Ulrich Teipel*
Georg-Simon-Ohm University
Nuremberg - Germany
ulrich.teipel@ohm-hochschule.de

Ulrich Förter-Barth
Institut Chemische Technologie
Pfinztal - Germany

*author for correspondence

Rheology of suspensions with aluminum nano-particles

Abstract: *Nano-scale aluminum particles are innovative materials increasingly used in energetic formulations. In this contribution, the rheological behavior of suspensions with either paraffin oil or HTPB as the matrix fluid and nano-scale aluminum (ALEX) as the dispersed phase is described and discussed. The paraffin oil/aluminum suspensions exhibit non-Newtonian flow behavior over a wide range of concentrations, whereas the HTPB/aluminum suspensions exhibit Newtonian behavior (i.e. the viscosity is independent of shear stress) up to a concentration of 50 vol.% aluminum. Both systems have unusual viscoelastic properties in that their elastic moduli are independent of the solids concentration.*
Key words: *Aluminum nano-particles, Rheology, ALEX, HTPB, Viscoelastic properties*

LIST OF SYMBOLS

$\eta(\dot{\gamma})$	Flow properties
γ	Deformation
$\hat{\gamma}$	Amplitude
ω	Radial frequency
$\tau(t)$	Sinusoidal shear stress
δ	Phase shift
$G^*(\omega)$	Shear modulus
$G'(\omega)$	Storage modulus
$G''(\omega)$	Loss modulus
η	Dynamic viscosity of
ρ	Density
S	Specific surface

INTRODUCTION

Aluminum particles are well known as an ingredient in energetic materials. The typical diameter of aluminum used in explosives and propellants is in the order of ~ 30 μm (Miller, 1991). To enhance aluminum reactivity, for instance during combustion of solid rocket propellants, it is advantageous to use particles with the largest possible specific surface area, i.e., particles with a smaller mean particle size are desirable. By vaporizing and subsequently condensing aluminum in argon, or by electric explosion of an aluminum wire, it is possible to produce aluminum particles in the nanometer size range (Ivanov and Tepper 1997, Tepper and Ivanov 1998). Particles in this size range exhibit physical properties very different than those in the micrometer range.

At such small sizes, interparticle interactions become significantly more important and, as a result, nano-scale particles have a higher tendency to agglomerate (Glotov, 2000).

At such small sizes, interparticle interactions become significantly more important and, as a result, nano-scale particles have a higher tendency to agglomerate (Glotov, 2000).

In addition, the changed material poses difficulties when they are mixed with a fluid polymer matrix. This work examines and discusses the rheological properties of suspensions containing nano-scale aluminum particles in steady state and oscillatory shear flows.

EXPERIMENTAL

Measurement Methods

The rheological behavior of suspensions filled with nanoscale aluminum was examined in steady state and oscillatory shear flow using a UDS 200 rotational rheometer manufactured by Physica Meßtechnik GmbH. The measurement fixtures included a modified coaxial cylinder (Mooney-Ewart-System) and a cone and plate. Under steady state shear flow, the characteristic material function can be described as follows:

$$\tau(\dot{\gamma}) = \eta(\dot{\gamma}) \cdot \dot{\gamma} \qquad (1)$$

Here, $\eta(\dot{\gamma})$ is a characteristic material function that describes the flow properties when the fluid is subjected to a rheometric flow.

In oscillatory shear flow, the fluid is subjected to a periodic (e.g., sinusoidal) deformation γ(t) with an amplitude $\hat{\gamma}$ at a radial frequency $\omega = 2\pi f$ (Fig. 1) (Teipel, 1999):

$$\gamma(t) = \hat{\gamma} \sin(\omega t) \qquad (2)$$

Subjecting the material to an oscillatory (sinusoidal) shear deformation at sufficiently small amplitudes, i.e. in the linear viscoelastic range, results in a sinusoidal shear stress

τ(t) output (Fig. 2). Viscoelastic material behavior is characterized by the existence of a phase shift δ between the shear stress output τ(t) and the deformation input γ(t):

$$\tau(t) = \hat{\tau} \cdot \sin(\omega t + \delta) \qquad (3)$$

By definition, the phase shift of a perfectly elastic solid is zero and that of a purely viscous fluid is $\pi/2$, whereas for viscoelastic fluids it is $0 \leq \delta \leq \pi/2$. The shear stress function can be described in terms of the frequency dependent complex shear modulus $G^*(\omega)$,

$$\tau(t) = \hat{\gamma} |G^*(\omega)| \cdot \sin(\omega t + \delta(\omega)) \qquad (4)$$

