Radiation-Assisted Synthesis of Polymer-Based Nanomaterials

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Nanotechnology is the science and technology of making and using very small structures called nanomaterials. As the scales of the constructions become smaller, the conventional methods of making these structures—lithography, etching, micromolding—reach physical limits and it becomes extremely difficult to apply these top-down methods at nanoscale dimensions. To overcome the limitations and create smaller and ordered structures, a so-called "bottom-up" approach must be used. As the component size decreases in nanofabrication, the "bottom-up" approach is being increasingly used in the preparation of nanomaterials, which are materials with at least in one dimension less than 100 nm in size.

Keywords: nanomaterials ; gamma radiation ; electron beam ; nanogels ; quantum dots ; nanoscale grafting ; advanced functional membranes

1. Overview

Radiation technology has long been proven as a simple, rapid, green and sustainable technology with macroscale applications in healthcare, industry and environment. Its merits, however, have not been fully utilized in today's ever growing nanotechnology. Ionizing radiation has beneficial effects for the synthesis and modification of structure and properties of nanomaterials.

2. Nanotechnology

The Japanese scientist Norio Taniguchi of Tokyo University was the first to use the term "nano-technology" in a 1974 conference to describe semiconductor processes such as thin film deposition and ion-beam milling exhibiting characteristic control on the order of a nanometer. His definition was that "nano-technology" mainly consists of the processing of separation, consolidation and deformation of materials by one atom or one molecule [1].

Nanotechnology is the science and technology of making and using very small structures called nanomaterials. As the scales of the constructions become smaller, the conventional methods of making these structures—lithography, etching, micromolding—reach physical limits and it becomes extremely difficult to apply these top-down methods at nanoscale dimensions. To overcome the limitations and create smaller and ordered structures, a so-called "bottom-up" approach must be used. As the component size decreases in nanofabrication, the "bottom-up" approach is being increasingly used in the preparation of nanomaterials, which are materials with at least in one dimension less than 100 nm in size.

The ionizing radiations by virtue of very high energies of γ photons (0.66–1.25 MeV) or accelerated electrons (several keV–10 MeV) and their ability to penetrate into solid materials generate free radicals homogeneously in the media they pass through. This allows irradiation of monomers or polymers in any state at—or if needed, below—room temperature. These unique properties make ionizing radiation a very useful tool for the preparation of nanomaterials [2][3].

Nanomaterials are currently categorized into four types:

1, Carbon-based nanomaterials;

2, Metal-based nanomaterials;

3, Polymer-based nanomaterials;

4, Composite nanomaterials.

Quantum dots can be considered as new-generation nano-systems with hybrid metalloid–polymer structures which can be included under metal-based nanomaterials. Materials prepared from graft copolymers with nanoscale graft chain lengths can also be considered as nanomaterials and will be discussed under a separate title.

Nanomaterials are synthesized by one of the three different approaches: chemical, physical or biological methods. Although various techniques are employed under one of these three approaches for the synthesis of nanomaterials, ionizing radiation is seldom mentioned as either a standalone technique or in combination with any conventional technique as a tool for the preparation of polymeric nanomaterials.

3. Carbon-Based Nanomaterials

The basic constituent of these nanomaterials is carbon in the form of carbon nanotubes (CNT), graphene and fullerenes. One of the major problems associated with this all-carbon nanomaterial family is their poor dispersion in aqueous and even organic media due to their hydrophobic and fused aromatic structures. The formation of agglomerates, clusters of these carbon-based nanomaterials limits their use for some applications such as in biomedical devices, drug delivery platforms, etc. CNTs, graphene and fullerenes are generally used as nanofiller for the preparation of polymer nanocomposites to achieve superior properties. However, their poor compatibility with commodity and engineering polymer matrices prevents these materials from achieving their full potential. To overcome these problems, surface modification of carbon nanomaterials by covalent and noncovalent functionalization has been elaborated [4]. Covalent functionalization of these fully aromatic compounds is best achieved via reactions to be initiated by irradiation with gamma rays or accelerated electrons.

Pre-irradiation of CNTs with gamma rays can be applied to disintegrate the agglomerates and disperse them into a polymer matrix and to maintain stable dispersions instead of using a dispersant or reducing agent [5]. Chemical functionalization and subsequent dispersion were better achieved for the irradiated CNTs as compared to pristine CNTs. Enhanced interaction between CNTs and polymer matrix help in uniform dispersion improving the electrical and mechanical properties of corresponding composites. Fullerene was shown to be functionalized with –OH groups by gamma irradiation in methanol solution for biosensor applications [6]. Water-soluble poly(acrylic acid) grafted multiwalled carbon nanotubes (MWCNTs) were prepared by two-step gamma irradiation [7]. Solution processable reduced graphene was prepared first by radiation-induced reduction of graphene oxide later grafted with poly(vinyl pyrrolidone) by pre-irradiation technique [8]. Green synthesis of water-dispersed graphene nanosheets was achieved by gamma irradiation and using natural capping agents [9]. The surface of CNTs was functionalized by radiation-induced grafting of acrylic acid, methacrylic acid, glycidyl methacrylate, maleic anhydride and 4-vinylphenylboronic acid [10]. The CNT/polymer nanocomposites were shown to be successfully prepared by radiation curing using epoxy resins [11]. These works and many other clearly show that ionizing radiation is a very useful tool to functionalize CNTs, graphene and fullerene to make them compatible with a variety of polymer matrices for the preparation of nanocomposites.

