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Study the Effect of Adding Iraqi Bentonite Kara Tepe on Some Optical Properties of Poly (Methyl Methacrylate)

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Abstract: Iraqi bentonite Kara Tepe was used as reinforcing phase in Poly Methyl Methacrylate PMMA matrix to form composites. Bentonite clay was prepared as a powder for particle size <25 and <45 μm, follow them calcinations process at 450°C for 2 h. PVA solution used as a coated layer covered the bentonite applied as a filler. The reinforced bentonite were added to PMMA solution in the rate of 1 and 2 wt.%.The transmittance value of PMMA inter V is and NIR region is equal to 80% but it decrease with increasing particles size of reinforced bentonite. The values of allowed and forbidden indirect transition optical energy gap decrease with increasing particles size of reinforced bentonite up to 3, 2.71, 2.45 and 2.6, 2.15, 1.8 eV and 3, 2.7, 2.4 and 2.6, 2.1, 1.7 eV, respectively. Refractive index, extinction coefficient of polymer reinforcement bentonite were done. The optical properties are influenced by the bentonite additives ratioand particles size.

Key words: PMMA, bentonite, optical properties, composite materials, reinforced, polymer

INTRODUCTION

The composite material is a mixture of two or more substances combined by a bond material, noting that there is no chemical reaction between the components of this mixture. The requirements of industrial development in the world led to 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 use (Umair, 2006; Hashim *et al*., 2016).

PMMA is an amorphous thermoplastic polymer. It has a good optical properties but has a poor scratch resistance and has a good weather resistance. PMMA is stable to alkal is and acid and has a good impact strength higher than that of glassor polystyrene. PMMA is widely used in many technological applications because ofits unique combination of excellent optical properties with chemical inertness, some good mechanical properties, thermal stability, electrical properties, weather resistance and easy shaping (Nahida, 2012).

Bentonite is a sematicclay which has a high montmorillonite content and the amount of less than other clay minerals. Other sematic group minerals include hectorite, saponite, beidelite and nontronite (Anonymous, 2005). Bentonite has a specific layer structure, each layer is composed of a central sheet of octahedral coordinated cations and two sheets of tetrahedral coordinated cations (Rautioaho and Korkiala-Tanttu, 2009). Bentonite group minerals show a colloidal structure in water, due to their internal structure and small particles 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 interact with the polymers (Grim, 1970). The aim of present research is to investigate the effect of adding Iraqi bentonite Kara Tepe on the optical properties of poly methyl methacrylate for used in different applications.

MATERIALS AND METHODS

The main material used in this research is Poly Methyl Methacrylate (PMMA). A chemical structure of the repeating unit of PMMA polymer shown in Fig. 1 (Nandi *et al*., 2009). Table 1 illustrate the most important properties of PMMA polymer (Billmeyer, 1984).

Bentonite Kara Tepe clay used in this study was supplied by state company of geological survey and minority in Iraq have the general structure consisting mainly AL_2O_3 $4SiO_2.H_2O$ (Al-Gohary *et al*., 1987). The chemical analysis of Iraqi bentonite Kara Tepe is listed in Table 2. The mineralogical analysis of the final powder of Iraqi bentonite Kara Tepe is listed in Table 3.

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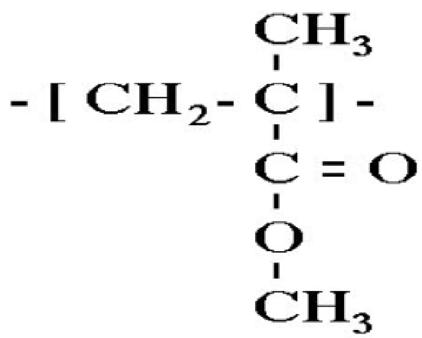

Fig. 1: Poly Methyl Methacrylate structure (Nandi *et al*., 2009)

Table 1: Most important properties of PMMA polymer Billmeyer (1984)

