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Optical Properties of Pure P3HT Doped with Multiwall Carbon Nanotubes Films

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Abstract: Optical properties includes measurements of absorbance and transmittance spectra as a function of wavelength for films prepared from combination P3HT solution with multiwall carbon nanotubes then calculating the absorption coefficient and other optical constants. These films prepared with different concentrations ratio of multiwall carbon nanotubes added to P3HT (0.00025, 0.00050 and 0.00075 g). The values of absorbance, absorption coefficient and refractive index values for pure and doped polymer are increasing with increasing of the concentrations ratio of MWCNTs. The results showed decreasing values of transmittance with all concentrations ratio of MWCNTs, the values of reflectance are increases with increasing of concentration ratio, also results showed decrease of energy gap for allowed direct transition with increasing of doping ratio.

Key words: Optical properties, P3HT, nano thin films, carbon nanotubes, calculating, concentrations

INTRODUCTION

The polymers are insulating materials electric but this image has changed after the discovery made by each of the (Heeger) and (MacDiarmid) and (Shirakawa) who reached the possibility of modification of polymeric materials to become a good conducts electricity like metal material (Kadhim *et al*., 2017). The polymer (P3HT), one of conductive polymers which received much attention in recently because of its optical properties and electrically similar to the connectors (Elmansouri *et al*., 2007).

It could be said that P3HT is one of the well-known π-conjugated polymers. It has attracted significant attention due to its outstanding properties including solution processability, excellent electronic properties, relatively high charge mobility (10^{-4}-10^{-1} cm^2 V^{-1} s^{-1}), excellent environmental stability and a strong trend towards creating a self-organized thin film that facilitates charge transport (Said *et al*., 2015). P3HT has a band gap of about 1.9 eV and can be further reduced by increasing the quinoidal character in the polymer (Holliday *et al*., 2016) (Fig. 1).

P3HT is one of the most investigated conducting polymers, due to its high chemical and thermal stability and the ease of polymerization, together with the relative low cost of production it alsohas the potential of many technological applications (Al-Mashhadani *et al*., 2014). P3HT enters in many applications, sach potential applications in many fields such as microelectronic devices, LEDs, diodes, catalysts, organic field-effect transistors, chemical sensors and biosensors (Abdulla and Abbo, 2012).

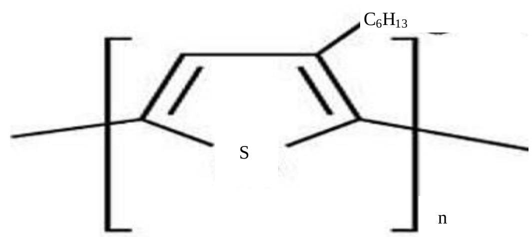

Fig. 1: Poly (3-hexylthiophene) (P3HT)

Carbon nanotube: In which the atoms are connected in a three-way curved foils a vicious form cylinder is obtained Carbon arc with the change of energy in order to become a continuous stream rather than AC and thus, can be obtained the tubular structures in a sediment on the pole. These pipes consisting entirely of carbon and has named nanotubes due to the diameter of a few nanometers. There are many ways to produce nanotubes composed of carbon molecules which are:

Action electrical analysis using electrodes table Ravit in molten salts, thermal catalyst for hydrocarbon analysis and evaporation of graphite using a laser. In addition, depending on the working methods of the nanotubes have different electronic properties, some are expected to be a metal while others are semiconductors. It turns out that these nanotubes are incredibly strong it hundreds of times stronger than steel and partly due to the geometric hexagon shape which can distribute forces and deformations due to the strength of the common wealth of carbon-carbon as well as consequently has the properties of electronic unusual.

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Carbon nanotubes have been used in many areas such as automotive fuel tanks industry, tennis rackets, golf, skiing and sticks on the snow and the coating of military materials that are not detected by radar. One of the new applications of nanotechnology, nano-carbon component of the ink tube is a ink was developed by Lee Jin Wong of the Korea Institute of Electrical Technology Research. The technique is highly developed it includes coating plastic surfaces, so, the ink to make a thin surface able to conduct electricity. It can be applied this technique on a variety of areas including touch screens and displays foldable.

MATERIALS AND METHODS

Experimental part

The materials used in the search:

- Conductive polymer (P3HT)
- Distilled water
- Carbon nano-tubes
- Slides of glass

Prepare polymer: To prepare the films are vestiges addition amount of carbon nano-tubes to the solution to form the two percentages by weight (1, 2, 3%) where the ratio of carbon nano-tubes are added (0.00025, 0.00050, 0.00075 g), respectively.

