Analysis of Band Gap Energy and Refractive Index of Electrospinning Polyacrylonitrile (PAN) Nanofibers

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Abstract

Polyacrylointrile (PAN) was prepared by electrospinning method in normal condition at the room temperature .The PAN nanofibers were investigated by XRD and SEM techniques .Optical properties of the thin film of PAN nanofibers were studied by the transmission and absorption spectra at room temperature within the wavelength of (300-700nm) . Optical energy gap E_{opt} and other parameters were calculated using Tauc relation . The dispersion relationship of refractive index were computed by using Wemple – Didomenico single oscillator model.

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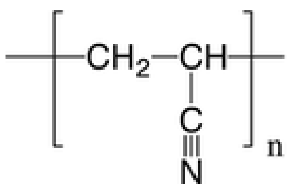
1. Introduction

Electrospinning is a low cost and simple technique for synthesis nanofibers or fiber mats from wide types of organic polymers [1]. In electrospinning, many properties of polymer nanofibers can be modified in order to get the requirements of a specific application. This change in polymer properties have been done by controlling the electrospinning parameters like: Viscosity, conductivity of the polymer, or by controlling of the electrospinning process parameters, like the DC applied voltage, flow rate feed and the distance between the needle and collector drum [2]. Accordingly, by electrospinning we can get polymer fibers with nanoscale diameters. One of the advantages of nanoscale material is the appearance of excellent advance properties like high surface area to volume ratio, flexibility and high mechanical tested [3]. At electrospinning process have two forces are dominating and playing an important role in forming nanofibers. The first force is surface tension and the second is the mutual repulsions force between droplets a solute polymer.

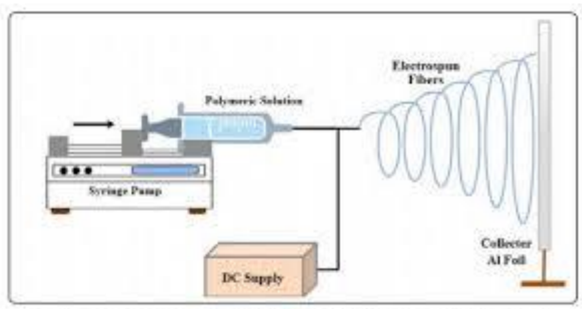
When high voltage applied on the end of a needle, surface tension force stabilizes the solution and tends to minimize its surface. The charge repulsion between charges reach a threshold value, the fluid jet form conical droplet at the end of capillary tube forming Taylor cone [4] . The solution jet travels in a straight path with bending motion like spiral shape, and finally collected on a screen material, which it is connected to a negative pole of a DC high voltage. There are many polymers have been prepared by electrospinning technique, one of these is PAN. The PAN has a semicrystalline structure and it takes the formula $(C_3H_3N)_n$, the nitrile (CN) functional group attached on polyethylene backbone as the unit structure, as shown in figure(1-a). The .Numerous applications are used PAN fiber in many technology branches, such as precursors in industry for the production of carbon fibers, sensor materials, and composite reinforcement or in medical application such as drug deliver wound dressing [5]. Optical techniques provide a good way of examining the properties of semiconductors, particularly measuring the absorption coefficient at the various energies, which it gives information about the band gaps of the material. The nature of bonding system and the number of atoms can be revealed from the energy difference between the orbitals. Knowledge of these band gaps is extremely important for understanding the electrical properties of a semiconductor, and therefore of great practical interest. Refractive indices of a variety of polymer materials can be tailored and precisely controlled to satisfied specific design purpose [6]. In the present study we are calculated the optical energy gap and dispersion optical parameters of PAN nanofibers thin film prepared by low cost technique ,i.e electrospinning. In addition , we have characterize them by measuring the XRD , SEM ,and UV-Vis- spectroscopy .

