On the Influence of Concentration on the Rheology of Polymer Solutions: Can Scaling Laws Be Found?

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Abstract:

The present work is concerned with the study of the rheology of polymer solutions spanning different concentration regimes and originates from a former round-robin research programme on this subject, the S1 project, involving a number of research groups and institutions. The base fluid for this programme was the so-called S1 fluid, which is a 2.5% w/w solution of Polyisobutylene (PIB) in a solvent consisting of a mixture of polybutene oil and dekalin. In this paper a set of solutions having different concentrations of PIB are studied in steady shear, oscillatory shear and in axi-symmetrical contraction flows. The focus of the study is on the possibility of finding concentration scaling laws for polymer solutions spanning each or several of the concentration regimes. The results in shear flows show that it is possible to find scaling laws both for temperature and concentration in all regimes. Extensional results show that the curves superimpose within each concentration regime, but not over the whole range of concentrations. Accordingly, concentration scaling laws were then found for both shear and extension, the latter depending on the concentration regime: dilute, semi-dilute or concentrated.

Zusammenfassung:

Die vorliegende Arbeit befasst sich mit der Untersuchung der Rheologie von Polymerlösungen, die verschiedene Konzentrationsbereiche abdecken. Sie entstammt einem früheren Ringversuch im Rahmen eines Forschungsprogramms auf diesem Gebiet, dem sogenannten S1 Projekt. Die Grundflüssigkeit für dieses Programm war das sogenannte S1-Fluid, welches eine 2.5% w/w Lösung von Polyisobutylene (PIB) in einem Lösungsmittel ist, welches aus Polybuteneoel und Dekalin besteht. In diesem Artikel wird ein Satz von Lösungen unterschiedlicher PIB Konzentrationen in stationärer Scherströmung, oszillatorischer Scherströmung, und in axialsymmetrischen Verengungsströmungen untersucht. Der Schwerpunkt der Untersuchung liegt in der Möglichkeit, Skalengesetze fuer die Konzentration zu finden, die für Polymerlösungen gelten, welche die einzelnen oder mehrere Konzentrationsregimes überspannen. Die Ergebnisse in Scherströmungen zeigen, dass es möglich ist, Skalengesetze für die Temperatur und die Konzentration in allen Bereichen zu finden. Die Ergebnisse in Dehnströmungen zeigen, dass die Kurven innerhalb eines jeden Konzentrationsbereiches superponierbar sind, aber nicht über den gesamten Konzentrationsbereich. Folglich wurden dann Skalengesetze für Scherung und Dehnung gefunden, wobei letztere vom entsprechenden Konzentrationsregime abhängig sind: verdünnt, halb-verdünnt bzw. konzentriert.

Résumé:

Le présent travail traite de l'étude rhéologique de solutions de polymères dans différents régimes de concentrations, et qui a été stimulé par un précédent programme de recherche, le projet S1, qui a impliqué un certain nombre de groupes de recherche et d'institutions. Le fluide de base pour ce programme fut le dénommé S1 fluide, qui est une solution de polyisobutylène (PIB) de 2.5% en poids, dans un solvant qui consiste en une mixture d'huile de polybutène et de décaline. Dans cet article, un ensemble de solutions possédant différentes concentrations de PIB est étudié en cisaillement en régime établi, en régime oscillatoire et en écoulement de contraction axi-symétrique. Le but de cette étude est de voir si il est possible de trouver des lois d'échelle en concentration pour des solutions qui appartiennent au même régime de concentration ou à des régimes différents. Les résultats en cisaillement montrent qu'il est possible de trouver des lois d'échelle pour toutes les températures et les concentrations quel que soit le régime. Les résultats en extension montrent que les courbes se superposent lorsqu'elles appartiennent au même régime de concentration, mais pas pour des régimes de concentrations différents. Ainsi, des lois d'échelle ont été trouvées pour le cisaillement et l'extension. Dans ce dernier cas, les lois d'échelle dépendent du régime de concentrations: dilué, semi-dilué ou concentré.

ly, there is a region of weak dependence on shear rate, followed by a second region of very strong dependence and, finally a third region of, again, a weaker dependency. This behaviour is well documented in the literature (see, for example, Cartalos and Piau [8]) and correspond to: First region – Purely viscous flow at low shear rates; Second region – Predominantly elastic flow at intermediate shear rates due to the unravelling of the polymer chains; Third region – Purely viscous flow at high shear rates due to the polymeric chains having attained their full stretch.

