A Review on Polymer/Nanodiamond Composites: Fabrication methods and applications

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A Review on Polymer/Nanodiamond Composites: Fabrication methods and applications

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Abstract: *The advent of nanodiamond-based polymer nanocomposites has been highlighted by recent studies and discoveries. ND particles offer numerous advantages over other carbon nanomaterials, with a variety of mechanical, chemical, optical, and biological properties. This review focuses on the fundamental characteristics and some synthetic methods of polymer/ nanodiamond nanocomposites, such as electrospinning, solution casting, and polymerization methods. Additionally, discusses biomedical and supercapacitor applications for nanocomposites.*

Keywords: Nanodiamond, nanocomposite, electrospinning, supercapacitor, and biomedical

1-Introduction:

Nanomaterials, including graphite, graphene, carbon nanotubes, carbon quantum dots, and nanodiamonds, have been investigated for mechanical, chemical, physical, and biomedical applications beyond their bulk materials [1–4]. One of the most appealing and promising carbon-based nanomaterials for use in cutting-edge technological applications is nanodiamond (ND). Therefore, it is crucial to be able to design and regulate the synthesis and structure of NDs. Because of their high surface-to-volume ratio and nanoscale size, ND particles might encourage the development of a unique interphase in polymer matrices, which could result in notable improvements in polymer characteristics even at low filler loadings. Since the first publication on nanodiamonds (NDs) in 1963, much has been made in their manufacture and uses [5]. NDs have exceptional mechanical, thermal, and optical capabilities due to their unusual extended carbon sp^3-hybridized structure. They also have a large specific surface area and an adjustable surface chemistry [6].

A wide variety of nanodiamonds (NDs) are currently available for study, which reflects the breadth of production methods created in recent decades. High-energy ball milling of high-pressure high-temperature (HPHT) diamond microcrystals [7], plasma-assisted chemical vapor deposition (CVD) [8], autoclave synthesis from supercritical fluids [9], ion irradiation of graphite [10], electron irradiation of carbon "onions" [11], detonation synthesis, laser ablation [12] Ultrasonic cavitation [13] is a few of these. The most often used techniques in commercial manufacturing are detonation synthesis and high-pressure high-temperature, which are two opposite approaches as shown in Figure 1.

Polymeric materials have been widely used in the construction of structural elements because of their broad applicability in a variety of industrial applications. To improve their mechanical and electrical qualities, researchers are still working to create new composite materials by adding nanoparticle fillers [14]. Because of their high surface-to-volume ratio, which greatly enhances interfacial interactions inside the composite matrix, spherical nanoparticles have become one of the most appealing nanofillers among these [15]. Recent years have seen a rise in interest in nanodiamond (ND)-based polymer composites, as indicated by the expanding corpus of research on the topic. For the creation of cutting-edge polymer-based products, NDs are very appealing due to their distinctive structural morphology and remarkable physicochemical characteristics. It is commonly known that adding NDs to polymer composites can greatly improve their mechanical, thermal, tribological, and rheological characteristics of polymer matrices [5,16]. Their potential for biomedical and other high-performance applications is further enhanced by their intrinsic biocompatibility [17,18].

Differentiating from background fluorescence can be made more difficult by the structural and functional changes that coupled nanodiamonds (NDs) may cause in related proteins. Additionally, other dispersion methods like sonication, vortex mixing, in situ polymerization, solution blending, and others are used to introduce NDs into polymer matrices. Strong interfacial contacts within the composite system can be facilitated by chemically bonding functionalized NDs to the amide and imide groups found in specific polymers using techniques like melt mixing and solution processing [19,20].

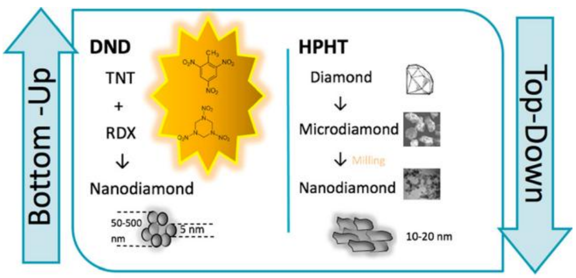

Figure 1. Schematic representation of the two main approaches for nanodiamond (ND) synthesis. Reprinted with permission from Ref [14]; Copyright 2021, American Chemical Society.

