

FT-NIR as a Determination Method for Reinforcement of Polymer Nanocomposites

Stephan Laske,¹ Milan Kracalik,¹ Michael Feuchter,² Gerald Pinter,² Günther Maier,³ Wolfgang Märzinger,⁴ Michael Haberkorn,⁵ Günter Rüdiger Langecker¹

¹Institute of Plastics Processing, University of Leoben, 8700 Leoben, Austria

²Institute of Materials Science and Testing of Plastics, University of Leoben, 8700 Leoben, Austria

³Material Center Leoben, 8700 Leoben, Austria

⁴i-RED Infrarot Systeme GmbH, 4020 Linz, Austria

⁵Upper Austrian Research GmbH, 4020 Linz, Austria

Received 21 July 2008; accepted 16 May 2009

DOI 10.1002/app.30765

Published online 7 July 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Layered silicates as nanoscale fillers have a great potential in improving polymer material properties. Depending on the composite structure (agglomerated, intercalated, or exfoliated) a significantly higher level of reinforcement of the virgin polymer can be achieved with a very small amount of filler. The morphology of the composites is usually characterized by XRD and microscopic methods (e.g., transmission electron microscopy). But the level of reinforcement of nanocomposites is not always proportional to morphology (delamination level of the silicate layers). A new approach for characterizing the material reinforcement level as a consequence of melt quality is to correlate the results of extensional rheometry (level of melt strength) with those of near infrared (NIR) spectroscopy. The advantage

of the NIR technique is the suitability for in-line implementation by using quartz based optics and optical fibers for the signal transfer from the measuring probe to the NIR spectrometer. The presented results show a direct correlation between the reinforcement level determined by rheometers measurements and the data analyzed from off-line NIR measurements. The results of the chemometric analysis of the NIR data shows that this in-line capable optical method provides quantitative information on the quality of the nanocomposite. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2488–2496, 2009

Key words: nanoparticles; polymer composite materials; FT-NIR spectroscopy

INTRODUCTION

Nanocomposites are modified polymers with particles, where at least one dimension is in the order of nanometers. Polymer material reinforced by nanoscale particles exhibit significantly higher performance, for example, higher elastic modulus, tensile strength, thermal resistance, lower gas and liquid permeability, reduced flammability, and enhanced rheological properties already for small amounts of the filler.^{1,2} For preparation of polymer nanocomposites, layered silicates (clay, especially montmorillonite, MMT) have been the most commonly used nanofillers due to the possibility to achieve aspect ratios ideally up to 1000. On the basis of MMT, nanocomposites containing polyamide, polyethers, polyesters, epoxides, polystyrene, and polypropylene have been prepared.^{2–16} Polymer/clay nanocomposites can generally be prepared by mixing during polymerization

(“*in situ*”), mixing in solvent and melt mixing.¹⁷ Additionally, possibilities of nanoparticle dispersion by application of electric fields,⁸ by ultrasonic mixing,¹⁸ or direct chemical bonding of polymer chains onto the surface of silicate platelets^{19–22} have been studied. Melt mixing (compounding) is the industrially most attractive method due to its technological simplicity (usage of common polymer processing machines in contrast to special equipment and procedures in chemical laboratories). According to the dispersion of MMT platelets in the polymer matrix, three composite structures (conventional composites, intercalated, and exfoliated nanocomposites) can be formed. In the first case, the MMT particles (tactoids) are dispersed in the polymer matrix in micrometer scale with the tactoids acting as a micro-filler. Intercalated (partially delaminated) systems show penetration of polymer chains into the interlayer gallery of silicate platelets whereas exfoliated (entirely delaminated) nanocomposites are characterized by homogeneous and uniform dispersion of silicate layers in the polymer. During the process, the structures, which are responsible for the reinforcement level, are formed by physical bonding between the hydrophilic clay, hydrophobic polymer matrix, and compatibilizer. The number and type of

Correspondence to: S. Laske (stephan.laske@unileoben.ac.at).

interactions depend on the processing conditions and can be monitored by NIR spectroscopy.

Near infrared (NIR) spectroscopy is a non-destructive, optical method to determine information on the composition of samples. Like mid infrared (MIR) spectroscopy, the NIR method measures the absorbance of light due to excitation of molecular vibrations of the substance under investigation. However, MIR, which exploits radiation in the wavelength range of 2500 to 25000 nm, measures the fundamental molecular vibrations, whereas NIR, operating in the spectral range between 780 and 2500 nm, detects the overtones and combinations of these vibrations. By placing the sample in the light path, the substances present in the sample absorb NIR radiation at specific frequencies according to their molecular structure, resulting in NIR sample spectra. As the frequencies, at which the absorbances take place, are depending on the energy, a molecular structure requires to be stimulated, the position of the absorbance bands in the NIR spectrum provides the information for identification of substances and for the existence of specific chemical functionalities present in the sample. By evaluating the intensity of the features identifying a substance or chemical functionality, the amount/concentration of the respective analyte can be determined. In polymer industry, NIR spectroscopy is used for example for examination of polymerization or copolymerization, moisture content, crystallinity, molecular weight, intermolecular interactions, tacticity, orientation, dispersion and alteration of the particle size of fillers, and density of polyethylenes. As described earlier, NIR spectroscopy in principle determines the chemical composition of samples. However, it is also capable of providing information on mechanical properties as these properties are generally linked to the chemical state of the sample. For example, the strength of coatings often depends on the degree of polymerization of polymers, which again can be monitored by determining the remaining amount of monomer functionalities which have not been converted by the polymerization reaction. Furthermore, some parameters can be determined by NIR spectroscopy although neither a chemical conversion is the basis for the phenomenon nor does the analyte show any activity in the NIR. For example, ions dissolved in water can be determined to a certain degree although they are not IR active and do not cause any specific chemical reaction. The reason for this is the fact that the charged ions interact with the water molecules, influencing the strength of the O—H bond and thereby shifting the water's O—H absorbance peak. In polymer nanocomposites, the silicate platelets form different levels of 3D physical network. Generally, in the real nanocomposite systems, both the intercalated as well as exfoliated structure

