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Real Time Monitoring of Morphologic and Mechanical Properties of Polymer Nanocomposites During Extrusion by near Infrared and Ultrasonic Spectroscopy

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Summary: Extrusion is one of the most applied technologies for the processing of polymer nanocomposites for applications in automotive, electrical and packaging industrial sectors. These nanostructured materials have advantages in comparison to traditional polymer materials, so that properties like tensile strength and modulus, barrier and surface properties, electrical properties and flame retardancy will be improved. There is a need to control amount and dispersion of the nanofillers in the polymer matrix during melt processing and to control the influence of the processing conditions on the nanocomposite formation. For an adequate real time characterization it is necessary to measure directly in the extruder. Spectroscopic methods and Ultrasonic measurements are outstanding methods for this kind of in-line monitoring. This paper deals with the real time determination of the dispersion and the impact strength of polymer nanocomposites in the melt during extrusion by Ultrasonic measurements and NIR spectroscopy. These in-line measurements were correlated with off-line rheological measurements, transmission electron microscopy and mechanical test measurements by multivariate data analysis. The polymers used are polypropylene and polyamide 6. As nanofillers we used different modified layered silicates. We determined the degree of exfoliation as an indicator for the dispersion of the nanofiller in the polymer matrix for different layered silicates and at different process conditions.

Keywords: exfoliation; nanocomposites; NIR spectroscopy; real time monitoring; Ultrasonic measurements

Introduction

The main aim of this work was the monitoring of the processing of innovative multifunctional polymer nanocomposites for applications in automotive, electrical and packaging industrial sectors. These multifunctional nanostructured materials have great advantages in comparison to traditional polymer materials, such as improving mechanical properties like tensile strength and Young's modulus, barrier and surface properties, electrical properties and flame retardancy. An overview of the state of the art of industry-relevant preparation, characterization and application of polymer nanocomposites is given by Leuteritz and Kretzschmar.[1] We used extrusion to process these nanocomposites because it is the most widely applied technology for mixing and modifying of polymers with fillers in the molten state. It is necessary to control the morphology of the nanofiller in the polymer matrix during melt processing and the processing conditions on the nanocomposite formation. In this context morphology describes the dispersion of nanofillers in a polymer matrix. Off-line analysis does not display the exact condition of the material during

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the extrusion process. For an adequate real time characterization, it is necessary to take measurements directly 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 of nanofillers in nanocomposites saves time, costs and raw material. We illustrate the effectiveness of in-line near infrared (NIR) spectroscopy and ultrasonic attenuation measurements (US) to analyze polymer nanocomposites in real time. For the correlation to morphology/dispersion and mechanical properties we used as off-line techniques such as transmission electron microscopy (TEM), rheological and mechanical test measurements.

An additional important point of our investigations was to study further the influence of different processing conditions, shown on different screw speeds, on the morphology.

Morphology - Determination of Dispersion

To determine the morphology of the nanocomposites is an important point in this paper. To accomplish this we investigated different layered silicates as nanofillers in polypropylene (PP) and polyamide 6 (PA6) polymers. This means in our case the measurement of the dispersion of layered silicates in the polymer matrices. Layered silicates intercalate and exfoliate in these both polymers. Often the processed material shows a structure between these states. So it is important to quantify the degree of exfoliation of the layered silicates in the polymer matrix. Our concept was to determine the shear thinning exponent from shear viscosity measurements as a degree for exfoliation according to a proposal by Wagener.[2] We determined this shear thinning exponent by off-line rheological measurements. Then we correlated the shear thinning exponent with in-line measurements using NIR and ultrasonic attenuation spectroscopy.[3–5]

Experimental Part

The investigated polymers were PA6 (Aquamid AQ500, Aquafil Technopolymers) and PP (Moplen HP500N, LyondellBasell). For this investigation PP was blended with 5 wt.% of PP modified with maleic anhydride (Polybond 3200, Crompton). This blend is marked in the paper as mPP. For the determination of dispersion, we measured the degree of exfoliation of different modified layered silicates in PA6 and mPP. The layered silicates used are montmorillonite (MMT) and a layered double hydroxide (LDH). MMT is hydrated sodium calcium aluminium magnesium silicate hydroxide, $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$. LDH is an aluminium magnesium layered double hydroxide, $Mg_6Al_2[(OH)_{16}|CO_3] \cdot 4H_2O$, in our application modified with hydrogenated fatty acid (Perkalite F100 (AkzoNobel)).

