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Rheological study of interactions between non-ionic surfactants and polysaccharide thickeners used in textile printing

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Abstract

The influence of four non-ionic surfactants (isododecyl and cetyl polyoxyethylene ethers) on aqueous polysaccharide solutions (sodium alginate, guar gum, and sodium carboxymethyl guar), applicable for textile printing pastes, were studied via rheological measurements.

Rheology of polysaccharide–surfactant solutions in aqueous matrices is primarily governed by polymer content, which imparts marked shear-thinning and viscoelastic character to the system. Such properties are modulated in moderate but sensible way by changes in surfactant concentration or type. Above 3% surfactants addition to non-substituted guar gum solutions results in a significant impact leading to phase separation and a particular strongly associated phase is formed due to hydrogen bonds between ethylene oxy units from the surfactant and primary hydroxyl groups in guar.

A satisfactory fitting of viscosity data is obtained with both the Cross equation and the Roberts–Barnes–Carew model. The experimental results of mechanical spectra can be described quite satisfactory with both the Friedrich–Braun and the generalized Maxwell models.

Keywords: Polysaccharide; Textile printing; Non-ionic surfactant; Polymer–surfactant interactions; Viscoelasticity

1. Introduction

From the variety of industrial application of polysaccharides, it is probably true to say that textile printing is one of the largest exploitations of the thickening properties of carbohydrate polymers. Thickeners are used in textile printing to modulate the rheological properties of the printing pastes during application and to obtain sharp, clean drawing patterns by preventing dye migration. Alginates, guar gum and its derivatives, methyl and carboxymethylcellulose, some exudate gums and xanthan are excellent thickeners for this application, since they can impart high viscosities at low concentrations and possess the adequate rheological behavior.

Color pastes employed in the machine printing of textiles are prepared by mixing a thickening agent solution and a dye solution or dispersion. The role of thickening agents in the formulation of printing pastes is of paramount importance since they impart adequate rheological properties to the pastes in the different flow conditions encountered in the printing process. During this process, the materials are moved by the sequence across the mask and through the screen openings, to the substrate. Thus, the pastes are subjected to flows with shear or extensional component, or both, at different strain rates. High strain rate conditions are present during the first steps of the application process, while after being forced through the screen openings and deposited on the fabric, the paste will continue to flow at very low shear rates. Hence, the thickening agents must ensure at the same time both a homogeneous distribution of the printing paste on the screen and its uniform flow through the screen openings. In other

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words, the paste must be characterized by a good screenability and a complete and uniform penetrability into the cloth; moreover, the best sharpness of definition must be achieved and flushing out prevented. It follows that the favorable properties for an easy application and a good performance of a printing paste are generally low viscosity values at high shear rates and high viscosities at low shear rates (or a presence of a yield stress), respectively.

Elasticity affects both the flow behavior of the paste through the screen openings to the fabric and the following step (flow through the fibers) by governing possible recovery of the paste immediately after its application. The selection of the thickening agent, which in most cases is confined to polysaccharides and their derivatives with high molecular weight, is determined by the fabric to be printed, the printing conditions, and, above all, the type of dye used. Depending on their chemical structure, dyes may interact with thickening agents, to form complexes or to give a chemical reaction, so causing a variation of the rheological properties of the printing pastes and, hence, of their application characteristics. However, in most cases the addition of a dye does not produce a qualitative change of the flow behavior, but only a limited increase in the rheological quantities.

Alginates and modified starches are used as thickeners, surface penetration and spreading controlling agents in textile printing with reactive dyes. Printing operations with this type of dye involve true chemical reactions of the dye with primary hydroxyl groups of the cotton fibers under alkaline conditions. Therefore, the ideal thickener must possess two essential features: its viscosity must be insensitive to high pH and the polymer itself must not interact with the dye. Alginate is the only hydrocolloid to have these requisites: besides being stable to alkali it has no free primary hydroxyl groups which can compete with cotton for dye fixation. The net result is that less dye is required to obtain a predetermined color yield and a better definition of the drawing (Lapasin & Pricl, 1995).

The application of guar gum in cellulose printing with reactive dyes causes direct or indirect (via reactive dye) chemical covalent binding of guar gum macromolecules with the cellulose substrate (Kokol, 1998). The occurred chemical cross-linking of guar gum on the fiber surface hinders washing-off and thus causes increased fabric stiffness and color changes of the printed substrate. Modification of guar gum, namely substitution of free primary hydroxyl groups with different substituents, decreases the chemical cross-linking. On the basis of high and low viscosity guar gum of different substitution levels, it was shown that the fabric stiffness strongly depends on the solid content. While high viscosity guar gum is suitable for nearly all reactive dyes, it is imperative to increase the substitution level of guar gum with increased solid content. The behaviour of monofunctional reactive dyes is more favourable than the behaviour of dyes with more reaction centres. High molecular weight guar gum can be used for printing with most reactive dyes, whereas low molecular weight thickeners are suitable only for monofunctional reactive dyes (Šostar & Schneider, 1999). To preclude chemical reaction of the guar gum with the reactive dye, an addition of an appropriate additive to the printing paste can alternatively reduce such undesired interactions (Kokol, 2002; Oblonšek, Šostar-Turk, & Lapasin, 2003). On the basis of the screening data, using non-substituted guar gum and bifunctional reactive dyes in printing pastes, reasonable additives have found to be ethoxylated stearyl alcohols and oleyl alcohols as well as some alkylpolyglycosides and some surfactants with amino-groups (Schneider & Šostar-Turk, 2003), but in some cases the results are still not satisfactory, since some surfactants form gels with guar gum. The rheological investigation of interactions between polysaccharide polymer thickener and reactive dye in the presence of polyoxyethylene stearylethers has shown that the breakup of the primary polymer cross-linked structure leads to stronger shear thinning and elasticity of the paste due to hydrogen and covalent ether bonds of surfactants as individual molecules (below critical micelle concentration), or as micelle aggregates (above critical micelle concentration) with the hydroxyl groups of the thickener (Kokol, 2002). The surfactant molecules tend to accumulate at polysaccharide interfaces and build an oriented monomolecular film on its interfaces (Kokol, Schneider, & Šostar, 1999). When the surfactant addition is contained at sufficiently low levels, only slight but different changes are observed for linear viscoelastic properties, ascribed to surfactant-induced intramolecular interactions and, consequently to slight conformational changes of polymer chains, whereas at higher surfactant concentrations the intermolecular connections promoted by micelles can prevail depending on micelle conformations and interactions, so leading to a moderate increase in viscosity and characteristic relaxation times (Oblonšek et al., 2003).

