Biological bioactive film of the propolis: morphological, optical and electrical properties

Film bioactif biologique de la propolis : propriétés morphologiques, optiques et électriques

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ABSTRACT. A large number of biological materials have outstanding environmental and technical properties. Propolis is a biological and bioactive honeybees product. We performed investigations on the microstructural, optical, and electrical properties of the propolis films. A stable, bioactive, green, and low-cost thin layers of this biocompatible material were produced. Transmittance spectrum shows that propolis film is opaque for blue and ultraviolet (UV) radiations which are responsible of the food oxidation, nutrient losses, flavor degradation, and discoloration. Propolis film reveals an energy gap of 2.88 eV at room temperature, which enables optoelectronic applications in the UV and blue ranges. The electrical study shows that the propolis film has semiconductor behavior. At low frequency range, a large variation of the conductance (10^{-8} - 10^{-5} S) was observed for a small variation of temperature (292 - 348 K). Therefore, the propolis film exhibits potential applications as a safe negative temperature coefficient sensor in bioelectronics.

RESUME. Un grand nombre de matériaux biologiques ont des propriétés environnementales et techniques exceptionnelles. La propolis est un produit biologique et bioactif pour les abeilles. Nous avons étudié les propriétés microstructurales, optiques et électriques des films de propolis. Des couches minces stables, bioactives, vertes et peu coûteuses de ce matériau biocompatible ont été produites. Le spectre de transmission montre que le film de propolis est opaque pour les rayons bleus et ultraviolets (UV) qui sont responsables de l’oxydation des aliments, des pertes de nutriments, de la dégradation de la saveur et de la décoloration. Le film de propolis révèle un écart d’énergie de 2,88 eV à température ambiante, ce qui permet des applications optoélectroniques dans les gammes UV et bleu. L’étude électrique montre que le film de propolis a un comportement semi-conducteur. Dans la gamme des basses fréquences, une grande variation de la conductance (10-8 - 10-5 S) a été observée pour une petite variation de température (292 - 348 K). Par conséquent, le film de propolis présente des applications potentielles en tant que capteur de coefficient de température négatif sûr en bioélectronique.

KEYWORDS. Biomaterials, Propolis, Thin films, Optical properties, Electrical properties, Bioelectronics, Organic semiconductors.

MOTS-CLÉS. Biomatériaux, Propolis, Couches minces, Propriétés optiques, Propriétés électriques, Bioélectronique, Semi-conducteurs organiques.

1. Introduction

Several biological materials have amazing environmental and technical properties [RIN 01], [OKA 98], [MUR 93], [ARK 96], [HAL 96], [AL-H 18]. Such properties should be studied and optimized in the goal to raise the potential of these green materials for technical applications and for a healthier environment [MOR 14], [AZE 09], [GUI 05]. Biological materials show fast optical and electrical response [TAK 91], [SIM 90]. They have intense optical absorption and emission coefficients. Furthermore, they have mixed electronic and ionic charge carriers [FAH 19]. As well, organic materials show semiconductor behavior. Nevertheless, if exposed to the air, no insulating oxide forms on their surface. The technical advances in organic light-emitting diodes [BUR 90], [BLO 98], [UOY 12] have opened up new perspectives for the organic photovoltaic cell sector. Even if their performance is not efficient enough, they enjoy a low production cost [HOP 04], [MEN 18].

Among these biological materials, we find the bioactive propolis substance (PS). It is produced by honeybees. They use it to seal cracks in their hive, disinfect their honeycomb, or mummify intruders. PS is a biologically active material used in a large number of drugs and it has a complex chemical composition. More than 300 active compounds have been found in the raw propolis [VIU 08]. PS is composed of resins (50%), wax (30%), essential oils (10%), pollen (5%), and other organic compounds (5%). We find phenolic and polyphenolic compounds, esters, flavonoids, terpenes, beta-steroids, aromatic aldehydes, sugars (fructose, glucose) and alcohols. In ancient Egypt, PS was used for embalming the dead. PS possesses antiviral, antifungal, antibacterial, anti-inflammatory, antioxidant, antitumor (cytotoxic), anesthetic, immune-stimulating, wound healing, and antiulcerogenic properties [WAG 13]. The integration of PS in polymers and natural rubbers, protects them from the degradation, prevents a rapid decrease in their lifetimes, and gives them a high potential for food and medical applications [ULL 19]. We find a great deal of research on pharmaceutical, medical, and food industry application of PS. However, there are few studies on the electrical and optical properties of PS. Drapak *et al.* created a heterojunction between indium monoselenide and Ukrainian PS [DRA 03]. The electrical properties of this heterojunction have been studied and the p-type semiconductor behavior of the PS has been deduced. Ukrainian propolis films were produced and the optical properties of these films have been investigated in the wavelength ranges $\lambda = 350$ - 1000 nm and $\lambda = 2750$ - 3500 nm [DRA 04], [DRA 07], [DRA 06]. An optical energy gap $E_g \approx 3.07$ eV was deduced from the absorption spectra and confirmed by the photoluminescence spectra at 2.86 eV. Ukrainian PS films reveal high optical absorption in near infrared (NIR) and ultraviolet (UV) regions.

