that the system is mainly heterogeneous and consists of some very dense aggregates that coexist and may be connected to entangled sticky associative chains.

The flow properties of these modified CMC in pure water are very peculiar. The present system shows a strong shear-thinning behavior with a large decrease of viscosity (often more than 1 decade) that occurs over a specific range of stresses (critical stress σ_c). The range of this critical stress is narrower when the polymer concentration is increased. Moreover, a thixotropic character has been evidenced together with a recovery of gel like structure at rest. Manipulation of behavior for specific applications can be envisaged by the choice of the polymer concentration (manipulated variable) for stress-control of the drastic shear-thinning behavior.

The effect of ionic strength (pure water, 0.1 and 0.01 M NaCl) on the flow behavior of the mono-grafted HMCMC is shown in Fig. 5. The viscosity drastically decreases as the salinity increases. Electrostatic repulsion ensure that both the solubility of the amphiphilic polymer and the high viscosity of the system are reduced by added salts. Consequently, the polymer chains can coexist at shorter distance and hydrophobic interactions are expected to be reinforced for synthetic water soluble associative polymers in dilute and semi dilute solutions by many authors (Magny, Iliopoulos, & Audebert, 1994; Wang, Iliopoulos, & Audebert, 1988). For most polyelectrolyte associative systems in the semi-dilute regime, the ionic strength induces a great increase in viscosity by reinforcing intermolecular hydrophobic associations, but in our case we did not observe this effect. To explain this difference, one can involve the lower solubility of HMCMC with increasing ionic strength (Senan, Meadows, Shone, & Williams, 1994) as compared to synthetic amphiphilic polymers (based on polyacrylates for example) because the charge density is lower in the case of HMCMC. In this way, the drastic fall of viscosity that has been observed in the case of HMHEC in the presence of salt could be explained by a local collapses occurring for the supposed aggregates but also due to sticky hydrophobic associations.

3.3. The rheological behavior of the bi-grafted HMCMC (comparison with the mono-grafted HMCMC)

3.3.1. Dynamic analysis

In order to compare the results obtained for the mono-grafted HMCMC, the same oscillatory measurements have been conducted on the bi-grafted polymer (CMC-$30C_4$-$3C_{12-18}$). Fig. 6 shows the frequency sweeps dependence of G' and G'' for 9 and 21 g L^{-1}. As for the mono-grafted HMCMC, only these two concentrations have been reported for clarity in Fig. 6.

A brief analysis of the results leads to similar conclusions to those obtained for the mono-grafted sample. The only slight difference occurs in the value of the storage modulus (G'), which is noticeably lower than obtained for the mono-grafted HMCMC at the same concentration. This observation is fully confirmed when taking a look at the Fig. 7 which represents the evolution of storage modulus (at 1 Hz) as a function of both mono and bi-grafted polymer concentration between 9 and 21 g L^{-1}. As a first remark, the number of sticky zone along the polymer are expected to be lower for the bi-grafted polymer than for the mono-grafted one. Bi-grafted polymer present 3% of C_{12-18} alkyl chains against 9% for the mono-grafted polymer, a loss of 6% which is expected to be compensated by the addition of

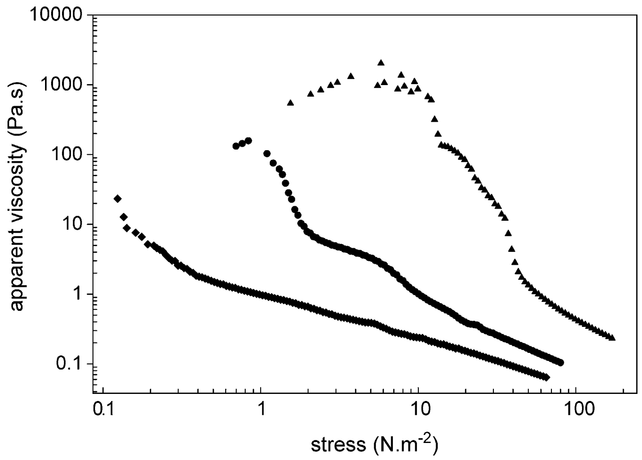

Fig. 5. Apparent viscosity as a function of stress for mono-grafted CMC (CMC-$9C_{12-18}$) at 25 °C and 16 g L^{-1} as a function of ionic strength (pure water ▲, 0.01 M NaCl ●, 0.1 M NaCl ◆).

