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Research article

Delving into the properties of polymer nanocomposites with distinctive nano-particle quantities, for the enhancement of optoelectronic devices

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ABSTRACT

The study focusses on synthesis and modification of structural, optical and electrical characteristics of nanostructured titanium dioxide anatase embedded Poly(methyl methacrylate) (PMMA) nanocomposite with different weight percentages (0.03, 0.06, 0.12, 0.18 and 0.24%) by the solvent casting method. Modification in the morphology of PMMA nanocomposites with an increasing amount of titanium dioxide anatase is studied by using a field emission scanning electron microscope (FE-SEM). Micrograms of FE-SEM show spherical shaped nanoparticles distribution in PMMA nanocomposites thin films. In optical characterization, transmission, optical band gaps, the real and imaginary part of dielectric constant, linear susceptibility, optical conductivity, refractive index and extinction coefficient are calculated using experimental data. It is observed that the optical band gap has an overall decreasing trend with increasing the weight percentage of TiO₂ (anatase) in PMMA nanocomposites. It is also found that values of all electrical parameters decrease with increasing the weight percentage of TiO_2 (anatase) in PMMA nanocomposites. All wavelength depending parameters are investigated in the wavelength range from 190 nm to 2700 nm. Single oscillator model is used to analyze the refractive index dispersion and estimation of the oscillator energy and dispersion energy of the films. The study is applicable to optical sensors and other optoelectronic devices.

1. Introduction

Poly(methyl methacrylate) (PMMA) is classified as acrylate polymers [1]. It is an optically transparent thermoplastic, and it is widely used as a substitute for inorganic glass due to high impact strength, weather resistance and scratch resistance. Intrinsically it is an insulator but with doping and mixing with metallic nano particles, it starts conduct electric charges. The drastic change in the properties of polymer nanocomposites are influenced by the type of integrated nanoparticles, their size, shape, their concentration and interaction with polymer matrix [2].

PMMA as a conducting polymer has attracted attention for use in many applications as optical components, optical sensors and in optoelectronics devices due to their low cost and excellent physical and chemical properties [3]. There has been a quick technological growth in the area of optics which is demanding the development of novel materials. incorporation nanoparticles within a polymer will introduce polymer nanocomposites that have different physical, chemical properties that of pure polymer, the changing of the polymer including chain dynamics as well as mechanical, thermal, optical and electronic properties to varying degrees [4, 5]. Nanophosphors of scarce-earth

ions doped alkaline earth borates (Sr₃B₂O₆:Dy3+) which are spreader in a polymer PMMA matrix by casting solution and their characteristics and structural measures have been studied by Khursheed et al. [6]. Photoluminescence emission and excitation spectra of PMMA composited film was studies, they found that embedding of the nano phosphors in the PMMA preserves their typical luminescence emission. But increase in the thermal stability as compared to pure PMMA.

PMMA/α-Fe₂O₃-ZnO nanocomposites films were synthesized with different weight percentage of nanoparticles, optical and dielectric properties were investigated, it was observed that optical transmittance reduced with increasing concentration of nanoparticles, the real and complex permittivity and dielectric loss values of PMMA/α-Fe₂O₃ is higher than those of pure PMMA, PMMA/ZnO and PMMA/α-Fe₂O₃-ZnO [7].

The optical properties of PMMA composites with different nanoparticles were studied like, PMMA/ZnO [8, 9, 10], metal chloride doped PMMA [5], PMMA/calcium carbonate (CaCO₃) [11], PMMA/carbon nano-dots [3].