Prepare thin films: Thin films were prepared by deposition of material on pieces of glass after clean samples and be a sedimentation process using a spin coating method.

Optical measurements: The absorbance and transmittance for solutions were measured by using instrument measuring the spectrum, made by (Shemadzo) company, Japan, type (Double-Beam Spectrophotometer (UV-1800)) where the range of wavelengths is 300-1100 nm. A computer programmer make scanned for all wavelengths and gave the value of wavelength that occurs in it a greatest absorption.

Theoretical calculations

Absorbance: Absorbance defined as the ratio between absorbed light intensity (I_T) by material and the incident intensity of light (I_o) (Mwolfe *et al.*, 1989):

$$A = \log \frac{I_o}{I_T} \quad (1)$$

The optical absorbance coefficient (σ_{opt}) of solution and film is given by the:

$$\alpha_{opt} = 2.303 \text{ A/d} \quad (2)$$

where, (d) represent a thickness of sample. The ratio (I/I_o) called (Transmittance), (T_r) connected with absorbance by Eq. 3 (Mwolfe *et al.*, 1989):

$$T_r = e^{-2.303\,A} \quad (3)$$

Refractive index (n): The refractive index can be given by the Eq. 4 (Mwolfe *et al.*, 1989):

$$n = \frac{c}{v} \quad (4)$$

where, defined as a ratio between the speed of light in a vacuum (c) to the speed of light in a medium (v) .

The values of refractive index were measured practically then applied in equation depending on the reflectance and the extinction coefficient (K_n) as shown in the following Eq. 5 (Saeed and Suhail, 2012). Then, refractive index will be.

Reflectance (R): The reflectance can be represented depending on the value of refractive index by the Eq. 5:

$$R = \frac{(n-1)^2+k^2}{(n+1)^2+k^2} \quad (5)$$

Reflectance also can be obtained from absorption and transmission spectrum in accordance to the law of conservation of energy by the relation (Nahida and Sekeb, 2016):

$$R+T+A = 1 \quad (6)$$

when light radiation passes from one medium into another having a different index of refraction, some of the light is scattered at the interface between the two media even if both are transparent.

Since, the index of refraction of air is very nearly unity. Thus, higher index of refraction of the solid, greater is the reflectivity. For typical silicate glasses, the reflectivity is approximately (0.05). Just as the index of refraction of a solid depends on the wavelength of the incident light, so, the reflectivity varies with wavelength. Reflection losses for lenses and other optical instruments are minimized significantly by coating the reflecting surface with very thin layers of dielectric materials such as magnesium fluoride (MgF_2) (Saeed and Suhail, 2012).

Extinction coefficient (k): Extinction coefficient (k) given by following Eq. 7 (Nahida and Sekeb, 2016):

$$k = \alpha_{op}\,\lambda/4\pi \qquad (7)$$

where, (λ) is the wavelength of incident photon. The extinction coefficient represents the amount of attenuation of an electromagnetic wave that is traveling in a material where it values depend on the density of free electrons in the material and also on the structure nature (Tintu *et al*., 2010):

$$n^* = n\text{-}ik \qquad (8)$$

Where:

n = The real part of refractive index
n* = Complex refractive index which depends on the material type, crystal structure (particle size), crystal defects and stress in the crystal

Electronic transitions: The optical data were analyzed from the classical relation for near optical absorption in semiconductor (Chopra, 1969):

$$\alpha = A[hf\text{-}E_g]^r/hf \qquad (9)$$

Where:

f = The frequency
h = Plank constant
r = (1/2, 3/2, 2, 3) for transition (direct allowed, direct forbidden, indirect allowed and indirect forbidden, respectively)

A is a constant and E_g is defined as the optical energy band gap between the Valence Band (VB) and the Conduction Band (CB). The type of transition depends on the absorption coefficient value when α value is larger than (104 cm^{-1}) the transition called (direct transition) where electron moves from VB-CB with the same wave vector (k) and momentum are conserved. While indirect transition occurs when the value of absorption coefficient is <10 4 cm^{-1} (Jamal *et al*., 2008) where the electrons transferred from VB-CB at the same wave vector (k). The momentum and energy must be conserved with phonon assistant (Abdulla and Abbo, 2012).