In summary, little research exists in the literature on the physical properties and potential technical applications of the PS films as a pure material or as a blend with other materials. To fill this lack of data and unravel the electrical and optical properties of PS, we undertook this study of PS thin films.

In this paper we present a detailed study of the morphological, optical, and electrical properties of propolis thin films and we highlight their potential technical applications.

2. Experimental

The raw PS was produced by Apis mellifera bee specie on the island of Djerba in Tunisia. We used ethanol (99.9% vol.) as a solvent for the PS extract solution. Amorphous glass and quartz substrates were used for the optical characterization, whereas tin oxide (SnO_2) substrates was used for electric characterization.

The ethanolic extract solution was obtained by the maceration of 10 grams of raw PS in 30 ml of the solvent at room temperature ranging between 20-25 °C during 7 days. The obtained solution is very stable. We used drop-casting technique to prepare PS films; a few drops of the ethanolic extract solution were cast on the heated substrates (80 °C) until the alcohol completely evaporated. The produced PS thin film show good performance stability.

The optical study was done by *Shimadzu UV-3101 PC* spectrophotometer. Electrical results were carried out using an *Agilent 4294 A* impedance analyzer. Surface morphology of the PS films was investigated by *XE-100 (Park Systems Corporation)* atomic force microscope (AFM) in a non-contact mode (NC-AFM).

3. Results and discussion

3.1. *Morphological properties*

The atomic force microscopy (AFM) topography of our PS thin film sample is displayed on the Figure1. The PS sample surface appears dense, well covered, and without cracks or other defects. This is an important observation, as a defect-free surface is often crucial for an electronics or biomedicine application. Small peaks appear on the sample surface. The root mean square (RMS) roughness value was calculated of an area of 100 μm^2 of the PS. It is found to be around 11 nm. This low RMS roughness value indicates that the surface of the PS film is smooth and adequate for optical applications.

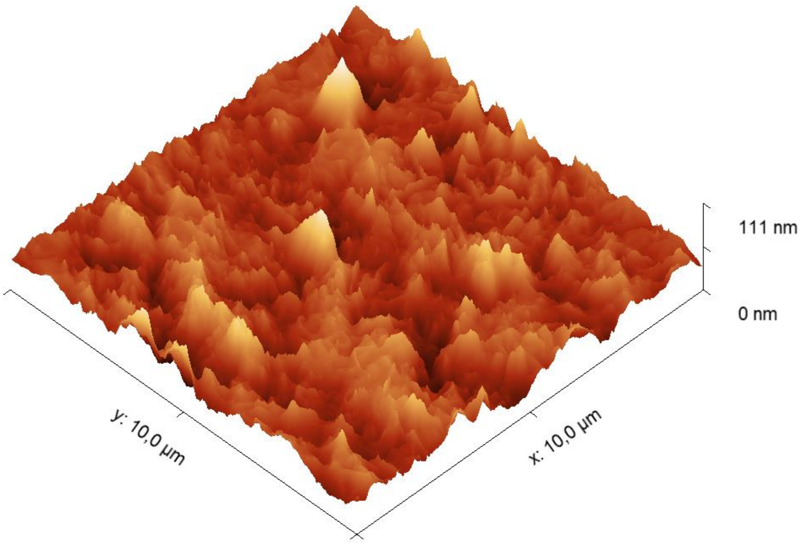

Figure 1. *AFM image of the PS film*

3.2. *Optical properties*

The optical properties were studied using UV-Visible-NIR spectroscopy. Figure 2 shows the transmittance spectrum of the PS film.

