Research Article

Electrical Switching in Thin Films of Nandi Flame Seed Cuticles

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Current-voltage (I-V) characteristics of Nandi flame seed cuticles (NFSCs) have been studied as a function of irradiation, annealing, and poling temperature. The cuticles showed memory and threshold switching. Threshold voltage $V_{th}$ was about 5 V which is almost five times higher than $V_{th}$ observed in synthetic polymers. The threshold voltage $V_{th}$ increased to 6–8 V after irradiation and annealing depending on the duration of annealing or irradiation. After switching, conductivity increased by an order of 10². In reverse bias, increase of current was observed and the memory hysteresis loop was at higher conductivity than at the time of switching. Switching effect was minimized at a poling temperature of 370 K. Formation of semiquinones and quinoid radicals from phenolic compounds may have contributed to electrical switching and hysteresis effect.

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1. Introduction

Electrical switching and memory is the basis of many potential molecular electronic devices, and has gained considerable attention of numerous research efforts in recent years [1–3]. Aviram and Ratner [4] described the first concrete idea of molecular conductance switching in which the chemical structure consisted of an electron donating molecule and a modified acceptor connected via a saturated (insulating) $\sigma$ bridge. According to their theoretical calculations, insulating molecule becomes conductive after applying a certain threshold voltage that brings the $\pi$-levels in resonance. A range of other molecular structures which exhibit electrical threshold switching have been reported [1] including self-assembled monolayers of phenylethynyl oligomers [5] and rotaxanes oriented between two conductors by Langmuir-Blodgett assembly [6, 7]. Conductance switching has also been reported in synthetic polymeric materials which consist of a large assemblies of molecules [8–12]. Whereas several biopolymers have well-documented properties as organic semiconductors [13–19], limited studies on electrical switching phenomenon of these biological assemblies have been done [20, 21].

Biopolymers are a rich resource for development of novel electronic devices, since there is tremendous natural variation in their composition [22]. Biopolymers also have the advantage of being biodegradable and biocompatible [23]. Plant seed cuticles have been shown to contain cutin and suberin biopolymers [24, 25]. Cutin is the main component (between 40% and 85%, w/w) of plant cuticles [26, 27]. Predominant aliphatic monomers of most cutins are C₁₆ and C₁₈ $\omega$-hydroxylated fatty acids, typically carrying in addition hydroxy- or epoxy groups in midchain positions. Besides aliphatic monomers, cutin also contains glycerol and small amounts of phenolic compounds [28, 29]. Suberin occurs at abscission zones such as chalazal region of seed coats formed during late stages of seed maturation [30, 31]. Suberin contains both aliphatic and aromatic monomers [32, 33]. The aliphatic part of suberin is mainly composed of C₁₆ to C₂₈ $\omega$-hydroxy fatty acids and C₁₆ to C₂₆ $\alpha,\omega$-dioic acids. The aromatic network is a hydroxycinnamate-derived polymer, primarily comprised of ferulic acid, N-feruloyltymamine, cinnamic acid, p-coumaric acid, or caffeic acid [33]. Kipnusu et al. [34] have reported that Nandi flame seed cuticle is an insoluble biomaterial which has high-specific heats and shows glass transition temperature...
comparable to glass transition of cutin reported elsewhere [35]. Three-dimensional structures of cutin and suberin macromolecules are not well understood, since their constitutive moieties can vary appreciably both in specific nature and relative abundance within macromolecular network [30]. However, Kolattukudy [36] suggested hypothetical models of cutin and suberin structures as shown in Figures 1 and 2, respectively.

In this paper, we present results of electrical switching properties of thin films of NFSC as a function of annealing temperature, irradiation with laser beam, and poling temperature. Fourier transform infrared (FT-IR) spectroscopy of NFSC is first analyzed and compared with FT-IR of cutin and suberin. Possible composition of monomers in NFSC is inferred from this comparison. Current-voltage (I-V) characteristics of NFSC under different conditions are analyzed and finally a discussion of possible electrical switching mechanism is presented.

