jet INTL JOURNAL OF ELECTRONICS AND TELECOMMUNICATIONS, 2025, VOL. 71, NO. 1, PP. 107-112
Manuscript received September 27, 2024; revised March 2025. doi: 10.24425/ijet.2025.153551

Biodegradable shellac-based substrates of various types for transient printed electronics

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***Abstract*—This work reports on the synthesis and properties of various shellac-based substrates for microelectronics applications. The analysis of the materials included temperature resistance and water solubility inspection. Low dielectric constant and dissipation factor as same as good integration of screen printed electrodes observed during SEM analysis, confirmed potential of shellac-based materials as substrates for transient, environmentally friendly electronic devices.**

***Keywords*—biodegradable electronics; shellac; dielectric substrates; printed electronics**

I. Introduction

WITH today's information and communications technology (ICT) landscape, there is a growing trend toward transformational change through the development of transient or time-varying electronic equipment. One of the examples can be a device that effectively performs designated functions (e.g. sensing system) throughout its lifetime and continues to remain environmentally neutral even at the end of its life cycle. Therefore, efforts are increasingly being made to produce and characterize biopolymer-based substrates for possible microelectronics applications, such as non-permanent electronics sensor systems for sustainable agriculture applications (assuming the sensor remains in the soil after it has served its purpose). Shellac, a natural polyester copolymer produced by female lac beetles, finds various applications in electronics due to its smooth surface suitable for microelectronic substrates. It allows for tape casting of substrates ranging from 200 to 500µm in thickness. When applied through thin film or spin coating deposition, it achieves surface smoothness below 1 nm Root Mean Square (RMS) [1]. Offering control over substrate thickness and viscosity, shellac can be successfully used as a dielectric ink for inkjet printing as same as a binder for conductive ink (replacing petroleum-derived polymers). Shellac-based electrically conductive inks, such as those developed by Poulin et al. in 2021, offer sheet resistance below $15\Omega\cdot sq^{-1}$, conductivity around $1000S\cdot m^{-1}$, mechanical flexibility (Young's modulus of 586±37MPa), and waterproofness [2]. It exhibits high value of the dielectric breakdown field similar to commonly used substrates [3], [4]. In organic field-effect transistors (OFET) applications, shellac is biocompatible and cross-links at 50-70°C [5]. Its dielectric properties make it suitable for constructing inverter circuits and organic thin-film transistors (OTFT), achieving mobility of $10-2cm^{2}\cdot V^{-1}\cdot s^{-1}$. Shellac's barrier properties qualify it as an insulator. It exhibits similar features to gelatin [6] and therefore its applications extend to FETs. Given the interesting known properties of shellac, it was decided to fabricate and characterize in terms of physical and electrical properties, a series of experimental substrates based on shellac orange (waxed and dewaxed) and lemon (dewaxed), as well as shellac substrates with the addition of propylene glycol (PG) and gelatin.

II. MATERIALS AND METHODS – SAMPLE PREPARATION

As a part of the research work, 6 starting materials were realized with the following compositions: shellac diluted with ethanol (sample no. I), shellac diluted with isopropanol (II), natural waxed shellac orange (III), dewaxed shellac orange (IV) and lemon (V) and shellac with addition of propylene glycol (PG) and gelatin (VI). Samples involving alcohol solvents were incubated in a water bath at 50°C and then poured into silicone molds to then be subjected to drying at room temperature in a fume hood with additional air supply for 24 hours, while samples consisting of shellac powders were stamped and molded under pressure into specially designed and prepared silicone molds, then placed in a GOLDBRUM 1450 vacuum dryer for 30 minutes at 90°C. This process resulted in solid, smooth wafers with a thickness of 1.65mm (III), 2.14mm (IV) and 2.18mm (V). Sample VI was obtained by mixing waxed orange shellac powder with distilled water and stirring in a water bath at 50°C for 30 minutes. The solution was then filtered three times, removing the undissolved precipitate. The clear solution was placed in a water bath for another 30 minutes at 50°C, and in the next step, powdered food gelatin

This work was supported by the National Science Centre Poland financed the work under project CHIST-ERA IV Programme (EU Horizon 2020 Research and Innovation Programme, under Grant Agreement no. 857925, UMO-2021/03/Y/ST7/00016). The work was also financed by the statutory funds at Łukasiewicz–Institute of Microelectronics and Photonics in 2024 (project No. 500-44200177).

