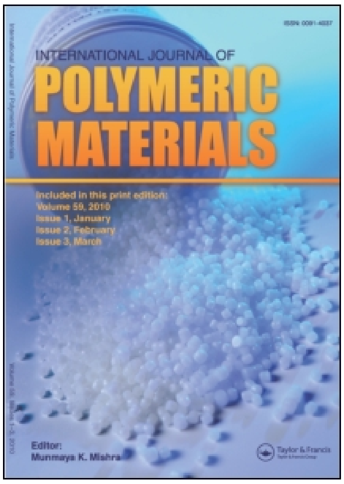

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OPTICAL PROPERTIES OF FULLERENE/PMMA

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The author has prepared high-quality fullerene/PMMA films in which fullerenes are uniformly embedded. The films are optically transparent. The products were characterized spectroscopically using UV/Vis and FTIR. The optical band gap of fullerene/PMMA films were reduced by increasing the fullerene concentration. The refractive index spectrum and absorption index spectrum of fullerene/PMMA films were determined in the wavelength range (200–2400 nm) from the combination of reflectance R and transmission T at normal incidence.

Keywords: PMMA, fullerene, refractive index

INTRODUCTION

The discovery of fullerene, a new carbon allotrope, has fascinated the scientific community, and the properties of fullerenes have understandably been a focus of intensive research [1]. Novel properties of fullerenes include superconductivity, ferromagnetism, and optical nonlinearity [2].

Application of fullerene in areas such as optical devices, semiconductor, chemical sensors, catalysis, solar energy conversion, and in the medical field have been predicted [3]. Thermal instability, low solubility, and tendency to form clusters have hindered the direct use of this material. In contrast, when doped with other host materials, such as silica, polymers, and metals, it can be of practical use.

Synthesis of fullerene-filled polymers is of interest from the viewpoints of both basic research and practical applications. Polymeric materials offer many advantages such as ease of processability and

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easy incorporation of functional molecular groups. Polymers have the added advantage that they are not as brittle as glass and do not break easily by bending or impact [4].

In this article, by simple method, the author has prepared high-quality fullerene/PMMA films in which fullerenes are uniformly embedded.

Fullerene/PMMA films are prepared by casting from toluene and are optically transparent. The products were characterized spctroscopically using UV/Vis and FTIR. The optical energy gap and band tails were calculated. The absorption index spectrum and refractive index spectrum of thick fullerene/PMMA Films were determined in the wavelength range 200–2400 nm, from the combination of transmission T and reflectance R at normal incidence.

EXPERIMENTAL

PMMA Mw = 996000, from Aldrich. Fullerenes obtained from Aldrich contain about 90% C_{60} and 10% C_{70}. They were kept in a dark place before use. Both PMMA and the fullerenes were dissolved in the same toluene solvent and cast on glass. After the films were dried, they were taken off the glass. The film thickness was 25 μm. The films are optically uniform and transparent. The content of fullerenes in the films were 0.5, 1, and 1.3 wt%.

The UV/Vis/NIR transmission and reflectance spectra were recorded with an UV- Vis- NIR spectrometer (UV- 3101 pc) Shimadzu. The FTIR spectra were measured on a Bruker Vector 22 spectrometer.

RESULTS AND DISCUSSION

Spectroscopic Characterization

The products were characterized spectroscopically using UV/Vis and FTIR spectrometers. Figure 1 shows the optical absorption of PMMA, and fullerene/PMMA films. Fullerene absorbs at 330 nm and PMMA absorbs at 207 nm. Fullerene/PMMA exhibit a band at 197 to 207 nm for PMMA and at 330 nm for fullerene, that is, it possesses the electronic transition characteristics of the two constituent parts. From Figure 1 it can be seen that the height of the fullerene absorption peak grows with increasing concentration of fullerenes, indicating that fullerene shows only a weak tendency to form clusters in PMMA. As the fullerene content increased, the PMMA band became broader and red-shifted, suggesting that the fullerenes are responsible for the spectral shift.

