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Effect of the Iraqi Bentonite Kara Tepe Filler on Optical Properties of Composites Based on Polystyrene

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Abstract: In this study, Iraqi bentonite Kara Tepe was used as reinforcing phase in Polystyrene (PS) matrix to form composites films. Bentonite clay was prepared as a powder for particles size <35 m and <65 μm, followed by calcinations process at 450°C for 2 h. PVA solution used as a coated layer covered the bentonite applied as a filler. The optical study showed good transmittance value of PS in the VIS and NIR regions but it decrease with increasing particles size of reinforced bentonite in polystyrene/bentonite composite films. The values of allowed and forbidden indirect transition optical energy gap decrease with increasing particles size of reinforced bentonite up to (2.6, 2, 1.8) and (2, 1.4, 1.27 eV), respectively which it is possible to apply in transistor, capacitors, solar cells, etc. Optical constants such as refractive index, extinction coefficient, real and imaginary part of dielectric constant of polystyrene/reinforcement bentonite composite films were done.

Key words: Polystyrene/bentonite composite, optical properties, composite materials, transmittance, transistor, imaginary

INTRODUCTION

The promising direction in polymer materials science is the fabrication of hybrid materials based on organic-inorganic systems. Effective way to solve this problem is to modify the polymer matrix by fillers insertion. A composite materials is made by combining two or more substances-often ones that have very different properties. There is no chemical reaction between the components of this mixture. The biggest advantage of modern composite materials is that they are light as well as strong. By choosing an appropriate combination of matrix and reinforcement material, a new material can be made that exactly meets the requirements of a particular application. Requirements for industrial development in the world may require the development of the science and technology of composite materials and the entry into the manufacture of new materials with special specifications determined by the required uses (Umair, 2006; Hashim *et al*., 2016).

Polystyrene (PS) is a thermoplastic polymer polystyrene is in a solid (glassy) state at RT but flows if heated above about 100°C its glass transition Temperature (T_g). It becomes rigid again when cooled. It is resists the action of many chemicals material (Anonymous, 2012).

Bentonites are defined as a sedimentary rock consisting of a large portion of expandable clay minerals with three-layer structures (smectites) such as montmorillonites (80%), beidellite, nontroniteetc with minor amounts of non-clay minerals such as quartz, calcite, dolomite and feldspar (Sarkar *et al*., 2008). Bentonite has a specific layer structure, each layer is composed of a central sheet of octahedrally coordinated cations (called octahedral sheet) and two sheets of tetrahedrally coordinated cations (called tetrahedral sheet) (Rautioaho and Korkiala-Tanttu, 2009). Bentonite group minerals show a colloidal structure in water due to their internal structure and small particle size. They have a large adsorption capacity for polymer compounds due to their unique crystal structure.

The polymer concentration, molecular weight, hydrolysis degree of polymer, clay particle's size, shape, surface charge, clay concentration in dispersion, clay's PH and temperature are effective factors when clay particles interact with the polymers (Grim, 1970). This study was aimed at producing polymer materials based on polystyrene and Iraqi bentonite Kara Tepe and the examination of the effect of particle's size of bentonite clay on the optical properties of PS for used in different applications.

MATERIALS AND METHODS

The polymer matrix used is Polystyrene (PS) polystyrene is a long chain hydrocarbon where in

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Table 1: The chemical analysis of Iraqi bentonite Kara Tepe

Constituent	Content (wt.%)
SiO_2	58.58
Fe_2O_3	2.00
Al_2O_3	15.80
MgO	6.10
CaO	2.77
Na_2O	0.70
SO_3	0.10
Loos on ignition	12.48

Table 2: The mineralogical analysis of Iraqi bentonite Kara Tepe

Minerals	Percentage
Montmorillonite ($[OH]_2\ Al_2SiO_{10}$)	97.54
Quartz (SiO_2)	2.46

alternating carbon centers are attached to phenyl groups. Polystyrene's chemical formula is $(C_8H_8)n$. Its dissolved in many solvents and that the user solvent is benzene in certain proportions and a temperature of 80°C.

