

Preparation and Study the Electrical Properties of Chitosan, Hydroxyethylcellulose, and Polyvinyl Alcohol polymer Blend Doped with Different ratios of 4-(2-Pyridylazo)Resorcinol Monosodium Salt Hydrate

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Received 29/10/2020 , Accepted 22/12/2020 , published:1/12/2021.

DOI: 10.18081/2226-3284/22-12/49-55

Abstract: The polymer blend of Chitosan: polyvinyl alcohol (PVA) (1:1) weight percent and hydroxyethyl cellulose (HEC) (0.5%) was prepared. The profile of the sample and its properties were measured by Fourier transfer Infrared spectroscopy (FTIR). The Scanning Electron Microscopy (FESEM) was used to describe the morphology of the polymer blend with two magnifications without any ratio of 4- (2-Pyridylazo) resorcinol monosodium salt hydrate and with 0.15 % of a 4-(2-Pyridylazo) resorcinol monosodium salt hydrate. The mechanical properties were demonstrated and characterized by Elongation and Young modulus. The polymer blend was incorporated with different weight ratios of 4-(2-Pyridylazo) of resorcinol monosodium salt hydrate, (0.03, 0.05, 0.07, 0.09, 0.15) gm of weight %. The current-voltage (I-V) characterization of prepared thin films showed ohmic behavior and the electrical conductivity was improved by increasing the ratio of dopant that leads all samples to reflect a semiconductor behavior.

Keywords:- Chitosan, PVA, 4-(2-Pyridylazo)resorcinol monosodium salt hydrate, Hydroxyethylcellulose, and current-voltage (I-V).

1. Introduction

In the past few years, researchers have directed to use of natural materials that do not pose a threat to the health of humans and biologically is degradable to not affect the environment. These polymers that have been used are chitosan, PVA, and hydroxyethylcellulose. Chitosan and its

derivatives that have drawn the attention of the distribution of acetyl groups, the degree of deacetylation of chitosan determined its solubility, the chain length, the molecular weight distribution, and the solubility polymer have a lot of attention by researchers [1-5]. we can synthesis chitosan from chitin by deacetylation [6,7], We also have hydroxyethylcellulose, which is very

available in nature, whether animal or vegetable, As cellulose has several properties and features, including mechanical durability and biological analysis, this leads to several applications, including medical, which are many and varied [8,9]. most Polymer blends exemplify a type of materials with perfect mechanical properties and biocompatibility than those of single ingredients and the basis of polymer/polymer miscibility may emerge from any specific interactions such as hydrogen bonding(H.B), and physical interaction such as dipole-dipole powers, and charge transfer complex for homopolymer combinations [10-12], In the context of the mixed substances, the mixture of polymers and natural dyes/ pigments play a vital role in our daily life due to the high-performance field of research with great potential. Consequently, the increase and benefit of doped polymers as diverse technological applications and as a major part of the daily routine was observed in recent years. For example, dyes/polymers are currently used in many medical applications, painting industries, analysis, and gas separations. [13,14]. These applications are specifically related to the existence of the dye which is mixed into the corresponding polymers. The affinity of certain polymers with dyes is used in the

treatment of wastewater after the dyeing process. All these attributes are very interesting for applications in different fields as dyeing of weaving, new employment dyes of organic light-emitting diodes, laser dyes, fluorescent labeling, and liquid crystal [15]. In this research, we prepared a polymer blend of three components of Chitosan, PVA, HEC, and with a doping component of different weight ratios of synthetic 4-(2-Pyridylazo) resorcinol monosodium salt hydrate. we used in this study biodegradable substances to produce a conducting polymer mixture to avoid environmental Contamination in this research.

1 . Instrument and Materials

Chitosan, PVA, HEC, PVA, 4-(2-Pyridylazo)resorcinol monosodium salt hydrate, and acetic acid were and bought from Merck and used as received, A universal testing machine (Zwick Rell) was used, device origin (Germany), from type (BTI-FR2.5TN.D14), power operating card (100-129 V / 4, 4-3,7A) at room temperature (RT). The FESEM measurement of samples was carried out using Leo-Supra 50vp (Carl Zeiss, Germany) available in Science College at Basra University the digital device: Keithley Series 2400 Meter (England) was used to study the electrical properties.

Polymer blends were recorded as KBr discs using the Fourier Transform Infrared Technique.

