Characterization and structural studies of CMC/PEDOT: PSS

Wessam Hany [b] , E. Salim [a] , A.G. Elshahawy [a] , A.H. Oraby [a]

[a] *Physics Department, Faculty of Science, Mansoura University, Mansoura, Egypt*

[b] *External biophysics, Faculty of Science, Mansoura University, Mansoura, Egypt*

Abstract: Thin films of an electrically conducting polymer blend, carboxymethyl cellulose (CMC)/ poly (3, 4-ethylenedioxythiophene) and poly (styrene sulfonate) (PEDOT:PSS) have been studied using ultraviolet photoelectron spectroscopy, FTIR, and XRD. A solution cast approach was used to study the characterization and structure of carboxymethyl cellulose (CMC)/polyethylene 3, 4-dioxythiophene: sodium polystyrene sulfonate (PEDOT: PSS). The FTIR spectroscopic study revealed the complexation between the blends. The X-ray diffraction (XRD) results infer the amorphous nature of the studied samples.

1. Introduction

The term "macromolecule" or "polymer" is derived from the Greek poly meaning "many, much" and meres which means "parts, segments". Thus, a polymer is a large molecule (macromolecule) formed by the replication of small units. The macromolecule has a high molecular weight of between 10000 and 1000000 g/mol [1,2]. The birth of polymer science persists in 1500, the development of rubber was initially recognized as a polymer [3].

In the 1830s, the work of Henri Braconnot was the first modern example of polymer science. Henri, along with Christian Schönbein and others, created natural polymer cellulose derivatives. In the 1833s, Jakob Berzelius invented the term "polymer" [4].

Polymer dissolution plays a major role in many industrial applications in several fields. Understanding the dissolving process enables the optimization of design and processing conditions as well as the choice of an appropriate solvent [5]. Polymers play a significant role in daily life; they are used to create a variety of high-tech items, including biomaterials (prosthetic hip and knee joints) and aerospace materials. The ease of processing polymers is one of the factors contributing to their enormous appeal [6]. A polymer blend, also known as a polyblend, is a mixture of two or more polymers (which could be homopolymers) that have been blended without covalent bonds to form a new material with different physical properties. Polymer composites, on the other hand, require at least one component. A polymer-nano filler system is a system in which the loaded filler is on a nanometric scale in at least one dimension and can be a single polymer, polymer blend, or copolymer. Around 30% of all polymers are solid in mixed form, according to estimates [7]. Biopolymers include chitin, chitosan, cellulose, starch, peptides, proteins (gelatin), DNA, and RNA, which are all created by living creatures. Sugars, amino acids, and nucleotides are their monomeric units, respectively [8]. The hydroxyl groups of the proteins react with reactive forms of dicarboxylic acids to form ester bonds [9,10]. Biopolymer nanofibrils are universal nano-building blocks in natural materials [11].

The most successful electronic conducting polymer with processibility is PEDOT:PSS, Poly (styrene-sulfonate), and poly (3,4-ethylenedioxythiophene). Antistatic coatings, conducting coatings, hole injection layers, electrochromic windows, photovoltaic devices, electroluminescent devices, and organic devices are some of the applications [12–18].

PEDOT:PSS has also been used as an excellent electrode material for biological and chemical sensors [19], pressure sensors [20], strain sensors [21,22], and electrocatalysts [23].

A lot of carboxyl groups are present in CMC, a biocompatible substance that is non-toxic and has strong chemical stability (-COOH) [24]. CMC is a cellulose derivative that is created when cellulose reacts with sodium hydroxide and chloroacetic acid. The cellulose molecule has been given several sodium carboxymethyl groups (CH2COONa), which encourage water solubility. The molecular weight of the polymer, the typical carboxyl content per anhydroglucose unit, and the distribution of carboxyl substituents throughout the polymer chains are the three variables that influence the different properties of CMC. The food industry, flocculation, drag reduction, deter-agents, textiles, paper, meals, and pharmaceuticals are just a few of the areas where CMC is used.

2.Experimental Work

2.1. Materials

Poly (2,3-dihydrothieno-1 ,4-dioxin)-poly (styrene sulfonate) (PEDOT : PSS), and carbo-xymethylcellulose (CMC) were purchased from Sigma-Aldrich. All the chemicals were analy-tically pure and used without purification.

