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SYNTHESIS AND CHARACTERIZATION OF A NOVEL NANOCOMPOSITE POLYMER

One-dimensional nanostructures of PANI: PVA-g-EI nanocomposite are prepared by the interfacial polymerization method. The properties of a resulting green powder are studied by the X-ray diffraction (XRD), energy-dispersive X-ray analysis (EDX), transmission electron microscopy (TEM), and infrared spectroscopy (FTIR). Prepared thin films were characterized by UV-Vis and photoluminescence (PL) spectroscopies. The XRD pattern of the nanocomposite shows that the higher volume fraction of crystalline phases corresponds to the PANI polymer with the accepted monoclinic unit cell of PVA. Nano-sized irregular particles arranged in clusters appear in the TEM measurements and SEM images, which testifies to the agglomeration without uniform packing. EDX confirms that the PVA-g-EI is incorporated in the structure of the polymer nanocomposite. A significant shift in the absorption edge with three PL independent emission peaks again confirms that PANI/PVA-g-EI form a nanocomposite.

Keywords: nanocomposite, thin films, polyaniline, dye, PVA.

1. Introduction

In the last decade, we have observed the increased interest in conjugated polymers which have π -electrons. This causes the electron to be delocalized along the polymer backbone, and this results in that the charge carriers will move along the polymer chain. The metallic or semiconducting properties of these polymers are therefore specified by the electronic construction, the number of repeated units being one example of this [1, 2]. Some of these polymers are the conductors which have been used in the optical devices, electroluminescent and photovoltaic devices, and as photoactive materials [3, 4]. Polyaniline (PANI) is one of the conductive polymers which were

discovered in the latter half of the 19th century which have drawn the increased attention due to a tunable property, good stability, synthesis simplicity, and low cost. This broadens their application to various fields such as light-emitting and electronic devices, biosensors, and energy storage units [5–8]. However, the poor process ability of polyaniline due to the insolubility in common organic solvents and the poor mechanical properties restrict the potential applications of PANI [9]. Attempts have been made to improve the solubility of conducting polymers and, thus, their processability and to increase the film quality by using PVA polymer to composite it with polyaniline. In fact, composite films could preserve their conductivity even under the humidity or at the heating [10]. Several methods have been used in the preparation of PANI /PVA composite [11, 12].

The visible spectral response of polyaniline is limited to a narrow range. So, with a view to improve and extend the parameters of conducting polymers to a wider region of the spectrum, dyes have to be

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integrated to the polymer matrix. The incorporation of dyes in the polymer matrix can expand the excitation spectrum of a polymer, by allowing one to prepare a multiemissive material as compared to the pure one [13]. Eosin (EI) belongs to a red fluorescent class of anionic dyes that are soluble in water. The International Union of Pure and Applied Chemistry (IUPAC) name of EI is 2-(2,4,5,6-Tetrabromo-6-oxido-3-oxido-3H xanthenes-9-yl) benzoate disodium salt. Eosin containing bromine atoms is used in the fields of dyeing, dye laser, dye-sensitized solar cells (DSSCs), and as a fluorescent pigment.

The main objective of this work is to prepare new advanced materials consisting of a PANI polymer matrix with polyvinyl alcohol grafted with eosin dye (PVA-g-EI) and to discuss the structure and optical properties of thin films prepared from this material.

2. Experimental

2.1. Materials

Eosin dye provided by Fluka, poly(vinyl alcohol) (PVA) provided by Aldrich Mw(110,000-106,000), Dimethyl Sulfoxid (DMSO) provided by BDH Ltd. Co. As a solvent, we took phosphoric acid (H_3PO_4) provided by Fluka as a catalyst. Aniline was purchased from Rankem; ammonium persulfate (APS), Carbon disulfide (CS_2) from Fisher Scientific, N-methyl-2-pyrrolidone (NMP), and acetic acid from Merck.

