



Spectroscopic Studies of Polyester – Carbon Black Composites

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Abstract

The optical properties of polyester – carbon black composites has been described by the measurement of changes in the UV-visible light absorption spectrum. Polymer composites Exhibits a new UV- visible absorption band at a wavelength range (226-235) nm, which is attributed to interchain interaction. The optical transmission method is successfully used to determine the absorption coefficient (α), dielectric constant and energy gap of four samples of polyester – carbon black composites. The optical characterization was carried out using UV-Visible spectrophotometer. The studies show which is strongly dependent on the nature of the material and the radiation type.

Keywords: Optical properties, UV- visible absorption, polymer composites.

Introduction

Composites have been developed to meet several industrial requirements, such as the need for easier processing and broadening the range of properties, either by varying the type, relative content or the morphology of each component¹. When carbon black is used as filler in polymer composite, the composite properties can change from insulator to conductive ones². Polyester and copolymers are susceptible to degradation by the action of sunlight. The action of the UV radiation is accompanied by the oxidation so that the overall degradation reaction is one of photo oxidation. The extent of degradation varies from location to location owing to differences in the intensity of radiation. This is of considerable importance in many applications because the degradation is reflected, in the case of transparent compositions, in a yellowing effect and generally in a loss of mechanical properties such as a lower elongation at break and reduced impact strength³.

Carbon materials are sometime added to polymer in order to obtain composites with improved electrical and mechanical properties. The most important of these substances is carbon black which is the most effective stabilizer for most polymers. The effectiveness of carbon black is dependent on first the type, second, the size of particles, and third, the degree of dispersion of the particles within the polymer. Carbon black is considerably more efficient as a weathering stabilizer than would be predicted on the basis of just its ability to screen the polymer from u.v. light. The increased efficiency of carbon black is usually ascribed to its ability to trap radicals produced during the photo oxidative processes which lead to chain degradation. Carbon black may also stabilize polymers by its ability to quench the excited state induced in the polymer by the absorption of u.v. radiation^{3,4}.

The study of effect of UV light on polymers has attracted considerable interest for many years. Spectroscopy is a fundamental part of such work. Polymers with pendant aromatic ring groups, such as polyester are known to show a new fluorescence band at longer wavelength under irradiation due to the interaction between excited and ground state aromatic groups, i.e. the formation of intermolecular excimers. This phenomenon has been widely used as a powerful tool in polymer structure studies⁵.

The irradiation of polymers with ionizing radiations leads to a wide variety of changes in their physicochemical properties which can generally be traced back to the rearrangement taking place in the chemical structure of the polymer as a result of energy deposition⁶.

Material and Methods

Materials and Samples: The polymers – carbon black samples with different percentage of CB content were prepared from 3 to 12 wt%. These samples having thicknesses of 0.15mm were cut into 2.6x2.8 cm² sized samples.

Experimental procedure of test: All samples were subjected to UV – Visible transmission and reflection studies by using Shimadzu double beam UV-VIS Spectrophotometer (UV-210 A) in the wavelength range 190-800 nm, the method of measurement has been described elsewhere⁶. Samples have been annealed in air at 30°C temperature.

Optical Calculation: Ultraviolet-visible absorbance was assumed to be zero above 700 nm therefore; the average sample absorbance between 700 and 800 nm was subtracted from the spectrum to correct for offsets due to instrument baseline drift, temperature, scattering, and refractive effects.

Absorbance units were converted to absorption coefficients follows⁷:

$$\alpha = 2.303 A / l \quad (1)$$

Where absorption coefficient (α) (m^{-1}) for the solutions. (A) is the absorbance for the solution, and (l) the thickness of samples. The extinction coefficient is calculated by using the following equation⁸:

$$K = \alpha \lambda / 4 \pi \quad (2)$$

Ultraviolet-visible (UV/Vis) spectroscopy has become an important tool to estimate the value of optical gap energy (E_g) in polymer. The optical absorption edge can be correlated to optical gap energy (E_g) using Tauc's equation [9]. The intersection of extrapolated spectrum with the abscissa yields the optical gap energy (E_g). The Tauc's equation is as follows^{6,8,9}:

$$\alpha h \nu = A (h \nu - E_g)^n \quad (3)$$

Since, λ is the wavelength, h is a Plank's constant $6.62617 \times 10^{-34} J.s$ and c the speed of light $3 \times 10^8 m/s$.

Results and Discussion

The Typical UV-Vis spectra of polyester – carbon black Composites are shown figure- 1. Typical normalized UV-Vis spectra of polyester with carbon black content (3 w%, 6 w%, 9 w%, 12 w%). It is shown that the adding of the filler to the

polymer lead to increase the intensity of peak. Critical analysis of UV-Vis spectra of polyester - carbon black composites shows that the highest shift in absorption wavelength is in the range 226-235 nm.