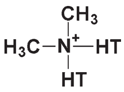
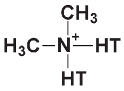
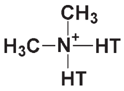
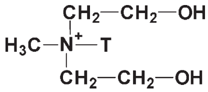
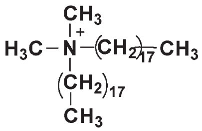
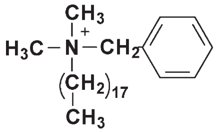
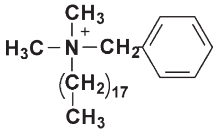
In case of the MMT we applied unmodified MMT (Cloisite Na^+) and MMTs modified with different quaternary ammonium salts (Nanofil 5, Nanofil 919, Nanofil 9, Cloisite 30B, Cloisite 15A, Cloisite 20A, Dellite 67G). The different quaternary ammonium salts used are described in Table 1.

All experiments were carried out using a Leistritz Micro 27 extruder with a measuring adapter at the end of the extruder as a bypass. This measurement adapter can be assembled with sensors for ultrasonic measurements (US), for NIR and Raman spectroscopy and for pressure and temperature measurements, shown in Figure 1.

We used different screw speeds (from 100 to 300 rpm) and different throughputs (from 6 to 10 kg/h) during extrusion. The temperatures were 200 °C for PP nanocomposites and 235 °C for PA6 nanocomposites and pressures between 20 and 100 bar.

For the off-line determination of the nanocomposite properties we used TEM (sample preparation: cryo ultracutting by Leica Ultracut UCT, layer thickness 80 nm, microscope: Jeol JEM 2010, 200 keV) to get an impression of the exfoliation state. For the measurement of impact strength

Table 1.
Notation and producer of the different modified MMT and the structure of the different organic modifiers and their concentration.

Notation (trade name) and producer of the different modified MMT	Structure of the different organic modifiers	cation exchange capacity [meq / 100 g MMT]
Cloisite Na^+ (Southern Clay Products)	-	-
Cloisite 15A (Southern Clay Products)	 $H_3C-\overset{CH_3}{\underset{HT}{N^+}}-HT$	125
Cloisite 20A (Southern Clay Products)	 $H_3C-\overset{CH_3}{\underset{HT}{N^+}}-HT$	95
Dellite 67G (Laviosa)	 $H_3C-\overset{CH_3}{\underset{HT}{N^+}}-HT$	108
Cloisite 30B (Southern Clay Products)	 $H_3C-\overset{CH_2-CH_2-OH}{\underset{CH_2-CH_2-OH}{N^+}}-T$	90
Nanofil 5 (Sued Chemie)	 $H_3C-\overset{CH_3}{\underset{(CH_2)_{17}-CH_3}{N^+}}-(CH_2)_{17}-CH_3$	75
Nanofil 9 fine powder (Sued Chemie)		75
Nanofil 919 Powder (Sued Chemie)		75

HT is hydrogenated Tallow (~65% C18; ~30% C16; ~5% C14); T is Tallow (~65% C18; ~30% C16; ~5% C14).

we used the Charpy test (ISO 179/1eU). 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 (dynamical frequency sweep: 0.05 Hz to 100 Hz) at 200 °C for PP and at 235 °C for PA6 nanocomposites. The absolute value of the initial slope at low frequencies (0.05 – 0.2 Hz) was used to calculate shear thinning exponents (STE).[2]

For the correlation of the off-line data with the in-line measured data we applied multivariate data analysis (chemometric analysis). The chemometric analysis used was the PLS-1 method. This method is a mathematical procedure and reduces the measured spectra to few principle components (PC). These PC can be related to properties of the investigated material by a calibration model. An important criterion to describe the significance of