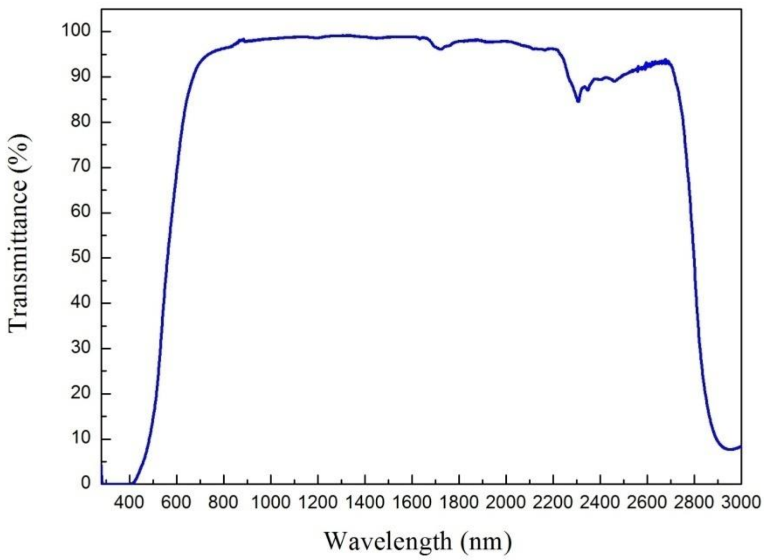

Figure 2. *Transmission spectrum of PS film*

The PS film is opaque for UV radiation and the blue components of visible light (wavelength $\lambda <$ 500 nm). Therefore, the PS film can be used as a UV barrier and a blue light filter. One of the most promising applications of this film is in food packaging, as PS film is a biological, healthy and eco-friendly product, to prevent food deterioration, since UV radiation induce oxidation of foods, leading to nutrient loss, degradation of flavors, and discoloration. Kim *et al.* claimed that propolis reveals protective effects against skin aging induced by UV-light [KIM 20] which is in agreement with our findings. For green and yellow light (~500 - 600 nm), PS film displays high absorption and the absorption coefficient abruptly changes. This rapid tendency corresponds to a fundamental absorption edge, typical of semiconductor behavior, which provides insight into the limit of the gap energy. On the other hand, for red and near infrared radiation (~ 600 - 2700 nm), PS film is transparent with a transmittance exceeding 95%. This makes it an excellent candidate for a wide range of optical applications, including high-quality optical lenses, which require materials with high transparency to transmit light without significant loss. Furthermore, it is suitable for the production of optical sensors, where high sensitivity and accuracy depend on the transparency of the material to the desired wavelengths of light. Moreover, in the 2700-3200 nm wavelength range, absorption increases sharply and PS films reveal significant photosensitivity and can be used as photosensors. Therefore, the PS film seems like a band-pass filter. Overall, the PS film's excellent transparency and optical properties make it a versatile and valuable material for numerous optical applications.

The transmission spectrum (Figure 2) reveals rapid absorption variation at low wavelength which corresponds to an energy gap E_g. This energy gap E_g was determined from the $(\alpha d h\nu)^2$ versus photon energy ($h\nu$) plot displayed on Figure 3 (typical of direct optical transition), where α is the absorption coefficient, d the film thickness, and h is Planck's constant. The estimated PS film energy gap is $E_g \approx 2.88$ eV at room temperature (~300 K). These results are in good agreement with the experimental findings of Drapak *et al.* [DRA 04], [DRA 07], [DRA 06] carried out from transmittance (3.07 eV) and photoluminescence spectra (2.86 eV) of Ukrainian propolis films.