2.2. Preparation of nanocomposite

Polyvinyl alcohol grafted with eosin dye (PVA-g-EI) has been prepared in the same way as in our previous research paper [14]. A three-neck reaction flask equipped with thermometers, mechanical stirrer, and condenser was charged with 1 mole of eosin dye, 0.01 mmol of PVA, 100 ml of DMSO, and three drops of H_3PO_4 . The reaction mixture was stirred and heated to 383 K for 7 h. Then the reaction mixture was evaporated by a rotary evaporater to remove the solvent at a reduced pressure of 0.1mmHg for 24 h at room temperature (RT).

In the present work, we use the interfacial polymerization to prepare PANI: PVA-g-EI nanocomposite. which is carried out at room temperature. The oil phase is CS_2 liquid and water as an aqueous phase. 5 ml of aniline with 1 ml of PVA-g-EI are dissolved in 75 ml of CS_2 with magnetic stirring for 30 min. In separate vial, we dissolved 4.680 g of APS in

1M HCl aqueous solution and then added it slowly and gently to the aniline solution. The polymerization reaction time is 12 h. The PANI nanofibers were formed in the oil phase. PANI: PVA-g-EI was extracted from the solution by a filter paper and washed several times by water and methanol. Then it was dried at room temperature. The green powder of the PANI: PVA-g-EI material has been used to prepare thin films by the spin coating method after dissolving it in NMP.

2.3. Characterization techniques

The thin films have been analyzed, by using an XRD diffractometer Philips PW-1729 with $Cu-K\alpha$ radiation. The scanning electron microscopy (SEM) and the elemental analyses were conducted by using a Jeol scanning electron microscope (JSM-6610 LV). Transmission electron microscopy (TEM) analysis was done using a Hitachi H7500 electron microscope operating at 80 kV. The FTIR spectrum of the solid sample was recorded by a Perkin-Elmer PE-RXI spectrometer. A computer-controlled Perkin-Elmer LAMBDA 750 spectrophotometer was used to obtain the various optical spectra of thin films in the 400-700 nm wavelength interval at room temperature. A Perkin-Elmer LS55 fluorescence spectrometer has been used to record the PL spectrum.

3. Results and Discussion

3.1. TEM and SEM results

Figure 1 shows the TEM image of the polymer nanocomposite powder. The figure depicts that there are many nanoparticles accumulate in clusters. This is due to a high concentration of PANI which forces the nanoparticles to aggregate and to form an extended connected network. Figure 1 also demonstrates the SEM images of the prepared polymer nanocomposite. The irregular nano-sized particles have appeared in the image which is a result of the agglomeration without uniform packing.

The composition of the prepared nanocomposite has been studied by the energy dispersive X-ray spectroscopy (EDX). The EDX spectrum of the copolymer in Fig. 2 shows the emission lines of carbon, nitrogen, oxygen, sulfur, and chlorine. In addition, the bromine element is apparent in the EDX figure which confirms the presence of the eosin dye in the structure of the nanocomposite. Oxygen and sulfur which are

