

In-line analysis of the degree of dispersion of nanofillers in nanocomposites during extrusion by ultrasonic measurements, near-infrared spectroscopy and light scattering

Ziel der Arbeiten war die Entwicklung innovativer multifunktionaler polymerer Nanocomposite-Materialien. Diese besitzen ein besseres Eigenschaftsprofil als konventionelle Polymermaterialien, insbesondere bei mechanischen, elektrischen, Barriere- und Oberflächeneigenschaften und beim Flammenschutz. Nanoskalige Füllstoffe werden in eine Polymermatrix durch Extrusion eingearbeitet. Hierbei ist es erforderlich schon bei der Verarbeitung den Einfluss der Prozessbedingungen und der Morphologie der Schmelze auf die späteren gewünschten Eigenschaften der Nanocomposites zu überwachen. Daher ist es notwendig in Echtzeit im Extruder zu messen. Die hierfür verwendeten In-line-Messmethoden sind die Nah-Infrarot- und Raman-Spektroskopie, Ultraschallmessungen und die Lichtstreuung. Speziell die Messung der Dispersion und der Partikelgröße der Nanofüllstoffe und die Korrelation der In-line-Messungen mit mechanischen Eigenschaften sind von großem Interesse. Insbesondere bei der Verarbeitung von Schichtsilikaten in Polymeren ist der Grad der Exfolierung der Schichtsilikate von beträchtlicher Bedeutung. Dieser wird in-line mittels einer Korrelation zwischen den In-line-Messungen und dem Scherverdünnungsexponenten aus Scherviskositätsmessungen, der als Maß für den Grad der Exfolierung dient, bestimmt.

Introduction

The main aim of this project was to develop innovative multifunctional polymer nanocomposites for application in automotive, electrical and packaging industrial sectors. These multifunctional nanostructured materials have great advantages in comparison to traditional polymer materials. Properties like tensile strength and Young's modulus, barrier and surface properties, electrical properties and flame retardancy will be improved. An overview to the state of the art of industry-relevant preparation, characterization and application of polymeric nanocomposites is given in [1]. We use extrusion to create nanocomposites because extrusion is the most applied technology for mixing and modifying of polymers with fillers in the molten state.

However, there is a need to control the morphology of the nanofiller in the polymer matrix during melt processing and on the influence of the processing conditions on the nanocomposite formation. In this context morphology describes the dispersion, particle size and distribution of the nanofiller in the polymer matrix. Off-line analysis does not display the exact condition of the material during the extrusion process. For an adequate real time characterization it is necessary to make measurements direct in the extruder. This real time information provides an improvement of the quality of the nanocomposite by controlling the process parameters immediately. Furthermore, an effective production process by real time analysis of dispersion and distribution of nanoparticles in nanocomposites saves time, costs and raw material.

An important point is to measure the degree of intercalation and exfoliation of layered silicates as nanofiller in a polymer matrix. Our concept was to determine the shear thinning exponent from shear

Keywords

process analytical technology (PAT)
in-line analysis
nanocomposites
extrusion monitoring
dispersion
particle size characterisation

Bearbeiter

D. Fischer
J. Müller
S. Kummer
K. Sahre
B. Kretzschmar
D. Pahlitzsch

Förderer

European Research Program
Integrated Project
Multihybrids

Kooperation

S. Große,
TOPAS GmbH, Dresden
SENTRONIC GmbH, Dresden
SONOTEC GmbH, Halle

viscosity measurements as a degree for exfoliation. Then we correlated this exponent with real time measurements. These real time measurements were spectroscopic, ultrasonic and light scattering measurements [2,3]. We illustrate the opportunities of in-line near infrared (NIR) spectroscopy, ultrasonic measurements and light scattering measurements to characterize polymer nanocomposites (NC) in real time. For correlation to morphology and mechanical properties we used different off-line techniques like transmission and scanning electron microscopy (TEM/SEM), rheology and mechanical test procedures.