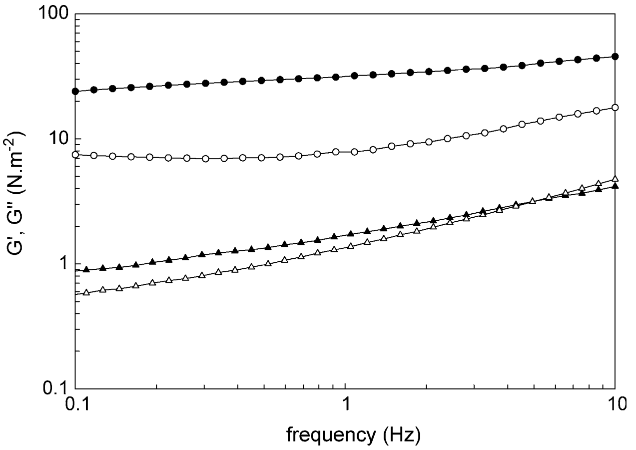

Fig. 6. Mechanical spectra for bi-grafted CMC (CMC-$30C_4$-$3C_{12-18}$) in pure water (25 °C) at 9 g L^{-1} (triangles) and 21 g L^{-1} (circles). G', full symbols and G'', open symbols.

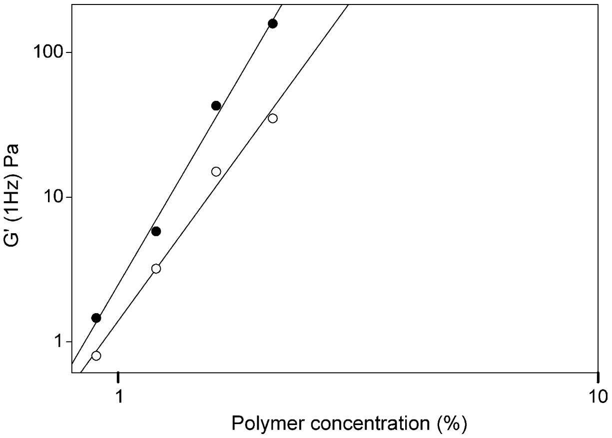

Fig. 7. Storage modulus (G' at 1 Hz) as a function of both HMCMC concentration in pure water (25 °C). ● For CMC-9C_{12-18}, ○ for CMC-30C_4-3C_{12-18}.

30% of C_4. It appears that the contribution of 30% of C_4 alkyl groups is not absolutely equivalent to such a loss of long chains. Therefore, the short chains probably make a contribution to the improvement of the rheological properties. The most important information is that the rheological properties, at low strains, of the bi-grafted polymer are qualitatively similar to that of mono-grafted polymer as shown in Fig. 8 which reports the values of tangent δ (G''/G') at 1 Hz for both HMCMC concentrations. However, it appears that the bi-grafted CMC evidences always a lower tangent δ in comparison with the mono-grafted one. This result seems to indicate the elastic contribution is much pronounced for the bi-grafted CMC. In fact, the bi-grafted CMC seems to present a lower number of associative zones ($G'_{\text{bi-grafted}} < G'_{\text{mono-grafted}}$) than the mono-grafted according to its lower extent of the long alkyl chain. At the same time, the presence of a large amount of short alkyl chains in the bi-grafted CMC seems to lead to more elastic associated zones ($\tan \delta_{\text{bi-grafted}} < \tan \delta_{\text{mono-grafted}}$) compared to the mono-grafted CMC.

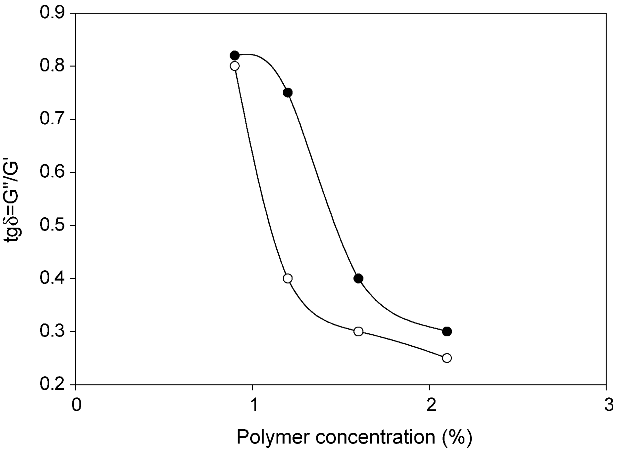

Fig. 8. Tan δ (1 Hz) as a function of both HMCMC concentration in pure water (25 °C). ● For CMC-9C_{12-18}, ○ for CMC-30C_4-3C_{12-18}.

