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Characterization and properties of cationic cellulosic fibres

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Abstract

This paper is devoted to the rheological properties of cationic cellulosic fibres with different degrees of substitution and swelling. Depending on the concentration of the fibre suspension, the system behaves as a solution ($C < 5$ g/l) or as a gel. The rheological characteristics of the suspensions are directly related to the degree of substitution, the degree of swelling and the degree of fibrillation of the material.

Keywords: Cationic cellulosic fibres; Rheology; Swelling; Suspension

1. Introduction

Water soluble polymers are developed for many applications for their role as thickeners, gelling, emulsifying polymers or stabilizers for the dispersion of solid particles [1–3]. They are neutral or charged, most generally anionic. Our work concerns the obtention of a new system based on cellulose, a natural and renewable polymer. The first objective was to prepare cationic cellulosic fibres playing the role of a flocculating new system [4]; but the cationic fibres have also other properties depending on their degree of substitution (DS) which impose their charge density and their degree of swelling in aqueous suspension. They present interesting rheological properties and especially a gel-like behaviour which is described in this paper.

2. Experimental

2.1. Materials

Cationic fibres were obtained by the chemical modification of cellulosic materials prepared from agricultural residues, the wheat bran previously fractionated and purified. The pretreatments of this residue are elimination successively of starch, hemicelluloses and lignin. The yield in cellulose in our substrate was around 93%. This cellulose has a $DP_v \sim 440$; it is semi-crystalline with 40% as degree of crystallinity based on cellulose I. The reaction is performed using a heterogeneous process in alkaline conditions with the reactive QUAB 151 from Degussa (QUAB 151 is a 2,3-epoxypropyltrimethylammonium chloride) [4]. Defibrillations of the derivatized fibres were realized under shear using a Nanojet equipment from Haskel General Pneumatic. This step is important to increase the division of the fibrous material and its rheological potential. Cellulosic fibres with different average degrees of substitution were obtained depending on the experimental conditions. When the average value of DS was around 0.6, we found that 15% (w/w) of the material become water soluble and has a DS $\approx$ 0.7 when the DS of the insoluble fraction is 0.4. Each sample was characterized by its average DS, the degree of swelling and the fraction of water soluble material (Table 1).

The xanthan sample used as reference is a commercial one from Rhône Poulenc (France).

2.2. Methods

The degree of swelling (τ in g H_2O/g dried matter) in water is obtained by thermogravimetry on a small sample dispersed in a large volume of water and then filtered. The TGA equipment is TGA-92-12 from SETARAM (France). The rheology experiments are performed with a plane-cone rheometer from TA Instruments with a cone of 4 cm diameter, a $3°59'$ cone angle and a 103 μm gap. All the experiments were performed at ambient temperature if no other temperature is indicated. The degree of substitution was determined by potentiometry from the determination of the chloride counterions and/or by microanalysis based on the yield of nitrogen and carbon.

The scanning electron microscopy was realized on a JSM-6100 from JEOL.

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Table 1
Some characteristics of cationic fibres in water

DS	0	0.026	0.11	0.2[a]	0.31	0.35[a]	0.45[a]	0.49	0.54[a]	0.62
τ (g/g)	9.9	9.5	10.5	28.2	51	52	51	53.5	56.1	57
% soluble	–	–	–	–	6.75	–	15	11	–	13.5

[a] Samples provided by ARD company.

