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Thermal and EPR Study of DNA – Based Membranes

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The present paper focuses on the results obtained from impedance spectroscopy, thermal analysis (DSC and DMA) and electron paramagnetic resonance (EPR) of membranes of DNA plasticized with glycerol and containing either poly(ethylene dioxythiophene) (PEDOT) or Prussian Blue (PB) and copper perchlorate ($CuClO_4$). The ionic conductivity values for the DNA-PEDOT-$CuClO_4$ and DNA-PB-$CuClO_4$ of 4.8×10^{-4} S/cm and 2.2×10^{-4} S/cm at 30 °C, respectively, were obtained. The DSC analysis of the samples showed two glass transition temperatures at about -80 and 50 °C and DMA a permanent deformation above 50 °C ascribed to a transition between elastic and plastic states. The EPR spectra evidenced that Cu^{2+} ions are in tetragonally distorted octahedral sites and the quantitative analysis of the EPR spin Hamiltonian $g_{\|}$ and $A_{\|}$ parameters revealed copper ions complexed by nitrogen and oxygen atoms. All these results suggest that DNA-biomembranes are interesting materials to be used in materials engineering science.

1. INTRODUCTION

The bio-materials are known ever since, but only recently a growing interest to study the natural macromolecules as potential materials for not only food

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industries [1, 2] and medical applications but also for opto-electronic devices is observed [3, 4]. In this context the biological systems and biologically important molecules, such as polysaccharides [3, 5], gelatin [6] and DNA are also investigated [7, 8]. It was already showed that the natural macromolecules are very interesting materials as charge injection interlayers for light emitting diodes [8] or ionic conducting membranes on substitution of liquid electrolytes in electrochemical devices as batteries, solar cells or electrochromic devices [9]. For such purpose, different polysaccharides and their derivatives [10-12], proteins [6, 13] and DNA [4, 14, 15] are investigated.

Among the natural polymers' membranes [9, 16, 17] DNA started to be investigated because of its high availability, as this polymer can be easily obtained from fish industry waste [18]. DNA is a water soluble natural macromolecule, which in solution forms polycations due to the phosphate group presence, i.e., forming a polyelectrolyte. Moreover, DNAs' biodegradability, non-toxicity, absorption and electrical properties led to its investigation for opto-electronic applications as, for example, field-effect transistors [19], solar cells [20] or optical wave guides [21] among others. Additionally, DNA biopolymers are also studied for endocrine disruptors [22], organic compounds [23] and Cu^{2+}, Ag^{+}, and Zn^{2+} removal [24].

Water and organic solvent soluble DNA can be blended with other polymers [25] or small organic and inorganic compatible molecule as glycerol and/or Prussian Blue (PB) [26]. To improve ionic conductivity inorganic salts as $LiClO_4$ or $LiCF_3SO_3$ are added. However, aiming to understand the natural polymers-based systems, especially the phenomena of metal-DNA interaction and/or metal coordination in DNA-based membranes copper perchlorate ($CuClO_4$) is added. Electronic Paramagnetic Resonance Technique (EPR) can then visualize the paramagnetic copper ions, when there are in the sample in small amount and the ions are spaced each other.

EPR is a sensitive spectroscopic technique for the study of local coordination environment of paramagnetic centers in a variety of liquids, gels and solid–state systems [27]. The EPR parameters, such as the electronic g tensor, and the hyperfine coupling constants spectroscopy can provide valuable information concerning the local environment of paramagnetic center and on the properties of the ligands. Recently, we have employed EPR spectroscopy in the study of chitosan bio-membranes with proton conductivity properties [28]. The knowledge of the interaction of metal ions with DNA can help to optimize adsorbent properties of this macromolecule. From another hand, copper is a transition metal of importance in many catalytic and biological systems and the EPR studies using Cu^{2+} ion as probe is appropriate for the understanding of magnetic properties and the local symmetry of copper incorporated in DNA bio-membranes. Thus, this technique can contribute to the natural macromolecules wastewater treatment understanding.

Dielectric properties in solids has been a subject of intense studies in physics domain since the 18th century [29], and can be used to obtain the ionic conductivity values of the samples [30]. Thermal analysis are important for possible practical applications where the informations, such as thermal transitions, degradations and thermal stability can be obtained.

In the present work, ionic conductivity, DSC and DMA thermal transitions in DNA-based membranes were analyzed. EPR experiments were carried out in samples doped with copper perchlorate in order to investigate the coordination environment of the metal cation in the sample. The spin-Hamiltonian parameters (**g**-tensor and hyperfine coupling constants) and the covalency bonding parameter of the copper ion were estimated from the EPR spectra.

2. EXPERIMENTAL

The DNA-based samples were prepared by dispersing 0.6 g of DNA in 100 mL of distilled water (Milli-Q) under stirring and without heating for 72 h [31]. The membranes were prepared by adding 2 wt% of either PEDOT/PSS or 0.3 wt% of PB, 0.001 M $CuClO_4$ and 1.25 g of glycerol under stirring. The final solution was poured into a Petri plate and dried at room temperature. The resulting transparent and freestanding membranes with thickness of 72-80 μm were stored in a dissecator to avoid the air humidity.