Materials

Investigated polymers were polyamide-6 (PA6), polypropylene (PP) and maleic anhydride-modified PP (PPm).

For the determination of particle sizes we used silicon dioxide nanoparticles with diameters of 90 nm (Aerosil R9200), 200 nm (Geltech 0.2) and 500 nm (Geltech 0.5), and talcum particles with primary particle sizes of 2.1 μm (Luzenac A7) and 1.2 μm (Luzenac A3).

For the determination of the dispersion we measured the degree of intercalation and exfoliation of different layered silicates (montmorillonites, MMT). First, we applied unmodified MMT (Cloisite Na⁺) for NC with bad exfoliation and then for a stepwise improvement of the exfoliation, we applied different modified MMT (Nanofil 5 and Cloisite 20A for PPm and Nanofil 919, Nanofil 919f and Cloisite 30B for PA6).

Experimental

All experiments were done at a Leistritz Micro 27 extruder with two different end adapters at the die (2 + 4 mm melt channel) and two side outlet adapters (2 + 4 mm melt channel) for measurements at different positions along the extruder. All measurement adapters were developed from the IPF and can be assembled with sensors for ultrasonic measurements (US), for NIR, UV/VIS and Raman spectroscopy, for light scattering/particle monitoring (PM) measurements and for pressure and temperature measurements, shown in Fig. 1. We used different screw profiles, different screw speeds from 100 to 400 rpm and different flow rates from 6 to 8 kg·h⁻¹ during extrusion. The temperatures were 220 °C for PP NC and 235 °C for PA6 NC.

With this equipment we are able to measure and monitor the following data in-line in real-time:

- Temperature and pressure,
- NIR transmittance and diffuse reflectance spectra,
- UV/VIS transmittance and diffuse reflectance spectra,
- Raman spectra,
- Extinction of light (660 nm) for particle monitoring,
- Ultrasonic velocity and attenuation (spectral and integral values).

To determine the desired properties of the NC it is necessary to correlate off-line determined data with data from the in-line methods. For the off-line determination of the NC properties we used SEM to measure particle sizes and carried out impact strength measurements by Charpy test (ISO 179/1) with flatwise impact. Furthermore, we carried out rheological measurements by an oscillatory rheometer (ARES rheometer, plate-to-plate: 25 mm plate diameter, 1 mm distance) to measure the shear viscosity

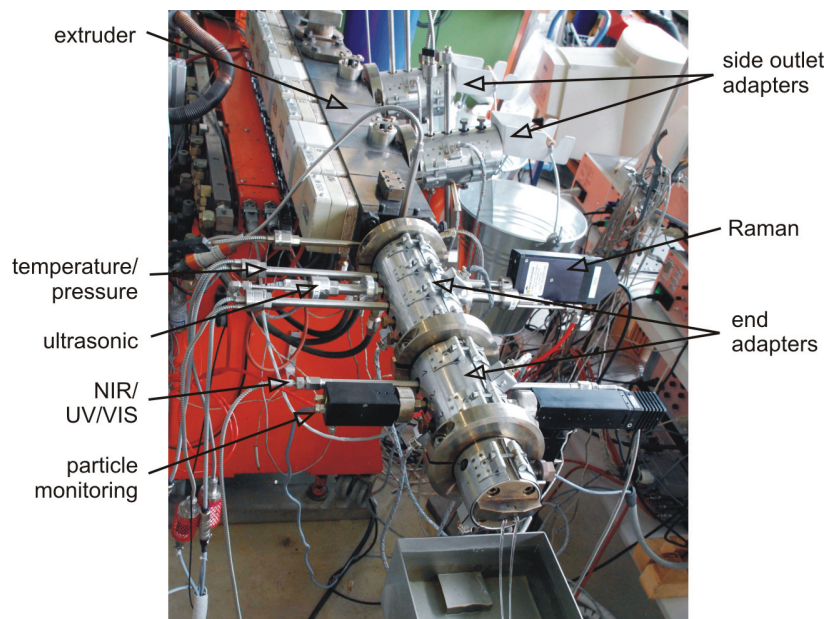


Fig. 1:
Leistritz Micro 27 extrusion system
with probe adapters used.

