EFFECT OF NANO TiO_2 ON THE OPTICAL PROPERTIES OF PVC CONTAINS TRIAZOLE MOIETIES

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ABSTRACT

Optical properties of pure and doped poly(vinyl chloride), PVC contain a triazole ring (P), with different concentration of nano titanium oxide TiO_2 were studied. The films prepared by using casting technique. Spectra of transmission, absorption and reflection were used to study the optical parameters. Different parameters such as the absorption coefficient, refractive index, extinction coefficient and energy gap were studied in the spectral range of 200-800nm. In this study we reveals that the doping of TiO_2 is effected on the optical properties of PVC contain triazole ring where the transmission spectrum and energy gap values were decreases with increasing percentage. The energy gap is decreased from 5.79 to 3.24 eV. Absorption coefficient, refractive index and extinction coefficient was increased with the increase of TiO_2 concentration.

Keywords: PVC polymer, Nano TiO_2 , Optical properties.

1. INTRODUCTION

Polymeric materials have attracted many of scientific and technological researchers, due to their wide industrial applications. In recent years, physical and chemical properties of polymer nanocomposite their have attracted great attention [1,2]. The presence of nanoparticles in polymer improves the mechanical, electrical and optical properties of the materials [3]. It is great importance to relate the chemical structure of polymers to their physical properties. Polymeric surface can be treated chemically or physically to induce desired properties to the surface layers. The surface analysis of polymers is of great importance in the understanding of adhesion

and in technical applications for insulation, isolation, passivation in microelectronics and compatibility of these materials [4]. The polymer of Polyvinyl chloride (PVC) is one of the best known polymers. PVC was seen as a replacement for glass in a variety of applications such as in glazing applications. In recent times, is being exploited as a polymer host. PVC is a commercially available, inexpensive polymer and is compatible with plasticizers such as dibutyl phthalate (DBP), dioctyladipate (DOA), dioctyl phthalate (DOP), polycarbonate (PC) and ethylene carbonate (EC). Various PVC based systems have been found to form electrolytes with conductivities ranging from 10^{-8} to 10^{-3} Scm^{-1} at room temperature. The electrical and

optical properties of polymers can be suitably modified by the addition of dopants depending on their reactivity with the host matrix [5]. Recently, optical properties of pure and iron- doped cellulose acetate (CA) were investigated in the 200-700 μ m wavelength region [7]. The optical properties of Poly vinyl chloride doped with different concentration of nanosize zinc oxide ZnO 1-20wt% [7]. The effect of continues CO₂ laser radiation on the optical properties of pure poly vinyl chloride and doped of ZnO nanoparticles was investigated [8]. Electrical conductivity was studied of poly aniline doped PVC-PMMA polymer blend [9]. Investigation on the dielectric properties of Carbon Black /PVC (cement) composites was done [10]. Analysis of the absorption spectra in the lower energy part gives information about atomic vibrations while the higher energy part of the spectrum gives knowledge about the electronic states in the atom. There are many researches on the optical properties of polyvinyl alcohol doped PVC-PVA thin films [11]. Optical properties of pure and doped PVA-CO-P4VPNO polymer films have been studied [12] and thermal, electrical and optical properties studies on the PVA based polymer electrolytes have been studied [12, 13]. Various research groups have studied the optical, structural and other properties of polymers films doped with multiple valance metal ions such as, I/KI, CuCl, ZnSe, CdS, MnCl₂, MgBr₂, CrF₃, FeCl₃, etc. These researches showed that a strong dependence of donor-acceptor mechanism between the metal ion and the polymer matrix. Also, these studies shows, the changes in the properties like crystallinity, structural and optical behavior of the polymer due to doping [14].

The aim of this work is to investigate the optical properties of PVC contains triazole ring and PVC films with different concentration.

2. EXPERIMENTAL

Poly(vinyl chloride) contains triazole ring was prepared by the method previously described by Ahmed [15] as in Figure 1 below:

Fig.1. Poly(vinyl chloride) contains triazole ring

PVC contains a triazole ring (P), doped with nano TiO₂. The P films with different weights (0.5, 0.10, 0.20) wt% were prepared by dissolving P and nano TiO₂ in THF with stirring the solution, using a magnetic stirrer for about 30 mins at room temperature for complete dissolving. The solution was poured into a clean glass plate and kept till dried 3 days at room temperature. The thickness of the produced films was 72 μ m measured using electronic digital caliper. The optical transmittance, absorbance and reflectance were recorded in the wavelength range 200-800nm using computerized UV-visible spectrophotometer (Shimadzu UV-1601 PC). Optical transmittance and absorbance were reported in order to study the effect of doping on the parameters under investigation.

3. RESULTS AND DISCUSSION

The UV–VIS transmittance spectrum in the region 200–800nm for doped and undoped films samples (a, b, c and d) are shown in Figure 2. The figure shows the transmittance is increased with the increase of wavelength for all films, while after doping it can be noticed that the transmittance decreases with increasing TiO₂ concentration. The results agreed with those reported by earlier workers [16, 17]. The absorption coefficient α can be calculated using the following relation [13]:

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

Where A is the absorption and t is the film thickness. The result of what is α ?

Figure 2 shows the dependence of the absorption coefficient on the wavelength. It is clear from this figure that a decreasing behavior for the absorption coefficient with increasing of the wavelength for all samples a-d. In contrast the absorption coefficient increases with increasing the doping concentration of TiO₂ this increasing may be attributed to the difference in carrier concentration or could be related to the existence of more transmissions from higher vibration levels of the ground state to higher sublevels of the first excited singlet state [18].