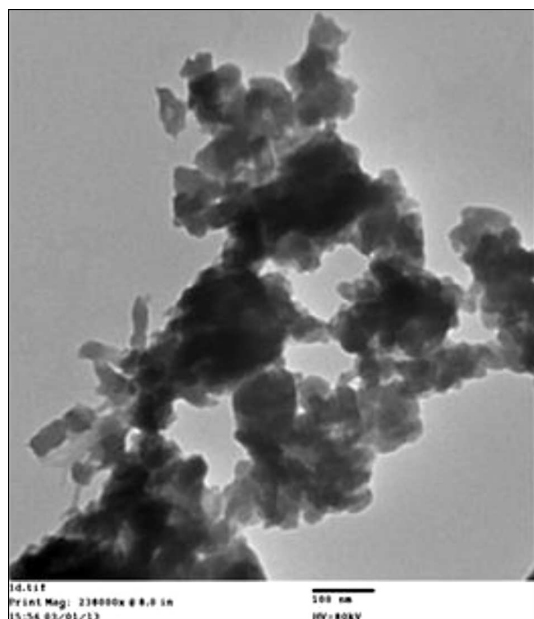


Fig. 1. Microscopic images of PANI/ PVA-g-EI

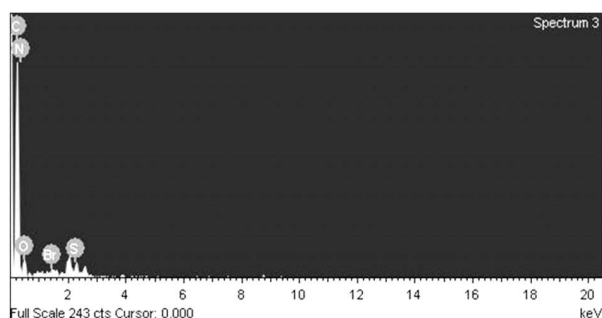
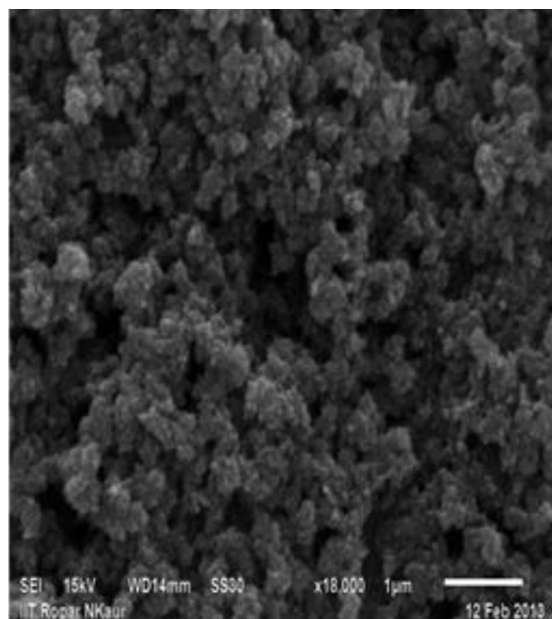


Fig. 2. EDX pattern of PANI/PVA-g-EI thin films

present in the EDS graph may be due to bound water molecules and the residual sulfate ions produced by the reduction of ammonium persulfate during the polymerization, respectively [15].

3.2. FTIR-IR spectroscopy

FTIR is one of the vibration spectroscopic tools which have been used to elucidate the Structure of PANI. Figure 3 shows the FTIR spectra of PANI/PVA film. The characteristic peaks at 1559 (aromatic C–C stretching (*B*)) and 1480 cm^{-1} (aromatic C–C stretching (*Q*)) matching to the vibrations of quinoid and benzenoid rings in PANi emeraldine salt, respectively [16, 17]. The 1299 and 1243

peaks indicate the N–H bending and asymmetric C–N stretching modes of the benzenoid ring [18]. The peak amplitude characteristic of the absorption upon a stretching vibration of quinoid ring at 1594 cm^{-1} is found quite close to that corresponding to the absorption of a benzene ring at 1487 cm^{-1} , which is a characteristic feature of the conductive form of polyaminoarenes [19].

3.3. Analysis. XRD data

Figure 4 shows the XRD pattern of PANI/PVA-g-EI. Pristine PANI is semicrystalline. The XRD pattern of the nanocomposite exhibits two weak peaks and one broad peak. The three peaks appeared at $2\theta = 15.4^\circ$, $2\theta = 20.82^\circ$, and $2\theta = 25.68^\circ$, these peaks in the diffraction pattern correspond to 121, 113, and 322 crystal planes [19, 20]. The crystal planes indicate the growth directions of chains, and the intensity (peak height) is referred to the population of crystallites in that plane [21]. The average crystallite size (*D*) is calculated by using the Scherrer formula [$D = K\lambda/\beta \cos\theta$], where $K = 0.9$ is the shape factor, and β is the full width at half maxima of the crystalline peak in radians] to the maximum peak ($D = 3.2 \text{ nm}$) [22]. The observed XRD pattern is matched with that reported in the literature [23]. No