(dynamical frequency sweep: 0.05 Hz to 100 Hz) at 220 °C for PP and at 230 °C for PA6 NC. The initial slope at low frequencies was used to calculate shear thinning exponents (STE) [4].

For the correlation of off-line data with the in-line measurements we used multivariate data analysis (chemometric analysis). The chemometric analysis was performed to find models (calibration procedure) to correlate particle size, mechanical properties and shear thinning exponents of the different nanocomposites with the in-line data. Then we used these models to predict unknown particle size, mechanical properties and shear thinning exponents in real time (validation procedure). A work flow chart is described in Fig. 2.

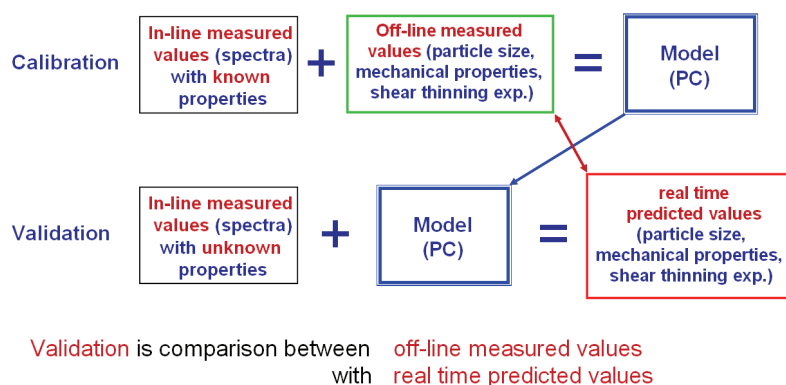


Fig. 2:
Work flow chart of the process of
multivariate data analysis.

The main criterion to describe the significance of a model is the calculation of the correlation coefficient R^2 of the regression between off-line measured and in-line predicted values.

Results

In-line prediction of particle sizes of nanoparticles in PA6

We measured in-line the particle sizes of silicon dioxide nanoparticles with source diameters of 90 nm (Aerosil R9200), 200 nm (Geltech 0.2) and 500 nm (Geltech 0.5), and talcum particles with source primary particle sizes of 2.1 μm (Luzenac A7) and 1.2 μm (Luzenac A3) in PA6. We added the different particles in

Fig. 3:
SEM images of Geltech 0.5 (left)
and Luzenac A7 (right) particles in
PA6.

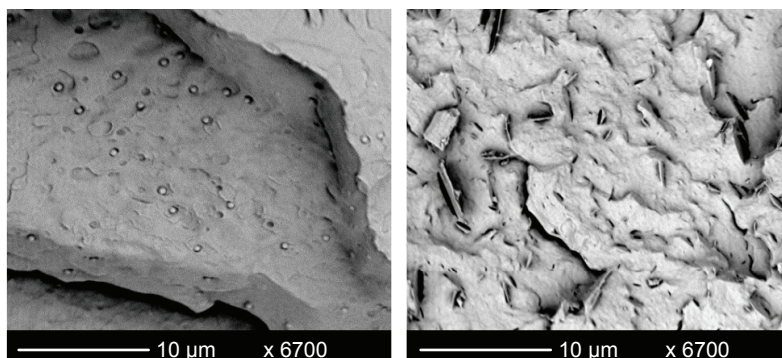


Table 1 and Table 2 show the SEM measured particle sizes compared with predicted particle sizes calculated using in-line NIR, Raman and US spectra. The average particle sizes of PM were calculated using the extinction coefficient [5].

Tab. 1:
Predicted particle sizes in PA6
matrix of the different methods with
5 wt-% content of nanoparticles.

