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Acoustically-enhanced particle dispersion in polystyrene/alumina nanocomposites

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Abstract. Polymer nanocomposites are advanced nanomaterials which exhibit dramatic improvements in various mechanical, thermal and barrier properties as compared with the neat polymer. Polystyrene/ alumina nanocomposites were prepared by an ultrasound-assisted solution casting method at filler loadings ranging from 0.2 to 2% and also at different ultrasonic frequencies, viz. 58 kHz, 192/58 kHz, 430 kHz, 470 kHz and 1 MHz. The composites were subjected to mechanical property tests (tensile and impact tests) and cavitation erosion tests to study the enhancement in functional properties. Filler dispersion in the polymer matrix was observed by SEM analysis. The effect of frequency on filler dispersion in the matrix was studied by SEM analysis and functional property enhancement of the composite material. The composites prepared at dual (high/ low) frequency (192/58 kHz) were found to show better property enhancement at low filler loadings as compared with neat polymer and also with composites prepared without ultrasound, thus reinforcing the finding that ultrasound-assisted synthesis is a promising method for the synthesis of nanocomposites.

Keywords: ultrasound; nanocomposites; dispersion; mechanical properties; cavitation erosion

1. Introduction

Polymer nanocomposites (PNCs) are synthesized by the incorporation of nano-sized inclusions into a polymer matrix. These materials exhibit significant improvement in physical properties as compared to those of neat polymer and also in comparison with micro and macro-composites (Giannelis 1996). PNCs are found to possess drastically different material properties compared to those of their constituents. The advantages they offer render them of great academic and industrial interest. Significant enhancement in properties such as stiffness, scratch resistance, abrasion resistance, barrier properties, solvent/ chemical resistance, erosion resistance, high temperature resistance, optical clarity, transparency, high weatherability, low water absorption, high refractive index, non-toxicity and biocompatibility shown by polymer nanocomposites is reported in literature. As a result, these materials find applications in automotive industry, packaging, protective coatings, flame retardant additives, performance plastics for office and home appliances, propulsion systems, optical systems such as hybrid solar cells, for corrosion resistance

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and in medical, dental and environmental fields (Alexandre and Dubois 2000, Ray and Okamoto 2003, Koo 2006).

Uniform incorporation of nanoparticles in a polymer matrix results in the formation of PNCs. Nanoparticles act as reinforcing agents in the matrix, and thereby change the overall behaviour of the matrix. Nanoparticles, being very small in dimension, possess ultra large interfacial area per unit volume, enabling enhanced interaction with the polymer matrix. This results in a dramatic improvement in functional properties (Ash *et al*. 2004).

Large scale preparation of nanocomposites is not realized yet due to the absence of cost-effective methods for controlled dispersion of nanoparticles in the polymer matrix. Nanoparticles have a strong tendency to agglomerate, which will nullify any advantages which could be obtained as a result of the lower dimension of particles. Currently, there is great difficulty in obtaining nanocomposites with acceptable homogeneity. Various physical and chemical methods are reported in literature for the synthesis of nanocomposites. Melt processing and solution blending are the major physical methods. Various in-situ polymerisation methods and sol-gel techniques fall in the category of chemical synthesis methods (Li *et al*. 2010). Some other methods such as spray drying and melt extrusion are reported elsewhere (Simon *et al.* 2008).

Ultrasound is a sound wave with frequency above the human threshold of hearing, i.e., sound of frequency above 20 kHz. Ultrasonic process intensification is an advanced and novel technology used in various scientific and medical fields. Acoustic cavitation and acoustic streaming are the two basic phenomena associated with any ultrasonic process. Like any other sound wave, ultrasonic waves also consist of compression and expansion cycles. When an ultrasonic wave is passed through a liquid, a positive pressure is exerted on the liquid during the compression cycle and a negative pressure is exerted during expansion cycle. During this negative pressure, molecules are pulled away from each other. This results in formation of cavities in the liquid. Over many cycles, these cavities grow and enlarge. Finally, implosion of the cavities occurs, creating temperatures of the order of 5000 K and pressures of 500 atmospheres (Suslick 1989).

Acoustic streaming is the phenomenon of time-averaged uni-directional flow that develops in a liquid when it is subjected to a high-intensity fluctuating beam component. In an ultrasonic tank, due to the presence of sound waves, unidirectional flow currents are formed. According to Lighthill (1978), the dissipation of acoustic energy flux creates gradients in momentum flux that result in acoustic streaming motion. Acoustic streaming, sometimes referred to as ‘quartz wind’, happens in the main body of the fluid. Raleigh streaming is associated with the boundary layer of solid surfaces (Lighthill 1978, Riley 1998). Both acoustic cavitation and acoustic streaming work together in all ultrasonic processes. But at low frequencies, acoustic cavitation dominates, and at higher frequencies (megahertz range), acoustic streaming dominates (Suslick and Doktycz 1990).