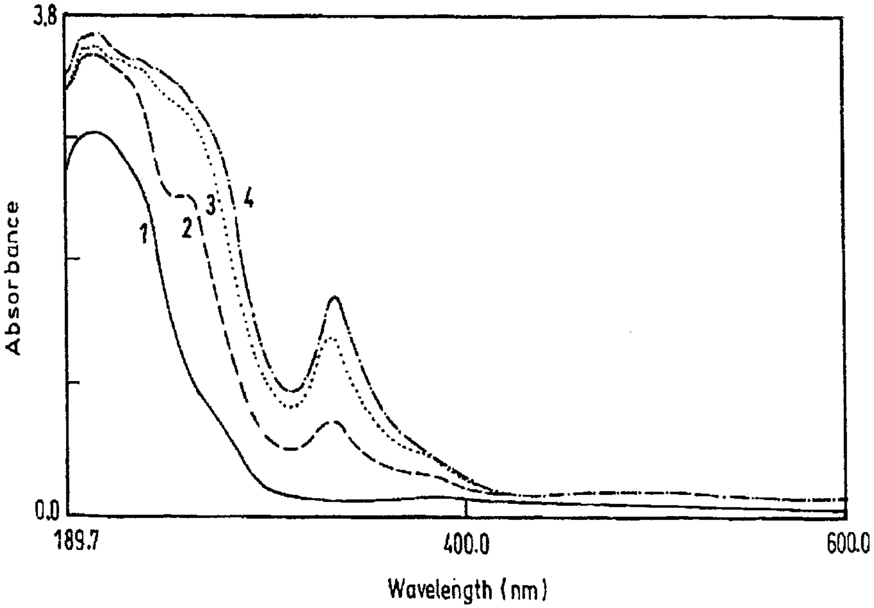

FIGURE 1 UV/V is spectra for (1) PMMA and (2,3,4) fullerene/PMMA of concentration (0.5, 1, and 1.3 wt%).

The broadening is attributed to transitions occurring from higher vibrational levels of the ground state to higher sublevels of the first excited singlet state [5]. Shifting and splitting of the degenerate electronic levels are accompanied by the broadening of the spectral bands [6].

Figure 2 shows FTIR spectra of PMMA, fullerene/PMMA, and fullerene. C_{60} shows an IR absorption band at 527 cm^{-1}, [7–8], which often survives in the functionalization of the C_{60}. The IR spectrum of fullerene/PMMA film was essentially identical to that of the starting PMMA except for a new weak band at 527.7 cm^{-1}.

Absorption Edge

The absorption coefficient α as a function of the photon energy ($E = \hbar w$) can be expressed by [9–10]

$$\alpha E = B[E - E_g]^n$$

where B is a constant, E_g is the optical energy and n is an index that depends on the transition type. Figure 3 shows the dependence of $(\alpha E)^2$ on photon energy E for PMMA and fullerene/PMMA films. It is shown