exist. During the compounding process, both structures are formed by the physical bounds between the hydrophilic clay, hydrophobic polymer matrix, and compatibilizer. The number and type of interactions between polypropylene chains, organic modifier based on organoclay (quaternary ammonium salt presented in Nanofil 5), polypropylene grafted with maleic anhydride (compatibilizer), and free maleic anhydride molecules (up to 0.1% in compatibilizer) depend on the processing conditions and can be monitored with NIR spectroscopy. A few studies studying the usage of vibrational (FTIR or Raman) spectroscopy to detect the changes in physical characteristics of polymers have been published up to now.^{23–31} Some of these studies proposed an approach to analyze the deformation behavior in polymer-clay nanocomposites.^{32,33} However, no study dealing with NIR spectroscopy for the determination of the reinforcement in polymer nanocomposites have been found in available literature.

EXPERIMENTAL

Preparation of polymer nanocomposites

The used polymer matrix was an isotactic polypropylene homopolymer (HC600TF; MFI 2.8 g/10 min, 230°C/2.16 kg; Borealis/A, Linz, Austria). As a nanofiller, a layered silicate intercalated with dimethyl distearyl ammonium chloride (Nanofill5, Sud Chemie/D, Munich, Germany) and as a compatibilizer a PP grafted with maleic acid anhydride (PP-MA, Scona TPPP 2112 FA, Kometra/D, Schkopan, Germany) was used. For the compounding process, a co-rotating twin screw extruder Theysohn TSK30/40D, Korneuburg, Austria with a string die has been used. The feed rate was set at 10 kg/h with a screw speed variation, between 75 and 400 rpm. The extruder temperature profile has been set to 160–200°C from the hopper up to the die. The melt pump temperature has been kept at 200°C. As listed in Table I, different nanocomposite systems have been prepared. In the first sample group (No. 1–16), masterbatches containing 20 wt % of compatibilizer with the same amount of organoclay have been prepared under different processing conditions (with or without melt pump, varying screw speed and screw geometry). In this sample group, a variation in melt pump adjustment has been performed: For $\Delta p_{\text{maximal}}$, a maximal negative difference (up to –100 bar) between the input and outlet pressure of the melt pump has been set. In this way, melt accumulation up to the 9th extruder section (~ 40 cm before the melt pump) has been achieved. In the $\Delta p_{\text{neutral}}$ mode, the input and outlet pressure were kept constant (around 10 bar), while in $\Delta p_{\text{positive}}$ mode, a positive pressure difference (around 5 bar) was set. The

TABLE I
Description of Samples

No.	Indication	Note	Clay/PP-MA content (wt %)	Screw speed (rpm)	Geometry
1	Osp65	Without melt pump	20/20	75	1
2	MB4-65rpm	$\Delta p_{\text{maximal}}$			
3	MB5-65rpm	$\Delta p_{\text{neutral}}$			
4	MB6-65rpm	$\Delta p_{\text{positive}}$			
5	Osp100	Without melt pump	20/20	100	1
6	MB1-100rpm	$\Delta p_{\text{maximal}}$			
7	MB2-100rpm	$\Delta p_{\text{neutral}}$			
8	MB3-100rpm	$\Delta p_{\text{positive}}$			
9	Osp2_75	Without melt pump	20/20	75	2
10	MB10-75rpm	$\Delta p_{\text{maximal}}$			
11	MB11-75rpm	$\Delta p_{\text{neutral}}$			
12	MB12-75rpm	$\Delta p_{\text{positive}}$			
13	Osp2_100	Without melt pump	20/20	100	2
14	MB7-100rpm	$\Delta p_{\text{maximal}}$			
15	MB8-100rpm	$\Delta p_{\text{neutral}}$			
16	MB9-100rpm	$\Delta p_{\text{positive}}$			
17	MB16-75rpm	$\Delta p_{\text{maximal}}$	20/20	75	3
18	MB13-100rpm			100	
19	MB19-150rpm			150	
20	MB20-200rpm			200	
21	MB21-300rpm			300	
22	G3-75	$\Delta p_{\text{maximal}}$	5/5	75	3
23	G3-100			100	
24	G3-150			150	
25	G3-200			200	
26	G3-300			300	
27	G4-75	$\Delta p_{\text{maximal}}$	5/5	75	4
28	G4-100			100	
29	G4-150			150	
30	G4-200			200	
31	G4-300			300	
32	G4-400			400	

second sample group (No. 17–21) consists of masterbatches prepared at different screw speed and the $\Delta p_{\text{maximal}}$ mode. The third sample group (No. 22–32) contains nanocomposites prepared by dilution of appropriate masterbatches to 5 wt % organoclay concentration under the same processing conditions used for masterbatches.

For the Rheotens measurements, the primary granulate obtained from the extrusion process has been used. The samples for near infrared have been prepared using a hydraulic vacuum press.

