

Gelatin: Chitosan Composite as Gate Dielectric

Gate dielectric layer in OFETs profoundly impacts the transistor performance in all aspects starting from operation voltage to electrical stability under different conditions like humidity, temperature, and mechanical stress. To utilize the OFET devices in various flexible and wearable applications for a long duration, high electrical stability is required for transistor performance upon applications of harsh bending conditions. For efficient transistor performance, high flexibility in the gate dielectric layers is essential to withstand repeated bending without degrading their dielectric properties and prevent the device from failure under mechanical stress. Gelatin is a promising biodegradable dielectric candidate, widely explored in various applications; however, it exhibits weak mechanical stability due to the deformation and breakage of polymer networks under stress. To enhance the flexibility, another natural polymer chitosan was integrated as a tuning agent in composite with gelatin in modulating the dielectric properties and enhancing the mechanical stability of the composite film. In this chapter, a composite gate dielectric of gelatin and chitosan was investigated with four different ratios to investigate their suitability as gate dielectric in flexible OFETs while enhancing their electromechanical stability through electrostatic interaction and strong hydrogen bonding between the functional groups of both polymers. This composite gate dielectric addressed the drawbacks of each polymer by combining their strengths, providing enhanced mechanical robustness, moisture resistance, and environmental sustainability for the demonstration of high-performance OFETs. TIPS-pentacene: PS was utilized to form the active layer for excellent p-channel transistor performance. The investigation of different gelatin to chitosan ratios in composites indicates that a controlled integration of chitosan (10:5) results in enhanced performance in transistors, alongside significant improvements in electromechanical and thermal stability. This work is recently published (Konwar, Saxena, Rahi, et al., 2022).

6.1 INTRODUCTION

The biocompatibility of natural materials and biopolymers makes them excellent candidates for implantable, edible, and skin-like electronics (Shi et al., 2020; L. Wang et al., 2021). Edible electronics has recently generated significant scientific enthusiasm by ideating a technology that is safe for consumption, eco-friendly, economical, and degrades within the body after performing its function, either through digestion or even metabolization (Sharova & Caironi, 2021; Sharova et al., 2020). OFETs have been explored as a very promising device for demonstration of flexible, sustainable, edible, or biodegradable electronics (Sirringhaus, 2014; Tang et al., 2019; Xiang et al., 2022). To achieve high performance in OFETs, various high- k dielectrics have been investigated by researchers (Y. Zhang et al., 2020; Zhu et al., 2018). However, many of these dielectrics were deposited at temperatures generally higher than 150 °C unsuitable for flexible plastic substrates and also due to their poor mechanical stability. In addition, these dielectrics are not suitable for biodegradability. Significant contributions have been made by researchers through the development of entirely or partially biodegradable transistors using numerous edible or biopolymer dielectrics like gelatin, cellulose, guanine, silk, adenine, chitosan, starch, dextran, etc (Konwar, Saxena, Raghuwanshi, et al., 2022c; Lee et al., 2018b; Shi et al., 2017; Xiang et al., 2022). The use of pristine biopolymers generally results in low electromechanical stability in devices due to inherent polar hydrophilic functional groups in these biopolymers which cause the device to

degrade rapidly (S. A. Mathew & S. Arumainathan, 2022). These hydrophilic groups can trap mobile charge carriers, constraining the performance with reduced drain current and induction of hysteresis (Kwon et al., 2021). However, chemical crosslinking of biopolymers can efficiently lower the polar hydrophilic functional groups of these dielectrics (Kim et al., 2017; Ren et al., 2018), making them suitable for fabrication of devices with enhanced electromechanical stability. Crosslinking of biopolymers with suitable materials can improve their mechanical, physical, chemical, and optical properties compared to those of individual films (Dhand et al., 2021; Kahle et al., 2017; Y. Yang et al., 2020). For example, composites like cross-linked poly(vinyl alcohol) (C-PVA), poly(4-vinyl phenol) (PVP), polydimethylsiloxane (PDMS), and fluorinated polymers were demonstrated as gate dielectric layers for fabrication of high performance transistor devices (Ren et al., 2018), though, these reports are rare. Moreover, the demonstration of crosslinked edible dielectric components with natural biopolymers can be very crucial for advancements toward future edible and biodegradable electronics.

Among various biopolymers, gelatin and chitosan are the most commonly explored materials as gate dielectric in transistors (Yu et al., 2018). Gelatin is easily soluble in water and forms complexes with other molecules because of the available functional groups acting as binding sites (S. A. Mathew & S. J. A. O. Arumainathan, 2022). This protein enables the formation of a smooth film with excellent dielectric properties for the development of low-voltage operated devices (He et al., 2016; Mandal et al., 2020a). Additionally, chitosan is a polysaccharide derived from chitin, containing amino polysaccharide molecules having a strong positive electrical charge, enabling it to bond very strongly with functional groups of gelatin (Crini, 2019). It is widely explored in oxide-based synaptic transistors and capacitors due to its advantages of mechanical stability, transparency, high capacitance for protonic mobile ions, and temperature stability (Fukada et al., 2021; Yu et al., 2018). The incorporation of chitosan in composite reduces the elastic modulus of gelatin film leading to increased elongation at break value indicating higher ductility for composite than the individual parent film (Samsi et al., 2019). The formation of strong hydrogen bonding between the ammonium groups of chitosan and the negatively charged side-chain groups in gelatin forms polyelectrolyte complexes resulting in film strengthening. This property is highly dependent on the ratio of chitosan content, deacetylation percentage, molecular weight, and film preparation process (Fukada et al., 2021; S. A. Mathew & S. J. A. O. Arumainathan, 2022). Composite of gelatin and chitosan have already been explored as an edible film in food and tissue engineering, although it has not been explored as gate dielectric in organic transistors (Bonilla & Sobral, 2016; Haghighi et al., 2019; Samsi et al., 2019).

In this work, for the first time, gelatin: chitosan composite was utilized as an edible gate dielectric to demonstrate the enhancement of electromechanical stability of the flexible organic transistors. The effect of enhanced properties of this composite is comprehensively investigated on various performance parameters for flexible organic transistors. For the same, different gelatin: chitosan ratios of 10:0, 10:1, 10:5, and 10:10 were explored in a combination of air-stable solution-processed semiconductor polymer blend TIPS-Pentacene: polystyrene (PS) (Konwar, Saxena, Raghuwanshi, et al., 2022a, 2022c) for p-channel transistor performance. All types of fabricated devices exhibited excellent p-channel performance for -5 V operation. Electromechanical stability of all the devices was studied using the application of bias stress, tensile bending, and continuous repeatability of electrical characteristics. Through this extensive study, it was observed that devices with 10:5 ratio exhibited excellent electromechanical stability along with high performance, better than other compositions. Less than 15% decay in I_{on} was observed for this composite, even after various electromechanical stability tests on device. Further, circuit utility of this device was explored in inverters showing decent switching. Finally, high environmental stability for 6 months was observed from these devices. These outstanding properties of this unique edible biopolymer composite can facilitate the demonstration of biodegradable and edible organic devices for ingestible, implantable, and artificial skin applications.

