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Short Communication: Test Method

Determination of additive content in polymeric compounds with terahertz time-domain spectroscopy

S. Wietzke[a,*], C. Jansen[a], F. Rutz[a,1], D.M. Mittleman[b], M. Koch[a]

[a]Institut für Hochfrequenztechnik, Technische Universität Braunschweig, Schleinitzstrasse 22, 38106 Braunschweig, Germany
[b]ECE Department, Rice University, Main Street 6100, Houston, TX 77005, USA

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Abstract

We present terahertz transmission time-domain spectroscopy measurements on a variety of additive-polymer combinations with differing additive contents. At lower terahertz frequencies, standard polymers are transparent. When processed into compounds, their terahertz properties are distinctively affected by additives in most cases. The materials under investigation are magnesium hydroxide in linear low-density polyethylene, glass-fibres in polyamide, and calcium carbonate, silicon or silicon dioxide in polypropylene. The extracted indices of refraction provide a reliable determination of the additive content of the material combination. Hence, terahertz time-domain spectroscopy is capable of characterising additive-polymer systems and it seems to be a promising non-destructive technique for quality control in compounding processes.

Keywords: Non-destructive testing; Terahertz spectroscopy; Polymeric compounds; Additive content

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1. Introduction

Plastic materials provide a high economic value for the industry, but synthesising new classes of polymers is hardly profitable any more. Hence, plastics manufacturers focus on adding various substances (fillers, fibres, colourants, flame retardants, plasticisers, etc.) in order to improve the properties of standard polymers for a variety of applications, ranging from commodities to high-tech products [1].

Within the plastics market, big companies rather concentrate their efforts on mass production than on the field of compounding, which is dominated by small and medium-sized enterprises. Consequently, it lies with the latter to offer highly customized products at low prices. These companies have to rely on a flexible, time- and cost-efficient quality management and process control, e.g. in order to be able to guarantee the precise composition of the materials with respect to their additive content.

The established measurement methods for compound characterisation, such as mechanical tests [2] or light microscopy, are standardised but mostly off-line, i.e. time-consuming and destructive. Recently, there have been several approaches in order to get closer to the compounding process with

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*Corresponding author. Tel.: +49 531 391 2010; fax: +49 531 391 2045.

E-mail address: steffen.wietzke@ihf.tu-bs.de (S. Wietzke).

[1] Present address: Fraunhofer Institut für Angewandte Festkörperphysik, Tullastr. 72, 79108 Freiburg, Germany.

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in- and on-line measurements using, e.g. the pressure filter test [3], ultrasonic testing [4] and spectroscopic monitoring, especially in the near infrared (NIR) frequency range [5,6].

However, each method is restricted to a small set of applications. The pressure filter test is not entirely reliable with higher additive concentrations and does not work with fibres. Ultrasonic testing is limited to applications that only require a low spatial resolution, while NIR delivers a very high resolution but is only suited for near-surface analysis or rather thin samples, as the penetration depth decreases with increasing frequency.

As we will show in the following sections, terahertz time-domain spectroscopy (THz TDS) [7–10] in the frequency range between 100 GHz and a few THz is a promising technique for non-destructive testing of polymeric compounds. It combines the high penetration depth of microwaves with submillimetre spatial resolution. THz TDS allows the extraction of both frequency-dependent refractive index and absorption coefficient, as phase and amplitude information of the propagated electromagnetic wave is obtained.

Most of the additives differ in their optical properties in the THz frequency range from the host polymers, such as polyethylene, polypropylene or polystyrene, so that the THz properties of the compound are expected to deliver a measure for the additive concentration. Compared to NIR or ultrasonic testing [11], extrusion conditions such as temperature or pressure are expected to have little effect on THz TDS, but this requires further investigation. THz TDS could be the basis for an in-line measurement system determining the concentration of additives in compounds.

In this paper, we show results of off-line THz TDS measurements of five concentration series with different additive–polymer combinations. The additives were selected to represent a variety of functions and particle geometries. Exhibiting a mostly linear correlation, the refractive index of the compounds seems to be a dependable measure for the volumetric additive content over a wide concentration range.

2. Experimental

2.1. Materials and sample preparation

We used the mineral flame retardant magnesium hydroxide (disc-shaped particles of $Mg(OH)_2$; Dead Sea Bromine Group's FR-20 100D-S7) within a matrix of linear low-density polyethylene (LLDPE; Dowlex 2035E), the cubic filler calcium carbonate (surface-treated $CaCO_3$; Omya's Hydrocarb 95 T) in polypropylene (PP; Basell's Moplen HP501M), glass fibres (GF; Cratec^{Plus} 173X from Owens Corning) and some additional performance additives in polyamide 66 (PA; BASF's Ultramid A3). Furthermore, PP (Basell's Moplen HP548R) was charged with silicon powder (Si; Possehl Erzkontor) or pulverised silica (SiO_2; Quarzwerke's Sikron SF 500).