This indicated the carbonization of the polymeric materials under irradiation. The shift in the absorption edge from UV to visible region could be attributed to an increase in conjugation length. In the present case the optical band gap energy can be correlated with the number of carbon atoms per conjugation length for a linear structure polymer^{6,7,11}.

The absorption of light energy by polymeric materials in UV and visible regions involves transition of electrons in n to π^* orbital from ground state to higher energy states. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200-700). These transitions need an unsaturated group in the molecule to provide the π electron⁶.

Figure-2 Shows the absorbance value as a function of carbon black concentrations of polyester. The result may be interpreted with interchain interaction in the outside of polymer coils. While polymer coils approach each other, interchain interaction in the outside of different polymer coils may induce the slight increase of absorbance. The local concentration of carbon black groups may increase linearly with polymer concentration. It is assumed that the micro viscosity increase slowly^{11,6}.

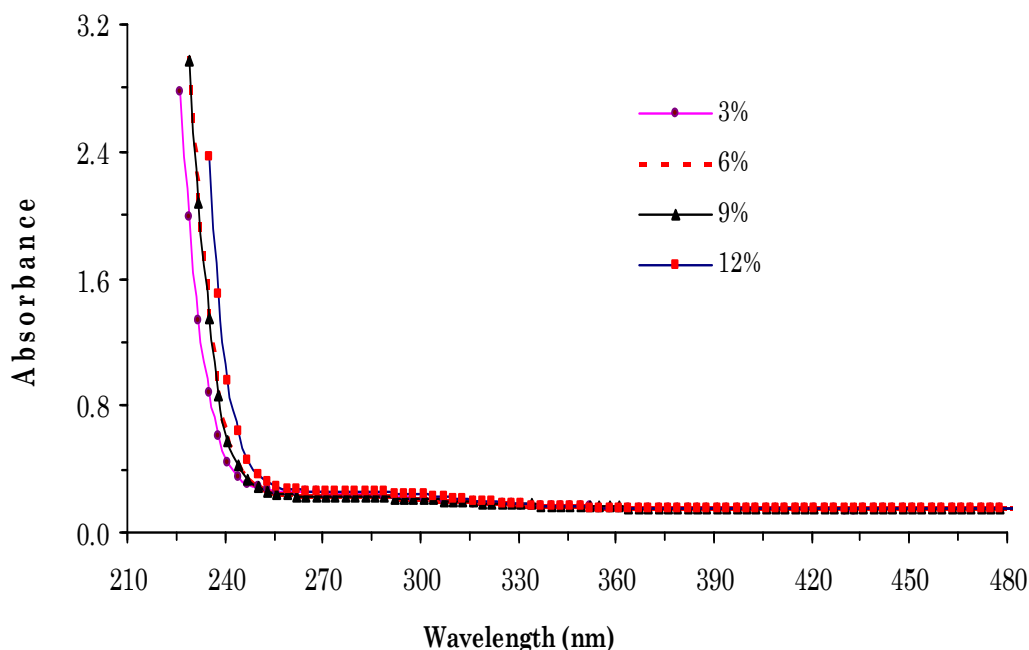


Figure-1
UV/Vis spectra of polyester-carbon black composites

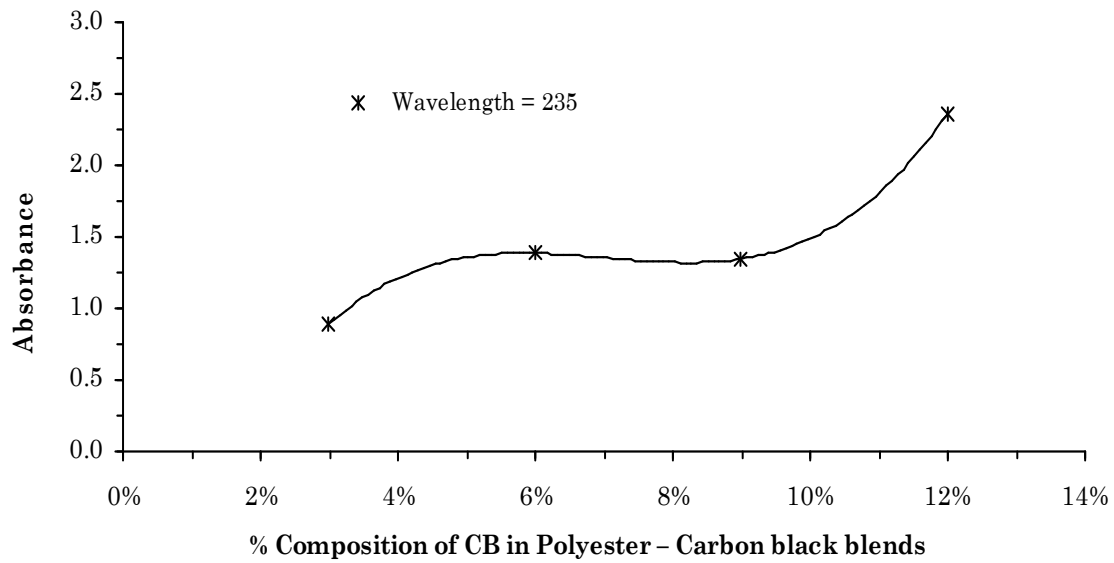


Figure-2
 The absorbance as function of CB content in polyester-carbon black composites

