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Interactions between polysaccharide polymer thickener and bifunctional bireactive dye in the presence of nonionic surfactants. Part 1: surface tension and rheological behavior of different polysaccharide solutions

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Abstract

The quality of textile printing is closely related to the rheological characteristics of the printing paste which depend on the chemical structure of the thickener used, its concentration and physico-chemical interactions with other paste components. The undesired interactions between the polysaccharide guar gum thickener and the bifunctional bireactive dye after the addition of a nonionic surfactant were investigated as a function of the degree of carboxymethylation (DS) of the guar gum polymer, the hydrophilic/hydrophobic structure of the surfactant, and the concentration of the surfactant and the reactive dye. The rheological investigations show that the destroying of the primary polymer cross-linked structure leads to stronger pseudoplasticity/elasticity of the paste due to hydrogen and covalent ether bonds of surfactants as individual molecules (below critical micelle concentration (CMC)), or as micelle aggregates (above CMC) with the –OH groups of the thickener. The interactions increase with the increasing HLB value and the surfactant concentration, and with the decreasing DS of the polymer. A highly hydrophilic surfactant produced a strong drop of viscosity and leads to phase separation. The addition of the reactive dye diminishes the hydrophilic interactions between the surfactant and the guar gum thickener probably due to interactions between the reactive dye and the surfactant. The micellization process of the surfactant is not influenced by the presence of reactive dye or guar gum molecules. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Printing paste; Polysaccharide; Guar gum; Reactive dye; Nonionic surfactants; Interactions; Critical micelle concentration; Viscosity; Viscoelasticity

1. Introduction

The importance of reactive dyes for cellulose printing has given rise to many studies which either promote sodium alginate as the most appropriate thickening agent for the preparation of printing pastes or propose economically and ecologically more appropriate thickeners, among which polysaccharide guar gum polymers have been recognized as the best alternative. In a sufficiently concentrated aqueous solution the incorporation of hydrophilic –OH groups into guar gum chains causes the formation of more or less entangled macromolecules (clusters/coils) due to inter- and intra- molecular H- bonds occurred between the polymers. Such a three-dimensional polymer network structure consequently produces a highly viscous solution (Kokol, 1998).

Beside the technological parameters of printing, the rheological behavior of the printing paste plays one of the most important roles in the process of printing because it affects the amount of the printing paste applied on the textile surface and consequently on the quality of the printed substrate. Namely, during the printing process (the action of the squeegee) the printing paste is exposed to deformation forces that change the arrangement of polymer chains in their primary cross-linked structure and thus cause a drop of viscosity and increased elasticity. The rheological properties of the printing paste are closely related to the chemical structure of the thickener used, its concentration and the physico-chemical interactions with other paste components (Smith, 1995; Parac Osterman, 1996).

The application of guar gum in the presence of a bifunctional bireactive dye in cellulose printing is still not possible because of the 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

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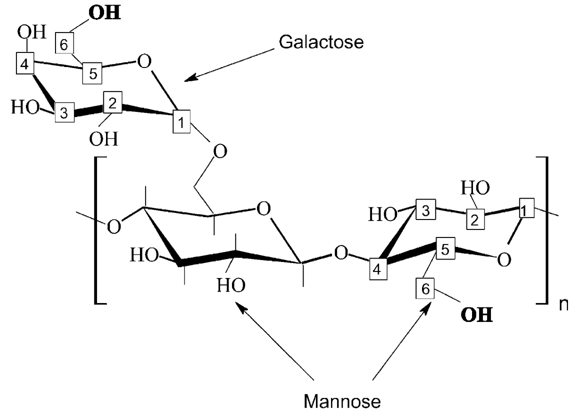

Fig. 1. Chemical structure of nonsubstituted guar gum (NSG).

changes of the printed substrate. The investigations conducted so far have shown that the modification of guar gum decreases the chemical cross-linking, but the results are still not satisfying.

An alternative way to reduce the mentioned undesired interactions is to add an appropriate additive into the printing paste (Kokol, 2001). It is proven (Kokol, Schneider, & Šostar-Turk, 2001) that some anionic and nonionic surfactants reduce the stiffness of so printed substrate to a certain degree. The connection between the chemical structure of the surfactant, its optimal concentration and its efficacy has not been revealed as yet. The objective of this and the following paper is so to ascertain the interactions occurring among the individual printing paste components (guar gum thickener, bifunctional bireactive dye and nonionic surfactants). The influence of the hydrophilic and the hydrophobic chain length and the role of the concentration of the surfactant will be presented, too.

Owing to the complexity of the system, several analytical methods were applied for every stage of the study. In the first paper the surface activity and the rheological behavior of different solutions will be studied, whereas in the second paper the size exclusion chromatography (SEC) will be used as an additional and a new alternative analytical method for the determination of mentioned interactions.

Table 1
The used polysaccharide guar gums

Guar gum	Abbreviation	DS	Concentration of solid (%)
Nonsubstituted	NSG	0	9.0
Carboxymethylised	CMG	0.4	8.0
Carboxymethylised	CMG	1.1	8.0

2. Experimental

2.1. Materials

2.1.1. Guar gums

Nonsubstituted (Fig. 1) and carboxymethylised (Fig. 2) guar gums were used as polysaccharide polymers. The –OH groups of carboxylmethylised guar gum were etherified with monochloroacetic acid to the required degree of substitution (DS). The abbreviation, the DS and the concentration of the solid (required for the stock paste preparation) of each guar gum thickeners used are shown in Table 1. All the guar gums were provided by Grünau Illertissen GmbH, Germany.

