Polymer Nanocomposites and Cr(VI) Removal from Water

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Abstract

The progress in nanocomposites is varied and used in many industries. Nanocomposites can be made with a variety of enhanced physical, thermal and other unique properties. They have properties that are superior to conventional microscale composites and can be synthesized using simple and inexpensive techniques. The addition of small amounts of nanoparticles to polymers has been able to enable new properties for the composite materials. In recent years polymer nanocomposites have received significant attention because of their importance both from academic and industrial point of view. Composites, Nanocomposites in general and Polymer nanocomposites in particular have been discussed. Different type of nanocomposites and their preparations have been reviewed in brief. Application of polymer nanocomposites for the removal of Cr(VI) from aqueous solution has been described taking the examples from the literature as well as our own results. It is found that nanocomposites can be used in an effective manner for the removal of Cr(VI), a highly toxic metal ion.

Keywords: Composite; Nanocomposite; Polymer; Cr(VI)

Introduction

Today's technologies require variety of materials with unusual combinations of properties which are generally not met by the conventional materials. The properties are obtained by a special class of materials known as composites. Composite materials are in general solids and obtained from the combination of two or more simple materials that develop a continuous phase and a dispersed phase. The examples of continuous and dispersed phases are polymers, metals, ceramics, etc. and glass fibers, carbon particles, silica powder, clay minerals, etc. respectively. The properties of the composites are essentially different from the components. Now the composites are being replaced by nanocomposites where nanoscale fillers are used and the materials give multifunctional properties. Even a small addition of nanoparticles has the potential to drastically transform the properties of the host polymer if it is used as a dispersed phase.

A nanocomposite is a multiphase solid material with one of the phases having dimensions less than 100 nanometers in one, two or three dimensions or structures having nanoscale repeat distances between the different phases that make up the

material. During the last few years polymer nanocomposites have received significant attention because of their importance both in academia and the industry [1-5]. The properties of nanocomposites depend on number of factors [6-10] such as the quality of dispersion, extent of interphase, processing methods, interfacial adhesion, loading of the particles, aspect ratio of the nanoparticles, modification of the surfaces of nanoparticles, compatibility of particle and host polymer, size of particles, and the properties of the constituents. The usefulness of nanocomposites lies in their multifunctionality which is generally not found in traditional materials.

In this article an overview of polymer nanocomposites is given in brief with special reference to their classification, preparation and applications. The removal of hexavalent chromium from water by polymer nanocomposites has been discussed.

Classification of composites

Before classifying the nanocomposites, a brief idea about the composites and their classification is essential and are given below:

Composite is a material consisting of two or more phases - matrix phase and dispersed phase. Matrix is a primary phase, having a continuous character. The second phase (or phases) is embedded in the matrix in a discontinuous form and is called dispersed phase. Dispersed phase is sometimes called reinforcing phase. Types of matrices and composites are given respectively in Figures 1 & 2.

Classification of nanocomposites

Nanocomposites are classified in number of ways. One way to classify is as:

- Inorganic filler in an inorganic matrix (inorganic - inorganic nanocomposites),
- Organic filler in organic matrix (organic - organic nanocomposites),
- Hybrid materials, i.e., organic in inorganic or inorganic in organic matrix.

Based on the nanomaterial's dimensional morphology,

nanocomposites have 1-D, 2-D, and 3-D structures.

The inorganic components in the nanocomposites can be three-dimensional framework such as zeolites, two-dimensional layered materials such as clays, metal oxides, metal phosphates, chalcogenides, and even one-dimensional and zero-dimensional materials [11-18]. Organic/inorganic nanocomposites are important for bio-ceramics and biomineralization in which *in-situ* growth and polymerization of biopolymer and inorganic matrix take place. Lamellar nanocomposites represent an extreme case of a composite in which interface interactions between the two phases are maximum. By judiciously engineering the polymer-host interactions, nanocomposites may be produced with a broad range of properties.

There are vast varieties of inorganic layered materials with well defined and ordered intralamellar space where other materials can be accommodated. This property enables them to act as matrices or hosts for polymers, yielding interesting hybrid nanocomposite materials.

There are two types of Lamellar nanocomposites, intercalated and exfoliated (Figure 3) [5]. In the intercalated polymer nanocomposites, there are alternating polymer chains with the

inorganic layers in a fixed compositional ratio and have a well defined number of polymer layers in the intralamellar space. In exfoliated nano-composites the number of polymer chains between the layers is almost continuously variable and the layers stand $>100 \text{ \AA}$ apart. The intercalated nanocomposites behave like compound because of stoichiometric polymer/layer ratio. This makes them interesting for their electronic and charge transport properties. On the other hand, exfoliated nanocomposites have superior mechanical properties.

