

POLYMER NANOCOMPOSITES WITH PRESCRIBED MORPHOLOGY: GOING BEYOND NANOPARTICLE-FILLED POLYMERS

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Introduction

Over the last decade, Polymer Nanocomposites (PNCs) have been one of the most extensively examined areas of polymeric nanomaterials. These efforts have led to numerous commercial successes, innovative approaches for fabricating and tailoring hybrid materials, and important fundamental insights on the behavior of polymers in confined environments^{1,2,3}.

Given the extensive variety of nanoparticles now commercially accessible (clays, carbon nanotubes, quantum dots, metals, silica, titania, zirconia, various oxides, etc.), the potential combinations of polymers and nanoparticles, and thus the tailorability of the property suite, is essentially endless. However, beyond maximization of the nanoparticle dispersion, the morphology of the vast majority of the polymer nanocomposites reported to date is uncontrolled, yielding isotropic nano-filled systems, not necessarily spatially 'engineered, designed and tailored' materials. Among the many challenges as PNCs move beyond commodity plastic applications, precise morphology control is paramount. Random arrangements of nanoparticles will not provide optimized electrical, thermal or optical performance for many potential high-tech applications, such as dielectric under-fills for electronic packaging, printed flexible electronics, engineered aerospace structural components, reconfigurable conductive adhesives and optical gratings to just mention a few. Two general approaches to this challenge of hierarchical morphology control are emerging, namely: external-in (directed patterning of nanoparticle dispersions) and internal-out (mesophase assembly of nanoparticles).

Directed patterning of nanoparticle dispersions using external electric fields is discussed.

Electric Field Alignment

Under an electric field, particulate additives, such as oxides or metals, reversibly form fibrous structures within a non-conducting fluid. These controlled aggregates are parallel to the applied field and can increase the viscosity of an electro-rheological fluid by up to 10⁵. Similar morphologies are found for magneto-rheological fluids where particle-particle interactions, which arise from induced magnetic dipoles, lead to chaining and subsequently long-range, periodic ordering of the particle chains parallel to the lines of magnetic flux.

Even with these proven successes, direct application of electric fields to large scale PNC production is challenging and rarely discussed⁴. Generating reconfigurable gradients in 3-dimensions with micron (or sub micron) features requires complex tooling with reconfigurable, patterned electrodes. As particle size decreases, the fields necessary to overcome thermal randomization increase considerably, and may approach the break-down strength of the matrix. This drastically limits sample thickness. Also anisotropic particles (rods and plates) drastically increase the complexity (and predictability) of field response with respect to the more commonly used spherical shapes. Finally, for thermoplastics, high viscosity results in long rotational and mass transport times, even over short sub-micron distances. Nevertheless, adaptations of these concepts to PNCs, especially thermosets where order can be 'stabilized' via post-processing polymerization, are now providing intriguing possibilities.

To better understand the limitations of electric field assisted patterning of nanoparticles, the impact of inherent (shape of particle, viscosity of the matrix, complex dielectric properties of the constituents) and external (temperature, frequency and magnitude of applied field) parameters on the torque generated on an isolated nanoparticle in a uniform electric field is calculated⁵. An applied electric field induces a dipole in a dielectric particle when it has a different permittivity from that of the media. When the shape of the particle is anisotropic, the orientation of the induced dipole does not necessarily coincide with the

applied field. The tendency of the dipole to orientate along the field causes a torque for the particle to rotate. Similarly, the conductivity difference of the particle and the medium causes charges to build up at the interface. This free charge dipole can also generate a torque. The torque is rigorously calculated using the Maxwell stress tensor, which is applicable to an arbitrary particle shape. Details of the model will be provided elsewhere⁵.