6.2 DEVICE FABRICATION AND ELECTRICAL CHARACTERIZATION

All materials including chitosan ($\geq 75\%$ deacetylation), gelatin (300 bloom A type), TIPS-Pentacene, and PS were purchased from sigma Aldrich and were used as it is. Flexible ITO-coated

PET substrate was used to fabricate the OFET devices using a conventional BGTC structure with ITO acting as a bottom gate electrode. Firstly, substrates were cleaned with standard cleaning processes with organic solvents. For the dielectric composite, chitosan and gelatin solutions were prepared separately and then mixed. For the same, a 2 wt. % chitosan solution in aqueous acetic acid was prepared by stirring at 50 °C for 6 hours. Similarly, 10 wt. % gelatin solution in DI water was prepared by stirring at 60 °C for 2.5 hours. Both the prepared solutions were mixed with different gelatin: chitosan ratios i.e. with 10:0, 10:1, 10:5, 10:10, and stirred for 1 hour. These composite solutions were spin-coated at 2000 rpm for 60 s and annealed at room temperature for 24 hours to form thin films of gelatin: chitosan edible dielectric. Blend of TIPS-Pentacene: PS layer was deposited over dielectric film using drop casting as reported in previous experiments. Finally, Au source/drain top contacts were deposited through a shadow mask. Figure 6.1 shows the schematic and picture of the fabricated transistors. Figure 6.1 shows the schematic and real image of the fabricated device on flexible substrate.

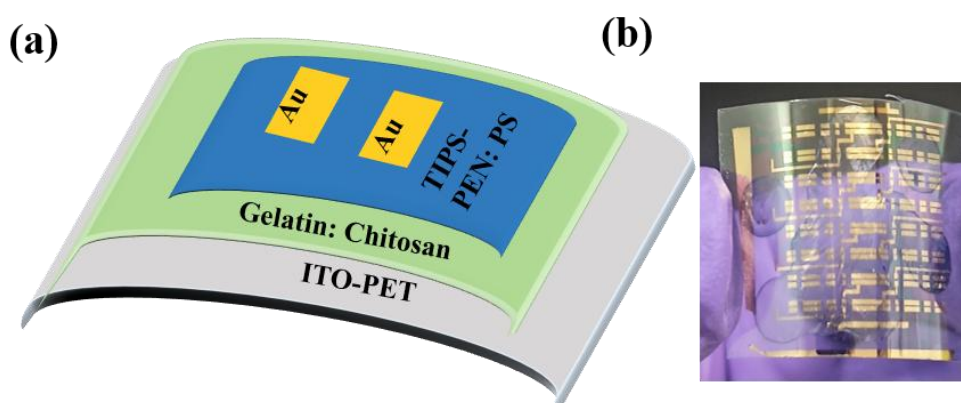


Figure 6.1 : (a) Schematic, and (b) digital image of flexible transistors with gelatin: chitosan edible gate dielectric composites.

Surface morphology for all dielectric composite films was investigated with the help of AFM images. The bonding between chitosan and gelatin was confirmed by FTIR measurements. TGA was used to identify the phase changes and to observe the physical properties of pristine biopolymers and their composites under temperatures ranging from 30 - 600 °C with the increment of 10 °C/min. Electrical characteristics of fabricated devices were measured in ambient air using Keithley 4200 SCS parametric analyzer, and important device parameters were extracted. C_i was measured from the MIS structure (i.e., ITO/gelatin: chitosan/TIPS-pentacene: PS/Au). Further, these values were used to calculate saturation regime μ values. Electrical and operational stability were characterized by performing multiple scans for transfer characteristics and bias-stress stability respectively. In addition, electromechanical stability was studied by inducing a tensile bending to the devices. Shelf-life stability was studied by observing the changes in the device performance with a time for 24 weeks. Resistive load-based inverter circuits were implemented and characterized to investigate the circuit applicability of these devices.

6.3 RESULTS AND DISCUSSION

6.3.1 Investigation of Film Properties of Dielectric Composite

Schematic representation of individual chitosan and gelatin and the formation of a crosslinked hybrid matrix is shown in Figure 6.2 (a), which helps in understanding the interactions between gelatin and chitosan. The chemical structures of chitosan and gelatin with their interactions to form hydrogen bonding among the functional groups are represented in Figure 6.2 (b). In general crosslinking agents are used to facilitate the formation of such composites (S. A. Mathew & S. Arumainathan, 2022). However, natural crosslinking is utilized in this study without using any cross-linking agent, with tuning of gelatin chitosan ratio for optimizing the gel network's thermal responsiveness. The hydroxyl and amino groups present in the chitosan help in intra and inter-molecular modification by forming hydrogen bonding

between them. Similarly, gelatin also has a large group of amino acids like glycine, hydroxyproline, glutamic acid, alanine, arginine, aspartic acid, etc. with a combination of single and double chains. The cross-linking process is aided by the electrostatic interactions between the NH_2 groups in chitosan and the COO groups in gelatin. As compared to gelatin, chitosan has an abundant number of amine groups, due to this little amount of chitosan integration can form strong hydrogen bonding, resulting in film strengthening. The gel strength is controlled by modifying the mixing ratio of the composite. To emphasize upon, confirmation of bonding and effect of temperature on composite will be discussed later through obtained results.