The complex shear modulus can also be expressed as

$$|G^*(\omega)| = \frac{\hat{\tau}(\omega)}{\hat{\gamma}} \qquad (5)$$

The complex shear modulus $G^*(\omega)$ of a viscoelastic material is composed of two material functions, a real and an imaginary component, called the storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$, respectively. The storage modulus $G'(\omega)$ is proportional to the deformation energy stored by the material (the elastic component), while the loss modulus $G''(\omega)$ is proportional to the amount of energy dissipated by the material (the viscous component).

$$|G^*(\omega)| = \sqrt{G'(\omega)^2 + G''(\omega)^2} \qquad (6)$$
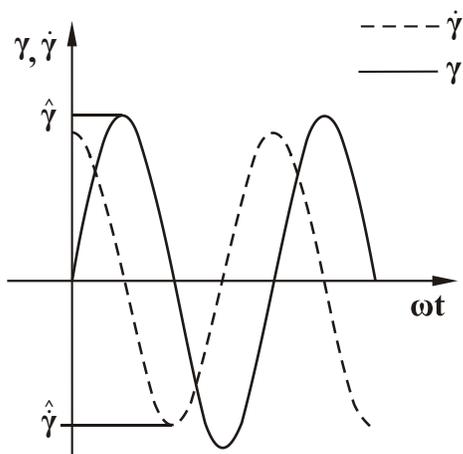

Figure 1: Deformation and shear rate profiles in oscillatory shear flow.

Oscillatory shear experiments must be conducted at deformations within the material's linear viscoelastic range. In this range, at a constant radial frequency , the deformation amplitude $\hat{\gamma}$ is proportional to the resulting shear stress amplitude $\hat{\tau}$, i.e., $\hat{\tau} \sim \hat{\gamma}$: This is only the case for sufficiently small oscillatory deformations. Within the linear viscoelastic region, the moduli $G'(\omega)$, $G''(\omega)$ and $G^*(\omega)$ are independent of the oscillatory amplitude in tests conducted at a constant frequency. The mean particle size and particle size distribution of the aluminum were determined via laser diffraction spectrometry or photon correlation spectroscopy. Scanning electron micrographs were accomplished to further characterize the material.
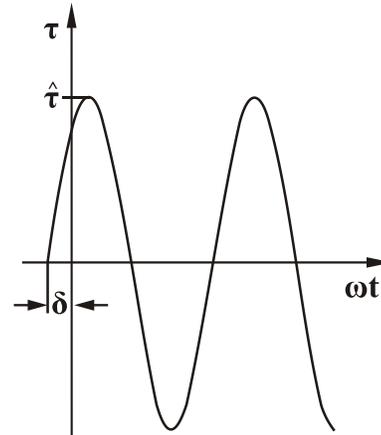

Figure 2: Shear stress profile of a viscoelastic fluid resulting from an oscillatory shear deformation.

Materials

The suspensions investigated consisted of nano-scale aluminum particles dispersed in paraffin oil or hydroxyl-terminated polybutadiene (HTPB). The paraffin oil exhibited Newtonian flow behavior with a dynamic viscosity of $\eta(20\,°C) = 198$ mPas. It had a $\rho = 874.7$ kg/m³ density and a $\sigma = 30.5$ mN/m surface tension. The hydroxy-terminated polybutadiene (designated HTPB R 45-M) also exhibited Newtonian flow behavior with a dynamic viscosity of $\eta(20\,°C) = 9300$ mPas.

The nano-scale aluminum (ALEX) was obtained from Argonide Corporation, Stanford, Florida/USA. The density of the aluminum particles was determined by gas pycnometry to be $\rho = 2.4$ g/m³ and the specific surface area determined by gas adsorption was $S = 11.2$ m²/g. A SEM image of the aluminum powder is shown in Fig. 3

Figure 3: Nano-scale aluminum powder.