1.2.Preparation of polymer blend film

Polymer blend film was synthesized according to the following procedure. Equal weights of PVA and HEC (1:0.5) weight ratio% are dissolved in distilled water at 80°C and mixed with 1 weight ratio of chitosan dissolved in 0.1 acetic acids aqueous solution with the continuous stirrer. the mixture was stirred at high speed and constant temperature of 30 °C yieldings (A) polymer blend Depicted in Figure 1.

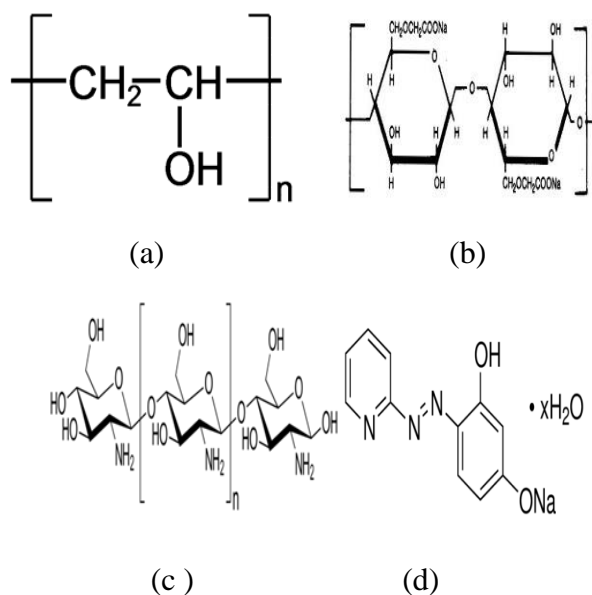
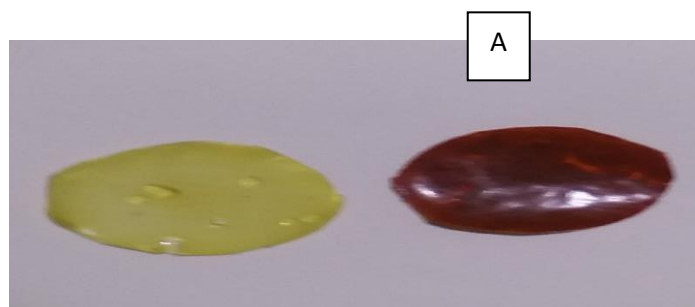


Fig. (1): chemical structure of (a) PVA, (b) CMC, (c) Chitosan, and (d) 4-(2-Pyridylazo)resorcinol monosodium salt hydrate.

1.3.Preparing doping solutions

Doping polymer blends with azo dye is achieved by adding 0.03, 0.05, 0.07, 0.09, 0.15 g wt.% of 4-(2-Pyridylazo)resorcinol monosodium salt hydrate dye to the Freshly prepared solution of PVA/ Chitosan/HEC (1:1:0.5) to yield (B, C, D, E, and F polymer blends respectively. The Resulted mixture was stirred well for 20 minutes to warranty that the homogeneous distribution of 4-(2-Pyridylazo)resorcinol monosodium salt in the polymer blend. Figure 2 represents the undoped film A and doped film F with 0.15 g of azo dye.



Figure(2): A undoped film and F doped film.

1.4.Samples preparation for electrical measurements

The glass slides were cleaned and drilled with acetone and Then distilled water. The glass slides were attached by a known wire diameter to the plastic pieces and fumigated by high-purity aluminum electrodes. After the evaporation process, the wires were raised and the process of molding the membranes to be examined was carried out. The electrodes on those slices connected them to the polar electrical circuit, which represents the digital device (Keithley Series 2400 Source Meter).

