Nanomaterials and Dispersion

1. Introduction

Nanomaterials have drawn a great interest and are one of the major focuses of research in recent years. Nanotechnology, along with its products and applications, has the potential to offer significant social and environmental benefits. The nanomaterials can potentially enhance the material’s properties because of the following two aspects: large relative surface area and new quantum effects. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity or heat resistance and can affect their strength. At the nano scale, quantum effects can become much more important in determining the material’s properties and characteristics, leading to extraordinary optical, electrical, and magnetic behaviors.

The nanomaterials have been applied in many commercial products. The range of commercial products available today is very broad and included stain-resistant and wrinkle-free textiles, cosmetics, sunscreens, electronics, paints, and varnishes. Nanocoatings and nanocomposites are used in diverse consumer products, such as windows, sports equipment, bicycles, and automobiles. There are novel UV-blocking coatings on glass bottles which protect beverages from damage by sunlight, as well as longer-lasting tennis balls using butyl-rubber/nano-clay composites. Nanoscale titanium dioxide, for instance, is applied in cosmetics, sun-block creams, and self-cleaning windows. Similarly, nanoscale silica is used as filler in a range of products, including cosmetics and dental fillings.

Innovations in nanomaterials are also driving advances in battery technology by increasing capacity, improving cyclability, and enhancing both rate capability and mechanical toughness. In medicine, proposed uses for nanomaterials include drug delivery, imaging, and the formation of bone composites [1-4]. Additionally, companies in the food and cosmetics industries have incorporated nanomaterials to enhance the quality of their products [5].

With the exception of the commercial products, defense and engineering scientists have shown that nanomaterials are potentially useful in electronics, sensors, munitions, and energetic/reactive systems involved with the advancement of propulsion technology [6].

2. Classification of Nanomaterials

Nanomaterials could be single-phase materials and multi-phase composites. The single nano phase materials are generally nanoparticles with particle sizes less than 100 nm in at least one dimension. The single-phase nanomaterials could also be bulk materials consisting of nanoparticle aggregate, cluster, or agglomerate. In this case, the expected properties many not be reached because of the agglomeration. In order to achieve the better properties and performance, the aggregated nanoparticles are necessary in order to be separated and dispersed.

Multi-phase nanocomposites are materials that are composed by adding nano phase materials into the matrices. These composites are most based on polymer matrices. By incorporating nanomaterials into existing products, they enhance certain properties or provide new functionalities, such as increased strength, improved heat or chemical resistance, better conductivity, etc. For example, higher performance polymeric composites contain 6-8 μm-diameter graphite fibers. However, the enhanced physical and mechanical properties of multi-phase composite materials depend on nanoparticles to be fully dispersed them at small length scales.

3. Importance of Uniform Dispersion of Nano Phase

The microstructure uniformity is of paramount importance to the bulk materials' properties and performance. The agglomeration of nanoparticles is a very significant and spontaneous phenomenon. Uncontrolled agglomeration of powders due to attractive van der Waals forces can give rise to microstructural inhomogeneities, which results in the desired properties' damaged.

The strong tendency of nanoparticles to form clumps and clusters ("agglomerates") is a serious technological problem that impedes the effective use of nanoparticles in many applications. For example, the nanoclay aggregates (as large as 10μm) could result in reduction of strength [7-8] in nanoclay/epoxy composites.

Therefore, the nanomaterials' uniform dispersion inside the matrix is a research focus. Effective means of deagglomerating and dispersing are needed in order to overcome the bonding forces after wettening the powder.

4. Dispersion Process

4.1 Single-Nano Phase Materials

In case of single-nano phase materials, the separation and dispersion of nanomaterials is by means of repulsive interparticle forces to prevent agglomeration.

In the case of solid nanoparticles, the dispersion process for single-nano phase materials generally doesn't occur through grinding method. The basic strategy is by surface modification to separate them since the surface modification can minimize the agglomeration by decreasing the particle surface energy.

For a solution, two methods are commonly used. **The first method** provides the dispersion by electrostatic repulsion. The repulsion results from the interactions between the electric double layers surrounding the particles. An unequal charge distribution always exists between a particle surface and the solvent. Electrostatic stabilization of dispersion occurs when the electrostatic repulsive force overcomes the attractive van der Waals force between the particles. This stabilization method is generally effective in dilute systems of aqueous or polar organic media. This method is very sensitive to the electrolyte concentration since a change in the concentration may destroy the electric double layer, which will result in particle agglomeration. **The second method** of stabilization involves the steric forces. Surfactant molecules can absorb onto the surface of particles, and their lyophilic chains will then extend into the solvent to interact with each other. The solvent-chain interaction, which is a mixing effect, increases the free energy of the system and produces an energy barrier to the closer approach of particles. When the particles come into closer contact with each other, the motion of the chains extending into the solvent becomes restricted and produces an entropic effect. Steric stabilization can occur in the absence of the electric barriers. Steric stabilization is effective in both aqueous and non-aqueous media, and is less sensitive to impurities or trace additives than electric stabilization. The steric stabilization method is particularly effective in dispersing high concentrations of particles.