Fig.2. The transmission spectra of TiO₂ doped PVC films as function of wavelength at different concentrations

Fig. 3. Variation the Absorption coefficient as a function of wavelength

The refractive index n is an important parameter for optical materials and applications. Thus, it is important to determine optical constants of the films and the complex optical refractive index [19]. The refractive index of the films has been determined from the reflectance, by the following relation:

$$n = \left(\frac{1+R}{1-R} \right) + \sqrt{\frac{4R}{(1-R)^2} - K^2} \quad (2)$$

Where R represents the reflectance, K is the extinction coefficient. Figure 3 shows the variation of the refractive index with wavelength for all samples. The refractive index shows an increase in the wavelength range 200–410nm for all PVC samples while for samples with different concentration, it shows a noticeable decreased with other wavelengths. The refractive index was increased with the increase of TiO₂ concentrations b, c and d respectively. This is in good agreement with the reported results of Faisal A [20]. The increasing in the refractive index is very useful for polymers in optics and photonics due to their ability to reduce reflection losses at interfaces [21].

Fig. 4. Variation the refractive index as a function of wavelength

The dependence of the extinction coefficient on the wavelength in the range 200-800nm of pure and doped samples is shown in Figure 5. It is clear that the extinction coefficient decreases with increasing wavelength for all samples before and after doped of TiO_2 . Extinction coefficient was increased with concentration this is due to the increase in absorption coefficient, where the extinction coefficient depending on the absorption coefficient by the equation [22, 23].

$$K = \alpha\lambda/4\pi \quad (3)$$

Fig. 5. Variation the extinction coefficient as a function of wavelength.

According to the inter-band absorption theory, the optical band of the films can be calculated using Tauc's relation [24]:

$$(\alpha h\nu)^p = A(h\nu - E_g) \quad (4)$$

where α is the absorption coefficient, A a constant, h is Planck's constant, ν the photon frequency, E_g is the optical band gap and p is an index which could take different values according to the electronic transition. The experimental data were fitted to the theoretical Eq (4) for different values of p and the best fit was obtained for $p=2$ this behavior directed that the transitions are allowed direct transitions. The direct allowed band gap was determined by plotting $(\alpha h\nu)^2$ as function of photon energy E for samples a, b, c, d are shown in Figures 6 to 9 respectively, the graph is a straight line and the value of E_g is obtained by extrapolating the linear portion of the graph to intercept the photon energy axis [25]. It was found that E_g reduces from 5.79eV of pure sample to 5.1, 4.05 and 3.24eV for samples b, c and d respectively. Showing the values of direct allowed gap is mentioned in Table 1. The decrease in E_g with increasing TiO_2 concentration can be understood by considering the mobility gap variation in the doped polymer. Furthermore, the decrements of E_g may be due to the transition between the molecular orbitals, which have highest occupied molecular orbitals instead of transition between valence-conduction band gap, polymers are usually amorphous insulators so one would consider the transition between the highest occupied molecular orbital and the lowest unoccupied molecular orbital instead of a valence-conduction band gap [26].

TABLE 1: THE OPTICAL ENERGY GAP OF PURE AND DOPED PVC CONTAINS TRIAZOLE RING(P) FILMS.

Sample	P+%Nano	E_g (eV)
A	P	5.79
B	P+0.05	5.1
C	P+0.1	4.05
D	P+0.2	3.24

Fig. 6. Variation the $(\alpha h\nu)^2$ as a function of photon energy for (a) film.

Fig. 7. Variation the $(\alpha h\nu)^2$ as a function of photon energy for (b) film.

Fig.8. Variation the $(\alpha h\nu)^2$ as a function of photon energy for (c) film.

Fig.9. Variation the $(\alpha h\nu)^2$ as a function of photon energy for (d) film.

4. CONCLUSIONS

The results indicate that TiO_2 can effectively dope PVC contains triazole ring and enhance its optical properties. The increase of TiO_2 concentration leads to decrease the transmission. The optical parameters such as absorption coefficient, refractive index and extinction coefficient were increased with the increase of TiO_2 concentration. Energy gap values shows dependence on TiO_2 concentration where decreased with increase percentage from 5.79 to 3.24 eV.

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تأثير اوكسيد التيتانيوم الثاني النانوي على الخصائص البصرية لأغشية بولي فينيل كلورايد المحتوية على حلقة التريازول

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الملخص:

تم دراسة الخصائص البصرية لأغشية بولي فينيل كلورايد النقية (PVC) المحتوية على حلقة التريازول (P)، والمطعمة بتركيزات مختلفة من ثاني أكسيد التيتانيوم النانوي (TiO_2) بعد تحضيرها باستخدام تقنية الصب. وقد استخدمت الأطياف الانبعاثية، الإمتصاصية والانعكاسية لدراسة العوامل البصرية المختلفة المتمثلة في: معامل الإمتصاص، معامل الإنكسار، معامل الخمود، وفجوة الطاقة وذلك ضمن مدى الأطوال الموجية (200-800) نانومتر من النطاق الطيفي.

وتكشف هذه الدراسة أن الخصائص البصرية من البلاستيك المحتوي على حلقة التريازول تؤثر بها المنشطات من ثاني أكسيد التيتانيوم النانوي (TiO_2)، حيث تنخفض قيمة الانبعاثية وفجوة الطاقة من 5.79 الى 3.24 إلكترون فولت. بينما زاد كل من معامل الإمتصاص، معامل الإنكسار ومعامل الخمود مع زيادة تركيز ثاني أكسيد التيتانيوم النانوي (TiO_2).