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Nanodiamond–polymer composites

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1. Introduction

Historically, polymer reinforcement has been one of the first and most obvious applications for nanoparticles, which emerged in the early 1990s. The first reports on polymer nanocomposites can be traced back to 1992 [1–5]. However, carbon-black-filled rubber, one of the premier materials engineering successes of the 20th century, can be considered as a polymer nanocomposite known from much earlier time. According to modern definition, *polymer nanocomposite* is a material consisting of a *polymer matrix* and *filler nanoparticles*, which have at least one dimension in the *nanoscale range* (less than 100 nm) and can be "organic" or "inorganic" in the sense these terms are used in chemistry [6]. In a typical case, the polymer matrix constitutes the main part of the nanocomposite's weight or volume. However, sometimes the ratio of polymer to nanoparticles is reversed, in which case the composite material can be considered as a polymer-impregnated porous solid body [7] or as self-suspended nanoparticle fluid also called "*nanoscale organic hybrid material*" [8]. The nanofillers can be *zero*, *one*, or *two-dimensional*, having 0, 1, or 2 dimensions larger than 100 nm, correspondingly. Among different nanofillers, carbonaceous nanoparticles such as graphene (2D), carbon nanotubes (CNTs — 1D) and nanodiamond (0D) are very promising due to their unique and highly tailorable combination of properties, such as mechanical strength, electrical conductivity, aspect ratio, etc [9].

The main benefits of nanoparticles are related to their small size and a much larger surface-to-volume ratio as compared to micrometer-

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sized particles. In polymer nanocomposites, the larger surface-to-volume ratio of the nanofillers results in a dramatic increase in the volume of the "*interphase*", i.e., the volume of the polymer which is close enough to a nanoparticle so that its properties are influenced by the nanoparticle and are different from the bulk polymer. In fact, when the filler size is reduced to the nanoscale, the volume of the interphase may exceed the volume of the particle, whereas for micrometer-sized fillers the volume of the particles always exceeds that of the interphase [5]. This, in turn, allows nanofillers to exert significant impact on the polymer properties even at low concentrations. For example, for 1 vol.% dispersion of 4 nm diameter nanospheres in a polymer, assuming the interphase thickness 6 nm around each nanoparticle, the volume fraction of the interphase in the composite is ~63 vol.% — more than half of the total volume [5]. Therefore, instead of adding 15–50 vol.% of standard fillers, the same improvements in mechanical properties can be achieved with only 5 vol.% of a nanofiller, resulting in reduced cost while also reducing weight [10] and preserving valuable properties of polymer matrix, e.g., plasticity and toughness. At larger sizes, however, the nanofillers quickly become less effective: with 1 vol.% of 40 nm diameter nanospheres and same interphase thickness, the interphase fraction reduces to 12 vol.% [5]. Small size provides other, less obvious benefits. For example, when the nanofiller particles are smaller than the random coil size or radius of gyration of the polymer, good dispersion is achievable even in cases when the particles and the matrix might be otherwise considered incompatible [11]. Besides small size, nanofillers bring in useful properties of the material they are made of. For example, carbon nanotubes and graphene are conductive and can be used to improve electrical and thermal conductivity of the polymers; luminescent semiconductor quantum dots impart luminescence to the composite, novel 2D transition metal carbides/nitrides (MXenes) may provide higher mechanical strength and conductivity, while in contrast to graphene being hydrophilic and strongly interacting with water-soluble polymers [12]. Finally, reactive chemical groups exposed on the surface of some nanoparticles can be used to form covalent bonds (a strong "*interface*") with the polymer matrix, which, in combination with the large surface-to-volume ratio of the nanoparticles (high fraction of the interphase) may result in super strong or highly thermally conductive polymer composites. Additionally, these surface functional groups can be used to improve the nanoparticle dispersion in the matrix through achieving favorable nanoparticle – polymer interactions, as well as suppressing unfavorable nanoparticle – nanoparticle interactions.

