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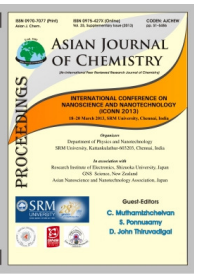

Analysis of Composite Spin Coated Thin Films [Polystyrene and Poly(methyl methacrylate)]†

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Solvent cast composite thin films of polystyrene and poly(methyl methacrylate) have been deposited by spin coating on silica substrate. Thin films of few μm thickness obtained have been examined using UV-visible, photoluminescence, XRD and SEM characterization methods. The band structure of polystyrene tailored by the addition of poly(methyl methacrylate), had 90 % transmittance. The amorphous nature of the material was confirmed using XRD analysis. Homogeneous crack free surface of the coated film has been observed by SEM analysis.

Key Words: Photoluminescence, Thin films, Polystyrene, Poly(methyl methacrylate).

INTRODUCTION

Polymers are of profound interest to society and are replacing other materials in diverse field of life, which can be further modified according to modern applications. Polymer materials have been widely used in various fields such as optical communications and electronics sensors[1]. In recent years thin polymer blend films have received much attention because of their technological importance. New materials with enhanced mechanical, optical and thermal properties can be created through the blending of polymers[2]. In general, polymer blends are formed by blending two or more immiscible polymers and the process of blending are usually classified by two routes, reactive route and non-reactive route[3]. Polymerization processes are the most common ways to synthesizing polymer blends *via* reactive route. Several means of non-reactive route have been reported in literature. The simplest method to form polymer blend is the dissolution of two polymers in an organic solvent, followed by evaporation of the solvent[4-6]. Blending of a polymer with another polymer, can change the structural, optical and mechanical properties of the primary polymer. In this article the changes in the optical properties of polystyrene by the addition of poly(methyl methacrylate) have been investigated.

EXPERIMENTAL

Polystyrene (99 % purity), poly(methyl methacrylate) (> 99 % purity), ethyl methyl ketone GR (> 99 % purity-Merck) were used to prepare polymer precursor solution. HCl GR (> 40 % purity-Merck), HNO_3 GR (> 60 % purity-Merck), acetone GR (> 99 % purity-Merck), double distilled water and extran were used to clean the microscopic glass slides.

Film preparation: The solution was prepared by dissolving known quantities of polystyrene (PS) and poly(methyl methacrylate) (PMMA) separately in ethyl methyl ketone (EMK) at room temperature to yield different molar solutions and then mixed. The reaction solution was heated to 40 ºC to ensure a homogeneous mixing of solvent. Then the solution was filtered using 0.5 μm Whatman filter paper to remove any undissolved impurities and dust before use. Thin films were deposited using spin coating unit. The rate of growth and thickness of the film depend on the nature of the substrate, the concentration, rmp and also the time of deposition. Spin coating unit (SCU 2007 model) supplied by Apex Instruments Co., Kolkata has been used during the first stage, the plate is spun at a low to moderate speed 500-1000 rpm for 5-10 s to evenly spread the solution. The thickness of the coating is then determined and controlled during the second stage by spinning the coating at a higher speed, between 2500-3000 rpm for time duration less than 1 min.

RESULTS AND DISCUSSION

Thin film characterization provides new challenges as they generally consist of a small amount of material and thus pose problems from an analytical point of view. The measurement of thin film properties is indispensable for the study of thin

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film materials and devices. Thickness of the coated films was measured by microbalance gravimetric technique. Thickness of the spin coated polymer films are given in Table-1 and it is observed that, film thickness increases as deposition time duration increases but decreases as rpm increases validating the technique adopted in this study.

TABLE-1
THICKNESS OF THE SPIN COATED FILMS

Constituents	Temp. (ºC)	Duration (h)	Thickness (µm)
2.0 g PMMA + 100 mL EMK	40	4	4.430
		5	4.930
		8	5.263
4.5 g PMMA + 1.8 g PS + 100 mL EMK	40	4	4.580

UV-Visible analysis: All UV-VIS spectrophotometric measurements of solution grown polymer films were made with LAMBDA UV/VIS spectrophotometer of Perkin-Elmer. The entire coated surface was illuminated by UV-VIS radiation and the spectroscopic data was taken for PS, PMMA and PS/PMMA. The UV-visible-NIR spectrum of PS films is shown Fig. 1a. The transmittance spectrum reveals a peak at 298 nm in the UV region and transmittance edge appears at 508 nm. The transmittance spectrum of PMMA films is shown in Fig. 1b, maximum transmittance peak is found to occur at 294 nm. The transmittance spectrum of composite film is shown in Fig. 1c. A sharp intense peak is observed at 300 nm *i.e.* in UV region and transmittance increases gradually as wavelength increases.

