

Multiphase Functional Nanomaterials

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Nanoscale interactions between polymers and nanoparticles are known to influence structure and properties of polymer materials containing dispersed nanostructures. This research project focuses on understanding how these interactions can be controlled and manipulated to produce functional nanomaterials incorporating nanostructures with specific functionality, surface chemistry, geometry, and size dispersed in model thermosetting and thermoplastic polymers. Specifically, we use sol-gel chemistry and electrospinning to produce metal oxide particles with a wide range of shapes (cubic, rod-like, fibrillar, and spherical), and silane chemistry to functionalize the surface of these particles with oligomer and polymer chains. These systems are dispersed in model host polymers possessing well-defined architectures, molecular weight distributions, and cross-linking density; allowing us to determine the fundamental effect(s) of particle/polymer and particle/particle interactions on structure and properties of polymer nanocomposites.

Tethering oligomers and polymers to particles

A simple procedure for tethering polymer chains of any chosen length at controlled coverage on silica nanoparticles has been developed. The procedure relies on initial introduction of vinyl groups to the particle surface. In the first step a well-mixed multicomponent self-assembled monolayer (SAM) comprised of unreactive alkyl-terminated and reactive vinyl terminated C10 chains is attached to the particle. The surface density of vinyl groups is controlled by varying the relative composition of vinyl and alkyl terminated chains in the bulk mixture. Since the binding constant for the alkylsilane species to silica are the same, the surface composition of vinyl groups is close to that in the bulk mixture. In the second step a living polymer chain of well-known molecular weight and narrow molecular weight distribution (in this case polyisoprene) is reacted with the vinyl groups to produce a two-tiered polymer corona on the particles (see Figure 1). Because the polymer molecular weight is known independently, thermal gravimetric analysis of particles functionalized with these chains could be used to independently quantify surface coverage.

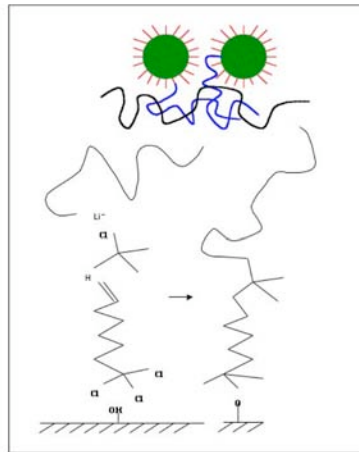


Figure 1: Scheme for functionalizing silica nanostructures with polymer chains

Synthesis of non-spherical nanostructures

Much of the scientific research to-date on polymer nanocomposites has focused on the effect of high aspect ratio, layered silicate clays on the host polymer properties. These materials are clearly effective, but the extremely large hydrodynamic volume of the sheets ($v_H \approx l^3$), where l is

the largest dimension $O(1-10\mu\text{m})$, means that even if polymer bridging can be avoided by controlling particle surface chemistry, significant levels of particle-particle contacts will occur in polymer composites reinforced by layered clays. Again this means that continuum, rather than the more popular non-continuum, physical models are perhaps more relevant for understanding how these anisotropic nanostructures reinforce polymers. To explore the effect of nanoparticle geometry on properties of polymer nanocomposites, we have used electrospinning and sol-gel chemistry to create nanostructures with novel fibrillar, cubic, and core-shell morphologies.

We have, for example, applied an acid-assisted technique for preparing surface functionalized multi-walled carbon nanotubes (MWNTs) and carbon nanofibers (CNFs), with carboxyl functional groups attached to the nanoparticle surfaces. A TEM micrograph of the modified MWNTs is shown in Figure. 2. A simple salt-mediated scheme has also

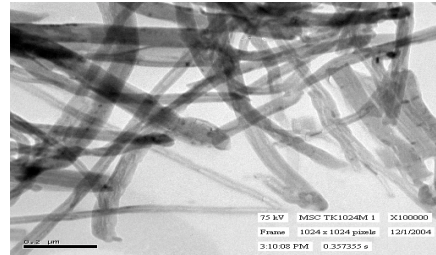


Figure 2: TEM of chemically modified multi-wall carbon nanotubes

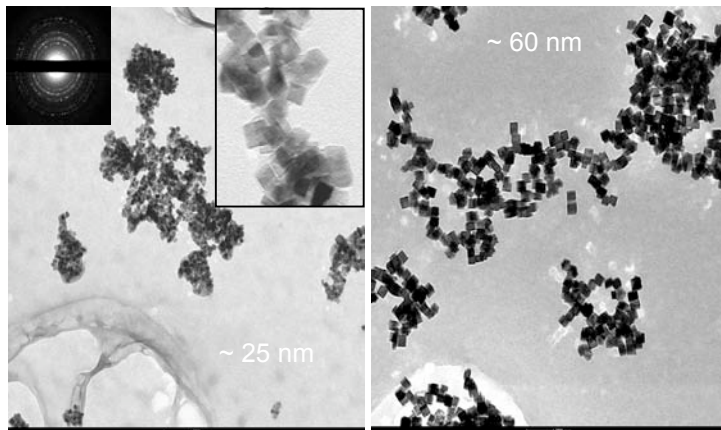


Figure 3: Co_3O_4 Spinel nanocubes with narrow particle size distribution

been used to synthesize Spinel Co_3O_4 nanocubes with uniform sizes in the range of 10 – 100 nm and a hydrothermal scheme for creating bohemite nanorods. Figure 3, for example, provides TEM micrographs of Co_3O_4 nanocubes with average particle sizes of 25 nm and 60 nm, respectively. These particles are observed to spontaneously aggregate to form large clusters.

