

Near infrared spectroscopy as a tool for in-line control of process and material properties of PLA biopolymer

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Abstract In the field of polymer processing NIR spectroscopy has been increasingly applied for an on-/in-line monitoring mainly at lab scale process development but also for production of high value materials. In this paper the bio-polymer polylactide (PLA) was investigated by NIRS in the range of 1.2 to 2.4 μm in order to identify additives like nanofil[®] and nano titanium oxide. A twin screw extruder (Haake Polylab PTW 16) was used to extrude polymer pellets mixed with the additives. The optical sensor probes (glass fibers) were placed between screw and nozzle to achieve a good optical throughput and to withstand typical temperature and pressure conditions during the extrusion (up to 220° C and a few 10 MPa). The on-line NIR spectroscopy enabled a real time information which might be used for process control or feeding control on the compound characteristics continuously. The chemometric data evaluation was able to quantify the measured values, especially the content of the additives in the compounds. The established statistical models predicted the actual values with high correlation coefficients (> 0.99). The additives altered viscosity of the melt and mechanical properties (Young's modulus) of injection moulded test samples of the compound.

1 Introduction

Bioplastics and biocomposites will become decisive and important materials for industrial sectors like e.g. automotive and aircraft applications and consumer products. Demands concerning process and product conditions are challenging tasks and new robust and reliable measurement systems must be utilized. Requirements of product quality

of Bioplastics and Biocomposites request to control effectively compositions and formulations and to run the processes at optimal conditions [1,2]. In-/on-line control method can monitor important parameters directly at the e.g. extruder at real time. Spectroscopy in the wavelength range from ultraviolet, the visible and especially the near and mid-infrared (NIRS and MIRS) is capable of providing in-line molecular information on involved constituents [3,4]. Application of MIR spectroscopy is limited because of not available fibre optics for the MIR range and is generally more sensitive in handling, the main focus was set on the NIRS for in-/online control, which has gained broad use in industrial processes [3–5]. For polymer processing and recycling NIR spectroscopy is widely used and commercial systems are available [6,7] For polymer processing NIRS supports effectively in-/on-line control if carefully calibrated and statistical data evaluation methods are applied like partial least square regression (PLSR) [8–13]. NIRS measurement techniques are applied to extrusion processes to measure the composition of input feed, compound composition, dispersion conditions or the stability of the process. They detect early e.g. deviations from the target properties, allowing immediate corrections by real time adaptation of process parameters. NIRS is also capable of monitoring additive or moisture content in the melt. In the present work, NIRS is applied to PLA matrix composites containing TiO₂ nanoparticles of about 100 nm to 200 nm diameter and nanofil[®] to study the monitoring of these additives and to correlate to mechanical properties of test samples. Nanofil[®] is composed of small nanometer sized clays layered as mineral silicates.

2 Near Infrared (NIR) Spectroscopy

The near infrared spectral region ranges from about 780 nm to about 2500 nm and is dominated by overtone and combination bands. Absorption bands originate mainly from functional groups containing hydrogen like CH, NH and OH. The optical path length for polymers is typically in the range of several millimetres hence measurements can be done in transmission configuration. In the transmission spectra either the absorption bands according to the functional groups can be evaluated for e.g. concentration determination or the stray light can be used for size measurements of e.g. nanoparticles [14]. Additionally, the use

of fibre optics allows long distances between the spectrometer and the probe which is a great advantage in case of difficult or hazardous places or surroundings. Due to the broad absorption bands in the near infrared spectral region the analysis of the spectra i.e. quantification of data via a regression has to be done typically with multivariate regression methods [15,16]. For the measurements a CARL ZEISS diode array spectrometer was used with a spectral range from 950 nm to 2400 nm with a spectral resolution of about 18 nm. Accumulation was five and integration time between 10 ms and 100 ms.