In the present research, the influence of isododecyl and cetyl polyoxyethylene ethers on the rheological properties of aqueous polysaccharide solutions is studied under steady and oscillatory shear conditions, in order to evaluate possibilities of an extended usage of a wider range of non-ionic surfactants in combination with guar gums and their derivatives for textile printing on cellulose.

2. Experimental

2.1. Polysaccharides

For the rheological investigation of polysaccharide–surfactant interactions three types of industrial polysaccharides (Fig. 1), produced by specialized manufacturer of natural thickeners for textile printing Lamberti S.p.a. (Italy), were used, namely sodium alginate (95% active content and 5% moisture), guar gum (85% active content, 5% proteins and 10% moisture) and sodium carboxymethylated guar gum (70% active content, 15% salts, 5% proteins and 10% moisture). Alginate is sodium salt of alginic acid

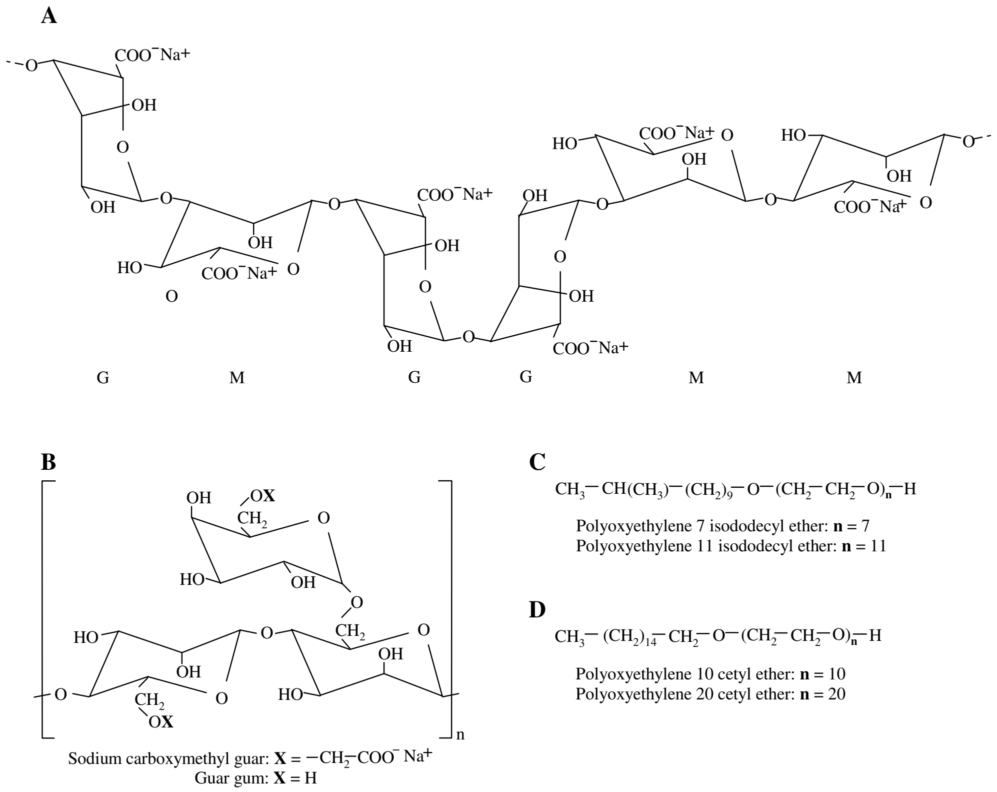

Fig. 1. (A) Idealized structure of sodium alginate with G-block, M-block and MG-block (B) idealized structure of guaran, the principal of guar gum and its derivatives, (C) monomer unit of polyoxyethylene isododecyl ethers and (D) monomer unit of polyoxyethylene cetyl ethers.

generally derived from brown seaweeds (*Phaeophyceae*). The alginate polymer is composed of two building blocks of monomeric units, namely 1–4-linked β-D-mannuronic acid (M) and 1–4-linked α-L-guluronic acid (G) in varying proportions and sequential arrangements, depending on the seaweed source. These monomers can be organized in blocks of consecutive G-residues (G-blocks), consecutive M-residues (M-blocks) or alternating M and G (MG-blocks) (Fig. 1, A). The dyadic frequency composition of sodium alginate thickener (F_{GG},F_{MM}, F_{GM+MG}) was determined via circular dichroism (Donati et al., 2003) at Department of Biochemistry, Biophysics and Macromolecular Chemistry, University of Trieste, Italy. The M/G ratio, determined from the dyadic frequency composition ($F_{GG} = 0.15$, $F_{MM} = 0.41$, $F_{GM+MG} = 0.44$) is 1.7, typical of alginates derived from *Macrocystis pyrifera* (Mancini, Montanari, Peresini, & Fantozzi, 2002; Panikkar & Brasch, 1996).