The impedance measurements were performed by sandwiching the 1.54 cm^2 round and about 5 μm thick membranes between two mirror-polished stainless-steel 304 electrodes [6]. The measurements were performed in vacuum using a home-made Teflon® sample holder and Solartron SI 1260 Impedance/Gain Phase Analyzer coupled to a computer. The frequency range was of 10^7 to 0.1 Hz with amplitude of 5 mV and temperature range from 303 K to 373 K controlled by an EDG 5P oven.

DSC measurements were performed with TA Instruments DSC-Q20 in the temperature range from – 120 to 120 °C with a heating rate of 10 °C/min. The thermal transitions were determined using Dynamical Mechanical Analysis (DMA) in the temperature range of -120 to 50 °C utilizing a TA Instruments DMA Q800 with deformation rate of 5 °C/min under N_2 atmosphere. EPR spectra at 9.5 GHz (X-band) were obtained with a Bruker Elexsys E580 spectrometer equipped with Oxford cryogenic system.

3. RESULTS AND DISCUSSION

The electrical impedance of the studied samples was measured as a function of temperature in order to analyze the ionic conductivity values and dielectric properties of the samples. The Nyquist plots used to obtain ionic conductivity values of the two types of DNA-based samples doped with $CuClO_4$ in two temperatures are shown in Fig. 1. As can be seen in Fig. 1, region of semicircle at high frequencies (Fig. 1 inset) in the complex plane

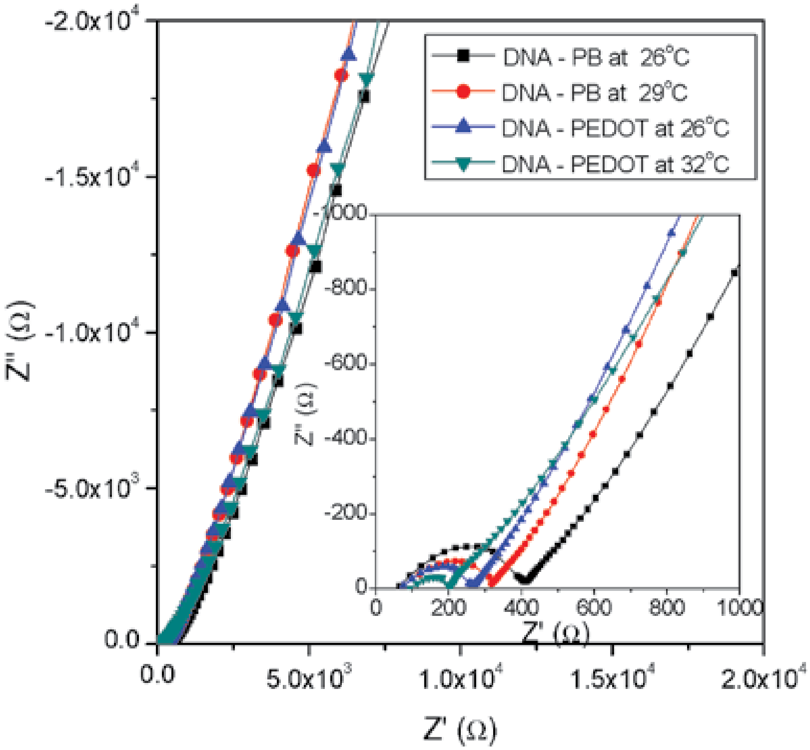

FIGURE 1
Nyquist plot of the DNA-PEDOT-$CuClO_4$ at 26 °C (▲) and at 32 °C (▼); DNA-PB-$CuClO_4$ at 26 °C (■) and at 29 °C (●).

corresponding to the electrolyte resistance display a small difference between these two samples revealing little lower real resistance for the samples containing PEDOT. As the samples contain only very small quantity of salt this difference can be due to the conducting properties of PEDOT. Moreover, all the samples showed a decrease in the semicircle with the increase of temperature from 26 to ~30 °C. The increase of ionic conductivity of the samples with increase of the temperature can be explained in terms of thermal movement of polymer chain segments and the dissociation of salt. These results are very similar to the results obtained with other DNA- [25] and pectin-based samples [5].

The electrolyte bulk resistance (R_b) was obtained from the intercept of the semicircle with the Nyquist plot Z' axis. Then, the *dc* ionic conductivity was deduced from the R_b values by employing the formula $\sigma = l/R_bA$, where l was the thickness of the electrolyte sample and A was the contact area between the electrolyte and the electrode. The ionic conductivity values of the DNA-PEDOT-$CuClO_4$ sample were of 2.7×10^{-4} S/cm at 26 °C and increased to 4.8×10^{-4} S/cm

