Terahertz Spectroscopy

A Powerful Tool for the Characterization of Plastic Materials

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Abstract— **Terahertz (THz) spectroscopy holds a high potential as non-destructive, contact-free testing tool for the analysis of macromolecules, the monitoring of plastic processing and the inspection of plastic components. Even molecular properties, such as the glass transition temperature of highly-crystalline polymers, can be derived from THz measurements. Furthermore, we have identified a plethora of emerging applications in the plastics industry. To appeal to these upcoming challenges, we developed the first THz time-domain spectroscopy (TDS) system for the inline monitoring of compounding processes, which was awarded the Otto von Guericke Prize 2009. It has been demonstrated that the filler content at the end of the extrusion line could be precisely determined by time-of-flight measurements. In addition, THz technology is capable of measuring the water content sensitively, THz birefringence measurements reveal the fiber orientation in reinforced plastics and the quality of plastic weld joints or adhesive bonds can be inspected by the interference evaluation of the THz data. Due to the outstanding dielectric contrast of materials at THz frequencies, even contaminations invisible to x-rays or ultrasonic measurements can be revealed by THz TDS imaging opening the door for a new generation of non-destructive, contact-free quality control systems.**

Keywords-terahertz spectroscopy; polymer; plastic; non-destructive testing; monitoring; compound; glass transition; fiber orientation; plastic weld joint; additive content; water content

I. Introduction

In the electromagnetic spectrum, the terahertz (THz) region is commonly defined by the frequency range of 0.3 THz to 10 THz. Located between the microwaves and the infrared, the non-ionizing THz radiation combines the great depth of penetration of microwaves with the lateral sub-millimeter resolution of the higher-frequency infrared region, especially when imaging techniques are employed [1]. Due to this exposed position, a variety of metrological applications with high impact on industries exists. However, as the number of optical and electronic devices that could access this frequency range was very limited, the THz gap remained a weakly illuminated spot on the spectral map for a long time. The rapid progress in (femtosecond, fs) laser science and microwave engineering finally allows full access to this long unexplored frequency band [2]. Now, a variety of terahertz sources exist. The recent advances in THz system technology [3] and a plethora of research projects currently pursued suggest that the market introduction is rapidly approaching. More and more industrial applications arise, which realize the high potential of this emerging technology. This contribution serves as an overview of selected applications in the plastics industry, especially focusing on those where existing measuring methods cannot deliver satisfactory solutions.

II. Terahertz Time-domain Spectroscopy on Polymers

We will focus on THz time-domain spectroscopy (TDS) providing lots of information in the time and the frequency domain. THz TDS employs a coherent generation and detection scheme. Therefore, this technique has access to both, the phase and the amplitude of the electric field in contrast to far-infrared absorption spectroscopy. Thus, THz TDS is capable of extracting the material's complex refractive index without the need for Kramers-Kronig relations [4]. Furthermore, an advanced data extraction algorithm allows for determining the real sample thickness d, the absorption coefficient α, and the refractive index n simultaneously [5].

Near- and mid-infrared spectroscopy considers absorption peaks that mainly arise from highly localized intramolecular deformation such as hindered rotation or stretching oscillation of covalent bonds [6]. However, THz waves interact with collective motions of large molecules. Polymer macromolecules interact much stronger with each other than gas molecules. These interactions result in much broader resonances compared to the sharp peaks of rotational spectra. By far-infrared absorption spectroscopy, complex inter- and intramolecular characteristics of polymers have been identified such as skeletal vibrations, liquid-lattice modes, intermolecular vibrations in the crystalline phase, or hydrogen bonds [7].

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Basically, polymers can be grouped by their dielectric properties in the THz regime into two classes:

1) Non-polar polymers including olefin polymers such as polyethylene (PE) and polypropylene (PP) have a very high transparency and a relatively low refractive index smaller than 1.55 at THz frequencies. Furthermore, they show hardly any dispersion.

2) Polymers comprising polar bonds without symmetric dipole moments such as polyamide (PA) exhibit a relatively high refractive index, which typically lies above 1.6. In contrast to the non-polar polymers, an anomalous dispersion is found. The dispersive behavior is due to orientation polarization of the permanent dipoles [8].

