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Effects of temperature and humidity on DNA-based biopolymers

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Organic biopolymers such as deoxyribonucleic acid (DNA) and its compounds are attractive materials to be printed into thin films for fabrication of electro-chromic organic electronic devices. This work reports results on the electrical characterization of two DNA compounds obtained using two cationic surfactants cetyltrimethylammonium (CTMA) chloride and benzalkonium (BZK) chloride. The resulted materials are subjected to climatic stress, specifically increased temperature or humidity. Subsequently, the two compounds are doped with a red organic dye, which is known to also influence conductivity, and tested again under climatic stress. In this paper, the resistivity of DNA-CTMA, DNA-BZK, DNA-CTMA-DR and DNA-BZK-DR1, is assessed by current-voltage (I-V) measurements. It results that the four compounds are electrical insulators and that in the case of DNA-CTMA and DNA-CTMA-DR the electrical resistivity is influenced by the concentration of the surfactant. Moreover, the conductivity of the compounds increases significantly when exposed to high relative humidity, but the samples exhibit thermal stability at temperatures as high as 85 Celsius degress and the behavior to thermal stress exposure indicates an ionic conduction.

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1. Introduction

Organic insulators and semiconductors are very attractive for use in low cost electronic products that can be produced by various additive deposition techniques such as spin-coating or ink-jet printing, on large area and flexible substrates. These organic electronic devices cover a broad range of applications in electronics and photonics such as organic thin film transistors [1-3], OLEDs [4-6], memory elements [7], light amplifiers [8], electro-optic modulators and waveguides [9] or passive devices [10]. Organic dielectric materials are often solution-based and allow low-temperature processing steps. High permittivity, optical transparency and chemical compatibility with a large number of other materials are further advantages, reported in [2, 5].

DNA-based biopolymers exhibit distinct qualities compared to other polymers. Some of their advantages are low optical loss over a broad wavelength domain and the stability of the double helical structure at temperatures exceeding 100 Celsius degrees. Also, the fact they are natural biological materials means that they are not only bio-degradable, but also renewable.

The samples presented in this work are based on the compounds of the biomolecule, deoxyribonucleic acid (DNA). There are many surfactants that can be mixed with it, of which CTMA has been previously reported in literature [2-5], while BZK does not appear to have been used with DNA. In all cases, purified DNA is modified by a surfactant cation exchange reaction to enhance solubility, processing and stability [11].

The compounds obtained in this manner are subjected to the investigation of the electrical characteristics. The electrical conduction is not yet fully understood, but several conduction hypotheses have been reported, in order to explain the mechanisms that determine the transfer of charge within the DNA molecular chain.

Charge migration in DNA is an intensely studied subject [12-17], mainly because of the variety of potential applications and the possibility of combining DNA with many surfactants [18-21] and dyes [22-24] that allow its use in opto-electronic devices.

2. Experimental procedure

2.1 Materials

DNA has a double helix molecular structure made up of two nucleotide chains. Each pair of nitrogenous bases is about 0.34 nm apart from its neighbour bases [25]. The diameter of the double helix is approximately 2 nm and the length of the DNA molecule depends on the number of base pairs, having approximately a third of a nanometer per base pair.

Charge transfer occurring in short DNA molecules, as described in [26-29], is the process which stands at the basis of the electronic characteristics of DNA-compounds. The charge transfer is said to occur by either super-exchange or molecular band conduction, depending on the energy level of DNA. The donor and the acceptor molecules can be dyes or other molecules intercalated or covalently bonded to

DNA. Conduction is possible due to the formation of a band of π-stacked base pairs [15], which acts as a path for migration of charges.

In principle, charge transport in disordered materials, such as DNA and other polymers, is believed to be done through a hopping mechanism, which is a tunneling mechanism between two localized discrete states [30]. The type of the hopping mechanism depends on the energy gap that the charges have to overcome in order to jump from their lower energetic state, identified as the highest occupied molecular orbital (HOMO), to the unoccupied state, identified as the lowest unoccupied molecular orbital (LUMO). It must be noted that the transition of electric charges depends on the temperature and its effectiveness decreases with the length of the chain [27].