Unlike the case of shear flows, it was not possible to superimpose all the entry pressure drop curves into one single mastercurve, mainly due to the different dependencies of ΔPe on shear rate in the second region. Thus, it was only possible to construct mastercurves for each concentration regime. The first mastercurve was constructed from S-0%, S-0.05% and S-0.1%, i.e., the solutions in the dilute regime, the second from the S-0.25%, S-0.5%, S-1% and S-1.5% (in this case S-1% was used as the reference concentration) and the last comprised only the S1-2.5% solution.

Figure 8 represents the superimposed entry pressure drop curves together with the slopes that quantify the dependence of the entry pressure drop on the shear rates for each regime. Analysing the figure, for the solutions in the dilute regime, labelled as A, there is an approximately linear dependency of ΔPe on shear rate, at low shear rates, in accordance with the predictions of Cartalos and Piau [8]. At intermediate shear rates the slope of the ΔPe curve is 2.5, which is slightly higher than the theoretically predicted value of 2 [8]. This may have to do with the fact that the Reynolds numbers are in the low hundreds and, therefore, inertial effects may be coming into play. Finally, the dependency is again linear, as predicted [8].

The second group, labelled B, comprises the solutions belonging to the semi-diluted regime, plus S-1.5% solution that, according to the shear results, already belongs or is in the transition to the concentrated regime. Their behaviour at low shear rates, closely resembles that of the dilute solutions, i.e. there is an approximately linear dependency of ΔPe on shear rate. At intermediate shear rates, however, the slope is 4.0 (instead of a value rounding 2), exactly as predicted by Cartalos and Piau [8] for semi-diluted
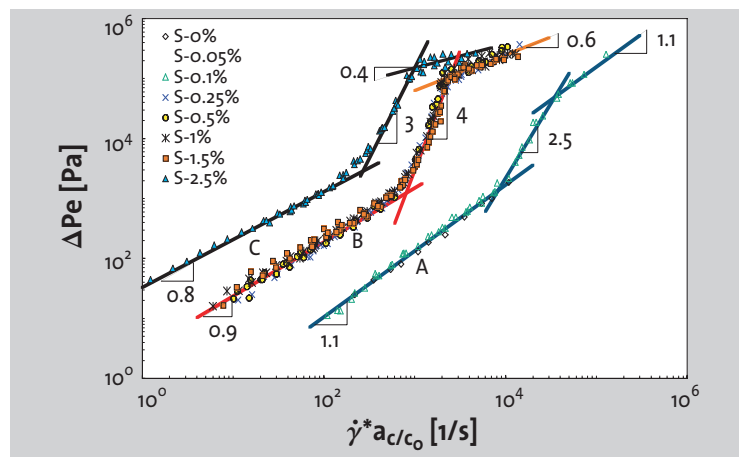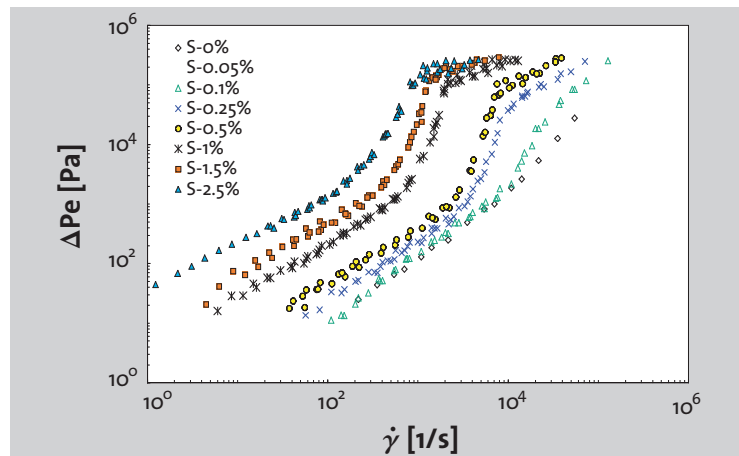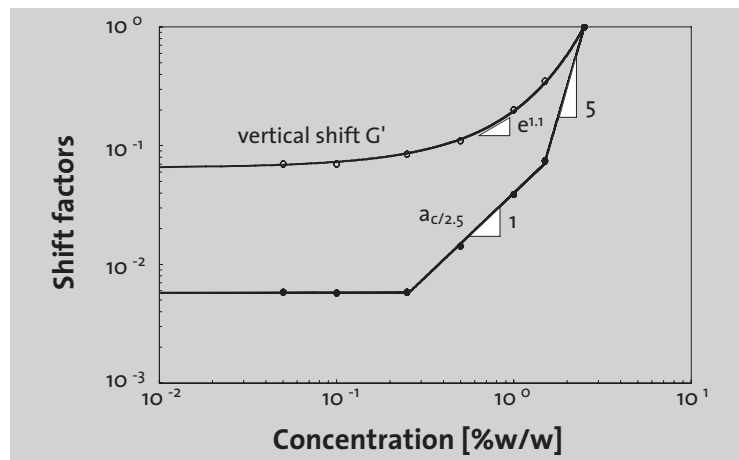
and concentrated solutions. At high shear rates the dependency of ΔPe on shear rate is very weak (the slope is approximately 0.6) and certainly lower than the theoretical value of 1 [8]. This may due to a number of reasons, a very strong possibility being the onset of flow instabilities that are known to be present in these flows and for these solutions at high shear rates [5, 6]. In this case the instabilities may be acting as extra stress-relief mechanisms and thus making the entry pressure drop decrease.