2. Experimental

2.1. Sample Preparation. FT-IR spectrometer of Hyper model 8400 series was used to obtain IR spectra of pristine and annealed samples. Cuticle samples cut out from a seed (Figure 3) were fitted into the sample holder of the FT-IR spectrometer. Annealing was done by placing the sample inside a temperature-controlled furnace that was fitted inside an electrically shielded cage of Lindberg/Blue Tube Furnace TF55035C. Samples were annealed at various temperatures of 320 K, 350 K, and 400 K for 30 minutes each. A mechanical mask was made by cutting circular holes of diameter 0.56 cm through a thin soft cardboard of dimensions 3 cm × 8 cm. Samples were mounted on each of the holes and then irradiated with He-Ne laser beam of wavelength 632.8 nm in a dark room. Irradiation was done separately on different samples for a time period of 10 minutes, 30 minutes, or 60 minutes each. Electrode coating on the film of pristine, preannealed, and preirradiated samples was done by using quick drying and highly conducting flash-dry silver paint obtained from SPI Supplies, Pa, USA. A mask of circular aperture of 0.56 cm diameter was used while coating to ensure uniformity in sizes of the coated regions. Circular aluminum foils of the same diameter were placed on the coated surfaces such that samples were sandwiched between two aluminum electrodes. The same flash-dry silver paint was used to connect thin wires onto the aluminum electrodes. A sample holder is shown in Figure 4. The thickness of the films was measured by a micrometer screw gauge and found to be 4 ± 0.02 μm.

2.2. Current-Voltage (I-V) Measurement. Before measuring voltage and current, the samples in Figure 4 were electrically...
annealed by driving high current through them. This was done by driving current of 0.3 A through the samples for 10–15 minutes. This reduced contact resistance and improved ohmic properties of the contact. Resistance of the contact was found to decrease considerably after it had been electrically annealed. $I-V$ for both annealed and irradiated samples was measured using Keithley 2400 source meter. The setup of the sample holder shown in Figure 4 was shielded with aluminum metal cage coupled with an electrical insulating material in order to minimize disturbances from electrical noise, temperature fluctuation, and electromagnetic waves. $I-V$ data for each treated sample was determined with

**Figure 2**: Hypothetical structure of suberin polymer.

**Figure 3**: Thin and transparent cuticle attached to the Nandi flame seed.

**Figure 4**: Sample holder. Thin wires are connected on both sides of the samples.
cable guard on. The cable guard of the source meter was activated in order to minimize leakage current. Step voltages of 0.1 V (within a range of 0.1 V–1.0 V), 1.0 V (within a range of 1.0 V–10.0 V), and 5.0 V (within a range of 10.0 V–40.0 V) were sourced for both forward and reverse biases. When measuring current at poling temperature, a sample sandwiched between aluminum electrodes was placed inside the Lindberg/Blue Tube. Furnace temperature was set to a constant value while recording current-voltage measurements.