2.2. Sample Preparation

Preparation of CMC/PEDOT: PSS: 0.2gm CMC dissolved in 10ml dis. water and made five samples then add for all PEDOT:PSS in different ratios as table (1):

Table (1): Different ratio of PEDOT: PSS on CMC

| Samples	CMC	PEDOT:PSS
S0	2gm/10ml dis. water	0
S1	2gm/10ml dis. water	.1
S2	2gm/10ml dis. water	.2
S3	2gm/10ml dis. water	.3
S4	2gm/10mldis. water	.4

3. Results and Discussion

3.1. X-Ray Diffraction Analysis (XRD)

The X-ray diffraction analysis technique is a powerful instrument for investigating the internal structural organization of a material and determining whether it is crystalline or amorphous based on the structural arrangement.

The constructive spectroscopic technique used to investigate the homogeneity and overlap of biopolymeric materials is analyzed using an X-ray diffraction scan (XRD). It is a highly useful instrument for providing information on the composition of the created substance's lattice (crystal/amorphous) and for providing extremely useful information on the level of the crystalline sample of the synthesized thin film. XRD examination is performed on pure samples as well as blended samples with various concentrations of CMC/PEDOT: PSS.

Figure (1) reveals the XRD pattern of CMC/PEDOT:PSS. Obtained data plotted as Bragg angle 2θ versus intensity reveals amorphous. The CMC film revealed a comparatively broad one peak [25] and PEDOT:PSS has two bands [26] when blended with the three peaks one broadband was observed as the result of the mix
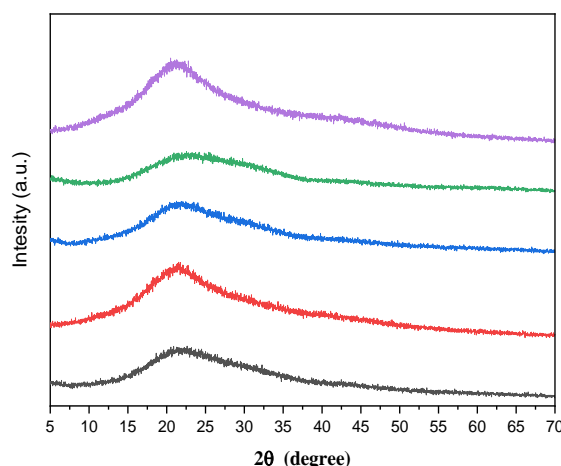
Figure (1) X-ray diffraction pattern of CMC / PEDOT: PSS.

### 3.2. UV/Visible optical absorption spectral data

UV/Visible optical absorption spectral data or electronic transitions can be considered a quantitative technique that is used to measure how much a chemical substance absorbs light. To do this, the amount of light passing through a sample is compared to the amount of light passing through a reference sample or a blank.

Spectra associated with molecules that absorb energy in the ultraviolet and/or visible regions to excite n-electrons from bonding or non-bonding states to higher anti-bonding orbitals can be used to estimate information about the electronic transitions of the examined material in various states. The difference

between higher and lower occupied molecular states (HUMO-LOMO) and the optical energy gap can likewise be derived from such spectral data.

Figure (2) shows the UV/Vis. electronic transition of the studied CMC / PEDOT : PSS S0 pure CMC, pure PEDOT : PSS ,S1cmc /PEDOT : PSS 0.1,p S1cmc / PEDOT : PSS 0.2, S1cmc / PEDOT : PSS 0.3, S1cmc / PEDOT : PSS 0.4.

