Small Angle X-Ray Scattering Analysis of PS/CdS, PVC/CdS & PMMA/CdS Polymeric Nanocomposites

V. Mathur*
Faculty of Science & Technology, The ICFAI University, Jaipur, India, and
Semi-conductor & Polymer Science Laboratory, Department of Physics, University of Rajasthan, Jaipur, India

K. Sharma
Semi-conductor & Polymer Science Laboratory, Department of Physics, University of Rajasthan, Jaipur, India
(Received 30 July 2014; Accepted 17 September 2014; Published 11 October 2014)

PS/CdS, PVC/CdS & PMMA/CdS polymeric nanocomposite samples were prepared through dispersion solution casting technique. The CdS nanoparticles were prepared by simple chemical method using CdCl₂ and H₂S gas produced from thiourea. The nanoscale morphology of the polymer nanocomposite samples was characterized using small angle x ray scattering (SAXS). SAXS reveals that CdS interact well with the polymer matrix and exhibit their nano nature. [DOI: 10.1380/ejssnt.2014.420]

Keywords: Small angle x ray scattering; Polymer nanocomposite; Polymer characterization

I. INTRODUCTION

New technologies require the use of materials exhibiting a performance that can only be achieved by combining several constituents [1, 2]. In this regard polymer composite materials are of great practical importance due the modification, and usually improvement, of the properties of the pure polymer [3]. The nanocomposites of CdS can provide the possibility to provide combinations of functionalities, such as thermally conducting composites with good mechanical properties that are optically clear. Such properties can result because CdS nanoparticles, with diameters distinctly below the Rayleigh scattering limit, still display their solid-state physical properties when embedded in transparent matrices. Basically CdS nanocomposites are optical composites and most of the studies of these are concerning optical characterization [4-7]. The different technological applications of CdS nanocomposites include biological labeling and diagnostics, LED’s, electro-luminescent devices, photovoltaic devices, lasers and single electrode transistors [8,9]. Vacatello [10] performed simulations of polymer systems filled with particles of a size comparable to the polymer chains and found that even in the absence of specific interactions with the polymer, the filler particles behaved as highly functional physical cross-links, reducing the overall mobility of the polymer chains compared to the unfilled polymer matrix. Li Chen et al. [5] reported controllable synthesis of CdS nanocrystal-polymer transparent hybrids by using poly methyl methacrylate (PMMA) as a polymer matrix. They studied thermo-gravimetric analyses (TGA) and fluorescence measurement study of the prepared samples. They concluded that PMMA/CdS sample exhibit better thermal stability and good optical properties as compared to pure PMMA sample. It is well known that material characterization is an important aspect of any study. The characterization of materials and phenomena has always made a major contribution to the development of science and technology. Polymer analysis continues to progress with improvements in instrumental techniques and computer-enhanced data analysis methods that provide deeper insight into materials characteristics. In the continuation of this, structural characterization of nanocomposite samples is primarily concerned to investigate that whether the dispersed nanoparticles are still within nano dimension within the sample. Literature reveals that techniques like scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), small angle x-ray scattering (SAXS), etc. are prominently reported by the researchers [11-14] in this regard. In contrast to SAXS, the other methods require a tedious sample preparation, longer measurement and data analysis times. There are many excellent textbooks on small angle scattering (SAS) in the field of colloids and polymers, which are the two building blocks of polymer nanocomposites we are interested in [15-17]. The present research paper reveals the morphology of CdS nanocomposites of PS, PVC and PMMA primary industrial polymeric material’s thin film samples through small angle x-ray scattering technique.

II. EXPERIMENTAL PROCEDURE

A. Material Preparation

In order to prepare polymeric blended-nanocomposite samples, firstly CdS nanoparticles have been prepared by simple chemical method using CdCl₂ and H₂S gas produced from thiourea. Then 6% wt CdS nanofiller particles were dispersed in PS, PVC & PMMA polymer matrix respectively during the solution casting process. Polymeric material used are of the laboratory grade and tetrahydrofuran (T.H.F.) is used as solvent. This solution was then stirred with the help of magnetic stirrer and then poured into flat-bottomed petri dishes to form film with a thickness of ~0.05 mm. The solvent is allowed to evaporate slowly over a period of 24 hours in dry atmosphere. The so obtained film was then peeled off and dried in vacuum at 50°C, well below the boiling point of solvent to avoid bubbling, for 24 hours in order to ensure the removal of the solvent [18-19].

