GAP EFFECTS IN A RHEOMETRICAL FLOW OF A HYDROPHOBICALLY ASSOCIATING POLYMER SOLUTION: APPARENT SLIP OR MATERIAL INSTABILITY?

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ABSTRACT
In this paper, we study gap effects and apparent slip phenomena in a torsional flow of a moderately concentrated hydrophobically modified associative polymer solution.Slip is investigated by varying the gap between concentric parallel disks, and the plate surface roughness.The onset of apparent slip is shown to occur when the associative network is destroyed, and the slip velocity to increase with increased shear stresses in the strong shear-thinning region of the flow curve.The apparent slip phenomenon is shown to be due to the associative character of the polymer solution; it has been attributed to the existence of clusters of associating polymers (microgels),which behave like soft particles in a low viscous dispersing medium once the associative network is destroyed.Apparent slip can be eliminated by using measuring plates with roughness of about 100µm, that is of the order of the characteristic size of the microgels.

ZUSAMMENFASSUNG
In diesem Beitrag wird der Einfluss der Spalthöhe und des scheinbaren Wandgleitens in einer mäßig konzentrierten, hydrophobisch modifizierten, assoziativen Polymerlösung in einer Scherströmung vorgestellt. Das Wandgleiten wurde durch die Variation der Spalthöhe zwischen zwei parallelen Platten und der Oberflächenrauhigkeit dieser Platten untersucht. Der Beginn des scheinbaren Wandgleitens erfolgt dann, wenn das assoziative Polymernetzwerk zerstört ist und die Wandgleitgeschwindigkeit mit steigender Schubspannung in dem stark strukturviskosen Bereich der Fließkurve zunimmt. Das Phänomen des scheinbaren Wandgleitens ist auf den Charakter der untersuchten Polymerlösungen zurückzuführen: Sobald das assoziative Polymernetzwerk zerstört ist, verhalten sich die clusterähnlich verbundenen Polymerketten wie weiche Partikel in einem niederviskosen Dispersionsmittel. Das scheinbare Wandgleiten kann mit Hilfe von Messplatten mit einer Rauhigkeit von 100 mm, welche ungefähr der Größenordnung der Mikrogele nahe kommt, eliminiert werden.

RÉSUMÉ
Dans ce papier, nous étudions les effets d'entrefer et les phénomènes de glissement apparent en géométrie plan-plan pour une solution modérément concentrée d'un polymère associatif modifié hydrophobiquement.Le glissement est étudié en faisant varier l'entrefer de mesure et la rugosité des plateaux.Ce glissement apparaît lorsque le réseau associatif est détruit, et la vitesse de glissement croît alors avec la contrainte imposée dans la région fortement rhéofluidifiante de la courbe d'écoulement.Le phénomène de glissement apparent est dû à la présence des associations intermoléculaires au sein de la solution et est attribué à l'existence d'amas de macromolécules associées (microgels) qui se comportent comme des particules molles dispersées dans un milieu faiblement visqueux lorque le réseau associatif est détruit.Le glissement sur les géométries de mesure peut être éliminé en utilisant des plateaux dont la rugosité est de l'ordre de 100 mm, c'est-à-dire de l'ordre de grandeur de la longueur caractéristique des microgels.

Key words: Slip, gap effects, associative polymer, heterogeneous solution, microgels

1 INTRODUCTION

The no-slip boundary condition for the fluid velocity close to a solid surface is known to be violated, above some shear stress, in numerous flowing complex fluids, from polymer fluids and melts to suspensions [1,2]. Obviously, concentrating on viscometry, the presence of slip phenomena strongly affects the rheological measurements, as studied thoroughly by Brunn *et al*. [3].

Direct evidence of slip can be obtained from visualization techniques, using particle tracers. The simplest method is to observe the kinematics of micron-sized particles suspended in the sample, using an optical microscope. The use of micron-sized particles allows to investigate the velocity field close to the geometry walls, as shown in the work by Archer *et al.* [4]. A technique of even higher resolution consists in using laser-differential microanemometry and total-reflec-