Figure 1 summarizes the relation between the equilibrium orientation of a plate-shaped particle and the processing conditions for ideal dielectric discs in an ideal dielectric medium. S_d (the Herman's Orientation Parameter 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, and is expressed as:

$$r = \frac{E^2 \epsilon_p V H_e}{2k_B T} \quad \text{and} \quad H_e = \text{Re} \left(\frac{(\epsilon_p / \epsilon_m - 1)^2}{\epsilon_p / \epsilon_m} \right) \quad (1)$$

E is the magnitude of the applied dc field, V is the particle volume, T is temperature, and k_B is the Boltzman constant. $\epsilon_i^* = \epsilon_i - j \sigma_i / \omega$ with p and m referring to particle and medium, respectively, and ϵ_i , σ_i and ω the permittivity, conductivity and frequency, respectively. To get appreciable alignment with $S_d > 0.1$, the electric field should be large enough to make $r > 1$. 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.

Consider a dielectric contrast of $\epsilon_p / \epsilon_m = 5$ and an applied field of 1 V/ μm , Figure 2a summarizes the equilibrium orientation at room temperature of plate-like particles as a function of particle volume, V (μm^3). For additional clarity, Figure 2b summarizes the impact of the radius, a (nm) for a plate of thickness 5 nm. Appreciable orientation does not occur until the particle is of substantial size (volume) or radius.

Experimentally, the impact of particle size is qualitatively observed during the electric field alignment of organically modified montmorillonite and laponite in epoxy. Details of the experiment can be found elsewhere⁴. In both cases, exfoliation of the layered silicates occur during epoxy cure, where as alignment of the layered silicates occurs in the uncured state, prior to complete exfoliation. Thus the effective particle size during alignment is substantially larger than an individual plate (montmorillonite: $\sim 100\text{nm} \times 1 \text{nm}$; laponite: $\sim 30\text{nm} \times 1 \text{nm}$). Nevertheless, the crystallite (tacoid) of laponite is substantially smaller than that of the montmorillonite. For the same processing conditions (Epon 862/Cure W, 1 V/ μm , room temperature, 3 wt% layered silicate, comparable CEC), the montmorillonite system exhibits alignment approaching $S_d \sim 0.6-0.7$. In contrast, laponite at best exhibits an $S_d < 0.1$. According to the model, the smaller the particle volume, the lower the equilibrium alignment that is possible. If the system was fully exfoliated, alignment would not occur due to the minuscule volume of a single nanoparticle. As an example of the experimental observations, Figure 3 summarizes the alignment of montmorillonite.

The alignment process may also be described energetically by considering a Boltzmann distribution of dipole orientation using the reduction in the system's internal energy due to dipole alignment.⁶ Here, the dipole is assumed to correspond to the long axis of the particle. This approach successfully accounts for the field dependence of particle alignment assuming a combination of induced and permanent dipoles (real part of the Clausius-Mossotti relation).

Finally, the aforementioned model (Equation 1) also provides insight into the impact of complex dielectric properties ($\sigma_i \neq 0$) of the particle and medium on the alignment of the particles. For an AC field, a frequency window is predicted in which a plate will orientate with its surface perpendicular to the applied field, where as at other frequencies, the plate will orientate with its surface parallel to the applied field as intuitively expected. Specifically, for a complex permittivity defined as $\epsilon_j^* = \epsilon_j - i \sigma_j / \omega$ for the plate and $\epsilon_m^* = \epsilon_m - i \sigma_m / \omega$ for the media, the rotation behavior depends on the ratio of the real and imaginary terms, $\beta_\sigma = \epsilon_j / \epsilon_m$ and $\beta_\sigma = \sigma_j / \sigma_m$. The rotation of the plate is frequency independent when $\beta_\sigma = \beta_\epsilon$. $\beta_\sigma > \beta_\epsilon$ makes the rotation faster. However, when $\beta_\sigma < 1$ and $\beta_\epsilon > 1$, or vice versa, there exists a frequency window so that the parallel alignment switches into perpendicular alignment. Fundamentally, this dual frequency behavior results from a balance between the instantaneous (β_ϵ) and frequency-dependent (β_σ) induced dipoles. Frequency switching of mesogen alignment is also observed for various nematic liquid crystals⁷. This prediction

suggests an exciting possibility to control the plate orientation via frequency and is currently being explored experimentally.

