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Rheological properties of sulfoacetate derivatives of cellulose[☆]

Gaëlle Chauvelon, Jean-Louis Doublier, Alain Buléon, Jean-François Thibault,
Luc Saulnier*

INRA Centre de Recherche Agro-Alimentaire, BP 71627, 44316 Nantes Cedex 03, France

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Abstract

Water-soluble cellulose acetate sulfate derivatives (CAS) have been prepared through chemical reaction involving sulfuric acid as a catalyst. These CAS have been obtained from cellulosic materials of different origins (pure cellulose, wheat bran, maize bran) and their rheological behavior in salt-free aqueous solution has been estimated in dilute and semi-dilute regime using dynamic viscoelastic and viscosity measurements. Influence of concentration, temperature of solubilization and temperature of measurement has been investigated. Weak gel-like properties were exhibited at elevated concentration (typically above 7–8 g/L). These systems also exhibited thixotropic properties: the structure was partly broken down upon shearing and recovered at rest. They also displayed thermoreversibility with large hysteresis, the melting temperature being ~15 °C higher than the temperature at which gelation took place. These overall observations clearly indicate that these distinctive properties arise from intermolecular association of the macromolecular chains of the cellulose derivative. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Cellulose; CAS; Water-soluble cellulose derivatives; Rheological properties; Gelling temperature; Melting temperature

1. Introduction

Cellulose derivatives, and in particular cellulose acetate have found important application in industry. A requirement for cellulose acetate to be water-soluble is that the degree of substitution should be lower than **1**.[2–6] At present, the only way to achieve this condition is the preparation of cellulose triacetate derivatives in a first step,[2,3,6,7] followed by its subsequent hydrolysis to cellulose monoacetate in an aqueous mineral acid solution[3,6] or by metal-catalyzed methanolysis of cellulose triacetate.[4,7] We described recently a new and efficient method to prepare water-soluble cellulose derivatives by direct acetylation of cellulose using sulfuric acid as catalyst.[1,8] This new cellulose derivative was a cellulose acetate sulfate esterified both by sulfuric acid (degree of sulfation of 0.3) and acetic anhydride (degree of acetylation between 1.8 and 2.4); a random distribution of sulfate groups was evidenced after deacetylation under mild hydrolysis conditions followed by partial enzymatic degradation.[9]

These derivatives seemed to exhibit outstanding properties as assessed from their behavior in dilute conditions. These would arise from a competition between hydrophilic groups (sulfate), which confer a good solubility in water, and hydrophobic groups (acetate), which probably mediate or modulate associations between polymer chains.[1] Another interest of direct acetosulfation is that depolymerization during the reaction appears to be minimized.[9] However, these CAS appeared insoluble in the presence of salt.[1] In the present work, water-soluble cellulose derivatives have been prepared following this procedure from pure commercial cellulose and cellulose-enriched residues from wheat bran and maize bran. The chemical composition of the cellulose derivative was similar and only the yield of esterified product was lower for cellulose-enriched residues due to the lower cellulose content in the starting material.[1] The rheological behavior of these CAS has been investigated in dilute and semi-dilute regime on the basis of the flow behavior and dynamic measurements.

[☆] Water-soluble cellulose esters,[1] Part 2.

* Corresponding author. Tel.: +33-2-40675062; fax: +33-2-40675066

E-mail address: saulnier@nantes.inra.fr (L. Saulnier).

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Table 1
Yield in esterified product (g/g), chemical composition (mg/g), degree of acetylation (DS_{Ac}) and sulfation (DS_{Sulf}) and intrinsic viscosity ([η], mL/g) of water soluble cellulose acetate sulfate

	Avi [a]	WB_3	WB_4	MB_1	MB_2
Treatment of starting bran	no	$NaClO_2$; KOH [b]	$NaClO_2$;KOH+$NaBH_4$ [c]	KOH+$NaBH_4$ [d]	KOH+H_2O_2 [e]
Yield in esterified product	1.7	1.2	1.2	1.2	1.3
Non-cellulosic sugar [f]	11	89	114	100	75
Glucose	531	408	434	443	445
Esterified acetic acid	330	320	285	262	308
DS_{Ac}	2.3	2.4	1.9	1.8	1.8
Esterified sulfuric acid	83	100	95	70	87
DS_{Sulf}	0.3	0.4	0.3	0.3	0.3
[η]25 °C in water	1470	1476	768	637	642

[a] Cellulose Avicel.
[b] Wheat bran treated with KOH 2 mol/L.
[c] Wheat bran treated with KOH 2 mol/L+1% (w/w) $NaBH_4$.
[d] Maize bran treated with KOH 1.5 mol/L+1% (w/w) $NaBH_4$.
[e] Maize bran treated with KOH 1.5 mol/L+1% (v/w) H_2O_2.
[f] Non-cellulosic sugar = arabinose, xylose, mannose and galactose.

2. Results

2.1. Chemical composition of CAS

The chemical treatment used to obtain cellulose-enriched residues from maize bran and wheat bran has been previously described.[10,11] The main differences between cellulose-enriched samples arose from the cellulose content (380–730 mg/g) and from the viscosity-average degree of polymerization of cellulose chains (DP_v between 270 and 1250).

The main physico-chemical characteristics of cellulose derivatives are given in Table 1. The cellulose derivatives obtained from the cellulose-enriched samples (WB_3, WB_4, MB_1 and MB_2) and from pure Avicel cellulose (Avi) had a similar composition.[1] For all the samples, the cellulose content was between 408 and 531 mg/g and a first difference dealt with the amount of non-cellulosic sugar since cellulose-enriched residues contained residual heteroxylans. The degree of acetylation was about 2.3 for Avi and WB_3 and about 1.8 for WB_4, MB_1 and MB_2. The degree of sulfation reached in every case 0.3–0.4. Large variations of the reduced viscosity in water were noticed. These ranged between 630 and 2130 mL/g at 0.5 mg/mL and 25 °C. The two samples with the highest degree of acetylation (Avi and WB_3) had the highest viscosity.