Particles (5 wt-%)	Average particle size (SEM) [nm]	Calculated particle size (US) [nm] $R^2 = 0.997$	Average particle size (PM) [nm]
SiO ₂ (Aerosil R9200)	140	160 ± 40	94
Talcum A3	1100	1099 ± 25	184
Talcum A7	1500	1500 ± 60	183

Tab. 2:
Predicted particle sizes in PA6
matrix of the different methods with
2 wt-% content of nanoparticles.

Particles (2 wt-%)	Average particle size (SEM) [nm]	Calculated particle size (NIR) [nm] $R^2 = 1.000$	Calculated particle size (Raman) [nm] $R^2 = 0.939$	Calculated particle size (US) [nm] $R^2 = 0.998$	Average particle size (PM) [nm]
SiO ₂ (Geltech 0.5)	600	665 ± 4	550 ± 30	600 ± 30	448
SiO ₂ (Geltech 0.2)	250	256 ± 5	230 ± 40	240 ± 60	173
SiO ₂ (Aerosil R9200)	140	160 ± 2	180 ± 70	138 ± 12	94
Talcum A7	1500	1466 ± 4	—	1500 ± 20	183

It is clearly to see, that we have a high correlation between the in-line NIR, Raman and US data and the off-line determined particle sizes. Data for particle monitoring show good results if the particles are smaller than 500 nm.

In-line prediction of shear thinning exponents of PA6/NC and PP/NC

PA6/NC

In principle, shear viscosity measurements at low frequencies show a pseudo-solid behaviour for nanocomposites with layered silicates [4, 6]. With decreasing frequency, an increasing viscosity is induced by interaction of the single layers of the layered silicates. We used different modified MMT to obtain NC with different degrees of exfoliation.

Fig. 4 shows the shear viscosity of PA6/MMT nanocomposites from 0.05 to 100 Hz. There is an increase of the shear viscosity at low frequencies for NC with modified MMT in comparison with NC

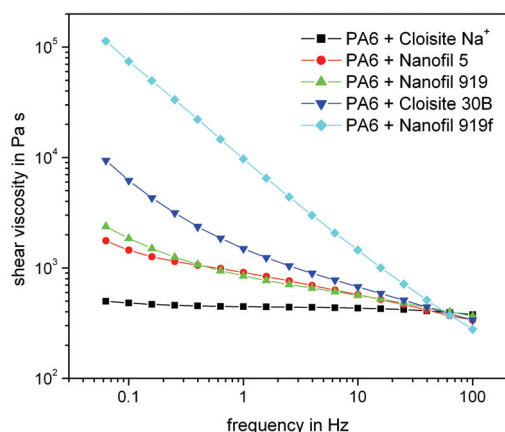


Fig. 4:
Shear viscosity of different PA6/MMT nanocomposites with 5 wt-% inorganic content of nanoparticles.

with unmodified MMT. The viscosity at low frequencies for NC with special for PA6 modified MMT (Nanofil 919f and Cloisite 30B) show a greater shear thinning exponent than NC with unmodified MMT (Cloisite Na⁺) and with not for PA6 modified MMT (Nanofil 5). The slope of the first four points was used to calculate the shear thinning exponent. The shear thinning exponents were used for a correlation with the in-line NIR- and US-spectra. Both in-line methods show a good correlation between in-line and off-line measurements. The values are listed in Table 3.

Nanofillers	Mean measured STE (ARES)	Calculated STE (NIR) R ² = 0.990	Calculated STE (US) R ² = 0.993
Nanofil 919f	-0.91 ± 0.05	-0.92 ± 0.06	-0.89 ± 0.04
Nanofil 919	-0.48 ± 0.04	-0.49 ± 0.02	-0.48 ± 0.04
Nanofil 5	-0.32 ± 0.03	-0.33 ± 0.02	-0.33 ± 0.03
Cloisite 30B	-0.78 ± 0.04	-0.77 ± 0.02	-0.78 ± 0.06
Cloisite Na ⁺	-0.07 ± 0.02	-0.03 ± 0.12	-0.12 ± 0.05

Tab 3:
Predicted shear thinning exponents (STE) of different MMT in PA6 matrix of the different methods with 5 wt-% inorganic content of nanoparticles.

