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Dispersion Techniques of Nanoparticles

Illy Athira Binti Azman
Faculty of Chemical Engineering
Universiti Teknologi MARA, (UiTM)
Shah Alam, Selangor, Malaysia.
illyathiraazman@gmail.com

Sakinah Binti Mohd Alauddin
Faculty of Chemical Engineering
Universiti Teknologi MARA, (UiTM)
Shah Alam, Selangor, Malaysia.
sakinah3676@salam.uitm.edu.my

Ruzitah Binti Mohd Salleh
Faculty of Chemical Engineering
Universiti Teknologi MARA, (UiTM)
Shah Alam, Selangor, Malaysia.
ruzitah@salam.uitm.edu.my

Mohammed Iqbal Bin Shueb
Agensi Nuklear Malaysia
Bangi, Selangor, Malaysia.
iqbal@nuclearmalaysia.gov.my

Abstract—**The distribution of the nanosized particles plays an important role in nanocomposite properties which are strongly dependant on the final morphology of the material. The dispersion of the nanosized particles remains obstacle for optimum nanocomposites applications. Therefore, this paper reviews the effect of three different techniques; sonicators, magnetic fields, and surfactants on the distribution performance of nanoparticles. From reviewed, it is obtain that the sonicators techniques will lead to a better nano particle dispersion, while magnetic field method applied with a parallel allignment will improve the thermal properties of the nano composite and agglomeration of nano particle can be avoided when surfactant used.**

Keywords— (Nanocomposites, Ultrasonic, Magnetic Fields, Sonicators, Nanoparticle dispersion)

I. INTRODUCTION

In recent years, composites nanoparticles are advanced materials that have gain attention at foreground of research due to their scientific and technological importance. It has a wide variety of applications like modifiers of polymer, catalyst with huge activity and specificity and metal semiconductor [1]. The addition of nanoparticle in composite can enhance it properties however problem arises when the nanoparticles tend to aggregate and bundle together due to strong interparticle attraction [2]. A few methods have been developed to encounter the agglomerate problems to enhance the dispersion of nanofiller including in situ polymerization, solution processing, spin casting and melt spinning [3, 4]. The processing such as method that has been utilized to enhance the dispersion of nanofiller are sonicators, magnetic fields, and surfactants [5]. Some researchers studied that the interaction between particles was based on electrostatic repulsion and the stabilization mechanism using a small-molecule anionic dispersant [6]. It was studied that nanoparticles exist as individually dispersed particles at points far away from the isoelectric point [7]. Nanoparticles show various degrees of coagulation, at points near the isoelectric point.

II. VARIOUS TECHNIQUES IN ENHANCE THE DISPERSION OF NANOFILLERS

A. Sonicator/Ultrasound

Ultrasound assisted single screw extrusion process for dispersion of carbon nanofibers (CNFs) in polymers was studied [8]. They added 1-20wt% of CNFs in polyetherimide (PEI). “*Fig. 1,”* shows a morphological sample result without ultrasonic treatment, the CNF bundles in the dry-mixed PEI/CNF composites.

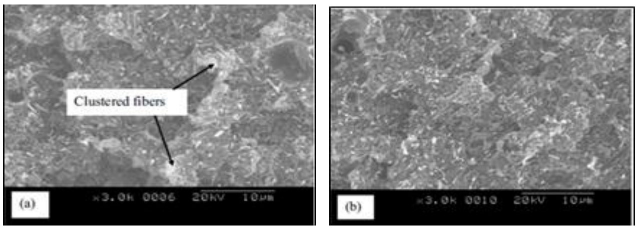


Fig. 1. SEM micrographs of cryofractured surface of 20 wt% CNF/PEI nanocomposites obtained without (a) and with (b) ultrasonic treatment.

However, with ultrasonic assisted it shows good dispersion of CNFs in PEI matrix. There are two factors that influence the dispersion which are the screw rotation speed and ultrasonic amplitude.[9]

The effect of ultrasonic treatment time on the mechanical properties of thermoplastic natural rubber (TPNR) nanocomposites was reported by Mou’ad A. Tarawneh, et al. [10]. “*Fig. 2,”* and *“Fig. 3,”* illustrate the X-ray diffraction (XRD) results for the sample. The ultrasonic treatment increased the distance between the layers of the clay thus provide more space for the polymer chain to interact and prevent agglomeration of clay to occurs. Without ultrasonic treatment, the layers still in ordered stacks in TPNR nanocomposites and the clay particles form big agglomerations. The optimum ultrasonic treatment time was obtained at 1 h with the addition of a 12% PP-g-MA as the coupling agent. They found that PP-g-MA which was used as compatabilizer can easily diffuse into the organoclay layers which increase its spacing indicating good homogeneous dispersion of clay inside the matrix [11].