2.2. Preparation conditions and overall rheological properties; definition

We previously reported that CAS is soluble in water but cannot be directly solubilized in NaCl solution.[1] In the present study, we report on the properties of salt-free CAS aqueous solutions. Cellulose derivatives were solubilized at various temperatures (25–100 °C) and kept for 1 h at this temperature. A solution was also kept for 16 h at 80 °C. In order to estimate the chemical stability of the solution, the amount of sulfate possibly released during solubilization experiments was measured (Table 2). Whatever the temperature, only very few free sulfate was detected in solution indicating a good chemical stability within the range of temperature investigated. This has also been reported by Klemm and co-workers[13] for cellulose sulfate in the purified acid-free state when stored at 100 °C for a long time.

Upon dispersion of CAS in water at room temperature, a turbid solution was obtained indicating incomplete solubilisation. This turbidity disappeared near 80 °C. Moreover, the solution remained clear upon cooling at room temperature. This is evidence that

Table 2
Amount of sulfate (mg/g) released after heating cellulose acetate sulfate solution (prepared from Avi)

	Temperature of solubilization (°C)				
Time of treatment	25	40	60	80	100
1 h	0.4	0.5	0.6	0.5	0.6
16 h	nd	nd	nd	0.9	nd

nd: not determined.

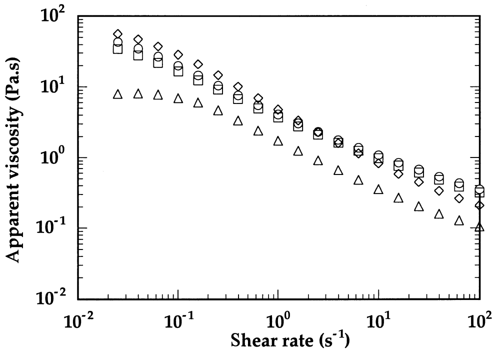

Fig. 1. Influence of the shear rate on the apparent viscosities at 20 °C of the cellulose acetate sulfate solution (10 mg/mL, prepared from Avi) after solubilization at 25 (circles) 45 (squares), 80 (lozenges) and 100 °C (triangles).

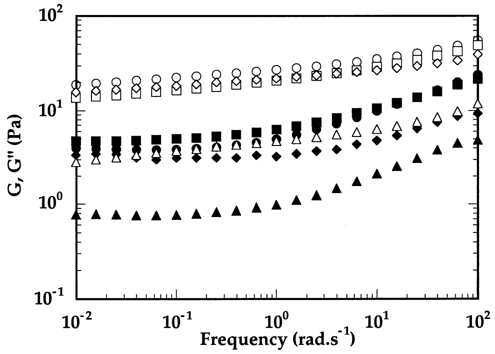

Fig. 2. Frequency dependence at 20 °C of the G' (open symbols) and G'' (closed symbols) modulii of the cellulose acetate sulfate solution (10 mg/mL, prepared from CA) after solubilization at 25 (circles), 45 (squares), 80 (lozenges) and 100 °C (triangles). Strain amplitude 0.5%.

heating improves solubilisation of CAS. The flow curves of 10 g/L CAS solutions (from pure cellulose) at four solubilization temperatures (25, 45, 80 and 100 °C) is shown in Fig. 1. Measurements were performed at 20 °C. We show here the results obtained after performing two thixotropic loops (see Section 4). As will be discussed latter, the curves that are displayed in Fig. 1 can be regarded as equilibrium curves after shearing at 100 s^{-1}. They all exhibited a shear-thinning behavior. However, clear differences between preparation temperatures were observed. The flow curves obtained at 25 and 45 °C had a similar profile. Surprisingly, heating to 80 °C yielded a more pronounced shear-thinning than at 25 and 45 °C: the apparent viscosity was higher at low shear rate and lower at high shear rate. The flow curve obtained after solubilization at 100 °C showed a Newtonian zone at low shear rate. The viscosity was much smaller in these conditions, indicating a possible thermal degradation. The flow curves obtained after solubilisation at 80 and 100 °C could be well described using the Carreau model (Eq. (1)) (Fig. 1), allowing one to estimate the Newtonian limiting viscosities η_0 and η_∞, towards the low shear rate and the high shear rate ranges, respectively.

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{(1 + (\tau\gamma)^m)^{1 - x/m}} \tag{1}$$

τ, relaxation time; γ, shear rate; η_0, viscosity at zero shear rate; η_∞, viscosity at infinite shear rate; m and x without dimension.

Value for η_0 was found to be 80 and 8 Pa s for solubilisation at 80 and 100 °C, respectively, and η_∞ was 0.17 and 0.07 Pa s after solubilisation at 80 and 100 °C, respectively. In contrast, the flow curves obtained after solubilisation at 25 and 45 °C could not be described using the Carreau model.

The viscoelastic behavior of CAS at these 4 solubilisation temperatures is illustrated in Fig. 2. For 25, 45 and 80 °C, the viscoelastic spectra appeared quite similar. The storage modulus (G') was much higher than the loss modulus (G''). G' increased slightly with the frequency while G'' was almost constant at low frequency but increased slightly beyond 1 rad/s. Such a behavior is reminiscent from the viscoelastic properties of a weak gel. Slight differences could be noticed however. From 25 to 45 °C, G' was slightly reduced whereas G'' increased. This means that there was a loss of the elastic character as can be illustrated by the comparison of tan δ ($= G''/G'$) values: 0.35 for 45 °C against 0.21 for 25 °C at 0.01 rad/s for example. At 80 °C, the frequency dependence of both moduli was slighter, indicating the gel like properties to be more pronounced. At 100 °C, G' and G'' moduli were dramatically depressed indicating clearly the elastic character to be less pronounced. This strong decrease in G' as well as in viscosity at 100 °C suggests a possible degradation of the macromolecules as has been showed by Klemm and co-workers[13] who reported a reduction of viscosity when keeping cellulose sulfate at 100 °C for a long time.

