SAND2013-10796C

Field-Assembled Polymer Composites

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ABSTRACT

In this paper we show that a wide variety of composite structures can be obtained from structuring with multiaxial fields. The properties of these composites are highly responsive to field structuring and so significant increases in a variety of properties can be obtained. These composites have application as high-strain actuators, strain and temperature sensors, chemical sensors, and as thermal interface materials. We discuss these issues and provide a general summary of the research we have done in this area.

INTRODUCTION

In many instances the properties of polymers can be usefully modified by the addition of particles. In some cases, such as carbon-black-filled polybutadiene, these particles enhance properties already inherent to the polymer, such as durability and strength. In other cases the particles modify the polymer so appreciably that entirely new functionalities, such as sensing and actuating, become possible. In either case most properties of the composite depend appreciably on the arrangement of the particles within the polymer, as well as their orientation, if the particles are anisometric. Accordingly, a number of obvious questions arise. For any given application what is the optimal particle arrangement? How is this arrangement modified if the desired composite properties are anisotropic? How can one create the necessary anisotropy? And how can magnetic or electric fields be used to answer any of these questions? The purpose of this manuscript is to answer these questions and to give examples of optimizing a variety of properties using magnetic fields. This article is essentially a review of the broad range of work we have done in this area, the references contain the details of this work.

RESULTS AND DISCUSSION

In all cases we start out with particles dispersed in a liquid. These particles can be spheres, rods, platelets or even more complex shapes, and do not need to be suspended. In fact, it is really no problem if the particles form a sediment at the bottom of the liquid, which is what they usually do. If the suspending liquid is a simple nonreactive fluid, then the application of various multiaxial, time dependent fields can create fluid vorticity [1-3] (and thus mixing) and various highly organized flow patterns, such as advection lattices [4] and vortex lattices [5]. These emergent effects are highly effective for noncontact heat and mass transfer, as discussed at length in various recent papers [6, 7]. However, the focus of this manuscript is on the case where the liquid phase is a thermosetting polymer resin, such as an epoxy. In this case the particles can be manipulated by the multiaxial magnetic fields to create a variety of composite structures.

So why should one use multiaxial fields to create composite materials? When one applies a spatially uniform magnetic (or electric) field to a suspension of magnetic (or dielectric) particles they will polarize. For such induced dipoles the contribution to the free energy will be minus one half the scalar product of the particle moment and the applied field. (For permanent dipoles there is another expression, and for those interested in the details of such things we have prepared an instructive paper on energy balance problems involving dipoles.) The suspension free energy will thus decrease as the particle moments increase. The particle moments are proportional to the local field, and even though the applied field is uniform, the local field is not, due to fact that all of the other particles in the suspension are polarized and produce fields of their own. Each particle thus maneuvers in the direction of increasing local field so as to increase its moment and reduce its free energy. This movement is due to the Kelvin force and is termed magnetophoresis, or dielectrophoresis in the case of an applied electric field. (This inconsistency in terminology for what is the same physics is really annoying, but derives from the fact that electrophoresis is already used for the migration of a charged entity in a uniform field. Because there are no free magnetic monopoles the term magnetophoresis is used for the migration of a magnetic dipole in a field gradient, even though "dimagnetophoresis" would be more consistent.) As the particles move so as to increase their moments, the magnetic permeability of the fluid increases linearly, since this quantity is related to the polarization density per unit applied field. In the presence of significant but decreasing thermal fluctuations the particles will eventually form the ground state structure that maximizes the fluid permeability. This structure (a bct lattice for spherical particles that subjected to a uniaxial applied field [8, 9]) can then be trapped by allowing the resin to polymerize. The result is a composite with a significantly enhanced permeability along the direction of the structuring field.

OK, so at this point we have argued that an applied field can optimize the magnetic permeability of a particle composite. What about other physical properties? In 1974 Batchelor [10] wrote a very nice paper pointing out that numerous physical properties of composites are actually isomorphic. This is because so many properties are related to a scalar field that obeys Laplace's equation and have the same boundary conditions. For example, the magnetic induction field obeys Laplace's equation, as does the thermal flux in steady-state heat transfer. The induction field has continuous flux lines, and the thermal flux is continuous in the absence of Kapitza resistance. So optimizing the permeability optimizes the thermal conductivity of a composite, which sounds a little strange because the conductivity is a transport property, but is true nonetheless. Other isomorphic properties include the dielectric permittivity, gas permeability, and the electrical conductivity (although there are some caveats in the latter case). Jack Douglas has pointed out that the suspension viscosity is also essentially isomorphic, but this observation does not really pertain to field-structured composites, though it does pertain to suspensions of spherical and anisometric particles [11]. So the bottom line is that applying a magnetic field causes particles to organize (and align) in such a way as to optimize many of the physical properties we call *Laplacian* properties.