3 Polymer processing Equipment

A twin screw extruder (Haake Polylab PTW 16) was used to extrude fed polymer pellets coated with the additive. The temperature profile of the extruder can be adjusted with up to four temperature zones whereby the extruder length was 40 cm. The extruder was fed by a single screw metering feeder. The polymer granulates and the additive powders, nano TiO₂ and nanofil[®], were weighted and subsequently mixed in a wobble mixer to achieve a good homogenisation of the two materials before the extrusion process whereas the PLA granules became coated in a bath of the particle dusts. The optical sensor probes (glass fibers) were placed between screw and nozzle to achieve a good optical throughput and to withstand temperature and pressure of 300° C and a few 10 MPa. In the probe body a sapphire window and appropriate optics are included. Extruded strands samples were obtained with a Babyplast[®]) mini-injection moulding machine equipped with a small standard test sample tool. The test samples were analysed by standard mechanical testing to determine Young's modulus, maximum strain and strain at break. 5 samples were 16 composite types, varying additive content, moisture, extruder temperature, screw design, momentum, were manufactured to apply statistical evaluation also to the mechanical properties influenced by the additives and processing parameters

4 Polylactide

Polylactide (PLA) and copolymers of lactic acid can be used on the one hand for medical applications like absorbable suture material and im-

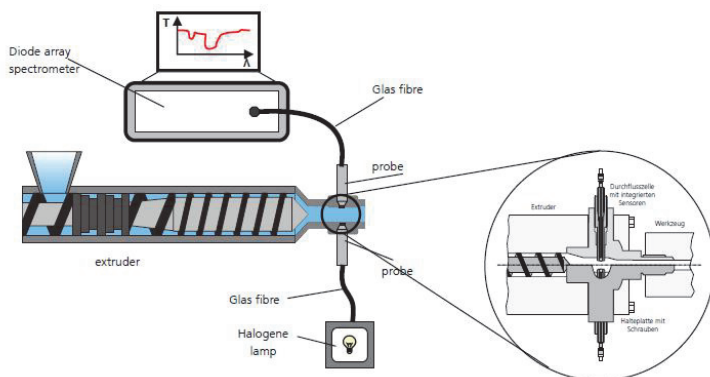


Figure 5.1: Drawing of the extruder equipped with probes for transmission measurement. The probes were installed in an adapter at the extruder die.

plants and on the other hand for biodegradable food packing [17]. For medical applications detailed NIRS investigations were performed in the past [18–20]. Bio-polymers PLA and starch are available commercially, and are suited for engineering biocomposites to be reinforced with natural fibres. In-/online monitoring of important parameters which might influence processing, the formulation itself, natural fibres and additives of the final bio-based materials have to be monitored or even on-/in-line controlled for quality assurance [21, 22]. A NIR spectrum recorded of a PLA raw material powder is shown in Fig.5.2. Main absorption peaks of functional groups in the near infrared spectral range are shown.

5 Effects of nanofil[®] TiO₂ Additives

The additive TiO₂ in PLA was already reported in the PPS23 and showed good correlation on calibration data [21]. In the present work nanofil[®] content in PLA was varied between 0 to 3 %. Both additives were also mixed and compounded with PLA. As an example for the influence to the spectral behaviour the results of the nanofil[®] additive are given.

