Dispersion of nanoparticles: From organic solvents to polymer solutions

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ABSTRACT

This work is devoted to a systematic study of nanoparticle dispersion by ultrasonication in different solutions: from organic solvents to polymer solutions. The cluster size of nanoparticles at different concentrations in both organic solvents and polymer solutions were directly characterized by Dynamic Light Scattering to study the effect of solid concentration, surfactant and polymer on the dispersion. It reveals that in stabilized suspensions, the smallest attainable size or aggregate size of nanoparticles is independent of solvent type and solid content over the tested range. Furthermore, nanoparticles in simple solvent and in polymer solutions had the similar evolution of cluster size and almost the same final size, which could be very helpful to optimize the dispersion of nanofillers in polymer solutions and nanocomposites. It is also shown that, with appropriate sonication amplitudes, the dispersion procedure developed for very dilute suspensions could be transferred to higher concentration suspensions or even to polymer suspensions.

1. Introduction

Suspensions of fine particles, especially nanoparticles, have attracted significant interest due to their large variety of application in chemistry, biology, medicine and material science [1–8]. Mixing of dry powders in a liquid phase has been one of the basic human operations in many areas of daily life. However, homogenous dispersion allowing taking full advantage of nanoparticles still remain a great challenge in numerous areas including coating, paints, inks, drug delivery, ceramic and nanocomposite processing.

During synthesis processes and post-processes, for example heating stage necessary to obtain the crystalline phase [9] or micelle removal stage in the reverse micelle-based synthesis technique [10], primary particles often form large clusters. Depending on the bond strength between primary particles, clusters can be divided into two types: aggregate created by covalent bonds between primary particles and agglomerates defined as looser and more open structures that can be separated into primary components [11–13]. In agglomerate structure, the components are held together by weak forces such as electrostatic, magnetic forces, or by weak material bridges between particles including hydrogen bonds or interaction of flocculants in suspensions [12].

High intensity ultrasound has been widely used to disperse powder in a liquid [14–20]. In spite of abundant studies on ultrasonic dispersion in aqueous and non-aqueous solutions, very little is known about the dispersion of nanoparticles in high viscosity polymer solutions, which is essential to optimize the dispersion of nanofillers in polymer nanocomposites. Furthermore, there are very different or even opposite results about the optimum processing conditions of nanoparticle dispersion in polymer solutions, for example in epoxy resin ([16] and references therein). The dispersion quality was usually characterized indirectly from transmission electron microscopy or scanning electron microscope image analysis or by measuring the particle size in diluted suspensions. It is worth noting that the cluster size in suspensions can be affected by various parameters including particle content, colloidal stabilization (electrical charges, absorbed surface layers) and also polymer interaction. Thus, the cluster size could change upon suspension dilution.

In this work, a systematic study of nanoparticle dispersion with different concentrations in Methyl Ethyl Ketone (MEK) and solutions of copolymer of vinylidene difluoride and trifluoroethylene (P(VDF-TrFE)) was accomplished. The cluster size was characterized directly in suspension at high nanofiller concentration, even in polymer solutions and compared with the result of aqueous suspensions in the previous study [18] to evaluate the dispersion quality.

2. Experimental

In the present study, commercial nanoparticles of Al_2O_3 (Aeroxide AluC®, Degussa, Germany) and ZnO (NanoGard®) were used. The primary particle size of Al_2O_3 and ZnO nanoparticles were respectively 13 nm and 60 nm, which were determined from Transmission Electron Microscopy (TEM) images. The diethyl octadecyl phosphonate, $C_{18}H_{37}P(O)(OC_2H_5)_2$ (P18Et2) was synthesized using the method adopted by Gaboyard [21]. The copolymer of

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vinylidene difluoride and trifluoroethylene (P(VDF-TrFE)) (70/30 mol.%), M_w = 1370000 from Piezotech S.A.S. (France) was dissolved in Methyl Ethyl Ketone (MEK) (Acros Organics) by stirring at 80 °C to prepare a 12 wt.% solution, which is often used to elaborate composites and devices [22–26].

The dispersion of nanoparticles in solutions was carried out with a Transducer Digital Sonifier® Model 450 (Branson Ultrasonics Corporation, USA). Its maximum power input and frequency are 400 W and 20 kHz, respectively. The ultrasonic horn that was immerged in suspension has a tip diameter of 13 mm and the sonication amplitude (tip movement) is in the range of 10–65 μm. To reduce the heating up of suspensions during sonication, the ultrasonic mode with a pulse ratio on/off 0.1/0.1 (s/s), which showed the same efficiency of deagglomeration with continuous irradiation [18], was used. The vessel of suspension was cooled using an ice-water bath.

The mean cluster size based on the intensity of scattered light (often given with the symbol Z-average) was measured by Dynamic Light Scattering (DLS, Zetasizer Nano ZS, Malvern Instruments Ltd.). The viscosity of suspensions was characterized by a rheometer (RheolabQC, Anton Paar). The available shear rate of this device is between $0.1\,s^{-1}$ and $5000\,s^{-1}$. The relationship between particle size and viscosity is described by the Stokes–Einstein equation:

$$d(H) = \frac{kT}{3\pi\eta D}$$

where d(H) is hydrodynamic diameter, D is translational diffusion coefficient, k is Boltzmann's constant, T is absolute temperature, η is dynamic viscosity.

