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Improving the Physical Properties of Polyvinyl Alcohol (PVA)-Melanin Doping

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Abstract

Polyvinyl alcohol (PVA) is an artificial polymer that used in many medical applications but it has a few disadvantages that can overcome by the addition of certain chemical compounds. The present study aimed to investigate the efficacy of melanin to improve the properties of biopolymer PVA. Doping may reinforce the PVA electrical, optical and mechanical properties. In the present work, dielectric relaxation and spectrophotometric techniques were used to characterize the biopolymer PVA doped melanin of different concentration. Increase melanin concentration cause reduction of both dielectric constant and relaxation times accompanied with increased in conductivity. Moreover, a small shift in Fourier Transform Infrared Spectroscopy (FTIR) of PVA with increasing the melanin concentration may be related to the increase OH. In conclusion melanin doping could improve the medical and the electronic industries applications of PVA.

Key words: PVA, melanin, electrical conductivity, dielectric constant, FTIR.

1. Introduction

Polyvinyl alcohol (PVA) as a biopolymer has many industrial, commercial, pharmaceutical and biomedical applications. That is due to its unique chemical and mechanical properties (e.g. water soluble, non-toxic, easy to form, whitish, tasteless,..) [1-5]. Adding varies dopant components to PVA allow gaining many mechanical, optical and electrical properties as a bio-combatable [2,3,6-12].

AC conductivity, dielectric constant, and dielectric loss of PVA/ cashew gum/ magnetite were found to be higher than those of the blend [13]. Moreover, succinic acid and silver nanoparticles doping enhance the dielectric properties of PVA [14,15].

Abdelaziz and Ghannam [16] found out that the addition of titanium chloride influences the optical and the dielectric properties of PVA films. Increasing the dopant level may cause decrease in the impedance due to the high degree of amorphization in the structures as well as decrease in relaxation time which may be due to increase in mobility of ions in the polymeric matrix.

ON the other hand, melanin is a well-known biopolymer that is widely distributed in most living organisms. Playing an important rules as photo-protection, metal ion chelation, antibiotic, anti-inflammatory, thermoregulation, free radical scavenging and some involvement in nervous system. The degree of melanin hydration influences the PVA electrical conductivity. A behavior can be used in electronic industries and medical applications such as synthetic muscle, heart surgery, an electrode of medical devices, smart skin and cartilage replacement or cartilage transplantation in clinical operation [17-19].

This work aimed to study the effect and benefit of PVA doped melanin to improve its electrical and optical properties.

2. Materials and Methods

2.1 Preparation of PVA solution

Thirty grams (30g) of PVA powder slowly added to 1L of cold water to avoid the formation of lumps. Mixture heated at 70 ºC and stirred thoroughly with a magnetic stirrer for 4h to obtain a homogenous mixture with a concentration of 30 mg/ml. The

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molecular weight PVA used in this study is approximately 30000 (fully hydrolyzed).

2.2 Preparation of Nigella Sativa L. melanin

The extraction and characterization of melanin from Nigella Sativa L. (black cumin seed) are prepared as described previously [18]. Briefly, the seed coats of Nigella sativa L. were solubilized in an alkaline solution of NaOH (pH 12.5) for 3 h, which yielded a dark brown solution. The solution was then centrifuged and filtered and melanin was precipitated from it at pH 2 using conc. HCl. The precipitate was thoroughly washed with distilled water, filtered out, dried at 80 ^{o}C and used to prepare solutions at pH 7 for biological studies by re-dissolving the desired amount of melanin powder (in w/w ratio) in NaOH solutions (at pH 12.5) and using conc. HCl to adjust the pH to 7. In this work, 50 mg of the dry powder was used to get a melanin stock solution of 1mg/ml.

2.3 PVA with melanin preparation

PVA Solutions of constant concentration (30 mg/ml) doped melanin were prepared with several different weight percent ratios of 100: (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.5, 2.0, 3.0, and 4.0) which is illustrated in table 1. All prepared samples stirred thoroughly with a magnetic stirrer for 12h to obtain a homogenous mixture. In details, a stock solution of melanin was prepared to get a net concentration of 1mg/ml and a stock solution of PVA was prepared to get a net concentration of 30mg/ml as explained in materials and methods section. Table 1 represent the preparation of Mel: PVA percentage ratios.

Table 1:The preparation of Mel: PVA percentage ratios.