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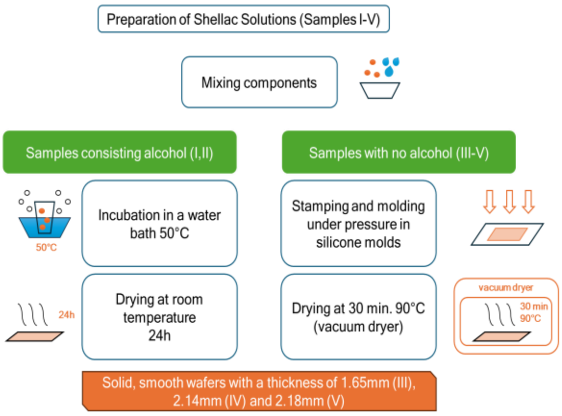

Fig. 1. Preparation of Shellac Solutions (Samples I-V)

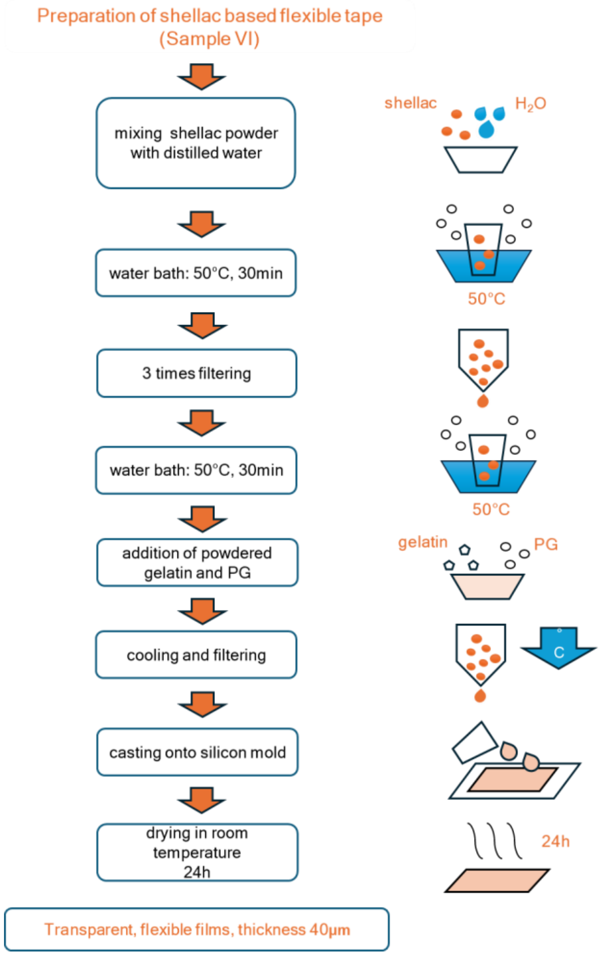

Fig. 2. Preparation of shellac based flexible tape

(binding strength of 180 bloom) and PG were added. The cooled and clear solution was poured onto a silicon mold, and then dried for 24 hours at room temperature with a medium-power air supply in a fume hood. The final result was transparent films with a slightly orange reflection, a thickness of 40µm and characterized by high elasticity, low brittleness and high resistance to creasing. Figures 1 and 2 show a diagrams of materials preparation procedure.

III. MEASUREMENTS AND DISCUSSION

For temperature resistance measurements, samples dimensions (X,Y) were measured before and after temperature treatment (range from 60 to 120°C, step 10°C, time 20 minutes) in a GOLDBRUM 1450 vacuum dryer. In the next step, shrink ratio (%) was calculated for each of the substrates. The behavior of the samples during heating demonstrates how various additives affect the thermal stability of shellac. Gelatin and propylene glycol increased the substrate's flexibility but due to the low thermal resistance of gelatin, also degraded its temperature resistance. A similar effect was observed with the addition of organic solvents. Samples III, IV, V without additives, due to their higher density and more homogeneous structure, exhibited higher temperature resistance (up to 110°C). Changes in the surface area of all tested samples as a function of temperature are shown in Figure 3.

