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Quality control of leather by terahertz time domain spectroscopy

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We use terahertz time-domain spectroscopy combined with effective-medium theory to measure moisture content and thickness of leather simultaneously. These results demonstrate that this method could become a standard quality control test for the industrial tanning process.

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1. Introduction

Tanning is the industrial process by which animal skins are converted into leather, which subsequently is used to manufacture a wealth of products that range from shoes to car seats. This process has seen relatively little changes since it was first used in ancient times. Although some automatic machines have been introduced, the process has not changed significantly. Most of the quality control is performed manually and even by subjective inspection of the finalized leather. Two parameters of extraordinary importance are the water content of the leather and its thickness. So far, the water content of leather is usually determined either indirectly, by measuring its electrical conductivity. Or by gravimetry, which is the process of taking a small sample of a leather hide, weighing it, drying it for 2 min at 90-100 °C and weighing it again.[1] Both of these methods are manually performed and either destructive or at least produce undesirable marks on the leather. The thickness is usually measured using a mechanical micrometer.[2] In order to prevent damaging the leather or producing a blockage of the conveyors that move the leather through the process, a non-contact method to measure these two parameters is desirable.

Terahertz radiation has attracted enormous attention owing to its potential of application in many fields. Advances in the technologies required to access this band of the electromagnetic spectrum have been reported in the last three decades by an active and growing community.[3, 4] One of the characteristics that make this radiation of interest is the fact that it is strongly absorbed by water,[5] therefore, terahertz can be used as a very sensitive non-contact and non-destructive probe of water content. This has been demonstrated for paper,[6] plants[7, 8] and other materials.[9] The transmission of terahertz radiation through leather samples has been reported, however, no quantitative information relevant to the quality control of this product has been extracted from such measurements yet.[10, 11] In this article we report transmission measurements of leather samples with different water content and thicknesses. We used an effective medium model for the combination of leather and water in order to quantitatively obtain the two variables simultaneously from the complex transmission spectra.

2. Qualitative measurements

In order to have a qualitative idea of whether the terahertz transmission technique could work as a moisture probe, a terahertz pulse was recorded after transmission through four samples of leather with different moisture levels. The measurements were performed using a terahertz time-domain spectrometer (THz-TDS) similar to the one described in Ref [12]. An intermediate state of the skins during the tanning process is called "Wet-Blue" (WB), as suggested by its name, this material contains high amounts of water. One sample of WB was measured as supplied from the factory (dripping wet, > 50 %wt), while two others where left drying for 15 minutes and 3 hours respectively before taking the measurement. In addition, a fully processed leather sample, with a water content below 10 %wt, was measured. The waveform of the pulses transmitted through the leather are displayed in Fig. 1. As shown in the figure, the pulse is completely absorbed in the sample with highest water content, while for the other samples, the amplitude of the pulse increases as the water content decreases, reaching a relatively large amplitude for the fully processed leather. This is a clear indication that the water content is related to the terahertz transmission. Furthermore, this demonstrates that in the latter stages of the process the leather is sufficiently transparent to obtain good transmission spectra and, therefore, a good signal-to-noise ratio on the measurement for quality control purposes.

3. Effective medium theory

Given that quality control of processed leather requires the determination of both the moisture content and thickness of each leather hide, we tried using the multiple echo method

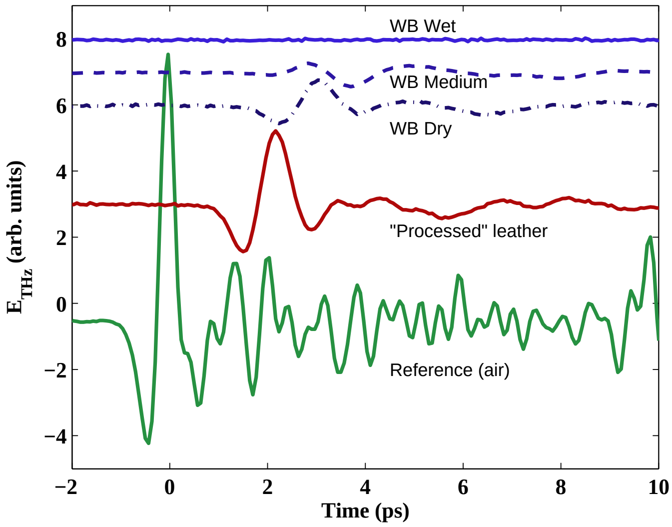

Fig. 1. (Color online) Terahertz pulses transmitted through leather samples with different humidity content. The amplitude of the pulse decreases as the water content of the sample increases. The curves on the figure are on the same scale and have been shifted vertically for clarity.

described by Duvillaret *et al.*[13, 14], however, the leather samples are not transmissive enough to obtain measurable FabryPerot reflections after the main pulse. Therefore we decided to investigate if effective medium theory can be used to obtain a quantitative measure for both of these parameters from the terahertz transmission spectra.

