



Study of the Optical Properties of Polyvinyl Alcohol/PluronicF-127 Blends Doped with Flavonoids Extracted from Hibiscus Sabdariffa L. plant

Zainab J. Sweah¹, Dalal K. Thbayh¹, and Sameerah Ahmed.Zearah²

University of Basra, Polymer Research Center¹

Department of Chemistry, College of Science, (Iraq -Basrah)

ABSTRACT

Thin films of the polymer blends (pluronicF127 and polyvinyl alcohol) doped with different ratios of flavonoids extracted from Hibiscus Sabdariffa L. plant (0.03, 0.05, 0.07, 0.09, 0.12, and 0.15) % wt., were prepared by a spin coating method. The optical properties of the prepared films were examined by Fourier transform infrared (FTIR), UV-Visible. The optical properties of synthesized polymer blends using absorbance spectra at wavelengths (200-900 nm). It is obvious that a maximum wavelength of polymer blends are dramatically increase until it reaches (400) nm with the increase of the weight ratios flavonoidsextracted from Hibiscus Sabdariffa L. plant from (0.03to0.15) wt% in the mixture of polymer blends/flavonoids. These shifts in the wavelength gave information on the samples that can absorb light in a quite broad spectral range up to the visible region. The values of the energy gap decrease from (4.87 eV) to (4.5 eV) as the increases flavonoids in the polymer blends.

Keywords: Polyvinyl alcohol, PluronicF-127, Hibiscus Sabdariffa L. plant and Optical properties.



1. INTRODUCTION

Polymers and semiconducting polymers have a wide range of technological applications such as adhesives, coating, lithograph, sensors and as solid-state electrochemical cells; they can be directly deposited on to chips in any shape or size. As well know, a great variety of low dimensional-related studies holds many researchers interest and attention because of their amazing optical properties and their possible applications in many fields [1, 2]. The substances made from biodegradable materials will generate increasing numbers of smart microelectronic, optical micro and photonic pieces and systems and novel generations of photovoltaic. These polymer compounds also can provide a good application in optics, electronics, Ionics, membranes, mechanics, protective and functional coatings [3] and catalysis, sensors and biology. in recent years, polyvinyl alcohol (PVA) polymers have interesting because of their variety of applications [4, 5]. Polyvinyl alcohol is a good compound having high dielectric strength, good charge depot ability and dopant-dependent electrical. VA with carbon chain backbone and hydroxyl groups attached to methane carbons, these OH group can be asource of hydrogen

bonding and hence help the coming into being of polymer blends [6]. Consequently, PVA has been used overall to synthesize films for disconnection and pressure have driven actions such as microfiltration, ultrafiltration, inverse osmosis and evaporation [7-13]. Pluronic F-127 triblock copolymers amphiphilic synthetic polymers with surface activity. The molecular structure of Pluronic F-127is an A-B-A block copolymer of poly (ethylene glycol) (PEG) and Poly (propylene glycol) (PPG) [14] as shown in figure (1). Polymer blends polyvinyl alcohol and Pluronic F-127 are a biodegradable polymer, with good film-forming properties and outstanding thermal, mechanical and chemical stability [15]. Roselle (*Hibiscus Sabdariffa* L. plant) could be used for various applications because it has several important chemical compounds such as flavonoids, anthocyanin, and many other compounds. The Roselle seed oil has high antioxidant activities [16] and many other benefits.

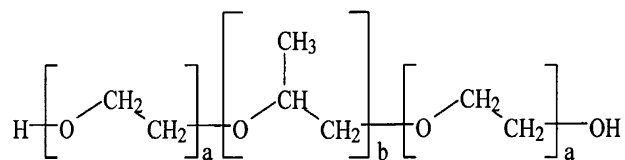


Figure 1.Pluronic F-127 molecular structure



In this work, we prepared biodegradable blends from PVA and Pluronic F-127, which were doped with flavonoid extract of the Roselle

2. Materials and Instruments

PVA, Pluronic F-127 were purchased from Merck and used as received flavonoid extract of the Roselle (*Hibiscus Sabdariffa* L. plant) was extracted from the commercial plant in the market in our laboratory. The polymer blend samples were coated to slides by Spin Coater on Backer Laboratory Equipment, vacuum pump, model: VE135N, Voltage: 230v/50-60Hz. The