Evaluation of testing methods for NIR calibration

As we have already presented elsewhere,³⁴ the level of real reinforcement in polypropylene nanocomposites is not only based on the delamination level (increase in interlayer distance) determined by the XRD method. The simple rule “a higher delamination leads to higher improvement in mechanical material properties” does not apply to all cases. The only way to find the ideal clay structure (e.g., type

and grade of mixture elements, degree of intercalation/exfoliation) in the polymer matrix for the best achievable material reinforcement is to combine the XRD and TEM technique with the characterization of mechanical properties. These methods require rather expensive scientific equipment and additional experimental time for the preparation of samples. Nevertheless, XRD, TEM, and tensile testing are the most approved methods for characterizing nanocomposites and can not be disclaimed when it comes to solid parts and their properties. But for monitoring the nanocomposite production and quality (e.g., melt homogeneity), it is necessary to examine the melt directly. We proved that the investigation of the melt strength level in compatibilized polypropylene nanocomposites using the Rheotens equipment enables to detect the material reinforcement level as a consequence of melt quality. A correlation between mechanical properties in the melt and solid state has been confirmed.³⁴ Concerning the suitability of the described methods for the polypropylene-nanocomposites characterization and the possibility for

Rheotens test being performed off- and on-line, we decided to correlate the results of Rheotens measurements (level of melt strength) with those of off-line near infrared spectroscopy to gain chemometric NIR calibration models.

Rheotens measurements

The advantage of Rheotens measurements consists in their simplicity without the need of expensive scientific equipment and additional time for sample preparation. The principle of the Rheotens measurement is shown in Figure 1. It is based on the elongation of the extruded string by two or four rotating wheels connected with a force transducer. The rotation speed is linearly increased up to the point when the molten string breaks. The tensile force applied to the wheels at a specific draw rate is the reference value for the melt strength level (stress at break). In our work, the Rheotens 71.97 equipment (Göttfert, Buchen, Germany) in combination with a capillary rheometer has been used. To compare the tensile force level of different nanocomposite systems (revealing different magnitudes of draw rate at break), the tensile force at a draw rate of 350 mm/s has been chosen as a comparative value. The data of at least three measurements for each sample with a measurement error of 2% was evaluated.

The silicate platelets form different levels of 3D physical network in the polymer matrix depending on their structure (intercalated or exfoliated). The different physical crosslinking and bonding between polymer chains and organoclay results in a diversity of viscoelastic response. Therefore, Rheotens measurements are used to identify changes of the elon-

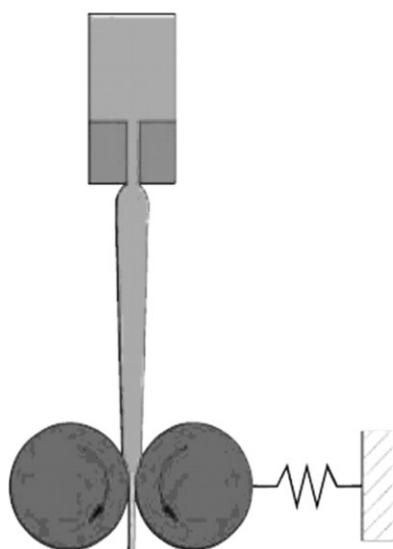


Figure 1 Principle of Rheotens measurements.³⁵

gational viscosity. Individual nanoparticles act as entanglement or crosslinking sites and raise the extensional stiffness of the composite. Depending on the degree of dispersion, this change is more or less pronounced compared to the polymer without filler.

Experimental setup for NIR measurements

The NIR spectra of the different samples were collected with the laboratory FT-NIR spectrometer Vertex 70 from Bruker Optics/D (Ettlingen, Germany). The samples were prepared as plates with a thickness of 0.8 mm and were measured in transmission by placing the plates in the optical path of the spectrometer in the sample chamber. All samples were measured three times at different lateral positions on the plate. The quantitative chemometric evaluation of the measured spectra was done with the software package OPUS from Bruker Optics/D. The measurement parameters for the acquisition of all spectra were:

- Detector: Extended InGaAs.
- Wavenumber range: 4000–10,000 cm^{-1} .
- Resolution: 8 cm^{-1} .
- Number of scans: 64.

Evaluation of NIR data

For the realization of efficient NIR spectroscopic process control applications, the extraction of process relevant information from the measured NIR spectra is essential. In the NIR region, typically, the spectral features of different species strongly overlap. This results in the need for more sophisticated evaluation methods.³⁶ In this case, the partial least squares (PLS 1) method was applied to extract quantitative information from NIR spectra and to evaluate the data for a desired parameter measured by NIR.

For example, NIR spectra are often used to estimate the amount of different chemical components in a sample. In this case, the so called “factors” are the wavelength specific measurements that comprise the spectrum. The parameters of interest, the so called “responses” are typically component amounts that the researcher wants to determine in future samples. In our case, the main response of interest is the level of reinforcement in the nanostructured materials produced by filling a polymer matrix with nanoparticles in different processing ways.