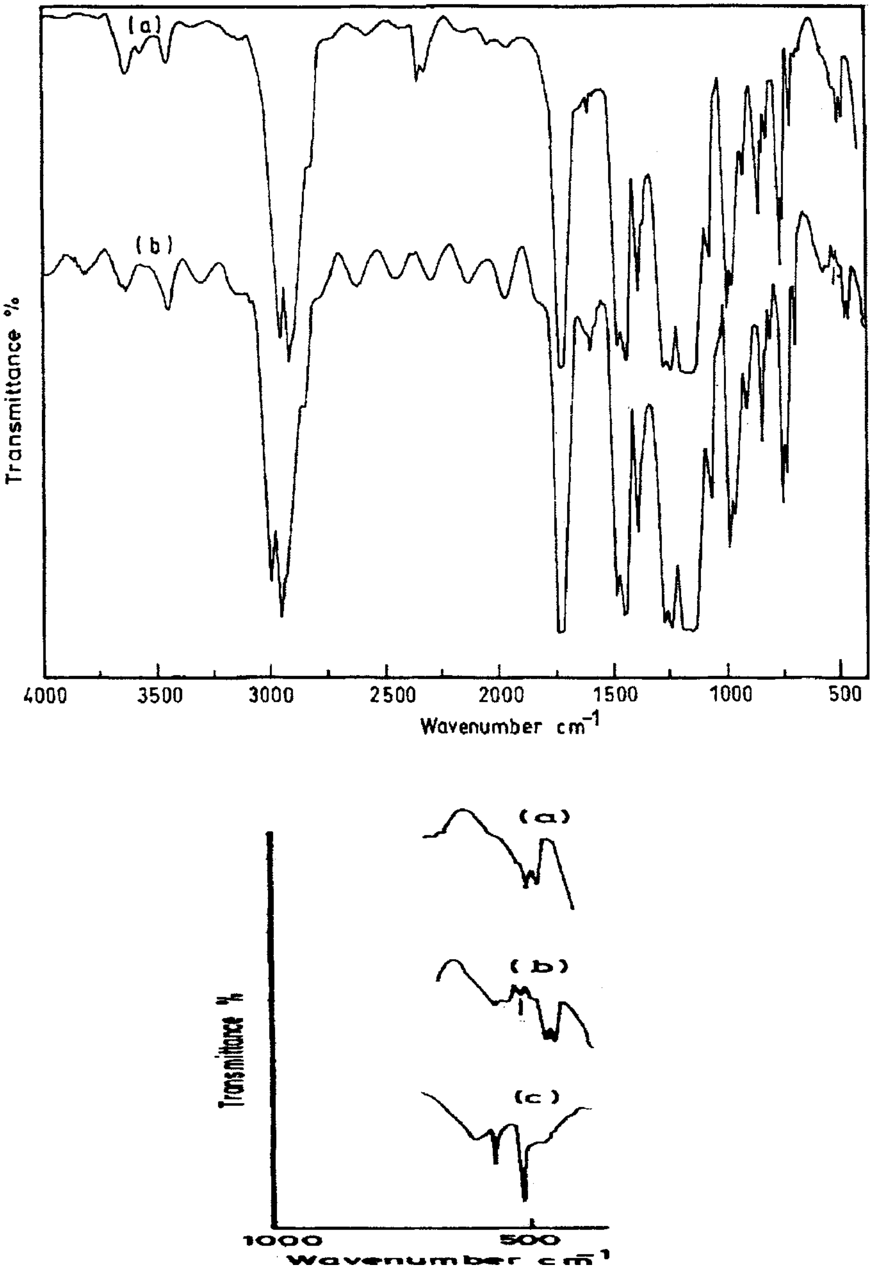

FIGURE 2 FTIR spectra for (a) PMMA, (b) fullerene/PMMA, and (c) fullerene.

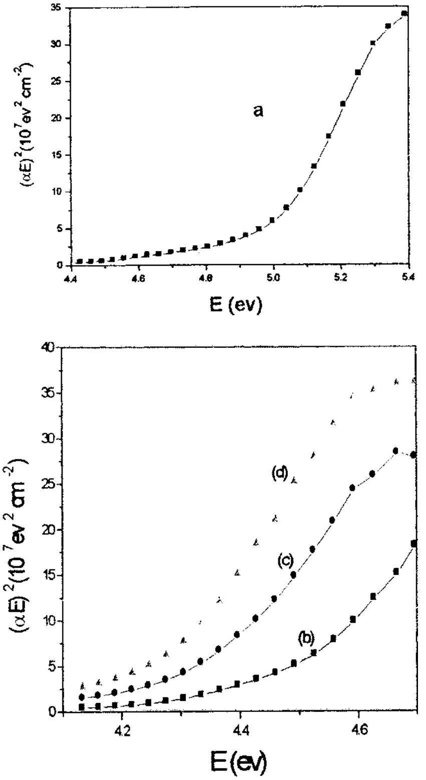

FIGURE 3 $(\alpha E)^2$ versus photon energy E for (a) PMMA and (b,c,d) fullerene/PMMA of concentration (0.5, 1, and 1.3 wt%).