3. Experimental

3.1 Extraction of flavonoid from *Hibiscus Sabdariffa*

Amount of 50 gm of the dried flower of *Hibiscus Sabdariffa* was defatted by Soxhlet apparatus with 500 ml of hexane. The solid residue was extracted with 500 ml of 80% methanol by stirrer at 25°C for 24 hours. The methanolic extract was filtered and evaporated to half volume under reduced pressure in a rotary evaporator, after that precipitation of a flavonoid extract by 1% Lead acetate. The

3.2 Preliminary phytochemicals analysis

Preliminary phytochemical study (color reactions) on flavonoid extract with performed using standard procedures in order to determine the presence of alkaloid (Dragendorff test), carbohydrates (Molish test), glycosides

(*Hibiscus Sabdariffa* L. plant) to prepared new biodegradable sensors, which can be degradable with time and less the pollution.

FTIR spectra were recorded IR spectra (KBr discs) on a JASCO FT/IR 4200, with a wave number range of 400-4000 cm⁻¹. The absorption spectra were measured in the range of 200-1100 nm for 10⁻³ by using UV-Visible spectrophotometer type Shimadzu UV-160A, that available at Polymer Research Center, Basrah University, Iraq.

precipitate was collected and dissolved in a mixture of (30 ml of conc. HCl and 25 ml of acetone). The mixture was filtered, and the solvent was evaporated to solid powder, which was dissolved in distilled water and mixed with the same volume of ethyl acetate and extracted by separating flask [17]. Ethyl acetate was collected and evaporated to dryness under reduced pressure in the rotary evaporator.

(Benedict test), steroids (Liebermann-Burchard test), phenolic compound (FeCl₃), flavonoids (Shinoda test) and terpenoids (Salkowsky test) [18,19].



Table (1): Qualitative analysis of flavonoid extract.

Chemical constituent	Remarks of flavonoids extract
Alkaloids	-
Carbohydrates	-
Glycosides	-
Phenolic compounds	+
Flavonoid	+
Steroids	-
Terpenoids	-

3.3 Preparation and Doping of the polymer blends

A mixture of polyvinyl alcohol (PVA) and PulronicF-127 with random ratio (1:1) was dissolved in distilled water and stirred with high-speed mixer at a constant temperature for 30 minutes. Doping polymer blends with flavonoids extract is carried out by adding the weighed flavonoids extract to the solution of PVA- PulronicF-127 after the prepared directly to give a polymer blend/flavonoid extract system containing (0.03, 0.05, 0.07, 0.09, 0.12 and 0.15) g wt.% of doping [20]. The mixture was stirred well for 15 minutes to guarantee that the homogenous distribution of flavonoids extract in the polymer matrix. Then the solutions

were poured in the above proportions on glass slides with dimensions of 2mm×2mm in the manner of spin coater.

4. Results and discussion

4.1 FTIR analysis

The spectra were showed the band at 2934 cm^{-1} assigned to aliphatic (C-H). Broadband resulting from hydroxyl group stretching (O-H) at 3317.9 cm^{-1} as shown in (Fig. 1). From the (Fig.2, Figure 3, and Figure 4) the band at 3435.5 cm^{-1} shows a weak band to a terminal hydroxyl group (O-H) of Pluronic F-127 and sharp band at 2886.9 to aliphatic (C-H). The graphs were indicated, that the nature of the bonding between the polymer blend chains

together is a physical interaction, as well as with flavonoids extract.