Ultrasound is used in a variety of applications such as surface cleaning, emulsification, degassing, crystallisation, extraction, for accelerating and performing chemical reactions (Contamine *et al*. 1994), and nanoparticle fabrication by sono-fragmentation (Gopi and Nagarajan 2008). Various studies have been reported in literature on the usage of ultrasound. Ultrasound had been effectively employed for cleaning in microelectronic industry (Nagarajan 1995), removal of soil contamination by ultrasonic washing (Mason *et al.* 2004), dye-degradation (Little *et al.* 2002), size reduction of particles (Kass *et al.* 1996), increasing rate of chemical reactions (Horst *et al.* 1996, Okitzu *et al.* 2005), etc.

The first example cited in literature for the preparation of nanocomposite was the incorporation of organoclay into a thermoplastic polyolefin matrix by Nahin and Backlund (1963). Since then,

there have been a huge number of reports on organic as well as inorganic fillers synthesized via various methods. The usage of ultrasound for the synthesis of nanocomposites is, however, sparingly reported in literature. A brief review is presented here.

Ryu *et al.* (2004) conducted studies on preparation of polymer-clay nanocomposites of various compositions by an ultrasonically-assisted polymerisation and melt-mixing process. They carried-out free radical polymerization of monomer in the presence of organically-modified clay by using sonication, and then carried out melt-mixing of the product so formed in an ultrasonically-assisted mixer. Lee *et al.* (2004) studied dispersion enhancement in nanocomposites by preparing polypropylene/clay nanocomposites in-situ in melt phase by ultrasound application. They concluded this to be an effective method to enhance dispersion of filler in thermoplastic-based nanocomposites.

Zhao *et al.* (2006) observed that subjection to ultrasonic oscillation during extrusion of nanocomposites lead to large improvement in mechanical properties such as elongation at break and impact strength. Zunjarrao *et al.* (2006) studied the influence of processing parameters and particle volume fraction on epoxy-clay nanocomposites. They prepared nanocomposites by ultrasonication and also by high shear mixing. They observed, in variance with other researchers, that high speed shear mixing was better than ultrasound-assisted mixing.

Swain and Isayev (2007) carried out experiments on the effect of ultrasound on HDPE/clay nanocomposites. Using a single-screw compounding extruder, they prepared nanocomposites at different clay compositions. Presence of ultrasound improved intercalation in the composite. Uniform dispersion of filler without the usage of an organic modifier was observed and reasonable enhancement in mechanical properties was obtained due to the ultrasonic treatment. In a different study conducted by Swain and Isayev (2009) with PA6/clay nanocomposites, they observed that usage of ultrasound helped in good dispersion of nanoparticles in the matrix without the use of any chemical modification. Mechanical, rheological and structural properties showed good improvement.

Chen *et al.* (2008) used high-intensity ultrasound for the preparation of chiral polyurethane/CdS-SiO_2 nanocomposites by ultrasonic irradiation with an ultrasonic horn directly immersed into the mixture solution. A silane coupling agent was used as a modifier for the filler so as to obtain better dispersion. They observed that usage of ultrasound reduced the crystallite size of the filler and resulted in enhancement of thermal stability of the filler. Tan *et al.* (2009) prepared polypropylene/silica nanocomposites by in-situ melt phase ultrasonication process. An organic modifier was used to control particle dispersion. The composites ultimately obtained were found to possess enhanced mechanical properties with particles finely distributed in the matrix. The aggregate size in the matrix was found to be 100 nm.

Isayev *et al.* (2005) in another study prepared nanocomposites based on carbon nanotubes using an ultrasonically-assisted twin-screw extrusion process. Effect of ultrasound on various properties was studied. Morphology and state of dispersion were investigated by means of HRSEM. This was a novel solvent-free process resulting in better dispersion without surface modification. Bittmann *et al.* (2011) synthesized TiO_2 /epoxy nanocomposites by dispersing nanoparticles into a commercially available epoxy resin using a horn-type ultrasonic device. Mechanical properties of these nanocomposites were observed to have an enhanced value, which proved the advantage of ultrasonic mixing. Composites prepared at 100% power input were found to possess the best dispersion of particles in the matrix.