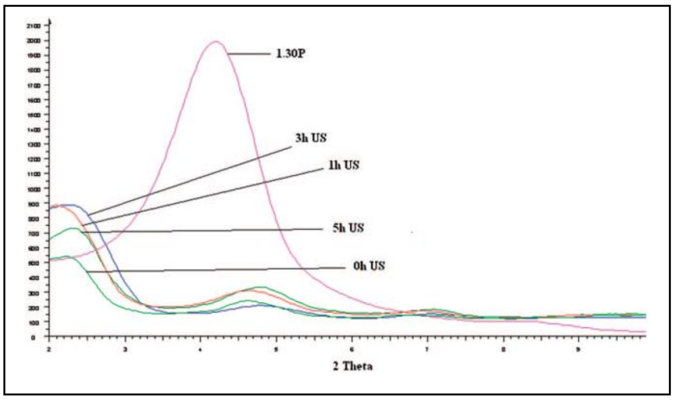


Fig. 2. XRD patterns of TPNR nanocomposites with different times for ultrasonic treatment (1, 3 and 5h) without a coupling agent.

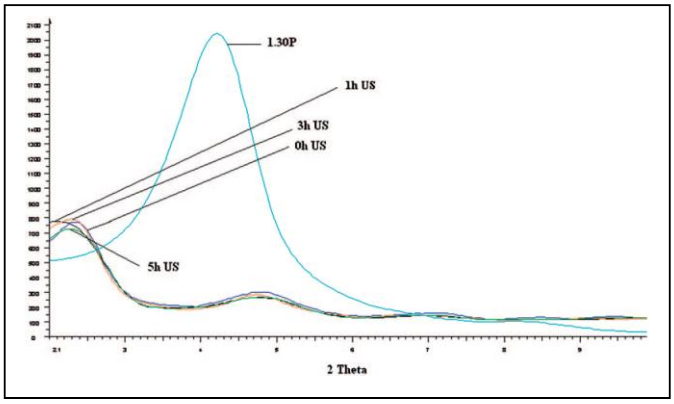


Fig. 3. XRD patterns of TPNR nanocomposites with different times for ultrasonic treatment (1, 3 and 5h) with a constant percentage of the coupling agent (12 % PP-g-MA).

Intensity of peak increased at 5h indicates the d-spacing of TPNR nanocomposites decreased with increased ultrasonic treatment which shows the tendency of clay to agglomerate inside the matrix. Increasing ultrasonic treatment time will lead to agglomeration of clay where it is difficult for the polymer chains to diffuse into the agglomerates and the clay interlayer.

While from TEM micrograph, there is a combination of intercalated-exfoliated structure of the TPNR composites with organic clay. *"Fig. 4," represents* the morphological characterization of transmission electron micrographs of the nanocomposite samples treated with different ultrasonics are shown in Figure 4(a)–(b). From the TEM micrographs, the dark lines shows the clay sheets while the light areas shows the PP phase and the darker areas represent the rubber phase. Without ultrasonic treatment, the layers still in ordered stacks in TPNR nanocomposites and the clay particles form big agglomerations. As can be seen, at 5 hours ultrasonic assisted the clay dispersed as intercalation and exfoliated in the rubber phase and PP which shows the ability of organoclay to open the layers which contributed for a better dispersion in the matrix.

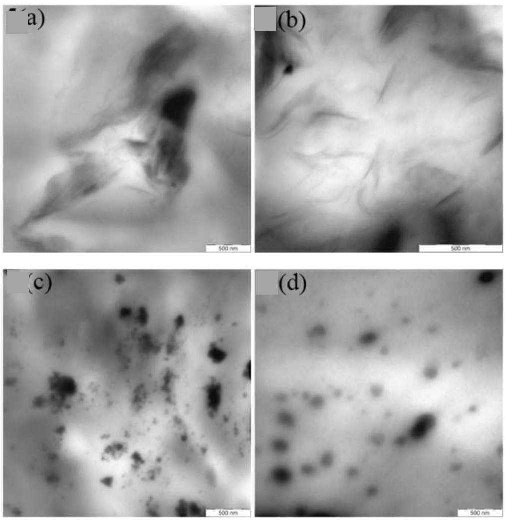


Fig. 4. TEM micrographs of TPNR/clay nanocomposites. Effect of ultrasonic treatment on TPNR/clay nanocomposites at: (a) 0h, (b) 1h, (c) 3h, (d) 5h.