Some additives, which can be used to disperse the nanoparticles, are useful, but they also present their own problems, especially in regard to the purity of the final product.

4.2 Multi-Phase Nanocomposites

The utilization of nanometer scale particulates, such as carbon nanotubes and nanoclay into polymers, is increasing due to potential improvements in thermo-physical properties. For instance, researchers at the Toyota Research Labs observed up to 60% increase in strength of nylon 6 sample with the addition of nanoclay. Similarly, Chen et al., fabricated nanocomposite samples by melt-compounding nanoclay with maleic anhydride modified polypropylene at loadings up to 50%. The authors observed monotonic improvements in tensile strength and stiffness, reaching 120% and 400%, respectively. However, the nanoclay aggregates (as large as 10μm) could result in reduction of strength [7].

Nonetheless, large macro-particles or clusters are detrimental to the properties of the composite materials since, they: (1) tend to have various types of defects at the atomic or molecular level, (2) may contain voids or impurities, and (3) facilitate ineffective load transfer at the interface due to their usually irregular shape. For such cases, mixing nanomaterials into other materials, whether they are polymeric or metallic, may degrade some of the original material properties.

Various proposed dispersion methods include: (1) directly mixing nanomaterials with a polymer, either in the solid or liquid form by a mechanical mixter, (2) using a sonicator or ultrasonic energy to enhance dispersion, (3) using an electric field after mechanical mixing to enhance dispersion (for instance, applying AC or DC voltage at various levels), (4) solid state mixing such as grinding nanomaterial and polymer together at room temperature, (5) mixing with a polymer during melting in the extruder before the extrusion or molding process (this method benefits from the high shear forces generated in an extruder to enhance dispersion), (6) cryo-mixing, or mixing at very low temperatures to make the polymer brittle enough so that polymer particles can be mixed with nanomaterials at a smaller length scale, and (7) heating the polymer to higher temperatures to decrease the viscosity of the polymer that will enhance the mixing.

Various mixing technologies, which employ the most common strategy, are available for the efficient processing of products containing nanomaterials depending on rheology and shear requirements [9].

Low-Viscosity Nanodispersions. The dispersion of nanomaterials into a low-viscosity formulation typically involves a pre-mix stage to combine the raw materials. This is done with the use of low-speed propellers, turbines, or simple agitators. Due to attractive forces between the individual nanoparticles, they combine with the liquid vehicle in the form agglomerates. High shear forces are necessary to break up these groups of agglomerates. How aggressive those shear forces need to be can vary from one formulation to another. One proven method is the use of Ross Ultra-High Shear Mixers, which are specially-engineered rotor/stator devices that run at extremely high Ross MegaShear used for dispersing and that have tip speeds up to 11,000 fpm.

Medium-Viscosity Nanodispersions. Higher loadings of nanoparticles can result in a premix of substantial viscosity, rendering single-shaft devices inadequate. For these requirements, a multi-shaft mixing system is recommended wherein two or more independently-driven agitators work in tandem such as a low-speed anchor agitator, a saw-tooth disperser blade, and a rotor/stator assembly equipped for powder induction. This configuration provides a unique combination of laminar bulk flow, high shear mixing, dust-free sub-surface powder addition, deagglomeration, and superior heat transfer. After a batch cycle, the nanodispersions may be further polished by running it through an Ultra-High Shear Mixer.

High-Viscosity Nanodispersions. As product viscosity continues to build up, a multi-shaft mixing system will eventually fail to produce adequate flow. When agitators with a fixed axis of rotation no longer suffice, a move to a planetary mixer is required. The agitators of a planetary mixer rotate and travel through the mix vessel by passing through every point within the batch, regardless of product rheology. Examples include the classic Double Planetary Mixer (DPM) and the “hybrid” planetary mixers, featuring one or two stirrer blades (similar to those in a DPM) and supplemented by one or two high speed disperser shafts. These shafts also revolve on their own axes while orbiting the mix vessel. For example, a three-roll mill has been used to mix nanoclay into the epoxy [10] matrix.

