

## NANOCOMPOSITES

## Stiffer by design

The full potential of nanoparticles in imparting new functionalities in polymer nanocomposites remains largely untapped. A widely applicable, two-solvent processing approach provides a hierarchical structure, affording unparalleled composite performance enhancement.

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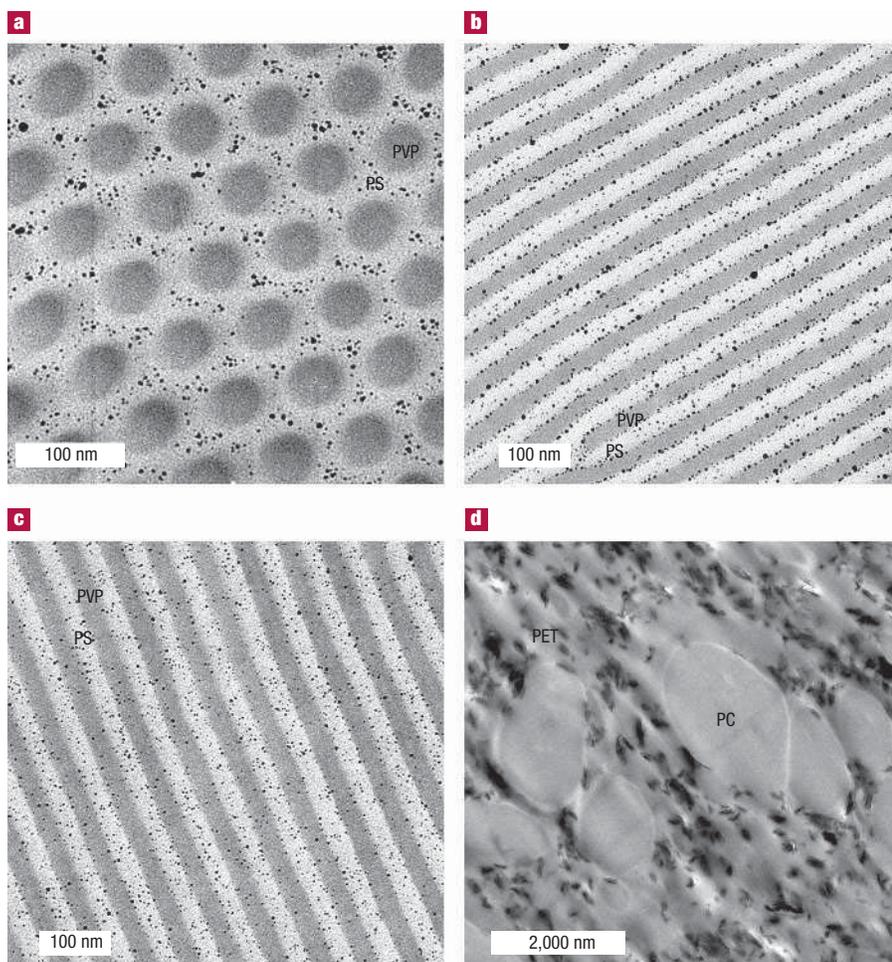
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**F**or most current applications of plastics, performance requirements, as well as cost and processing considerations, necessitate the introduction of additives and fillers into the polymer matrices. The use of nanoscale fillers push this strategy to the next level by exploiting the advantages that

nanometre-size particulates offer compared with macro- or microscopic fillers, such as huge surface area per mass, ultra-low filler levels required for connectivity through the sample (low percolation threshold), extremely small interparticle separations in a polymer matrix, and often very high length-to-width, or aspect, ratios. Most of the research efforts, and almost all of the commercial examples, of polymer-based nanocomposites to date have revolved around introducing nanoscale fillers into polymers and simply capitalizing on the

filler properties to enhance performance of the composites — this produces a class of polymer/inorganic materials that is perhaps better described by the term ‘nano-filled polymers’. On the other hand, the formation of ‘genuine’ nanocomposites introduces new physical properties and novel behaviours that are absent in the unfilled matrices, effectively changing the nature of the original polymer. This class of materials can be termed as ‘polymer/inorganic hybrids’ or ‘molecular composites’<sup>1</sup>. On page 76 of this issue, McKinley and colleagues<sup>2</sup> present



**Figure 1** A variety of multiphase polymer systems with selectively positioned nanofillers. **a–c**, polystyrene-bearing gold nanoparticles in a polystyrene–poly(2-vinylpyridine) block-copolymer (PS-*b*-PVP): gold nanoparticles selectively sequestered in the PS phase of a cylindrical PS-*b*-PVP morphology<sup>3</sup> (**a**), copyright (2005) Wiley-VCH; gold nanoparticles preferentially dispersed at the PS/PVP interface of a lamellar morphology (**b**) and in the PS lamellae (**c**)<sup>4</sup>, copyright (2006) American Chemical Society. **d**, Montmorillonite layered silicates selectively dispersed in the poly(ethylene terephthalate) domains of a poly(ethylene terephthalate)/polycarbonate blend. All these examples rely on highly sensitive and system-specific tailoring of thermodynamics to control the nanofiller partitioning. The approach presented by McKinley and colleagues<sup>2</sup> is a more general solvent-based approach that should enable similar preferential reinforcements in a wide variety of multiphase polymer systems.

a generally applicable approach to creating polymer nanocomposites with hierarchical structure, which fall into the latter category. By selectively reinforcing certain domains of a phase-separated block copolymer with an inorganic nanofiller using a two-solvent processing method, they achieve unprecedented performance improvements in stiffness, strength and heat resistance, without losses in elasticity of the composite. Their approach should be applicable to other combinations of materials, providing a new direction for future nanocomposite design.