III. Monitoring Polymeric Compounding Processes

While polymers offer a relatively high transparency to THz waves, commonly used fillers exhibit a significantly higher permittivity. Offline measurements on representatively selected material combinations have shown that the filler content can be reproducibly determined using THz TDS [9]. In addition, an advanced quasi-static effective medium theory allows for modeling these heterogeneous dielectric mixtures [10]. This way, polymeric compounds can be employed for THz devices in return [11].

In order to demonstrate the potential of THz technology for non-destructive inline monitoring in the plastics industry, we have developed a fiber -coupled THz spectrometer designed to operate in a rough industrial environment. First inline measurements on molten polymers and polymeric compounds were performed during compounding processes [12]. However, making the move from the laboratory setup to the practical and user-friendly inline monitoring system requires some innovative engineering. To meet the requirements of flexibility, transportability and robustness, a partially fiber-coupled THz spectrometer relying on fiber-coupled antennae has been developed. The free space elements, including an 800 nm Ti:Sa laser and an optical delay line, are packaged in a hermetically sealed metal box mounted on a transportable, shock-absorbing, optical bench (Fig. 1a). The innovative fiber coupling relies on the fact that the fs laser beam is launched into a glassfiber that is directly glued onto the antenna chip [13]. This connection method enhances the flexibility (vertical setup possible) and the robustness of the entire system tremendously. Modern fiber lasers, an all-fiber setup and further integration techniques will reduce not only the size but also the cost of such a system in the near future. The vision is a compact THz probe at the end of the compounding line (Fig. 1b).

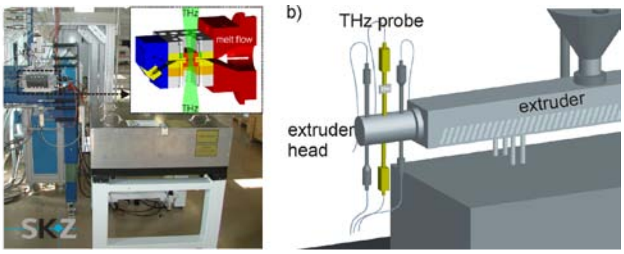

Figure 1. A first industrial-use fiber coupled THz spectroscopy system (a) and the scenario of a compact probe at the end of an extrusion line (b).

Measuring the THz signal at a fixed time position allows for a sensitive real-time monitoring [12]. Even small shifts of the measured THz pulse that arise from altered composition of the molten compound under test affect the measured signal noticeably. For instance, the current concentration of $CaCO_3$ in a PP matrix has been monitored successfully (Fig. 2). The filler content was altered several times at the dosing unit. The results show that the THz signal could also be applied to monitor the residence and the wash out time of the compounding process. These first real-time measurements demonstrate the applicability of THz technology as a valuable technique for the inline control of production processes, which was awarded the Otto von Guericke Prize 2009.

IV. Non-Destructive Testing of Plastic Components

A. Determining the Water Content

Water strongly absorbs THz radiation. Actually, this high sensitivity to water can be used for determining even low water contents. Recently, first application such as the investigation of the water content in plant leafs [14] or in paper [15] have been demonstrated successfully using THz radiation. Furthermore, the diffusion of solvents into a polymer can be investigated by THz technology [16].

A model for the dielectric material behavior depending on the water content was developed and verified by THz TDS measurements. The modeling considers an effective medium theory, bound and free water, as well as density-corrections due to swelling of the compound [17]. Fig. 3 displays the refractive index (a) and the absorption coefficient (b) at 0.6 THz as a function of the water content in PA 6 (Ultramid B3, BASF). A good agreement between measurement and simulation results is observed. The refractive index shows a slightly non-linear behavior, which is caused by the increase of the effective density. The sensitivity of THz radiation to water can provide a non-destructive, contactless tool for determining the water content in hygroscopic polymers, plastics and compounds.