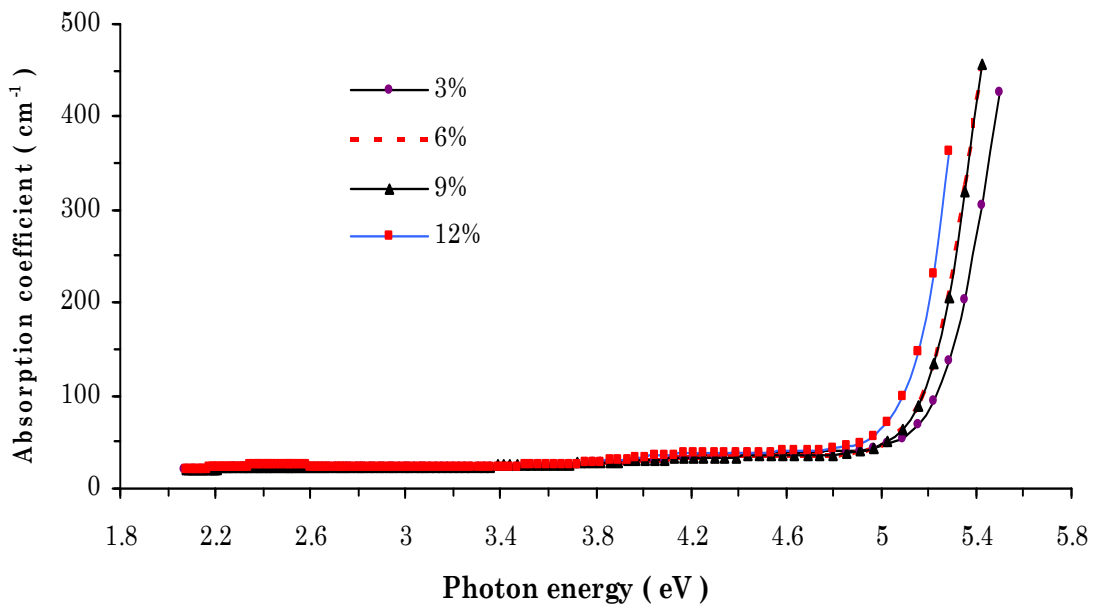


Figure-3
 The absorption coefficient for polyester-carbon black composites as a function of photon energy

The absorption coefficient α were determined for each sample by using the equation (1). It is clear that α must be a strong function of the energy $h\nu$ of the photons. figure- 3 Shows that for $h\nu < E_g$, no electron hole pairs can be created, the material is transparent and α is small. For $h\nu \geq E_g$, absorption should be strong^{10,12}.

The optical energy gap will be estimated from the optical measurements by analyzing the optical data with the expression for the optical absorbance, and the photon energy, $h\nu$ using equation 3. The optical band gap can be obtained by extrapolating the linear portion of the plot of $(\alpha h\nu)^{1/n}$ versus $h\nu$ to $\alpha=0$. Using the value $n=2$, the relation found to be straight line as shown in figure- 4 Representing direct transition⁹.

Figure- 4 reveals that the optical gap of the polymer - carbon black composites has the value 5.1, 5.02, 4.99 and 4.9 eV for the CB concentrations (3% , 6% , 9%,12%) respectively. This behavior of decreasing the values of optical gap with increasing with CB content which may be attributed to the decrease in the packing density with increasing CB content of polymer^{6,9,10}.

The variation of extinction coefficient (k) with wavelength for polyester-carbon black composites is shown in FIGURE- 5, indicating that the extinction coefficient increase with increasing the weight percentage of the added carbon black to the polyester and decreases with increasing the incident wave length. The behavior of extinction coefficient can be described according to high absorption coefficient. This result indicates that the doping atoms of carbon black will modify the structure of the host polymer.