Guar gum is a galactomannan, obtained from the seed of the legume *Cyamopsis tetragonolobus*. Guaran (Fig. 1, B), the functional polysaccharide in guar gum is a chain of (1 → 4)-linked β-D-mannopyranosyl units with single α-D-galactopyranosyl units connected by (1 → 6) linkages to, on the average, every second main chain unit (Whistler & BeMiller, 1993). Carboxymethylated guar gum is guar ether, generally prepared at elevated temperature under aqueous conditions using strong NaOH and monochloroacetic acid. An average of three hydroxyl groups is available for derivatization on every sugar unit in guar, so a maximum degree of hydroxyl group substitution (DS) of three can be achieved. Carboxymethylated guar gum used in this research has DS = 0.3.

An estimate of the viscosity average molecular weight (M_v) of the polysaccharides was established, using intrinsic viscosity $[\eta]$ data and the appropriate Mark–Houwink relationship, given as $[\eta] = KM_v^{\alpha}$, where K and α are constants depending on the polymer–solvent pair. Since the published relationships are known to be reasonably robust, we can assume that the weight average molecular weight, $M_w \approx M_v$.

For the determination of intrinsic viscosity the samples were previously purified as described in Azero and Andrade (2002) and Beer, Wood and Weisz (1999). The efflux times of the dilute polysaccharide solutions were measured using the Ubbelohde capillary viscometer ($k = 0$–0109). The viscometer was immersed in a precision water bath (thermostat Petrotest, Petrotest Instrument GmbH & Co. KG, Germany) to maintain constant temperature. The results are shown in Table 1.

2.2. Surfactants

Two branched non-ionic polyoxyethylene surfactants (Fig. 1C) produced by Lamberti S.p.a. (Italy), namely TR 8 (polyoxyethylene 7 isododecyl ether) and TR 12 (polyoxyethylene 11 isododecyl ether); and two linear

Table 1
Intrinsic viscosity, η, and estimated weight average molecular weight, M_w, of sodium alginate, guar gum and sodium carboxymethylated guar gum

Sample	Conditions	Reference	$K \times 10^6$	α	$[\eta]$ (dL/g)	M_w (g/mol)
Sodium alginate	0.1 M NaCl, 25 °C	K and α values are derived from experiments of Donnan and Rose (1950)	122.8	0.963	5.78	7.11×10^4
Guar gum	aqueous solution, 25 °C	Robinson, Ross-Murphy, and Morris (1982)	380	0.723	10.61	1.41×10^6
Sodium carboxymethyl guar gum (DS = 0.3)[a]	0.1 M NaCl, 25 °C	Risica, Dentini, and Crescenzi (2005)	193	0.739	7.12	1.51×10^6

[a] For carboxymethylated guar gum (DS = 0.3) Mark–Houwink constants are not available in the literature, therefore the weight average molecular weight was estimated using the Mark–Houwink parameters for methyl guar gum (DS = 0.3) determined by Risica et al. (2005).

non-ionic polyoxyethylene surfactants (Fig. 1D) produced by Sigma–Aldrich (Germany), namely Brij(R) 56 (polyoxyethylene 10 cetyl ether) and Brij(R) 58 (polyoxyethylene 20 cetyl ether), were used.

2.3. Sample preparation

All aqueous systems were prepared by adding a proper amount of polymer (marks: A (sodium alginate), G (guar), CG (sodium carboxymethyl guar)) to a corresponding solution of single surfactant under stirring conditions. The surfactants, marked as S7 (TR 8), S11 (TR 12), S10 (Brij(R) 56) and S20 (Brij(R) 58), were dissolved in distilled water with slight heating, prepared at three different concentrations for each polymer system ($w = 1\%$, 3% and 5%) and the same polysaccharide concentration (4% for A and CG solutions and 1% for G systems). All the systems were left in the refrigerator to swell overnight. A phase separation was observed for G-S7 ($w_{S7} = 3\%$ and 5%), G-S11 ($w_{S11} = 5\%$), G-S10 ($w_{S10} = 5\%$) and for G-S20 ($w_{S20} = 3\%$ and 5%), whereas slight inhomogeneity and turbidity was displayed by CG-S7 ($w_{S7} = 3\%$ and 5%).

2.4. Apparatus

Rheological measurements (flow curves, stress sweep and frequency sweep) were carried out at 25 °C and performed with a rotational controlled stress rheometer Haake RS150 with different measuring devices: cone and plate (C60°/1) and parallel plates with serrated surfaces (PP35 Ti). The latter device was used to investigate flow properties and linear viscoelastic behavior of the polymer-rich phase of the G systems, where phase separation was evident, and also of inhomogeneous CG systems to avoid wall slippage effects.

3. Results and discussion

3.1. Steady shear properties

In most cases the results obtained from steady shear tests indicate the shear-thinning properties peculiar to ordinary polymer solutions. The surfactant contribution to rheological properties on the polymer solution depends on surfactant concentration and is most evident in G systems where phase separation due to polymer–surfactant interactions appears at higher surfactant concentrations. Such behaviour could be ascribed to the saturation of the polymer surface with surfactant molecules. Stronger interactions between hydrophilic ethylene oxy (EO) units from the surfactant and primary hydroxyl groups of the G polymer could cause the orientation of the hydrophobic part of the surfactant toward the aqueous medium. Such polymer-surfactant complexes become hydrophobic on the surface and consequently separation into two phases appears.

