Insulating characteristics of polyvinyl alcohol for integrated electronics

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The aim of this work is to evaluate the effects of molecular weight, hydrolysis degree, and cross-link on the performance of Polyvinyl Alcohol (PVA) when applied as dielectric material in organic field effect transistors. For this purpose, metal–insulator–structures and polymeric films were characterized. The polymer structure was analyzed by thermogravimetry and calorimetry, and the electrical characterization of the films was performed through current–voltage and capacitance–voltage curves; and dielectric spectrometry. Cross-linkage, followed by hydrolysis degree, presented the major impact on polymer properties, due to the strong influence on chain mobility. The chain mobility increases the dielectric response and decreases the insulation capacity, generating the need to compromise between these two properties. The largest drawback encountered was the high sensitivity of the films to ambient humidity. The best performance of the organic insulator was obtained from cross-linked films made of an incompletely hydrolyzed PVA.

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1. Introduction

Organic field effect transistors (OFETs) have been a hot topic in the last 20 years due to their potential to produce low cost, high volume and flexible electronics. These structures offer a good basis to develop materials that will be applied in tomorrow’s electronics [1–3].

Extensive studies have been done on semiconductor materials to understand and improve charge transport, but much less attention has been paid to dielectric materials [4]. The path to development of an all-organic transistor and flexible electronics requires the definition of an organic gate insulator. The structure of the gate dielectric imparts various surface and bulk characteristics that strongly influence a device’s performance [5]. A large variety of polymers have been tested as dielectric layers; among them the most studied are poly(4-vinylphenol) [6,4], polyimide [7], poly(methyl methacrylate) [8], poly(vinyl pyrrolidone) [9], poly(vinyl alcohol)(PVA) [10,11], and photoalignment layers [12]. Reports have been made on the use of self-assembly monolayer [13,14], multilayer [15], high-k inorganic/smooth organic bilayer structures [16,17], polymer electrolytes and ion gels [18,19]. However the integration of these layers would add complexity, raising fabrication cost and sacrificing flexibility. Therefore a single organic dielectric layer is desired to allow a simple, cost effective solution at low temperatures [20].

PVA is probably the most studied polymer to be applied as a dielectric material in organic thin-film transistors due to its versatility, high solubility in water, low cost, non-toxicity, flexible hydrophilic network and, above all, due to its electronic characteristics such as great insulating properties and notably high dielectric permittivity [21]. PVA is a semi-crystalline polymer, which is predominately produced and used for non-electronic applications. PVA is produced by the hydrolysis of polyvinyl acetate (PVAc) obtained by the polymerization of vinyl acetate monomer. The hydrolysis reaction is incomplete resulting in polymers with different degrees of hydrolysis [22]. Considering that hydroxyl groups act as cross-linking sites and form hydrogen bonds between adjacent chains, PVA with different hydrolysis degrees and chain sizes gives rise to different polymer structures. While there is a good amount of work applying PVA as a dielectric material in OFETs, detailed work exploring the influence of its forms on electrical properties is much less prevalent.

The electrical nature of many insulating materials, including PVA, is only partially understood. Some important parameters have been extensively studied. The effect of impurities has been discussed by Egginger et al., which recommends extensive purifications to minimize hysteresis [21,23]. A comparison between PVA and PVP polymers indicated that devices’ characteristics are significantly affected by the concentration OH group in the gate dielectric [4]. PVA chain-cross-linking
was evaluated by Bettinger et al., which states that devices fabricated on non-cross-linked PVA films exhibited generally enhanced performance compared to similar devices fabricated on cross-linked PVA dielectrics [24]. However, the insulating properties of PVA can be significantly improved using a cross-linking process, enhancing immunity against moisture and solvent [25]. The composition ratio of cross-linking agent was evaluated previously [25,26]. Results for PVA cross-linked with glutaraldehyde were presented by Wang et al., demonstrating the structural flexibility of the film [27]. Additionally a detailed study of the PVA molecular dynamics by dielectric spectroscopy and dynamic mechanical analysis in a wider temperature range was conducted to shed light into PVA molecular motions [28].