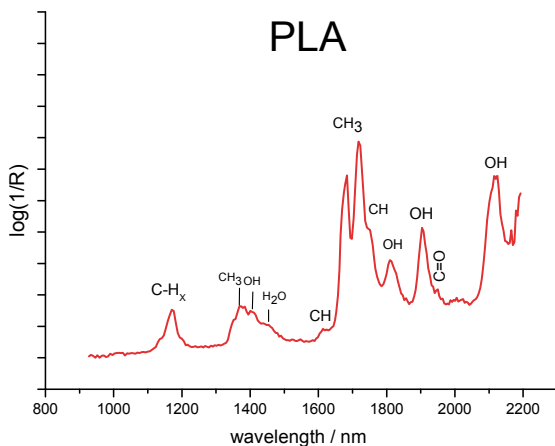


Figure 5.2: NIR spectrum of PLA powder

In Figure 5.3 a SEM picture is given which shows a PLA sample with a TiO_2 / nanofil[®] mixture. The nanofil[®] additive shows a well dispersed homogenous structure in the PLA matrix with TiO_2 nano particles spread between the nanofil[®] component. The nanofil[®] material is also oriented in different directions and not in clumps indicating that intercalation and exfoliation had happened. This might be because of the extrusion conditions like screw speed, throughput of the material or geometry of the twin screw. The TiO_2 particles can also act like small grinding stones fostering the dispersion process of the nanofil[®]. This must be verified in subsequent trials.

6 NIR Measurements PLA / nanofil[®]

PLA was mixed with increasing amount of nanofil[®] material and extruded. Nanofil[®] was in the range of 0% (m/m) to 3% (m/m). NIR spectra were measured at the extruder die (Fig.5.1). During extrusion

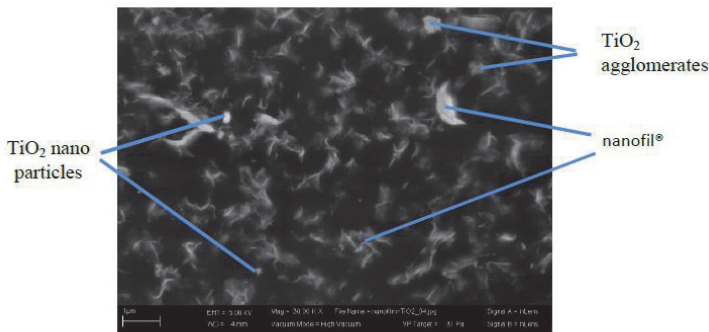


Figure 5.3: SEM picture of a injection moulded test sample of PLA with nano-TiO₂ and nanofil[®], ——— 1 μ m. Content of nanofil[®] was 1% (m/m).

the temperature and screw speed were kept constant to ensure a stable process. Hence influences by process conditions are minimized and spectra evaluations give more reliable results. First the intensity of a PLA sample $I(\lambda)_{\text{PLA}}$ was measured in the NIR range and used as reference $I(\lambda)_{\text{PLA}}$ with λ the wavelength. After that PLA samples with increasing nanofil[®] content were measured giving the intensity $I(\lambda)_{\text{mix}}$. Spectral transmission $T(\lambda)$ was calculated as

$$T(\lambda) = \frac{I(\lambda)_{\text{mix}}}{I(\lambda)_{\text{PLA}}} \quad (5.1)$$

The results of the measurements of selected samples are shown in Figure 5.4. There is a correlation between nanofil[®] content and transmission. Samples with higher content of nanofil[®] show a lower transmission over the whole spectral range. Each sample shows increasing transmission from lower to higher wavelengths. This behaviour is caused by light scattering of the nanoclay particles and therefore correlated with the amount of nanoclay. Beside this physical spectral information also chemical information is contained in the spectra. The absorption peak at about 1650 nm to 1680 nm can be assigned to OH and SiO / SiO₂ functional groups. There is also a small peak at 1400 nm which can be assigned to OH functional group [23]. The gap between layers in the

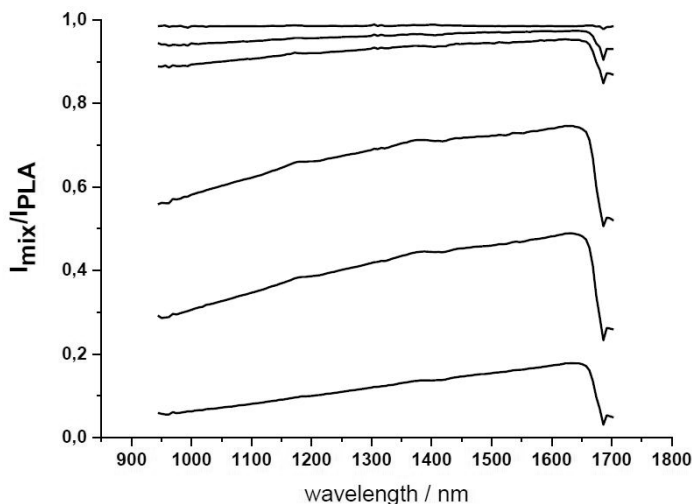


Figure 5.4: NIR spectra of PLA / nanofil[®] mixture samples. Amount of nanofil[®] is given in mass percent (m/m%) at each of the spectra.