Looking at the typical composition of guar gum thickeners they are generally contaminated with 5–6% of impurities such as proteins (Whistler & BeMiller, 1993), which could be considered as an indication to strong interactions between surfactant and proteins in G-surfactant systems. It is known that when ionic charged surfactants or micellar systems are added to protein solutions, generally the protein is denatured or biologically inactivated as a result of binding. Nonetheless, it has been found that non-ionic (non-charged) surfactants do not bind to these biomolecules to a significant extent and do not denaturate proteins (Helenius & Simons, 1972; Makino, Reynolds, & Tanford, 1973; Sahito, 1987). Moreover, taking this into consideration, it must also be emphasized that substituted guar, used in this research, also contains 5% of protein impurities (as provided by the producer), but the rheological effects produced by the addition of non-ionic surfactants in CG systems, do not seem to be quantitatively important (see Fig. 4) and indicate that the interactions between the surfactant and protein contents are not so strong, thus supposed of secondary importance.

Oblonšek et al. (2003) investigated changes in the rheological properties after the elimination of proteins from non-substituted guar, with purification by extraction method, carried out by the producer. The application of the purified guar to reactive printing using standard printing paste recipe, prepared with the thickener and addition of non-ionic surfactant, bifunctional reactive dye, urea, sodium carbonate and reduction substance, showed that printing results on viscose were still not satisfactory, due to highly elastic printing pastes resulting from an entanglement of the polymer with other components of the printing paste.

In the present research, the removal of soluble proteins from guar with purification by precipitation in ethyl alcohol as described in Beer et al. (1999) and Azero and Andrade (2002), was performed. As in the cases observed for unpurified guar the addition of surfactant to aqueous solutions of purified guar likewise leads to phase separation. To summarize the previous observations, it can be concluded that strong interactions in G-surfactant systems, where phase separation appears, are primarily governed by hydrogen bonding between G and surfactant, as discussed further.

The investigation of the polymer-rich phases show a dramatic increase of viscosity (Fig. 2) and, correspondingly, much longer relaxation times, as it will be deduced later from the analysis of the mechanical spectra reported in Fig. 6.

As shown in Fig. 2, the flow curves of G-S7 systems (black symbols) are compared with those of the corresponding pure G aqueous solutions (open symbols) having the same polysaccharide concentration and it can be seen that the asymptotic values of the viscosity at zero shear stress nearly coincide.

Looking at the guar solutions (Fig. 2, open symbols), an appreciable increase in the low shear viscosity of almost three orders of magnitude is observed passing from 1% to 3% polymer concentration. Increasing polymer concentration leads not only to an increase of the topological constraints posed to each individual chain by the temporary polymer network but also enhances the role of hydroxyl groups and the resulting hydrogen-bond intermolecular interactions.

It can be seen from Fig. 2 that the flow curves of G-S7 polymer-rich phases show an anticipated viscosity drop in the middle shear region with respect to the corresponding pure G aqueous systems. It is obvious that the surfactant molecules participate in the polymer intermolecular associations, binding via hydrogen bonds with their hydrophilic units towards the guar gum hydroxide groups, giving origin to the formation of polymer–surfactant complexes, so replacing the intermolecular interactions and associations promoted by hydrogen bonds between individual polymer chains. The application of higher shear stresses causes the break-up of such complexes, the consecutive uncoiling of polysaccharide chains and decrease in viscosity.

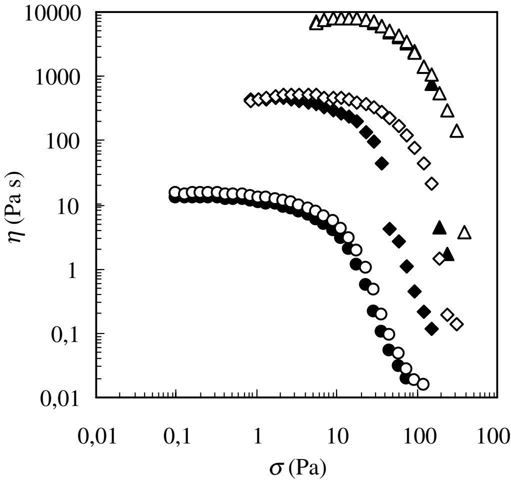

Fig. 2. Steady shear viscosity vs. shear stress for G, G-S7 (●, G$_{(w = 1\%)}$–S7$_{(w=1\%)}$; ○, G$_{(w=1\%)}$; ◆, G$_{(w=1\%)}$–S7$_{(w=3\%)}$-conc. phase; ◇, G$_{(w = 2\%)}$; ▲, G$_{(w = 1\%)}$–S7$_{(w = 5\%)}$-conc. phase and △, G$_{(w=3\%)}$).

Comparing flow curves of the G polymer-rich phases (Fig. 3) makes evident that their properties result from the combination of several condition factors, such as guar gum concentration, surfactant concentration, EO chain length and hydrophobic group as well. In the particular case of G-S10 and G-S20 polymer-rich phases with 5% surfactant addition, it can be seen that the contribution of surfactant to the properties of the polymer-rich phases depends on the number of EO groups in the surfactant molecule, causing a more concentrated phase and, consequently, higher viscosity values at higher EO number. The properties of systems G$_{(w=1\%)}$–S10$_{(w = 5\%)}$-conc. phase and G$_{(w = 1\%)}$–S20$_{(w = 3\%)}$-conc. phase coincide in the linear regime at low shear stresses, whilst at higher shear stresses the profile shape of complex G$_{(w=1\%)}$–S10$_{(w = 5\%)}$-conc. phase shows an anticipated viscosity drop, indicating the influence of surfactant structure and concentration.

