Soft Polymer Magnetic Nanocomposites: Microstructure Patterning by Magnetophoretic Transport and Self-Assembly

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Supplementary Materials

Supplement 1 – Determination of Magnetic Field

The experimental setup consisted of a pair of 1 inch cube N52 grade NdFeB magnets (K & J Magnetics, Inc.), shown in the schematic in Figure 1 (d), that are placed 12.7 mm apart. Magnetic nanoparticles were dispersed in diluted prepolymer and cured in plastic cuvettes at three positions relative to these magnets, labeled A, B and C. Numerical values for $\mathbf{B}^{ext}$ are obtained from the Finite Element Method Magnetics (FEMM) software at the substrate posed by the cuvette walls and confirmed by using a Hall probe magnetometer. Values of $d\mathbf{B}^{ext}/dx$ are obtained from this by a central difference scheme. A map of these values is shown in Figure S1 pointing out positions used to determine the magnetic control variables which are separated from the surface of the magnet by the thickness of cuvette walls. The values are listed in Table 1.

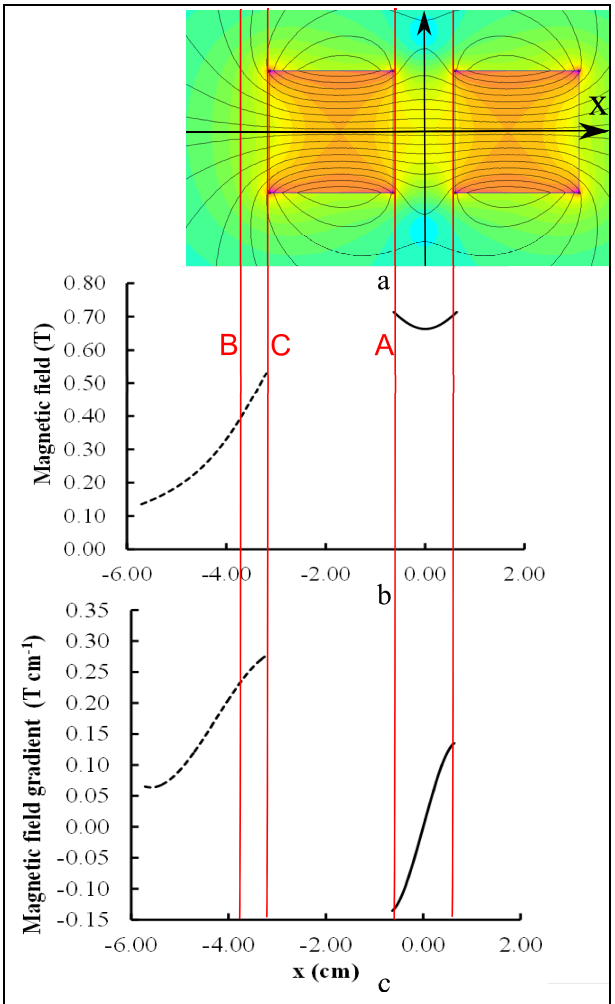

Figure S1 (a) Map of magnetic field strength $|\mathbf{B}^{ext}|$ with values of the x-components of (b) $\mathbf{B}^{ext}$, and (c) its gradient $d\mathbf{B}^{ext}/dx$ determined from FEMM software.

Supplement 2 – Scaling analysis relating magnetophoretic velocity to particle size

Each dipole is an MNP cluster of submicron length. The particle inertia thus plays a negligible role in its dynamics so that the magnetophoretic force is balanced only by the fluid drag. From Stokes' formulation, the drag on a spherical particle in a fluid

$$\mathbf{F} = -6\pi\mu a\mathbf{U}, \tag{S2.1}$$

where a denotes the particle radius and μ the dynamic viscosity of the fluid. For nonspherical particles, the drag force $F \sim \mu a U$ where a is an estimate of the particle size. This equals the magnetophoretic force, i.e.,

$$|(\mathbf{m}\cdot\nabla)\mathbf{B}| \sim \mu a U . \tag{S2.2}$$

The magnetic moment $|\mathbf{m}| \sim a^3 M_s$ where M_s is the saturation magnetization of the constituent material. Thus, it follows from Eq. S2.2 that the magnetophoretic speed of a particle scales as

$$U \sim a^2 . \tag{S2.3}$$

Supplement 3 – Scaling Analysis for Structure Anisotropy

The anisotropy metric ϑ is a representative measure of the cone angle of the filaments. Thus, a lower value of ϑ indicates higher shape anisotropy. Its lowest value is achieved for a single chain of dipoles that represents the highest conceivable shape anisotropy. The source of microstructure anisotropy is the long range orientation of the dipole-dipole bonds in the direction of the field. A larger $|\mathbf{B}^{ext}|$ induces greater alignment of these bonds and thus leads to smaller ϑ. However, ϑ increases monotonically with the gradient of the external magnetic field $|d\mathbf{B}^{ext}/dx|$, as seen in Figure 2 (i), while its variation with $|\mathbf{B}^{ext}|$ is not monotonic. This is