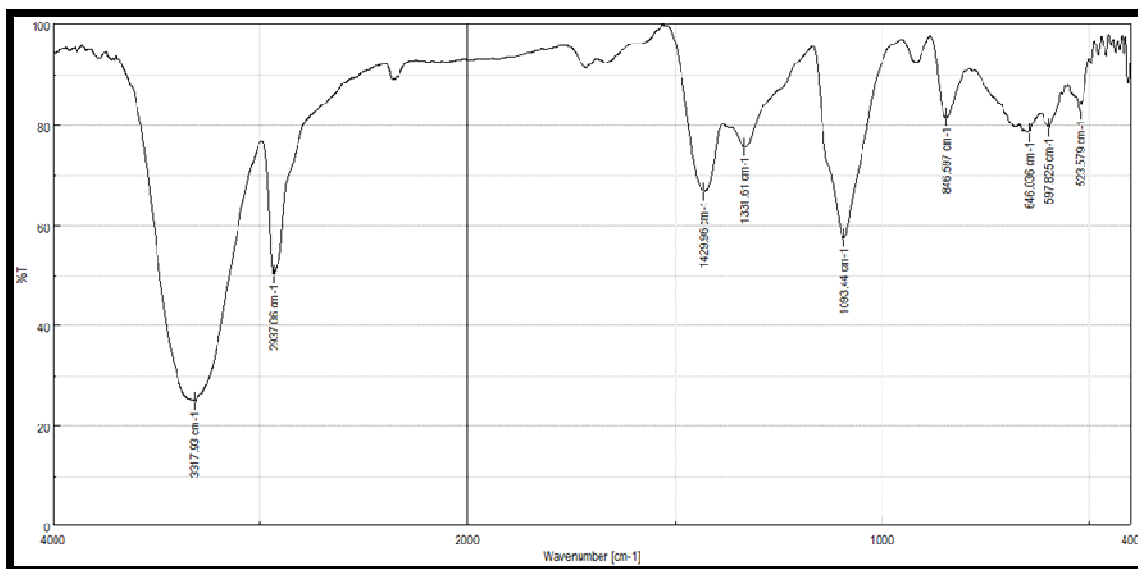


Figure (1): FTIR of PVA.

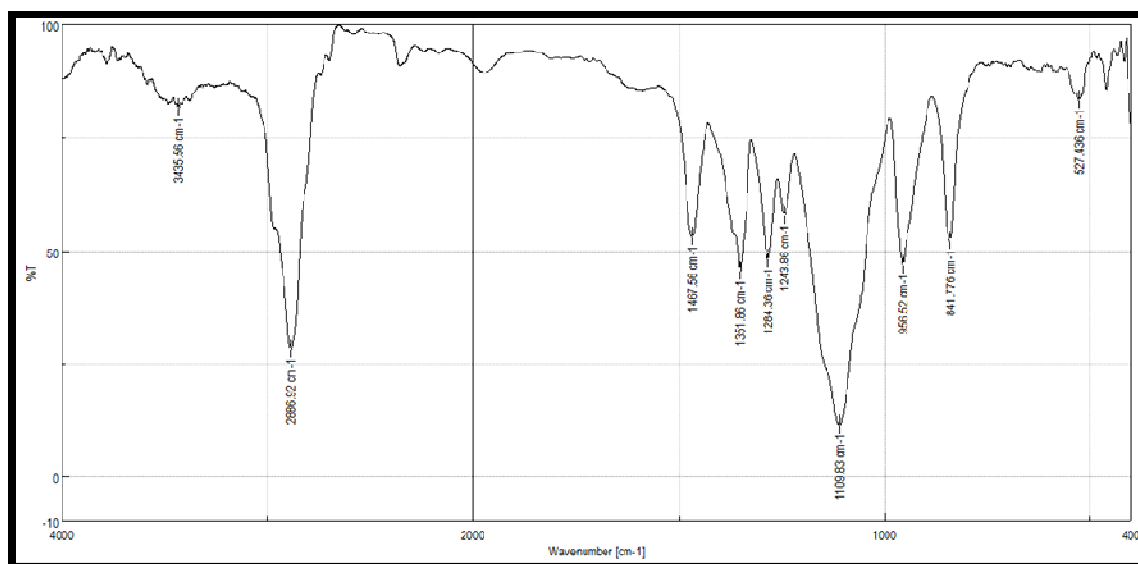


Figure (2) FTIR of Pluronic F-127.

