Limitations and Opportunities for Electric Field Assisted Patterning of Polymer Nanocomposites

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INTRODUCTION

Arguably, the goal for the vast majority of polymer nanocomposite (PNC) investigations is to achieve increased thermo-mechanical performance through dispersion at the single-particle level. The resulting PNCs are treated much as an isotropic, filled polymer. Thus from a historical perspective, nanocomposites today are really nanoparticle-filled plastics. The use of the moniker '*composites,*' though, invokes strong parallels to traditional continuous fiber-reinforced composites (CFRC) and the ability to spatially *'engineer, design and tailor'* materials performance for a given application. The pay-off of CFRC manufacturing technologies is exemplified by the incredible material advancements that enable current aerospace systems, both military and civilian. Current processing and fabrication approaches for PNCs fall well short of this fabrication and design capability. [1]

Modeling efforts to establish structure-performance correlations further support the need for more refined processing techniques. Reports predict huge dividends in mechanical, barrier and electrical performance if processing could prescribe precise spatial arrangement of nanoparticles. For example, Gusev et al. showed that comparable shear moduli could be obtained at only half the volume fraction of particles if a web-like morphology could be generated rather than random or hexagonal arrangement [2]. Additional work by Gusev and coworkers on barrier properties [3] and the coefficient of thermal expansion (CTE) [4], and by Boyce et al [5] and Balasz et al [6] on mechanical reinforcement further point to the importance of nanoparticle arrangement in achieving maximum effect at minimum filler loading.

Ultimately, two general approaches to this challenge, paralleling nanofabrication concepts, are emerging, namely: external-in (top-down) and internal-out (bottom-up). For external-in, *directed patterning of nanoparticle dispersions (DPND)* relies on the creation, by an external means, of a multi-dimensional morphology directing potential, such as a spatially varying field or susceptibility within the material. This transforms a random distribution to a prescribed, ordered construction. For internal-out, *mesophase assembly of nanoparticle (MANP)* relies on the ability to tailor interparticle interactions, both particle-particle and particle-matrix, to result in thermodynamically stable (and defined) mesophases.

Establishing the limitations of these various approaches, whether with regard to nanoparticle size, processing time or feasibility of complex morphologies, is paramount to incorporating these concepts into commercially relevant devices and parts. Here in, the limitations and opportunities of DPND-motivated electrical field directed assembly of oblate (plate-shaped) dielectric nanoparticles within a dielectric matrix are considered. The correlation between theory for single particle alignment and experiment with layered aluminosilicates (NanoClays) in epoxy is summarized. Particle-particle interactions leading to particle chaining, similar to that observed in electro- and magneto-rheological fluids are discussed elsewhere.[7]

TORQUE ON AN ISOLATED, IDEAL DISC

An imposed AC electric field on oblate particles suspended in a viscous medium will result in an induced dipole moment on the particles originating from the difference in the dielectric properties between the medium and the particles. Consequently, the exerted time-average electric torque, T_o, on the particles tends to align the particles parallel to the electric field [8]. According to equilibrium statistics, the orientation parameter (Sd) is a function of the applied field, Brownian thermal energy kT and the anisotropy of the electric polarizability tensor which depends on particle geometry, size and the dielectric properties of the particle and medium.
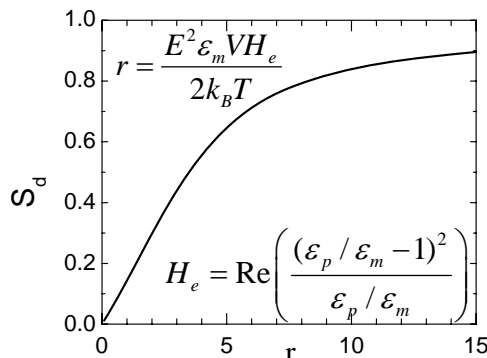

$$r = \frac{E^2 \varepsilon_m V H_e}{2k_B T}$$

$$H_e = \mathrm{Re}\left(\frac{(\varepsilon_p / \varepsilon_m - 1)^2}{\varepsilon_p / \varepsilon_m} \right)$$

Figure 1. Orientation parameter Sd as a function of r (competition between Brownian motion ($\sim k_B T$) and torque ($\sim E^2 \varepsilon_m V H_e$)).

