Resonant cavity dielectric spectroscopy for quality assurance evaluations of secure documents[#,†]

Mary Kombolias[a], Jan Obrzut[b], and Yaw S. Obeng[c]

[a]Plant Operations, United States Government Publishing Office, 732 North Capitol Street, NW,
Washington, DC 20041, USA
[b]Materials Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau
Drive, Gaithersburg, MD 20899, USA
[c]Physical Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau
Drive, Gaithersburg, MD 20899, USA

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ABSTRACT

Paper is a biphasic bio-composite material. The complexity of paper from a material science point of view is increased when it is manufactured for or used as a substrate in security printing products. However, most tests to evaluate such printing and graphic arts substrates are destructive and ex situ, resulting in a loss of information. Other tests may be non-destructive but may only provide visual assessments without any correlation to the chemical and physical properties of the substrate. There is a need to explore new metrologies which can interrogate security printing substrates in a non-destructive and contactless manner and yield data which corresponds to visual and physicochemical attributes. Resonant cavity dielectric spectroscopy provides a means to gather information on printing substrates derived from cellulose as well as those from synthetic polymers. In this paper, we provide four case studies demonstrating the broad utility of the resonant cavity dielectric spectroscopy technique in the analyses of unprinted substrates and surface modifications. The inherent forensic capabilities of this technique lend it well to further applications in secure document manufacturing.

Keywords: Dielectric spectroscopy, resonant cavity, non-destructive analysis, printing substrates, quality assurance, quality control

1. INTRODUCTION

Paper continues to serve as the most widely used graphics arts substrate for secure documents. Manufacturers of secure documents employ substantial levels of sampling and quality assurance / quality control (QA/QC) testing of the raw materials which are used in document production as well as the finished products. However, many test methods are destructive and time consuming as they are rooted in 20th century wet bench chemistry. Non-destructive evaluations of the optical properties and visual characteristics may be subjective in some instances and those which are quantitative yield limited information; the lack of established objective, instrument-based characterization of the relevant features influencing inspections in secure documents factors into the speed at which innovations are adopted in the business of optical document security [1].

A prime example of this is the current state-of-the art method for analyzing the fiber content of paper, TAPPI T 401 “Fiber analysis of paper and paper board” [2]. Originally developed in the early 20th century, this method is relied upon by the paper industry, forensics laboratories, and secure credential manufacturers for verifying the types and quantities of fiber species in paper. The TAPPI method depends upon visual acuity and level of experience of a specially-trained human analyst, is time intensive, and necessarily destroys the analyte. These factors limit the throughput, accuracy, and reliability associated with this method.

Paper is a heterogeneous matrix comprised of inorganic and organic compounds of varying polarizabilities. It is also manufactured to contain approximately 5% water. This water is hydrogen bonded to polar polymers, like cellulose, within the paper matrix. Dielectric characterization of materials relies upon examining the relaxation dynamics of dipoles and mobile charge carriers in response to an alternating electric field. While dielectric spectroscopy techniques are most commonly used to evaluate semiconductors and microelectronic components [3], the application to paper has been limited largely to moisture content determination [4-8]. On the other hand, by using the water confined in the matrix as a probe molecule to yield chemical and structural information, we have recently applied a contactless, non-destructive, and fast resonant cavity dielectric spectroscopy technique to distinguish between natural, cellulosic papers on the basis of the plant species of the fibers, recycled fiber content, and the relative age of papers of the same furnish [9-12]. In this publication, we present four case studies illustrating the broad utility of this technique to characterize both natural cellulosic and synthetic printing substrates and surface modifications of each.

