COMMENTARY

Polymer/carbon-nanotube nanocomposites: from innovation to commercialization

Arun K. Kota

University of Michigan, Department of Materials Science and Engineering,
Ann Arbor, MI 48109, USA
arun_kota@yahoo.com

With the availability of new and improved processing and characterization techniques, researchers have become increasingly interested over the past decade in altering homogeneous polymeric-matrix materials by adding nanoscale fillers (less than 100 nm in at least one dimension) to create what are now being called polymer nanocomposites. The most notable structural feature of the polymer nanocomposites is the enormous interfacial area between the nanoscale fillers and the polymer matrix. This becomes clearly evident when polymer composites containing microscale fillers are compared with those containing nanoscale fillers. For example, consider two different polymer composites containing the same volume fraction of the filler, but one with 1-μm-diameter spherical filler particles and another with 1-nm-diameter ones. As the radius of the spherical filler particles drops from the microscale to the nanoscale, the number of filler particles increases by one billion times, the mean particle–particle separation decreases by one thousand times, and the total interfacial area increases by a thousand times.

Due to the large surface area of nanoscale fillers, polymer nanocomposites have a large volume of interfacial polymer, as shown in Fig. 1. Almost the entire matrix can be interfacial polymer even at filler volume fractions as small as 5 vol.% [1]. This is critical because the interfacial polymer can have significantly different morphology and material properties compared to the bulk polymer (which is not at the interface). Thus, the resulting polymer nanocomposite may exhibit synergistic material properties that are well beyond those predicted by simple additive models for traditional microcomposites. In polymer nanocomposite literature, this synergy is sometimes termed as the *nano effect* or the *nano advantage*.
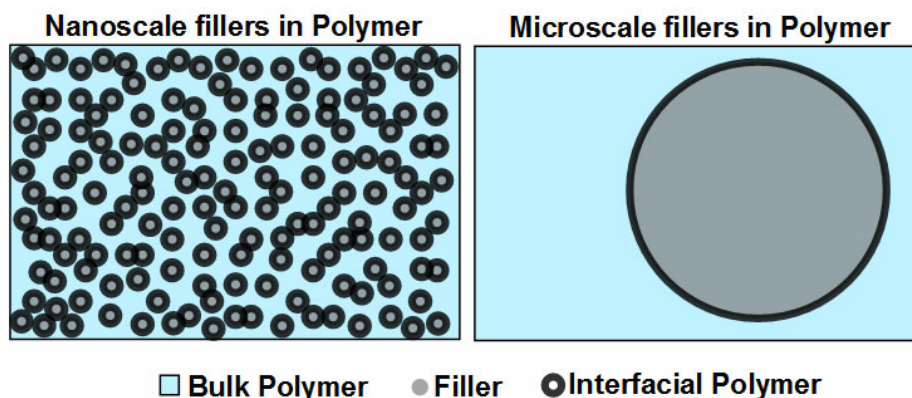

Fig. 1. Schematic showing the significant difference in the volume of the interfacial polymer (black) in polymer composites with nanoscale and microscale fillers.

Among the various nanoscale fillers, carbon nanotubes (CNTs), both single- and multi-walled, have been identified by materials scientists as having the greatest potential to revolutionize the technological landscape of the century ahead. Their extremely high surface-to-volume ratios along with their high electrical conductivity ($\sim 10^4$ S/cm), high thermal conductivity ($\sim 6 \times 10^3$ W/m K), high mechanical modulus (~ 1 TPa), and low density make them particularly attractive [2]. When added to polymeric matrix materials, they form polymer/CNT nanocomposites, which in turn show significant promise for applications in diverse high-performance and multifunctional materials.