The Landau-Lifshitz-Looyenga model[15] has been used before to calculate the effective complex dielectric function mixtures of materials that can be considered homogeneous on length scales comparable to the wavelength of the radiation. If two materials with complex dielectric constants ϵ_w and ϵ_l are mixed at volumetric fractions a_w and $1 - a_w$ respectively, then the model predicts that the mixture will have a complex dielectric function given by

$$\sqrt[3]{\epsilon_{\text{mix}}(\omega)} = a_w \sqrt[3]{\epsilon_w(\omega)} + (1 - a_w)\sqrt[3]{\epsilon_l(\omega)}. \tag{1}$$

The complex refractive index of the mixture is given by $n + i\kappa = \sqrt{\epsilon_{\text{mix}}}$; therefore, a mixture sample of thickness d will have a transmission coefficient given by [16]

$$T(\omega) = t_{12} t_{21} e^{-\frac{\omega}{c}(\kappa + \kappa_{\text{scatt}})d} e^{i\frac{\omega}{c}(n-1)d}, \tag{2}$$

where $t_{12} = 2\tilde{n}/(\tilde{n} + 1)$ and $t_{21} = 2/(\tilde{n} + 1)$ are the Fresnel transmission coefficients at the

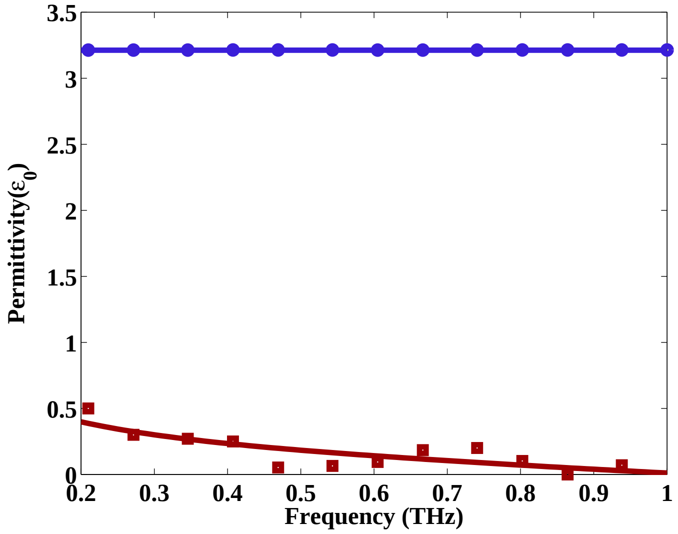

Fig. 2. (Color online) The real (circles) and imaginary (squares) parts of the dry leather dielectric function are plotted. The symbols represent actual measured points and the continuous lines are polynomial fits that were used for the effective medium model. The real and imaginary parts are approximated by the polynomials $Re(\epsilon) = 3.7 \times 10^{-39}\epsilon_0\,\mathrm{THz}^{-2}\nu^2 - 4.9 \times 10^{-27}\epsilon_0\,\mathrm{THz}^{-1}\nu + 3.19(\epsilon_0)$ and $Im(\epsilon) = 1.2 \times 10^{-2}\epsilon_0\,\mathrm{THz}^{-2}\nu^2 - 7.4 \times 10^{-2}\epsilon_0\,\mathrm{THz}^{-1}\nu + 0.0132(\epsilon_0)$.

air-sample and sample-air interfaces and

$$\kappa_{\mathrm{scatt}} = \frac{c}{\omega d}\left[(\sqrt{\epsilon_{\mathrm{mix}}} - 1)\frac{4\pi\tau\cos\theta}{\lambda}\right]^2 \tag{3}$$

is a correction to the imaginary part of the refractive index caused by scattering losses at the rugous interfaces of the mixture.[17] Here τ is the rugosity of the sample's interfaces measured as the standard deviation of the surface height profile and θ is the incidence angle.

