Talanta 143 (2015) 169–177

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Qualitative and quantitative analysis of calcium-based microfillers using terahertz spectroscopy and imaging

Andreja Abina [a,*], Uroš Puc [a,b], Anton Jeglič [a,b], Jana Prah [c], Rimvydas Venckevičius [d], Irmantas Kašalynas [d], Gintaras Valušis [d], Aleksander Zidanšek [a,e,f]

[a] Jožef Stefan International Postgraduate School, Jamova 39, SI-1000 Ljubljana, Slovenia
[b] Faculty of Electrical Engineering, University of Ljubljana, Tržaška cesta 25, SI-1000 Ljubljana, Slovenia
[c] Calcit d.o.o, Stahovica 15, SI-1242 Stahovica, Slovenia
[d] Optoelectronics Department, Center for Physical Sciences and Technology, LT-01108 Vilnius, Lithuania
[e] Department of Condensed Matter Physics, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia
[f] Faculty of Natural Sciences and Mathematics, University of Maribor, Koroška cesta 160, SI-2000 Maribor, Slovenia

ARTICLE INFO

Article history:
Received 27 February 2015
Received in revised form
5 May 2015
Accepted 12 May 2015
Available online 27 May 2015

Keywords:
Calcium-based microfillers
Granulation
Surface treatment
Terahertz pulsed imaging
Terahertz time-domain spectroscopy

ABSTRACT

In different industrial applications, several strictly defined parameters of calcium-based microfillers such as average particle size, particle size distribution, morphology, specific surface area, polymorphism and chemical purity, play a key role in the determination of its usefulness and effectiveness. Therefore, an analytical tool is required for rapid and non-destructive characterization of calcium-based microfillers during the synthesis process or before its use in a further manufacturing process. Since spectroscopic techniques are preferred over microscopy and thermogravimetry, particularly due to its non-destructive nature and short analysis time, we applied terahertz (THz) spectroscopy to analyse calcite microfillers concentration in polymer matrix, its granulation and chemical treatment. Based on the analysis of peak absorbance amplitude, peak frequency position, and the appearance of additional spectral features, quantitative and qualitative analysis was successfully achieved. In addition, THz imaging was also applied for both quantitative and qualitative analysis of calcium-based microfillers. By using spatial distribution map, the inhomogeneity in concentration of calcium carbonate in polymer matrix was characterized. Moreover, by THz spectroscopy and imaging different calcium compounds were detected in binary mixtures. Finally, we demonstrated that the applied spectroscopic technique offers valuable results and can be, in combination with other spectroscopic and microscopic techniques, converted to a powerful rapid analytical tool.

1. Introduction

Calcium carbonate, i.e. $CaCO_3$, is one of the most abundant raw materials that normally naturally occurs as a white mineral with a stable crystal polymorphic arrangement of calcite. Due to unique properties the calcium carbonate has become an important commercial product that is used as a filler, pigment or functional additive [1] in various industrial applications ranging from construction products, paints, glass, ceramics, adhesives, composites, paper, and plastics to animal feeds, food, pharmaceuticals, cosmetics, etc. The manufacturing of different products demands specific grades of calcium carbonate that depend on its physico-chemical properties like colour, hardness, chemical purity, average particle size, and particle size distribution which are all determined by controlling the temperature, pressure, concentration, and time during the production process [2,3]. Since the new applications of calcium carbonate constantly are being developed it is expected that its use will continue to grow in the next decade especially on account of technologically developed products with enhanced physical and mechanical properties. For this reason an analytical tool is required for rapid and non-destructive characterization of calcium carbonate during the precipitation process or before its use in a further manufacturing process.

For qualitative analysis of calcium-based microfillers several techniques showed a potential such as Fourier transform infrared (FTIR) spectroscopy [4], electron microscopy [5,6], powder X-ray diffraction [7], and Raman spectroscopy [7,8]. The spectroscopic methods are preferred over microscopy and thermogravimetry particularly due to its non-destructive nature and short analysis time. The infrared (IR) spectroscopy has already been used to discriminate between calcium carbonate polymorphic forms of

* Corresponding author. Fax: +386 1 477 31 10.
E-mail addresses: andreja.abina@mps.si (A. Abina), aleksander.zidansek@ijs.si (A. Zidanšek).

http://dx.doi.org/10.1016/j.talanta.2015.05.027
0039-9140/

calcite, aragonite, and vaterite within binary and ternary mixtures in frequency range from 700 cm^{-1} to 1800 cm^{-1} [9] and from 680 cm^{-1} to 800 cm^{-1} [4], respectively. Moreover, the temperature dependence of absorption for calcite of different grain shapes in frequency range between 83 cm^{-1} and 5000 cm^{-1} measured by FTIR is also reported [10]. Lately, novel analytical techniques have been applied to confirm the polymorphic forms of calcium carbonate such as terahertz (THz) spectroscopy [11–13] and surface analysis techniques, containing X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectroscopy [14]. Besides qualitative analysis, FTIR spectroscopy has been also used as a quantitative analysis method for the determination of ratios of calcium carbonate against other compounds in mixtures [15,16] as well as for the detection of different calcium carbonate crystal concentrations in powder mixtures [23]. Hence it follows that spectroscopic techniques can meet the industrial requirements for rapid and non-destructive qualitative characterization of calcite and its quantitative determination in mixtures.