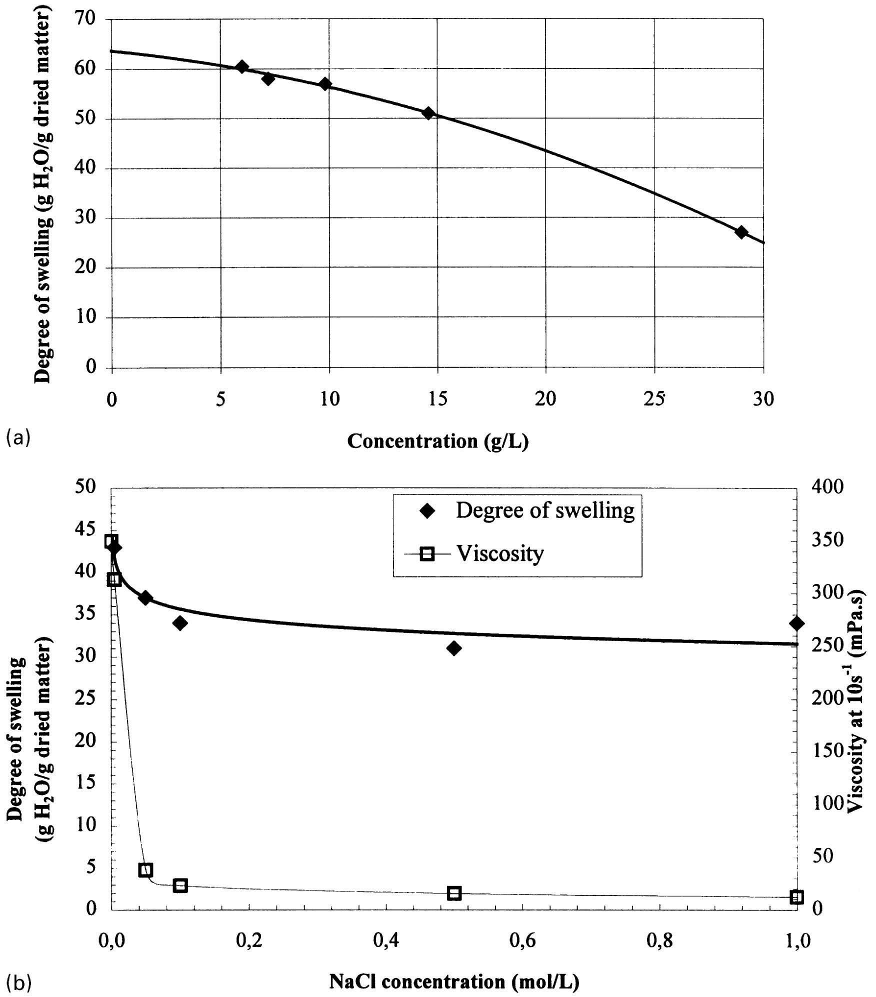

Fig. 1. Degree of swelling of cationic fibres: (a) as a function of the fibre concentration in water; and (b) of the external ionic concentration at constant fibre concentration ($C = 9.83$ g/l, DS = 0.45). Viscosities of the suspensions at 10 s^{-1} shear rate in the same conditions are also given.

Table 2
Degree of swelling for cationic fibres in ethanol/water (v/v) solvents ($C_p = 7$ g/l)

Solvent	τ (g H_2O/g)
0/100	57.9
50/50	47.7
75/25	34.7

3. Results and discussion

3.1. Characterization of the cellulosic fibres

The first characteristic of the material is the average degree of substitution. At this point, we have demonstrated that in our experimental conditions, the average degree of substitution of the derivative must be lower than 0.3 to remain completely insoluble (Table 1). This limit depends on the experimental conditions adopted for the derivatization (especially, the hydroxide concentration which controls the initial degree of swelling of cellulose) [5]. The related

