Preparation of Structured Polymer Composites Using an Ultrasonic Focusing Technique

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Introduction

This research uses ultrasonic standing waves to arrange sub-micron size particles within polymeric materials in layered or stratified configurations. Such composites have the potential to exhibit unique mechanical and transport properties. Through the combination of ultrasonics, polymer science, and particle science, it is hoped that a range of advanced thin-film materials can be developed as barrier materials and for proton exchange membranes (PEM) fuel cells. In the present study, silicon dioxide particles have been arranged in poly(butylmethacrylate) and studied as a model composite material. The scope of our current work explores the fundamental relationships between particle characteristics, acoustic parameters, and effects of the polymer matrix, to determine how they affect the acoustic focusing process.

Theory and Concepts

The primary acoustic radiation force on a solid particle (or liquid droplet or gas bubble) of radius R, suspended in a fluid, under the condition that the particle dimension is much less than the acoustic wavelength in a one-dimensional resonant field is

$$F_{1,ac} = 4\pi R^3 \kappa E_{ac} F \sin(2\kappa x) \tag{1}$$

where κ is the wave number of the acoustic field, E_{ac} is the energy density of the acoustic field, F is the acoustic contrast factor, and x is the distance from a pressure antinode of the standing wave[1]. The acoustic contrast factor F, determines whether a particle will travel to a pressure node or antinode under the influence of the sound field,

$$F = \frac{\Lambda + 2(\Lambda - 1)/3}{1 + 2\Lambda} - \frac{1}{3\sigma^2 \Lambda} \tag{2}$$

where Λ is the ratio of the particle density to the fluid density and σ is the ratio of the longitudinal sound speed in the particle to that in the fluid[2]. If F has a value of greater than zero, particles will collect at pressure nodes. Conversely, if F has a value that is less than zero, particles will collect at pressure antinodes. Particles are pushed to these stable equilibrium points within the sound field, depending on the value of F. The distance between consecutive pressure nodes (or antinodes) is equal to one-half the wavelength of the acoustic field.

In addition to the primary acoustic force, secondary acoustic forces also arise due to the interaction of the sound field scattered by the particles. The secondary acoustic force ($F_{2,ac}$) between two similar particles is attractive, and may promote particle aggregation.

The secondary force between two particles (labeled as 1 and 2) is given by

$$F_{2,ac} = \frac{\kappa^2 E_{ac}}{2\pi}\left(1-\frac{\gamma_{p1}}{\gamma_f}\right)\left(1-\frac{\gamma_{p2}}{\gamma_f}\right)\frac{V_{p1}V_{p2}}{d^2} \quad (3)$$

where γ_p is the compressibility of the particle, γ_f is the compressibility of the fluid, V_p is the volume of the particle, and d is the distance between particles[3]. Usually the secondary force is small relative to the primary acoustic force, however as particles concentrate at a pressure node (or antinode), the secondary force can become significant as the aggregate volume becomes large or the interparticle distance becomes smaller, both of which can induce further agglomeration.

Experimental Setup and Technique

The acoustic chamber where the ultrasonic focusing occurs consists of a glass housing, of which one face is comprised of a lead zirconate titanate (PZT) piezoelectric ceramic transducer which produces the sound field, and another face parallel to the transducer which is a stainless steel plate, acting as a reflector. The two other housing walls are made of glass, forming a "tank" in which a fluid can be added. The combination of the transducer and reflector creates a standing sound wave in the fluid medium when a sound field is applied. At the pressure nodes, the pressure is equal to zero, and at the pressure antinodes, the pressure is at a maximum. A homogeneously dispersed particle/monomer solution with a photoinitiator is added to the acoustic chamber. A schematic of the acoustic chamber is shown in Figure 1.

