Dielectric spectroscopic studies of biological material evolution and application to paper

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ABSTRACT: Current product composition and quality test methods for the paper and pulp industry are mainly based on manual ex-situ wet-bench chemistry techniques. For example, the standard method for determining the furnish of paper, TAPPI T 401 "Fiber analysis of paper and paperboard," relies on the experience and visual acuity of a specially trained analyst to determine the individual plant species present and to quantify the amount of each constituent fiber type in a sheet of paper. Thus, there is a need for a fast, nondestructive analytical technique that leverages intrinsic attributes of the analytes.

In this paper, we demonstrate an application of dielectric spectroscopy (DS) as a potential metrology to differentiate between nonwood pulp and wood pulp fibers. This in-situ, noncontact and nondestructive assessment method has inherent forensic capabilities and is also amiable to quality assurance techniques such as gauge capability studies and real-time statistical process control (SPC).

Application: The dielectric spectroscopy results presented in this paper can nondestructively determine the amount of lignin in paper products and are in principle comparable to the performance specifications of the TAPPI Standard Test Method T 401. This DS method should enable the sources of printing substrates to be both authenticated and validated in real time in a paper testing laboratory environment.

TAPPI Standard Test Method T 401 om-88, "Fiber analysis of paper and paperboard," is currently the most commonly used method to determine the fiber types and their ratios within a paper sample [1]. For example, the TAPPI T 401 Test Method is used to distinguish between the type of pulping process used, i.e., kraft fibers versus sulfite or groundwood processes. The test method is also utilized in applications such as secure credentials manufacturing, law enforcement, custom inspections, archeology, and art conservation. However, the TAPPI T 401 test has many inherent limitations, such as being a manual, colorimetric technique that relies upon the visual acuity and level of experience of an analyst viewing chemically-stained fiber samples mounted onto glass slides via an optical microscope [1]. Sample preparation for the T 401 test is physically laborious and time consuming, requiring boiling, maceration, and acid/base treatments to liberate constituent fibers from a sheet. Finally, the T 401 test results are fraught with multiple sources of imprecision and inaccuracies [2], and liberated fiber samples are also often subject to the effects of atmospheric oxidation once a reagent stain has been applied, making it difficult to archive samples for preservation or specimen banking.

Dielectric spectroscopy (DS) probes the relaxation dynamics of dipoles and mobile charge carriers in response to an alternating electric field and provides information on the molecular fluctuations of dipoles within a matrix in response to rapidly changing electromagnetic fields [3]. This molecular polarization involves rotational reorientation in rapidly changing electromagnetic fields, making DS particularly well suited to examine the dynamics of molecules in confined spaces, such as in paper products. In this work, we leverage water as a probe molecule. The water molecule is hydrogen-bonded to the various polar polymers, such as cellulose and lignin, confined within a sheet of paper. Hydrogen bonding, especially with the adsorbed water molecules, influences the level of cross-linking within the cellulose structure and the level of polarizability [4]. In DS, the dielectric loss profile is a measure of the polarization relaxation, and the magnitude of the polarization is related to the length scale of the displacement. It depends on the electronic polarizability of the polar molecules and can be obtained by summarizing the characteristic polarizabilities, $\alpha 0$, of its covalent bonds. Cellulose is a syndiotactic polymer with many sites available for water to bind via hydrogen bonding, while lignin is a polarizable heteropolymer containing polar and polarizable conjugated bonds, all of which contribute to the dielectric loss function. The value of the dielectric function is also dependent on the density and on moisture content [5]. The total dielectric response of a material results from a vector sum of all the dipole moments of the system in its present orientation; thus, DS is able to distinguish different molecular units of a polymeric system,

like cellulose, in relation to the rate of their orientational dynamics [6].

While there is a significant body of work that uses DS techniques to study cellulose, wood, pulp, and paper, these studies have typically been focused on moisture content determination in the prediction of the mechanical properties based upon the dielectric anisotropy [7-12]. In this paper, we demonstrate the application of DS to test paper beyond moisture and mechanical properties to distinguish and understand the relationships between the various types of fiber present in an analyte [13]. This in-situ, nondestructive assessment method is also amiable to quality assurance techniques such as gauge capability studies and real-time statistical process control (SPC).