For evaluating NIR spectroscopy as a method capable of measuring a certain sample attribute (responses: e.g., reinforcement level) a straight forward approach was applied. Experimentally NIR spectra of samples with varying but known

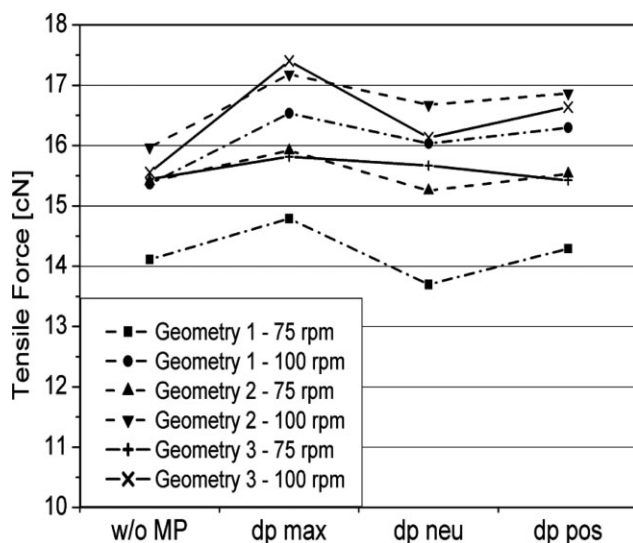


Figure 2 Melt strength of nanocomposite masterbatches prepared by different processing conditions.

responses were measured. Then PLS 1 was used to generate a linear calibration model for calculating the responses from the measured NIR data (factors).

By looking at correlation parameters [like correlation coefficient R^2 and root mean square error of cross validation (RMSECV)] of the resulting model, it is possible to evaluate whether the model shows sufficient predictive ability or not. R^2 and RMSECV are determined as follows with Y_k as the reference parameter value and Y_p as the predicted parameter value:

$$R^2 = \frac{\sum_{i=1}^n (Y_{pi} - \bar{Y}_k)^2}{\sum_{i=1}^n (Y_{ki} - \bar{Y}_k)^2}$$

$$\text{RMSECV} = \sqrt{\frac{\sum_{i=1}^n (Y_{ki} - Y_{pi})^2}{n}}$$

RESULTS AND DISCUSSION

Rheotens testing

As can be seen in Figure 2, nanocomposite masterbatches processed with screw geometry 2 (applying higher shear energy) as compared to those processed with screw geometry 1 (lower shear configuration) revealed a higher level of melt strength. The difference in screw speed shows a clear trend: a higher screw speed (generating higher shear rate) for a certain screw geometry results in a higher magnitude of tensile force (level of melt strength). Comparing

the tensile force level of masterbatches prepared using geometry 2 and 3, respectively, no significant difference occurred. This is attributed to the moderate diversity between both geometries, which differed only in the sequence of the identical screw elements.

The tensile force level of nanocomposites prepared by dilution of appropriate masterbatches using different screw geometries can be observed in Figure 3. It is obvious that for a certain screw geometry, a critical screw speed with optimal shear energy as well as residence time occurs. For geometry 4, this critical screw speed is shifted from 100 rpm (geometry 3) up to 150 rpm, because no kneading blocks in geometry 4 have been assembled and the shear rate acts proportionally to the screw speed. That means, with higher screw speed, higher shear energy is applied to the melt and a lower amount of kneading blocks is required.

The presented results show a direct relation between the melt strength level (reinforcement level) and the processing conditions (screw speed, geometry, etc.). This means that Rheotens equipment can be used for characterization of polymer nanocomposites in the molten state due to reflection of structural changes caused by different processing conditions. Furthermore, this technique can be applied on-line using a by-pass flow channel.

Near infrared spectroscopy

Sample group 1 (No. 1–16)

The samples discussed in this section were generated by running the extruder with different melt pump operation modes. Running the melt pump in

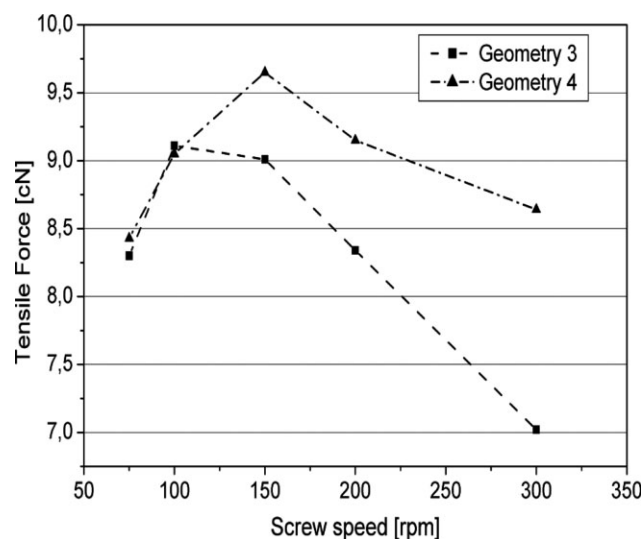


Figure 3 Melt strength of nanocomposites prepared by different processing conditions.

different operation modes enables a variation of residence time of the polymer and the nanomaterial in the extruder, and thus, results in a variation of the mechanical treatment of the material. The different degrees of mechanical treatment again result in different mechanical sample properties.

In the following figures (Figs. 4–7), the steps from the raw measurement to a calibration model are demonstrated. In Figure 4, raw measurement data is shown. As can be seen, the spectra are shifted by varying offset values. The differences are mainly caused by variations in transparency and light scattering properties from sample to sample.

Basically, a chemometric algorithm works in two steps:

Pretreatment: The spectra are pretreated to get rid of parasitic measurement effects like light straying, positioning variations or granularity, and to exclude spectral regions with irrelevant spectral information regarding the specific parameter of interest (response).

Evaluation: A scalar product of the pretreated spectrum vector with the regression coefficient (or loading) results in the numerical value of the parameter of interest (response).