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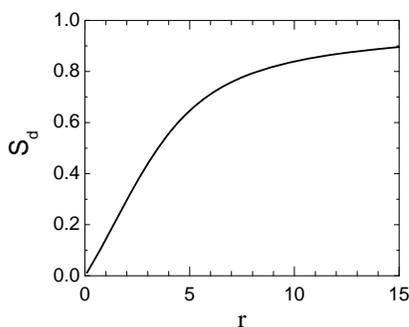


Figure 1. Relation between the extent of particle alignment, S_d , and the ratio of the energy decrease of the particle due to alignment and the thermal energy of the system, r .

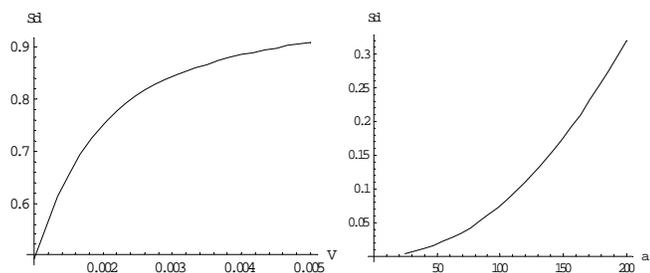
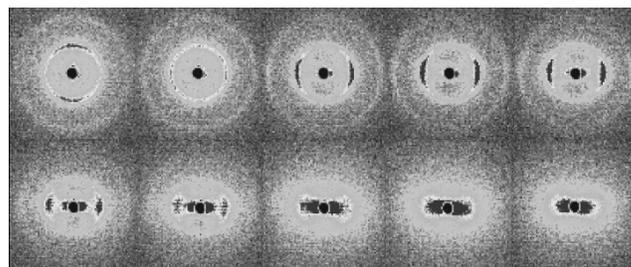


Figure 2. Dependence on plate orientation (S_d) on (left) plate volume, V (μm^3) and (right) radius, a (nm), of a 5 nm thick plate. ($\epsilon_p/\epsilon_m = 5$, $E=1$ V/ μm)

No E, RT E, 35 °C E, 75 °C E, 100 °C E, 125 °C



E, 150 °C E, 175 °C E, 200 °C E, 250 °C No E, RT

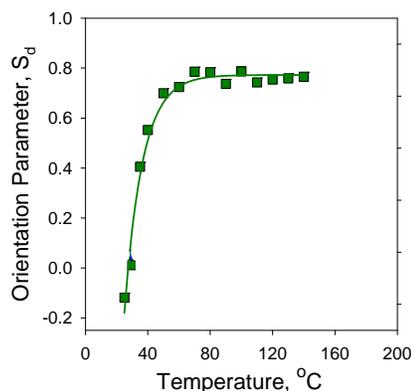
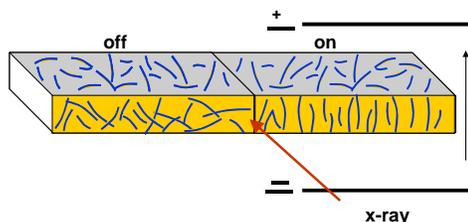


Figure 3.⁴ (middle) Schematic of the relative orientation of the applied electric field, montmorillonite layers and x-ray scattering used to determine orientation parameter. The montmorillonite layers are represented with black lines corresponding to the edge of the sheet. (top) A series of representative frames from in-situ, time-resolved X-ray scattering experiments for 6wt% Nanocor I.30E in Epon 862/W aligned in an electric field of 2V/ μm at 500Hz upon curing. The electrodes (and gap) are oriented horizontally, while the electric field direction is oriented vertically. The initial preferential alignment of the layers parallel to the electrode surface is due to flow occurring during sample preparation. This alignment is rotated 90° upon application of the E-field. The layer spacing increases (reflections migrate toward the beam stop) as cure progresses (temperature increases). (bottom) Herman's orientation parameter, S_d , (squares) determined from the in-situ scattering (3 °C/min). Note that the intensity of the basal reflection ($d001 = 36\text{\AA}$) rapidly decreases above 120 °C, effectively disappearing by 180°C. Orientation parameter above 120 °C was estimated from the featureless scattering around the beam stop.