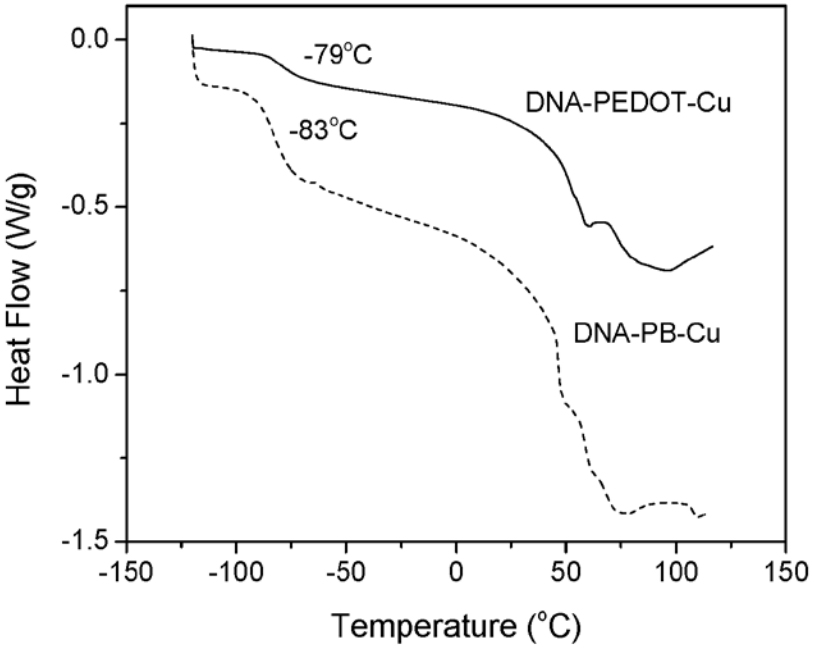

FIGURE 2
DSC curves of the DNA-PEDOT-CuClO$_4$ (——) and DNA-PB-CuClO$_4$ (-----).

at 32 °C. The sample of DNA-PB-CuClO$_4$ showed comparable ionic conductivity values of 1.5×10^{-4} at 26 °C and 2.2×10^{-4} S/cm at 29 °C.

Differential Scanning Calorimetry (DSC) was performed in order to observe the transition temperatures of the samples. From Fig. 2, for the DNA-based membranes with 0.001 M of CuClO$_4$, two thermal transition temperatures can be observed in the temperature range studied. The first one marked as change of the baseline is characteristic to the second order transition occurring at -79 and -83 °C for the sample of DNA-PEDOT-CuClO$_4$ and DNA-PB-CuClO$_4$, respectively. This transition can be attributed to glass transition temperature, Tg, which frequently occurs at low temperatures and could be related to the glycerol or to the movement of molecules and polymers side chains [32]. The second transition starts above 25 °C and is marked with second baseline change at about 50 °C. As in other studies [26], this transition at ~50 °C can be related with double to single stranded DNA, which is usually assigned to occur in the temperature range of 30 to 80 °C [33]. In both samples, a start of an endothermic feature, which can be attributed to the melting of crystalline phase followed by a degradation process of the samples or added PEDOT [34], can be observed.

Aiming to verify the thermal transitions and to obtain information about mechanical properties, the samples of DNA-based membranes have been subjected to DMA measurements in the temperature range from -120 to 60 °C and

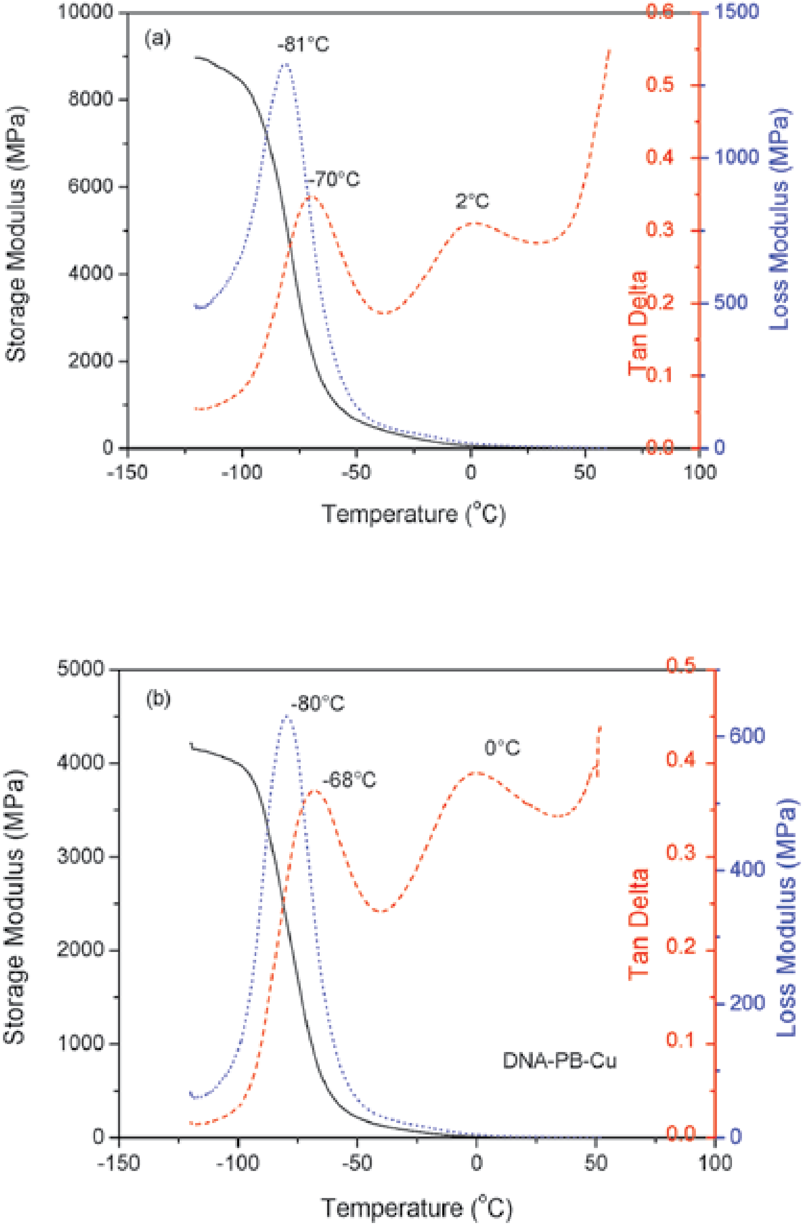

FIGURE 3
DMA curves of the DNA-PEDOT-$CuClO_4$ (a) and DNA-PB-$CuClO_4$ (b). Storage modulus (—), loss modulus (·····) and tan δ (----).

