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Tailoring the Optical Properties of Polymers Blend Nanocomposites**Y.K. Saraswat¹ Shalini Agarwal² Vibhav K. Saraswat^{3*}**

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ABSTRACT

The presented work deals with the structural and optical properties of chemically synthesized TiO₂ nanoparticles filled PC/PS blend nanocomposites. A series of PC/PS (100/0, 50/50, 0/100 wt%/wt %) -TiO₂ (1, 2, 3 wt %) blend nanocomposites have been prepared by solution casting method. Prepared blend nanocomposites have been subjected to XRD, SEM and FTIR for structural analysis. Optical constants have been analyzed using UV-Vis spectroscopy. The XRD, SEM and FTIR spectrum confirms the formation of PC/PS-TiO₂ blend nanocomposites. Results reveal the decrease in band gap and enhancement in optical constants like, extinction coefficient, refractive index and dielectric constants of blend nanocomposites with nanofiller TiO₂ content.

1. Introduction

Polymers, due to their versatility and wide variety of applications, have been creating a worldwide demand. Common polymers used in many applications as raw material are acrylics, *acrylonitrile*, polyethylene, polypropylene, polystyrene and polycarbonates^[1-3]. Among these polymers polycarbonate (PC) has attracted considerable attention, since polycarbonate is amorphous, transparent, fully recyclable, made from natural resources and one of the most widely used engineering polymers. It can withstand all sorts of extreme and adverse environmental conditions. It is also helpful in minimizing the carbon footprint. It shows very good thermal and mechanical properties^[4-8]. Moreover, amorphous materials have a lot of useful potential applications concerned with

their electrical and optical properties. Many electronic equipment is made up of Polycarbonates like CDs and DVDs, automobile parts, sports safety equipment, reusable water bottles, containers for food-storage due to its toughness and heat resistance^[9,10]. Polystyrene (PS), a versatile thermoplastic polymer, is one of the commercial polymers widely used in various industrial fields, packaging and biomedical applications. When combined with various colorants, additives or other plastics, polystyrene (PS) is used to make appliances, electronic, automobile parts, toys etc.^[11,12].

In the large field of nanotechnology, combining the properties of the polymer matrix and the inorganic filler provides a new economic way to obtain tailored high-performance materials, as they can provide the necessary stability and easy process-ability with interesting optical

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properties [9-12]. Polymer nanocomposites possess unique material properties which make them suitable for optical applications. The addition of nanoparticles into a polymer matrix makes it wear and scratches resistant. The large surface-to-volume ratio of nanoparticles allows significant improvement and modification of material properties [13-19]. Inorganic filler titanium dioxide (TiO₂) has drawn enormous attention in recent years due to its importance in a variety of practical applications: photo catalysis, optics, sensing, optical-interference coatings and electric devices such as varistors, in paints (as a pigment). TiO₂ is biologically and chemically inert, non-toxic, abundantly available and cheap [20-24].

TiO₂ is the promising material as semiconductor having high photochemical stability and low cost [25]. A great deal of research effort has been focused on both synthesis of nanocomposites and their linear and nonlinear optical properties. M. T. Ramesan et.al [21] has reported about conductivity studies of copper sulphide nanoparticles incorporated polypyrrole (PPy)/polyvinyl alcohol (PVA) blend by in situ chemical oxidative polymerization. Thin films of polystyrene and polystyrene-TiO₂ nanocomposites have been prepared by spin coating and exposed to UV irradiation, the reduced values of optical band gap have been found in the range from 4.54 eV in pure PS to 4.45eV for PS-TiO₂ nanocomposites prior to irradiation [26]. Ruchuan Liu et. al [27] has reviewed recent progress on hybrid photovoltaic systems of inorganic semiconductors and organic conducting polymers.

The measurement of the optical absorption coefficient, particularly near the fundamental absorption edge, provides a standard method for investigation of optically induced electronic transitions. This also provides some ideas about the band structure and energy gap in both crystalline and non-crystalline materials [28-30]. The work described in this paper is concerned with the structural and optical properties of PC/PS-TiO₂ blend nanocomposites.

2. Experimental

The polycarbonate, Polystyrene (in granular form), Titanium III Chloride (TiCl₃) (mw~154.2) and Ammonium Hydroxide (NH₄OH) have been procured from Sigma Aldrich (USA). Di-ChloroMethane (DCM) (density=1.325) has been procured from Merck Pvt Ltd (India).