Multiphase Functional Nanomaterial Characterization

To investigate the effect of nanostructures on polymer properties, it is important to develop repeatable dispersal strategies. Silica-based particles are easily dispersed in hydrophilic polymers such as PEO using a freeze-drying technique. In this approach strong interactions between the particles and polymer in aqueous solutions are exploited to trap the system into a homogeneous mixed state. Mechanical measurements performed using annealed composites produced in this manner reveal two to three orders of magnitude enhancement of the elastic modulus at particle loadings as low as 3v%, confirming good dispersal. Carbon nanofibers(CNFs) and multiwall carbon nanotubes(MWNT) have been dispersed in a thermoset polymer matrix by combining chemical modification with various dispersal methods. The CNFs and MWNTs were modified with carboxylic acid groups to enhance spontaneous mixing with the host. The effect of surface modification on dispersion and alignment of CNFs on the coefficient of thermal expansion (CTE) is depicted in Figure 4. Particle alignment was achieved using a mechanical shear field. It is apparent from the figure that this results in nanocomposite materials with lower CTE values, relative to systems where particles are randomly dispersed in the host. This result was confirmed by measuring the CTE both parallel and perpendicular to the flow field. Samples

which contain chemically modified nanoparticles exhibit a further lowering of the CTE, suggestive of enhanced polymer-nanoparticle interaction. A maximum Tg enhancement of 23°C was also observed.

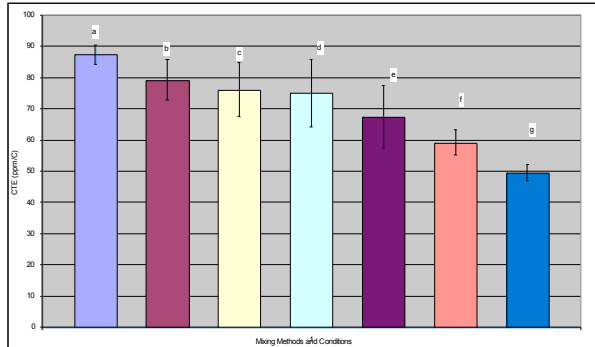


Figure 4: Coefficient of Thermal Expansion (CTE) of thermosets containing nanofibers and nanotubes. a- neat Epon 815C; b- unmodified mechanically mixed; c- modified mechanically mixed; d- unmodified sheared (perpendicular, p); e- modified; f - unmodified sheared-p); g- modified sheared-p .

Approaches to improve the toughness of thermosets, such as rubber toughening, increasing the molecular weight between crosslinks, and replacing rigid backbone segments with more flexible ones, all result in decreases in Tg, oxidative stability, dimensional stability and mechanical properties. The use of high performance thermoplastic nanofibers thus provides an exciting potential alternative to enhance the toughness without sacrificing other properties.

Nanofibers can be incorporated into the thermoset as random entities or as aligned mats. We have utilized an electrostatic spinning process to prepare nanoscopic fibers of Nylon 6. These fibers, in the form of a random mat, were infiltrated with epoxy resin.

As shown in Figure 5 a-d, when the nanoscopic fibers, which have an average diameter of 200 nm (shown in a) are infiltrated with epoxy resin, followed by curing, a transparent nanocomposite results (shown in b). For a very low loading of nylon nanofiber, 0.5 wt%, the nanocomposites exhibit a 17% enhancement in both the strength and the strain at failure. The epoxy-nylon miscibility is relatively low, based on the SEM micrograph in Figure 5(c).

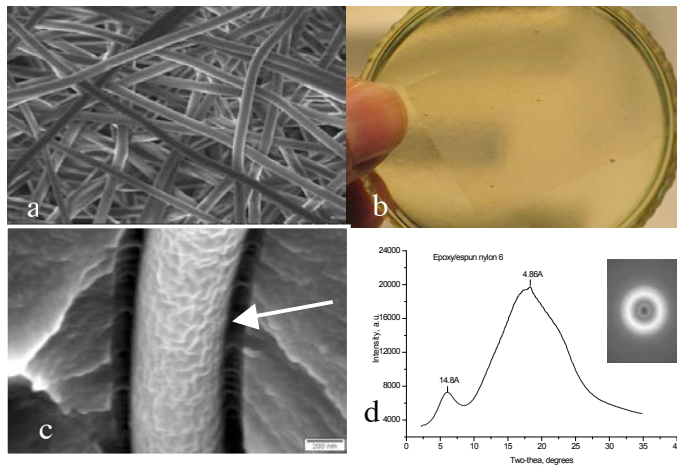


Figure 5: a.) Electrospun fibrils from nylon 6. b.) Nylon 6/epoxy nanocomposite. c.) SEM of nylon fiber dispersed in epoxy. d.) XRD of nylon 6/epoxy nanocomposite. XRRD of nylon/epoxy nanocomposite.

the nanocomposites exhibit a 17% enhancement in both the strength and the strain at failure. The epoxy-nylon miscibility is relatively low, based on the SEM micrograph in Figure 5(c).

In summary, several methods have been developed for synthesizing nanostructures with well-defined geometries, sizes and surface chemistries. These structures have been dispersed in thermoplastic and thermosetting polymer hosts to produce materials with enhanced mechanical and highly anisotropic

thermal properties. Our ongoing work seeks to establish fundamental relationships between the shapes of nanostructures and properties of polymeric materials reinforced by these structures. Related work seeks to determine the effect of external fields on the spatial distribution and properties of these materials.