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Method Development for Contactless Resonant Cavity Dielectric Spectroscopic Studies of Cellulosic Paper

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Attention: Jialan Zhang, Ph.D.

Science Editor

March 12, 2019

Dear Editor:

My co-authors and I respectfully submit for your consideration our manuscript entitled “Method Development for Contactless Resonant Cavity Dielectric Spectroscopic Studies of Cellulosic Paper.” This work is a joint effort between the United States Government Publishing Office and the National Institute of Standards and Technology and a continuation of our earlier efforts [Kombolias, M., et al, Dielectric Spectroscopic Studies of Biological Material Evolution and Application to Paper, TAPPI Journal, 2018. 17(9): p. 501-505] to develop a contactless, non-destructive means of fiber analysis of paper and graphic arts substrates which is objective and machine repeatable.

Dielectric spectroscopy is a powerful analytical technique which can simultaneously provide both chemical and structural information on a material under test; it was recently utilized to examine materials for performance-limiting defects in advanced semiconductor devices. We have adapted dielectric spectroscopy for the fiber analysis of paper and graphic arts substrates by leveraging a resonant cavity which enables additional advantages such as contactless, non-destructive, and quantitative measurements of paper samples. With our new test method, measurements can be performed in minutes rather than hours and by anyone without the need for specialist training. This technique is easily automated and eliminates numerous sources of error associated with the traditional, manual process, and is amenable to statistical process control.

An unanticipated result of our research efforts has been that we are able to determine the relative age of paper produced in the modern era. To demonstrate the sensitivity of our method, we can discriminate between office papers of different fiber blends (recycled and virgin) both before and after artificial aging – papers which would otherwise be indistinguishable from another via conventional physical and chemical analyses. The data from our experiments allow us to simultaneously corroborate composition and color. We believe our technique is poised to provide an alternative to Carbon-14 dating of documents and other cellulose-based questioned documents.

Thank you for your time and consideration, and we look forward to your feedback.

Very respectfully,

Yaw Obeng

TITLE:

Method Development for Contactless Resonant Cavity Dielectric Spectroscopic Studies of Cellulosic Paper

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KEYWORDS:
Resonant Cavity, dielectric spectroscopy, paper, fiber analysis, paper aging, recycled content

SUMMARY:
A protocol for the non-destructive analysis of the fiber content and relative age of paper.

ABSTRACT:
The current analytical techniques for characterizing printing and graphic arts substrates are largely ex situ and destructive. This limits the amount of data that can be obtained from an individual sample and renders it difficult to produce statistically relevant data for unique and rare materials. Resonant cavity dielectric spectroscopy is a non-destructive, contactless technique which can simultaneously interrogate both sides of a sheeted material and provide measurements which are suitable for statistical interpretations. This offers analysts the ability to quickly discriminate between sheeted materials based on composition and storage history. In this methodology article, we demonstrate how contactless resonant cavity dielectric spectroscopy may be used to differentiate between paper analytes of varying fiber species compositions, to determine the relative age of the paper, and to detect and quantify the amount of post-consumer waste (PCW) recycled fiber content in manufactured office paper.

INTRODUCTION:

Paper is a sheeted, heterogenous, manufactured product comprised of cellulosic fibers, sizing agents, inorganic fillers, colorants, and water. The cellulose fibers may originate from a variety of plant sources; the raw material is then broken down through a combination of physical and/or chemical treatments to produce a workable pulp consisting primarily of cellulose fibers. The cellulose in the paper product may also be recovered secondary, or recycled fiber[1]. The TAPPI Method T 401, "Fiber analysis of paper and paperboard," is currently the state of the art method for identifying fiber types and their ratios present within a paper sample and is utilized by many communities[2]. It is a manual, colorimetric technique reliant on the visual acuity of a specially trained human analyst to discern the constituent fiber types of a paper sample. Furthermore, sample preparation for the TAPPI 401 method is laborious and time consuming, requiring physical destruction and chemical degradation of the paper sample. Staining with specially prescribed reagents renders fiber samples subject to the effects of oxidation, making it difficult to archive samples for preservation or specimen banking. Thus, the results from TAPPI Method T 401 are subject to human interpretation and are directly dependent upon the visual discernment of an individual analyst, which varies based upon that individual's level of experience and training, leading to inherent errors when comparing results between and within sample sets. Multiple sources of imprecision and inaccuracy are present as well[3]. Additionally, the TAPPI method is incapable of determining the quantity of secondary fiber or the relative age of paper samples[4,5].

In contrast, the resonant cavity dielectric spectroscopy (RCDS) technique we describe in this article offers analytical capabilities that are well-suited for paper examinations. Dielectric spectroscopy probes the relaxation dynamics of dipoles and mobile charge carriers within a matrix in response to rapidly changing electromagnetic fields, such as microwaves. This involves molecular rotational reorientation, making RCDS particularly well-suited to examine the dynamics of molecules in confined spaces, such as the water adsorbed on the cellulose fibers imbedded within a sheet of paper. By using water as a probe molecule, RCDS simultaneously can extract information on the chemical environment and physical conformation of the cellulose polymer.

