Effect of Kaolin Clay Concentration and Irradiation on the Electronic Transitions of Polyvinyl Alcohol Films

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Abstract

Pure and (1 and 3 wt%) kaolin doped PVA films were synthesized by solution casting method, and exposed to ^{60}Co-γ-rays, activity 2μCi for two weeks, The optical characterizations of the films were carried out using UV-Vis transmittance spectrophtometer in the wavelength range 300–900 nm. The results show that in the visible region the transmittance of the films increases as the kaolin concentration increase clearly as comared with the same film before irradiation. The dominant transmittance band of UV region increases after irradiation while the reverse is the case with the reflectance. Also results indicates that PVA films have an indirect band gap that decreased from 3.7 to 3.55 eV as the doping concentration increases to 3wt%. Also the energy band gap of the irradiated films appeared to be decreased from 3.9 eV down to 3.4 eV.

Keywords: PVA-Kaolin composite, Solution casting method, Optical energy gap

تأثير تركيز الكؤلين والتشعيع على الأنتقالات الألكترونية لأغشية بولي فنايل الكحول

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قسم الفيزياء –كلية التربية-الجامعة المستنصرية

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الخلاصة

حضرت أغشية البولي فينايل الكحول غير المشوبة والمشوبة (1%, 3%) كاولين بطريقة الصب , وعرضت لأشعة كاما الناتجة من الكوبلت – 60 بنشاطة 2μCi لمدة اسبوعين, تم دراسة الخصائص البصرية باستخدام مطياف الأشعة فوق البنفسجية المرئية لمدى الاطوال الموجية 300 – 900 نانومتر. أثبتت النتائج ان النفاذية في المنطقة المرئية تقل بزيادة تركيز الكاولين عند مقارنتها مع الأغشية غير المشوبة. تزداد حزمة النفاذية المهيمنة في منطقة فوق البنفسجية بعد التشعيع بينما يحدث العكس في حالة الانعكاسية. كذلك فان النتائج تشير الى ان أغشية (PVA) ذات انتقال غير مباشر ويقل من 3.7 الى 3.55 eV بازدياد نسبة 3% . ان فجوة الطاقة المباشرة للأغشية المشععة تشير الى تناقص الفجوة من 3.9 الىeV 3.4 .

الكلمات المفتاحية: مركب بولي فنايل الكحول-كؤلين, طريقة صب المحلول, فجوة الطاقة البصرية.

Introduction

Polyvinyl alcohol (PVA) is a non-toxic, water-soluble synthetic polymer that has good film forming ability and adhesive properties. Its molecular formula is $(C_2H_4O)_x$, and has a density between (1.19 and 1.31 g/cm^3) [1]. It has a large number of hydroxyl groups which allows it to react with many types of functional groups to form composites [2]. Polymer matrix composites are very popular due to their low cost, high strength to weight ratio, noncorrosive and simple fabrication methods. Polymer matrix composites reinforcement by strong fibrous network is characterized by the high tensile strength, high stiffness, high fracture toughness, good abrasion and corrosion resistance. Composites containing at least two materials with different physical properties exhibit often new properties. The composites can provide improved characteristics that not obtainable by any of the original components alone, they are not only combining the advantageous properties of dopant and polymers but also exhibit many new properties that single-phase materials do not have [3], and are used in a wide variety of industrial products. A variety of additives are used in the composites to improve the material properties, aesthetics, manufacturing process, and performance.

The structural, optical, and electrical properties of these polymeric materials can be enhanced by incorporation of filler into polymer matrix, because dispersed filler will enhance various physical properties of the host polymer [4].

In this paper, we report and discuss the characterization of the kaolin doped PVA films prepared by the casting technique.

Experimental details

Polyvinyl alcohol PVA of molecular weight 10000 g/mol as a matrix element supplied by (BDH chemicals) with high purity and kaolin clay as a filler agent with weight percent (0, 1, and 3 wt%). these materials were prepared by solution casting method. PVA were dissolved in redistilled water and ethanol of distilled to obtain a pure PVA film. The doped films to (1 and 3) wt% where prepared by adding 0.1 and (0.3 g) of kaolin light into the pure PVA solution. The complete dissolution was obtained using a magnetic stirrer at temperature (90 ˚C)for 1 hr. Then the solution was poured on to a clean glass plate dishes and dried for 24 at (40˚C). The thickness of the films was controlled by the volume of polymer solution, and they were in the range of 20 μm. The optical studies were carried out using double beam spectrophotometer (Shimadzu UV- probe Japan) in the wavelength range (300-900) nm. The prepared were cut down into small films with dimensions of (5x5) cm and subjected to (Co^{60}-γ-rays) ,activity 2μCi for two weeks.