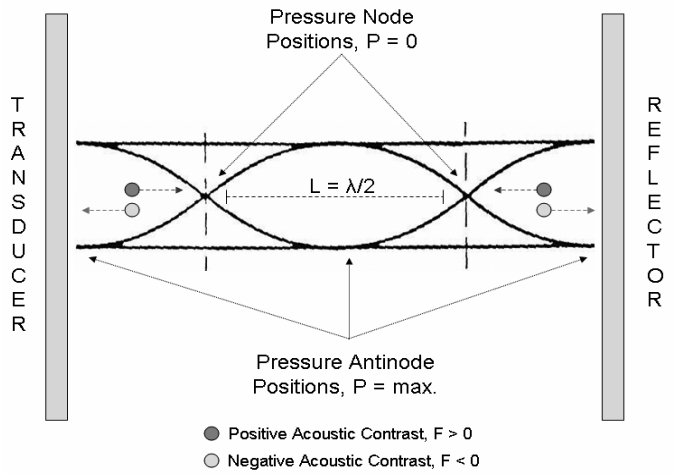


Figure 1 – Acoustic Chamber Schematic

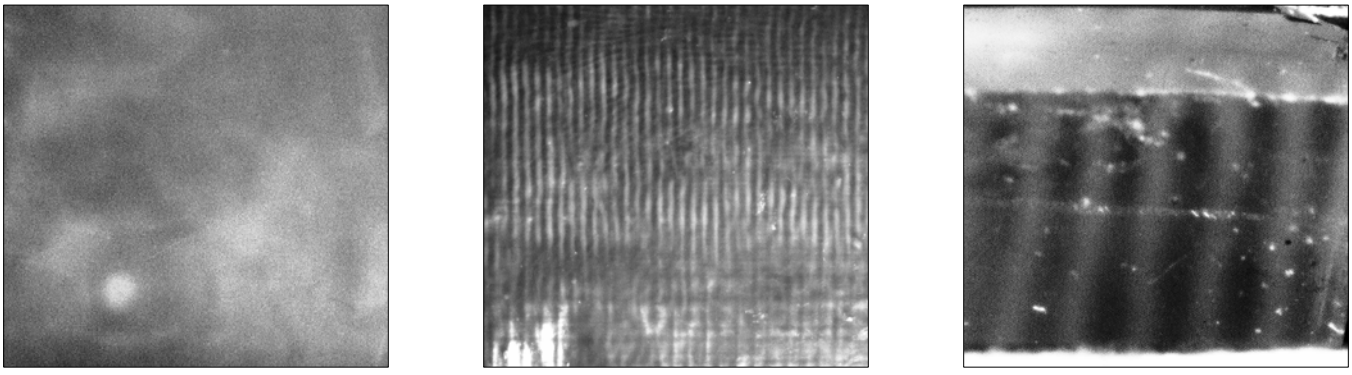
Once the particle/monomer dispersion is added to the acoustic chamber, the sound field is applied at a given frequency and intensity causing particles to travel to pressure nodes (or antinodes) which produce particle bands at intervals equal to one-half the wavelength of the sound field parallel to the faces of the transducer and reflector. The distance between bands is strictly a function of the frequency. Operating at higher frequencies leads to smaller

wavelengths which reduces the distance between pressure nodes and particle bands. Once banding has occurred, ultra-violet light is used to initiate free-radical polymerization, which "freezes" the particles in their banded states. The resultant structured polymer composite can be removed from the chamber and analyzed in greater detail.

Current Results and Discussion

In current experiments, a system consisting of 500-nm silicon dioxide particles dispersed in butylmethacrylate is being employed as a model system. The reason for using silicon dioxide is its availability in a wide variety of sizes and the ability to functionalize its surface with different chemical species which could be useful for future applications. Butylmethacrylate was chosen as the monomer/polymer due to its transparency in both the monomer and polymer states. This permits visual observation of particle movement during the focusing process and for analysis of particle bands once polymerization is complete. The *F* value for the SiO_2/butylmethacrylate system is 0.59, which indicates that the silicon dioxide particles are expected to collect at the pressure nodes under the influence of the acoustic field. The size of the silicon dioxide particles in the initial dispersed state was confirmed using laser light scattering.

Figure 2(a-1) shows a top-down view of a homogeneous dispersion of 500-nm silicon dioxide (0.75% by volume) in butylmethacrylate in the acoustic chamber prior to application of the sound field. Figure 2(a-2) shows the same dispersion, now banded, after the application of the sound field at 725 kHz, where the inter-band spacing is approximately 1 mm (centerline distance between white bands). The white banded regions have a high concentration of silicon dioxide particles and the black bands are polymer regions with a much lower particle concentration. The overall dimension of the polymer is 5 cm by 5 cm, with a thickness of about 2 mm. Figure 2(b) shows a side view of a SiO_2/poly(butylmethacrylate) system (initially 2 vol. % particle concentration) showing uniform banding throughout the polymer cross-section.