3. Results and Discussion

Figure 5 shows FT-IR spectrum of pristine NFSC. IR absorption bands of NFSC are compared with IR bands of cutin and suberin biopolymesters found in plant cuticles. IR bands and band assignments are listed in Table 1. Cutin and suberin IR data bands and comments in Table 1 are based on literature [33, 37–39]. The IR spectrum of NFSC shows a wide band at 3348 cm$^{-1}$ assigned to O–H stretching vibration. This band is correlated to absorptions at 3300 cm$^{-1}$ and 3464 cm$^{-1}$ in cutin and suberin, respectively, and is caused by presence of alcoholic and phenolic hydroxyl groups involved in hydrogen bonds [40]. Bands located near 2900 cm$^{-1}$ and 2300 cm$^{-1}$ resulted from C–H asymmetric and symmetric stretching vibrations of methoxyl and methylene groups, respectively [37, 39]. Methylene is the most repeated structural unit in the cutin biopolyester [37]. Around 1750–1630 cm$^{-1}$ wavenumbers, absorption bands are caused by stretching vibrations of carbonyl groups. Absorption around 1603 cm$^{-1}$ and 1513 cm$^{-1}$ is assigned to the stretching of C=O–C bonds and the stretching of benzenoid rings. Absorption bands in the range 1300–1210 cm$^{-1}$ are related to asymmetric vibration of C–O–C linkages in ester to esters or phenolic groups. Other IR absorption band assignments of NFSC in comparison with those of cutin and suberin are summarized in Table 1. IR bands of NFSC between 3300–1500 cm$^{-1}$ result from components of both cutin and suberin while bands around 1400–1200 cm$^{-1}$ are more related to those of suberin components as shown in Table 1. Types of monomers in cutin and suberin are shown in Table 2. Figure 6 shows FT-IR spectrum of pristine NFSC in comparison with spectrum of NFSC sample annealed at 400 K. The spectra show that IR absorption peaks for pristine and annealed samples occurred at nearly the same frequency. This means that annealing (400 K) does not destroy the functional groups in the sample. Figure 7(a) shows $I$–$V$ characteristics of pristine and annealed samples. $I$–$V$ curves were drawn as log-log plots because in many cases drastic conductivity changes of several orders of magnitude were observed. It is noted that at certain threshold voltage, $V_{th}$, current rises rapidly by an order of about $10^4$. There are two distinct regions for forward bias regime. High-impedance region, which occurs before $V_{th}$, is referred to as OFF state and low-impedance region, which occurs after $V_{th}$, is known as ON state. At low voltages, log$I$ versus log$V$ plots are approximately linear with a slope of 1, while at higher voltages, above a well-defined threshold voltage $V_{th}$, the plots are again approximately linear with a slope of $1.8 \pm 0.2$. The plots show that at low voltages, OFF state, current follows ohms law but after switching to ON state at higher voltages, current follows a power law dependence given by $I = V^n$, where $n = 1.8 \pm 0.2$ obtained from the slopes. This shows that the ON-state region is governed by space charge limited current (SCLC) controlled by single trapping level, the injecting carrier concentration dominating the thermally generated carriers. Current increased by an order of $10^2$ after switching to ON state. It was also noted that current did not follow the same path on decreasing applied electric field, hence indicating that the samples exhibit electrical switching with memory. This hysteresis effect was not erased by annealing or irradiating the samples. The threshold voltage $V_{th}$ for pristine samples was $5 \pm 0.5$ volts which is higher than $V_{th}$ reported for some synthetic polymers; polymethylmethacrylate (1.6 V), polystyrene (4.5 V) [12], phthalocyanine (0.3 V) [41], 2,6-(2,2-bicyanovinyl) pyride (5.01 V) [42], Langmuir-Blodgett (1.0 V) [43]. The width of $V_{th}$ or transition voltage during switching from OFF to ON states was about 1.0 V. All samples returned to OFF state after about 30 minutes. Figure 7(b) shows that $V_{th}$ increased nonuniformly from 5–9 V, with increase in annealing temperature. A decrease in magnitude of the negative dielectric anisotropy during annealing is a major reason for the increase in $V_{th}$ for the annealed samples [41].

Figure 8(a) shows that irradiated samples have similar $I$–$V$ switching properties as annealed samples. The curves show electrical switching and memory effect with $V_{th}$ that
Table 1: FT-IR frequencies (cm\(^{-1}\)) of cutin, suberin, and NFSC. *Benitez et al. [37], Cordeiro et al. [39].