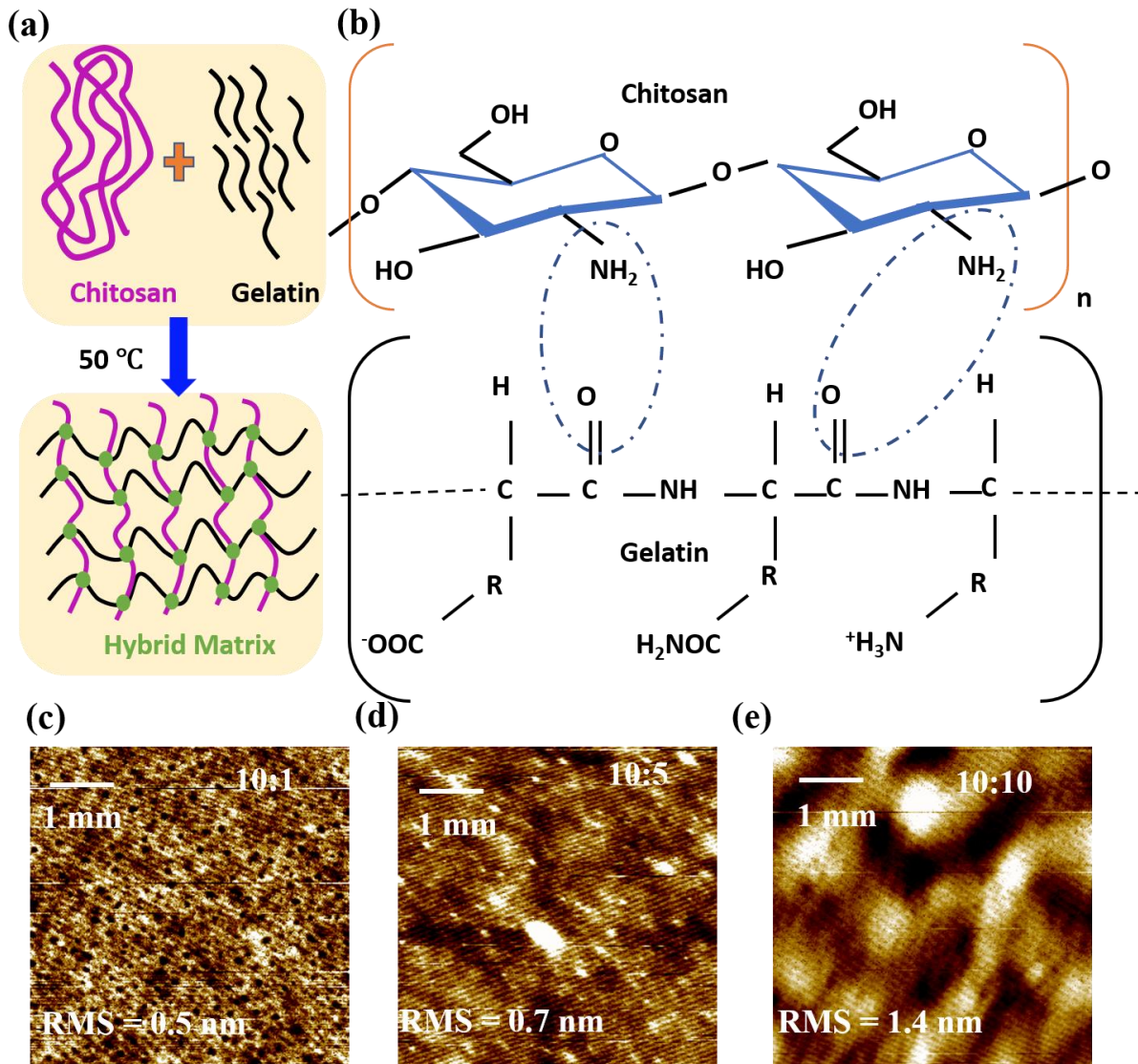


Figure 6.2 : (a) Schematic illustration of the formation of chitosan: gelatin hybrid matrix. (b) Representation of hydrogen bonding between molecules through chemical structures of chitosan and gelatin. AFM images showing surface morphology for 10:1 (c), 10:5 (d), and 10:10 (e) for gelatin: chitosan dielectric composite.

Surface morphology of dielectric films was investigated using AFM and root mean square (RMS) values of surface roughness were used to estimate the smoothness of the dielectric surface. Morphology of bare gelatin has been earlier reported on multiple instances showing the RMS roughness values ranging between 0.3 to 0.6 nm (Mao, Hwang, et al., 2014). The AFM images for the composite layers are shown here in Figure 6.2 (c, d, and e). RMS roughness values of 0.5 nm, 0.7 nm, and 1.4 nm were obtained for 10:1, 10:5, and 10:10 dielectric films respectively. In general, a smoother dielectric surface is preferred for low interfacial mismatches and trapping sites at the interface of semiconductor and gate dielectric (Don Park et al., 2007). Increasing the rate of chitosan content increases the roughness due to the porous nature of chitosan and limits the device's performance. Though almost identical smoothness was achieved for 10:1 and 10:5

composites, a relatively higher roughness was observed for 10:10 composites. The thickness of gelatin: chitosan dielectric layer was measured by Dektak XT surface profiler and was found to be $0.56 (\pm 0.03) \mu\text{m}$. The combined thickness of TIPS-Pentacene: PS polymer blend was found to be $\sim 1.2 (\pm 0.2) \mu\text{m}$. The thickness of the PS layer after vertical phase separation had been earlier explored by our group to be $\sim 140 \text{ nm}$.

6.3.2 Performance of Flexible OFETs with Different gelatin: chitosan composites

The output and transfer characteristics for all the p-channel flexible organic transistors with an edible composite gate dielectric, with gelatin: chitosan ratios of 10:0, 10:1, 10:5, and 10:10, are shown in Figure 6.3 (a & b, c & d, e & f, and g & h) respectively.

