Chapter 7

SYNTHESIS, STRUCTURAL AND OPTICAL PROPERTIES OF POLYMER/CERIA NANO COMPOSITES

7. 1. Introduction

The synthesis of polymeric matrixes embedded with nanoparticles has attracted much interest in the field of nanomaterials. Polymers are considered as good choice as host materials, because they can be designed to yield a variety of bulk physical properties, and they normally exhibit long term stability and possess flexible reprocessability. This new class of inorganic-polymer composites may afford potential applications in molecular electronics, optics, photo electrochemical cells, solvent-free coatings etc. Synthesis of polymer/nanoparticles composite materials is very important in advanced material science. These materials combine both the unique properties of nanoparticles and polymers and possess new properties which are not specific to the original components. The polymer matrix also prevents extremely active nanoparticles from aggregation. The addition of inorganic spherical nanoparticles to polymers allows the modification of polymers physical properties as well as the implementation of new features of inorganic nanoparticles.
Polymer nanocomposite structures provide a new method to improve the processability and stability of materials with interesting optical properties. Inorganic/polymer nanocomposites benefit from physical flexibility and ease of processing, which are typical features of polymers. Further, nanocrystals dispersed in suitable solid hosts can be stabilized for long period of time [1]. In the present work, four different polymers are used as the matrix for nanocerium oxide in the nanocomposite. In this study, CeO$_2$ nanocrystals have been prepared by hydrolysis assisted chemical method which could be suitably embedded in four polymer matrices (polyvinylidene fluoride (PVDF), polyvinyl alcohol (PVA), polymethyl methacrylate (PMMA) and polystyrene (PS)).

PVDF is a special plastic material in the fluoropolymer family; it is used generally in applications requiring the highest purity, strength, and resistance to solvents, acids, bases and heat. Compared to other fluoropolymers, it has an easier melt process because of its relatively low melting point of around 177 °C. It has a low density (1.78 g/cc) and low cost compared to the other fluoropolymers. Polyvinyl alcohol (PVA) has excellent film forming, emulsifying and adhesive properties. It has high tensile strength and flexibility. PVA is fully degradable and dissolves quickly. PVA has a melting point of 230 °C. It decomposes rapidly above 200°C as it can undergo pyrolysis at high temperatures. Polymethyl methacrylate (PMMA) is a transparent thermoplastic, sometimes called acrylic glass. Chemically, it is the synthetic polymer of methyl methacrylate. Polystyrene (PS) is an amorphous, optically clear thermoplastic material, which is often chosen as a host matrix because of its ideal properties for investigating optical properties. It is one of the most extensively used plastic materials.
7.2. Experimental techniques

7.2.1. Synthesis

CeO$_2$ nanoparticles were prepared by hydrolysis assisted precipitation method as explained in chapter 3. PVDF/ CeO$_2$ nanocomposite solutions were prepared by adding 10 wt % of CeO$_2$ powder sample into PVDF solution (10% w/v) in NMP. The mixtures were then stirred for 2h and then sonicated for 10 min [2]. Using the same procedure PVA (dissolved in water)/ CeO$_2$, PMMA (dissolved in Tetrahydrofuran)/CeO$_2$ and PS (dissolved in tetrahydrofuran)/CeO$_2$ nanocomposites were also prepared.

7.2.2. Characterizations

XRD studies were carried out for the polymer/CeO$_2$ nanocomposites using a Rigaku Ultima-III X-Ray Diffractometer using Cu K$\alpha_1$ radiation in the 2$\theta$ range from 10$^\circ$ to 70$^\circ$. Optical absorption studies were carried out using JASCO V 570 Spectrophotometer at room temperature. Photoluminescence spectra of composite samples were obtained using Fluoromax-3 Spectrophotometer at room temperature under an excitation of 325 nm.