For particle monitoring, differences between the 5 PA6/MMT NC can be detected. The average particles sizes calculated from extinction measurements are shown in Fig. 5, together with the calculated particle sizes for the both PA6/talcum NC.

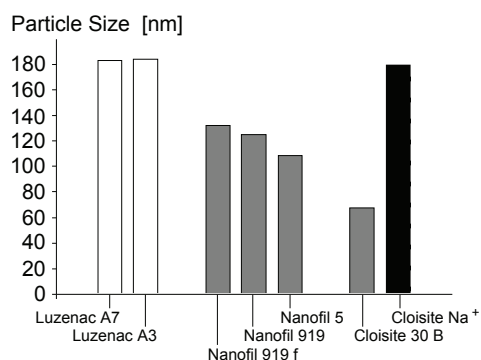
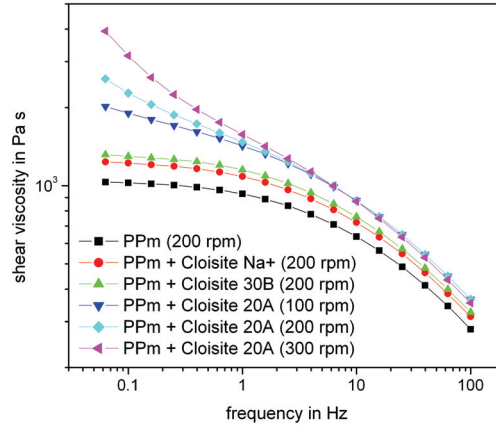


Fig. 5:
Results of particle monitoring for different PA6/NC: Average particle size of nanofillers dispersed in PA6 from real-time light extinction measurements at twin screw extrusion (particle size = extinction cross section equivalent circle diameter).
□ unmodified talc; ■ modified MMT; ■ unmodified MMT

PP-NC

The shear viscosity measurements of PPm/MMT nanocomposites from 0.05 to 100 Hz are presented in Fig. 6. These curves show also an increase of the shear viscosity at low frequencies for NC with MMT in comparison with pure PPm. The viscosity at low frequencies for the NC with specially for PP modified MMT (Cloisite 20A) show a greater shear thinning exponent than NC with unmodified MMT (Cloisite Na⁺) and with not for PP modified

Fig. 6:
Shear viscosity of different
PPm/MMT nanocomposites with
5 wt-% inorganic content of
nanoparticles and at different screw
speeds.

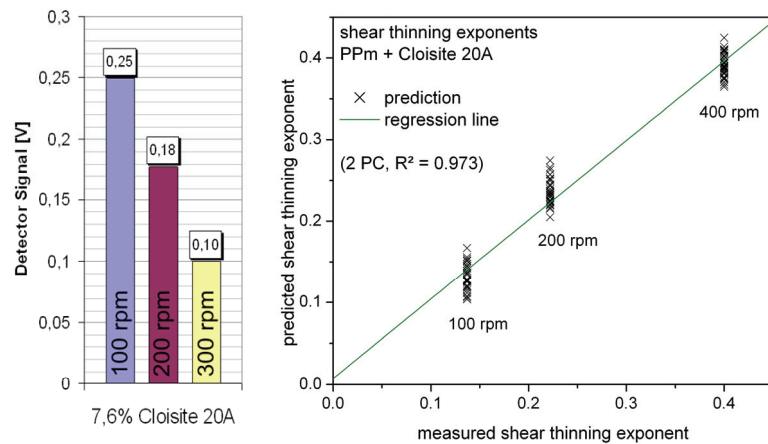


Tab. 4:
Predicted shear thinning exponents
of different MMT in PPm matrix
calculated by US and NIR with 5 wt-
% inorganic content of
nanoparticles.