N.	PVA Vol (ml) (30mg/ ml)	Total PVA weight (mg)	Mel. Vol (ml) 1mg/ml)	Total Mel. weigh t (mg)	Mel/ PVA W/W (%)
1	100	3000	0	0	0.0
2	80	2400	5	5	0.2
3	80	2400	10	10	0.4
4	80	2400	15	15	0.6
5	80	2400	20	20	0.8
6	80	2400	25	25	1.0
7	80	2400	30	30	1.2
8	70	2100	32	32	1.5
9	50	1500	47	47	3.0
10	50	1500	64	64	4.0

2.4 Electrical Parameter Measurement

The electrical measurements were taken at room temperature in the frequency range from 20Hz–3MHz with a WYANE precision component analyzer device, model 6440 B (UK). The electrical cell used is composed of two platinum black electrodes used to form a parallel plate capacitor with cell constant 1cm^{-1}. For a dielectric material placed between two parallel plates capacitor, the measured values of the capacitance, C and resistance, R as a function of the applied frequency, were used to calculate the electric filed (E) , dielectric constant (έ), dielectric loss (ε"), conductivity(σ) loss tangent (tanδ, D) and relaxation time (τ) using the following equations: [16, 20,21]. $E = \frac{\sigma}{\varepsilon'} = \frac{V}{d}$, $\acute{\varepsilon} = Cd/\varepsilon_o A$, $\varepsilon'' = \acute{\varepsilon} \tan\delta$, and $\sigma = G\,(d/A) = d/RA$ where d is the cell inter electrode distance (m), A is the electrode area (m^2), so d/A is the cell constant in which for our cell, G is the conductance (Ω^{-1}), ε_o is the permittivity of free space and $\tan\delta = 1/2\pi fRC$.

2.5 FTIR spectroscopy

The Fourier transform infrared spectroscopy (FTIR) used to detect structures (functional group) of a sample PVA-Mel solution using Thermo-Scientific Nicolet 6700 in the range 4000-400 cm^{-1} to stretch or bend the vibration of the peak of particles. The wave's number at the peak indicates the function of the group.

3. Results and Discussion

The conductivity $(\Omega m)^{-1}$of all samples as a function of frequency is shown in figure1. Conductivity at saturation region for all studied samples are summarized in table2. It clear from the figure1 and table (2) how the conductivity of PVA increased with the concentration of melanin (wt. %) due to the carrier charges (ions) are increased. The findings agree with data obtained previously [22].

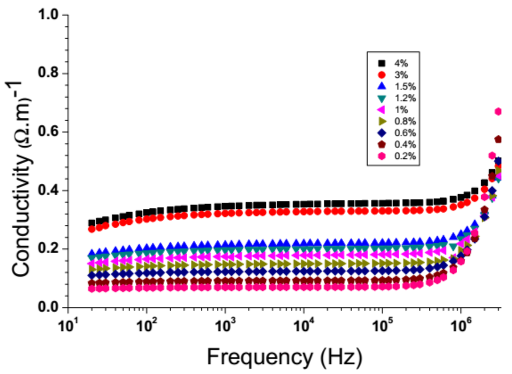

Fig.1 Conductivity of melanin 1mg/ml, pure PVA 30mg/ml and PVA doped with melanin of different concentrations.

Figure 2 shows electric filed (V/m) as a function of frequency, the electric filed increasing with increasing of capacity (F).