Laboratory extruder setups were employed to compound concentration series of the material systems. The produced granulate was injection moulded into appropriate specimens (sheets and thin planar slabs with thickness up to 2 mm) with smooth surfaces to avoid scattering when performing the measurements. In the case of $Mg(OH)_2$ and $CaCO_3$, we produced pellets from additive powder in order to complete the concentration series. Remaining cavities due to imperfect pressing were corrected considering bulk density and linear extrapolation [12].

2.2. Measurements and data processing

We determined the refractive index and the absorption coefficient of the samples with THz TDS in a transmission setup [13,14]. A sample pulse and a reference pulse without sample in the propagation path were measured. In order to remove unwanted multiple reflections (Fabry–Pérot effects), a window function was applied to the time-domain data [15]. The phase and amplitude information of the Fourier spectra of the pulses yields the frequency-dependent indices of refraction $n(f)$ and absorption coefficients $\alpha(f)$ of the samples when their thickness is known [16]. Furthermore, as the materials under observation are hardly dispersive, the refractive index was averaged over a dependable frequency range. This mean value is denoted as $\langle n \rangle$.

3. Results and discussion

The material combinations LLDPE–$Mg(OH)_2$, PP–$CaCO_3$ and PA–GF were compounded gravimetrically in weight percentage (wt%) as is customary in the compounding industry. Fig. 1 shows the refractive indices $n(f)$ of the LLDPE–$Mg(OH)_2$ concentration series from 0.2 to 1.6 THz. In this presentation, the gap between the individual

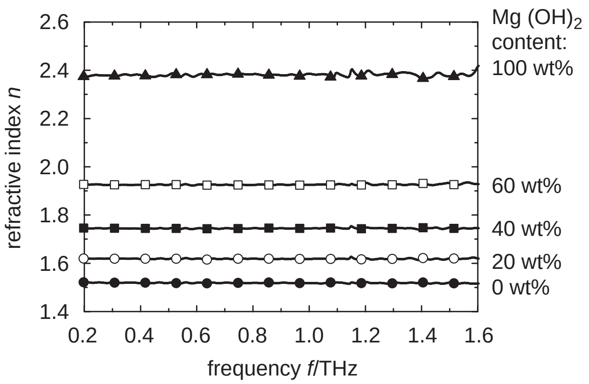

Fig. 1. Refractive index over frequency in the terahertz range with different magnesium hydroxide content (wt%) in LLDPE.

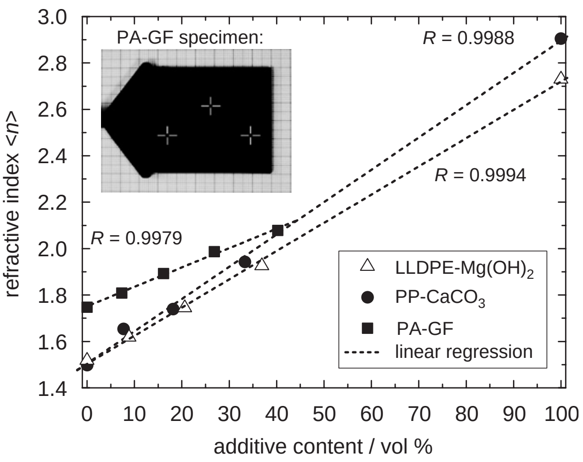

Fig. 2. Refractive index $\langle n \rangle$, averaged in a dependable frequency range, over volumetric content of the additives magnesium hydroxide, calcium carbonate and glass-fibres in standard polymers: the regressions and their correlation coefficients R lead to the assumption of a linear dependency.

levels of the refractive index broadens with increasing additive content. Assuming incompressibility during compounding, which is a good approximation for a polymeric matrix and mineral additives, it is possible to convert the gravimetric content into the volumetric content $V_{\text{additive}}/V_{\text{compound}}$ considering the specific gravity of the components. After this conversion, a mostly linear dependence of $\langle n \rangle$ on the additive content is revealed, which is illustrated in Fig. 2. The triangles represent the frequency-averaged refractive indices for different concentrations of $Mg(OH)_2$ in LLDPE. The linear regression is shown as a dashed line. A linear relation also holds true for the measurement data set of $CaCO_3$ in PP, displayed as dots. Also, the volumetric glass-fibre content can be regressed linearly against the indices of refraction of the reinforced PA, which is shown by squares and a dashed line. Compared to LLDPE–$Mg(OH)_2$ and PP–$CaCO_3$, the slope of the characteristic line is lower because of the smaller difference in the refractive index between GF and PA, but still provides a clear determination of the additive content. The high correlation coefficients R confirm the accuracy of all regressions. Hence, knowing the slope parameter from two measured points, this easy calibration allows a reliable determination of volumetric additive content with high precision and sensitivity compared to other measurement methods mentioned earlier.