nanoclays is in the nanometer range. Water can be bound between these layers and can dominating the NIR spectra and influence also mechanical properties of the matrix material. Therefore a control of the nanofil[®] content is essential for producing polymers with reproducible properties. Transmission spectra were measured and a multivariate prediction (PLSR) model was generated (Figure 5.5). NIR spectra of the composite with additives gave results which led to correlation better than 0.996 indicating the possibility to control their PLA content on processing.

7 Light Scattering

There is light scattering in the PLA / nanofil[®] caused by the nanoclay composite. Light scattering can be described by Mie theory whereby the presumption is that the particles are non-interacting and spherical [24, 25]. The nanoclays are not spherical and an interaction cannot

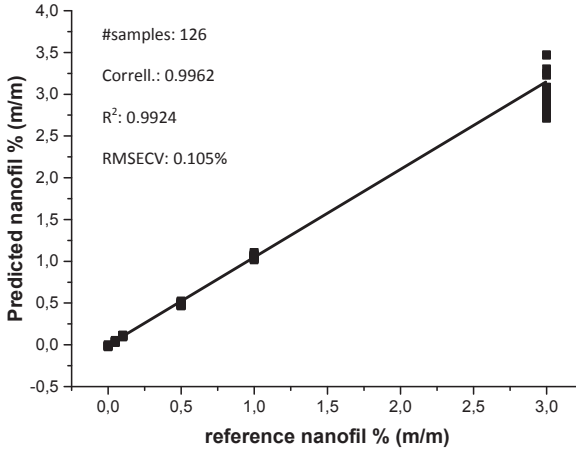


Figure 5.5: PLSR prediction model of the nanofil® content (0 – 3%) in PLA with a correlation better than 0.996. Spectral pre-treatment: vector normalization. Validation method: cross validation

be excluded for higher filling factors. Nevertheless an evaluation based on Mie theory was tried to get information out of the spectral measurements. Light intensity is either decreased by absorption or scattering in the material. The intensity loss through light scattering can be described by:

$$I(\lambda) = I_0(\lambda) \exp(-NC_{\text{sca}}d) \quad (5.2)$$

$I_0(\lambda)$ is the incident intensity, $I(\lambda)$ the intensity of the beam emerging after a distance d , N is the number of scattering particles and C_{sca} the scattering cross section of the particles [14,24]. In case if quotient of particle radius r and wavelength λ is $r/\lambda < 0.8$ the Rayleigh approximation can be used for C_{sca} . For the present evaluation in the wavelength range from about 1000 nm to 2000 nm it was assumed that this approximation

and assumption is valid. Equation (5.2) was transformed to

$$\frac{1}{d} \ln(T(\lambda)) = \tau = \frac{1}{d} \ln \left(\frac{I(\lambda)}{I_0(\lambda)} \right) = -NC_{\text{sca}} \quad (5.3)$$

$$\text{with } \tau = \frac{1}{d} \ln(T(\lambda)) \quad (5.4)$$

τ is called turbidity. The scattering cross section C_{sca} was described in the Rayleigh limit as $C_{\text{sca}} = A/\lambda^n$. The parameter A is a function of particle radius and refractive index of the matrix and the particle and number of particles. For Rayleigh scattering the exponent n is 4. But for increasing particle radius n decreases from 4 to 0 and can be used as an indicator for e.g. particle growth or agglomeration processes [25]. The measurements of Fig. 5.4 were fitted to

$$\frac{1}{d} \ln(T(\lambda)) = \frac{1}{d} \left(\frac{I_{\text{mix}}(\lambda)}{I_{\text{PLA}}(\lambda)} \right) = \frac{A}{\lambda^n} \quad (5.5)$$