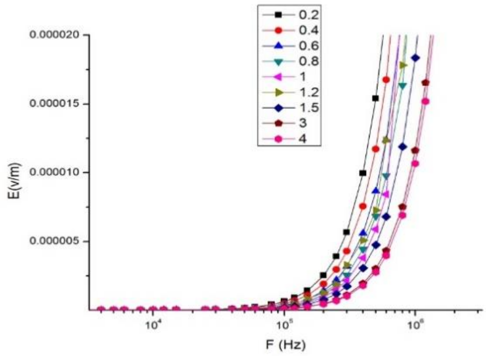

Fig.2 Electric field of PVA doped with melanin of different concentrations

Figure 3 shows the dielectric constant of PVA-Mel with different concentration. The presented dielectric data indicates that PVA-Mel systems have a strong dielectric dispersion corresponding to the alpha relaxation region in the frequency range used which identified as anomalous frequency dispersion. A rapid decrease in the dielectric constant may be attributed to the tendency of dipoles to orient themselves in the direction of the applied field in the low-frequency range. The loss tangent D of PVA-Mel with different concentration is represented in figure 4. It is noticed that, loss tangent D increased with low frequency therefore dropped toward high frequency. At low frequency, dipoles can arrange themselves according to the electric field direction before it changes direction causing increased polarization and increasing the dielectric constant and loss. At high frequency, there was no extra charge diffusion in the direction of the electric field due to the field changing so quickly that there was no time for charges to arrange. Increase or decrease of dielectric constant and loss was related to the increasing or decreasing polarization. Polarization results in accumulation of charge diffusion in the direction of the field. A decrease of charge accumulation diffusing in the direction of the filed decreased the polarization [11, 22-23]. The peak for PVA shown in figure 4 shifts toward higher frequency with doping with different concentrations of melanin. With a higher concentration of PVA-Melanin, the value of loss energy (tanδ) decreased as frequency increased [22]. Abdelaziz and Ghannam [16] reported that dielectric constant continuously decreases with increasing frequency and reaches a constant value at high frequency. For higher doped samples the value of tanδ decreased as frequency increased. Relaxation times were found to decrease with increase of titanium content. Polarization due to charge accumulation decreased, leading to decrease in the loss factor. Relaxation times decreases with an increase of melanin content. and a data are summarized in table 2 and represented in figure 5 a,b.

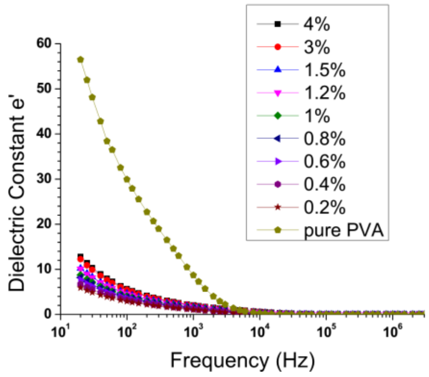

Fig.3 Dielectric constant of melanin 1mg/ml, pure PVA 30mg/ml and PVA doped with melanin of different concentrations.

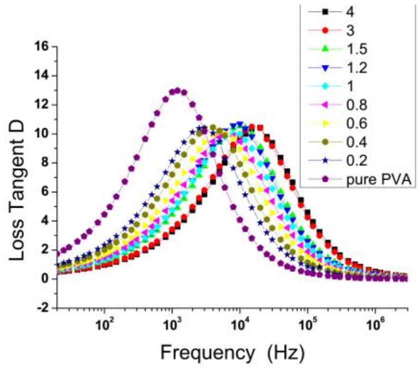

Fig.4 Loss tangent D of melanin 1mg/ml, pure PVA 30mg/ml and PVA doped with melanin of different concentrations.

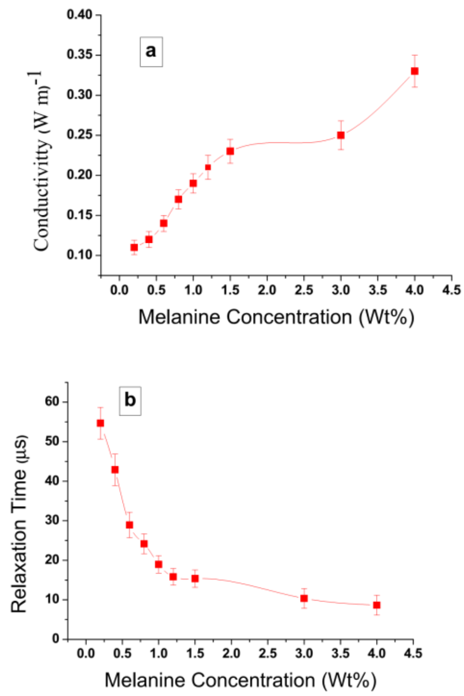

Fig.5 a) Melanin Conductivity at saturation as a function of melanin concentrations
b) Relaxation Time as a function of melanin concentrations

Table 2 :Conductivity$(\Omega m)^{-1}$ and relaxation time as a function of melanin concentration (wt.%)

Melanine Concentration (Wt %)	Conductivity $((\Omega m)^{-1}$	Relaxation Time (μs)
0.2	0.11±0.009	54.68±4.0
0.4	0.12±0.010	42.88±4.0
0.6	0.14±0.010	28.94±3.2
0.8	0.17±0.012	24.16±2.5
1.0	0.19±0.012	18.95±2.2
1.2	0.21±0.015	15.82±2.1
1.5	0.23±0.015	15.36±2.2
3.0	0.33±0.018	10.36±2.5
4.0	0.35± 0.020	08.65±2.5

*Values are means ± SEM.