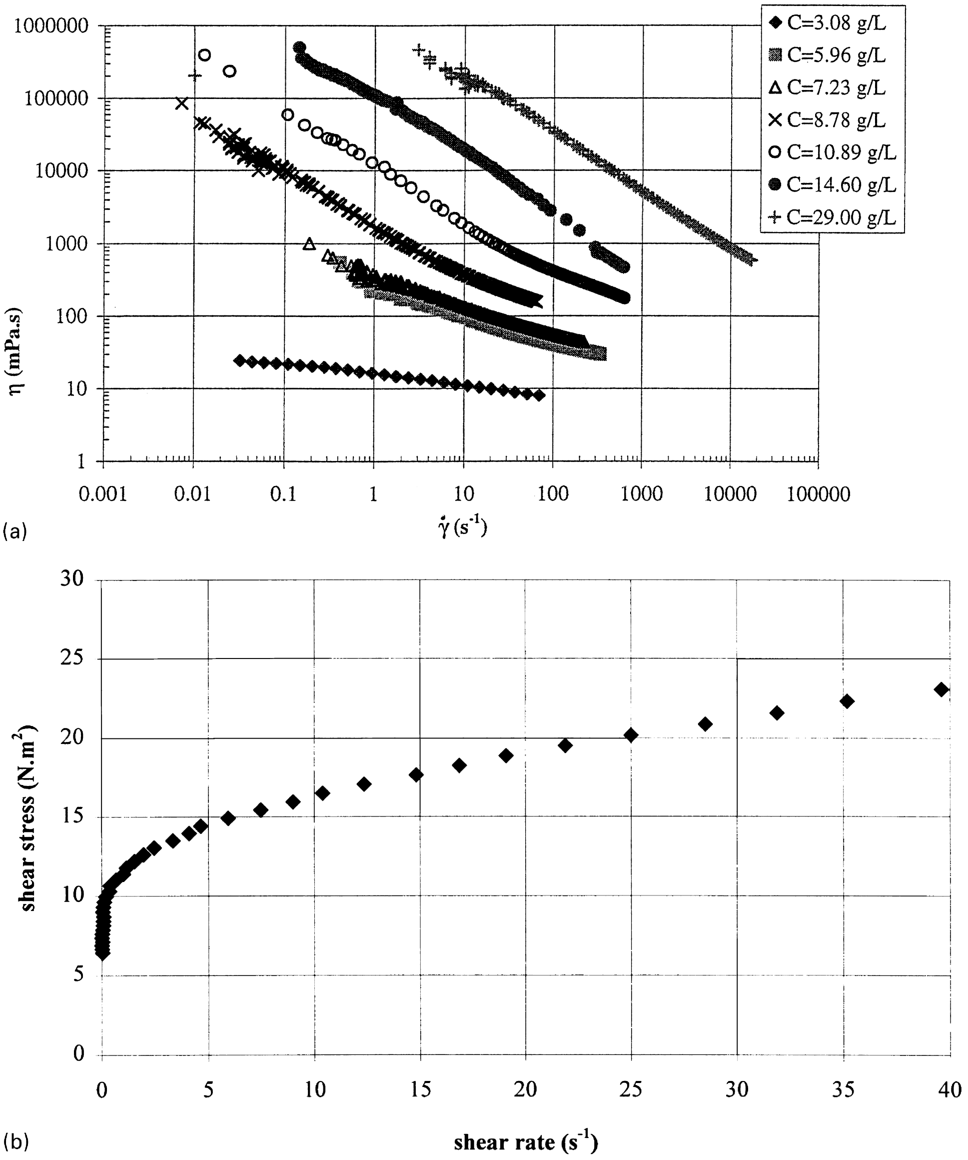

Fig. 2. Viscosity of suspension: (a) as a function of concentration and shear rate in water; (b) Flow experiment at 10.89 g/l showing the existence of a yield stress, DS = 0.45.