2. MATERIALS AND METHODS

2.1 Sample Preparation

Commercially available graphic arts substrates were studied. To accommodate the dimensions of our resonant cavity apparatus, analyte samples were in the form of paper strips of width 0.5 cm and roughly to 8 cm in length cut from 21.6 by 27.9 cm (i.e., 8-1/2” by 11”) sheets with a rotary cutter. (The cavity sees only the bottom 1 cm from the specimen edge.) Strip angles were measured using a student’s protractor with the basis of the machine direction set to 90°, while the cross direction was set to 0°. The samples were stored between glass microscope slides in a nitrogen-filled dry box. Moisture content of the paper analytes was assumed to be 5%, at ambient conditions as specified by the manufacturers. The thickness of the paper specimen was determined through an average of ten caliper measurements.

2.2 Dielectric Loss Measurement

The complex relative permittivity, ϵ_r ,of the paper analytes is the sum of real and imaginary parts ($\epsilon_r = \epsilon_r' - j\epsilon_r''$) and was measured at a frequency of 7.435 GHz using a non-contact cavity perturbation method. In our earlier work [15-17], we showed that for a small specimen inside a rectangular cavity operating in the TE_{10} mode, the classical perturbation equation can be simplified to linear equations:

$$y' = (\varepsilon_r' - 1)2x - b' \tag{1a}$$

$$y'' = \varepsilon_r'' 4x - 2b'' \tag{1b}$$

where x, y' and y'' are defined by the following relations:

$$x = V_s/V_0\ ,\ y' = (f_0 / f_s) / f_0\ ,\ \text{and}\ y'' = 1/Q_s - 1/Q_0 \tag{2}$$

In equation 2, the resonant frequency of the empty cavity is, f_0, f_s is the resonant frequency with the specimen present, V_0 is the volume of the cavity, V_s is the volume of the specimen ($V_0 >> V_s$). Q_0 is the resonance quality factor of the empty cavity and Q_s is the resonance quality factor of the cavity loaded with the specimen. The resonance quality factor is obtained from the resonant peak according to the conventional half power bandwidth formula as $Q_s = f_s / \mathrm{w}f_s$. where $\mathrm{w}f_s$ is the bandwidth of the resonant peak. The real permittivity ε_r' and the dielectric loss ε_r'' can be determined from the slope of equations (1a) and (1b) respectively, where intercepts are the constants, b' and b''.

Our cavity test fixture employs a WR90 waveguide, operating in the microwave frequency range of 6.7 GHz to 13 GHz. The fixture is connected to a network analyzer (Agilent N5225A) with semi-rigid coaxial cables and near cross-polarized coaxial to WR90 coupling adapters. The network analyzer measures the transmission scattering parameter S_{21}. The resonant frequency, f_s, and the half power bandwidth, $\mathrm{w}f_s$, are determined for the TE_{103} resonant mode. In these measurements, the cavity with $V_0 = 29.49672\ \mathrm{cm}^3$, was operated at the resonant frequency of 7.4355 GHz, which corresponds to the TE_{103} resonant mode. The specimen is inserted into the cavity through a slot in the center of the cavity, where the TE_{103} electric field attains a maximum value. The specimen insertion and the corresponding volume of the material in the cavity (V_s) are controlled by a stage. During the measurements, the specimen is partially inserted in small steps, ΔV_s, while the magnitude of the scattering parameter, S_{21}, is recorded. The measured frequency span is typically $2\mathrm{w}f_s$, recorded with a resolution of ± 50 kHz. The dynamic range of the noise level in the $|S_{21}|$ magnitude is typically below –65 dB. The dielectric constant, ε_r', is determined with the combined uncertainty of $\pm 2 \times 10^{-3}$ and in the dielectric loss, ε_r'', the combined uncertainty is within $\pm 5 \times 10^{-4}$. The measurement data for equation 1b are used to determine the value of ε_r'', which is equal to the slope of the plot.

3. RESULTS

3.1 Discrimination between natural cellulosic and synthetic printing substrates

Security documents, such as smart cards, are manufactured from synthetic polymer substrates commonly known as "synthetic paper" and increasingly documents such as passports are being manufactured to contain a mix of substrates. Quality assurance / quality control testing of unprinted lots of synthetic papers often require destructive and time-consuming analytical techniques such as differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The time required to execute these processes inherently lowers the throughput of testing. We used our resonant cavity dielectric spectroscopy method to differentiate synthetic papers from natural, cellulosic papers and between each other. Synthetic substrates contain significantly less water than natural, cellulosic papers making the differentiation between these two classes of materials clear cut as show in figure 1. Even between synthetic papers, differentiation is possible. Figures 2a-b highlight the differences between the synthetic polymeric substrates.