Properties	Specification
Chemical formula	$(C_5O_2H_8)_n$
Tg (k)	379
Molecular weight (g/mol)	Various
Melting point	473
Refractive index (k)	1.49

Table 2: Chemical analysis of Iraqi bentonite Kara Tepe

Constituent	wt. (%)
SiO_2	58.58
Fe_2O_3	02.00
Al_2O_3	15.80
MgO	06.10
CaO	02.77
Na_2O	00.70
SO_3	00.10
Loss on ignition	12.48

Table 3: Mineralogical analysis of Iraqi bentonite Kara Tepe

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

The bentonite particles were dispersed in de-ionized water (PH = 7.09 measured at RT) which has electrical conductivity 23.6 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 30 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 <25 and <45 μm and the calcinations process 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 (Bussetti and Ferreiro, 2004). The mixture was mixed by a magnetic sterile type Sturt-Germany manufacture under 80°C continued to get slurry form and to insure homogeneity with high viscosity (the mixing process was adopted according to the method by Greenland (1963) then dried, milled and sieved to particle sizes <25 and <45 μm. A solution have been prepared by solving 2 g of PMMA in 30 mL of the benzene and using magnetic stirrer to mix the materials to obtain more homogeneous solution at 70-80°C for 30 min. The reinforced bentonite of <25 or <45 μm sizes were added to PMMA with weight of percentage 1 and 2 wt.%, respectively and mixed for 50-60 min to make acreamy solution color homogeneous. The casting method is used to get the composites cast on glasses petri dish and then left to dry for 2 days. The choice of the casting method in the preparation of PMMA was due to the require no advanced techniques and complex devices and by which they can prepare samples with a large area and equal thickness.

The absorption spectrum of (PMMA-Iraqi bentonite) composites at thickness 30-37 μm have been recorded in the wavelength range 280-1100 nm by using the double beam spectrophotometer (Shimadzu, UV-1800 Å, Japan).

Basic relation: The absorption coefficient (α) can be calculated from the Eq. 1 (Pankove, 1971):

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

where, t is the sample thickness. The reflectance (R) of thin films was calculated from the Eq. 2 (Pankove, 1971):

$$R = 1 - \left[\sqrt{T_{exp}(\alpha t)}\right] \tag{2}$$

The refractive index (n) was calculated from the Eq. 3 (Pankove, 1971):

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

The extinction coefficient (k) is related to the exponential decay of the wave as it passes through the medium and it is defined to be Eq. 4 (Chopra, 1969):

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

where, λ is the wavelength of the incident radiation. The optical energy gap (E_g^{opt}) for indirect transition type is given Eq. 5 by (Sze and Ng, 2007):

$$\alpha h\upsilon = B\left(h\upsilon - E_g^{opt} \pm Eph.\right)^r \tag{5}$$

Where:

Eph = Energy of phonon
(-) = When phonon absorption
(+) = When phonon emission
r = 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

The PMMA polymer was characterized by using (FTIR) spectrum in the region (4000- 500) cm^{-1} using KBr disk samplingas shown in the Fig. 2. After a comparison of the general behavior of the schemes was to make sure that the material used in the search is PMMA with a high degree of purity which are in accordance with international standards.

Figure 3 and 4 show the optical transmittance spectrum versus wavelength of incident light on PMMA and PMMA-Iraqi bentonite) filmsin the rate of 1 and 2 wt% for particles size <25 and <45 μm, respectively.The optimum value of transmittance about 80% for pure PMMA film at high wavelength (Vis-NIR). The transmittance decrease with the increasing particles size of reinforcement bentonite additive. This result is due to the following; The chemical analysis of bentonite indicates that the enforcement clay powder additive consists of oxides of varying proportions (Table 2) and