Result of the fitting procedure delivers an exponent of the wavelength of about 1.44 for a content of 0.05% of nanofil[®]. Figure 5.6 shows the plot of the scattering behaviour depending on wavelength. The exponent decreases for increasing content of additive to about 1 for a filling factor of 3% (Fig.5.7). The results of the fitting procedure for all samples are given in Table 5.1.

nanofil [®] content %	A	n
0.05	1330	1.44
0.1	21424	1.77
0.5	3320	1.25
1	3033	1.14
3	2035	0.95

Table 5.1: Result of the fitting procedure according to equation 3. The n value of sample with 0.1% nanofil[®] might be caused by agglomeration or incomplete exfoliation.

8 Mechanical Properties

It is well known that nano-particles influence the mechanical properties of composite materials [26,27]. This is also true for nano TiO₂ and

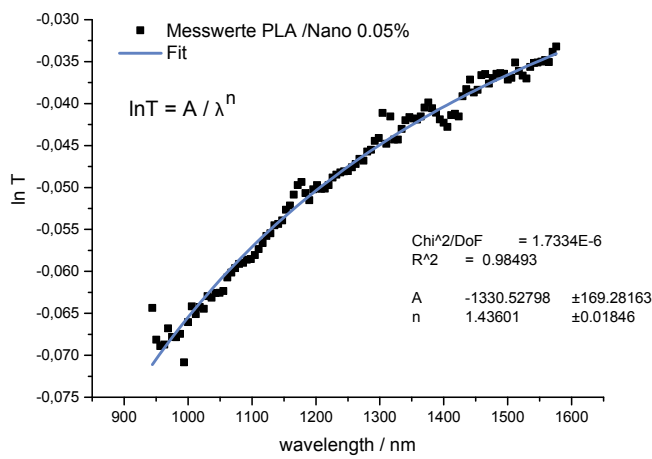


Figure 5.6: Spectral data PLA-0.05% nanofil[®] with a least squares fit of the scattering relation according to equation (5.5).

nanofil[®]. The statistical evaluation of the 80 samples of 16 types enabled an analysis of significant influences the additive content, the moisture content, extruder temperature and momentum. Both nano-particles, if present as single additives, increase significantly Young's modulus but decrease maximum strain. However, if both additives are present then the maximum strain increases significantly.

9 Summary

NIR spectroscopy can be used to measure additive content during processing of PLA biopolymer. Transmission spectra can be used to generate multivariate regression models to predict content of nanoclay. Main spectral information is the light scattering of the nanoparticles. Light scattering can also be used to make assertions of state of particle agglomeration and size changes.

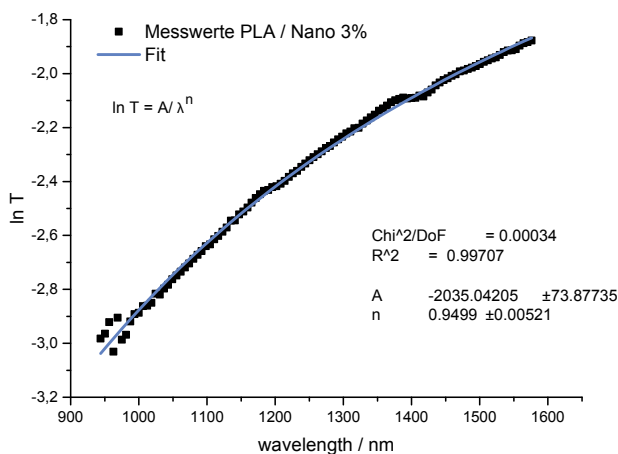


Figure 5.7: Spectral data PLA-3% nanofil[®] with a least squares fit of the scattering relation according to equation (5.5).

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