The chemical precipitation method has been employed to synthesize TiO₂ nanoparticles. In this method, solution mixture of TiCl₃ solution and NH₄OH aqueous solution in a volume ratio 1:6, has been stirred for 48 hrs at room temperature. Then, solution has been centrifuged and white precipitate has been further washed in isopropyl alcohol. White powdered TiO₂ nanoparticles have been obtained after drying precipitate at room temperature [31].

PC and PS have been used as precursor. PC and PS have been taken in 100/0, 50/50, 0/100 weight ratio and dissolved in solvent (DCM). TiO₂ nanoparticles, with 1, 2 and 3 wt %, have been added in this solution and is sonicated for 10 min. Resultant solution has been cast and dried on to the glass Petri dish. Self- sustainable film has been peeled off from Petri dish and used for characterization.

3. Theory

The optical absorption coefficient (α), can be calculated from the optical absorbance spectra using the relation [32,33]

$$\log\left(\frac{I_0}{I_t}\right) = 2.303 A = \alpha t \quad (1)$$

Where, I_0 be the intensity of incident beam, I_t be the intensity of the transmitted beam, A be the optical absorbance, and t be the film thickness.

The transmission coefficient (T) can be calculated using the relation [33];

$$T = 10^{(-A)} \quad (2)$$

While, the values of reflectance have been obtained from absorbance and transmission coefficient using the relation;

$$R = 1 - (A + T) \quad (3)$$

The absorption edge for transitions can be obtained according to the model proposed by Tauc [34,10] as;

$$\alpha h\nu = C_0(h\nu - E_g^{opt})^n \quad (4)$$

Where, E_g^{opt} be the energy, which is independent constant related to the properties of the valance and conduction bands, $(h\nu)$ be the photon energy, E_g^{opt} be the optical energy band gap of the material. The value of 'n' for allowed direct transition is taken as 1/2 [6]. The variation of $(\alpha h\nu)^2$ against $(h\nu)$ yields a good straight line fit to the absorption edge and the extrapolated $(h\nu)$ for $(\alpha h\nu)^2 = 0$ provides the E_g^{opt} .

The extinction coefficient k can be obtained from the relation [35] as

$$k = \frac{\alpha \lambda}{4\pi} \quad (5)$$

Where, λ be the wavelength of light.

The variation of the refractive index 'n' can be calculated by [36].

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (6)$$

Refractive index 'n' determines how reflective and refractive a film made from this material will be [37].

The real (ϵ_r) and imaginary (ϵ_i) parts of the dielectric constant have been given by the following equations [38].

$$\epsilon_r = n^2 - k^2 \quad (7)$$

$$\epsilon_i = 2nk \quad (8)$$

4. Results and Discussion

4.1 X-Ray Diffraction (XRD)

X-Ray Diffraction of prepared TiO₂ nanoparticles and TiO₂-PC/PS blend nanocomposites have been recorded, using Bruker D8 Advance with Cu (K α) radiation ($\lambda=1.54$ Å), in the range of $2\theta = 20^\circ-70^\circ$. Figure 1 shows X-ray diffractogram of TiO₂ nanoparticles and a representative XRD pattern of PC50%/PS50% and its TiO₂ blend nanocomposites.

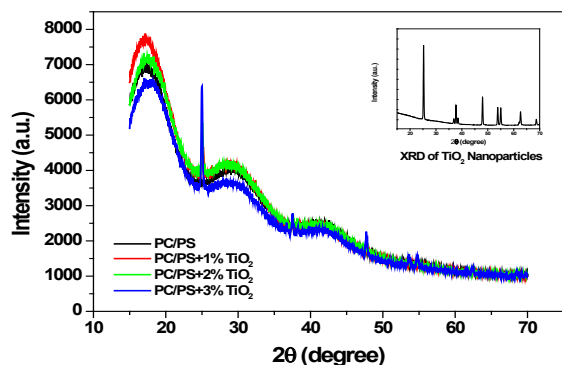


Figure 1. XRD pattern of (a) TiO₂ nanoparticles (b) PC50%/PS50% and its TiO₂ blend nanocomposites

The appearance of sharp crystalline reflections indicates the high purity and crystallinity of the nanoparticles. Their average crystallite size has been estimated, according to the Scherrer equation [39], as ~19 nm. On the other hand, the diffractogram of PC50% / PS50% shows broad reflections indicative of its amorphous character. These wide peaks in the diffractograms of the blend nanocomposites, together with those characteristics of the nanoparticles, confirm that the crystalline structure of the nanoparticles is maintained in the blend nanocomposites.