Bentonite Kara Tepe clay ($Al_2O_3\ 4SiO_2\ H_2O$), supplied by state company of geological survey and minority in Iraq was used as a filling agent (Al-Gohary *et al.*, 1987). The chemical analysis of Iraqi bentonite Kara Tepe is listed in Table 1. The mineralogical analysis of the final powder of Iraqi bentonite Kara Tepe is listed in Table 2.

The bentonite clay was dispersed in de-ionized water (pH = 7 measured at RT) which has electrical conductivity 24.6 μS and shaken extensively for 24 h at RT. The washing process was repeated seven times during which the floating water was reduced every 24 h. The result of the test of the electrical conductivity of the bentonite clay after the last wash was 34 μS which is an acceptable result. The product was dried at 100°C for 24 h by using the dryer type F.G. BODE and CO-Laboratory-Equipment-Hamburg-90. Particle sizes selected for Iraqi bentonite Kara Tepe is <35 and <65 μm and the calcinations was performed at 450°C for 2 h.

The addition of PVA has pH = 6 is one of the requirements to obtain the best adsorption on the surface of the clay before applied it as filler (De Bussetti and Ferreiro, 2004). The mixture was mixed (using a magnetic sterile type-Sturt-Germany manufacture) with heat treatment in 80°C continued to get slurry form and to insure homogeneity with high viscosity (the mixing process was adopted according to the method of green land (Greenland, 1963) then dried, milled and sieved to particle sizes < 35 and <65 μm 1.5 g of PS was dissolved in 30 mL benzene by using magnetic stirrer to mix the mixture to obtain more homogeneous solution at 70-80°C for 30 min. The reinforced bentonite of <35 and <65 μm sizes were added to PS with weight of percentage 2 wt.% using a delicate electronic scale of up to 10^{-4} g and mixed for 30 min. to make the mixture more homogenous. The casting method is used to get the composites cast on glasses betray dish and then left to dry for 1 day.

The absorption spectrum of polystyrene/bentonite composite films at thickness around 0.30 mm to size 35 μm and 0.37 to size 65 μm (by using electronic digital device-Micrometer-to measure thickness) have been recorded in the wavelength range (280-1100) nm by using the double beam spectrophotometer (Shimadzu, UV-1800 A, Japan). The absorption spectrum have been recorded at RT. A computer program (UV Probe Software) was employed to obtain the absorption coefficient, extinction coefficient, refractive index, dielectric constant (real and imaginary parts) and optical energy gaps.

Basic relation: The absorption coefficient (α) was calculated using the expression (Pankove, 1971):

$$\alpha = \ln(1/T)/t \tag{1}$$

where, t is the sample thickness. The Reflectance (R) and refractive index (n) of thin films were calculated from the Eq. 2 and 3, respectively (Pankove, 1971):

$$R = 1-\sqrt{T\exp(\alpha t)} \tag{2}$$

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \tag{3}$$

The extinction coefficient (K) defined to be (Chopra, 1969):

$$K = \frac{\alpha\lambda}{4\pi} \tag{4}$$

where, λ is the wavelength of the incident radiation. The real (ε_r) and imaginary (ε_i) parts of the dielectric constant related to (n) and (k) values can be written as in following Eq. 5 and 6:

$$\varepsilon_r = n^2-K^2 \tag{5}$$

$$\varepsilon_i = 2nK \tag{6}$$

The optical Energy gap (E_g^{opt}) for indirect transition type is given by Sze and Ng (2007):

$$\alpha h\upsilon = B(h\upsilon-E_g^{opt}\pm E_{ph.})^r \tag{7}$$

where, $E_{ph.}$ Energy of phonon, (-) when phonon absorption and (+) when phonon emission, r is the exponential constant its value depends on the type of transition, r = 2 for the allowed indirect transition and r = 3 for the forbidden indirect transition.

