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Microphotometric Detection of Particles/Inhomogeneities in Flowing Polymer Melts

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Summary: By application of different unique microphotometric sensors it is possible to detect and quantify disturbing particles (gels, unmolten resins, black spots, additive agglomerates, bubbles) within a flowing polymer melt in realtime during extrusion processing. These particles result in disadvantageous optical and mechanical properties of a final polymer product. Sensors can be adapted inline and online to different extruders at various positions. This seems to give technical and economic benefit to quality control and process optimisation in polymer processing.

Keywords: extrusion monitoring; gels; light scattering; quality control; sensor

Introduction

Achieving best possible product qualities with production costs as small as possible has to be challenged these days, whereas this is not limited to polymer processing. New applications for polymer products demand an increased level of process- and quality-control. These new applications include for example optical elements, storage media, multi layer pipes, high voltage cable coatings and medical parts (micro-tubes). The smallest amount of particulate inhomogeneities disturbs not only the optical sensation of such "high–sophisticated" products, it results in disadvantageous mechanical properties too. Failure and as an extreme case the breakdown of a polymer component is possible because of this fact. Disturbing particles in a polymer melt are for instance so called gels and black spots, gas bubbles, incomplete molten resins and insufficient dispersed additive agglomerates, but also environmental dust or insects. Figure 1 shows such a particulate

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inhomogeneity included in one layer of a multi-layer pipe as it is used for fuel transportation or heating circuit water. It can be strongly assumed that the failure was caused by inclusion of an impurity. Under pressure load a crack might be generated at this special position.

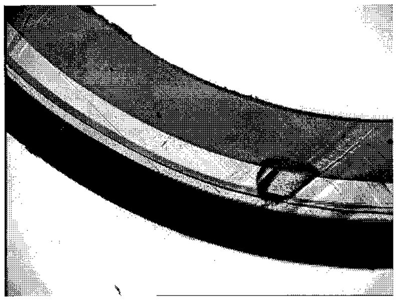


Figure 1. Failure of a multi-layer pipe caused by a particulate inclusion, light-microscopic image of a fractured surface

Polymer industry tries to meet the mentioned concerns by optimising extruder designs and processing conditions and the application of melt filters. But it can not be excluded that there are particulate inhomogeneities remaining in the final product. Therefore instruments for quality control have to be implemented to the polymer process. From the current state of the art quality control is done in most of the cases offline by laboratory methods like film observation or microscopic with a quantitative image analysis afterwards. These procedures lead to a big lag of time between the moment of taking a sample and getting a quality result. During laboratory analysis product quality of the running process is unknown. Either the polymer is directed to a buffer store during that time or low quality batches have to be accepted. Besides these laboratory procedures are high degree time and cost consuming. Because of these circumstances development and testing of novel inline particle sensors which provide realtime quality data of a flowing polymer melt was claimed to be objective of our work. These particle sensors are based on a microphotometric measuring method which is already applied to different industries (i.e. brewing-, refinery-industry) for process control and quality assurance. Now a transfer of this technique to polymer processing has to be tackled. To be accepted by the user an inline particle monitoring system has to give realtime results without constraining polymer processing. It has to handle extrusion typical temperatures and pressures up to 300°C and 150bar, environmental pollution and vibrations. Surrounded by these harsh conditions an inline particle sensor has to give accurate results for a long lifetime.

Experimental

Extruder setup

Three different extruders which belong to the technical equipment of the IPF Dresden can be used to adapt the microphotometric sensors. The first of them is a single-screw extruder "Davo Viskosystem". Furthermore two corotating twin-screw extruders (ZSK40-Coperion Werner & Pfleiderer, Micro27-Leistritz) have been applied on microphotometric measurements. Such twin-screw extruders can be mounted modularly and therefore optimal extruder configurations for special processing tasks are possible. With these three extruders lots of microphotometric measurements have been carried out. Extruder setup and processing parameters have been chosen within an array as shown in Table 1 according to different test series.

Table 1. Array of extrusion parameters for microphotometric measurements

length / diameter	(L/D)	20 ... 32
mass flow	(kg/h)	5 ... 20
screw speed	(min^{-1})	50 ... 400
barrel temperature	(°C)	170 ... 260

Process-Micro-Photometer (PMP)

These sensors are based on light scattering principle. Figure 2 shows the interactions between an incident light beam and a particle. Light will be absorbed and scattered by this particle, whereas reflection, deflection and refraction contribute to the scattering effect. By summation of all these energy loss effects the term "extinction" is defined. As a special features of these photometric sensors the highly focused measuring volume with a diameter of about 30μm has to be mentioned. Because of this fact sensors are called *Micro*-Photometer. By minimising the measuring volume the abidance of more than one particle within can be eliminated and therefore multiple scattering effects will not appear.