4.2 Fourier Transform Infrared (FTIR)

A Fourier transform infrared spectrum has been employed for structural characterization of blend nanocomposites. FTIR spectroscopy is one of the

powerful tools for identifying and investigating the presence of various functional groups in polymers. FTIR has been performed in transmission mode using Bruker Alpha-T spectrometer. The spectra have been recorded in the wave number range of 500-4250 cm⁻¹.

Figure 2 shows the FTIR spectra of PC 50%/ PS 50% (wt/wt) with TiO₂ (1, 2, 3 wt %) nanoparticles as a representative case. The absorption bands of PC, PS and TiO₂ have been observed in IR spectrum. Table 1 lists the absorption band modes observed in FTIR spectra.

Table 1. Observed bands and modes in FTIR spectra

S.No.	Mode	Wavenumber (cm ⁻¹)
1	C=O stretching band	1773
2	ring (C-C) vibrational mode	1507
3	O-C-O stretching vibrational mode	1013
4	aromatic C-H stretching	3026
5	aliphatic C-H stretching	2849
6	aromatic C=C stretching	1601, 1493
7	C-H deformation vibration band of benzene ring	758
8	Ring deformation vibration	700
9	Ti-O vibrational group	547, 551, 593

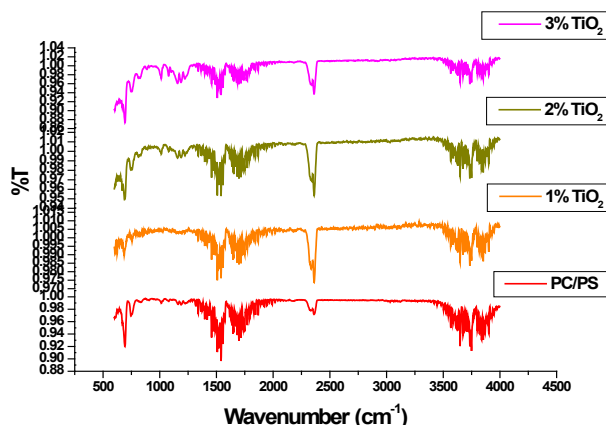


Figure 2. FTIR spectra of PC50%/PS50% and its TiO₂ blend nanocomposites

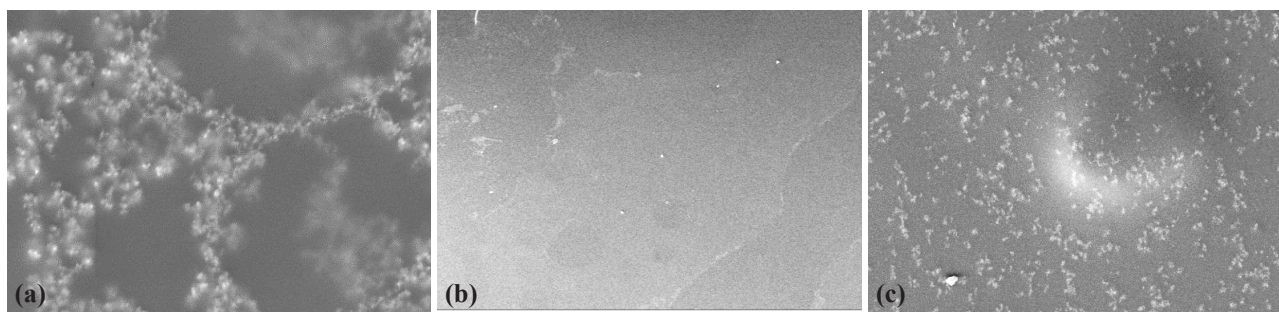


Figure 3. SEM images of (a) PC100%+2% TiO₂ (b) PC50%/PS50%+2% TiO₂ (c) PS100%+2% TiO₂ blend nanocomposites