The chemical environment of the cellulose fibers influences the extent of hydrogen bonding with water molecules, hence the ease of motion in response to the fluctuating electromagnetic fields. The cellulosic environment is determined, in part, by the concentrations of hemicellulose and lignin in the paper analyte. Hemicellulose is a hydrophilic branched polymer of pentoses, while lignin is a hydrophobic, cross-linked, phenolic polymer. The amounts of hemicellulose and lignin in a paper fiber are a consequence of the paper-making process. Adsorbed water in paper partitions between the hydrophilic sites, and the hydrogen bonding within the cellulose polymer, especially with the adsorbed water molecules, influences the level of cross-linking within the cellulose structure, the level of polarizability, and the architecture of pores within the cellulose polymer[5]. The total dielectric response of a material is a vector sum of all the dipole moments within the system and can be distinguished via dielectric spectroscopy through the use of effective medium theories[6,7]. Similarly, the capacitance of a dielectric material is inversely proportional to its thickness; hence, resonant cavity dielectric spectroscopy is ideal to study sample-to-sample thickness reproducibility of ultra-thin films materials such as paper[8-10]. While there is a significant body of work pertaining to the use of dielectric spectroscopy techniques to study wood and cellulose products, the scope of those studies has been limited to paper manufacturability issues[11-13]. We have taken advantage of the anisotropic nature of paper to demonstrate the application of RCDS to testing paper beyond moisture and mechanical properties[14-16] and to show that it yields numerical data that can be used in quality assurance techniques such as gauge capability studies and real-time statistical process control (SPC). The method also has inherent forensic capabilities and can be used to quantitatively confront environmental sustainability concerns, support economic interests, and detect altered and counterfeit documents.

Resonant cavity dielectric spectroscopy (RCDS) theory and technique

RCDS is one of several dielectric spectroscopy techniques available[17]; it was chosen specifically because it is non-contact, non-destructive, and experimentally simple in comparison to other methods of dielectric spectroscopy. In contrast to other analytical techniques used to study the properties of paper, RCDS eliminates the need for duplicate sets of measurements to account for the two sides of a sample sheet[18]. The resonant microwave cavity technique has the advantage of being sensitive to both the surface and bulk conductivity. For example, the surface conductance of a sample material is determined by tracking a change in the quality factor (Q-Factor) of the cavity as a specimen is progressively inserted into the cavity in quantitative correlation with the specimen's volume[18-20]. Conductivity can be obtained by simply dividing surface conductance by the specimen thickness. The surface conductance of a thin, sheeted material like paper functions as a proxy for the dielectric profile of a material under test (MUT), as it is directly proportional to the dielectric loss, ε'', of the MUT[18-20]. Dielectric loss is an indication of how much heat is dissipated by a dielectric material when an electric field is applied across it; materials with greater conductance will have a higher dielectric loss value than less conductive materials.

Experimentally, the dielectric loss, ε'', associated with the specimen's surface is extracted from the rate of decrease of cavity resonance quality factor (Q) (i.e., energy loss), with increasing volume of specimen[19]. The Q is determined at the resonant frequency *f* from the 3 dB width, Δf, of the resonant peak at the resonant frequency *f*, Q = $\Delta f\ /f$. This relation is quantitatively correlated with the slope of the line given by Equation 1 below, where $\left(Q_s^{-1} - Q_0^{-1}\right)$ represents the difference of the reciprocal of the Q-factor of the specimen from the Q-factor of the empty cavity, $\frac{V_s}{V_0}$ is the ratio of the volume of the inserted specimen to the volume of the empty cavity, and the line intercept, b'', accounts for the non-uniform field in the specimen, as shown in **Figure 1**[19].

$$\left(Q_s^{-1} - Q_0^{-1}\right) = \varepsilon'' \frac{4V_s}{V_0} - 2b'' \qquad \text{(Equation 1)}$$

In this article, we illustrate the broad utility of this technique by determining the ratios of fiber species (speciation), determining the relative age of naturally and artificially aged papers, and quantifying the recycled fiber content of white office copier paper analytes. Whereas the RCDS technique may be suitable for studying other topics, such as aging issues in paper insulation in electric power apparatus, such studies are outside the scope of the current work but would be interesting to pursue in the future.

PROTOCOL:

1. Setup of materials

1.1. Record all manufacturing information provided with the ream of paper (e.g., basis weight, manufacturer's advertised PCW content, and manufacturer's advertised brightness).

1.2. Take an average of ten thickness measurements along a sheet from the ream, using a caliper.

1.3. Identify the machine and cross directions of the sheet (i.e., the machine direction is the long dimension).

1.4. Using a protractor identify and cut the paper along the desired stripe angle between the machine and cross directions.

1.5. Using a rotary cutter, slice test strips 0.5 cm wide by 8 cm long in the target orientation for the sample.

1.6. Label samples from one end and store between glass microscopy slides. Store until testing under nitrogen atmosphere.

NOTE: It is advisable to wear gloves and perform handling with tweezers to avoid creasing and / or contaminating the paper samples.

2. Accelerated paper fade testing

NOTE: Paper samples are aged under UV-light at elevated temperature at laboratory ambient humidity. The aging is performed using an accelerated weathering chamber equipped with 340 nm UVA bulbs, at an irradiance of 0.72 W/m^2 at 50 °C for 169 h, by following the following protocol.

2.1. Calibrate the UV-sensors, by running the calibration radiometer routine pre-preprogrammed in the UV-based accelerated weathering chamber.

2.2. Calibrate the temperature sensors by running the **P4 calibrate panel temperature** program pre-preprogrammed in the weathering chamber.

2.3. Measure the pre-post-aging color of the paper samples using a portable spectrophotometer operating in the visible wave range from 400 nm to 800 nm.

2.4. Select appropriate standard test cycles pre-preprogrammed in the weathering chamber.

2.5. Mount whole sheets of test papers on the flat panel (optionally, mount one sheet of either side of the flat panel).

2.6. Fasten the flat panels to the sample holders with snap rings, pushing the rings snugly against the panel.

2.7. Install the panel holders with the stop pin down.

2.8. Attach aluminum blanks to mount in the panel holders for condensation.

2.9. For uniform exposure, reposition the test samples (at least five times) during the test cycle.

2.10. Measure the post-aging color of the paper samples using a portable spectrophotometer.

2.11. Cut sample strips out of the aged paper samples to fit the resonant cavity. The typical specimen area is 0.5 mm (width) x 15 mm (length).