that this relation is linear and this indicates the existence of a direct transition. The addition of fullerene to PMMA causes a decrease in the value of E_g from 4.9 eV for PMMA to 4.3 eV for high concentration of fullerene in PMMA. For $1 \leq \alpha \leq 10^4$ cm^{-1}, there is usually an Urbach [11] tail where the absorption coefficient depends exponentially on the photon energy E as

$$\alpha(\nu) = \alpha_o \exp(E/E_u)$$

where ν is the frequency of the radiation, α_o is a constant and E_u is the width of the tails of the localized states in the gap region, and in general represents the degree of disorder in amorphous material. The plot of Ln α versus photon energy E in Figure 4, gives the value of $E_u = 0.18$ ev for PMMA, and increases with addition of fullerene to 0.34 ev for the higher concentration.

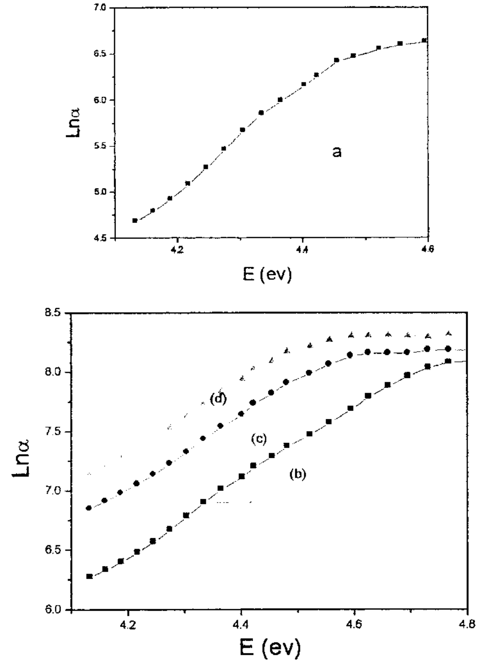

FIGURE 4 Ln α versus photon energy E for (a) PMMA and (b,c,d) fullerene/ PMMA of concentration (0.5, 1, and 1.3 wt%).

Optical Constants

The optical constants of solids can in principle be determined in two ways, either from intensity measurement (unpolarized light) or from polarization measurements (nonnormal incidence) [12–13]. This article considers only the intensity methods at normal incidence. The combination of reflectance R and transmission T gives the most accurate value of n – ik [14].

Consider an ideal film with plane-parallel faces, perfectly characterized by its thickness d and the complex refractive index $\tilde{n} = n + ik$ of the homogeneous material of which it is composed. If no interference observed [15],

$$T = \frac{(1-R)^2\left[1+(K/n)^2\right]\exp(-\alpha d)}{1-R^2\exp -2\alpha d}$$

where k and α are the absorption index and absorption coefficient. In case of $k^2 \ll n^2$