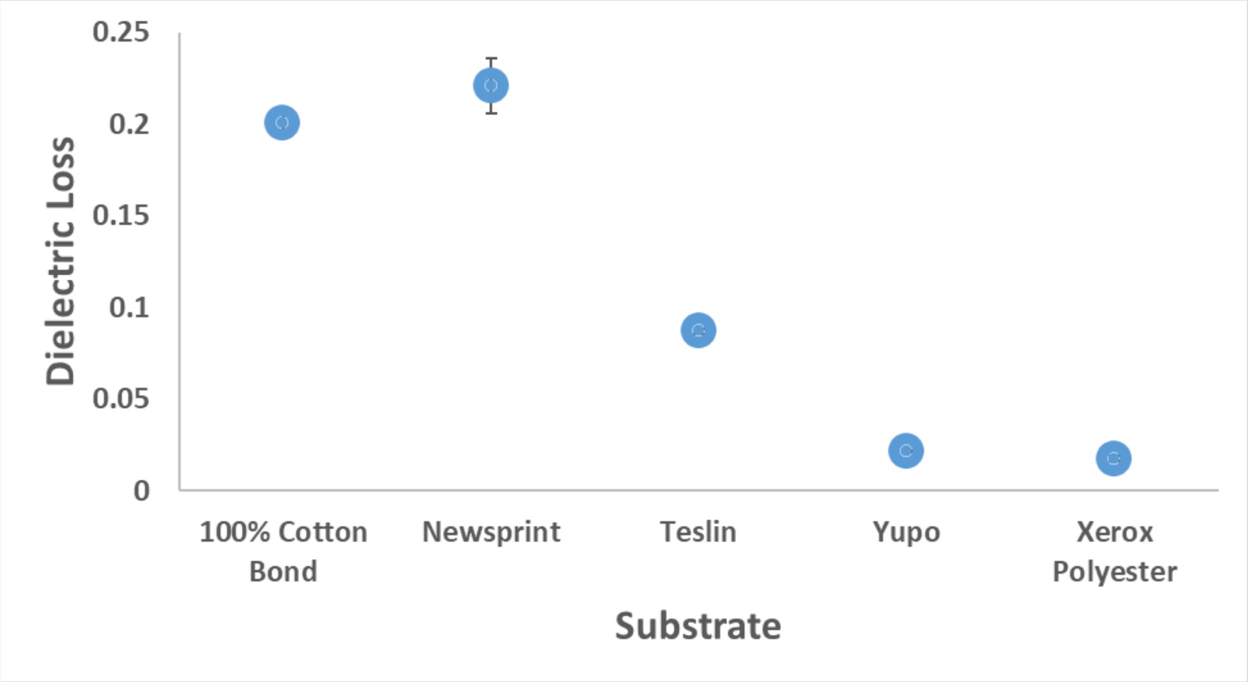

Figure 1. A comparison of the dielectric loss profiles of natural cellulosic paper (100% cotton bond and newsprint) versus synthetic papers (Teslin (PPG Specialty Coatings and Materials, Monroeville, PA, USA), Yupo Octo (Yupo Corporation. Tokyo,) and Xerox Polyester (Xerox, Norwalk, CT, USA). Measurements were conducted at 90 degrees at ambient laboratory temperature and humidity. The error bars for the synthetic papers were substantially smaller than the data points.

