A “Layered Look” for Spherical Nanoparticles in Semicrystalline Polymers

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In 1993, researchers at Toyota Central R&D reported that 5 wt % of an exfoliated clay could double the room-temperature modulus of nylon-6, a semicrystalline engineering plastic, and raise its heat distortion temperature by more than 80 °C—all without sacrificing toughness.1 That work stimulated a worldwide effort to synthesize and study polymer–matrix nanocomposites—and it also highlighted the importance of high filler aspect ratio, and good filler dispersion, in achieving these properties. In this issue of ACS Central Science, Zhao et al.2 demonstrate a more general route to nanoparticle reinforcement of semicrystalline polymers, achieving similar increases in modulus, again with no reduction in toughness—with spherical nanoparticles, rather than plate-like clay layers—simply by controlling the relative rates of particle diffusion and crystal growth.

The nylon-6-clay composites developed at Toyota were made by an in situ polymerization of the nylon-6 monomer, after it had swollen an organically modified clay.3 While this approach succeeds in exfoliating (and thereby thoroughly dispersing) the clay layers, such exfoliation is difficult to achieve for most polymer–filler combinations, and in situ polymerizations can be difficult to execute at the commercial scale. One would prefer to simply blend together preformed nanoparticles and polymer, much as one adds carbon black or silica to rubber to reinforce it for tire treads. And over the past few decades, a variety of effective approaches to graft spherical nanoparticles with polymer chains have been developed, to enable these particles to disperse well in a range of polymer matrices. But to produce significant stiffness increases in plastics (vs rubbers) requires high loadings of such spherical nanoparticles—much more than the ∼5 wt % required when the filler is a plate-like clay sheet. Indeed, nature recognized long ago the value of plate-like architectures, which it employs in seashell nacre (mother-of-pearl): an organic–inorganic composite showing both excellent stiffness and toughness, arising from its structure on multiple length scales and complex deformation mechanisms.4 Semicrystalline polymers also form a layered nanoscale structure, consisting of alternating crystalline and amorphous layers with a typical periodicity of 10–50 nm. If the nanoparticles could be selectively sequestered within the amorphous layers, then even modest overall nanoparticle loadings would translate to high local nanoparticle fractions, rendering those amorphous layers stiff—much like exfoliated clays. This is precisely what Zhao et al.2 have achieved.

Growing polymer crystals can concentrate nanoparticulate fillers into the amorphous layers between crystals, enhancing the stiffness of polymer–matrix nanocomposites.

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separated by large liquid-free regions (gas cells). At slower diffusion rates, the noncrystallizing component becomes incorporated between intraspherulitic fibrils, at the micron scale.\textsuperscript{5} Nanoparticles diffuse more slowly still, so they can segregate only on much smaller length scales: either “sandwiched” between the growing polymer crystals at the 10–50 nm scale, or if they cannot diffuse even that distance, they are essentially immobile and become “engulfed” by the growing crystals, a regime not seen in molecular mixtures. Zhao et al. observed this transition from “engulfed” to “interlamellar” nanoparticles in blends of poly(ethylene oxide) homopolymer, PEO, with spherical silica nanoparticles of 14 nm diameter, grafted with either poly(methyl methacrylate) or poly(methyl acrylate) chains (PMMA or PMA), by raising the crystallization temperature and thereby slowing PEO crystal growth.\textsuperscript{2}

The qualitative results of changing crystallization rate, shown by the TEM images in Figure 1, are striking: the nanoparticles are transformed from a uniform distribution at fast crystallizations, to an obviously layered structure at slow crystallizations. This change in structure is accompanied by a significant change in properties: an increase in modulus by \(\sim 40\%\) for the layered (vs engulfed) case, after accounting for the influence of crystallization rate on PEO crystallinity.

While the extent of segregation is difficult to quantify from the TEM images, by modeling the small-angle neutron scattering patterns from the nanocomposites, the authors estimated that only 26\% of the nanoparticles (whose silica cores comprise only 3.5 vol \% of the composite) are segregated into the intercrystalline regions. In other words, only 1\% of spherical silica nanoparticles—if selectively segregated into layers—can raise the composite modulus by 40\%.

![Figure 1](image.png)

**Figure 1.** Schematic of the transition between “engulfed” (isolated) and “interlamellar” (layered) spherical nanoparticles observed by Zhao et al.\textsuperscript{2} as the crystallization rate is reduced. Left: melt structure of nanocomposite, showing spherical silica nanoparticles (black, 3.5 vol \% of total) grafted with PMMA or PMA chains (red), dispersed in a matrix of molten PEO (blue). Center: schematics of solid-state structures, with PEO crystal stems shown as straight line segments, where the particles are principally engulfed (top) or principally interlamellar (bottom). Right: transmission electron micrographs (TEMs)\textsuperscript{2} reveal the order of the nanoparticles (black) in the PEO matrix (white). Scale bar = 200 nm.

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This proof of concept paper will doubtless spark further work in the area. One immediate question is the nature of the crystal surrounding the “engulfed” particles, which is represented only conjecturally in Figure 1: do the lamellar crystals, which are two-dimensional entities (and thus extend above and below the plane of Figure 1) “surround” the engulfed particle, leaving a particle-size “hole” in the plate-like crystal? Or does the growing crystal “bend” around the particle? There are also a number of practical avenues for
future research. Foremost among these would be to extend this work to polyolefins, by far the largest-tonnage polymers produced, and particularly to isotactic polypropylene (PP). PP is of interest for structural applications, such as automotive body panels and appliance housings, but its low glass transition temperature gives it a relatively low modulus compared with engineering plastics. To achieve the required stiffness, PP is typically reinforced with fibers (usually glass, sometimes carbon or aramid), but the large diameter of these fibers (10 μm or more) precludes their selective incorporation into the interlamellar amorphous layers, instead impacting structure at the level of polymer spherulites.\(^6\) To achieve a good dispersion of nanoparticles in PEO, Zhao et al. employed particles grafted with PMMA or PMA, both of which show favorable enthalpic interactions (negative Flory \(\chi\) parameter) with PEO, but this will be more challenging to achieve with polyolefins. Second, to achieve interlamellar segregation of nanoparticles, Zhao et al. needed to employ very slow crystallization rates, with crystallization times of as much as a week, compared with typical injection molding cycle times of seconds. To accelerate nanoparticle diffusion, the nanoparticle diameter could be reduced; the particles could be grafted with shorter (less entangled) chains; and the molecular weight (melt viscosity) of the polymer matrix could be reduced, but the practical limits of these approaches have yet to be explored. Finally, although this initial work reports only on mechanical properties, selective segregation of nanoparticles into layers by crystallization might also be expected to significantly influence the gas barrier, optical, and dielectric properties. Since crystals are easily oriented during processing, not only the mean values of such properties, but also their anisotropy, could be controlled through crystallization. In short, Zhao et al. have opened up a new route to tuning structure and properties in polymer–matrix nanocomposites, and this initial work can only hint at the many possibilities to follow.

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