Moreover, given that the localized states in an unordered material are at different distances, the charges will select the easiest path, decided either by proximity or by reduced energy requirements. The charge transfer changes with the increase in temperature, which helps define the two aforementioned distinct hopping mechanisms, super-exchange and molecular band conduction. Molecular band conduction, similar to the nearest neighbor hopping mechanism, implies that at high enough temperature, the charges have enough energy to jump to the neighbor within the smallest distance. This ensures an improved conduction. As shown in Figure 1, this would imply the jump of electrons to an Adenine/Thymine (A/T) pair from a Guanine/Cytosine (G/C) pair.

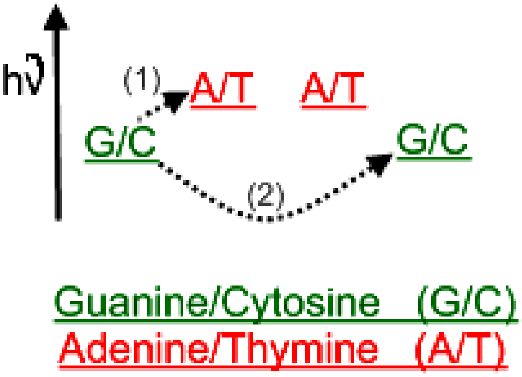

Fig. 1. Charge transfer in DNA by molecular band conduction (1) or super exchange (2)

On the other hand, if the temperature is not high enough, then the super-exchange mechanism is probable. This is similar to the variable range hopping mechanism [30]. In this case, the electrons do not have enough energy to jump to the LUMO level and hop to the next G/C pair, which is in the same energy band.

In this work, four DNA-based compounds have been synthesized. The compound, DNA-CTMA, can be obtained by precipitation of the purified DNA in water with a cationic surfactant complex. The cationic surfactant used is hexadecyltrimethylammonium chloride (CTMA) [31-33] and the resulting aggregate is obtained through an ion exchange reaction. By this process, the solubility of DNA is changed from water soluble to chemical soluble.

As described in [5], CTMA has a positive charge on the nitrogen, which is counter balanced by the negatively charged chlorine. Thus, mixing the DNA and CTMA aqueous solutions leads to ion exchange reactions, which replace the ionic bonded Na ions on the DNA molecule with the CTMA, resulting into a DNA-CTMA precipitate.

Similarly, the second compound, DNA-BZK, is obtained using benzalkonium chloride (BZK), an alcohol-free antimicrobial compound, which has been widely used in the health care industry for more than 30 years. BZK is a mixture of alkylbenzyldimethylammonium chlorides of various even-numbered [34, 35] alkyl chain lengths. This product is a nitrogenous cationic surface-acting agent belonging to the quaternary ammonium group and is also used as a cationic surfactant.

Further, the experiment had a second processing step, in which a second batch has been produced by doping the compounds with a red dye [36]. Doping DNA with organic dyes such as Disperse Red, which has an absorption maximum in the range, 360-590 nm depending on the solvent [24], not only has effects on its electrical conductivity, but also enables the use of such organic materials in opto-electronics.

2.2 Test structure

The layout of the test structure, as presented in Figure 2, includes two interdigitated electrodes separated by a channel which has a 500 μm width and a length of 130 mm. Only the area where the S-D digits are completely overlapped is taken into account. Thus, each of the 13 channel interspaces has 10mm, which are summed. The copper electrodes have been obtained by milling using a LPKF Protomat M100/HF milling machine.