RESULTS AND DISCUSSION

FT-IR test: Infrared spectrum (FTIR) of samples P3HT recorded using infrared spectroscopy infrared (Bruker victor 22 FTIR Spectrophotometer) where thin disks of P3HT were prepared in KBr. To ensure the drought of these samples, we had to dry the studied samples by a dryer for 6 h in 30°C and then record the spectra. Figure 2 shows the spectrum infrared transmittance that we have got (Table 1).

Table 1: Experimental values for the number of wavelengths of the absorption peaks and the corresponding bond

No. of the function	Wavelength (cm^{-1})	Functional groups
1	829	C = CH
2	1296	CH_3
3	1489	C-C
4	2711	C = C
5	2721	C-H
6	2746	CH_2
7	2980	CH_3
8	3412	C = CH

Table 2: Morphological characteristics of P3HT: MWCNTS nano films doping with different ratio

P3HT: MWCNTs samples	Roughness average Sa (nm)	Root mean Square Sq (nm)	Average diameter (nm)
0.00	5.16	6.03	79.70
0.01	4.03	4.83	83.61
0.02	8.35	9.65	83.77
0.03	5.56	6.44	84.04

Atomic Force Microscope (AFM): The results of the tests (AFM) for pure (P3HT) and doped with different ratio of (MWCNTs) films which prepared by spin coating which showed a uniform granular surface morphology as in Fig. 3-6. Where notice that the roughness increased with increasing the ratio of doped. As well as the Root Mean Sequare (RMS) increased with increasing of ratio of doped film, also the average grain diameter. Exhibits the same behavior as in Table 2. This is consistent with the findings of the researchers (Bkakri *et al*., 2015).

Absorbance spectrum: Absorbance measurements of (P3HT) before and after doping were plotted as a function of wavelength as shown in Fig. 7. Figure 7 shows that the absorbance of pure polymer and its additives are increasing with the increase of the concentrations of carbon nanotubes.

Figure 7 represent the relation between the absorbance with wavelengths for pure P3HT and doped for different ratio of doping. We can note from this figure, the values of absorbance increase when concentration increase because the absorbance is directly proportional with concentration according to the Lambert-Beer law, this is because the addition led to increase the values of concentration in same volume, then increase the number of particles that absorb the energy of incident light according to the Lambert-Beer law, this is agreement with.

Refractive index: The colculated values of refractive index of (P3HT) before and after doping (are shown in Fig. 8 and 9). Figure 9 shows that the refractive index values of pure and doping polymer are increasing with the increase of the concentrations of doping ratio.

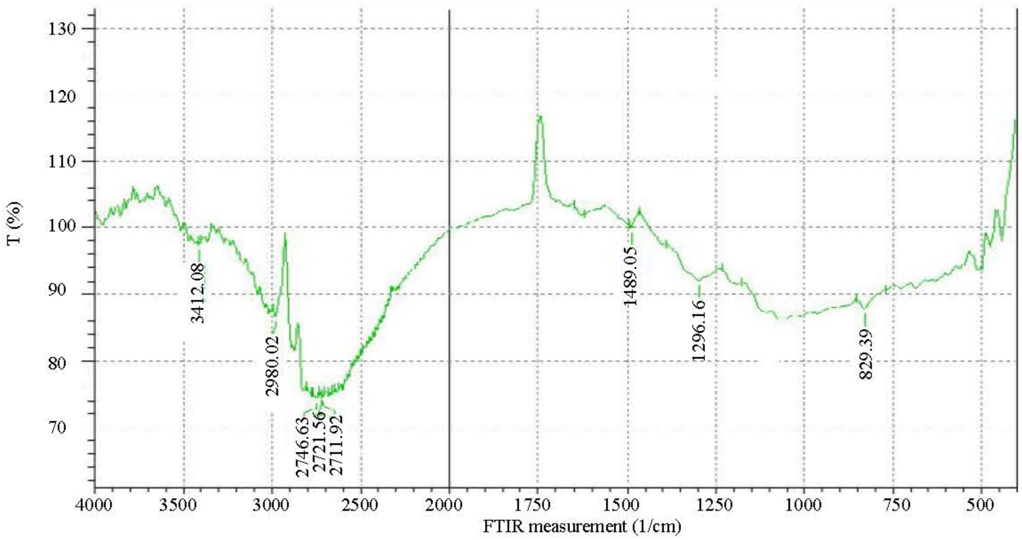

Fig. 2: FT-IR spectra of (P3HT)