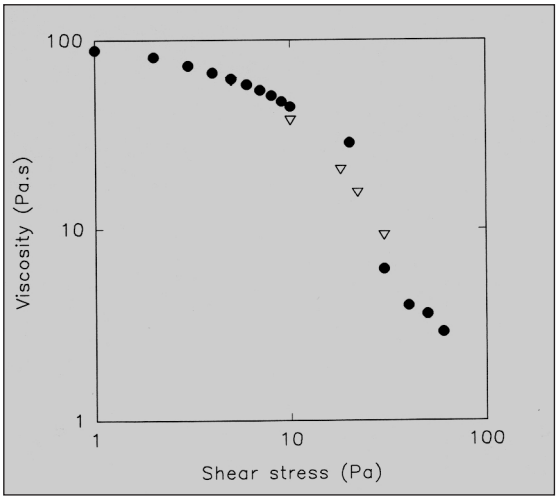

Figure 6 (left): Actual (▽) and apparent (●) steady shear viscosity as a function of imposed shear stress for a 1% w/w hydrophobically modified (hydroxypropyl) guar aqueous solution. The apparent values are determined at a rheometer gap of 500 µm.

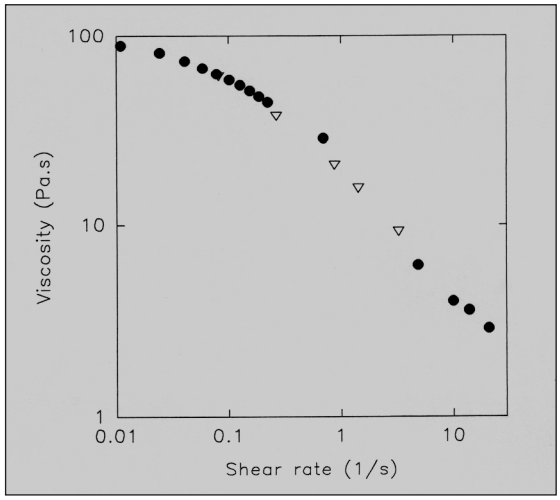

Figure 7 (right): Steady shear viscosity as a function of actual (▽) and apparent (●) shear rate for a 1% w/w hydrophobically modified (hydroxypropyl) guar aqueous solution. The apparent values are determined at a rheometer gap of 500 µm.

slip occurs at the polymer-wall interface and not in the polymer bulk, which is in favor of slip by depletion at the walls. Moreover, tests with only one plate roughened have clearly proved that polymer slips on both disks.

The true flow curve, that is the one taking into account the actual shear rate at the rim, τ_R, (calculated from the results plotted in Fig. 4), has been compared to the apparent flow curve at a gap spacing of 500 µm in Fig. 6 and in Fig. 7, so as to evaluate more directly the influence of apparent slip on rheological results. These data show that the actual shear-thinning region is smoother than the apparent one, but is still a rather marked nonlinear region. Therefore, this result does not question, but rather qualify the microstructural interpretations of the non-linear rheological properties of hydrophobically modified (hydroxypropyl) guar solutions given in our previous paper [12]. Microgels certainly do not play a key role, contrary to that played by the reversible hydrophobic network, in the rheology of such associative polymers; however, they certainly cannot be ignored since they can perturb and modify some rheological results, at least in the shear region where the associative network is destroyed. Thus, from a rheological point of view, at high shear rates or stresses, the system cannot be seen simply as nearly similar to the precursor, but has to be considered rather as a suspension of soft particles in a precursor solution

4 CONCLUSION

The study of gap-dependent effects in a moderately concentrated hydrophobically modified (hydroxypropyl) guar aqueous solution has shown that apparent slippage occurs in the drastic shear-thinning region of the flow curve. Slip phenomena have been shown to be due to the hydrophobic modification of the polymer chains and have been attributed to the presence of microgels, that is clusters of associating chains which bear a few tens of hydrophobic groups. The existence of microgels, expected to be frequent in "commercial" associative polymer solutions, can influence the linear and the non-linear rheological properties of such systems. Indeed, microgels give a colloidal nature to the system, and behave like soft particles in a low viscous non-associative medium, once the associative network is destroyed. Apparent slip has been shown to disappear when using measuring plates, with roughness of about 100µm, that is of the order of the characteristic size of the microgels.

Future work on the associative polymer solutions studied in this work should address microscopic characterization, via visualization techniques, of the heterogeneous states under flow conditions. Such investigation has just begun at the laboratory, where microgels have been observed during shear experiments. The first results, not presented in the paper which is devoted to mechanical investigation, have confirmed the existence of apparent wall slip by the study of the kinematics of microgels close to the walls.

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