More complex particle assemblies can be produced with more complex fields and these structures can have tailorable property enhancements in one, two, or three directions. Biaxial fields, consisting of two orthogonal fields with at least one being alternating, produce negative dipolar interactions and give rise to a composite of parallel

particle sheets that form in the plane of the field [12, 13]. Triaxial fields, consisting of three orthogonal fields with at least two components alternating, give rise to networks of particle chains [14]. However, if two or three of the alternating field components are close in frequency, such the suspension dynamics can follow the heterodyne beat frequency (or frequencies), then very surprising particle assemblies [14] emerge as the viscosity of the polymerizing resin continuously increases. If two field components heterodyne the result is an anisotropic cellular composite, a bit like a honeycomb. If three components heterodyne the result is an open-celled particle foam. Of course, it is possible to create imbalances in the relative magnitudes of the field components, and these lead to distortions in the various composite structures, with commensurate changes in the anisotropy of physical properties.

To predict the property enhancements of these various structures we have developed an effective medium theory for structured composites that is based on a self-consistent local field calculation [9]. This theory uses an equivalent site approximation and takes into account composite structure through an order parameter that in essence averages the dipolar fields created by the nearby dipoles. The far-field dipole contribution through the Lorenz cavity field. This order parameter is zero for random particle composites and can be either positive or negative for structured composites. To compute this order parameter requires information about the composite structure. This information could be obtained from x-ray tomography of real composites, but we obtain composite structures from *Brownian Dynamics* simulations of structural evolution in multiaxial fields [9, 12, 13, 14]. This effective medium theory is able to account for the trends of essentially all of the data we have taken on spherical particle composites in uniaxial and biaxial fields, but fail to predict increases in the properties of triaxial composites produced in balanced field. This is because the equivalent site assumption is inaccurate for these composites. To address this issue requires an effective medium model that does not make this assumption, and such a model has been developed [15]. The properties can also just be calculated directly from the simulation structures without any assumptions. We will now discuss the enhancements we have achieved in various properties.

Magnetic permeability

Measurements of the magnetic permeability and the related susceptibility are of particular interest because they are a direct measurement of the magnetostatic energy of the composite. We have published rather exhaustively on this subject, having made measurements on dozens of composite structures, and so will only give a few highlights here. SQUID magnetometer measurements were made on composites machined into cubes or solid rectangles. These measurements give the applied field and the magnetic moment of the sample. To compute the magnetic susceptibility requires that the macroscopic internal field of the sample is known, but this is not measured. To determine this field we numerically modeled the macroscopic field inside solid rectangles having a range of magnetic susceptibilities. By intelligently fitting these data to a functional form [16] we are able to self-consistently determine the internal field of the composite, which can be several times smaller than the applied field, and thus accurately compute the material susceptibility and permeability. Uniaxial composites have a

susceptibility that is greatly enhanced along the structuring field and slightly suppressed, relative to that of a random composite [16]. Biaxial composites have a susceptibility that is greatly enhanced in the plane of the structuring field and strongly suppressed orthogonal to this plane [16]. Triaxial composites have a susceptibility that is somewhat enhanced in all three directions [15].

The greatest enhancements were for the heterodyned composites [15]. Strangely, a triaxial field with two alternating components heterodyned shows strong enhancements in all three directions, but especially in the direction of the field component that is not heterodyned (this component is normally dc). The imbalance is significantly greater if the dc component is made to be 25% greater than the heterodyned components. In fact, this gives the greatest enhancements we observed, because the heterodyning acts like an artificial source of thermal fluctuations that helps the rough particles move over energy barriers. 3-D heterodyning gives substantial enhancements in all three directions and field imbalances can be used to create controlled anisotropy in the composite properties. This is really the best way to make optimized composites. But even better enhancements can be obtained for composites of superparamagnetic particles, but that is quite an involved story [17].

Our work on the magnetic permeability may be viewed as an experimental validation of the concept of structuring with multiaxial fields. In general the experimental results are very consistent with the predictions from simulations.

Thermal conductivity

Talking about the thermal conductivity is redundant, because it is isomorphic to the magnetic permeability, so the story is just the same. However, I'm going to discuss this anyway because it is more intuitive than the permeability, which helps to make some important points about composites, and there is a definite need for better thermal interface materials to remove heat from microsystems.