Finally, the third group, labelled C and denoting the concentrated regime, is made up of the 2.5% solution (S1) and shows behaviour that

Figure 6 (right above): Shift factors in oscillatory shear.

Figure 7 (right middle): Entry pressure drops for all solutions.

Figure 8 (right below): Reduced entry pressure drops: Group A – Dilute regime (c ∈ [0, 0.1] %); Group B – Semi-dilute regime (c ∈ [0.25, 1.5] %); Group C – Concentrated regime (c = 2.5 %).
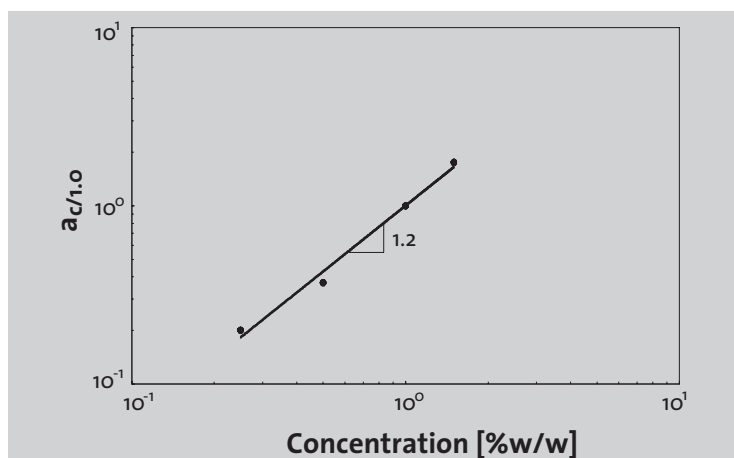
Figure 9: Shift factors for reduced entry pressure drops of solutions in the semi-dilute regime.

is similar, albeit with slightly weaker dependencies of ΔPe on shear rate, to that of the second group. At low shear rates this points to a possible initial extension-thinning behaviour by S1 [6] before becoming extension-thickening, at the onset of the second region. At this point, and corresponding to a shear rate of 98 s^{-1}, the flow is known to become unstable [6] with an oscillating instability developing in the vicinity of the orifice and propagating towards the bulk with increasing shear rate. This eventually leads to the complete destruction of the flow structure in the third region (shear rates above approximately 1000 s^{-1}), with very large instabilities being present. Thus, the power 3 dependence of ΔPe on shear rate observed at intermediate shear rates and power 0.4 observed at high shear rates, instead of the powers 4 and 1, respectively, predicted theoretically supports the hypothesis of the instabilities acting as extra stress-relief mechanisms.

The concentration shift factors versus polymer concentration of the solutions, for the semi-dilute regime are represented in Fig. 9. The values can be related by a power law equation exhibiting a dependence of approximately $c^{1.2}$ on the polymer concentration, which is very similar to the values found in shear ($c^{1.0}$ for steady shear and $c^{1.4}$ for oscillatory shear).

4   CONCLUSIONS

The aim of the present work was to study the possibility of finding concentration scaling laws for polymer solutions spanning several of the concentration regimes, which would be very useful, for example, in aiding the development of solutions with specific properties, since it would allow polymer concentration to be treated as another variable, such as temperature or rate of strain.

The results obtained showed that, in shear flows, both time-temperature and time-concentration superposition holds for the studied solutions, much in the same way as for some surfactant solutions [7], enabling master curves to be found for these materials in all concentration. In fact, the data showed that by means of a time-concentration superposition method, the various flow curves could be superimposed into a single mastercurve. Hence it becomes possible to find concentration scaling laws for both the viscous and linear viscoelastic response in rheometrical shear flows for polymer solutions spanning all the concentration regimes – dilute, semi-dilute and concentrated. For extension dominated flows, the curves of the entry pressure drops only superimpose in each of the concentration regimes, mainly due to the behaviour at intermediate shear rates, where the polymer chains are unravelling and elasticity plays a leading role in the flow behaviour.

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