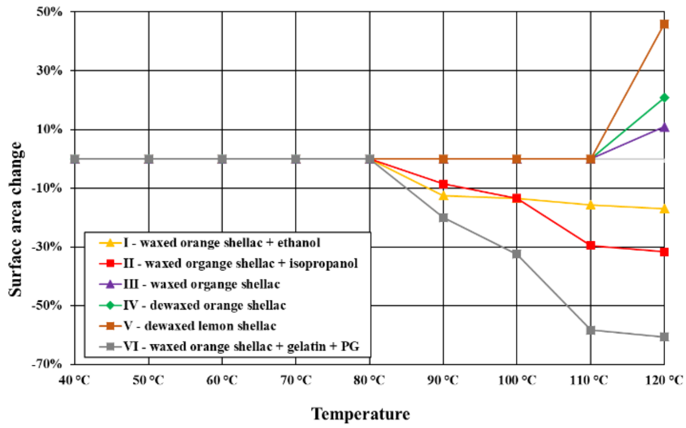

Fig. 3. Change in the surface area of shellac-based substrates after temperature treatment (%)

Water solubility/water absorption test was realized by placing each sample in a container of distilled water (100ml) and after 2, 4, 8, 24, 48, 72, 96 and 120 hours of incubation. Each time the sample was removed from the water, changes in the mass, color and texture of the sample were recorded. Changes in the mass of all tested samples as a function of time are shown in Figure 4.

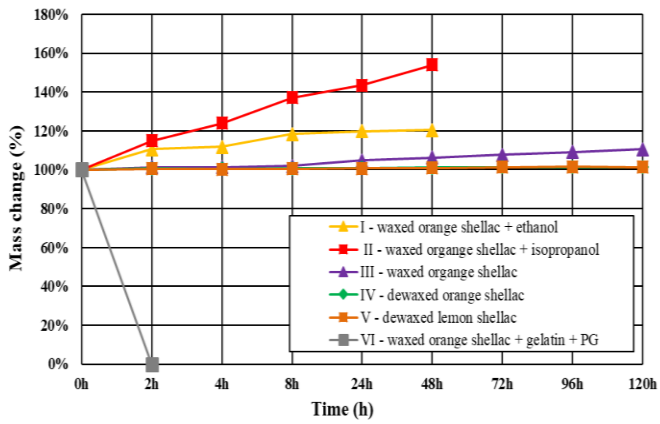

Fig. 4. Mass change of shellac-based substrates after water soaking

Additionally, pH and conductivity of the solution were measured. Samples containing polar solvents (I, II) or additives with polar functional groups (VI) are characterized by high hygroscopicity and low resistance to degradation in water environment. The absence of wax in samples IV and V provides a lower porosity of the material compared to shellac with wax. This is why it results in less susceptibility to water absorption and greater hermeticity. Figure 5 shows the pH changes of aqueous solutions for all tested samples over time, remaining within ±2. This suggests that during biodegradation in water, the samples would have minimal impact on environmental pH with relatively low risk to organisms.

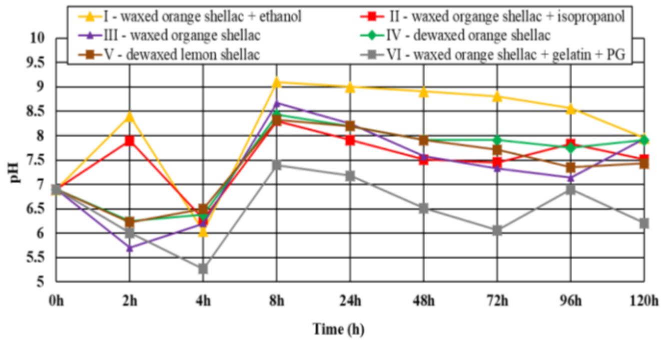

Fig. 5. pH changes of aqueous solutions for all tested samples over time

IV. SURFACE ANALYSIS (SEM)

To examine the sample's surface, scanning electron microscopy (SEM) images were acquired in BSE (backscattered electrons) and SE (secondary electrons) modes at 300x magnification.

