POLYMER-NANOCOMPOSITES

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ABSTRACT

Composites are the materials in which two or more materials are mixed together combine some of the advantages of the component materials forming some novel materials. Dispersions of nanoparticles in polymers (or any other medium) give rise to nanocomposites. Nanocomposites have a great potential for different applications as a new generation of multifunctional materials. In this article, few of our research activities on metal-polymer nanocomposites are outlined. A discussion some on synthesis and characterization methods on polymer nanocomposites are discussed. Some possible applications of these novel materials in memory devices, sensors, optical filters, etc. have been discussed.

1. INTRODUCTION

Past two decades have witnessed a tremendous growth of nanoscience and nanotechnology. This can be attributed to the realization that all the materials, whose at least one dimension is smaller than some critical size characteristic of each material, have size dependent properties. It has been observed that all the properties like mechanical strength, thermal, optical, magnetic, conducting, etc. are size dependent. The critical size is usually below ~ 100 nm. Important question would be why is there any size dependence? Nanomaterials with reduced dimensions are neither like bulk solids nor like atoms or molecules. Their electronic structure differs from bulk solids and atoms or molecules. In the intermediate size regime the nanomaterials also have large number of atoms on the surface as compared o those in the interior. The surface atoms usually are very reactive and are responsible for some surface related properties. All these have opened a new branch in science known as Nanoscience. Nanoscience deals with the synthesis, analysis and finding out the ways to manipulate the materials. Nanotechnology on the other hand is the design, utilization, production and application of functional structures, devices and systems by controlling shape and size at the nanometer scale [1,2]. Often the words Nanoscience and Nanotechnology are used synonymously.

Nanomaterials can be synthesized by variety of physical, chemical, biological or hybrid methods. All the synthesis technique are often divided into two types viz. so called 'top down' and 'bottom up' approach. In top down approach materials are brought down from a larger size to nanometric dimension. On the other hand it is also possible to start with atoms or molecules, bring them together o make the required particles or assemblies of nanometer size. One can also use an approach known as 'self assembly' in which assemblies of nanoparticles are obtained.

Scientists have realized now that Nature has employed nanomaterials to make animal and plant kingdom very efficient, functional and rich in variety. It has developed various sensor organs, reproduction mechanism, day to day life functions by using nanomaterials. They are now trying to mimic some of them in the laboratories so as to obtain efficient materials which can be useful, cost effective and better than previously available materials.

By integrating two or more materials of different kind together one can obtain a composite material which takes the advantage of the integrated materials. Such materials are known as 'composites'. Often polymers are filled with ~ 30 to 40% of metals, clays etc. to make the composites. Polymers are usually flexible and light weight materials. One can put metal

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fillers in some non-conducting polymers so as to obtain novel conductors, sensors, actuators and so on. By incorporating metal nanoparticles in the insulating polymers one can not only arrest the nanoparticles but obtain some novel polymer-nanocomposites. It is expected that the amount of nanomaterials required to fill the polymers is less than that normally required (percolation threshold) amount. Without going into the details of it and assuming the result, we can immediately see the emerging advantage. The amount of filler material being small, we save filler material, make the composite lighter and take the additional advantage of 'nano' material.

We have synthesized a variety of metal (gold, silver, copper, iron, nickel etc.) and semiconductor (ZnO, ZnS, ZnSe, CdS, CdSe etc) nanoparticles , in the size range of ~ 1 to 50 nm and used for variety of applications. We have made nanoshell particles and recently some nanocomposites. Fig. 1 shows some Scanning Electron Miicroscopy images of ZnO nanoparticles synthesized in our laboratory.

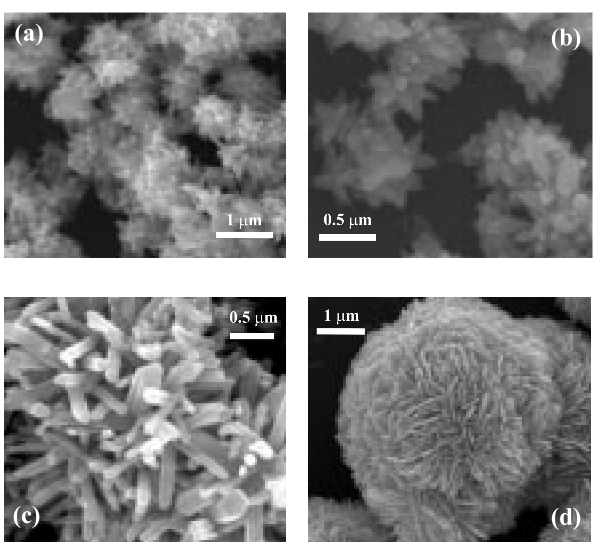

Figure 1 : SEM images of (a), (b) ZnO flowers, (c) ZnO rod like, (d) a single ZnO papilla and (e) TEM image of gold nanoparticles.