The thermal conductivity of polymers is generally about 0.2 W/m-K, so using thermosetting resins to bond microprocessors or other devices to heat sinks creates a significant thermal barrier. It would seem logical enough to add some particles of a high conductivity to boost the thermal conductivity, such as diamond, with a thermal conductivity of ~2000 W/m-K. One might guess that adding 10% diamond powder might create a composite with a thermal conductivity of ~200 W/m-K, but this is very optimistic. In reality the composite thermal conductivity will increase by 30%, to about 0.26 W/m-K. The reason for the small increase is that within each spherical diamond particle there is very little thermal gradient, in comparison to the applied thermal gradient. Because the interior is nearly isothermal, there is little additional heat conduction. In fact, the additional conduction is virtually independent of the thermal conductivity of the material of which the particle is comprised, once that is greater than that of the polymer.

By forming high conductivity spherical particles into chains and other structures with applied magnetic fields of various sorts we have managed to make composites with thermal conductivities that are as high as 1.5 W/m-K [18]. This is because of the much greater penetration of the thermal gradient into particles that are strategically organized by fields. However, to obtain much better enhancements we have taken advantage of the

much greater thermal gradient penetration that occurs when thin magnetic platelets are aligned and agglomerated with a uniaxial field. These platelets can be solid Ni, with a thermal conductivity of 90 W/m-K, or can be more complex multilayered structures such as a Ni core coated with Al and over coated with magnesium fluoride layers. These multilayer platelets can be used to make electrically insulating composites. In the best case platelets gave a composite thermal conductivity of 4.5 W/m-K at a volume fraction of 16%. A summary of the specific thermal conductivity enhancements of composites made of a variety of particle shapes and field structuring strategies is shown in Figure 1. Field-structured composites comprised of platelets give almost a 30x greater enhancement that randomly dispersed spheres. The composites made with multilayered platelets [19] are nearly as conductive as the solid platelets [20], but are electrically insulating.

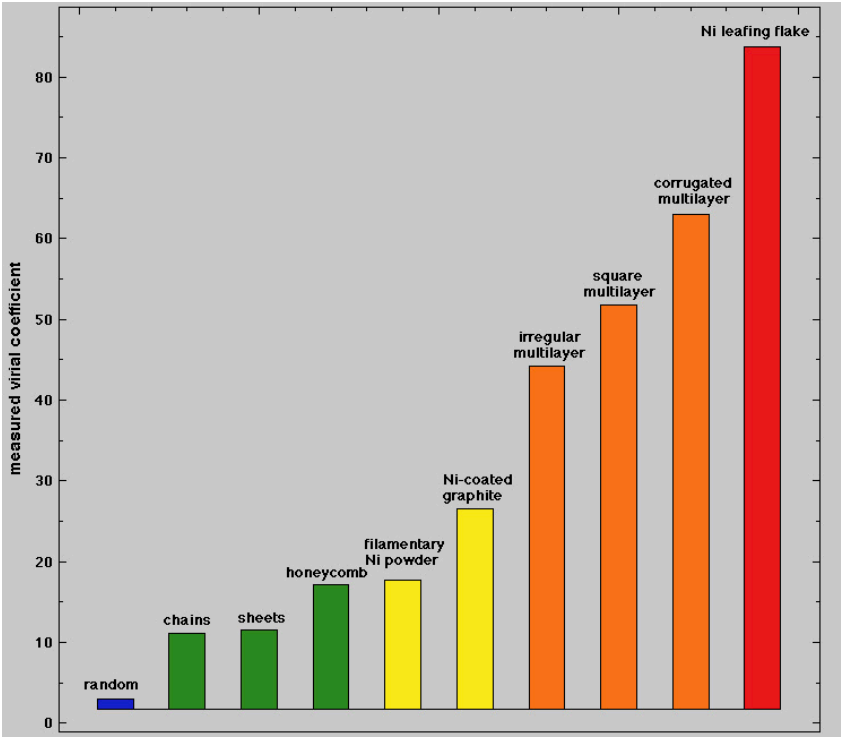

Figure 1. The specific thermal conductivity enhancements (the relative increase in thermal conductivity per unit volume fraction of particles, also known as the transport virial) is shown for a variety of particle geometries. Randomly dispersed spheres give a value of 3, whereas the best platelets give 84, a 28x improvement.

