THz Spectroscopy for the Inline Control of Polymeric Compounding Processes

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***Abstract* — We present non-destructive and contactless inline measurements on the molten polymer polypropylene and on the polymeric compound polypropylene-$CaCO_3$ carried out with a THz spectrometer. The effect of temperature and pressure on the THz properties of the molten polymeric material is investigated. Additionally, we analyze the additive content of the compound during the extrusion processing and compare this data with offline results. Further measurements on wood plastic composites demonstrate the capability of detecting the degree of dispersion of compounds with THz-spectroscopy.**

I. Introduction

Presently, several inline measuring systems exist to monitor polymeric compounding processes[1-3]. The most common method to determine the additive content of a compound is via its dielectric conductivity. A rather new technique which is capable of determining the dispersion quality uses ultrasonic waves. Yet, offline testing methods are still widely used to analyze these material parameters during the extrusion process. Hence, there is a strong demand for supplementary inline techniques that are suitable for monitoring both, the additive content and the dispersion quality, simultaneously.

Here, we demonstrate that THz technology holds great potential to fill this gap. We present a robust and mobile THz spectrometer for non-destructive and contactless inline measurements on molten polymers and compounds[4]. Using this system we study the effect of temperature and pressure on the dielectric THz properties of molten polypropylene. Furthermore, we carry out THz inline measurements for polypropylene-$CaCO_3$ compounds and obtain reliable information on their additive content. In addition, we perform offline experiments on wood plastic composites with different degrees of dispersion. A clear distinction between well and badly dispersed samples is possible, demonstrating the high potential of THz spectroscopy for inline characterization.

II. Results

The experimental data that is shown in the following have been measured inline during the extrusion process. Therefore, we adapted our THz inline spectrometer to a custom made injector unit positioned at the end of an extruder in a semi-industrial environment. Only the dispersion degree measurements have been taken offline.

Measurements on pure molten polymers

First, we investigate the polypropylene "Basell Moplen HP501M". We perform measurements at various melt temperatures and a constant pressure as well as at various pressures and a constant temperature. We determine no measureable influence of the melt pressure on the THz parameters in the range from 0 bar to 18 bars. Additionally, no significant change in the absorption of the material is detected for melt temperatures from 225 °C to 290 °C. In contrast, the refractive index shows clear temperature dependence (see Fig. 1). We calculated the specific gravity of polypropylene using the PVT-diagram. Although the differences in the refractive index are very small, an expected linear relation between the refractive index of the polymer and its specific gravity can clearly be observed (see Fig. 1). The linear fit of our measured data meets the literature value[5] of the refractive index of propylene at room temperature. This shows the reliability of our data as well as the high quality of the THz inline spectrometer.

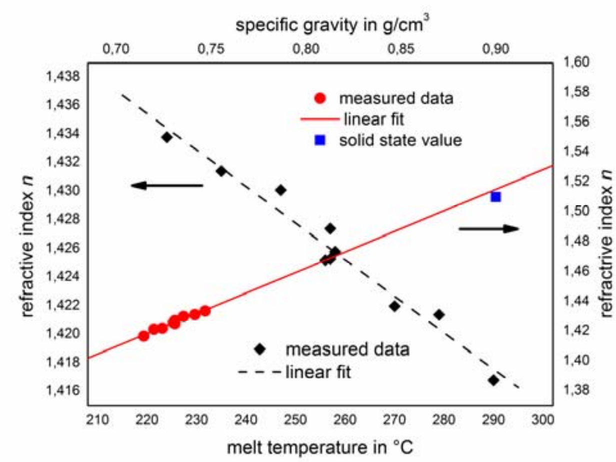

Fig. 1: Refractive index n of molten polypropylene as a function of temperature (diamonds) and as a function of the specific gravity (circles)[5]. The room temperature value (square) of the refractive index of polypropylene[6] (n=1.51) is added to confirm the high quality of the experimental data. These values represent the average of the refractive index in the frequency range from 0.20 to 0.35 THz.