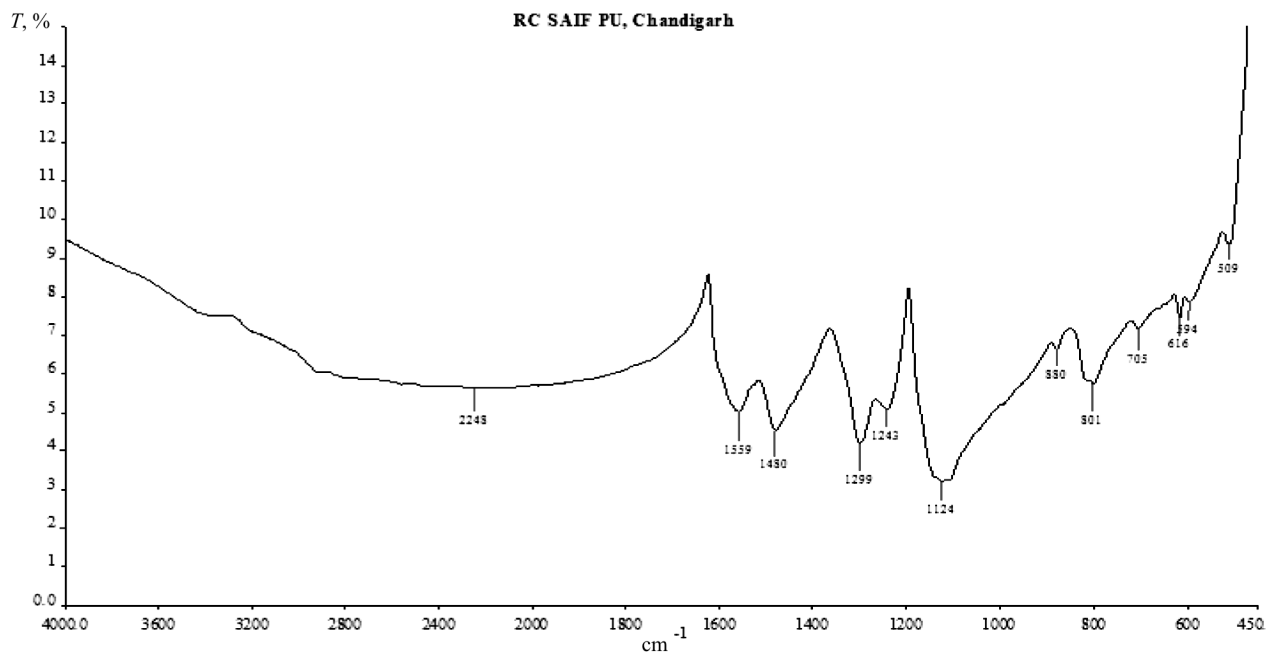


Fig. 3. The FT-IR spectrum of PANI/PVA-g-EI

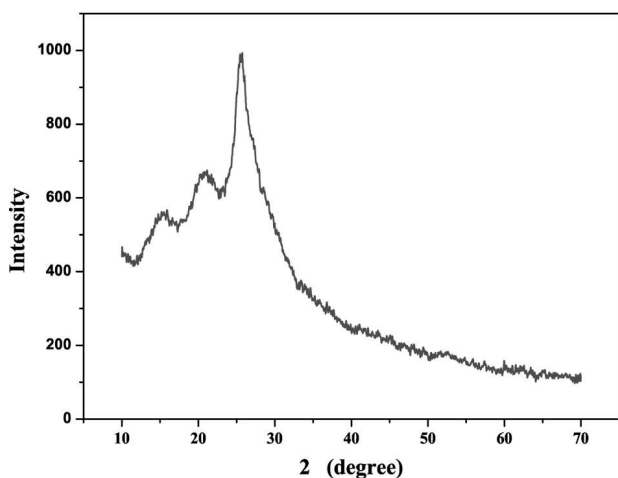


Fig. 4. The XRD pattern of PANi/PVA-g-EI

peaks are observed due to other composite materials, indicating that the materials are amorphous in nature, as well known.

