

Polymer nanocomposites: Synthesis and applications

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Abstract

Environmental nanotechnology is considered to play a principal role in shaping current environmental engineering and science. Looking at the nanoscale has stimulated the development and use of novel and cost-effective technologies for catalytic degradation, adsorptive removal and detection of contaminants as well as other environmental concerns. Polymer-based nanocomposites (PNCs) which incorporate the advantages of both nanoparticles and polymers, received increasing attention in both academia and industry. This introductory review focuses on the general introduction of the nanocomposites, and the synthetic routes of nanocomposites. It will explore the application of nanocomposites for environmental remediation as well.

Keywords: nanotechnology, PNCs, synthesis, applications

1. Introduction

Nanotechnology refers broadly to manipulating matter at the atomic or molecular scale and using materials and structures with nano sized dimension, usually ranging from 1 to 100nm. Due to their nanoscale size, nano particles have unique physical and chemical properties such as large surface area to volume ratios or high interfacial reactivity. Till now increasing nanoparticles have been demonstrated to exhibit specific interaction with contaminants in waters, gases, and even soils, and such properties give hope for exciting novel and improved environmental technology (Klefenz et al., 2011; Masciangioli et al., 2003). However, the small particle size also brings issues involving mass transport and excessive pressure drops when applied in fixed bed or any other flow-through systems, as well as certain difficulties in separation and reuse, and even possible risk to ecosystems and human health caused by the potential release of nanoparticles into the environment. An effective approach to overcoming the above technical bottlenecks is to fabricate hybrid nanocomposite by impregnating or coating the fine particles onto solid particles of larger size. The widely used host materials for nanocomposite fabrication include carbonaceous materials like granular activated carbon (Jang et al., 2008), silica (Badr et al., 2007), cellulose (Hunne et al., 2008), sands (Hansen et al., 2001), and polymers (Szecsody et al., 1994), and polymeric hosts are particularly an attractive option partly because of their controllable pore space and surface chemistry as well as their excellent mechanical strength for long-term use. The resultant polymer-based nanocomposite (PNC) retains the inherent properties of nanoparticles, while the polymer support materials provide higher stability, processability and some interesting improvements caused by the nanoparticle–matrix interaction. The choice of the polymeric supports is usually guided by their mechanical and thermal behavior. Other properties such as hydrophobic/hydrophilic balance, chemical stability, bio-compatibility, optical and/or electronic properties and chemical functionalities (i.e. solvation, wettability, templating effect, etc.) have to be considered to select the organic hosts (Sinsawat et al., 2003). Here a review is provided on the synthesis of the PNCs along with their environmental application.

2. Preparative Methods for Polymer nanocomposites

Polymeric nanocomposites are usually synthesized through solution route and because of this; the use of a large amount of organic solvents is required and this may pollute the environment. Therefore, effective and green synthetic methods have attracted much interest. Supercritical carbon dioxide (scCO₂) may be an alternative to the conventional processing. Generally, polymer/ inorganic filler nanocomposites can be synthesized in three different ways (Haldorai et al., 2012). The methods are (i)

direct mixing or blending of the polymer and the inorganic fillers either as discrete phases (known as melt mixing) or in solution (solution mixing), (ii) sol-gel process which starts with a molecular precursor at ambient temperature and then forms metal oxide framework by hydrolysis and condensation and (iii) in-situ polymerization of monomers in the presence of fillers.

2.1 Solution processing: In this method the layered silicates are dispersed in a suitable solvent in which the polymer is soluble. On evaporation of the solvent, the silicate sheets sandwich the polymer to form an ordered, multilayered structure. This process is also known as Exfoliation/adsorption process.

2.2 Melt Processing: The process has the greatest interest because of economical and flexible formulations (Paul et al., 2008). Layered silicate is mixed with the polymer in the molten state. If layer's surfaces are compatible enough with the selected polymer, it can be inserted into the interlayer space and form the final nanocomposite. In this case no solvent is required.

2.3 In-situ polymerization: In this case monomers with initiators are taken and allowed to polymerize in presence of clays. The polymer chains as they grow separate the clays and enter in the interlayer space forming polymer-clay nanocomposite.

2.4 Formation of nanoparticles via Polymerization: In this method nanoparticles are synthesized via polymerization of colloidal sols containing metal ions and monomers. The particle size depends on temperature, properties of the colloidal sols, thermal coagulation and Ostwald ripening.