Other preparation parameters play a role in the properties of CAS dispersions. The effect of the cooling rate is illustrated in Fig. 3. Large differences were found when cooling the dispersions at 5 °C/min instead of 1 °C/min. A slow cooling resulted in much higher G' values (370 Pa instead of 135 Pa at 0.01 rad/s) while the shape of the curves was similar (tan δ at 0.01 rad/s of the order of 0.2). It is worth noting that the system changed upon ageing as illustrated in Fig. 3. A long storage (30 days) resulted in much higher G' values (220 Pa instead of 135 Pa at 0.01 rad/s). Low cooling rate and storage time appear favorable to the structuration of the system. The present results show that a heating treatment of 80 °C followed by a slow cooling rate can be taken as a good compromise for the preparation of aqueous CAS dispersions.

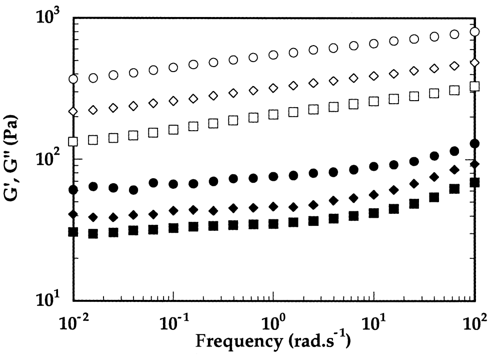

Fig. 3. Frequency dependence at 20 °C of the G' (open symbols) and G'' (closed symbols) modulii of the cellulose acetate sulfate solution (20 mg/mL, prepared from Avi) cooled at 1 °C/min (circles) and at 5 °C/min ($t = 0$ squares; $t = 30$ days lozenges).

2.3. Influence of CAS concentration

2.3.1. Flow properties. The flow properties have been assessed in two steps as described in Section 4. In a first step, two successive cycles have been linearly programmed with shear rates varying linearly from zero to 100 s^{-1} and then back to 0. This provides a way to estimate the shear susceptibility of the system and the 'up' and 'down' plot is therefore referred to as 'thixotropic loop'. After performing these two cycles, step rate measurements were performed with a logarithmic programming from 100 s^{-1} down to 0.025 s^{-1} in order to describe the flow curve with a higher accuracy.

The 'thixotropic' loops of CAS solutions at various concentrations (5, 10, 15 and 20 g/L) are showed in Fig. 4. A strong influence of the polymer concentration was observed. At concentrations lower than 4 g/L, the behavior was Newtonian (not shown). At 5 g/L, the dispersions exhibited a shear-thinning (non-Newtonian) and non-thixotropic behavior (curve a). At higher concentrations (10–20 g/L), the CAS dispersions exhibited a highly thixotropic behavior with a large loop between the first 'up' and 'down' shear rate cycle. Only results from the first cycle are displayed: the second cycle resulted in superimposed 'up' and 'down' curves which furthermore coincided with the 'down' curve of the first cycle. This disappearance shows that a pseudo-equilibrium state is attained which is defined by the upper imposed shear rate (100/s). This justifies the fact that step-rate measurements can be performed to describe this pseudo-equilibrium state as illustrated by the results shown in Fig. 1. On the other hand, the extent of thixotropy could be estimated from the relative area of the loops as defined by the ratio of the area of the loop to that delimited by the 'down' curve and the x-axis.

At 10 g/L, a highly thixotropic behavior with a large loop appeared, indicating that the structure is quite easily broken down. The stress overshoot seen at ~2 s^{-1} indicates a high elasticity of the system. At 15 g/L, the overshoot was still present and the thixotropic behavior was much more pronounced as shown by the increase of the relative area of the loops (79% at 15 g/L instead of 44% at 10 g/L). At 20 g/L, the overshoot and the thixotropic behavior were still more pronounced. However, the 'up' curve appeared rather irregular. This may be ascribed to a high heterogeneity of the system likely due to the presence of aggregates. Furthermore, when performing the second cycle, a loop was still seen although its area was limited. A third cycle probably would be required to yield its total disappearance. Another point to be mentioned is the recovery of the structure. This can be easily evaluated by performing a second loop after a resting time. For example, for the 15 g/L dispersion, after a resting time of 1 h, about 77% of the structure was recovered as estimated from the area of the thixotropic loop (the area of each loop was estimated and the ratio of the second to the first one was determined).

