

Rheology of polyethylene-coated aluminum nanoparticles suspensions.

Baptiste MARY¹, Charles DUBOIS¹, Pierre J. Carreau¹ and Patrick Brousseau²

1-Ecole Polytechnique de Montréal, Department of Chemical Engineering, Montréal, (Quebec), Canada. C.P.6079, Succ. Centre-Ville, Montréal, Quebec, H3C 3A7.

2-Defense Research and Development Canada (DRDC), 2459 Pie XI, Blvd North, Val-Bélair, QC, G3J 1X5, Canada.

Abstract

Ultrafine aluminum powders have been identified as very promising fuels for novel energetic materials formulations. However, the large specific surface area that gives these powders a high reactivity also makes them particularly difficult to maintain in an unoxidized state and different coating processes have been proposed to solve this problem. The rheology of viscous suspensions of nanoparticles still remains poorly understood and the effect of the coating of these powders on the flow behavior is even more difficult to assess. We have studied the rheology of ultrafine aluminum suspensions prepared from two low molecular weight polymers of different viscosities: a hydroxy-terminated polybutadiene and a polypropylene glycol. The nanosize aluminum powders had previously been coated by a thin layer of high density polyethylene using an in-situ polymerization process. The rheological characterization of the suspension was conducted by the means of steady and oscillatory shear flow measurements for similar concentrations of particles and the effect of the coating process on the suspension rheology is discussed.

1.Introduction

In spite of the high expectations about the potential use of ultrafine aluminum powders in energetic materials, several problems remained to be overcome before being able to fully benefit of their large specific area. Among these difficulties, the control of the thickness of the oxide layer at the surface of the particles has received a particular attention. The alumina content of ultrafine aluminum powders has an important effect on the performance of energetic materials formulations containing them. Several coating approaches have been proposed to reduce or prevent the oxidation of these powders during their storage and handling. Among them are coating by carbon deposition[1], stearic acid and aluminum diboride deposition[2], polyvinylidene fluoride deposition by SCF carbon dioxide [3] and polystyrene polymerization [4]. In the recent years, we have studied an in-situ polymerization reaction as a means of forming a thin layer of high density polyethylene (HDPE) on nanosize aluminum particles [5-6]. The coating process is a modified Ziegler-Natta polymerization where the surface of the aluminum particle is used to attach the catalyst system. The reaction is conducted by suspending the ultrafine powders in a solvent.

Even if metal nanoparticles have shown promising combustion properties, their use in energetic materials formulations remains conditional to identifying appropriate mixing

conditions for their compounding. Contemporary plastic bonded explosives and solid rocket propellants are composite materials prepared from suspensions that contain more than 80 % w/w in solids. In propellant formulations, the metal particles often account for about one quarter of the dispersed phase. The rheology of these highly loaded systems is sensitive to even small changes in composition. Therefore, there is a real interest in investigating the effect of using nanoparticles on the processability of these suspensions. In a recent work, Teipel *et al* studied the rheology of suspensions containing Alex (Argonide Corporation, USA) nanosize aluminum particles having a specific surface area of 11.2 g/m² [7]. In their work, they considered two suspending fluids: a paraffin oil and a hydroxy-terminated polybutadiene (HTPB). They found that with increasing concentrations of aluminum particles, the paraffin based suspension exhibits a clear shear-thinning behavior while the HTPB blend, of higher viscosity, remained Newtonian up to a shear rate of about 100 s⁻¹.

As a general rule, colloidal suspensions are classified as such when containing particles of a size in the range of 1 nm to 1000 nm [8]. Accordingly, if properly dispersed, the suspensions prepared from ultrafine aluminum particles, with average diameters of less than 250 nm, should present colloidal characteristics. The surface effects are very important in these suspensions and the forces governing their behavior arise from several sources: Van der Waals forces, Brownian forces and forces imparted by the flow field. The attractive and repulsive forces are not the only parameters of importance to the rheology of colloidal suspensions since the volumetric concentration, the particle size and the particles shape can also have a significant effect [8]. In addition to the difficulty of getting a good grasp on some theoretical aspects of their rheological behavior, the experimental investigations on suspensions are themselves quite challenging. Therefore, our first objective in this exploratory work was to establish a reliable and reproducible process to prepare the suspensions of interest. In a second time, we wanted to study the effect of the HDPE coating of aluminum nanoparticles on the rheology of the suspensions. Finally, we wanted to assess, if any, the presence of interactions between the coating and the suspending fluid and how these interactions are affected by the type of fluid used.