SEM images present the surface structure of III - waxed orange shellac with and without added solvents (Fig. 6, Fig. 7, Fig. 9) and in dewaxed form IV - dewaxed orange shellac (Fig. 8). The use of ethanol and isopropanol resulted in a decrease of open porosity due to lowering surface tension of the mixture during its solidification and may have a positive effect on achieving even smoother, non-porous surface layer.

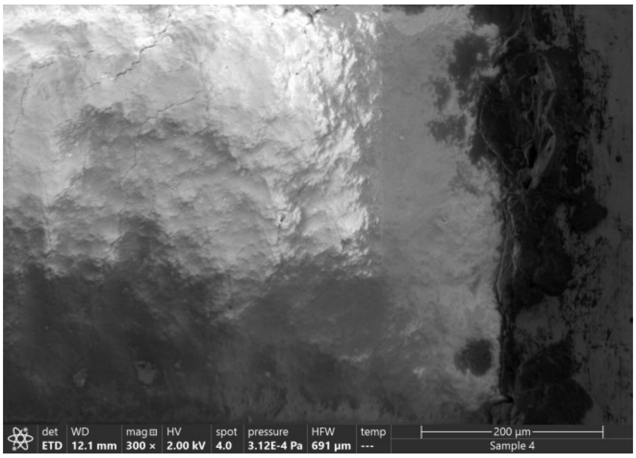

Fig. 6. Surface of substrates based on waxed orange shellac dissolved with ethanol

In addition, due to the presence of natural waxes, which can increase the porosity and permeability of the coating, waxed orange shellac (Fig. 9) is less resistant to water adsorption.

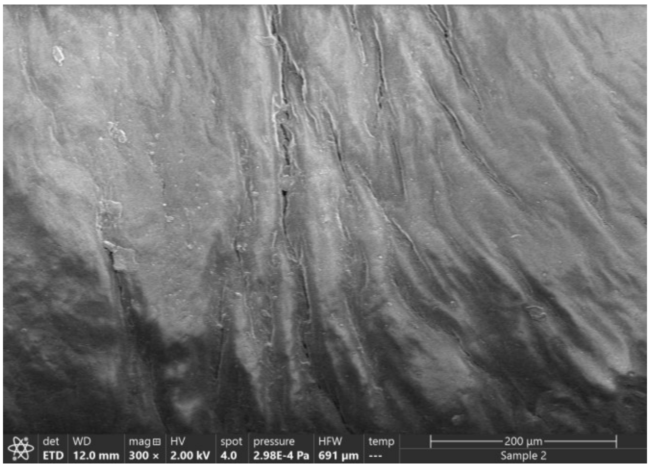

Fig. 7. Surface of substrates based on waxed orange shellac dissolved with isopropanol