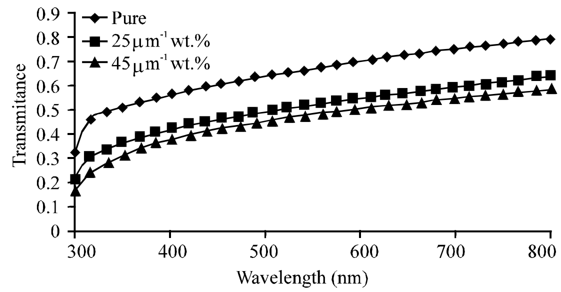

Fig. 3: The transmittance versus wavelength for pure PMMA and (PMMA -1 wt.%Iraqi bentonite) films

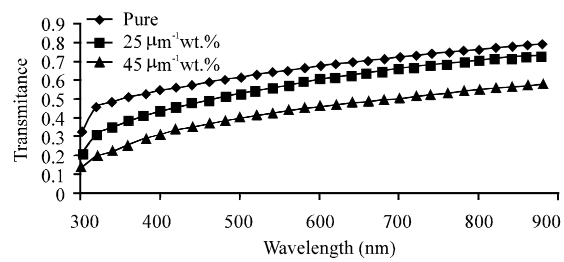

Fig. 4: The transmittance versus wavelength for pure PMMA and (PMMA -2 wt.%Iraqi bentonite) films

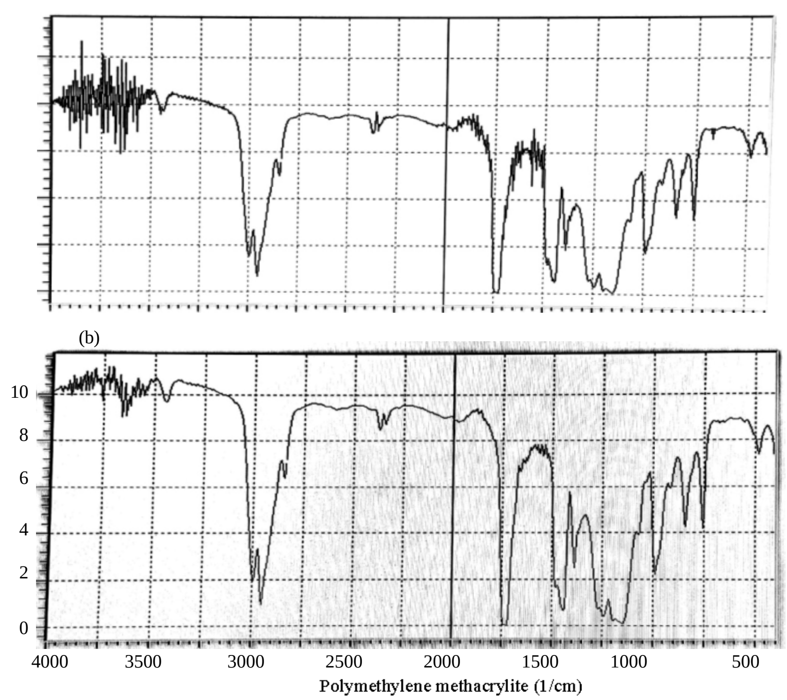

Fig. 2: FTIR forPMMA polymer: a) Under study and b) Standard scheme

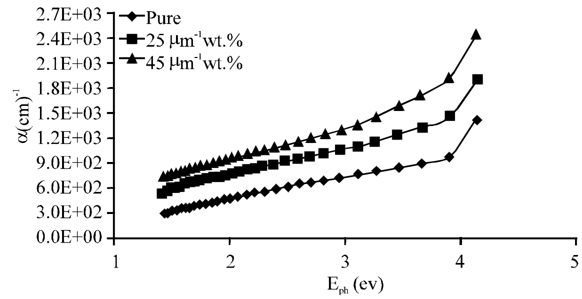

Fig. 5: The absorption coefficient α $(cm)^{-1}$ versus photon energy for purePMMA and (PMMA-1 wt.% Iraqi bentonite) films

