Polymer Communication

Rheological study of compositional heterogeneity in an associative commercial polymer solution

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Abstract

The compositional heterogeneity of a concentrated aqueous solution of a commercial hydrophobically associating polysaccharide and its precursor has been investigated, using optical and rheometrical characterization. Optical observations proved that the non-associating precursor solution was rather homogeneous, whereas significant compositional heterogeneity was present in the associating one, containing soft polymeric particles with a size of order 100 μm. Linear and non-linear rheological measurements were carried out on the centrifuged and non-centrifuged associating polymer solution in order to study the rheological influence of these objects and their nature. The results tend to prove that the soft polymeric particles are mainly composed of polymer chains bearing the longest hydrophobic groups. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Hydrophobically associating water soluble polymers form a class of macromolecules with great interest in pharmaceutical, biotechnological and industrial applications [1–3], where they are used mainly as rheology modifiers [4,5]. These amphiphilic polymers are hydrophilic polymers containing few hydrophobic groups, in the form of side chains or terminal groups. Among these polymeric materials, particular attention has been paid to naturally occurring or chemically modified polysaccharides and their hydrophobic derivatives [6]. One of such polysaccharide derivatives, hydroxypropyl guar gum, has been thoroughly studied in the recent years, mainly from a rheological point of view [7–11]. All these studies were performed with relatively well-characterized samples synthesized in laboratory conditions [12]. Indirect rheometrical evidence of the existence of compositional heterogeneous states in aqueous solutions of such well-characterized hydrophobically modified hydroxypropyl guar has been reported very recently [11]. Indeed compositional heterogeneity is often encountered in associative polymer solutions, because of a delicate balance between association and phase separation [13]. The existence of heterogeneous polymeric parts in associative polymer solu-

tions is influenced by the number, the length and the location of the hydrophobic units, thus it is all the more expected as the polymer is closer to its commercial form, which often present a large distribution of those molecular characteristics. The aim of the present paper is to study a commercial hydrophobized hydroxypropyl guar gum and its precursor, focusing on macroscopic compositional heterogeneity, characterized by optical and rheometrical investigation techniques.

2. Materials

2.1. Polymers

The commercial polymers used for this study have been synthesized by Fratelli Lamberti s.p.a. (Albizzate, Italy) [14]. Two types of polymers have been used.

1. The precursor, that is the parent non-associative guar gum derivative, containing an average of one hydrophilic substituent (hydroxypropyl or hydroxybutyl group) per monomer. The weight average molecular weight is about 2×10^6, corresponding to a degree of polymerization of about 3000, and the dispersity index is approximately 1.5. The structure of the repeating unit of guar and hydroxypropyl guar is shown in Fig. 1.
2. The hydrophobically modified polymer, obtained by

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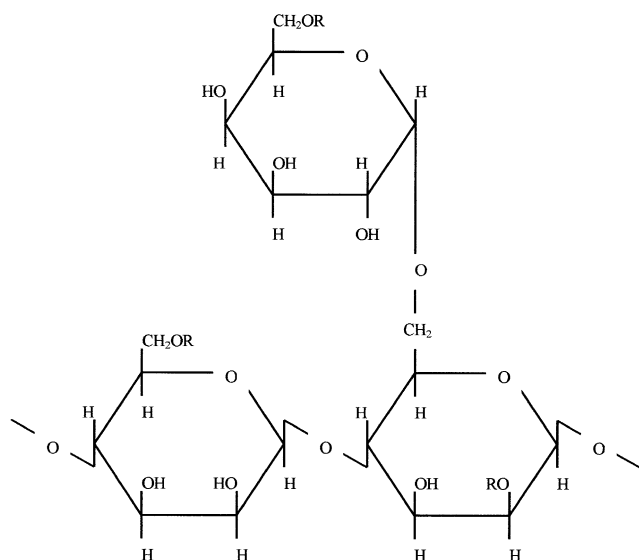*E-mail address:* thierry.aubry@univ-brest.fr (T. Aubry).