Polystyrene is a very common plastic used in a large variety of applications, despite its highly brittle nature at reasonable temperatures of practical use. Enhancement of the properties of this

material in terms of flexibility, modulus and strength would increase the durability and uses of the material. Preparation and characterization of nanocomposites based on polystyrene and alumina are reported in literature. Afsharimani *et al.* (2010) carried out polystyrene/alumina nanocomposite synthesis by a solution casting method using alumina flakes of about 100 nm size which were synthesized by a solution combustion method. These composites exhibited enhancement in dielectric and mechanical properties as compared to pure polystyrene. Kaush and Michler (2007) prepared nanocomposites with polymers PS, PMMA, PC and alumina, silica nanoparticles and carbon nanotubes as fillers. They used the solution casting technique and obtained a good level of dispersion. Siengchin *et al.* (2007) have used melt-mixing method and prepared alumina-filled polystyrene nanocomposites. The dispersion status of polymer in filler was obtained by TEM and SEM. Zhang *et al.* (2009) carried out a review on the effect and application of ultrasound on the synthesis of polymer nanocomposites, mainly on systems such as polymer/carbon nanotubes, polymer/clays and polymer nanocomposites with magnetic particles. The effect of sonochemistry in accelerating the rate of the polymerisation reaction and dispersing the particles uniformly in the polymer matrix is studied.

An explorative study (Philip *et al.* 2012) had earlier been published by the authors on sono-synthesis of polystyrene/alumina nanocomposites. Polystyrene/alumina nanocomposites had been prepared by an ultrasound-assisted method at two different frequencies (viz., 430 kHz and 192/58 kHz) and at five filler loadings ranging from 0.2 to 1.0% by weight. Mechanical properties of these composites were studied. Cavitation erosion studies and SEM analysis also were conducted. No attempt was made to optimize the ultrasonic parameters for the synthesis of nanocomposites. Later, the importance of ultrasonic frequency as a critical parameter for the dispersion of particles in the matrix has been identified. The present study is focussed on studying the effect of ultrasonic frequency on the dispersion of nanoparticles in the polymer matrix with nanoalumina as the filler. Different frequencies were applied for synthesis, viz., 58 kHz, 430 kHz, (192/58) kHz, 470 kHz and 1 MHz.

2. Experimental

2.1 Materials used

General purpose polystyrene (GPPS, Grade SC206), obtained from Supreme Petrochem Industries, was used for the study. The density of polystyrene is 1.04 g/cc, molecular weight is approximately 200,000 and softening temperature is 99^0C. THF (Tetrahydrofuran) ultrapure, obtained from Sisco Research Laboratories, was used as a solvent for polystyrene. Nanoalumina, supplied by Alfa Aesar with approximate mean particle size of 200 nm, was used as filler. Ultrasonic tanks, provided by Crest Ultrasonics, Trenton, NJ, of frequencies 58 kHz, 430 kHz, 192/58 kHz (dual frequency), 470 kHz and 1 MHz were utilized for the study. The tanks were utilized at a power of 500 W.

2.2 Methodology

2.2.1 Preparation of polymer solution

Polymer solution was prepared by dissolving weighed amount of polystyrene granules in the solvent tetrahydrofuran by sonicating for about 1 hour.

2.2.2 Preparation of filler dispersion

A dispersion of the nanoparticles was prepared by adding the required amount of nanoalumina particles to the solvent THF, and then subjecting this mixture to a low-frequency ultrasound (25 kHz) for 20 minutes. This helps in formation of a uniform dispersion and also prevents particle agglomeration.

2.2.3 Preparation of polystyrene/alumina nanocomposites

Polystyrene/alumina nanocomposites were prepared at different filler loadings ranging from 0.2% to 2% by weight. The nanoalumina dispersion in THF was transferred to the already-prepared polymer solution. The so-obtained polymer-filler mixture solution was then left for sonication in an ultrasonic tank for about three hours. This is intended to achieve homogenization of the mixture. The dispersion so obtained is cast into a petri-dish and left for drying. Specimens for testing were cut from the dried composite sheet as per ASTM standards.

3. Characterization studies

The tensile strength and modulus of the composites were measured using a Zwick Roell UTM. Impact strength measurement was carried out in an Izod un-notched impact tester. SEM was used to study the dispersion of particles in the polymer matrix. A cavitation erosion test was carried out to measure the erosion resistance of the surface of the composite. The data for impact strength, tensile modulus, and cavitation erosion for composites prepared at frequencies 430 kHz and 192/58 kHz (dual frequency) have been published in a previous study (Philip *et al*. 2012).

4. Results and discussion

4.1 Tensile tests

PS/alumina nanocomposites were prepared by an ultrasound-assisted method. The composites were subjected to tensile tests as per ASTM D 638 standards. Dumbbell-shaped specimen were prepared for the tests as specified. The tensile properties of the composites were obtained. These tests were conducted in a Zwick Roell UTM. Composites were prepared at frequencies of 58 kHz, 192/58 kHz (dual frequency), 430 kHz, 470 kHz & 1 MHz. The filler loadings used for composite preparation were 0.2, 0.4, 0.6, 0.8 and 1% by wt. For dual frequency alone, composites were also prepared at higher filler loadings of 1.5% and 2% by wt. Composites were prepared without ultrasound for filler loadings 0.4 and 1%. A comparison is also made between composites prepared with and without ultrasound.