2.1.2. Surfactants and reactive dye

Five nonionic surfactants of different hydrocarbon chain lengths (hydrophobic part) and different numbers of ethyleneoxide (EO) units (hydrophilic part) in their molecules were chosen. The chemical structure, the abbreviation, the general specification (molecular weight M_w, Hydrophilic Hydrophobic Balance—HLB value, percent of EO units) and the producer of all surfactants used are presented in Table 2. All the surfactants were used in the commercial non-purified form.

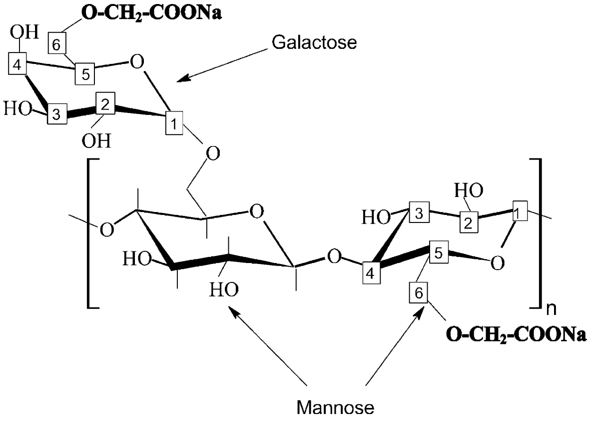

Fig. 2. Chemical structure of carboxymethylised guar gum (CMG).

Table 2
The specification of surfactants used

Chemical structure	Abbreviation	M_w	HLB value	EO (%)	Producer
$CH_3–(CH_2)_{17}–O–(CH_2CH_2O)_4–H$	$C_{18}EO_4$	446	7.9	39.5	Grünau Illertissen GmbH
$CH_3–(CH_2)_{17}–O–(CH_2CH_2O)_{10}–H$	$C_{18}EO_{10}$	710	12.4	62.0	Fluka Chemie AG
$CH_3–(CH_2)_{17}–O–(CH_2CH_2O)_{20}–H$	$C_{18}EO_{20}$	1150	15.3	76.5	Grünau Illertissen GmbH
$CH_3–(CH_2)_{15}–O–(CH_2CH_2O)_{10}–H$	$C_{16}EO_{10}$	682	12.9	64.5	Fluka Chemie AG
$CH_3–(CH_2)_{11/13}–O–(CH_2CH_2O)_5–H$	$C_{12/14}EO_5$	406/434	10.5/9.8	52.4/49.0	Schill and Seilacher GmbH

2.1.3. Reactive dye

A commercially available bifunctional bivinylsulphonyl dye C.I. Reactive Black 5 (Remazol Black B 133%) of the firm DyStar GmbH, Germany was used. The reactive dye present in Fig. 3 is a dye with a molecular weight M_w of 993.

2.2. Printing paste preparation

In accordance with the corresponding polysaccharide guar gum thickener and in order to set a constant viscosity of the stock paste, the defined quantity of solid (Table 1) and demineralized water were stirred in a mixer and left in a refrigerator overnight to attain full swelling. To prepare the printing pastes 60% of the stock paste of each thickener, 2.5% of $NaHCO_3$, 0% (1, 5%) of reactive dye and required amount of demineralized water were stirred for another 15 min. All the printing pastes were adjusted to a constant viscosity ($\eta = 7000 \pm 500$ mPa s) at the shear rate of $\dot{\gamma} = 10\ s^{-1}$ and $T = 25$ °C using the rotation rheological method. The required amount (0, 1, 3, 5%, …) of individual nonionic surfactant was added to each paste and stirred again to obtain homogeneous solution.

2.3. Methods

The surface tension and the critical micelle concentration (CMC) of different solutions containing surfactant were obtained with a K12 processor tensiometer (Krüss GmbH, Germany) using the plate Wilhelmy method. The Rheometrics Fluids Spectrometer (RFS II) (Rheometrics, USA) with a cone and plate measuring system (KP 25/0.05 mm, $d = 25.0$ mm) was used for the rheological properties of printing pastes determination. Viscosity measurements were performed with the rotation method at shear rates in the region of $\dot{\gamma} = 0.1–500\ s^{-1}$, whereas viscoelasticity was determined by the oscillation method. First, the linear viscoelastic region (Amplitude Sweep) at a constant frequency of oscillation $\omega = 10$ rad s^{-1} and at different amplitudes of deformation in the region between 0.1 and 100% was determined. The drop of the resulting curve determines how great the deformation amplitude or shear could be without destroying the inner structure of the sample. Regarding to this the viscoelastic properties were determined at a constant but the maximal (15.8%) amplitude of deformation (Frequency Sweep) in a frequency interval between $\omega = 0.1$ and 100 rad s^{-1}. The rheological measurements were performed in the I. Newtonian and structural viscosity region. The relations between the viscous-loss (G'') and the elastic-storage (G') modulus were expressed by the dynamic viscoelasticity parameter tan δ (loss factor). All the experiments were carried out at $T = 25.0 \pm 0.5$ °C.

3. Results and discussion

In order to establish the interactions between the guar gum thickener and reactive dye in aqueous alkali solution after the nonionic surfactant addition, the individual components of the printing paste were progressively introduced in the preparation of solutions. Interactions between the guar gum and the surfactant and then the interactions between the guar gum, surfactant and reactive dye were examined. The investigation was focused on the following influential parameters: (1) the chemical structure and the concentration of the surfactant in combination with the nonsubstituted guar gum, (2) the presence of the reactive dye and its concentration in combination with the nonsubstituted guar gum and different surfactants and (3) the degree of carboxymethylation (DS) of guar gum.