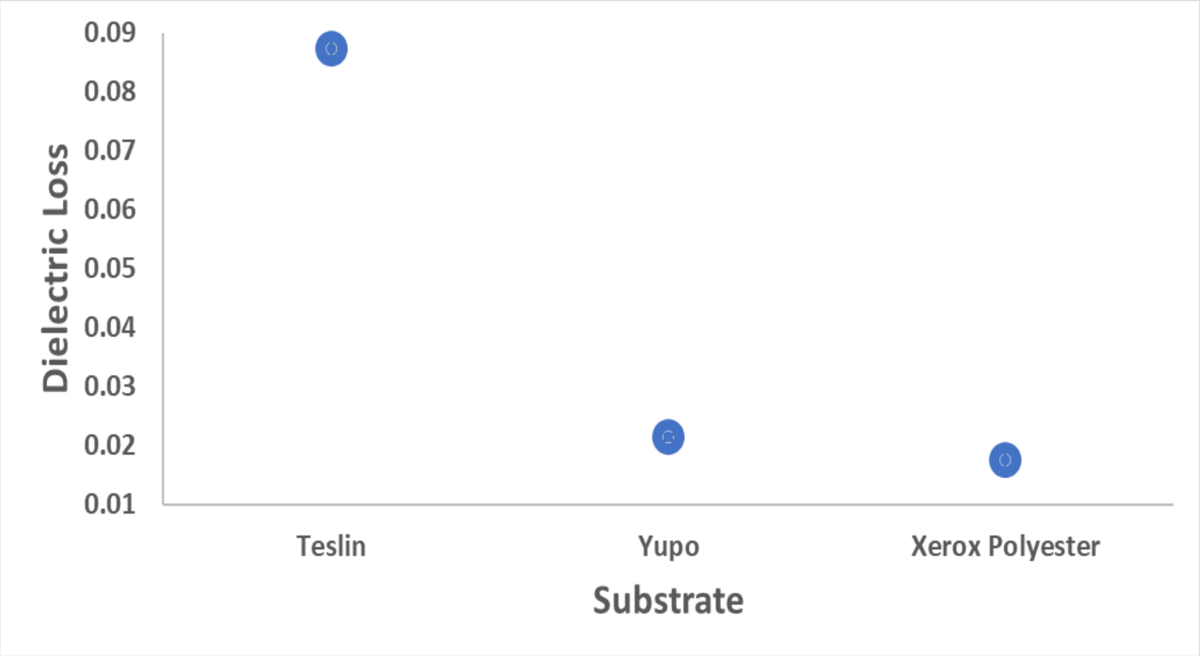

Figure 2a. Comparison of the dielectric loss profiles of three synthetic substrates from figure 1.