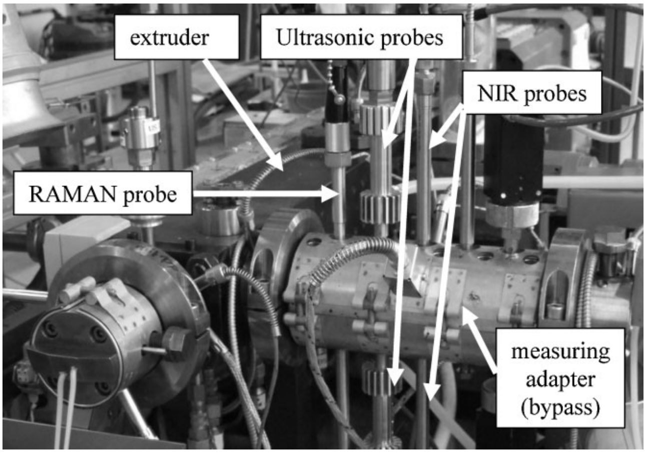


Figure 1.
Leistritz Micro 27 twin screw extruder with measuring adapters and sensors.

the calibration model is the correlation coefficient R^2 of the regression between off-line measured and in-line predicted values. For all multivariate data analysis we utilized the program UNSCRAMBLER (CAMO).

Results

Real Time Monitoring of the Degree of Exfoliation of Different PA6 Nanocomposites by Prediction of the STE

In principle, shear viscosity measurements at low frequencies show a pseudo-solid behaviour for nanocomposites with layered silicates.[2,6] With decreasing frequency, an increasing viscosity is induced by interaction of the single layers of the layered silicates. Thus, the higher the absolute value of the STE, the better the filler is exfoliated in the nanocomposite.

We used different modified layered silicates to obtain PA6 nanocomposites with different degrees of exfoliation to study the influence of the nanofiller on the exfoliation behaviour.

We analysed TEM images to get an impression of the exfoliation behaviour. The left image in Figure 2 shows a very good exfoliated nanocomposite, the system PA6 with 5% Nanofil 9. For this system we

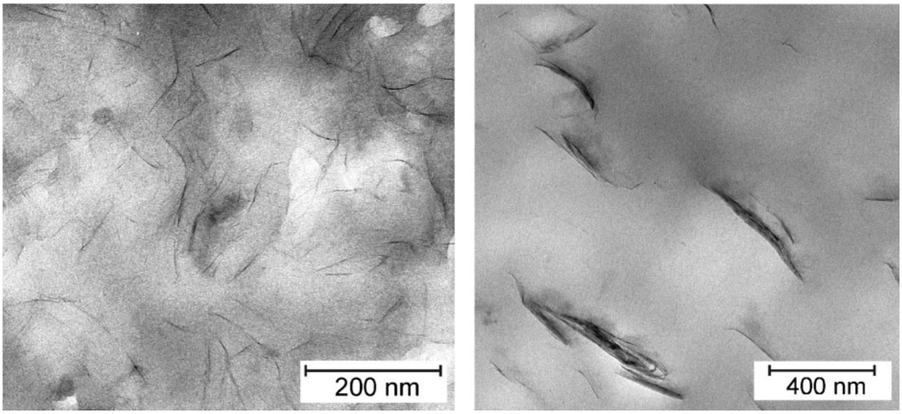


Figure 2.
TEM images of PA6 with 5% MMT Nanofil 9 (left) and of mPP with 5% MMT Cloisite 20A (right).

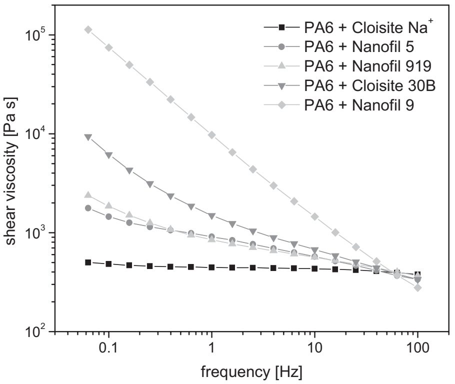


Figure 3.
Shear viscosity of PA6 nanocomposites with different MMT (5 wt.% inorganic content).

calculated the highest STE. In comparison to this system, shows the right image an intercalated nanocomposite, the system mPP with 5% Cloisite 20A, where the exfoliation is poor.

