Combined FT-IR and diffuse reflectance spectroscopy for research of paper-solvent interaction

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In pulp and paper research much investigation effort is made on the drying process in order to improve the product quality and to make the manufacturing environmentally friendly. The major challenge in moisture detection is the high porosity of paper, which leads to multiple scattering of light. We apply two complementary methods, which allow to quantify the drying process in paper.

1 Introduction

Paper-solvent interaction, which occurs during drying of paper is a very energy consuming process. Therefore much investigation effort is made on this process in order to make paper industry more environment friendly and to improve the end product quality. The main challenge in this context is the high porosity of paper, which leads to multiple scattering of light in the sample. We apply two complementary methods, which allow to analyze the microscopic structure of paper under the influence of solvents from which we can determine the local solvent concentration. This information is important in order to understand different drying processes, which occur in paper during production.

2 FT-IR Spectroscopy

Our primary measurement technique is Fourier Transform Spectroscopy in the mid-infrared regime. The spectrometer (Bruker Vertex 80v) is operated in transmission mode with a spectral resolution of 4 cm-1. Water is currently our main solvent under investigation. The drying of paper is sampled 40 times every 15 seconds resulting in 10 minutes for the overall measurement time. The spectrum is recorded in the range between 500 cm-1 and 5000 cm-1. The resulting spectrum is depicted in Fig. 1. The spectrum reveals two different processes, that occur during drying. In the range between 1500 cm-1 and 2700 cm-1 the sample is becoming more transparent with time. This is due to evaporation of water molecules (at 1540 cm-1 and 3790 cm-1). Apparently there are also some chemical bounds between water and paper constituents, which absorb radiation in the vicinity of water bands. The second process (above 4200 cm-1) is non-monotonic in time and introduces a transmission minimum (after about one minute) during drying. This effect is caused by scattering within the sample which is becoming dominant in the dry state. Scattering occurs predominantly at fibers and pores. The size of pores and their content is dependent on the local concentration of the solvent. Scattering in the sample increases the variance of optical path lengths and restricts therefore the validity domain of Lambert-Beer law. For deeper understanding of the structural changes in paper during drying a second experimental setup has been developed.

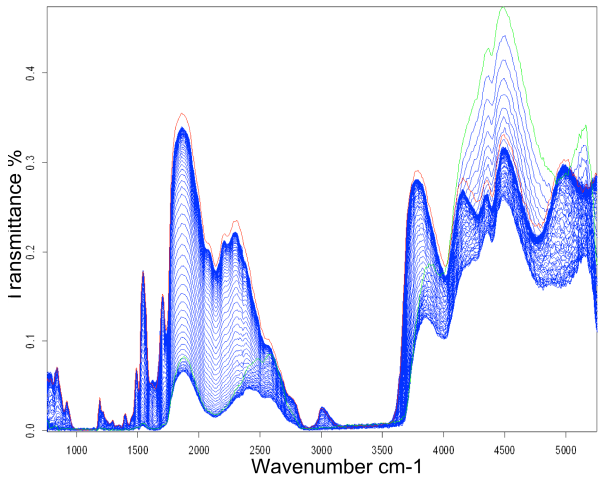

Fig. 1 *FT-IR transmission spectrum of paper during drying; the green curve is the beginning and the red curve is the end of the measurement;*

3 Diffuse Reflectance Spectroscopy

In order to account for multiple scattering in the sample we use a method for quantifying its absorption coefficient μ_a and scattering coefficient μ_s, respectively (both denoted as optical parameters in the following). The main objective of the method is to measure the local scatterer size distribution. This information can be used to derive the local drying behavior of the sample. The main challenge in determining scattering and absorption coefficients of porous materials is the strong coupling between these two properties. Because direct and independent measurements of the samples optical properties are impossible, indirect parameter determining techniques are applied. In order to de-

termine optical parameters indirectly one performs experiments, where absorption and scattering have different impact on the measurement signal. Afterwards a numerical simulation or an analytical model is exploited in order to extract the parameters from the measured data.

