In-line monitoring of polymer extrusion processes with ultrasonic attenuation spectroscopy

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Introduction

Direct control of extrusion processes during polymer nanocomposite (NC) production by in- and on-line monitoring is important for the following reasons. First, real time information about nanofillers and polymer can provide an improvement of the quality of the nanocomposite by controlling the process parameters immediately. Then, effective production process by real time analysis of dispersion and distribution of nanoparticles saves time, costs and raw material.

The aim is to find out the opportunities of ultrasonic spectroscopic measurements as technique for in-process monitoring to characterize polymer nanocomposites in the melt. Therefore, different approaches were performed in the past [1, 2].

An in-line process application in extrusion was built up with a measuring adapter and adapted ultrasonic probes. Measurements of polymers with nanofillers of different particle sizes and different nanofiller concentrations were carried out.

Materials

The investigated polymer in this paper was polyamide 6 (PA6). It is an important polymer e.g. for automotive purposes. For the determination of particle sizes in the polymer matrix we used silicon dioxide nanoparticles with different diameters (Geltech 0.2 and 0.5, Aerosil R9200) and furthermore two types of talcum particles with different primary particle sizes (Luzenac A3 and A7).

Experimentals

All experiments were carried out at a Leistritz Micro 27 extruder with an end adapter at the die. The processing temperatures were 235 °C for PA6 NC. The measurement adapter was developed from the IPF and can be assembled with sensors for ultrasonic measurements (US), for NIR, UV/VIS and Raman spectroscopy, for light extinction measurements and for pressure and temperature measurements. The ultrasonic measurements were performed using self made ultrasonic probes and software. With this equipment we were able to measure and monitor ultrasonic data in-line in real-time.

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 of the nanofillers in the PA6 matrix.

For the correlation of off-line data with the in-line measurements we used multivariate data analysis (MVA). The MVA was performed to find models in a calibration procedure for the correlation of particle sizes with the in-line data. Then, we used these models to predict unknown particle size of nanofillers in real time in a validation procedure.

Results of measurements

The extrusion process was performed by adding the nanoparticles described above to a PA6 polymer melt with different concentrations. Ultrasonic attenuation spectra of the NC melts with a spectral range of 3-10 MHz were measured during extrusion, shown in figure 1.

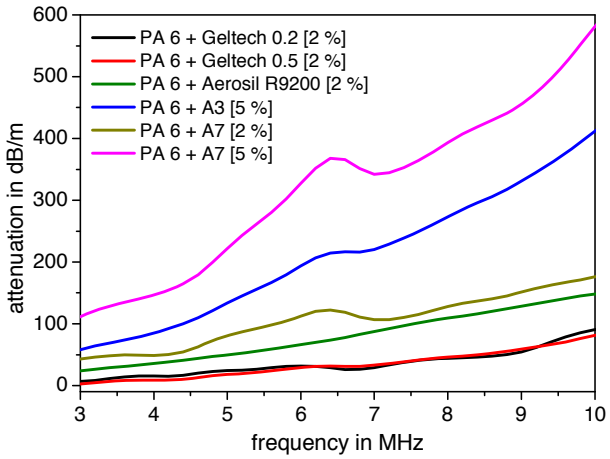

Fig.ure 1: Ultrasonic attenuation spectra of the different NC melts.

We can see a strong dependence of the attenuation spectra on the particle size and on the particle concentration. After extrusion, SEM was used to determine the real particle sizes in PA6.

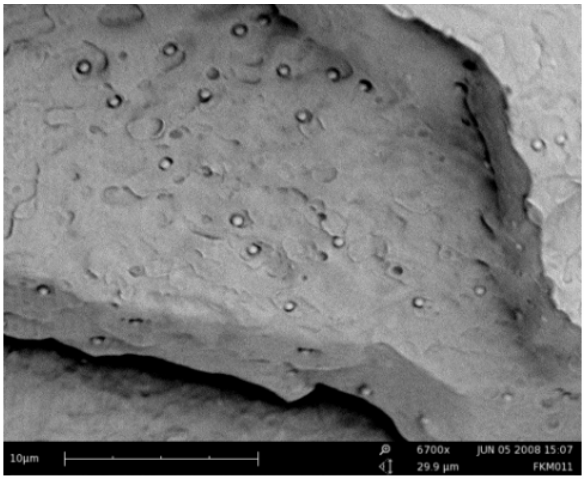

Figure 2: SEM image of Geltech 0.5 nanoparticles in PA6.

As an example, figure 2 shows Geltech 0.5 particles in PA6. The mean particle sizes of all nanoparticles are shown in table 1 and table 2, together with the results of MVA.