They also found that, the mechanical properties of TPNR nanocomposites with or without the coupling agent were improved after 1 hour ultrasonic treatment however if the ultrasonic treatment takes more than 1 hour, the particle will tends to aggregate and weaken the tensile properties, Young's modulus, Elongation at break and Impact strength. The longer time for ultrasonification will introduce defects somehow; it is an accepted technique for dispersing aggregated nanoparticle composite [12,13]. It was concluded that, ultrasonic treatment can improve the compatibility of organoclay filler and the TPNR matrix and enhance dispersion of the clay in TPNR [14].

Katherine Dean et al, prepared and characterized melt-extruded thermoplastic starch/clay nanocomposites [15]. They used two types of clays which one based on naturally occurring sodium montmorillonite (Na-MMT) clay and synthetic fluoromican (Na-FHT) and water as the plasticizer. The formulations were prepared by dry blending, conventional dispersion and ultrasonic dispersion followed by extrusion. *"Fig. 5,"* shows the Transmission Electron Microscopy (TEM) of the samples.

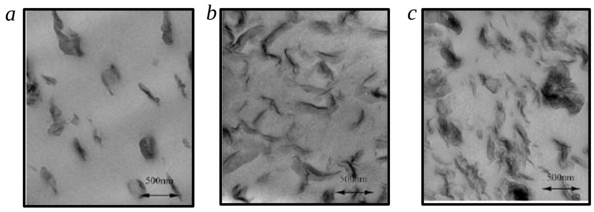


Fig. 5. (a) TEM image of low water content (13 wt%) Na-FHT gelatinized starch nanocomposites 1 wt% clay (conventional dispersed 30 min) , (b) TEM image of medium water content (18 wt%) Na-MMT/gelatinized starch nanocomposites with 2 wt% clay (ultrasonically treated 2 h), (c) TEM image of high water content (20 wt%) Na-MMT/gelatinized starch nanocomposites with 3.2 wt% clay (ultrasonically treated 2 h).

They reported that the medium water content 18 wt%, 2 wt% Na-MMT with ultrasonic treatment the nanocomposite shows an exfoliated type structure. Some agglomeration of clay platelets was observed even dispersion of platelets was still good as the clay content was increase to 3.2 wt%, although in systems containing higher amounts of water to 20 wt%. Both intercalated and exfoliated structures can be produced depending on levels of nanoclays, types of nanoclays, dispersion methodologies, and processing conditions [16].

Fangzhi Zhang et al, studied the surface treatment of magnesium hydroxide to improve its dispersion in organic phase by ultrasonic technique [17]. The ultrasonic frequency and power of the ultrasound were constant at 25 kHz and 100 W, respectively. Nano magnesium hydroxide $Mg(OH)_2$ was modified by ultrasonic method with stearic acid (SA) as modifier in water. *“Fig. 6(a)”* and *Fig. 6(b)”* represent the dispersion image of unmodified $Mg(OH)_2$ and SA-$Mg(OH)_2$ (SA 6 wt%) in xylene. Bad agglomeration of $Mg(OH)_2$ can be seen in *“Fig. 6(a)”* while good dispersion of SA-$Mg(OH)_2$ captured as shown in *“Fig. 6(b)”* due to hydrophobic properties of SA-$Mg(OH)_2$. Their result indicates, that all SA was chemically bonded into the surface of the $Mg(OH)_2$ forming a coating layer. Compared with the unmodified $Mg(OH)_2$, the modified $Mg(OH)_2$ has better dispersion property in xylene because of slower sedimentation velocity of dilute suspension in xylene correspond to the hydrophobic interaction between the $Mg(OH)_2$ and SA. The modified $Mg(OH)_2$ also exhibits lower viscosity of suspension in paraffin liquid reflecting that it can easily blended within the polymer matrix during the melt compounding due to its own chemical property, $Mg(OH)_2$ tends to agglomerate. In organic phase, modified $Mg(OH)_2$ could have better dispersion than the unmodified $Mg(OH)_2$. The interfacial region between the $Mg(OH)_2$ and polymer matrix must be modified to solve this problems and the dispersion quality of $Mg(OH)_2$ must be improved. Modification of $Mg(OH)_2$ and SA by sonication will leave a good treatment effect to the sample. The interactional mechanism between both $Mg(OH)_2$ and SA, and the dispersion of $Mg(OH)_2$ in organic phase (xylene and paraffin liquid) have been studied.