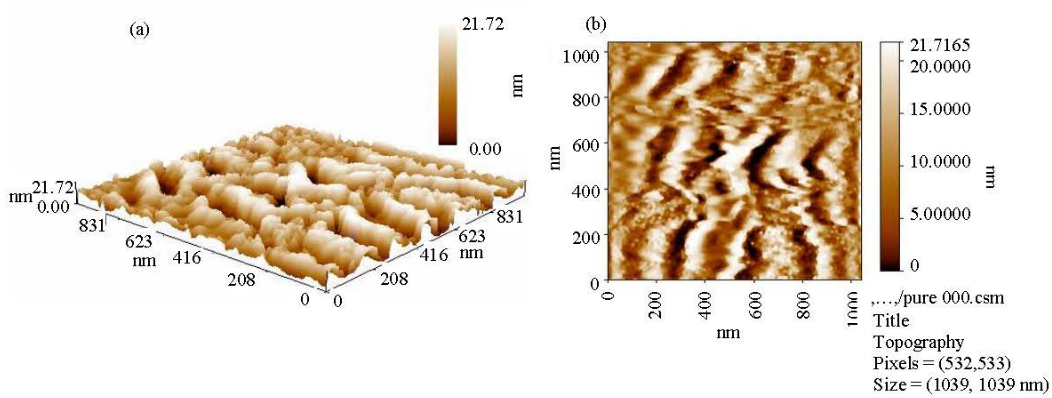

Fig. 3: AFM images of pure P3HT nano films for; a) 3-D and b) 2-D

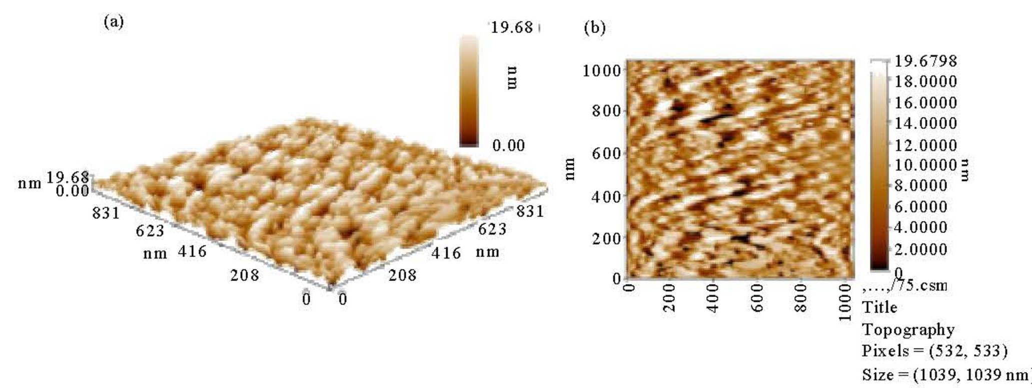

Fig. 4: AFM images of P3HT: 1% MWCNTS for; a) 3-D and b) 2-D

Absorption coefficients: The values of α for all thin films are found to be >104 cm^{-1} in the visible region which means that the films have a direct optical energy gap. The variation of the absorption coefficient (α) of (P3HT) films is shown in Fig. 10 and 11 as a function of wavelength. This is consistent with the findings of the researchers (Saeed and Suhail, 2012).

Direct energy gap: The optical band gap determined from the plot of $(\alpha\ h\upsilon)^2$ versus photon energy is shown in Fig. 12 and 13.

Extinction coefficient: The calculated values of extinction coefficient (k) of (P3HT) before and after doping are shown in Fig. 14 and 15 and Table 3.