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Titanium dioxide or Titania is currently the focus of intense research due to their interesting chemical, electrical and optical properties [12]. Titania can be found in four different structures anatase, rutile, brookite and TiO_2 (B) [13]. The optical properties of TiO_2 thin film were studied by Essalhi et. al. [14], Evtushenko et. al. [12], Khan et al [15], Szindler et. al [16]. In addition, the optical and electrical properties of TiO₂ nanoparticles incorporated in different polymers were studied by many researchers. For instance, Ehsani et. al. studied TiO₂ nanoparticles/polytyramine composite film [17], TiO₂ rutile structure was synthesizes and composite to polyvinylpyrrolidone and poly(vinyl alcohol) (PVAL) by Nussbaumer et. al [18]. They reported Strong UV absorption of the nanocomposites and the maximum absorption was reported at 225 nm for PVAL-TiO2 nanocomposite. In 2012, Chand et. al [19]. reported an Improvement in thermo mechanical and optical properties of PMMA/TiO2 nanocomposite. They showed that peak of UV absorption has blue shifted with the doping of TiO₂ and the absorption has increased up to approximately 397%. The nanocomposites also showed an increase of up to 40% in tensile strength and modulus up to 16%

AL-Baradi [20] studied the optical properties of PMMA/TiO₂, in our work the thin films has a different process to synthesis, also the studying covers a wide range of spectrum in the UV-VIS-NIR that is from (190–2700) nm, also more optical properties was studied like optical conductivity, extinction coefficient, and the refractive index dispersion parameters, moreover the electrical properties of the PMMA/anatase nanocomposites was studied as a function in wavelength such as real and imaginary part of dielectric constant and the electrical susceptibility.

In present work, TiO_2 nanoparticles (pure anatase structural) embedded PMMA polymer thin films are synthesized by solvent casting method with different weight percentage. Structural, optical and electrical characteristics of these films are investigated.

2. Experimental

In order to study titanium dioxide (anatase structure) (TiO2 anatase structure with average particle size is 10-30 nm (99% purity, Nanostructured & Amorphous Materials Inc., USA) nanoparticles embedded PMMA, a thin film of PMMA/TiO₂ nanocomposite was synthesized using the solvent casting method. In the first step, PMMA polymer (from SABIC, Saudi Arabia) was dissolved in chloroform (99.4% pure from Sigma-Aldrich) at room temperature and stirred by a magnetic stirrer for an hour to totally dissolve to make a homogeneous solution. In the second step, a different amount of anatase structures of TiO₂ 0.03, 0.06, 0.12, 0.18, and 0.24 wt. % was added to the prepared solution for each percentage amount. The polymer nanocomposites solution was then placed for 20 min in ultrasonication, then again put into the magnetic stirrer for about 1-2 h until a homogeneous dispersion was obtained. The resulting solutions were then poured into separate petri dishes and left to dry for 2 days. The dried films were peeled off from the Petri dish when there were no more traces of the solvent. The thicknesses of the prepared thin films were measured by conventional micrometers and found that were 0.42, 0.40, 0.50, 0.30, and 0.44 mm for the 0.03, 0.06, 0. 12, 0.18, and 0.24 wt. %respectively.

In order to determine the crystal structure of PMMA/TiO₂ anatase thin films, single-crystal X-ray diffraction studies were carried out using diffractometer (XRD- Bruker D8 advance, Germany) with Cu Kα radiation $\lambda = 1.54060$ Å source with 20 ranging from 0 to 100°. The morphology of PMMA/TiO₂ nanoparticles composites was monitored by field emission scanning electron microscope (FE-SEM) (JEOL -JSM-7600F; JEOL Ltd., Akishima, Tokyo, Japan) after platinum coating on the surfaces and operated at an accelerated voltage 5 kV. The optical absorption and transmission spectra of PMMA/TiO₂ nanocomposites were recorded in the range 190–2700 nm using Jasco-V770 spectrometer.

3. Results and discussion

The crystallinity of the PMMA/TiO₂ anatase nanocomposites was analyzed by XRD method. XRD patterns of the pure PMAM and PMMA/TiO₂ anatase (0.06 and 0.24 wt.% of anatase) nano composite film and the TiO₂ anatase nanoparticles are shown in Figure 1. The XRD pattern of pure PMMA with triclinic structure matches with COD card no. 2224612 [21] for PMMA polymer. The XRD pattern of TiO₂ confirms that the TiO₂ has anatase tetragonal structure according to COD card no. 5000223 for anatase tetragonal nanoparticles [22].