<table>
<thead>
<tr>
<th></th>
<th>Cutin(^*)</th>
<th>Suberin(^*)</th>
<th>NFSC</th>
<th>Band assignment</th>
<th>Comments(^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3300</td>
<td>3464</td>
<td>3348</td>
<td></td>
<td>(\nu (O-H))</td>
<td>Alcoholics and Phenolic hydroxyl groups</td>
</tr>
<tr>
<td>2924</td>
<td>2919</td>
<td>2916</td>
<td></td>
<td>(\nu_{\text{as}} (C-H)),</td>
<td>Aliphatic stretch,</td>
</tr>
<tr>
<td>2852</td>
<td>2851</td>
<td></td>
<td>2615</td>
<td>(\nu (C-H))</td>
<td>Methoxylic groups, Methylenes groups</td>
</tr>
<tr>
<td>1736</td>
<td>1738</td>
<td></td>
<td>1682</td>
<td>(\nu_{\text{as}} (\text{COO}^-)),</td>
<td>Ester carbonyl, Ketone groups</td>
</tr>
<tr>
<td>1731</td>
<td></td>
<td></td>
<td></td>
<td>(\nu (C=O))</td>
<td></td>
</tr>
<tr>
<td>1630</td>
<td></td>
<td>1635</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1530</td>
<td>1513</td>
<td>1603</td>
<td></td>
<td>(\nu (C=C))</td>
<td>Conjugated double bonds, benzenoid rings</td>
</tr>
<tr>
<td>1463</td>
<td></td>
<td></td>
<td></td>
<td>(\delta (C-H))</td>
<td>Aromatic ring</td>
</tr>
<tr>
<td>1437</td>
<td></td>
<td>1427</td>
<td></td>
<td>(\nu_{\text{as}} (C-H))</td>
<td></td>
</tr>
<tr>
<td>1364</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1300</td>
<td>1319</td>
<td>1157</td>
<td></td>
<td>(\nu_{\text{as}} (C-O-C))</td>
<td>Esters linkages, Phenolics, Glycosidic link.</td>
</tr>
<tr>
<td>1210</td>
<td></td>
<td>1157</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1167</td>
<td>1130</td>
<td>1157</td>
<td></td>
<td>(\nu (C-O))</td>
<td>Aliphatic alcohols or Aliphatic esters</td>
</tr>
<tr>
<td>1100</td>
<td></td>
<td>1157</td>
<td></td>
<td>(\nu (C-H))</td>
<td>Benzene ring</td>
</tr>
<tr>
<td>1055</td>
<td>1050</td>
<td>1033</td>
<td></td>
<td>(\delta (O-H)),</td>
<td>Primary and secondary alcohols</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\nu (C-O))</td>
<td></td>
</tr>
</tbody>
</table>

increased (from 5 to 8 V) with the increase in irradiation time. It is also noted that irradiation increased electrical conductivity especially in the reverse bias. It also increased the gap between OFF state and ON state currents in the forward bias. Increase in conductivity for irradiated samples can be attributed to dissociation of primary valence bonds into radicals. The dissociation of C–C and C–H bonds leads to degradation and cross-linking which improves electrical conductivity [44]. Exposure of polymers to ionizing radiation produces current carriers in terms of electron and holes which may be trapped in the polymer matrix at low temperatures [45]. If the original conductivity is small, then the presence of these carriers produces an observable increase in the background conductivity of the polymer. Irradiation of polymers also results in excitations of its molecules and creation of free electrons and ions that migrate through the polymer network till they are trapped. The electronic and ionic configurations created cause changes in the electric conductivity. Figure 8(b) shows that \(V_{\text{th}}\) increased almost linearly with the increase in irradiation time. Since irradiating time is associated with an increase in irradiation dose [46], increasing duration of irradiation could have led to an increase in the number of chain ends acting as trapping sites which increased \(V_{\text{th}}\).

