Research articles

Tunable one-dimensional assembly of magnetic nanoparticles using oscillating magnetic fields at low frequencies for polymer nanocomposite fabrication

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ABSTRACT

Tunable, one-dimensional (1D) nanofiller assembly using oscillating magnetic fields in the low frequency range (< 5 Hz) is studied as a scalable and energy-efficient method to structure nanofillers within viscous matrices to deliver anisotropic, multi-functional polymer nanocomposites (PNCs). In this work 1D assembly tailoring was first experimentally studied and demonstrated using the model system of superparamagnetic iron oxide nanoparticles (SPIONs, 15 nm, 0.02–0.08 vol%) in DI water using varying magnetic fields (0–5 Hz frequency, 10–100 G magnetic flux density, and square and sinusoidal waveforms). In addition to lateral assembly of nanofillers, when the field oscillation is turned on, transverse assembly can be introduced as the magnetic moments of the particles respond to the changing fields by Brownian rotation. The degree of transverse assembly, in balance with lateral assembly and the resulting nanofiller patterns, was observed to be determined by the magnetic field parameters, magnetic responsiveness of the nanofillers, and the matrix viscosity. Based on this assembly study, PNCs consisting of ferrimagnetic iron oxide nanofillers in a thermoset polymer, with two different linear nanoparticle patterning, were successfully fabricated using small magnetic fields (< 100 G) even in a viscous matrix (70 cP) with a short assembly time of 30 min. This work can contribute to scalable manufacturing and thus bulk application of multi-functional PNCs enabled by more precise nanofiller and interface structuring.

1. Introduction

Bulk application of polymer nanocomposites (PNCs), consisting of nanofillers (carbon, ceramic, metal, etc.) and polymers (thermoset, elastomer, etc.), have been desired for their high mass-specific multi-functional properties (mechanical [1–9], thermal [10], electrical [3,7–9,11,12], magnetic [13,14], and smart [12,15,16]), but has not been achieved due to unknown multi-scale structure-property relationships and missing scalable fabrication. PNCs often exhibit smaller property improvement than theoretical prediction when characterized in macro scale, even with organized implementation of nanofillers [17–20]. While driven by the advanced properties and structuring of nanofillers [8,9,12], PNC properties are critically affected by their boundary conditions (between nanofiller and between nanofillers and polymers) [7,21] as nanofillers alter polymer chains' static and dynamic behaviors and the boundary surface area per volume is large. Such boundary effects on PNC properties are different for each property; for example, with implementation of carbon nanotubes, mechanical

toughness increased by mitigating crack-growth due with nanofiller-polymer debonding, void growth, and crack deflection [8,9], while thermal transport property improvement is minimum due to high thermal boundary resistance (Kapitza resistances) [19]. Thus, precise and tunable tailoring of nanofiller structures, including their boundary conditions (inter-nanofiller contacts and nanofiller-polymer bonding), is critical to study these scaling effects per property and to achieve the PNC properties close to the theoretical predictions, but is currently missing.

Nanofiller assembly using oscillating magnetic fields at low frequencies is potentially a solution to the scalable manufacturing of PNCs with tailored nanostructures and nanofiller contacts. While nanofiller integration by deposition on micro-components (such as fibers and cloths [22–24]) is currently a popular method, active nanofiller assembly using external fields has the balanced benefits of scalability and precise structuring of the nanofiller. Nanofiller assembly has been attempted using magnetic fields [20], electric fields [25,26], acoustic fields [27], and even strain deformation [28]. Among these field

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options, the focus of this work is on magnetic assembly due to their non-contact, energy-efficient, fast assembly and patterning capabilities [20,29]. In addition, magnetic assembly does not have limitations set by the dielectric breakdown or electrode polarization using electric fields [3] or by set-up complexity using acoustic fields [27] or strain fields [28]. The nanofiller surfaces can be treated to enhance their dispersion and suspension, and to tune the bonding conditions between nanofillers and polymers [30].

In the past, assembly of microfillers (sphere [31], rods [20], platelets [20,32], etc.) in polymers has been demonstrated using rotating magnetic fields with low flux density (10 G) in a short time (1 h) to fabricate sizable PNCs (50 mm long) [20] with tunable microstructures and mechanical properties [29,32,33]. The magnetic assembly of nanofiller in low viscosity matrices has also been investigated. Both experimental and analytical studies exist about magnetic nanofiller assembly using static or rotating magnetic fields [34–37]. In addition, nanofiller tailoring capability using pulsed fields has been experimentally demonstrated in water; a model system of colloidal suspensions of superparamagnetic latex nanoparticles were assembled through the balancing between particle thermal diffusion and attractive magnetic dipole-dipole interactions [38]. While the effects of gravity decreases due to the nano size, the hydrodynamic forces are size-dependent, and often prevent nanofiller movement especially within viscous polymers [12]. Due to this, thermal diffusion of nanofillers in a polymer matrix is limited, leading to pulsed waveforms being a poor choice for this matrix type. Thus, oscillating magnetic fields, especially of the low frequency range (< 1 Hz), are a novel method to assemble and tailor nanofillers and their interfaces in polymer matrices where transverse particle assembly can be enhanced due to field switching.