NOTE: For these tests, we use commercially produced colored 90 g/m^2 (gsm) (24 lb) office paper of two different compositions: virgin and 30% recycled fibers (i.e., 0% and 30% post-consumer waste [PCW] recycled fiber content, respectively).

3. Setup of equipment and taking resonant cavity measurements

NOTE: The resonant cavity testing fixture consists of an air-filled standard WR-90 rectangular waveguide. The cavity has a 10 mm x 1 mm slot machined in the center for specimen insertion. The waveguide is terminated on both ends by the WR-90 to coax adapters that connect the cavity with a microwave network analyzer via semi-rigid coaxial cables. The coupling adapters are nearly cross polarized with respect to the waveguide polarization angle, which creates sharp impedance discontinuities at both waveguide ends and consequently the cavity walls. The polarization angle is about 87°, which is sufficient to achieve optimal power loading into cavity while maximizing the quality factor. The quality factor, Q_0, and the resonant frequency, f_0, of the empty cavity at the third odd resonant mode TE_{103} at which we make the measurements are 3.200 and 7.435 GHz respectively. The measurements are performed in ambient laboratory conditions by following the protocol listed below.

3.1. Record the temperature and relative humidity and take the initial reading of the quality factor Q_0, and the resonant frequency f_0 of the empty cavity.

3.2. Position the specimen secured in the sample holder above the slot at the center of the cavity. During the measurements, the specimen is inserted into cavity through this slot in steps of increasing volume $V_x = h_x \cdot w \cdot t$, where h_x is the specimen length inserted into cavity, and w and t are the specimen width and thickness respectively.

3.3. Using the Vernier caliper on the sample mount, insert the sample into the cavity by Δh_x = 50 µm increments and take readings of the quality factor and resonant frequency at each step until the sample has been lowered 10 mm (1 cm) into the cavity.

3.4. Retract the sample from the interior at the same increments of 50 µm and take readings of the quality factor and resonant frequency until the sample has been fully retracted.

3.5. Store the sample between glass slides and return them to nitrogen atmosphere.

3.6. The dielectric loss, ε'', of the paper samples is obtained from the slop of the perturbation (Equation 1). Optionally, the dielectric constant, ε' can be obtained from the measured V_x, and the resonant frequency f_x by solving the perturbation equations for ($\varepsilon' - 1$) as described in elsewhere[18-20].

REPRESENTATIVE RESULTS:

Rationale for choosing the 60° strip angle

The cut orientation of the test sample influences the magnitude of the dielectric response, as shown in the graph in **Figure 2**. In initial experiments, test stripes were cut from the orthogonal angles of the sheet, as is standard practice for measuring physical properties in paper science; however, strips cut from non-orthogonal angles along the paper sheet have provided the greatest resolution between paper types, particularly at the 45° and 60° orientations[15]. This response difference can be rationalized on the basis on the preferential orientation of the cellulose chain, that deviates approximately 30°–45° from the normal, within the cellulose microfibril structure inside the cell walls of living plants[21,22]. Dielectric studies on fiber orientation of factory-manufactured paper sheets have shown that along both the wire and felt sides of the sheet, the orientation of the cellulose polymer chains is about 30° from the machine direction, which corresponds to our designation of the 60° orientation along the paper sheet[23,24].

Effect of concentrations of cotton fiber on the dielectric loss

Figure 3 shows the dielectric loss profiles of cotton-containing bond papers procured by the US Federal Government using 60° strips. The error bars represent the standard deviation of the individual measurements. The data clearly demonstrate the resonant cavity's ability to differentiate between bond papers of various concentrations of cotton fiber. This is consistent with our previous work, in which we used the RCDS technique to distinguish between papers of varying non-wood fiber concentrations derived from plant sources such as the herb sage, cocoa husks, and bamboo[15].

Impact of environmental conditions on test results

It is important to maintain control over laboratory temperature and humidity during the testing of materials. Paper is naturally hygroscopic mixture. In our work we found that temperature has a very nominal influence on the dielectric profile of a paper sample. However, the relative humidity (RH) of the laboratory wields a much greater influence on the results. **Figure 4** compares the results of testing 100% cotton bond paper procured by the Federal Government at 47% RH and 49% RH, respectively. In general, we obtained more reproducible sample-to-sample dielectric loss results at higher relative humidity. Therefore, it is advisable to test paper samples under well controlled environmental conditions to enable sample comparisons.

Relative age of paper

The RCDS technique has incredible utility beyond speciation. We have demonstrated in our other work the resonant cavity's ability to distinguish between relative age cotton bond papers of the same content manufactured 40 years apart. Older paper samples exhibit lower average dielectric loss values than newer papers, suggesting the loss of polarizability as a result of the degradation of the cellulose polymer[25].

Our experiments on artificially aged paper analytes also demonstrate clear differences between the before- and after-UV light fading experiments on both virgin (0% PCW) and (30% PCW) papers. As shown in **Figure 1**, after 169 h of UV-accelerated aging, the degradation of the cellulose polymer is discernable as the average dielectric loss values had decreased for both the virgin and recycled varieties. It is notable that the technique can distinguish between the virgin and recycled materials even after the accelerated aging period[25].