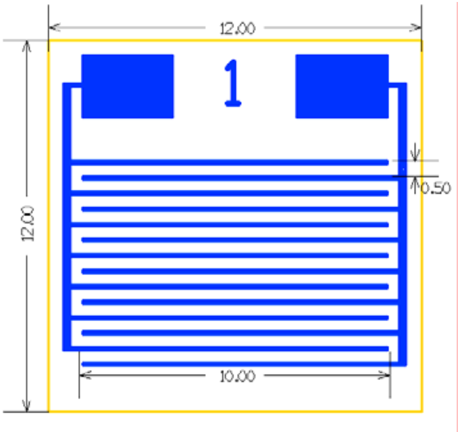

Fig. 2: Layout of the test structures designed with OrCAD Cadence Layout Editor

The area onto which the DNA compounds have been deposited through spin coating is approximately 8 mm long and 10 mm wide, as shown in Figure 3. The thin films were deposited using a Laurell WS-400B-6NPP/LITE spin coater, which was programmed at 1500 rotation/minute for one minute.

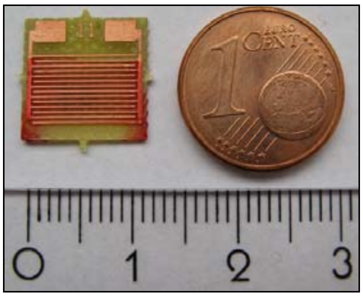

Fig. 3. Electrodes obtained by milling the copper plated textolite epoxy glass (FR-4) sheets

For the highest concentration of surfactant, the film can be as thick as 1 µm, as shown in the optical profilometer measurements in Figure 4. It can be observed that there is a step between the area where the compound is coated, indicated by the left vertical bar, and the area with the clean substrate, indicated by the right marker bar. The level difference is approximately 11000Å.

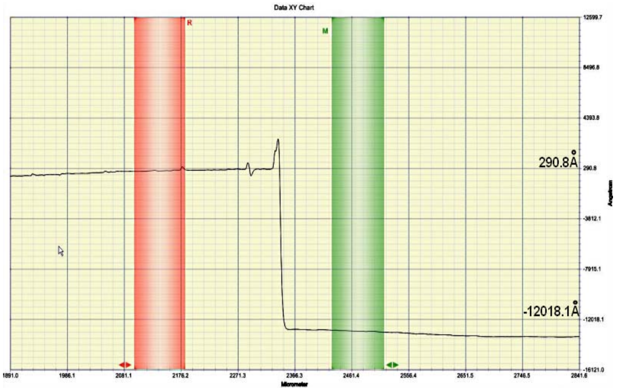

Fig. 4: Profilometer caption for the DNA film thickness.

For this measurement, the compound was spin-coated onto a silicon wafer, because this has a smoother surface than FR-4, resulting in a more precise level profile.

3. Results and discussion

DNA can be synthesized in any desired base sequence and thus can be used to create various chemical composites, from dielectrics to semiconductors, depending on the cationic surfactant of choice. The cationic surfactants used in this work lead to the fabrication of dielectrics, with a low permittivity constant.

The chemical compounds are synthesized in various concentrations of surfactant: 15%, 30%, 40% and 60%, respectively. These surfactant concentrations influence the thickness of the material in a directly proportional manner.

Current-voltage measurements have been performed with a Keithley 617 Programmable Electrometer. The aim was to determine the values of the sheet resistivity and evaluate the stability of these materials, prior and after doping with Disperse Red dye, at high temperature and humidity, respectively.

The resulting resistance-voltage (R-V) plots for the DNA-CTMA and DNA-BZK compounds can be observed in Figs. 5 and 6.

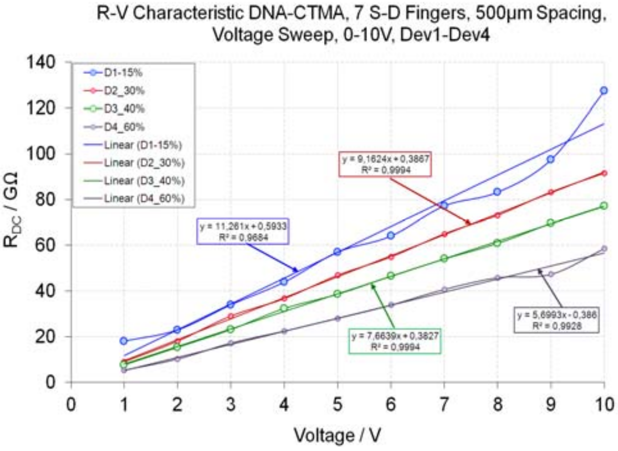

Fig. 5: R-V characteristics for the DNA compound with CTMA in various concentrations.