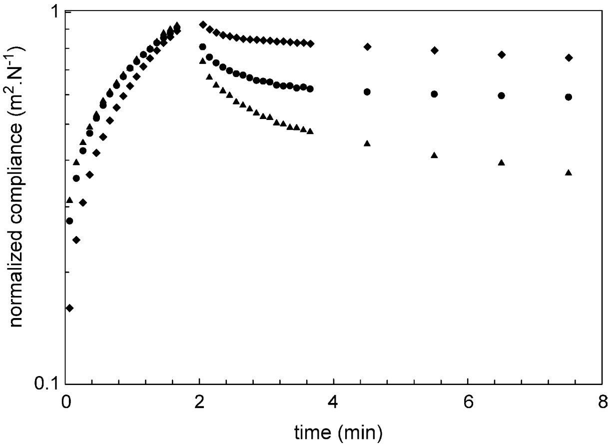

Fig. 9. Creep curves for bi-grafted CMC (CMC-30C_4-3C_{12-18}) in pure water at 16 g L^{-1} as a function of temperature (▲, 15 °C; ●, 25 °C; ◆, 40 °C).

Creep experiments have been conducted on bi-grafted HMCMC solutions in the conditions described before for the mono-grafted polymer (i.e. 15, 25 and 40 °C). The results are reported on the Fig. 9. Once again both modified polymer present the same behavior: a loss of elastic properties as the temperature increases. This result is significant of an sticky entangled chain behavior. It seems that for the higher temperature (40 °C) the elasticity remains slightly larger for the bi-grafted polymer as compared to the mono-grafted one. This observation suggests that if the number of association zones is probably lower for the bi-grafted polymer than for the mono-grafted, the high amount of C_4 moieties together with the longer chains give rise to stronger hydrophobic association than long chains alone. These results appear consistent with the dynamic ones reported above.

3.3.2. Flow measurements

As for the mono-grafted polymer, flow measurements have been conducted on the bi-grafted HMCMC. Fig. 10(a) and (b) represents, respectively, the apparent viscosity as a function of stress and the shear rates as a function of stress (increasing and decreasing sweeps). The behavior is similar for both mono and bi-grafted polymers. A strong and drastic shear-thinning flowing is evidenced that occur for a very narrow range of stresses, which indicates an extreme rheological behavior. For the same range of concentrations, the bi-grafted polymer presents slightly lower zero shear viscosity than the mono-grafted polymer. This result appears consistent with the above dynamic ones.

Some differences in the flow behavior between both modified polymers can be, however, pointed out. First of all the yield stress characteristics that have been evidenced for the mono-grafted polymer is not so obvious for the bi-grafted CMC even at the higher concentration. The second point, which appears important regardless to potential