Recovered fiber content of white office papers

We have compiled the dielectric loss data on white office papers from several manufacturers featuring varying percentages of advertised brightness (mainly due to proprietary additives) and PCW recycled content[26]. There appears to be some yet to be understood relationship between the recycled fiber content and the advertised brightness of the paper analyte. In general, within cohorts of papers of the same quality the average dielectric loss deceased with increasing manufacturer's advertised brightness, although the advertised brightness values for the same type of papers examined varied substantially from manufacturer to manufacturer. **Figure 5** presents a contour plot based a linear regression fit showing the dielectric loss of white office copier paper based upon the manufacturer's advertised brightness and recycled waste paper content (% PCW) of the analytes. The data suggest that the dielectric loss is also sensitive to optical brighteners and other additives the various manufacturers use to obtain the advertised brightness.

FIGURE LEGENDS:

Figure 1: Changes in cavity quality factor (equation 1) as a function the specimen inserted volume, V_x, for several specimens: 25%-(red triangles), 50% (blue circles) and 100% bond cotton paper samples (green squares), respectively. The slope of the plots represents the dielectric loss, ε'', for each sample.

Figure 2: A comparison of dielectric response by stripe angle (0°, 45°, 60°, and 90°) for virgin 'As-Received" blue 24-lb office papers before (green circles) and after UV-fading for 169 h (red

squares). The error bars represent the standard deviation of at least five individual measurements.

Figure 3: Dielectric loss profiles cotton-containing bond paper specimens containing of different amounts of cotton cut into 60° strips. The error bars represent the standard deviation of at least five individual measurements.

Figure 4: A comparison of dielectric response of 100% cotton bond paper in changing ambient humidity, showing that the dielectric loss appears to be more reproducible at higher relative ambient humidity. The error bars represent the standard deviation of at least five individual measurements.

Figure 5: A contour plot, based on a linear regression fit, showing the expected dielectric loss of white office copier paper based upon the manufacturer's advertised brightness and the recycled waste paper content (% PCW) of the analytes. The data suggest that the dielectric loss is also sensitive to optical brighteners and the other additives various manufacturers use to obtain the advertised brightness. The data used in this figure were collected with 60° test strips.

DISCUSSION:

We have shown elsewhere that the presence of lignin content of fibers does significantly alter the dielectric behavior of manufactured papers[15]. Speciation is not only important in the QA/QC testing of modern papers but of great interest in the study of historical papers which were predominantly manufactured from non-wood plant sources, such as bamboo, hemp, flax, and papyrus. As shown in **Figure 3**, our technique can distinguish between non-wood plant sources (100% cotton paper versus 90% bamboo / 10% cotton paper). This is consistent with previous work employing other dielectric spectroscopic techniques to distinguish between purified forms plant, bacterial, animal, and reconstituted celluloses and between white wove paper and newsprint which are manufactured with different types of wood pulp using different processes[6,27,28]. Thus, dielectric loss profiles can confirm the morphological differences in cellulose chains originating from different plant fiber species and plant fiber species mixtures. The protocol and the results presented in this paper relies on interrogating the sample cut at 60° degrees relative to the machine (90°) direction of the paper. This approach is novel to paper sample analysis; currently measurements of physical properties of paper are performed at orthogonal angles along what are known as the machine (90°) and cross (0°) directions. We found, through experimentation, that the 60° angle affords the best discrimination based on the polarizability of those materials between a wide range of industrially manufactured samples than the 0°, 45°, and 90° orientations for all the purposes discussed in this article: speciation, determination of relative age, and determination of PCW fiber content.

The resonant cavity dielectric spectroscopy provides paper scientists with a powerful tool to discriminate between paper samples. The determination of the relative age of paper and the identification and quantification of PCW fiber content in paper are possible with this technique because both problems are rooted in the degradation of the cellulose polymer. The degradation of the cellulose polymer changes the degree of polymerization and the environment into which water is adsorbed and ultimately the amount of polarizability of the sheet[29,30,31]. Thermal degradation accelerates and magnifies the extent of hydrolysis and oxidative damage to the polymer, and the amount of total degradation to the sheet of paper is also influenced by the constituent materials within the sheet or the document. Secondary fibers undergo both chemical and physical degradation, as they may be subjected to multiple iterative bleaching cycles at temperatures ranging from 60°C to 80°C after enduring the mechanical chopping and shredding mechanisms of re-pulping[32] . These processes render the secondary fibers shorter than virgin fibers, as well as chemically degrading the secondary fibers. Another consequence of the recycling process and source of degradation for secondary fibers is hornification, or the annealing, shrinking and hardening of the cellulose polymer, thereby altering the morphology of the polymer chain and the environment in which water is to be adsorbed[33]. The loss of hemicelluloses due to recycling also differentiates virgin from recycled fiber content[34-36].

To the best of our knowledge, non-destructive, contactless methods such as microwave cavity, have not been employed to determine the constituent fiber species or the presence and amount of secondary fiber within a paper sheet. Secondary fiber content is currently certified via forensic accounting methods by third party auditing organizations[37,38]. Historically, analytical methods for the identification and quantification of secondary fiber in paper have been well received because they do not appear to have the necessary accuracy required by the paper manufacturing community (i.e., at best, an accuracy of ±50% of advertised claim)[39,40]. Similarly, traditional paper testing protocols, elemental analysis, and isotopic analysis of commercially available white office papers have been unable to distinguish with any statistical confidence between papers of virgin and secondary fiber content[41-43]. Methods to determine the age of paper, like Carbon-14 dating, are also laborious and destructive and cannot be performed with any reasonable accuracy on contemporary samples. The resonant cavity dielectric spectroscopy method we have demonstrated here is versatile enough to meet and exceed the metrological limits of the TAPPI T 401 method of fiber analysis. Our work demonstrates that the contactless, in situ technique is well suited to characterize materials based upon the types and amounts of cellulose polymer they contain, as well as the level and types of degradation experienced by the cellulose polymer, regardless if that degradation is present due to age (natural or accelerated) or via the presence of secondary fiber. So far, we have not examined hand sheets or other types of handmade papers and therefore cannot comment on the effect of sample orientation on papers which are not industrially manufactured. It is not necessary to perform moisture determination of paper samples (which is performed in a laboratory oven at 105 °C) as the permittivity measurements, in essence, serve as a proxy for moisture content determination[44]. Temperature and humidity do contribute to the values measured, and it is important to compare samples analyzed under the same environmental conditions.