Results and discussion

The spectral dependences of transmittance for the pure and kaolin doped PVA films are shown in Fig.1(a). The results indicate that transmittance of the films increases with the increasing of the incident photons wavelength λ, also it can be notice that increasing doping ratio improves their transparency. The figure shows that the percentage of transmission for the pure PVA film is approximately 42% in the visible region, increased to 48% and 54% with increasing the kaolin concentration to 1wt% and 3wt% respectively. Fig.1(b) shows that the transmittance of irradiated pure PVA film increases clearly as compared with the same film before irradiation [5]. The dominant transmittance band of UV region increases after irradiation. The absorption and transition peaks at UV region were used to study the optical characteristics. The visible bands correspond to the excitation of outer electrons provide information on the electronic transitions of the molecules in the samples.

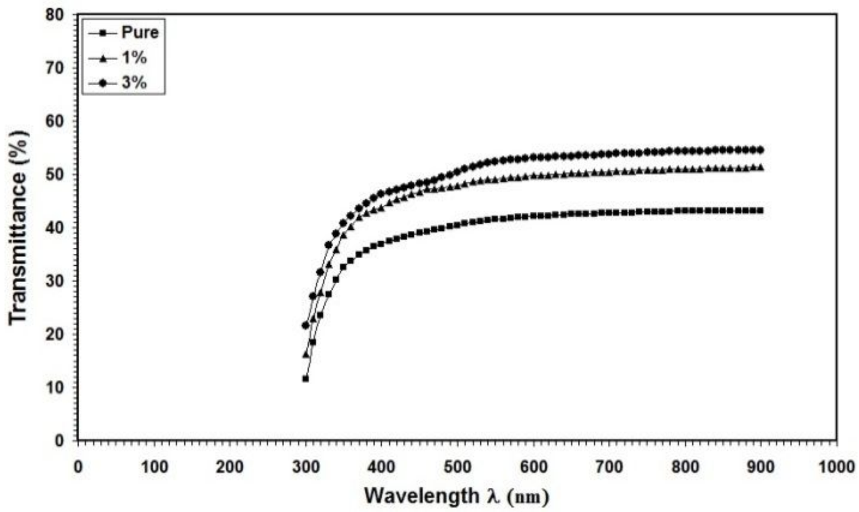
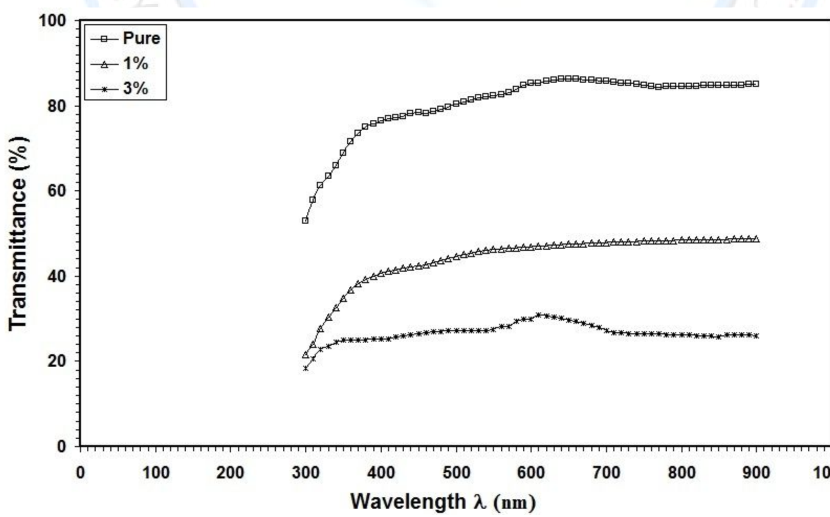


Fig. (1): Transmittance versus wavelength for Pure and kaolin doped PVA films :(a) Before irradiation



(b)

Fig. (1): Transmittance versus wavelength for Pure and kaolin doped PVA films (b) After irradiation

Fig. 2(a) shows that in the visible region, the reflectance average value for the pure and doped films before irradiation were about 0.20%, while with increasing kaolin concentration to 3wt% the reflectance for the films slightly decreased and have the average value of 0.19%.It can be seen that the reflectance in the visible region is limited only by the surface reflectance. Furthermore, it is clear form Fig. 2(b) that the reflectance for the 3% kaolin doped film doesn't affect by irradiation. While, for the 1% and pure PVA films the reflectance decreases to the average values 1.5 and 0.08 respectively.