Fig

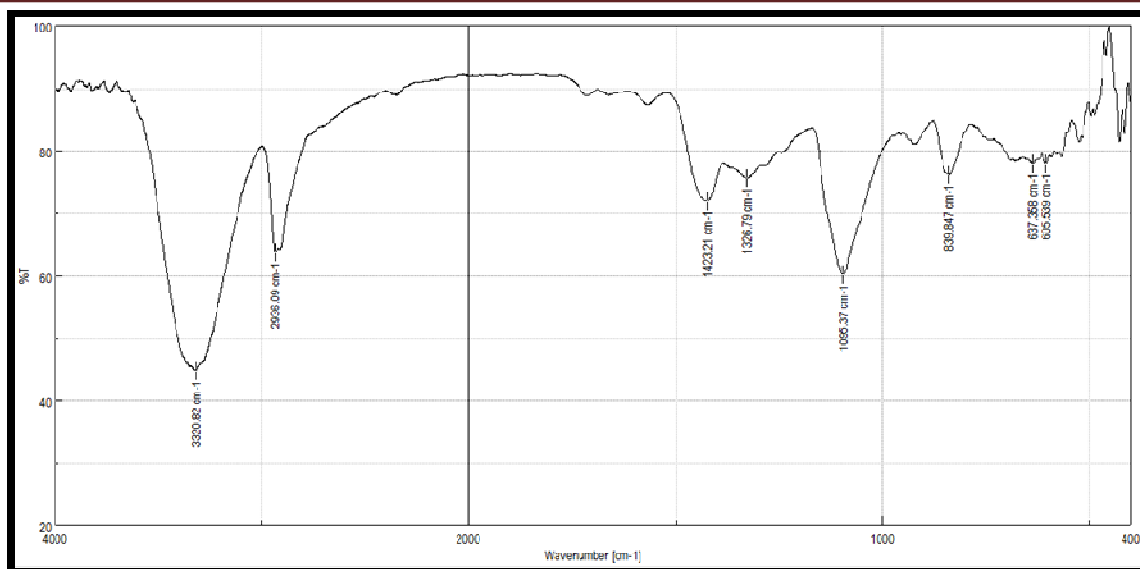


Figure (3): FTIR of a polymer blend of Pluronic F-127 and PVA.

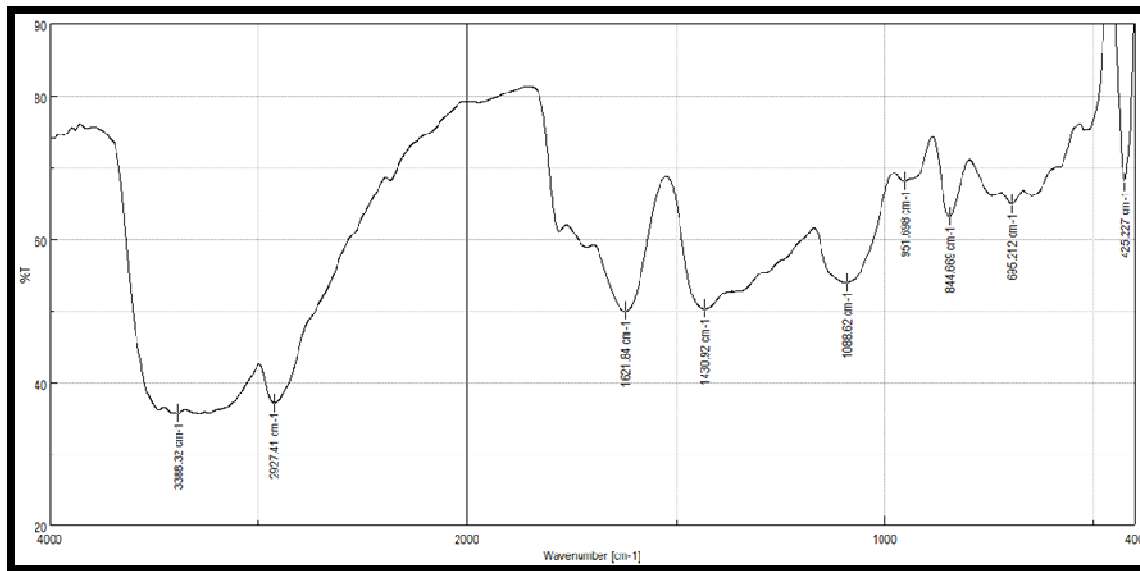


Figure (4): FTIR of a polymer blend with 0.12% of Flavonoid extracted from Hibiscus Sabdariffa L. plant.