The most critical steps within the protocol presented in this work involve precisely matching the sample test strips to the volume of the microwave cavity used. However, other microwave cavities and sample holders may be designed to be able to interrogate larger volumes of sample without the need to mutilate the sample to perform an analysis, bypassing this experimental limitation.

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DISCLOSURES:

This is a contribution of the National Institute of Standards and Technology, and not subject to copyright. Certain commercial equipment, instruments, or materials are identified in this report to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology or the United States Government Publishing Office, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose. The authors have nothing to disclose.

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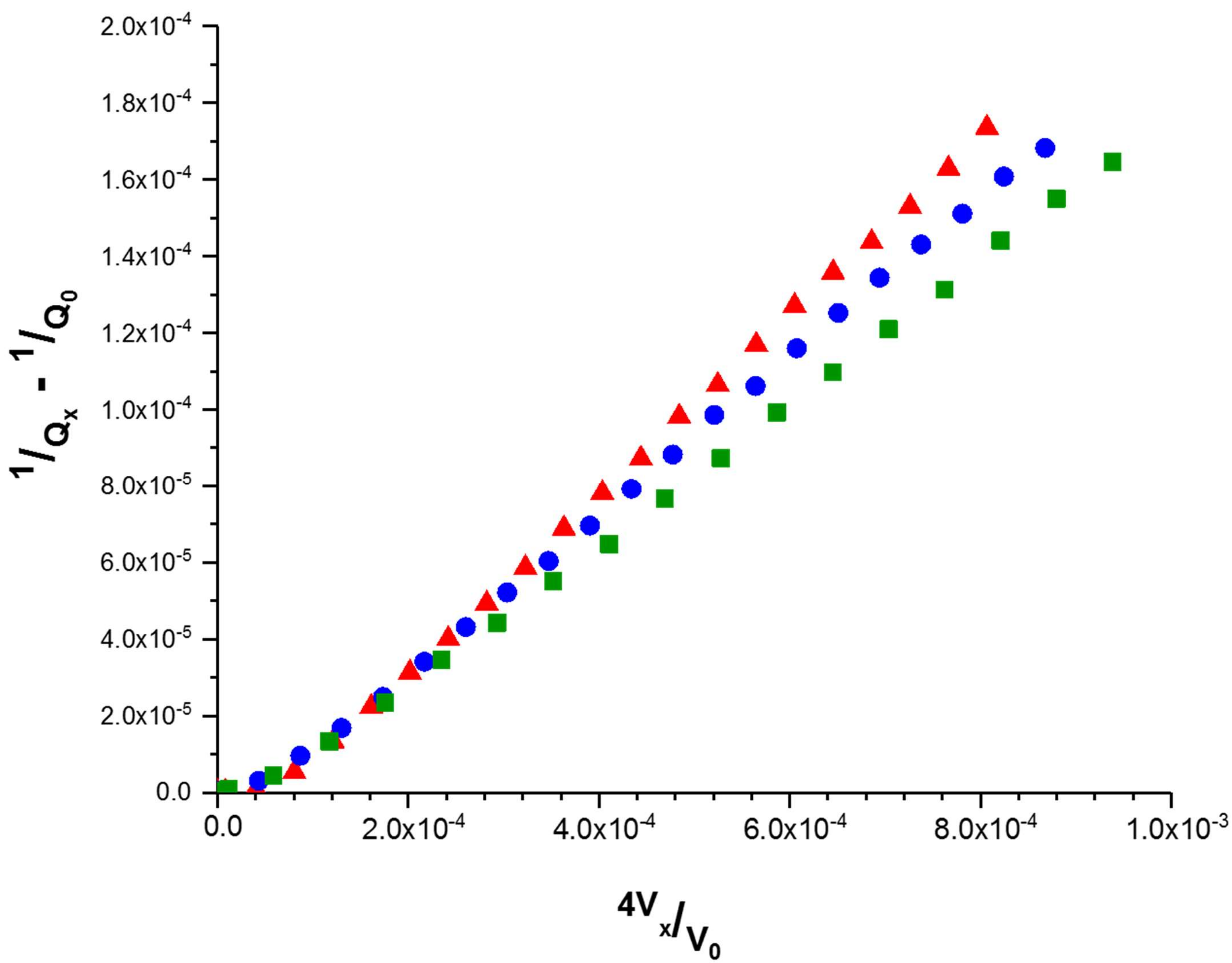
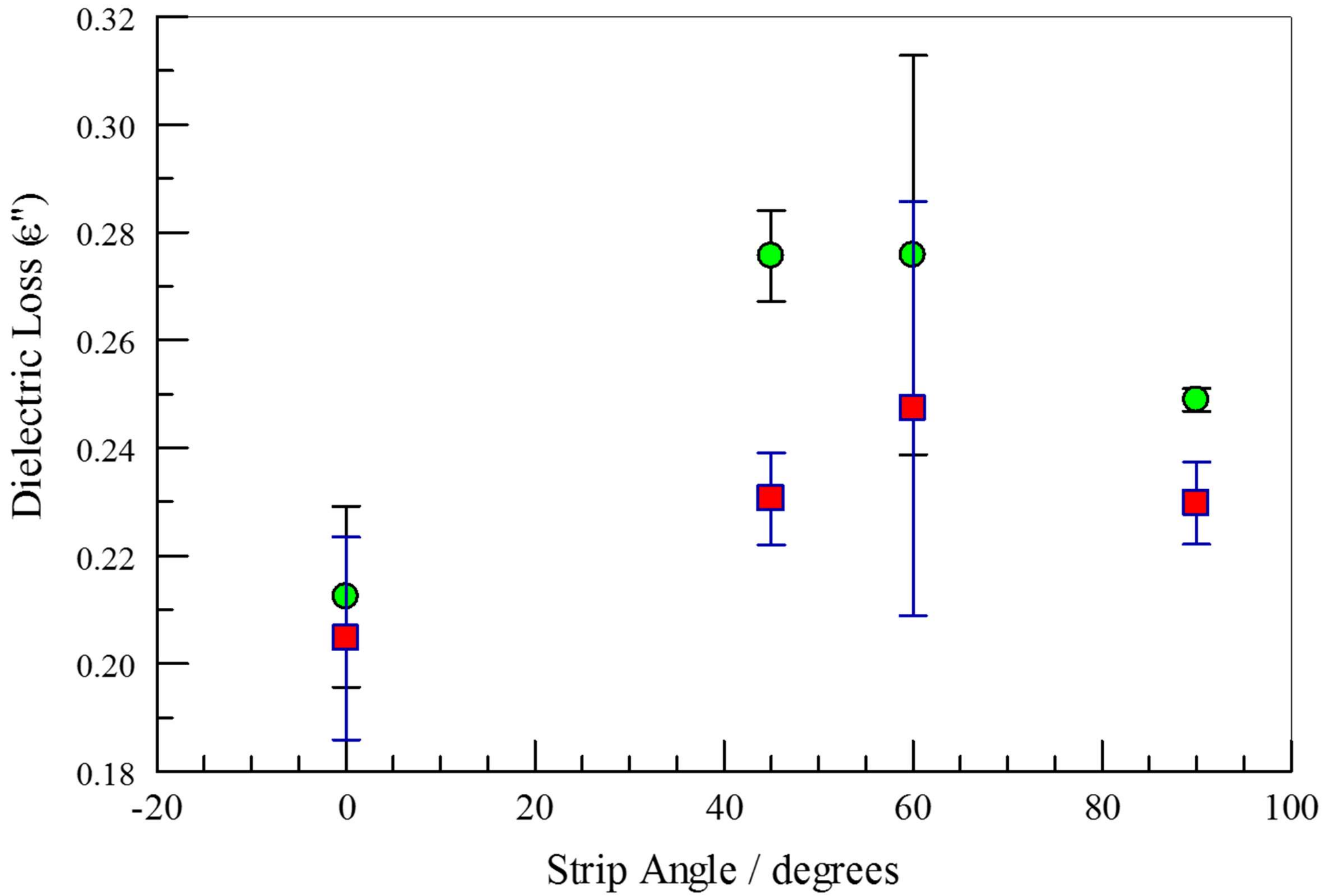
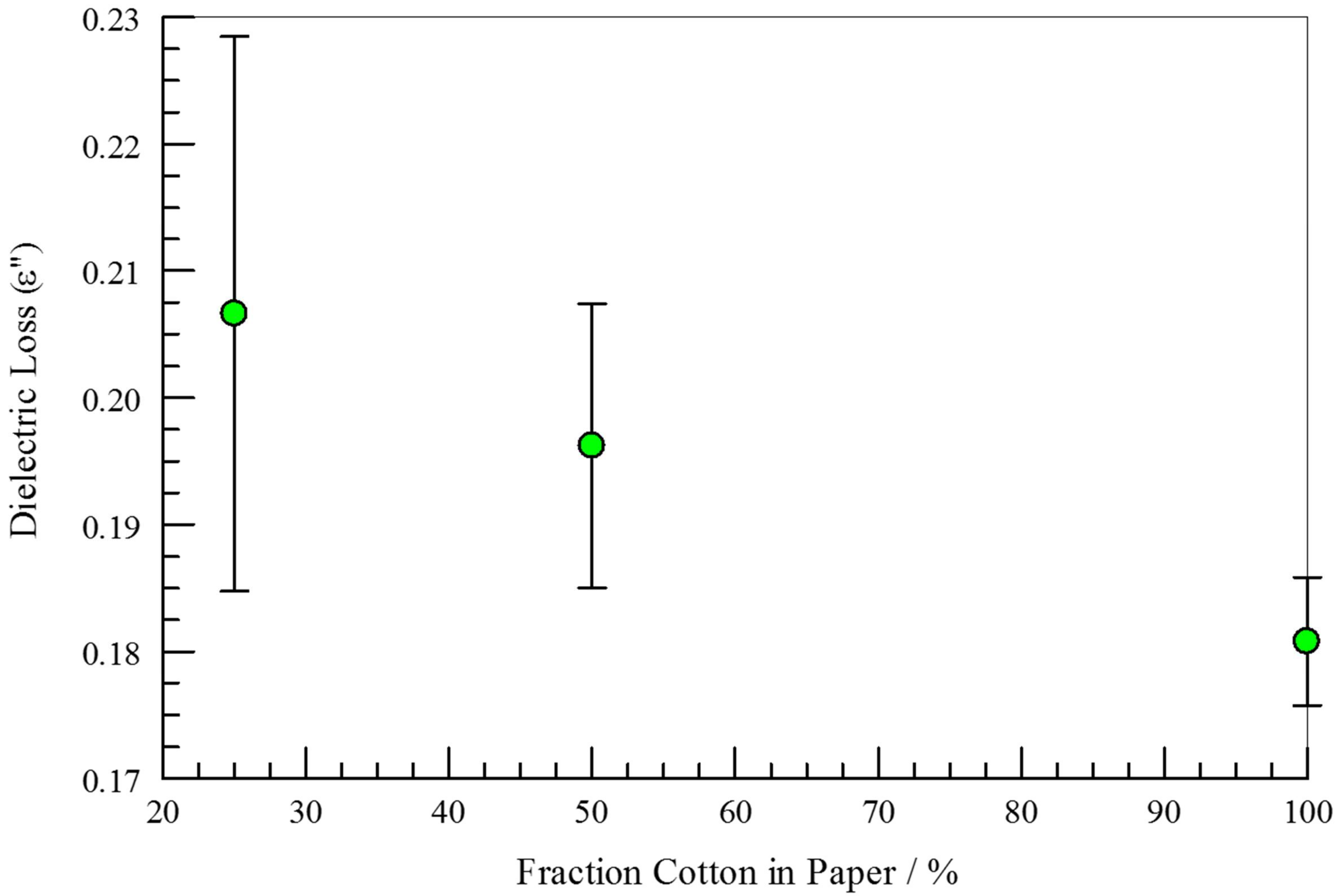