RESULTS AND DISCUSSION

Figure 1 shows the optical transmittance spectrum versus wavelength of incident light on pure PS and (PS/bentonite composite) films. The optimum value of transmittance about 62% for pure PS film at high wavelength (VIS-NIR). The transmittance decrease with increasing particles size of reinforcement bentonite up to 38 and 34% for <35 and <65 μm sizes, respectively. This result can be attributed to what follows: the chemical analysis of bentonite indicates that the enforcement clay powder additive consists of oxides of varying proportions as in Table 1 and that the electrons available in it can absorb the electromagnetic energy of the incident light and travelto higher energy levels. This process is not accompanied by emission of radiation because the traveled electron to higher levels have occupied vacant positions of energy bands, thus, part of the incident light is absorbed by the substance and dose not penetrate through it. This is because the breaking of electron linkage and moving it to the conduction band needs to photon with a high energy (Dahshan, 2002).

Figure 2 shows the absorption coefficient (α) versus photon energy for PS and (PS/bentonite composite) films. It can be seen that the absorption coefficient is the smallest at a low energy that means the possibility of electron transition is little because the energy of the incident photon is not sufficient to transmission of the electron from the valence band to the conduction band. The values of α is $<10^4$ cm^{-1} which means that the electron transitions is indirect.

Both the allowed and forbidden indirect transition optical energy gap are shown in Fig. 3 and 4, respectively. E_g^{opt} decreases with the increasing particles size of reinforced bentonite as shown in Table 3. This results due to the creation of localized levels in the forbidden energy gap.

Figure 5 shows the change in refractive index for PS and (PS/bentonite composite) films versus wavelength. In visible region (630 nm), the refractive index decrease with increasing particles size of reinforcement bentonite but in the VIS and NIR regions over 630 it gets the opposite.

Figure 6 shows the change of extinction coefficient (k) for PS and (PS/bentonite composite) films versus wavelength. It can be noted that k increase with increasing particles size of reinforcement bentonite in all regions. This is related with the absorption coefficient.

Table 3: Optical energy gap for the allowed and forbidden indirect transition of (PS/bentonite composite) films

(PS-Iraqi bentonite) samples	Particale size (μm)	Allowed indirect transition (eV)	Forbidden indirect transition (eV)
Pure PS	-	2.6	2
PS-2 wt.% bnt.	35	2.0	1.4
PS-2wt.% bnt.	65	1.8	1.27

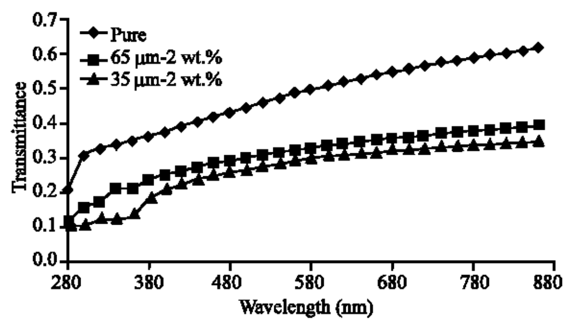

Fig. 1: The transmittance versus wavelength for PS and (PS/bentonite composite) films

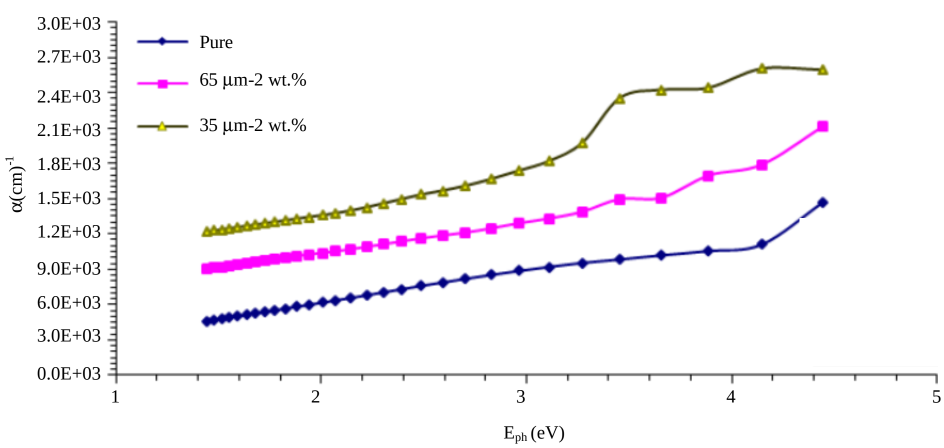

Fig. 2: The absorption coefficient versus photon energy for pure PS and (PS/bentonite composite) films