Methods to fabricate polymer/CNT nanocomposites have overwhelmingly focused on improving CNT dispersion because, in most cases, better dispersion correlates with better material properties. Among the various methods employed, three techniques are very common: solution blending, melt mixing, and in-situ polymerization. In solution blending, the CNTs are dispersed in a suitable solvent, the polymer is separately dissolved in the same solvent, the two solutions are mixed together and the nanocomposite is recovered by precipitation or evaporation of the solvent. In melt mixing, the CNTs are added (as a powder or a suspension) to the polymer melt at a high temperature, high shear forces are employed to achieve the desired mixing, and the nanocomposite is obtained after cooling to room temperature. In in-situ polymerization, the CNTs are dispersed in the monomer followed by polymerization to obtain the nanocomposite. Each of these three methods has its own merits and demerits. While solution blending is a small-scale laboratory technique, melt mixing is an easily scalable industrial technique. However, the high viscosity of the nanocomposite melt limits good dispersion in melt mixing to low loadings. While in-situ polymerization can be done both via solution blending and melt mixing, it is significantly more complicated. Thus, the choice of the process is significantly influenced by the eventual performance targets of the investigation.

Once the process has been identified, the mixing of CNTs and the polymer must be optimized. Too mild mixing would lead to aggregates of CNTs, while too aggressive mixing would lead to damaged CNTs. Most researchers have used isotropic dispersion of CNTs as a benchmark for this optimization. However, dispersion of CNTs is a subjective measure when studied only via optical, confocal or electron microscopy. Recently, researchers have started using x-ray scattering in tandem with electron microscopy to quantify dispersion in terms of size, dimensionality and structure of the primary particle, the secondary aggregate, and the hierarchical agglomerate [3].

Provided that there is good dispersion, a major advantage of the polymer/CNT nanocomposites is their potential to exhibit material properties similar to the highly loaded conventional polymer/carbon-fiber microcomposites, at relatively low loadings. Over the past decade, researchers have found impressive electrical and thermal properties in polymer/CNT nanocomposites at low loadings, but mechanical properties were far below the expectations [1-4]. In general, the most impressive performance enhancement has been the improvement of electrical conductivity by more than 15 orders of magnitude higher than that of the polymer matrix to values as high as 100 S/m [5] with percolation thresholds as low as 0.002 vol.% [6]. The most promising results in thermal conductivity show an improvement of 2 to 3 times that of the polymer matrix at loadings on the order of 0.5 vol.% [7]. The lesser increase in thermal conductivity is because the difference in thermal conductivities of CNTs and polymers is not as significant as their difference in their electrical conductivities. The mechanical properties, which are considered to be the most important deliverables of these nanocomposites, showed an improvement that is below an order of magnitude that of the polymer matrix at loadings as high as 5 vol.% [1]. These modest improvements are significantly below the idealized theoretical predictions that in turn are attributed mainly to poor load transfer.

Although there have been significant strides in realizing the potential applications of polymer/CNT nanocomposites, the hype surrounding the claims has far exceeded the delivery of the product. Research activity on these nanocomposites is quickly reaching a stage where

the research front has to move from innovation to production and growth. In order to do so, the following fundamental and production challenges need to be addressed quickly and efficiently:

- **Interface Dynamics:** The mechanical properties are very sensitive to the interfacial adhesion between the polymer and the CNTs. It cannot be emphasized enough how important it is to tailor these interfaces such that the carefully chosen polymer matrix and the functionalized or non-functionalized CNTs have favorable interactions. While there have been significant efforts in this regard, there is a need for a breakthrough to obtain a synergy that is beyond simple additivity.

- **Property Prediction:** In addition to experimental studies, it is important to develop theoretical models and simulation that can predict the macroscopic material response in order to help elucidate the underlying physical mechanisms and consequently enable efficient design of the nanocomposites [8]. While there have been several modeling efforts so far, they are all faced with one big challenge: the properties of the interfacial layers are not known.

- **Significant Variable Identification:** Most of the studies conducted so far have focused on establishing the structure-property relationships and very few systematic studies were conducted to identify the effect of processing conditions on the resulting structure. Knowledge of the significant process variables is extremely crucial in scaling-up a process and should be gathered hand-in-hand with the structure-property screening.

- **CNT Cost**: Although there have been substantial property improvements, the cost of CNTs, while decreasing, is not low enough to warrant a competition of these nanocomposites to existing alternatives or their penetration of newer markets. It is incumbent on CNT manufacturers to convince potential customers of the viability of these nanocomposites.

In summary, there is a pressing need for more systematic studies and some significant breakthroughs in the next five years for true commercialization of polymer/CNT nanocomposites. Until the fundamental questions are resolved, they remain limited to research laboratories and high-value niches where the end-users see a significant benefit in such materials.

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