data are shown in Fig. 3. As seen from Fig. 3, the storage modulus of the DNA-PEDOT-$CuClO_4$ sample (Fig. 3a) is about twice than those of the DNA-PB-

$CuClO_4$ sample (Fig. 3b) in the temperature below -100 °C. As the difference between both samples is electrochromic additive, i.e., PEDOT or PB this difference should be due to the additive. An increase of the temperature promotes a decrease of the storage modulus at about -100 °C reaching zero at 0 °C. At the same time, the loss modulus of both samples starts to increase reaching the maximum at -81 °C for DNA-PEDOT-$CuClO_4$ and -80 °C for DNA-PB-$CuClO_4$. The curves of tan δ (red lines in Fig. 3) are in agreement with G' results. From this analysis, one can observe two maxima at -70 and 2 °C for DNA-PEDOT-$CuClO_4$, and at -68 and 0 °C for DNA-PB-$CuClO_4$. The lowest transition temperature is attributed to the glass transition temperature as already observed in DSC analysis (Fig. 2) and the transitions at ~0 °C can be due to the melting of water absorbed by the glycerol-containing system. Above 50 °C the tan δ starts to increase continually until the loss of response. The visual analysis of the samples revealed a permanent deformation; thus, above this temperature a transition between elastic and plastic behavior is observed.

Comparing the results obtained by DSC and DMA for DNA-PEDOT-$CuClO_4$ and DNA-PB-$CuClO_4$ one can observe 8 and 15 °C differences, respectively between the first glass transition temperatures. Aiming to investigate the nature of this difference the sample of DNA-PEDOT-$CuClO_4$ was subjected to cooling-heating-cooling cycle and the storage modulus, loss modulus and tan δ were recorded. The results of this analysis are shown in Fig. 4, where one can observe an increase of the Tg value from -68 to -80 °C on heating-cooling cycle between -120 and -40 °C. This hysteresis with

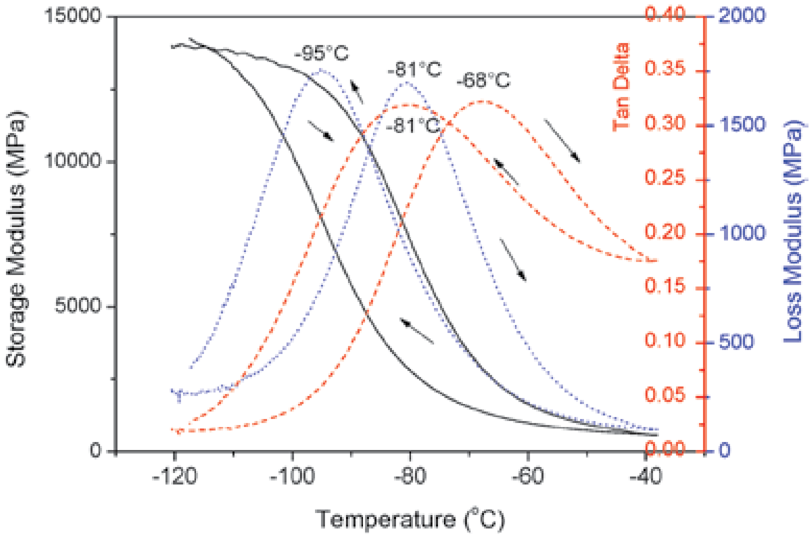

FIGURE 4
DMA curves of the DNA-PEDOT-$CuClO_4$ during heating-cooling cycle. Storage modulus (——), loss modulus (·····) and tan δ (----).

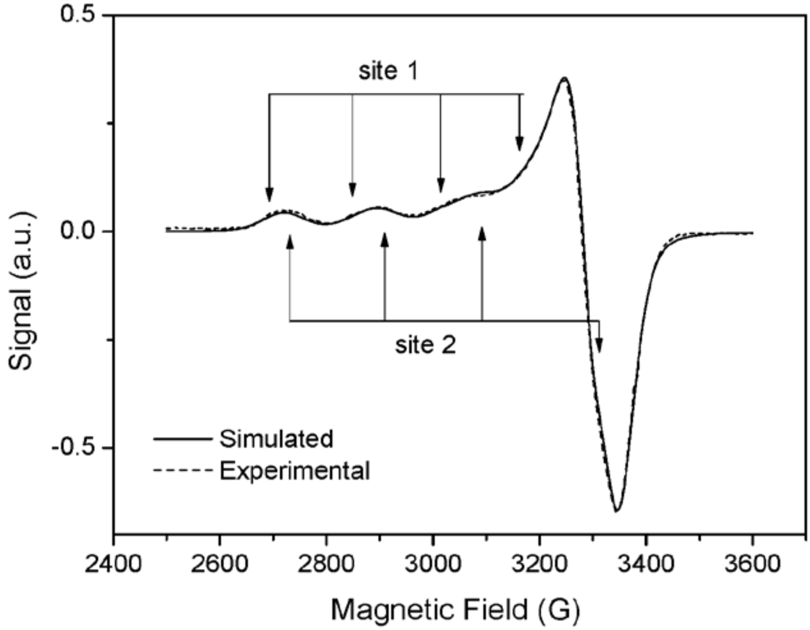

FIGURE 5
Experimental and simulated EPR spectrum of DNA-PEDOT-$CuClO_4$ membrane. The parallel hyperfine peak positions of both Cu^{2+} species are presented in the figure.