The spectroscopic technique which uses electromagnetic radiation between microwave and near-infrared (IR) frequencies to study the properties of materials [17] is known as THz spectroscopy. The applications where this spectroscopy has shown a potential are increasing over the last two decades mainly due to more accessible instruments which typically operate within the frequency range 0.1–3.0 THz. Currently, the major research is devoted to applications in pharmaceutical industry [18], security [19], medicine [20], and materials characterization [21]. However, some studies reported that calcium carbonate exhibits strong absorption at around 3 THz due to the vibration of calcite molecules [11,22]. The absorption of a single crystal depends on the crystal direction, crystal size, and crystal shape due to the large birefringence [11]. For powder samples the angle dependence disappears due to the random directions of the crystals. By calculating optical properties the volumetric additive content for various concentrations of calcium carbonate in polymer matrix can be determined [23]. Furthermore, the THz spectra of natural calcium carbonate also show the presence of impurities in powder samples [11] and can differentiate between calcite and aragonite polymorphic forms [13]. In addition, the spectroscopic THz imaging system with the performance optimized for fingerprint-frequencies measurement can be applied for samples imaging in the transmission and reflection geometry. The results obtained by employing the continuous wave spectroscopic THz imaging with InGaAs bow-tie diodes [24], semiconductor-based THz pulsed technology [25], THz antenna coupled field-effect transistors [26], and microbolometers [27] were in good agreement with the FTIR spectroscopy data and provided the spatial distribution of the components in the samples using principal component analysis (PCA). The reported results pointed out that the THz spectroscopy and imaging have a potential to be used for both qualitative and quantitative research in room environment and real time.

The aim of this study was to undertake the analysis of calcium-based microfillers using THz spectroscopy and imaging in order to demonstrate that the applied technology has a potential to quantitatively and qualitatively characterize pure and modified microsized particles in a powder form. The method is applied for the discrimination between various concentrations of microfillers in polyethylene matrix and various granulations of calcite samples as well as for the detection of additives and surface-modifying agents within calcite microfillers which are present in numerous application cases. In addition, we show that THz spectroscopy is capable to follow the reactions of decarbonation/carbonation route through the detection of formation of chemical reaction products including calcium carbonate, calcium oxide and calcium hydroxide, or the presence of reactants in an incomplete chemical reaction. According to this study, THz spectroscopy can be used as an analytical method for rapid calcium-based microfillers characterization before they are used in a process what is especially desired for quality control aspects in industry.

2. Material and methods

2.1. Materials and its physicochemical properties

Calcite samples were obtained from Slovenian supplier Calcit d.o.o. which produces calcium carbonate fillers from naturally high-quality white marbled limestone deposit in Slovenia. The particle size distribution was determined by laser granulometer RODOS for samples C-5, C-15, C-40, C-5T and by Micromeritics Sedigraph 5120 for samples C-EX, C-1, C-EXT and C1T. Last method uses the sedimentation technique which measures the gravity-induced settling rates of different size particles in a liquid with known properties. Both data are given for additive-treated samples, i.e. first five samples in Table 1, and surface-modified samples, i.e. last three samples in Table 1 marked with additional letter *T*. The Mohs hardness for all samples has value of 3. In Table 1 also data from chemical analysis are given which are the same for all samples. We selected two series of calcite samples, the additive-treated one and the second where the samples are additionally surface-modified, what makes them hydrophobic. Moreover, we measure the additional natural calcite sample obtained from manufacturer that was not treated in any way, labelled as C-5L.

Apart from calcite powder samples gained from manufacturer, three additional calcium compounds in powder form obtained from Sigma-Aldrich were analysed: calcium carbonate (ACS reagent, $\geq$ 99.0%), calcium oxide (meets analytical specification of FCC, $\geq$ 96.0%), and calcium hydroxide (ACS reagent, $\geq$ 95.0%). As a reference material we selected polyethylene (PE) powder with 53–75 μm particle size obtained from Sigma-Aldrich.

Table 1
Physicochemical properties, average particle size and particle size distribution of calcite samples from limestone deposit (summarized from the manufacturer specifications). d50 is defined as the average diameter particle size distribution and d98 as a top cut or maximum particle size distribution.

Sample mark	Particle size distribution		Physical properties			Chemical analysis		
	d50 (μm)	d98 (μm)	Specific surface area (m^2/g)	Density after tamping (g/ml)	Moisture absorption (g/100 g)	$CaCO_3$ (%)	Fe_2O_3 (%)	SiO_2 (%)
C-EX	0.75–0.9	3.5	9.69	0.6	34.0	98	0.01	0.02
C-1	1.4–1.8	6.0	6.34	0.7	31.0	98	0.01	0.02
C-5	4.0–4.5	17.5	2.10	1.0	26.0	98	0.01	0.02
C-15	12.0–16.0	70	0.75	1.2	26.0	98	0.01	0.02
C-40	16.0–25.0	90.0–150.0	0.67	1.4	24.0	98	0.01	0.02
C-EXT	0.75–0.9	3.5	9.69	0.6	Hydrophobic	98	0.01	0.02
C-1T	1.4–1.8	6.0	6.34	0.9	Hydrophobic	98	0.01	0.02
C-5T	4.0–4.5	17.5	2.10	1.1	Hydrophobic	98	0.01	0.02