Study of optical properties of potassium permanganate (KMnO₄) doped poly(methylmethacrylate) (PMMA) composite films

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Abstract. We have developed films of pure polymethylmethacrylate (PMMA) (0.5, 1, 2 and 5%) and potassium permanganate (KMnO₄)-doped PMMA composite films of thickness ($\sim 100 \mu\text{m}$) using the solution-cast technique. To identify the possible change that happen to the PMMA films due to doping, the optical properties were investigated for different concentrations of KMnO₄ by recording the absorbance (A) and transmittance ($T\%$) spectra of these films using UV–Vis spectrophotometer in the wavelength range of 300–1100 nm. From the data obtained from the optical parameters viz. absorption coefficient (α), extinction coefficient (κ), finesse coefficient (F), refractive index (n), real and imaginary parts of dielectric constant (ϵ_r and ϵ_i) and optical conductivity (σ) were calculated for the prepared films. The indirect optical band gap for the pure and the doped-PMMA films were also estimated.

Keywords. PMMA–KMnO₄ composite films; optical properties; energy band gap; dielectric constant.

1. Introduction

The desire for high performance combined with reduction in size, weight and manufacturing-cost and the amenability for moulding into various desirable shapes suggests that polymers are promising potential materials to develop things of desired properties. One significant aspect is that these properties can be tailor-made for specific applications by use of filler/doped material. A careful literature survey reveals that the addition of small quantity of dopant filler significantly changes the optical, electrical, mechanical and thermal properties of polymeric materials, which assist in the development of novel materials with high-end applications for device industry. These changes in physical properties depend on the chemical nature of the dopant and on the interaction mechanism between the dopant and the host polymer. Recently, in their pursuit to develop suitable electrically conductive polymer composite materials for use within the electronics industry as suitable shielding for electromagnetic interference applications, we have developed potassium permanganate (KMnO₄)-doped polymethylmethacrylate (PMMA) composite films as explained in refs [1–3].

The optical properties of PMMA-based polymer nanocomposites, in particular, were found to have dopant-dependent optical and electrical properties [4–8]. A meticulous literature survey also reveals that although a great deal of work was reported in literature to the optical properties of filler-doped PMMA composite films, but no report can be seen in the literature about the optical properties of KMnO₄-doped PMMA films. Hence, it was significant for us to investigate

the optical properties of these prepared samples. The research would be significant as knowledge of optical constants like optical band gap, refractive index, extinction coefficient aid in examining their potentials to be used in optoelectronic devices. Thus, in this present work, we have tried to investigate the optical properties of PMMA–KMnO₄-based solid polymer composite films by measuring the absorbance (A) spectra and transmission ($T\%$) spectra of these composite films using UV–visible absorption spectroscopy as a tool.

2. Experimental

2.1 Materials

KMnO₄ was obtained from Himedia Laboratories (99.9%), and dichloromethane, purity of 99.8%, was purchased from Merck Specialties Private Limited, Mumbai. PMMA granules were purchased from M/s Gadra Chemicals, Bharuch. All chemicals were used as received.

2.2 Sample preparation

Films of pure PMMA and its composites with different wt% of KMnO₄ were prepared by solution-casting technique. A predetermined amount of granular PMMA is measured and dichloromethane is added as a solvent. The molten PMMA is stirred uniformly on a magnetic stirrer for 2 h and to this, prepared solution of different concentrations of KMnO₄ (0, 0.5, 1, 2 and 5% by weight) were dispersed

Figure 1. The prepared samples of varying thicknesses.

in PMMA matrix separately, using magnetic stirrer, where dichloromethane was used as a solvent. The solutions were thoroughly stirred using a magnetic stirrer at 60°C for 6 h to assure the dispersion of metal oxide nanoparticles aggregations throughout the solvent, until the homogeneous viscous molten state was obtained. The solution was cooled up to room temperature. Then, poured into a flat-bottomed glass Petri dish (diameter 76.2 mm) floated over mercury for 24 h, and the solvent was allowed to evaporate slowly at ambient temperature under atmospheric pressure for almost 24 h. The dried samples are peeled off by tweezers clamp. Transparent yellow flexible nanocomposite polymer films of thickness around 100 μm are obtained.

The illustration of the preparation procedure of polymer composite films and prepared samples of varying concentrations of KMnO_4 is shown in figure 1.