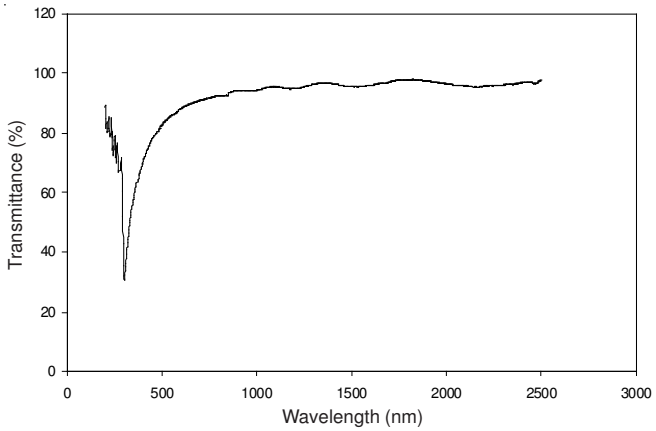

Fig. 1 (a). Transmittance spectrum of polystyrene

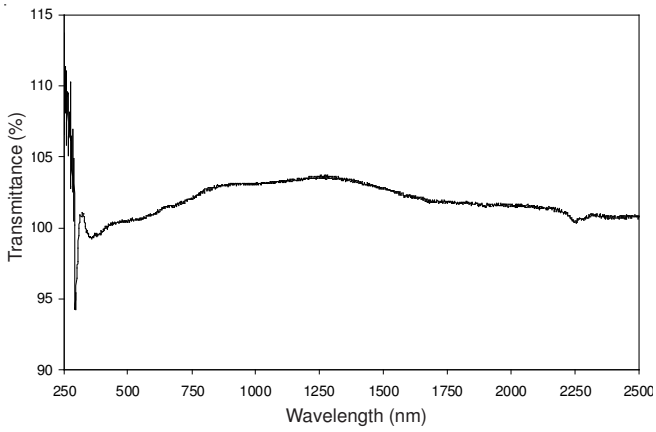

Fig. 1 (b). Transmittance spectrum of poly(methyl methacrylate)

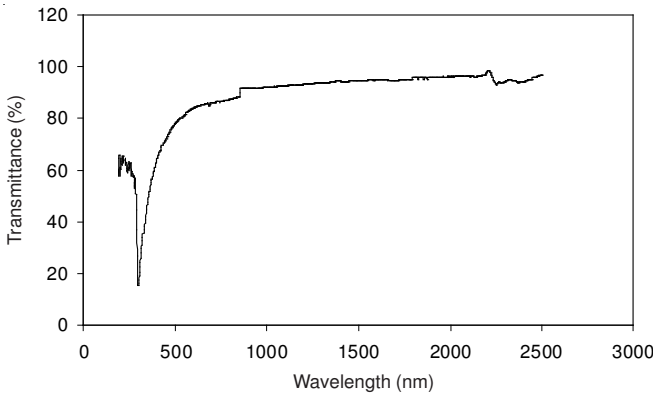

Fig. 1 (c). Transmittance spectrums of composite thin films

Photoluminescence spectrum analysis: Photoluminescence behaviour of all thin film samples deposited in this study are excited at 300 nm and emission spectrum has been recorded from 318 to 587 nm. The photoluminescence behaviour of polystyrene film is shown in Fig. 2(a), which shows a sharp emission at 539 nm. The photoluminescence spectrum of PMMA film is shown in Fig. 2(b), revealing prominent emission at 542 nm. The photoluminescence spectrum of composite is shown in Fig. 2(c), which shows the emission occurrence at 373, 389 and 501 nm.