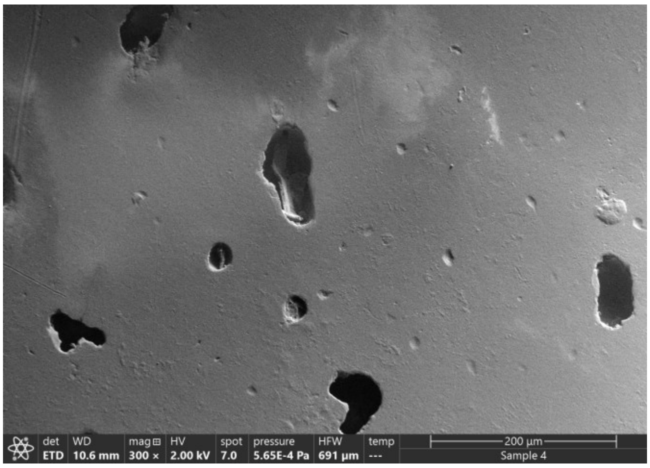

Fig. 8. Surface of substrates based on dewaxed orange shellac with no additives

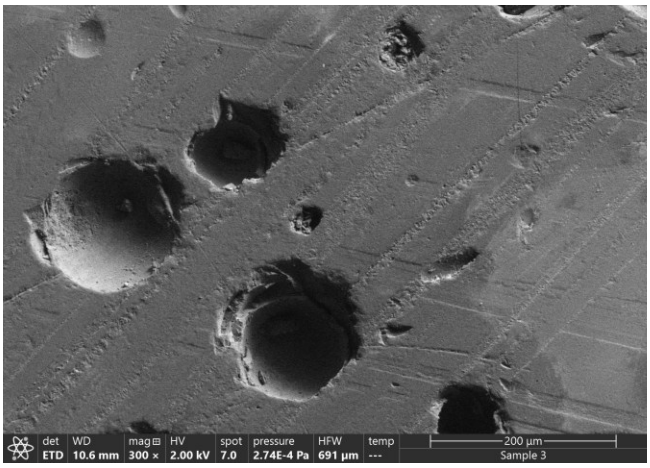

Fig. 9. Surface of substrates based on waxed orange shellac with no additives

It is worth highlighting that the appearance of open and closed porosity (visible in cross-sections) has a direct impact on the dielectric properties of the substrates. Porosity, as an additional gas phase introduced into the material, can be characterized by a dielectric constant value approaching 1, modulating final dielectric properties of the material.

V. DIELECTRIC PROPERTIES

Dielectric properties measurements were made with the following instruments at a room temperature of 21°C: electrical capacitance and dissipation factor were examined with a QuadTech 7600 RLC meter and resistance with KEITHLEY 2002 multimeter, and a KEITHLEY 8002A. The capacitance (C) expressed in pF and dissipation factor (DF) of the materials were measured in the frequency range from 1kHz to 1MHz. The dielectric constant of the materials (ε_r) was then calculated using the formula given below:

$$C = \varepsilon_0 \times \varepsilon_r \times \frac{S}{d} \tag{1}$$

C - electrical capacitance, ε_0 - electric permittivity of free space, ε_r – relative electric permittivity (dielectric permittivity, dielectric constant) of examined material, S - surface area of examined material, d - thickness of material, ε_0=8.854·10pF·m^{-1}.

The resulting calculations are presented in the form of graphs showing dielectric constant (ε_r) as a function of frequency (Fig.10, Fig.12) and dielectric loss tangent tanδ (dissipation factor) as a function of frequency (Fig.11, Fig.13).

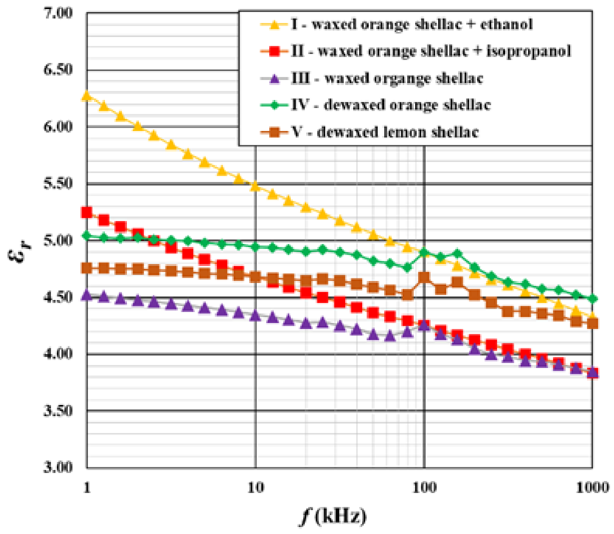

Fig.10. Dielectric constant (ε_r) of shellac-based substrates as a function of frequency (1-1000kHz)

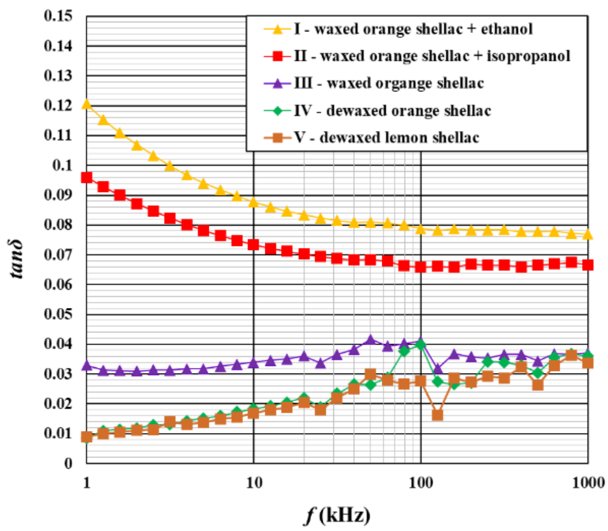

Fig.11. Loss tangent (tanδ) of shellac-based substrates as a function of frequency (1-1000kHz)