Compositions of nanoparticles with other materials have a great potential for variety of application. Nanocomposites are new generation of multifunctional materials which have attracted great interest in the last few years as they are novel materials which combine the advantages of different constituting materials. The challenge is to produce nanocomposites with monodisperse fillers in medium matrix. There are various techniques to fabricate well dispersed nanocomposites. In these kinds of materials, the nano-size fillers influence the composite's properties to a much greater extent than corresponding conventional composites with micro-size fillers. Polymers are able to provide required immobilization of nanoparticles avoiding their coalescence or segregation; thus protecting the novel size dependent properties of nanomaterials. However, depending upon the size and the shape of the particles and polymer species as well as concentration of nanoparticles, properties of nanocomposites may change. Particularly the electrical resistivity of metal nanoparticles-polymer composite shows strong dependence upon metal particle concentration. Noble metal nanoparticle-organic polymer composite materials are of wide interest because of their potential in optical, electrical and biomedical applications.

2. FABRICATION OF METAL-POLYMER NANOCOMPOSITES

As we mentioned earlier, the main challenge is to fabricate monodispersed nanoparticles in polymer matrix. Both simple and complex methods have been developed for this purpose. The methods used in the preparation of nanocomposites range from chemical means to vapour phase deposition. In relation to the polymer composites, in general, these techniques can be classified as *ex situ* and *in situ* methods. In the *ex situ* process, there are two subgroups: direct mixing and solution mixing.

Direct mixing consists of elastomeric mixing or thermal mixing in which nanoparticles and polymers are mixed directly to make polymer-nanocomposites.

In solution mixing, first the metal nanoparticles are synthesized chemically or physically and passivated with proper molecules. Then the nanoparticles are dispersed into either a polymer solution or monomer solution which is then polymerized to form metal-polymer nanocomposite. The nanocomposite so made, can be isolated from solution by casting a film, solvent evaporation or precipitation.

In the *in situ* routs, first the polymer solution is provided by dissolving the commercial polymer in proper solvent or polymerization of monomer in solution. Then metal ions are introduced into the polymer solution and chemically, thermally or by electromagnetic irradiation reduced inside the polymer matrix.

Here we shall discuss some polymer-metal nanocomposites with examples mostly from our own laboratory.

2.1 *Ex situ* formation of nanocomposites

2.1.1 Direct mixing

Some nanocomposites can be produced with this traditional method. For example, nanoscale silica (SiO_2) and polypropylene have been successfully mixed in a two-roll mill [3]. Some nanoparticle fillers in Nylon matrix also have been processed using thermal spraying method [4]. The main limitation of direct mixing process is that by increasing the filler concentration the viscosity increases rapidly, which in turn can limit the viability of this technique.

2.1.2 Solution mixing

It is possible to overcome some of the limitation of direct mixing if the nanoparticles and polymer dissolve in solution. This allows modification of the particle surface (like ligand-exchange process) among the polymer matrix, which reduces particle accumulation and agglomeration.

For example, it has been shown that the synthesized gold nanoparticles capped with oleylamine can properly disperse in polymethylmethacrylate [PMMA] matrix using modified solution mixing, to fabricate Au-PMMA nanocomposites by a ligand-exchange process [5]. The Ag-PMMA nanocomposite also has been produced using modified solution mixing method, with different amounts of nanoparticle filling. Figure 2 shows the absorption spectra of silver nanoparticles in a 300 to 800 nm range. Inset shows the FWHM and intensity of the UV-vis spectra of silver nanoparticles. By increasing the time of heating, the intensity of the spectra is increased and the FWHM of them is decreased.