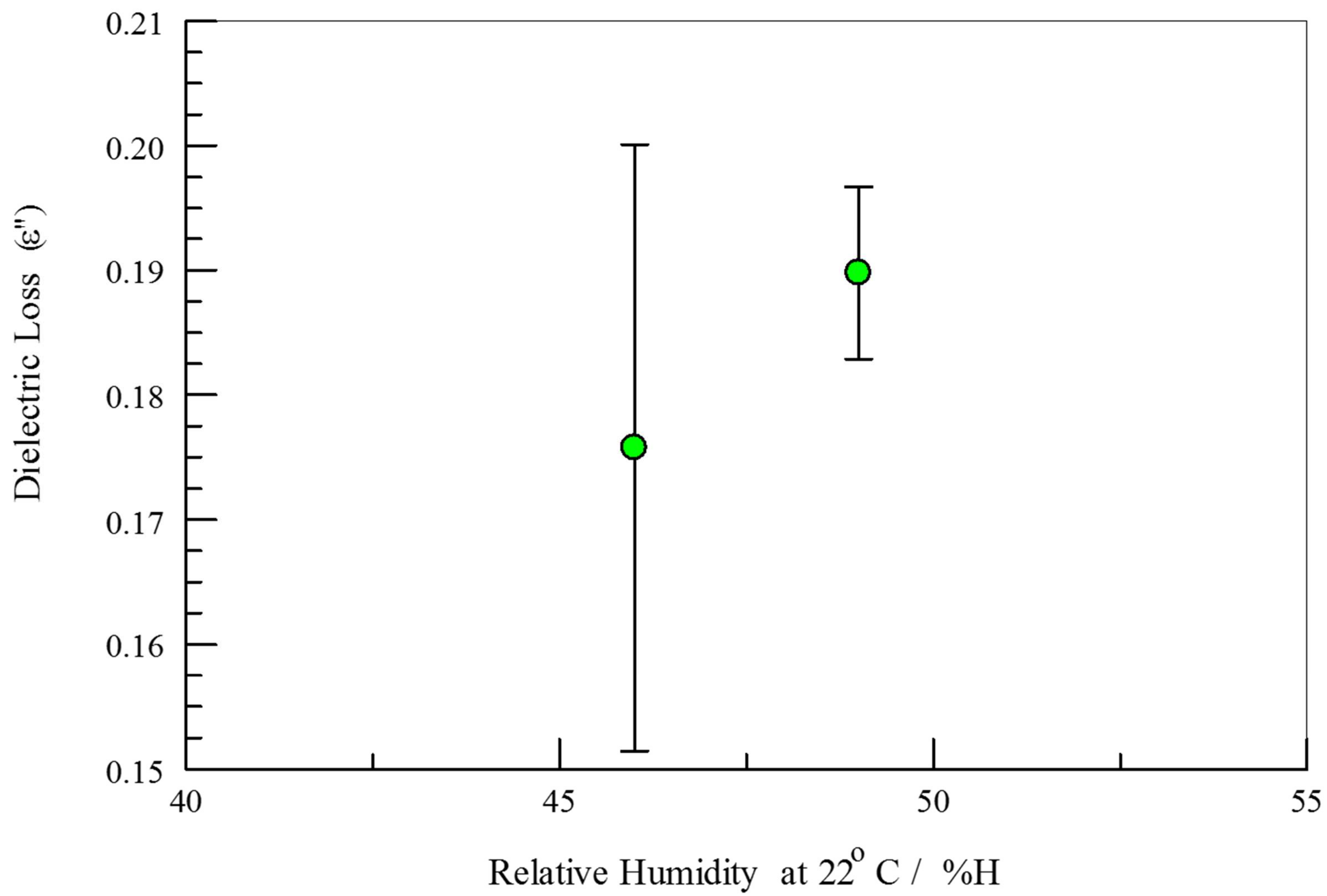
2.0x10-4
1.8x10-4
1.6x10-4
1.4x10-4
1.2x10-4
1.0x10-4
8.0x10-5
6.0x10-5
4.0x10-5
2.0x10-5
0.0
1/Qx - 1/Q0
0.0
2.0x10-4
4.0x10-4
6.0x10-4
8.0x10-4
1.0x10-3
4Vx/V0