Although several examples of conductance switching have been investigated extensively, switching mechanism in most cases is unknown and is the subject of some controversy [5]. Several possible mechanisms for the conductance transition observed in NFSC were considered. This resulted in the identification of a possible mechanism that is in agreement with the available electrical conductance data and possible structure of this system. The first mechanism considered was the quantum interference of different propagation parts within the molecules which involve permutation of highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) [48]. This can be explained by considering the potential barrier distinction between the metal contact regions. Under the positive bias, the electrons are easier to inject from the electrode into the molecule and are more difficult to transfer from the molecule to the opposite electrode, thus resulting in the charging of the molecule. In this bias, charging (charging energy) in the molecule moves the HOMO up with respect to Fermi level, whereas under negative bias, the deficit of electrons in the molecule moves the HOMO down [49]. Consequently, it can be reasonably concluded that a smaller (larger) positive (negative) bias is necessary to drive the HOMO into the HOMO-LUMO gap, hence allowing large currents to flow. This could also result from permutation of frontier orbitals, HOMO\(_{−1}\), and LUMO\(_{−1}\). In the absence of electric field, HOMO\(_{−1}\) is localized on the acceptor group...
### Table 2: Types of monomers and their % abundance in cutin and suberin biopolysters. Pollard et al. [30].

<table>
<thead>
<tr>
<th>Monomer type</th>
<th>Abundance (%) and common monomers</th>
<th>Cutin (Example)</th>
<th>Suberin (Example)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unsubstituted fatty acids</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxylated fatty acids</td>
<td>1–25%</td>
<td>C16:0, C18:0, C18:1, C18:2</td>
<td>C18:0 to C24:0</td>
</tr>
<tr>
<td><strong>ω-Hydroxy fatty acids</strong></td>
<td>1–32%</td>
<td>C16:0, C18:1, C18:2</td>
<td>11–43%, C18:1 to C24:0</td>
</tr>
<tr>
<td><strong>α,ω-Dicarboxylic acids</strong></td>
<td>Usually &lt;5% in Arabidopsis</td>
<td>C16:0, C18:0, C18:1, C18:2</td>
<td>24–45% C18:1, C18:2, C16:0 to C26:0</td>
</tr>
<tr>
<td><strong>Mid-chain functional monomers</strong></td>
<td>0–34%</td>
<td>C18:0 (9,10-epoxy)</td>
<td>C18:1 (9, 10-epoxy)</td>
</tr>
<tr>
<td><strong>Epoxy-fatty acids</strong></td>
<td>16–92%</td>
<td>C16:0 (10,16-dihydroxy)</td>
<td>C18:0 (9,10, 18-trihydroxy)</td>
</tr>
<tr>
<td><strong>Polyhydroxy fatty acids</strong></td>
<td>Traces</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Polyhydroxy α,ω-dicarboxylic acids</strong></td>
<td>0–8%</td>
<td>C18:0 (9,10-dihydroxy)</td>
<td></td>
</tr>
<tr>
<td><strong>Fatty alcohols</strong></td>
<td>0–8%</td>
<td>C16:0, C18:1</td>
<td>1–6%</td>
</tr>
<tr>
<td><strong>Alkan-1-ols and alken-1-ols</strong></td>
<td></td>
<td>C18:0 to C22:0</td>
<td></td>
</tr>
<tr>
<td><strong>α,ω-Alkanediols and α,ω-alkenediols</strong></td>
<td>0–5%</td>
<td>C18:1</td>
<td>0–3%</td>
</tr>
<tr>
<td>Glycerol</td>
<td>1–14%</td>
<td></td>
<td>14–26%</td>
</tr>
<tr>
<td>Phenolics</td>
<td>0.1% Ferulate</td>
<td></td>
<td>0–10% Ferulate, Samller amounts of coumarate, sinapate, cefeate</td>
</tr>
</tbody>
</table>

and LUMO+1 on the donor group. When the external field is applied, electron orbitals are “pulled” toward the acceptor group reducing the HOMO-LUMO gap of frontier orbitals and the switching and hybridization between HOMO−1 and LUMO+1 take place. As the strength of the field increases, the HOMO-LUMO gap in the molecular spectrum becomes smaller and the HOMO, HOMO−1, and LUMO orbitals split into the HOMO-LUMO gap, and hence become delocalized. Figure 10 shows a schematic diagram of the switching effect under an electric field. However, this explanation does not account for the formation of hysteresis and the return of the samples to OFF state within 30 minutes.