Electro- and magnetostrictive actuators

These structured composites have significant electro- and magnetostriction, which make them attractive as actuators. Generally speaking magnetostriction is due to a distortion of the crystalline lattice of a ferromagnetic material in response to an applied field. This distortion reduces the interaction energy between the spins. In a composite material an applied field will thus cause a distortion of the ferromagnetic particles within the composite, but this effect is small for our materials. The principal effect is the magnetic interactions between particles, which have both dipolar and multipolar components. We have developed a point dipole theory of electro- and magnetostriction

of structured particle composites [21] that shows that structuring increases striction enormously. Optical cantilever measurements of magnetostriction confirm the theoretical predictions, and the trends follow that of the permeability measurements. This is not obvious, since magnetostriction depends on a second, higher-order order parameter. In any case, strains of 10,000 ppm have been measured [22] for the best samples, which is a value about two orders of magnitude greater than that of piezoelectric actuators. Under the proper conditions the accompanying magnetoresistance can be very large, as much as a six order of magnitude increase in conductivity with an applied field of only 600 G.

Chemical, thermal and strain sensors

We have developed chemical and strain sensors whose transduction mechanism is a change in electrical conductivity. The electrical conductivity is a very complicated property and is not at all a Laplacian property in the systems we have investigated, even though theory tells us otherwise. This reminds of a Yogi Berra quip, "*In theory, theory and practice are the same. In practice they are different.*" A simple experiment we performed highlights how different the electrical conductivity is from the Laplacian properties we have investigated, which have property enhancements that are only on the order of 25x or less. Electrical conductive, Au-plated Ni particles were dispersed in a thermosetting resin in a square cuvette. These particles were organized into chains with a uniaxial field and the electrical conductivity of the sample was measured parallel to the structuring field during cure. The conductivity changed very little up to the gel point, at which time the magnetic field was turned off, being no longer necessary to hold the particles in place. As the resin continued to cure the conductivity *increased by 8 orders of magnitude*, due to the cure shrinkage of the resin. This shrinkage caused strong positive contact pressure between the particles, creating ohmic contacts over an increasing contact area after the gel point. If the polymer was then swollen by solvent sorption or heating, the contact pressure decreased, causing the conductivity to drop by many orders of magnitude.

The extreme dependence of the conductivity on composite swelling and strain makes these composites ideal for sensor applications [23]. We have developed these materials as temperature and strain sensors, but have spent quite a bit of effort developing these as chemical sensors [24, 25]. At this point we are able to sense volatile organics at extremely low vapor pressures and can tune the sensor sensitivity over ~3 orders of magnitude by controlling the stress within the polymer phase. By applying a tensile strain to a single sensor we are able to reversibly tune the sensitivity of a single sensor by 2 orders of magnitude [26]. Some degree of selectivity can be achieved by tailoring the polymer affinity to the target analyte, or by using sensor arrays of various polymers. However, a simpler approach is to extract the *saturation* vapor pressure of an unknown analyte from the response kinetics [27]. Because saturation vapor pressures vary over many orders of magnitude this approach is a reasonable basis for identifying an unknown analyte.

CONCLUSIONS

A wide variety of composite structures can be obtained from structuring with multiaxial fields. The composite properties are highly responsive to field structuring and significant increases in a variety of properties can be obtained. These composites have application as high-strain actuators, strain and temperature sensors, chemical sensors, and as thermal interface materials.

ACKNOWLEDGEMENTS

Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000. This work was supported by the Division of Materials Science, Office of Basic Energy Sciences, U.S. Department of Energy (DOE).

