Effect of Temperature and Doping Ratios on Electrical Conductivity of Polymer Blend Films of PluronicF127 and Polyvinyl Alcohol with Flavonoid Extract of Hibiscus Sabdariffa (Roselle)

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Abstract. Electrical conductivity of polymer blend films doped with different ratios of flavonoid extract of Hibiscus Sabdariffa (Roselle) (0.03, 0.05, 0.07, 0.09, and 0.12) % wt., were studied. The composite films prepared using solvent casting method. The result showed that the conductivity increased with increasing temperature and doping ratios. The values of activation energy decreased with increasing temperature and doping ratios of flavonoid for all ratios except that of (0.12%) doping, so, it was concluded that the ratio (0.09%) is the best appropriate one for doping.

1 Introduction

Polymer blends played a large role in the progress in scientific research and commercial application. Scientists and development of polymeric blended materials for suitable applications. Poly (vinyl alcohol) (PVA) has excellent film forming, water-soluble, adhesion, emulsification and barrier properties, which has been used in fibers, films and adhesive agents widely [1-4]. Polyvinyl alcohols (PVA) are hydrophilic polymer was been found to be non-immunogenic and non-carcinogenic in humans with many other polymers [5]. PVA is an important material regarding its large-scale applications; it is used in surgical devices, implantation, blend membrane, Poly (vinyl alcohol) films are clear and colorless, the polymer films exhibit good mechanical properties, crack resistance and good light fastness. It is resistant to oils, fats, greases and waxes. It has good pigment binding capacity and good compatibility with pigment and extenders used in the industry. However, disadvantage of poly (vinyl alcohol) is its weak water and electrolyte resistance. Recent researches indicated that poly (vinyl alcohol) has potential as polymer electrolyte for energy devices such as fuel cell and battery [6, 7].

Pluronic F-127 is approved poly (ethyl oxide)/poly (propylene oxide)/poly (ethylene oxide) (PEO-PPO-PEO) a triblock copolymers amphiphilic synthetic polymers with surface activity [8, 9]. The molecular structure of PluronicF-127 is an A-B-A block copolymer of poly (ethylene glycol) (PEG) and Poly (propylene glycol) (PPG), as shown in figure 1.
Figure 1: Pluronic F-127 molecular structure.

Roselle (Hibiscus Sabdariffa L) could be used for various applications because it has several of important chemical compound such as flavonoids, anthocyanin, and many other compounds. The Roselle seed oil have high antioxidant activities and anticorrosion.

Hibiscus is one of the most ordinary flower plants grown worldwide. More than 300 species of Hibiscus can be found around the world, growing in both tropical and subtropical regions. Most of the varieties of hibiscus plant are used as decorative plants; and partly for fiber and food but only Hibiscus Sabdariffa (Roselle) provides swollen red and green calyxes which are helpful for both food and non-food applications [11]. 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 and anticorrosion.

Flavonoid and anthocyanin and on the pharmaceuticals and healthcare and presently used as a natural colorant [12], antioxidant [13], anticancer and to avoid premature aging, Therefore, isolated anthocyanin from rosella petals have chance susceptible to degradation due to the effect of light [14, 15]. The aim of this study was preparation a series of doping biodegradable polymer blends and study of the electrical properties to synthesis a biodegradable semiconductor materials which decrease the pollution in our system

2 Materials and Instruments
PVA and 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 FTIR spectra were recorded IR spectra (KBr discs) on a JASCO FT/IR 4200 instrument, with a wave number range of 400-4000 cm$^{-1}$. This technique provided information about structure and chemical bonding of material. Available at Polymer Research Center, Basrah University, Iraq.

2.1 Extraction of flavonoid from Hibiscus Sabdariffa
50 gm. of dried flower of Hibiscus Sabdariffa was defatting by soxhlet apparatus with 500 ml of hexane. The solid residue were extracted with 500 ml of 80% methanol by stirring 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 flavonoids extract by 1% Lead acetate. The precipitate was collected and dissolved in mixture (30 ml of conc. HCl and 25 ml of acetone). The mixture was filtered, and the solvent was evaporated, then the solid powder, which was dissolved in distilled water. The solution was mixed with same volume of ethyl acetate and extracted by separating flask [16]. Ethyl acetate was collected and evaporated to dryness under reduce pressure in rotary evaporated to afford dry extract.

2.2 Preliminary phytochemicals analysis
Preliminary phytochemical study (color reactions) on flavonoid extracted with performed using standard procedures in order to determine the presence of alkaloid (Dragendorff test), carbohydrates (Molish test), glycosides (Benedict test), steroids (Liebermann-Burchard test), phenolic compound (FeCl$_3$), flavonoids (Shinoda test) and terpenoids (Salkowsky test) the results were showed in table 1. [17, 18].

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

Table (1): Qualitative analysis of flavonoid extract
2.3 Preparation and Doping of the polymer blends
A mixture of polyvinyl alcohol (PVA) and Pluronic F-127 (1:1) were dissolved in distilled water and stirred with high-speed mixer at constant temperature for 30 minutes. Doping polymer blends with Flavonoid was carried out by adding the weighed of extraction Flavonoid to the solution of PVA- Pluronic F-127 after the prepared directly to give a polymer blend/Flavonoid system containing (0.03, 0.05, 0.07, 0.09 and 0.12) g wt.% of doping. The mixture was stirred well for 15 minutes to guarantee that the homogenous distribution of Flavonoid in the polymer matrix.

