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Natural polymers for disposable organic thin film transistors

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ABSTRACT

In this study, eco-friendly PTCDI-C8–based organic thin film transistors (OTFTs) were fabricated by incorporating polymers from renewable sources as gate dielectrics and substrates. Chitosan, a polysaccharide obtained from the deacetylation of chitin, and natural rubber (NR), extracted from natural rubber tree, have good dielectric properties, biocompatibility, and biodegradability. To examine the practical applicability of these materials, we fabricated OTFTs using bilayer PVPy/NR and chitosan/NR films as gate dielectric materials. NR not only improved the insulation properties of the dielectric film but also acted as a surface modifier. The fabricated OTFT incorporating chitosan/NR dielectric operated under a low driving voltage, with values of μ and V_{th} of 0.027 $cm^2V^{-1}s^{-1}$ and 0.83 V, respectively. It also displayed an electrical response in the presence of DNA at different concentrations. Because, chitosan possesses high transparency and good mechanical properties, it can be readily cast to form transparent flexible substrates. Accordingly, a flexible disposable OTFT device was fabricated using PVPy/NR as the dielectric material on chitosan as the substrate. The disposable device exhibited a carrier mobility of 0.011 $cm^2V^{-1}s^{-1}$, a value of V_{th} of 0.83 V, and an on/off ratio of 10^3, while being workable over 100 bending cycles.

1. Introduction

Electronic devices play important roles in modern human life. Many advanced and sophisticated electronic devices have been invented to make human life easier and more efficient. Unfortunately, increasing demands for electronic appliances lead to increasing amounts of electronic waste (E-waste) that can threaten living organisms by polluting the water, soil, and even the air. It is estimated that 50 million tons of E-waste is produced each year [1]. The US Environmental Protection Agency estimates that only 15–20% of electronic waste is disposed and recycled properly; the rest goes directly into landfills and incinerators [2]. One potential way to lessen the accumulation of E-waste is to prepare them using materials that can be fully or partially naturally degraded or decomposed. Some organic materials having such capabilities are being studied and developed for their potential to build devices with high flexibility and stretchability—characteristics not afforded by silicon or other inorganic materials. Moreover, devices made with organic materials have the potential to interface with biological systems, and promise more sustainable electronic technologies with potential for biodegradability or recyclability [3].

Polymers from renewable resources are interesting materials for use in electronic devices because of environmental concerns and as substitution for petroleum derived materials [4]. Such polymers can be classified into three groups: natural polymers, synthetic polymers, and polymers from microbial fermentation [5]. A number of polymers derived from renewable resources have been employed in electronic applications as substrates or dielectric materials, including synthetic polymers (e.g., polylactic acid [6,7], polycaprolactone [8], polyvinyl alcohol [9,10]) and naturally occurring polymers (e.g., paper [11–14], silk [15,16], gelatin [17–19], cellulose-based polymers [20–22]). In this study, we examined the use of a combination of synthetic polymer and polymers from renewable resources within thin film transistors. The first polymer is polyvinylpyrrolidone (PVPy), a water-soluble synthetic polymer made from the monomer *N*-vinylpyrrolidone; it provides good transparency, biocompatibility, non-toxicity, and high chemical stability. PVPy has found broad applications as a food additive and in cosmetic, medicine, and pharmaceutical technologies [23–26]. The second material is chitosan, a natural polysaccharide obtained from the deacetylation of chitin, the second most widespread natural polysaccharide on Earth after cellulose [27]. Chitin is the structural material found in

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the shells of crustaceans and insects and fungal cell walls [28]. Chitosan has high transparency and good mechanical properties that make it a suitable material for applications requiring flexible substrates. Chitosan films are also proton conductors displaying high specific gate capacitance, useful in transistor and synapse applications [29,30]. In addition, chitosan is a biocompatible material applied widely as a scaffold material in tissue engineering [31,32]. The third material we explored is natural rubber (NR), a *cis*-polyisoprene extracted from the rubber tree (*Hevea brasiliensis*). The utility of NR has been known since the early seventeenth century; it has excellent insulating properties, with a volume resistivity on the order of 10^9 Ωcm, and is used as a high frequency insulator [33]. These properties make PVPy, chitosan, and NR ideal candidates for the fabrication of environmentally friendly electronic devices. Because chitosan has moderate insulating properties and high capacitance, combining PVPy and chitosan with NR should provide dielectric films with attractive electrical properties.

The use of OTFTs in chemical and biological sensing application has received great attention in recent decades, for example detection of gas [34], metal ion [35–37], pH [38], DNA [39,40], or protein [41,42]. The sensing principle is based on the interaction of a charged species with the interface of the organic semiconductor or the sensing layer which caused a change in surface potential and affects the current that flows in the conducting channel of OTFTs [43]. The sensor response is determined by comparing the electrical characteristics before and after analyte exposure to the device [44].

In this study, we fabricated flexible and disposable *N*,*N*′-dioctyl-3,4,9,10-perylenedicarboximide (PTCDI-C8)–based organic thin film transistors (OTFTs) incorporating bilayer dielectric PVPy/NR and chitosan/NR films on glass and chitosan substrates. Devices prepared with the chitosan/NR dielectric functioned at low operating voltage and could be used as sensors for deoxyribonucleic acid (DNA). In addition, we prepared a device incorporating the PVPy/NR dielectric fabricated on a chitosan substrate that functioned as a flexible disposable transistor. These renewable polymers are promising materials for the development of inexpensive, sustainable, biocompatible, and eco-friendly organic electronics for a wide range of applications—from disposable systems to biosensors and biomedical applications.