Fig. 1 shows the variation of relative tensile strength (ratio of tensile strength of the composite to tensile strength of neat polymer matrix, E/E_m) with filler loading for composites prepared at various frequencies. Composites prepared at 430 kHz, 470 kHz and 1MHz, compared with the neat polymer, show an initial increase in property value at filler loadings of 0.2% and 0.4% by wt. As the filler loading is increased further, the property value is found to degrade and level off. Composites prepared at 58 kHz do not show a significant enhancement. Composites prepared at dual frequency are observed to have better enhancement in property value in comparison with those prepared at all other frequencies. Tensile strength of composites prepared at 1.5% and 2% by

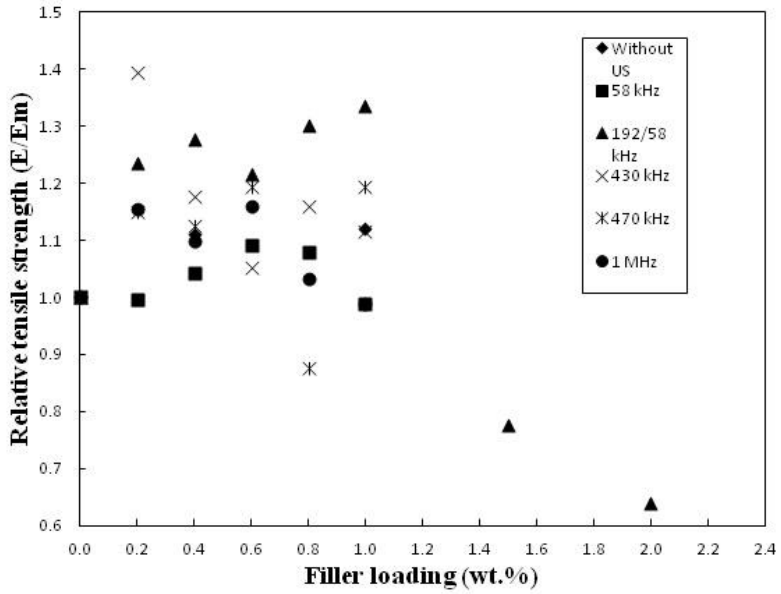


Fig. 1 Variation of tensile strength with filler loading

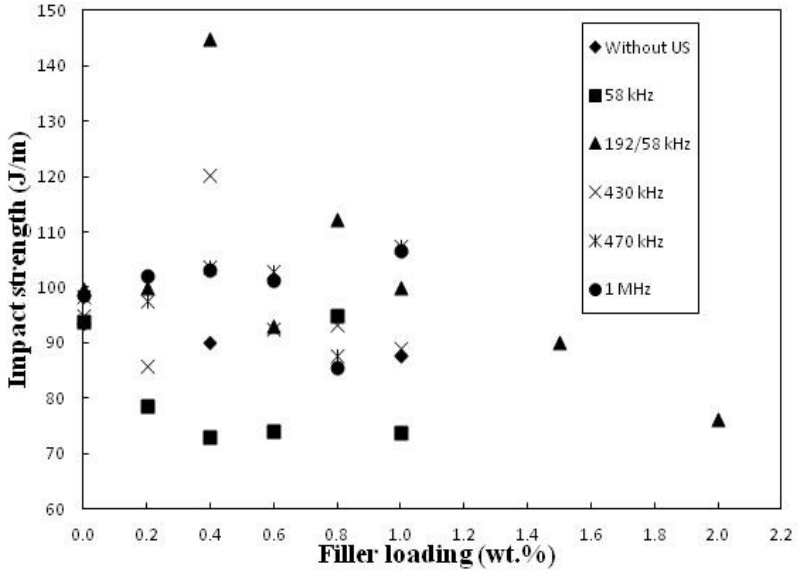


Fig. 2 Variation of impact strength with filler loading

weight (dual frequency) was found to drop off to a value much lower than that of the neat polymer. This might be due to the possible agglomeration of particles in the polymer matrix. Composites were prepared without using ultrasound for filler loadings of 0.4 and 1% by weight. These composites showed lower property values emphasizing that subjection to ultrasound results in better dispersion of particles in the matrix.

4.2 Impact tests

The composites were subjected to Izod un-notched impact test as per ASTM D 256 standards. Samples were prepared according to ASTM standard dimensions. Impact test gives a measure of the toughness of the material.