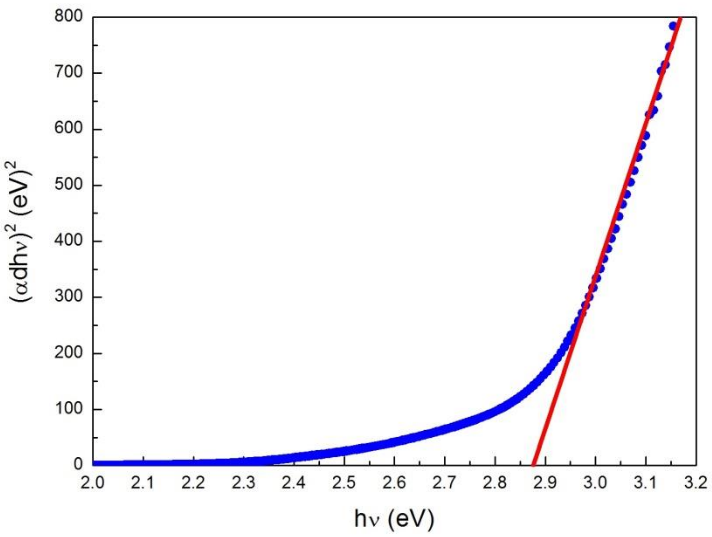

Figure 3. *Energy gap estimation, experiment (full circles) and extrapolation of absorption edge (full line)*

In the light of these optical results for the PS film, this biological and bioactive material presents numerous potential applications in short wavelength optoelectronics (photodetectors, light-emitting diodes operating in blue and UV ranges,...) and in transparent electronics.

3.3. *Electrical properties*

The structure displayed on the Figure 4 was used to investigate the electrical properties of PS film. This structure is composed of amorphous glass substrate, tin oxide layer (transparent conducting oxide TOC), PS film, and silver layer. SnO_2 and silver layer were used as ohmic contacts.

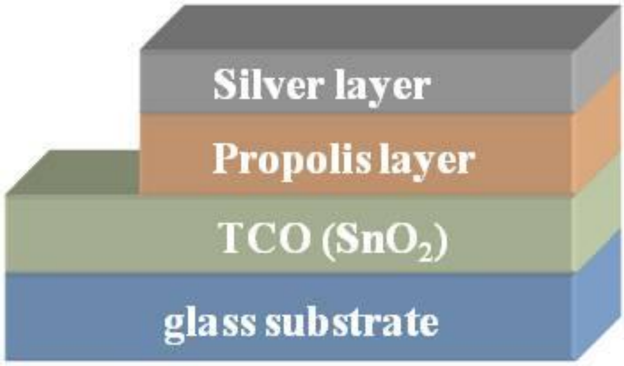

Figure 4. *Schematic illustration of the electrical investigation cell*

3.3.1. *Electrical conductance*

Electrical conductance is an important physical quantity in materials characterization. In this electrical study, the AC complex impedance spectroscopy was carried out for a large frequency range (40 Hz to 10 MHz), at different temperatures (292-348 K), and in ambient air. Figure 5 displays AC conductance versus frequency *(f)* at different PS film temperatures (*T*). At low frequency band, the conductance is approximately constant and represented by a plateau. However, at higher frequencies, we observe a dependent frequency region. We notice that the electrical conductance increases with the temperature, so does with the frequency, this is a sign of semiconductor behavior. We observe a significant variation of the conductance (10^{-8}-10^{-5} S) for a relatively small variation of temperature (292-348 K) at low frequency range. So, PS film can have a potential application in a safe biocompatible negative temperature coefficient sensor, in current-limiting device, and in thermal threshold control in bioelectronics. Especially since these latter properties are observed at temperatures quite close to room temperature and to human body temperature. Therefore, PS film can be a potential bioactive layer in future medical thermometers.