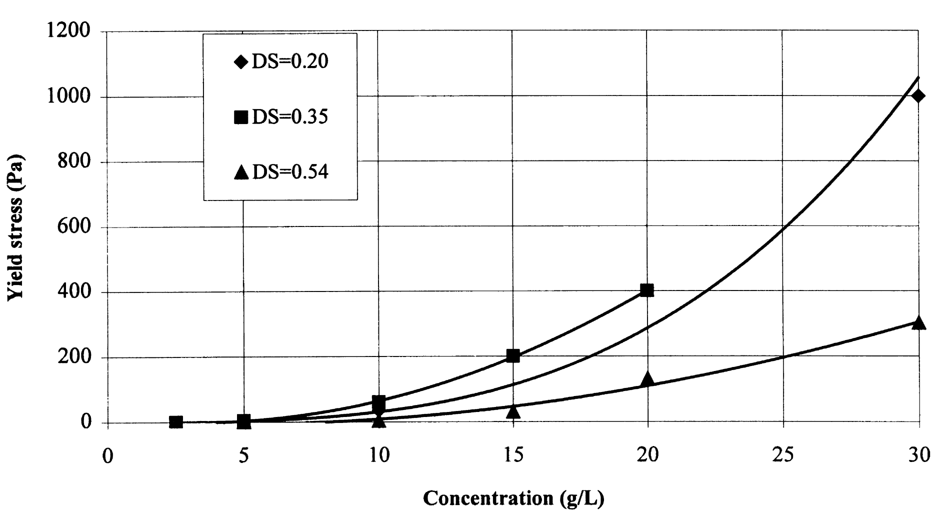

Fig. 3. Influence of suspension concentration and DS (one run of defibrillation) on the yield stress.

Table 3
Determination of α and β parameters relating viscosity with suspension concentration and shear rate, respectively

DS	α at 10 s^{-1}	β^a at 2%	β^a at 1.5%
0.2	2.57	− 0.74	
0.35	2.99	− 0.68	− 0.81
0.54	3.49	− 0.79	− 0.76

[a] β parameter in the range of 0.1–100 s^{-1}; $-0.8 < \beta < -0.6$ in the range of concentration (0.5–3%) and for the different DS.

Table 4
Evolution of the viscosity (in mPa. s) of the suspension as a function of temperature (comparison with the behaviour of a xanthan in solution, solvent: H_2O; $\dot{\gamma} = 300\ s^{-1}$)

	T (°C)			
	20	35	50	60
Xanthan 2 g/l	490	400	270	–
Cationic fibres				
DS = 0.45; 21 g/l	3500	5000	6000	–
DS = 0.45; 15 g/l	740	880	980	1100

important parameter is the degree of swelling expressed as the water content in gram of water per gram of dried material. It depends on the concentration of the suspension and on its ionic concentration (Fig. 1). This is related to the ion exchanger properties of the suspended fibres. The degree of swelling decreases to a plateau over NaCl 0.1 M and the value stabilizes to 33 g H_2O/g which remains much higher than for the underivatized initial cellulose (9.9 g H_2O/g). The viscosity of the suspension decreases under the same conditions. These salt effects are due to the screening of electrostatic interactions.

The suspension was examined in the presence of an organic solvent; the results are given for different contents of ethanol as a non-solvent in Table 2. The degree of swelling remains high in the presence of ethanol (34.7 g H_2O/g for a EtOH/H_2O mixture 75/25 v/v).

It must also be mentioned that suspensions are stable in water over a critical concentration in the range of 3–5 g/l; in other words, there is no sedimentation of the fibres.

At the end, the cationic fibres were dried and redispersed; the swelling was demonstrated as reversible as well as the viscosity of the suspension [4]; this interesting characteristic is also directly related to the electrostatic repulsions.

3.2. Rheology of cationic fibre suspensions

Flow and dynamic experiments were realized for fibre suspensions in deionized water. Fibers with different average degrees of substitution (DS = 0.2, 0.35 and 0.54) but also different degrees of defibrillation characterized by the number of runs through the Nanojet equipment were investigated.

3.2.1. Flow properties

From the beginning of this work, one understands that these cationic fibres were not only ion exchanger materials (or even cationic flocculants) but also a thickening polymer-like substance. The rheology of the relatively diluted suspension was first tested in flow experiments. These suspensions are non-Newtonian over 3 g/l at least and present a yield stress when the concentration increases in the range of 10 g/l (Fig. 2).

In Fig. 2(a), the evolution of the viscosity (mPa s) as a function of the suspension concentration and of the shear rate in water is given for a suspension of fibres with a DS equal to 0.45. But, the viscosity is strongly influenced by the ionic concentration as shown in Fig. 1(b). In addition, in salt excess, a Newtonian plateau appears for these suspensions in the range of 3 s^{-1} when the salt content is higher than 0.1 M.