Resonant microwave cavity measurement was chosen for this initial work because it is noncontact, nondestructive, and experimentally simple in comparison to other methods of DS analysis. It is also particularly suited to characterize thin, sheeted materials, such as paper, as it eliminates the need for duplicate sets of measurements to account for the two sides of a sample sheet [14]. Resonant microwave cavity measurements have the advantage of being sensitive to both the surface and bulk conductivity, and the surface conductance of a sample material is determined by monitoring 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 surface area and volume [14-16]. In a thin, sheeted material, the surface conductance is a good proxy for the dielectric profile of a material under test (MUT), as it is directly proportional to the dielectric loss,ε'', of the MUT [14-16]. Dielectric loss is an indication of how much heat is dissipated by a dielectric material when an electric field is applied across it; more conductive materials will have a higher dielectric loss value than less conductive materials.

The dielectric loss, ε'', associated with the specimen, is represented as the slope of the line given by Eq. 1 as follows:

$$(Q_s^{-1} - Q_0^{-1}) = \varepsilon'' \frac{4V_X}{V_0} - 2b'' \quad (1)$$

where $(Q_s^{-1} - Q_0^{-1})$ represents the difference of the reciprocal of the Q-factor of the specimen from the Q-factor of the empty cavity, and $\frac{V_X}{V_0}$ is the ratio of the volume of the inserted specimen to the volume of the empty cavity [15].

MATERIALS AND METHODS

Sample preparation

Paper strips were cut using a rotary cutter. Strip angles were measured using a student's protractor with the basis of the machine direction set to 90°, while the cross direction is set to 0°. Paper strips of width 0.5 cm were cut roughly to 8 cm in length to accommodate the sample holder of the resonant cavity device setup. Sample strips were placed between glass microscope slides and stored in a nitrogen-filled dry box. The samples were re-equilibrated with ambient conditions for several hours before the microwave measurements. The reported thickness of the paper was determined through an average of ten caliper measurements.