3.4. Optical properties

The absorbance spectra of PANI thin films over the wavelength interval 300 to 1000 nm are shown in Fig. 5. Figure 5 shows two distinct absorption peaks

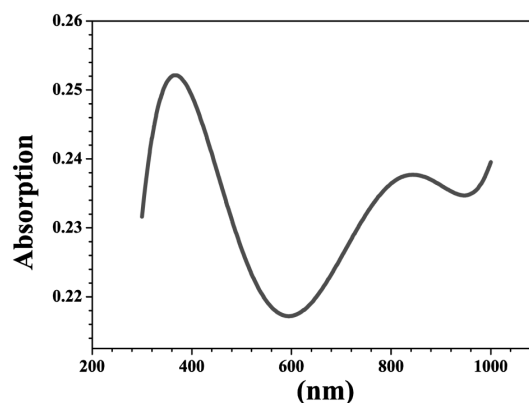


Fig. 5. The absorbance spectra of PANI/ PVA-g-EI thin films

at about 360 and 840 nm which are characteristic of PANI. The peak at 360 nm correlates to localized polarons, which are associated with the presence of protonated PANi in the nanocomposite polymer [20]. The other peak (840 nm) is attributed to the bipolaron band transitions, which is characteristic of the “salt form” of PANI [24].

As can be seen from Fig. 5, the superior PANI/PVA-g-eosin polymer nanocomposite produced via the in situ polymerization of aniline monomers with PVA-g-eosin is completely in the doped state.

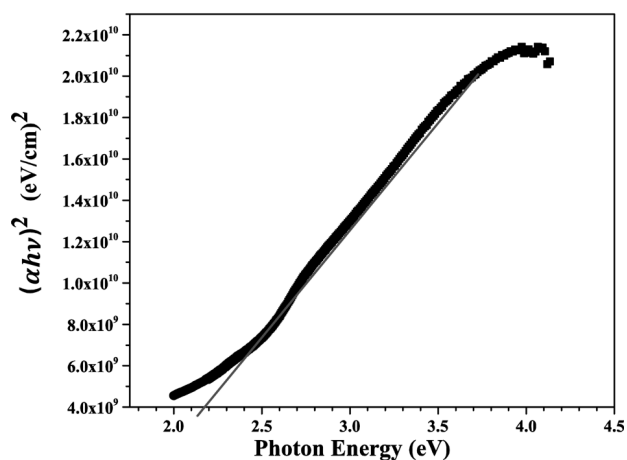


Fig. 6. Direct allowed transition energy for PANI/ PVA-g-EI thin films

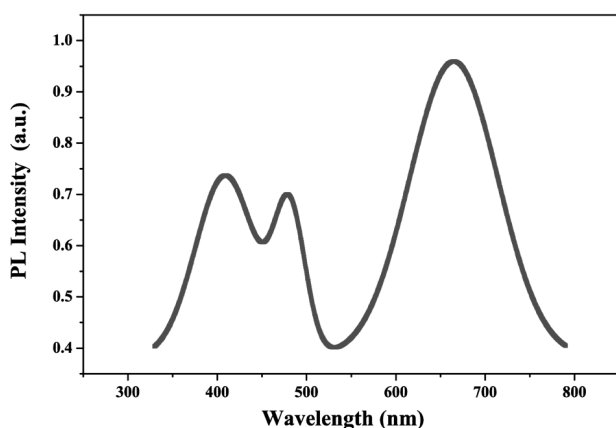


Fig. 7. PL spectra of PANI/ PVA-g- EI thin films

The optical band gaps in the thin film can be determined from the relation between α and the incident photon energy $h\nu$: [25]

$$\alpha h\nu = B(h\nu - E_g)^n, \quad (1)$$

where B is a constant, E_g is the band gap of the material, and the exponent n depends on the type of transition. For the direct allowed ones, $n = 1/2$; and, for the indirect allowed transitions, $n = 2$.