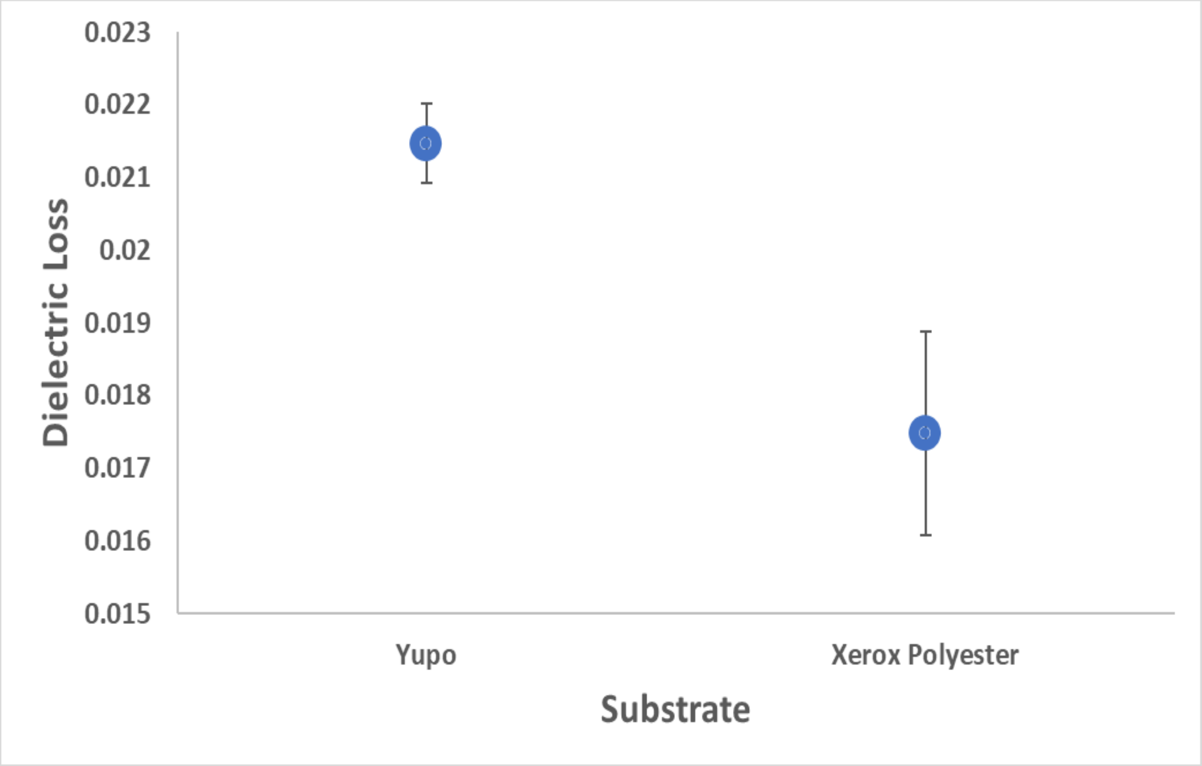

Figure 2b. Magnified view of the dielectric profiles of Yupo Octo and Xerox Polyester substrates from figure 1.

3.2 Distinguishing between Colored Cellulosic Papers

We have previously found that the presence of optical brightening agents influences the dielectric loss profiles of white office copier papers [5]. We have also demonstrated the ability to distinguish between two office papers – one virgin and the other with 30% post-consumer fiber content of the same shade of blue and from the same manufacturer – which could not be differentiated from each other by color measurements both before and after artificial aging experiments [10]. Thus, there is applicability for this technique in the QA/QC testing as well as forensic evaluation of paper in a non-destructive manner for which color space data and other physical measurements may not be able differentiate a genuine substrate from a substituted or counterfeited substrate. As shown in figure 3, our resonant cavity dielectric cavity technique can distinguish office papers by colors which are perceptible to the human eye. This is due to the changes in the cellulose matrix into which the water is adsorbed because of the presence of the respective colorants, which differ for each hue. The polarities of the colorants (dye molecules and insoluble pigments) influence the total dielectric response of each sample color sheet per effective medium theory [13-16].