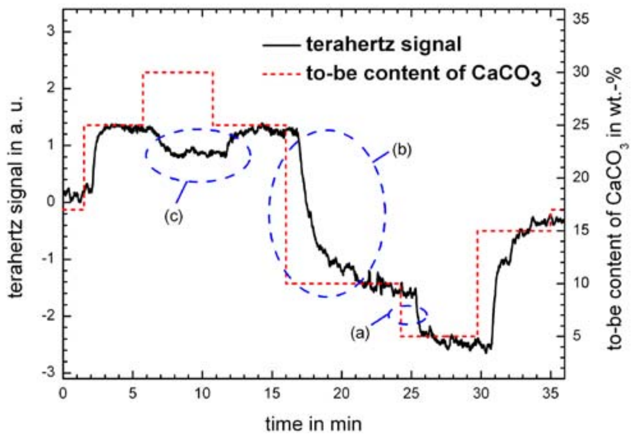

Figure 2. Real-time THz signal (solid curve) measured on $CaCO_3$-filled polypropylene the concentration of which is varied during the course of the measurement (dashed): (a) residence time of the additive inside the extruder, (b) wash out time; (c) $CaCO_3$ concentration outside the effective measurements range (but could be covered by adjusting the THz pulse).

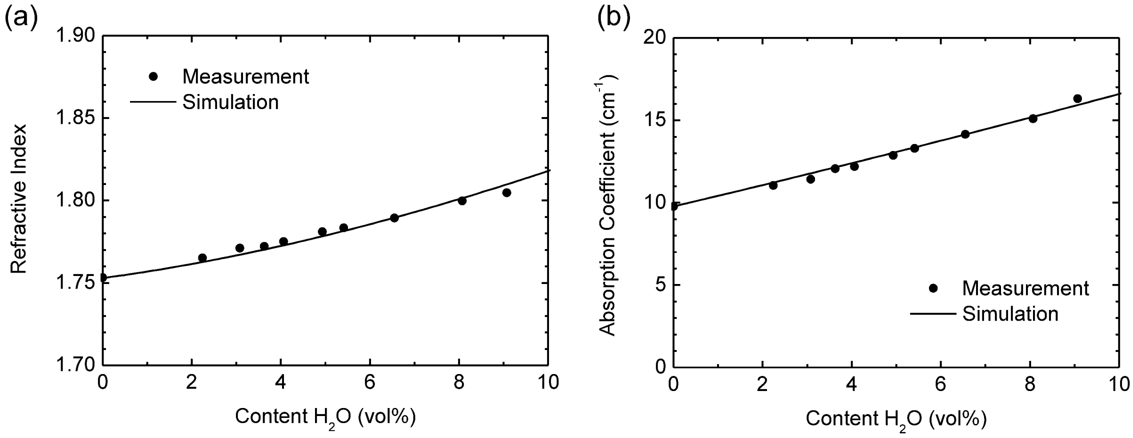

Figure 3. Refractive index (a) and absorption coefficient (b) at 0.6 THz over water content in PA 6.

B. *Revealing Fiber Orientations*

Another class of polymeric materials that can benefit from THz technology are fiber-reinforced plastics, widely used for applications in the aviation and the automotive industry. The mechanical properties of the component strongly depend on the fiber content and the fiber orientation within the sample. Therefore, the knowledge of these parameters is of immediate importance if such materials are used for safety-critical components. However, non-destructive testing methods are extremely rare and limited to specialized cases.

Recently, THz testing has been introduced to the evaluation of glass fiber reinforcements in terms of detecting voids, delaminations, mechanical and heat damage [18]. Moreover, the orientation of the fibers inside the host medium directly results in a birefringent behavior of the composite material for THz waves. Therefore, THz TDS can be employed to identify the fiber orientation. Polarization imaging of a component made of fiber-reinforced liquid crystal polymer has been presented by Rutz et al. [19]. Yet, no angular resolution was obtained.

Our new algorithm allows for extracting the actual fiber orientation at a specific spatial position, indicated by an arrow [20]. The direction and the length of the arrow represent the preferential fiber orientation and the fraction of orientated fibers, respectively. The longer the arrow, the more pronounced is the birefringence, which corresponds to a higher degree of fiber orientation as long as the fiber content is spatially invariant. Fig. 4 displays the results of measurements on an injection-molded specimen made of polyamide that is reinforced with 30 wt% short glass fibers. The fiber orientation was investigated at seven distinct spatial positions by extracting the refractive index at a frequency of 0.6 THz. A mold flow simulation verifies the results [20].