For the glass-fibre-reinforced polyamide, a statistical analysis was performed by measuring three points on a sample sheet for each additive concentration. Considering a normal distribution, the doubled standard deviation with respect to the mean refractive index can be seen as the half-width $\Delta\langle n \rangle$ of a confidence interval which encloses the real value of the measurand with a possibility of $P = 95.45\%$ [17]. The associated relative error is smaller than $\Delta\langle n \rangle / \langle n \rangle = 0.5\%$. We did not plot the error bars since they are much smaller than the symbols themselves. In order to exclude systematic measuring errors due to the sample preparation, the results of different injection moulded specimens of the same assumed additive concentration were also compared. No significant discrepancies were observed (relative error for $P = 95.45\%$ is below 0.1%). Hence, this method can be considered as reproducible.

The linearity also holds true for the material systems PP–Si and PP–SiO_2 (Fig. 3). The measured data of the PP–Si compounds are shown as dots, the triangles stand for the values of silica in polypropylene. Again, the dashed lines represent linear regressions with corresponding correlation coefficients. However, extrapolating to 100% silicon, a refractive index of $\langle n \rangle = 5.15$ is found. We note that this value is much higher than the reported literature refractive index [18]. The origin of this discrepancy is not clear yet and currently under investigation. It may be that the relation between the refractive index and the silicon content becomes non-linear and tails off for silicon contents higher than 50 vol%. Such concentrations have not been investigated yet, as they are challenging to produce. On the contrary, the extrapolated refractive index of $\langle n \rangle = 2.08$ representing 100% SiO_2 meets other

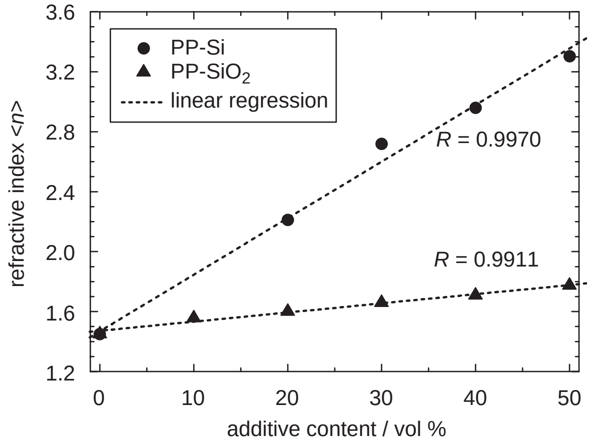

Fig. 3. Refractive index $\langle n \rangle$, averaged in a dependable frequency range, over volumetric content of the additives silicon and silica in polypropylene: a linear correlation can be assumed.

measurement results of 2.04 for fused quartz (polycrystalline SiO_2) very well [19].

The absorption coefficient does not provide a very useful figure of merit to determine the additive content since $\alpha(f)$ rises with increasing frequency. In addition, compared to the sensitivity and accuracy of $n(f)$, the measured $\alpha(f)$ shows a high uncertainty, in particular due to the long-term intensity noise of the laser [16,20]. Hence, the absorption is less reliable than $\langle n \rangle$ as a measure for the additive concentration in compounds.

In conclusion, we have shown terahertz time-domain spectroscopy measurements on different polymeric compounds. With all material systems analysed in this paper, the frequency averaged refractive index $\langle n \rangle$ scales nearly linearly with the volumetric additive content for all concentrations observed. Nevertheless, the linear regression has to be considered an empiric approximation for the measured data and does not necessarily hold true for all material systems and concentrations. However, non-linear fits could also serve for a calibration in the same manner. Since correlation does not imply causation, a description using physical models is currently being analysed in detail. In addition, the monitoring of dispersion quality of additive particles is a subject of active investigation. This said, we have demonstrated, that terahertz time-domain spectroscopy is a promising tool for non-destructive, contactless quality assurance and compounding process development. Presently, a THz spectroscopy system for in-line measurements is under construction.

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