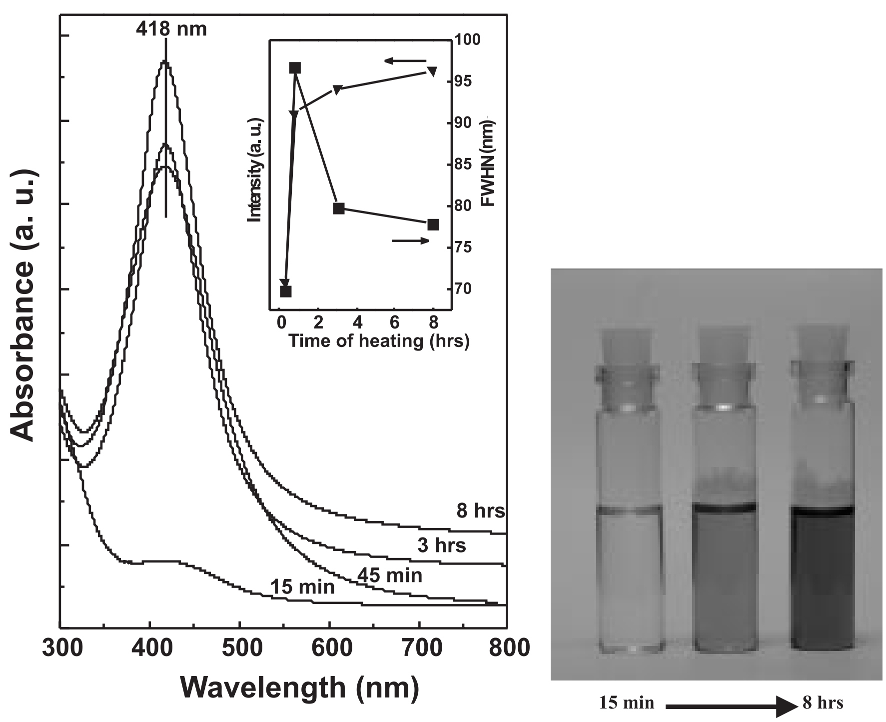

Figure 2 : Optical absorption spectra of Ag nanoparticles collected at different heating times. The inset shows intensity and FWHM as a function of time of heating. Photograph on the right hand side is of the actual samples.

2.2 *In situ* formation of nanocomposites

In this process, the formation of the nanoparticles occurs in the presence of a protective polymer, which immobilizes the particles and limits the size of the particles. Once a stable suspension of metal particles is prepared in the presence of a polymer, the composite can be cast to form a nanocomposite. There are several techniques which can be introduced as *in situ* technique, like: thermolysis, electrochemical, photoreduction, etc.

Photoreduction method is amongst the simplest methods which can be used to fabricate noble metal nanoparticles-organic polymer composites. There are many efforts to investigate the formation of gold nanoparticles in solid or liquid polymer matrix and also to produce well defined geometries of gold nanoparticles by photoreduction method [6-8]. It is shown that gold nanoparticles can be formed in the polymethylmethacrylate (PMMA) with an *in-situ* photoreduction method using UV irradiation [9]. Depending upon the initial loading of gold precursor, particles are more or less uniformly distributed in the films. Smaller particles are formed at higher loadings of $HAuCl_4$ in PMMA. Triangular gold nanoparticles were observed for some specific concentrations. It was also observed that the gold nanoparticles and polymer interact with each other through ester functional group of PMMA.

3. PROPERTIES OF NANOCOMPOSITES

3.1 Optical Properties

It is known for more than hundred years that the small metal particles show a strong absorption peak at a particular wavelength due to surface plasmoan resonance (SPR). This was theoretically proved by Mie [10]. The FWHM, intensity and position of the SPR peaks depend on the size and shape of the metal nanoparticles. Incorporation of metal nanoparticles in transparent polymers can make nanocomposites attractive as decorative materials. The characteristic SPR peaks of metal-polymer nanocomposites depend on the size and shape of metal nanoparticles in polymer matrix as well as inter-particle separation which can be controlled by particle concentration. Typically gold, silver, copper and platinum embedded in various polymer media are prepared by using different methods to examine their optical properties [11]. These nanocomposites open up new applications in areas such as optoelectronic devices, nonlinear optical devices and color filters.

3.2 Magnetic Properties

Magnetic nanoparticles embedded in polymer matrix have been, and continue to be, of great interest due to their applications in high-density magnetic recording, magnetic sensor, electromagnetic interference suppression, etc [12]. Incorporation of magnetic nanoparticles in polymer matrix prevents the particles' aerial oxidation as well as immobilizes them with the lowest surface contamination (magnetization is highly sensitive to surface contamination). Ultra fine cobalt and nickel particles are prepared in polymer matrix by in situ γ-irradiation at room temperature [13]. The magnetic nanocomposite of polymethylmethacrylate (PMMA) doped with iron nanoparticles are produced using *ex situ* melt blending technique which exhibited a somewhat large coercivity [14].