Fig. 1. Structure of the repeating unit of guar (R = H) and hydroxypropyl guar (R = CH$_2$CH$_2$CH$_2$OH).

reaction of the parent polymer with a mixture of C$_{18}$ to C$_{28}$ n-alkyl epoxides. The number of hydrophobic substituents per polymer chain lies between 0 and a few 10s and their distribution along the chain is supposed to be a random one. Moreover we assume that the chemical hydrophobic modification of the precursor leads to no molecular degradation, as suggested by Caritey [12].

We would like to point out that the associative and parent guar gum derivatives previously studied [7–11] were laboratory samples, whereas those studied in this work, though of the same type, are commercial samples.

2.2. Polymer solutions

Solutions were prepared by dissolving the solid polymer under gentle stirring in distilled water, then left at rest for 24 h at 4 °C before any measurement. The concentration range of parent polymer solutions, studied in this work, lies between 0.01 and 1% w/w, and that of the associative polymer solutions lies between 0.01 and 0.6% w/w. These polymer concentration domains include the dilute regime and the semi-dilute to concentrated regimes, the overlap concentration being about 0.1% w/w [12].

3. Techniques

All polymer solutions were centrifuged at 18,000 rpm for 1 h, at ambient temperature. After each centrifugation, at least when a dense, opaque phase, referred to as bottom phase in the paper, was observed at the bottom of test container, the supernatant was removed and centrifuged again; this process was continued till no visible phase separation was obtained. Three types of samples were studied: the non-centrifuged solutions, the supernatants

obtained at the last centrifugation step, and a mix of all bottom phases collected after each centrifugation step.

After centrifugation, the polymer concentration was determined at different levels in the test container, using the total organic carbon (TOC) technique: a small sample of supernatant is heated at 680 °C in an O$_2$ atmosphere, so that all carbon atoms are transformed in CO$_2$, whose concentration is determined by spectrometry. The polymer concentration was inferred only after knowing the chemical structure of the polymer. The concentration profiles measured using this technique are only indicative of the average hydrodynamic effects felt by macromolecular chains submitted to centrifugation.

Rheological measurements were performed at 25 °C, using a Rheometric Scientific AFES strain controlled rheometer, equipped with either Couette or parallel-plate geometries, depending on the viscosity of the sample. The two surfaces of the parallel-plate geometry were roughened with waterproof abrasive paper of roughness of about 100 μm, in order to avoid slippage [11].

The rheological investigation was completed by optical microscopy. Drops of non-centrifuged solutions were dried in a drying oven at 50 °C for 24 h, then observed using an optical microscope. The drying technique was used to improve the contrast of the polymeric objects observed.

4. Results and discussion

4.1. Heterogeneity of the non-associative polymer solutions

The first result to be mentioned is that the volume of the dense phase, collected at the bottom of the test container after centrifugation, is too small to allow a rheometrical investigation. Moreover, the polymer concentration profile was shown to be quite uniform within the supernatant.

Fig. 2 shows an optical micrograph of a non-centrifuged 0.4% w/w solution. This picture is quite illustrative of what is observed in any parent polymer solutions tested in this
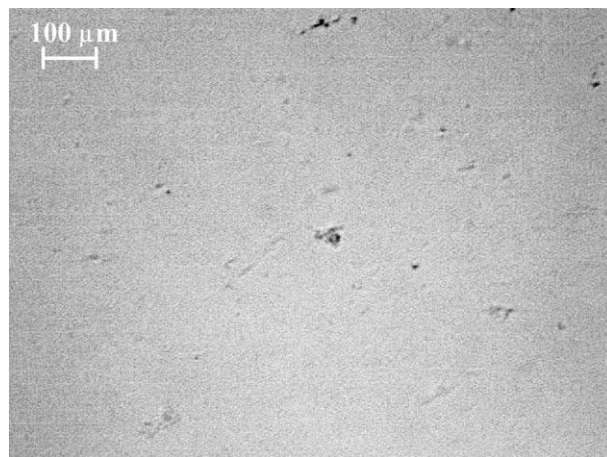