In this work, experimental studies were first conducted to understand the effect of the magnetic field (frequency, flux density, and waveform) and nanofiller volume fraction on assembly, including nanofiller contacts, using oscillating magnetic fields. The model system of superparamagnetic iron oxide nanoparticles (SPIONs) dispersed in deionized (DI) water was selected for this parametric study so that magnetic remanence and hydrodynamic drag are minimum. Second, ferrimagnetic nanoparticles were assembled and tailored within DI water and in a polymer matrix. Based on the above assembly studies about the SPIONS, the assembly trends were studied and the capability to tailor nanofillers and their contact conditions within viscous matrices was preliminary demonstrated. Findings from this work will contribute to the development and bulk application of tailored PNCs with advanced, multi-functional properties by enabling scalable manufacturing of PNCs with more precise control of nanofiller structures and their interfaces. The nanofiller volume fractions are kept low (< 0.1%) in this work for easier observation of magnetic assembly and inter-nanofiller distances; relevance of this study to other material systems and to resulting PNC performances will be discussed later.

2. Material and methods

2.1. Magnetic assembly study with SPIONs in DI water

The magnetic assembly behavior of the SPIONs with a low-frequency oscillating magnetic field was captured in real-time and analyzed (see Fig. 1a and b). The SPIONs (Sigma-Aldrich, I7643, 15 nm) are amine-terminated and suspended in an aqueous suspension (50 mg per ml in 1 mM EDTA, pH 7.0), but aggregate (1–5 μm) due to van der Waals forces, electrostatic potential, and/or chemical interactions (see Fig. 1c). The SPION aqueous solutions were prepared to have low volume fractions (0.02–0.08 vol%) to enable observation. SPION aggregates larger than 150 nm will settle [39], and thus the local, as observed, SPION volume fractions were calculated to be higher (approximately 7.5–11.7 vol%) based on processing of the captured images. Superparamagnetism of the SPIONs was confirmed through the anhysteretic magnetic response measured using a vibrating sample

magnetometer (MicroSense, ±1200 kA/m) as shown in Fig. 1d. The measured magnetic saturation of 20.6 emu/g and maximum susceptibility of 0.61 are comparable with the values of iron oxide nanoparticles in the literature [40,41].

The magnetic assembly of the SPION aggregates is achieved and captured in real-time using the set-up illustrated in Fig. 1e. In this paper, aggregates refer to the initial SPION groupings as shown in Fig. 1a, and assembly refers to the assembled line features after the field application as shown in Fig. 1b. The SPION aqueous solutions were ultrasonicated (35 kHz) for 5 min, encapsulated in a KOVA Glasstic slide (6 mm × 6 mm area, 0.1 mm height), and mounted between a solenoid pair. Images of SPION assembly were captured using a digital optical microscope (Olympus BX51WI) before and after 15 min of magnetic field application; assembly did not noticeably change beyond 15 min [38]. The solenoid pair (570 turns, 14.8 cm length, 6.51 cm inner diameter, 16-gauge enameled wire, 410 stainless steel core) were connected in series, and driven by a bipolar power supply (Kepco BOP 20–10 M, ± 20 V, ± 10 A) and a function generator (BK Precision, 4014B). The applied magnetic field was varied about the frequency (static, and up to 5.0 Hz), waveform (50% duty cycle square and sinusoidal) and magnetic flux density (peak of ± 10 G, ± 50 G, and ± 100 G for square waves, and RMS peak of ± 14.1 G, ± 70.7 G, and ± 141.4 G for sinusoidal waves). Symmetric square or sinusoidal waveforms were selected, instead of the previously tested pulsed fields [38], to reinforce controlled assembly by switching of the external field direction, rather than by thermal diffusion. The frequency range was kept below 5 Hz to fully enable SPION magnetic moment rotation for the Brownian reorientation mechanism [31]. The minimum flux density was set as 10 G based on the previous related work [20]. The spatial distribution of the magnetic flux density was monitored using a gaussmeter (LakeShore Model 425), and the flux density gradient across the sample was kept below 5% to minimize SPION migration towards the magnetic poles. The captured optical microscope images were processed using Matlab to quantitatively evaluate assembly morphology (see Fig. 1f): the length and width of each assembly, and the separation between the assemblies. The processing details can be found elsewhere [42]. One sample was prepared for each assembly condition, and the characteristic dimensions of the assemblies were averaged over ~100–1000 assemblies for each sample/condition.

3. Theory

Assembly of SPION aggregates using oscillating magnetic fields is governed by forces produced by the external magnetic field, inter-particle magnetic forces, hydrodynamic drag, thermal energy, van der Waals forces, and electrostatic forces. Among these forces, van der Waals and electrostatic forces are assumed to be negligible due to their non-directionality. The forces produced by the external magnetic field are also ignored in this work because only uniform external magnetic fields, while time-varying, were applied to the SPION aggregates. The SPION aggregates are collections of small single-domain (SD) SPIONs, or homogeneous magnetic dipoles [43], and thus have no magnetic remanence due to random reorientations of the SPIONs magnetic moments. The inter-particle magnetic forces due to the locally induced, non-uniform magnetic fields of the aggregates, or the magnetization (*M*), are expected to largely contribute to assembly of the SPION aggregates [44–46].

3.1. SPION assembly behaviors in magnetic fields

As illustrated in Fig. 2, upon application of a magnetic field, magnetic moments of the SPIONs align along the field direction. When the distance between neighboring spherical aggregates is smaller than the capture radius of $r_c = 2a\lambda^{1/3}$(m), the magnetic attraction overcomes thermal diffusion, and the aggregates form needle-like, elongated assemblies along the field direction (*lateral* assembly) due to the locally