For ideal dielectrics (no dielectric loss at applied frequency), the equilibrium orientation, Sd, with respect to the in-plane axis of the particle and the direction of applied field, increases as r increases, where *r* is the ratio of the energy decrease due to alignment and the thermal energy of the system. *E* is the magnitude of the applied field, V is the particle volume, T is temperature, and k_B is the Boltzmann constant. $\varepsilon_i^* = \varepsilon_i - j\,\sigma_i / \omega$ with *p* and *m* referring to particle and medium, respectively, and ε_i, σ_i and ω the permittivity, conductivity and frequency, respectively. H_e is a shape function. Note that the viscosity of the medium does not impact the *equilibrium orientation*, but it does substantially impact the *rate* at which alignment or randomization will occur.

SIZE LIMITATION

The competition between applied field and thermal energy leads to limitations on the size of the smallest rotatable particle. To get appreciable alignment with $S_d > 0.1$, the electric field has to be large enough to make *r*>1 to overcome Brownian motion. Assuming dielectric properties appreciated for a layered silicate [9] and epoxy matrix, Sd ~ 0.6 are only possible with disks around 20nm in thickness and 400 nm in radius.

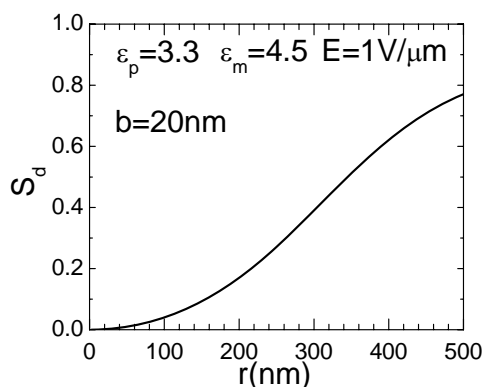ε_p=3.3 ε_m=4.5 E=1V/μm

b=20nm

Figure 2. Orientation parameter as a function of particle size for experimentally observed dielectric constants of layered aluminosilicate and epoxy under 1V/μm field strength.

Figure 3 summarizes alignment data (XRD, d_{001}) for two different layered silicates. For the same processing conditions (Epon 862 epoxy medium, 1 V/μm, room temperature, 3 wt% layered silicate, comparable CEC), the montmorillonite system (Cloisite 30B) exhibits alignment approaching S_d ~ 0.6. In contrast, Laponite at best exhibits

an $S_d < 0.1$. This is consistent with larger particles leading to better alignment. Also, alignment levels of Sd ~ 0.6 for Cloisite 30B implies rotation of tactoids (crystallites) occur, not individual 1-nm thick layers. This is consistent with microscopy observations [8].
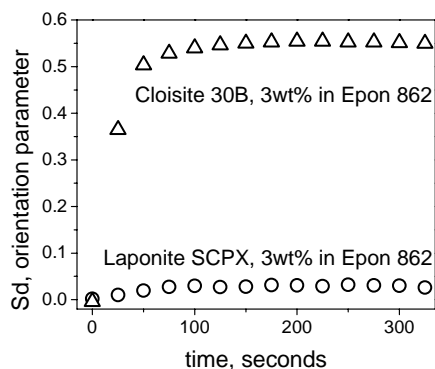

Figure 3. Orientation parameter (XRD, d_{001}) as a function of time for two different types of layered silicates (△ Cloisite 30B: 2r=100nm, ○ Laponite SCPX: 2r=30nm).