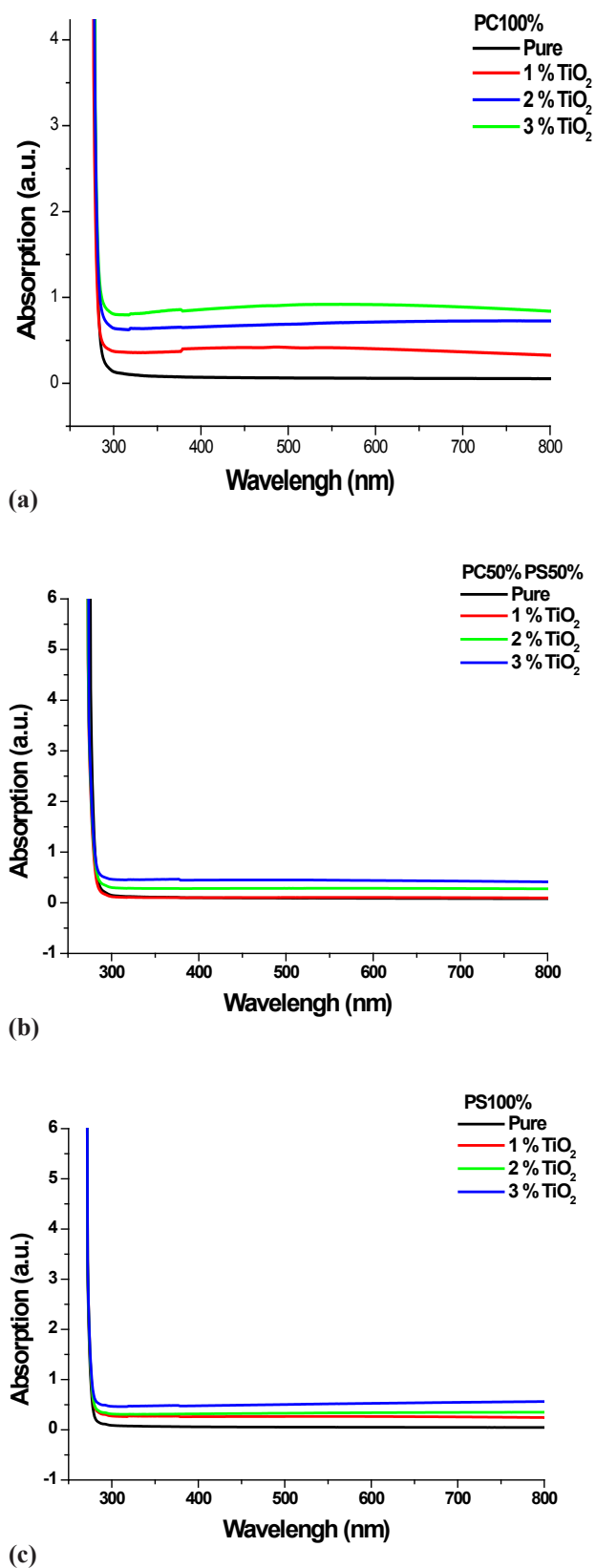


Figure 4. Absorption spectra for TiO₂ blend nanocomposites of (a) PC100% (b) PC50%/PS50% (c) PS100%

4.3 Scanning Electron Microscopy (SEM)

SEM provides very useful information about the particle size and location of filler on the surface of the material. Zeiss EVO 18, Scanning Electron Microscopy machine, has been employed to investigate the dispersion of nanoparticles in the polymer blend matrix. Figure 3 shows the SEM images of PC 100%, PC50%/PS50% and PS100% embedded with 2 wt% TiO₂ as representative cases. TiO₂ nanoparticles have tendency to agglomerate due to very high surface energy. Random and homogeneous TiO₂ distributions have been observed in polymer blend nanocomposites.

4.4 UV-Vis Spectroscopy

Perkin Elmer LAMBDA-750 UV/Vis/NIR spectrophotometer has been employed to record the absorption spectra in the wavelength range of 250-800 nm. Figure 4 shows the absorption spectra of blend nanocomposites under test. Red shift i.e. higher absorption has been observed in TiO₂ blend nanocomposites as compared to pure polymer matrix.

Absorption increases as TiO₂ content increase due to absorbance of the incident light by the free charge carriers. These absorption spectra have been used to calculate band gap using Tauc relation (eq.-4). Figure 5 shows the variation of $(\alpha h\nu)^2$ against $(h\nu)$ and calculation of band gap according to Tauc relation and the values of band gap have been listed in Table 2. A decreasing trend in the values of optical band gap is observed with the increase in TiO₂ wt% in the polymer blend samples under test. The lowest band gap (4.22 eV) has been found for PC50%/PS50% with 3% TiO₂ content.