12 °C difference can be due to the slow macromolecular arrangements as well as glycerol resulting in lowering of glass transition after second cooling process.

Figs. 5 and 6 show the X-band EPR spectra measured at 50 K of DNA-PEDOT-$CuClO_4$ and DNA-PB-$CuClO_4$ bio-membranes doped with copper perchlorate. No EPR signal was observed in the spectra of undoped bio-membranes indicating that no paramagnetic impurities were present in the starting materials. When copper ions are introduced into the bio-membranes all the investigated samples exhibit resonance signals. The Cu^{2+} ion has a $3d^9$ electronic configuration and spin $S = ½$. The nuclear spin for for the ^{63}Cu (natural abundance 69 %) and ^{65}Cu (natural abundance 31 %) isotopes is $I = 3/2$. Therefore, four perpendicular and four parallel hyperfine components could be expected. These hyperfine structures result from the dipole-dipole interaction between the magnetic moment of the nucleus and the electronic moment of the paramagnetic ion. These spectra are well resolved and indicate the presence of isolated monomeric Cu^{2+} ions distributed over the bio-membranes. Superhyperfine structure due to the interaction of the nuclear spin of the ^{14}N ($I = 1$) with the unpaired electron of Cu^{2+} are not observed. The spectra in Fig. 5 and 6 are similar to those previously reported for chitosan bio-

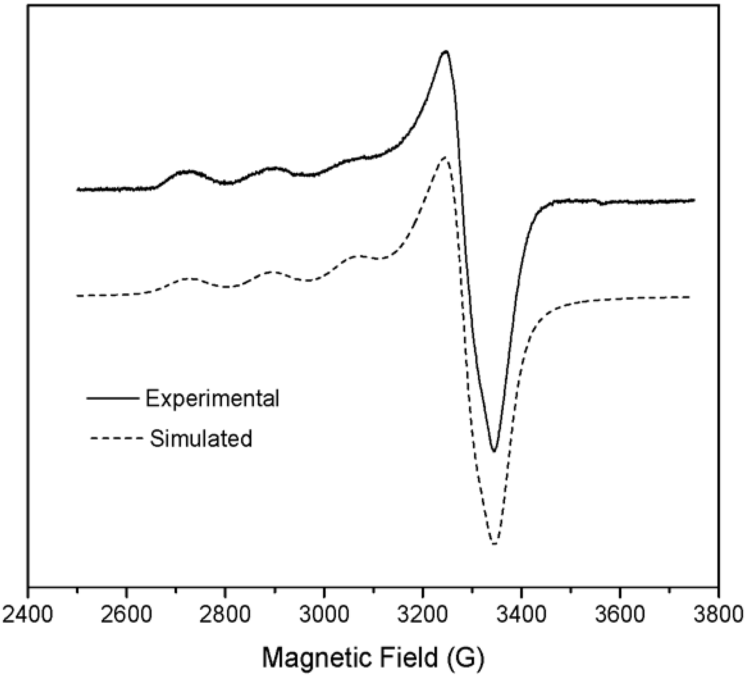

FIGURE 6
Experimental and simulated EPR spectra of the DNA-PB-$CuClO_4$ membrane.

membranes doped with $Cu(ClO_4)_2$ [28] and are typical of paramagnetic Cu^{2+} ions in axially distorted sites. An axial spin Hamiltonian, which includes the hyperfine interaction has been used to describe the EPR spectra.

$$H = g_{//}\beta H_Z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{//} I_z S_z + A_{\perp}(I_x S_x + I_y S_y)$$

where z is the tetragonal symmetry axis; $g_{||}$ and $g_{\perp}$ are the parallel and perpendicular components of the anisotropic g tensor, $A_{||}$ and $A_{\perp}$ are the parallel and perpendicular hyperfine components of the hyperfine tensor A; and the other symbols have their usual meaning [28]. The experimental Cu^{2+} EPR spectra were analyzed by numerical simulation of the spin Hamiltonian. A closer examination of the line shape in the parallel region of the DNA-PEDOT-$CuClO_4$ bio-membrane reveals that the experimental spectrum is a superposition of two spectral components corresponding to two different copper species. The spin Hamiltonian parameters, deduced from the simulated spectra are collected in Table 1.