Because the surface tension is an important thermodynamic function used to explain the micellization process of surfactant solutions as well as the distribution of surfactant molecules in the presence of an additive (Schick, 1966), the surface activity and the micelle formation of nonionic surfactants in combination with other solution components were studied additionally.

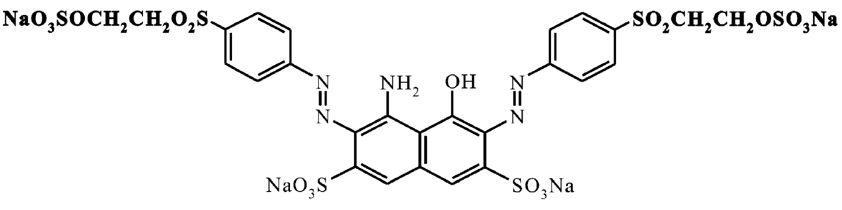

Fig. 3. Chemical structure of bifunctional bireactive dye.

Table 3
CMC values of pure nonionic surfactant solutions and in combination with NSG/0 thickener or reactive dye (/: not measured)

Surfactant	CMC ($g\,l^{-1}$)		
	Pure solution	Surfactant/NSG/0	Surfactant/r. dye
$C_{18}EO_{10}$	0.0128	0.0128	0.0128
$C_{18}EO_{20}$	0.0094	/	/
$C_{16}EO_{10}$	0.0057	/	/
$C_{12/14}EO_5$	0.0168	/	/

The obtained 'surface tension/surfactant concentration' curve in case of the $C_{18}EO_{10}$/guar gum and $C_{18}EO_{10}$/reactive dye mixture solutions showed only one equilibrium value which is the same as the CMC of the pure surfactant solution ($CMC = 0.0128\,g\,l^{-1}$) (Table 3). Since no special transition for Critical Association Concentration (CAC, Gilanyi & Wolfram, 1975; Lindman et al., 1993) is obtained, results indicate that the micellization process is not influenced by the presence of guar gum or reactive dye molecules, or that micelles of the same size and aggregation number are formed either in their pure solution or in the presence of guar gum or reactive dye molecules. Suchlike changing of CMC values with the changing chemical structure of the surfactants used can be explained by the impurity of surfactant components.

3.1. Interactions between surfactant and guar gum

3.1.1. The influence of the structure of the surfactant

The influence of the structure of the surfactant on the viscosity of nonsubstituted NSG/0 solutions (without the reactive dye) is shown in Fig. 4 for 1% and in Fig. 5 for 5% surfactant concentration. The addition of a surfactant causes an increase of viscosity at lower shear rates (in the I. Newtonian region) and a viscosity drop at higher shear rates (in the structural viscosity region) compared to pure guar gum solution. This effect is much more expressed and noticeable at a higher surfactant concentration (Fig. 5) indicating that the system becomes more shear sensitive or more pseudoplastic after the surfactant addition.

Such an effect of surfactant molecules on the viscosity behavior of polysaccharide guar gum solution can be explained by the particular orientation and adsorption properties of surfactant molecules in the studied aqueous solutions since the decrease of the viscosity curve, above all in the structural viscosity region, depends on the strength of the cross-linked polysaccharide structure (Kokol, 1998). In such a solution the individual surfactant molecules will migrate to polysaccharide hydrophilic –OH groups and participate in a polymer inter-molecular associations: they will orient with their hydrophilic EO units and final –OH group in the direction of polysaccharide –OH groups, while the hydrophilic carbon chains will orient toward the solution. Individual surfactant molecules will so bind to –OH groups of the guar gum macromolecules with their hydrophilic EO units via H- bonds as well as with their final –OH group with a covalent ether bond (due to the alkali medium pH = 8–9, Krässig, 1993). A suchlike orientation of the surfactant molecules will in the first step and at enough higher surfactant concentration form a monomolecular film on a polysaccharide surface which will break the inter-molecular H- bonds between individual polymer clusters and separate them into individual complex formations. As the surfactant concentration is increasing, the surfactant molecules will start to associate into micellar aggregates which will bind on the polymers in the same way; thus the cluster structures will become separated, but still connected to each other via surfactant micellar aggregates with H- or ether bonds.

An increase of the viscosity at lower shear rates is so the result of system thickening owing to the enveloping of the polysaccharide macromolecular structure of guar gum with

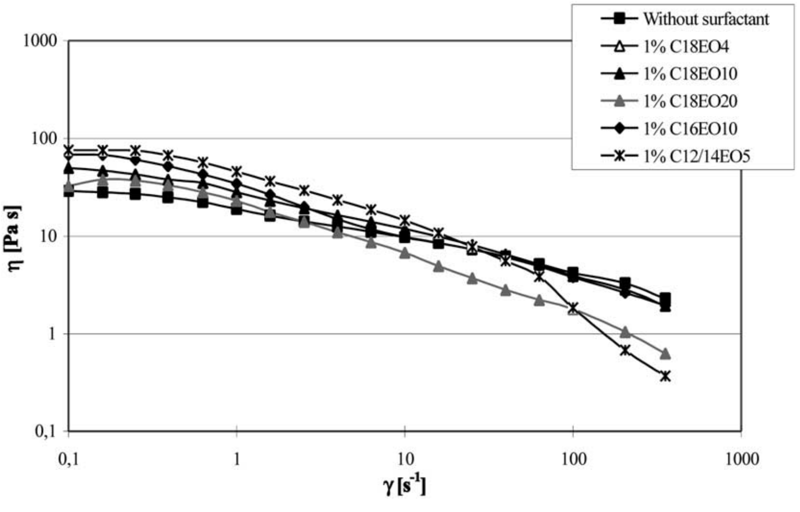

Fig. 4. The influence of different surfactants (1%) on the viscosity of NSG/0 solutions without the reactive dye.