REFRENCES

1. J. E. Martin, *Theory of strong intrinsic mixing of particle suspensions in vortex magnetic fields*, Phys. Rev. E **79** 011503-011514 (2009).
2. J. E. Martin, Shea-Rohwer L, Solis K J, *Strong intrinsic magnetic mixing in vortex magnetic fields*, Phys. Rev. E **80** 016312-016317 (2009).
3. K. J. Solis, R. C. Bell, J. E. Martin, *Vortex magnetic field mixing with anisometric particles*, J. Appl. Phys. **107** 114911-1 to 114911-4 (2010).
4. K. J. Solis, J. E. Martin, *Isothermal magnetic advection: Creating functional fluid flows for heat and mass transfer*, Appl. Phys. Lett. **97**, 034101 (2010).
5. K. J. Solis, J. E. Martin, *Stimulation of vigorous rotational flows and novel flow patterns using triaxial magnetic fields*, Soft Matter **8**, 11989-94 (2012).
6. K. J. Solis, J. E. Martin, *Controlling the lattice spacing in isothermal magnetic advection to enable tunable heat and mass transfer*, J. Appl. Phys. **112**, 049912-7 (2012).
7. K. J. Solis, J. E. Martin, *Multiaxial fields drive the thermal conductivity switching of a magneto-responsive platelet suspension*, Soft Matter 9, 9182-9188 (2013).
8. T. J. Chen, R. N. Zitter, R. Tao, *Laser diffraction determination of the crystalline structure of an electrorheological fluid, Phys. Rev. Lett.* **68**, 2555-2558 (1992).
9. J. E. Martin, R. A. Anderson and C. P. Tigges, *Simulation of the athermal coarsening of composites structured by a uniaxial field*, J. Chem. Phys. **108** 3765-3787 (1998).
10. G. K. Batchelor, *Transport properties of two-phase materials with random structure*, Ann. Rev. Fluid Mech. 6 227-255 (1974).
11. E. J. Garboczi, J. K. Douglas, *The intrinsic viscosity and the polarizability of particles having a wide variety of shapes*, Advances in Chemical Physics **91**, 85-153 (1995).
12. J. E. Martin, R. A. Anderson and C. P. Tigges, *Simulation of the athermal coarsening of composites structured by a biaxial field*, J. Chem. Phys. **108** 7887-7900 (1998).

13. J. E. Martin, R. A. Anderson, C. P. Tigges, *Thermal coarsening of uniaxial and biaxial field-structured composites*, J. Chem. Phys. **110** 4854-4866 (1999).
14. J. E. Martin, R. A. Anderson, and R. L. Williamson, *Generating strange magnetic and dielectric interactions: Classical molecules and particle foams*, J. Chem. Phys. **118** 1557-1570 (2003); J. E. Martin, R. A. Anderson, and R. L. Williamson, *Generating strange interactions in particle suspensions*, Composites Science and Technology **63** 1097-1103 (2003).
15. J. E. Martin, E. Venturini, G. Gulley, J. Williamson, *Using triaxial magnetic fields to create high susceptibility particle composites*, Phys. Rev. E **69** 21508-1 to 15 (2004). J. E. Martin, *Using triaxial magnetic fields to create optimal particle composites*. Composites Part A **36** 545-8 (2005).
16. J. E. Martin, E. Venturini, J. Odinek, and R. A. Anderson, *Anisotropic magnetism in field-structured composites,* Phys. Rev. E. **61** 2818-2830 (2000).
17. J. E. Martin, E. Venturini, and D. L. Huber, *Giant magnetic susceptibility enhancement in field-structured nanocomposites*, Journal of Magnetism and Magnetic Materials **320** 2221-2227 (2008).
18. J. E. Martin and G. Gulley, *Field-structured composites for efficient, directed heat transfer*, J. Appl. Phys. **106** 084301-084307 (2009); also in Virtual Journal of Nanoscale Science & Technology **20** [19] (2009).
19. K. J. Solis, J. E. Martin, *Field-structured magnetic platelets as a route to improved thermal interface materials*, J. Appl. Phys. **111**, 054306-10 (2012).
20. J. E. Martin, K. J. Solis, D. Rademacher, V. Raksha, *Field-structured, multilayered platelets enable high-performance, dielectric thermal composites*, J. Appl. Phys. **112**, 073507-10 (2012).
21. J. E. Martin and R. A. Anderson, *Electrostriction in field-structured composites: Basis for a fast artificial muscle?* J. Chem. Phys. **111** 4273-4280 (1999).
22. J. E. Martin, R. A. Anderson, D. H. Read, G. Gulley, *Magnetostriction of field-structured magnetoelastomers*, Phys. Rev. E **74** (5) 051607-051624 (2006).
23. J. E. Martin, R. A. Anderson, J. Odinek, D. Adolf and J. Williamson, *Controlling percolation in field-structured particle composites: Observations of giant thermoresistance, piezoresistance, and chemiresistance*, Phys. Rev. B **67** 94207-1 to 11 (2003).
24. D. H. Read and J. E. Martin, *Field-structured chemiresistors*, *Advanced Functional Materials,* **20** (10), 1577–1584 (2010).
25. D. H. Read and J. E. Martin, *Master transduction curve for field-structured chemiresistor calibration*, Anal. Chem. **82**, pp. 5373-9 (2010).
26. D. H. Read and J. E. Martin, *Strain-tunable chemiresistor*, Anal. Chem. **82** (5), pp 2150–2154 (2010).
27. D. H. Read and J. E. Martin *Analyte discrimination from chemiresistor response kinetics,* Anal. Chem. **82**, pp. 6969-75 (2010).