2. Experimental

The electrospinning process is carried out by dissolved, 0.3g of PAN in the 10ml DMF as a solvent .Then, the solution is stirred over night at the room temperature, after that transferred to a 5ml plastic syringe (23G) . A high voltage about 8kV was applied by a copper electrode connected with syringe needle with a 0.5ml/h feed rate and the distance between needle and target was about 10 cm. All the tests were conducted at ambient atmosphere . Figure(1-b) illustrated the electrospinning diagram.



a



b

Figure 1 : (a) PAN chemical structure and (b) The electrospinning diagram

3. Results and discussion

3.1 Structural and morphological properties

XRD measurement of prepared PAN nanofibers thin films were carried out by using a Rigaku RINT Ultima –III with the angle 2θ in the range 10 to 40° at ambient condition . Figure(2) show the XRD chart for pure PAN nanofibers, there are three clear peaks, which are indicated that semicrystalline structure of PAN. The first strong peak at 2θ =17.1°, the second ,weak peak at 2θ = 27.9° .The same result are found by Fung He et.al.in the previous studied [7].

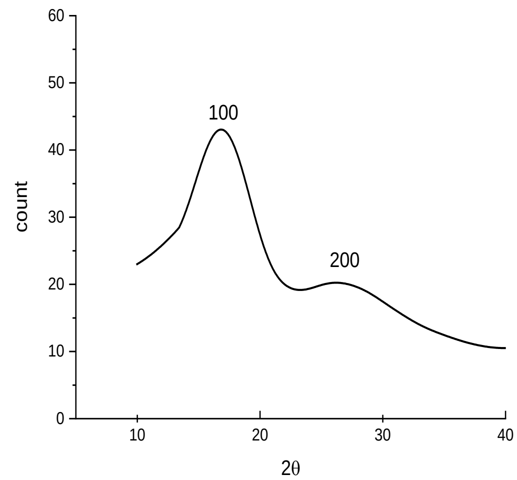


Figure 2: XRD pattern of prepared PAN nanofibers

The morphology of pure PAN nanofibers thin film was observed under a scanning electron microscope(FEI NOVANanosem 4501,Japan) as shown in figure (3) . The SEM images show that, the formation of fibers mat structure with a average diameter 147.63nm. Non-aligned nanofibers as there in spite of using drum collector ,because the low speed rotation is no efficient to aligned the nanofibers [8] ,from figures it seen that formed beads , these are related to the solution concentration where it is play significant role to effect at the diameter of nanofibers . Lower solution concentration leads to narrowest diameters, however at the identical time enhanced to bead formation .On other side, increase in a concentration causes that increasing in a diameter [9]. The travel path distance to the collector effect on the diameter of the polymer fibers, where the shorter distance lead to wet fiber with bead [10].