2. Experimental

A. Materials and synthesis

The ultra fine aluminum powders used for this study were obtained from TEKNA Plasma Systems (Sherbrooke, Quebec). They had a mean diameter of 120 nm, a 16.5m²/g specific surface area and a density of 2.4g/cm³. The coating of these powders with high density polyethylene was carried out by a Ziegler-Natta polymerization with a coordination catalyst grafted on the surface of the particles. A complete description of this process has been published by Roy *et al* [5-6]. The HDPE content in the powders that we used for this investigation was measured at 20 % w/w by means a thermogravimetric analysis. The commercial grade liquid prepolymer hydroxy-terminated polybutadiene (HTPB) obtained from Arco Chemicals, had a nominal molecular weight (Mn) of 2800 g/mol, a polydispersity index of 1.8 and a density of 0.90 g/cm³. An amount of 0.5% w/w of di-terbutyl hydroxy quinone (DTBHQ) was dissolved in the polymer to prevent early

oxidation. The HTPB was found to have a Newtonian behavior for up to 100 s^{-1} with a viscosity of $8.7 \text{ Pa}\cdot\text{s}$ at 25°C . The second suspending fluid used was a polypropylene glycol (also called dihydroxyl terminated polypropylene) Arcol TM PPG-3025 polymer, with a nominal molecular weight (M_n) of 3000, a polydispersity index of 1.1 and a density of 1.01 g/cm^3 . The polypropylene glycol had a Newtonian behavior with a steady shear viscosity of $0.61 \text{ Pa}\cdot\text{s}$ at 25°C .

B. Rheological measurements

The powders, stored in hexane, were first filtered and then placed in a vacuum oven at 60°C overnight to ensure a complete solvent removal. The dried powders were sieved with a $600\mu\text{m}$ diameter sieve. The required amount of sieved powders were then mixed in 100 ml of the liquid polymer using a Brinkman high shear rate homogenizer. An intermittent mixing cycle of 30 minutes was used to obtain a first reduction in the size of the aggregated particles. This was followed by a three minutes ultrasonic treatment using a 1.25 cm probe (SONICS) with a pulse amplitude of 50% (360W). This procedure ensured an optimum homogenization of the suspensions that were then placed in vacuum oven at 60°C for 60 min. in order to remove the entrapped air in the sample.

All rheological data were obtained in a controlled-strain Rheometric Scientific ARES rheometer. The rheometer was used to conduct strain sweep and steady shear measurements with a Couette geometry (inner diameter: 32 mm, outer diameter: 34.4mm length: 33.35 mm) with a gap of 1.20 mm for all tests. For suspensions, the interactions between the particles are often responsible for the formation of a structure that is time and shear dependant. Accordingly a preconditioning treatment consisting of a constant shear rate pre-shearing of 300 s^{-1} for 60 sec and a rest time of 500sec was applied to each sample in order to ensure the same condition at the beginning of all tests. The particle size characterization experiments were carried out in a MALVERN Mastersizer 2000 light scattering apparatus and ultrasounds were applied to the samples just before measuring the particle size distribution, by means of a 1.25 cm probe (SONICS) operating at a pulse amplitude of 50% and a power level of 360W for 3 minutes.