Figure 3 shows the shear viscosity curves of PA6 nanocomposites from 0.05 to 100 Hz. There is a clear increase of the shear viscosity at low frequencies for nanocomposites with modified layered silicates in comparison to nanocomposites with unmodified layered silicates.

The shear viscosity at low frequencies for especially for PA6 modified layered silicates (Nanofil 9 and Cloisite 30B) show a higher shear thinning exponent than the nanocomposite with unmodified layered silicate (Cloisite Na$^+$) and those with modified layered silicates, which are not optimized for use in PA6 (Nanofil 5). These shear thinning exponents were used for a correlation with the in-line NIR and US spectra by multivariate data analysis using the PLS method. The results of these calibrations, in order to the correlation coefficient R^2, show for both in-line methods a good agreement with the off-line STE, calculated from the shear viscosity measurements with the rheometer ARES. All values are listed in Table 2.

These results demonstrate that the state of exfoliation during extrusion for nanocomposites with different modified layered silicates can be measured in real time using chemometrics.

For the real time monitoring of the degree of exfoliation we investigated three PA6 nanocomposites, PA6 with Nanofil 5, Nanofil 919 and Nanofil 9. As model for the prediction of the STE by NIR spectroscopy and Ultrasonic measurements we used the calibrations shown in Table 2. The results show, that we could clearly differentiate between the three nanocomposites for both in-line methods. There is a remarkable accordance of the two independent in-line methods, results are shown in Figure 4.

As a result of this monitoring we could demonstrate that the best exfoliation behaviour (highest STE) was found for Nanofil 9, a good exfoliation for Nanofil 919 and the lowest exfoliation for Nanofil 5 in PA6.

Real Time Monitoring of the Degree of Exfoliation of a PP Nanocomposite at Different Process Conditions by Prediction of the STE

We determined the degree of exfoliation for modified PP with the layered silicate Cloisite 20A at different screw speeds to investigate the influence of the screw speed on the exfoliation behaviour. The real

Table 2.
Measured and predicted shear thinning exponents (STE) of different MMT in PA6 (5 wt.% inorganic content); ARES: STE, calculated from shear viscosity measurements; NIR: STE, calculated from NIR in-line spectra; US: STE, calculated from in-line ultrasonic attenuation spectra.

Layered silicate in PA6	mean meas. STE (ARES)	calc. STE (NIR) $R^2 = 0.990$	calc. STE (US) $R^2 = 0.993$
Nanofil 9	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

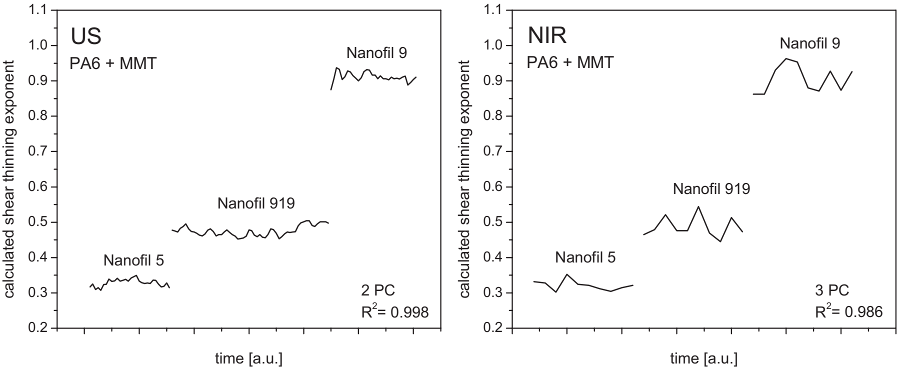


Figure 4.
Real time predicted shear thinning exponents of PA6 with Nanofil 5, Nanofil 919 and Nanofil 9, calculated by ultrasonic attenuation and NIR absorbance.

values of the shear thinning exponents (Table 3 and x-axis in Figure 4) were calculated off-line from shear viscosity measurements. The predicted shear thinning exponents (Table 3 and y-axis in Figure 4) were calculated using ultrasonic attenuation and NIR spectra. For the correlation of the in-line data with the shear thinning exponents we used again the multivariate data analysis.