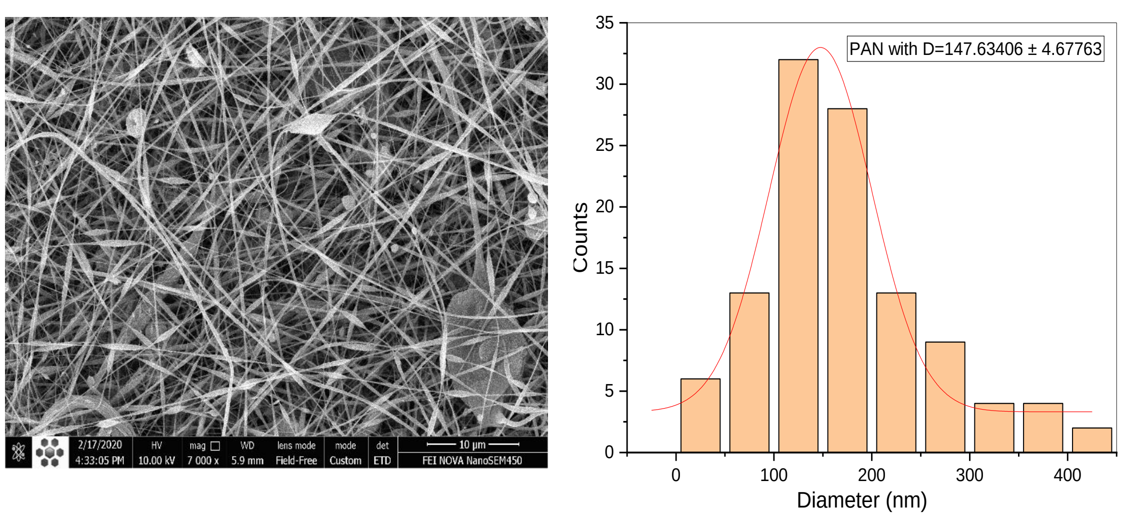


Figure 3: FESEM of PAN nanofibers prepared at 8 kV DC

3.2 Optical properties

The absorbance (A) and transmittance (T) spectrum of PAN nanofiber films were are illustrated in figure (4) and figure(5) respectively. The absorbance spectrum of film shows sharp edge at ultraviolet region at 300 nm related to n - π* transition [11]. Furthermore, the films appear low absorption at the long wavelength region. The transmittance spectrum increases with increasing the wavelength, which is due to the weak absorbance in the region above 400nm. The reflectance spectrum can be calculated from the relation [12]:

$$A+T+R=1 \qquad (1)$$

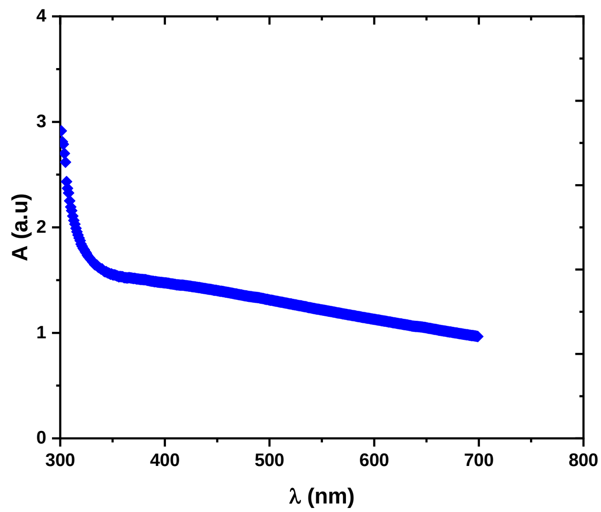


Figure 4: The absorbance spectrum of prepared PAN nanofiber

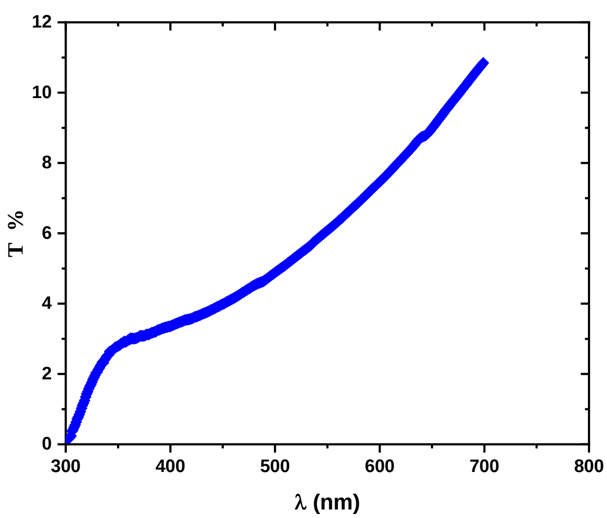


Figure 5: The transmittance spectrum of prepared PAN nanofiber

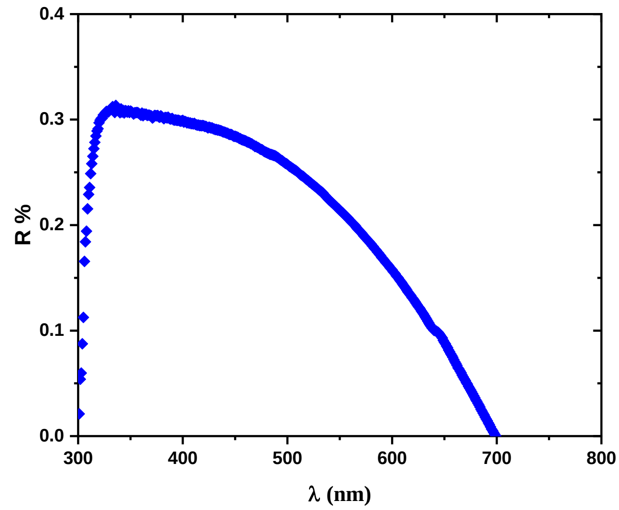


Figure 6: The reflectance (R) spectrum of prepared PAN nanofiber

Figure 6 shows the reflectance against wavelength, where the reflectance spectrum shows an increase with increasing wavelength at the range (300–350nm) then decrease in the range (400-700nm). The maximum value of reflectance of film is 30% at 323nm.