6. Application Examples

6.1 Silver Particle Dispersion

The comparison of mechanical mixing with a three-roll mill and sonication are conducted to disperse the nanosized silver particles in ethylene glycol. The measurement results show that mixing with a three-roll mill is an effective tool to break the agglomerates of silver nanoparticles in solvent, resulting in a better dispersion [11].

A uniform dispersion of silver nanoparticles into a binder solution is also achieved in a Ross Double Planetary Mixer under a vacuum. After mixing, the paste is fed into a Ross Three-Roll Mill, a kind of mill providing high shear force, to break down any agglomerates. The milled material exhibits a markedly glossier, more homogenous appearance, further indicating an improvement in dispersion quality.

6.2 Nanocomposites with Carbon Nanotubes

Polymer matrix nanocomposites with fillers such as carbon fiber, fiber glass, or other polymer fibers render high mechanical properties, high electrical conductivity, high electrostatic discharge, high electromagnetic interference, and high thermal conductivity, with which the regular polymer can't provide. Carbon nanotubes have high mechanical properties from their high aspect ration, high electrical conductivity, high thermal conductivity, and high thermal stability. By adding carbon nanotubes into the polymer, it is possible to improve the polymer matrix in terms of solvent resistance, stiffness, glass transition temperature (Tg), and to reduce thermal shrinkage. However, it requires a high loading (about 10 to 25 wt%) and a good dispersion to reach the desired polymer properties. The smooth sidewall surface of carbon nanotubes, incompatible with most solvents and polymers, results in poor dispersion of carbon nanotubes in polymer matrixes.

However, the potential of using nanotubes as a constituent of polymer composites is not presently recognized because of the difficulties associated with dispersion and processing. High aspect ratio combined with high flexibility increases the possibility of nanotube entanglement and close packing. The low dispersity comes from the tendency of pristine nanotubes to assemble into bundles or ropes as shown in Fig. 1 [12]. Thus, a significant challenge in developing high-performance CNT-polymer composites is to introduce the individual CNTs in a polymer matrix in order to achieve better dispersion and alignment and strong interfacial interactions, all of which is to improve the load and electron transfer across the CNT-polymer matrix interfaces.

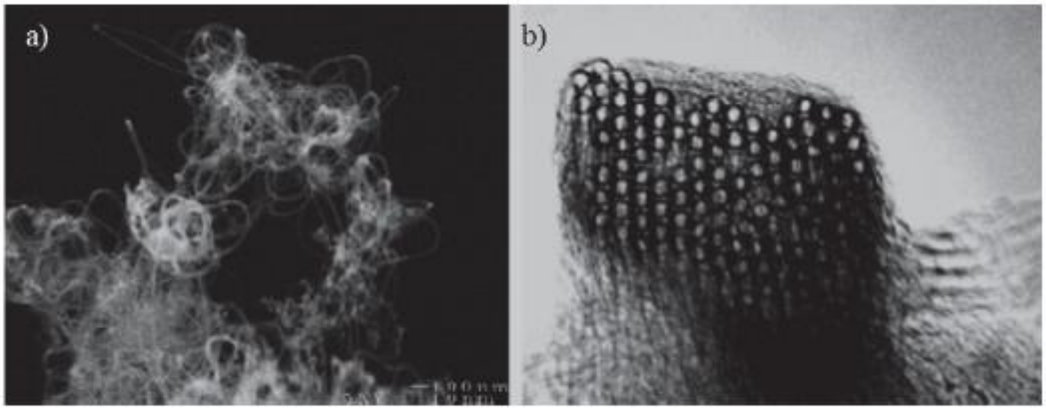

Figure 1. *(a) SEM image of entangled SWCNT agglomerates and (b) TEM image of a SWCNT bundle [12].*

Here, we compare the most commonly employed methods listed in part 4.2 (1), (2), and (4) for CNT dispersion [13].

Ball milling is a method that is typically used to grind bulk materials into fine powder. During milling, a high pressure is generated locally due to the collision between the rigid balls in a sealed container (Fig. 2). The cascading effect of the balls reduces the size of material to fine powder. Balls are usually made by ceramic, flint pebbles, and stainless steel. Ball milling has been successfully applied to CNT dispersion into polymer matrices. To obtain narrow length and diameter distributions of CNTs and to open the nanotubes for improved sorption capacity for gases, ball-milling is a very useful method [14]. However, it has also been observed that a large amount of amorphous carbon is created, which clearly indicates that the tubes are damaged in different ways, and that ball milling is a destructive method [15].