Thus, the task of finding the best chemometric model for a specific measurement problem is the task of finding the best pretreatment method and regression coefficient. This can be done by testing different pretreatment methods applied to different wavenumber ranges and by searching for a model which gives the best correlation properties with the desired response.

For the first series of measurements, the response of interest is the tensile force value normally deter-

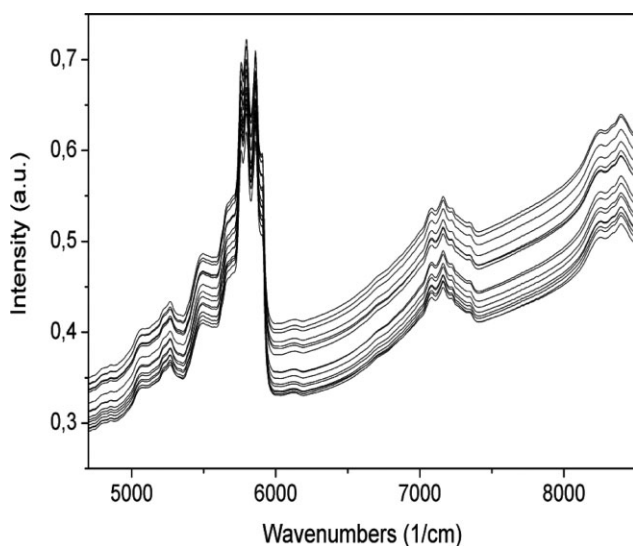


Figure 4 Absorbance data of samples 1–16. Spectra are shown as measured without any data treatment.

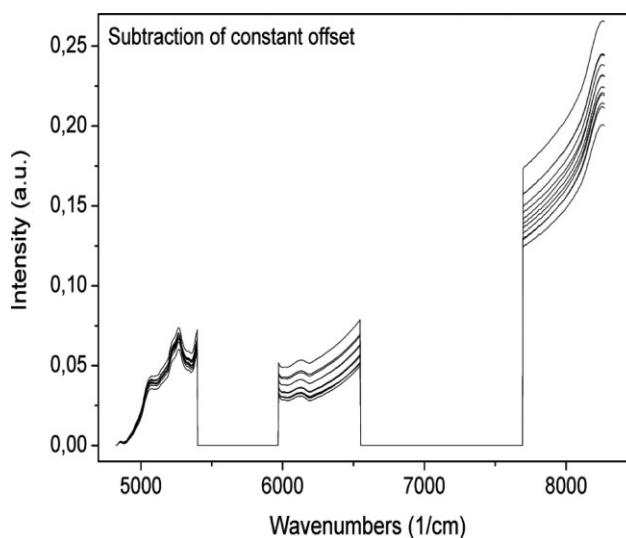


Figure 5 Selected regions of NIR absorbance spectra after subtraction of constant offset values.

mined by Rheotens measurement. In the following pictures, the final result of an iterative model optimization procedure is shown. The gained chemometric model should be near to the best model for the evaluation of the tensile force value from NIR measurements.

In Figure 5, the resulting spectral vectors after pretreatment are given. Optimization in terms of best correlation parameters led to the elimination of selected wavelength ranges and to the pretreatment method “subtraction of constant offset.” This means that the pretreatment method subtracts a constant value from each spectrum.

In Figure 6, the wavenumber dependent coefficients of regression are shown. The PLS 1 algorithm

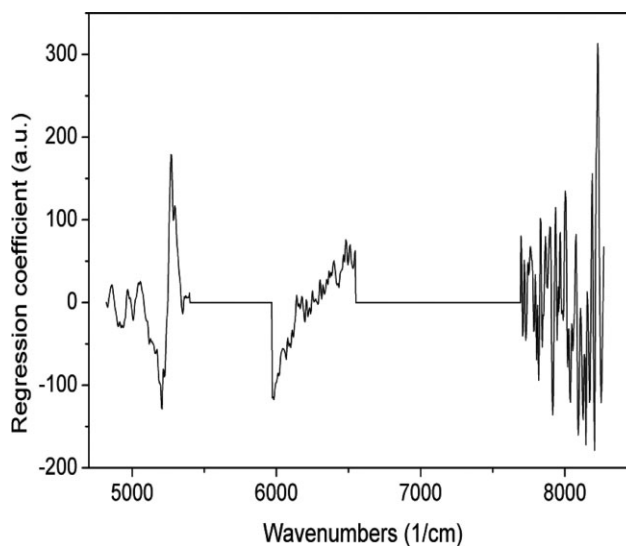


Figure 6 Wavelength dependent coefficient of regression calculated by PLS 1 algorithm.

TABLE II
Comparison of Drawing Force Values Evaluated by Rheotens Method and Calculated Values from the NIR Spectra for Sample Group 1 (Samples 1, 5, 9, and 13 Excluded Due to Different Processing Procedure as Explained in the Text)