The XRD pattern of PMMA/TiO₂ anatase (0.06 and 0.24 wt.% of anatase) nanoparticles also corresponding to the literature [23] which demonstrates that PMMA pure polymer, consists of a broad non-crystalline peak of the amorphous polymer at 15° and very low intensity of TiO₂ anatase peaks at around 25°. The appearance of very low intensity peaks of TiO₂ anatase in the XRD pattern of nanocomposite is due to the very low quantity of anatase nanoparticles in the nanocomposites.

Elastic strain also calculated from XRD pattern using Williamson-Hall (W–H) formula [24] as in Eq. (1).

$$\beta \cos(\theta) = \varepsilon (4 \sin(\theta)) + \frac{k\lambda}{D}$$
(1)

where β is the FWHM of the peak, θ position of the peak in radiance, ε is strain, k is constant equal to 0.9, λ is the wavelength of X-ray source and D is particle size. A plot is drawn with 4sin θ along the x-axis and β cos θ along the y-axis for PMMA/anatase nanocomposites, from the linear fit to the data, the strain ε was estimate from the slope of the fit.

The relation between wight percentage of anatase and strain is show in the Figure 2, the results suggested that elastic strain is decrease slightly with increase the anatase in polymer matrix.

The surface morphologies of the samples were observed using field emission scanning electron microscopy. Figure 3 exhibit the FE-SEM image of the pure PMMA and PMMA with anatase nanocomposites thin films. It can be seen in the Figure 3 (F) that TiO_2 nanoparticles have spherical and uniform shapes, the average sizes of anatase nanoparticles are determine from SEM micrographs as 50–75 nm. Roughened surface is aggregation of TiO_2 nanoparticles on the surface, usually nanoparticles tend to form agglomerates in polymer matrix due to its surface chemistry and high surface energy [25], in this work during the preparation of nanocomposites, to reduce the agglomeration; ultrasound treatment was used, which is one of the methods that used to control and avoid aggregations [26].



Figure 1. X-ray diffraction spectra of the PMMA/TiO₂ anatase nanoparticles composites films.



Figure 2. The relation between elastic strain and the weight percentage of anatase in PMMA polymer.

Transmittance of the materials has a vital role in the application of optoelectronic devices. Transmittance vs wavelength curve of pure PMMA and the nanocomposites with various amount of TiO_2 (anatase) is depicted in Figure 4. The Figure 4 demonstrates that transmittance decreases with increasing amount of TiO_2 (anatase) and the decrease in transmittance in the visible region is very high. The decrease in transmittance *T* of the nanocomposites is mainly due to light scattering by randomly dispersed spherical nanoparticles. If *r* is the radius and \emptyset_p is volume fraction, then according to theory of Rayleigh scattering, the

transmittance can be explained by the Eq. (2), the Rayleigh scattering formula [27].

$$T = \frac{I}{I_0} = exp \left\{ -\frac{32\pi^4 \varpi_p x r^3 n_m^4}{\lambda^4} \left[\frac{\left(n_p / n_m \right)^2 - 1}{\left(n_p / n_m \right)^2 + 2} \right]^2 \right\}$$
(2)



Figure 4. Transmittance spectra for PMMA/TiO₂ anatase structural.



Figure 3. FE-SEM of PMMA anatase nanocomposite A) pure PMMA B) 0.03, C) 0.06, D) 0.12, E) 0.18 and F) 0.24 wt.% of anatase.

where I and I_0 are the intensities of the transmitted and incident light respectively, x is the optical path length, λ is the wavelength of light, and n_p and n_m represent refractive indices of the particles and the matrix, respectively.

The optical absorption coefficient α can be computed using transmittance by the relation mentioned in Eq. (3) [28].

$$\alpha = \frac{\ln(1/T)}{d} \tag{3}$$

d: thickness, T: transmittance.