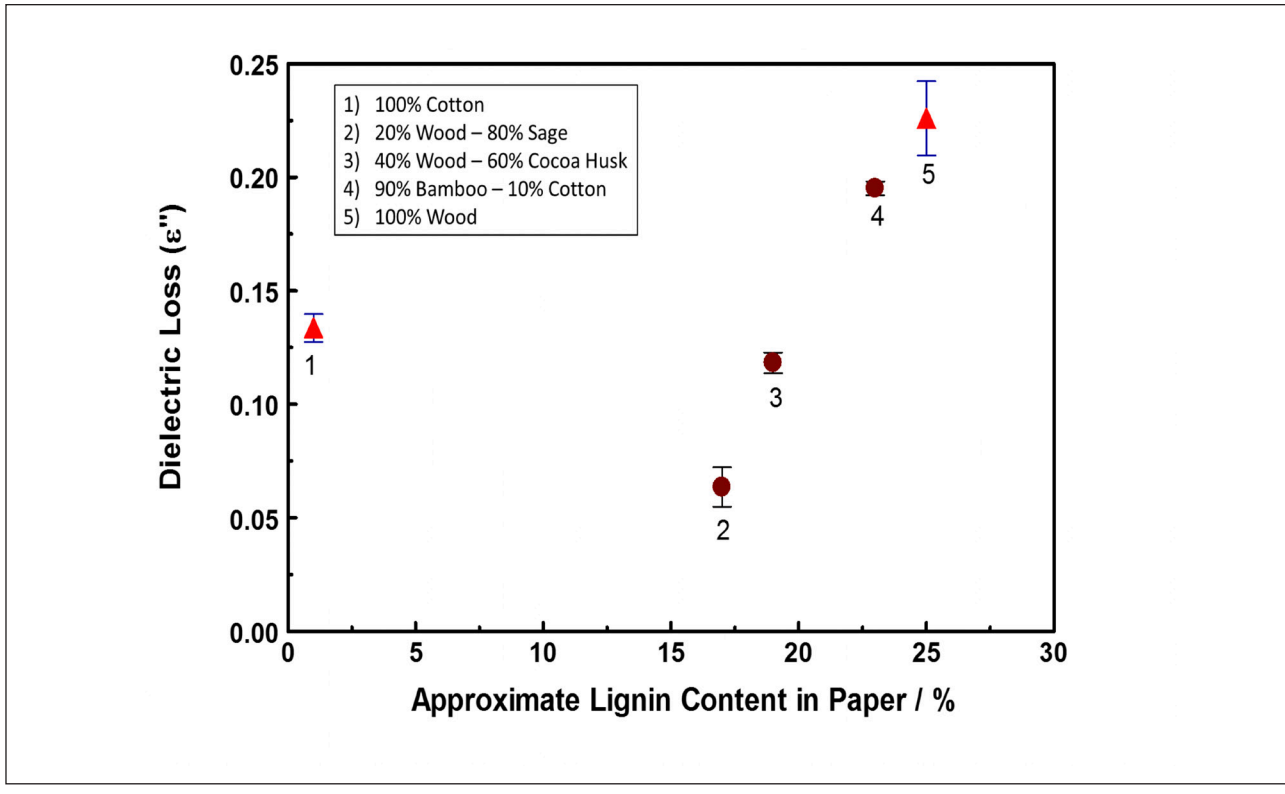
Resonant cavity

The resonant cavity fixture used in this work consists of an air-filled standard R100 rectangular waveguide (Agilent Technologies, Santa Clara, CA, USA; a = 10.16 mm, b = 22.86 mm, l_z =127.0mm), with an operating microwave frequency range of 6.700–13.000 GHz. The cavity is connected to an Agilent N5225A network analyzer with semirigid coaxial cables and coaxial to R100 coupling adapters. The coupling adapters are nearly cross polarized in respect to the waveguide polarization angle, which makes sharp impedance discontinuities at both waveguide ends and consequently the cavity walls. The polarization angle is about 87°, which results from the standard dimensions of the R100 flange and is sufficient to achieve optimal power loading into cavity while maximizing the quality factor. The specimen is inserted into the cavity through a slot machined in the center of the cavity, where the electric field, E_x, attains a maximum value at each odd TE_{10n} mode.

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. During measurements, the specimen is partially inserted into cavity in steps to a certain volume, V_x, while the quality factor, Q_x, and the resonant frequency, f_x, is recorded. Dielectric permittivity of the paper samples was obtained by plotting the measured V_x, f_x, and Q_x data and solving the two linear perturbation equations for complex permittivity as described in references [14-16]. The measurements were performed in ambient laboratory conditions. The storage history of the samples did not appear to impact the measurements.

RESULTS AND DISCUSSION

Nonwood fibers serve as a source of low environmental impact pulp that is quicker to bring to market than wood-based pulps. Historically, documents of interest to archeologists and historians have often been produced on papers manufactured from nonwood fibers [17]. In the modern era, cotton is the most common nonwood fiber used in papermaking for secure and nonsecure high-value printing papers. Cotton fiber is easily distinguishable from wood fiber via optical microscopy by its dimensions and morphology, as well as its reaction to iodine-based stains, such as Graff's C-Stain [12,13,15]. However, the quantitative determination of cotton content in paper is still a lengthy and onerous task if one relies upon an optical microscope and the TAPPI T 401 procedure. This is because the determination of the cotton content depends upon the correct identification and calculation of the ratios of hardwood and softwood fibers in cotton-blend papers, via optical microscopy. By examining papers with varying proportions of wood to nonwood fiber, we hope to show that resonant cavity dielectric spectroscopy can dis-



1. Dependence of dielectric loss profiles (slope, see Eq. 1) on estimated weighted lignin fraction in the analyte. The weighted lignin fraction was calculated from the average literature values of lignin content in each fiber source weighted for the advertised composition.

cern between wood and nonwood fibers. The discriminating metric, the dielectric loss profile, is presented as the slope of the change in the Q-factor of the cavity as the specimen volume is varied.

Chemically, a typical plant-based paper product is comprised of cellulose (40%–50%), hemicellulose (15%–35%), and lignin (20%–40%). Functionally, lignin combines with the hemicellulose to impart mechanical strength to the composite raw materials. However, lignins are generally undesirable contaminants in paper products, as they age poorly, turn brown, and become acidic, resulting in paper embrittlement with time. While lignins make up 20% to 30% of wood-based paper products, they are only about 1% in cotton-based bond paper. Figure 1 compares the dependence of the observed dielectric loss profile of papers of varying furnishes based on the estimated weight fraction of lignin in each analyte. For this work, test strips cut at 60° relative to the paper's cross direction were used. Inspection of the figure shows that two paper types that were nominally advertised as containing no wood fiber, namely, 100% cotton bond paper and bamboo blend paper (90% bamboo, 10% cotton), showed different dielectric loss responses. The presence of the bamboo fiber significantly elevated the average dielectric loss profile in comparison to the pure cotton bond paper. This disparity in response is attributed to the high lignin content in bamboo [18]. In fact, the lignin content in bamboo (20%–26%) is substantially higher than the normal range of lignin in nonwoody biomass (11%–27%), and closely resembles the ranges reported for softwoods (24%–37%) and hardwoods (17%–30%) [19]. Thus, based on lignin content, the 90% bamboo paper is in fact more chemically like 100% wood paper products. It must be emphasized that in these comparisons the precise chemical structure of the lignins was not considered, although there are many different types of lignins.