2. Experimental

2.1. Materials and solution preparation

PTCDI-C8, chitosan (medium molecular weight, 85% deacetylated), and PVPy (molecular weight: 360,000) were purchased from Sigma–Aldrich and used without further purification. Acetic acid (99.5% pure) was obtained from Acros Organics. Toluene, MeOH, and diiodomethane (reagent plus, 99.5%) were purchased from Sigma–Aldrich. 6045 BP DNA (Fig. S1, ESI†) was diluted in deionized (DI) water into three different concentrations: 1 μg/ml, 3 μg/ml and 5 μg/ml. NR sheets were bought from a Tamil Nadu (India) farmer. A solution of chitosan was prepared by dissolving chitosan powder in a mixture of water and acetic acid (2%, v/v). The NR sheet was stirred continuously in toluene until it dissolved completely.

2.2. Device fabrication

Bottom-gate top-contact OTFTs were fabricated on ITO/glass substrates that had been cleaned with detergent, acetone, and isopropyl alcohol and then treated in a UV-ozone cleaner for 30 min. Bilayer chitosan/NR and PVPy/NR films were used as dielectric materials. PVPy (4 wt% in MeOH) was spin-coated (1000 rpm) onto the gate electrode and then baked at 75 °C for 30 min; NR (0.75 wt% in toluene) was then spin-coated (800 rpm) on the PVPy layer and baked at 75 °C for 30 min. Similarly, chitosan (1 wt% in water/acetic acid) was spin-coated (1000 rpm) onto an ITO/glass substrate and then baked at 90 °C for 30 min, followed by deposition of NR as mentioned above. The thickness of Chitosan/NR and PVPy/NR are 300 and 375 nm, respectively. PTCDI-C8 (50 nm) was thermally evaporated under pressure of 5×10^{-6} torr onto the PVPy/NR film; following the preparation of the active layer, Au source and drain electrodes (40 nm) were thermally evaporated through a shadow mask [channel width (W): 200 μm; channel length (L): 2000 μm]. A flexible chitosan substrate was prepared by casting a chitosan solution (2 wt% in water/acetic acid) into a Petri dish and heating at 90 °C for 4 h to evaporate the water. A Au gate electrode was thermally evaporated on the chitosan substrate, followed by spin-coating of the PVPy/NR dielectric layer and thermal evaporation of the PTCDI organic semiconductor and Au source/drain electrodes. The capacitance of polymer dielectrics were measured using metal-insulator-metal (MIM) structure consisting of polymer layers sandwiched between ITO bottom and Au top electrodes with active area of 0.1 cm^2.

2.3. Electrical and material characterization

The electrical performance of the fabricated devices was measured using a Keithley 4200 semiconductor analyzer inside a N_2-filled glove box. Tapping-mode atomic force microscopy (AFM) images were recorded using a Bruker Dimension Icon atomic force microscope. The capacitance of the dielectric films was measured using an Agilent E4980A Precision LCR Meter. Film thickness was measured using Bruker Dektak surface profilometer. Bending tests of flexible devices were performed at a bending radius of 1.5 cm; the changes in electrical performance were measured after 25, 50, 75, and 100 cycles. The DNA sensor (a device incorporating a chitosan/NR dielectric on an ITO/glass substrate) was tested after placing droplets (2 μL) of solutions of DNA on top of the channel and then drying for 60 min under vacuum. The threshold voltage shift was determined by dividing the threshold voltage value in the presence of DNA (V_{th}) by the initial threshold (V_{0th}). Contact angles were measured using a MagicDroplet model 100 goniometer, with DI water (polar) and diiodomethane (dispersive) as probe liquids. The mechanical properties of the chitosan substrates were characterized through tensile tests. The tensile test specimens were prepared by cutting 4-inch chitosan substrates into strips (1 × 5 cm) and stretching at a constant rate (0.33 mm s^{-1}) using an MTS Tytron 250 pull tester.

3. Results and discussion

The n-channel OTFTs were fabricated on ITO/glass by using PVPy/NR and chitosan/NR as bilayer dielectrics; later, they were fabricated on a 50-μm flexible chitosan substrate to form a disposable device. Fig. 1 (a) illustrates the device structure used in this study. Fig. 1 (b) presents the chemical structures of PVPy, NR, chitosan, and PTCDI-C8. The device fabricated with a single layer of PVPy worked at 60 V, while the device failed when incorporating only chitosan. When a thin layer of NR was introduced, the device featured a clearer linear and saturated region when compared with that of the device featuring single-layer PVPy (Fig. S2, ESI†).

Fig. 2 presents the output and transfer characteristics of n-channel PTCDI-C8 transistors, measured at various gate voltages (V_G) and drain–source voltages (V_{DS}). Devices fabricated using the PVPy/NR dielectric functioned at an operating voltage of 20 V [Fig. 2(a) and (b)]; those containing the chitosan/NR dielectric functioned at a lower operating voltage of 10 V [Fig. 2(c) and (d)]. The capacitance (Ci) was measured for both the PVPy/NR and chitosan/NR dielectrics, using the sandwiched structure ITO/polymer/Au.

Fig. 3 plots the measured values with respect to frequency. The PVPy and PVPy/NR films exhibited stable capacitance upon increasing the frequency from 20 Hz to 1 MHz. In the case of chitosan/NR, however, the value of Ci was high (8.03 nF) at low frequency (20 Hz) and then dropped tremendously upon increasing the frequency. This behavior was presumably due to the mobile ions present in the chitosan film