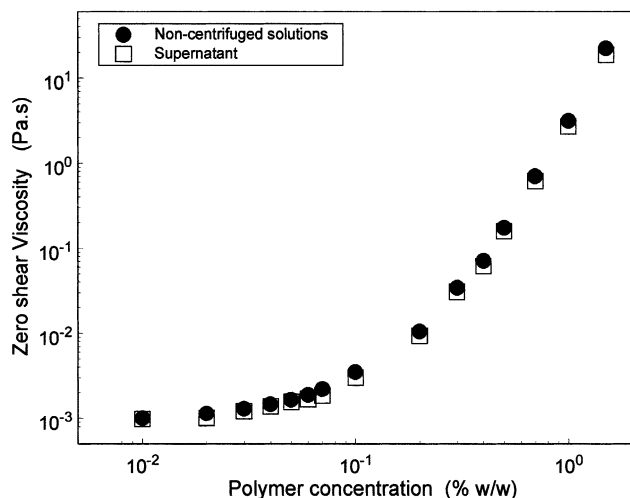Fig. 2. Optical micrograph of a 0.4% w/w non-associative precursor solution.

Fig. 3. Zero-shear viscosity as a function of polymer concentration for non-associative precursor solutions and for supernatants obtained after complete centrifugation.

Fig. 4. Optical micrograph of a 0.4% w/w associative polymer solution.

work. Indeed, no visible significant heterogeneity has ever been observed in these materials.

Fig. 3 shows the zero-shear viscosity versus polymer concentration, for the non-centrifuged solutions and for the supernatants after centrifugation. In the concentration range studied, there is no significant difference in Newtonian viscosity between the two types of samples.

These macro and microscopic results tend to prove that the non-associative parent polymer solutions are rather homogeneous in composition, at least in the concentration range of the study.

4.2. Heterogeneity of the associative polymer solutions

The volume of the dense phase, collected at the bottom of the test container after centrifugation, is quite sufficient in volume to allow a rheometrical investigation. We have to point out that this first qualitative significant difference between the two polymers cannot be attributed to the centrifugation of the macromolecules of the highest hydrodynamic volume, since both polymers are supposed to have nearly the same molecular characteristics. Besides, the polymer concentration profile was shown to be rather uniform within the supernatant after centrifugation.

Fig. 4 shows an optical micrograph of a non-centrifuged 0.4% w/w associative polymer solution. This picture illustrates the type of polymeric objects observed in non-centrifuged solution above 0.1% w/w, that is above the overlap concentration. The average size and number of the polymeric particles increases with polymer concentration above 0.1% w/w; for a 0.4% w/w solution, the average characteristic size is about 100 μm, as shown in Fig. 4. Below the overlap concentration and for all the supe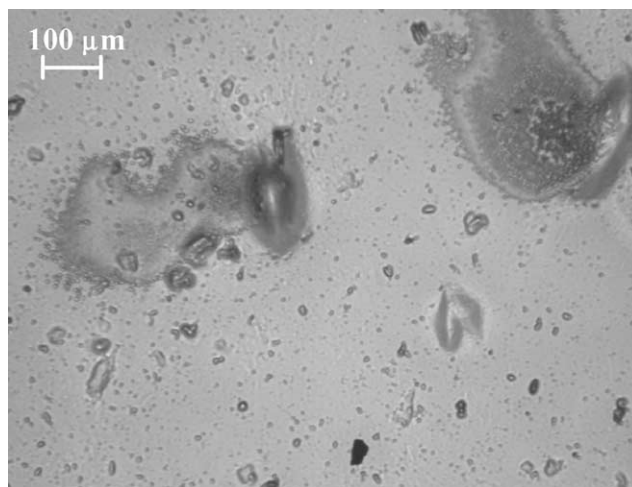rnatants, the micrographs present the same features as those observed for non-associative polymer solutions, where no significant heterogeneity appears.