4.2 Optical measurement of the polymer blend

The optical characterization of the polymers blends give information about other physical properties, e.g. band gap energy and band structure, optically active defects etc. and may be of endurable interest for several different applications. The absorption spectra of the blends PVA- PulronicF-127 as well as PVA- PulronicF-127 doped with flavonoids extract are shown in figure (5). It is clear from the figure that the spectrum of PVA- PulronicF-127 (Pure) exhibits a maximum wavelength around (250) nm, but apparently, one peak was sharp and creep up toward higher wavelength. It is obvious that the maximum wavelength raises dramatically until it reaches to (400) nm with increasing the weight ratios of the flavonoids extract to the mixture. These shifts in the wavelength pointing to the formation on the samples can absorb light in a quite broad spectral range up to the visible region [21, 22]. Therefore, VA- PulronicF-127/ flavonoids extract films are excellent UV absorber. The optical band gap of the films has been calculated using Eq. (1):

$$(\alpha h\nu) = A_0(h\nu - E_g)^{1/2} \quad (1)$$

where $h\nu$ is the photon energy, A_0 is a constant, E_g is the band gap energy [23], and α is the absorption coefficient that is defined by the Beer-Lambert's law using Eq.(2):

$$\alpha = \frac{2.303A}{d} \quad (2)$$

Where A is the absorbance and d is the film thickness, which was about 1 micrometer [24]. The band gap energy can be calculated by plotting $(\alpha h\nu)^2$ versus $h\nu$. The figures (6) and (7) show the relationship between absorption coefficient and photon energy for pure and the different ratios of flavonoids extracting the blends (PVA- PulronicF-127). The value band energy gap of photon E_g decreases from (4.87 eV) to (4.5 eV) when flavonoids extract increase from 0% to 0.15 as indicated in the table (2). After that, we have noted the value of the energy gap remained at the same level of 4.5 eV despite the increase of the ratio flavonoids extract to 0.15% in the blend. This can be attributed to the arrival of the polymeric blends to the saturation of the added flavonoids extract so it does not have a clear effect on the value of the energy gap.

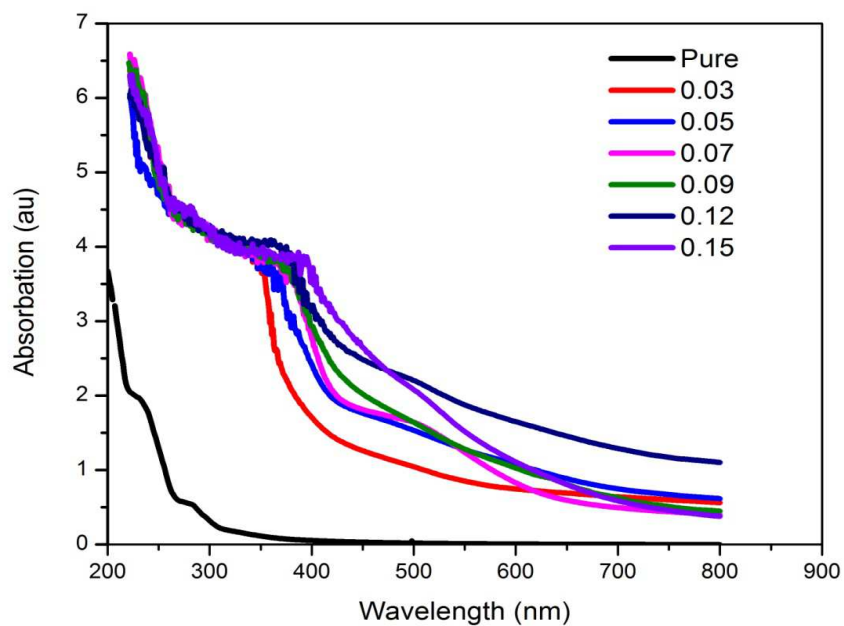


Fig 5. The absorbance spectra as a function of wavelength for PVA- PultronicF-127 flavonoids extract for all concentration ratios.