7.3. Results and discussion

XRD patterns of various polymer/ceria nanocomposites are shown in figure 7.1. These indicate broad non crystalline peaks of polymer and sharp peaks of cerium oxide. The diffraction peaks corresponding to (111), (200), (220) and (311) planes indicate cubic structure of CeO$_2$ (JCPDS 34-0394). The broadening of XRD peaks indicates formation of nanosized particles in the as-prepared sample. The presence of CeO$_2$ produces neither new peaks nor peaks shift with respect to polymer showing that nano CeO$_2$ filled polymer composites consist of two phase structures.
Figure 7.1: XRD patterns of the polymer/ CeO$_2$ nanocomposites

UV-Vis absorption spectra of the polymer/CeO$_2$ nanocomposites are shown in figure 7.2. Pure ceria shows a sharp absorption peak around 298 nm and an absorption edge at 387 nm which is explained in chapter 3.3. In PMMA, PVA and PVDF/ceria nanocomposites the absorption edge shifts to longer wavelength side. But in PS/ceria nanocomposite absorption edge is almost at 300 nm. In all the composite samples there is a UV absorption window. The width of the window is from 250 nm to 350 nm for all polymer/ceria nanocomposites except for PS/ceria nanocomposite for which it is from 250 nm to 300 nm.
Figure 7.2: UV-Vis absorption spectra of the polymer/ CeO$_2$ nanocomposites

Pure polymers don’t show appreciable UV absorption. But polymer/ceria nanocomposites are covering UV A and UV B regions and part of UV C region, thus showing prospects of acting as efficient UV filters. The mechanism of UV absorption in these materials involves the use of photon energy to excite electrons from the valence band to conduction band.

Figure 7.3: Band gap energy of the polymer/ CeO$_2$ nanocomposites
Direct and indirect band gap energies of polymer/CeO₂ nanocomposites are shown in figure 7.3 (a & b). Table 7.1. shows direct and indirect band gap energies of polymer/CeO₂ nanocomposites.

**Table 7.1:** Direct and indirect band gap energies of polymer/CeO₂ nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Direct band gap (eV)</th>
<th>Indirect band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF/Ceria</td>
<td>2.43</td>
<td>2.05</td>
</tr>
<tr>
<td>PVA/Ceria</td>
<td>2.75</td>
<td>2.14</td>
</tr>
<tr>
<td>PMMA/Ceria</td>
<td>2.87</td>
<td>2.26</td>
</tr>
<tr>
<td>PS/Ceria</td>
<td>4.13</td>
<td>3.99</td>
</tr>
</tbody>
</table>

The present findings reveal an enhanced band gap in the range of 4.13 eV for PS/ceria nanocomposite. So it could be used as a better photocatalyst. Light below this wavelength has sufficient energy to excite electrons and hence absorbed by CeO₂. Light having a wavelength longer than the band gap energy (towards the visible light) will not be absorbed. Therefore PS/CeO₂ nanocomposite is an excellent UV absorber [3].

![Figure 7.4: PL spectra of the polymer/ CeO₂ nanocomposites](image_url)
PL spectra of the as-prepared polymer/CeO$_2$ nanocomposites are shown in figure 7.4. PL studies of polymer/ceria nanocomposites are done to investigate the effects of the polymer matrix on the PL characteristics of ceria. Pure ceria shows a series of high intensity PL emission peaks in the blue-green region and also lower intensity peaks in the UV region which are well explained in chapter 3.3. Polymer matrix provides surface passivation of the ceria nanoparticles and hence modifies the PL spectrum. Passivation effect is highly pronounced in PMMA/Ceria nanocomposite. The PMMA/Ceria nanocomposite has the most intense PL emission peak at 466 nm compared to pure ceria and other polymer composites.

It is observed that free standing films of PS/ceria, PMMA/ceria and PVDF/ceria can be obtained with thickness around 1 µm using solution casting. These nanocomposite films also show high dielectric constant value around 20. Due to time constraint, detailed investigations on the various properties of these films could not be carried out.

7.4. Conclusion

Polymer/ceria nanocomposites using four different polymers have been successfully synthesized. These nanocomposites show good UV absorption window regions. Polymer matrix provides surface passivation of the ceria nanoparticles and hence modifies the PL spectra. Passivation effect is highly pronounced in PMMA/Ceria nanocomposite.

It is observed that free standing polymer nanocomposite films of ceria can be prepared using PS, PMMA and PVDF which show considerably high dielectric constant values (\(\sim 20\)). These free standing high dielectric constant nanocomposite films can be of profound applications as gate electrodes for metal oxide semiconductor devices.
Chapter 7

References


    Polym. Int., 60 (2011) 1263