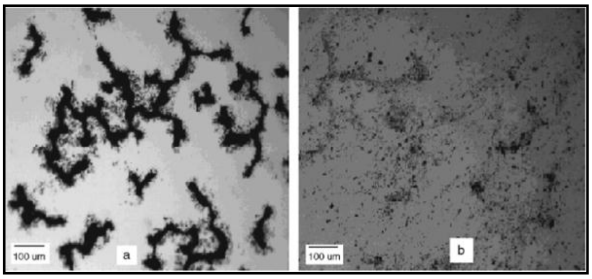


Fig. 6. The dispersion character pictures of $Mg(OH)_2$ in xylene: (a) $Mg(OH)_2$, (b) SA-$Mg(OH)_2$ (SA 6 wt.%).

B. Magnetic Field

Polymer/carbon nanotube (CNT) composites are expected to have good processability characteristics of the polymer and excellent functional properties [18]. Few methods have been introduced by Biercuk et al, to enhance the dispersion of nanoparticle like CNTs in a polymer matrix *“Fig. 7(a),”* , including optimum blending, in situ polymerization and chemical functionalization and *“Fig. 7(b),”* the alignment of CNTs in the matrix can be enhanced by ex situ techniques, force and magnetic fields, electrospinning and liquid crystalline phase-induced methods.

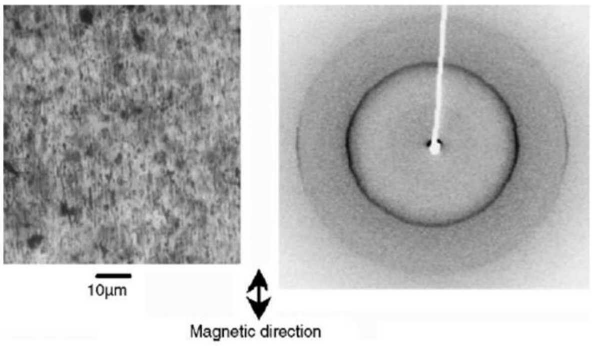


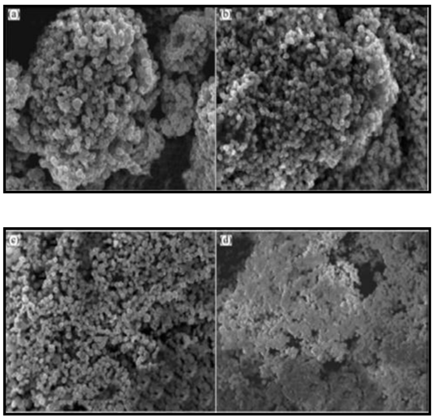
Fig. 7. Optical micrograph (a) and wide angle X-ray diffraction (WAXD) pattern (b) of PC/carbon fiber nanocomposites treated in molten state under a magnetic field.

Aggregation of nanoparticles is a common problem in nanotechnological production processes because it reduces the advantages associated with the large surface area of single particles [19]. Microwaves, ultrasound, homogenization, media and jet milling have been used to disperse the aggregation [20, 21]. New magnetic field assisted dispersion technique has been applied in industry, including planetary ball milling, ultrasonic and ultraturrax techniques and jetmilling with respect to particle size and energy efficiency in the treatment of silica suspension. Smallest particle size can be obtained by applying ultrasonic and ultraturrax treatment. Jet milling and magnetic treatment produced nearly same size particle, while larger particles produced from planetary ball mill method. The magnetic field assisted dispersion technique was the best method in producing uniform particle size [19].

The enhancement of thermal and electrical properties of carbon nanotube polymer composites by magnetic field processing was studied [22]. The addition of small quantities of carbon nanotubes (CNTs) to polymer composites will increase the thermal conductivity of the polymer host [23].The introduction of magnetic alignment will improve the properties of nanocomposite of CNT [24,25]. Based from their result, the parallel direction of magnetic alignment CNT mat samples give the thermal conductivity five to eight times larger compared to perpendicular direction [24,25], while 10% improvement of the thermal conductivity on the composite can be seen. They also dispersed the CNTs ultrasonically with small amount of ethanol which to avoid particle agglomerate and also to enhance the distribution of CNTs on the surface of composite. By applying magnetic field on the nanotubes, the usage of magnetic field directly towards the nanotube will reassemble the CNTs in a polymeric medium. The authors revealed that the cooperation alignment of nanotubes was the cause of increasing in thermal conductivities. Electrical transport analysis test outcome shows that the magnetic field process will leads to formation of single wall carbon nanotubes (SWNT) bundle. The formation of SWNT bundle will improve the thermal conductivity when significant works applied. SWNT bundle also may enhance the electrical conductivity of the composite. Authors conclude that, it is desired to use a method that will aligned CNT composite in order to have a better nanotube separation.