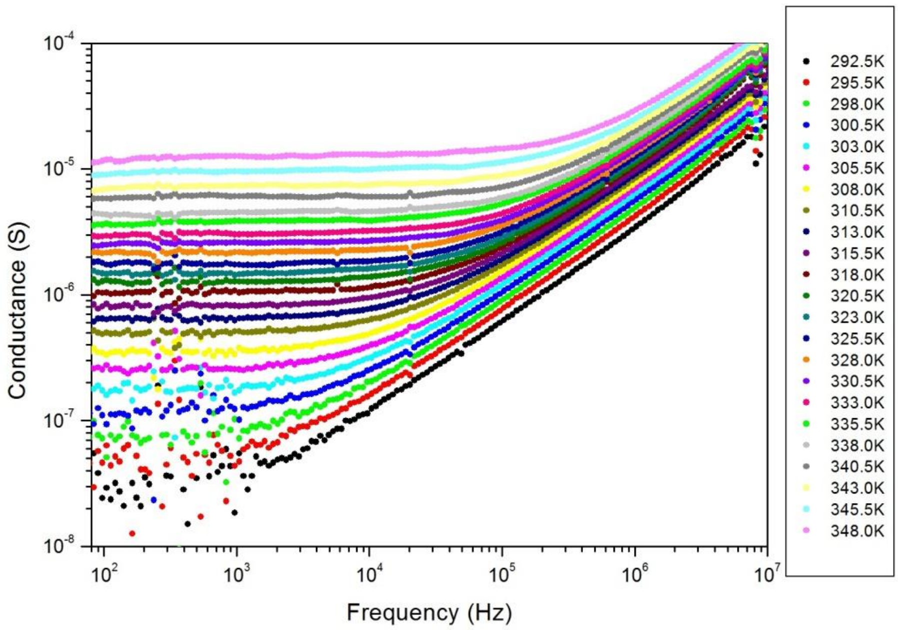

Figure 5. *AC conductance versus frequency at several temperatures of the propolis film*

We carried out the "DC" regime conductance (frequency-independent conductance G_{DC}) from the low frequency plateau. Figure 6 shows the G_{DC} evolution as a function of 1000/T in an Arrhenius plot. In this figure, three linear slopes appear. These linear curves reveal thermally activated processes. Therefore, G_{DC} can be represented by an Arrhenius behavior [MOT 79]:

$$G_{DC} = Aexp(-\frac{E_a}{K_B T}) \quad [1]$$

where A is a pre-exponential factor, E_a is the thermal activation energy, K_B is the Boltzmann constant, and T stand for the PC film absolute temperature. The three slopes give three activation energy values summarized in the Table 1 and displayed in Figure 6. These different activation energies correspond probably to several emission centers of charge carrier and represent a priori a clue to the coexistence of various conduction mechanisms and charge carriers. The same activation energy has been obtained using other physical quantities [MEZ 22].

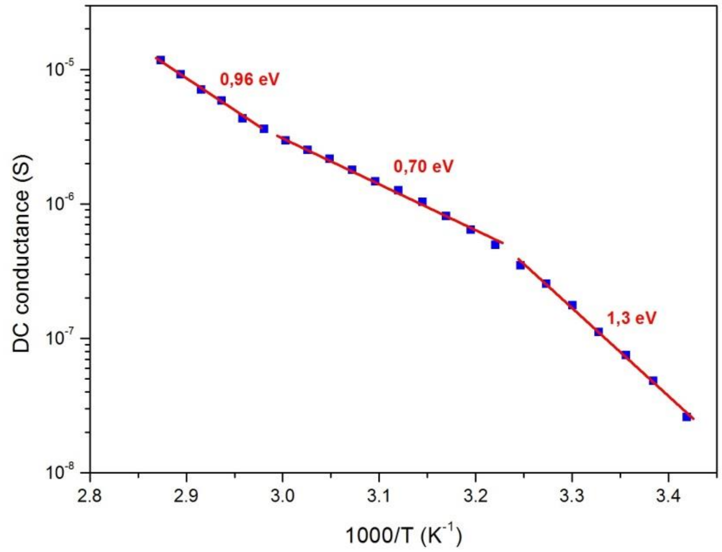

Figure 6. *Measured DC conductance (full squares) versus 1000/T and its linear fit (full lines) with the activation energy values*

Temperature range (K)	E_a (eV)
292-309	1.30±0.03
309-334	0.70±0.02
334-348	0.96±0.03

Tableau 1. *Activation energies (EA) obtained from Arrhenius plot of G_{DC}, with the corresponding temperature ranges*

3.3.2. *Electrical impedance*

The real part Z' and imaginary part Z'' of the complex impedance Z of the PS thin film were carried out for a large frequency range (40 Hz to 10 MHz), at several temperatures (292-348 K), and in ambient air.

$$Z(\omega) = Z'(\omega) + jZ''(\omega) \qquad [2]$$

where $j^2 = -1$; ω is the angular frequency. The real part Z' stand for the resistance to the current flow, and the imaginary part Z" represents the opposition to voltage or current flow fluctuations (capacitive and inductive effect).