Conversely, in the case of the systems prepared with branched non-ionic surfactants, an increase in the number of EO groups leads to lower viscosity values and anticipated viscosity drop (compare the polymer-rich phases of G$_{(w = 1\%)}$–S11$_{(w = 5\%)}$ and G$_{(w = 1\%)}$–S7$_{(w = 5\%)}$).

A satisfactory fitting of viscosity data is provided with the Cross equation (Cross, 1965), using shear rate as the independent variable:

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\lambda\dot{\gamma})^n} \qquad (1)$$

where η_0 and η_∞ are the asymptotic values of the viscosity at zero and infinite shear rates, respectively, λ is the characteristic time and n rules the shear dependence in the power law region.

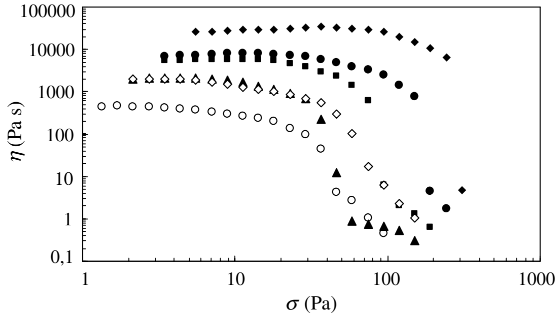

Fig. 3. Steady shear viscosity vs. shear stress for polymer rich phases (○, G$_{(w = 1\%)}$–S7$_{(w = 3\%)}$-conc. phase; ●, G$_{(w=1\%)}$–S7$_{(w = 5\%)}$-conc. phase; ■, G$_{(w = 1\%)}$–S11$_{(w = 5\%)}$-conc. phase; ▲, G$_{(w=1\%)}$–S10$_{(w = 5\%)}$-conc. phase; ◇, G$_{(w=1\%)}$–S20$_{(w = 3\%)}$-conc. phase and ◆, G$_{(w=1\%)}$–S20$_{(w = 5\%)}$-conc. phase).

Since the concentrated G systems, that result after phase separation, due to strong interactions between guar and surfactant, show a gradual fall-off in the viscosity before the precipitous drop, a quite satisfactory data fitting can also be obtained with the Roberts–Barnes–Carew (RBC) model (Roberts, Barnes, & Carew, 2001). The model represents a modified version of the Ellis model which is more flexible in virtue of the increased number of adjustable parameters. The previous parameters η_0 and η_∞ are redefined so that they become functions (η'_0 and η'_∞) of the shear stress, σ, as follows:

$$\eta = \eta'_\infty + \frac{\eta'_0 - \eta'_\infty}{1 + (\sigma/\sigma_c)^m} \tag{2a}$$

where

$$\eta'_0 = \frac{\eta_0}{1 + (\sigma/\sigma_1)^p} \tag{2b}$$

$$\eta'_\infty = \eta_\infty(1 + (\sigma/\sigma_2)^s) \tag{2c}$$

and σ_c is a critical shear stress. The number of adjustable parameters can be reduced, setting s equal to −1,5. Even if the RBC model provides adequate data fitting also for some G-surfactant solutions, the Cross equation appears to be more suitable and convenient to describe the shear thinning behavior of these systems. Table 2 shows a comparison of the model parameters and the quality of the fitting with the Cross and RBC models, respectively. The objective function (O.F.) used in the minimization procedure is given as:

$$\text{O.F.} = \sum_{i=1}^{N} \left(1 - \frac{\eta_{i,\text{cal}}}{\eta_{i,\text{exp}}}\right)^2 \tag{3a}$$

the average percentage deviation (APD):

$$\text{APD} = \sum_{i=1}^{N} \left|1 - \frac{\eta_{i,\text{cal}}}{\eta_{i,\text{exp}}}\right| \cdot \frac{100}{N} \tag{3b}$$

and number of runs is defined as:

$$\text{no.runs} = \sum_{i=2}^{N} \left|\frac{\text{sign}(\eta_{i,\text{cal}} - \eta_{i,\text{exp}}) - \text{sign}(\eta_{i-1,\text{cal}} - \eta_{i-1,\text{exp}})}{2}\right| \tag{3c}$$

In order to examine surfactant contribution, viscosity data (calculated with the Cross equation) of the polymer–surfactant systems were compared with polymer aqueous systems with no surfactant addition (Fig. 4).

In the case of CG-S10 systems (triangles) the surfactant gradually reduces the viscosity of the polysaccharide matrix over the whole shear region. The effects of polymer-surfactant interactions in the case of CG systems added with S7 (3% or 5%, circles) are not quantitative important but appear evident only under steady shear conditions where inhomogeneous flow is observed in the non-linear region and the behaviour becomes boundary dependent. A viscosity reduction is evident above 1 Pa, especially for the systems with higher surfactant concentration, which indicates that the different effects produced by the surfactant addition are strictly related to the different structural features of the polymer matrix under different shear conditions. Above the critical stress the polymer–surfactant interactions are substantially broken setting a significant fraction of polysaccharide molecules free in solution.