Composites were prepared at five different frequencies, viz., 58 kHz, 192/58 kHz, 430 kHz, 470 kHz & 1 MHz for different filler loadings, 0.2, 0.4, 0.6, 0.8 and 1.0% by weight. For dual frequency alone, composites were also prepared at higher filler loadings of 1.5% and 2% by wt. The results of the impact strength are shown in Fig. 2. Impact tests were carried out as per ASTM D 256 standards. Samples cut from the dried composite sheets to conform to ASTM standard dimensions were used for the tests. Mean values are shown in the plot. A comparison is made between composites prepared with and without ultrasound. The impact strength of the composites prepared at different filler loadings for 58 kHz frequency is found to decrease compared with the neat polymer and also in comparison with the composites prepared without ultrasound. Composites prepared at 430 kHz and 192/58 kHz (dual frequency) show an initial increasing trend in property value which degrades or levels off at higher loadings as the filler loading is increased. For composites prepared at 1 MHz and 470 kHz, filler loading does not have much of an effect on property enhancement. Composites prepared at frequencies of 430 kHz and 192/58 kHz (dual frequency) show almost similar trends and are found to give better results compared to those prepared at other frequencies. The enhancement in property might be attributed to the proper dispersion of particles in the polymer matrix. For composites prepared at dual frequency, at an initial concentration of 0.2%, property enhancement is not observed to a significant extent. But as filler concentration is increased, at 0.4% filler loading, there is noticeable increase in impact strength. As the filler loading was increased to 1 %, property value is found to level off. The results suggest that of all the frequencies used, dual frequency gives the best property enhancement, which leads to the conclusion that the best particle dispersion occurs at the dual frequency setting. At higher filler loadings of 1.5% and 2%, property value is found to degrade. This is presumably due to difficulty in polymer processing or particle agglomeration. Negligible property enhancement is seen with composites prepared at 470 kHz and 1 MHz.

4.3 Cavitation erosion tests

Cavitation erosion test was conducted to quantify the material eroded from the surface of the composites when subjected to low-frequency ultrasound. Cavitation erosion gives an indirect measure of the strength of the composite. The composite sample that was taken in a beaker with water was subjected to sonication in low-frequency ultrasound (58 kHz) for about thirty minutes. The water in the beaker was tested for the number of particles (of size >1 micron) before and after sonication using a Laser Particle Counter Spectrex LPC 2200.

Fig. 3 shows the results of cavitation erosion tests conducted on the composites. C/C_o is the ratio of cavitation erosion from the surface of the composite to that of the neat polymer. A comparison is made between the erosion from the surface of the neat polymer and the composites, and also between composites prepared with and without ultrasound. For composites prepared without ultrasound the erosion from the surface is similar to that of the neat polymer. For composites prepared at lower filler loadings, there is a reduction in erosion from the surface compared with the neat polymer. But as filler loading is increased, erosion is more or less equal to that of neat polymer. For composites prepared at 58 kHz and 470 kHz, there is not much change in

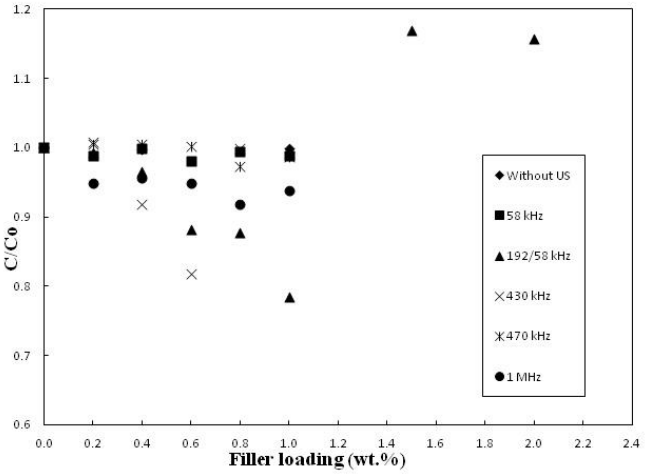


Fig. 3 Variation of cavitation erosion with filler loading

erosion as compared with that of the neat polymer. Composites prepared at 430 kHz and 1 MHz show a reduction in erosion at low filler loadings, but the value increases and levels off at higher filler loadings. For composites prepared at dual frequency, there is progressive decrease in erosion with increase in filler loading. At higher filler loadings of 1.5% and 2%, cavitation erosion is found to be higher. The results substantiate the fact that the composites prepared at dual frequency have the best filler dispersion. The property reduction at higher filler loadings is likely due to the agglomeration of particles resulting in the strength reduction of composites.

4.4 Scanning electron microscopy results

Scanning electron microscopy was used to study the dispersion of particles in the polymer matrix.