3. Results and Discussion
3.1. FTIR analysis
(FTIR) analysis with of each component of the polymer blends were done to study the nature of the physical bonding that can occur between the physical mixing of prepared polymer blends as well as the Flavonoid extract of Hibiscus Sabdariffa L. plant. The spectra were showed band at 2934 cm\(^{-1}\) assigned to aliphatic (C–H), and Broad band for hydroxyl group stretching at 3317.9 cm\(^{-1}\) (figure 2). From the (figure 3) the band at 3435.5 cm\(^{-1}\) was showed week band to hydroxyl group (O-H) of Pluronic F-127 and sharp band at 2886.9 cm\(^{-1}\) to aliphatic (C–H). Figure (4) was showed Broad band at 3388 cm\(^{-1}\) for hydroxyl group stretching(O-H) from the study and observation of the graphs, we were noted that the nature of the mixing between the polymer blend chains and the extracted flavonoid together according to hydrogen bonding as a Physical coherence between the polymeric chains and in same time with flavonoid.

Figure 2: FTIR of PVA.
3.2. Electrical conductivity

The electrical measurements for the already prepared samples as Al/polymer/Al were performed by two-point probe method. Electrical conductivity measurements were carried out by using DIGIT MULTIMETER 8808A, PWS2185 DC Power supply 0-18,5A. Figures (5) - (10) show the relationship between current-voltage characteristics of polymer blend films with different ratios at the temperature range (303-363) K. Ohmic behavior was observed at low voltage of less than 10V at all ratios. This can be explained by the fact that there is a slight injection of charge carriers from the aluminum electrode to the polymer blend films, because the thermally generated charge carriers are greater than the injected charge from electrodes [19]. The current increases with increasing temperature and the applied voltage is identical to the characteristics of semiconductor materials.

When temperature increases, more localized electrons have the energy to bridge the gap and the routine becomes more ordered, then decreasing amount of localized states present accepting for more mobile of charge carriers. On other hand, the molecular structure of the polymer greatly influences the charge carrier's mobility according to the (I-V) characteristics. Namely, polymer blends do not have side chain that lead to higher charge carriers mobility compared to the polymers with long side chains.
Figure 6: (I-V) Characteristics at different temperatures for weight ratio (0.03%) of doping polymer blend films.

Figure 7: (I-V) Characteristics at different temperatures for weight ratio (0.05%) of doping polymer blend films.

Figure 8: (I-V) Characteristics at different temperatures for weight ratio (0.07%) of doping polymer blend films.
Figure 9: (I-V) Characteristics at different temperatures for weight ratio (0.09%) of doping polymer blend films.

Figure 10: (I-V) Characteristics at different temperatures for weight ratio (0.12%) of doping polymer blend films.

Figure 11 shows the effect of doping ratio with flavonoid enhanced electrical conductivity in this order: (pure < 0.03 < 0.05 < 0.07 < 0.12 < 0.09) % wt. This is due to electrostatic interaction in emulsion and powder between flavonoid and polymer blend films, and the small amount of flavonoid, which make it; diffuse within the matrix of polymer blend films.
Figure 11: The relationship between $\sigma_{dc}$ and weight ratio of doping polymer blend films at different temperatures.

Figure 12 shows the connection between effect of temperature and dc conductivity for polymer blend films with doping percent. The $\sigma_{dc}$ increases with increased temperature between (30-90) °C because of the increasing charge carrier in conduction band, this indicating semiconductor-like behavior, which was fit to the following Arrhenius exponential equation [20].

$$\ln \sigma_{dc} = \ln \sigma_0 - \frac{E_a}{kT} \quad (1)$$

The increase of dc conductivity between 348 K to 363 K can be related to segmental movement as a result of increasing temperature. However, the electrical conductivity increases linearly after 38 K as perfectly detected for another system.

Figure 12: DC conductivity for doping polymer blend films with different temperatures.

Figure 13 shows the relation between $\ln \sigma$ and $1/KT$ (eV) (equation 1) from where activation energy of polymer blend films with different percent's of doping can be calculated from the slope of the straight line. It was found that the values of activation energy decrease with the increase of the ratios of doping for all ratios except that of (0.12%) doping where the activation energy increases with the increase in doping ratio. So, it is concluded that the ratio (0.09%) is the best appropriate one for doping. The results of activation energies $E_a$ is listed in the Table (2).
Figure 13: The relationship between $\ln \sigma_{dc}$ and $1/kT$ for polymer blend films with different ratio.

Table 2: Activation energies for doping polymer blend films with different doping ratio.

| Doping ratio % | $E_a$  |
|---------------|--------|
| 0.00          | 0.48   |
| 0.03          | 0.40   |
| 0.05          | 0.37   |
| 0.07          | 0.34   |
| 0.09          | 0.31   |
| 0.12          | 0.42   |

4 Conclusion

The prepared biodegradable polymer blends were interconnected with the flavonoid extract of Hibiscus Sabdariffa L. plant. by hydrogen bonding as a Physical coherence. Temperature dependence of conductivity of doped polymer blend films with different ratios of flavonoid suggests a transition from insulator nature to semiconductor nature with increase in temperature. The conductivity is increase with increasing the ratio of flavonoid as the temperature increase the conductivity is increase too in a behavior similar to the semiconducting materials. This make possibility of preparation biodegradable semiconductor it can be decomposed after a period of time and thus it is possible to reduce the occurrence of pollution in the environment.

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