3-Fabrication methods of polymer/ND composites

3.1- Electrospinning method

One of the simplest and most effective physical processes for creating conductive polymer nanostructures is electrospinning. Understanding how to control the production of nanofibers and the complex electrospinning process has advanced significantly since the early 1990s [21,22]. It may be used to produce continuous micro/nanofibers in large quantities from a variety of polymers and composites. Electrospun fibers have many advantages, such as an inexpensive process, homogeneity, high surface porosity, a high surface area-to-volume ratio, and better mechanical strength.

Figure 2. represents steps of solution preparation and fabrication of nanofibers, which involve, firstly, a very volatile solvent dissolving the polymer [23]. When creating smooth and bead-free electrospun nanofibers, the solvent is crucial [24] for easy processing. It is better to use volatile solvents because they help the nanofibers develop through evaporation as they go from the capillary tip to the collection surface. However, because of their low boiling points and quick rates of evaporation, extremely volatile solvents are usually avoided as they may cause the jet at the needle tip to dry up. The electrospinning process may be hampered by a clog at the needle tip brought on by this drying action [25]. Alcohols, dichloromethane, chloroform, tetrahydrofuran (THF), dimethylformamide (DMF), acetone, dimethyl sulfoxide (DMSO), hexafluoroisopropanol (HFIP), and trifluoroethanol are some of the solvents that are widely utilized.

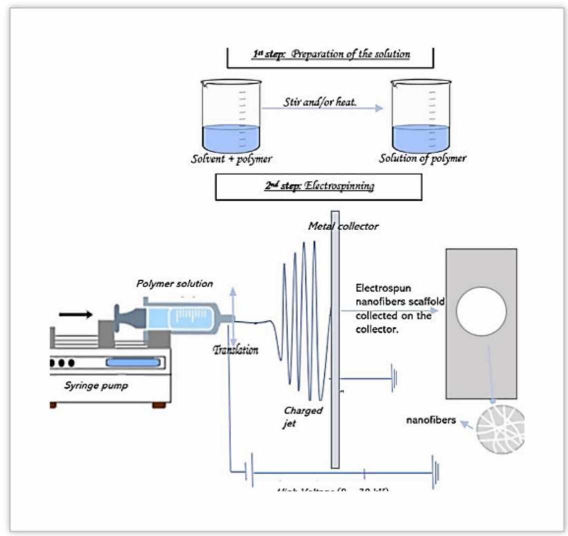

Figure 2. Schematic diagram of the electrospinning method [23].

As seen in Figure 2, the setup of this process typically consists of four major parts: a spinneret, a syringe pump, a high-voltage power source, and a conductive collector. Because of the enhanced electrostatic field between the collector and spinneret, electrospun fibers are created when the repulsive force of a charged solution overcomes the solution's surface tension. The jet can be simultaneously stretched, elongated, pulled, and bent by the electrical force, which accelerates solvent evaporation and produces nano/microfibers [26]. The structure and morphology of the resulting polymer nanofibers, as well as the success of the electrospinning process, are often described by a collection of characteristics pertaining to the polymer, solvent, polymer solution, processing parameters, and ambient conditions [27,28].

The electrospinning process was effectively utilized to achieve a fine dispersion of nanodiamond (ND) particles within various polymeric matrices, which Guk Young Ahn et al. [29] have created electrospun PCL/ND composite fiber. Scanning electron microscopy (SEM) pictures of polycaprolactone (PCL) fibers with different nanodiamond (ND) particle concentrations showed that the fibers were discovered to be oriented in various orientations, and by adjusting the flow rate and voltage during the electrospinning procedure, their thickness was maintained at about 1.8 µm. Notably, the development of thicker fibers can have a beneficial effect on the scaffold's tensile strength as well as cell proliferation [30,31]. In a different work, the electrospinning process was effectively used to create polyurethane/nanodiamond (PU/ND) composite membranes [32]. The resultant fibers had a clean surface morphology, a consistent thickness distribution, and a noticeable rise in average fiber diameter as the nanodiamond content rose, as explained in Figure 3.a. FTIR confirms interactions between polymer and nanodiamond as shown in Figure 3.b, which indicates that the crystallinity of the polyurethane matrix is improved by the incorporation of nanodiamonds (NDs), as demonstrated by the intensified characteristic absorption peaks observed near 1700 cm^{-1} in the FTIR spectra.