The UV-visible absorbance spectra at 200 to 1100 nm wavelength ranges for CMC-based films [25].
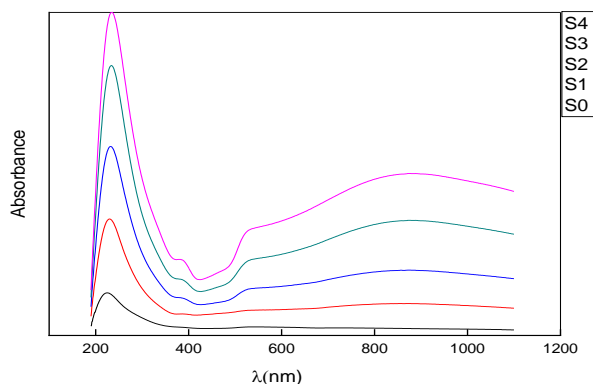
Figure (2) The UV/Vis. electronic transition of the studied CMC/PEDOT:PSS

3.2.1. Direct and indirect band gaps

A semiconductor's band gap might be one of two forms in semiconductor physics: direct band gap or indirect band gap. In the Brillouin zone, the conduction band's minimum energy state and the valence band's maximum energy state are both defined by a crystal momentum (k-vector). The material has an "indirect gap" if the k-vectors are different. When the crystal momentum of electrons and holes in both the conduction and valence bands is the same, the band gap is called "direct," and an electron can emit a photon directly.

A photon cannot be released in a "indirect" gap because the electron must transit through an intermediary state in order to transmit momentum to the crystal lattice.