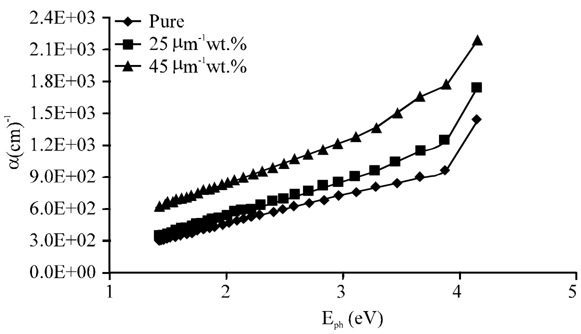

Fig. 6: The absorption coefficient α $(cm)^{-1}$ versus photon energy for pure PMMA and (PMMA-2 wt.% Iraqi bentonite) films

that the electrons available in it can absorb the electromagnetic energy of the incident light and travel to 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, on the other hand, the PMMA polymer has high transmittance because it does not contain free electrons (Dahshan, 2002). This is agree with previous research related to it (Abd-Alkareem , 2016).

Figure 5 and 6 show the absorption coefficient α $(cm)^{-1}$ versus photon energy for (PMMA-Iraqi bentonite) films. It can be seen that the absorption coefficient is the smallest at a low energy. This means that the possibility of electron transition is little because the energy of the incident photon is not sufficient to move the electron from thevalence band to the conduction band. While at high energies we find that absorption is good. The values of the absorption coefficientis $<10^4$ cm^{-1} which explains t the electron transitions is indirect.

Both the allowed and forbidden indirect transition optical energy gap are shown in Fig. 7 and 8, respectively.

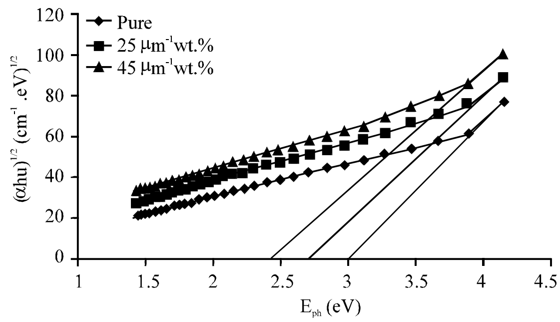

Fig. 7: Optical energy gap for the allowed indirect transition $(\alpha h\tilde{o})^{1/2}$ versus photon energy of pure PMMA and (PMMA-1 wt.% Iraqi bentonite) films

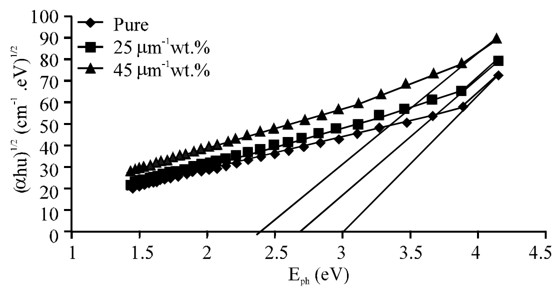

Fig. 8: Optical energy gap for the forbidden indirect transition $(\alpha h\upsilon)^{1/3}$ versus photon energy of pure PMMA and (PMAA-2 wt.% Iraqi bentonite) films

Table 4: Values of the optical energy gap for the allowed and forbidden indirect transition of PMMA and (PMMA-Iraqi bentonite) films

Samples	Particale size μm	Allowed indirect transition (eV)	Forbidden indirect transition (eV)
PMMA	-	3	2.60
PMMA-1 wt.% bnt.	25	2.71	2.15
PMMA-1 wt.% bnt.	45	2.45	1.80
PMMA-2 wt.% bnt.	25	2.7	2.10
PMMA-2 wt.% bnt.	45	2.4	1.70

The values of optical energy gap decrease with increasing both concentrations and particles size of reinforced bentonite additives (Table 4) which it is possible to apply in transistor, capacitors, solar cells, electrical equipment, etc. This results attributed to the creation of localized levels in the forbidden energy gap.

Figure 9 and 10 show the change of refractive index for PMMA and (PMMA-Iraqi bentonite) films versus wavelength. In visibleregion, the refractive indexincrease with increasing particles size of reinforcement bentonite. This attributed to the high transmittance of pure PMMA in compare with that values of composite (PMMA-Iraqi bentonite). But in the UV regionit gets the opposite.