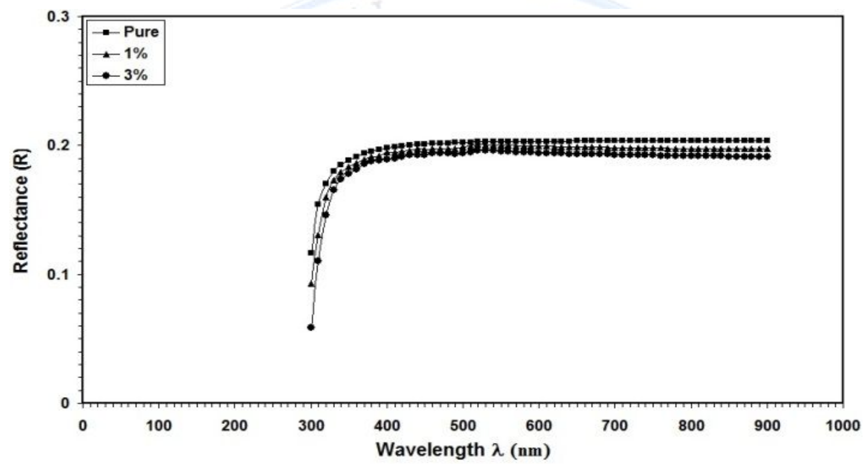


Fig. (2): Reflectance versus wavelength for pure and kaolin doped PVA films

(a) Before irradiation

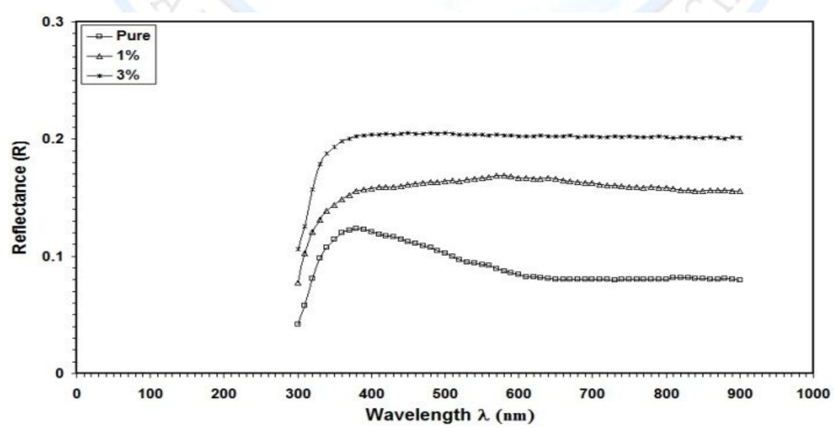


Fig. (2): Reflectance versus wavelength for pure and kaolin doped PVA films

(b) After irradiation

According to the inter-band absorption theory, the optical band of the films can be calculated using Tauc's relation [6]:

$$(\alpha h\upsilon) = A(h\upsilon - E_g)^n \qquad \ldots\ldots\ldots\ldots(1)$$

where α is the absorption coefficient, A a constant, h is Planck's constant, υ the photon frequency, E_g the optical band gap and n is an index which could take different values according to the electronic transition.