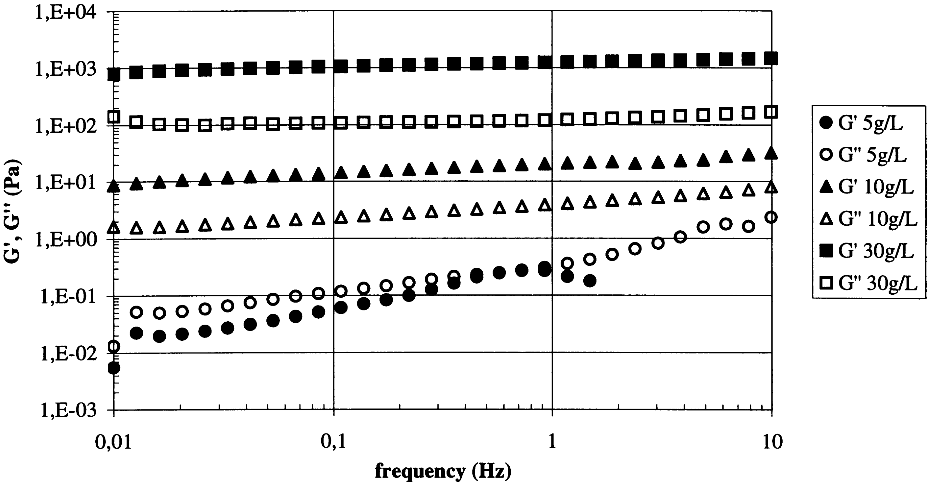

Fig. 4. Rheological characterization of fibre supensions (DS = 0.2, one run of defibrillation) for different concentrations ($C = 5$ g/l $G'' > G'$ for $\omega < 1$ Hz; $C > 5$ g/l $G' > G''$).

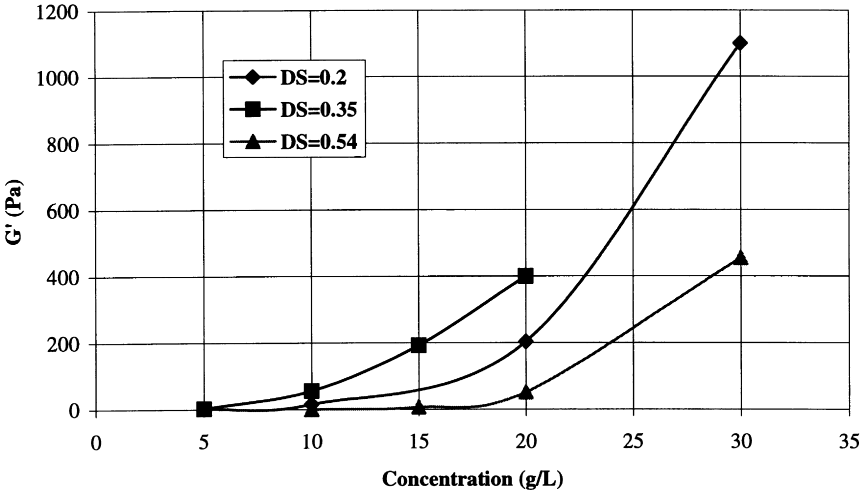

Fig. 5. Elastic modulus of suspension determined as a function of polymer concentration for different DS. Conditions: 25°C, 0.17 Hz, one run of defibrillation.

In flow experiments, the yield stress was determined; it appears as soon as the concentration becomes higher than a critical value C^* in the range of 5 g/l but depending on the DS and the degree of fibrillation (Fig. 3). At the same time a gel-like behaviour is shown in dynamic experiments. The viscosity of the suspension is non-Newtonian in all the range of the shear rate covered whatever the tested concentration, especially in water. Then, the viscosity of the suspensions depends on the fibre concentration (C) and on the shear rate ($\dot{\gamma}$) following a relation similar to that proposed for a polymeric solution

$$\eta \propto C^{\alpha}\dot{\gamma}^{\beta}.$$

The parameters α and β were determined from the dependence of η with C at a given shear rate and dependence with shear rate at a constant concentration (Table 3). These parameters are in the same range as for polymers in a semi-dilute regime ($\alpha \sim 3.4$; $\beta \sim -0.8$).