Z' measurements are displayed in Figure 7 for different frequencies and temperatures. Z' decreases with the increase of the frequency and the temperature. This observation confirms that PS films behave like semiconductors.

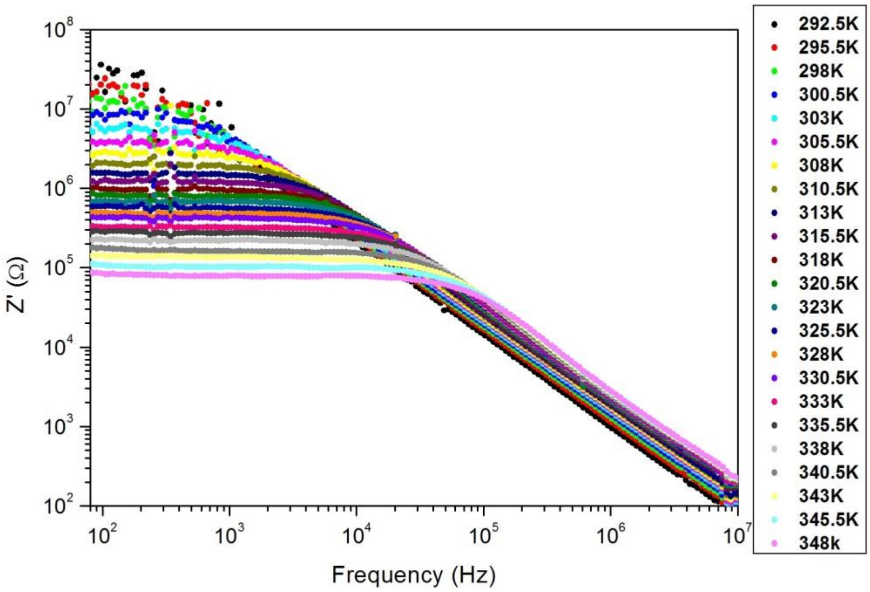

Figure 7. *The impedance real part (Z') of PS film as a function of the frequency for different temperatures*

The variation of the imaginary part Z'' as a function of frequency is displayed in Figure 8 for different temperatures. Z" spectra exhibit peaks at specific frequencies f_r, which confirms the presence of polarization phenomena. These peaks correspond to the relaxation frequencies for different temperatures. As shown in Figure 8, the relaxation frequency increases with the temperature, which is due to the enhancement of charge carriers mobility. We observe that the peak height decreases with temperature which is a sign of the decrease of the resistive properties [LI 12]. These results confirm once more the semiconductor behavior of the PS layer. The relaxation time τ_r associated to the f_r frequency is given by:

$$\tau_r = \frac{1}{2\pi f_r} \quad [3]$$

However, at high frequencies , Z" decreases sharply and merges for all sample temperatures. At high frequency, the period of the electrical signal becomes smaller and smaller compared to the relaxation time. Thereby, the polarization phenomena vanishes at high frequency.

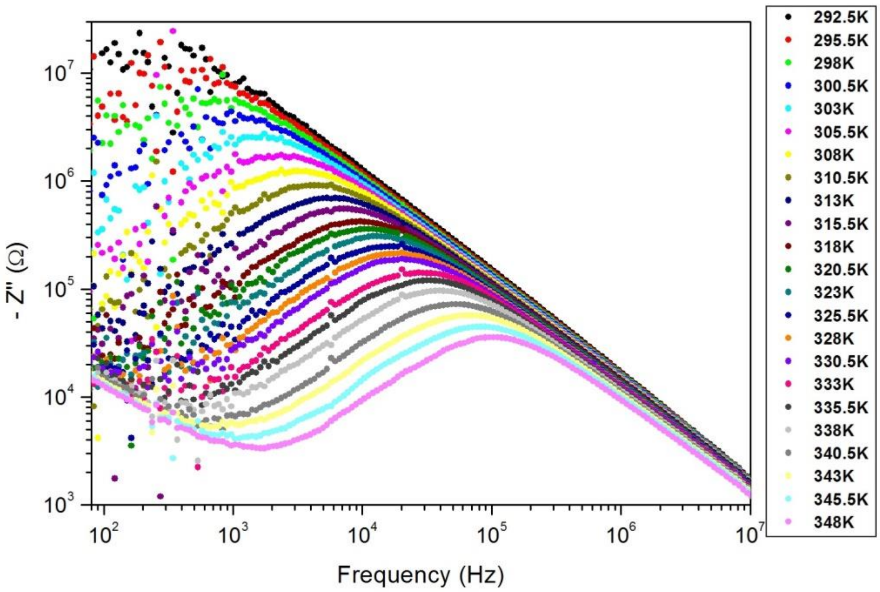

Figure 8. *The impedance imaginary part (Z") of PS film as a function of the frequency for different temperatures*