Polymer nanocomposites

During the last few years a considerable interest developed in polymer nanocomposites. Varieties of nanoparticles can be incorporated into the polymer matrix to form polymer nanocomposites. There are two type of nanocomposites - thermoplastic and thermoset nanocomposites.

3.3.1. Thermoplastic nanocomposites: These materials are divided into two broad categories-

(i) Commodity and (ii) Engineering resins. Nanomaterials filled thermoplastics have different properties than thermoplastics filled with conventional materials.

Figure 1: Classification of matrices.

Figure 2: Type of composites.

3.3.2. *Thermoset nanocomposites*: these nanocomposites are less important commercially but can be produced easily.

Following fillers may be used for the preparation of nanocomposites.

- Montmorillonite organoclays(MMT)
- Carbon Nanofibers (CNFs)
- Carbon nanotubes (CNTs)
- Metallic nanoparticles
- Ceramics
- Others

Polymer nanocomposites can also be classified based on the synthesis procedure.

1. Direct incorporation of nanomaterials into a solution or

polymer melt [19].

2. *In-situ* generation of nanoscale building blocks in a polymer matrix (reduction of metal ions in polymer matrix) [19]. For example polyaniline/cadmium sulfide nanocomposite was prepared by dissolving polyaniline in dimethyl formamide solution and adding dimethyl cadmium. Subsequently H_2S was passed through the solution to have polyaniline/cadmium sulfide nanocomposite (Figure 4) [20].

3. Polymerization of monomers in the presence of nanoscale building blocks [19].

4. A combination of polymerization and formation of nanoscale building blocks [19].

Once the polymer is selected, basically there are two issues:

(i) Choice of nanomaterial compatible with the polymer with appropriate interfacial interaction.

Figure 3: Intercalated and exfoliated nanocomposites.

Figure 4: Polyaniline/Cadmium sulphide nanocomposite.

(ii) Processing technique involving uniform dispersion of the nanomaterial within the polymer matrix.

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 (scCO_2) may be an alternative to the conventional processing. Generally, polymer/inorganic filler nanocomposites can be synthesized in three different ways (Figure 5) [21]. 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 (Figure 6).

4.1. Solution processing: In his 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 (Figure 7). This process is also known as Exfoliation/adsorption process.

4.2. Melt Processing: The process has the greatest interest because of economical and flexible formulations [22]. 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 (Figure 7). In this case no solvent is required.

4.3. 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 (Figure 8).

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

4.5. Sol-gel process: This includes two approaches-hydrolysis of the metal alkoxides and then polycondensation

Figure 5: The three general approaches for preparation of polymer/inorganic filler nanocomposites in scCO_2 . Polymer-clay nanocomposites have been prepared in a number of ways as given in Figure 6.

Figure 6: Synthesis of nanocomposites.

Figure 7: Nanocomposite by solution/melt processing.

Figure 8: Nanocomposite by *in-situ* polymerization.

Figure 9: Melt mixing of CNT with thermoplastic polymer.

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 hybrids.

4.6. *Mechanical mixing of nanoparticles with polymers:* This

method involves the direct mechanical mixing of a polymer solution with a pre-synthesised, highly dispersive nanoparticle solution. CdS/polyacrylamide nanocomposites have been synthesised by gamma-irradiation.

4.7. *CNT-polymer nanocomposites:* Due to changes in the properties there has been considerable interest in nanocomposites of polymer and carbon nanotubes (CNT). In the preparation of CNT-polymer nanocomposite there is a

Figure 10: Relationship between metal generation, exposure pathway and environmental impact. Different sources in polluting water by heavy metals are given in Figure 11.

Figure 11: Different sources discharging heavy metals in water.

problem of dispersion of CNT into polymer matrix. However the nanocomposite can be prepared by suspensions of CNT in polymer solutions and preparation of thin films or *in-situ* polymerization in the presence of CNT. Nanocomposite can also be prepared by melt mixing of nanotubes with polymers. Melt mixing can be done as shown in Figure 9.