The last series of experiments concerns the role of temperature. It is well known that usually with a water soluble polysaccharide the viscosity decreases when the temperature increases. The exception should be with amphiphilic polymers [6]. In these experiments one compares the behaviour of the suspension with that of a xanthan solution (Table 4). The originality of these suspensions is that their viscosity increases when temperature increases due to the swelling of the fibres. This is an advantage for application; the level of the viscosity remains lower at the same weight concentration than that of xanthan in an aqueous solution.

3.2.2. Dynamic measurements

The dynamic moduli (G' and G'') were determined in

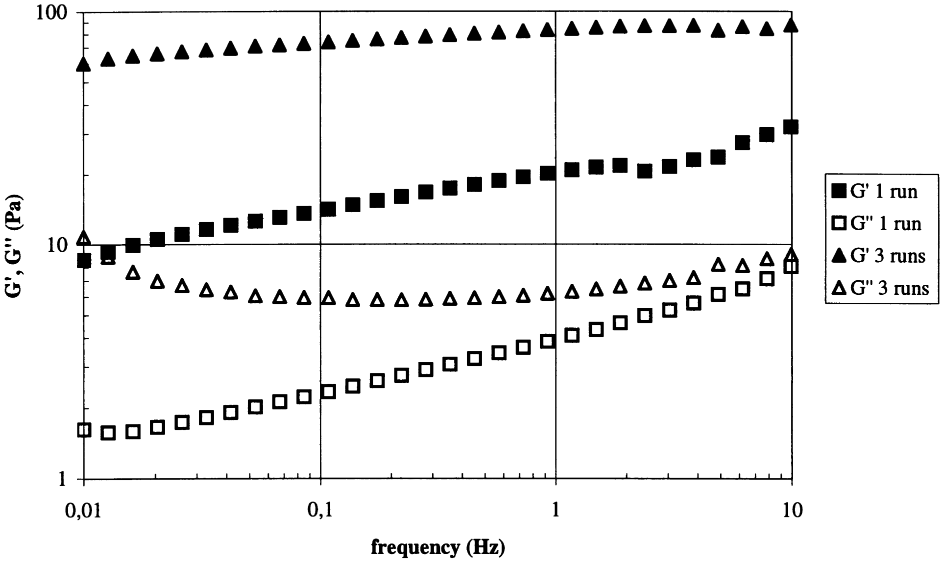

Fig. 6. Role of the number of defibrillation runs on the dynamic moduli of the suspensions. Conditions: DS = 0.2; $C = 10$ g/l; $T = 25$°C.

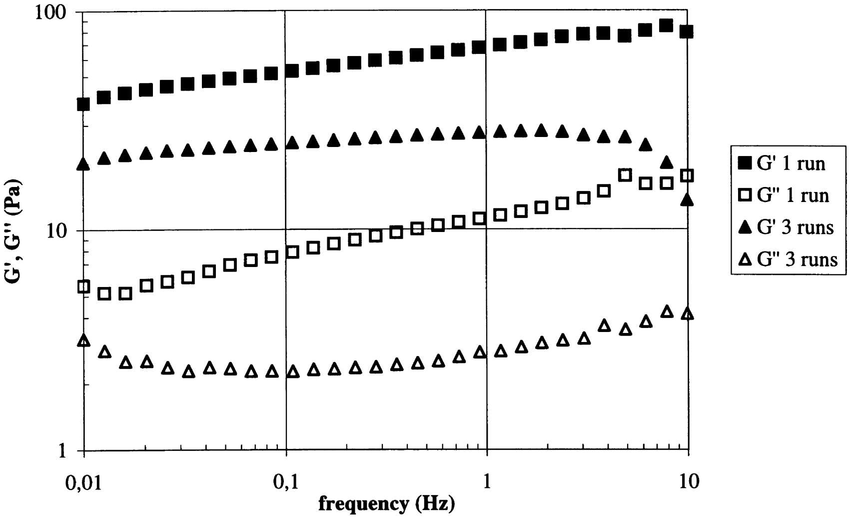

Fig. 7. Role of the number of defibrillation runs on the dynamic moduli of the suspensions. Conditions: DS = 0.35; $C = 10$ g/l; $T = 25$°C.