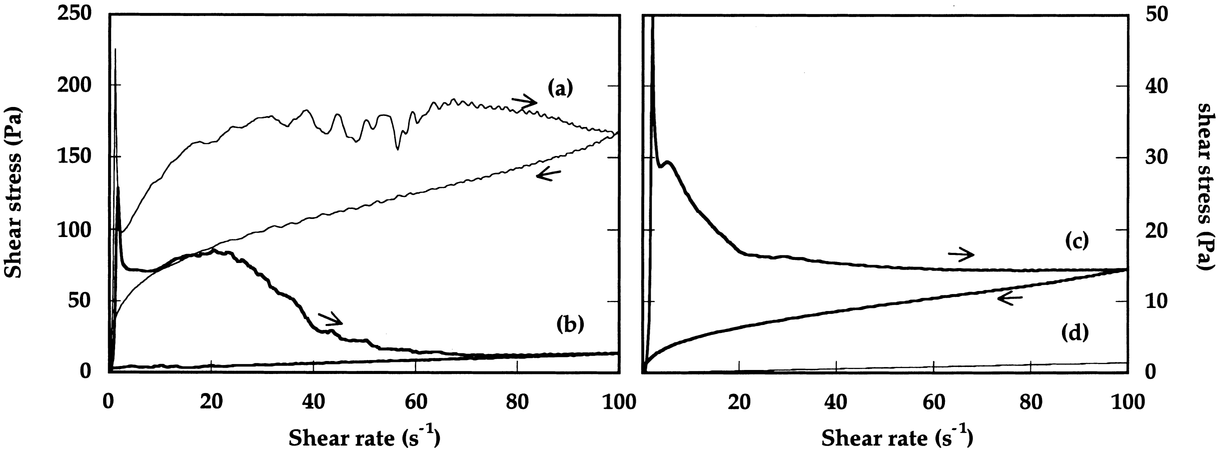

Fig. 4. Flow curves at 20 °C of the cellulose acetate sulfate solution (prepared from Avi) at 20 (a), 15 (b), 10 (c) and 5 mg/mL (d). Arrows indicate up and down phase of shear rate cycle.

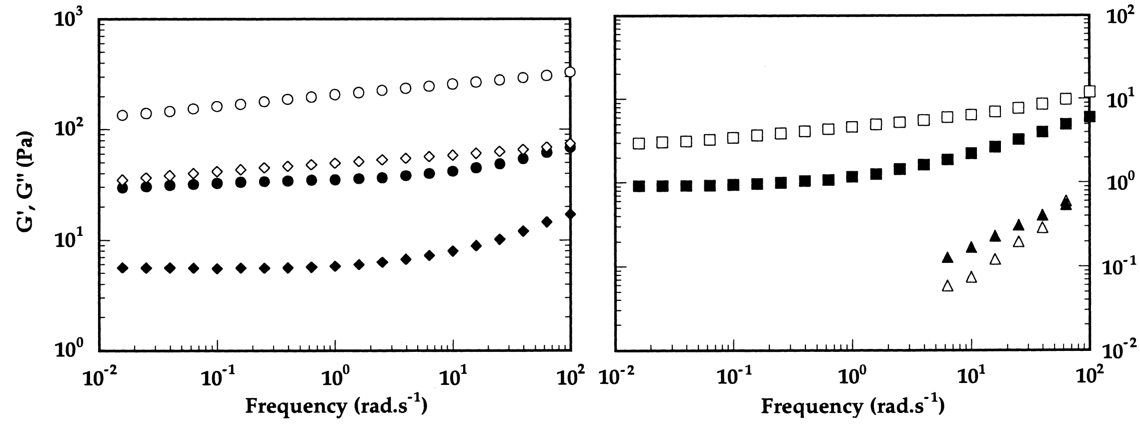

Fig. 5. Frequency dependence at 20 °C of the G' (open symbols) and G'' (closed symbols) modulii of the cellulose acetate sulfate solution (prepared from Avi) at 20 (circles), 15 (lozenges), 10 (squares) and 7.5 mg/mL (triangles). Strain amplitude 0.5%.

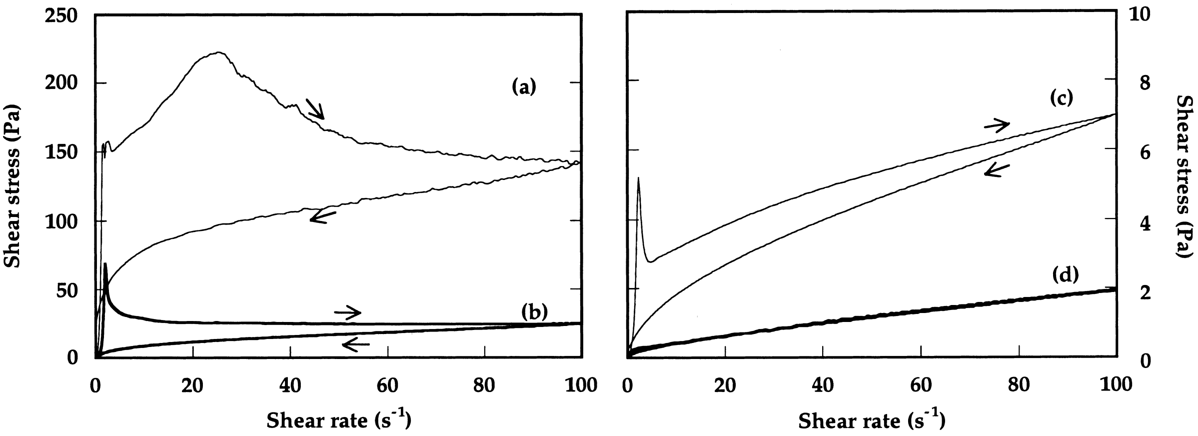

Fig. 6. Flow curves at 20 °C of the cellulose acetate sulfate solution (prepared from MB_2) at 20 (a), 15 (b), 10 (c) and 5 mg/mL (d). Arrows indicate up and down phase of shear rate cycle.

2.3.2. Viscoelastic properties. The viscoelastic behavior of these CAS dispersions is illustrated in Fig. 5. For the lowest concentration (7.5 g/L), G' and G'' increased with frequency with G' lower than G'' at low frequency and a crossover at high frequency, the slopes of $G'(\omega)$ and $G''(\omega)$ were 0.6 and 1, respectively (Fig. 5). Such a behavior is reminiscent of a macromolecular solution despite the theoretical slopes at low frequency should be 1 and 2, for G'' and G', respectively. For concentrations of 10 g/L, G' was higher than G'' over the all frequency domain. G' increased slightly with frequency while G'' was almost constant at low frequency but slightly increased beyond 1 rad/s as already mentioned. At 15 and 20 g/L, G' and G'' were much higher while tan δ was of the same order for these two concentrations (~ 0.2 at 0.01 rad/s) and lower than for 10 g/L dispersions (0.3 at 0.01 rad/s), indicating the elastic character to be more pronounced when the concentration increases.