Water Pollution

When toxic substances enter water bodies, they get dissolved or lie suspended or get deposited on the bed. This results in the pollution of water. Because of pollution, chemical, physical or biological changes may occur in the water. This will have a

harmful effect on any living thing that drinks or uses. Polluted water diminishes the aesthetic quality of lakes and rivers, destroys aquatic life and reduces its reproductive ability. Also, it is a hazard to human health. Water pollution by heavy metal ions is considered to be one of the major environmental issues due to the adverse effects of heavy metals on ecosystem and on human health. Metal generation, exposure pathway and environmental impact are shown in Figure 10.

Chromium removal from aqueous solution

Polluted water and industrial wastewater are contaminated with chromium (III) and Cr(VI) ions. Chromium and its ions used

Figure 12: Effect of concentration on removal of Cr(VI) from solution by polypyrrole/graphene oxide nanosheet.

Figure 13: Removal of potassium dichromate from solution at different interval of time in the presence of ZnFe2O4- Polyvinyl Alcohol film.

Figure 14: (a) Formation of ZnFe₂O₄-Polyvinyl Alcohol nanocomposite. (b) Adsorption of Cr⁶⁺ on the surface of ZnFe₂O₄-Polyvinyl Alcohol nanocomposite 41.

in different industries, such as: metallurgy, in steel production, anodizing of aluminum plating, dye production, textile dyeing, for metal surface cleaning processes, leather tanning, wood preservation, as a corrosion inhibitor in water-cooling towers and more (Figure 11) [23]. Hexavalent chromium (Cr(VI)) is extremely toxic and harmful whereas Cr(III) is relatively nontoxic. Long time interaction with Cr(VI) can cause many diseases, such as respiratory disease, nose bleeds, chronic headaches, reproductive failure, live failure, bone or organ deterioration and any type of cancer [24]. Therefore, it is necessary to remove Cr(VI) from wastewater before it is discharged to the natural water bodies. Various treatment technologies such as ion exchange, electrolytic removal, membrane filtration, reverse osmosis, chemical precipitation, adsorption, and solvent extraction have been reported for the removal of Cr(VI) from waste water [25-38]. Most of these technologies are associated with high operational and maintenance cost.

However, adsorption is found to be the most promising method particularly at low concentrations [39]. Many types of adsorbents have been used for the removal of Cr(VI). Some nanostructured adsorbents have been found to have excellent ability for removal of Cr(VI). Two defects have seriously restricted their practical applications. First, nanostructured adsorbents, especially nanoparticles, are very easy to aggregate, depriving them of their unique and excellent properties. Second, the high surface energy and the small size of nano range make them very difficult to be separated from the liquid phase after

use, which restricts their recyclable applications. The best way is to use the nanoparticles in the form of nanocomposites. In this context, recent advances in nanotechnology have explored the use of nanocomposites with unique properties as adsorbents for Cr(VI). As adsorption is a surface phenomenon, nano adsorbents offer high sorption efficiency and rapid process kinetics due to their large surface area and easily accessible sorption sites [25]. A number of nanocomposites have been reported as efficient sorbents for Cr(VI) removal from aqueous solution. It is reported that polypyrrole/Fe₃O₄ nanocomposite is a very good adsorbent for the removal of Cr(VI) from wastewater [25]. Adsorption is found to be time dependent and increases with temperature and concentration. The effect of the Cr(VI) initial concentration on the Cr(VI) removal by the Polypyrrole/Graphene Oxide composite nanosheets (Figure 12) has been studied [40]. Adsorption is found to be time dependent and the efficiency is higher at lower concentration.

The removal of chromium from aqueous solution of potassium dichromate of different concentrations in the presence of ZnFe₂O₄-Polyvinyl Alcohol nanocomposite film was carried out [41]. The film was kept in solution of different concentrations of K₂Cr₂O₇. Change in dichromate concentration was determined at different time intervals and plotted in Figure 13. It is seen that the concentration of dichromate decreased with time and became constant within 15 minutes. It appears that dichromate ions are adsorbed at the surface of zinc ferrite-Polyvinyl alcohol nanocomposite and the process is time dependent. When the

surface is covered with large number of dichromate ions, the efficiency of adsorption is reduced.

The formation of ZnFe_2O_4 -Polyvinyl Alcohol nanocomposite and adsorption of Cr^{6+} on the surface of nanocomposite is shown in Figure 14.

Conclusion

Discharge of metal containing effluents into water has been a cause of major concern. It is reported that water pollution causes harmful effects and particularly heavy metals in water are much more harmful to health. Traditional treatment methods are proving to be ineffective and expensive. Cr(VI) present in water even in smaller amounts is hazardous for health. Polymer nanocomposites can be very efficient and economical for removal of Cr(VI) from water solution.

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