3. Results and discussion

The experimental investigation began by assessing the effect of the HDPE coating on the particle size distribution (PSD) of the ultrafine aluminum powders. The PSD (number and volume averages) of non-coated aluminum powders are shown in Figure 1a). The number average diameter of the particles is found to be close to the nominal value of 120nm reported by the manufacturer (Tekna). On Figure 1b) the PSDs of the HDPE-coated particles after an ultrasound treatment are also presented. It is concluded that with a proper post-synthesis dispersion treatment (ultrasounds), the coating process does not affect significantly the PSD of the powders. In both cases, however, the volume average size distribution reflects the fact that a small number of very large particles are found in the suspensions. The PSD characterization of the coated and non-coated powders was carried out in hexane. In results that we do not present here, the PSDs of coated powders not

treated by the ultrasonic processor were found to be shifted to significantly higher diameter values.

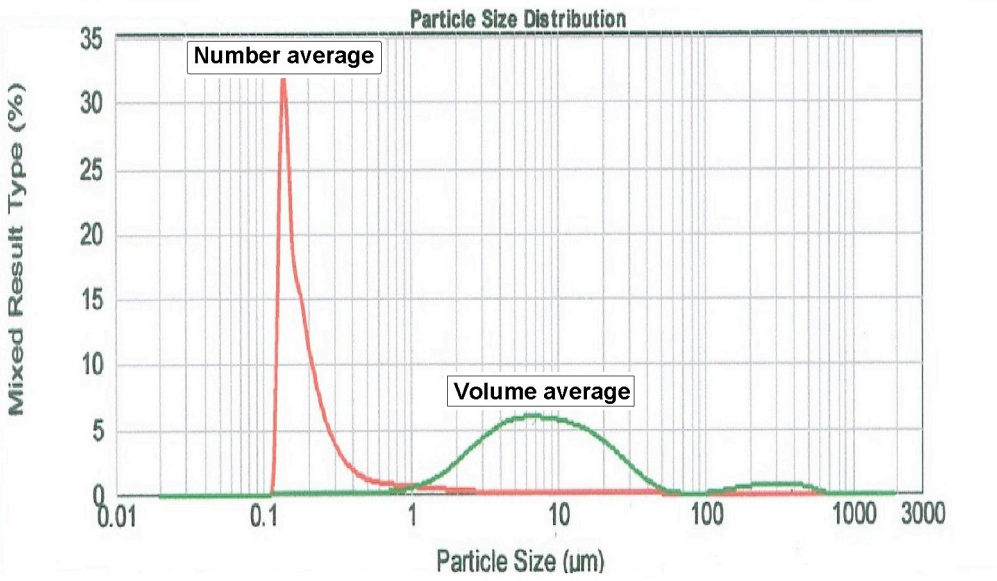


Figure 1 a) PSD of non-coated TEKNA aluminum powders.

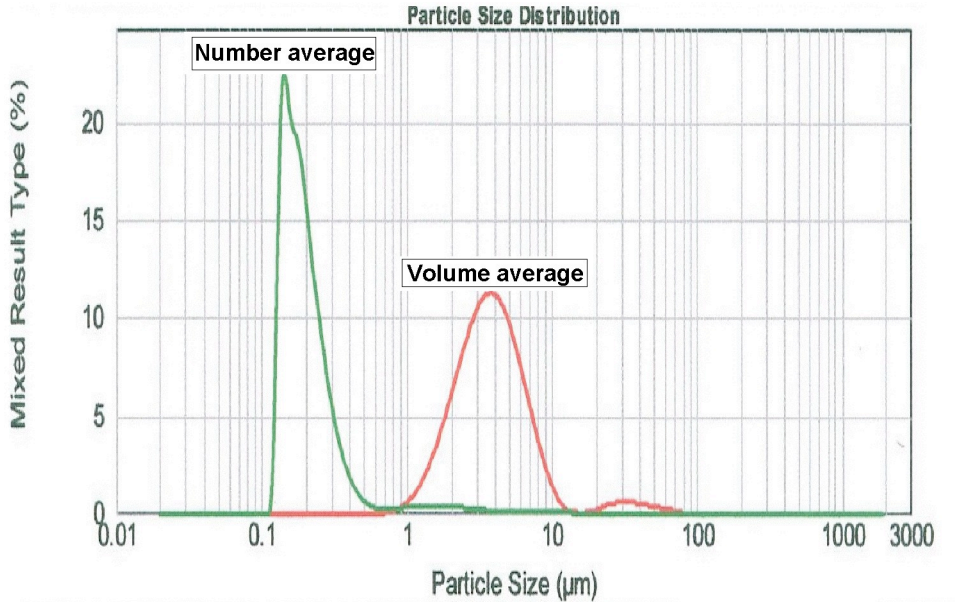


Figure 1 b) PSD of HDPE-coated TEKNA aluminum powders.