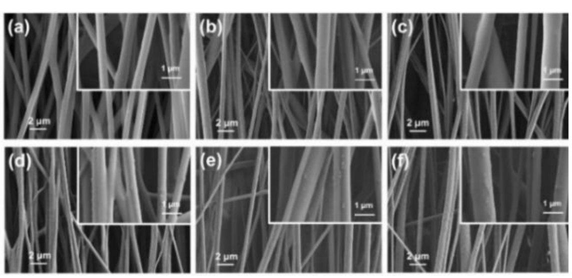

Figure 3.a. SEM morphology of PU/NDs composite with varying of nanodiamond (a-f). Reprinted with permission from Ref [32]; Copyright 2024, American Chemical Society.

Similarly, Poly (vinyl alcohol) (PVA)/ND were electrospun into nanofibers and induced homogenization and shrinkage of composite nanofibers [33].

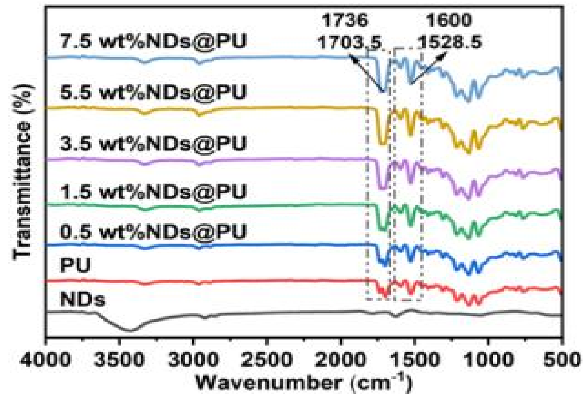

Figure 3.b. FTIR spectra of PU/NDs composite with varying amounts of nanodiamond. Reprinted with permission from Ref [33]; Copyright 2024, American Chemical Society.

3.2- Solution casting method

This is a historically significant and rather easy method of fabricating nanocomposite materials. One of the earliest techniques for making plastic films was first created by Eastman Kodak in the 19th century for the manufacture of photographic films. A simple and adaptable method for creating composite thin films or sheets is the solution casting technique. This method involves dissolving the polymer matrix in either water or a volatile non-aqueous solvent first, then adding nanoscale additives. After that, the mixture is poured onto a level surface. The desired polymer nanocomposite is obtained by separating the dried film from the substrate after solvent evaporation [34]. Using the solution casting method, Asima Siddiqa et al. prepared PVDF-PANI/NDs composite membranes [35]. *N, N*-dimethyl formamide (DMF 99%) was used to dissolve the polymer with amounts of PANI/ PVDF in ratio 2:1 (wt%) while NDs with different concentration from (1-5) wt%. in this work, there is no discernible segregation of nanodiamonds (NDs) on the surface, suggesting that the matrix (PANI/PVDF) and the filler material (NDs) interact effectively [36] as shown in SEM images. Additionally, the existence of ND in the PANI/PVDF polyblend is confirmed by FTIR spectra.

3.3- In situ polymerization

In situ polymerization represents a widely utilized technique in the field of polymer chemistry for the synthesis of polymer nanocomposites. This procedure entails creating the composite material while the nanoparticles are still in the polymerization mixture. Short-chain molecules called unstable oligomers are required in many chemical processes. It's crucial that these oligomers are created in situ—that is, inside the reaction mixture itself—as opposed to being created separately beforehand, because they may be extremely reactive or short-lived. In situ polymerization creates a hybrid material by fusing nanoparticles and polymer chains. An initiating phase precedes several polymerization stages, which culminate in the production of the intended nanocomposite [37]. PDA/PPy/ND TEM pictures [38] provide greater in-depth information about the material's hierarchical structure by displaying its interactions and organization at the nanoscale, which confirms the existence of ND after the polymerization. Additionally, the XRD pattern shows the full preservation of ND crystals in the composite with the emergence of the distinctive peak at 2θ= 43.6o, which corresponds to the ND (111) plane [39].