Results of this calibration are shown in Figure 5. We could differentiate clearly between the various screw speeds from 100 to 300 rpm.

Table 3.
Measured and predicted shear thinning exponents (STE) of mPP/C20A (5 wt.% inorganic content); ARES: STE, calculated from shear viscosity measurements; NIR: STE, calculated from NIR in-line spectra; US: STE, calculated from in-line ultrasonic attenuation spectra.

nanocomposite	mean meas. STE (ARES)	calc. STE (NIR) $R^2 = 0.990$	calc. STE (US) $R^2 = 0.993$
mPP + Cloisite 20A (100 rpm)	0.14 ± 0.02	0.14 ± 0.02	0.14 ± 0.03
mPP + Cloisite 20A (200 rpm)	0.22 ± 0.03	0.22 ± 0.02	0.25 ± 0.03
mPP + Cloisite 20A (300 rpm)	0.40 ± 0.05	0.40 ± 0.02	0.39 ± 0.03

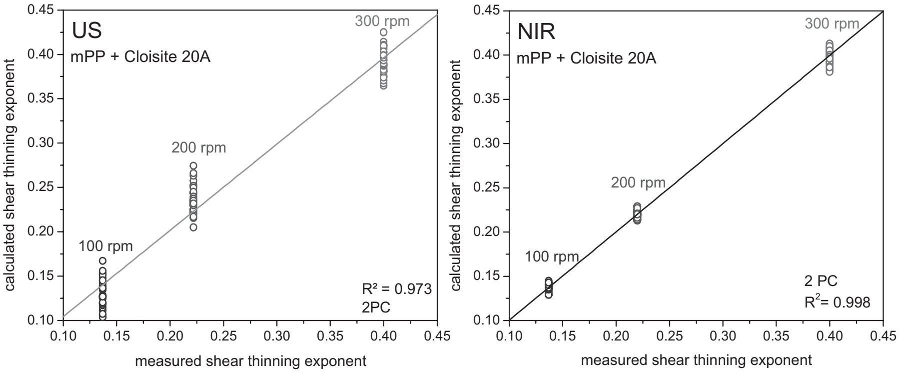


Figure 5.
Predicted shear thinning exponents of modified PP with Cloisite 20A at different screw speeds (calibration).

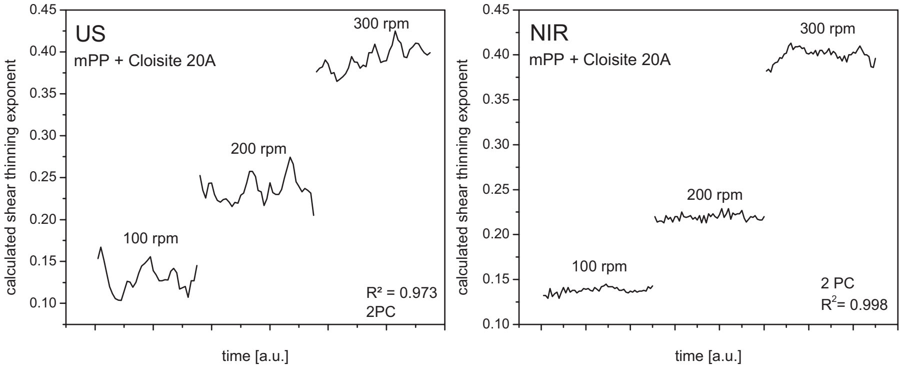


Figure 6.
Real time predicted shear thinning exponents of modified PP/Cloisite 20A, calculated by ultrasonic attenuation and NIR spectra, at different screw speeds.

After this calibration, we used the calibration model for monitoring the STE by NIR and Ultrasonic attenuation for the mPP/Cloisite 20A nanocomposite during processing at different screw speeds. Also in this real time monitoring we found a remarkable agreement for both methods, shown in Figure 6.

