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A study of the optical properties of polypropylene based polymer composite films

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SUMMARY: The optical clarity of the polymeric material can be influenced by changing the preparations parameters and thus the polymer structure. In this study, the transmittance, absorptance and reflectance of the polypropylene (PP) based polymer composites, synthesized by pressing method, changing the thickness between 8 – 29 μm, are investigated. Infrared and ultraviolet spectra of PP/diamond and PP/fiber composite in the wavelength range 200-25000 nm are examined. Optical absorption spectra recorded in the UV-Visible range are presented; the determined values of energy gaps are listed. The results indicate that both mechanism, direct and indirect transitions may exist. The analysis of absorption peaks corresponding to oxygen groups, for PP/diamond (0.3-0.5 %) and PP/fiber (20-30 %) composites, show low optical densities which complies with our other studies.

Introduction

Polymers have a wide range of important applications such as optical switching, pyroelectricity, thermochromic applications. In optical tools as filters, lenses, prisms; polymer materials have replaced conventional inorganic materials. The advantage of using polymers lies in their relative ease of processing, better impact resistance and lightness compared to their inorganic glass counterparts$^{1)}$. There has been an increasing interest in synthesizing new polymers and composites that possess high optical, thermal stability and good mechanical properties. In the optical properties of polymers, e.g luminesance , the absorption process plays an important role. Longer infrared (IR) wavelengths are absorbed selectively by the functional groups in the polymer molecule, providing useful means for the analysis of structure. At the other extreme, short ultraviolet (UV)wavelengths from the sun are abt to be absorbed and activate unstable bonds in the polymer molecule$^{2)}$. UV spectroscopy is an attractive method for analysis for many additives. Principal advantages over IR spectroscopy include greater sensitivity arising from higher extinction coefficients and a lack of interfering absorptions from the polymer matrix$^{3)}$.

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Recently the need for examining the properties of polymer composites has arose. As it is well known, the classical zone theory is not valid for noncrystalline and semicrystalline materials. Polymers are also materials of this type. In this case, formation of the zone tails in the forbidden band and the equations related are taken into consideration[4]. The study of absorption of polypropylen/polyethylen(PP/PE); PP/diamond and PP/PPfiber composites provides the deeper understanding of the interaction between optical excitation and phonon spectra.

The measurements of the absorption give an opportunity to obtain information about the nature of the chemical bonds. In polyolefins the values of the bond energies for C-C; C-H; C-O etc. show differences when it is calculated with different methods and change in very large ranges.

To find the proper value of these energies is very important to understand the mechanism of degradation and stabilisation times. These values can be calculated properly by using optical measurements. On the other hand, using these measurements one can also find out how the inorganic (diamond) and organic (fiber) additives which are added in the polyolefins are bound to the main structure by the chemical bonds or as a simple filler.

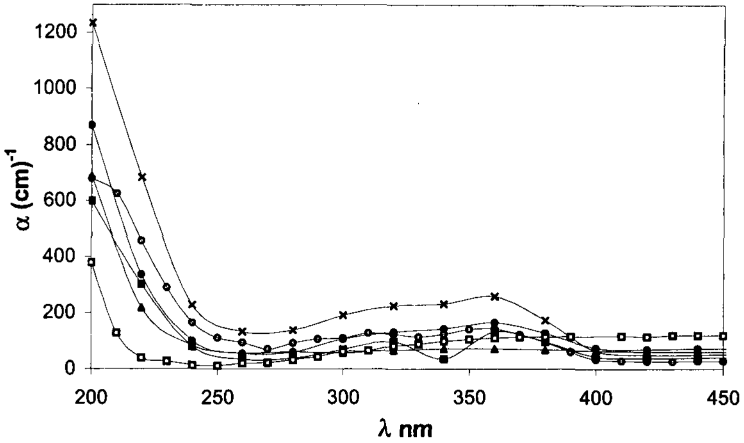

Fig. 1: Absorption spectra vs. wavelength for ● = P8, ■ = P9, ▲ = P12, ✕ = P13
○ = P10, □ = P14

The objective of this article is to examine the absorption spectra in the (PP/PE); PP/diamond and PP/PPfiber composites and to explain the mechanisms of the structural variations.