4- Polymer/ND composite applications

Numerous studies have been conducted on the application of nanodiamonds (NDs) as fillers in polymer composites, including elastomeric materials, thermosets, thermoplastics, and products based on biopolymers. These studies have demonstrated that adding NDs to such materials improves their mechanical qualities. The propensity of nanodiamonds (NDs) to aggregate and disperse unevenly inside the matrix is one of the primary disadvantages of their use in polymer composites. They are less able to physically reinforce the material because of having a smaller effective surface area. To overcome this issue, additional compatibilizers are commonly used to enhance the interactions at the interface between the filler and the polymer matrix.

4.1- Biomedical application

Because of their huge surface area, high aspect ratio, and porous structure—features that are especially beneficial in the medical field—fibers are frequently used in biomedical applications, mainly in the form of electrospun nanofibers [40]. Nanofibers based on nanodiamond (ND) polymers have demonstrated promise for usage in several biological applications, including medication delivery systems, sensing, imaging, wound dressings, and scaffolds for cell growth [17,41–43]. Solvent casting was used to create a PVA-ND film with improved mechanical properties for broader biological applications [44]. Brady et al. reported on the electrospinning of PLGA with ND. In contrast to pure PLGA, the fibers in PLGA-ND composites were noticeably thicker, and the void areas between the fibers were found to be smaller. In comparison to pure PLGA, the results demonstrated that using primary human stem cells from humans to seed the nanocomposites improved cell spreading. The oxygen termination on the surface of the diamond nanoparticles causes the ND-loaded scaffolds to become more hydrophilic, was credited with this improvement [45]. Another important consideration for biological applications is toxicity. A human embryonic kidney (HEK) cell line was used to assess the harmful effects of PANI/ND nanocomposites [46]. The cytotoxic effect was determined to be minimal when the PANI/ND nanocomposite was administered to the cells at a dose of 0.05 ppb. At low doses, the nanocomposite's toxicity was negligible. Furthermore, throughout the incubation phase, the addition of the nanocomposites had no effect on the morphology of the cells. The use of NDs improved the stability of the film. Additionally, a bacterial strain—specifically, E. coli—was used to investigate the toxicity of the PANI/ND nanocomposite.

4.2- Supercapacitors application

Technological developments in supercapacitors have created a multitude of possible uses in fields such as electronics, batteries, electric cars, energy storage, power and energy management, and compressed air energy storage [47]. Nevertheless, despite these advancements, no supercapacitor device to date has completely satisfied the technological and financial needs of contemporary energy storage systems. Notably, the utilization of conducting polymer-based nanocomposites in applications involving supercapacitors has led to notable advancements [48]. PANI-ND composites [49] was applied as electrodes for Symmetric supercapacitors with 3–28 wt% ND. This composite's electrochemical experiments were conducted using 1 M H_2SO_4 electrolytes in a symmetrical two-electrode configuration. In this study, cycle stability and capacitance retention at high sweep rate were improved, as the specific capacitance of the chosen PANI electrodes implanted with nanodiamonds (NDs) rose to 640 F g^{1-1} after 10,000 galvanostatic charge-discharge cycles. Also, creation of the ITO/PANI-g-ND structure, Gopalan et al. [50] employed an electrochemical technique to graft polyaniline (PANI) chains onto nanodiamonds (NDs) supported on indium tin oxide (ITO). Kausar A. [51] prepared PVDF/PEDT/PANI-ND composite by the in-situ method and reinforced in combination. For this work, every nanocomposite's electrical conductivity rose, with PVDF/PEDT/PANI-ND5 achieving the highest value (3.0 S cm−1), and after 300 cycles, Spectroscopy of electrochemical impedance showed 90% Efficiency of Coulombs and 900 mA h g^{-1} specific capacity.

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