Detailed quantitative information on the coordination environment of Cu^{2+} ions in the bio-membranes can be obtained by analyzing the EPR spin Hamiltonian parameters. The principal values of the g-tensor ($g_{//} > g^{\perp} > g_e$) indicate

Sample		%	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (10^{-4} cm^{-1})	$A_{\perp}$ (10^{-4} cm^{-1})	α
DNA – PEDOT	Site 1	50	2.308	2.064	191	15	0.84
	Site 2	50	2.267	2.068	210	15	0.84
DNA – PB			2.283	2.066	186	7.5	0.83

TABLE 1
Summary of the EPR spin Hamiltonian parameters and the bonding parameter *a* of Cu^{2+} in the DNA-PEDOT-$CuClO_4$ and the DNA-PB-$CuClO_4$ membranes.

the Cu^{2+} ions are co-ordinated by six ligands, which form an octahedron elongated along the z-axis, the ground state being the d_{x2-y2} orbital (B_{1g} state). The parameter *G*, which is a measure of the exchange interaction between the copper centers in the bio-membranes, can be calculated by using the expression apropriate for axial EPR spectra, $G = (g_{\parallel} - g_e)/(g_{\perp} - g_e)$, where $g_e = 2.0023$ is the free electron g value [35]. If $G < 4.0$, considerable exchange coupling is present in the complex; if it is greater than 4.0, exchange interaction is considerer negligible. Since the *G* values calculated for the DNA-PEDOT-$CuClO_4$ and DNA-PB-$CuClO_4$ bio-membranes by using the spin Hamiltonian parameters in Table 1 are whithin the range 4.0 – 5.0, exchange coupling effects are not significant in the studied samples. The empirical factor $f = g_{\parallel}/A_{\parallel}$ (cm), which is a measure of the tetrahedral distortion around the metal in tetragonally coordinated copper complexes [36], can also be calculated for our samples. The *f*-values of our samples are within the range 105-135 cm assigned for tetragonal structures, suggesting that this copper does not undergo a significant distortion when complexed in the DNA bio-membranes.

In order to discuss the nature of the copper ligand bonding in terms of the magnetic parameters, the bonding coefficients can be calculated by the molecular orbital theory approach [27]. According to this approach, the nature of the bonding is described in terms of the covalency parameter α^2, which describes the covalency of the in-plane s-bonding between a copper 3d orbital and ligand orbitals, quantifying the delocalized electronic density on the ligand atoms. Its value decreases with increasing covalency to a minimum value of $\alpha^2 = 0.5$ for a completely covalent copper-ligand bond, up to a maximum value of $\alpha^2 = 1.0$ for a completely ionic bond. The covalency parameter α^2 can be evaluated from the EPR spin Hamiltonian parameters by using the simplified expression [27, 28]

$$\alpha^2 = \frac{A_{II}}{P} + \left(g_{II} - 2\right) + \frac{3}{7}\left(g_{\perp} - 2\right) + 0.04, \tag{3}$$

where $P = 0.036$ cm^{-1} is the dipolar hyperfine coupling constant for free Cu^{2+}. The values of α^2 for the DNA bio-membranes studied here are in the range α^2

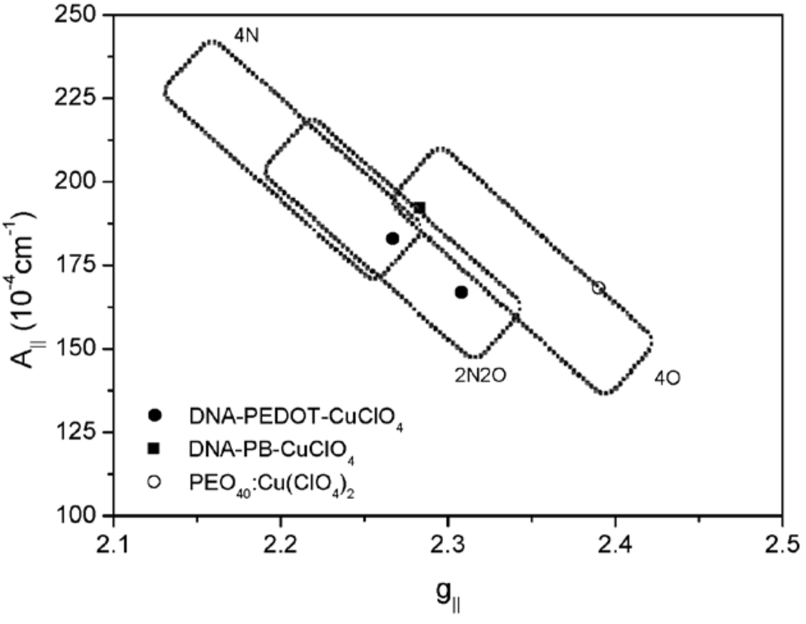

FIGURE 7
Correlation plot of $g_{||}$ and $A_{||}$ Cu^{2+} spin Hamiltonian parameters of the DNA-PEDOT-$CuClO_4$ (●) and the DNA-PB-$CuClO_4$ (■) membranes. The data of the polymer electrolyte PEO:$Cu(ClO_4)_2$ is also included (○). The areas represent the varying oxygen and nitrogen coordinations about Cu^{2+} centres according to Peisach and Blumberg.

= 0.83 - 0.84 (Table 1) indicating a moderate covalency for the *s*-bonding. These values are comparable to the $\alpha^2 = 0.86$ that we calculated from the EPR parameters reported for copper amino acid complexes bound to DNA fibers by Harada et al [37].

Finally, we used the empirical model originally suggested by Blumberg and Peisach to obtain quantitative information on the coordination environment of Cu^{2+} ions in the bio-membranes. When the EPR Cu^{2+} $g_{||}$ and $A_{||}$ parameters are plotted, a correlation can be found between these values and the nature of the equatorial coordinating atoms. Fig. 7 shows the so called Peisach-Blumberg plot for the bio-membranes samples using the $g_{||}$ and $A_{||}$ values from Table 1. The values ($g_{||} = 2.39$ and $A_{||} = 141\times10^{-4}$ cm^{-1}) of the poly(ethylene oxide)-based polymer electrolyte, PEO:$Cu(ClO_4)_2$ are also included in Fig. 7 [38]. As expected, the $g_{||}$ and $A_{||}$ parameters of the DNA bio-membranes fall within the specific region corresponding to the coordination of Cu^{2+} ions with nitrogen atoms and oxygen atoms, whereas those of the PEO:$Cu(ClO_4)_2$ fall in the region corresponding to copper ions coordinated only by oxygen atoms [27].