Fig. 5 shows the Newtonian viscosity of the non-centrifuged solutions and the supernatants after centrifugation, as a function of polymer concentration. This figure clearly shows that the zero-shear viscosity of supernatants is lower than that of the non-centrifuged solutions, at least at concentrations above 0.1% w/w; that is above the overlap concentration where an entanglement network and a reversible associative network superpose [7]. This difference in zero-shear viscosity level was attributed to the presence of the polymeric objects, microscopically observed in the non-centrifuged solutions, which contribute to the flow resistance. It has to be noticed that the difference between the zero-shear viscosities of the two samples decreases at concentrations above 0.25% w/w. This trend reveals that the centrifugation technique is less and less efficient as the polymer concentration further increases and can be attributed to a reinforcement of the entanglement network, which hinders the 'suspended' polymeric objects from being centrifuged.

Hence there is a clear evidence that the associative polymer solutions are heterogeneous in composition above the overlap concentration, contrary to the solutions of the non-associative parent polymer. This difference can thus be attributed to the presence of the hydrophobic intermolecular junctions within the associative solutions. Moreover, the presence of micrometric polymeric objects was shown to modify the rheological properties of the associative solutions, as suggested in a previous work [11].

Linear and non-linear rheological investigation was then performed in order to get some physical insight into those polymeric objects. Results are shown for a 0.4% w/w polymer solution.

Fig. 6 shows the steady state viscosity versus shear stress of the non-centrifuged solution and the supernatant, obtained after one or two centrifugations. The non-centrifuged
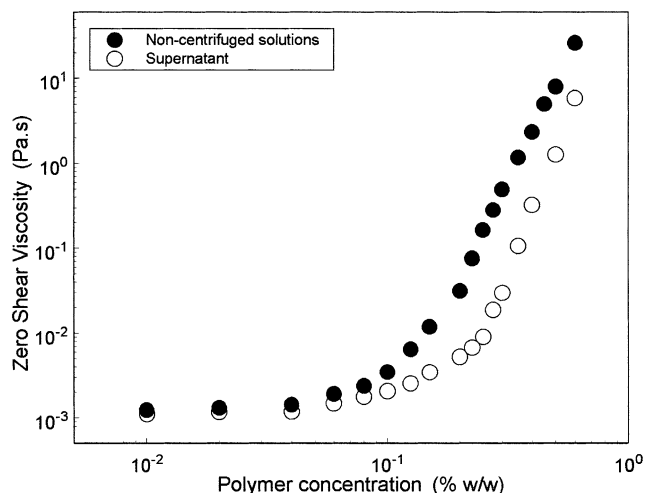
Fig. 5. Zero-shear viscosity as a function of polymer concentration for associative solutions and for supernatants obtained after complete centrifugation.
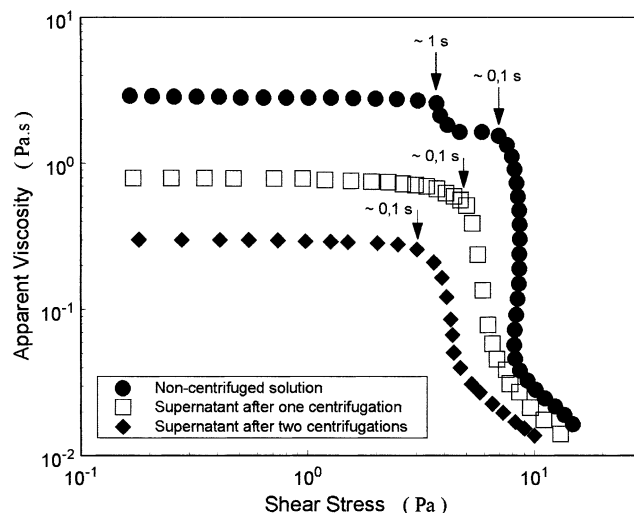