4.4.1 Comparison of composites at same filler loadings and different frequencies

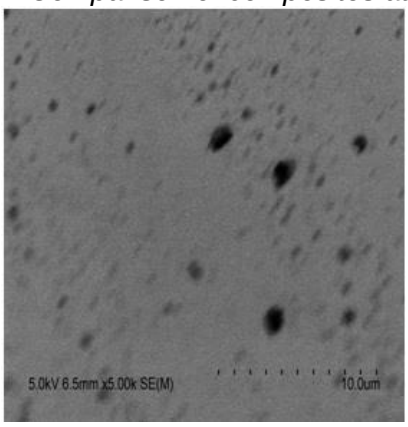


Fig. 4 PS/alumina nanocomposite prepared without ultrasound at 0.4% filler loading

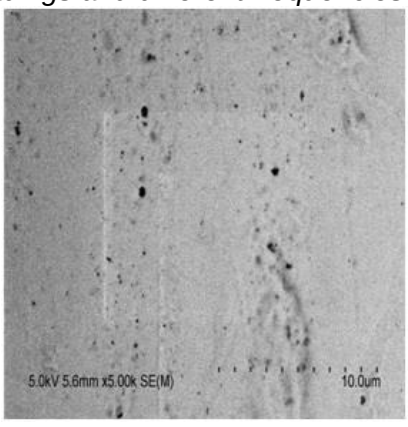


Fig. 5 PS/alumina nanocomposite prepared at 58 kHz frequency and 0.4% filler loading