In polymer systems with an existing phase-separated morphology, such as polymer blends and copolymers, selective reinforcements can lead to genuine

nanocomposite formation offering exciting opportunities and novel properties, for example, preferential reinforcement of one phase<sup>3</sup> or targeted reinforcement of the interphase<sup>3,4</sup>, filler-induced changes in phase morphology<sup>4</sup> or phase alignment, filler-induced compatibilization of immiscible polymer phases, and changes of thermo-mechanical transitions<sup>5</sup>. Figure 1 shows examples of systems where nanofillers have been selectively placed in certain regions of phase-separated blends. These have all been made possible by exploiting thermodynamic mixing of the filler with one component of the polymer phase.

McKinley and co-workers used an elastomeric block copolymer composed

of hard segments and soft segments; the hard segments phase segregate to form hard crystalline domains through hydrogen bonding. The authors used a two-solvent processing approach to disperse nanoparticles of Laponite — a layered silicate clay — preferentially within the crystalline hard domains, while the soft domains remained largely unaffected. Pristine Laponite is not thermodynamically miscible with hydrophobic polymers such as the one used by McKinley and colleagues, but this solvent exchange approach kinetically traps the inorganic nanofillers within the hard domains. The two solvents are selected to form a co-suspension of polymer and nanofillers and, during the evaporation of the second solvent, the inorganic fillers are immobilized within the hard domains owing to strong hydrogen-bonding interactions.

The selective reinforcement, combined with filler loadings above the percolation threshold and a choice of particulates that are comparable in size to the hard domains, leads to the formation of an extended interconnected network of hard microdomains. This morphology gives rise to unprecedented increases in stiffness of up to 23-fold and concurrent improvements in strength and heat deflection temperature (by up to 100 °C), while the elastic properties of the polymer are retained. This is a remarkable and unique set of property improvements that is impossible to obtain through traditional composite approaches and originates directly from the hierarchical morphology of these nanocomposites. The improvement in stiffness without sacrificing elasticity arises from the fact that the nanofillers are preferentially located in the hard domains. When the nanofillers are also dispersed in the soft domains, the elastic properties are lost<sup>2</sup>; in the extreme case, where the nanofillers are preferentially dispersed in the soft domains, the strength and ultimate extensibility of the nanocomposite are dramatically reduced<sup>6</sup>. In addition to this preferential reinforcement of the hard domains, the ultra-high magnitude of stiffness improvement is only possible because the fillers are of similar size to the hard domains (about 10 nm) and their volume fraction is high enough to allow for the development of interconnected network structures. When the volume fraction is below the level needed to create these extended structures, the magnitude of stiffness improvement is substantially smaller (about threefold<sup>2</sup>) and comparable to that of polyurethane elastomers 'nano-filled' by montmorillonite layered silicate particles<sup>7</sup> that are ten times larger. Larger nanofillers usually provide greater stiffness enhancements, so the preferential location of the filler in McKinley and co-workers' composites is critical to the magnitude of improvement in properties.

The impacts of the above study reach far beyond improving the thermomechanical properties of polyurethane elastomers by layered-silicate fillers, particularly because this approach is not limited to the system studied. For example, a natural extension of the above design principles aiming to selectively disperse carbon-nanotube fillers in shape-memory polyurethane matrices<sup>5</sup> would almost certainly lead to large improvements of the shape-memory properties of these systems — an idea that is pointed out by the authors. In another example, selective reinforcement of the hydrophobic phase of a fuel-cell proton-exchange membrane — aiming to increase its stiffness by formation of an

extended network — would also prevent collapse of the hydrophilic domains at low hydration levels, thus extending the fuel-cell operation to much higher temperatures than currently possible. The two-solvent approach put forward by McKinley and co-workers would allow for such a preferential reinforcement of the selected/appropriate phase in both the above examples, as it relies on selective solvation of filler and polymer rather than polymer/filler thermodynamics of mixing.

These materials are a paradigm of exploiting the hierarchical nanocomposite structure, rather than the inherent physical properties or the reinforcement ability of the nanofillers, to give rise to novel properties.

This work thereby exemplifies a shift in focus from ‘nano-filled’ composites to genuine ‘molecular-composite hybrids’, where the interconnection of selectively reinforced domains leads to new functionalities.

#### References

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