2.Results and discussion

2.1. FTIR characterization

The Fourier Transform Infrared spectra the Chitosan /PVA/HEC (A) without azo dye and Chitosan/ PVA/HEC (with a 0.15% weight ratio) of 4-(2-Pyridylazo) resorcinol monosodium salt hydrate salt (F) powders were recorded as KBr discs using the Fourier Transform Infrared Technique (FTIR). showed the peak at $(3230.6) \text{ cm}^{-1}$ which represents the stretching of the hydroxyl group (O-H), $(2925) \text{ cm}^{-1}$ Symmetric amide, and (C-H), $(1664.27) \text{ cm}^{-1}$ coincides to (C=O), stretching vibration of (CH_2) group at 1433.35 cm^{-1} [16], see Figure 3. In Figure 4, the FTIR of (F) sample, represents the values of the strong groups initiated to shift, These signals are an interplay between the dye and the polymer because the suitable polymer blend composition many bonds can interconnect with added 4-(2-Pyridylazo) resorcinol monosodium salt hydrate. The spectrum showed a peak at $(3407.65) \text{ cm}^{-1}$ which represents the (O-H) stretching, 2936.09 cm^{-1} symmetric amide (C-H), 1664.27 cm^{-1} represents (C=O) stretching vibration of (CH_2) group in 1432.85 cm^{-1} , $(1316.13) \text{ cm}^{-1}$, $(1156.02) \text{ cm}^{-1}$ vibration band (C-N), and $(1078.01) \text{ cm}^{-1}$ for (C-O) group [17].

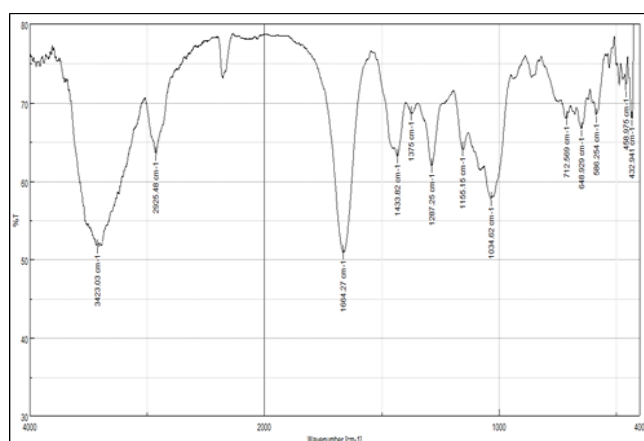


Fig. 3: FTIR spectrum of (A) Polymer Composite.

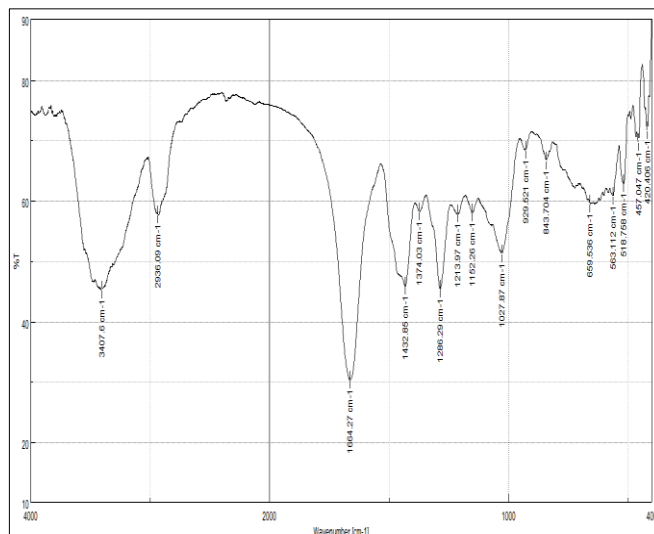


Fig.4: FTIR spectrum of (F) Polymer Composite.

2.2. Field Emission Scanning Electron Microscopy (FESEM)

For cross-section analysis, samples were cryo fractured after inundation in liquid nitrogen. The FESEM images were acquired on a ZEISS SUPRA 55 (Carl Zeiss, Germany) field-emission scanning electron Microscope. The images were taken at random positions of the films. The FESEM micrographs of (A) polymer blend are magnified by 8000x and 25000x times and 800x for F film. (FESEM) observations were carried out to gain a good insight into the homogeneity and the microstructure analysis of the blend film. FESEM images of the surface of the polymer blend (A) film, was presented. It was remarked that (A) film was arranged in the film template, smooth and with good structural good surface Figure 5 (a₁ and a₂) while (b) represents of The FESEM of blend film, FESEM images uncovered that A film had a smooth surface of the blend structure. Where No clumps or breaks were shown in SEM pictures, indicating good compatibility between the mixed materials.