The transmittance of PMMA usually lies above 90 %, the PMMA-PS composite in ethyl methyl ketone exhibits transmittance around 90 % and also has consistent transmittance over the entire IR range (*ca.* 1000-2400 nm). Hence this feature of

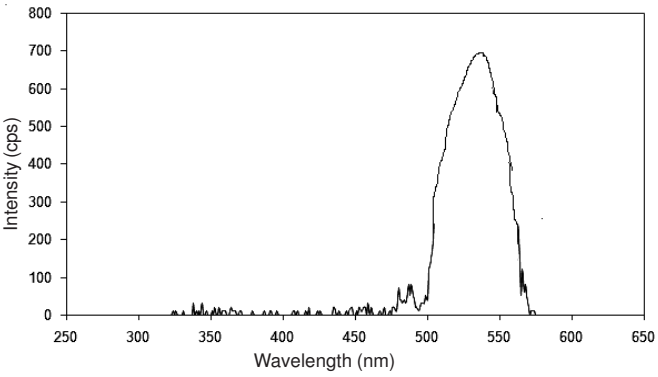

Fig. 2(a). Photoluminescence spectrum of polystyrene

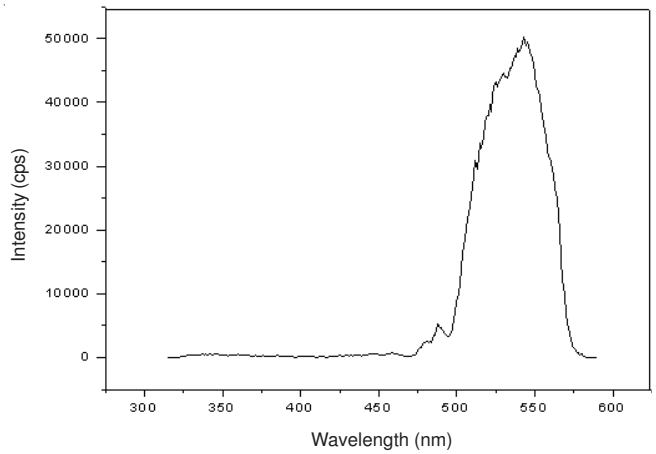

Fig. 2(b) Photoluminescence spectrum of poly(methyl methacrylate)

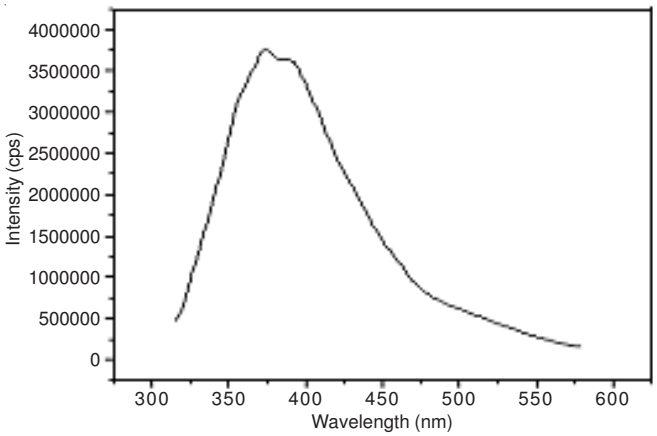

Fig. 2(c). Photoluminescence spectrum of composite thin film

the film will be favourable for IR therapy. Comparing PS and composite film, it is observed that the emission of PS at 539 nm has shifted to 501 nm in the composite. Pristine PS is noted to have an emission at 510 nm. This indicates that the addition of PMMA with PS in the present study has reduced the band gap from 510 to 501 nm. The value of FWHM is 70 nm for composite film, whereas the FWHM value of PMMA is 50 nm from UV-visible spectra which is shown in Fig. 3.

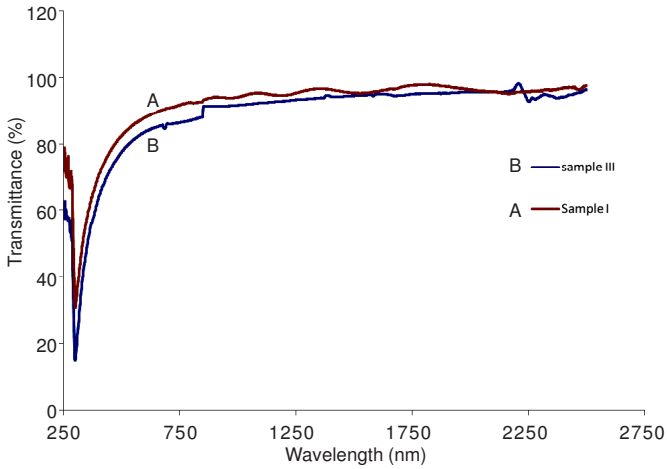

Fig. 3. Shift in bandgap

An energy level diagram shown in Fig. 4, utilizing the absorption and emission spectra obtained.