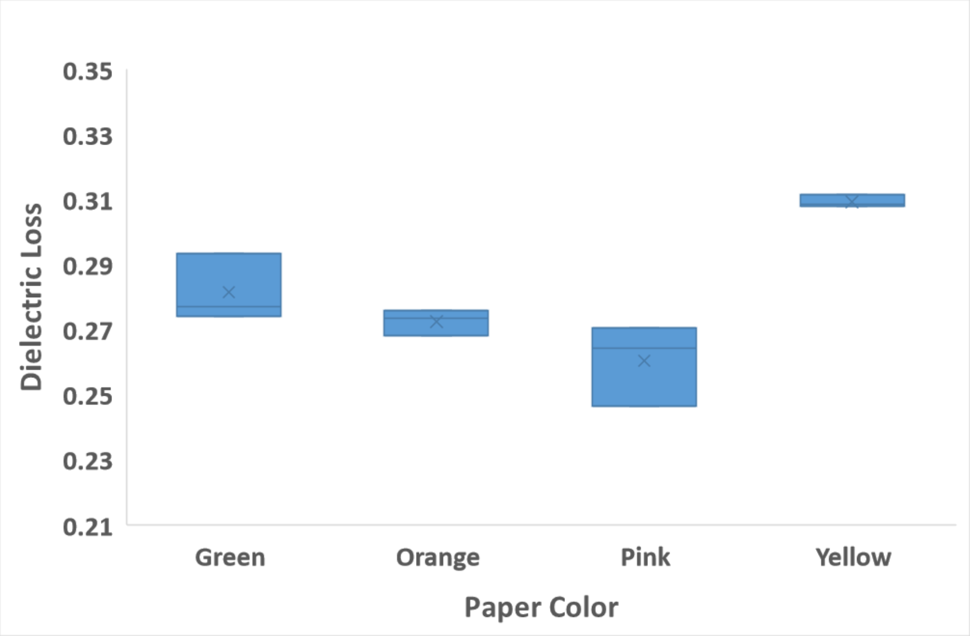

Figure 3. Box plot of the dielectric loss profiles of highly saturated colored office papers (24 lb) measured at 90 degrees and under ambient laboratory conditions. The height of the box plots represents the range of sample-to-sample variability in replicate measurements of the dielectric loss.

3.3 Measurement of UV Ink Applied to a Synthetic Substrate

Security documents are typically designed to contain authentication features which become apparent when exposed to UV light. These features include threads, fibers, planchettes, ribbons, and printing with UV inks, typically offset. In this demonstration, Teslin was chosen as the substrate onto which to simulate offset printing with UV ink as it has little to no chemi-adsorbed water in its matrix. Unlike many grades of natural, cellulosic paper, it is free of optical brightening agents which would fluoresce under UV light. In these experiments, lines of UV ink (pink) were traced onto sample strips of Teslin using a commercially available UV ink pen. As shown in figure 4, the average dielectric loss value decreases with increasing numbers of lines (i.e., quantity) of UV ink applied to sample strips. This suggests that dielectric spectroscopy may offer a novel way of corroborating the density of UV inks on a substrate without a visual inspection or performing separate UV fluorescence measurements.