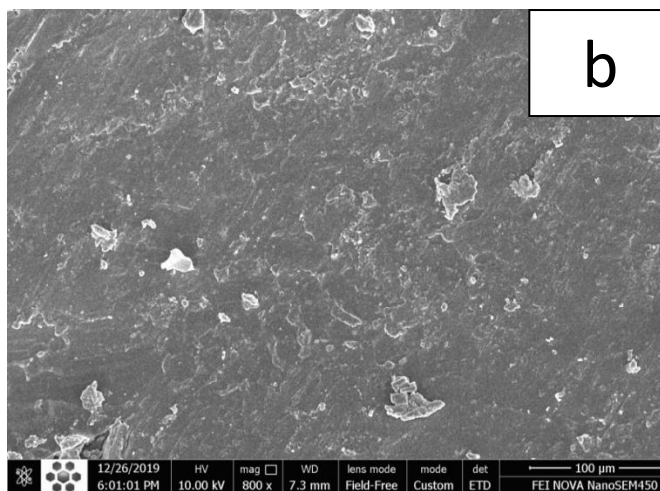
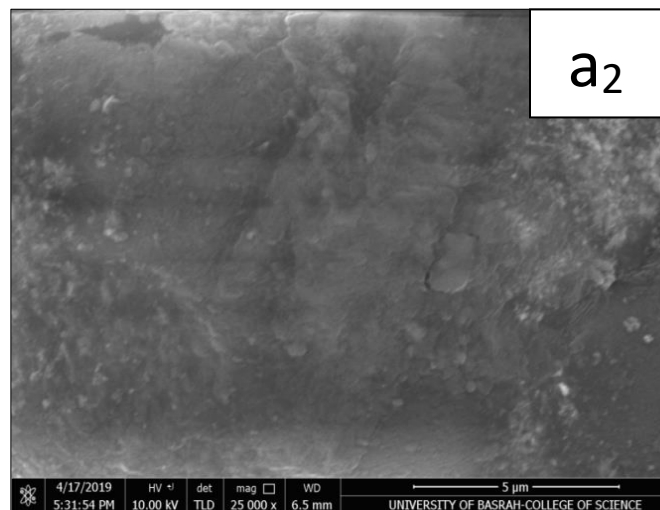
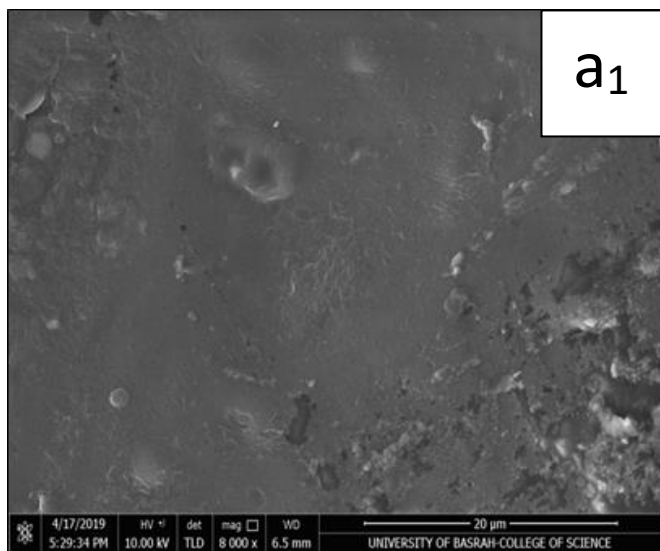


Fig.(5): FESEM of (A) polymer blend without azo dye (a1)8000amplifier and (a2) with25000amplifier and Polymer blend (F) (b) 800 amplifier.

2.3.Study of Mechanical Properties.

Mechanical properties of the A film, like young’s modulus and elongation at break, were determined. Tensile strength was estimated as the maximum load on the film before breakdown was divided by the cross-sectional area of the sample. Elongation was known as the Alteration percentage in sample length compared to the primary length between the grips. Three replicate measurements were performed. Figure 6, illustrates the relationship between the stress at the yield strength representing the stress at which the material begins to mess or

plastic distortions preceding the yield point the material will distort elastically and will restore to its primary shape when the used stress is removed. Noting that the value of Young’s modulus of (A) film was 0.798 Mpa and Maximum Elongation ϵ_m was=12%. the Hardness at its weakest point σ_Y = 9.58 Mpa, and the Elongation at break was $\epsilon_B\%$ = 16.4, these properties make the prepared polymer blend films suitable for thin conductive and biodegradable films.