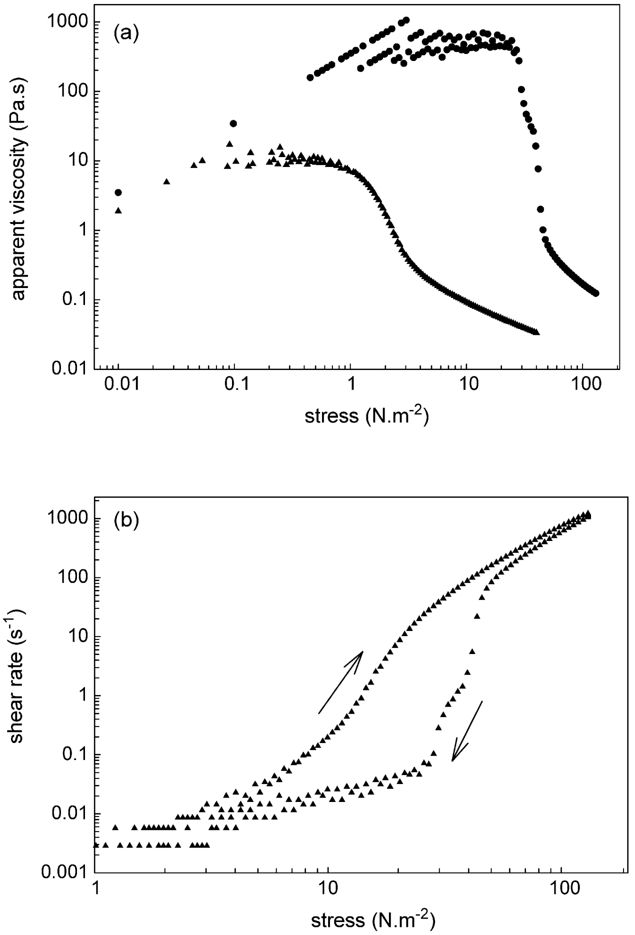

Fig. 10. Apparent viscosity (a) and shear rates (b) as a function of stress for bi-grafted CMC (CMC-30C_4-3C_{12-18}) in pure water (25 °C) at 9 g L^{-1} (▲ for a and b) and 21 g L^{-1} (● for b). For (b), increasing and decreasing sweeps of stress are identified by up and down arrows, respectively.

applications, concerns the thixotropy that is really more pronounced in the case of the bi-grafted polymer. Considering that long alkyl chains are the most effective in association and so in rheological improvement, the lower extent of C_{12-18} for the bi-grafted CMC, as compared to the mono-grafted CMC, may explain that the reformation of reversible physical and associated entanglement needs more time.

The effect of an increase of the ionic strength has also been studied for the bi-grafted polymer throughout flow measurements (Fig. 11). Compared to the mono-grafted CMC, one can observe the same tendency that means a strong decrease of the viscosity. The explanations are similar to those above exposed. However, it appears that the phenomenon is less drastic in the case of the bi-grafted CMC as showing by the viscosity fall between pure water and 0.01 M NaCl that is higher for the mono-grafted CMC as compared to the bi-grafted homologue. The supposed collapse seems less pronounced for bi-grafted polymer. This result should confirm the previous discussions, which indicate that the association zone is mainly due to long alkyl moieties.

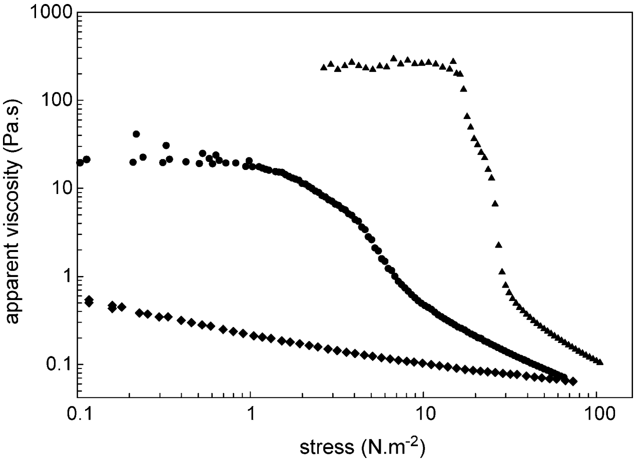

Fig. 11. Apparent viscosity as a function of stress for bi-grafted CMC (CMC-30C_4-3C_{12-18}) at 25 °C and 16 g L^{-1} as a function of ionic strength (pure water ▲, 0.01 M NaCl ●, 0.1 M NaCl ◆).

4. Conclusion

The main objective of this work was to compare the rheological properties of two different hydrophobically modified CMC varying by their HLB.

A mono-grafted CMC bearing 9% of a mixture of long alkyl chain (C_{12-18}), called CMC-9%C_{12-18}, develop in concentrated solution very interesting and surprising rheological properties. A large increase of viscosity is observed as the concentration increases, and more interesting a drastic shear-thinning behavior that occurs in a very narrow range of stress values. This behavior is accompanied with a slight thixotropy, which decreases as the concentration is increased. In fact, this behavior might be described by a compromise between a sticky entangled polymer system and a colloidal dispersion. This point of view can be consistent with the establishment of fluctuating and reversible hydrophobic junction zone (sticky entanglements) and the establishment of very compact hydrophobic zone acting as local hydrophobic collapse which can be connected or not to the entanglement (colloidal dispersion look like). Such a system may be consistent with the drastic collapse observed with ionic strength.

The second main result shows that it appears possible to maintain the very interesting rheological properties of the mono-grafted CMC together with increasing the hydrophobic character. This has been evidenced by the similitude in rheological behavior between the mono-grafted CMC-9C_{12-18} and the bigrafted CMC-30C_4-3C_{12-18}. As a consequence, it is probably possible to largely improve the interfacial properties (by adding a large amount of short alkyl moieties) together with the storage of very specific rheological properties. This may open a large field of investigation in specific application such as cosmetic, paints etc.

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