UV-shielding efficiency of TiO$_2$-polystyrene thin films prepared by solution cast method

Aman Deep Acharya$^{1,2,*}$, Bhawna Sarwan$^{1,2}$, R Sharma$^1$, S Moghe$^1$, S B Shrivastava$^1$ and V Ganesan$^3$

$^1$Vikram University, Ujjain 456010, MP, India
$^2$Lovely Professional University Phagwara 144411, Punjab, India
$^3$UGC-DAE Consortium for Scientific Research, Khandwa Road, Indore, MP 452001, India

Email: $^*$acharyaphysics2011@gmail.com

Abstract. In order to evaluate the UV-protection efficacy of TiO$_2$ doped polystyrene (PS/TiO$_2$) films with concentrations 0.5%, 0.75% and 1% have been fabricated by using solution cast technique. The effect of doping on the microstructure and morphological properties was studied. The obtained results reveal that the better the dispersion of filler particles, larger the UV-protection efficiency of the composite material.

1. Introduction
Incorporation of small amount of inorganic nanoparticles can considerably improve the bulk performance of polymer matrix in optical, electrical, mechanical, thermal properties etc. [1-4]. Most promising inorganic material is TiO$_2$, which have wide band-gap energies of around 3 eV have been widely used as inorganic UV absorbers due to its significant optical properties [5]. Consequently, TiO$_2$ doped polystyrene thin film nanocomposite has been considered as an excellent candidate for UV shielding applications. In present work, we have prepared TiO$_2$/PS thin films having different concentration of the dopant by using solution cast method. The structural and morphological properties of films were studied by using X-ray diffraction (XRD), atomic force microscopy (AFM) measurements. Transmittance of the films has been recorded by using UV-Vis spectroscopy.

2. Experimental
The polystyrene was dissolved in dichloromethane in a 25 ml borosil glass beaker to cast a defect free film. The viscous solution was then poured over a smooth casting surface of a flat-bottomed petrie dish. In order to get the uniformity in the membrane thickness, the dish was made to float on the mercury. The solvent was allowed to evaporate slowly over a period of 12 - 24 hrs in a dry atmosphere and the membrane was peeled off the surface of petrie dish. For preparing doped polystyrene thin films, the dopant concentration was calculated from the following equation.

$$W (wt\%) = \frac{w_f}{w_p + w_f} \times 100$$  \hspace{1cm} (1)

where $w_f$ and $w_p$ represent the weight of dopant and the polymer, respectively.
3. Structural and morphological analysis

It can be seen in figure 1, XRD pattern of pure polystyrene film shows an amorphous polymeric structure without any peaks. The patterns of the 0.5 wt% TiO$_2$/PS thin film indicates low intensity diffraction peaks attributed to the crystalline domains of the PS chains. In case of 1 wt%, the peak was slightly shifted towards lower diffraction suggesting an interaction between the filler particle and the polymer structure, leading to a rearrangement of the PS chains. The intensity increased of these peaks with higher amount of filler loading implies that the slowing of the crystallization rate caused due to inclusion of filler particles.

Figure 1. X-ray diffraction pattern of PS/TiO$_2$ thin films

Figure 2 shows AFM images of PS-TiO$_2$ at content of 0.5, 0.75 and 1.0 wt %. The addition of 0.5 wt% TiO$_2$, some rods were seen (see figure 2b) on the surface of pure PS. The formation of rods assumes the random aggregation of nucleates or acting as efficient nucleating agents.

Figure 2. AFM images of PS/TiO$_2$ film
Additionally, as can be seen from figure 2c, TiO$_2$ lead to fractal type of aggregation on addition of 0.75 wt% filler content. Moreover in figure 2d the nucleates randomly agglomerate in the continuous phase and increase of titania particle volume fraction made the area larger and causes their overlap which led to opaque PS/TiO$_2$ films [6-7]. This suggests that the 0.75 wt% PS/TiO$_2$ films have large particle agglomerates, while the 0.5 wt% PS/TiO$_2$ films have improved dispersion as well as higher interface area and therefore possess higher UV-absorption efficiency.

4. PS/TiO$_2$ UV–Vis Shielding

In figure 3, pure PS film seems rather transparent in the visible region (400-800 nm), whereas films with increasing TiO$_2$ content continuously adsorb more UV light as a result of empty conduction band and filled valence band. However, UV protection behaviour was observed with 0.5 wt% content of TiO$_2$ and extensive UV-blocking effect with visible transmittance more than 70% in the region below 355 nm was seen. With the further addition of 0.75 wt% TiO$_2$, the material appeared opaque to eye observation and had significant absorbance in the visible region as well as in the UV region. In addition, the cluster sizes of films became more nonuniform, and irregular with increasing TiO$_2$ content up to 1 wt% which causes a reduction in transmittance.

![Figure 3. The transmittance spectra of PS/TiO$_2$ films](image)

Figure 3. The transmittance spectra of PS/TiO$_2$ films

Figure 4 shows that the bandgap energy of samples was found to be 3.00 and 2.61 eV, for pure PS and 0.5 wt% TiO$_2$/PS respectively. This variation in the calculated optical band gap may reflect the role of dopant particles in modifying the electronic structure of the PS matrix due to appearance of various polaronic and defect levels [8-9]. The decrease in bandgap also reflects the increase in degree of disorder in the films which arises due to the change in polymer structure.

![Figure 4. Plot of $(a_0h\nu)^2$ v/s photon energy (h\nu) of PS/TiO$_2$ thin films](image)

Figure 4. Plot of $(a_0h\nu)^2$ v/s photon energy (h\nu) of PS/TiO$_2$ thin films
5. Conclusions
XRD results reveals that low intensity diffraction peaks showed crystalline domains of the PS chains. Morphological studies show that the titania particles were aggregates of loosely associated primary particles. With 0.5 wt % content of TiO$_2$, extensive UV-blocking effect in the region below 355 nm was observed. This confirms the introduction of matrix compatible polymer chain doped with TiO$_2$ particles increased the UV shielding ability of PS film.

Acknowledgement
The authors would like to thank the Director and Center Director of UGC-DAE CSR, Indore for their concern to avail the characterization facilities and Dr. Y.K. Vijay (Prof. University of Rajasthan, Jaipur) for providing the experimental facilities to study positron lifetime.

References
[1] Pavlidou S, Papaspyrides C D 2008 Prog. Polym. Sci. 33 1119
[2] Yoon K B, Hwang Y Y, Noh S K and Lee D H 2008 Polym. J. 40 50
[3] Jordan J, Jacob K I, Tannenbaum R, Sharaf M A, Jasiuk I 2005 Mater. Sci. Engg. A 393 1
[4] Zaragoza contreras E A, Hernandez escobar C A, Mendoza duarte M E, Flores-Gallardo S G, Ibarra gomez R, Marquez lucero A 2009 Polym. J. 41 816
[5] Acharya A D, Moghe S, Panda R, Shrivastava S B, Gangrade M, Shripathi T, Phase D M and Ganesan V 2012 Thin Solid Films 525 49
[6] Menga X, Zhanga Z, Luo a N, Caoa S, Yangb M 2011 Poly. Sci. A 53 977
[7] Scrosati B 1988 in Solid States ionic Devices ed Chowdari B V R and Radhakrishna S (World Scientific Publishing Co.) 133
[8] Devi C U, Sharma A K and Rao V V R N 2002 Mater. Lett. 56 167
[9] Rozra J, Saini I, Sharma A, Chandak N, Aggarwal S, Dhiman R and Sharma P K 2012 Mater. Chem. Phys. 134 1121