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# 23. Nanostructured Polymeric Materials

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**Abstract:** The field of nanotechnology has been one of the most popular thrust areas of contemporary research in almost all scientific and technical disciplines. In fact, viewing materials in the nano-scale, and manipulating properties at this level has its own advantages and potential applications. Polymeric materials, due to their unique properties like high mechanical flexibility, low cost, good mechanical strength, and environmental stability have attracted much attention, both in basic and applied fields. Polymer based properties derive benefits on addition of nano-scale filler or fiber. The ''nano-effect'' of nano-particle or nano-fiber inclusion has much importance, when compared to their larger scale counterparts. In this article, the current trends of nano-structured polymeric materials, their various applications and characterization techniques are discussed. Scanning Electron Microscope (SEM) images of nano-structured polymeric material which is obtained by incorporating cadmium salt in a polymer blend matrix are shown, for illustrative purposes. For comparison purposes, the micro-structural features obtained by incorporating lead salt in the same polymeric blend are also presented in this paper.

**Keywords:** Polymer nano-structure; PVA- PVP blends; Cadmium nano-structures; Pb micro-structures; SEM images.

## 1. Introduction

In earlier days of polymer science and technology, polymers were used as insulators in electrical and electronic applications, mainly due to their high electrical resistivity and dielectric properties. But, after the discovery of conducting polymers, polymeric materials were extensively used for electronic and optoelectronic applications also. The most popular area of current research is nanotechnology, as the critical dimension scale for modern devices is below 100 nano-meters (nm). Nanotechnology obviously includes polymer science; this field of polymer nanotechnology includes a wide range of topics like microelectronics, nano-electronics, polymer based biomaterials, nanoparticles drug delivery, fuel cells (electrode polymer bound catalysts), layer-by-layer self-assembled polymer films, electro spun nanofibers, polymer blends and nanocomposites. The field of nanotechnology is not new to polymers, but was not referred to as such, until recently.

Polymer nano-composites (PNC) refer to a polymer or copolymer having nanoparticles or nano-structures in the polymer matrix. These may have various shapes (e.g., platelets, spheres, rods and flower-shaped nano-features); but, at least one dimension must be in the range varying from 1 nm up to 300 nm. In essence, the nano-scale of dimensions is the transition zone between the macro- level and molecular level. Two of the major factors which are involved in the transition from micro- to nano-particles are the increase in ratio of the surface area to volume, and the reduced size of the constituent particles in the material. The surface area-to-volume ratio, which increases as the particle agglomeration gets smaller, leads to an increasing dominance of behavior of atoms on the surface of the particle over that of those in the interior of the nano-particle. This modifies the properties of these particles, especially when they are reacting with other particles. In fact, due to the higher surface area of these nano-particles, the interaction with other particles within the mixture is more, and this leads to desirable properties of the resulting material, like for example, an increase in the mechanical strength, heat resistance and many other properties.

## 2. Applications

Reinforcement aspects of nanocomposites have gained much interest among researchers; their potential applications include barrier properties, flammability resistance, electrical/electronic properties, optoelectronic properties and compatibilization of polymer blends. Interesting observations involving exfoliated clay, and more recent studies wherein, the incorporation of carbon annotates, carbon nanofibers, exfoliated graphite (graphene), nanocrystalline metals into the host polymeric matrix has added flavor to research work in this area. It was reported in a recent study that, for nano-fillers multiwall carbon nano-tubes (MWCNT), carbon nano-fibers (CNF) and high structure carbon black (HS-CB) nanostructures in acrylonitrile-butadiene-styrene (ABS) polymeric host, a comparative study on electromagnetic interference shielding effectiveness (EMI SE) revealed that the EMI SE, permittivity and electrical conductivity of the nanocomposites decreased in the following order: MWCNT > CNF > CB [1].

The environmental applications of PNCs includes abatement of contaminants from various environmental media like groundwater or industrial effluents, gases, soils; the main mechanism responsible for their environmental application are catalytic degradation and adsorption. For example, titanium dioxide ($TiO_2$) along with polyhydroxybutyrate (PHB) is used to degrade methylene blue pollutant [2]. Also, PNCs are extensively explored for sensing and detecting pollutants particularly at trace levels, as well as for green chemistry, in order to minimize the discharge of pollutants into the receiving environment. Tin oxide ($SnO_2$) incorporated polystyrene/polyaniline (PSS/PANI) polymer nano-composite is used as gas sensor for the detection of the dangerous pollutant, carbon monoxide (CO) [3].