Sample Preparation and Measurements

Samples are prepared by hot pressing method at 423 K and 15 MPa. Samples, which are kept 10 minutes at 423 K and 15 MPa are cooled by dipping into water at room temperature. Samples are low density polyethylene (LDPE), PP and PP based PE, PPfiber and diamond composites obtained with various percentages (0.5 - 80%). The percentage and thickness of samples (9 – 29 μm) are given in Table 1. Absorption spectra are taken in the range 200 – 25000 nm with the help of Perkin Elmer UV-VIS Lambda 2 and Watson 1000 FTIR spectrophotometers. Hemispherical transmittance (T), reflectance (R) are measured by using Perkin Elmer UV-VIS-NIR Lambda 9 spectrophotometer in order to determine the band gap E_g and absorption coefficents of the above mentioned films. α values have been calculated

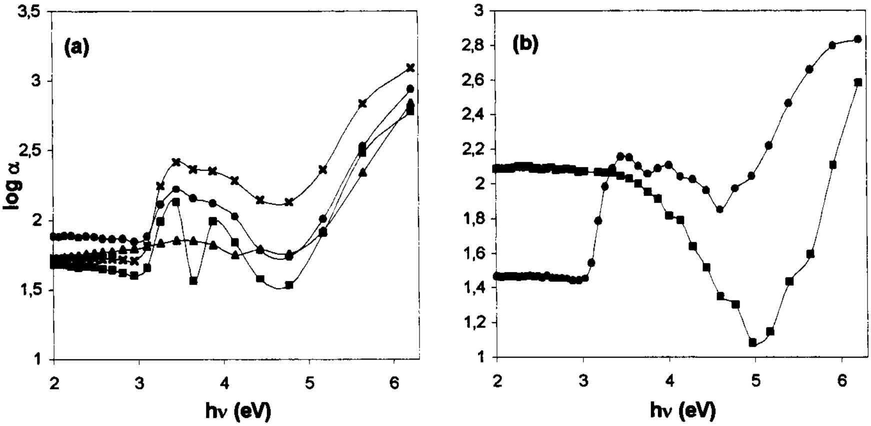

Fig. 2: Variation of the absorption coefficient as log α vs. photon energy for (a) ● = P8, ■ = P9, ▲ = P12, × = P13 (b) ● = P10, ■ = P14

from the optical transmittance and thickness. From the absorption spectra, approximate absorption edges and optical activation energies can be calculated using the Tauc equation:

$$\alpha h\nu \sim (E-E_g^{opt})^n \qquad (1)$$

Where E_g^{opt} is optical energy gap; n is a constant and α is absorption coefficient.

Tauc graphs $[(\alpha h\nu)^{1/n}$ and $(\alpha h\nu)^n$ vs.hν] are plotted for different films. Extrapolation of the straight line region onto the x axis gives an estimate of E_g^{opt} 4). E_g varies in the range from 0 eV for metalic films to approximately 3-10 eV for PP/PE and composites.

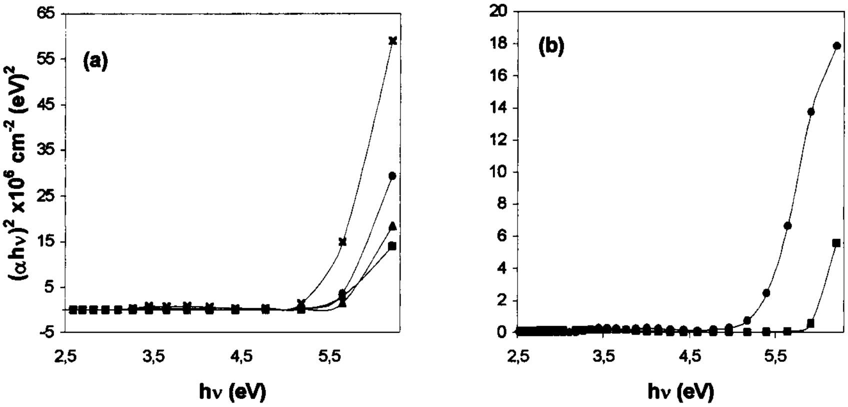

Fig. 3: Tauc plot of $(\alpha h\nu)^2$ vs. photon energy for (a) ● = P8, ■ = P9, ▲ = P12, × = P13 (b) ● = P10, ■ = P14