4. Metal-Based Nanomaterials

Metal nanoparticles have a number of potential applications in many fields such as electronics, energy, medicine, magnetics, sensors, catalysis, optical devices, antibacterials and fungicide. A variety of metal nanoparticles were fabricated by top-down approaches such as mechanical milling, grinding, etching, sputtering, laser ablation, etc. These methods are generally costly, energy-intensive, with loss of starting materials or maybe harmful to the environment; therefore, more environment friendly procedures should be developed that will make the whole process greener [12].

Nano-sized materials have special characteristics that can be exploited for a number of advanced functional applications. However, difficulty in handling these very small objects has represented a strong limitation to their use. In addition, most of nano-sized metals are very instable. They can aggregate because of the high surface free energy and can be oxidized by air, contaminated by surrounding atmosphere. Metal nanoparticles are generally utilized as embedded in an appropriate matrix. The embedding of nanoscopic metals into polymers is particularly interesting since they have a variety of characteristics. Polymer embedding is the easiest and most convenient way for the stabilization and use of nanometals. The universal method for the controlled synthesis of metal nanoparticles is by in situ reduction of metal ions.

5. Polymer-Based Nanomaterials

The above mentioned conventional techniques and more sophisticated ones developed typically involve expensive chemicals, difficult processing techniques and specialized chemistry. However, treatment with ionizing radiation of monomers or polymers with the same aim has been shown to be a simple, rapid and so-called green technique operated at ambient conditions [3].

Polymer-based nanomaterials can be prepared by irradiating either polymers or monomers with ionizing radiation to comply with the two basic approaches of nanotechnology, namely top-down and bottom-up. The polymers predominantly degrading with radiation are suitable for lithographic applications and developing track-etched membranes, demonstrating typical top-down applications already matured to industrial level. However, there is more room in the preparation of polymer-based nanomaterials by the bottom-up approach. In the following examples, bottom-up synthesis of polymer-based nanomaterials by ionizing radiation is discussed.

Radiation-induced grafting has been successfully used to functionalize track-etched membranes, improve properties of fuel cell membranes, make the surfaces of cell culture dishes thermoresponsive and develop specialty adsorbents and molecularly imprinted polymer matrices, just to name the most established applications. Irradiation of aqueous solutions of polymers leads to the formation of nanoparticles, nanogels, polymer–clay nanocomposites, and polymer–metal nanocomposites.

6. Composite Nanomaterials, Polymer Nanocomposites

Polymer nanocomposites consist of a polymer or copolymer having nanoparticles or nanofillers with at least one dimension in the range of 1–100 nm dispersed in a polymer matrix; therefore, they are composed of almost 95% polymers. One of the most interesting aspects of the use of nanofillers is the low concentration that needs to be added to the polymer system to obtain desired property improvements. These systems combine the best properties of each component through synergistic effect. The addition of low content nanofillers can lead to improvements in their mechanical, thermal, electrical, barrier and flammability properties without adversely affecting their processability. Among the most frequently used nanofillers, carbon nanotubes, graphene, nanoclays, nano-oxides, nanocellulose and metallic nanoparticles can be mentioned. In the previous sections, nanomaterials prepared by using CNTs, graphene and metal nanoparticles are were discussed. Among nano-oxides, TiO_2 and SiO_2 are the most frequently used nanofillers. Clays received particular attention as nanofillers due to their natural abundance, variety of types and ease of modification and processing. Montmorillonite (MMT) has been shown to be a very good nanofiller as the silicate layers are 1 nm thick with cross-sectional area of 100 nm^2. Clays are hydrophilic and incompatible with most commodity and engineering polymers, which are hydrophobic and nonpolar. To make these binary systems compatible, either clay particles must be rendered organophilic or polymers should be chemically modified (e.g., by incorporating maleic anhydride) to impart hydrophilicity or polarity. Ionizing radiation can be used in different ways for the preparation of polymer–clay nanocomposites. Gamma radiation can be used to initiate in situ polymerization of vinyl monomers in the presence of dispersed clay particles. Electron beam-induced reactive in situ modification of pristine MMT in polypropylene has been achieved by investigating the effect of electron energy and absorbed dose on the final structure of nanocomposites [13]. In a recent study, natural MMT was modified by first intercalating with a charged monomer and then radiation-induced in situ polymerization of monomer in between the silicate layers. Radiation modified clay was successfully used in the preparation of EVA-MMT nanocomposites [14]. Gamma-irradiated polypropylene was used as a compatibilizer in the preparation of short carbon fiber reinforced polypropylene composites. Shortened PP chains due to radiation degradation and simultaneous oxidation by air irradiation enhanced the interactions between the carbon fiber and pristine PP with the formation of the nanocomposite [15]. The mechanical and barrier properties of some polymer–clay nanocomposites can be improved by radiation-induced crosslinking of polymer matrix. A critical review recently published provides an overview of the preparation, properties and uses of polymer nanocomposites by using basically three major types of nanofillers [16].

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