RESULTS

Flow Behavior of the Paraffin Oil/Aluminum Suspensions

Prior to the rheological characterization, the paraffin oil/aluminum suspensions were stirred for a number of hours and the aluminum was well dispersed using an ultrasound homogenizer. This process ensured that aluminum agglomerates were broken down and the suspension was adequately homogenized. After mixing, the flow behavior was characterized under steady shear flow. Fig. 4 illustrates the relative viscosity as a function of shear rate for the suspensions, which ranged in solids concentration from 2 to 45 vol.%, as well as for the pure paraffin oil.
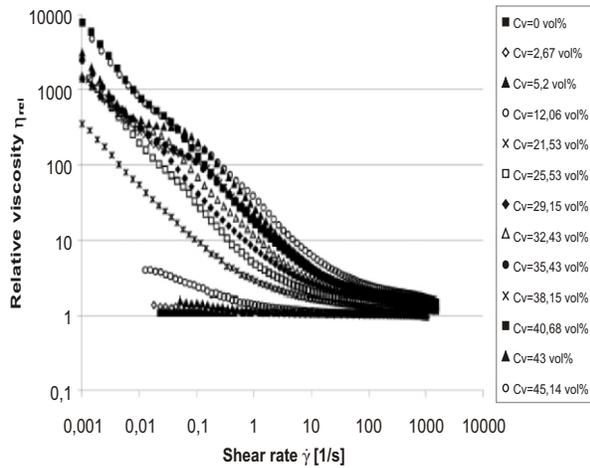

Figure 4: Relative viscosity of the paraffin oil/aluminum suspensions as a function of shear rate; = 20 °C.

The relative viscosity rel is defined as the ratio of the viscosity of the suspension to that of the matrix fluid at a constant shear rate $\dot{\gamma}$:

$$\eta_{rel} = \frac{\eta_{suspension}|\dot{\gamma}}{\eta_{matrixfluid}}$$

(7)

With increasing aluminum concentration the suspensions exhibit more and more distinct shear thinning behavior. This non-Newtonian response can be attributed to particleparticle interactions and the changed hydrodynamics of the suspension compared to the single phase fluid. At small shear rates, the viscosity increase as a function of concentration is particularly pronounced. In this shear rate range, the interparticle forces dominate the relatively weak hydrodynamic forces, so that the rheological response of the suspension is strongly dependent on the solids concentration and the resulting structural interactions. As the shear rate is increased, the hydrodynamic forces also increase, leading to flow induced structuring of the nano-scale particles and a corresponding decrease in the viscosity at a given solids concentration. The effect of solids concentration on the suspension

viscosity is much less pronounced at higher shear rates because of the flow induced structuring of the system.

Figure 5 shows the relative viscosity of the suspension as a function of solids concentration for the limiting viscosity at zero shear rate ($\dot{\gamma} \to 0$) and at a relatively high shear rate, $\dot{\gamma} = 1000\,s^{-1}$.
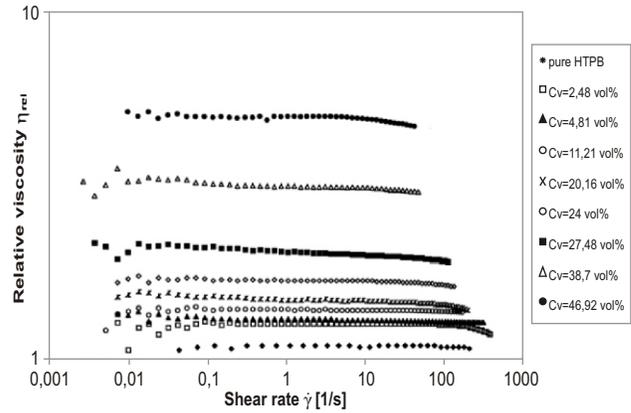

Figure 5: Relative viscosity of paraffin oil/aluminum suspensions as a function of solids concentration.

At the highest shear rate examined, a linear increase in the relative viscosity as a function of solids concentration is observed, up to a $C_V \approx 25$ vol.% concentration. At very low concentrations, there is almost no difference in the relative viscosity determined at the minimum and maximum shear rate. In this range of concentration, sufficient distance between the particles contributes to small particleparticle interactions, and likewise flow induced orientation of the particles has a relatively minor effect on the viscosity. Increasing the concentration leads to an increased contribution of the viscosity from particleparticle interactions. The quiescent particle structure formed with increasing concentration at low shear rates is one of the reasons for the strong concentration dependence of the limiting viscosity at zero shear rate, as shown in Fig. 5.

At higher shear rates a flow induced structure is formed leading to a reduction in the relative viscosity at a given solids concentration. The difference of the viscosity function at the two shear rates $\dot{\gamma} \to 0$ and $\dot{\gamma} = 1000\,s^{-1}$, which increases with increasing solids concentration, can be attributed primarily to the behavior of the particles in the Couette flow. At a concentration of 45 vol.%, the viscosity difference is nearly of the order of 104.