The optical absorption coefficient (α) can be calculated according to the relation [13]:

$$\alpha = \frac{2.303\log(\frac{1}{T})}{d} \qquad (2)$$

Where ***α*** and ***d*** are the absorption coefficient and thickness of film, respectively. Figure 7 shows the relation between absorption coefficient α against photon energy hν at the range (1–eV) for PAN nanofibers film .

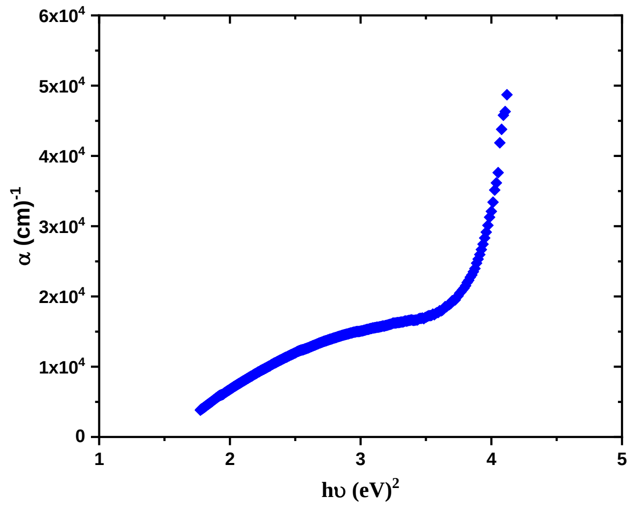


Figure 7: α versus photon energy of prepared PAN nanofiber

The extinction coefficient k was calculated for PAN nanofibers film from absorption coefficient values according to the relation [14]:

$$k = \frac{\alpha\lambda}{4\pi} \qquad (3)$$

As seen the k decrease with increasing wavelength due to low absorbance in the long wavelength, similar to the corresponding α . The magnitude of k is about 0.11 at 301nm. The values of refraction index n can be calculated according to the relation [15]:

$$n = \left(\frac{1+\sqrt{R}}{1-\sqrt{R}}\right) \qquad (4)$$

The values of n are increasing with wavelength increment in the region < 400 nm. Higher values of n related to slow down of light speed in this region, while at the long wavelength region > 400 nm ,the value of n is decreasing . The maximum value of n is about 3.49 at 327nm. Figure (8) shows the refractive index and excitation coefficient as a function of wavelength.

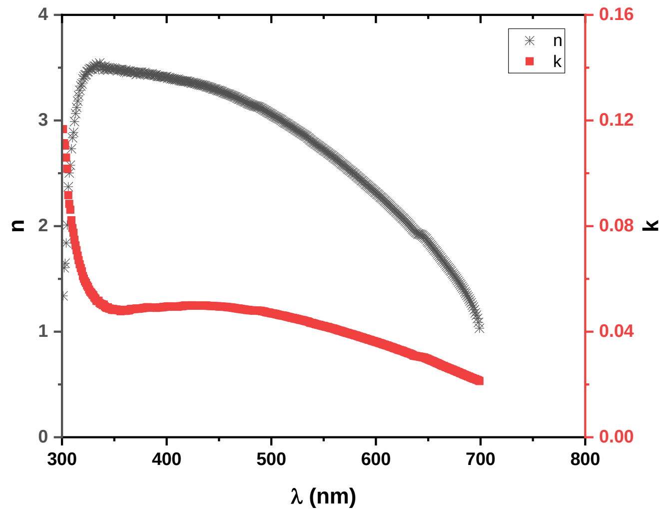


Figure 8: The relation between n and k as a function to wavelength of prepared PAN nanofibers

The optical energy gap E_g of PAN nanofiber films are calculated using Tuac's relation [16]:

$$\alpha h\upsilon = A(h\upsilon - E_g)^r \quad (5)$$

where ***hυ*** is energy of the incident photon, A is the probability parameters of the transition , and r is nature of transition . From the value of absorption coefficient α is $\geq 10^4$ cm^{-1}, the type of transition is allowed indirect transition ,So figure (9) show the relation of $(\alpha h\upsilon)^2$ as a function of photon energy hυ, from the figure the straight line fit at high energy region give the value of energy gap E_g . The values of energy gap for PAN are listed in Table 1. T. Tanski et.al. calculated that Eg for PAN, which was about 3.92eV,indicated the dielectric nature mats of this material [11] ,while other authors have been found Eg is equal to 2.57eV and 2.44 eV by using spectroscopy and ellipsometry techniques, respectively [17].