C. Effect of surfactance

Conducted a research on fine face-centered cubic (FCC) nickel powders that synthesized by liquid phase reduction with different surfactants [26]. The nickel powders were synthesized by reducing nickel sulfate in aqueous hydrazine solution with a variety of surfactants including cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS), PVP, PEG, poly oxyethylene tert-octylphenyl (Trion X-100), triethanolamine (TEA) and polyethylene glycol sorbitan monostearate (Tween). They used liquid phase reduction method to produce high-purity FCC nickel powders with favourable dispersion and investigate the effect of surfactants on the dispersion and morphology of the products. *"Fig. 8,"* illustrate SEM image of the 6 different sample.



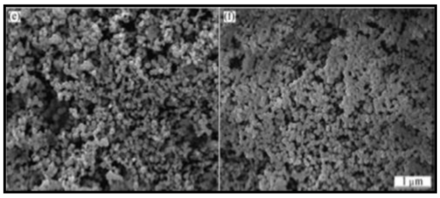


Fig. 8. SEM images of samples prepared with non-ionic surfactants: (a) Nothing; (b) PVP; (c)PEG-600; (d)TEA;(e)Triton X-100; (f) Tween-40.

The nonionic surfactants PEG-600 and Tween-40 were found to show best performance in nanoparticle dispersion.

The carbon nanotubes tend to self-associate into micro-scale aggregate, different approaches were suggested to decrease the nanotube agglomeration [27]. General dispersion procedure, when the surfactant adsorbed at the nanotube surface, the ultrasonification will apply due to reduce the bundle of nanotubes by electrostatic repulsions. They also found that after surfactant was added, the outermost nanotubes are treated more than the innermost tubes where it is remain predominantly [28,29]. To have individual carbon nanotubes, mechanical exfoliation of surface treatment must occur. Basically, ionic surfactants are chosen for CNT/watersoluble solutions while nonionic surfactants are chosen when organic solvents used. Ultrasonication and high shear mixing methods introduced to change the surface chemistry of the tubes either covalently functionalization or adsorption. It can be concluded that the behavior of surfactants in dispersing the carbon nanotubes is similar to that of dispersing solid particles such as classical colloidal chemistry [30].

Researchers found that in order to have heat transfer enhancement to develop a homogeneous, stable and have new heat exchange medium of high conductivity, they started by applying nanomaterial technologies in this medium. Dispersing nanoparticles into conventional heat transfer fluids will produce nanofluids like water, glycol, or oil, was coined by Choi in 1995 at Argonne National Laboratory of USA [31]. To have better stability compared to those fluids containing micro- or milli-sized particles and have higher thermal conductive capability than the basic fluids were the benefit of nanofluids. However, it is easily to coagulate and difficult to disperse in water since high surface energy of nanoparticles. In reducing the coagulation of nanoparticles in the nanofluids, they suggested by applying agitation [32,33] and adding surfactants. Theoritically, by adding the surfactant will cover the external surface of nanoparticles which mean by electrosteric potential but from their result shows that the adsorption of surfactants onto nanoparticles changes the electrical interaction between the particles [34].

III. CONCLUSION

Better dispersion of nanofiller in matrices will enhanced the polymer composites performance. It can be summarized that with the ultrasonic assisted the nanocomposite will have better dispersion in polymer, the material flow will be improved and also will give less breakage in a drawing process, which contribute to improve production yields. The surface quality of the composites can be improved while use ultrasonic assisted. Usage of magnetic field techniques with some others additional method such as planetary ball milling, ultrasonic and ultraturrax will help in the nano particle dispersion and it is also would gave a uniform particle size of nanocomposite. Applying the parallel magnetic field direction towards the nanocomposites would lead to the enhancement of the thermal and electrical conductivity of the nanocomposite. Surfactant such as cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS), PVP, PEG, poly oxyethylene tert-octylphenyl (Trion X-100), triethanolamine (TEA) and polyethylene glycol sorbitan monostearate (Tween) have been used to cover the surface of nano particle to avoid the nano particle from being agglomerate, coagulate and being attached to each other. Each technique of nanoparticle dispersion enhancement has its specific effects on the composites itself based on their needs.

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