Table 2. Values of band gap for PC/PS-TiO₂ blend nanocomposites

Sample	Pure	Band Gap (ev) 1%TiO ₂	2%TiO ₂	3%TiO ₂
PC100%	4.38	4.36	4.35	4.34
PC50%PS50%	4.26	4.24	4.23	4.22
PS100%	4.40	4.37	4.36	4.35

k , the extinction coefficient, has been calculated using equation (5). Figure 6 shows the dependence of k on λ for polymer blend nanocomposites. Results reveal that behaviour of k is nearly similar to corresponding absorption spectra (Figure 4) as, k is directly proportional to α . It has also been observed that values of k increase with increasing TiO₂ wt%.

The values of reflectance R have been obtained by

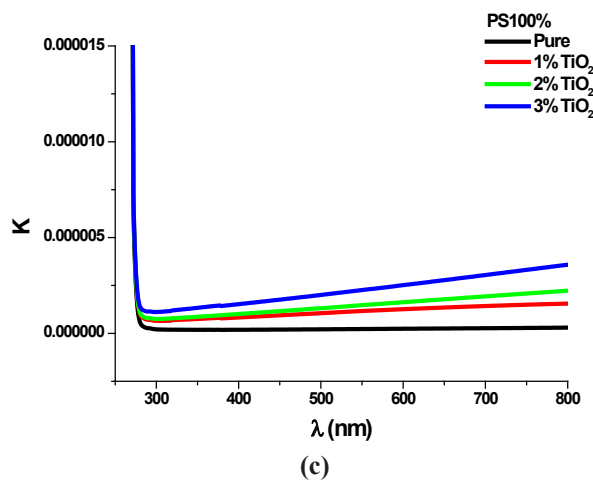
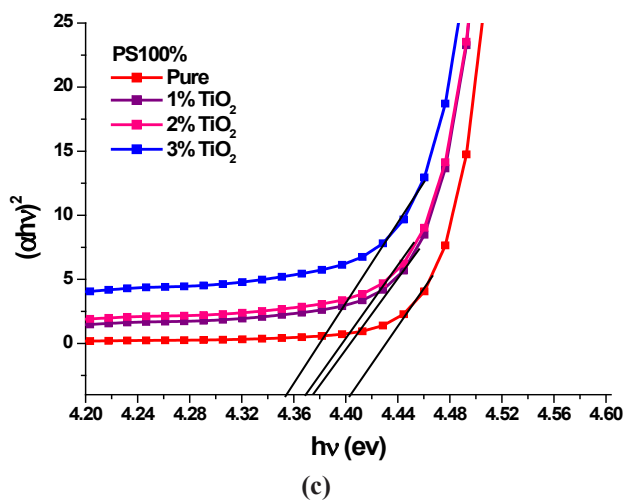
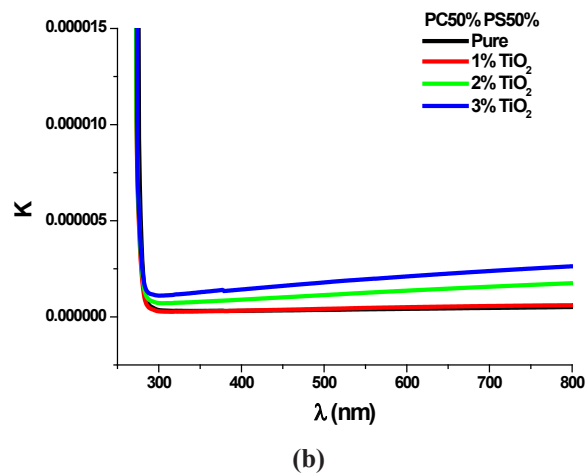
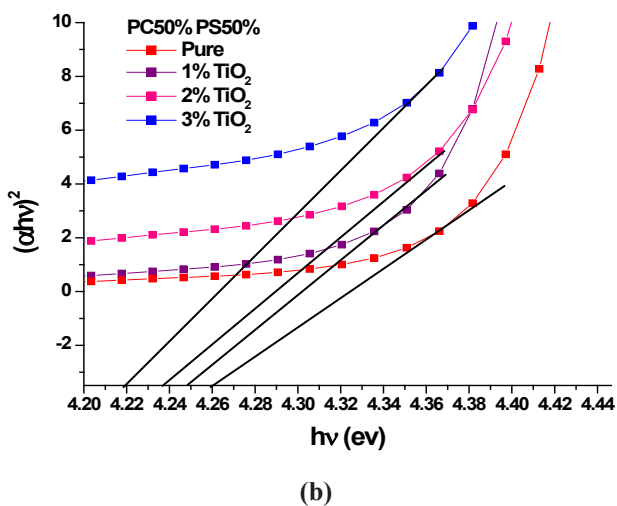
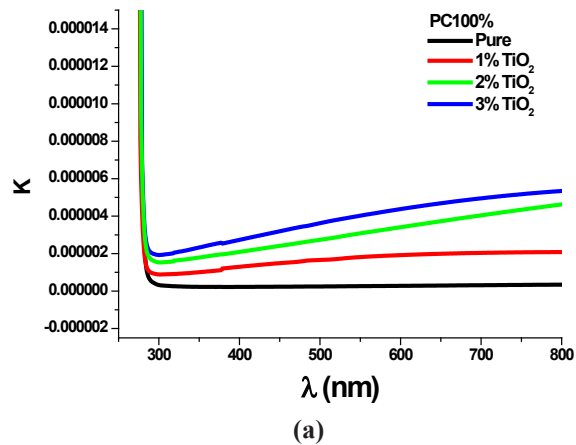
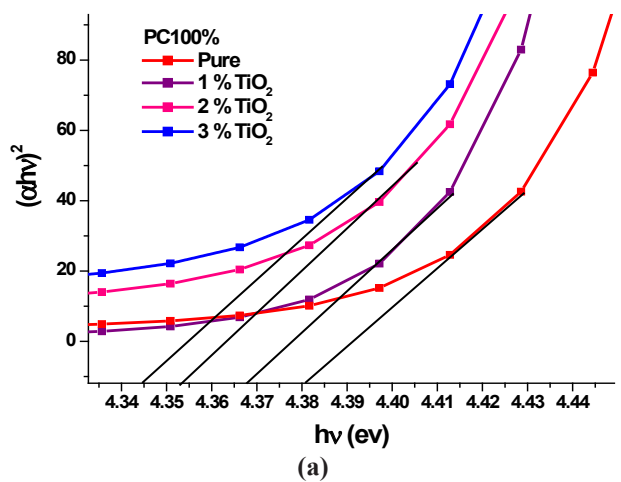