TORQUE ON A DIELECTRIC-LOSSY DISC

At relatively low frequencies, most fluids exhibit dielectric loss (conductivity) due to impurities. Also, many non-covalent surface functionalization approaches result in nanoparticles with finite dielectric loss.[9] Thus, the frequency behavior of particles in an electric field needs to consider the complex dielectric characteristics, ε_i^*. Traditional theory looks at an 'effective' field on each particle and does not apply to low/intermediate frequency range. The details of the local field distribution increases in importance as the shape anisotropy increases or the applied frequency corresponds to dielectric resonances. In these cases, the shape function He in Figure 1 is frequency dependent and leads to dual frequency behavior of particles in electric fields. The ratio of particle/matrix conductivity and dielectric constant determines whether an anisotropic particle aligns with its long axis along the field direction or perpendicular to it.
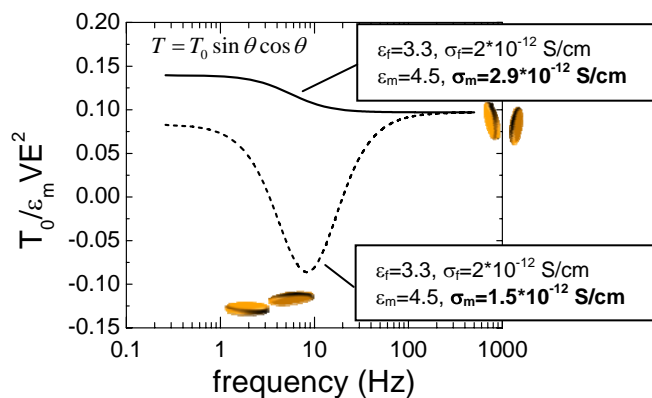

Figure 4. Normalized torque, $T_0/(V\varepsilon_m E^2)$ as a function of frequency for a particle-matrix system with different conductivity contrast ($\sigma_m/\sigma_f > 1$, solid line; $\sigma_m/\sigma_f < 1$, dashed line).

Figure 4 illustrates that the frequency window for switching particle orientation depends on minor differences in materials parameters. The theory predicts a possible window at lower frequencies for layered silicates in epoxy matrices.
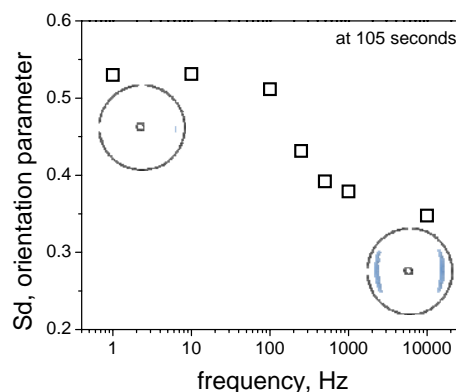

Figure 5. Orientation parameter as a function of frequency for layered silicate Cloisite 30B in Epon 862.

Figure 5 summarizes the experimental frequency dependence for the Cloisite 30B system in Figure 3. The orientation parameter decreases with higher frequencies as quantitatively predicted in Figure 4. Experiments on a layered system with much larger dielectric constant (AgBehenate) exhibited a partial switch in alignment direction, but with retention of the extent of order (Sd). This is qualitatively consistent with change in the sign of the induced torque on the particle, but maintenance of the magnitude of the torque.

CONCLUSIONS

The theory for isolated particle alignment predicts that below a critical particle size, alignment is undetectable (e.g. via X-ray) due to the counteracting Brownian motion. This can be addressed by assembly of particles into domains thereby increasing the effective particle size, by larger fields or by increasing the dielectric constant contrast ($\varepsilon_p/\varepsilon_m >> 1$). Consideration of complex dielectric characteristics also reveals a frequency window in which the torque on the particles changes sign, leading to either parallel (low frequencies) or perpendicular (high frequencies) alignment of oblate particles. This opens up opportunities to fine-tune orientation of particles with frequency. The viscosity of the matrix/particle system only impacts the rate of alignment, not the ultimate state. However for practical processing times (< mins), equilibrium alignment is reached only for low viscosities.

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