Table 2
Model parameters of cross and RBC model and fitting quality parameters for the concentrated systems G-S7, G-S11, G-S10 and G-S20 after phase separation

	G-S7 conc. phase.		G-S11 conc. phase	G-S10 conc. phase	G-S20 conc. phase	
	($w_{S7} = 3\%$)	($w_{S7} = 5\%$)	($w_{S11} = 5\%$)	($w_{S10} = 5\%$)	($w_{S20} = 3\%$)	($w_{S20} = 5\%$)
Cross-model						
η_0(Pa s)	494.9	8890	6740	1848	1646	26526
η_∞(Pa s)	0.043	0.203	0.487	0.176	0.055	0.066
λ (s)	18.3	72.6	93.9	40.4	33.4	69.1
n	0.870	0.943	0.972	0.980	0.890	1.034
O.F.	0.0457	0.0447	0.0157	0.5427	0.7357	0.6309
APD	3.47	4.49	4.06	18.73	16.96	11.63
No. runs	5	4	6	4	6	8
RBC model						
η'_0(Pa s)	1023	8414	6064	1539	1465	26098
η'_∞(Pa s)	0.001	0.002	0.001	0.256	0.001	0.121
σ_c(Pa)	0.623	56.8	37.0	29.5	29.6	174.4
m	0.339	2.06	2.48	11.79	4.62	3.60
σ_1(Pa)	24.5	157.9	76.6	1909.2	1909.2	275.8
p	5.48	29.5	23.9	19.8	19.8	61.0
σ_2(Pa)	7293	35616	30844	181	6405	689
s	−1.5	−1.5	−1.5	−1.5	−1.5	−1.5
O.F.	0.8976	0.0281	0.0161	1.9229	1.4846	0.4335
APD	14.50	2.95	5.70	9.25	12.80	5.29
No. runs	6	7	8	6	6	8

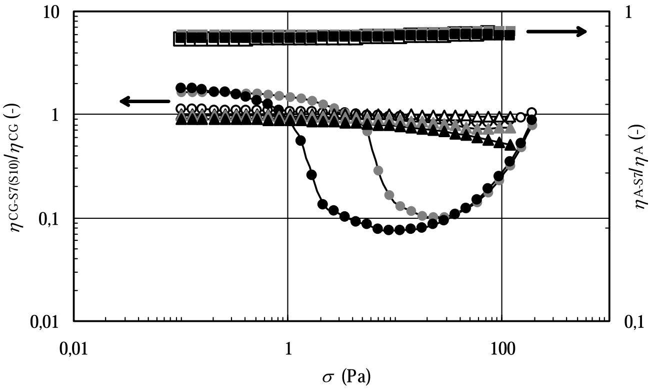

Fig. 4. Ratios between Cross viscosities of A-S7 and A systems; CG-S7 and CG systems; CG-S10 and CG systems at the same polysaccharide content and at different surfactant concentration (A-S7: $w_{S7} = 1\%$ (□), 3% (▨), 5% (■); CG-S7: $w_{S7} = 1\%$ (○), 3% (●), 5% (●); CG-S10: $w_{S10} = 1\%$ (△), 3% (▲), 5% (▲)).

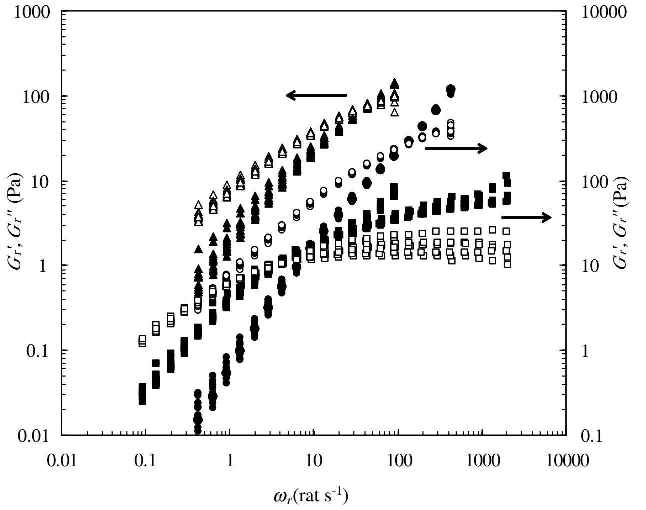

Fig. 5. Relative master curves of the mechanical spectra of A (●, G'; ○, G''), G(■, G'; □, G'') and CG(▲, G'; △, G'') systems at different surfactant additions, obtained by horizontal shift along the frequency axis; reduced frequency (ω_r) is identical to the applied frequency for the single polysaccharide solutions without surfactant.

The alginate–surfactant systems (Fig. 4, squares) show slight decrease of the steady shear viscosity due to surfactant addition over the whole shear region. These effects can be ascribed to reduction in the connectivity of the polymeric matrix induced by the entrapped surfactant micelles, hindering intermolecular interactions and associations between the polysaccharide chains.

3.2. Linear viscoelastic properties

From the preliminary step in the analysis of the oscillatory flow data, namely stress sweep tests, the limit of the viscoelastic regime was determined. The Soskey–Winter equation is used for the description of viscoelastic moduli vs. deformation (Soskey & Winter, 1984):

$$\frac{G^*}{G_0^*} = \frac{1}{1 + b\gamma^n} \tag{4}$$

where G^* is the complex modulus, G_0^* is the complex modulus in the linear viscoelastic regime, γ is the strain and b and n are adjustable parameters. The critical strain value γ_c^0 marking the upper limit of the linear viscoelastic regime is arbitrarily set in correspondence with $G^*/G_0^* = 0.95$.

For CG and A systems the critical strain values are typical of ordinary polymer solutions, lying in the ranges 0.2–0.4 and 0.6–0.8, respectively, while γ_c^0 varies between 0.01 and 0.07 for the polymer-rich phases (G systems), so indicating a proximity to weak gel condition.