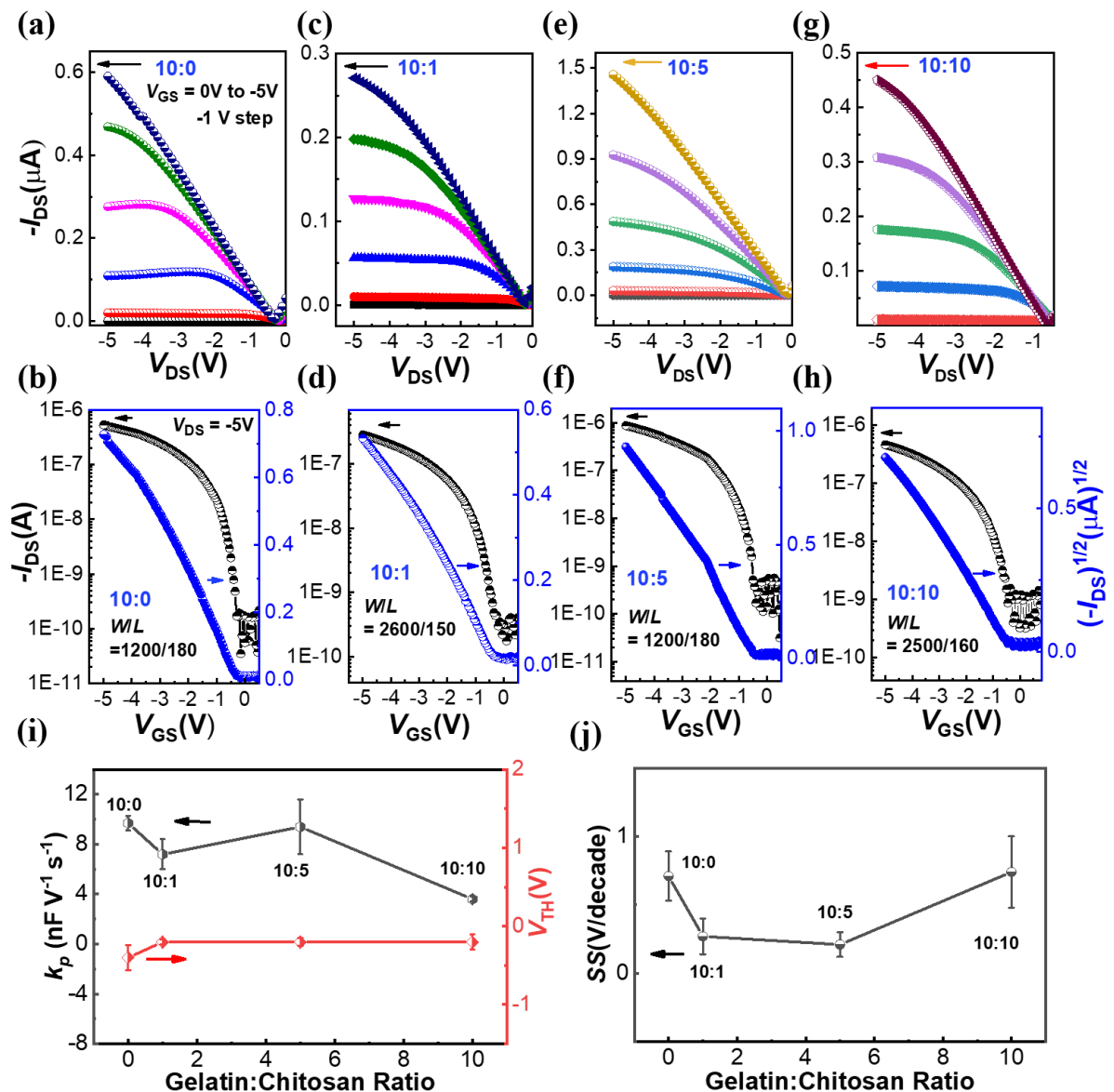


Figure 6.3 : Output and transfer plots of p-channel transistors for gelatin: chitosan dielectric composition of 10:0 (a), (b); 10:1 (c), (d); 10:5 (e), (f) and 10:10 (g), (h), respectively. The V_{GS} is varied from 0 V to -5 V in -1 V step in the output characteristics. The transfer curve is plotted for saturation region with V_{DS} of -5 V. Comparison of performance parameters, (i) Process transconductance (k), V_{TH} , and (j) SS for all gelatin: chitosan compositions.

Transfer characteristics in saturation region were obtained at V_{DS} of -5 V while sweeping the V_{GS} between 1 to -5 V. Similarly, output characteristics were obtained for V_{DS} range of 0 to -5 V by changing the V_{GS} from 0 to -5 V in steps of -1 V. Excellent saturation in output characteristics and sharp switching in transfer characteristics were observed for 10:5 gelatin: chitosan composite as shown in Figure 6.3 (e & f). In general, contact effects are observed in solution-processed

organic devices due to the combined effect of injection barrier between metal contacts and organic semiconductor (OSC) and morphology of OSC. Theoretically, the schottky barrier between Au and TIPS-Pentacene can be obtained from energy band structure. Considering the work function of Au as -5.1 eV, HOMO and Fermi levels of TIPS-pentacene as -5.3 eV, and -4.6 eV respectively, a schottky barrier of ~1 eV is estimated (Griffith et al., 2010; Xu et al., 2017). However, contact issues are not evident in the output characteristics of the best case (10:5) devices. Low voltage operation in these devices indicates a strong accumulation of holes in the channel due to the properties of the gate dielectric capacitance formed by these natural composites. To study and compare the performance of the transistors of various composite ratios, the main performance parameters such as k_p (μ^*C_i), V_{TH} , SS , and I_{on}/I_{off} were calculated from the I_{DS} vs V_{GS} plot at saturation regime. The μ_{sat} was estimated from k_p values extracted from the electrical characteristics as given above, C_i was measured through the MIS structures at 1 kHz for all compositions. The D_{it} was estimated from the actual SS values and C_i was measured at 1 kHz using the standard equation for estimation (Held et al., 2015). It is important to note that these C_i values can be higher at much lower frequencies, which is observed for natural biopolymers (Sharova & Caironi, 2021). Hence, k_p was chosen for comparison, which is indicative of the actual current driving capacity of the device and a fairly normalized parameter for comparison of transistor devices addressing the structure and dielectric variations. The fluctuation of k and V_{TH} , for different dielectric compositions, is shown in Figure 6.3 (i). Similarly, corresponding SS for devices is shown in Figure 6.3 (j). Table 6.1 summarizes the directly derived and estimated device parameters for all compositions of gelatin: chitosan edible dielectric. As it can be seen from the performance summary, devices with 10:5 composition outperformed the other counterparts in terms of sharper switching (lower SS values) and higher I_{on}/I_{off} . Among all, 10:10 composition shows inferior performance compared to others as also indicated by the higher surface roughness for this dielectric composite through RMS values obtained from AFM.

Table 6.1 : Summary of average and maximum device parameters for all dielectric compositions

Device parameters	10:0	10:1	10:5	10:10
k_p (nF V ⁻¹ s ⁻¹)	9.7(±0.6)	7.2(±1.2)	9.4(±2.2)	3.6(±0.2)
$k_{p,max}$ (nF V ⁻¹ s ⁻¹)	13.5	9.0	14.0	5.2
V_{TH} (V)	-0.4(±0.16)	-0.2(±0.03)	0.2(±0.05)	-0.2(±0.1)
SS (V/dec)	0.71(±0.18)	0.27(±0.13)	0.21(±0.09)	0.74(±0.26)
I_{on}/I_{off}	~ 6×10 ³	~ 10 ³	~10 ⁴	~ 5×10 ²
* C_i (nF/cm ²)	7.5	8	8.5	8.7
μ_{sat} (cm ² V ⁻¹ s ⁻¹)	1.3(±0.05)	0.9(±0.2)	1.1(±0.27)	0.4(±0.02)
* μ_{max} (cm ² V ⁻¹ s ⁻¹)	~ 1.8	~ 1.1	~ 1.65	~ 0.6
D_{it} (cm ⁻¹ eV ⁻¹)	3.1×10 ¹¹	1.8×10 ¹¹	1.3×10 ¹¹	6.2×10 ¹¹

C-V was measured from the frequency range of 1 kHz to 1 MHz, and * C_i for the lowest value of frequency, i.e. for 1 kHz was considered.

