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Black Carbon Incorporation Effect on Optical Properties of Poly-Methyl Methacrylate Films

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ABSTRACT

The optical properties of poly-methyl methacrylate (PMMA) films with difference filling levels of black carbon (BC) were studied in the visible and ultraviolent wavelength regions. It was found that the optical absorption is due to allowed- and, forbidden- direct transitions and the energy gaps decrease with increasing BC content for all transitions, while the width of the tail localized states increase with increasing BC content. The optical constants refractive index n, extinction coefficient k, the real ϵ_r and imaginary ϵ_i parts of the dielectric constant have been also calculated. The dielectric constant increased in the composite samples as compared with the pure PMMA sample prepared by the same method.

Keywords: polymer, composite, fillers, optical properties, dielectric constant

INTRODUCTION

It is well known that the physical properties of polymers may be affected by filling. Certain structural, optical, mechanical, electrical and magnetic properties of the selected polymer can be controllably modified owing to the type of the filler used, its concentration and the way in which it penetrates and interacts with the chains of the polymer. Detailed studies of polymer filled with different filling levels of a certain filler allow the possibility of choice of the desired properties [1-5].

Poly-methyl methacrylate (PMMA) has been widely used in architecture, automobile, air and railway transport systems due to its superior optical and mechanical properties [6-7]. This wide range of applications of PMMA can be even more extended by incorporation of filler into PMMA matrix, because well dispersed filler may enhance various physical properties of PMMA. The aim of the present work is too concerned with the investigation of the effect of black carbon filler of various filling levels on the optical properties of poly-methyl methacrylate (PMMA) films.

OPTICAL BAND GAP

Practically the optical absorption coefficient $\propto$ can be calculated from the relation [8]:

$$ln\left(\frac{I_o}{I_t}\right) = 2.303\ A = \propto d \tag{1}$$

where I_o and I_t are the intensities of the incident and transmitted beams respectively, A the optical absorbance and d is the film thickness [5,9].

The extinction coefficient K, is related to the absorption coefficient α, through $K = \alpha\lambda/4\pi$, where λ is the wavelength of light [10-12].

The refractive index as a function of wavelength can be determined from the reflection coefficient data R and the extinction coefficient K using equation [13]:

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

The absorption edge for direct and non-direct transitions can be obtained in view of the models proposed by Tauc et al [14-17]:

$$\propto hv = C_o(hv - E_g^{opt})^n \tag{3}$$

where C_o is a constant related to the properties of the valance and conduction bands [18], $h\nu$ is the photon energy, $\propto$ is the absorption coefficient, E_g^{opt} is the optical energy band gap of the material and$n = 1/2, 3/2, 2, or\ 3$ for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively [19-22].

A plot of $(\propto h\nu)^{1/n}$ versus $(h\nu)$ often yields a reasonably good straight line fit to the absorption edge and the extrapolated $(h\nu)$ at which $(\propto h\nu)^{1/n} = 0$ provides a convenient experimental benchmark for the optical band gap E_g^{opt} [23].

The optical absorption coefficient $\propto (\nu)$ near the band edge shows an exponential dependence on photon energy $(h\nu)$ and obeys an empirical relation due to Urbach [24-26]

$$\propto (\nu) = \propto_o \exp(h\nu/E_t) \qquad (4)$$

where $\propto_o$ is a constant and E_t is related to width of the band tails of localized states in the forbidden band gap. it should be mentioned that this equation is applicable only in the low absorption region ($\propto = 10^3 - 10^4 cm^{-1}$).

EXPERIMENTAL DETAIL

Films of PMMA-BC composite were prepared by solution casting: $2g$ of pure poly-methyl methacrylate (PMMA) supplied from Sigma-Aldrich company has been dissolved in $20ml$ of dicholoro methylene to obtain a pure PMMA film, then the same amount of PMMA was dissolved with $0.01, 0.02, and\ 0.03$ of CB to prepare the different filling levels of the PMMA-BC composites, these homogeneous solutions were spread on a glass plate and allowed to evaporate the solvent slowly in air at room temperature for $24h$. The thickness of the films was in the range of $(100 - 470)\mu m$, it was determined using micrometer at different places in each film and an average was taken.

RESULTS AND DISCUSSION

The optical absorption spectra of all films were recorded at room temperature, by UV-VIS double beam spectrometer (Model: Lambda 25) in the wave length range from 190 to 1100 nm. The optical band gap of these samples was evaluated from the photon energy absorption plot.