* Corresponding author: wishalmathur@gmail.com
B. Small Angle X-Ray Scattering (SAXS)

Small-angle x-ray scattering (SAXS) provides information about the morphology of a polymer matrix on length scales from a few nanometers to several micrometers. Because of electron-density fluctuations, the incident x-rays are scattered, which leads to characteristic patterns. The scattering intensity, $I(q)$, is usually shown as a function of the scattering vector ($q$)

$$q = (4\pi/\lambda) \sin(\theta/2),$$

where $\theta$ and $\lambda$ correspond to the scattering angle and the wavelength of the incident x-rays, respectively [20].

The Small angle X-ray diffraction pattern of the samples were collected at room temperature on a Philips X’Pert Pro diffractometer, equipped with Cu target X-ray tube with step size of 0.020 $^\circ \theta$ and time per step of 0.3 s with Cu Kα radiation of wavelength 1.54 Å. It is performed on an X’Pert Pro MPD system to investigate the size of the. In order to determination of particle size, shape and distribution of CdS-nanoparticles within nanocomposite samples, the obtained data files from X’Pert Pro MPD system are matched with the analysis templates that are provided with EasySAXS software.

III. RESULTS AND DISCUSSION

A. Small angle X-ray scattering analysis

Figures 1 shows the scattering intensity as a function of angle ($2\theta$) for PS, PVC, PMMA & their CdS nanocomposites respectively. It is observed that SAXS pattern of CdS embedded polymer nanocomposites show higher scattering intensity as compared to without CdS dispersed samples. The nano-crystals of CdS act as independent scattering centers in the respective polymer matrices and add to the total scattering intensity in the respective SAXS pattern. These SAXS patterns are used for elucidating the shape and size of CdS nano-crystals by subtracting the background scattering intensity (without CdS embedded polymeric phase) from scattering intensity of CdS embedded polymeric nanocomposite phases with the help of EasySAXS software. SAXS characterization reports of respective nanocomposites suggest that CdS nanofiller particles have been distributed evenly within the available polymer/blend matrix and have very little tendency to form agglomerates.

Figure 2 shows the particle size distribution curves for PS/CdS, PVC/CdS, and PMMA/CdS nanocomposites. In this figure curves (a), (b) and (c) are for the PS/CdS, PVC/CdS and PMMA/CdS nanocomposites respectively. The particle size distribution reports of respective nanocomposites suggest that the distribution is well approximated by a Gaussian. The minor oscillations in the distribution curve around zero towards larger particle radii may be regarded as insignificant.

Table I depicts the summary of analysis obtained from these particle size distribution curves. It is observed that all of these curves approximately centered at $R = 1.3$ nm and it means that the most frequent radius ($R$) of CdS nanofillers is 1.3 nm and major volume fraction of these CdS nanoparticles is exhibiting radius within 0.6 nm to 2.3 nm. The CdS nanoparticle size distribution curves exhibit relative standard deviation of 25% (approximately) for all the three samples. The surface-to-volume ratio ($S/V$) was calculated from the distribution curve for each sample which lies about 0.07 Å$^{-1}$ for all respective samples. The surface-to-volume ratio ($S/V$) value can be used to calculate the specific surface area of respective polymer nanocomposite sample.
FIG. 2. Particle size distribution curves for PS/CdS, PVC/CdS and PMMA/CdS.

TABLE I. Summary of particle size distribution curves analysis.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample</th>
<th>Most frequent radius</th>
<th>Average radius</th>
<th>Relative standard deviation</th>
<th>Surface to volume ratio S/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PS/CdS</td>
<td>1.5 nm</td>
<td>2.23 nm</td>
<td>24.62 %</td>
<td>0.07013(1/Å)</td>
</tr>
<tr>
<td>2</td>
<td>PVC/CdS</td>
<td>1.2 nm</td>
<td>2.19 nm</td>
<td>25.01 %</td>
<td>0.06712(1/Å)</td>
</tr>
<tr>
<td>3</td>
<td>PMMA/CdS</td>
<td>1.4 nm</td>
<td>1.93 nm</td>
<td>24.84 %</td>
<td>0.06911(1/Å)</td>
</tr>
</tbody>
</table>

IV. CONCLUSION

Characterization of physical structure of CdS nanoparticles embedded in PS, PVC, & PMMA polymer matrix respectively using SAXS technique reveal that it can elucidate the morphologies of polymer nanocomposites. The observed values of average particle size of CdS nanoparticles in all respective nanocomposite samples lies within nano dimensions (i.e. below 100 nm) and implies that the prepared samples retain their nanocomposite nature.