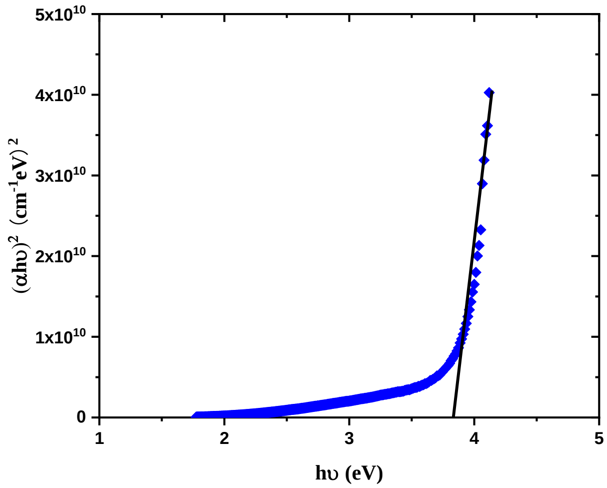


Figure 9: $(\alpha h\upsilon)^2$ against $h\nu$ of prepared PAN nanofibers

For many materials, it is assumed that the absorption coefficient α close to the band edge appears an exponential dependent on photon energy hν .This dependence is given by using the relation achieved from Urbach energy tailing which characterizes the optical absorption in this material . The Urbach energy tailing of the optical absorption edge in the material follows the empirical Urbach law [18] :

$$\alpha(\upsilon) = \alpha_o e^{\frac{h\nu}{E_t}} \qquad (6)$$

where $\boldsymbol{\alpha_o}$ is a constant and $\mathbf{E_t}$ is the Urbach energy tail. The origin of E_t can be considered as thermal vibrations in the lattice [19]. The exponential dependence of α on hυ for the film indicates that it obeys Urbach's formula [20]. Figure 10 shows the logarithm of α against photon energy for PAN nanofibers film. The reciprocal of the slope at the linear portion of the curve represented E_t, *the* value of Urbach tail E_t was calculated about 956meV.

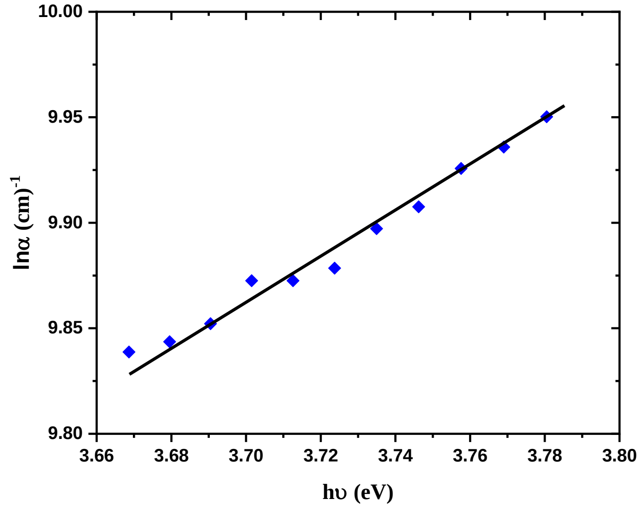


Figure 10: The relationship between ln α and $h\nu$ of prepared PAN nanofiber

One of the methods that used to determine the dispersion of refractive index n is Wemple and Didomenico model whereas the analyzed refractive index data below the inter-band absorption edge .The relation between refractive index n and photon energy obeys to the single effective oscillator equation [21,22]:

$$n^2 = 1 + \frac{E_o E_d}{E_o^2 + (h\nu)^2} \qquad (7)$$

where E_o is the single oscillator energy and E_d is the dispersion energy which measures the average strength of inter band optical transition. Experimental investigation of Eq. 7 can be given by plotting $(n^2-1)^{-1}$ against $(h\upsilon)^2$ as shown in Figure(11), from the slope $(E_oE_d)^{-1}$ and intercept (E_o/E_d) can be calculated the values of E_o and E_d are about (3.81) and (18.19) eV respectively.