Flow Behavior of HTPB/Aluminum Suspensions

Figure 6 shows the relative viscosity of the HTPB/aluminum suspensions as a function of shear rate for solids concentrations from $0 \le C_V \le 47$ vol.%. Hydroxy-terminated polybutadiene, HTPB R 45-M, without additives exhibits Newtonian flow behavior, see Fig. 6 (Hordijk, 1996 and Muthiah, 1996).
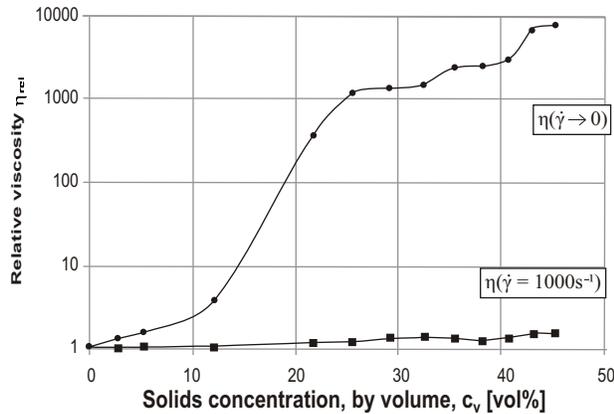
Figure 6: Relative viscosity of HTPB/aluminum suspensions as a function of shear rate, $=20°C$.

In contrast to the paraffin oil/aluminum suspensions, the HTPB suspensions exhibited Newtonian behavior over a wide shear rate range up to a solids concentration of ~ 50 vol.%. With increasing concentration, the relative viscosity of the suspensions increased; however, the behavior remained linear. Figure 7 shows the relative viscosity of the suspensions as a function of solids concentration.
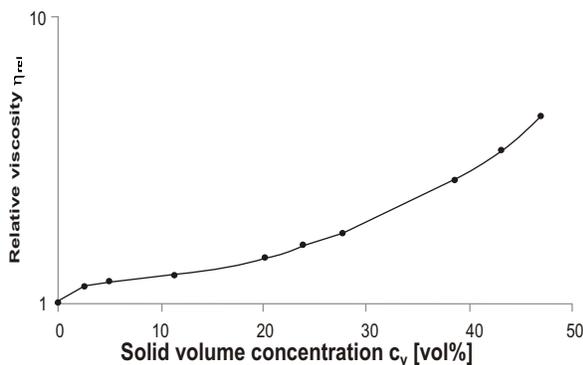

Figure 7: Relative viscosity of the HTPB/aluminum suspensions as a function of solids concentration.

The rheological characterization of the HTPB-based suspensions filled with nano-scale aluminum yielded the following relationship for the relative viscosity as a function of solid volume concentration:

$$\eta_{rel} = \frac{\eta_{suspension}|\dot{\gamma}}{\eta_{HTPB}} = 1 + 5.5 \cdot C_V - 31.4 \cdot C_V^2 + 74.5 \cdot C_V^3$$

$$(8)$$

Eq. (8) is valid for solid volume concentrations C_V up to 50 vol.%.

Viscoelastic Properties of the Suspensions

Viscoelastic material properties can be determined by oscillatory shear experiments. The complex shear modulus determined by dynamic experiments in the linear viscoelastic region can be expressed in terms of two material functions (as shown in Eq. (6)), the storage modulus G'(ω) and the loss modulus G''(ω). The storage and loss modulus functions of the paraffin oil/aluminum suspensions are shown in Fig. 8 for various solids concentrations.
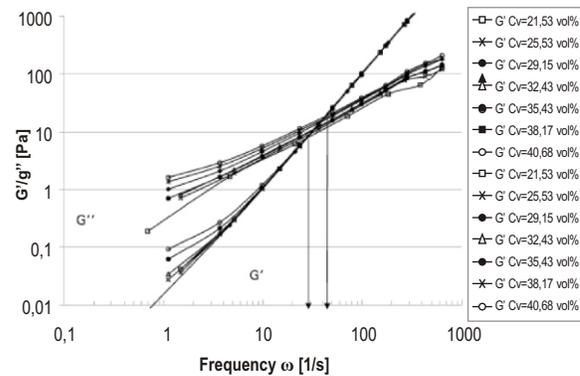

Figure 8: Storage and loss modulus functions of the paraffin oil/aluminum suspensions.