different conditions. A gel-like behaviour ($G' > G''$ over a large range of frequencies) appears over a critical concentration C^*. The elastic plateau strongly depends on the suspension concentration, the DS and the degree of defibrillation. Fig. 4 shows the existence of the critical concentration separating the solution behaviour from that of a gel-like behaviour over 5 g/l. The influence of suspension concentration on the elastic modulus is shown in Fig. 5 for the three investigated degrees of substitution. The medium with fibres having a DS of 0.35 is still a suspension with nearly no soluble fraction but having a large swelling degree which favours the gel-like behaviour; a DS of 0.54 is too large and the cellulosic material partially soluble and a DS of 0.2 is not in the optimum efficiency with one run of defibrillation. When the microfibres are mechanically defibrillated by three runs through the device and when DS = 0.2, the rheology of the suspension is optimized. On the contrary for DS = 0.35, this effect is negative. The interpretation comes from the larger degree of swelling and the ability of disruption of this material under shear which then loses its performances due to a too large degree of breaking of the fibrillar structure (see Table 1). The results are represented in Figs. 6 and 7.

The last interesting result is that the gel-like behaviour is increased when temperature increases just as mentioned for viscosity (Fig. 8). This is again an advantage compared with other physical gels such as carrageenan or gellan based on H-bonds whose performances decrease when temperature increases [7,8].

4. Conclusion

In this paper, the rheological properties of cationic fibre

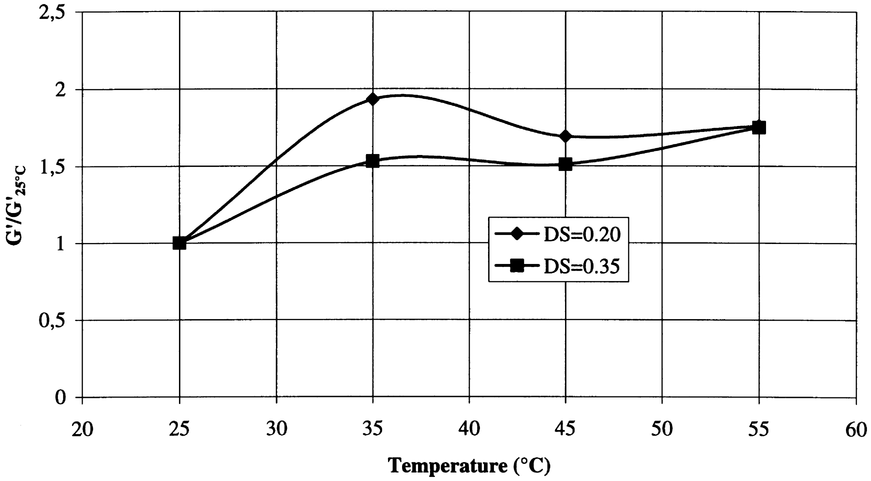

Fig. 8. Role of the temperature on the elastic modulus (expressed by the ratio $G'/G''_{25°C}$) of suspensions with different DS. Conditions: $C = 20$ g/l; 0.17 Hz; one run of defibrillation.

suspensions are described in relation with their average degree of substitution and degree of swelling. Their flow properties are non-Newtonian and show an yield stress when fibre concentration is larger than ~5 g/l. For larger concentrations, they present a gel-like behaviour ($G' > G''$) whose performance depends on the degree of substitution of the cellulosic fibres and the degree of fibrillation. The optimum properties are obtained for a given degree of fibrillation of the derivatized materials which has to be optimized in relation with their average degree of substitution.

One advantage of these cationic fibres is to develop their rheological characteristics when the temperature increases in contrast to the usual behaviour of water soluble polymeric solution. Comparison with xanthan is done to demonstrate this point.

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