No.	Indication	Note	Rheotens (cN)	NIR 1 (cN)	NIR 2 (cN)	NIR 3 (cN)	Average NIR (cN)
2	MB4-65rpm	$\Delta p_{\text{maximal}}$	16.54	16.52	16.41	16.46	16.46
3	MB5-65rpm	$\Delta p_{\text{neutral}}$	16.03	15.97	16.09	16.11	16.06
4	MB6-65rpm	$\Delta p_{\text{positive}}$	16.30	16.20	16.27	16.06	16.18
6	MB1-100rpm	$\Delta p_{\text{maximal}}$	14.90	14.92	15.14	14.63	14.90
7	MB2-100rpm	$\Delta p_{\text{neutral}}$	13.70	13.75	13.95	13.74	13.81
8	MB3-100rpm	$\Delta p_{\text{positive}}$	14.29	14.22	14.08	14.04	14.11
10	MB10-75rpm	$\Delta p_{\text{maximal}}$	17.18	16.98	16.92	17.19	17.03
11	MB11-75rpm	$\Delta p_{\text{neutral}}$	16.68	17.00	16.68	16.82	16.83
12	MB12-75rpm	$\Delta p_{\text{positive}}$	16.87	16.92	16.81	16.62	16.78
14	MB7-100rpm	$\Delta p_{\text{maximal}}$	15.92	15.90	15.40	15.72	15.67
15	MB8-100rpm	$\Delta p_{\text{neutral}}$	15.25	15.23	15.78	15.32	15.44
16	MB9-100rpm	$\Delta p_{\text{positive}}$	15.53	15.58	15.50	15.90	15.66

searches for linear correlations between spectral data (factors) and reference values (responses). The diagram shows the wavelength regions which are changing with the effect of interest as well as how these regions are changing. Positive values mean that the spectral value is increasing with increasing response value. Negative values mean that the spectral value is decreasing with increasing response value. The response value in this case is the tensile force.

Table II and Figure 7 give an overview of the resulting chemometric model. In Table II, the single measurement values and the corresponding average value of the NIR method are shown and can be compared with the Rheotens values. In Figure 7, the tensile force values evaluated by Rheotens method (horizontal axis) are plotted versus the calculated values from the NIR spectra (vertical axis). The quality of the chemometric model and thus the ability of the NIR spectroscopic method to measure the tensile force value can be quantified by the values R^2 and RMSECV. The correlation coefficient R^2 shows the correlation of the NIR data with the reference values of the investigated response parameter. Values of R^2 are between 0 and 100. Typically, models with R^2 values above 90 enable quantitative calculation of the response parameter of interest. Correlation coefficients above 70 allow qualitative evaluations. If R^2 lies below 70, the response is not well pronounced in the factors (the spectral data) and thus can not be evaluated with reasonable practical relevance.

The root mean square error of cross validation (RMSECV) is determined by calculating a predictive model by using all samples except for one. This model is applied to the sample left out for prediction of the desired response parameter. RMSECV is calculated by doing this procedure for every sample and by summing up the root mean square errors of the deviations of the calculation results from the assumed true reference values. This value is a mea-

sure for the error of the developed NIR measurement method.

The chemometric model given in Figure 7 shows a very good correlation with the Rheotens method and allows absolute quantification of tensile force values by the NIR method. It was necessary to exclude samples 1, 5, 9, and 13 due to their different processing procedure. Including these samples in the chemometric model design led to a chemometric model with R^2 value of 83. With this model, semi-quantitative evaluation of the tensile force parameter would still be possible. Samples 1, 5, 9, and 13 were produced without melt pump. In the experimental procedure, all other samples were produced first, then the melt pump was detached and samples 1, 5, 9, and 13 were extruded. It is assumed that the change in the experimental setup has caused not only changes in the mechanical treatment in the extruder

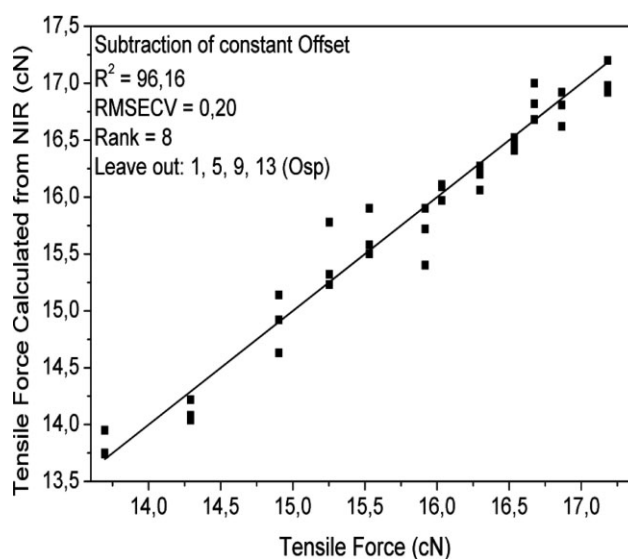


Figure 7 Drawing force values calculated versus measured for samples 1 to 16.

TABLE III
Drawing Force Values Calculated Versus Measured for Samples 17–21

No.	Indication	Note	Rheotens (cN)	NIR 1 (cN)	NIR 2 (cN)	NIR 3 (cN)	Average NIR (cN)
17	MB16-75rpm	$\Delta p_{\text{maximal}}$	17.40	17.37	17.44	17.07	17.29
18	MB13-100rpm		15.81	15.74	16.00	16.06	15.93
19	MB19-150rpm		17.14	16.56	17.33	16.76	16.88
20	MB20-200rpm		17.12	17.12	17.02	16.59	16.91
21	MB21-300rpm		12.90	13.63	13.28	13.74	13.55

but eventually also led to slight differences in chemical composition, transparency, or light stray properties of the samples.

The procedure shown in detail for samples 1 to 16 was also done with the other sample groups which are identical in chemical composition. For the other groups, only the final result, the comparison of the reference values and the values determined by NIR spectroscopy is shown.

Sample group 2 (No. 17–21)

In this sample group, the extruder was operated with the melt pump at maximal pressure difference. The PP-MA and organoclay content was constant at 20 wt % for all samples. Differences were achieved by changing the screw speed in the range from 75 to 300 rpm.