FTIR of all studied samples show two bands, 3256.07 and 1635.01 cm^{-1} . The 3256.07 cm^{-1} band of pure melanin of 10 mg/ml (Fig 6) indicated to OH or NH stretching vibration modes of carboxylic acid, and phenolic and the second in 1635.01cm^{-1} indicated to Stretching vibration of symmetric of C=C aromatic ring or stretching of C=N with strong intensity and sharp peak and C=O double bond (COOH) of carboxylic function. The vibration from 500-400cm^{-1}indicated to C-Cl aromatic which was a very weak vibration of C-C. FTIR of pure PVA of 30 mg/ml (Fig 7) shows broadband in 3307.06cm^{-1}indicated to OH stretching vibration of hydroxyl groups and is sharp with 1638.87cm^{-1}indicated to stretching vibration of C-C or C=O group which bonding with the OH. The higher intensity for PVA solution is due to the formation of strong hydrogen bonds between oxygen and hydrogen atoms.

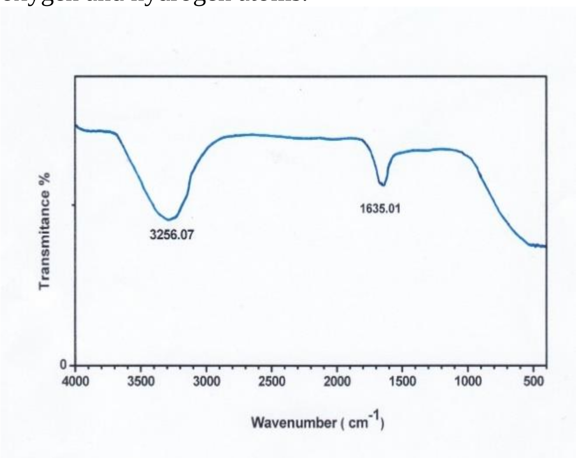

Fig. 6 FTIR of pure melanin 10mg/ml

Effects of PVA: Melanin is shown in figure (7). FTIR of pure PVA is similar to PVA: Melanin shape curves because PVA joined with melanin by H-bonding without any chemical interaction. Stretching bond OH of PVA is shifted from 3307 to 3288.82, 3270.86, 3303.03, 3301.29, 3266.37, 3268.24, 3274.63, 3323.75, 3294.18 cm^{-1} The second peak at 1638.87$cm^{-1}$of PVA shown in figure (7) shift to 1635.30, 1634.91, 1635.41, 1638.71, 1635.20, 1636.71, 1634.95, 1633.70, 1635.06, 1635.58 cm^{-1} which indicated to C=N and C=C or C-C groups. Band at 455 cm^{-1} is shifted to 472, 460.66, 472, 437, 438.43, 503.80, 487, and 449.89 cm^{-1}. OH bonding of PVA reducing with added melanin into the structure of PVA, increasing OH of melanin caused destroy order of PVA chains. A Small position reflects the concentration change of melanin. This result is an agreement with Wang et al. [23] and Hao and Wen [11]. The change in the spectra reflects the change in the concentration of carboxylic groups not bonded to metals ions [24-26].

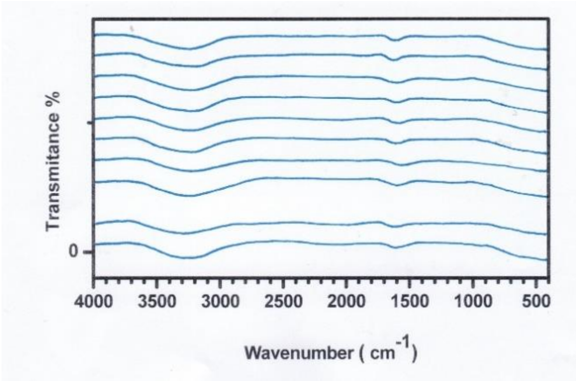

Fig.7 FTIR of PVA: Mel for different melanin concentration (Pure PVA) 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.5, 3.0, 4.0 (Wt.%)

4. Conclusions:

The presented study highlight the dopant effect of melanin on the electrical and optical behaviour of PVA polymer properties. That effects are confirmed by the conductivity measurement which is increased with increasing concentration of melanin due to the increasing of the carrier charge that diffused through the polymer. The Reduction of dielectric constant of pure PVA after doping with melanin causes increased electrical conductivity systems. This behaviour can be used in electronic industries and medical applications such as synthetic muscle, synthetic heart surgery, an electrode of medical devices, smart skin and cartilage replacement or cartilage transplantation in clinical operation. Finally, decreasing polarization leads to a reduction of dielectric constant, dielectric loss, and loss tangent.

5. Statistical data analysis

Data analysis was carried out with the software package, Microsoft Excel, Version 2010 and origin software, version 8.1(Northampton, Massachusetts, USA). Results are expressed as mean ± standard error.

6. Conflicts of interest

There are no conflicts to declare.

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