### 3.2.2. Formula for absorption (tauc equation)

The absorption coefficient (alpha) is generally connected to photon energy (hν) by the well-known equation:

$\alpha = \beta / (h) (h\nu - Eg)^n$

Alternatively,

$(\alpha h\nu)^{1/n} = \beta(h\nu - Eg)$

Where, β the band tailing parameter is a constant, Eg is the energy of the optical band gap, and n is the power factor of the transition mode, which depends on whether the material is crystalline or amorphous. Tauc's relation states that graphing $(\alpha h\nu)^{1/2}$ vs photon energy (hν) results in a straight line in a specific location. The (hν)-axis will be intercepted by the extrapolation of this straight line, yielding the value of the indirect optical energy gap (Eg). Figures (3&4) shows the direct and indirect UV energy gap for samples S0, S1, S2, S3, and S4, respectively.
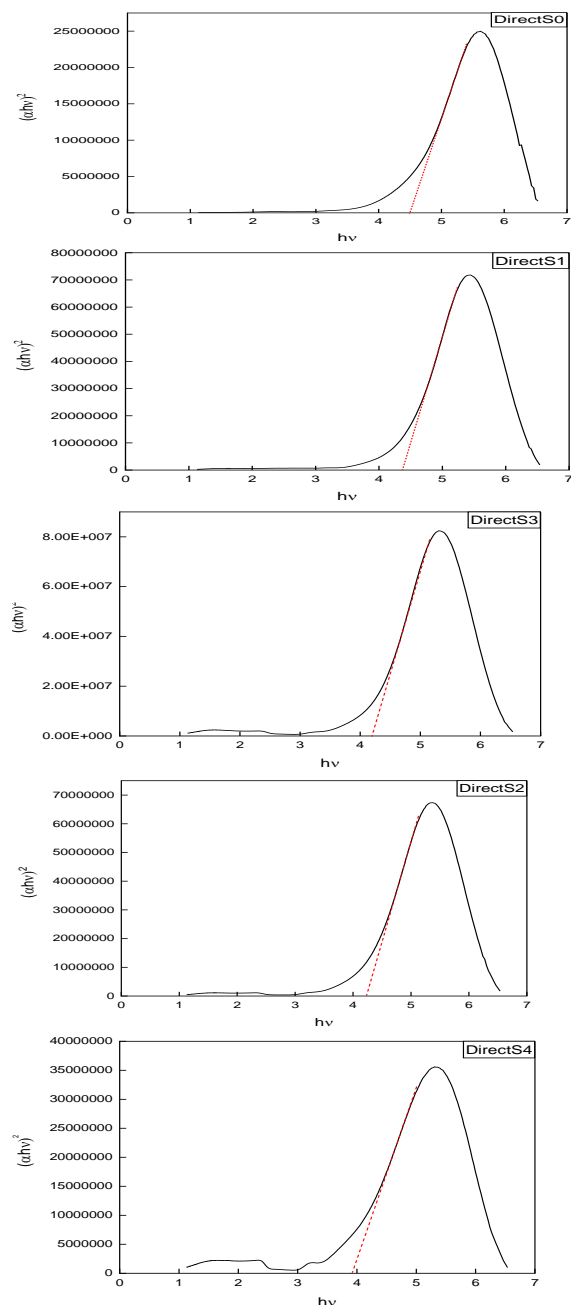
**Figure (3)** Direct energy gap for all ample S0, S1, S2, S3, and S4.
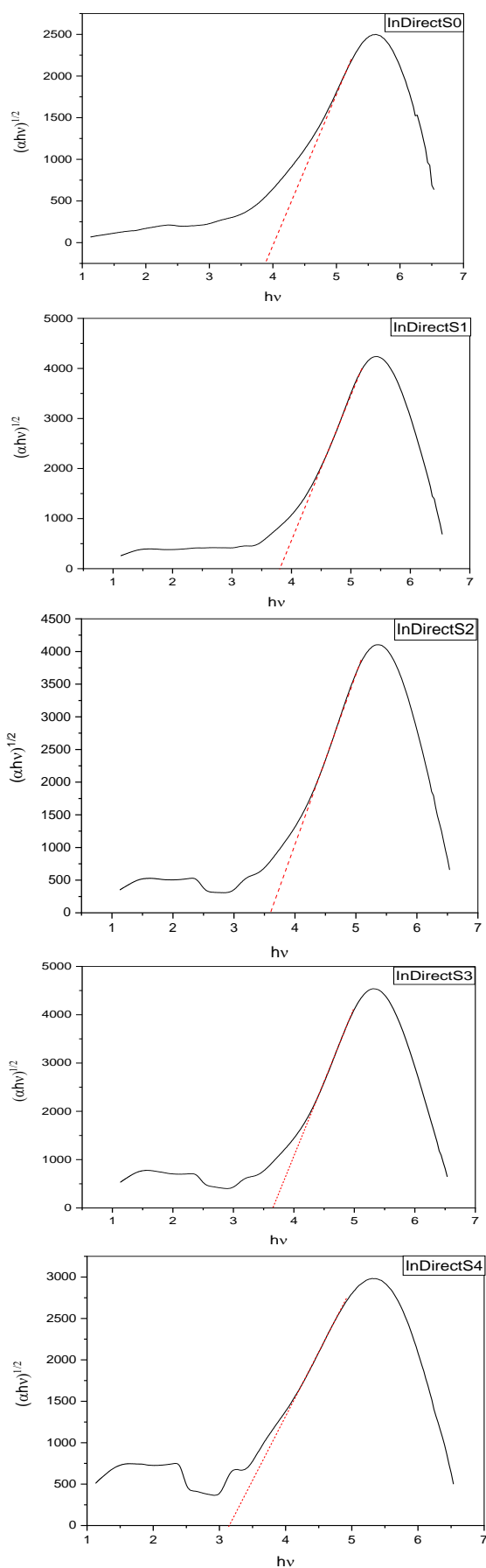
Figure (4) Indirect energy gap for all samples S0, S1, S2, S3, and S4**.**