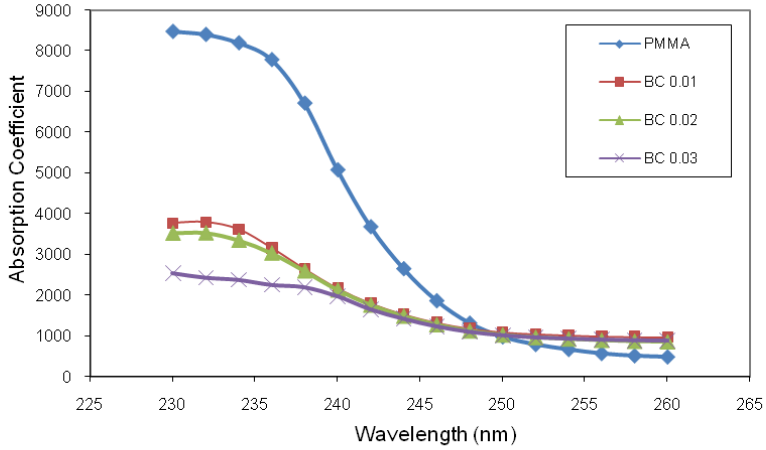

Fig. 1 Optical absorption coefficient for PMMA with BC content

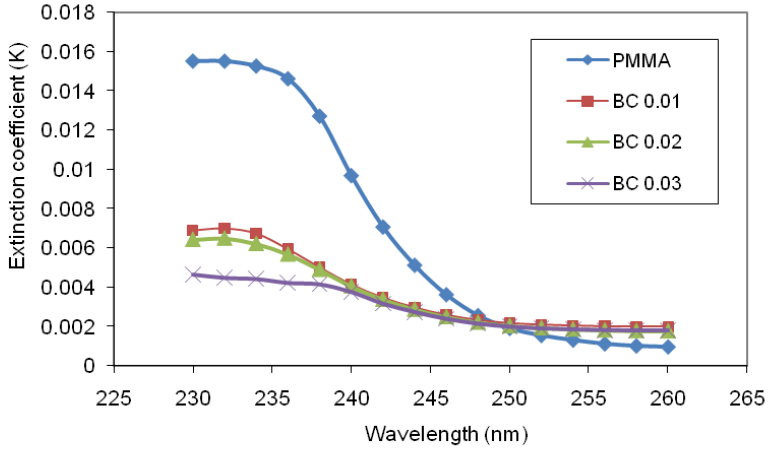

Fig. 2 Extinction coefficient K as a function of wavelength for PMMA polymer with BC content

Figure1 shows the absorption coefficient as a function of the wavelength for pure PMMA and different concentration of BC filers, for low wavelengths, in the UV region the absorption coefficient is decreasing exponentially. The extinction coefficient K over the exponential absorption region $(230 - 260)nm$ for all polymer samples are given in Fig. 2. The variations of refractive indices n of all films with photon energy are shown in Fig. 3. It is clear from these figures, that the refractive indices n and extinction coefficient K are decrease with increase of wavelength. The increase of BC content to the polymer lead to more stability of refractive indices at high values, which are useful in the industry of reflectors.