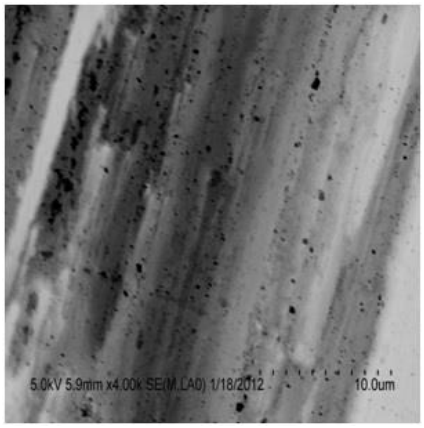


Fig. 6 PS/alumina nanocomposite prepared at 192/58 kHz at 0.4% filler loading

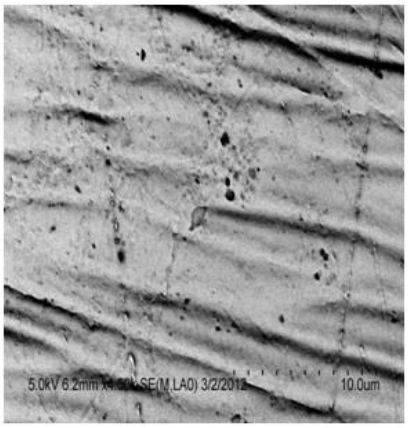


Fig. 7 PS/alumina nanocomposite prepared at 1 MHz at 0.4% filler loading

4.4.2 Comparison of composites prepared at same frequency and different filler loading

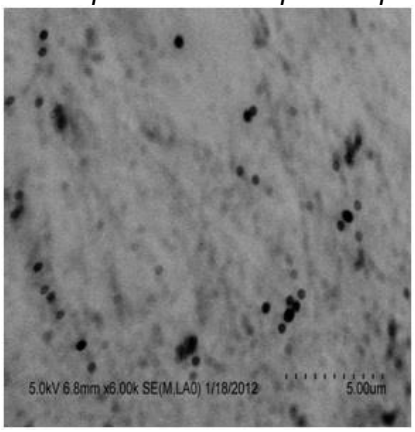


Fig. 8 PS/alumina composite prepared at 192/58 kHz and 0.2 % filler loading

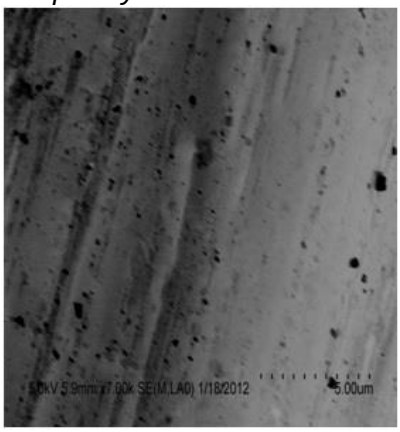


Fig. 9 PS/alumina composite prepared at 192/58 kHz and 0.4% filler loading

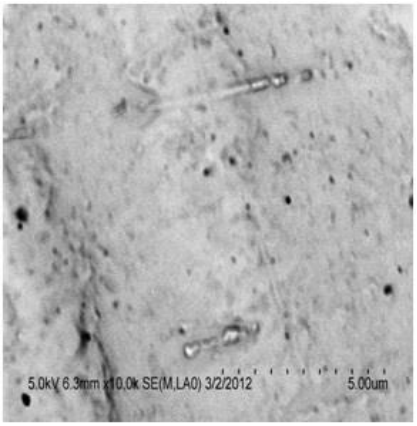


Fig. 10 PS/alumina composite prepared at 192/58 kHz and 0.8% filler loading

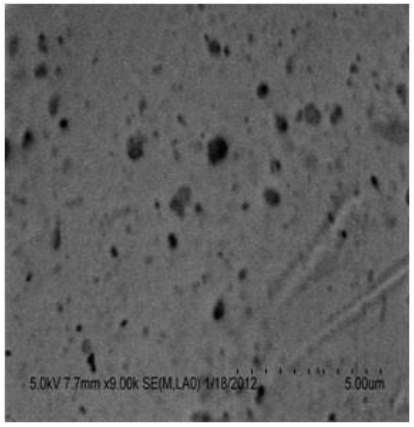


Fig. 11 PS/alumina composite prepared at 192/58 kHz and 1.0% filler loading

4.4.3 SEM images of composites prepared at higher filler loadings

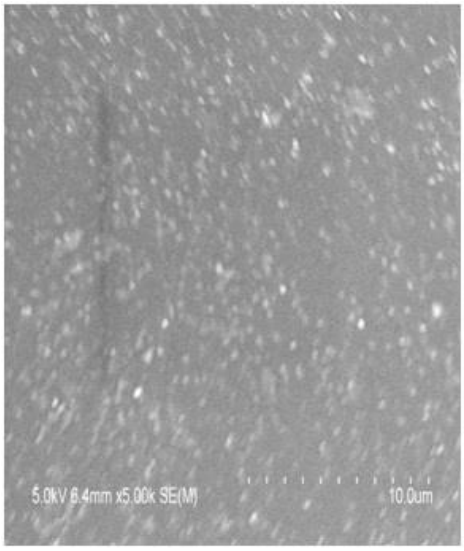


Fig. 12 PS/alumina composite prepared at 192/58 kHz and1.5% filler loading

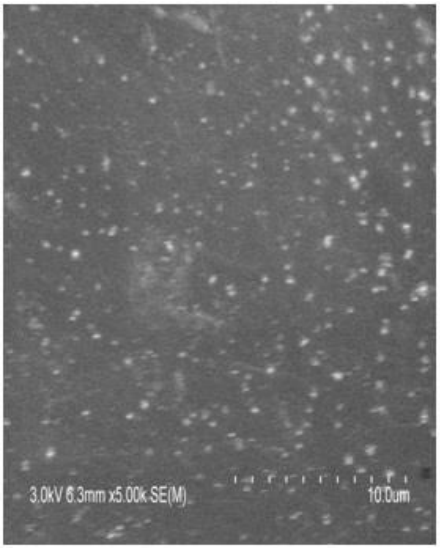
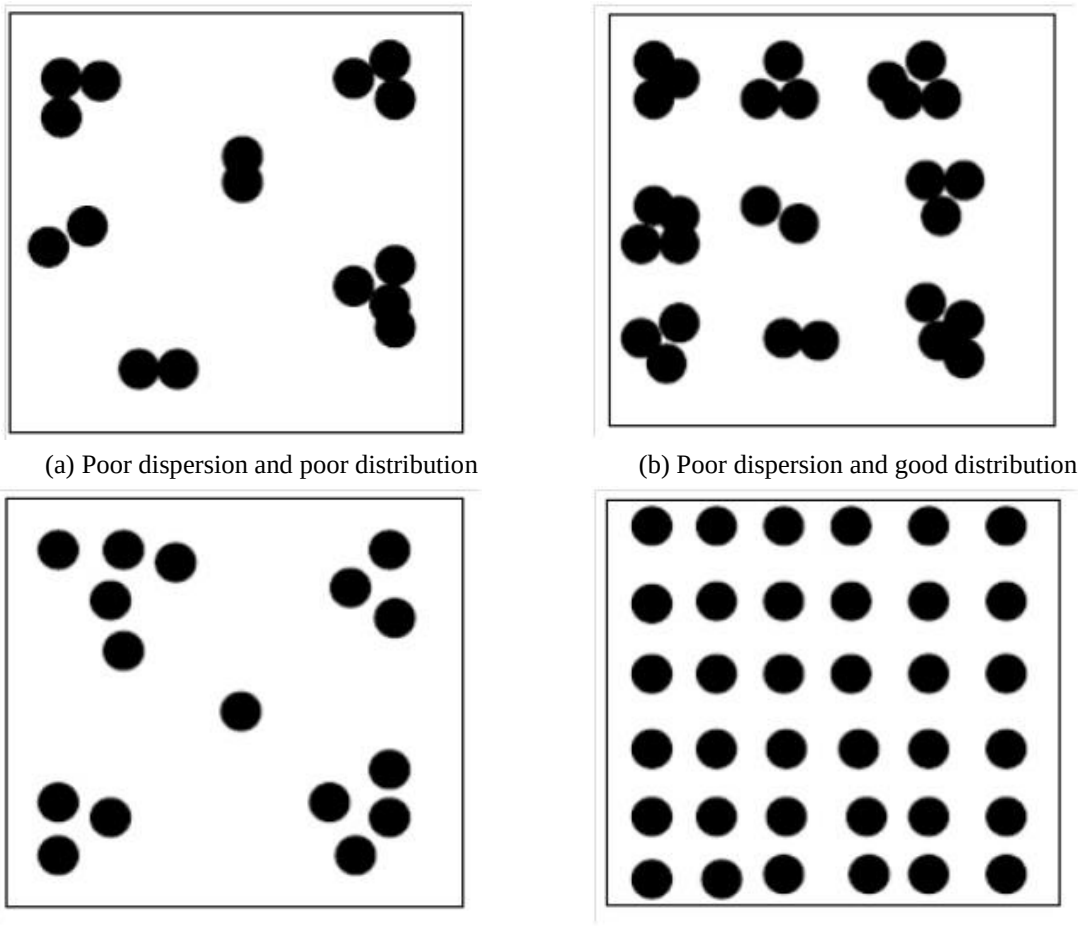