Table (2): The variation of optical properties for CMC blended PEDOT:PSS.

ConC.	γ_{edge}	E_{direct}	$E_{indirect}$	$E_{tanc}(1242/\gamma_{edge})$
S0	344.870	4.418	3.894	3.601
S1	348.939	4.383	3.800	3.559
S2	359.233	4.203	3.610	3.457
S3	365.218	4.093	3.649	3.400
S4	402.089	3.824	3.184	3.088

3.3. Fourier transform infrared (FTIR)

Figure (5) reveals FT-IR optical absorption spectra of the CMC/PEDOT:PSS spectra. The peak at 2930 cm^{-1} is attributable to the CMC film's CH stretching vibration, and the broadbands around 3520 and 3260 cm^{-1} are related to OH groups. The COO groups' peak is at 1620 cm^{-1} and 1410 cm^{-1}, respectively. In comparison to the CMC film, the CMC-PEDOT: PSS composite film showed weaker peak intensities for the OH, CH, and COO groups. In addition, the presence of PEDOT:PSS caused noticeable peak alterations in the range of 600 to 1320 cm1, with the peaks at 600, 707, and 900 cm1 corresponding to C–S bonds in the thiophene rings and s–phenyl bonds in the sulfonic acid of PEDOT:PSS, respectively. Peaks at 1590 ,1420 and 1320 cm^{-1} are related to the C—C or C¼C stretching vibration of thiophene rings.
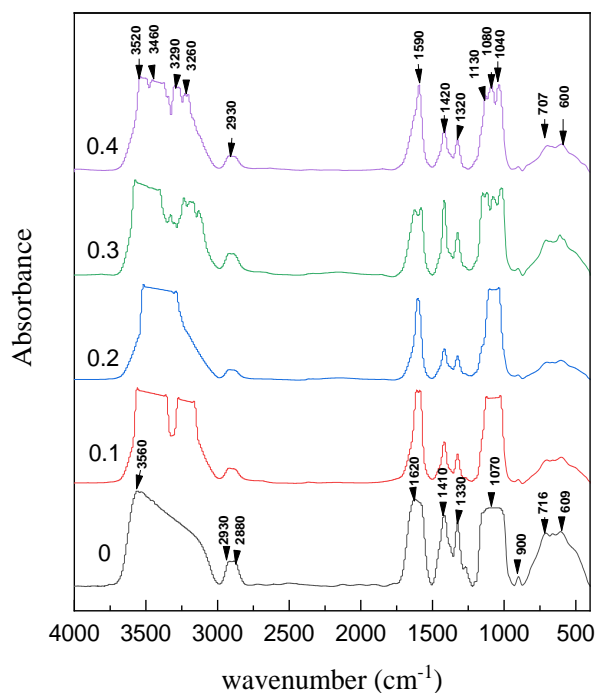
Figure (5) FTIR Absorbance of the synthesized *cmc/PEDOT:PSS*

Table (3) Assignments of the FT-IR characterization bands of the blend CMC and PEDOT : PSS.

Peak position(cm)$^{-1}$	Band Assignment (cm)$^{-1}$
—OH group	3520_3260
C—H stretching vibration	around 2930
the carboxylate group	1620and 1410
the C—O—C stretchingvibration	1080 and 1040
.As for PEDOT:PSS	.As for PEDOT:PSS
the Cvibration—S bondstretching	peaks at 600, 707, and 900
the C—C or C¼C stretching vibration of thiophene rings.	Peaks at 1590,1420and 1320
attributed to the stretching of C—O—C bonds	Peaks at 1080, 1040, and 1130

4. Conclusions

Utilizing ultraviolet photoelectron spectroscopy, FTIR, and XRD, thin films of the electrically conducting polymer mixture carboxymethyl cellulose (CMC)/polyethylene 3,4-dioxythiophene: sodium polystyrene sulfonate (PEDOT : PSS) have been investigated. Carboxymethyl cellulose (CMC)/ poly (3,4-ethylenedioxythiophene)and poly(styrenesulfonate) (PEDOT:PSS) has been made with varying concentrations utilizing the solution cast method for the study of characterization and structure. The complexation between the blends was discovered using FTIR spectroscopic research. Results from X-ray diffraction (XRD) suggest that the phase is amorphous.