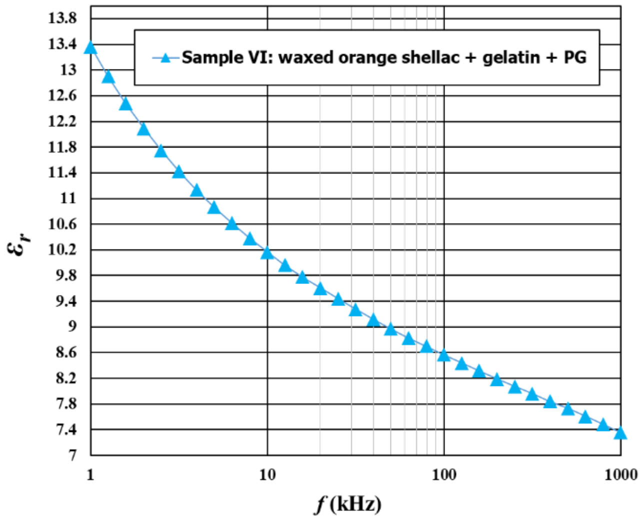

Fig.12. Dielectric constant (ε_r) as a function of frequency (sample VI – shellac+gelatin+PG)

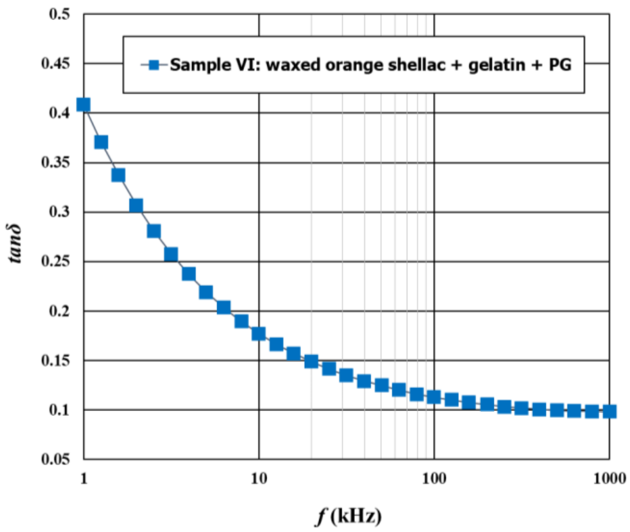

Fig.13. Loss tangent (tanδ) as a function of frequency (sample VI – shellac+gelatin+PG)

Resistance measurements have confirmed the dielectric character of all substrates. Some samples (IV and V) are strongly insulating with the resistance of 5TΩ and some exhibit a moderate resistance of 8.79MΩ (sample VI). In alternating electric field, the dielectric permittivity is a complex quantity composed of the real (ε') and imaginary (ε'') part. Some of the energy in a material is dissipated as heat due to dielectric losses which are proportional to the imaginary part of dielectric permittivity. Loss tangent is proportional to the imaginary part of dielectric permittivity (tanδ=ε''/ε'). Real dielectrics in the alternating electric field exhibit power losses in the polarization process. Below microwave frequencies, dielectric losses comprise predominantly relaxation losses which originate from dipole (orientational) polarization, space charge polarization and Maxwell-Wagner polarization (resulting from accumulation of electric charge at phase boundaries or at the dielectric-pore boundaries in a non-uniform and porous dielectric material). Furthermore, in a non-ideal dielectric there occur losses caused by electric current flow (leakage) which are dissipated as Joule-Lenz heat.