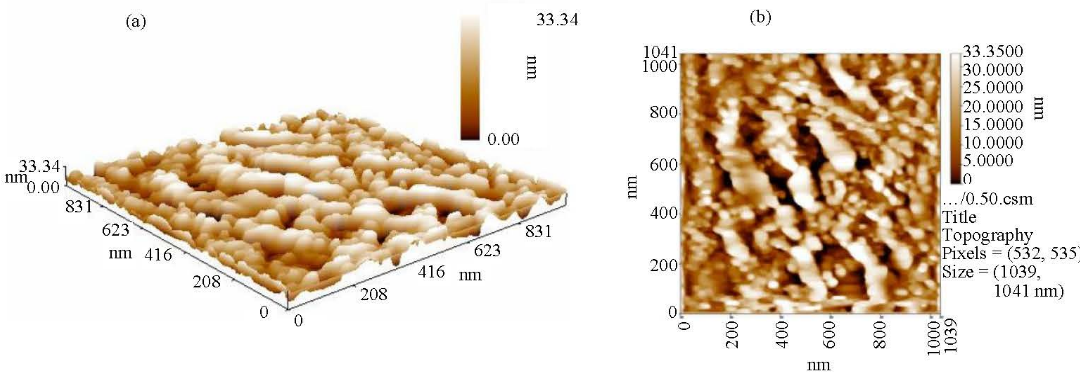

Fig. 5: AFM images of P3HT: 2% MWCNTS for; a) 3-D and b) 2-D

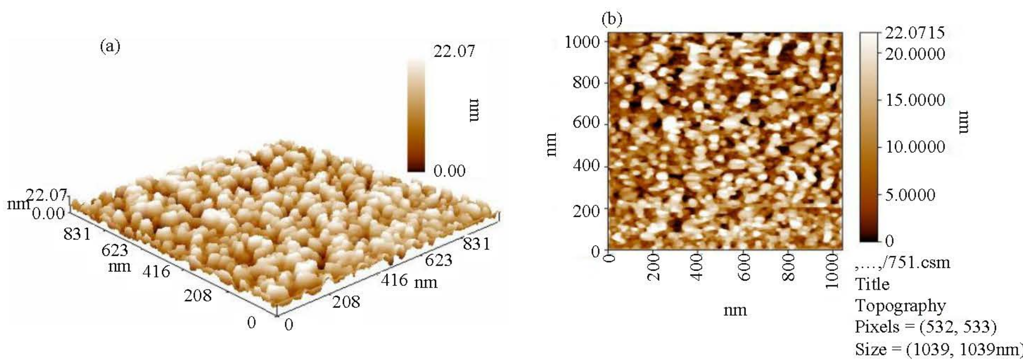

Fig. 6: AFM images of P3HT: 3% MWCNTS for; a) 3-D and b) 2-D

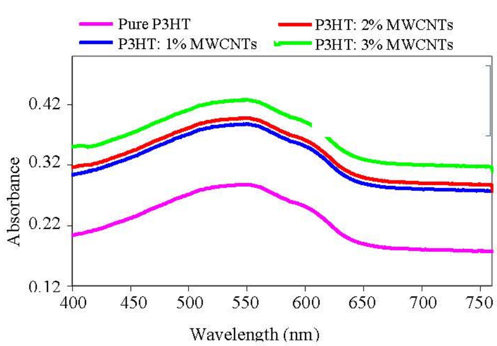

Fig. 7: Absorbance as a function of wavelengths for P3HT: MWCNTs

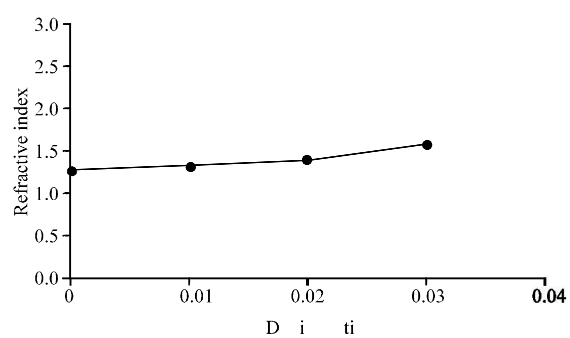

Fig. 9: Refractive index as a function of doping ratio

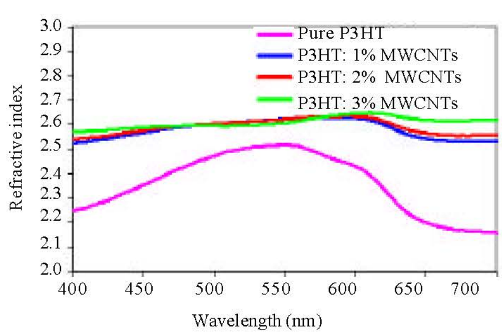

Fig. 8: Refractive index as a function of wavelengths for P3HT: MWCNTs

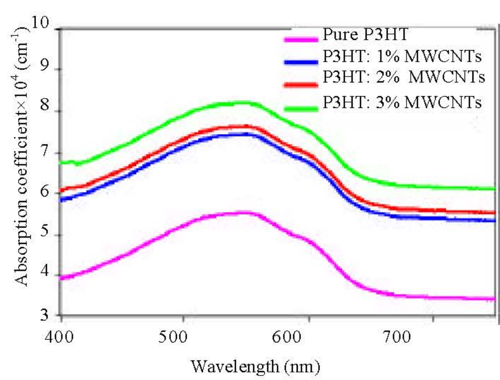

Fig. 10: Absorption coefficients as a function of wavelength for P3HT: MWCNTs

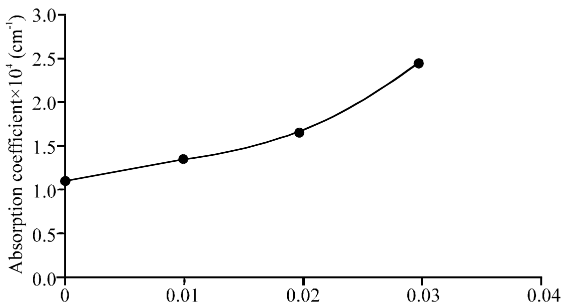

Fig. 11: Absorption coefficients (α) as a function of doping ratio

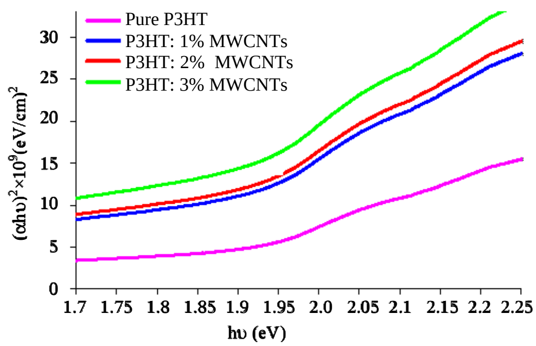

Fig. 12: Relation between $(\alpha h\upsilon)^2$ versus photon energy

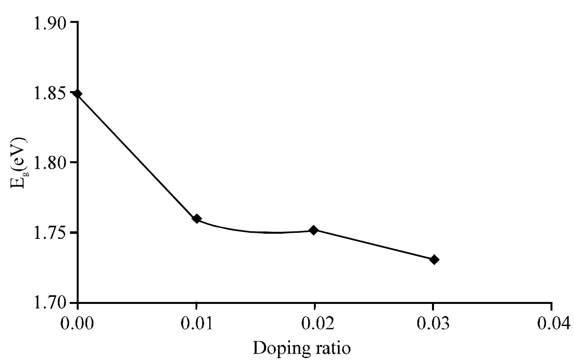

Fig. 13: Relation between E_g and doping ratio

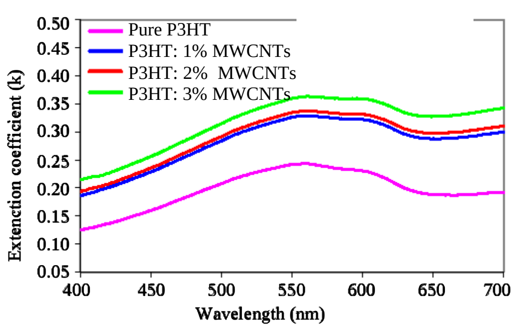

Fig. 14: Extinction coefficients as a function of wavelength for P3HT: MWCNTs

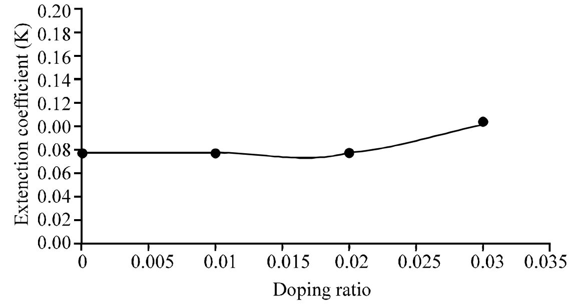

Fig. 15: Extinction coefficients (k) as a function of doping ratio

Taple 3: Optical parameters of P3HT:MWCNTs at λ = 550 nm

P3HT: MWCNTs sample	$\alpha\times10^4$ (cm^{-1})	E_g (eV)	n	k
0.00	1.098	1.85	1.267	0.076
0.01	1.361	1.76	1.328	0.077
0.02	1.612	1.75	1.395	0.078
0.03	2.401	1.73	1.558	0.102

Figure 15 shows that the extinction coefficients values of pure and doping polymer increasing with the increase of the concentrations of doping ratio.

CONCLUSION

The summarized results from this research are the following: spin coating technique is a good technique in the preparation of thin films. It is found through a study that these polymers possess random installation. The addition of carbon nano tube does not change the installation of the polymer. It is found through the study that these polymers appear a continuous change in the optical properties as a result of adding (carbon nanotube) to the polymer. The addition of carbon nanotube to (P3HT) led to the improvement optical properties. And get a lower energy gap. It was also found that the roughness of the surface increased by increasing the concentration and thus increase the conductivity to increase the surface area which reduces the resistance.

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