Composite properties depend on its composition and structural characteristics. Taking into consideration mechanical properties, for example, the Young's modulus enhancement depends on intrinsic properties of the matrix and the filler, as well as the interactions between them. Tensile strength and ultimate strain, on the other hand, are more sensitive to defects. Due to a complex interplay of these structural characteristics, as well as additional factors such as thickness and properties of the interface and interphase, nanofiller dispersion quality, intrinsic properties of the nanoparticles, etc., it is not surprising that creating a quantitative theory of nanocomposite properties is a very challenging task [13], necessitating the need to use simplified models (such as additive schemes) or adaptation of predictive models developed for traditional composites (for example composite micromechanics models), as well as extensive use of computational atomistic-level modeling [14,15]. However, special care should be exercised when micromechanics models developed for traditional composites with moderate concentrations of the microfiller are transferred to nanocomposites where the nanofiller concentration is typically much lower, because traditional theories of micromechanics do not account for a meaningful change in properties when so little material is replaced. Thus, the mechanics must be understood as arising from load transfer as much as from load bearing [1], emphasizing again the role of the interface between the components of the nanocomposite. In view of this, three-phase micromechanics models taking into consideration the matrix, the filler, and the interphase are being developed [16–19], producing an overall better agreement with experimental and atomistic computational modeling results.

Current research in polymer nanocomposites has many facets, aiming at discovering novel nanofillers, improving dispersion and bonding (interface) between the nanoparticles and the matrix, developing nanocomposite theory, resolving manufacturing issues such as unacceptably high viscosity of some polymer-nanofiller melts, etc. Although our understanding of all these aspects has considerably improved over the past years, the promises of nanocomposites to a large extent still remain elusive. Similar to a majority of other engineering materials, the man-made nanocomposites are either stiff (high Young's modulus) but brittle (low strain at failure), like ceramics or extensible but weak, like rubber. At the same time, nature-made nanocomposites such as

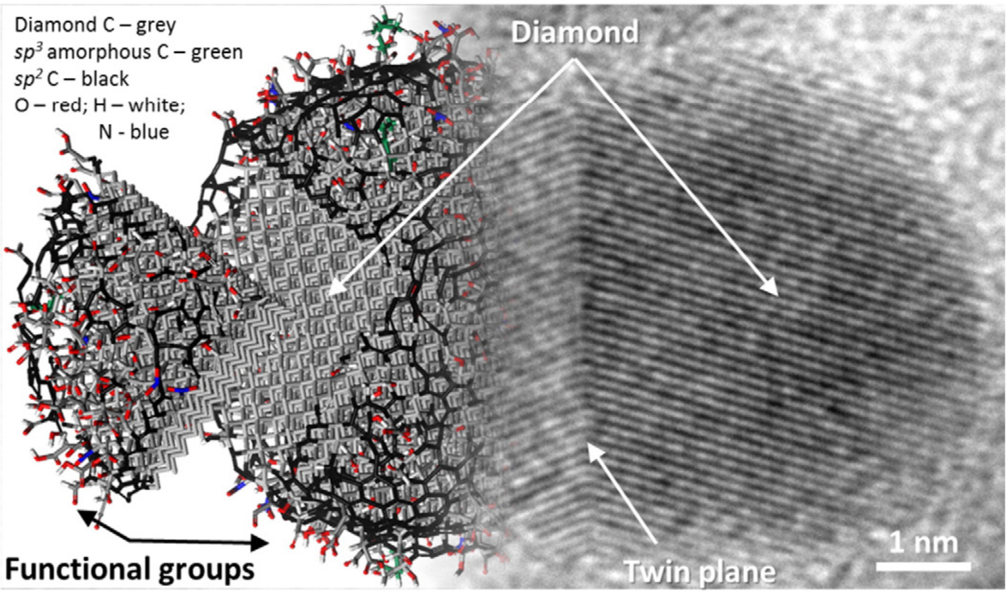

Fig. 1. Blended high resolution TEM and atomistic model of a single ND particle, showing internal diamond structure with a typical twin defect and surface functional groups.