In this paper, we report a study concerning the effect of different molecular weight, hydrolysis degree, and reticulation on the performance of the PVA for use as a dielectric material in OFETs. The aim of the work is to compare the different types of PVA structures and seeking for maximizing dielectric properties that would be useful in organic electronics applications, such as low leakage current, high dielectric constant and low hysteresis. For this purpose, MIS structures and polymeric films were prepared and characterized. We have focused on the dielectric alone, excluding the influence of the organic semiconductor and therefore no transistor was manufactured.

### 2. Experimental

Four grades of PVA obtained from Sigma-Aldrich, 99.7% purity, described in Table 1, were evaluated. Ammonium dichromate (ADC), 99.9% purity, supplied by B. Herzog (São Paulo/Brazil), was used as a cross-linking agent for PVA. All materials were used as received.

PVA solutions were prepared by dissolving 5% w/w of PVA in hot distilled and deionized water (60–80 °C). The solutions were then filtrated to eliminate any particulates. The PVA solutions were prepared according to PVA grade. The solutions without cross-linking agent were named PVA1, PVA2, PVA3, PVA4, and those with ADC at a concentration of 0.8% w/w were named PVA1–ADC, PVA2–ADC, PVA3–ADC and PVA4–ADC.

PVA films were prepared by casting the PVA solutions (5 ml) into a polystyrene Petri dish, drying it at 60 °C for 36 h and annealing the obtained films at 90 °C in air for 24 h.

Thermal degradation behavior of the PVA films was investigated using a thermogravimetric analyzer (TGA 2050, TA Instruments) within a temperature range of 25–900 °C, at a heating rate of 20 °C/min under nitrogen atmosphere. The degradation temperature, wherein percentage weight loss was determined as a function of temperature, and ash content were recorded using 20 mg samples. The PVA characteristic thermal properties such as glass transition and melting point were determined on a Differential scanning calorimeter (DSC 2910, TA Instruments). 5 mg samples at a heating/cooling rate of 10 °C/min, under nitrogen atmosphere, were heated and hold at 110 °C for 7 min (first run), cooled down to 20 °C, and then heated up to 250 °C (second run). Temperature calibration was performed using Indium as a reference (Tm = 156.6 °C and Heat flow = 28.5 J/g) and the baseline was calibrated without pans.

MIS structures were prepared by spin coating of the PVA solutions on top of p-type(100) silicon wafers simulating the gate dielectric in
organic field effect transistors. These films were prepared with constant rotational speed of 2000 rpm for 50 s and then annealed at 90 °C for 2 h on a hot plate in air. The thickness of these films was measured by ellipsometry and optical reflectance techniques.

Aluminum circular contacts with diameters of 200 μm and thicknesses of 0.5 μm were obtained by resistive evaporation through a mechanical mask. Indium gallium alloy was manually applied to the rear surface to obtain ohmic contacts. For characterization of the MIS capacitors, a HP4155A Semiconductor Parameter Analyzer was used to measure current–voltage (I–V) characteristics and a HP4284A LCR Meter was used for capacitance–voltage (C–V) measurements with variable frequency.

3. Results and discussions

Fig. 1 presents the TGA (weight loss versus temperature) and DTA(derivative) curves of the samples (weight loss and its derivatives with respect to the temperature) and Table 2 summarizes the thermal events observed. The thermal degradation of the non-cross-linked PVAs follows the pattern described in the literature for these polymers [24]. TGA thermograms of PVA show three weight loss events. The first is associated to water evaporation ($T_{\text{max}}: 90–125 °C$), since it is a hydrophilic polymer, the second to chain decomposition ($T_{\text{max}}: 270–330 °C$) and the third to sub-products degradation ($T_{\text{max}}: 430–460 °C$) due to cyclic conjugated compounds. A detectable difference can be observed between thermal degradation curves of the PVA with different hydrolysis degrees (Fig. 1a and b). PVAs with a higher hydrolysis degree degrade under lower temperatures, which is consistent with the thermal degradation mechanism described in the literature [29]. In degradation process, the earliest step is the removal of hydroxyl groups from the chain. Polymers with a higher concentration of hydroxyl groups are prone to start this process earlier, and therefore are more heat sensitive.

The same effect is noticed on the cross-linked PVA films (Fig. 1c and d), however in a more subtle way.