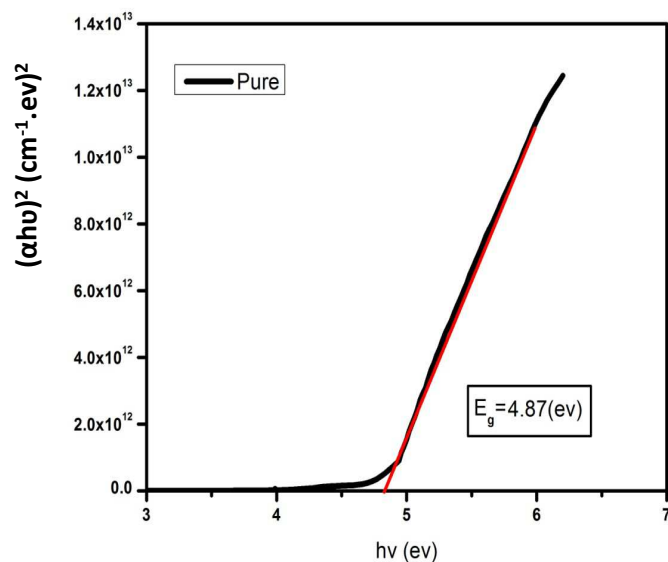


Fig 6. The relationship between $(\alpha hv)^2$ as function of photon energy for PVA- PultronicF-127 (Pure).

