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THz ATR Spectroscopy for Inline Monitoring of Highly Absorbing Liquids

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Abstract We present a THz attenuated total reflection (ATR) setup which allows for inline measurements of highly absorbing liquids. As a proof of principle, we investigate a mixture of water and ground calcium carbonate (GCC) from 5 to 40 wt%. Inline measurements prove that our THz ATR setup allows for the distinction of various concentrations. As an example, we show inline THz ATR measurements for 30 to 40 wt% for GCC watery solution, as this concentration range is of technical relevance. We obtain a sensitivity better than 2 wt%.

Keywords ATR THz- TDS · Inline measurements · Industrial application

1 Introduction

Paper coating is an important step in the paper production process by adding value to the final product. It improves several characteristics of the end result, like surface uniformity of fiber-based paper, better white tint, and reduced transparency [1]. Here, we want to concentrate on the so-called coating color. The coating color is a mixture of minerals, including clay, ground calcium carbonate (GCC), precipitated calcium carbonate (PCC), titanium dioxide (TiO_2), and talc [1]. The coating procedure poses a considerable percentage of the overall production costs in the paper industry. In order to save valuable resources and to keep production costs low, it is necessary to find a suitable inline technique to monitor the quality of the coating process.

A promising technique to address this problem is THz time-domain spectroscopy (TDS) [2, 3]. There are already several examples for inline measurements in industrial applications [4–7]. Particularly, Banerjee et al. reported on THz TDS measurements for determining the moisture

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content of paper [8]. In 2009, Mousavi et al. reported on a similar technique which allows to determine the moisture and thickness of the paper simultaneously [9]. However, we are interested in monitoring the coating process at the earliest possible opportunity. At this point, the coating substance is a moist suspension with a high amount of water. Since THz radiation is strongly absorbed by water [10–12], conventional THz TDS transmission measurements reach their limit. An appropriate technique to circumvent this problem is THz ATR spectroscopy [13]. Using this approach, merely, an evanescent wave interacts with the strongly absorbing sample [14]. This principle allows for spectroscopic measurements of highly absorbing substances in the THz frequency range [12, 15, 16].

Yet, inline measurements with a continuous turnover of the liquid have not been reported with THz ATR spectroscopy so far. This is the point of the present work which demonstrates that THz ATR spectroscopy is in principle suitable to be used in an industrial environment. Here, we use a GCC solution as an example for a highly absorbing coating substance. First, we classify solutions with different water concentration by regular THz ATR measurements. To simulate an industrial application, a closed system with a pump is implemented in the THz ATR spectrometer. This enables us to monitor GCC suspensions with different water concentration in an inline measurement system.

2 Experimental Setup

The THz ATR system used in this work is based on an ultrafast Er:fiber laser with fiber-coupled photoconductive antennas. A scheme of the setup can be seen in Fig. 1a. The laser is coupled into free space, where the beam is split into two parts. One part is used for the THz generation at the emitter antenna, while the other part is used to optically gate the receiver antenna. In order to sample the THz field, a delay line is employed in the receiver arm. The setup is designed to have a high phase and amplitude stability, which is compulsory for long-term measurements [17].

The key part of the setup is a silicon prism with a refractive index of 3.418 [2] and a specific resistivity of 10 kΩ cm^{-1}. On top of the prism are two separated measurement chambers. One chamber is used for reference measurements, while the other serves as sample chamber [17]. The prism is mounted on a linear translations stage which enables alternating measurements of the two chambers. This configuration permits continuous referencing during long-term measurements and avoids errors due to misalignment. In order to avoid systematic errors, the characteristics of both chambers were measured in advance and taken into account for the post processing [18].

A picture of the setup is shown in Fig. 1b. The sample chamber has an inlet and outlet which are connected to the sample reservoir and the pump by flexible hoses. The flow rate of the liquid was set to 100 ml/min. The setup emulates an industrial setting where a highly absorbing liquid can be continuously monitored inline in the THz frequency domain.

3 Experimental Results

To verify that the THz ATR measurement scheme is capable of distinguishing between different concentrations of a watery GCC solution, preliminary measurements with known compositions were performed. We used the prism described in the previous section without

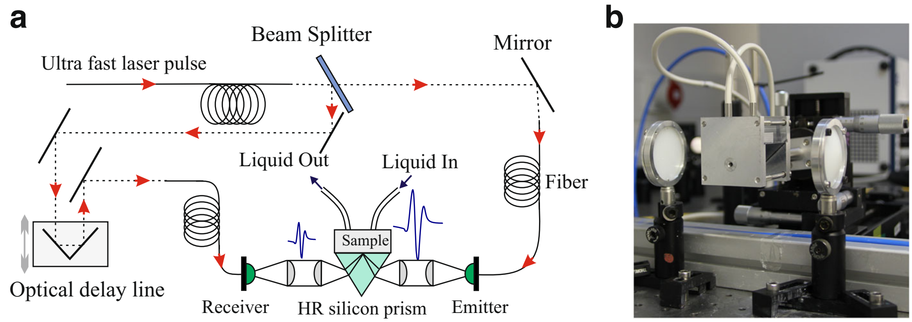

Fig. 1 **a** Schematic and **b** picture of the THz ATR setup

further modification for the inline emulation and examined GCC/ water mixtures with a percentage of 5, 10, 20, 30, and 40 wt% of GCC. After each measurement, the sample chamber was carefully cleaned. The complex refractive index of the sample was obtained by the algorithm described in [18], which minimizes the influence of slight variations in the signal during long-term measurements.