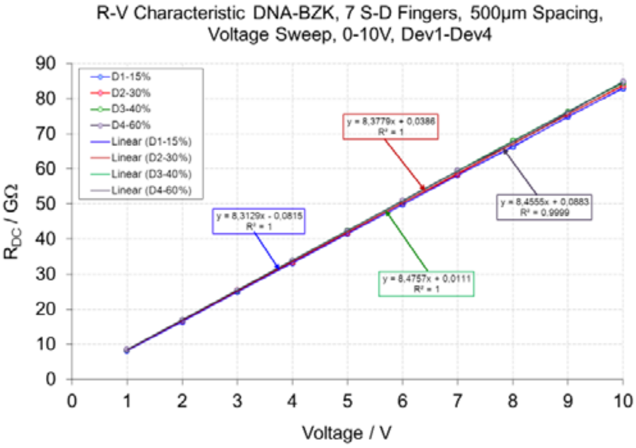

Fig. 6: R-V characteristics for the DNA compound with BZK in various concentrations.

From the measurements, it can be inferred that with the increase in thickness of the dielectric film, the resistivity decreases when CTMA is used as a surfactant. Conversely, the concentration of BZK does not appear to influence the resistivity of the film, as this remains relatively constant irrespective of the concentration of surfactant.

The sheet resistivity was computed according to equation (1):

$$\rho = R \cdot t \cdot \frac{W}{L} \tag{1}$$

where R is the measured resistance, t is the film thickness, W the width and L the length of the channel.

The obtained resistivity for DNA-CTMA is around 10^{11} Ωcm. For the other compound, DNA-BZK, the resistivity is around 10^{14} Ωcm.

For the environment stress testing, an Espec SH-241 climatic chamber was used, the temperature being set to 85 Celsius degrees. In the second stage, the relative humidity was set to 85 %, in accordance to the 85/85 testing standard. Figures 7 and 8 indicate the climatic stress results for the two composites with a concentration of surfactant of 60 % .

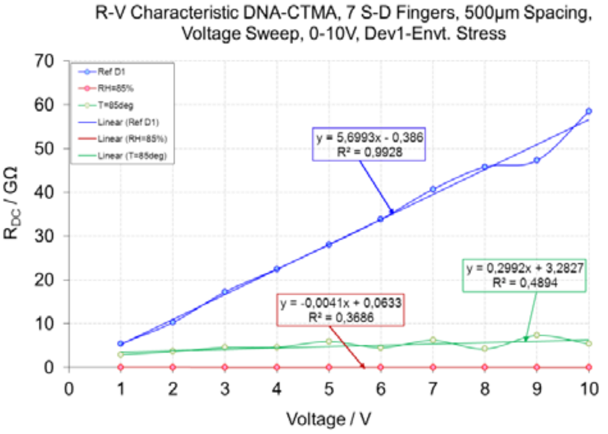

Fig. 7. R-V characteristics for DNA-CTMA under climatic stress

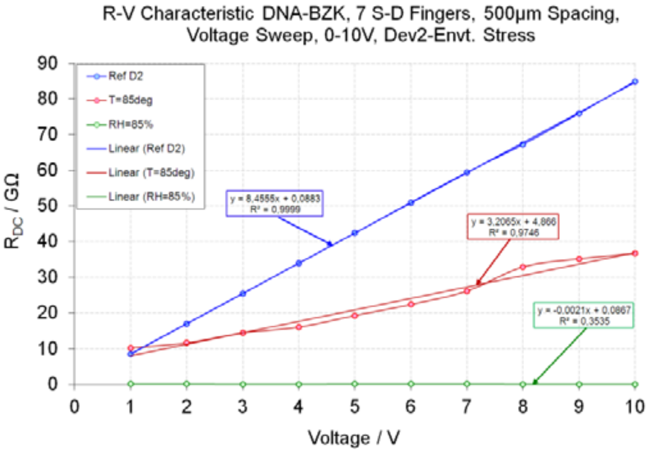

Fig. 8. R-V characteristics for DNA-BZK under climatic stress.