(a-1) **(a-2)** **(b)**

Figure 2 – Photographs of SiO_2 banded in poly(butylmethacrylate): (a-1) Top-down view of a homogeneous 500-nm SiO_2 dispersion (0.75% by volume) in butylmethacrylate. (a-2) Banded SiO_2 after application of sound field at 725 kHz and photopolymerization, with an inter-band spacing of approximately 1 mm. (b) Side view of 500-nm SiO_2 particles banded at 725 kHz in poly(butylmethacrylate) with a thickness of 3 mm (for this case, the total concentration of particles is 2% by volume and the centerline band-to-band distance is about 1 mm).

These images verify the principle of using acoustic fields to focus sub-micron sized particles in a monomer and preserve the banded structure via photo-polymerization. Based on the transducer frequency of 725 kHz and the speed of sound through butylmethacrylate (1196 m/s) the wavelength of the sound field is 1.7 mm (where the wavelength is equal to the speed of sound in the monomer divided by the frequency)[4]. Thus, according to theory, the distance between bands (or pressure nodes) should be 0.85mm. From a close-up view of a banded region within the polymer using an optical microscope, the distance was found to be 0.90 mm, which is in good agreement with the theory. Variations in inter-band distance (center of one band to another) can deviate from theory due to waviness in the bands caused by non-uniformities of the sound field (e.g., localized regions of higher and lower energy density).

Beyond analyzing the distance between bands, it also important that the particle bands pass through the entire cross-section of the polymer as demonstrated in Figure 2(b) Sedimentation of particles can be a problem if the individual particles or particle agglomerates are too large. To avoid sedimentation, the polymerization must be sufficiently rapid to halt the banding process before agglomerates within the band become exceedingly large and sink. If the sound field were applied indefinitely with no polymerization, the particles would agglomerate in the region of the acoustic chamber that had the highest energy density resulting in a single large mass of particles. On the other hand, if polymerization occurs too early, the resistance to particle movement will become infinite prior to the particles reaching the acoustic node positions. The exact time to start polymerization can be determined via direct experimental observation or by performing a force balance on the particles and using acoustic field models (which determine the theoretical energy density of the sound field in the monomer) in order to calculate when the particles should reach the pressure node positions. Such analyses will be discussed in a future paper.

Applications

There are many potential applications for structured polymer composites created via ultrasonic focusing. The ability to create banded particle structures that run through the cross-section of a polymer film lends itself to applications such as proton exchange membranes for fuel cells (where the banded particles are surface treated with protonic moieties). In such an application, the particles could be organized into bands, creating concentrated proton conducting conduits that run through the cross section of the membrane. By segregating the particles into bands, a particle percolation threshold can be achieved at a much lower initial particle loading. Thus, for a homogeneous composite membrane, the particle concentration percolation threshold for proton conductivity would be about 30%, whereas the average particle concentration in a banded film would be 15-20% (in which case the particle concentration in the bands could be as high as 40%). Reducing the initial particle loading may decrease costs and would certainly improve the mechanical properties of the membrane since high particle loadings would cause the films to be brittle. In addition to fuel cell applications, acoustically focused particle/polymer membrane could be used as barrier films (where the particles are banded parallel to the membrane surface) and for anti-static films (where electronically conductive particles are employed). In all applications, the overall concentration of particles in the membrane will be much lower than that in the banded layers, which should provide significant advantages of this technique over traditional composite membrane morphologies.

Conclusions

Proof-of-principle experiments were successful in arranging sub-micron particles into banded structures via ultrasonic fields and then preserving the banded morphology through free-radical polymerization. Models of the ultrasonic focusing process, which track focusing time and particle trajectory, while accounting for the effects of, viscosity, frequency, sound field intensity, and particle size, compared favorably with experimental results. Additional experimentation is needed to better understand the particle orientation and concentration within the bands (e.g., the use of scanning electron microscopy). Experiments involving smaller functionalized particles, higher loadings, and multi-dimensional sound fields will also be performed. The ultimate goal is to produce one and two-dimensional particle structures in thin polymer films for a variety of applications including proton exchange membrane fuel cell membranes and barrier membranes.

References

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