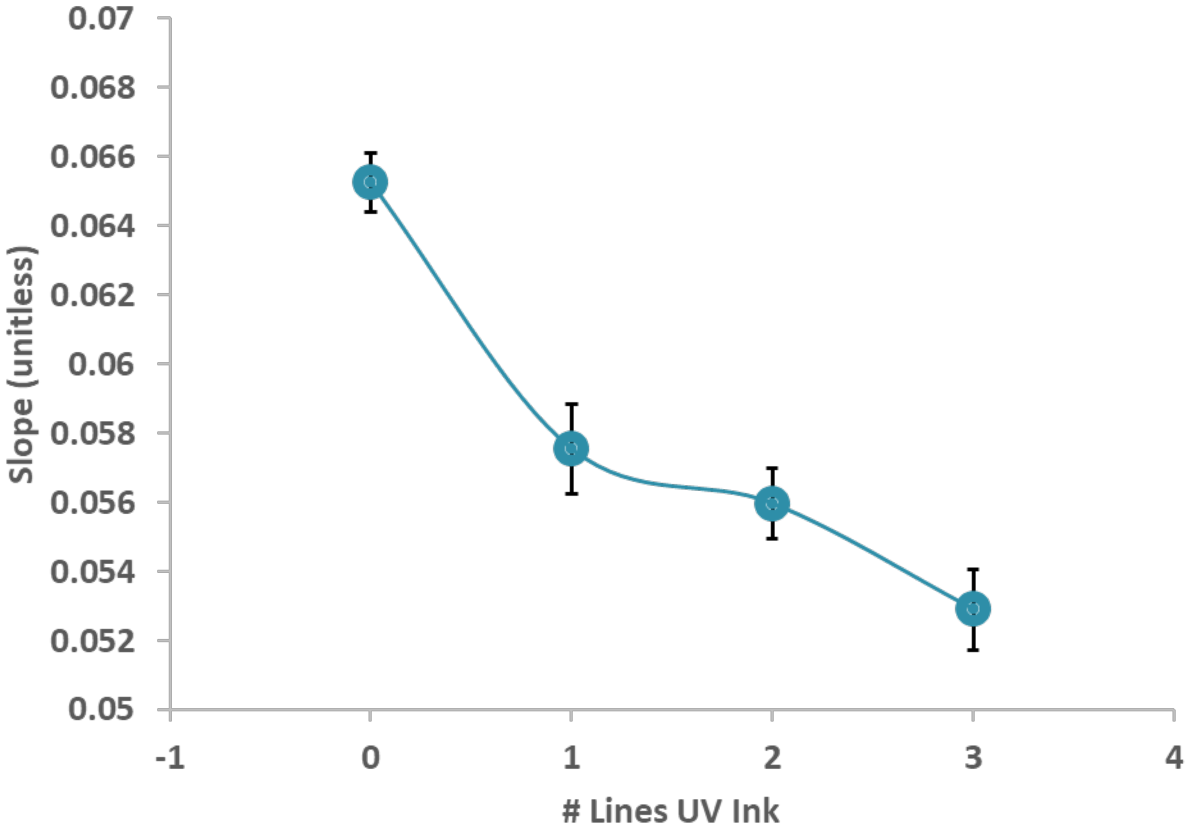

Figure 4. The change in dielectric loss of Teslin synthetic substrate with increasing concentration of UV ink applied to the surface via a commercially available UV ink pen. 90° sample strips were measured at 21% relative humidity.

3.4 Characterization of Physical Surface Modifications

Calendering is a physical modification to the surface of manufactured papers whereby the pressure of heated rollers is applied in order to increase the density, smoothness, and gloss of the paper [17]. Calendered and uncalendered samples comprised of 80% sage and 20% unbleached softwood kraft (UBSK) fiber were characterized dielectrically in the microwave resonant cavity. Though the furnishes and manufacturing process for each is identical, the dielectric behavior of differs substantially, as shown in figure 5. The calendering process not only decreased the thickness of the sample, but it also altered the dielectric characteristics of the material. Because calendering is known to further align the fibers in a sheet toward the machine direction (90°), two non-orthogonal angles were chosen to monitor the anisotropy, 45 degrees and 60 degrees. The anisotropy increased more in the calendered specimens than in the uncalendered specimens, as the dielectric loss value increased approximately 15% from 45 to 60 degrees for the calendered sage blend paper but only about 2% for the uncalendered variety (figure 6).

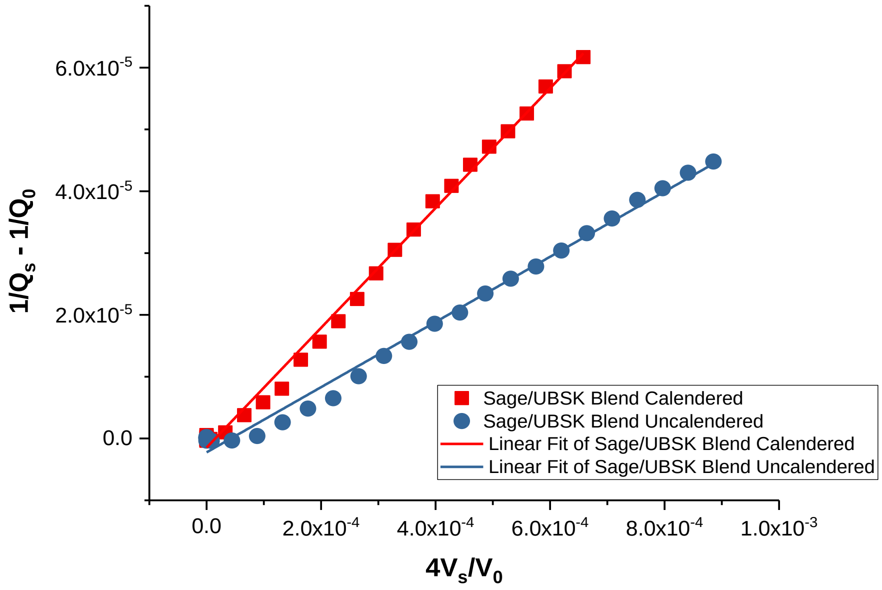

Figure 5. Plots of equation 1b for ε_r'' for sage/UBSK blend calendered and uncalendered papers at 32% relative humidity from 60 degree test strips. Solid lines represent linear fits for each sample.