C. *Quality Control of Plastic Weld Joints*

Plastics have also gained importance as construction materials. This draws the attention to joining methods such as welding. Contaminations, air bubbles or delaminations can reduce the strength of the weld dramatically, eventually leading to a loss of structural integrity. Since welding is normally

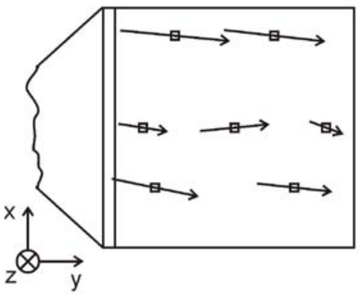

Figure 4. Arrows denote the preferential fiber orientation extracted from THz TDS measurements at distinct positions of a glass-fiber-reinforced PA 6 specimen.

placed near the end of the value creation chain, ensuring the quality of plastic weld joints is also important for non-structural applications due to economical reasons.

Non-destructive testing of plastic weld joints seemed to be a permanent obstacle. We have developed a THz imaging system to overcome these restrictions. Fig. 5 shows backlighted photos and the corresponding THz image (normalized amplitude) of HDPE welded with contaminations. Metal and sand inclusions can be resolved since they significantly reduce the transmitted intensity of the THz pulses. The drilled holes become visible due to a higher intensity surrounded by a small area of lower transmittance due to diffraction. For a better comparison, translucent HDPE was employed as material under test, but also optically opaque plastics can be investigated by THz waves. Even the delamination of a weld contact area can be revealed by THz TDS imaging [21], e.g. by displaying interference effects in the frequency range or

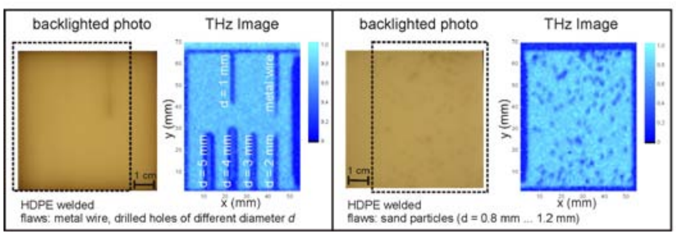

Figure 5. THz imaging reveals flaws in plastic weld joints (lighter color represents a higher transmission)

considering echo pulses from inner surfaces.

V. Determining the Glass Transition of Polymers

The glass transition temperature T_g marks the transition from the glassy to the rubber-like state of a polymer [22]. However, the glass transition is still an active field of discussion. Since the glass transition is a core feature of the amorphous domains, T_g is hard to identify with highly-crystalline polymers by conventional methods such as differential scanning calorimetry (DSC) or dynamic mechanical analysis (DMA) [23].

We have demonstrated the suitability of THz TDS as a tool to monitor the glass transition in highly-crystalline polymers [24]. Below T_g, segmental motions along the polymer chain are frozen due to the lack of free volume between neighboring macromolecules. Above T_g, there is enough free volume available so that the segmental motion of the macromolecular chain can start. We show that this transition also reflects in the temperature dependence of the refractive index at THz frequencies. Two regimes can be identified, which differ in their sensitivity to temperature changes. Extrapolating the low- and the high-temperature regime simply reveals T_g as the intersection of two linear fits.

VI. Conclusion

Terahertz (THz) technology offers an extensive set of quality inspection tools, often superior to existing measurement methods. In particular, THz testing provides a non-destructive, contactless technique for polymer analysis, process monitoring, and quality control of plastic components.

Acknowledgment

We gratefully acknowledge the Federal Ministry of Economics and Technology (BMWi) whose budget funds, provided by the Arbeitsgemeinschaft industrieller Forschungs-vereinigungen "Otto von Guericke" e.V. (AiF), have supported our work within project number 182 ZN and 269 ZN. We thank the Federal Ministry of Education and Research (BMBF) for financial support within the research project no. 13N8572, 13N9406, and 13N9466. The Marburg group acknowledges financial support by the BMBF and the Optodynamics Research Center. Furthermore, the authors would like to express their gratitude towards T. Grunwald, S. Lüders, E. Kraus, and D. Kraft for technical assistance. N. Vieweg thanks the Studienstiftung des deutschen Volkes for financial support.

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