From the table, it can be observed that both 10:0 and 10:5 compositions have almost similar k_p values, however, remaining parameters such as V_{TH} , SS , D_{it} , I_{on}/I_{off} are higher in 10:5 devices. Though the impact of thickness is not explored here, it is worth mentioning that the variation in thickness of dielectric and semiconductor layers will impact on switching voltage and speed of transistors, primarily due to corresponding variation in values of capacitances. Further, switching speed of these devices is expected to be low due to large L of the devices and complete overlap of source/drain electrodes with gate, leading to high value of parasitic capacitance (Klauk, 2018). Patterned gate can help in eliminating the overlaps and increasing the operation speed. It is important to note that edible dielectrics are rarely reported in literature for solution-processed

flexible organic transistors. The k value of $14.0 \text{ nF V}^{-1} \text{ s}^{-1}$ is higher than those exhibited by other reports on flexible transistors with edible gate dielectrics such as $8.7 \text{ nF V}^{-1} \text{ s}^{-1}$ for alginate (Dumitru et al., 2015), and $6.2 \text{ nF V}^{-1} \text{ s}^{-1}$ for almond gum (Seck, Mohammadian, Diallo, Faraji, Erouel, et al., 2020). This high k value from 10:5 composite corresponds to an average and maximum μ_{sat} of $1.1(\pm 0.27)$ and $1.65 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively using the C_i measured through a value of 8.5 nF/cm^2 . The $I_{\text{on}}/I_{\text{off}}$ values were lower (on the order of 10^1 to 10^3) for those reports compared to $\sim 10^4$ exhibited by the proposed 10:5 gelatin: chitosan composite in our work. Recently, honey, a natural edible material, was explored as an excellent electrolytic gate dielectric for organic transistors and logic circuits operating in ambient air at very low voltages (Sharova & Caironi, 2021), with higher k values exhibited from transistors, however, those devices were demonstrated on rigid corning glass. Similar explorations are essential on flexible substrates for emerging fields of edible electronics.

In addition, very low V_{TH} values were obtained for gelatin: chitosan composite devices, which is essential for low power consumption and is one of the potential uses for eco-sustainable technologies for portable electronics. SS represents the minimum V_{GS} required to modulate I_{DS} by one order of magnitude. Lower SS values correspond to sharper switching of the devices and lower off currents which leads to low power consumption when devices are in standby mode. Devices with 10:5 composite exhibited a low SS value of 0.2 V/dec. , which is among the lowest values reported for flexible organic transistors with solution-processed semiconductors and dielectrics (Seck, Mohammadian, Diallo, Faraji, Erouel, et al., 2020). Moreover, these low values are difficult to find for edible gate dielectrics in literature to date even with vacuum evaporated organic semiconductors (Shi et al., 2017). The low values of SS for transistors result in low estimated values of D_{it} , signifying a good quality interface formed between the semiconductor and dielectric of TIPS-Pentacene: PS/ gelatin: chitosan structure, which is vital for optimal carrier conduction.

6.3.3 Effect of Bias-stress and Bending on Transistor Performance

Further, operational and electrical stability upon mechanical stress or bending were extensively performed to explore the utility of devices for real-world flexible applications and are summarized in Figure 6.4. Further, to investigate the electromechanical stability, a tensile strain was applied to the devices using 100 repeated mechanical bending cycles at a radius (r_{bend}) of 5 mm, followed by the bias-stress measurements on the same device. Maintaining the transistor characteristics under mechanical bending is crucial for devices for reliable operation in flexible electronics. The bending strategy is shown in inset of Figure 6.4 (a). Normalized I_{DS} decay upon bias-stress before and after 100 cycles of bending was studied, as given in Figure 6.4 (a), (b), (c), and (d) for the composite of 10:0, 10:1, 10:5, and 10:10 respectively. A typical decay in I_{DS} is observed for all the devices which is very obvious for any polymer dielectrics due to the presence of functional groups (Lee et al., 2006). From these plots, it can be observed that the devices with 10:5 composition have excellently maintained the bias-stress characteristics even after this extreme bending condition. On the other hand, the devices with pristine gelatin could not sustain the bias-stress as can be seen in Figure 6.5 (a). Moreover, a significant decay followed by a slight increase later is seen in the case of gelatin, which can happen for a polar dielectric due to the polarization generating extra charge carriers and traps at the interface during the stress period (Subbarao et al., 2015). The composition with equal amounts of gelatin and chitosan (10:10) showed the poorest bias-stress stability among all, indicating the importance of gelatin: chitosan ratio in obtaining high electromechanical stability. Change in V_{TH} during the stress period was estimated from I_{DS} decay, as shown in Figure 6.5 (e) and (f) respectively for before and after 100 cycles of bending. Percentage of I_{DS} decay in all compositions and their corresponding variation V_{TH} of after the stress period for unbent as well as after 100 cycles of bending are listed in Table 6.2. Among all these, 10:5 device exhibited the least decay of 12% after combined effect of bias-stress and bending, compared to others which were 18%, 23%, and 32% for the devices 10:0, 10:1, and 10:10 respectively. Moreover, a significantly lower V_{TH} shift of 0.3 V was observed for 10:5 composition, indicating the lowest charge trapping at the dielectric interface. The reduction of

device performance after tensile bending possibly occurs due to the formation and propagation of microcracks/defects in the semiconducting film under strain, or due to variations in the dielectric film's characteristics (Choi et al., 2020).