The optical band gap is another important parameter required for the designing of optoelectronic devices. The optical band gap is evaluated from optical absorption coefficient α near the absorption edge by Tauc plot using the following Eq. (4) [29].

$$(\alpha h\nu)^m = A(h\nu - E_g) \tag{4}$$

where A is constant of energy for a material within the measured optical material frequency range, E_g is the optical band gap, *h* the plank's constant, and ν the frequency of the incident photons. *m* is a constant which determines the type of the optical transition. For allowed direct transition m = 2. Figure 5 shows the Tauc plot for the direct optical band gap of pure and TiO₂ (anatase) nanoparticle embedded PMMA thin films. The intercept to x-axis of linear part of $(\alpha h\nu)^2 vs.h\nu$ curves give optical band gap values which are tabulated in Table 1. It is observed that the optical band gap has an overall decreasing trend with increasing the weight percentage of TiO₂ (anatase) in PMMA.

Reflectance of the nanocomposites vs wavelength in the range of 190 nm–2700 nm is depicted in Figure 6. It can be seen that the increasing amount of TiO_2 (anatase) nanoparticles in PMMA, reflectance is decreased but it does not change the profile of the reflectance vs wavelength.

The parameters, refractive index, dielectric constant, electrical susceptibility and optical conductivity etc. are very important for lightmaterial interactions in energy conversion for development of optoelectronics devices [7, 30, 31]. These parameters have been determined for the nanocomposites with varying amount of TiO₂ nanoparticles from experimental data. The dependence of these parameters on wavelength has also been investigated.

Refractive index is a fundamental physical property of a material which is a measure of propagates of light through a material. The higher the refractive index the slower the light propagation, which causes a correspondingly increased change in the direction of the light within the material. The refractive index *n* could be calculated from Fresnel's formula as given in Eq. (5) [29].

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{\left(1-R\right)^2} - k^2}$$
(5)

Where *R* is reflectance and *k* are extinction coefficient. The extinction coefficient is an intrinsic property of material depending on their structure and is measure of how strongly a material absorbs light at a particular wavelength. It is given by the fraction of light lost due to scattering and absorption per unit distance in participating medium. It can be calculated from the Eq. (6) [32].

$$k = \frac{\lambda \alpha}{4\pi} \tag{6}$$

The absorption coefficient α is calculated from Eq. (3), the dependence of the refractive index and extinction coefficient on the wavelength for pure PMMA and embedded TiO₂ (anatase) nanoparticles at various quantity is shown in Figures 7 and 8 respectively. From these figures, we can see that the refractive index is almost constant except with two valleys at $\lambda = 1687 \text{ nm and } 2250 \text{ nm}$. With increasing the concentration of TiO₂ (anatase) the refractive index

decreases accordingly (see Figure 7). Generally, the extinction coefficient increases with increasing the amount of TiO_2 (anatase) which means more loss of energy by scattering with increasing amount of TiO_2 .

Light propagation in absorbing materials can be described using a complex-valued refractive index. The imaginary part, k, handles the attenuation, while the real part, n, accounts for refraction.

The real part n and imaginary part k are related to the complex dielectric constant. The real part of the dielectric constant shows how much it will slow down the speed of light in the material, whereas the imaginary part shows how much a dielectric material absorbs energy from an electric field due to the dipole motion [33].

The dielectric constant is given by the relation $\varepsilon = \varepsilon_r + \varepsilon_i$ whereas, the real and imaginary parts are related to refractive index and extinction coefficient as follow in Eqs. (7) and (8) [30].

$$\varepsilon_r = n^2 - k^2 \quad (\text{real part})$$
 (7)

$$\varepsilon_i = 2nk \quad (\text{imaginary part}) \tag{8}$$

Dependence of real part of the dielectric constant, ε_r and imaginary part, ε_i on wavelength for pure PMMA and nanocomposite at various amount of TiO₂ is shown in Figures 9 and 10 respectively. The Figure 9 demonstrate that with increasing the amount of nanoparticle of TiO₂ anatase, the value of ε_r decreases. The profile of ε_r also changes with changing amount of TiO₂. With increased number of nanoparticles in PMMA, there is little variation in ε_r with increasing wavelength.