In Table III and Figure 8, the detailed results of the chemometric evaluation of this sample group are given. Very good correlation of Rheotens and NIR tensile force values can be achieved by designing an optimized chemometric model. The chosen spectral pretreatment method was “subtraction of constant

offset” as in sample group 1. Even though the coefficient of correlation R^2 is in the same region as in group 1, the results can not be judged with the same relevance, because of the low number of samples and because of the non-uniform distribution of the sample parameter values over the parameter interval (effectively only three really different tensile force values in sample set 2).

Sample group 3 (No. 22–32)

For the sample group 3, the extruder was operated with the melt pump at maximal pressure difference. The PP-MA and organoclay content was constant at 5 wt % for all samples. Differences were achieved by changing the screw speed in the range from 75 to 400 rpm and by changing the geometry of the extruder screw.

The results of the chemometric evaluation are shown in Table IV and Figure 9. The best spectral pretreatment method for this chemometric model for the determination of the tensile force values from NIR spectra, is “first derivative and multiplicative scatter correction (MSC).” The coefficient of correlation R^2 of 82 for this model is lower than for the models of the other sample groups but still enables qualitative evaluation. The chemometric model enables an evaluation of the mechanical properties of the samples generated with three different extruder

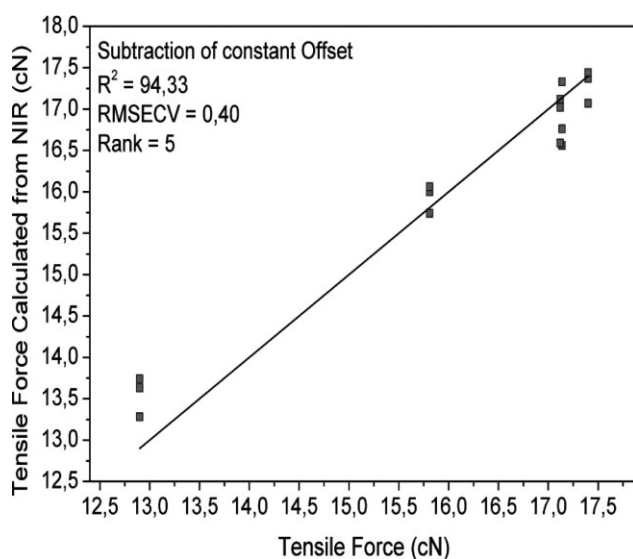


Figure 8 Drawing force values calculated versus measured for samples 17 to 21.

TABLE IV
Drawing Force Values Calculated Versus Measured for Samples 22–32

No.	Indication	Screw speed (rpm)	Rheotens (cN)	Average NIR (cN)
22	G3-75	75	8.30	8.84
23	G3-100	100	9.11	8.68
24	G3-150	150	9.01	9.15
25	G3-200	200	8.34	8.42
26	G3-300	300	7.02	6.84
27	G4-75	75	8.43	8.86
28	G4-100	100	9.05	8.67
29	G4-150	150	9.65	9.59
30	G4-200	200	9.15	9.31
31	G4-300	300	8.64	8.65
32	G4-400	400	7.66	7.66

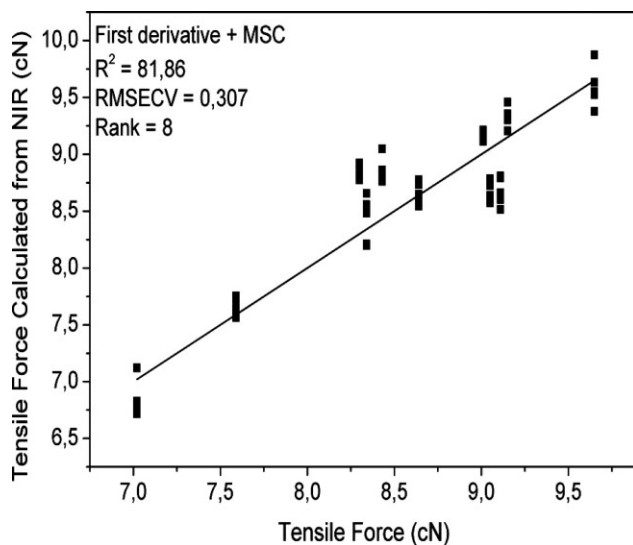


Figure 9 Drawing force values calculated versus measured for samples 22 to 32.

screw geometries. The chemometric model itself will improve significantly, when measurements are taken in-line at the extruder, without any postprocessing of the material.

CONCLUSION

It can be seen that the material reinforcement (level of melt strength) exhibits good correlation with NIR data analyzed by the partial least squares method. NIR spectroscopy was shown to be a qualitative and predominantly quantitative method for monitoring nanocomposite quality of all sample groups investigated, although the extruded sample material had to be cooled down, granulated, and processed to plates for measurements with the off-line NIR system. Therefore, it is crucial to measure the quality of the nanocomposites in-line without any additional processing, to prevent any negative effect on the material structure or reinforcement level. Unknown changes in the samples caused by these postprocessing procedures are negatively affecting the shown chemometric models. In-line-measurement of NIR data is technically possible for the extruder and would lead to a higher quality of the chemometric models due to omission of postprocessing steps. Rheotens and NIR measurements could be done simultaneously on the extruder if the NIR system is implemented in-line and the Rheotens measurements are done on-line through a bypass die system.