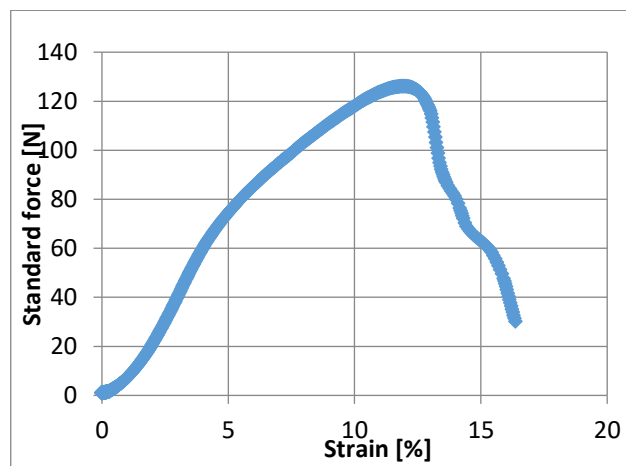


Fig. (6): Mechanical properties of the polymer blend (A).

2.4. Electrical Properties

Current-Voltage (I-V).

current-voltage characteristic of the thin films prepared A, B, C, D, E, F was calculated within voltage range (2-12 Volt) at a temperature of 28 ° C. It is noted from Figure 7 that the relationship between voltage and current is an umbrella relationship, i.e. increasing the current by increasing the voltages within the current range and the voltages at a constant temperature. Generally, the electrical conductivity increases as a result of the doped polymer, due to the increase in the ratio of free electrons present, which depends on the conduction mechanism of N = N group of azo compounds [18]. The polymeric characteristic presented in this study has been verified by dielectric properties. The latter becomes more important at the best deformation rate of the mixture E (Chitosan – PVA-HEC-0.09% 4-(2-Pyridylazo) resorcinol monosodium salt hydrate). Electrical characteristics are ultimately quite useful as the desired characteristics occur in semiconductors.

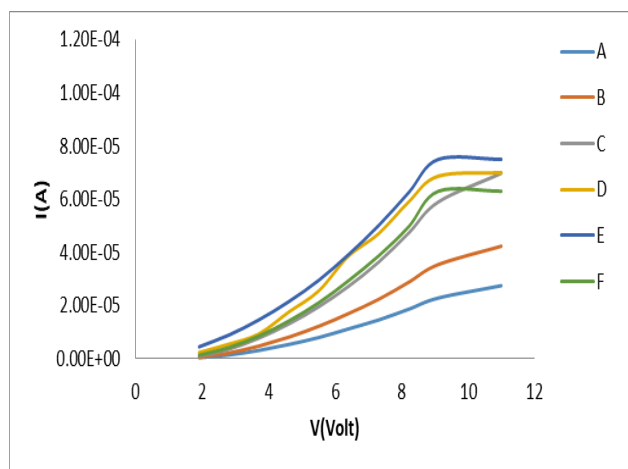


Fig.(7): current-voltage (I-V), the relation between the voltage and the current for polymer blend with 4-(2-Pyridylazo)resorcinol monosodium salt hydrate (A, B, C, D, E, and F).

3. Conclusion

In summary, A blend of (Chitosan –PVA-HEC) was prepared And doped with 4-(2-Pyridylazo) resorcinol monosodium salt hydrate. It is found that the mixing process is effective and successful. The effect of adding the azo dye to the mixture was demonstrated as well. The FTIR records showed that the Bands of the effective groups were spectrally shifted and changed their behavior due to the presence of materials doping. The polymeric characteristic presented in this study has been verified by dielectric properties. The polymer blend becomes more important at the best deformation rate of the mixture E (Chitosan –PVA-HEC-0.09% 4-(2-Pyridylazo) resorcinol monosodium salt hydrate). Electrical characteristics are ultimately quite Important as the wanted characteristics happen in the semiconductor.

References

- 1-Walaa A. Abbas, I. cell M. Sharafeldin Mostafa M. Omar and Nageh K. Allam, Novel mineralized electrospun chitosan/PVA/TiO₂ nanofibrous composites for potential biomedical applications: computational and experimental insights, Electronic Supplementary Material (ESI) for Nanoscale Advances.,2, 1512-1522,(2020).
- 2-Adora Reis Rodrigues, Maria Madalena de Camargo Forte, Denise Scherman Azambuja and Katia R.L. Castagno, Synthesis and characterization of hybrid polymeric networks (HPN) based on polyvinyl alcohol/chitosan, Reactive & Functional Polymers 67,708–715 (2007).