Electrical susceptibility indicates the degree of polarization of a dielectric material in response to an applied electric field. The greater the electric susceptibility, the greater the ability of a material to polarize in response to the field, and thereby reduce the total electric field inside the material.

Electrical susceptibility can be calculated using the Eqs. (9) and (10) as follow [32].

$$\varepsilon_r = \varepsilon_0 + 4\pi \chi_c = n^2 - k^2 \tag{9}$$

$$\chi_c = \frac{n^2 - k^2 - \varepsilon_0}{4\pi}$$
(10)

The variation of electrical susceptibility χ_c of PMMA nanocomposites at wavelength from 190 nm to 2700 nm with increasing amount of TiO₂ nanoparticles, is depicted in Figure 11. It can be noted from Figure 11 that the electrical susceptibility decreases with increasing amount of TiO₂ nanoparticles correspondingly with



Figure 5. Tauc plot for determination of direct optical band gap of PMMA/ anatase nanocomposite.

Table	1. Optical	band gap,	dispersion	optical	parameters	of PMMA/T	iO ₂ anatas	e nanocomposites	films at	various	quantity	of anatase
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	PMMA pure	0.03 wt.% anatase	0.06 wt.% anatase	0.12 wt.% anatase	0.18 wt.% anatase	0.24 wt.% anatase
E _g (eV)	4.39	3.75	4.33	2.01	1.50	1.56
E ₀ (eV)	19.54	9.50	11.02	10.57	13.55	13.09
E _d (eV)	42.30	10.63	13.50	11.55	13.32	8.34
M ⁻¹	2.16	1.12	1.22	1.09	0.98	0.64
M ⁻³ ×10 ⁻³	5.7	12.4	10.1	9.8	5.3	3.7
n _∞	1.78	1.45	1.49	1.45	1.41	1.28



Figure 6. The reflectance spectra of the PMMA/TiO₂ anatase nanoparticles composites films.



Figure 7. The variation of refractive index with wavelength of the PMMA/TiO₂ anatase nanocomposites films at various quantity of TiO₂ (anatase).

increasing wavelength. This might be due to decrease in polarization with increasing number of nanoparticles at same electric field.

Optical conductivity is one of a good tool for the investigation of atomic structure of the material. It links the current density to the electric field with exposure of material at different wavelengths of light and depends mostly on absorption coefficient and refractive index of the material. The optical conductivity of PMMA/TiO₂ anatase nano-composites at different energies of light photons with changing various amount of nanoparticles of TiO₂ is investigated using Eq. (11) [34].



Figure 8. Extinction coefficient vs. wavelength for PMMA/TiO₂ anatase nanocomposites films at various quantity of TiO₂.



Figure 9. Real part of the dielectric constant vs. photon energy for $PMMA/TiO_2$ anatase nanocomposites films at various quantity of anatase with increasing wavelength from 190-2700 nm.

$$\sigma_{opt} = \frac{\alpha nc}{4\pi} \tag{11}$$

 α : Absorption coefficient, *n*: Refractive index *c*: The velocity of light.

Variation of optical conductivity with incident photon energy for PMMA/TiO₂ anatase nanocomposites films at various quantity of TiO₂ anatase is shown in Figure 12. It can be observed that optical conductivity increases with photo energy and at around 5 eV it increases rapidly its value increases more than 20 times the previous value. This rapid increase is due to increase in absorption at corresponding wavelengths.



Figure 10. Imaginary part of the dielectric constant vs. photon energy for $PMMA/TiO_2$ anatase nanocomposites films at various quantity of anatase with increasing wavelength from 190-2700 nm.



Figure 11. The electrical susceptibility variation with wavelength for PMMA/ TiO_2 anatase nanocomposites films at various quantity of anatase.



Figure 12. Optical conductivity vs. photon energy for PMMA/TiO₂ anatase nanocomposites films at various quantity of TiO_2 anatase.