The increasing ε'' values with the lignin content are evident in Fig. 1. The effect represents the extent of polarization of water molecules with the paper sample; the more polarized the environment around the water molecule, the larger ε''. Thus, Fig. 1 suggests that the relaxation time of water changes with increasing lignin content of the paper analyte. This is reasonably consistent with the current understanding of the physicochemical impact of lignin in wood. Water molecules in paper may be bound within the fiber wall or adsorb to the surface as free water [20]. Nuclear magnetic resonance (NMR) studies show that the molecular motions of sorbed water in paper depend upon the physical state and crystallinity of the cellulose polymer. The water molecules that are tightly bound to cellulose will exhibit restricted motion as compared to free water [21,22]. Lignins modulate the water mobility in paper by cooperatively binding with hydrophilic polysaccharides to displace the bound water within the fibril network [23]. The lignins also form slightly hydrophobic domains, and water molecules in these channels have higher mobility than tightly bound ones [24]. The presence of less hydrophilic lignin, how-

ever, reduces some of the opportunities for water to associate with the more hydrophilic cellulose polymer but does not necessarily generate unbound water. The mobility of water molecules associated with the lignin hydroxyl regions is significantly reduced due to hydrogen bond formation, but the mobility of the water associated with the bulky methoxyl groups is only slightly restricted, due to steric and hydrophobic effects [25,26]. This restricted motion translates into a lower dielectric loss response. The limited lignin content puts pure cotton paper in a physicochemically distinct class that is different from wood-containing paper in terms of the structure of water in paper.

With this understanding, the DS results clearly illustrate the impact of the chemical composition of the paper analyte on the dielectric loss response, and are consistent with investigations of wood species and cotton using other dielectric spectroscopy techniques [3]. The results suggest that resonant cavity DS could be a useful tool for discriminating between paper of different compositions.

CONCLUSIONS

We have successfully applied resonant cavity DS to nondestructively determine the amount of lignin in paper products. The DS results presented in this paper are in principle comparable to the performance specifications of the TAPPI Standard Test Method T 401 and should enable the sources of printing substrates to be both authenticated and validated in real time. Moreover, DS offers an objective metrology approach that does not rely on the qualitative judgments of an analyst and can be adapted as a means of inline quantifying the amount of lignin present during the manufacturing of paper products. The technique can also be automated and easily integrated into a paper testing laboratory setting to increase the throughput of quality assurance/quality control (QA/QC) acceptance testing and can be extended to disciplines beyond the paper, pulp, and printing industries.

Further studies under tightly controlled test environments will be necessary to assess the technique's robustness and reliability. A proper evaluation of the DS technique must include studies to understand the impact of such product variables as lignin chemistry, filler type and percentage, and pulping process type, at a minimum.

ABOUT THE AUTHORS

We chose to study this topic because the paper and pulp industry needs fast, objective, and nondestructive metrologies for material analyses and quality control. The most challenging aspect of this research was that traditional paper testing angles (i.e., the machine and cross directions) provided poor resolution. This required trying nonorthogonal angles, which are not normally selected when performing physical testing of paper.

In contrast to the traditional TAPPI Standard Test Method T 401, we found there are nondestructive ways to perform fiber analysis without a specially trained human analyst. Also, we observed that nonorthogonal sample angles can yield better information and should be investigated while performing other testing of the physical properties of paper. Measuring samples from a nonorthogonal angle (60°) provided better resolution between paper analytes than measurements taken along the machine and cross directions.

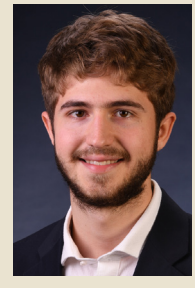
The approach here could ultimately help mills authenticate and validate fiber content of printing substrates in real time, and this technique can be automated and integrated into a paper testing laboratory setting to increase the throughput of QA/QC acceptance testing.

In the future, further studies under tightly controlled test environments will be necessary to assess this technique's robustness and reliability. A proper evaluation of the technique must include studies to understand the impact of such product variables as lignin chemistry, filler type and percentage, and pulping process type, at a minimum.

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clude studies to understand the impact of such product variables as lignin chemistry, filler type and percentage, and pulping process type, at a minimum. Such studies should be carried out at the handsheet level rather than at the commercial product level. It is our hope that other researchers will contribute to the further development of the measurement technique.

PUBLICATION NOTES

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