At low frequencies the storage modulus is smaller than the loss modulus, meaning that the viscous properties are dominant in this frequency range. Both functions increase steadily with frequency; however, the slope of the storage modulus function is greater than that of the loss modulus and, as a result, the two functions intersect at a characteristic frequency ωi, which differs depending on the solid volume concentration. Above this frequency, the elastic properties are dominant. The structural relaxation time λ is equal to the reciprocal of the frequency at which the storage and loss moduli intersect:

$$\omega_i \cdot \lambda = 1 \qquad (9)$$

For the paraffin oil/aluminum suspensions up to solids concentrations $C_V \leq \%40$ vol.%, the structural relaxation time range is from 0.24 s $\leq$ λ 0.37 s. It was also observed that the storage modulus G'(ω) was essentially independent of the aluminum concentration. One concludes that for these suspensions, filled with nano-scale particles, the stored (elastic) deformation energy is independent of the particle concentration.

The storage and loss modulus functions of the HTPB/aluminum suspensions are shown in Figure 9 for various solids concentrations. As in the previous case, the storage modulus G'(ω) is independent of solids concentration. However, the structural relaxation times for

the HTPB-based suspensions are significantly smaller than those of the paraffin oil-based suspensions, falling in the millisecond range ($0.0021\,s \leq \lambda \leq 0.0062\,s$)
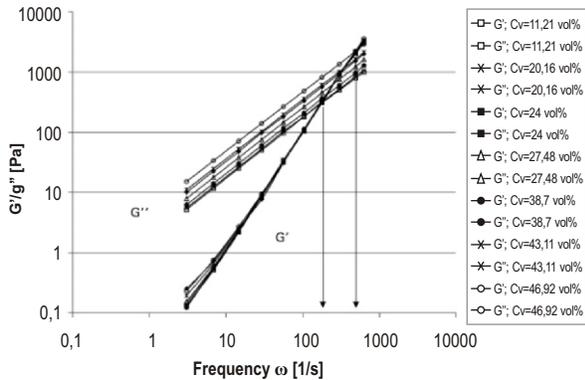

Figure 9: Storage and loss modulus functions of the HTPB/aluminum suspensions.

CONCLUSION

The paraffin oil/aluminum suspensions exhibit non-Newtonian flow behavior over a wide range of concentrations, whereas the HTPB/aluminum suspensions exhibit Newtonian behavior (i.e. the viscosity is independent of shear stress) up to a concentration of 50 vol.% aluminum. Both systems have unusual viscoelastic properties in that their elastic moduli are independent of the solids concentration.

REFERENCES

Glotov, O. G., Zarko, V. E, and Beckstead, M. W. , 2000 "Agglomerate and Oxide Particles Generated in Combustion of Alex Containing Solid Propellants", 31st International Annual Conference of ICT, Karlsruhe, Germany, June 2730, pp. 130/1130/15.

Hordijk, A. C., Sabel,H. W., Schonewille, R. L. and Meulenbrugge, J. J., 1996, "The Application of Rheological Equipment for Improved Processing of HTPB based PBXs", 27th International Annual Conference of ICT, Karlsruhe, Germany, June 2528, pp. 3/13/11.

Ivanov, G. V. and Tepper, F., 1997, "Activated Aluminum as a Stored Energy Source for Propellants", in: K. K. Kuo (ed.) "Challenges in Propellants and Combustion, 100 Years after Nobel", Begell House, pp. 636-645.

Miller, R. R., Lee, E. and Powell, R. L., 1991, "Rheology of Solid Propellant Dispersions", Journal of Rheology , Vol.35, No. 5, pp.901-920.

Muthiah, R, Krishnamurthy, V. N. and Gupta, B. R., 1996,"Rheology of HTPB Propellant: Development of Generalized Correlation and Evaluation of Pot Life", Propellants, Explosives, Pyrotechnics, Vol. 21, pp.186-192.

Teipel,U., 1999, "Rheologisches Verhalten von Emulsionen und Tensidlösungen", Dissertation, Universität Bayreuth; Wissenschaftliche Schriftenreihe des Fraunhofer ICT, Band 22.

Tepper, F., Ivanov,G. V., Lerner, M. and Davidovich, V., 1998, "Energetic Formulations from Nanosize Metal Powders", 24th International Pyrotechnics Seminar, Monterey, California, USA, July 2731, pp. 519-530.