3- Parul Sharma, Garima Mathur, Navendu Goswami, Sanjeev K. Sharma, Sanjay R. Dhakate, Subhash Chand and Ashwani Mathur

Evaluating the potential of chitosan/poly(vinyl alcohol) membranes as alternative carrier material for the proliferation of Vero cells, *e-Polymers* | Volume 15: Issue 4,2015.

4-Ezequiel de Souza Costa-Júnior¹, Marivalda M Pereira, Herman S Mansur, Properties and Biocompatibility of Chitosan Films Modified by Blending With PVA and Chemically Crosslinked, *J Mater Sci Mater Med.* 20(2):553-61,(2009).

5-Esam A. EL-Hefian, Mohamed Mahmoud Nasef, and Abdul Hamid Yahaya, Preparation and Characterization of Chitosan/Poly(Vinyl Alcohol) Blended Films: Mechanical, Thermal, and Surface Investigations, *E-Journal of Chemistry*, 8(1), 91-96, (2011).

6-P.Negrea, A.Caunil, I.Sarac, M.Butnariu, The Study of Infrared Spectrum of Chitin and Chitosan Extract as Potential Sources of Biomass, *Digest Journal of Nanomaterials and Biostructures* Vol.10, No.4,p:1129-1138,(2015).

7- Rayane Santa Cruz Martins de Queiroz Antonino, Bianca Rosa Paschoal Lia Fook, Preparation and Characterization of Chitosan Obtained from Shells of Shrimp (*Litopenaeus vannamei* Boone), *Mar. Drugs*, 15, 141;(2017): DOI:10.3390/md15050141

8- Khalil, H.P.S.A., Davoudpour, Y., Islam, M.-N., Mustapha, A., Sudesh, K., Dungani, R., Jawaid, M., Production, and modification of nano fibrillated cellulose using various mechanical processes: a review. *Carbohydr. Polym.* 99, 649e665,(2014).

9- Navarra, M.A., Bosco, C.D., Moreno, J.S., Vitucci, F.M., Paolone, A., Panero, S., Synthesis, and characterization of cellulose-based hydrogels to be used as gel electrolytes. *Membranes* 5, 810e823,(2015).

10.M. D, Abubakar, Pattern of energy consumption in millet production for selected farms in Jigawa, Nigeria. *Australia Journal of Applied Sciences*, 4(4), p.665-672, (2010).

11- A.A Hammajam, Z.N, Ismarrubie, S.M, Sapuan; Fouth Postgraduate Composites Symposium, Universiti Putra Malaysia, PP.54-58, (2011).

12- K. Behzad, *Journal of Thermoplastic Composites Materials*, (23), PP. 1–10, (2014).

13-Carolin Fleischmann, Melanie Lievenbrück, and Helmut Ritter, *Polymers and Dyes: Developments and Applications*, *Polymers*, 7, 717-746, (2015). doi:10.3390/polym7040717.

14-H. M. Zidan¹, N. A. El-Ghamaz, A. M. Abdelghany, A. Lotfy, Structural and Electrical Properties of PVA/PVP Blend Doped with Methylene Blue Dye, *Int. J. Electrochem. Sci.*, 11 ,9041 – 9056, (2016) .doi: 10.20964/2016.11.08.

15- K. Hunger "Industrial Dyes, Chemistry, Properties, Application",3-527-30426-6,(2003).

16- Shahida Yasmeen, Mrinal Kanti Kabiraz, Badhan Saha, Md. Rakibul Qadir, Md. Abdul Gafur³ and Shah Md. Masum¹, Chromium (VI) Ions Removal from Tannery Effluent using Chitosan-Microcrystalline Cellulose Composite as Adsorbent, *International Research Journal of Pure &Applied Chemistry*,10(4): 1-14, (2016).

17- Abraham A., Soloman P.and Rajini V., perturbation of chitosan –polyvinyl alcohol blends and on thermal and mechanical on emerging trends in engineering, science, and technology *Procardia technology*,24,741-748, (2016).

18- Hassania Hadi Dhannoun Hoda Abd Al-Azar Al-Bakry Hisham Anwar Saleh. Preparation and study of the effect of bilateral deformation on the electrical and optical properties of polymers, *Journal of Education and Science* Volume 27 Issue 4 of (2018).