2.4. Origin of cellulosic materials

The previous results have been obtained from CAS from pure Avicel cellulose (Avi). Similar results have been obtained when preparing CAS from cellulose-enriched wheat and maize bran. This is illustrated in Figs. 6 and 7 for CAS from MB_2. The non-Newtonian and shear-thinning behavior appeared for a concentration of about 4 g/L. At 5 g/L, a non-thixotropic and shear-thinning behavior was shown, as previously described for Avi at the same concentration. The viscosity was also comparable for the two samples. A thixotropic loop was seen at a concentration between 5 and 10 g/L. At 10 g/L, a thixotropic behavior also was experienced but this was less pronounced than for CAS from Avi (Fig. 4, curve c). Also, the viscosity was slightly lower for MB_2. Again, the higher the concentration the more noticeable the thixotropic behavior. However, this was less pronounced for CAS obtained from MB_2 than

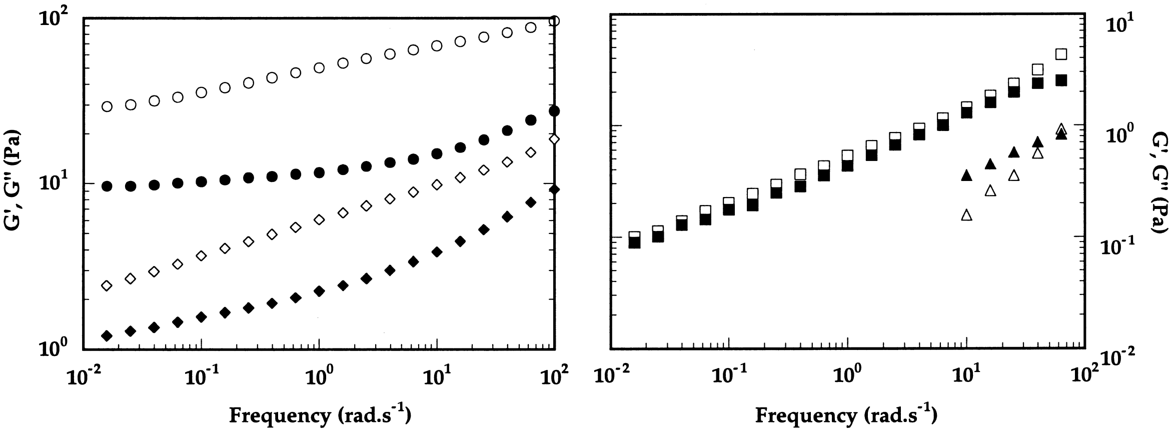

Fig. 7. Frequency dependence at 20 °C of the *G′* (open symbols) and *G″* (closed symbols) modulii of the cellulose acetate sulfate solution (prepared from MB_2) at 20 (circles), 15 (lozenges), 10 (squares) and 7.5 mg/mL (triangles). Strain amplitude 0.5%.

from Avi. For instance, in the case of 15 g/L, the relative area of the thixotropic loop was of 36% for MB_2 instead of 78% for Avi.

The viscoelastic spectra of CAS from wheat and maize bran also showed a behavior similar to that from pure cellulosic material. Thus, at 7.5 g/L (Fig. 7), the behavior of CAS from MB_2 was typical of a macromolecular solution as it could be expected from the non-thixotropic behavior. At 15 and 20 g/L, weak gel-like properties were exhibited. However, 10 g/L presented a quite different behavior when compared with the viscoelastic spectra observed for CAS from Avi at the same concentration. *G′* and *G″* were of the same order over the all frequency range and strongly dependent upon frequency with a slope of about 0.5. Clearly, this behavior is typical of a gelling system lying close to the gel point that is near the sol–gel transition.

Similar observations have been made with the other cellulose-enriched residues. Overall, these results clearly evidence that CAS with distinctive rheological properties can be prepared from such cellulose-enriched materials such as wheat or maize bran. The main differences can be ascribed to differences in molar mass or to the presence of residual heteroxylans.

2.5. Influence of temperature

2.5.1. Behavior in dilute medium. Variations of the reduced viscosity as a function of concentration in dilute conditions at 40, 70 and 80 °C are showed in Fig. 8. The overall variations are reminiscent of the behavior of a polyelectrolyte in salt-free aqueous solutions. Apparently, this polyelectrolyte behavior was more pronounced at 80 °C than at lower temperatures. Furthermore, a dramatic decrease of the reduced viscosity was experienced from 40 to 80 °C. This is more accurately showed in Fig. 9 where the reduced viscosity at 0.5 g/L is plotted as a function of temperature. A sharp decrease was evidenced at ~40 °C while little variation was experienced above 60 °C. Also it is worth mentioning that the values were large with respect to the degree of polymerization of the starting cellulose ($\overline{DP}_v = 210$, evaluated by the Mark Houwink relation, the intrinsic viscosity being determined in cupriethyl-

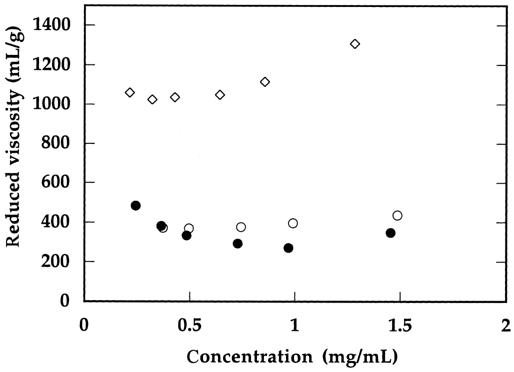

Fig. 8. Concentration dependence of the reduced viscosity of cellulose acetate sulfate solution (from Avi) at 40 (open lozenges), 70 (open circles) and 80 °C (closed circles).