Experimental Results and Discussion

Optical absorption spectroscopy provides an insight into the energy gap, optically induced transition and band structure of materials. The absorption spectra of most organic composites in visible and near UV region is a wide band containing one or several maxima depending on electron transitions5). It is observed that two distinct linear relations are found corresponding to different interband absorption processes6). The lower energy range n=2 is typical of an indirect allowed transition. Optical energy gap E_I^{opt} can be obtained from the plot of $(\alpha h\nu)^{1/2}$ vs. hν (Fig. 4a and b) while the direct energy gap E_d^{opt} can be obtained from the plot of $(\alpha h\nu)^2$ vs. hν (Fig. 3a and b). Their values are listed on Table 1. The quantities are observed to rise with photon energy near the band edge, having a tail of electronic states in the band gap. In our case, the values were found to be in the range 4.77-5.08 eV for direct and 3.73-5.82 eV for indirect transitions. These values show a great difference with the values of previous measurements7).Considering these wide range of values, the thicknesses have been chosen with more precision. The width of the band tail can be evaluted from the following relation:

$$\ln \alpha = \ln \alpha_1 - h\nu/\Delta E \qquad (2)$$

ΔE values are also listed on Table 1. The absorbance vs. wavelength plots (Fig. 1) show sharp rise in the absorbance at the higher energies. Log α vs. photon energy plots are almost flat up to 3 eV. At higher photon energies ($E_{ph} > 3$ eV) they show fluctuations and sharp absorbtion peaks (Fig 2.).

As it is well known, the covalent bond energies of the bounds in polymer chains are in 250-500 kJ/mole which is more than 3 eV and it is natural that the polymer chains can be affected starting from the values higher than 3 eV of the light energies.

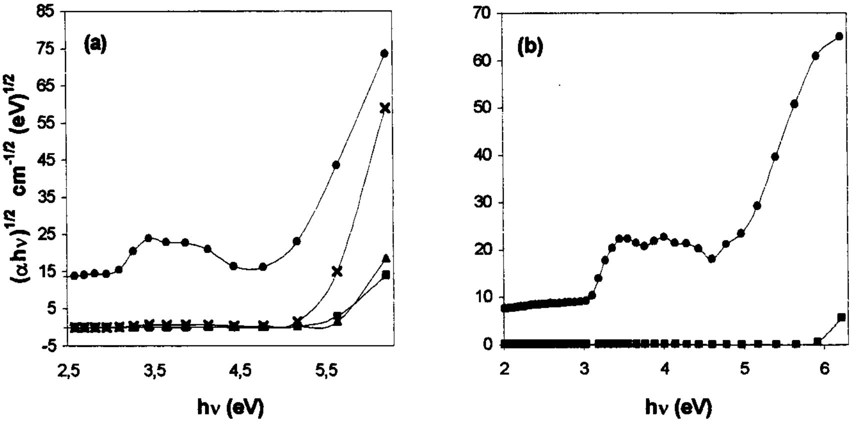

Fig. 4: Tauc plot of $(\alpha h\nu)^{1/2}$ vs. photon energy for (a) ● = P8, ■ = P9, ▲ = P12, × = P13
(b) ● = P10, ■ = P14

Conclusion

As seen from the table and the figures, the activation energies for the PPfiber and diamond additives display considerable differences. This situation explains how various additives effect different mechanisms. Depending on the previous studies, the following results may be stated:

1) The organic additives positioned at the supermolecular formation limits, effect the semicrystalline polymer structure, by forming monolayers, i.e. they play the role of impurities.

2) Fiber additives form crystallization centers and change the amorphous-crystalline ratio, in other words effect the physical structure.

According to these results, it may be concluded that diffusion of O towards polymer chains becomes harder to attain and prevents the generation of peroxide groups. Actually, it may be observed for the cases of diamond (0.3-0.5 %) and fiber (20-30 %) additives, the intensity of the peaks (C = O) in the range 1710-1790 cm^{-1} at the IR spectrum is seen to decrease considerably.

Table 1. Optical properties of polymer composites.

Samples	Composition	Thickness (μm)	$E_d^{opt}(eV)$	$E_i^{opt}(eV)$	ΔE
P8	PP / 50% LDPE	10	5.08	3.73	1.06
P9	PP / 20% LDPE	15	4.77	4.73	0.90
P10	PP / 40% PP Fiber	29	4.78	4.50	1.13
P13	PP / 20% PP Fiber	15	5.02	4.99	1.10
P12	Granule PE / <0.5% Diamond	21	5.08	5.05	1.11?
P14	LDPE / 0.5% Diamond	9	5.70	5.82	0.57

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