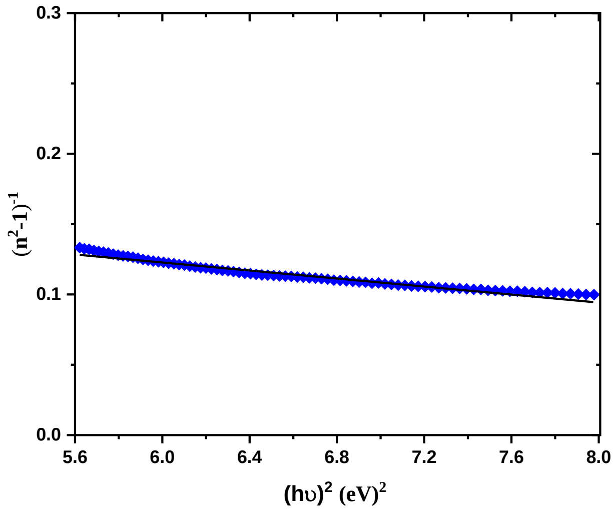


Figure 11: $(n^2-1)^{-1}$ against $(h\upsilon)^2$ for PAN nanofiber

The static refractive index n_0 for the PAN films is determined by extrapolation the WDD dispersion relation to the value of the incident photon energy hν approaching zero which gives by:

$$n_0 = [\, 1 + E_d / E_0 \,]^{1/2} \qquad (8)$$

The statically refraction index and static dielectric constant, $\varepsilon_o = n_o^2$ is evaluated and tabulated in table 1. It can be seen that the values of parameters obtained from WDD model were close to the values obtained by the Tauc's model.

M_{-1} and M_{-3} are define the moment of optical dispersion spectra , it can be calculated by using the equation [23]:

$$\left.\begin{aligned} E_o^2 &= \frac{M_{-1}}{M_{-3}} \\ E_d^2 &= \frac{M_{-1}^3}{M_{-3}} \end{aligned}\right\} \qquad (9)$$

The moment optical dispersion parameters of the film are tabulated in Table 1. The relation between real part ε_1 and λ^2 can be estimated by [24]:

$$\varepsilon_1 = n^2 - k^2 = \varepsilon_\infty - \frac{e^2 N}{\pi\, c^2 m^*} \lambda^2 \qquad (10)$$

Where ε_∞ is infinite frequency dielectric constant, e is the electronic charge, c is the velocity of light, and N/m^* is the ratio of carrier concentration to the effective mass. Figure 12 shows the relationship between n^2 against λ^2 , from the slope obtained the values of N/m^* whereas ,from the extrapolating the linear part of wavelength to zero give value of ε_∞ . The obtained values of ε_∞ and N/m^* are listed in the Table 1.

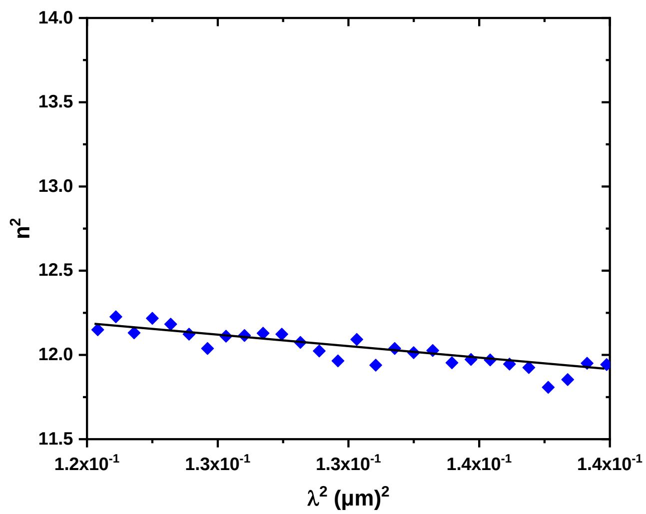


Figure 12: n^2 against λ^2 for PAN nanofiber

The average inter-band oscillator wavelength λ_o can be calculated by the following [25]:

$$\frac{n_o^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2 \qquad (11)$$

n_o is the refractive index at infinite wavelength λ_o, the plotting $(n_o^2-1)^{-1}$ verses λ^{-2} as illustrated in Figure (13) shows linear part, n_o^2 at λ_o equal to ε_∞. The average oscillator strength is given by:

$$S_o = \frac{n_o^2 - 1}{\lambda_o^2} \qquad (12)$$

The values of λ_o and S_o are listed in Table 1. The optical conductivity is a measure of frequency response of material when irradiated with light, it is determined from the following equation [26]:

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \quad (13)$$

Optical conductivity σ_{opt} versus photon energy hν is illustrated in the Figure 14, it is observed that a hump in spectrum and peak at highest photon energy is attributed to inter atomic transitions .

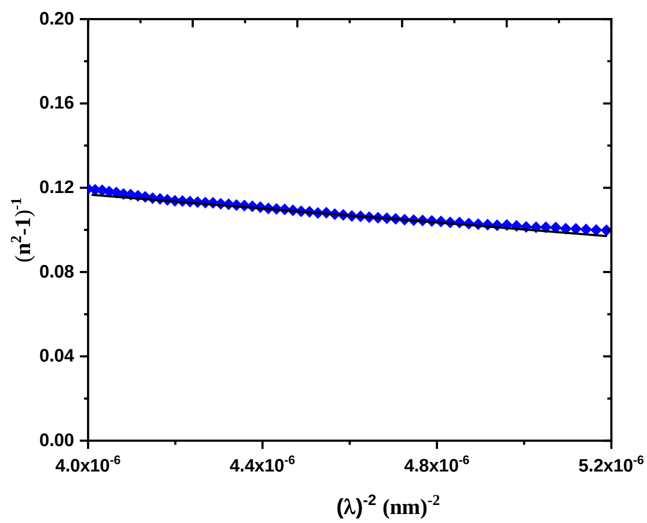


Figure 13:. $(n^2-1)^{-1}$ against λ^{-2} of prepared PAN nanofiber

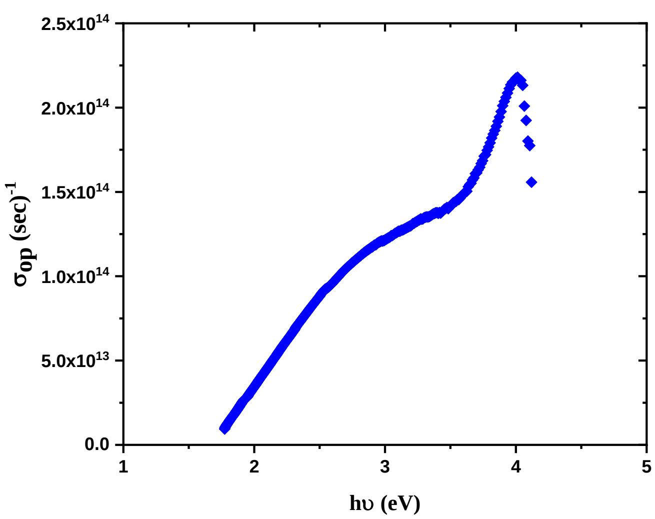


Figure 14: σ_{opt} against hν of prepared PAN nanofibers

It is well known that polarizability of any solid is proportional to its complex dielectric(ε^*) constant ,therefore ,ε^* is an important quantity for designing the highly efficient optoelectronic devices [27].

Therefore we define the complex dielectric constant ε_r according to [28]:

$$\left.\begin{aligned} \varepsilon^* &= \varepsilon_1 - i\varepsilon_2 \\ \varepsilon_1 &= n^2 - k^2 \\ \varepsilon_2 &= 2nk \end{aligned}\right\} \quad (14)$$

Where ε_1 is the real part and ε_2 is the imaginary part of the dielectric constant. The photon energy dependence of ε_1 and ε_2 of PAN nanofiber films are given in Figure 15. Both the value of ε_1 and ε_2 increase with increasing photon energy ,The real part of the dielectric constant is higher than that of the imaginary part of the dielectric constant. The dielectric constant ε_1 shows a value 12.39 at a peak 3.8eV , whereas the imajanary part ε_2 is small than real part is about 0.44.