Polymeric materials are preferred in many applications, due to their advantages such as easy processing, low cost, flexibility, high strength, good mechanical properties, low density, low thermal conductivity, easy synthesis and versatile processability. The use of polymeric materials in the preparation of polymer-inorganic thermo electric (TE) nano-composites appears to have a great potential for producing relatively low cost and high-performance TE materials. It is reported that, in a series of alternating poly(2,7-carbazole) derivatives synthesized (by Aich *et al* in 2009) [4], a maximum power factor value of 19 $\mu W\ m^{-1}\ K^{-2}$ (doped film) was obtained due to a high electrical conductivity (up to 500 S/cm) and relatively high Seebeck coefficient (up to70 $\mu V/K$), with the additional advantage of the material being stable in air.

During last decade, the optical properties of polymer containing materials have attracted the attention of researchers due to their widespread applications in Polymer Solar cells (PSCs), Polymer Light Emitting Diodes (PLEDS) and Polymer Light Emitting electrochemical cells (PLECs). The development of PSCs represents one of the innovations in materials science. Poly [2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV), developed by Wudl and Srdanov [5] was one of the earliest PSC polymer developed. Wudl also invented the fullerene derivative, 6, 6- Phenyl C61- Butyric acid Methyl ester (PCBM), a methano-fullerene, which a PSC acceptor which is still widely used. Another example for application of polymeric nano-structured material is that of a nano-polymer silicon nano-spheres containing material, which show modified properties in range 10–100 nm, and these materials are much harder than silicon, their hardness being between that of sapphire and diamond [6].

## 3. Methods

There are three methods to prepare nano structured polymers. The preparation methods are solution casting method, melt blending and in-situ polymerization. The authors have used the solution casting method for preparation of the nano-structured polymeric materials. In solvent casting method, a polymer, a solvent and nano-reinforcement (dopant/ filler) are combined and thoroughly mixed by ultrasonication or by constant stirring and the solvent is allowed to evaporate in a air cooled , temperature controlled oven by maintaining the temperature at 40°C , leaving behind the nano-composite, typically as a film. An example for solution casting method to prepare a polymeric nano-composite is the preparation of polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) blend films wherein there is incorporation of cadmium nanostructures, by the process of doping PVA-PVP aqueous blend with cadmium chloride monohydrate. The experimental details of this study, by B. M. Baraker and B. Lobo, are presented elsewhere [7, 8].

## 4. Characterization

Observation is the key to new discoveries, and this is especially true in the nano-scale. Observations on nano-structured materials are done with a probe which may consist of photons, electrons, neutrons, atoms, ions, or even an atomically sharp tip. The probe i.e., light or particle (invoke the dual nature of matter/ radiation as a wave/ particle ) has frequencies ranging from that of gamma radiation to that of infrared rays or even beyond in the case of photons. In the case of particles, the kinetic energies of the same may vary from hyper-thermal (<100eV) to relativistic energies. The data obtained can be processed to yield spectra, which reveal vital information about the topographic, geometric, structural, chemical and physical details about the material.

The experimental investigation of DC (direct current) electrical conductivity measurements gives information about the charge carrier transport in nano-structured polymeric materials, through which the activation energy for mobility of mobile charge carriers in the material can be determined. By analyzing the absorption spectra (UV-VIS or UV-VIS/NIR) of the materials, optical parameters can be calculated. Fourier transform infrared (FTIR) studies give information about different stretching vibrations, and hence, functional groups present in the polymer sample can be identified. Degree of crystallinity and crystallite size can be studied with the help of Differential Scanning Calorimetry (DSC) and X-Ray Diffraction (XRD) studies.