2.3 Theory for optical characterization

The absorbance and transmittance spectra were recorded using double beam UV-Vis spectrophotometer in the wavelength range of 300–1100 nm at room temperature. When light of intensity (I) is incident on a film of thickness (t), relationship between incident intensity (I) and penetrating light intensity (I_0) is given by

$$I = I_0 \exp(-\alpha t). \quad (1)$$

So that

$$\alpha t = 2.303 \log I/I_0, \quad (2)$$

or absorption coefficient

$$\alpha = 2.303(A/t), \quad (3)$$

where α is the absorption coefficient in cm^{-1} and the I/I_0 amount is defined as transmittance, so that $\log(I_0/I)$ is the absorbance (A).

The amount of optical energy gap from this region was evaluated from the Mott and Davis relation:

$$\alpha h\nu = C(h\nu - E_g)^m, \quad (4)$$

where $h\nu = E$ is the photon energy, C the proportional constant depending on the specimen structure, E_g is the allowed or forbidden energy gap of transition and the exponent m is an index, which determines the type of electronic transition responsible for absorption. It can take values 1/2, 3/2 for direct and 2, 3 for indirect allowed and forbidden transitions, respectively.

Reported literature [7,8] suggests that if the amount of absorption $\alpha > 10^4 \text{ cm}^{-1}$, the electronic transitions is direct, otherwise indirect one. If plotting α vs. E (i.e., $h\nu$) shows an $E^{1/2}$ dependence, then, plotting α^2 with E will show a linear dependence. Therefore, if a plot of $h\nu$ vs. α^2 forms a straight line, it can normally be inferred that there is a direct band gap, measurable by extrapolating the straight line to the $\alpha = 0$ axis. On the other hand, if plotting α vs. E (i.e., $h\nu$) shows an E^2 dependence, then, plotting $\alpha^{1/2}$ with E will show a linear dependence. So, when a plot of $\alpha^{1/2}$ vs. $h\nu$ forms a straight line, it can normally be inferred that there is a indirect band gap, measurable by extrapolating the straight line to the $\alpha = 0$ axis.

Further, the extinction coefficient is calculated using the relation:

$$k = \alpha\lambda/4\pi, \quad (5)$$

where λ is the wavelength of the incident ray.

The reflectance R is obtained from absorbance A and transmittance T using the following relation:

$$R + A + T = 1. \quad (6)$$

The refraction index (n) was calculated using the relation:

$$n = (4R/(R-1)^2 - k^2)^{1/2} - (R+1/R-1). \quad (7)$$

Also, the finesse coefficient is given by:

$$F = 4R/(1 - R^2). \quad (8)$$

The real (ϵ_r) and imaginary (ϵ_i) parts of the dielectric constant are related to n and k values accordingly:

$$\epsilon_r = n^2 - k^2 \quad \text{and} \quad \epsilon_i = 2nk. \quad (9)$$

The optical conductivity is related to light speed and can be expressed by the following equation:

$$\sigma_{\text{opt}} = nc\alpha/4\pi. \quad (10)$$

3. Result and discussion

UV-Vis double beam spectrophotometer is a simplest tool to probe the optical properties to estimate band gap energy and to determine the types of electronic transition within the materials. We have used Shimadzu UV-Vis double beam spectrophotometer to record the absorbance and transmission spectra of the prepared sample films in the wavelength range of 300–1100 nm.

Figure 2 shows the absorbance spectra as a function of wavelength of the incident light for PMMA film with different concentrations of KMnO_4 . It is clear that increase in the concentration of KMnO_4 in the polymer matrix leads to increase in the peak intensity. Thus, there is chemical interaction between the two components in the matrix and the increment in the absorption is attributed to the increment in the concentration of KMnO_4 , which is the absorbing component. An ample literature survey also reveals similar behaviour for different salts doped in PMMA, whether PMMA doped by methyl blue and methyl red composite films [4], or PMMA doped with CrCl_2 [5], or the couramine-102/PMMA thin films [7], or iron chromate doped PMMA [11] or PMMA doped with diarylethene compound [12].

Figure 2. Variations in absorbance as function of wavelength for PMMA films with different concentrations of KMnO_4 .

Figure 3. Variations in transmittance as function of wavelength for PMMA films with different concentrations of KMnO_4 .