Fig. 6. Steady-state viscosity as a function of shear stress for a 0.4% w/w associative polymer solution and for the supernatant obtained after one or two centrifugations.

solution exhibits a well-defined Newtonian viscosity, followed by two strong shear-thinning regions, separated by a small viscosity plateau. The second discontinuity is much more abrupt than the first one. The viscosity jump corresponding to the first and second discontinuity in the flow curve is about 35 and 95%, respectively, compared to the Newtonian viscosity level and viscosity plateau, respectively. After one centrifugation, the zero-shear viscosity of the supernatant decreases and the flow curve exhibits only one discontinuous shear-thinning region. The effect of the second centrifugation is to reduce the Newtonian viscosity level of the supernatant and to decrease the height of the viscosity jump corresponding to the discontinuous shear-thinning domain. These non-linear rheological results can be discussed in terms of microscopic characteristic time scales. Indeed the inverse of the shear rate, just before a discontinuity in the flow curve, has been shown to define a characteristic time scale corresponding to the time needed for a hydrophobic group to exit from an associative micelle [7]. Applying this process to the 0.4% w/w solutions tested leads to define two characteristic times, of about 0.1 and 1 s, for the non-centrifuged solution, and only one characteristic lifetime, of about 0.1 s for the supernatant. This result suggests that the associative solution contains mainly two populations of hydrophobic groups, one characterized by a short lifetime, which does not seem to be significantly affected by the centrifugation, and the other one, characterized by a longer lifetime, which is highly sensitive to centrifugation. Moreover, if the height of the discontinuity is considered as a measure of the density of hydrophobic junctions present in the solution, as suggested by Aubry and Moan [7], then the non-centrifuged solution is shown to contain a large majority of hydrophobic groups of short lifetime.

These results are confirmed and completed by the study of the rheological properties of the bottom phase. Fig. 7

shows the flow curve of the bottom phase of a 0.4% w/w associative polymer solution. The apparent viscosity of this sample does not exhibit a Newtonian plateau at low shear stresses, but a smooth shear-thinning region, followed by a discontinuous shear-thinning domain at higher stresses. The latter shear-thinning region appears at a characteristic time of 1 s, corresponding to the longest association lifetime defined before, as expected. However, contrary to the non-centrifuged solution, the bottom phase cannot be considered as a dense macromolecular system. Indeed, the existence of a less marked shear-thinning region at low shear rates, without any measurable Newtonian viscosity, tends to show that the system rather behaves like a structured colloidal system. This set of non-linear rheological results leads to think that the bottom phase is a dispersion of polymeric particles composed of macromolecules interacting via hydrophobically associating junctions of the longest lifetime.

The discussion of the time scales, attributed to association lifetimes, prevailing in the various systems studied can be presented in molecular terms: the shorter and longer lifetimes being characteristic of the shorter and longer hydrophobic groups, respectively, as studied by Annable et al. [15]. However, the discussion is restricted to a qualitative molecular interpretation; indeed the absence of data on the molecular weight distribution of the hydrophobic substituents prevents us from discussing the results in terms of carbon content of the hydrophobic units.

Linear viscoelastic measurements were performed in order to complete the rheological characterization and particularly to study the dynamics of the polymeric systems on longer time scales.

First of all, we have to notice that the storage and loss modulus of the supernatants were too low to be measured, therefore the study of the linear viscoelastic properties was limited to the non-centrifuged solution and to the bottom
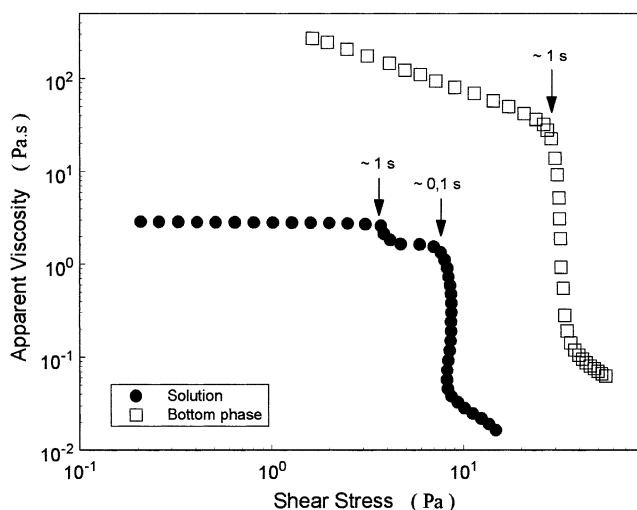
Fig. 7. Steady-state viscosity as a function of shear stress for a 0.4% w/w associative polymer solution and for the bottom phase obtained after one centrifugation.