Figure 5. Band gap calculation for TiO₂ blend nanocomposites of (a) PC100% (b) PC50%/PS50% (c) PS100%

Figure 6. Variation of *k* with respect to λ for TiO₂ blend nanocomposites of (a) PC100% (b) PC50%/PS50% (c) PS100%

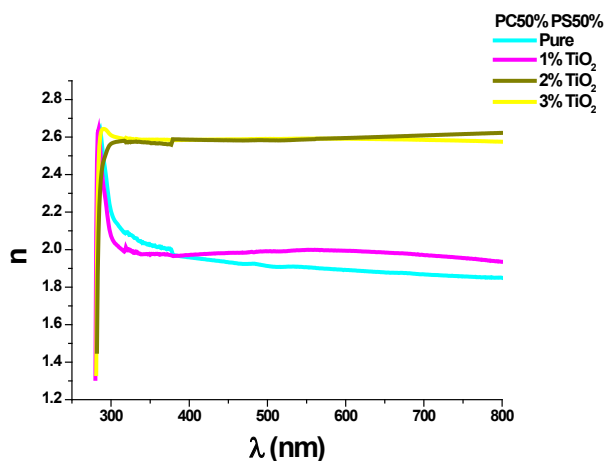


Figure 7. Variation of n with respect to λ for PC50%/PS50% and its TiO₂ blend nanocomposites

equation (3). Using formula (6), refractive index n has been calculated. Variation of n with respect to λ for PC50%/PS50% and its TiO₂ blend nanocomposites, as a representative case, has been shown in Figure 7. Most organic materials like poly (methyl methacrylate) (PMMA), PS, PC have a small adjustable refractive index range (1.3-1.7) due to their chemical structure limitation^[40]. Figure 7 illustrates the improvement in refractive index of blend nanocomposites in comparison with pure polymer matrix. Nearly equal values of refractive index have been observed for high (2 & 3wt %) TiO₂ content. The obtained result has been attributed to the high refractive index of TiO₂ nanoparticles.