The nanoparticles were also characterized by Transmission Electron Microscopy (TEM, Philips CM 200). The samples were prepared by placing a drop of suspension after ultrasonication on a carbon film coated copper grid and then dried at room conditions. For analyzing the dispersion of nanoparticles in polymer nancomposite, TEM images of 100-nm thick films prepared by spin-coating directly on copper grid from solution of the polymer in MEK were done. The average cluster diameters were measured manually from the images.

3. Results and discussion

3.1. Dispersion of nanoparticles at low concentration in solvent

The dispersion of alumina nanoparticles in low concentration suspension was investigated in previous work [18]. The results showed that aqueous suspensions of Al_2O_3 nanoparticles are stabilized by electrostatic forces and the enhancement of colloidal stability using electrostatic repulsion (by changing pH or ionic strength), steric hindrance (using surfactants) has no significant effect on the aggregate size. Despite the Al_2O_3 primary particle size of 13 nm, the agglomerates are reduced to hard aggregates that could not be broken into individual nanoparticles and the smallest attainable size is about 150 nm (the value from intensity distribution). This aggregate size could not be reduced even for a very long irradiation time, but the reagglomeration could be occurred during long ultrasonication [15,18]. For low viscosity suspensions, the sonication amplitude is optimized at 30% as higher amplitudes do not improve the deagglomeration of nanoparticle clusters [18].

In organic solvents, the nanoparticles are generally stabilized by steric effect. In this study, diethyl octadecyl phosphonate (P18Et2) was used for the stabilization. The suspensions of alumina at 1 mg/ml in MEK were stabilized against reagglomeration by adding 0.8 mg/ml P18Et2. Particle size distribution (PSD) of Al_2O_3 in MEK suspensions after magnetic stirring showed bi-modal feature

with large agglomerates (∼1700 nm) and smaller components (∼220 nm) (Fig. 1). With increase of ultrasonication time, the large agglomerates were broken into smaller fragments and progressively reduced to aggregates.

The evolutions of alumina mean cluster size as a function of ultrasonication time in water and MEK are presented in Fig. 2. The values of the final size of alumina clusters in both solutions were identical. This result reveals that when nanoparticles were stabilized, the smallest size of aggregates after ultrasonication was independent of solvent. However, in the same conditions, the cluster size was reduced faster in water than in MEK. In aqueous suspensions, the nanoparticles are stabilized by electrostatic repulsion of the permanent electrical charges on their surface. In non-aqueous systems, colloidal stability is mostly controlled by steric repulsion induced by adsorbed dispersant layers (adlayers). Such organic molecules should be strongly anchored around the particle surface. However, the bonding between surfactant and particles can be broken under ultrasonic irradiation [17] and the steric stabilization is therefore slowed down. As can be seen in Fig. 2, the cluster size decreases faster in the suspension of P18Et2/MEK at 1 mg/ml than that at 0.8 mg/ml. Since the adsorption rate increases with concentration of the surfactant, the new surfaces of cluster could be stabilized more quickly against reagglomeration with higher concentration of surfactant. However, there is a greater tendency to form larger agglomerates due to the material bridge between particle surfaces at high surfactant concentration [18].

3.2. Dispersion of nanoparticles at high concentration in solvent

Nanoparticle concentration could affect the cluster size and viscosity of the suspension. The rheological behavior of suspensions depends strongly on the solid loading and has been studied in several contributions [27,28]. In the present study, the suspensions of alumina in water up to 50 mg/ml exhibited the *Newtonian viscosity plateau* at shear rate between $500\,s^{-1}$ and $1100\,s^{-1}$ (Fig. 3). The values of the *Newtonian plateau,* at the shear rate of $880\,s^{-1}$, were used to calculate the size of the clusters in the Stokes–Einstein equation. The *Newtonian* viscosity (Fig. 3) and cluster size (Fig. 4) of Al_2O_3 suspensions decreased with increasing ultrasonication time. The similar results were also observed for TiO_2 nanoparticle suspensions [14].

As shown in Fig. 4, between 1 and 50 mg/ml, the cluster size showed almost the same final value and evolution as a function of ultrasonic time. It reveals that the concentration of alumina
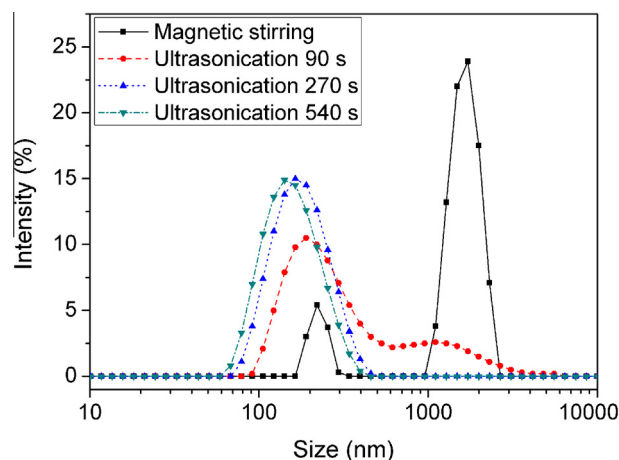

Fig. 1. Particle population of Al_2O_3/P18Et2/MEK 1 mg/1 mg/ml as a function of ultrasonic time.