Another possible mechanism considered for electrical switching in NFSC is nondifferential resistance (NDR) which results from the injection of electrons from electrodes leading to build up of space charges across the metal electrodes and formation of high-field domains (or an accumulation layer due to dipole formation) [49, 50]. Formation of high-field regions leads to elongation of low-field regions till the interface separating the high- and low-field regions lies on
the same potential and is perpendicular to the current flow direction [51]. Electron injection into molecules sandwiched between metal electrodes was originally proposed to explain NDR [50] but was criticized due to the requirement for a counterion to neutralize the resulting space charge. The mechanism would also generate a negative space charge in the molecules, which cannot be compensated easily. As more charge is injected, space charge potential will increase, and the voltage required for charge injection also increases. While space charge effects may not be favorable for electrical switching, they do not appear to prevent switching a minority of molecules in the absence of counterions [5].

The most likely source of conductance switching in NFSC is the formation of quinoid and semiquinone structures from phenolic compounds present in plant cuticles [52, 53] and which are presumably present in NFSC. It has been observed that electrical switching molecules are likely to have one or more phenyl rings and hemiquinone structures [5, 54]. Organic conductors are assemblies of molecules whose HOMO orbitals are partially filled [55]. This allows for easy proton-electron transfer within molecules which incidentally may cause conductance switching. Aviram et al. [54] suggested that electron-proton motion within hemiquinones molecules that comprised of catechol and o-quinone, molecules between two contacts may switch the molecules to low-impedance (ON) state due to the formation of semiquinones-free radicals. When an electron is injected into the molecules from the metal contact, it is gained by an electron acceptor (o-quinone) molecule. An electron donor (catechol) molecule then transfers the electron to

Figure 7: (a) I-V Switching characteristics for pristine and annealed samples. (b) Variation of threshold voltage \( V_{th} \) with annealing temperature.

Figure 8: (a) I-V switching characteristics for irradiated samples. (b) Variation of threshold voltage \( V_{th} \) with irradiation time.
highly conjugated compared to phenyl groups. As the electric field increases, quinoid structures become delocalized over the entire structure. This is the basis for the change of conductance state from OFF to ON state. In addition to increased conjugation and planarity, a decrease in HOMO-LUMO gap in the quinoid structures occurs in all forms of “switching” molecules [5]. Benzene ring rotation and bond length changes during the formation of quinoid result in activation barriers which are presumably the origin of the temperature dependence conductance. Activation barrier associated with the structural rearrangement is responsible not only for the activation barrier but also for the switching hysteresis. The quinoid form is apparently the higher energy form in the absence of an electric field, but is the favored form in a high field [5]. Reorganization energy is sufficiently large that the quinoid form survives after the field is removed, at least for several minutes to several hours [5]. High conductance high field of the reverse regime may also be due NDR and Fowler-Nordheim field emission process which involves tunneling of free carriers in the bulk of the material [56].

4. Conclusion

$I-V$ characteristics of Nandi flame seed cuticle biomaterial have shown reproducible switching and memory properties. The switching and memory effects are explained in terms of formation of semiquinones and quinones structures from phenolic compounds due to redox processes. The switched samples lost memory within 10–30 minutes. Threshold voltage $V_{th}$ for pristine samples was about 5 V. $V_{th}$ increased to about 6–8 V after irradiation with laser light of wavelength 632.8 nm. Annealing also increased $V_{th}$ by the same magnitude. Hysteresis effect in the $I-V$ curves is due to the presence of quinoid radicals. At a poling temperature of 370 K, both switching and memory effects almost disappeared. Current in the OFF state was ohmic but after switching to ON state, current was governed by space charge-limited current (SCLC). These results have shown that NFSC has electrically switchable molecules which can be explored further for their application in gas sensing and electrical switching circuits.

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References