4. CONCLUSIONS

DNA-based membranes with $CuClO_4$ were obtained and characterized. The characteristic properties of the samples were examined by using DSC, DMA, EPR and the electrochemical impedance method. The impedance measurements revealed the ionic conductivity values for the DNA-PEDOT-$CuClO_4$ and DNA-PB-$CuClO_4$ of 4.8×10^{-4} S/cm and 2.2×10^{-4} S/cm at ~ 30 °C, respectively. The DSC results indicated two glass transition temperatures, the first one at about -80 °C probably due to the glycerol or to the movement of molecules and polymers side chains, and the second one at 50 °C related with double to single stranded DNA. The DMA analysis evidenced a permanent deformation above 50 °C that was ascribed to a transition between elastic and plastic states. The EPR experiments indicated that the Cu^{2+} ions are located in axially distorted sites and the analysis of the spin Hamiltonian parameters showed that the copper ions are coordinated to nitrogen and oxygen atoms. Moreover, the evaluation of the Cu^{2+} bonding parameter evidenced moderate covalency for the *s*-bonding for DNA-based bio-membranes. In summary, the presented results on the physical-chemical properties of the natural polymer membrane confirmed its possible application in bio-electrochemical devices.

5. ACKNOWLEDGEMENTS

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REFERENCES

[1] Pawlicka A., Grote J., Kajzar F., Rau I. and Silva M.M., Agar and DNA bio-membranes for electrochromic devices applications, *Nonlin. Optics Quant. Optics* 45, 113 (2012).

[2] Giavasis I., Harvey L.M. and McNeil B., Gellan gum, *Critical Reviews in Biotechnology* 20(3), 177 (2000).

[3] Nogi M. and Yano H., Transparent Nanocomposites Based on Cellulose Produced by Bacteria Offer Potential Innovation in the Electronics Device Industry, *Adv. Mater.* 20, 1849 (2008).

[4] Zhang Y., Zalar P., Kim C., Collins S., Bazan G.C. and Nguyen T.-Q., DNA Interlayers Enhance Charge Injection in Organic Field-Effect Transistors, *Adv. Mater.* 24(31), 4255 (2012).

[5] Andrade J.R., Raphael E. and Pawlicka A., Plasticized pectin-based gel electrolytes, *Electrochim. Acta* 54(26), 6479 (2009).

[6] Vieira D.F. and Pawlicka A., Optimization of performances of gelatin/LiBF4-based polymer electrolytes by plasticizing effects, *Electrochim. Acta* 55, 1489 (2010).

[7] Kawabe Y., Wang L., Horinouchi S. and Ogata N., Amplified spontaneous emission from fluorescent-dye-doped DNA-surfactant complex films, *Adv. Mater.* 12(17), 1281 (2000).

[8] Zalar P., Kamkar D., Naik R., Ouchen F., Grote J.G., Bazan G.C. and Nguyen T.Q., DNA Electron Injection Interlayers for Polymer Light-Emitting Diodes, *J. Am. Chem. Soc.* 133(29), 11010 (2011).

[9] Pawlicka A. and Donoso J.P., Polymer electrolytes based on natural polymers. In: Polymer Electrolytes: Properties and Applications. Sequeira C.A.C., Santos D.M.F. (Ed). Cambridge, Woodhead Publishing Limited, 95 (2010).

[10] Pawlicka A., Sabadini A.C., Raphael E. and Dragunski D.C., Ionic conductivity thermogravimetry measurements of starch-based polymeric electrolytes, *Mol. Cryst. Liq. Cryst.* 485, 804 (2008).

[11] Pawlicka A., Danczuk M., Wieczorek W. and Zygadlo-Monikowska E., Influence of plasticizer type on the properties of polymer electrolytes based on chitosan, *J. Phys. Chem. A* 112(38), 8888 (2008).

[12] Fuentes S., Retuert P.J. and Gonzalez G., Lithium ion conductivity of molecularly compatibilized chitosan–poly(aminopropyltriethoxysilane)–poly(ethylene oxide) nanocomposites, *Electrochim. Acta* 53, 1417 (2007).

[13] Vieira D.F., Avellaneda C.O. and Pawlicka A., Conductivity study of a gelatin-based polymer electrolyte, *Electrochim. Acta* 53(4), 1404 (2007).

[14] Leones R., Fernandes M., Sentanin F., Cesarino I., Lima J.F., Bermudez V.d.Z., Pawlicka A., Magon C.J., Donoso J.P. and Silva M.M., Ionically conducting Er3+-doped DNA-based biomembranes forelectrochromic devices, *Electrochim. Acta* 120, 327 (2014).

[15] Stadler P., Oppelt K., Singh T.B., Grote J.G., Schwodiauer R., Bauer S., Piglmayer-Brezina H., Bauerle D. and Sariciftci N.S., Organic field-effect transistors and memory elements using deoxyribonucleic acid (DNA) gate dielectric, *Organic Electronics* 8(6), 648 (2007).