2.5 Sol-gel process: This includes two approaches- hydrolysis of the metal alkoxides of the hydrolyzed intermediates. Inorganic metal oxides can be prepared from organic metal alkoxides, halides, esters etc. using this method. Transparent films of organic-inorganic hybrid materials have been made via co hydrolysis and polycondensation of alkyltrimethoxysilane-tetramethoxysilane mixtures. The sol-gel process using metal alkoxides is an effective way to produce inorganic-organic hybrid.

3. Applications

3.1 Adsorption of pollutants

Adsorption techniques are widely used in water treatment and gas purification as one of the most effective and simplest approaches to removing toxic and recalcitrant pollutants. Many environmentally benign inorganic particles, namely, metal (hydro) oxides (e.g., Fe(III) (Swallow et al, 1980; Fan et al, 2005), Mn (IV) (Trivedi et al, 2001; Kawashima et al, 1986) and $M(\text{HPO}_4)_2$ ($M = \text{Zr}, \text{Ti}, \text{Sn}$) (Pan et al., 2007) have been exploited as efficient adsorbents for enhanced removal of targeted pollutants. When the particle size gets into nanoscale, they appeared to be more efficient because of the extremely large surface area and high reactivity. Till now increasing nanocomposite adsorbents were designed by impregnating the inorganic nanoparticles onto the conventional polymers, namely, alginate (Zouboulis et al., 2002), cellulose (William et al., 2008), porous resins (Katsoyiannis et al., 2002) and ion-exchangers (Pan et al., 2009), to avoid issues caused by the ultra-fine particle size such as transition loss and excessive pressure drops. Porous polymeric adsorbents or ion exchangers have proved to be ideal alternatives to fabricate similar hybrid adsorbents when considering their excellent mechanical strength and adjustable surface chemistry of the polymeric supports (Blaney et al., 2007). The immobilized charged functional groups bound to the polymeric matrix are believed to enhance permeation of inorganic pollutants of counter charges, which can be interpreted by Donnan membrane principle. A new hybrid adsorbent HMO-001, which was fabricated by impregnating nanosized hydrous manganese dioxide (HMO) onto a porous polystyrene cation exchanger resin (D-001) (Tang et al., 2006). Lead adsorption onto HMO-001 was tested and the maximum capacity of HMO-001 toward lead ion was about 395mg/g. HMO-001 exhibited highly selective lead retention from waters in the presence of competing Ca(II), Mg(II), and Na(II) at much greater levels than the target toxic metal. Fixed-bed column adsorption of a simulated water indicated that lead retention on HMO-001 resulted in a conspicuous decrease of this toxic metal from 1mg/l to below 0.01mg/l (the drinking

water standard recommended by WHO). The exhausted adsorbent particles were amenable to regeneration by the binary NaAc–HAc solution for repeated use without any noticeable capacity loss. Another typical example is hydrated ferric oxides, which can selectively bind anionic ligands (e.g., arsenate, phosphate) through inner-sphere complex formation (Pierce et al., 1984). They are also environmentally benign and cost effective. Like HMO, they cannot be directly employed in fixed-bed columns or any other flow-through systems due to the fine or ultrafine particles.

3.2 Biosensor

The total effect of a biosensor is to transform a biological event into an electrical signal, as illustrated in Fig. 7. Biosensors have found extensive applications in environmental pollution control for measuring toxic gases in the atmosphere and toxic soluble compounds in waters. By far the largest group of direct electron transfer biosensors is based on co-immobilization of the enzyme in a conducting polymer, namely polypyrrole (Kajiya et al., 1991) and polyaniline (Mu et al., 1991). For example, a cholesterol biosensor was fabricated by co-immobilize cholesterol oxidase, cholesterol esterase and peroxidase onto electrochemically prepared polyaniline films (Singh et al., 2006). This polyaniline-based cholesterol biosensor has a response time of about 240 s, and can be used to estimate cholesterol concentration upto 500 mg/dl. These polyaniline/cholesterol oxidase/cholesterol esterase films have a detection limit of 25 mg/dl. The enzyme films were found to be thermally stable up to 48°C and have a shelf-life of about 6 weeks when stored at 4°C.

Conclusion

The environmental applications of PNCs are interesting and endless. The widespread use of PNCs in photo/chem-catalysis degradation, adsorption of pollutants, and pollutant sensing and detection result in less pollution and benign products. Till now, numerous PNCs are available for environmental purpose, and currently fabrication of new PNCs of high efficiency and low cost is still a hot topics. Also, we hope the polymeric hosts are available through cleaner processes instead of environmental unfriendly ones. In addition, further insights into the interplay between the host polymers and the encapsulated NPs are still required. Besides, most of the recent achievements are still based on laboratory-level tests. Many issues may need to be solved in the mass production and field application.

Conflict of interest:

Authors declare that they have no conflict of interest.

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