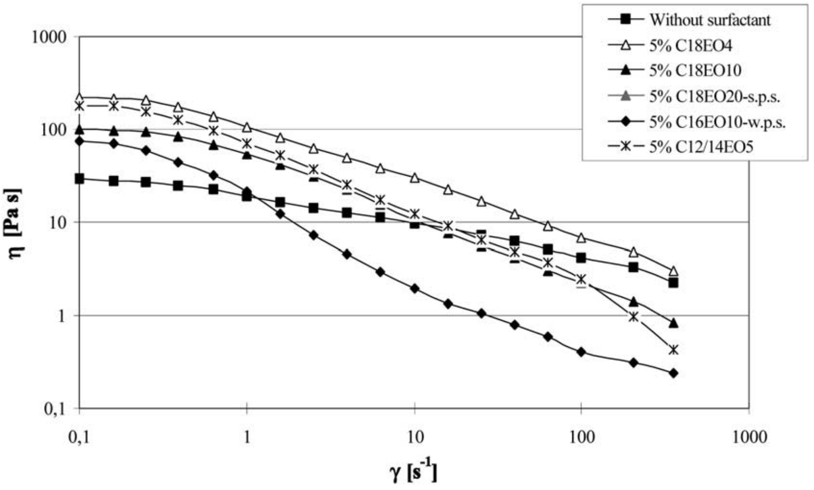

Fig. 5. The influence of different surfactants (5%) on the viscosity of NSG/0 solutions without the reactive dye.

a surfactant molecules/micelles or owing to the incorporation of surfactant micellar structures into inter-molecular associations. An applied shear rate cause the breaking of inter-molecular H- bonds between the surfactant and polymers (the breaking of complex formations) and at the same time provoke an uncoiling of the polysaccharide polymers which must be much more readily aligned than in its pure solutions since the drastic pseudoplasticity effect of those solutions is observed.

It is also evident from the viscosity measurements (esp. from the degree of pseudoplasticity) that the changes of a polysaccharide cross-linking structure depends beside of the surfactant concentration also on the length of the hydrophobic and the hydrophilic part of the surfactant molecule (HLB value) particularly at higher (≥5%) surfactant concentrations (Fig. 5). In the case of $C_{18}EO_{20}$/NSG/0 system the viscosity could not be measured because of the instant strong phase separation (s.p.s.) with the added surfactant, whereas in the case of $C_{16}EO_{10}$ surfactant a weak phase separation (w.p.s.) is appeared which is also probably the reason for a very short Newtonian behavior at lower shear rates and an important decrease of viscosity in the structural viscosity region. Such a rheological behavior of a studied mixtures could be the consequence of the saturation of the polymer surface with surfactant molecules before it starts to uncoiling. Quantitatively greater interactions between hydrophilic EO units and –OH groups of polymers the most probably cause the orientation of the hydrophobic hydrocarbon chains towards the water; since such agglomerate-like forms become hydrophobic on the surface (i.e. hydrophobically modified) a separation of the system in two phases occur. From the comparison of four surfactants ($C_{18}EO_4$, $C_{12/14}EO_5$, $C_{18}EO_{10}$, $C_{18}EO_{20}$) it can also conclude that the pseudoplastic behavior of NSG/0 solutions increases with the increasing HLB values (7.9, 10.5/9.8, 12.4, 15.3; Table 2). A highly hydrophobic surfactant ($C_{18}EO_4$) does not interact strongly with the polymer, whereas as it was described a very hydrophilic surfactant ($C_{18}EO_{20}$) causes the phase separation. However, the variation of the hydrophobic carbon chain length at a constant number of the hydrophilic EO units (in case of $C_{18}EO_{10}$ and $C_{16}EO_{10}$) has a greater impact on the pseudoplasticity of the system than the variation of the number of EO units at a constant carbon chain length (in case of $C_{18}EO_4$, $C_{18}EO_{10}$ and $C_{18}EO_{20}$).

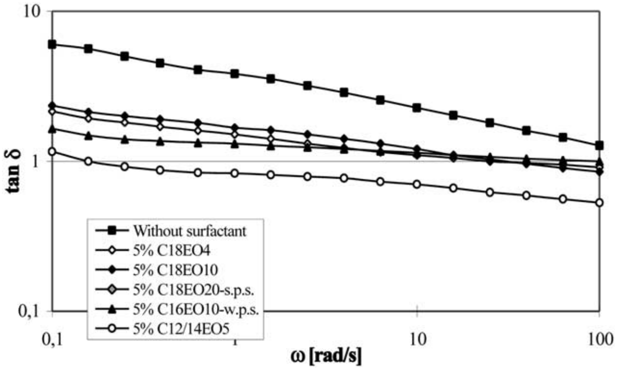

Fig. 6. The influence of surfactant (5%) on the tan δ of NSG/0 solutions without the reactive dye.