[16] Arvanitoyannis I.S., Formation and properties of collagen and gelatin films and coatings. Boca Raton, CRC Press (2002).

[17] Gennadios A., Mchugh T.H., Weller C.L. and Krochta J.M., Edible coatings and films based on proteins. In: Edible coatings and films to improve food quality. Krochta J.M., Baldwin E.A., Nisperos-Carriedo M. (Ed). Lancaster, Technomic Pub. Co., 210 (1994).

[18] Singh T.B., Sariciftci N.S. and Grote J.G., Bio-Organic Optoelectronic Devices Using DNA, *Organic Electronics* 223, 189 (2010).

[19] Singh T.B., Sariciftci N.S. and Grote J.G., Bio-Organic Optoelectronic Devices Using DNA. In: Organic Electronics. 223, 189 (2010).

[20] Bandyopadhyay A., Ray A.K. and Sharma A.K., Use of DNA in the fabrication of solid state dye sensitized solar cells, *J. Appl. Phys.* 102(6) (2007).

[21] Yaney P.P., Heckman E.M., Diggs D.E., Hopkins F.K. and Grote J.G., Development of chemical sensors using polymer optical waveguides fabricated with DNA, *Organic Photonic Materials and Devices VII* 5724, 224 (2005).

[22] Zhao C.S., Shi L., Xie X.Y., Sun S.D., Liu X.D., Nomizu M. and Nishi N., DNA-modified polysulphone microspheres for endocrine disruptors and heavy metal ions removal, *Adsorption Science & Technology* 23(5), 387 (2005).

[23] Zhao C.S., Yang K.G., Liu X.D., Nomizu M. and Nishi N., DNA-immobilized porous polysulfone beads for organic compounds and heavy metal ion removal, *Desalination* 170(3), 263 (2004).

[24] Yang K.G., Zheng B.X., Li F., Wen X. and Zhao C.S., Preparation of DNA-encapsulated polyethersulfone hollow microspheres for organic compounds and heavy metal ions removal, *Desalination* 175(3), 297 (2005).

[25] Firmino A., Grote J.G., Kajzar F., M'Peko J.-C. and Pawlicka A., DNA-based ionic conducting membranes, *J. Appl. Phys.* 110, 033704 (2011).

[26] Pawlicka A., Sentanin F., Firmino A., Grote J.G., Kajzar F. and Rau I., Ionically conducting DNA-based membranes for eletrochromic devices, *Synth. Met.* 161(21-22), 2329 (2011).

[27] Pilbrow J.R., Transition Ion Electron Paramagnetic Resonance. Oxford, New York, Oxford University Press (1990).

[28] Pawlicka A., Mattos R.I., Tambelli C.E., Silva I.D.A., Magon C.J. and Donoso J.P., Magnetic resonance study of chitosan bio-membranes with proton conductivity properties, *J. Membrane Sci.* 429, 190 (2013).

[29] Jonscher A.K., Dielectric relaxation in solids, *Journal of Physics D-Applied Physics* 32(14), R57 (1999).

[30] Macdonald J.R., Impedance Spectroscopy, *Annals of Biomedical Engineering* 20, 289 (1992).

[31] Samoc A., Galewski Z., Samoc M. and Grote J.G., Prism coupler and microscopic investigations of DNA films, *SPIE* 6646, 664607 (2007).

[32] Angles M.N. and Dufresne A., Plasticized starch/tunicin whiskers nanocomposites. 1. Structural analysis, *Macromolecules* 33(22), 8344 (2000).

[33] Holbrook J.A., Capp M.W., Saecker R.M. and Record M.T., Enthalpy and heat capacity changes for formation of an oligomeric DNA duplex: Interpretation in terms of coupled processes of formation and association of single-stranded helices, *Biochemistry* 38(26), 8409 (1999).

[34] Kiebooms R., Aleshin A., Hutchison K., Wudl F. and Heeger A., Doped poly(3,4-ethylenedioxythiophene) films: Thermal, electromagnetical and morphological analysis, *Synth. Met.* 101(1-3), 436 (1999).

[35] Procter I.M., Hathaway B.J. and Nicholls P., The electronic Properties and Stereochemistry of Copper(2) Ion .I. Bis(Ethylenediamine)Copper(2) Complexes, *Journal of the Chemical Society a -Inorganic Physical Theoretical*10.1039/J19680001678 (7), 1678 (1968).

[36] Patel R.N., Shukla K.K., Singh A., Choudhary M., Chauhan U.K. and Dwivedi S., Copper(II) complexes as superoxide dismutase mimics: Synthesis, characterization, crystal structure and bioactivity of copper(II) complexes, *Inorg. Chim. Acta* 362(14), 4891 (2009).

[37] Harada W., Nojima T., Shibayama A., Ueda H., Shindo H. and Chikira M., How amino acids control the binding of Cu(II) ions to DNA .1. The role of the hydroxyl group of serine and threonine in fixing the orientation of the complexes, *Journal of Inorganic Biochemistry* 64(4), 273 (1996).

[38] Donoso J.P., Cavalcante M.G., Bonagamba T.J., Nascimento O.R. and Panepucci H., Magnetic-Resonance Study of Water-Absorption in Some Peg-Lithium Salt Polymer Electrolytes, *Electrochim. Acta* 40(13-14), 2357 (1995).