From figure 3, it is clear that the transmittance decreases with the increase in the concentration of KMnO_4 . The pure PMMA has high transmittance because there are no free electrons (electrons are strongly linked to their atoms through covalent bonds) and the breaking of electron linkage and moving to the conduction band need photon with high energy. KMnO_4 molecules contain free electrons, which absorb photons of the incident light, thus, transporting to higher energy levels. This process is not accompanied by emission of radiation because the electron that moved to higher levels has occupied vacant positions of energy bands. Thus, part of the incident light is absorbed by the substance and does not penetrate through it.

3.1 Band gap analysis

The absorption coefficient (α) shown in figure 4 was calculated using equation (3). It can be noted that absorption is relatively small at high wavelengths, i.e., the possibility of electron transition is low, because the energy of the incident photon is not sufficient to move the electron from the valence band to the conduction band ($h\nu < E_g$). At low wavelengths i.e., at high energies, absorption is high, this means that there is a great possibility for electron transitions. As mentioned in literature [4–8], when the values of the absorption coefficient is high ($\alpha > 10^4 \text{ cm}^{-1}$), it is expected that direct transition of electron occurs. On the other hand, when the values of the absorption coefficient is low ($\alpha < 10^4 \text{ cm}^{-1}$), it is expected that indirect transition of electron occurs. The coefficient of absorption for the PMMA in the presence of KMnO_4 as dopant is $< 10^4 \text{ cm}^{-1}$, which explains that the electron transition is indirect.

In figure 5, the intercept of the extrapolation of the linear portion of curves to zero absorption on $h\nu$ axis, gives the value of optical band gap energy E_g listed in table 1. From

Figure 4. Variations in absorption coefficient α (cm^{-1}) as function of photon energy for PMMA films with different concentrations of KMnO_4 .

Figure 5. Absorption edges $(\alpha h\nu)^{1/2}$ for composite films as function of photon energy. At the extension of curve, to the values of $(\alpha h\nu)^{1/2} = 0$, we get indirect allowed gap transition.

table 1, it can be inferred that the values of energy gap E_g decrease with increase in the wt% of KMnO_4 . This decrease in behaviour of optical band energy on doping a polymer with KMnO_4 was reported in ref. [6]. Further, as also reported by several researchers, the modification in electronic structure may affect the optical properties of composites. The decrease in E_g values is a consequence of the generation of new energy levels (traps) between the HOMO and LUMO, due to the formation of the disorder in the composite films. This leads to an increased density of the localized states in the mobility band gap of the PMMA matrix.

Table 1. Optical energy band gaps for PMMA– KMnO_4 composite films.

Samples	E_g , eV
PMMA doped with 0.5% KMnO_4	1.91
PMMA doped with 1% KMnO_4	1.71
PMMA doped with 2% KMnO_4	1.27
PMMA doped with 5% KMnO_4	1.14

Figure 6. Variations in extinction coefficient (k) as function of wavelength for PMMA films with different concentrations of KMnO_4 .

3.2 Refractive index study

The fundamental optical parameters like the extinction coefficient, refractive index and dielectric constant are necessary to be evaluated to understand the polarizability of the samples, and their consequent applications.

3.2a Extinction coefficient: The change in extinction coefficient k as a function of wavelength is shown in figure 6. It is noted that k increases with increasing KMnO_4 content and incident photon energy. This can be ascribed to the variation in the absorption coefficient α with increased doping percentages of added salt ions, as it is directly proportional to α optical absorption coefficient and the incident wavelength described in equation (4). The extinction coefficient of pure PMMA remains almost a constant for the entire wavelength range as reported by others [4,5,8,11], but for the doped composites, the attenuation coefficient behaviour is different for different doped salts. It was reported by Abdullallah *et al* [11] that the attenuation coefficient increases with increasing wavelength when PMMA is doped with iron chromate. Similar behaviour was noted by Najeeb *et al* [12] when PMMA is doped with diarylethene compound. On doping PMMA with methyl blue or red, the attenuation coefficient initially increases in the

Figure 7. Variations in refractive index (n) as function of wavelength for PMMA films with different concentrations of KMnO_4 .

wavelength region from 200 to 600 nm and then, decreases in the higher wavelength region till 900 nm [4]. The decrease in the value of k with increasing wavelength was previously observed on doping PMMA with CrCl_2 in ref. [5]. The doping of a polymer with KMnO_4 as reported by Abdullah *et al* [8] gives similar results as observed for our composite samples.