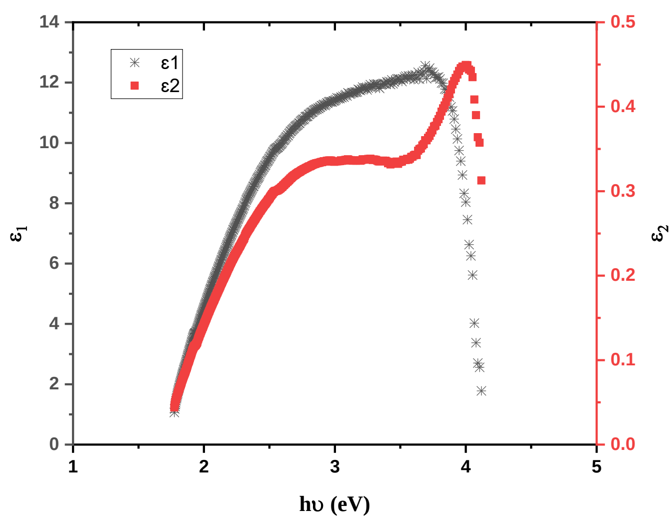


Figure 15: The relationship between ε_1 , ε_2 and hν of prepared PAN nanofiber

Table 1: Optical constants of prepared PAN nanofibers

Quantity	Value	Quantity	Value
$E_g^T (eV)$	3.84	$\varepsilon_\circ$	5.76
$E_t\ (meV)$	956	$N/m^*(cm^3.g)^{-1}$	1.52x10^{52}
$E_\circ(eV) = E_g^{WDD}$	3.81	ε_∞	13.83
$E_d(eV)$	18.19	$\lambda_\circ\,(nm)$	148.60
$M_{-1}(eV)^2$	4.77	$S_\circ(m^{-2})$	2.15x10^{14}
$M_{-3}(eV)^2$	0.32		
$n_\circ$	2.4		

4. Conclusions

The summarized results from this work are the following:

1- Electrospinning is simple technique and low cost to prepare polyacrylonitrile nanofibers thin films .

2- The XRD spectrum for PAN thin film show a semicrystalline structure ,while the SEM images shown the nanofiber mats with average diameters is 147.63nm.

3- The optical energy gap were calculated by using two methods , Tauc's relation and Wemple-DiDomenico single oscillator model, the computed values are (3.84eV,3.81eV) respectively .

4- Localized tail states were also discussed and Urbach energy was calculated using absorption spectrum.

5- The dispersion of the refractive index of the nanofiber films followed the single oscillator model, where many oscillator parameters were obtained such as E_o,E_d,ε_o,n_o,λ_o,S_o,N/m* .

6- The results of the calculations of energy gap and other parameters by different approaches were found to be consistent with the data of the literatures.

7- Optical conductivity (σ_{opt}) was increase with increasing photon energy .

8- The real part of the dielectric constant was higher than that of the imaginary part of the dielectric constant, which are equal to 12.39 at a peak 3.8eV and ε_2 is about 0.44, respectively.

9- Finally, we can using polyacrylonitrile in optoelectroinc deviceses.

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المستخلص

تم تحضير بولي اكريلونترايل (PAN)بطريقة الغزل الكهربائي بالظروف الاعتيادية وبدرجة حرارة الغرفة. تم تشخيص الالياف النانوية المحضرة من PAN بوساطة حيود الأشعة السينية XRD والمجهر الالكتروني الماسح SEM . درست الخواص البصرية للألياف النانوية من PAN ضمن الطول الموجي (700-300) نانومتر . تم حساب فجوة الطاقة البصرية من معادلة تاوك ومن نموذج المتذبذب الاحادي ليومبل –ديديمنكو تم حساب معامل الانكسار ومن ثم مقارنة النتائج المستحصل عليها من الطريقتين .