The value E_g corresponding to the indirect band gap transition was calculated from the curve of $(\alpha h\upsilon)^2$ versus hυ, using the formula:

$$(\alpha h\upsilon)^2 = A(h\upsilon - E_g) \qquad \ldots\ldots\ldots\ldots(2)$$

The extrapolation of the linear part of the curve $(\alpha h\upsilon)^2$ to the energy axis indicates the indirect band-gap energy for the pure PVA film and found to be 3.7eV as shown in Fig. 3(a). Noticeable increase in the optical energy gap of the pure PVA is observed after radiation as shown in Fig. 3(b). It can be seen from figures 4(a) and 5(a) that the energy gap of the films is tend to decrease with the increasing of kaolin concentration, this decrease can be attributed to a decrease in crystallinity disorder of the films. The optical band gap of the PVA films is obviously affected by the defects and the crystallinity, such decrease in the PVA energy gap due to doping was also obtained by other researchers [8, 9]. The effect of radiation on the optical energy gap is shown in figures 4(b) and 5(b), which shows that the gap decreases after irradiation due to the increment degree of structural disorder. This could be attributed to the interaction of an electron with the polymer molecule which results in an excited state, followed by ionization. With the decreasing of E_g, the degree of disorder will increase. This concurs with the results from this study. Consequently, when exposing the films to radiation, the spin density increases, hence more unpaired electron forms in the unfilled band which results in the decrease of E_g values.