When subjected to climatic stress the samples remain relatively stable, in the range of Giga Ohms, at high temperatures. However, their conductivity increases significantly, getting in the range of Mega Ohms, at high humidity. The resistivity is slightly smaller when the temperature increases, which is an indicator that the material conduction is ionic in nature.

In the second stage, a new batch of samples has been fabricated. The shape of the electrodes was preserved. The DNA-CTMA and DNA-BZK films have been doped with a red dye, Disperse Red. This was done in order to investigate what effects doping has on the conductivity of the films. The aim was to also verify whether doping with this dye can be performed successfully, in view of potential applications in the area of photonics.

The resistivity does not appear to decrease significantly after doping and thus, as mentioned in [37], DNA – PEDOT – cationic surfactant compounds could be processed to increase conductivity. Other types of electrodes made of metals with closer work functions to the DNA energy levels could also lead to higher conductivity.

The resistance-voltage representation for the DNA-CTMA-DR and DNA-BZK-DR polymers can be observed in Figures 9 and 10.

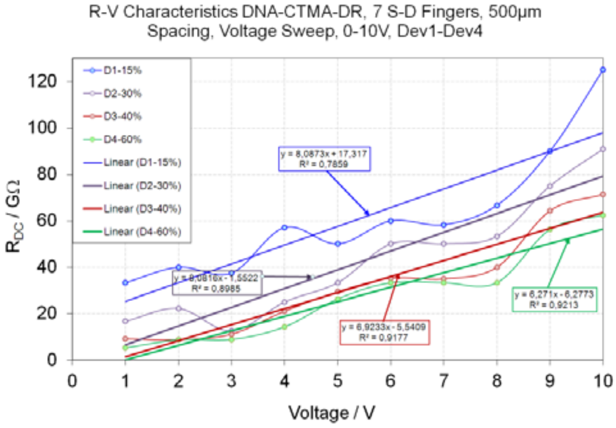

Fig. 9. R-V characteristics for the DNA-CTMA compound doped with Disperse Red dye

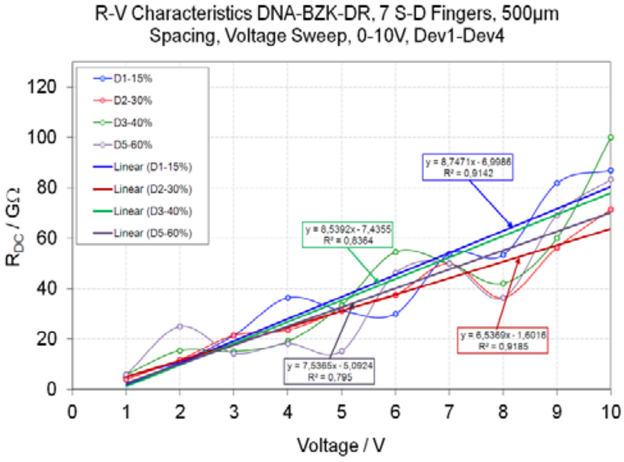

Fig. 10. R-V characteristics for the DNA-BZK compound doped with a Disperse Red dye.

From the resistance-voltage characteristics, it can be inferred that doping DNA biopolymers does reduce their resistance, but the decrease in electrical resistivity is small. Therefore, other dyes should be used if the scope of the experiment is to obtain a material with active semiconductor properties, as explained in [38].