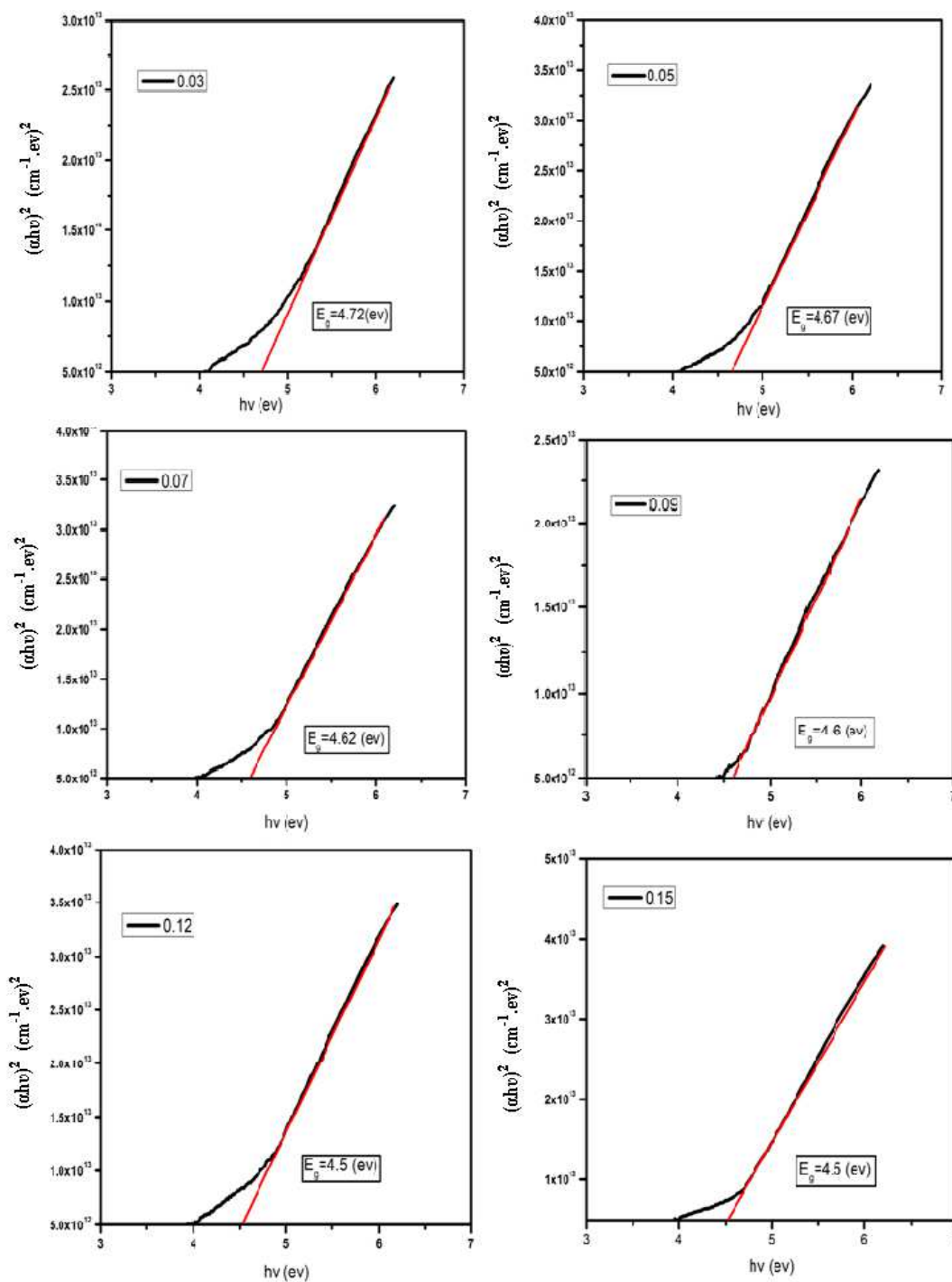


Fig 7. The relationship between $(\alpha h\nu)^2$ as function of photon energy for PVA- PultronicF-127 /flavonoids extract for all concentration ratios.



Table 2. The energy gap for all concentration of blend (PVA- PulronicF-127 /flavonoids extract) ratio.

Wt% flavonoids extract in PVA- PulronicF-127	Energy Gap Eg(eV)
0	4.87
0.03	4.72
0.05	4.67
0.07	4.62
0.09	4.6
0.12	4.5
0.15	4.5

4. Conclusion

In this study, the polymer blends of PVA and Pluronic F-127 doped with different ratios of flavonoids extract that extracted from Hibiscus Sabdariffa L. plant the study was made the effect of incorporating flavonoids extract on the PVA and Pluronic F-127 blends through the study of optical properties. The prepared biodegradable polymer blends were interconnected with the flavonoids extract by hydrogen bonding as a Physical coherence. From the results of the blends we can conclude that the Spectral investigations revealed that the spectra show some noticeable changes in peak absorption and location relative to the wavelength with an increase flavonoids extract in the mixture and this may be due to the

link between the flavonoids extract and the polymer. Also, it has been found that the films have excellent absorption of ultraviolet radiation. The analysis of the optical measurement data showed the energy gap decrease from 4.87eV to 4.5eV, as the flavonoids extract ratio increase from 0% to 0.12% in the mixture. Therefore, these compounds can play multiple roles to prepare a new-doping polymer tools with good protection from the harmful effects of ultraviolet rays. This makes possibility of preparation biodegradable materials, which can be decomposed after a period of time and thus it is possible to reduce the occurrence of pollution in the environment.



References

1. R. M. Ahmed 1 and M. Saif. "Optical Properties of Rhodamine B Dye-Doped in Transparent Polymers for Sensor Application". *Journal C, Physics*, 51(3):511-521, 2013.
2. Gernot Wirmsberger, Peidong Yang, Brian J. Scott, Bradley F. Chmelka, Galen D. Stucky, "Mesostructured materials for optical applications: from low-k dielectrics to sensors and lasers", *Spectrochimica Acta Part A* 57, 2049–2060, 2001.
3. Wenting Lan, Li He and Yaowen Liu, "Preparation and Properties of Sodium Carboxymethyl Cellulose/Sodium Alginate/Chitosan Composite Film", *Coatings*, 8, 291, 2018,
4. Saeed Nazeri, Esmat Mirabzadeh Ardakani, Hamid Babavalian, Ali Mohammad Latifi, "Evaluation of Effectiveness of Honey-Based Alginate Hydrogel on Wound Healing in Rat Model" *Journal of Applied Biotechnology Reports*, Volume 2, Issue 3, 293-297, 2015.
5. Mariagrazia Cascone, Bushra Sim, Sandra Downes, " Blends of synthetic and natural polymers as drug delivery systems for growth hormone" *Biomaterials* 16(7):569-74, 1995.
6. K.A. Abdelkader, Z. Anwar, "Spectroscopic studies of polyvinyl alcohol", *Journal of Applied Polymer Science* 2:1146-1151, 2006.
7. Meihong Liu, Choumou Zhou, Bingyan Dong, Zhefeng Wu, Lizhong Wang, Sanchuan Yu, and Congjie Gao, "Enhancing the perm-selectivity of thin-film composite poly(vinyl alcohol) (PVA) Nanofiltration membrane by incorporating poly(sodium)", *J. Membrane. Sci.* 463, 173–182, 2014.
8. Brian Bolton, Thuy Tran, Manh Hoang, and Zongli Xie., "Cross-linked poly (vinyl alcohol) membranes", *Prog. Polym. Sci.* 34 (9), 969–981, 2009.
9. Yang Liu, Ran Wang, Hongyang Ma, Benjamin Chu, " High-Flux Microfiltration Filters Based on Electrospun Polyvinyl alcohol Nanofibrous Membranes", *Polymer* 54 (2):548–556, 2013.
10. Xuefen Wang, Xuming Chen, Kyunghwan Yoon, Dufei Fang, Benjamin S. Hsiao, and Benjamin Chu, " High Flux Filtration Medium Based on Nanofibrous Substrate with Hydrophilic Nanocomposite Coating", *Environ. Sci. Technol.*, 39 (19), 7684–7691, 2005.
11. Fubing Peng, Xiaofei Huang, Anna Jawor, and Eric M.V. Hoek, " Transport, structural, and interfacial properties of poly (vinyl alcohol)– polysulfone composite nanofiltration membranes", *Journal of Membrane Science*, 353, 169–176, 2010.
12. Steve Yijie Hu, Yufeng Zhang, Darren Lawless, and Xianshe Feng, "Composite membranes comprising of polyvinyl amine-poly(vinyl alcohol) incorporated with carbon nanotubes for dehydration of ethylene glycol by evaporation", *Journal of Membrane. Sci.* 417–418, 34–44, 2012.
13. Kian Fei Yee, Yit Thai Ong, Abdul Rahman Mohamed, and Soon Huat Tan " Novel MWCNT-buckypaper/polyvinyl alcohol asymmetric membrane for dehydration of etherification reaction mixture: Fabrication,