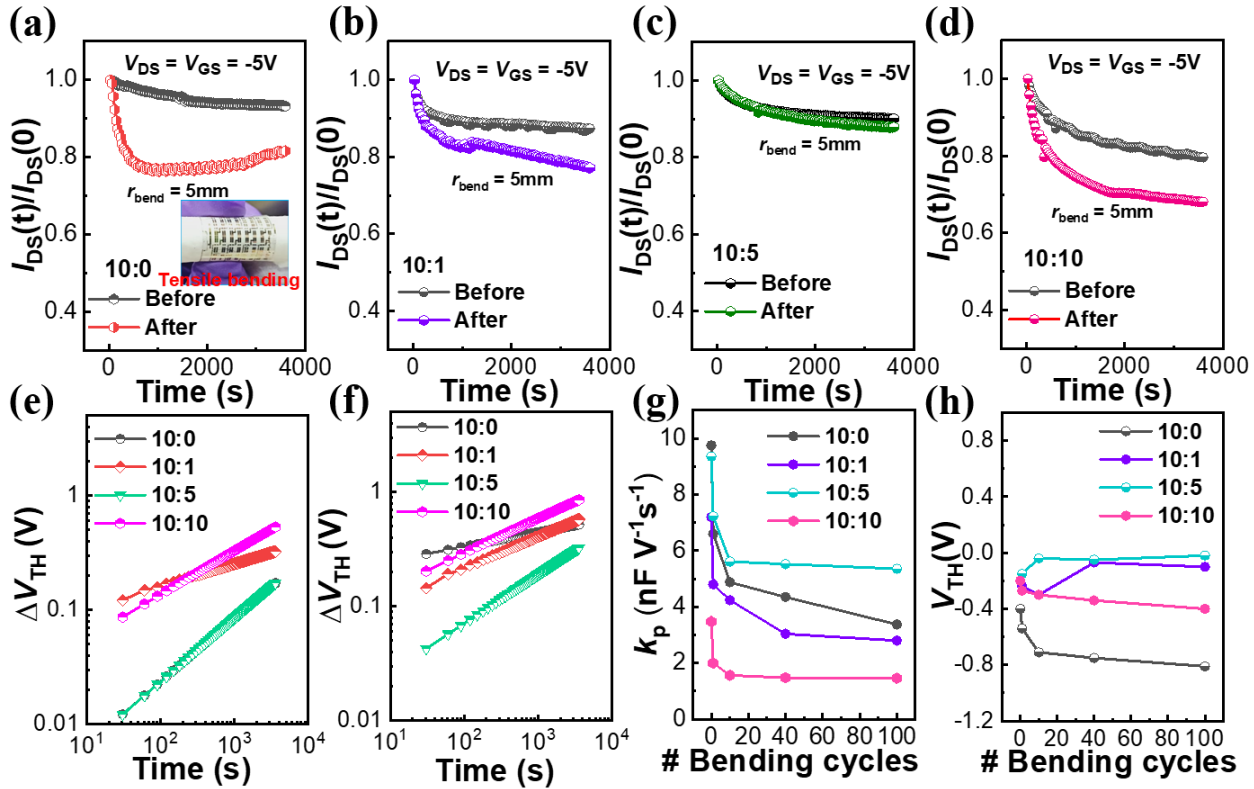


Figure 6.4 : Electromechanical stability exploration involving electrical bias-stress with $V_{DS} = V_{GS} = -5$ V for 3600 s and application of 100 cycles of bending causing tensile stress on devices. Bias-stress induced decay for gelatin: chitosan composite of (a) 10:0, (b) 10:1, (c) 10:5, and (d) 10:10 respectively; showing normalized I_{DS} decay before and after bending. Corresponding bias-stress induced shift in V_{TH} for unbent devices (e), and after 100 cycles of bending (f), for all dielectric compositions. Variation of the average values of k (g), and V_{TH} (h), at different bending cycles.

Table 6.2 : Summary of percentage decay in I_{DS} and change in V_{TH} after the 1 hr bias-stress for unbent and devices with 100 cycles of tensile bending.

Device condition	Parameters	10:0	10:1	10:5	10:10
Unbent	$\Delta I_{DS}(\%)$	7	12	10	20
	ΔV_{TH}	0.18	0.32	0.18	0.53
100 times of tensile bending	$\Delta I_{DS}(\%)$	18	23	12	32
	ΔV_{TH}	0.52	0.58	0.32	0.86

However, the addition of suitable chitosan content to gelatin increases the dielectric film's mechanical stability, which in turn reduces the effect of bending on dielectric film and results in more consistency in device properties. The average value variation of crucial performance parameters k and V_{TH} for different bending cycles 1, 10, 40, and 100 for all four compositions are shown in Figure 6.4 (g) and (h) respectively. For k , the decay of 65%, 62%, 42% and 60% are observed for devices of 10:0, 10:1, 10:5, 10:10 gelatin: chitosan compositions. Again, device with 10:5 composition has shown the least percentage of decay in k during the bending process, confirming the better electromechanical stability compared to other compositions. Similarly, this device showed a negligible variation of V_{TH} at different bending cycles as shown in Figure 6.4 (h).

These enhanced properties were attributed to the excellent hydrogen bonding between gelatin and chitosan.

6.3.4 FTIR and TGA Characteristics

The bonding between gelatin and chitosan was confirmed through fourier transform infrared spectroscopy (FTIR) measurements. FTIR spectrum for 10:5 composite is shown in Figure 6.5 (a). Gelatin showed the characteristic absorption at 3566 cm^{-1} (O-H stretching vibration), 1704 cm^{-1} (C=O stretching vibration), 1571 cm^{-1} (N-H bending vibration), and 1083 cm^{-1} (C-O stretching vibration). Similarly, chitosan absorption bands appear at 3463 cm^{-1} (O-H and N-H stretching vibrations), 1677 cm^{-1} (C=O bending vibrations), 1575 cm^{-1} (N-H bending vibration), and 1155 cm^{-1} (C-O-C stretching vibrations). From these results, it can be observed that the peak at 1704 cm^{-1} is shifted to 1706 cm^{-1} , whereas 1571 cm^{-1} is shifted to 1575 cm^{-1} , indicating strengthening due to the strong hydrogen bonding between ammonium ($-\text{NH}_3^+$) ions of the chitosan and the carboxyl ($-\text{COO}^-$) ions of gelatin (Peng et al., 2020). To further investigate the reasons for high performance and stability of devices with 10:5 composite, thermogravimetric analysis (TGA) was performed and the phase changes under a range of temperatures were studied for bare gelatin, chitosan, and their 10:5 composite. For this analysis, temperature ranging from 30 to $600\text{ }^\circ\text{C}$ with an increment of $10\text{ }^\circ\text{C}/\text{min}$ was applied. The TGA results are shown in Figure 6.5 (b).