The absorption coefficient (α) of the thin film is obtained from the absorbance measurement, Fig. 4, using the relation:

$$\alpha = 1/d \ln(1/A), \quad (2)$$

where d is the thickness of the film, and A is the absorbance.

As can be seen from Fig. 6, the line fit has been obtained, which means that the electronic transition is direct allowed one. The corresponding E_g value which has been obtained by extrapolating the straight-line portion of the $(\alpha h\nu)^2$ vs. $h\nu$ plot on the $h\nu$ axis at $(\alpha h\nu)^2 = 0$ is 2.2 eV.

3.5. Photoluminescence studies

Photoluminescence of organic molecules is an important property of compounds under study. Their emission extends over a wide range from the violet to the red and can also be combined in several different forms to produce white light. One category of organic materials with photoluminescence properties is conjugated organic polymers [26].

Because the eosin dye is a fluorescent dye, it is advisable to confirm the doping of PANI-PVA using the fluorescence spectroscopy. PL spectra were measured in the interval 300–800 nm at room temperature and are shown in Fig. 7. The PANI: PVA-g-EI nanocomposite thin film shows three independent emission wavelengths, namely, 409 (3.031 eV), 480 (2.58 eV), and 665 nm (1.86 eV), when excited with UV light (300 nm). The first two peaks at 409 and 480 nm are specified on the scale of blue-green light and are due to the benzenoid/amine groups of the oxidized/reduced PANI [27]. It was obtained (M. Sharma *et al.*, 2006) that the presence of these peaks in the PL spectra of thin film indicates the possibility of the existence of multiple electronic states which are responsible for the photo-excitation process [28]. It has been also established that the energy splitting between the two excited states will increase, as the interchain distance is reduced [29]. So, we see these electronic states in our PL measurements due to the nanostructure of our samples. The emission peak at 665 nm is a characteristic emission peak of PVA-g-eosin [30], which again confirms that PANI/PVA-g-eosin is a nanocomposites. As the eosin dye is incorporated into the polymer nanocomposite, the photoluminescence spectrum of the polymer nanocomposite covers a greater range than that of pure PANI, where red light is emitted.

4. Conclusion

In this work, we have prepared and studied a new polymer nanocomposite with improved properties. As indicated by the SEM and TEM measurements,

the PANI/PVA-g-eosin polymer nanocomposite produced via the in situ polymerization of aniline monomers with PVA-g-eosin contains nanoparticles in its structure. The X-ray diffraction pattern indicates that the PANI polymer has a larger volume fraction of the crystalline phases in the polymer nanocomposite. The PANI/PVA-g-eosin absorption peaks are characteristic of PANI in the doped state. Photoluminescence of PANI/PVA-g-eosin has a truly unique properties where cover a greater range than that of pure PANI. The optical properties of PANI can be controlled on a large scale by a nanocomposite with the polymer grafted with an organic dye.

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СИНТЕЗ ТА ХАРАКТЕРИСТИКИ НОВОГО ПОЛІМЕРУ-НАНОКОМПОЗИТА

Методом міжфазної полімеризації виготовлено одновимірні наноструктури із полімерів PANI: PVA-g-EI. Їхні властивості вивчено з використанням дифракції рентгенівських променів (XRD), аналізу дисперсії енергії цих променів (EDX),

трансмісійної електронної мікроскопії (ТЕМ) та спектроскопії інфрачервоних променів (FTIR). Для виготовлених тонких плівок виміряно спектри фотолюмінесценції та спектри в ультрафіолетовому і видимому діапазонах. Методом XRD знайдено, що значна об'ємна частина кристалічних фаз відповідає PANI полімеру з моноклінною елементарною коміркою, яка характерна для PVA. Методами TEM і SEM показано існування кластерів наночастинок, що свідчить про агломерацію і відсутність однорідного пакування. Крім того, формування нанокompозита з полімеру PANI/ PVA-g-EI підтверджено результатами вимірювання методом EDX та значним зсувом межі поглинання з трьома незалежними піками фотолюмінесценції.

Ключові слова: нанокompозит, тонкі плівки, поліанілін, фарбник, PVA.