- characterisation and application", *Journal of Membrane. Sci.* 453, 546–555, 2014.
14. Domínguez-Delgado CL, Fuentes-Prado E, Escobar-Chávez JJ, Vidal-Romero G, Rodríguez-Cruz IM, and Díaz-Torres R. "Chitosan and Pluronic F-127: Pharmaceutical Applications". *Encycl Biomed Polym Polym Biomater*, 1513-1535, 2016.
15. Wail Falath, Aneela Sabir, and Karl I. Jacob, "Highly improved reverse osmosis performance of novel PVA/DGEBA cross-linked membranes by incorporation of Pluronic F-127 and MWCNTs for water desalination" *Desalination* 397, 53–66, 2016.
16. Hai-Yao Wu, Kai-Min Yang and Po-Yuan Chiang," Roselle Anthocyanins: Antioxidant Properties and Stability to Heat and Ph", *Molecules*, 23, 1357, 2018.
17. Luc Takongmo Ngouadjo, Andre Youmssi, Steve Carly Desobgo Zangue, and Joseph Kayem, "Optimization of the extraction of Roselle (*Hibiscus Sabdariffa* L.) dried calyxes juice", *International Journal of Innovation and Applied Studies* 2(4), 2013.
18. Harborne JB and Baxter HH "Phytochemical Dictionary: A handbook of a bioactive compound from plants "Taylor and Francis; Washington, 237-240, 1993.
19. Khandelwal KR "Practical Pharmacognosy" Nirali Prakashan: Pun. 16th edition, 149-153, 2005.
20. M. Abdelaziz, Magdy M. Ghannam "Influence of titanium chloride addition on the optical and dielectric properties of PVA films" Elsevier, *Physica B* 405, 958–964, 2010.
21. P.M. Baros, I.V.P. Yoshida, M.A. Schiavon, "Boron-containing poly (vinyl alcohol) as a ceramic precursor", *J. Non-Cryst. Solids* 352, 3444- 3450, 2006.
22. Z. Ambras, N. Balazs, T. Alapi, G. Wichmann, P. Sipos, A. Dombi, K. Mogyorsi, "Synthesis, structure and photocatalytic properties of Fe(III)-doped TiO₂ prepared from TiCl₃", *Appl. Catal. B: Environ*, 81, 27-37, 2008.
23. Sze, S.M. and K.K. Ng, *Physics of semiconductor devices*. John Wiley & Sons, 2006.
24. N. Ghobadi, "Band gap determination using absorption spectrum fitting Procedure," *International Nano Letters*, vol. 3, 1-4, 2013.