In order to apply this model to leather we need to determine the dielectric function of "dry" leather. For this we baked a sample of processed leather for 2 hours at 95°C. The sample was immediately transferred to the TDS system. A transmitted and a reference pulse where measured under a nitrogen atmosphere to prevent absorption from atmospheric water vapor. The complex dielectric function was subsequently calculated. This was achieved by Fourier transforming the reference (nitrogen) and sample waveforms. These two functions were divided in order to obtain the complex transmittance function. From the phase and amplitude of such function it is possible to obtain the real and imaginary parts of the refractive index, and therefore of the dielectric function of the material. Further details of the formalism are presented in Ref. [18]. The dielectric function for dry leather is shown in

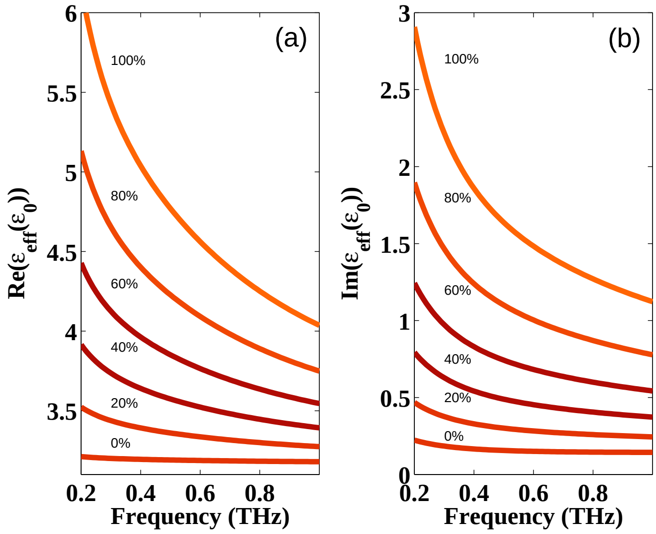

Fig. 3. (Color online) Real (a) and imaginary (b) parts of the dielectric function of leather for various moisture levels calculated from the effective medium model.

Fig. 2. The real part of the dielectric function, related to the propagation speed of radiation in the sample is almost constant. The imaginary part, that measures the absorption of the material, shows small ($<0.5\,\epsilon_0$) positive values. This is most likely related to vibrational absorption of the proteins present in the sample.

By using Eq. 1 combining the dielectric function of water, obtained from a double Debye model[19], and the dielectric function of dry leather it is possible to obtain the complex dielectric function of wet leather with different humidities. Both the real and imaginary part of such dielectric functions are shown in Fig. 3. As expected from the measurements in the previous section, both the real and imaginary parts of the dielectric function of the mixture have an important dependence on the water content. The real part almost doubles and the imaginary part increases by a factor of 15 (at 0.2THz) when the water content goes from 0 % to 100 %. It is important to notice that provided the volumetric proportions of water and leather it is relatively easy to calculate the dielectric function of the mixture, however, the calculation of the proportion of water and leather from the measured dielectric function of the mixture is, in general, not trivial, for this an iterative fitting algorithm, such as the one described in the following section is required.

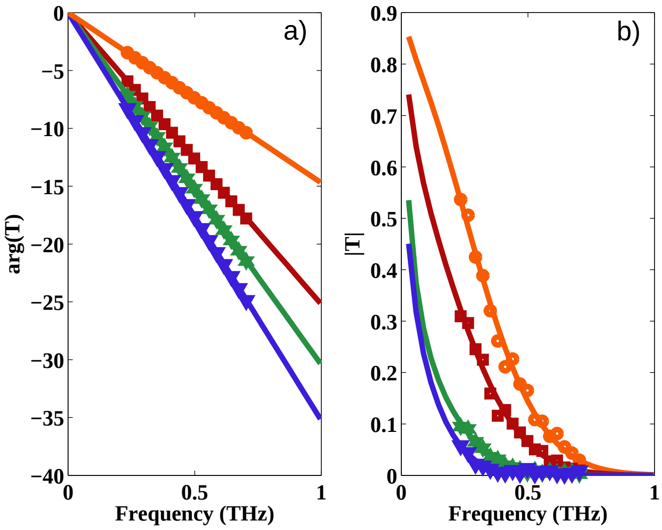

Fig. 4. (Color online) Phase (a) and amplitude of the transmission coefficient of various leather samples. The symbols represent measured values, while the continuous curves are fits of the effective medium theory model. The symbols correspond to samples a humidity and thickness of: 19 %, 1.7 mm (circles); 24 %, 1.7 mm (squares); 42 %, 2.1 mm (stars) and 45 %, 2.2 mm (triangles) respectively as measured by *conventional* methods.