The TGA curves of the cross-linked PVAs show different thermal profile due to the chain reticulation process involving the hydroxyl groups. Although the weight loss of the first event is the same for the non- and cross-linked PVA, it decreased significantly in the second event, since the hydroxyl groups are linked to the cross-linking agent ADC changing the chain scission mechanism. Therefore, there was an increase in the third weight loss and residue content. The second peak of the chain scission overlaps the temperature where the pure ADC undergoes decomposition, around 180 °C [30]. The residual mass fraction of the cross-linked PVA samples was about 8–11 times larger than that of the non-cross-linked ones. Differences on the curves thermal profiles, on the weight loss and larger residual mass indicate the occurrence of a reaction between ADC and PVA that delayed overall PVA thermal degradation and induced char formation. No effect of the molecular weight on the thermal degradation of PVA was observed.

Fig. 2 presents the DSC endothermic curves and Table 3 summarizes the thermal transitions of the PVA films. The annealing of the PVA films 110 °C for 7 min (1st run) eliminated any moisture of the cross-linked samples and no endothermic peak due to water evaporation was seen in the 2nd endothermic run. Non-cross-linked PVA films presented a small amount of moisture after the annealing and a small endothermic peak was also present in 2nd run.

The non-cross-linked PVA films presented glass transition ($T_g$) and melting ($T_m$) temperatures, as expected. The PVA samples with higher hydrolysis degree (PVA2 and PVA4) presented higher crystallinity (high enthalpy) and crystallites that are more homogeneous (well-defined $T_m$ peak) compared to the samples with lower hydrolysis degree (PVA1 and PVA3). PVA with higher hydrolysis degree has higher hydroxyl content and higher density of intermolecular interactions between these groups that favors the polymer crystallization. On the other hand, a higher interaction between the hydroxyl groups decreases the chain mobility; therefore PVA2 and PVA4 present higher $T_g$ (75 °C) than PVA1 and PVA3 (68 °C).

The cross-linked PVA films did not present thermal transition related to $T_m$, since the reticulation process with ADC avoids any chain crystallization. The wide endothermic peak over 150 °C is due to the endothermic sublimation of ADC–PVA compounds, formed during the PVA

![Fig. 2. DSC curves of the PVA films.](image-url)
The cross-linked PVA films were amorphous and presented more rigid structure than the non-cross-linked ones. No T_g could be detected until 150 °C by this technique.

Fig. 3 presents the DC insulation response of the PVA films. As the substrate is p-type Si, the measurements were done applying a negative voltage to the top contact to maintain the MIS structure in accumulation and to assure that the voltage drop fell only on the PVA layer. Considering that the insulation effect on any layer is strongly dependent on its thickness, the responses to the electrical field were normalized, dividing the applied voltage by the PVA thickness.

Cross-linking reduces leakage current by more than an order of magnitude, due to the reduction in chain mobility and due to the reduction of PVA hydrophilicity. This result is in agreement with what was previously presented in literature [26]. The electric insulation response of all cross-linked PVA films was very slight. On the non-cross-linked samples, M_w plays an important role. PVA3 and PVA4 with higher M_ws allow lower leakage currents. High M_w is known for reducing chain mobility of high polymer chains, since the density of chain entanglements and the density of chain extremities are, respectively, higher and lower than low M_w polymers. In a polymer, the extremities have higher mobility than the chain segments and both entanglements and extremities stay on the amorphous region of a semi-crystalline polymer [31]. In a semi-crystalline polymer, the charge transport involves mostly the amorphous region, leaving a less important role for crystalline region.

Figs. 4 and 5 show the variation of the relative dielectric constant and tan δ, respectively, of the different PVA films versus temperature and frequency. An increase of dielectric constant is related to polarization which is dependent on chain freedom of movement which, in turn, is dependent on time and temperature.

For non-cross-linked PVA films the dielectric response decreases with the increase of frequency and increases with the increase of temperature. The coordinated bond movements necessary for polarization are time dependent. For each temperature, there is a resonance frequency where the dipole movements are in phase with the electric field. At this resonance frequency there is a jump in capacitance; loss is minimized and tan δ reaches a maximum. The higher the temperature is, the freer the chain movements are, resulting in a higher resonance frequency. For lower temperatures, low resonance frequencies were not reached due to equipment limitations.

Polarization is also dependent on the concentration of permanent dipoles in the polymer chain. At lower temperature and lower frequencies, PVA2 and PVA4, due to their higher density of hydroxyl groups, have a higher dielectric constant. Hydroxyl groups function as strong permanent dipoles that can align to the field, increasing polarization. PVA2, having a lower T_g and less rigid amorphous region, has a higher dielectric constant than PVA4.