3.2b Refractive index: The values of refractive index can be obtained from the reflection coefficient R and extinction coefficient k data using the Fresnel formulae defined through equation (6). Figure 7 shows that the refractive index decreases at the greatest wavelengths and increases at greatest dopant concentration, because the transmission of the longest wavelength is more. The observed increase in the refractive index due to incorporation of different salts in polymer was reported elsewhere too [4,5,8–10,12]. The increasing trend of refractive index (n) upon KMnO_4 addition can be understood in view of the intermolecular hydrogen bonding between K^+ ions and the adjacent ion of PMMA polymer chains and thus, the polymer films are dense, and hence, higher refractive indices can be achieved, according to the well known Clausius–Mossotti relation [13,14].

3.2c Finesse coefficient: Figure 8 shows the values of finesse coefficient against wavelengths at different concentrations of PMMA– KMnO_4 . The finesse coefficient increases with increase in doping percentage as expected and reported in ref. [12], because of doped additives that lead to change in reflectance as F is dependent on R . It was observed that F values decreases after a certain value at lower wavelengths for each sample. The positions of the peaks in the spectrum are also shifted as we move towards the maximum concentration of doping.

Figure 8. Variations in finesse coefficient (F) as function of wavelength for PMMA film with different concentrations of KMnO_4 .

3.2d Dielectric analysis: The real (ϵ_r) and imaginary (ϵ_i) parts of the dielectric constant are related to (n) and (k) values according to equation (8). Figure 9a and b shows the change of these constants with wavelengths. The values of the real dielectric constant are high with respect to the imaginary dielectric constant, because they are dependent on n and k values. It was observed that the real and imaginary dielectric constants increase on increasing the doping content similar to the behaviour exhibited on the addition of different salts in polymer as reported in literature [4–12]. The observed value of real part of dielectric constant varies within the range of 2–7 for our samples. It was reported that the addition in different concentrations of methyl red and blue in PMMA produce a variation in ϵ_r between 4–15 [4], while the addition of CrCl_2 in PMMA make the variation in ϵ_r between 2–8 [5], whereas it presents a drastic change from 20–100 for ϵ_r on doping PMMA with different concentrations of diarylethene compound [12]. The imaginary part of dielectric constant shows an increase on increasing the doping content, similar to the reported data in refs [4,5,11,12]. The values of ϵ'' for our samples decrease with increase in wavelength similar to the behaviour reported by refs [4,5] and in contrast to others [11,12], where it increases with increase in wavelength.

3.3 Optical conductivity analysis

The optical conductivity (σ) for pure PMMA- and KMnO_4 -doped PMMA samples was calculated using the absorption coefficient α and the refractive index n data using the relation expressed in equation (10). An increase in optical conductivity is observed on increasing the doping percentages and increase in photon energy as shown in figure 10. This aspect of optical conductivity was seen in ref. [8], where KMnO_4 was doped in PVA. This means that the generation

Figure 9. Variations in (a) real and (b) imaginary dielectric constants (ϵ_r) as function of wavelength for PMMA films with different concentrations of KMnO_4 .

Figure 10. Variations in optical conductivity (σ) as function of wavelength for PMMA films with different concentrations of KMnO_4 .

of KMnO_4 ion percentages increases the contribution of electron transitions between the valence and conduction bands, which lead to the reduction of energy gap.

4. Conclusion

In this work, solid polymer films of PMMA– KMnO_4 were prepared by the casting technique. Optical quantities such as absorption coefficient, optical energy gap, refractive index,

optical conductivity, extinction coefficient and dielectric constants were determined from the absorbance and transmittance ($T\%$) of UV–visible spectra analysis. From the obtained results, it was found that the indirect optical band gap energy extensively decreased with increasing KMnO_4 concentration, thus, band gap can be plausibly tuned. The increase in optical conductivity of polymer upon the addition of KMnO_4 salt is attributed to an increase in charge carrier concentration. The observed increase in refractive index and dielectric constant in the doped samples is related to added salt and are decisive for optoelectronics application. The results of the present work show that all the optical parameters are significantly affected by KMnO_4 .

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