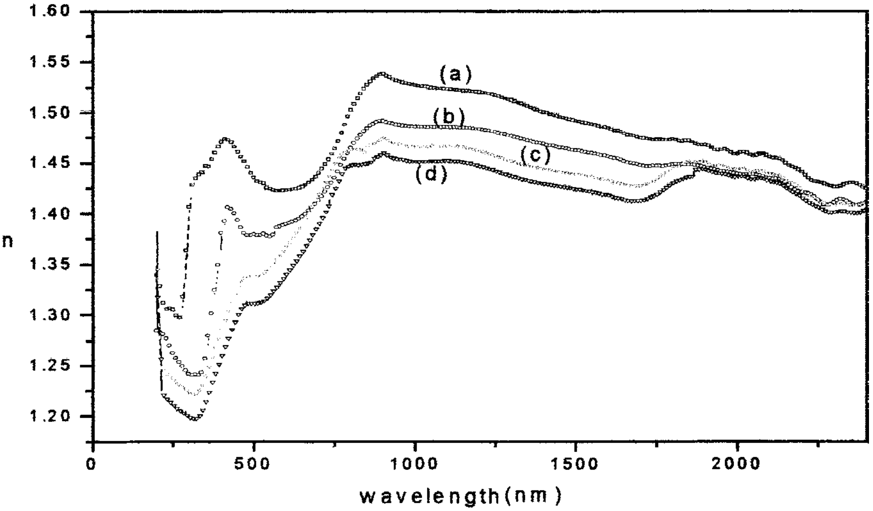

FIGURE 5 Index of refraction for (a) PMMA and (b, c, d) fullerene/PMMA films of concentration (0.5, 1, 1.3 wt%).

$$T = \frac{(1-R)^2 \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)}$$

$$\therefore \alpha = \frac{4\pi k}{\lambda} = \frac{1}{d} \ln \frac{(1-R)^2 \pm \sqrt{(1-R)^4 + 4T^2R^2}}{2T}$$

The reflectance of an absorbing surface in air for normal incidence is given by

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

The spectral distributions of n and k for fullerene/PMMA films are shown in Figures 5 and 6 respectively. It can be seen that an increase in fullerene content leads to a decrease in refractive index of the blend.

The refractive index of materials depends on the linear polarizability and the number density of molecules, as indicated by Lorentz–Lorenz equation

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3}\pi N \alpha$$

where n, N, and α are refractive index, the number density of molecules, and linear polarizability, respectively. In the case of doping

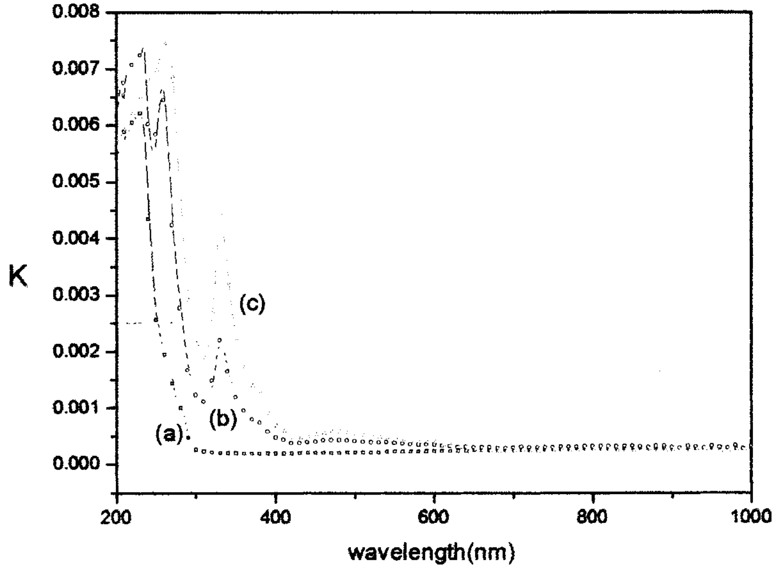

FIGURE 6 Absorption index for (a) PMMA and (b, c) fullerene/PMMA films of concentration (0.5, 1 wt%).

fullerene in PMMA, both linear polarizability and the refractive index decrease.

According to a recent work by Tang et al. [16], when the fullerene content is low, the giant three-dimensional spheres may act as plasticizers, increasing the free volume among the polymer chains. These results suggest that it is possible to control the refractive index of polymeric materials.

CONCLUSION

The author prepared high-quality fullerene/PMMA films in which fullerenes are uniformly embedded. The films are optically transparent. The products were characterized spectroscopically using UV/Vis and FTIR. The IR spectrum of fullerene/PMMA film was essentially identical to that of the starting PMMA except for a new weak band at 527.7 cm^{-1}.

The optical band gap of fullerene/PMMA films was reduced by increasing the fullerene concentration. The refractive index spectrum and absorption index spectrum of fullerene/PMMA films were determined in the wavelength range 200–2400 nm. The doping of fullerene in

PMMA induces a decrease in refractive index. These results suggest that it is possible to control the refractive index and energy gap of polymeric materials.

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