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 during extrusion. In the first experiments, we tried to correlate off-line measured impact strength of different modified PP nanocomposites with in-line NIR and Ultrasonic spectroscopy. Table 4 shows the measured impact strength (Charpy) for pure modified PP and for different PP nanocomposites and the calculated impact strength with multivariate data analysis using NIR and US spectra. The nanofillers used were two single layer silicates (Dellite 67G, Cloisite 20A) and one with a layered double hydroxide (Perkalite F100). Additionally, we extruded mPP/Cloisite 20A with a masterbatch extrusion procedure.

The correlation plots for both methods are given in Figure 7. The x-axis shows the measured impact strength and the y-axis shows the calculated impact strength by a calibration with NIR and Ultrasonic data. Both in-line measurements show a good correlation to the off-line determined impact strength. Thus, one can distinguish between two samples with different impact strength values. Therefore, these preliminary results show that it is possible to monitor mechanical properties of the final nanocomposites with NIR and Ultrasonic measurements.

Table 4.
Measured and predicted impact strength of different mPP nanocomposites, calculated using US and NIR (5 wt.% inorganic content; MB: masterbatch processing).

Layered silicate in modified PP	meas. impact strength [kJ/m^2]	calc. impact strength [kJ/m^2] NIR $R^2 = 0.999$	calc. impact strength [kJ/m^2] US $R^2 = 0.942$
pure mPP	108 ± 6	108.7 ± 1.5	103.4 ± 1.6
mPP/Perkalite F100	81 ± 13	81.0 ± 1.2	81 ± 5
mPP/Cloisite 20A MB	45 ± 3	44.6 ± 1.5	49 ± 5
mPP/Dellite 67G	37 ± 3	38.5 ± 1.8	36 ± 8
mPP/Cloisite 20A	36 ± 3	31.6 ± 1.7	36 ± 8

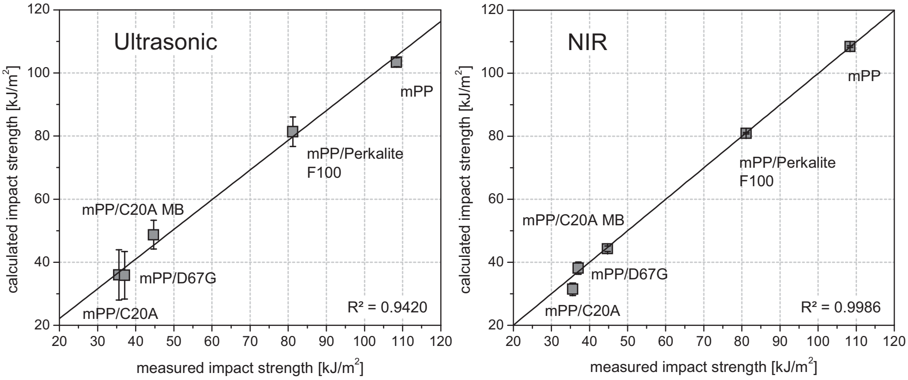


Figure 7.
Predicted impact strength of different mPP nanocomposites.

Conclusion

We were able to show that on-line sensors for ultrasonic measurements and for NIR spectroscopy would be successfully adapted at the end of an extruder.

We used different off-line methods to determine dispersion (exfoliation) and impact strength of various nanofillers (different modified layered silicates) in modified PP and PA6. These different analytical methods were TEM, rheological measurements and mechanical testing.

Ultrasonic attenuation measurements and NIR spectroscopy can be used to determine in-line in the melt during extrusion in real time the degree of exfoliation as a quantity for dispersion by using the shear thinning exponent from shear viscosity measurements, and the impact strength, as an example for the measurement of mechanical properties, by correlation with off-line determined values.

Furthermore, it is possible to measure different dispersion states caused by different processing conditions and caused by different modified layered silicates. Thereby we found an improvement of the exfoliation state at higher screw speeds and we could distinguish between different modified layered silicates.

The combination of both independent analytical methods, NIR spectroscopy and Ultrasonic measurements, which are in excellent agreement, give ancillary a high reliability of the achieved process monitoring results.

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