3.3 Electrical Properties

Dispersion of metal nanoparticles in conductive or insulating polymers can enhance their electrical conductivity. Additionally, the electric breakdown strength of nanocomposites can be enhanced. The percolation threshold has been shown to be lower in nanocomposites than in conventional micron-sized filled composites [15]. These nanocomposites have found various applications in heating devices, as antistatic materials, electromagnetic shielding and specially, they might lead to the development of highly sensitive components for the measurements of temperature and pressure. However, the resistivity of metal nanoparticles-polymer nanocomposites shows dependence upon the polymer species, size and shape, as well as concentration of nanoparticles. It is shown that the electrical resistivity of gold nanoparticles-PMMA nanocomposites shows a thermally assisted transition with an onset at ~165 K and exhibits a semiconductor like conductivity at higher temperatures and temperature independent conductivity at lower temperatures [5]. The resistivity of the PMMA polymer filled with silver nanoparticles shows also semiconductor-like to insulator behavior but, at a thermally assisted transition with lower onset.

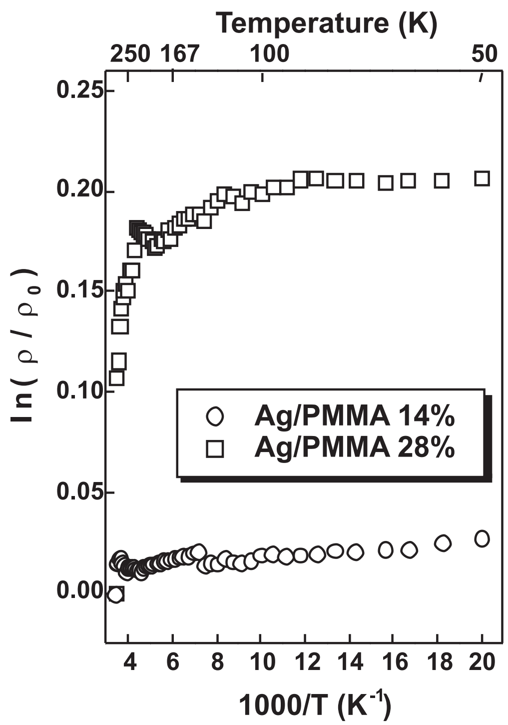

Figure 3 : Normalized logarithm of resistivity versus inverse temperature for Ag-PMMA nanocomposite films with different silver nanoparticles concentration, (O) 14%, (□) 28%.

Figure 3 exhibits the normalized logarithm of dc resistivity of Ag-PMMA nanocomposites with different concentrations as a function of temperature. The more concentrated sample is more sensitive to the temperature.

4. APPLICATIONS OF NANOCOMPOSITES

Metal-polymer nanocomposites are potentially applicable for a number of technological purposes, e.g. sensors, conductive shielding materials, color filters, optical limiters, polarizers, memory devices, etc [16,17]. The metal-polymer nanocomposites can be used as pigments in optical plastics due to their surface plasmon absorption band. In addition, they can be used as color filters using e.g. gold, silver, palladium and copper nanoparticles. Incorporation of metal nanoparticles in polymer media and subsequently reorganizing them into pearl-necklace arrays, results to the nanocomposites which exhibit a polarization dependence and tunable color. This behavior can be used to fabricate liquid-crystal color displays and special electro-optical devices.

These functional composite materials can be used to modify the refractive index of optical plastics using characteristic ultrahigh-low refractive index nanoparticles. These nanocomposites have found wide application in the waveguide and optical fibers technology.

Metal nanoparticles (e.g., gold and silver) have attracted great interest due to their nonlinear optical polarizability which is attributed to the quantum confinement of the metal electron cloud. By incorporating these particles into a clear polymeric matrix, nonlinear optical devices can be made in a readily processable form. These materials are used to prepare a number of devices for photonics and electro-optics.

Various methods have been also developed to produce nanocomposites which are biocompatible and found numerous applications as biosensors. For example, functionalized platinum nanoparticles have been conjugated onto the multi wall carbon nanotubes and the assemblies have been incorporated into the polypyrrole matrix using electropolymerization technique [18]. Resulting nano-biocomposites are highly electrocatalytic and exhibit high sensitivity, useful for a biosensor. Additionally, the biocompatible polymers like, 'Arabinnogalactan' can be applied for reducing and stabilizing noble metals; e.g. Au, Ag, Pd, Pt [19].

CONCLUSIONS

We have briefly discussed here the metal-polymer nanocomposites which have attracted great attention in last few years. The metal-polymer nanocomposites can be produced by either *in situ* or *ex situ* procedures. The polymer nanocomposites exhibit various properties like optical, magnetic, electrical, etc. better than the polymer composites with large micrometer size particles. These advanced functional materials have found large applications in different areas.

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