Figure 9 displays Nyquist diagrams (-Z" versus Z') of the PS layer at different temperatures. All the experimental curves display a single semicircle. The skewed circular arcs have their centers below the real axis. This trend is representative of a deviation from the ideal Debye type behavior and confirms the presence of a non-Debye relaxation phenomenon. This non-ideal behavior can be attributed to several sources such as the presence of many charge carrier types, different trap types, different conduction paths, etc. Furthermore, the semicircles radius decreases with the increase of temperature. Consequently, this confirms that PS film has a negative temperature coefficient resistance behavior. This tendency also demonstrates that conduction processes are thermally activated and that PS film has semiconductor properties. At low temperatures below 298 K, we observe a linear response of Z" in logarithmic scale. This indicates that the relaxation time is relatively large and therefore a highly insulating behavior of PS film at low temperatures. Therefore, the electric properties of the PS film have to be described by a modified Debye model [JON 74], [JON 74a], [JON 75b] in which the adequate equivalent circuit is a parallel set of a pure resistance (R) and a constant phase element (CPE) as shown in the insert of Figure 9. The CPE has been introduced to improve the experimental impedance spectra fitting by the equivalent electrical circuit models and it is defined as a frequency-dependent capacitance [JON 74], [JON 74a], [JON 75b].

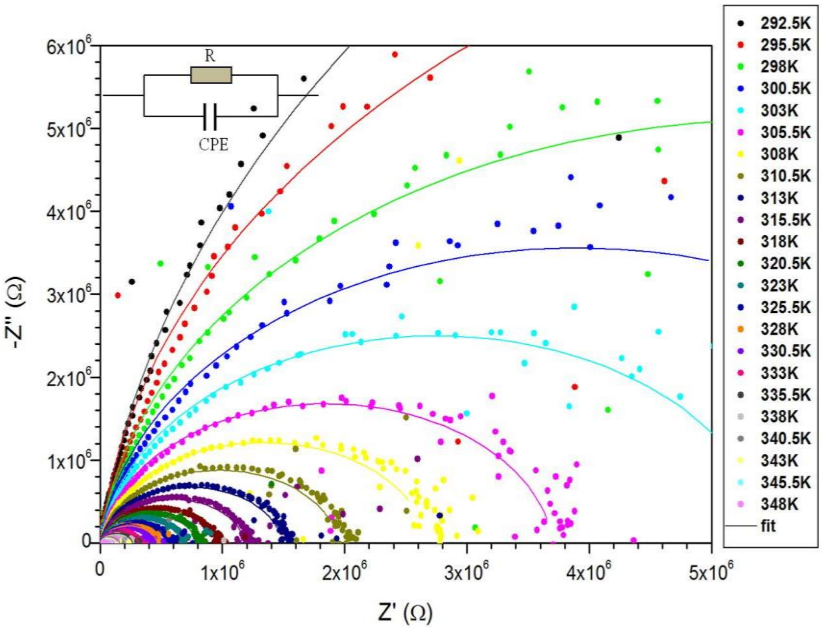

Figure 9. *Nyquist plot at different temperatures of PS film. Full lines are the fitting curves using the inserted equivalent electric circuit*

As shown in Figure 9, the Nyquist diagrams are well adjusted by the electrical equivalent circuit (R-CPE), which proves that the electrical equivalent circuit R-CPE parallel set represents a suitable model and perfectly fits the electrical properties of the propolis layer.