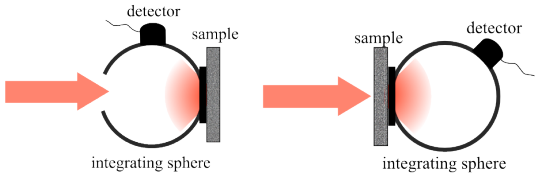

Fig. 2 *Measurement setup for Diffuse Reflectance Spectroscopy; diffuse reflection and transmission of the sample are captured by two integrating spheres;*

Our preferred experimental method, diffuse reflectance spectroscopy (DRS) is based on two integrating sphere setups (Fig. 2). The drying sample is illuminated by a semiconductor laser diode in the visible regime. The two setups perform measurements of diffuse reflectance and transmittance of the drying sample respectively (3).

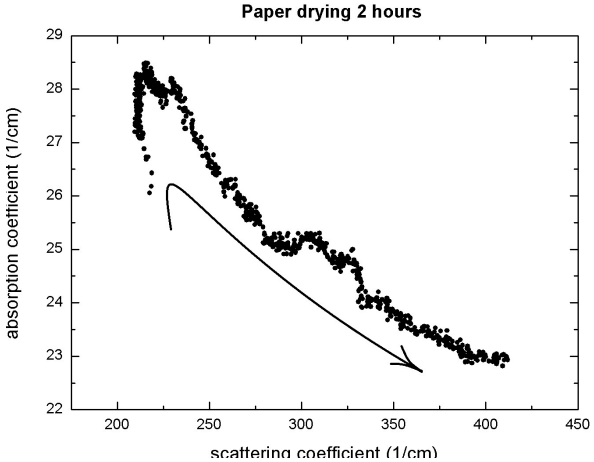

Fig. 3 *Scattering and absorption coefficients during drying of paper measured with DRS;*

After the integrating sphere measurements it is necessary to perform simulations in order to be able to extract the optical parameters properly. A very important step is the choice of the right model. Most models in this context are based on a macroscopic approximation of Maxwell Equations, the Radiation Transfer Equation (RTA) (1). However RTA has poor performance in case of complex sample geometries and requires usually further approximations. An analytic approximation of RTA is the Diffusion Approximation (DA). It shows good performance but adds strict constrains to the sample properties. The DA becomes invalid, if either the amount of absorption is close to the amount of scattering or the detection is close to the entry point of light into the sample (direct light). Our method of choice is the numerical approximation of RTA by Monte Carlo simulation. This method is very time consuming but gives results with arbitrary precision. One of the biggest advantages of the Monte Carlo simulations is the absence of any constrains on the sample geometry. The program code of the Monte Carlo simulation is based on the MCML code (2).

The measurement results of DRS using Monte Carlo simulations for parameter extraction are depicted in Fig. 3. The sample was illuminated by a semiconductor laser diode (650 nm). The diffuse transmittance and reflectance of the drying paper sample are captured every 10 seconds within the first 2 hours. At the beginning of the drying process the absorption coefficient increases from 26 cm^{-1} to 28,5 cm^{-1}. The scattering coefficient remains constant. After the first 10 minutes the scattering coefficient starts to increase and the absorption coefficient decreases. The non-monotonic behavior of the optical parameters of the sample is consistent with the measurements using the FT-IR spectrometer.

4 Conclusion

Multiple scattering of light in the paper sample makes the measurement of moisture content to a challenging task. In order to understand the drying process of paper, which consists of several competing processes, we apply two complementary measurement techniques. The FT-IR measurement setup shows a rich drying dynamics, which occurs in paper and is reflected in the mid-infrared regime. The integrating sphere setup combined with a Monte Carlo based parameter extraction delivers the optical parameters of the sample during drying. A third technique, photoacoustic tomography is currently under development in order to overcome multiple scattering effects and to improve the spatial resolution of the measurement.

References

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