Results of multivariate analysis

First of all, a principle component analysis (PCA) was performed to detect differences of the ultrasonic spectra of the different NC mathematically.

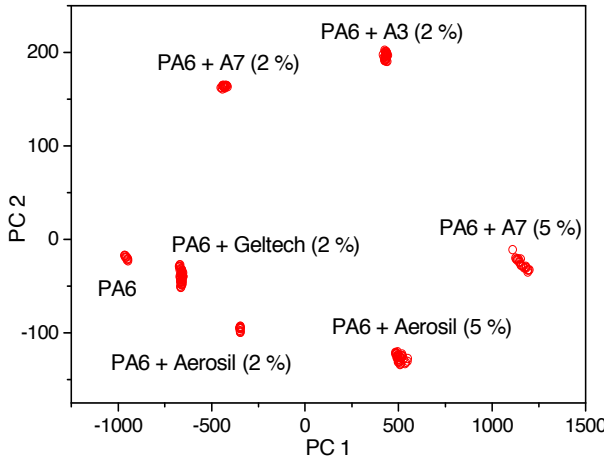

Figure 3: MVA of ultrasonic attenuation spectra (PCA results).

Figure 3 shows the reduction of the frequency range to just two principle components (PC). The measured spectra for the different nanocomposites with either different nanoparticles or amounts can be distinguished very well.

We used the off-line SEM results of the particle sizes to build a multivariate model with the ultrasonic attenuation spectra for the prediction of particle sizes by performing a partial least squares (PLS) regression.

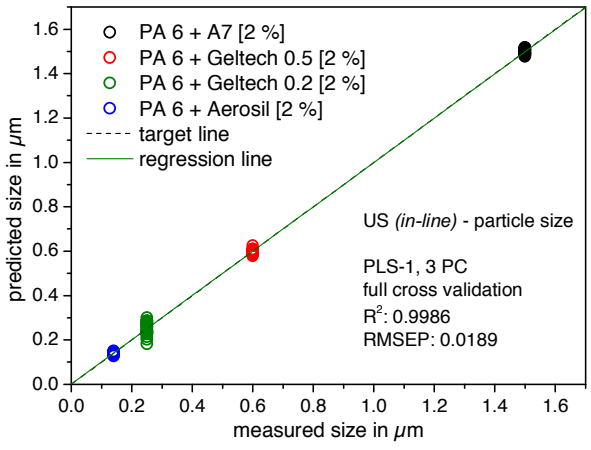

Figure 4: Prediction of particle sizes by ultrasonic attenuation spectra (PLS-1 results).

Figure 4 shows a calibration plot of the PLS regression. A good correlation between the ultrasonic spectra and the particle size can be found with the use of only three principle components in case of 2 wt.% nanofiller concentration.

Table 1 and Table 2 show an overview of the SEM measured particle sizes compared with predicted particle sizes calculated by real time ultrasonic attenuation spectra.

particles (5 wt.%)	**av. particle size (SEM) [nm]**	**calc. particle size (US) [nm] 2 PC $R^2 = 0.997$**
SiO_2 (Aerosil R9200)	140	160 ± 40
Talcum A3	1100	1099 ± 25
Talcum A7	1500	1500 ± 60

Table 1: Predicted particle sizes with 5 wt.% content of particles.

particles (2 wt%)	**av. particle size (SEM) [nm]**	**calc. particle size (US) [nm] 3 PC $R^2 = 0.998$**
SiO_2 (Geltech 0.5)	600	600 ± 30
SiO_2 (Geltech 0.2)	250	240 ± 60
SiO_2 (Aerosil R9200)	140	138 ± 12
Talcum A7	1500	1500 ± 20

Table 2: Predicted particle sizes with 2 wt.% content of particles.

In case of both NC with different concentration of nanoparticles, a good correlation of ultrasonic attenuation spectra to the particle size can be found.

Conclusions

We performed extrusion to produce polymer nanocomposites of polyamide 6 with different nanoparticles. We adapted ultrasonic sensors at the end of the extruder to measure ultrasonic attenuation spectra of the nanocomposite melt in real time.

We determined the particle sizes of the different nanoparticles using scanning electron microscopy. Then, by applying multivariate data analysis on the ultrasonic attenuation spectra, we predicted the particle sizes of nanoparticles in a polyamide 6 melt in real time. A good correlation between the prediction and the off-line measurements was found.

Ultrasonic attenuation spectra as a real time method thus can be used for the prediction of particle sizes of nanofillers in polymer matrices.

References

[1] D. Fischer et al., GIT **11** (2006), 1017

[2] I. Ahlig et al., Macromol. Symp. **230** (2005), 51