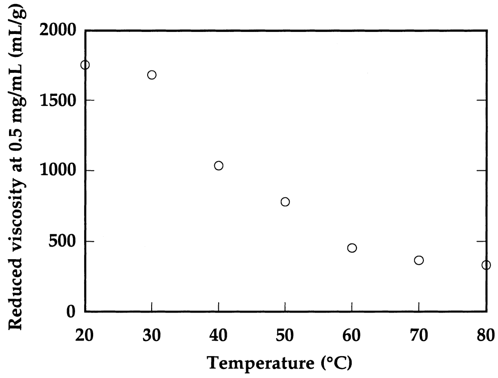

Fig. 9. Temperature dependence of the reduced viscosity of cellulose acetate sulfate solution (0.5 mg/mL, prepared from Avi).

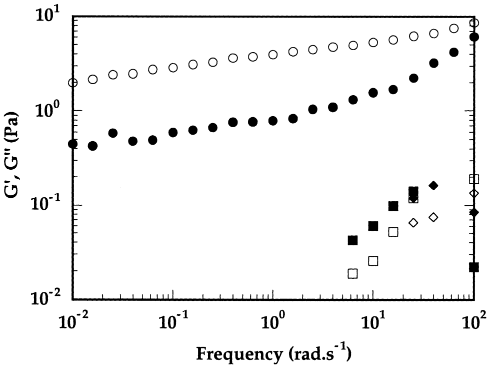

Fig. 10. Frequency dependence of the G' (open symbols) and G'' (closed symbols) modulii of cellulose acetate sulfate solutions (10 mg/mL; from Avi) at 80 °C (starting measurement: lozenges; final measurement: squares) and at 20 °C (circles). Strain amplitude: 0.5 and 5% at 20 and 80 °C, respectively.

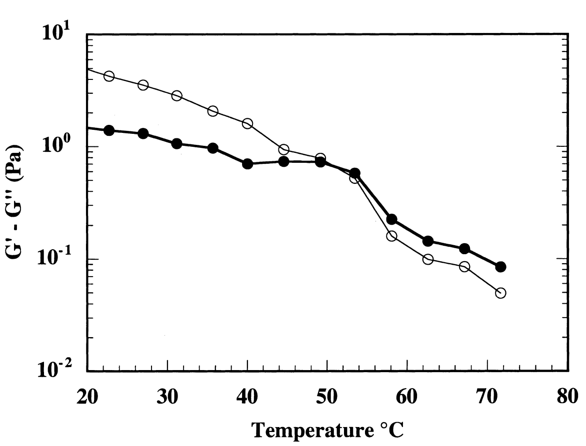

Fig. 11. Temperature dependence of the G' (open symbols) and G'' (closed symbols) moduli at 1 rad/s of cellulose acetate sulfate solution (10 mg/mL, from Avi). Strain amplitude: 0.5% in the 20–40 °C range, 5% in the 45–80 °C range.

enediamine[10,11]) or the cellulose sulfate obtained by deacetylation of CAS ($\overline{\mathrm{DP}}_p = 166$ as determined by HPSEC in $NaNO_3$,[9]). Such values of the reduced viscosity probably do not correspond to the isolated macromolecules but rather to large aggregates. The dramatic decrease (1750–330 mL/g at 0.5 mg/mL) observed when temperature increases from 20 to 80 °C reflects large changes in the volume of these aggregates. This suggests a dissociation of aggregates as temperature increases.

2.5.2. Behavior in concentrated medium. The effect of temperature was also studied during cooling and heating between 80 and 20 °C, every ~ 5 °C, by plotting viscoelastic spectra from 0.1 and 100 rad/s. The dispersion was prepared at 80 °C and measurements were performed from 80 down to 20 and then from 20 to 80 °C. At 80 °C (Fig. 10), the viscoelastic behavior was typical of a macromolecular solution with G' lower than G'', both moduli varying strongly with frequency (with slopes of ~ 0.9 for G' and ~ 1.8 for G'', respectively). Upon cooling, at 20 °C, the dispersion exhibited the behavior of a weak gel as already described.

During the cooling experiment, gelation took place in the range 50–55 °C (Fig. 11): G' and G'' were intermingled but still strongly frequency dependant with a slope of about 0.5. As we previously discussed for the effect of concentration, this is the behavior of a system at the sol–gel transition. When plotting G' and G'' (at 10 rad/s) as a function of temperature (Fig. 11) a cross-over was found at 51.5 °C. Upon reheating, similar variations were exhibited with however an important shift in the melting temperature with respect to the gelling one: weak gel properties were still exhibited at 68 °C and the melting point was close to 70 °C. Furthermore, the viscoelastic spectra measured at 80 °C upon reheating were totally superimposed to the spectra obtained at 80 °C at the beginning. CAS aqueous systems appear thermoreversible but exhibit a large thermal hysteresis.

3. Discussion

The present results are clear illustration that CAS exhibit outstanding rheological properties in salt-free medium. Depending upon concentration, the properties are typical of a macromolecular solution ($c \leq 7.5$ g/L) or of a weak thermoreversible gel ($c \geq 10$ g/L). The best conditions to induce gel formation are a thermal treatment at 80 °C followed by slow cooling, probably owing to an enhancement of association of the cellulose chains. A long storage time also favors the structure formation of the system.