This work was done within the project Nano-comp—0901 PlaComp1 funded by the Austrian Nano Initiative. Parts of the FT-NIR research work were done within the FH Plus—Project AMiESP (Advanced Methods in Embedded Signal Processing).

References

- Gilman, J. W.; Kashiwagi, T.; Lichtenhan, J. D. *Sampe J* 1997, 33, 40.
- Ray, S. S.; Okamoto, M. *Progr Polym Sci* 2003, 28, 1539.
- Sanchez-Solis, A.; Garcia-Rejon, A.; Manero, O. *Macromol Symp* 2003, 192, 281.
- Sanchez-Solis, A.; Romero-Ibarra, I.; Estrada, M. R.; Calderas, F.; Manero, O. *Polym Eng Sci* 2004, 44, 1094.
- Ishida, H.; Cambell, S.; Blackwell, J. *Chem Mater* 2000, 12, 1260.
- Vaia, R. A.; Giannelis, E. P. *Macromolecules* 1997, 30, 8000.
- Pinnavaia, T. J.; Beall, G. W. *Polymer-Clay Nanocomposites*; New York, 2000.
- Kim, D. H.; Park, J. U.; Cho, K. S.; Ahn, K. H.; Lee, S. J. *Macromol Mater Eng* 2006, 291, 1127.
- Hasegawa, N.; Kawasumi, M.; Kato, M.; Usuki, M.; Okada, A. *J Appl Polym Sci* 1998, 87, 67.
- Maxfield, M.; Shacklette, L. W.; Baughman, R. H.; Christiani, B. R.; Eberly, D. E. *PCT Int Appl WO* 1993, 93, 04118.
- Lee, S. S.; Kim, J. *Polym Mater Sci Eng* 2003, 89, 370.
- Kracalik, M.; Mikesova, J.; Puffr, R.; Baldrian, J.; Thomann, R.; Friedrich, C. *Polym Bull* 2007, 58, 313.
- Kracalik, M.; Studenovskiy, M.; Mikesova, J.; Sikora, A.; Thomann, R.; Friedrich, C.; Fortelny, I.; Simonik, J. *J Appl Polym Sci* 2007, 106, 926.
- Kracalik, M.; Studenovskiy, M.; Mikesova, J.; Kovarova, J.; Sikora, A.; Thomann, R.; Friedrich, C. *J Appl Polym Sci* 2007, 106, 2092.
- Kracalik, M.; Pospisil, L.; Slouf, M.; Mikesova, J.; Sikora, A.; Simonik, J.; Fortelny, I. *Polym Compos* 2008, 29, 437.
- Kracalik, M.; Pospisil, L.; Slouf, M.; Mikesova, J.; Sikora, A.; Simonik, J.; Fortelny, I. *Polym Compos* 2008, 29, 915.
- Gilman, J. W.; Morgan, A. B.; Harris, R. H., Jr.; Trulove, P. C.; DeLong, H. C.; Sutto, T. E. *Polym Mater Sci Eng* 2000, 83, 59.
- Messersmith, P. B.; Giannelis, E. P. *Chem Mater* 1994, 6, 1719.
- Hoffmann, B.; Kressler, J.; Stöppelmann, G.; Friedrich, C.; Kim, G. M. *Colloid Polym Sci* 2000, 278, 629.
- Lepoittevin, B.; Pantoustier, N.; Devalckenaere, M.; Alexandre, M.; Kubies, D.; Calberg, D.; Jérôme, R.; Dubois, P. *Macromolecules* 2002, 35, 8385.
- Messersmith, P. B.; Giannelis, E. P. *Chem Mater* 1993, 5, 1064.
- Messersmith, P. B.; Giannelis, E. P. *J Polym Sci Polym Phys Ed* 1995, 33, 1047.
- Tashiro, K. *Vibr Spectr Polym* 2007, 143.
- Loo, L. S.; Gleason, K. K. *Macromolecules* 2003, 36, 6114.
- Sakurai, T.; Kasahara, T.; Yamaguchi, N.; Tashiro, K.; Amemiya, Y. *PMSE Preprints* 2003, 88, 352.
- Nakamoto, S.; Tashiro, K.; Matsumoto, A. *Macromolecules* 2003, 36, 109.
- Tashiro, K. *Sen'i Gakkaishi* 2002, 58, 253.
- Kitagawa, T.; Tashiro, K.; Yabuki, K. *J Polym Sci Part B: Polym Phys* 2002, 40, 1269.
- Wang, H.; Palmer, R. A.; Manning, C. *J Appl Spectrosc* 1997, 51, 1245.
- Sonoyama, M.; Shoda, K.; Katagiri, G.; Ishida, H. *Appl Spectrosc* 1997, 51, 346.
- Tashiro, K. *Korea Polymer J* 1996, 4, 166.
- Kalra, A.; Parks, D. M.; Rutledge, G. C. *Macromolecules* 2007, 40, 140.
- Loo, L. S.; Gleason, K. K. *Macromolecules* 2003, 36, 2587.
- Laske, S.; Kracalik, M.; Gschweilt, M.; Feuchter, M.; Maier, G.; Pinter, G.; Thomann, R.; Friesenbichler, W.; Langecker, G. R. *J Appl Polym Sci* 2009, 111, 2253.
- Goettfert Ltd. Buchen, Germany. Available at: <http://www.goettfert.com>.
- Brerenton, R. G. *Chemometrics Data Analysis for the Laboratory and Chemical Plant*, ISBNs: 0-471-48977-8 (HB); 0-471-48978-6 (PB), 2003.