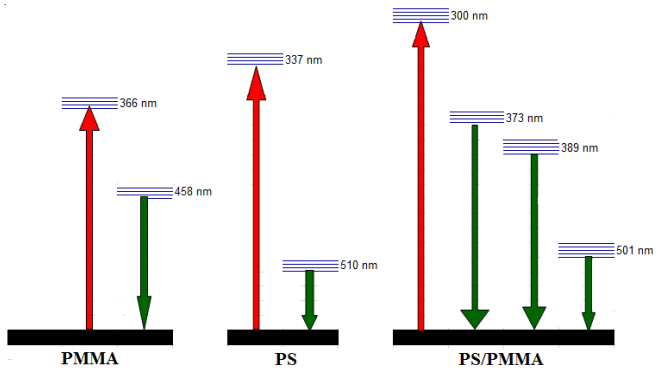

Fig. 4. Energy level diagram

The analysis of emission from PS, PMMA and the composite of PMMA and PS in ethyl methyl ketone shows the emission at 373, 389 and 501 nm for the similar excitation at 300 nm. This suggests that PMMA/PS composite with especially the solvent used as EMK can be a perspective candidate for UV pass filters. While looking at the FWHM of the absorption peaks, the bandwidth has been found to shift from 50 to 70 nm, an additional 20 nm band broadening indicates that ample amount of transition probability has been allowed due to the composite film formation compared to pristine PMMA films. Hence PS/PMMA composite films can act as UV pass filters for the solar simulator experiments.

XRD analysis: The X-ray diffraction studies were carried out using Pananalytical Xpert pro X-ray diffractometer with CuK_α radiation of wavelength $\lambda = 1.54060$ Å in the angle range $2\theta = 10^\circ$ to 80° with step size of 0.0170°. The X-ray diffraction pattern of PS, PMMA and composite film are shown in Figs. 5a-5c, respectively. XRD pattern of PMMA and composite shows only two broad peaks indicating amorphous nature. Table-2 shows the measured values of XRD parameters and the calculated values of interchain distance (r). The interchain distance between PMMA polymer chain is 3.5295 Å (computed from first peak) and the distance between pendant groups ($COOCH_3$) is 1.5536 Å (computed from second peak) respectively.

TABLE-2
XRD PARAMETERS

Sample	Position (2θ) (º)	β (º)	d-spacing	r (Å)
PMMA	31.6625	0.0502	2.82596	3.5295
	76.5972	0.8029	1.24393	1.5536
Composite	31.6647	0.2007	2.82578	3.5292
	36.4440	0.4015	2.46542	3.0792

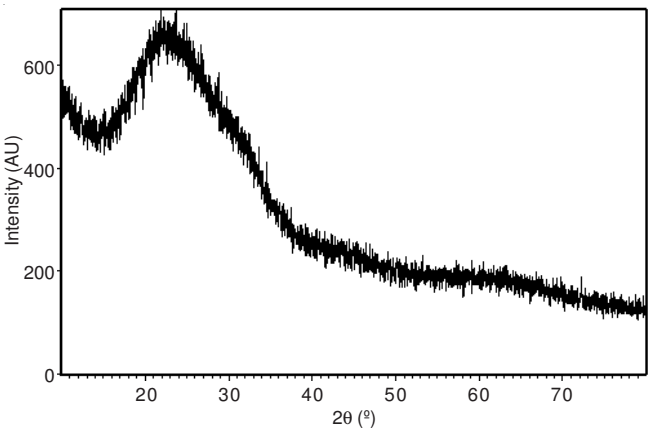

Fig. 5(a). XRD pattern of polystyrene

Surface analysis: The surface morphology of composite PS/PMMA thin film was analyzed using FEI Quanta FEG 200 high resolution scanning electron microscope (HRSEM), (Fig. 6).The micrograph of the film indicates homogeneous, continuous and crack free nature of the surface. The film is found to have randomly oriented rod like grains. Both short and long rods are present in the SEM image of PS/PMMA composite film, having a length of 1.61 and 2.89 μm, respectively.