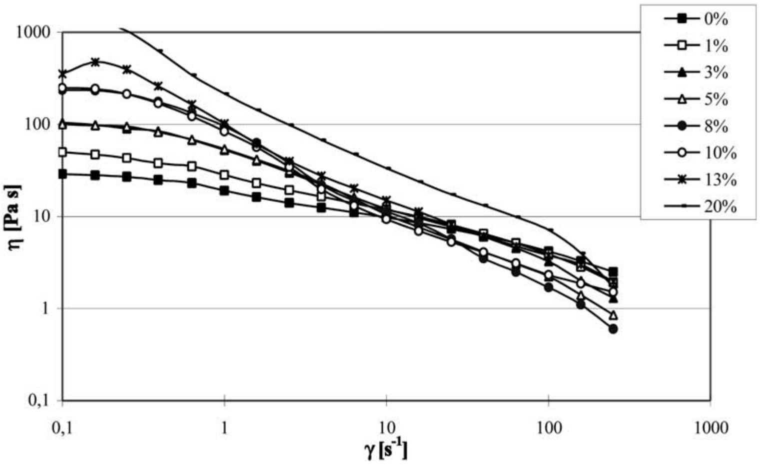

Fig. 7. The influence of the $C_{18}EO_{10}$ surfactant concentration on the viscosity of NSG/0 solutions without the reactive dye.

The viscoelasticity behavior of these surfactant/NSG/0 mixtures presenting in Fig. 6 coincide with the results of viscosity measurements. Higher values of tan δ indicate that the G'' is higher than the G' or that the viscous component, which is most strongly expressed at the NSG/0 solution without the surfactant, is predominant. The greater the stress applied to such a solution, the more elastic and the less viscous it gets because the tan δ values decrease with the increasing oscillation frequency in all measured region. The addition of a surfactant to the NSG/0 solution results in a much more elastic system, which shows in much lower tan δ values obtained already at lower oscillation frequencies. The $C_{12/14}EO_5$ surfactant results to the most elastic system whereas the mixtures containing other surfactants show an intermediate behavior of elasticity. Considering the effect of the chemical structure of the surfactant in the guar gum solution, we can conclude that the elasticity of the system increases with the increasing hydrophilic part and with the shortening hydrophobic part of the surfactant where the carbon chain length has a greater effect than the number of EO units. The higher the HLB value the more elastic is the system.

3.1.2. The influence of the concentration of the surfactant

The course of the viscosity curves of $C_{18}EO_{10}$/NSG/0 (Fig. 7) and $C_{16}EO_{10}$/NSG/0 (Fig. 8) mixtures confirms the occurrence of inter-molecular interactions between surfactants and guar gum polymers. The increase of the viscosity in the I. Newtonian region is, as described previously, the result of the participation of surfactant in a polymer inter-molecular cross-linking resulting into more dense system: the contribution of individual surfactant molecules (under CMC) is negligible whereas the increasing concentration of surfactant monomers and micelles (above CMC) have an important impact since it is known that the viscosity of a pure surfactant solution increases with the increasing surfactant concentration (Kokol, 2001; Pisarcik & Bakos, 1994). At very high surfactant concentrations a transition from a close-packed micellar phase containing spherical micelles to a phase with rod or later to a phase with hexagonal structures could also be possible.

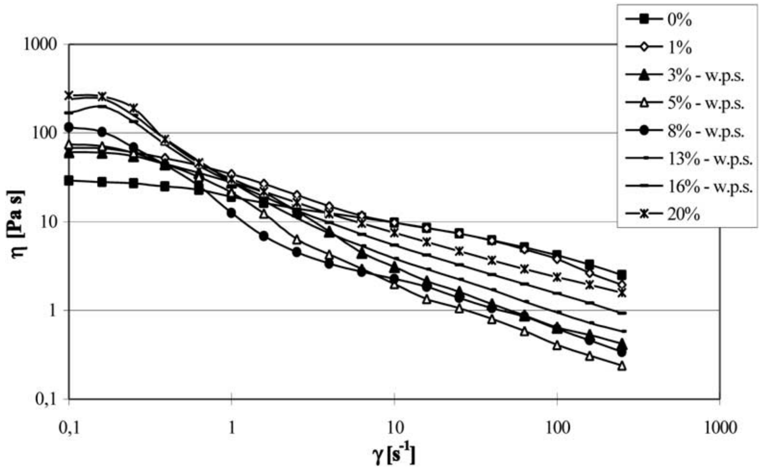

Fig. 8. The influence of $C_{16}EO_{10}$ surfactant concentration on the viscosity of NSG/0 solutions without the reactive dye.

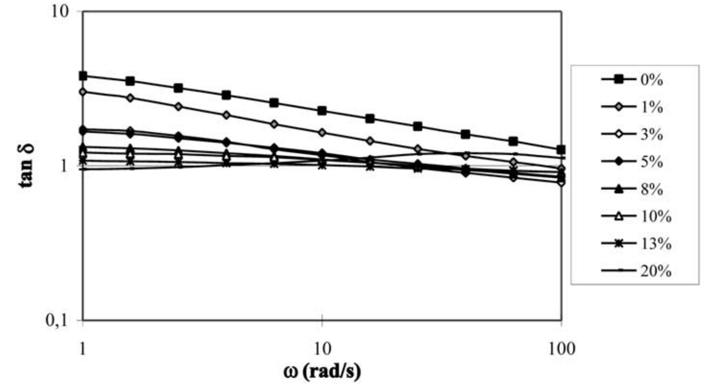

Fig. 9. The influence of different $C_{18}E_{10}$ surfactant concentration on the tan δ of NSG/0 solutions without the reactive dye.