4. Calculation of thickness and moisture

In order to obtain both the thickness and moisture content of leather samples, we implemented an iterative algorithm that makes a complex least-square fit to an experimental transmission spectra. This algorithm adjusts the parameters a_w and d of Eq. 2 which depend on Eq. 1. More details about the algorithm can be found in Ref. [7]. For consistency with standard practices in the tanning industry, the humidity presented in this article refers to the mass fraction that water represents of the leather sample expressed in percentage. The conversion between volumetric and mass fraction can be found in the article just referenced.

In order to test the algorithm and validate the technique, four processed leather samples were prepared. Different amounts of water were added to each one of them and they were left in sealed plastic bags for 4 days in order to ensure the water was evenly diffused into the tissue. Each sample was cut in two and each half was placed in separate sealed bags. A set of samples was sent to the tannery facility to be characterized with conventional methods and a second set was taken to the THz-TDS system. None of the two people performing the characterization knew the amount of water added to each sample.

The characterization in the tannery was performed by gravimetry, using a commercial

OHAUS MB45 humidity analyzer. With this equipment, each sample was weighted, baked at 200 °C and weighted again to measure its water content. The thickness was determined using a micrometer with 0.1mm resolution. For the terahertz characterization a transmitted waveform was recorded for each sample together with a reference waveform. All of these measurements were done in air in order to test the technique under conditions as close as possible to those of a real production line. The transmission spectra were calculated and are shown in Fig. 4. Subsequently the iterative algorithm described in the previous section was applied in order to obtain fits to the experimental points (also shown in Fig. 4), and therefore, the thickness and water content of each sample was determined. In terms of computation each calculation took ∼0.9 s, which is acceptable for quasi-real-time monitoring in an industrial environment. As seen in the figure, there is an excellent fit between the model and the experimental data for all the samples. For the fitting process, the parameter $\tau \sim 90\,\mu m$ was measured for the leather surface using a perfilometer. The angle of incidence θ was assumed to be zero.

The results from the tannery and the parameters of the fitting process are plotted together in Fig. 5 for comparison purposes. There is excellent match in both variables with mutual standard deviations between the measurements of 2% for humidity and 0.15 mm for thickness. It is important to notice that for samples with water content higher than ∼45% the uncertainty of the terahertz measurement is expected to increase significantly given that the amplitude of the transmitted pulse gets smaller and therefore the poor signal-to-noise ratio of the transmission spectra results in a worse estimation of both parameters.

5. Final remarks

In this article we demonstrated that it is possible to use THz-TDS in combination with effective medium theory to simultaneously quantify the water content and thickness of leather. The comparison between the measurements using THz radiation and conventional methods match very well and the mutual deviation of such measurements is perfectly acceptable for quality assurance purposes. The fact that this is a non-contact technique allows its implementation on production-line conveyors for automated quasi-real time characterization of each hide produced which is impossible with the methods currently used. This tool promises to be extremely useful for the quality control in the tanning industry.

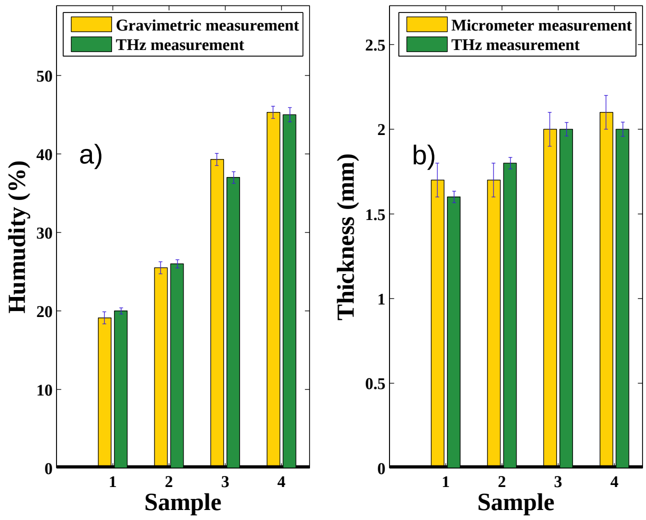

Fig. 5. (Color online) Comparison of measurements of humidity (a) and thickness (b) for various samples obtained using conventional methods (gravimetry and a micrometer) and the parameters obtained from the terahertz measurements. There is excellent correlation between the conventional and THz measurements with a mutual standard deviation of 2% and 0.15 mm respectively.

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