Nanofillers	Mean measured STE (ARES)	Calculated STE (NIR) $R^2 = 0.998$	Calculated STE (US) $R^2 = 0.986$
Cloisite Na ⁺	-0.036 ± 0.012	-0.05 ± 0.02	-0.04 ± 0.02
Cloisite 30B	-0.03 ± 0.02	0.00 ± 0.02	-0.04 ± 0.04
Cloisite 20A	-0.222 ± 0.023	-0.24 ± 0.02	-0.22 ± 0.03

Furthermore, we investigated the nanocomposite PPm/MMT by NIR, US and PM at three different screw speeds to study the influence of changes in process conditions. The results demonstrate that we can distinguish between the different screw speeds. This is shown in Fig. 6 for the off-line shear viscosity measurements. The explanation is that different screw speeds induces changes in the degree of exfoliation which can be seen in the in-line NIR and Ultrasonic spectra. The correlation between US in-line spectra and off-line STE measurements are displayed in Fig. 7 (right graphic). Using particle monitoring, differences in the in-line measured signals between the 3 PPm/MMT NC can also be detected. This is also shown in Fig. 7 (left graphic).

Fig. 7:
Determination of measurement
signal differences caused by
different screw speeds for PM
(detector signal) and US (spectra)
for the NC PP/Cloisite 20A.



Our results show that it is possible to monitor with NIR, US and PM the shear thinning exponent as a degree for exfoliation. This degree can be used as a description for the dispersion of layered silicates in PA6 and PPm nanocomposites [4].

Real time monitoring of shear thinning exponents of PP-NC

The chemometric models (calibration) created for prediction of the shear thinning exponents of NC in the melt can easily be applied to the extrusion process to monitor this parameter in real time. We repeated the extrusion process with NC which were unknown for the evaluation program to validate our calibrations (validation). The real time predicted STE's calculated by chemometrics using the NIR and US spectra are shown in Fig. 8.

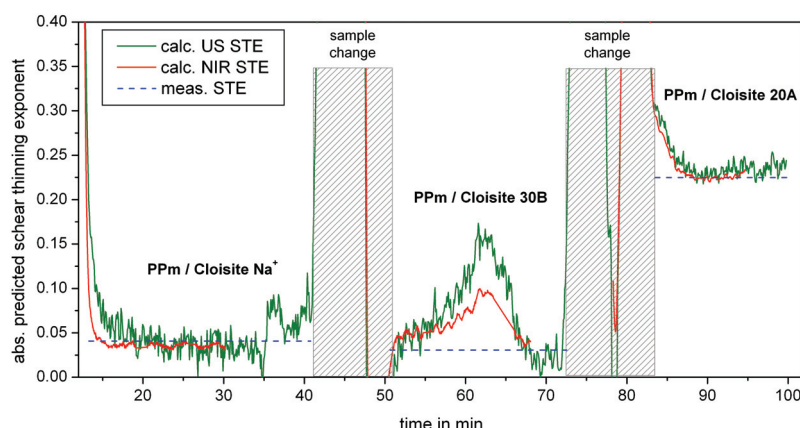


Fig. 8:
Real time prediction of the shear thinning exponent of different PPm nanocomposites by NIR (red) and US (green), calculated by chemometrics (true off-line values: blue lines).

We monitored the values of the shear thinning exponents of different nanocomposites at the end of the extruder. The STE's calculated using ultrasonic spectra are shown in green and the STE's calculated using NIR spectra are shown in red. The off-line measured values (true values) of the STE's are drawn as blue dotted lines. After changing the NC addition, (marked with grey boxes in Fig. 8) it needs some minutes to stabilize the melt mixture in the extruder. After stabilizing, the calculated values of the STE's agree with the true off-line measured shear viscosity values.