The impedance measurements showed the decrease of dielectric constant and loss tangent with the increase of frequency. Low values of ε_r (4.53-3.82 for sample III, waxed shellac) prove the positive effect of material porosity, which can be considered as an additional gas phase with dielectric constant aiming at 1. The low dissipation factor is the result of covalent bonds responsible for supporting the shellac's molecular structure and chemical purity (no precipitation of other phases). The lowest tanδ (0.009-0.023) was observed for substrates based on dewaxed shellac as a result of reduced porosity and the reduction of van der Waals and hydrogen bonds present in waxes. The low dielectric losses of samples III, IV, V are matched by greater thermal stability (confirmed by temperature resistance tests) compared to waxed substrates and those with added solvents. Also worth noting is the relatively low value (tanδ 0.024) for the waxed orange shellac (III) with a lower dielectric constant value at the same time. Due to the different character of gelatin-based substrate with the addition of shellac and PG, its dielectric properties are summarized in the separated figures (Fig.12, Fig.13). The dielectric permittivity showed greater temperature dependence and tanδ seems to stabilize at 0.01 at frequencies above 100kHz. The ε_r decreases with frequency reaching a value of 7.35 for 1MHz. The different dielectric character of the material results from proportion of gelatin, PG and bound water (indicating ionic/dipole polarizations). The presence of multiple phases results in a less uniform structure, which translates into higher dielectric losses.

VI. EXPERIMENTAL SCREEN PRINTING

The compatibility of substrates with screen-printed conductive layers was verified by realizing test prints using silver-based (DP5000) and carbon-based (DP7105) paste. The integration of the paste with the substrate material was examined using SEM images with and without prints at 300x magnification which were selected for detailed comparative analysis. The samples were then subjected to SEM analysis (to confirm the quality of the prints and the degree of integration between the electrode and the substrate). Shellac is hydrophobic and bioadhesive, based on aliphatic and alicyclic hydroxy acids, serving as a natural alternative to plastics in high-performance electronics as a dielectric and smoothener [7].

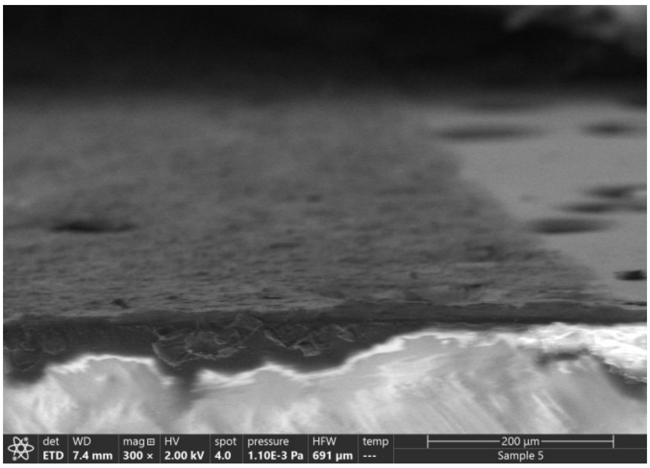

Fig.14. SEM image of shellac substrate materials showing integration with screen printed electrodes: dewaxed lemon shellac - carbon print

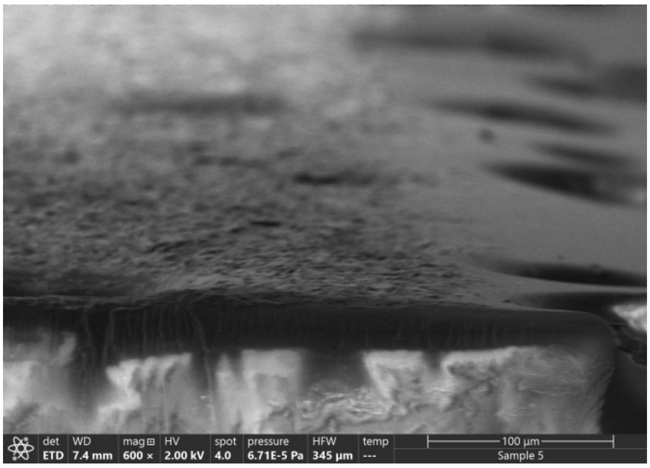

Fig.15. SEM image of shellac substrate materials showing integration with screen printed electrodes: dewaxed lemon shellac - silver print.

