In the early 1960s, polymer composites are in the spotlight and this field is treated as a new template for prototyping high-performance materials for exploration in different applications. In the past two decades, polymer nanocomposites took the limelight away from conventional polymer-based composites due to their promising potential. One facet that is often highlighted as a reason for their dominance is their ‘size-dependent functionality’. Auffan et al. [1] concluded that there is a critical size that is considerably smaller than 100 nm at which properties of particles change. They identified this critical size of about 20–30 nm by relating the exponential increase in the number of atoms localized at the surface to the size of nanoparticles (Figure 1.1). This excessive increase in surface energy of nanoparticles results in crystallographic changes [1, 2], and subsequently effects their interfacial reactivity [3, 4].

Even size dependence of optical and electronic properties as well as bactericidal effects is well reported [5–7]. Silver nanoparticles, for instance, show highest bactericidal effect in the 1–10 nm range, where there are more highly reactive {111} surfaces [6]. These nanoparticles penetrate cell membranes of bacteria to strongly interact with sulphur- and phosphorus-containing compounds. In the process, they release toxic silver ions. In fact, this suggests that particle dissolution is another parameter that is size-dependent. Solubility, although dependent on solvent properties, is also dependent on solute (nanoparticles) properties like specific surface area (in turn, surface energy and interfacial reactivity),

Edited by Aravind Dasari and James Njuguna.
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surface morphology, and dispersion state [8]. More interestingly, these properties are manipulated by changing interactions between them and organic ligands. An example is the use of alkylamines as capping ligands in the control of the size and shape of ruthenium nanoparticles (spherical or rod-like) [9]. Another example is boehmite. By controlling the pH and ionic strength of the synthesis medium, 100-nm-sized fibres (or rods) and even 10–25-nm-sized diamond-shaped particles are formed [1, 4]. Importantly, fibres have (100) as lateral faces and (010) basal planes; and diamond-shaped particles are with (101) lateral faces.

The above discussions suggest that the presence of nanoparticles in a polymer system provides an opportunity to alter many of the base properties of the system. The extent of alteration and the potential of these materials to exhibit superior properties are dependent on two major aspects: interface between polymer and matrix and confinement of polymer matrix chains at the nano-level.

1. **Interface**: It is generally believed that interface is a region with altered chemistry, altered polymer chain mobility, and altered crystallinity [10]. Figure 1.2 shows a schematic of interface region in two systems: micro-composites and nanocomposites [11]. With the same volume fraction of filler, the higher radius of curvature of nanoparticles ensures that more polymer is involved in the interfacial regions. This huge interfacial area created by well-dispersed nanoparticles is shown to influence the surrounding polymer matrix for several radii of gyration [12], fundamentally influencing the glass transition temperature, $T_g$ and mechanical properties of the matrix. This suggests the importance

Figure 1.1 Percentage of atoms localized at the surface of a nanoparticle as a function of its diameter. Grey line indicates the boundary below which non-bulk properties emerge. Auffan et al. [1]. Reproduced with permission of Nature Publishing.
of having a greater degree of control on the interface in polymer nanocomposites. Changes in $T_g$ are particularly important, not only because they yield insights into the fundamental changes in polymer chain dynamics, but also because the associated gains in thermal stability are critical. With many nanoparticles (particularly those with high aspect ratio), results showed that a noticeable change in $T_g$ occurred only when inter-particle distances are less than 500 nm [13]. As an example, Figure 1.3 shows changes in $T_g$ for some polymer nanocomposites (based on graphene and carbon nanotubes) [14]. Though this number (500 nm) is qualitative and subjective (and much larger than that predicted by theory [15]), it indicates that inter-particle spacing is important in influencing intrinsic properties of a polymer.

2. Nanoscopic confinement of polymer chains: It is known that under conditions of nanoscopic confinement, conformation of chains and segmental mobility are highly affected, suppressing the conventional spherulitic superstructures and resulting in growth of structures with specific crystal orientations. These concepts of confinement/restricted mobility in well-defined geometries and different dimensions versus crystallization have been the subject of many investigations [16–18]. Various reasons are considered for the formation of interfacial zones ranging from chemisorption (e.g. interaction of polar groups with inorganic fillers), to geometric confinement.

Geometric (spatial) confinement specifically hypothesizes that nanoparticles like carbon nanotubes might be treated as macromolecules as their diameters are similar to the radius of gyration of a polymer. Their highly curved surfaces result in strong geometric confinement (by allowing preferential orientation of lamellae) even if (lattice) matching between polymer chain and the filler (graphitic sheet) is absent. This is termed ‘soft epitaxy’ [19, 20]. While in the case of large diameter particles, as the surface curvature is small, the polymer behaves as if it is on a flat surface and, therefore, require crystallographic lattice matching for preferential lamellae organization. The behaviour of large-diameter carbon fibres and
small-diameter carbon nanotubes is shown in Figure 1.4. However, there are many other studies that reported the absence of soft epitaxy despite a uniform dispersion of nanoparticles with sizes similar to or less than individual lamellae. This suggests the complexity in analysing an interface as it is affected by even the slightest change of shape, size and surface modification (influencing the surface energy) of the particles along with their dispersion/inter-particle distances.

Regardless of these discrepancies about interfacial zones, it is rather more important to identify whether their presence would enhance the filler-polymer interfacial strength and ultimately result in improved mechanical properties. Though mostly positive results are reported in the literature on stiffness and strength of polymer nanocomposites, toughness/ductility is often dramatically reduced (in line with the scaling/dimension arguments) [21]. Nevertheless, their promising potential is realized, in particular with functional and physical properties. On this positive note, in this book, we cover a range of functional and physical properties of these materials, with basics as well as advanced and in-depth knowledge on various facets of these properties. These include optical, magnetic, thermal, energy scavenging, biosensing, gas/water barrier, anti-microbial, and biodegradability. As discussed earlier, it is also important to understand how the

![Figure 1.3 Changes in T_g for some selected polymer nanocomposites. FGS, functionalized graphene sheets produced by rapid thermal expansion of completely oxidized graphite oxide; PAA, poly(acrylic acid); PAN, poly(acrylonitrile); PMMA, poly(methyl methacrylate); SWNTs, single-walled carbon nanotubes. Adapted from Ref. [14]](image-url)
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nanoparticles are dispersed and distributed (inter-particle spacing) in a polymer matrix as many intrinsic properties of polymers are influenced by this. Therefore, to kick-start the proceedings, an entire chapter is dedicated towards three-dimensional microstructural characterization of nanocomposites.

References

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