Measurements on molten polymeric compounds

Offline studies on injection molded specimen have shown a linear correlation between the THz refractive index and the volumetric additive content[7] for several compounds. We show that this linear relation also holds for molten compounds. In

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Fig. 2 we directly compare our new inline data with offline results that are already presented in[7]. Considering the influence of the abovementioned decreased density of the molten polymer, the refractive index of pure polypropylene in the molten state is lower. In contrast, the $CaCO_3$ particles are still in the solid state at temperatures of about 250°C. Hence, the slopes of both graphs differ slightly.

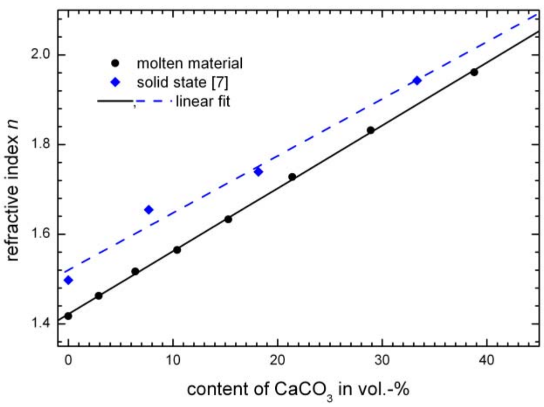

Fig 2.: Refractive index *n* of the compound polypropylene-$CaCO_3$ at various additive contents. These values represent the average of the refractive index in the frequency range from 0.20 to 0.35 THz. Compared are offline solid-state data that have been published in reference # 7 and the result of inline measurements that are taken during the extrusion process[5].

Measuring the degree of dispersion of compounds

Exemplarily, we took offline measurements on well and badly dispersed wood plastic composite specimen with varied additive content. Wood is a material that is compressible. Different production techniques to achieve the different dispersion qualities lead to a slightly different compression of the wood particles. Hence, the refractive indexes of both charges also differ slightly. However, this effect is negligible for the following argumentation.

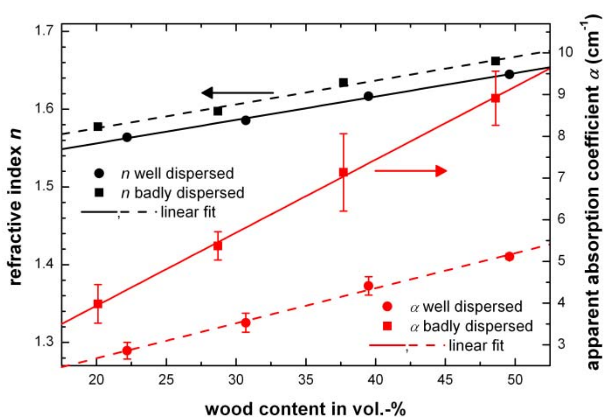

Fig. 3: Refractive index *n* and the apparent absorption coefficient as a function of the volumetric wood content in well and badly dispersed wood plastic composites. These values represent the average of the refractive index in the frequency range from 0.20 to 0.8 THz.

The degree of dispersion can clearly be distinguished by analyzing the apparent THz absorption coefficient that includes the effect of scattering. The terahertz signal is scattered on particles with dimensions close to the wavelength of the THz radiation. Almost no effect is detectable if the filler is homogenously dispersed in the polymer matrix. A bad degree of dispersion leads to agglomerates. Once the size of the clusters is large enough this causes Mie scattering which affects the measured data considerably. As a result, the apparent absorption coefficient of the investigated sample increases as can be seen in Fig. 3.

III. Summary

Studies on molten polypropylene which are performed during the extrusion process show the high quality of our measured data. Even smallest changes in the refractive index caused by different processing temperatures can be reliably determined. The linear relation between the volumetric additive content and the refractive index of several compounds in the terahertz frequency range, which was up to now only shown with offline measurements taken at room temperature, is confirmed with the investigation of the molten compound polypropylene-$CaCO_3$. Offline measurements on well and badly dispersed wood plastic composites show the possibility of determining the degree of dispersion of polymeric compounds with THz spectroscopy. The apparent absorption coefficient is dramatically higher for the badly dispersed samples due to scattering on agglomerates.

In summary, THz spectroscopy is an extremely valuable technique for the inline monitoring of industrial compounding processes.

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