

## RHEOLOGICAL PROPERTIES OF SUSPENSIONS WITH SPHERICAL PARTICLES IN SHEAR AND ELONGATIONAL FLOWS

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### ABSTRACT:

The rheological behaviour of model suspensions with spherical particles was experimentally investigated in shear and elongational flows. Particular attention was focussed on the main parameters affecting the flow behaviour of suspensions such as particle size distribution, particle size, particle surface, humidity, temperature and viscosity of the matrix fluids. All variables were investigated depending on the pre-shear conditions. In this regard the validity of the time-temperature-superposition and the Trouton-ratio was verified for suspensions with spherical particles.

### 1 INTRODUCTION

Highly filled suspensions are frequently encountered in several manufacturing and transport processes. Paints, printing inks, tar or food stuff are only some examples for industrial applications of suspensions. For an optimization of processing parameters it is essential to predict the rheological behaviour of suspensions depending on the predominating deformation (i.e. shear flow, elongational flow). Although it is well known that the steady shear flow behaviour of suspensions is strongly influenced by the properties of the filler (i.e. volume fraction  $\Phi_t$ , particle shape and size distribution, specific surface area of the particles) and by the matrix properties [1-5] still many open questions remain. In this connection particular attention is focussed on the relevance of the maximum packing fraction  $\Phi_{max}$  which especially for concentrated bidisperse suspensions has been shown to be the dominating parameter in the high-shear-(stress)-state.

In comparison to the extensive information available on the viscosity function in steady shear flow there are only few studies which focus on the development of the viscoelastic material functions of colloidal and non colloidal concentrated suspensions [6-8]. Furthermore only little literature can be found on investigations of the validity of the time-temperature superposition principle for concentrated suspensions [7-10]. Although it is well known that the actual state of suspension architecture strongly influences its rheological behaviour it is worth mentioning that a systematic investigation of the rheological properties of suspensions depending on the

pre-shear conditions cannot be found in literature.

The intention of the Ph.-D.-work was to experimentally contribute to open questions in the field of suspension rheology in shear and elongational flows. Since the flow behaviour of suspensions is very complex for experiments in shear flow model suspensions containing defined spherical particles in Newtonian fluids were examined. Using the Münstedt tensile rheometer (MTR) suspensions of spherical particles in non-Newtonian fluids were additionally investigated in elongational flows. In this review, however, three important findings in shear flow will be presented whereas all results shown were obtained by applying a systematic pre-shearing. First it will be demonstrated how the polydispersity of a particle size distribution influences the maximum packing fraction  $\Phi_{max}$  and hence the rheological behaviour in the high shear-(stress)-state of a concentrated suspension. Furthermore it will be shown that the time-temperature superposition principle is valid for the model suspensions investigated if a systematic pre-shearing is applied prior to the determination of the dynamic moduli.

At last it will be demonstrated that depending on the actual particle structure the magnitude of the elasticity of suspensions can exceed the elasticity of polymer melts by decades.

### 2 MATERIALS

As the matrix fluids three Newtonian non-polar low molecular weight polyisobutylenes (PIB 1, PIB 2, PIB 3) with a density of  $\text{g/cm}^3$  were chosen. Their weight average molecular weight  $M_w$  and

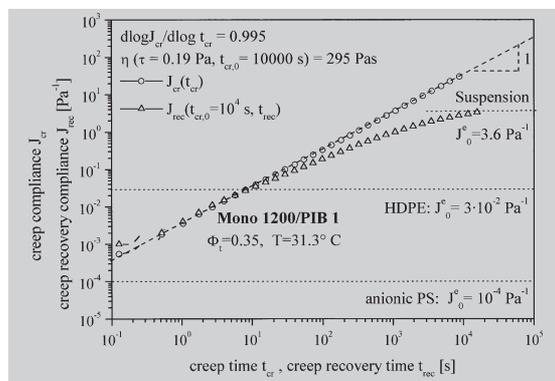


Figure 6: Creep compliance  $J_{cr}(t_{cr})$  and creep recovery compliance  $J_{rec}(t_{rec}, t_{cr}, \omega)$  for a very low shear stress of  $\tau = 0.19$  Pa (system Mono 1200/PIB 1,  $\Phi_t=0.35$ )