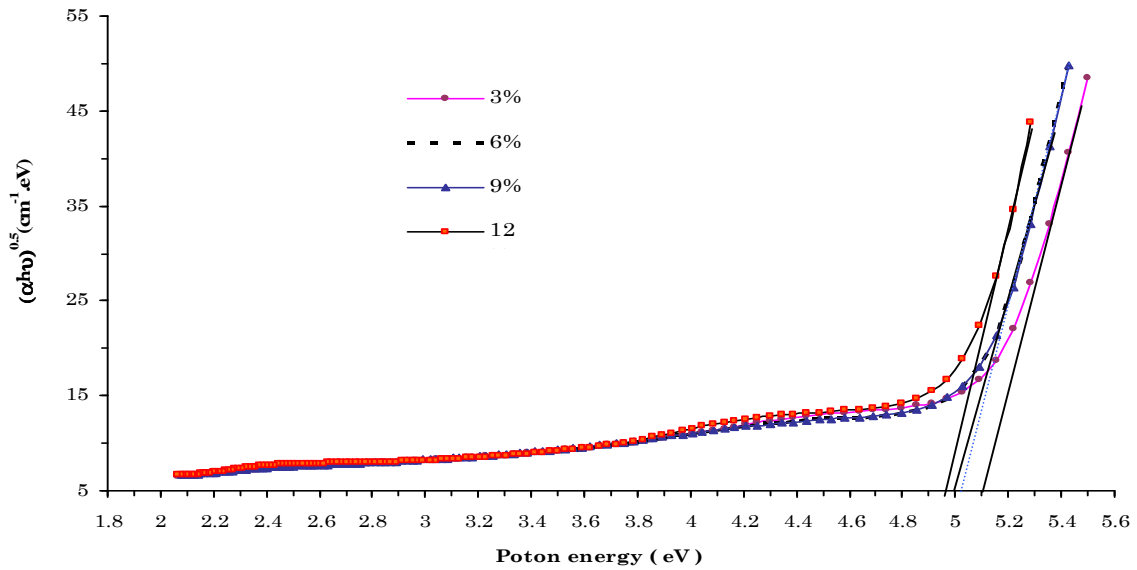


Figure-4
 Plot of $(ah\nu)^{0.5}$ vs $h\nu$ for polyester-carbon black composites

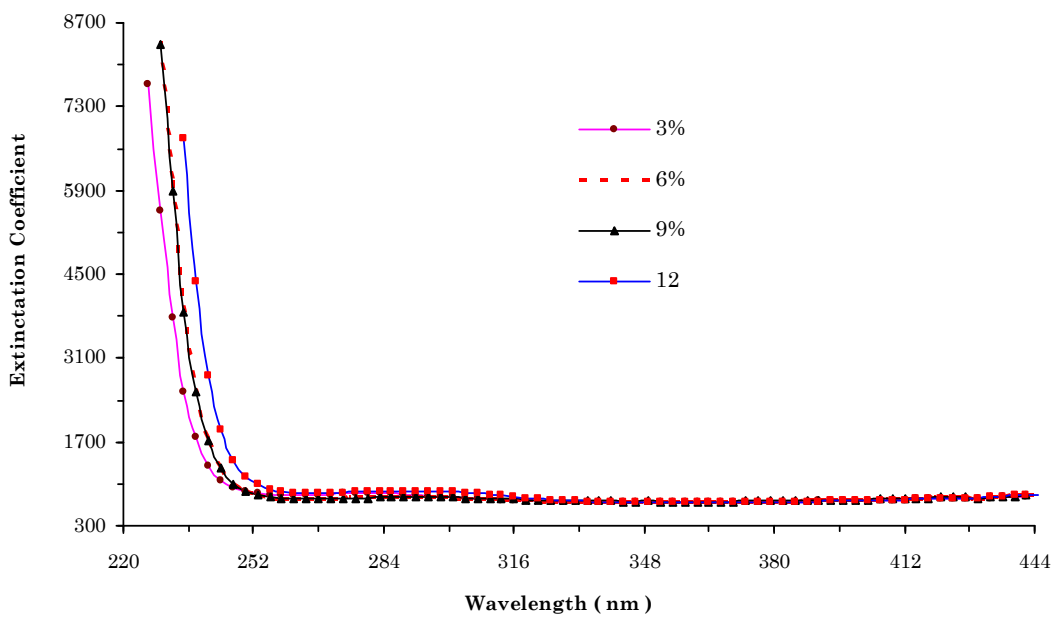


Figure-5
 The variation of extinction coefficient for polyester-carbon black composites with incident wavelength

Conclusion

There are many parameters which affect the composite structure and properties. In this work we have described an optical method for measurement of polyester-carbon black composites, which uses total reflectance of the polymer composites sample at a wavelength rang 190-800 nm. The results showed the optical properties of composites can be changed using the modified CB. The absorption coefficient is increasing with increasing of the filler wt. % content. The optical energy gap was decrease with increasing the concentration of CB in polyester. The extinction coefficient (k) increase with increasing the weight percentage of the added carbon black to the polyester and decreases with increasing the incident wave length.

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