The patterns of the mechanical spectra of A-surfactant and CG-surfactant systems are typical of ordinary polymer solutions and do not change substantially with increasing surfactant concentration, so that, a generalized representation can be easily derived by superposing the individual profiles through simple shifting procedure (Fig. 5).

Slight deviations from the ordinary profiles are observed for G systems (polymer-rich phases after phase separation), reasonably due to interactions between surfactant and guar molecules (Fig. 6). The formation of polymer–surfactant complexes leads to a significant increase of both moduli and relaxation times as well, as it can be evinced by double shifting of the crossover condition towards higher values and lower frequencies.

The experimental data from oscillatory tests, namely frequency sweep, can be described quite satisfactorily with the Friedrich–Braun model (Friedrich & Braun, 1992), based on fractional derivatives, as well as with the classical generalized Maxwell model (composed of 4 Maxwell elements in parallel). The following relationships can be derived from the Friedrich–Braun fractional model in order to describe the frequency dependence of the storage G' and loss G'' moduli, respectively:

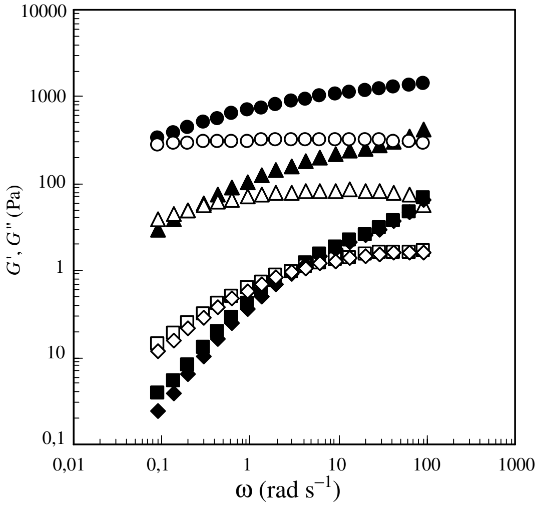

Fig. 6. Mechanical spectra for G and G-S20 systems ($G_{(w=1\%)}$ (◆, G'; ◇, G''); $G_{(w=1\%)}$–$S20_{(w=1\%)}$ (■, G'; □, G''); $G_{(w=1\%)}$–$S20_{(w=3\%)}$-conc. phase (▲, G', △, G''); $G_{(w=1\%)}$–$S20_{(w=5\%)}$-conc. phase (●, G'; ○, G'')).

$$G'(\omega)=\Delta G\frac{(\lambda\omega)^d\left[\cos\frac{\pi}{2}d+(\lambda\omega)^c\cos\frac{\pi}{2}(d-c)\right]}{1+2(\lambda\omega)^c\cos\frac{\pi}{2}c+(\lambda\omega)^{2c}} \tag{5a}$$

$$G''(\omega)=\Delta G\frac{(\lambda\omega)^d\left[\sin\frac{\pi}{2}d+(\lambda\omega)^c\sin\frac{\pi}{2}(d-c)\right]}{1+2(\lambda\omega)^c\cos\frac{\pi}{2}c+(\lambda\omega)^{2c}} \tag{5b}$$

where λ is a characteristic time, c and d are related to the derivation orders of the differential operators, and ΔG rules the magnitude of both moduli. The Friedrich–Braun model parameters obtained from data fitting for A-S11 systems (Fig. 7) show no significant discrepancies. This indicates that no physical interactions via hydrogen bonds between alginate and surfactant appear in these systems, being the surfactant micelles hosted inside the polysaccharide network.

The constitutive equation for the corresponding generalized Maxwell fluid is obtained by summing the contribution τ_k of each of the N Maxwell elements:

$$\tau=\sum_{k=i}^{N}\tau_k \tag{6a}$$

where each contribution is given by the constitutive equation of the Maxwell element:

$$\tau_k+\lambda_k\frac{\partial\tau_k}{\partial t_k}=G_k\dot{\gamma} \tag{6b}$$

Accordingly, the model yields the following expressions for the viscoelastic quantities under small-amplitude oscillatory motion (storage G' and loss G'' moduli, respectively):

$$G'=\sum_{k=1}^{N}\frac{G_k\lambda_k^2\omega^2}{1+(\lambda_k\omega)^2} \tag{6c}$$

$$G''=\sum_{k=1}^{N}\frac{G_k\lambda_k\omega}{1+(\lambda_k\omega)^2} \tag{6d}$$

From the results of data fitting using the generalized Maxwell model expressed through the corresponding relaxation time distribution G_k (λ_k) (Fig. 8), canonical profiles can be recognized for relaxation spectra of A and CG systems, but the profiles of the spectra for G systems show increasing contribution of higher relaxation times, due to a more complex and strongly associated structure produced by the effect of higher concentrations of surfactant addition and higher contribution of thickener in the polymer-rich phases.

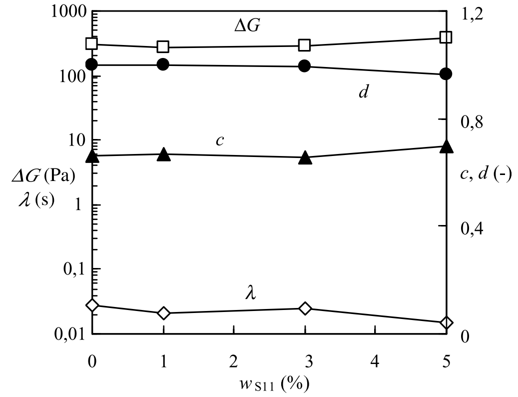

Fig. 7. Concentration dependence of the Friedrich–Braun model parameters for A-S11 systems.