Upon shearing the gelled systems ($c \geq 10$ g/L) in steady conditions (flow measurements), continuous viscosity decay was experienced, the network being broken down by shearing but almost totally recovered at rest. Such a behavior is typical of a thixotropic system.[22] Klemm and co-workers[13] also reported a thixotropic behavior for cellulose sulfate.

These overall rheological properties might arise from intermolecular associations resulting in the formation of micro-aggregates, which would yield the formation of a particulate network when concentration is high enough. The presence of aggregated structures is supported by viscosity measurements in dilute conditions. Indeed, we were unable to determine intrinsic viscosity of our samples owing to their polyelectrolyte character. However, from the determination of reduced viscosity in dilute conditions it was possible to make some comparisons with literature. At room temperature, the reduced viscosity of our samples was high (between 630 and 2130 mL/g, depending upon the cellulose source, at 0.5 mg/mL and 25 °C[1]). These values are of the same order as to other water-soluble cellulose derivatives such as carboxymethylcellulose whose the intrinsic viscosity can be as high as 1230 mL/g.[14] This high reduced viscosity reflects the likely presence of supermolecular structures resulting from associations between chains. The drop in reduced viscosity as temperature increases suggests the size of these supermolecular entities to be depressed strongly. At 80 °C, the supermolecular organization is lost, the macromolecules being individualized as suggests the fact that the reduced viscosity is of the same order as that of cellulose sulfate obtained by deacetylation. The progressive decrease in both viscoelastic and flow properties upon increasing temperature is also to be ascribed to the disruption of aggregates, the system tending to a macromolecular solution at 80 °C, the cellulose macromolecules being individualized. Moreover, similar viscoelastic spectra have been obtained after successive heating and cooling treatment (Fig. 10), indicating complete thermoreversibility although a large hysteresis was experienced. This temperature dependency may be of practical interest in industrial applications.

Whatever the cellulose source, either from pure cellulose or from cellulose-enriched samples, the overall rheological behavior was similar. However, viscoelastic moduli or the apparent viscosity were slightly lower for CAS from cellulose-enriched materials. This can probably be ascribed to the presence of residual heteroxylans as suggested by the presence of non-cellulosic sugars such as xylose and arabinose (Table 1). It implies that CAS with gel-like properties can be produced from low-cost cellulosic materials as well as from pure cellulose.

Thixotropic and shear-thinning characters have been shown for numerous cellulose derivatives such as carboxymethylcellulose,[16] or hydrophobically modified cellulose derivatives such as hydroxyethycellulose or carboxymethylcellulose.[17,18] Associative properties induced by intramolecular associations have been observed for hydrophobically modified carboxymethylcellulose derivatives.[15] The formation of thermoreversible gel in the presence of potassium ions was also reported for cellulose sulfate.[13] The rheological properties of the CAS systems appear comparable, at least with some respects, to the rheological behavior of associative polymers. These latter derivatives are prepared from a water-soluble polymer (carboxymethylcellulose, carboxymethylpullulan or hydroxyethylcellulose) by grafting hydrophobic groups to carbohydrate units.[17] The level of incorporation of the hydrophobic groups is limited in order to keep the polymer water-soluble.[21] These derivatives exhibit a high apparent molar mass and they form an important class of thickeners due to the balance between hydrophobic and hydrophilic characters.[19] Their peculiar rheological properties are ascribed to molecular association of neighboring hydrophobic substituents.[15,17,18,20] In the present study, the CAS samples are highly hydrophobic (degree of acetylation between 1.8 and 2.4) with a few hydrophilic groups (degree of sulfation of 0.3) whose distribution is homogeneous.[1,8,9] Their chemical structure is therefore quite different from hydrophobically modified polymer. However, the rheological properties of CAS systems display some similarities and their properties are also controlled by the balance between hydrophobic and hydrophilic characters. It is likely however that the mechanisms involve other interactions between chains. Further studies have to be undertaken to better understand the rheological behavior of these cellulose derivatives.

4. Experimental

4.1. Materials

Cellulose Avicel PH-101 (Avi) was purchased from Fluka. Wheat bran and maize bran devoid from starch were obtained from ARD (Pomacle, France) and Ulice (Chappes, France), respectively. These raw materials have been submitted to various alkaline treatments to prepare various cellulose-enriched residues referred to as WB_3 and WB_4 for wheat bran and MB_1 and MB_2 for maize bran, respectively (see Table 1).[10,11]

4.2. Chemical modification

Chemical modification of cellulose was performed as previously described.[1,8] Cellulose (1 g) was activated in glacial AcOH and then dispersed in a mixture of glacial AcOH and H_2SO_4 (20 mL and 0.24 g, respectively) and anhydride acetic was finally added (3.2 mol/mol anhydroglucose). The mixture was stirred during 30 min at 40 °C. The reaction was stopped by addition of a mixture of water in AcOH (3:7) and residual particles were removed by centrifugation (2250*g*, 10 min, 35 °C). Supernatant was recovered and slowly added in de-ionized water to precipitate cellulose triacetate (CTA). After 16 h at 4 °C, CTA were removed by centrifugation (17,500*g*, 20 min, and 4 °C). Supernatant was neutralized at pH 7.5 by addition of NaOH (4 mol/L), dialyzed and the water-soluble ester was finally freeze-dried.

4.3. General methods

All results are expressed relative to the dry matter content determined by drying at 120 °C for 3 h. The methods to characterize CAS (neutral sugar, AcOH and H_2SO_4) were previously described.[1,12] CAS solutions were prepared at 20 °C in de-ionized water under magnetic stirring during 1 h at room temperature and then heated at 80 °C during 1 h.