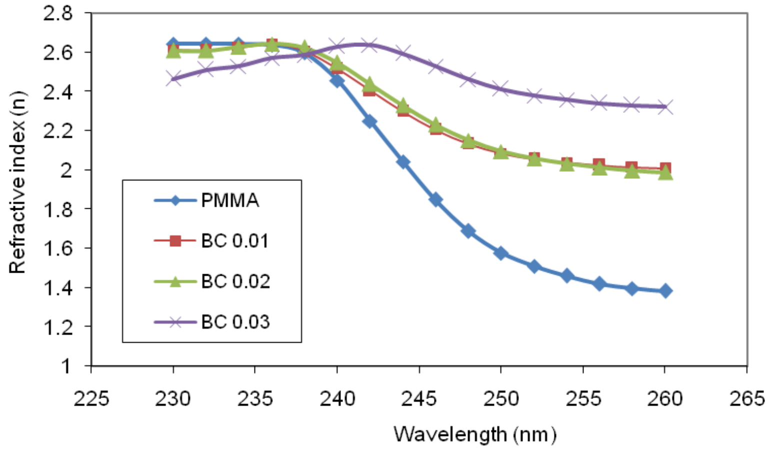

Fig. 3 Refractive index as a function of wavelength for PMMA with BC content

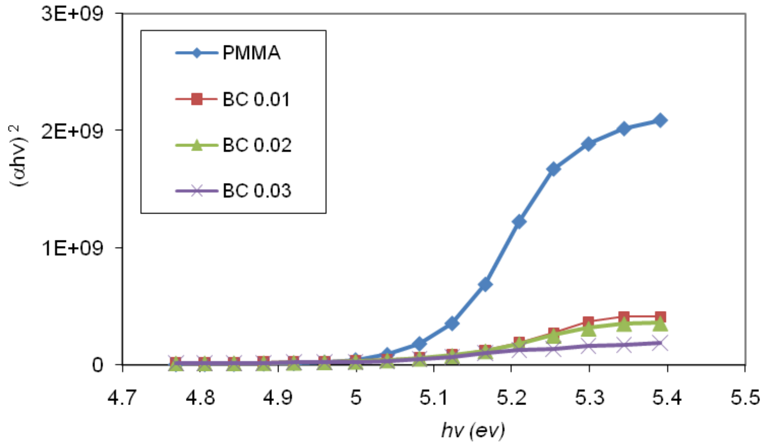

Fig. 4 Relation between the $(\propto \mathrm{hv})^2$ and hv for PMMA with BC content

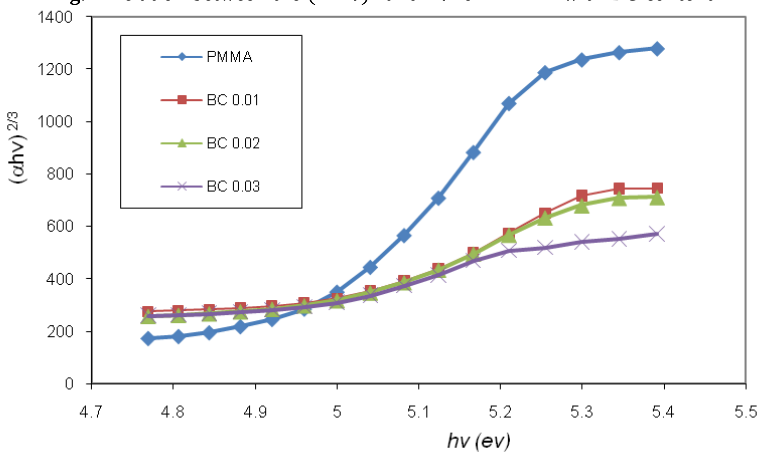

Fig. 5 Relation between the $(\propto \mathrm{hv})^{2/3}$ and hv for PMMA with BC content

Figures4 and 5, shows the dependence of $(\propto hv)^{1/n}$ on the photon energy (hv) for direct allowed $(n = 1/2)$, direct forbidden $(n = 2/3)$ transitions, respectively. It is to be noticed that the curves are characterized by the presence of an exponentially decaying tail at low photon energy. The optical energy gap E_g^{opt} was estimated from the extrapolation of the linear portion of the graph to the photon energy axis. It is observed that E_g^{opt} decreased with black carbon content. All plots show straight lines with some deviations from linearity at the lower of $\propto$, which were suggested by many researchers [27-30] as possibly due to imperfections in the material, but this region of the curve is still not fully understood. The mean vale of E_g^{opt} for direct-, allowed and forbidden transitions are tabulated in Table -1.

The Urbach plot is presented in Fig. 6 in which the natural logarithm of absorption coefficient is plotted as a function of photon energy $h\nu$. The slop of each line yields the magnitude of $1/E_t$. The measured values of width tails localized states in the band gap for all samples are tabulated in Table -1.Table1 shows that the optical energy gap E_g^{opt} decreases with increasing BC contents for all transition, on the other hand the width of the band tails of the localized state shift towards higher energies which range from (*0.1234 eV*) for pure PMMA to (*0.3058 eV*) for 0.03 filer concentration. This may be attributed to the increase in the disorder caused by the changes in the degree of crystallization, which is known to increase the width of the localized states, thus reduce the value of the optical gap. Such a change has been reported by others for different polymer compositions [11,31].

Table -1 Optical Energy Band and Band Tail for PMMA with BC Content

Type of transitions	Pure PMMA	PMMA-0.01 BC	PMMA-0.02 BC	PMMA-0.03 BC
Direct allowed	5.1024 eV	5.0455 eV	4.9805 eV	4.9642 eV
Direct forbidden	4.9715 eV	4.7833 eV	4.6875 eV	4.6597 eV
Width of band tail	0.1234 eV	0.2978 eV	0.2822 eV	0.3058 eV