In this case the guar gum clusters will place between such micellar structures or the micelles structures will act as cross-linkers between individual polymer clusters. An intensively pseudoplastic effect of those solutions at higher shear rates coincide with this explanation since formed micelle/polysaccharide complexes are much more shear sensitive than guar gum coils in their pure aqueous solutions; the insertion of surfactant micelles into polymer cross-linking structure obviously causes their degradation.

Comparing the effect of different surfactant concentrations in NSG/0 solution it can be see that the transition from the I. Newtonian to the structural viscosity region in case of solutions containing the $C_{18}EO_{10}$ (Fig. 7) occurs at much higher shear rates ($\dot{\gamma} = 10.0\ \mathrm{s}^{-1} \pm 0.3\%$) compared to solutions containing the $C_{16}EO_{10}$ (Fig. 8) ($\dot{\gamma} = 0.8\ \mathrm{s}^{-1} \pm 1\%$) and that the pseudoplasticity effect is much more expressed at the $C_{16}EO_{10}$/NSG/0 system (it starts already at a 3% concentration). This indicate that the cross-linked structure of the $C_{18}EO_{10}$/NSG/0 complex solution is much more dense than the $C_{16}EO_{10}$/NSG/0 one. It is difficult to establish why so similar nonionic surfactants cause so different viscosity behaviors but it could predict that the surfactant micellar aggregation number plays an important role in defining those complex structures.

As could be seen from the Fig. 9, the tan δ values of NSG/0 solutions decrease with the increasing $C_{18}EO_{10}$ surfactant concentration and the flow curves of solutions containing $\geq$10% surfactant depend no longer on the oscillation frequency, which indicates that the ratio of the G' and the G'' moduli is almost constant, or that the systems are entirely elastic. Also, the higher the surfactant concentration, the lower the frequencies at which the transition from viscous to elastic behavior takes place. It is obvious from the Fig. 10 that in the case of solutions containing the $C_{16}EO_{10}$ surfactant this transition takes place at a much lower frequency and a lower surfactant concentration (5%) than in case of solutions containing the $C_{18}EO_{10}$ surfactant (10%) which could ascribe to intensive interactions between the surfactant and guar gum. Such a behavior again confirm the formation of a dense cross-linking structure in case of the $C_{18}EO_{10}$/NSG/0 solution.

3.1.3. The influence of the DS of guar gum

The DS of guar gum polymers has an important influence on the course of viscosity curves before as well as after the addition of a surfactant (Fig. 11). The CMG/0.4 solution exhibits a Newtonian character at lower shear rates for a longer period of time and a more strongly expressed pseudoplastic behavior at higher shear rates than the NSG/0 solution; the incorporation of inter-molecular electrostatic

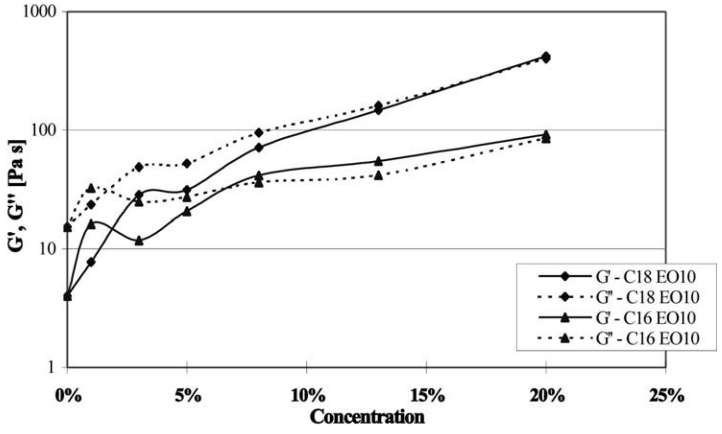

Fig. 10. The influence of different surfactant concentration on the storage (G') and the loss (G'') modulus ($\omega = 1.0\ \mathrm{s}^{-1}$) of NSG/0 solutions.

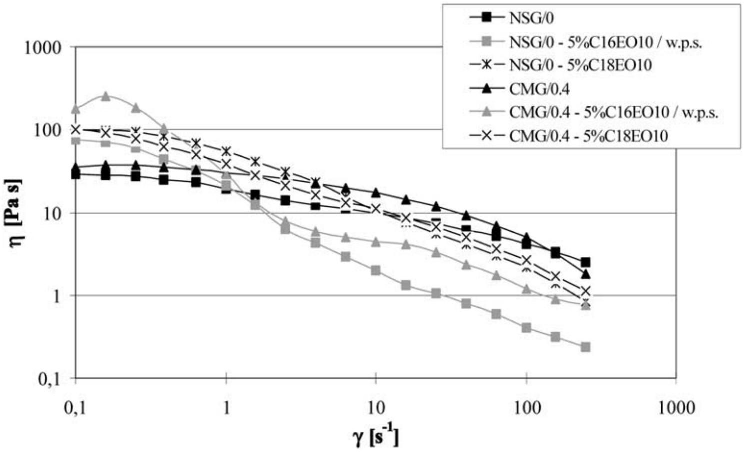

Fig. 11. The influence of different surfactant (5%) and guar gums on the viscosity of solutions without the reactive dye.

repulsion interactions between –COO$^-$ anions in case of CMG/0.4 thickener cause faster extension of polymer macromolecules compared to the NSG/0 thickener. A stronger drop of the viscosity curve, especially at higher shear rates, is observed when the $C_{16}EO_{10}$ surfactant is added to those polysaccharide solutions compared to the $C_{18}EO_{10}$ one. The decrease of viscosity is more intensive with the NSG/0 than with the CMG/0.4 mixtures because a smaller number of –OH groups in case of the CMG/0.4 thickener leads to less interactions with surfactant and consequently to slower uncoiling of polymers.