Since the ultrasound processing appeared to be effecting in breaking agglomerates of particles when dispersed in a low viscosity solvent like hexane, it was decided to evaluate as well its efficiency when preparing the nanoaluminum suspensions in polymers. Suspensions of 15 % w/w in aluminum (coated and non-coated) were prepared in PPG and HTPB and their viscosity in steady shear measured at 25 °C after, or not, an ultrasounds treatment. The results for HTPB and PPG suspensions are given in Figure 2 and 3 respectively. It is seen on Figure 2 that for a dispersion of non-coated ultrafine aluminum powders in HTPB at a concentration of 15 %w/w, the behavior of the suspension is essentially Newtonian over the range of shear rate considered (100 s^{-1}). In this case, the use of ultrasounds seems to decrease slightly the suspension viscosity. However, if one considers the coated particles then a completely different rheology is observed. Firstly, over the same range of shear rates, there is no longer a Newtonian plateau and the suspension is clearly shear-thinning. Secondly, It can also be observed that the viscosity of the coated powders suspensions is increased when treated by the ultrasounds processor. Because it is known from PSD measurements that the ultrasonic treatment is efficient in breaking agglomerated powders in smaller particles, it can be assumed that the treated suspensions have a higher specific surface area. Accordingly, their higher viscosity, in comparison with the non-coated powder suspensions, can be explained by a contribution of an interfacial phenomenon and thus an effect of the compatibility between the HDPE coating and the suspending liquid polymer can be suspected.

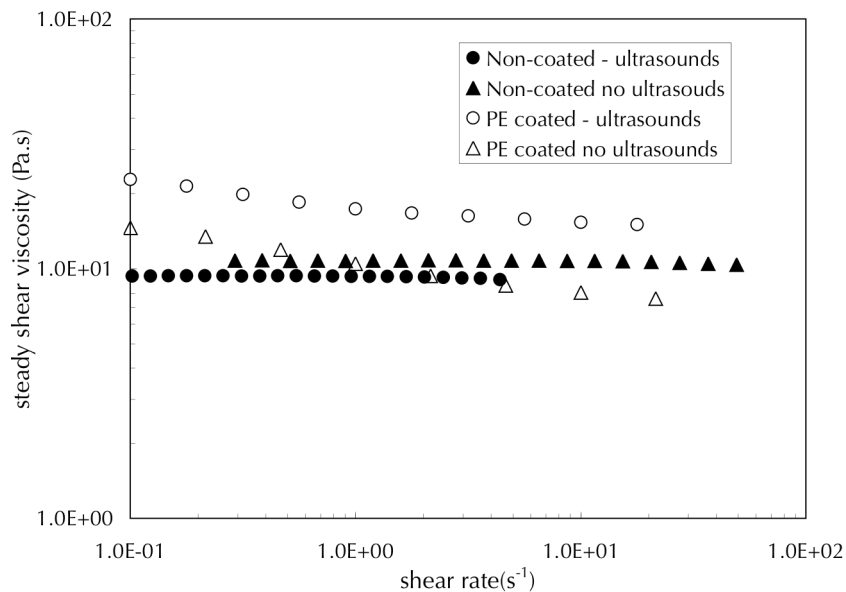


Figure 2: Effect of coating and ultrasounds pre-treatment on the rheology of a 15% w/w aluminum suspension in HTPB at 25 °C.