Figure 11 and 12 show the change of extinction coefficient (k) for pure PMMA and (PMMA-Iraqi bentonite) films versus wavelength. It can be noted that

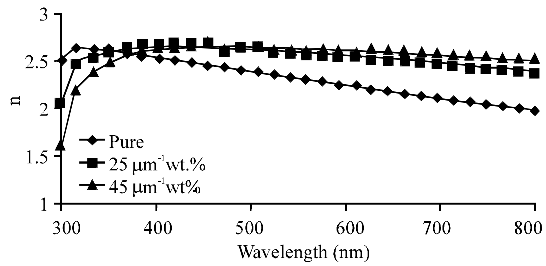

Fig. 9: The refractive index (n) versus wavelength for pure PMMA and (PMMA-1 wt.% Iraqi bentonite) films

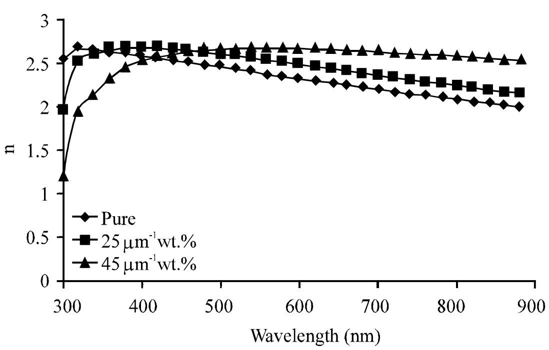

Fig. 10: The refractive index (n) versus wavelength for pure PMMA and (PMMA-2 wt.% Iraqi bentonite) films

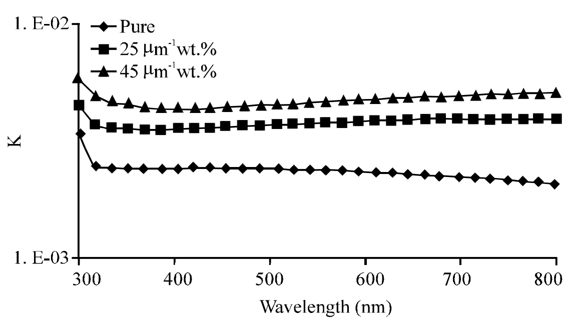

Fig. 11: The extinction coefficient versus wavelength for pure PMMA and (PMMA-1wt.% Iraqi bentonite) films

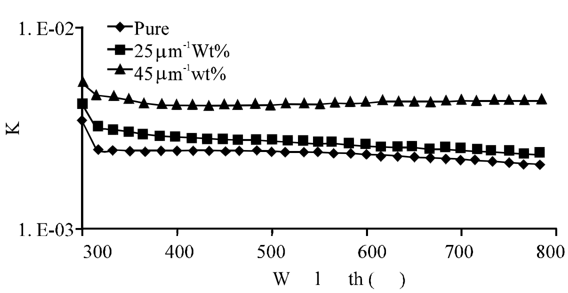

Fig. 12: The extinction coefficient versus wavelength for pure PMMA and (PMMA-2 wt.% Iraqi bentonite) films

k increase with increasing particles size of reinforcement bentonite in all regions. This is attributed to increase absorption coefficient with the increase of the particles size of reinforcement bentonite. Absorption coefficient (α) has a direct related with k as in the Eq. 4.

CONCLUSION

The optical study showed good transmittance value of PMMA, inter VIS and NIR region but it decreases with the increasing particles size of reinforced bentonite additive.

The energy gap for indirect transition (allowed and forbidden) decreases with increasing both concentrations and particles size of reinforced bentonite additives and which it is possible to apply in transistor, capacitors, solar cells, electrical equipment, etc.

The refractive index and extinction coefficient of pure PMMA and (PMMA-Iraqi bentonite) films are increasing with the increase of particles size of reinforcement bentonite.

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