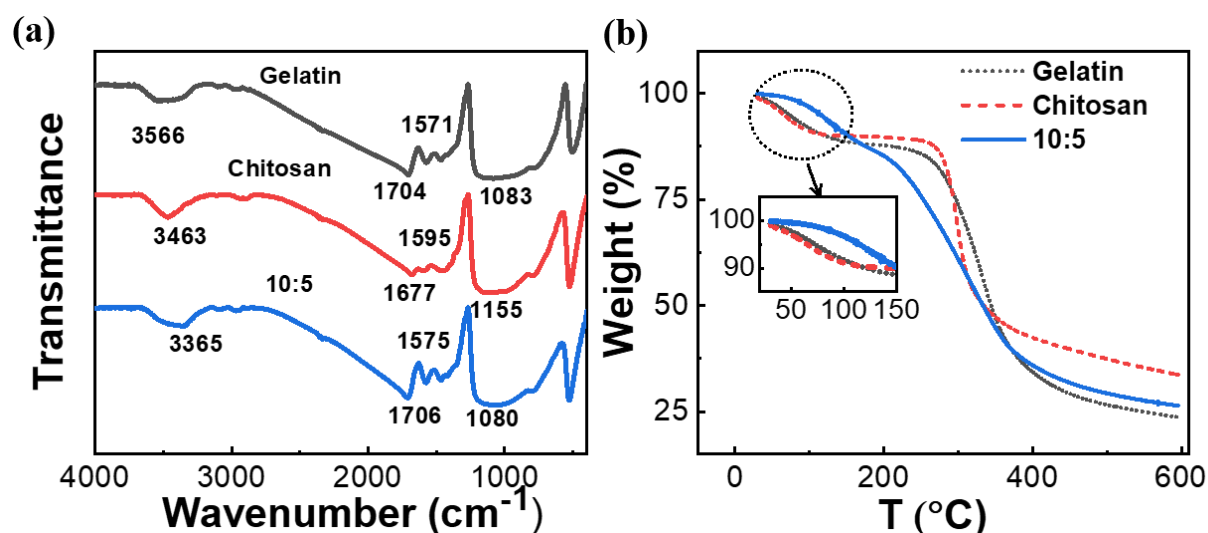


Figure 6.5 : (a) FTIR spectrum and, (b) TGA characteristics for a temperature range of $30\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$ for bare gelatin, chitosan, and 10:5 composite. Inset of (b) highlights the suitability of 10:5 composite over others.

In TGA plot, the weight loss is observed at three different regions of temperature. In the first region, i.e from $30\text{--}150\text{ }^\circ\text{C}$, the weight loss primarily happens due to the removal of moisture content from the materials. At $150\text{ }^\circ\text{C}$, bare biopolymers as well as 10:5 composite show $\sim 10\%$ of weight loss. However, at lower temperatures such as $100\text{ }^\circ\text{C}$ which is a commonly used annealing temperature for most of the solution-processed organic devices, the stability of composite ($\sim 3\%$ of weight loss) is significantly higher than the pristine ones which are $\sim 8\%$ and $\sim 9\%$ of weight loss for gelatin and chitosan respectively. This finding is indeed remarkable indicating a huge potential of composite in tuning the material properties for enhancement of device performance. In the second region between $150\text{ }^\circ\text{C}$ to $360\text{ }^\circ\text{C}$, a significant weight loss of 50% is observed due to the depolymerization of molecules by breaking of the chemical bonding and generation of free radicals. After that, at $600\text{ }^\circ\text{C}$, loss of 24% , 33% , and 26% remained in the mass respectively for gelatin, chitosan, and 10:5 composite. It is interesting to see that, at this stage, the composite does slightly better performance than pristine gelatin. From these results, it can be observed that there is a sharp degradation in both pristine gelatin and chitosan upon application of temperature, at about $265\text{ }^\circ\text{C}$, whereas the composite shows a comparatively linear decay in the weight for most parts of the temperature range. More interestingly, from $30\text{ }^\circ\text{C}$ to $150\text{ }^\circ\text{C}$, a very encouraging aspect of the composite is observed, as also highlighted in the inset of Figure 6.5 (b). Up to $150\text{ }^\circ\text{C}$, which is a widely accepted maximum operating and annealing temperature for flexible electronics and

most flexible plastic substrates, the composite has done exceptionally well compared to the pristine biopolymers.

6.3.5 Repeatability and Environmental Stability

To further investigate the suitability of 10:5 gelatin: chitosan composite gate dielectric in real world applications, transistor performance was investigated with this gate dielectric for repeatability and environmental stability, as shown in Figure 6.6. An excellent overlapping of transfer characteristics was observed upon continuous scanning for 100 cycles, as shown in Figure 6.6 (a).

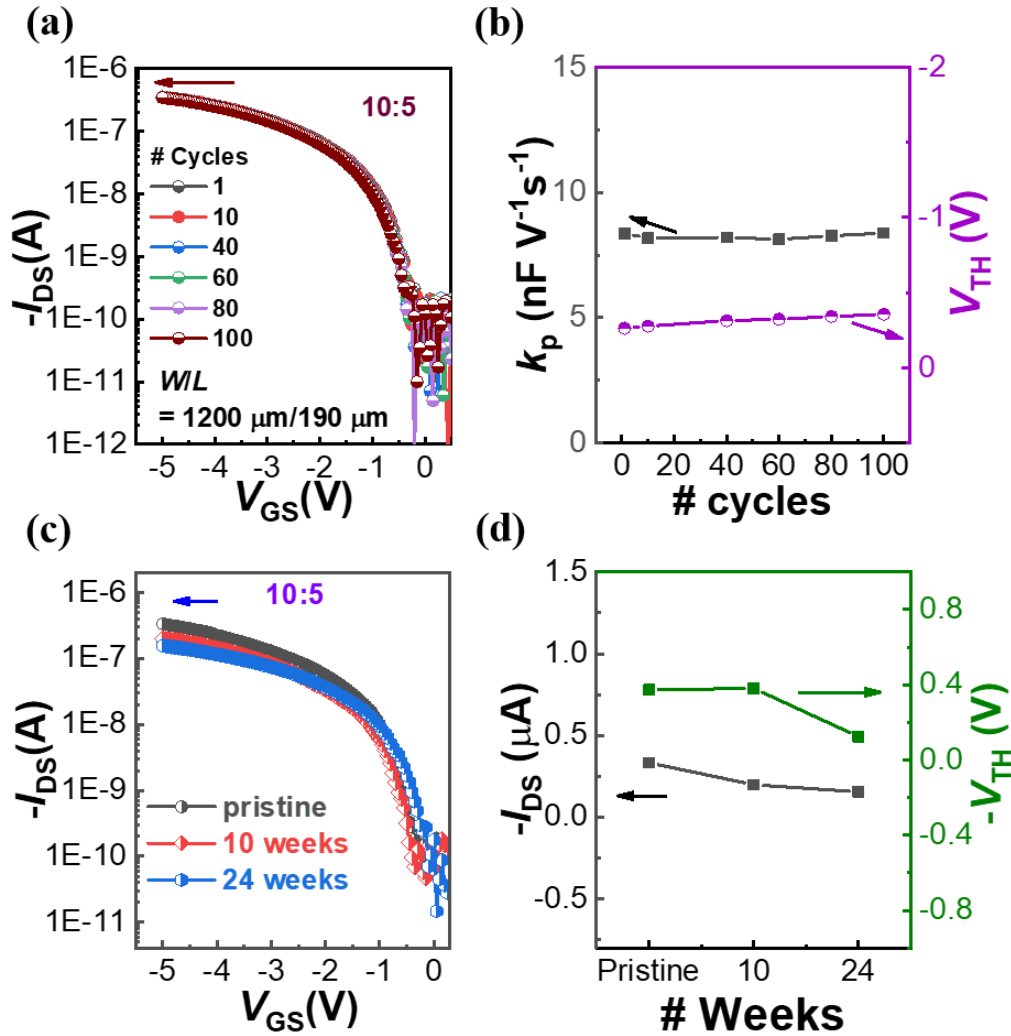


Figure 6.6 : (a) Repeatability of transfer characteristics for 100 times continuous scanning, and (b) corresponding changes in k and V_{TH} values. (c) Transfer characteristics showing environmental stability for a period of 24 weeks, and (d) corresponding variation of I_{DS} and V_{TH} for the 10:5 composition indicating high shelf-life stability.