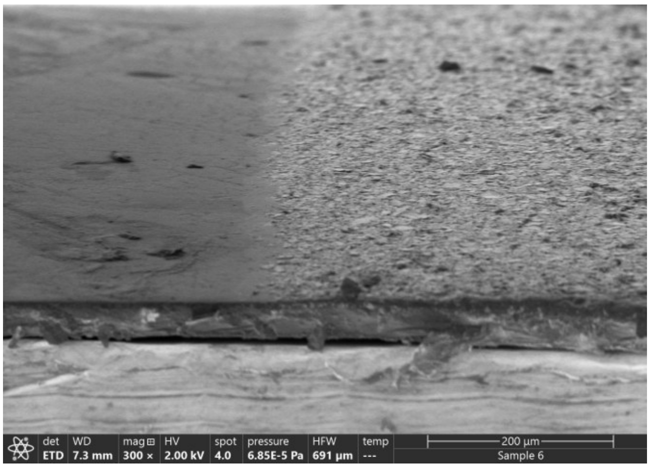

Fig.16. SEM image of shellac substrate materials showing integration with screen printed electrodes: shellac+gelatin+PG – silver print.

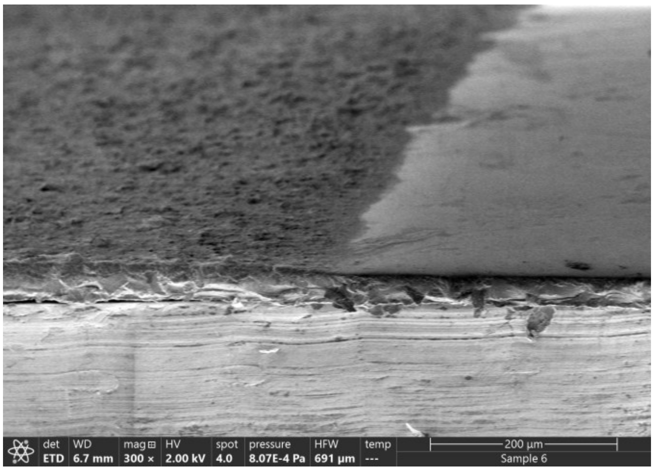

Fig.17. SEM image of shellac substrate materials showing integration with screen printed electrodes: shellac+gelatin+PG – carbon print.

For both carbon-based (Fig.14, Fig.17) and silver-based (Fig.15, Fig.16) paste prints, no delamination of the conductive layer from the substrate was observed. It is also noticeable that the pastes effectively penetrate the open pores, smoothing the surface of the material. The functionalization of the substrate to close the porosity, accordingly, is the next method after the use of solvents to make it homogeneous. Treatment with temperature (50°C) to consolidate the print did not negatively affect the surface of the material.

Conclusion

As a result of the research, shellac-based substrates of various thicknesses and flexibility were produced, demonstrating insulating capabilities and favorable dielectric properties (e.g. tanδ 0.02, and ε_r of approximately 4.23 for dewaxed orange shellac). The outcomes of dielectric measurements provide grounds to believe that at higher frequencies, these materials will exhibit favorable properties for applications in transient electronic devices (e.g. soil sensors).The dielectric response is significantly affected by the moisture content in the environment. The low dissipation factor of the developed materials contributes to reduced power consumption, promotes miniaturization, and increases frequency selectivity. Owing to their higher density and homogeneous structure, dewaxed shellac substrates exhibited increased temperature resistance (up to 110°C). A particularly interesting candidate for microelectronic applications is a flexible, semi-transparent shellac-based material with gelatin and PG, which has demonstrated optimal integration with printed layers and sufficient resistance to temperature (90°C) and humidity. Due to its remarkable properties, including elasticity, versatility, and complete biodegradability, gelatin serves as a key component in the fabrication of durable electronic systems [8]. Additionally, the mechanical flexibility of shellac can be enhanced by PEG (polyethylene glycol), further improving compatibility with printed layers [9]. This makes the shellac+gelatin+glycol substrate also interesting for various applications in transient electronics.

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