Fig. 8. The storage modulus G' and the loss modulus G'' as a function of pulsation ω for a 0.4% w/w associative polymer solution and for the bottom phase obtained after one centrifugation.

phase after centrifugation. Fig. 8 shows the storage modulus, G', and loss modulus, G'', of the non-centrifuged solution and of the bottom phase as a function of the pulsation. For the non-centrifuged solution, G' and G'' are proportional to ω^2 and $\omega^{0.9}$, respectively, at low frequencies, that is in the terminal portion of the curves, as observed in dense macromolecular systems, where long time dynamics is governed by reptation [16]. The reptation time, roughly corresponding to the crossover of the G', G'' curves, is about 30 s for a 0.4% w/w solution, which is of the order of magnitude expected for sticky reptation dynamics, that is reptation hindered by the association/dissociation process [7,17].

The linear viscoelastic behavior of the bottom phase exhibits quite different qualitative features. The pulsation dependence of G' and G'' moduli, at the lowest frequencies, is $\omega^{0.8}$ and $\omega^{0.5}$, respectively, as shown in Fig. 8. This behavior shows that the bottom phase, contrary to the non-centrifuged solution, is not a dense macromolecular system, whose long time dynamics is governed by (sticky) reptation. This result confirms by the way that the bottom phase is not composed of the longest macromolecules, i.e. the molecules of the highest hydrodynamic volume. The weaker power-law dependence of G' and G'' in this terminal region could reflect the presence of the polymeric particles, which behave as soft microgels in the bottom phase, as thoroughly studied in the work by English et al. on another associative polymer [18].

5. Conclusion

The optical and rheometrical results reported in the paper clearly show that the solutions of a commercial hydrophobically modified polymer solutions are more heter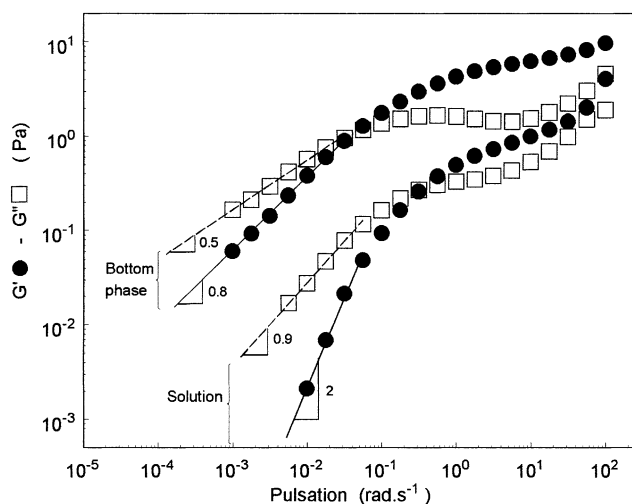ogeneous in composition than the solutions of the parent non-modified polymer. The associative polymer solutions contain micrometric soft polymeric particles which are mainly composed of macromolecules strongly interacting via hydrophobically associating junctions of the longest lifetime. Moreover, the rheometrical study suggests that the polymeric particles behave like microgels, which interact with 'free' macromolecules in the solution, via hydrophobic associations. The concluding schematic picture of the associative solution we propose is that of a continuum associative medium with compositional heterogeneities, located in soft microgels composed of the macromolecules bearing the longest hydrophobic groups.

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