Fig. 13 PS/alumina composite prepared at 192/58 kHz and 2.0% filler loading

SEM images of the composites prepared without ultrasound and at different frequencies of 58 kHz, 192/58 kHz, 1 MHz at a filler loading 0.4% by wt. are shown in Figs. 4 to 7. From the images, it can be observed that the composites prepared with dual-frequency ultrasound have more uniformly distributed particles than those prepared at other frequencies. Composites prepared at same frequency (192/58 kHz) but at different filler loadings (0.2, 0.4, 0.8 and 1.0) are shown in Figs. 8 to 11. It is observed from the images that composites prepared at a filler loading of 0.4% by wt. show good particle dispersion with less agglomerate formation. In Figs. 12 and 13, SEM images of composites prepared at higher filler loadings of 1.5% and 2% are shown where particles are seen to be crowded in the matrix. This may be the reason for reduction in property values at this filler loading.

In a low-frequency ultrasonic system, acoustic cavitation dominates, which results in disruption of clusters and agglomerates and in fragmentation of particles. Hence, low-frequency ultrasound will result in dispersive mixing which involves size reduction as well as breakage of agglomerates in the system. In high-frequency ultrasound, acoustic streaming dominates, resulting in a uniform mixing of the fluid. This results in distributive mixing, which refers to uniform spreading of the particles throughout the matrix. Subjecting of the polymer /filler system to a single frequency alone results in either a dispersive mixing or a distributive mixing. But in the case of dual-frequency system, where a low and high frequency are coupled, both acoustic streaming and acoustic cavitation are present simultaneously, which brings about both dispersive and distributive mixing. The enhancement in properties shown by the composites prepared at dual frequency, as well as the uniformity in particle distribution of these composites seen in the scanning electron microscopy, may be attributed to the above-mentioned phenomenon.

A schematic (Fig. 14) of distributive and dispersive mixing is shown below.



(a) Poor dispersion and poor distribution (b) Poor dispersion and good distribution

(c) Good dispersion and poor distribution d. (d) Good dispersion and good distribution

Fig. 14 Schematic representation of dispersive and distributive mixing (Manaz-Zloczower 1997)

5. Conclusions

PS/ alumina nanocomposites were prepared by an ultrasound-assisted method. Composite preparation was carried out at five different frequencies, namely 58 kHz, 430 kHz, dual frequency (192/58 kHz), 470 kHz and 1 MHz. Composites were prepared at five filler loadings ranging from 0.2 % to 1% by weight. For dual frequency alone, composites were prepared at higher loadings 1.5 and 2.0% also. The composites were subjected to mechanical property tests (impact and tensile tests) and measured values were compared to that of the pristine polymer. Property enhancement is seen at filler loadings of 0.2 and 0.4 wt. %. On further addition of filler, the property values are found to level off or degrade, which might be attributed to particle agglomeration. This is corroborated by SEM images showing that at a filler loading of 0.4%, particles are more uniformly distributed with least agglomeration compared to those at other filler loadings. Of all the frequencies used for composite synthesis, composites prepared at 430 kHz and dual-frequency show similar trends. Composites prepared at the 58 kHz, 470 kHz and 1MHz frequencies do not

show much enhancement. From the SEM images, it is observed that composites prepared at dual-frequency have the best dispersion of particles in the polymer matrix. Cavitation erosion studies conducted also affirm this, reinforcing the observation that composites prepared at dual-frequency undergo the least surface erosion. Based on the quantitative results and qualitative observations obtained in this study, it is recommended that an appropriate combination of low- and high-frequency ultrasonic/ megasonic fields be deployed in synthesis of nano-composites in order to ensure optimum distributive and dispersive mixing-an essential requirement in order to achieve enhanced properties.

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