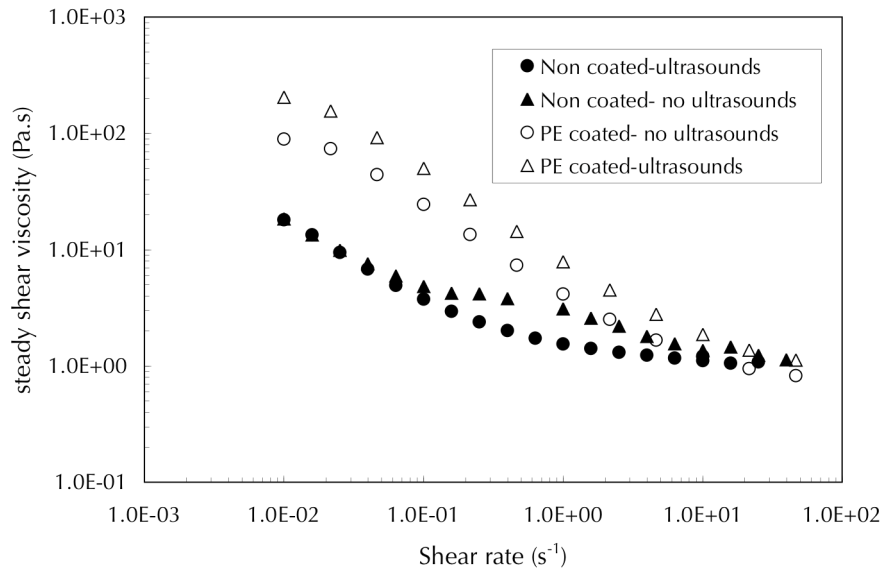


Figure 3: Effect of coating and ultrasounds pre-treatment on the rheology of a 15% w/w aluminum suspension in PPG at 25 °C.

The effect of ultrasound processing on the rheology of suspensions of coated and non-coated aluminum powders in PPG is also somewhat similar, as shown in Figure 3. For the non-coated powders, the effect of ultrasounds is negligible except for what appears to be an experimental anomaly in the curve of the non-coated suspension not treated with ultrasounds. In that case, however, the suspension has a shear thinning behavior even for the non-coated powders. This was not observed with the more viscous HTPB based suspension but it confirms the results of Teipel *et al* obtained on a suspension of Alex nanoparticles in a low viscosity oil [7]. Figure 3 also shows that PE-coated aluminum powders are better dispersed by the use of an ultrasound treatment and again, an increase in the viscosity is observed as the viscosity-shear rate curve is vertically shifted to higher viscosity values. Again, since the specific surface area of the powders is increased by the sonic treatment, one may assume that significant interfacial forces are at work in shaping the rheological behavior of the suspensions.

In order to obtain a confirmation of the presence of polymer-polymer interactions in the case of suspensions of coated powders, it was decided to look at the rheology of suspensions made from PPG and HTPB at temperatures where the two suspending fluids have the same zero shear rate viscosity. A simple rheological characterization of pure HTPB and PPG showed that for these two fluids $\eta_0 = 3.40$ Pa.s at 40°C and 1.2 °C respectively. The complex viscosity of the corresponding aluminum suspensions at these temperatures is reported in Figure 4 from strain sweep experiments conducted at 1 Hz. This figure reveals a clear difference in the level of interactions between the suspending polymer fluid, HTPB or PPG, and the HDPE particle coating. At low deformation levels, the complex viscosity of the PPG-based suspension is three times higher than its HTPB-

based counterpart, indicating a stronger level of interactions between the HDPE and the PPG.