The averaged refractive index as well as the absorption coefficient of 25 measurements for each concentration can be seen in Fig. 2a, b. A higher GCC concentration leads to a higher refractive index and lower absorption coefficient. This correlates with the properties of the solvent which is water in this case. Pure water has a higher absorption coefficient and a lower refractive index than GCC. As consequence, a higher ratio of GCC reduces the absorption coefficient while increases the refractive index. Figure 2c presents the refractive index and absorption coefficient variation for the concentration between 5 and 40 wt% at 800 GHz. We note that absorption coefficient and refractive index do not vary linearly with the concentration. This may be due to concentration-dependent sizes and shapes of GCC clusters. Yet, to unveil the origin of this behavior is beyond the scope of this paper.

It has been reported that the THz permittivity of water changes with temperature [19]. To ensure high accuracy of the measurements, we therefore kept the sample temperature constant at 20 ± 0.1 °C.

Figure 3 shows the standard deviation obtained for five concentrations and frequencies around 800 GHz. On this basis, it is already possible to distinguish between concentrations varying by 5 %. The standard error of the mean (given by the standard deviation divided by the square root of the number of measurements) for the data in Fig. 2a, b are very small, i.e., only 30 % of the symbol size. Therefore, we did not plot the corresponding error bars in Fig. 2a, b.

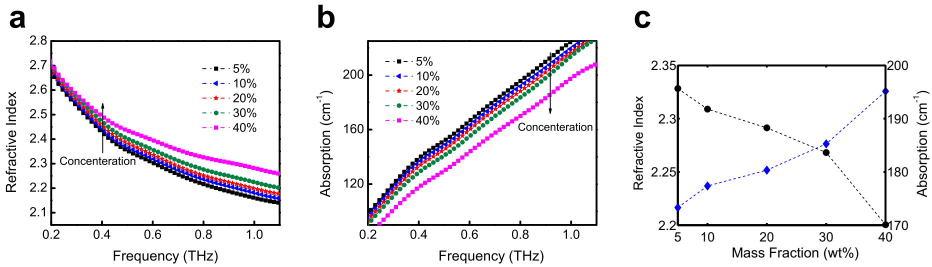

Fig. 2 **a** Refractive index and **b** absorption coefficient for GCC ratios between 5 and 40 %. **c** The variation of refractive index and absorption coefficient between 5 and 40 wt% at 800 GHz

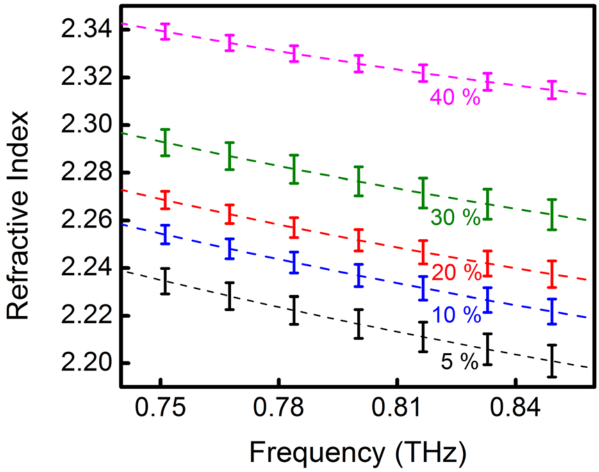

Fig. 3 Standard deviation for refractive index of the GCC measurements around 800 GHz

Hence, after a careful calibration, one can very reliably determine the present concentration using a lookup table.

With these results, we moved to the inline measurement. We stepwise increased the amount of water in the system in order to decrease the GCC concentration from 40 to 30 wt%. The reason why we use this concentration range is that it fully falls within is range of practical relevance in the paper production process for the coating colors examined. The online monitoring of the composition of the mixture is the actual task of the ATR setup. For each concentration, eight reference and sample measurements were alternately performed and averaged. We extracted the refractive index and the absorption coefficient and integrated both parameters between 300 and 650 GHz. In contrast to considering the parameters at a single frequency, this approach is more robust to noise. The averaged refractive index (red squares) and the absorption coefficient (black circles) can be seen in Fig. 4 for GCC ratios varying between 30 and 40 wt%. The trend for an increasing refractive index and a decreasing absorption coefficient is in good agreement with the previous measurements.

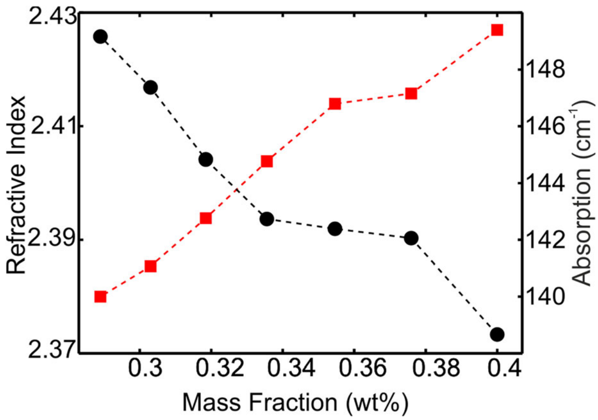

Fig. 4 Refractive index (*red squares*) and absorption coefficient (*black circles*) extracted from the inline measurements. Both parameters were averaged between 300 and 650 GHz

4 Conclusion

In this paper, we measured GCC in aqueous solution with concentration from 5 to 40 wt% by employing THz ATR time-domain spectroscopy. The results show that our proposed measurement scheme allows us to distinguish various GCC/water ratios in inline measurements. We focused here on the concentration range between 30 and 40 wt% as it is of technical relevance. In this range, we obtained the sensitivity better than 2 wt%. The key to obtain these results is the THz ATR technique combined with a prism with two measurement chambers. This configuration allows for continuous measurements which is necessary for inline monitoring. In principle this method can be used for inline monitoring of other highly absorbing liquids in industrial processes.

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