0.32
0.30
0.28
0.26
0.24
0.22
0.20
0.18
Dielectric Loss (ε")
-20
0
20
40
60
80
100
Strip Angle / degrees



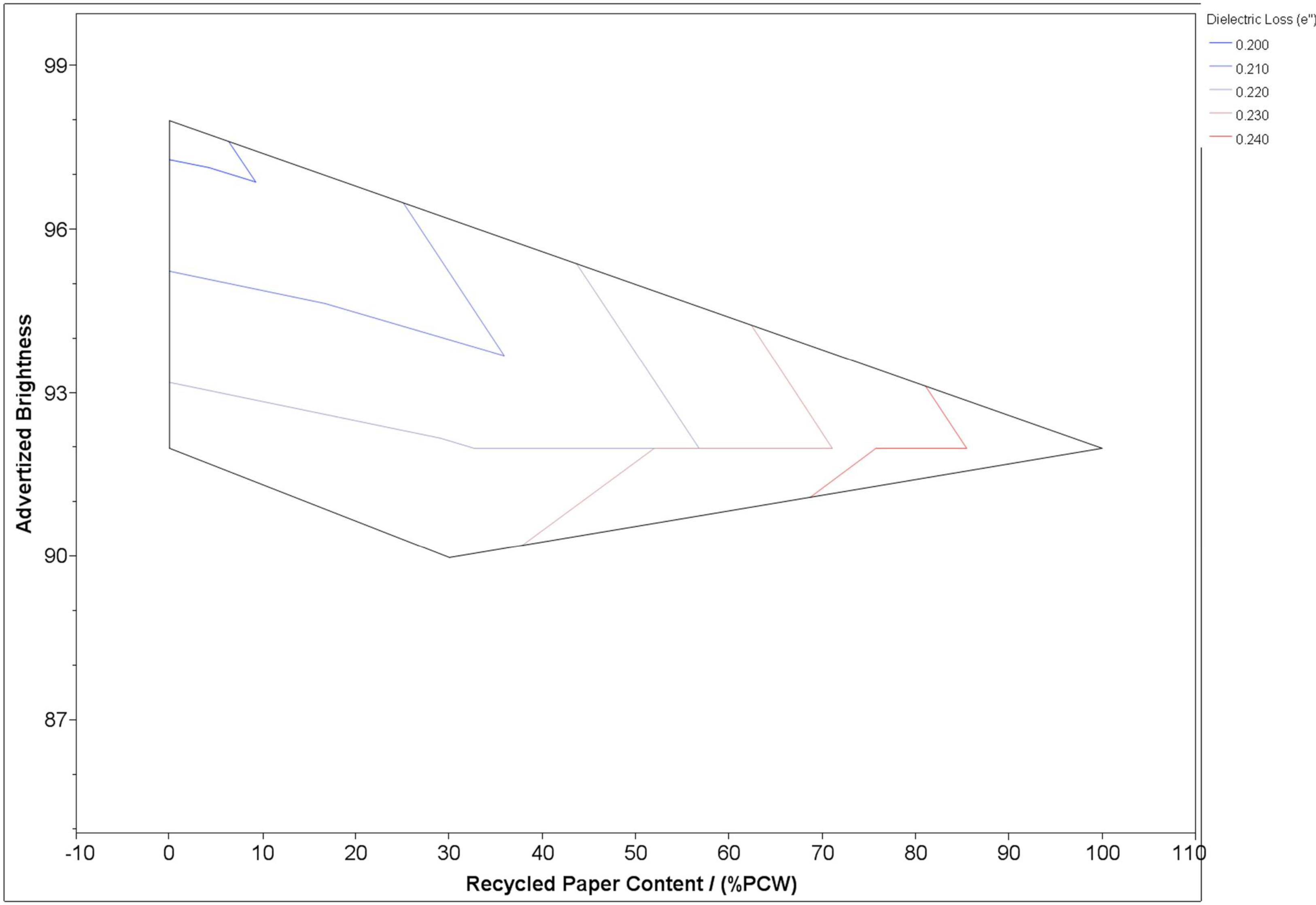
0.23
0.22
0.21
0.20
0.19
0.18
0.17
Dielectric Loss (ε")
20
30
40
50
60
70
80
90
100
Fraction Cotton in Paper / %



0.21
0.20
0.19
0.18
0.17
0.16
0.15
Dielectric Loss (ε'')
40
45
50
55
Relative Humidity at 22° C / %H

Figure

Click here to access/download;Figure;fig 5.pdf



Name of Material/Equipment	Company	Catalog Number
commercially produced colored office paper	Neenah Paper	
Q-Lab QUV accelerated weathering chamber	Q-Lab Corporation, Westlake, OH	
X-Rite eXact	X-Rite, Inc., Grand Rapids, MI	
Agilent N5225A network analyzer	Agilent Technologies, Santa Rosa, CA	
WR90 rectangular waveguide	Agilent Technologies, Santa Rosa, CA	
JMP data analysis software	SAS, Cary, NC	

Comments/Description

Purchased from Staples

R 100 (a = 10.16 mm, b = 22.86 mm, l_z =127.0mm)

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1) All requested editorial changes have been made:
    a. Figures have been modified as required
    b. Discussion section has been changed to conform to the editorial out line
    c. Reference have been changes to superscript style
    d. Commercial language has been removed
    e. Document has been thoroughly revised, and spell checked
2) Changes suggested by reviewer have been incorporated (highlighted in yellow) in the new manuscript.

We hope the revisions we have made in the manuscript and figures meet the editor's expectations.

Sincerely,

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4/12/2019