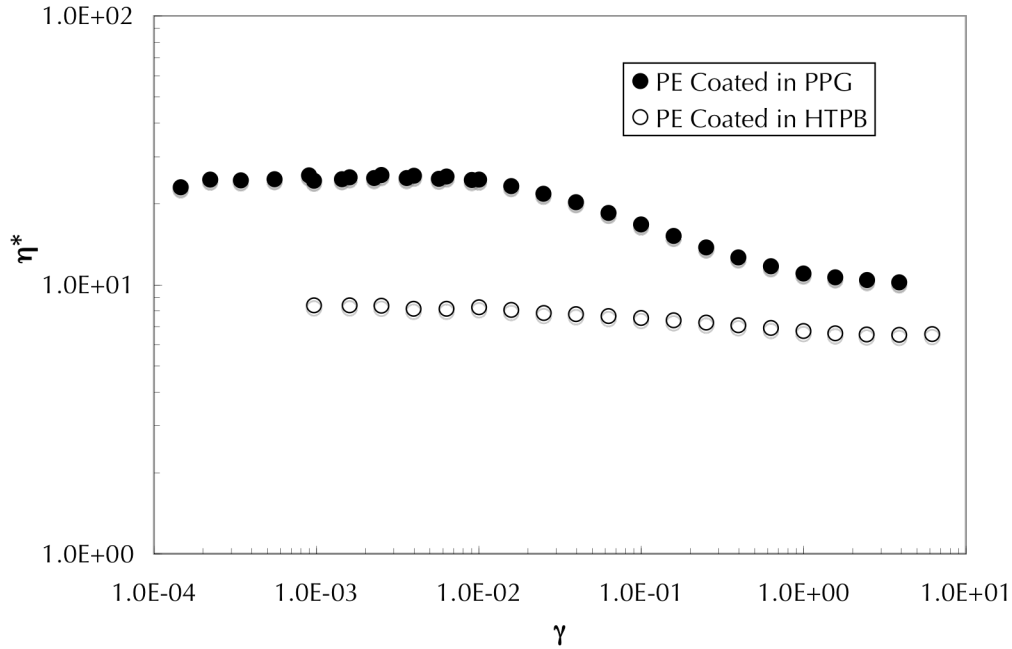


Figure 4: Dynamic viscosity of 15% w/w suspensions obtained from strain sweep experiments at 1Hz, at two different temperatures: $\eta_0 = 3.40$ Pa.s at 40°C (HTPB) and 1.2 °C (PPG)

The adhesion of a polymer on a solid can be characterized by the thermodynamic work of adhesion, i.e. by the work needed to separate two different bodies in contact. The work of adhesion can be defined as [9]:

$$W_a = \gamma_l(1 + \cos\theta)$$

We report in Table 1 experimental values of surface tensions and contact angles for the systems of interest, and the corresponding values of W_a and S_a . It is seen that $W_{a,PPG-HDPE}$ is higher than $W_{a,HTPB-HDPE}$ and we find stronger interactions between the PPG and the HDPE coating than with the case of HTPB suspending fluid, thus confirming our rheological measurements.

Table 1: Parameters of adhesion between the HDPE coating and the suspending fluids

	γ_l (mN/m)	γ_{sl} (mN/m)	Contact angle θ (rad)	W_a
PPG	35.6-36.8	8.6-9.4	39.2	59.1-59.9
HTPB	48.6-52.6	32.3-33.1	25.7	52.0-56,3

4. Conclusion

In this paper we conducted our first investigations on the rheological behavior of viscous suspensions of polymer coated ultrafine aluminum powders. A special interest was devoted to observing any effect of the compatibility between the coating and the suspending fluid. It was found that the HDPE coated powders used for this work were partially agglomerated due to the coating process and a treatment with an ultrasonic processor was successful in returning the powders to their pre-polymerization PSD. The rheological behavior of the suspensions prepared in HTPB and PPG, two Newtonian low molecular polymers, was found to depend on the viscosity of the suspending fluid. When blend with non-coated powders, the more viscous HTPB suspensions kept the Newtonian behavior of HTPB. On the other hand, the less viscous PPG-base suspensions of non-coated powders exhibited a shear-thinning behavior indicating that other factors that only hydrodynamic forces affect their rheology. With both fluids, the use of HDPE-coated powders was found to change the rheology of the suspensions. By conducting a rheological characterization of suspensions at temperatures where the viscosity of the HTPB and PPG suspending fluids are the same, it was found that coating-fluid interactions were stronger in the case of the HDPE-PPG system. The rheological behavior of these suspensions is clearly colloidal in nature. In a future work, a more precise investigation of these phenomena will be conducted and a modeling of these forces will be attempted.

Acknowledgements

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