Figure 10 displays the capacitance of the electrical capacitive cell as a function of frequency at different PS film temperatures. This cell is made up of two electrodes, one in silver and the other in SnO_2, separated by a propolis film as the dielectric layer (see Figure. 4). At high frequency band, the capacitance is approximately constant and represented by a plateau. However, at low frequencies, we observe a dependent frequency region and high capacitance values. This relaxation phenomena is probably due to the electrical orientation polarization of the polar hydroxyl groups of phenolic and polyphenolic compounds present in the PS film. Orientation polarization exhibits high resonance for frequency less than almost 1 kHz - 1 MHz, which is in agreement with our capacitance spectrum. Consequently, PS thin layer can be used as a high performance dielectric layer in capacitors.

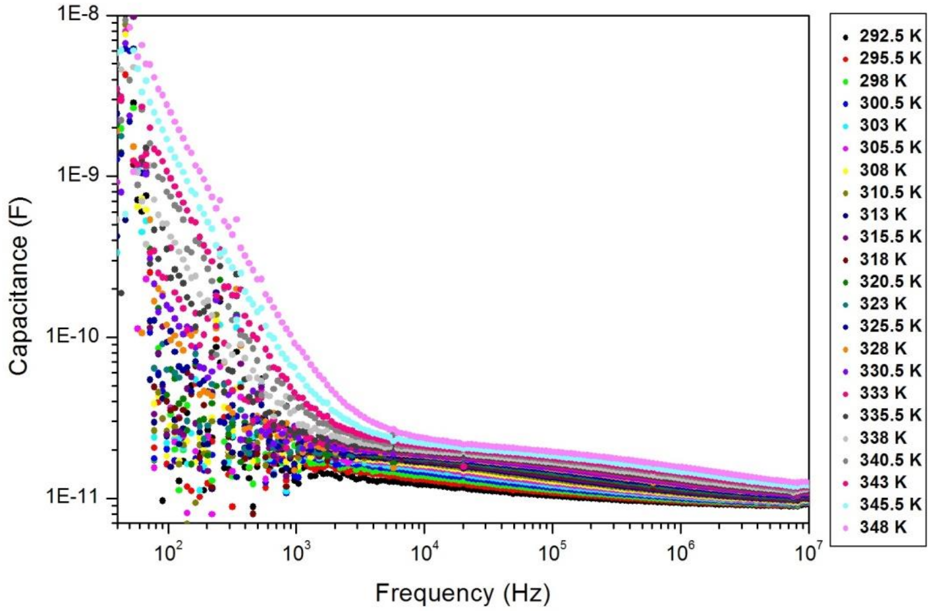

Figure 10. *The capacitance of the electrical capacitive cell as a function of frequency at several PS film temperatures.*

3. Conclusion

The morphological, optical, and electrical properties of the biological bioactive propolis film were studied. The drop-casting technique was used to produce the propolis films. The raw propolis was produced by Apis mellifera bee specie on the island of Djerba in Tunisia. We made-up a stable, bioactive, green, and low-cost thin films of PS.

The PS thin films is dense, without pinholes or cracks, smooth, and well cover the substrates surfaces.

The optical study shows that the PS film is opaque to UV radiation and to the blue components of visible light. UV radiation induces food oxidation and leads to nutrient losses, flavor degradation, and discoloration. Therefore, PS film can be used in food packaging to prevent food deterioration. For green and yellow light (~500 - 600 nm), the absorption coefficient abruptly changes. However, for red and near-infrared radiation (~ 600 - 2700 nm), PS film presents high transparency (> 95%). PS film reveals significant photosensitivity between near-infrared and mid-infrared wavelengths (~-2700 - 3200 nm) and thus can be used as a photosensor. An energy gap $E_g \approx 2.88$ eV was estimated, which, in principle, allows optoelectronic applications.

We studied the electrical properties of the PS film by complex impedance spectroscopy for a large frequency range (40 Hz to 10 MHz), at different temperatures (292-348 K), and in ambient air. The electrical conductance of PS film increases with temperature and with frequency, which is an evidence of semiconductor behavior. Thus, PS film can have a potential application in a safe biocompatible negative temperature coefficient sensor and in thermal threshold control in bioelectronics. A non-Debye relaxation phenomenon has been demonstrated .

In addition to its interesting applications in pharmaceutical, medical, and food industries, the green and bioactive film of propolis seems to be a promising candidate for food packaging, transparent electronics, optoelectronics, biocompatible temperature sensors, and bioelectronics.

Acknowledgment

This work is funded by the Tunisian Ministry of High Education and Scientific Research through the budget allowed to the implied Tunisian lab.

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