seemingly counterintuitive but is clarified by considering that dipole-dipole bonds are oriented not along $|\mathbf{B}^{ext}|$ but along the local direction of the magnetic field. This above analysis is thus valid only when $|\mathbf{B}^{ext}| \sim |\mathbf{B}^{dip}|$. For a nonhomogeneous field, the magnetophoretic force due to the magnetic field gradient also influences the anisotropy. In order to analyze the dependence of microstructure anisotropy on the magnetic control variables $|\mathbf{B}^{ext}|$ and $|d\mathbf{B}^{ext}/dx|$, we consider a simple system comprised of the two dipoles shown in Figure S2.

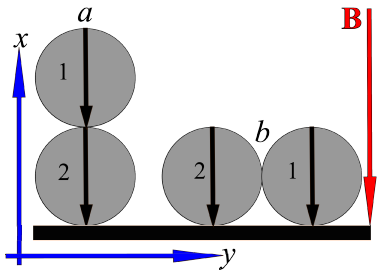

Figure S2 A simplified two particle system demonstrates how anisotropy increases with increasing gradient of the magnetic field.

In a homogeneous external field, stronger magnetic fields induce greater alignment of the dipoles and thus a higher anisotropy. However, as the field strength increases above a critical value, the degree of alignment saturates. This critical value can be estimated by comparing $|\mathbf{B}^{ext}|$ with the field produced at a point due to neighboring dipoles, as noted above. For the configuration in Figure S2 (b), the magnetic field at the center of dipole 1 due to the presence of its neighbor is $\mathbf{B}_1^{dip} = \mu_0 M_s / 24\ \mathbf{e}_x$. Considering magnetite particles, $M_s = 446\times10^3$ Am^{-1} leads to $|\mathbf{B}_1^{dip}| \sim 0.023$ T, which is an order of magnitude smaller than the applied value of $|\mathbf{B}^{ext}|$ in our experiments. As $\mathbf{B}^{ext}$ is directed along (–x), the net magnetic field experienced by dipole 1 is also similarly directed towards the externally imposed field. It is reasonable to assume that all dipoles in the system encounter a local magnetic field that is directed along (–x), and the alignment effect of the magnetic field is well past saturation.

Corresponding to our experiments, we consider $\mathbf{B}^{ext} = -B(x)\mathbf{e}_x$. The total potential energy of the system

$$U_{tot} = -\sum_i \mathbf{m}_i \cdot \mathbf{B}^{ext}(\mathbf{r}_i) + \frac{\mu_o}{4\pi}\left(\frac{\mathbf{m}_1 \cdot \mathbf{m}_2}{r^3} - \frac{3(\mathbf{m}_1 \cdot \mathbf{r})(\mathbf{m}_2 \cdot \mathbf{r})}{r^5}\right), \tag{S3.1}$$

where **r** denotes the position vector of one dipole relative to the other. Thus, the potential energies for cases (a) and (b) in Figure S2 are, respectively,

$$U_{tot}^a = -m(B(a) - B(3a)) - \frac{\mu_0}{4\pi}\frac{m^2}{4a^3}, \text{ and} \tag{S3.2}$$

$$U_{tot}^b = -2mB(a) + \frac{\mu_0}{4\pi}\frac{m^2}{8a^3}. \tag{S3.3}$$

Here, *a* denotes the radius of the dipolar particle. The difference between these two values indicates whether anisotropic chains are formed along the magnetic field or if all nanoparticles are pulled to the substrate. This difference,

$$\Delta U_{tot} = m\big(B(a) - B(3a)\big) - \frac{\mu_0}{4\pi}\frac{3m^2}{8a^3}. \tag{S3.4}$$

A two-particle chain transitions to a morphology where both particles lie on the substrate when $\Delta U_{tot} > 0$. Approximating $B(a) - B(3a) \sim |dB/dx|(2a)$, the criteria for this transition is,

$$\frac{16a\,|dB/dx|}{\mu_0 M_s} > 1. \tag{S3.5}$$

Thus, a larger magnitude of the magnetic field gradient renders a smaller anisotropy in the resultant structure. In more complicated systems that consist of several dipoles, simplified

expressions for such equations cannot be determined. However, the dimensionless number obtained from Eq. (S3.5),

$$\Pi = \frac{a\,|\,dB/dx\,|}{\mu_0 M_s} \tag{S3.6}$$

provides guidance about the anisotropy of the system. Smaller values of Π lead to higher anisotropy in the microstructure, forming long filaments with small ϑ whereas a high value of Π will drag all dipoles to the substrate forming an uniform coating with the highest conceivable value of ϑ.