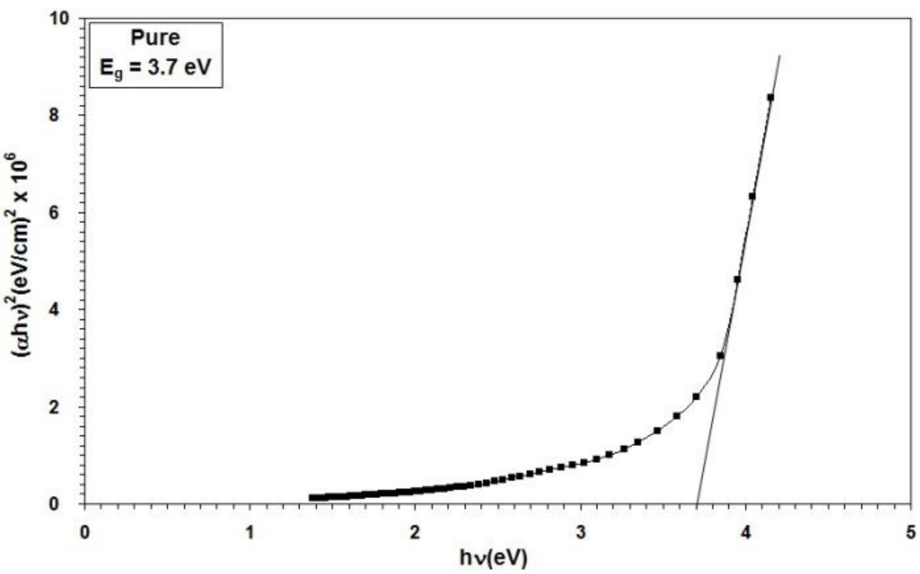


Fig (3) $(\alpha h\upsilon)^2$ for pure PVA films : (a) Before irradiation

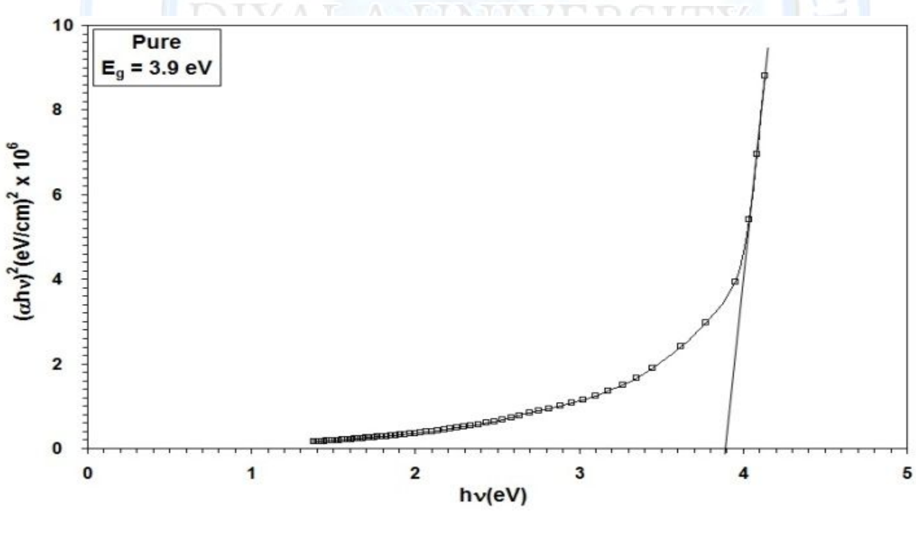


Fig (3) $(\alpha h\upsilon)^2$ for pure PVA films: (b) After irradiation

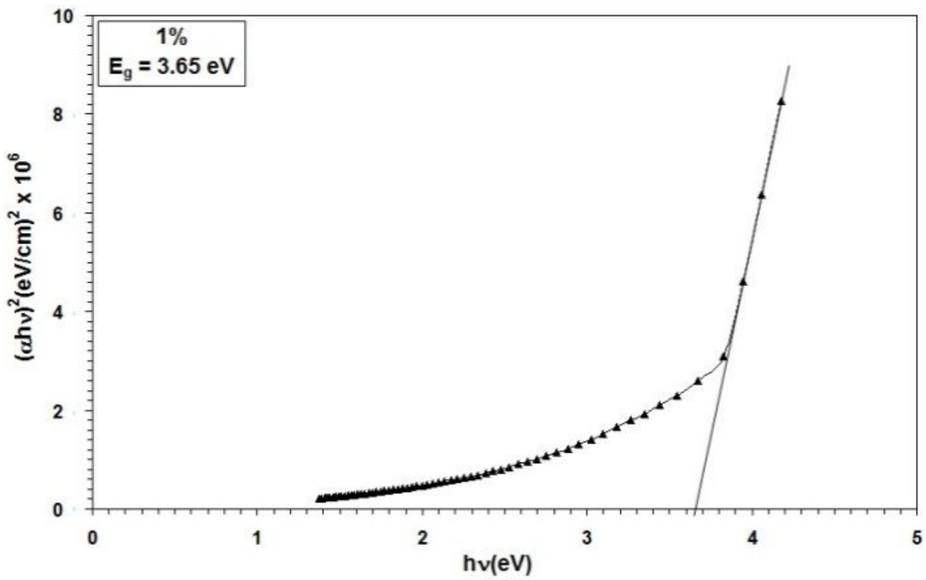


Fig (4) $(\alpha h\upsilon)^2$ for 1% kaolin doped PVA films: (a) Before irradiation

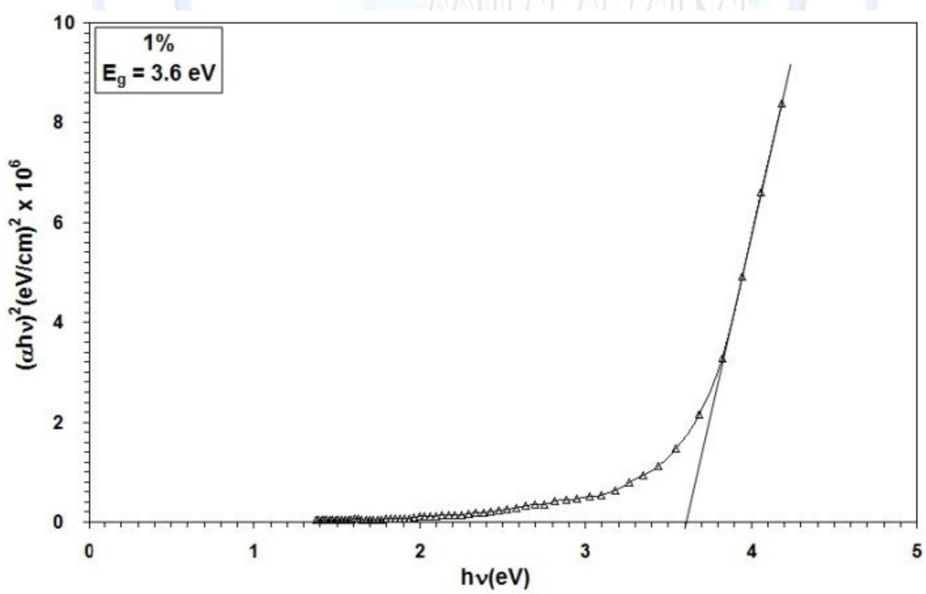


Fig (4) $(\alpha h\upsilon)^2$ for 1% kaolin doped PVA films : (b) After irradiation