Reduced viscosity was determined in an Ubbelhode viscometer (diameter 0.52 mm, viscologic TI.1 SEMATech, Nice-France). Six measurements were realized for each dilution (1.5, 1.0, 0.75, 0.5, 0.38 and 0.25 g/L). Determinations were performed at different temperatures ranging from 20 to 80 °C. The solutions were filtered (pore diameter 15 μm) before measurement.

Rheological measurements were performed using a controlled strain rheometer (Rheometrics Fluid Spectrometer II) in steady and oscillatory shear with either a cone-plate geometry (diameter 5 cm, angle 0.0397 rad) or a coaxial cylinder attachment (internal diameter 3.2 cm, external diameter 3.4 cm, height 3.3 cm). Most of measurements performed at 20 °C were carried out with the cone-plate device. However, when temperature had to be varied, the coaxial cylinder attachment was used. The samples were prepared at various concentrations (20.0, 15.0, 10.0, 7.5 and 5.0 g/L).

The viscoelastic behavior was assessed by performing oscillatory shear measurements as a function of frequency (viscoelastic spectra) within the range 0.01–100 rad/s. Gelling and melting temperatures were determined performing viscoelastic spectra at different temperatures from 80 to 20 °C and then while heating between 20 and 80 °C. For all the samples, the strain amplitude in oscillatory shear was imposed at 0.5% when measurements were carried out between 20 and 40 °C and 5% between 45 and 80 °C. It was checked that the strain amplitude lay within the linearity limits of the viscoelastic behavior.

The flow behavior was assessed by performing two successive 'thixotropic' loops, that is by programming linearly the shear rate from 0 to 100 s^{-1} and back to 0 for each loops. Then, further viscosity measurements were performed with a shear rate range between 0.025 and 100 s^{-1}. The 'thixotropic' loops were performed prior to viscosity measurements to reach a quasi-stable state defined by the upper shear rate applied (100 s^{-1}).

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References

1. Chauvelon, G.; Buléon, A.; Thibault, J.-F.; Saulnier, L. *Carbohyd. Res.* **2003**, *338*, this issue, doi:10.1016/S0008-6215(03)00008-9.
2. Fordyce, C. R. Cellulose esters of organic acids. *Adv. Carbohydr. Chem. Biochem.* **1945**, *1*, 309–326.
3. Tanghe, L. J.; Genung, L. B.; Mench, J. W. Cellulose. *Methods Carbohydr. Chem.* **1963**, *3*, 193–212.
4. Buchanan, C. M.; Edgar, K. J.; Wilson, A. K. *Macromolecules* **1991**, *24*, 3060–3064.
5. Engelhardt, J. *Carbohydr. Europe* **1995**, *12*, 5–14.
6. Samios, E.; Dart, R. K.; Dawkins, J. V. *Polymer* **1997**, *38*, 3045–3054.
7. Buchanan, C. M.; Edgar, K. J.; Hyatt, J. A.; Wilson, A. K. *Macromolecules* **1991**, *24*, 3050–3059.
8. Chauvelon, G.; Saulnier, L.; Buléon, A.; Thibault, J.-F. FR. Patent 2789080, 2000.
9. Thomas, M.; Chauvelon, G.; Lahaye, M., J.-F.; Saulnier, L. *Carbohydr. Res.* **2003**, *338*, this issue, doi:10.1016/S0008-6215(03)00010-7.
10. Chauvelon, G.; Saulnier, L.; Buléon, A.; Thibault, J.-F.; Gourson, C.; Benhaddou, R.; Granet, R.; Krausz, P. *J. Appl. Polym. Sci.* **1999**, *74*, 1933–1940.
11. Chauvelon, G.; Gergaud, N.; Saulnier, L.; Lourdin, D.; Buléon, A.; Thibault, J.-F.; Krausz, P. *Carbohydr. Polym.* **2000**, *42*, 385–392.
12. Chauvelon, G.; Renard, C. M. G. C.; Saulnier, L.; Buléon, A.; Thibault, J.-F.; Benhaddou, R.; Granet, R.; Krausz, P. *J. Appl. Polym. Sci.* **1998**, *68*, 331–337.
13. Klemm, D.; Philipp, B.; Heinze, T.; Heinze, U.; Wagenknecht, W. *Comprehensive Cellulose Chemistry*; Wiley-Vch: Weinheim, 1998; Vol. 2, pp 115–133.
14. Mitchell, J. R. Rheology of polysaccharide solutions and gels. In *Polysaccharides in Food*; Blanshard, J. M. V.; Mitchell, J. R., Eds.; Butterworths: London, 1979; pp 51–72.
15. Charpentier, D.; Merle, L.; Muller, G. *Les Cahiers de Rhéologie* **1997**, *15*, 251–260.
16. Coffey, D. G.; Bell, D. A.; Henderson, A. Cellulose and cellulose derivatives. In *Food Polysaccharides and their Application*; Stephen, A. M., Ed.; Dekker, Inc: New York, 1995; pp 123–153.
17. Tanaka, R.; Meadows, J.; Phillips, G. O.; Williams, P. A. *Carbohydr. Polym.* **1990**, *12*, 443–459.
18. Charpentier, D.; Mocanu, G.; Carpov, A.; Chapelle, S.; Merle, L.; Muller, G. *Carbohydr. Polym.* **1997**, *33*, 177–186.
19. Bataille, I.; Huguet, J.; Muller, G.; Mocanu, G.; Carpov, A. *Int. J. Biol. Macromol.* **1997**, *20*, 179–191.
20. Tanaka, R.; Meadows, J.; Phillips, G. O.; Williams, P. A. *Macromolecules* **1992**, *25*, 1304–1310.
21. Landoll, L. M. *J. Polym. Sci. Polym. Chem.* **1982**, *20*, 443–455.
22. Mewis, J. *J. Non-Newton. Fluid Mech.* **1979**, *6*, 1–20.