Since the drop of the viscoelasticity curve for the CMG/0.4 solution (without a surfactant) present in Fig. 12 is greater than that obtained with the NSG/0 solution, the elasticity of the CMG/0.4 solution increases faster with the increasing oscillation frequency than to the NSG/0 one.

The addition of the $C_{16}E_{10}$ or $C_{18}E_{10}$ surfactant (5%) to the used guar gum solutions results in much lower tan δ values in all measured regions and in a much smaller slope of their curves compared to the solution without the surfactant; meaning that the elasticity of the systems is higher and that it increases with the increasing frequency. The tan δ curves for both guar gum thickener solutions become identical upon the addition of the $C_{18}E_{10}$ surfactant (5%), whereas the addition of the $C_{16}E_{10}$ (5%) to the CMG/0.4 solution indicates lower tan δ values and additionally a smaller slope of the curve compared to the $C_{16}E_{10}$/NSG/0 system. It is obvious that the carboxymethylation of guar gum polymers contributes to a higher elastic modulus when the $C_{16}E_{10}$ surfactant is used.

3.2. Interactions between surfactant, reactive dye and guar gum

Previous investigations (Kokol, 1998) have shown that the type as well as the concentration of the reactive dye has an important influence on the rheological behavior of printing pastes prepared from different guar gum thickeners. Due to this fact, the curves that present the rheological behavior of printing pastes containing 1 or 5% of reactive dye (at the absence of surfactant) are overlapping. But at could be seen from the Fig. 13, the concentration of the reactive dye has an important influence on the viscosity behavior of the paste containing a nonionic surfactant and that this behavior dependent on the concentration of the surfactant used. This influence is clearly expressed at higher

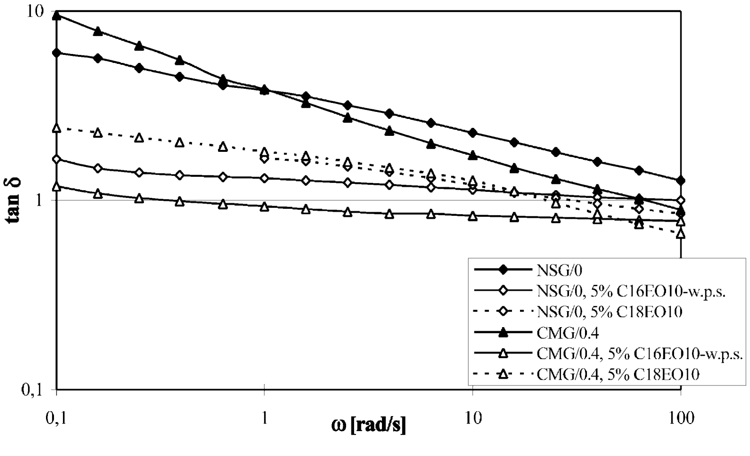

Fig. 12. The influence of different surfactants on the tan δ of NSG/0 and CMG/0.4 solutions without the reactive dye.

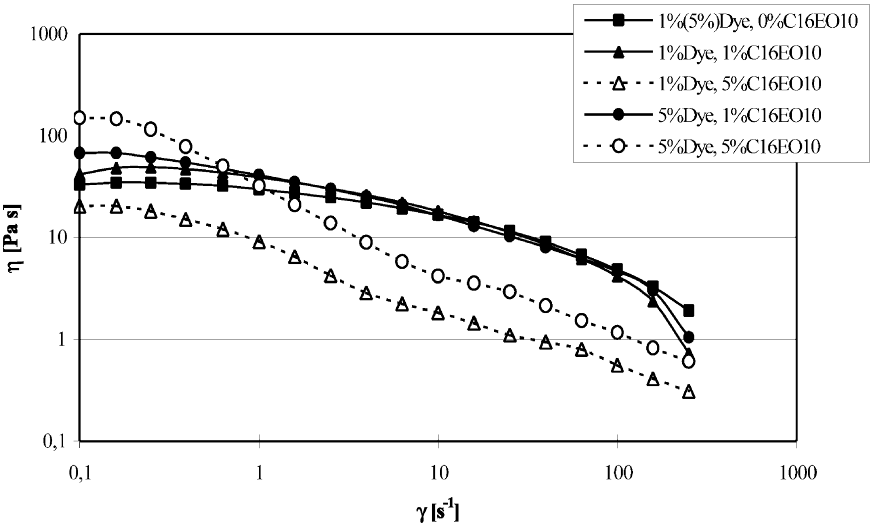

Fig. 13. The influence of different reactive dye concentration on the viscosity of the CMG/0.4 solutions with 5% of $C_{16}EO_{10}$ surfactant.

surfactant concentration (5%) where the viscosity values in both measured regions and with the system containing 5% reactive dye are higher than the system containing 1% of reactive dye. The obviously diminishing difference between the obtained two viscosity curves with the increasing shear rates indicate that at a higher dye concentration a more stable system is obtained. It can be assume that the interactions between the surfactant and guar gum polymer diminish due to the occurrence of interactions between the surfactant and the reactive dye molecules.