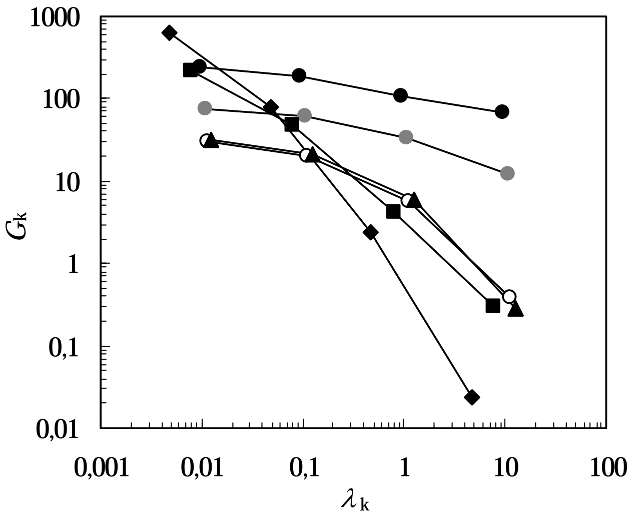

Fig. 8. Relaxation spectra of G-S7, G, A and CG systems (G$_{(w\,=\,1\%)}$–S7: $w_{S7}=1\%$ (○), 3%-conc. phase ●, 5%-conc. phase (●); G$_{(w\,=\,1\%)}$ (▲); A$_{(w\,=\,4\%)}$ (◆), CG$_{(w\,=\,4\%)}$ (■)).

Comparing experimental data obtained under continuous and oscillatory flow conditions, it can be seen that in the case of pure G and CG solutions the curve of $\eta^*(\omega)$ essentially coincides with that of $\eta(\dot{\gamma})$ over nearly two decades of ω and $\dot{\gamma}$ (Fig. 9, squares and diamonds). The empirical Cox–Merz rule (Cox & Merz, 1958) states that the shear-rate dependence of the steady-state viscosity, $\eta(\gamma\cdot)$ is equivalent to the frequency dependence of the complex viscosity, $\eta^*(\omega)$:

$$\eta(\dot{\gamma})=|\eta^*(\omega)|_{\omega=\dot{\gamma}}=\sqrt{\left[(G'/\omega)^2+(G''/\omega)^2\right]_{\omega=\dot{\gamma}}} \tag{7}$$

where G' and G'' are the storage and loss modulus, respectively. Discrepancies between the surfactant effects on steady and oscillatory shear properties are underlined by the failure of the rule for G-surfactant systems (Fig. 9, triangles) or, as in the case of CG-surfactant systems, a divergence between the curves are noticed as both ω and $\dot{\gamma}$ increase. In the case of A systems discernible deviations from the prediction of the Cox-Merz rule appear (Fig. 9, circles). The functional dependence of $\eta^*(\dot{\gamma})$ is substantially different from that of $\eta^*(\omega)$, and steady and oscillatory shear quantities show only slight tendency to converge.

Conclusions

The rheological investigation of the influence of four non-ionic surfactants on different polysaccharides in general shows marked shear thinning and viscoelastic character of the systems.

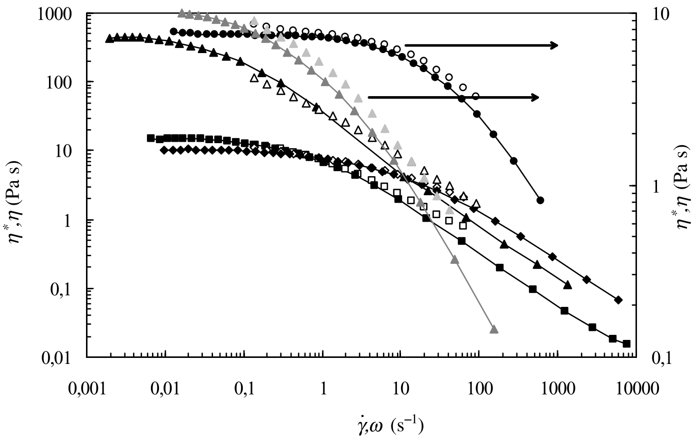

Fig. 9. Cox–Merz rule for A (○, η^*; ●, η), CG (◇, η^*; ◆, η); G (□, η^*; ■, η) $G_{(w = 1\%)}$–$S7_{(w=3\%)}$-conc. phase (△, η^*; ▲, η) and $G_{(w=1\%)}$–$S11_{(w = 3\%)}$ (▲: η^*, ▲: η).

Since alginate polymer has no free primary hydroxyl groups, the slight changes in rheological properties are the result of reduction in the connectivity of the cross-linked polysaccharide matrix induced by incorporation of surfactant micelles that become entrapped in the associative structure of the polymer.

The different effects produced by the surfactant addition in the case of carboxymethyl guar systems are strictly related to the different structural features of the polysaccharide matrix under different shear conditions, but in general the rheological behaviour is governed by polymer content. To avoid possible interactions via hydrogen bonds between carboxymethyl guar and non-ionic surfactant, a higher substitution degree of free primary hydroxyl groups in carboxymethyl guar is recommendable for its usage as thickening agent in reactive printing.

Significant effects, ascribed to the physical interactions (via hydrogen bonds) and associations between the polymer chains induced by surfactant micelles, lead to a sequestration of the guar gum polymer in a ‘gel-like’ phase with a particularly extended and strong associated structure, characterised with high viscosity, low critical strain value and higher relaxation times. The possible usage of the investigated non-ionic surfactants in non-substituted guar gum based reactive printing pastes is limited to lower surfactant content.

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