In-line prediction of impact strength of PP nanocomposites

It is of great interest to correlate off-line determined mechanical properties with in-line measurements to monitor the quality of an extruded product. In first experiments we tried to correlate off-line measured impact strength of different PPm nanocomposites with in-line NIR and US spectra. Table 5 shows the impact strength of pure PPm and different PPm nanocomposites in comparison with chemometric results using NIR and US spectra. The NC used for extrusion were two MMT's (Dellite 67G, Cloisite 20A) and one double layered silicate (Hydrotalcite F100). Furthermore, we extruded Cloisite 20A at two different extrusion procedures. Both, NIR and US spectroscopy, show a good correlation to the off-line determined impact strength. It is possible to distinguish between different impact strength values.

Nanofillers	Measured impact strength [kJ·m ⁻²]	Calculated impact strength (NIR) [kJ·m ⁻²] R ² = 0.999	Calculated impact strength (US) [kJ·m ⁻²] R ² = 0.942
no nanofiller	108 ± 6	108.7 ± 1.5	103.4 ± 1.6
Dellite 67G	37 ± 3	38.5 ± 1.8	36 ± 8
Hydrotalcite F100	81 ± 13	81.0 ± 1.2	81 ± 5
Cloisite 20A	36 ± 3	31.6 ± 1.7	36 ± 8
Cloisite 20A MB	45 ± 3	44.6 ± 1.5	49 ± 5

Tab. 5:
Predicted impact strength of different PPm/NC, calculated using US and NIR with 5 wt-% inorganic content of nanoparticles (MB = masterbatch processing).

Furthermore, these first results show that it is possible to monitor the mechanical properties of the final nanocomposites with NIR and US.

Summary

We adapted extruder sensors for ultrasonic measurements (US), for NIR, UV/VIS and Raman spectroscopy and for light scattering/particle monitoring (PM) measurements at the end and at different positions along the extruder.

We used different off-line methods to determine particle size, dispersion (intercalation/exfoliation) and mechanical properties of different nanoparticles and nanofillers (layered silicates) in PPM and PA6. The different analytical methods were SEM, TEM, Raman, FTIR, Rheology and mechanical testing.

The suitability of the methods to determine in-line in real-time was verified for particle size, degree of exfoliation, change of processing conditions and mechanical properties of PPM and PA6 NC.

We could determine particle size, dispersion (intercalation/exfoliation: shear thinning exponent) and mechanical properties (impact strength) in-line in real-time in the melt during extrusion by correlation of off-line values with different in-line methods.

Furthermore, it was possible to measure different dispersion states (degree of intercalation/exfoliation) caused by different processing conditions by using the shear thinning exponent.

References

- [1] A. Leuteritz, B. Kretschmar, D. Pospiech, F.R. Costa, U. Wagenknecht, G. Heinrich: Industry-relevant preparation, characterization, and applications of polymer nanocomposites.— in: Polymeric nanostructures and their applications. Vol. 2: Applications / Ed. H.S. Nalwa.— American Scientific Publishers, 2007, pp. 99-151 (ISBN 1-588-83070-7)
- [2] D. Fischer, K. Sahre, M. Abdelrhim, B. Voit, V.B. Sadhu, J. Pionteck, H. Komber J. Hutschenreuter: *Compt. Rendus. Chem.* 9 (2006), pp. 1419-1424
- [3] I. Alig, D. Fischer, D. Lellinger, B. Steinhoff: *Macromol. Symp.* 230 (2005), pp. 51-58
- [4] R. Wagener, T.J.G. Reisinger: *Polymer* 44 (2003), pp. 7513-7518
- [5] M. Stephan, S. Große, U. Blankschein, M. Stintz: *Kunststoffe Plast Europe* 95 (2005), pp. 160-163
- [6] J.X. Ren, A.S. Silva, R. Krishnamoorti: *Macromolecules* 33 (2000), pp. 3739-3746