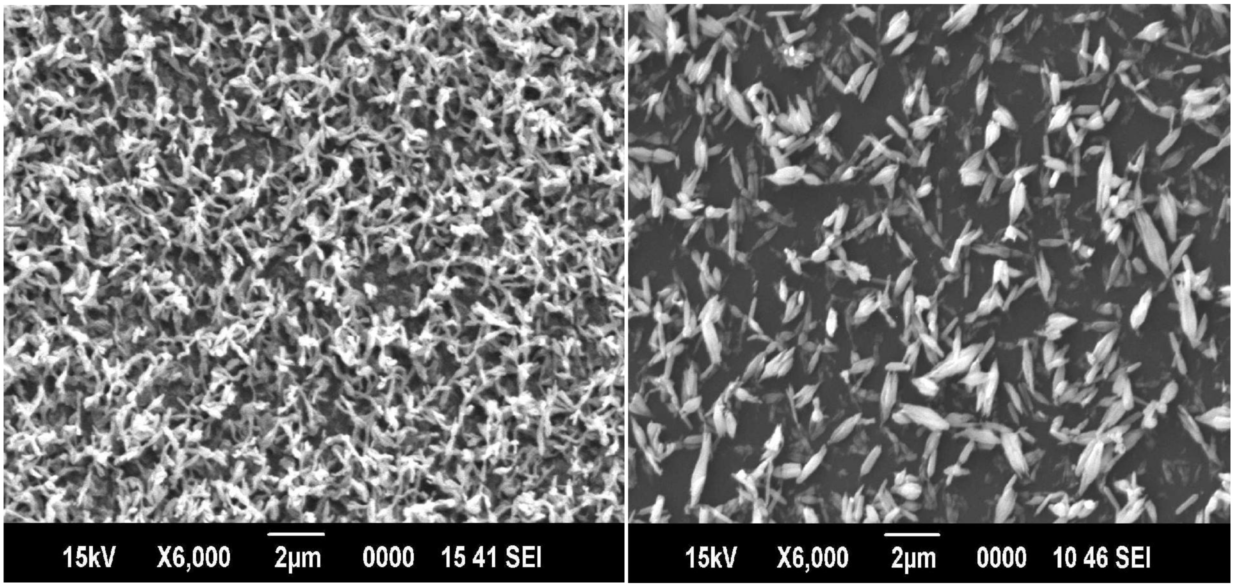


**Figure 1.** Nano- flower shaped cadmium nano-structures in PVA-PVP polymeric blend at 3.3 wt% and 4.4 wt% of cadmium chloride in the polymeric host. See reference [7] for details about this material.

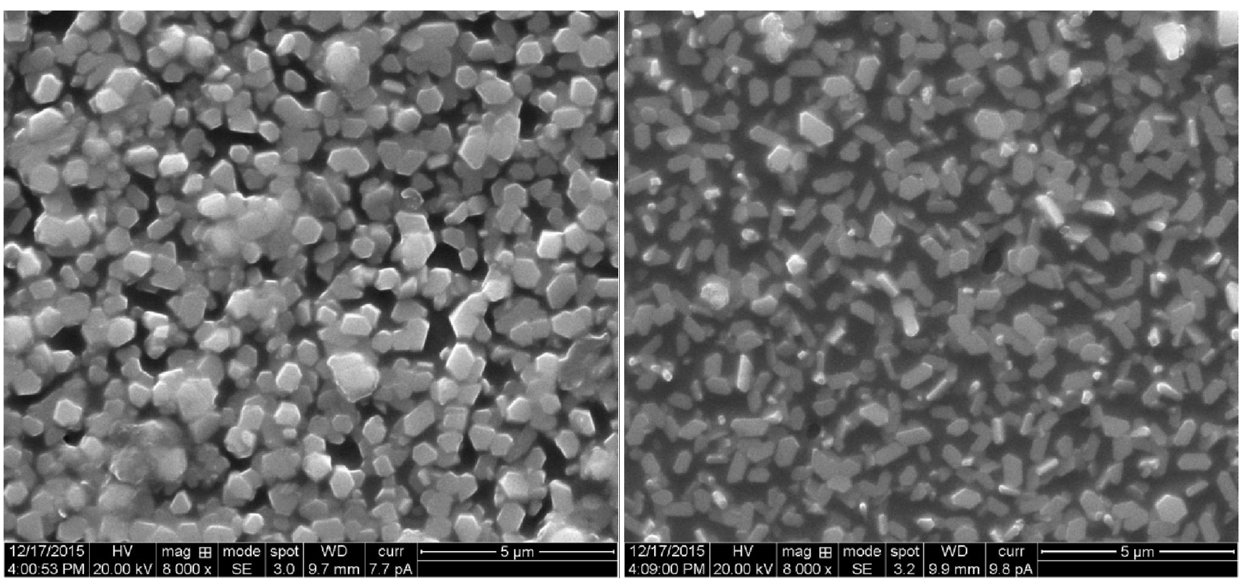


**Figure 2.** The micro-structures of lead (Pb) in lead nitrate doped PVA-PVP composite polymeric system. See reference [12] for further details about this material.

The mechanical properties of the nano-structured polymeric material can be studied using a Universal Testing Machine (UTM). Scanning Electron Microscopy (SEM), Transmission

Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) can be used to study the morphology of the sample. The SEM images (see reference [9]) of polyaniline (PANI) nano-structures reveal their size distribution (like diameter and length of the nano-structures). Features like Nanospheres, Nanorods and Nanofibers have been visualized, using SEM [9]. The SEM images of nano-structured polymeric material which is obtained by incorporating cadmium salt in a polymer blend matrix (PVA-PVP blend) are shown in Fig. 1, for illustrative purposes [10]. For comparison purposes, the micro-structural features obtained by incorporating a lead (Pb) salt in the same polymeric blend (PVA-PVP blend) are shown in Fig. 2 [11, 12].

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