5. References

1. Jenkins, A. D., Kratochvíl, P., Stepto, R. F. T., & Suter, U. W. (1996). Glossary of basic terms in polymer science (IUPAC Recommendations 1996). *Pure and applied chemistry*, **68(12)**, 2287-2311.
2. Barcelo D., (2008). Comprehensive analytical chemistry*, Elsevier*,
3. Neser G., (2017). Polymer based composites in marine use: history and future trends, *Procedia engineering*, **194,** 19-24.
4. Weast R.C., (1985). Handbook of chemistry and physical 65th ed., CRC press,
5. Miller-Chou, B. A., & Koenig, J. L. (2003). A review of polymer dissolution. *Progress in Polymer Science*, 28(8), 1223-1270.
6. Puoci, F., Iemma, F., Spizzirri, U. G., Cirillo, G., Curcio, M., & Picci, N. (2008). Polymer in agriculture: a review. *American Journal of Agricultural and Biological Sciences*, **3(1),** 299-314.
7. Flokes M. J., P.S. Hope, (1993) . Polymer Blend and Alloys, springer link, *https: // link. springer. com / book / 10.1007 / 978-94-011-2162-0.*
8. G. Akovali (2001).Hand Book of Composites Fabrication. Ankara, Turky,
9. Folkes, M. J., & Hope, P. S. (Eds.). (1993). Polymer blends and alloys (pp. 49-52). *London: Blackie Academic & Professional.*
10. Xu, K. (2004). Nonaqueous liquid electrolytes for lithium-based rechargeable batteries. *Chemical reviews*, **104 (10),** 4303 - 4418.
11. Ling, S., Chen, W., Fan, Y., Zheng, K., Jin, K., Yu, H., ... & Kaplan, D. L. (2018). Biopolymer nanofibrils: Structure, modeling, preparation, and applications. *Progress in Polymer Science*, **85**, 1-56.
12. Yue R.R., J.K. Xu, (2012) Poly(3,4-ethylenedioxythiophene) as promising organic thermoelectric materials: a mini-review, Synth. *Met*. **162,** 912–917.
13. Kirchmeyer S., K. Reuter, (2005) Scientific importance properties and growing applications of poly(3,4-ethylenedioxythiophene), *J. Mater. Chem*. **15,** 2077-2088
14. Elschner A., S. Kirchmeyer, W. Lovenich, U. Merker, K. Reuter, PEDOT: (2010). Principles and Applications of an Intrinsically Conductive Polymer, *CRC Press*.
15. Ouyang J.Y., C.W. Chu, F.C. Chen, Q. Xu, Y. Yang, (2005). High - conductivity poly (3,4 ethyl enedio xythio phene) : poly (styrene sulfonate(film and its application in polymer optoelectronic devices, *Adv. Funct. Mater*. **15** 203–208.
16. Heuer H.W., R. Wehrmann, S. Kirchmeyer, (2002). Electrochromic window based on conducting poly (3,4-ethylene dioxy thiophene) : poly (styrene sulfonate), *Adv .Funct. Mater*. **12,** 89–94.
17. Xia Y., K. Sun, J. Ouyang, (2012). Highly conductive poly(3,4-ethyl enedio xy thio phene :(poly (styrene sulfonate (films treated with an amphiphi licfluoro compound as the transparent electrode of polymer solar cells, *Energy Environ. Sci.* **5** (.5332 –5325.

18. Xia Y., J. Ouyang, (2011). PEDOT : PSS films with significantly enhanced conductivities induced by preferential solvation with cosolvents and their application in polymer photovoltaic cells, *J. Mater. Chem*. **21,** 4927–4936.

19. Nikolou M., G.G. Malliaras, (2008). Applications of poly(3,4-ethylenedio xythiophene (doped with poly(styrene sulfonic acid) transistors in chemical and biological sensors, *Chem. Rec*. **8,** 13–22.

20. Silva F.A.R., L.M. Silvaa, A.M. Ceschin, M.J.A. Sales, S.G.C. Moreira, C.E. Viana‹ (2008). KDP / PEDOT : PSS mixture as a new alternative in the fabrication of pressure sensing devices, *Appl. Surf. Sci*. **255** , 734–736.

21. Liu N.S., G.J. Fang, J.W. Wan, H. Zhou, H. Long, X.Z. Zhao, (2011). Electrospun PEDOT: PSS–PVA nanofiber based ultrahigh-strain sensors with controllable electricalconductivity, *J. Mater. Chem*. **21,** 18962–18966.

22. Lang U., P. Rust, J. Dual, (2008) . Towards fully polymeric MEMS: fabrication and testing of PEDOT / PSS strain gauges, Microelectron. *Eng*. **85,** 1050–1053.

23. Wang, Y., Qu, Z., Wang, W., & Yu, D. (2021). PVA/CMC/PEDOT: PSS mixture hydrogels with high response and low impedance electronic signals for ECG monitoring. *Colloids and Surfaces B: Biointerfaces, 208*, 112088.

24. Achachlouei, B. F., & Zahedi, Y. (2018). Fabrication and characterization of CMC-based nanocomposites reinforced with sodium montmorillonite and TiO_2 nanomaterials. *Carbohydrate polymers*, *199*, 415-425.

25. Kim, J., Park, C., Im, S., Lee, H., & Kim, J. H. (2019). Effect of molecular weight distribution of PSSA on electrical conductivity of PEDOT : PSS. *RSC advances,* **9(7),** 4028-4034