The largest increase of dielectric constant occurs around the polymer T_g, between 50 °C–110 °C, and at lower frequencies when the polymer has sufficient time to align its dipoles to the electric field.

For cross-linked polymers, temperature has a less pronounced effect on the chain mobility. The rigidity of the structure and the lower density of dipoles (cross-linking compromises hydroxyl groups) generate lower dielectric constant. Nevertheless, PVA2–ADC and PVA4–ADC present higher amounts of dipoles when compared with PVA3–ADC and PVA1–ADC and therefore show higher dielectric constants.

Another effect found in cross-linked PVA films is that the increase of temperature reduces the dielectric constant due to water loss. Water molecules, when present in the PVA structure, function as plasticizers.
They embed the polymer chains increasing the free volume and reducing T_g. A plasticizing effect of small amounts of water on T_g can lead to slight differences in the T_g values reported elsewhere [32]. Elimination of these water molecules, therefore, decreases chain mobility and consequently reduces dielectric constant. This effect is stronger in crosslinked PVA because chain mobility is less sensitive to the rise of temperature.

The dielectric constants obtained in this work are in agreement with what have been reported in different evaluations of PVA as a gate dielectric, between 5 and 10 [23,25–28].

Fig. 6 shows the hysteresis C–V curves of the studied films and Table 4 presents the resulting sheet concentrations of mobile charges calculated from these graphs. These concentrations are obtained by multiplying the voltage differences between both curves by the maximum capacitance in accumulation. Cross-linked films present a higher hysteresis than non-cross-linked films. This indicates the presence of contaminants in the film structure that are most likely introduced by the reticulation process. The cross-linking process introduces ionic species that, once hydrated, behave as mobile charges considerably increasing the hysteresis of the film. On non-cross-linked PVA films, the excess moisture absorbed functions as fixed charges, allowing high current passage and reducing hysteresis.

Hysteresis has been a commonly reported problem arising from the use of polymers as gate dielectric in OFETs. The hysteresis and memory behaviors in OFETs are normally proposed to be due to the charge storage, slow polarization of the gate dielectric and electron trapping in the semiconductor [10]. Although hydroxyl density plays a hole on the film hysteresis [33], a more relevant part is played by the ionic contaminates that are generally present in the dielectric film. Impurities such as Sodium Acetate or ADC residual ions move with the applied electrical field leading to charge separation within the electrically neutral dielectric giving rise to strong electrode effects [23]. It was found that remnant cations, especially for solutions containing larger amounts of cross-linking agent, resulted in a lowering of the electric field strength of the c-PVA film. This suggests that Cr^{+5} and NH_4+ radicals play an important role with respect to the gate leakage current of a transistor with a cross-linked gate insulator [26,34].

4. Conclusions

PVA is a promising candidate to be used as a gate dielectric in OFET structures due to its suitable properties such as low leakage current, high dielectric constant, simple application and good film properties. The engineering of its structure can provide a more efficient dielectric
material considering the device structure and its components. Control of cross-linking, hydrolysis degree, molecular weight and moisture content can be used to optimize the characteristics of the film, depending of the desired properties. Insulation and dielectric response are in antithesis; the increase of one results in the decrease of the other since both are affected, either positively or negatively, by the chain mobility. This generates the need to compromise between these two properties.

The major impact on the polymer properties is given by reticulation. The largest drawback encountered for the studied PVA films was the high sensitivity to environmental conditions, especially moisture. The methodology used for this study proved to be efficient in the sense of concentrating on the analysis of the gate dielectric properties and associating them with the characteristics encountered through polymer structural analysis. Classical tools for polymer thermal analysis, such as TGA and DSC, provided a good characterization of the structures and allowed for complete structure and properties analysis.

The choice of PVA for an organic insulator must be on cross-linked polymer with high Mw and incomplete hydrolyzation. The large hysteresis allowed for complete structure and properties analysis. Classical tools for polymer thermal analysis, sense of concentrating on the analysis of the gate dielectric properties and associating them with the characteristics encountered through polymer structural analysis. Classical tools for polymer thermal analysis, such as TGA and DSC, provided a good characterization of the structures and allowed for complete structure and properties analysis.

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References