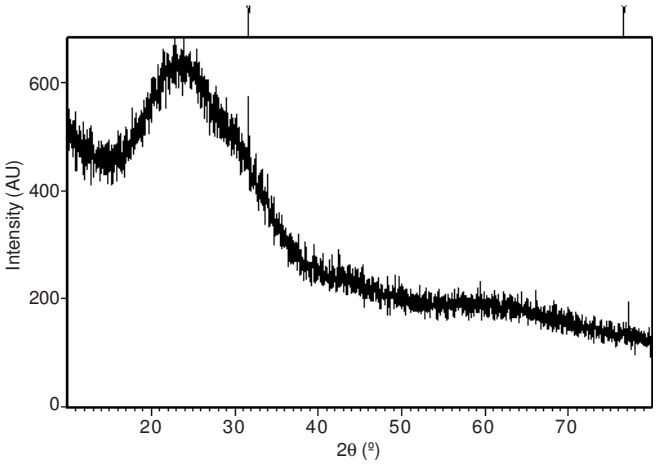

Fig. 5(b). XRD pattern of poly(methyl methacrylate)

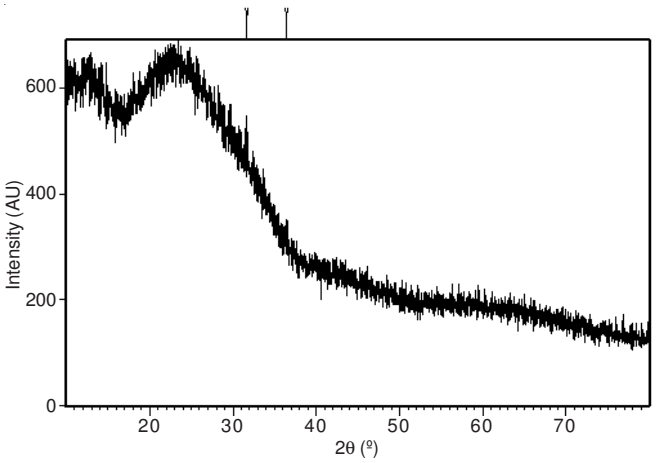

Fig. 5(c). XRD pattern of PS/PMMA film

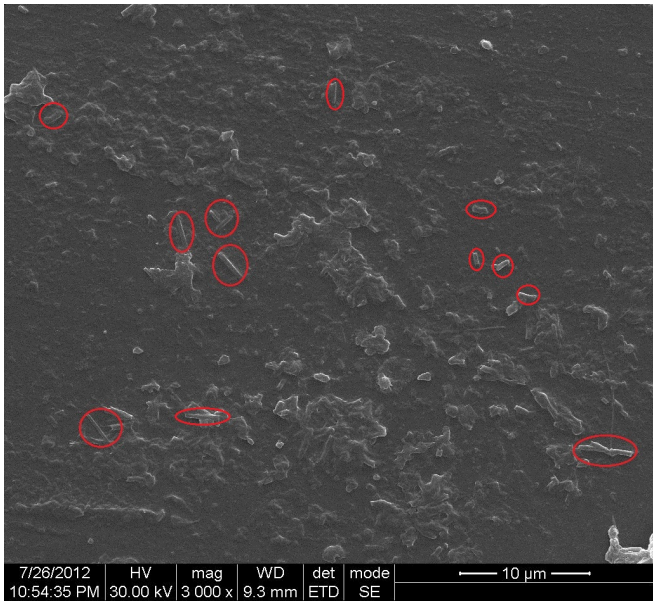

Fig. 6. SEM Image of PS/PMMA composite film

Conclusion

The composite PS/PMMA thin films prepared by spin coating method, which is a convenient and economical way. The structural and optical properties of the coated films were analyzed using various characterization methods. The XRD studies indicate the amorphous nature of the material and the SEM analysis indicates the crack free nature of the coated composite film. The coated PS/PMMA film has 90 % transmittance so it can be used as an alternative to glass in many applications and it was found that by the addition of PMMA, band gap of PS has been tailored. This property can be utilized in the area of UV pass filters for the solar simulator experiments and microbial activity studies.

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