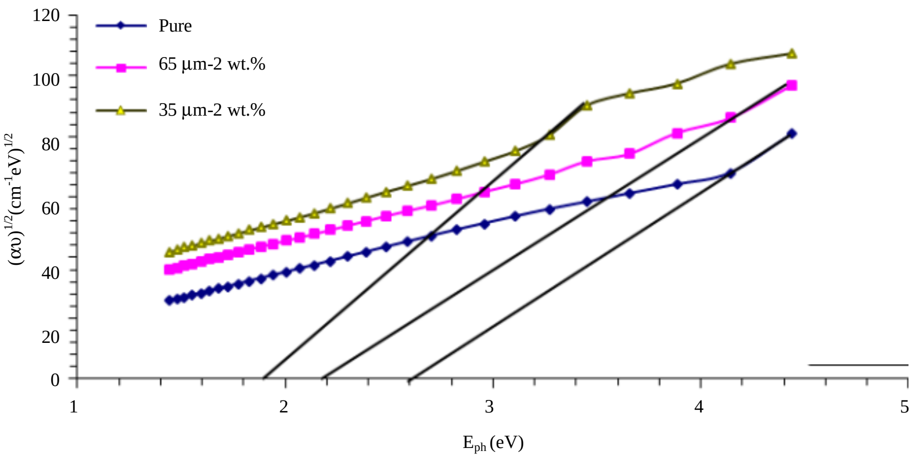

Fig. 3: The energy gap for the allowed indirect transition $(\alpha h\upsilon)^{1/2}$ versus photon Energy (E_{ph}) of PS and (PS/bentonite composite) films

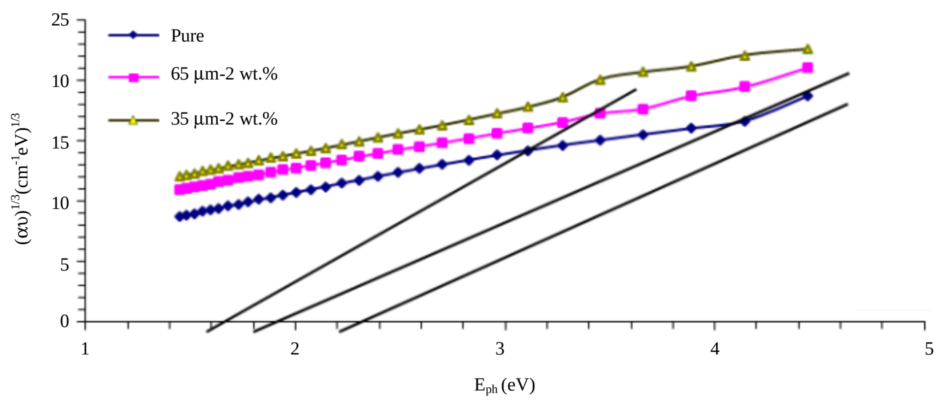

Fig. 4: Optical energy gap for the forbidden indirect transition $(\alpha h\upsilon)^{1/3}$ versus photon Energy (E_{ph}) of PS and (PS/bentonite composite) films

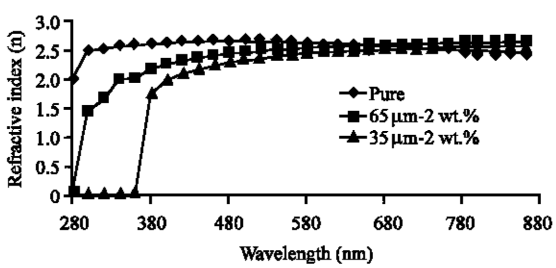

Fig. 5: Refractive index (n) versus wavelength for PS and (PS/bentonite composite) films