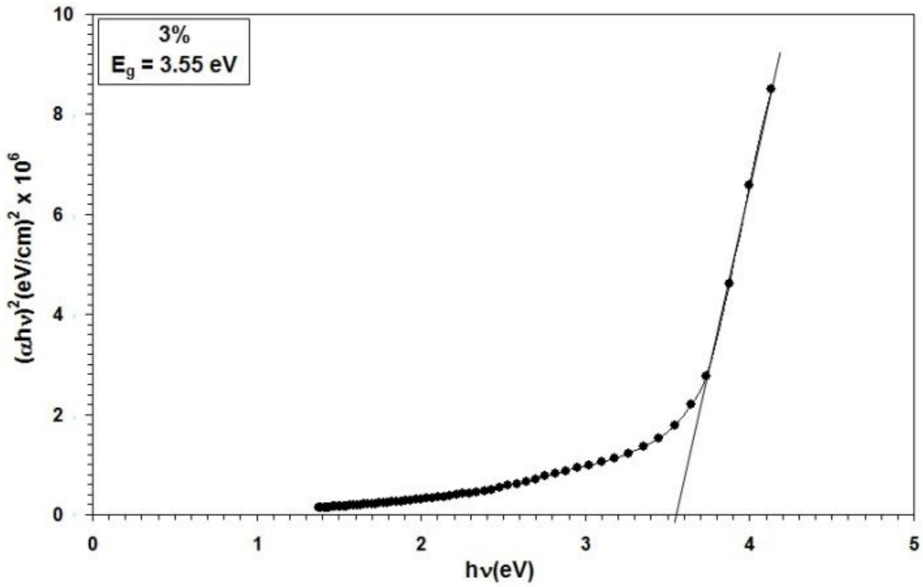


Fig (5) $(\alpha h\upsilon)^2$ for 3% kaolin doped PVA films:(a) Before irradiation

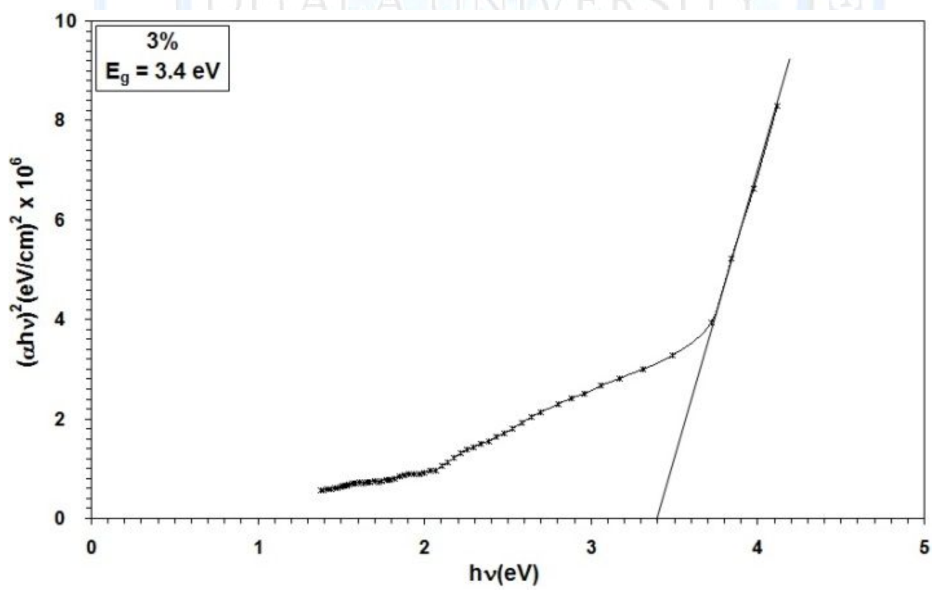


Fig (5) $(\alpha h\upsilon)^2$ for 3% kaolin doped PVA films (b) After irradiation

Conclusion

The physical properties of the films before and after irradiation were characterized. All samples were optically characterized by using (UV-VIS) technique and the results were systematically presented. It was found that the transmittance of the pure PVA films in the visible domain reaches 42% while an increase to 54% was obtained with increasing the kaolin concentration to 3wt%. Furthermore, results indicate that the E_g values were found to be decreases with the increasing of kaolin ratio and have the values of 3.7, 3.65, and 3.55 eV, while after irradiation the Eg values 3.9, 3.6, and 3.4 for the pure, 1wt%, and 3wt% kaolin doped PVA films respectively.

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