Wemple-DiDomenico single oscillator model is used to analyze the refractive index dispersion below the inter-band absorption edge using the relation in Eq. (12) [35, 36]

$$n^{2}(E) = 1 + \frac{E_{d}E_{o}}{\left(E_{o}^{2} - E^{2}\right)}$$
(12)

n: refractive index, E_o : is oscillator energy, E_d : dispersion energy.

The above equation calculates the inter band optical transition strength. The dispersion has an important role in the research for optical materials. Dispersion phenomena is a significant factor in the field of optical communication and in manufacturing devices for spectral dispersion. Graph of $(n^2 - 1)^{-1}$ vs. $(h\nu)^2$ in Figure 13(A,B) allows us to determine the oscillator parameters E_o and E_d values from slope and intercept on the vertical axis of the plot. The calculated values of E_o and E_d are given in Table 1. It is observed that adding anatase nanoparticles in to the PMMA decreases the oscillator energy of the film, because TiO₂ filling increases the electron transition probability between electronics bands.

Refractive index at the longest wavelength n_{∞} and moment of ε (*E*) (M_{-1} and M_{-3}) are calculated using $E_{\circ}^2 = \frac{M_{-1}}{M_{-3}}$, $E_d^2 = \frac{M_{-1}^3}{M_{-3}}$ and $n_{\infty}^2 - 1 = \frac{E_d}{E_{\circ}}$ (see Table 1). The refractive index at longest wavelength



Figure 13. The plot of $(n^2-1)^{-1}$ vs. $(h\nu)^2$ of the PMMA/TiO₂ anatase nanocomposites films (A) from 14 eV to 18 eV energy and (B) films from 14 eV to 18 eV energy of photon.

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decreases with increasing the concentration of TiO_2 anatase in nanocomposites of PMMA.

4. Conclusion

PMMA/TiO₂ nanocomposites, with using only anatase nanostructure of titanium dioxide are synthesized by solvent casting method with different weight percentage of TiO₂. The structural properties of the nanocomposites thin films are analyzed by XRD which confirms the single anatase structure of titanium dioxide. The morphology is studied by FE-SEM. It shows existence of spherical shaped anatase nanoparticles in the polymer. Optical, and electrical parameters of the PMMA/TiO₂ nanocomposites are investigated.

The optical band gaps of the PMMA/TiO₂ anatase nanocomposites are estimated with Tauc plot. The values of optical band gaps change from 4.39 eV to 1.56 eV with increasing the weight percentage of TiO₂ (anatase) in PMMA. Study of wavelength dependent refractive index, extinction coefficient, dielectric constant and susceptibility of the nanocomposites reveals that the value of these parameters decreases with increasing amount of TiO2 in nanocomposites. It is also noticed that the profile of these parameters with wavelength variation from 190 nm to 2700 nm remain almost identical. In case of optical conductivity, its value increases with increasing amount of TiO₂ corresponding to incident photon energy and at around 5 eV it increases tremendously, more than 20 times the previous value. This rapid increase is due to increase in absorption at corresponding wavelengths. The dispersion of refractive index parameters is calculated by signal oscillator model, the refractive index at longest wavelength decreases by increasing the concentration of anatase in PMMA nanocomposites. The dispersion energies Ed of the thin films are in 42.30 eV for pure PMMA and decrease to average 10 eV in case adding anatase to PMMA. It is shown that the optical properties of PMMA nanocomposite can be controlled by the amount of anatase in the polymer. The present investigations are useful for the development of optics, Optical sensors and other optical instruments or optoelectronic devices.

Declarations

Author contribution statement

Nafeesah Yaqub: Performed the experiments; Analyzed and interpreted the data.

W. A. Farooq: Conceived and designed the experiments; Wrote the paper.

M. S. Alsalhi: Contributed reagents, materials, analysis tools or data.

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Data availability statement

The data is available in the material lab physics and astronomy department King Saud university Riyadh.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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