ian behaviour whereas at  $\tau = 0.19$  Pa a non-Newtonian behaviour was observed. The Newtonian matrix PIB 1 can be considered as purely viscous since its creep recoverable compliance  $J_{rec}$  was lower than the resolution of the magnetic torsional bearing rheometer. For both applied shear stresses (i.e.  $\tau = 0.19$  Pa and  $\tau = 200$  Pa) in good approximation a constant slope of the creep compliance  $J_{cr}(t_{cr})$  is reached after a creep time of  $t_{cr} = 10^4$  s. Interestingly no significant recoverable creep compliances  $J_{rec}$  can be obtained after applying a shear stress of  $\tau = 200$  Pa in the creep test for the suspension investigated. This strongly indicates that in this state the suspension behaves a purely viscous, as well.

After applying low shear stress of  $\tau = 0.19$  Pa in the creep test a significant recoverable creep compliance can be observed, however. For the findings obtained after applying a shear stress of  $\tau = 0.19$  Pa in the creep test the creep compliance  $J_{cr}(t_{cr})$  and the recoverable creep compliance  $J_{rec}(t_{rec})$  are plotted in Fig. 6 on a double logarithmic scale as a function of the creep time  $t_{cr}$  and the creep recovery time  $t_{rec}$ , respectively. The magnitude of the resulting creep recoverable compliance  $J_{rec}(t_{rec})$  obtained for the suspension is compared with the upper and lower boundary of the steady state recoverable compliance  $J_e^0$  that can be found in literature for different polymer melts [29-33]. As can be seen from Fig. 6 a steady-state recoverable compliance of approximately  $J_e^0 \approx 3.6 \text{ Pa}^{-1}$  is obtained for our suspension which exceeds the largest steady-state recoverable compliances  $J_e^0$  of polymer melts by more than 2 decades. Considering the fact that the same suspension does not show significant creep recoverable compliances after applying a shear stress of  $\tau = 200$  Pa in the creep test and hence behaves as a viscous liquid the results from Fig. 6 are even more fascinating. This outstanding finding clearly demonstrates the strong influence of the present particle structure on the elastic properties of suspensions.

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## REFERENCES

- [1] Dabak T and O Yucel: Shear viscosity behaviour of highly concentrated suspensions at low and high shear rates, *Rheologica Acta* 25 (1986) 527-533.
- [2] van der Werff JC and CG de Kruif: Hard-sphere colloidal dispersions: The scaling of rheological properties with particle size, volume fraction and shear rate, *Journal of Rheology* 33 (1989) 421-454.
- [3] Tsai SC, D Botts, J Plouff: Effects of particle properties on the rheology of concentrated noncolloidal suspensions, *Journal of Rheology* 37 (1992) 1291-1305.
- [4] Tsai SC and B Viers: Effects of liquid polarity on rheology of noncolloidal suspensions, *Journal of Rheology* 31 (1987) 483-493.
- [5] Chang SH, ME Ryan, RK Gupta: The effect of pH, ionic strength and temperature on the rheology and stability of aqueous clay suspensions, *Rheologica Acta* 32 (1993) 263-269.
- [6] Matsumoto T, Ch Hitomi, S Onogi: Rheological properties of spherical particles in polystyrene solution at long time scales, *Transactions of the Society of Rheology* 19 (1975) 541-555.
- [7] Shikata T and DS Pearson: Viscoelastic behaviour of concentrated spherical suspensions, *Journal of Rheology* 38 (1994) 601-616.
- [8] Watanabe H, ML Yao, A Yamagishi, K. Osaki, T Shikata: Non-linear rheological behaviour of a concentrated spherical silica suspension, *Rheologica Acta* 35 (1996) 433-445.
- [9] Choi GN and IM Kieger IM: Rheological studies on sterically stabilized model dispersions of uniform colloidal particles, *Journal of Colloid and Interface Science* 113 (1986) 101-113.
- [10] Rueb CJ and CF Zukoski: Rheology of suspensions of weakly attractive particles: Approach to gelation, *Journal of Rheology* 42 (1998) 1451-1476.
- [11] Schmidt M: Rheological properties of suspensions with spherical particles in shear and elongational flows, Ph.D.-thesis, Institute of Polymer Materials, University Erlangen-Nuremberg, Shaker-Verlag, Aachen, Germany (2000).