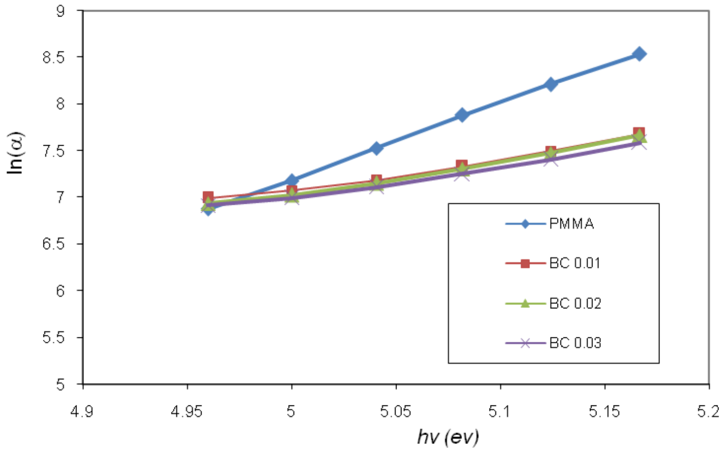

Fig. 6 Relation between the $\ln(\propto)$ and hv for PMMA with BC content

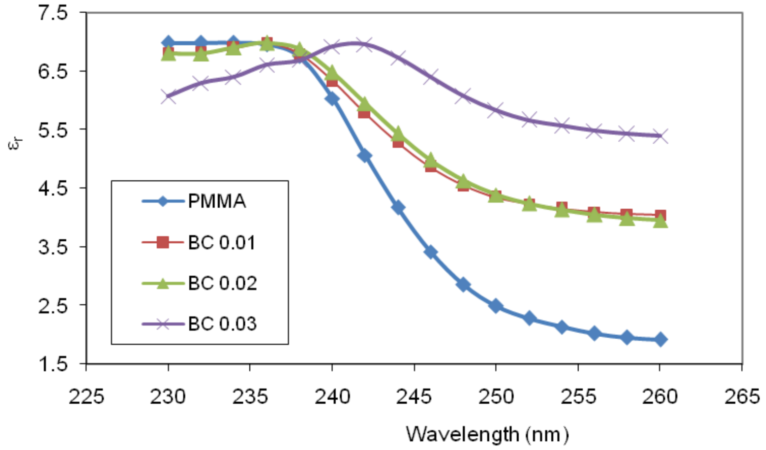

Fig. 7 Relation between the real part of dielectric constant ϵ_r and wave length for PMMA with BC content

The real and imaginary parts of dielectric constant can be calculated by using equation [32]:

$$\epsilon_r = n^2 - K^2, \quad \epsilon_i = 2nK \tag{5}$$

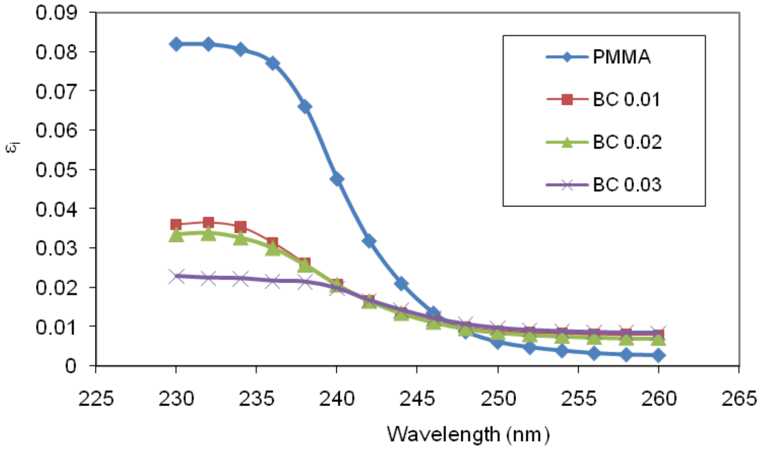

Fig. 8 Relation between the imaginary part of dielectric constant ϵ_i and wave length for PMMA with BC content

Figures7 and 8, show the dielectric constants ϵ_r and the dielectric loss factor ϵ_i versus the photon energy for all samples. The significant decrease of loss factor can be observed in the wavelength range $(235 - 245)nm$ and finally reaches nearly a constant value.

Both the electric nature of the polymer and the effect of BCs in the composites can be understood by correlating the dielectric constant values with the refractive index. If the sample is non-polar insulator, the dielectric constant ϵ_r for long wavelength can be expressed by Maxwell's equation $\epsilon_r = n^2$ [33]. The difference between the squared refractive index and the dielectric constant is a result of permanent dipoles and the semi-conductive character of the sample [34-36]. The difference between ϵ_r and n^2 for the pure sample is greater than that observed in the composites samples, wich indicated that the PMMA has permanent dipoles.

CONCLUSION

The optical properties of poly-methyl methacrylate (PMMA) films with difference concentrations of black carbon (BC) were investigated at room temperature. The band tail width obeys Urbach's empirical relation. The optical absorption is due to all direct and indirect transition. Generally, the optical band gap decreases with increasing BC contents for all transitions. The value of refractive indices and dielectric constant were tended to be more stability at high values by increasing the black carbon content in PMMA matrix, through the investigated range.

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