As in the previous experiment, the concentration of the cationic surfactant is a relevant factor in the case of DNA-CTMA-DR. The sheet resistance of the DNA-CTMA-DR film varies with thickness, according to equation (1), meaning that the resistance increases when the thickness decreases.

On the other hand, from the electrical characteristics for the DNA-BZK-DR compound, it can be observed that the resistivity values do not appear to shift significantly with the changes in the thickness of the film.

Similarly, the new materials are subjected to environment stress for the same humidity and temperature values, with results presented in Figs. 11 and 12.

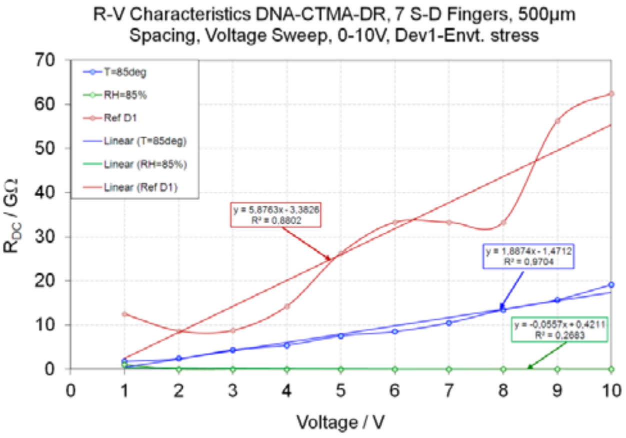

Fig. 11. R-V characteristics for DNA-CTMA-DR under climatic stress

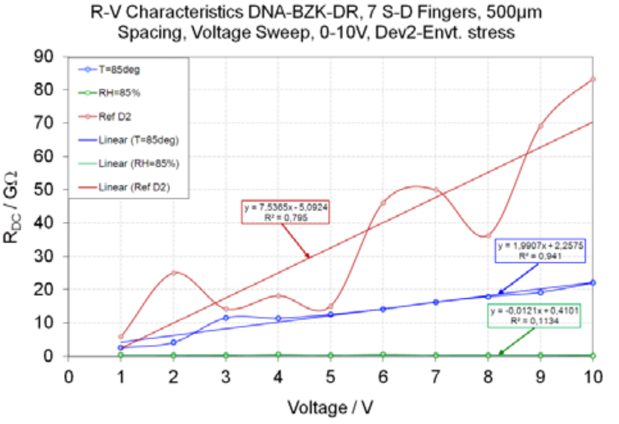

Fig. 12. R-V characteristics for DNA-BZK DR under climatic stress.

As prior to doping with the red dye, the samples exhibit the same thermal stability. However, at high relative humidity, the conductivity increases significantly as the resistance is in the range of tens of Mega Ohms, instead of Giga Ohms.

4. Conclusions

Four DNA-compounds have been characterized from an electrical point of view: DNA-CTMA, DNA-BZK and their counterparts doped with the Disperse Red dye. These proved to be low-k dielectrics, which allow their use in capacitive structures or, as dielectric thin films, in photonic active devices.

Also, it resulted that the resistance of the DNA- CTMA film decreases with the film thickness increase, while the resistance of the DNA-BZK compound remains relatively constant.

Moreover, while doping does modify the compound conductivity, the samples maintain their dielectric character. The main advantage of doping with the Disperse Red dye is the possibility to use the compound in photonic applications.

In terms of stability with respect to climatic stress, it resulted that the samples exhibit thermal stability when the temperature is increased. A slight decrease in resistance with temperature increase was observed, which indicates that an ionic conduction process takes place.

However, the samples do not appear to maintain their low conductivity at high values of the relative humidity. As a consequence, new investigations into encapsulation of the final electronic devices need to be considered for highly humid environments, like the case of biosensor applications. Also, the possibility of cross-linking the DNA materials with a surfactant that would increase the compound hydrophobic character should be considered.

Moreover, other DNA compounds should also be synthesised and deposited on various types of metallic electrodes, in view of their use as dielectric films for organic thin film transistors (OTFTs) and organic light emitting devices (OLEDs).

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