- [12] Schmidt M and H Münstedt: Packing of spheres and its effect on the viscosity on concentrated polydisperse suspensions, *Proceeding of the XII-th International Congress on Rheology*, Cambridge, UK, Eds. DE Binding, NE Hudson, J Mewis, JM Piau, CJS Petrie, P Townsends, MH Wagner, K Walters (2000).
- [13] Schmidt M and H Münstedt: Rheological behaviour of concentrated monodisperse suspensions as a function of preshear conditions and temperature: an experimental study, accepted for publication in *Rheologica Acta* (2001a).
- [14] Schmidt M and H Münstedt: On the elastic properties of suspensions as investigated by creep recovery measurements in shear, accepted for publication in *Rheologica Acta* (2001b).
- [15] Sengun MZ and RF Probststein: Bimodal model of slurry viscosity with application to coal slurries - Part 1 : Theory and experiment, *Rheologica Acta* 28 (1989) 382-393.
- [16] Probststein RF, MZ Sengun, TC Tseng.: Bimodal model of concentrated suspension viscosity for distributed particle sizes, *Journal of Rheology* 38 (1994) 811-829.
- [17] Shapiro AP and RF Probststein: Random packing of spheres and fluidity limits of monodisperse and bidisperse suspensions, *Physical Review Letters* 68 (1992) 1422-1425.
- [18] Poslinski AJ, ME Ryan, PK Gupta, SG Sheshadri, FJ Frechette: Rheological behaviour of filled polymeric systems. 2. The effect of bimodal size distribution of particulates, *Journal of Rheology* 32 (1988) 751-771
- [19] Krieger M, *Rheology of monodisperse latices*, *Advances in Colloid Interface Science* 3 (1972) 1-136.
- [20] Kitade S, A Ichikawa, N Imura, Y Takahashi, I Noda: Rheological properties and domain structures of immiscible polymer blends under steady and oscillatory shear flows, *Journal of Rheology* 41 (1997) 1039-1060.
- [21] Bousmina M: Effect of interfacial tension on linear viscoelastic behaviour of immiscible polymer blends, *Rheologica Acta* 38 (1999) 251-254.
- [22] Palierne JF: Linear rheology of viscoelastic emulsions with interfacial tension, *Rheologica Acta* 29 (1990) 204-214.
- [23] Fahländer M and Ch Friedrich: Rheological properties of polymer blends with sphere in sphere morphology, *Rheologica Acta* 38 (1999) 206-213.
- [24] Graebing D, R Muller, JF Palierne: Linear viscoelastic behaviour of some incompatible polymer blends in the melt. Interpretation of data with a model of viscoelastic liquids, *Macromolecules* 26 (1993) 320-329.
- [25] Ohl N and W Gleissle: The characterization of the steady state shear and normal stress functions of highly concentrated suspensions formulated with viscoelastic liquids, *Journal of Rheology* 37 (1993) 381-406.
- [26] Aral BK and DM Kalyon: Viscoelastic material functions of noncolloidal suspensions with spherical particles, *Journal of Rheology* 41 (1997) 599-620.
- [27] Gabriel C and J Kaschta: Comparison of different shear rheometers with respect to creep and recovery measurements, *Rheol. Acta* 37 (1998) 358-364.
- [28] Plazek DJ: Magnetic bearing torsional creep apparatus, *J Polym Sci Part A2* 6 (1968) 621-638.
- [29] Plazek DJ, N Raghupathi, RF Kratz RF, WR Miller WR: Recoverable compliance behaviour of high-density polyethylenes, *J Appl Polym Sci* 24 (1979) 1305-1320.
- [30] Agarwal PK and DJ Plazek: Shear creep recovery behaviour of IUPAC low density polyethylenes, *J Appl Polym Sci* 21 (1997) 3251-3260.
- [31] Gabriel C, J Kaschta, H Münstedt: Influence of molecular structure on rheological properties of polyethylenes; Part I: creep recovery measurements in shear, *Rheol. Acta* 37 (1998) 7-20.
- [32] Gabriel C and H Münstedt: Creep recovery behaviour of metallocene linear low-density polyethylenes, *Rheol Acta* 38 (1999) 393-403.
- [33] Kraft M, J Meissner, J Kaschta: Linear viscoelastic characterization of polymer melts with long relaxation times, *Macromolecules* 32 (1999) 751-757.