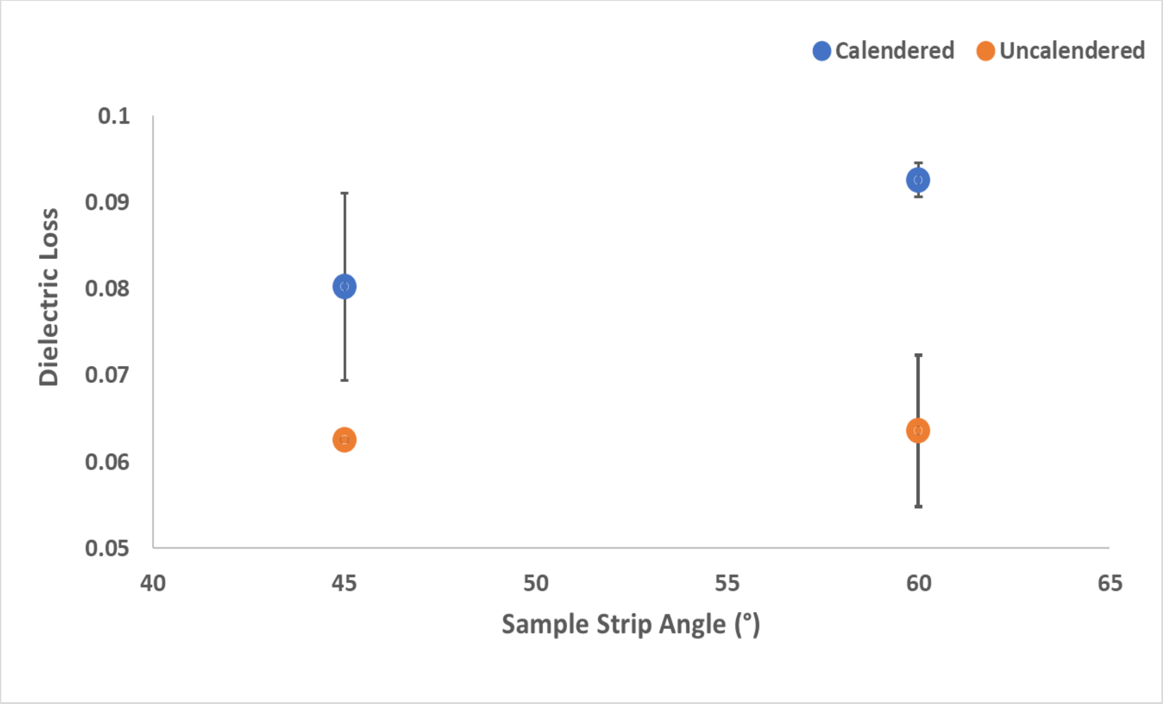

Figure 6. Dielectric loss profiles of calendered and uncalendared sheets comprised of 80% sage / 20% unbleached softwood kraft fiber blend. Samples were measured at approximately 32% relative humidity.

4. CONCLUSION

Resonant cavity dielectric spectroscopy can readily provide numerical, machine repeatable data which can corroborate optical and physical measurements of natural cellulosic and synthetic polymer graphic arts substrates, both of which are used in the manufacture of secure documents and identity credentials. The technique is rapid, with each sample evaluated in less than two minutes, and non-destructive, which enables sample banking and the creation of reference libraries. Because of its ability to differentiate between materials even of the same composition, this method has inherent forensic capabilities as well. Further work on other materials (i.e., foils, holographic elements) and printing modalities (i.e., Intaglio) used in the manufacture of secure documents is necessary to discover its full utility.

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