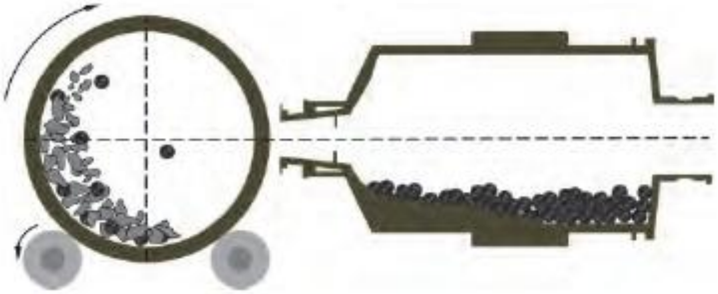

Figure 2. *Schematics of ball milling technique*

Ultrasonication is a very effective method of dispersion and deagglomeration of CNTs, as ultrasonic waves of high-intensity ultrasound generates cavitation in liquids (Fig. 3). Ultrasonication disperses solids primarily through a microbubble nucleation and collapse sequence. Ultrasonication of fluids leads to three physical mechanisms: cavitation of the fluid, localized heating, and the formation of free radicals. Cavitation, the formation and implosion of bubbles, can cause dispersion, but it also damages the CNT structure. Another study found hardness deteriorated in hardness for sonication greater than 10 minutes [7]

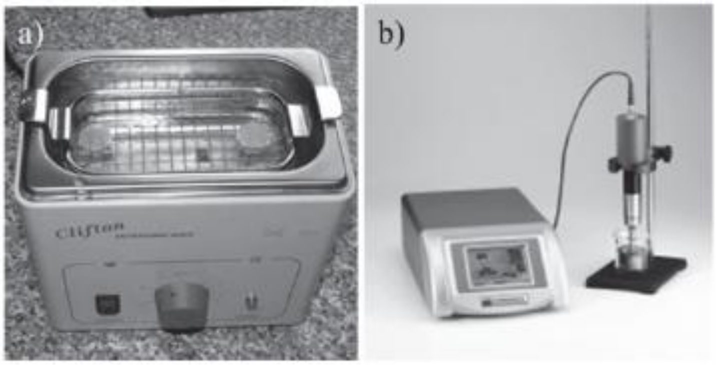

Figure 3. *(a) Bath type, (b) horn type sonicator*

Calendering, also commonly known as three-roll-milling (Fig. 4) is a dispersion technique that employs both shear flow and extensional flow created by rotating rolls of different speed to mix and disperse CNTs or other nanoscale fillers into polymers or other viscous matrixes. The first and third rollers (usually called the feed and apron rolls, respectively) in Fig. 5 (b) rotate in the same direction while the center roller rotates in the opposite direction. In order to create high shear rates, angular velocity of the center roll must be higher than that of feed roll ($\omega 2 > \omega 1$). As the resin suspension is fed into the narrow gap (δ) between the feed and center rolls, the liquid mixture flows down, covering (and essentially coating) the adjacent rolls through its surface tension under intensive shear forces. At the end of each subsequent intended dwell time, the processed resin suspension is collected by using a scraper blade in contact with the apron roll. This milling cycle can be repeated several times to maximize dispersion.

One of the unique advantages of this technique is that the gap width between the rollers can be mechanically or hydraulically adjusted and maintained, thus it is easy to obtain a controllable and narrow size distribution of particles in viscous materials. In some operations, the width of gaps can be decreased gradually to achieve the desired level of particle dispersion [16].

Due to the powerful shearing forces of the three-roll mill, the dispersion of the agglomerates for the carbon nanotubes is ideal. The carbon nanotubes remain undamaged, and the requisite high aspect ratio (length to diameter) is retained. The surface area of the carbon nanotubes wet by epoxy resin continues to grow. As a result, the viscosity rises steadily from 10 cPoise to as much as 100.000 cPoise [17].

Figure 4. *Torrey Hills T65 three roll mill used for CNT dispersion into a polymer matrix*

Conclusion

The combination of nanoparticles and dispersion is an important topic in both academic research and industrial application. Generally, the grinding method is only used for part of nanocomposites. Three-roll mill machine is a very appealing process and benefits the environment by eliminating the solvent. The three-roll mill is an extremely effective dispersion route for nanocomposites, containing fibers such as carbon fiber, glass fiber, carbon nanotube, etc. The mixer can reach a higher degree of intercalation/exfoliation within a short period of time. The main reason is that the high shear force from three-roll mill could disperse the fibers with great effect.

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