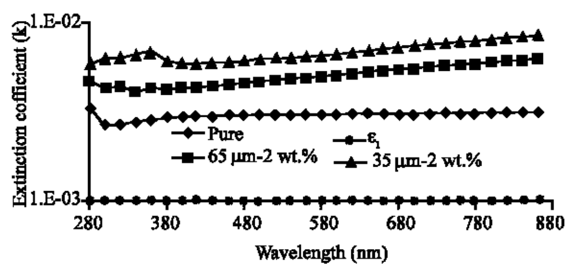

Fig. 6: Extinction coefficient versus wavelength for PS and (PS/bentonite composite) films

The dielectric constant for two parts real ε_1 and imaginary ε_2 for pure PS and (PS/bentonite composite) films versus wavelength are shown in Fig. 7 and 8, respectively. It can be seen that ε_1 considerably depends on n^2 due to low value of κ_0^2, so in visible region (over 580 nm), the ε_1 increased with the increase of the particles size of reinforcement bentonite. The change of ε_2 dependent on K_o values that change with the absorption coefficient due to the relation between α and K_o. The optical conductivity versus photon energy for PS and (PS/bentonite composite) films is shown in Fig. 9. The increase in optical conductivity with increasing photon energy is due to electron exited by photon energy.

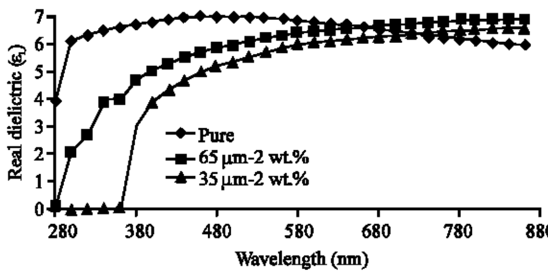

Fig. 7: The real dielectric constant (ε_1) versus wavelength for PS and (PS/bentonite composite) films

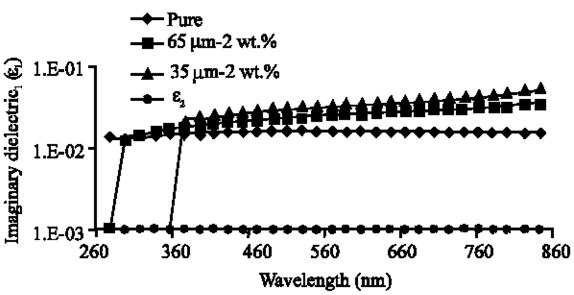

Fig. 8: The imaginary dielectric constant (ε_2) versus wavelength for PS and (PS/bentonite composite) films

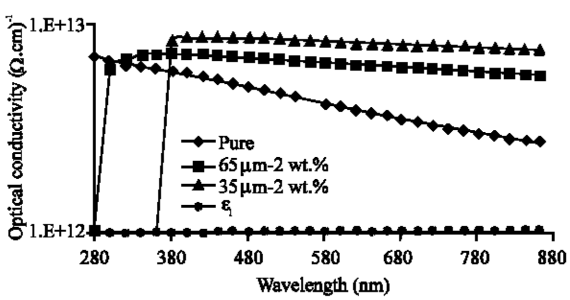

Fig. 9: Optical conductivity versus photon energy for pure PS and (PS-Iraqi bentonite) films

CONCLUSION

The optical study showed good transmittance value of PS, inter VIS and NIR region but it decreases with the increasing particles size of reinforced bentonite additive. The energy gap of indirect transition (allowed and forbidden) decreases with increasing particles size of reinforced bentonite. The optical constant such as refractive index, extinction coefficient and dielectric constant (real and imaginary) are increasing with the increase of particles size of reinforced bentonite.

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