It is also clearly evident from the Fig. 14 that the elasticity of printing pastes containing NSG/0 thickener and 5% $C_{16}EO_{10}$ surfactant obviously increases with the increasing reactive dye concentration and from the Fig. 15 that the DS of the guar gum additionally increase the elasticity component and reduce the viscosity one at higher (5%) reactive dye and surfactant concentrations.

4. Conclusion

The rheological changes of printing paste containing the polysaccharide guar gum thickener and the bifunctional bireactive dye after the nonionic surfactant addition indicate on it's interactions with all paste components. The most important interactions are those between the surfactant and guar gum polymer since they change the primary cross-linked structure formed by polymer clusters in an aqueous alkali medium and results to more pseudoplastic and more elastic system. The intensity of interactions depends on the chemical structure and the concentration of the surfactant and on the type of guar gum thickener used. At low surfactant concentrations (below the CMC) individual surfactant molecules bind with H- bonds (via hydrophilic EO units) or ether bonds (via end –OH groups) with the –OH groups of guar gum polymers. Increasing

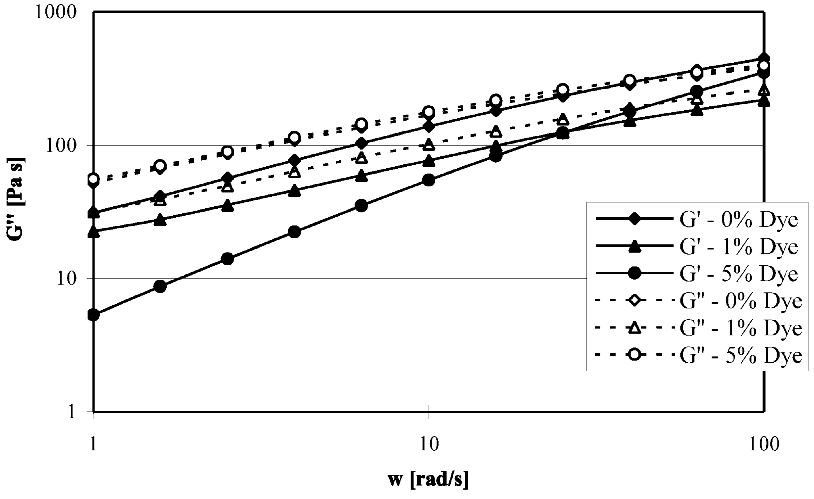

Fig. 14. The influence of different reactive dye concentration on the G' (elasticity) and G'' (viscosity) modulus of NSG/0 guar gum solutions with 5% of $C_{16}E_{10}$ surfactant.

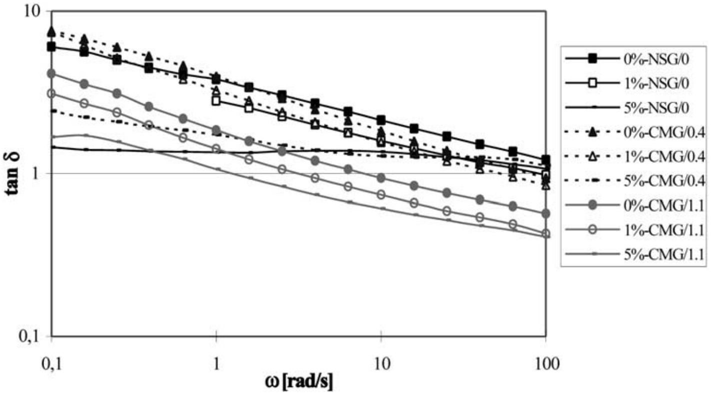

Fig. 15. The influence of $C_{18}E_{10}$ surfactant concentration on the tan δ of different guar gum solutions with 5% reactive dye.

surfactant concentrations form in the first step a monomolecular film on polysaccharide cluster surfaces and in the second step (above the CMC) the micelles of surfactants envelop the individual cluster structures; the complex formations occur. Further increasing of surfactant concentration could results in a higher forms of micelle aggregates (rod-like, hexagonal, lamellar) which should be freely formed in the solution after the saturation on guar gum cluster structures. The micellization process is not dependent on the presence of guar gum molecules.

The intensity of interactions between surfactant and guar gum polymers increases with the increasing HLB value of the surfactant ($C_{18}EO_{20} > C_{16}EO_{10} > C_{18}EO_{10} > C_{18}EO_4$). At higher concentrations (≥5%) the most hydrophobic surfactant ($C_{18}EO_4$) has no relevant influence on the changes in the polysaccharide cross-linking structure, while the most hydrophilic one ($C_{18}EO_{20}$) causes the separation of the system into two phases. The shortening of the hydrophobic chain ($C_{18}EO_{10}$, $C_{16}EO_{10}$) has a greater influence on the intensity of interactions than the increasing number of hydrophilic EO units ($C_{18}EO_4$, $C_{18}EO_{10}$, $C_{18}EO_{20}$). The interactions decrease with the increasing carboxymethylation degree of the polymer (due inter- and intra- molecular electrostatic repulsion forces acting between $-COO^-$ anions) and with the increasing concentration of the reactive dye. The presence of reactive dye most probably causes interactions between the surfactant and reactive dye which additionally increases with the increasing hydrophilic EO units number and concentration of the surfactant.

The rheological measurements do not provide direct information about the amount of redistributed surfactant into the surfactant/reactive dye/guar gum solution but the method could be used above all for the study of interactions between surfactant and guar gum thickener. In the next paper the investigation of all types of interactions will be studied using SEC method.

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