The corresponding changes in k_p and V_{TH} at each cycle extracted from the transfer curve are shown in Figure 6.6 (b), exhibiting negligible changes during the repeatability tests indicating high reliability of the devices. The transfer characteristics for pristine as well as after 10 and 24 weeks, and corresponding changes in I_{DS} and V_{TH} within this time period are shown in Figure 6.6 (c) and (d). The transistor retains its properties even after 24 weeks with very low variation in the performance parameters, indicating remarkable environmental stability. We attribute it to the strong hydrogen bonding present in the edible dielectric film confirmed by FTIR, and the temperature stability supported by TGA, both helping to make it highly resistant to environmental conditions including humidity and temperature, facilitating air stability in devices. Due to the demonstrated robustness, electromechanical, and environmental stability, these devices with edible composite dielectric have the potential to be employed in edible electronics as well as real-time sensing and circuit applications. To summarize, composites of

gelatin and chitosan biopolymers offer great potential for the advancement of sustainable and edible flexible electronics.

6.3.6 Resistive-load Inverter

Further, the circuit applicability of the OFET device with 10:5 gate dielectric composite was examined by implementing a resistive load inverters with connecting external load resistance varying from 10 MΩ to 50 MΩ for. The circuit implementation is shown in inset of Figure 6.7 (a).

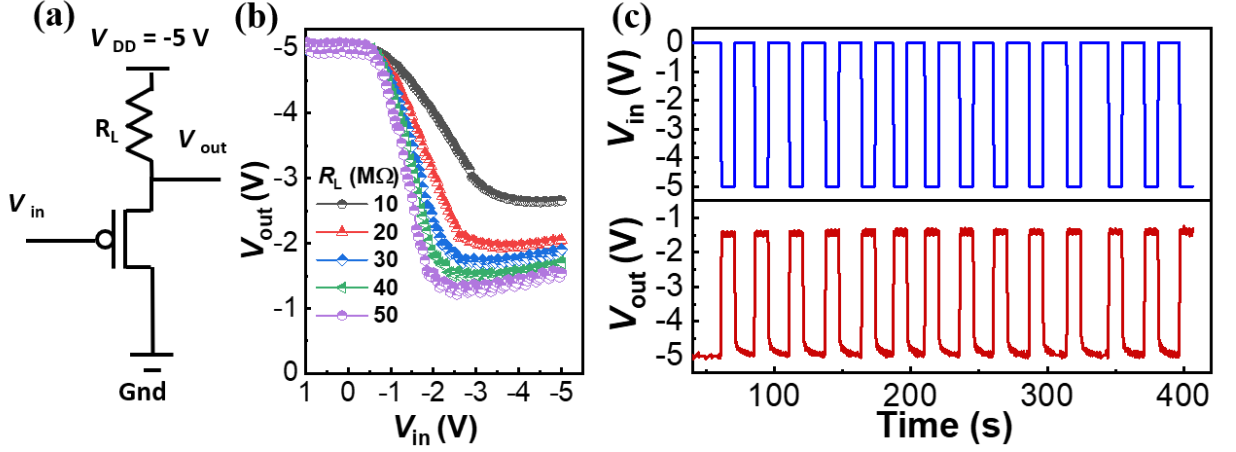


Figure 6.7 : (a) Voltage transfer characteristics with varying load resistance from 10 MΩ to 50 MΩ. The inverter circuit is shown in the inset. (b) Time dependent dynamic switching characteristics for load resistance of 50 MΩ.

First the voltage transfer characteristics (VTC) was analysed for an operating voltage (V_{DD}) of -5 V and shown in Figure 6.7 (a). As it can be seen from VTC, a perfect high logic 1 is achieved for all R values. For logic 0 at output when V_{in} is high, the potential is divided corresponding to device ON resistance and load resistance R , and V_{out} is calculated as following:

$$V_{out} = V_{DD} - I_{DS} \times R_L \quad (6.1)$$

This indicates that a higher value of R_L is needed to have better values of logic 0. The time-dependent dynamic response of inverter for R_L of 50 MΩ is shown in Figure 6.7 (b). Upon application of 0 to -5 V pulse at input, an excellent output swing between logic 1 (-5 V) and logic 0 (-1.5 V) was observed indicating excellent dynamic switching. From these findings, it can be summarized the gelatin: chitosan composite exhibits better dielectric properties in comparison to parent polymer with showing additional functionalities for the demonstration of high performance OFETs.

6.4 CONCLUSION

In this chapter, a composite of natural biopolymers gelatin and chitosan are demonstrated as excellent low-cost edible gate dielectric candidate for flexible electronics. Tuning the ratio of biopolymers in the composite has been illustrated as an effective way to enhance the performance and electromechanical stability of devices. Gelatin: chitosan dielectric composite ratios of 10:0, 10:1, 10:5, and 10:10 with increasing chitosan components were used for fabrication of flexible transistors to demonstrate the tuning capability of dielectric. Appropriate incorporation of chitosan into gelatin leads to strong hydrogen bonding between the functional groups of individual biopolymers, as confirmed by FTIR. These devices exhibited excellent p-channel characteristics with high process transconductance (mobility-capacitance product) and low threshold voltage values, for -5 V operation. Among all the explored ratios of the dielectric composites, 10:5 exhibited the most superior overall performance compared to others with the lowest subthreshold swing value of ~0.20 V/decade, low threshold voltage of -0.2 V, high on/off current ratio of 10^4 , and process transconductance value of $14 \text{ nF V}^{-1} \text{ s}^{-1}$, rare to find for flexible transistors with edible gate dielectrics. From electromechanical stability tests including multiple cycles of bending and bias-stress, it was found that the devices with 10:5 composition maintained

an excellent level of bias-stress stability even after upon application of extreme tensile bending. Our experiments confirmed that the addition of suitable chitosan content to gelatin increased the mechanical stability of dielectric film which in turn reduced the effect of bending on performance and stability of the transistors. The stability of the 10:5 composite for flexible transistor application was further confirmed by the TGA. At temperature of 100 °C, a commonly used processing temperature for most of the solution-processed organic devices, the stability of composite was found to be significantly higher than the pristine ones. A high environmental stability in ambient up to 24 weeks and decent inverter operation is also demonstrated indicating the reliability and circuit applicability of the devices with the proposed composite. Our investigation shows that this proposed unique edible gate dielectric composite can be an excellent alternative for future edible and ingestible electronics.

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