The real (ϵ_r) and imaginary (ϵ_i) parts of the dielectric constant have been calculated using equation (7) and (8). Figure 8 shows the variation of real and imaginary parts of the dielectric constant of PC50%/PS50% and its TiO₂ blend nanocomposites, as a representative case. The real part of the dielectric constant increases on increasing TiO₂ wt%. Furthermore, nearly equal values of real part of dielectric constant have been observed for high (2 & 3wt %) TiO₂ content. It has been concluded that the variation of ϵ_r mainly depends on (n^2) because of small values of (k^2), while ϵ_i mainly depends on the (k) values which are related to the variation of absorption coefficients.

Keen observation of all optical properties leads an interesting inference that PC50%/PS50%-TiO₂ blend nanocomposites have the modified optical properties in comparison of pure polymer matrix. Such type of polymer blend nanocomposites can be useful for photovoltaic devices, solar cells etc.^[41,42]

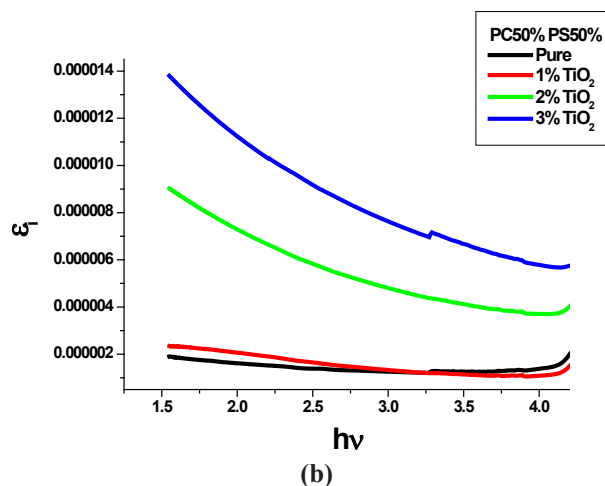
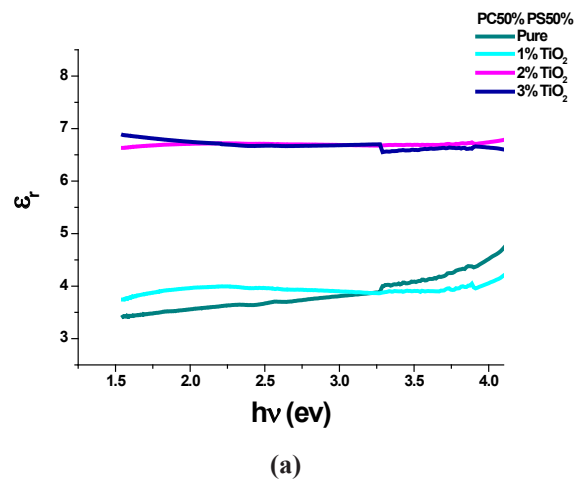


Figure 8. Variation of (a) real and (b) imaginary part of the dielectric constant of PC50%/PS50% and its TiO₂ blend nanocomposites

5. Conclusions

The discussion of the results obtained in present work leads to the following conclusions.

A series of PC/PS-TiO₂ blend nanocomposites have been prepared by solution casting method. The average crystallite size of chemically synthesized TiO₂ nanoparticles has been estimated using Scherrer equation and it comes out to be ~19 nm.

X-ray diffractograms of PC50%/PS50% and its TiO₂ blend nanocomposites show that the nanoparticles remain in nano-regime during blend nanocomposites preparation process. FTIR spectra shows the presence of various functional groups in blend nanocomposites, which confirms the formation of polymer blends and nanocomposites. SEM analysis provides the information about homogeneous distribution of TiO₂ in polymer blend nanocomposites.

Increase in absorption has been observed by increasing TiO₂ content in PC/PS matrix. Optical band gap decreases with increase in TiO₂ wt% in the polymer blend system. The lowest band gap (4.22 eV) has been found for PC50%/PS50% with 3% TiO₂ content. The enhancement in extinction coefficient, refractive index and dielectric constants of blend nanocomposites has also been observed. Such blend nanocomposites of PC/PS with modified optical constants are useful for photovoltaic applications.

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