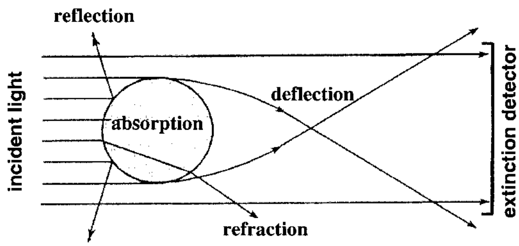


Figure 2. Interactions of an electromagnetic field (light) with particles [1]

A second feature of microphotometric particle sensors is the ability to record and analyse signals with differing time resolution from minute- to millisecond-scale (Figure 3).

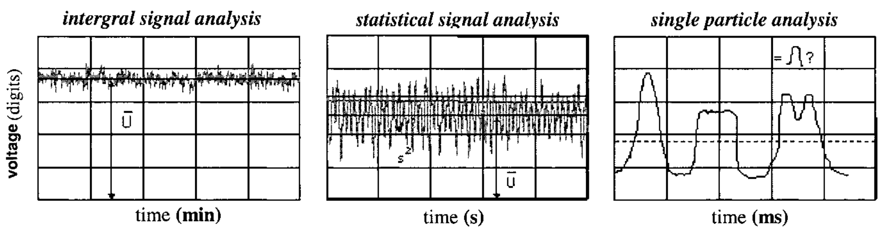


Figure 3. Signal analysis with the Process-Micro-Photometer [2]

With integral signal analysis a classical turbidimetry can be done. From a combination of integral and statistical signal analysis it is possible to calculate average particle sizes of diluted polymer systems with the help of the *Lambert/Beer`s* – law: [3]

$$E = \ln\frac{1}{T} = A_V \cdot c_V \cdot L$$

E – extinction
T – transmission
c_V – volume concentration of particles
L – optical path length
A_V – volume specific extinction cross-section

Volume specific extinction cross-section A_V depends on the main particle characteristics (size and optical properties) and the wavelength of the applied laser. This correlation was described by *Mie* in detail.[4] There are approximations for these calculations too.[5]

$$A_V = f(d,\lambda,m)$$

A_V – volume specific extinction cross-section
d – particle diameter
λ – laser wavelength
m – relative refractive index

By using these theoretical calculations it is possible to estimate particle dimensions of a diluted polymer system from extinction measurements with the Process-Micro-Photometer if volume concentration of particles, its optical properties and some sensor parameters are known. On the other hand signal analysis in stochastically mode enables the Process-Micro-Photometer to perform a single particle analysis. Time resolution in a millisecond-scale separates single particle impulses. These voltage impulses are caused by particles interrupting the laser beam. By calibration with model systems impulse amplitudes can be correlated with particle sizes.

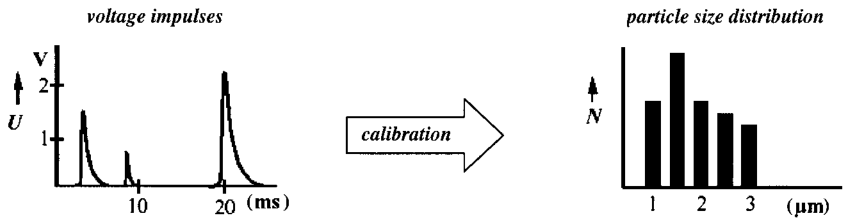


Figure 4. Transformation of single particle impulses to a particle size distribution

Most of such single particle counters provide a multi-channel analysis whereas particles are classified by a number of size classes. As it can be suspected by the term "counter" size and concentration of particles can be determined simultaneously by using this method. Thus it is suitable for applying to purity control where very low concentrated particles have to be detected. Today three different Process-Micro-Photometers are present. First of them is a patented [6] prototype-inline sensor PMP691 which can be adapted to the head of an extruder via a special slit die as it is shown in Figure 5. Figure 6 demonstrates its optical setup. The beam of a laser diode is directed by a beam splitter via diverse optical elements to the centre of the slit die. Interactions of particles within the polymer melt will be recognised by an extinction detector. Additional there is a backscatter detector implemented to receive backscattered light from particles. A reference detector controls

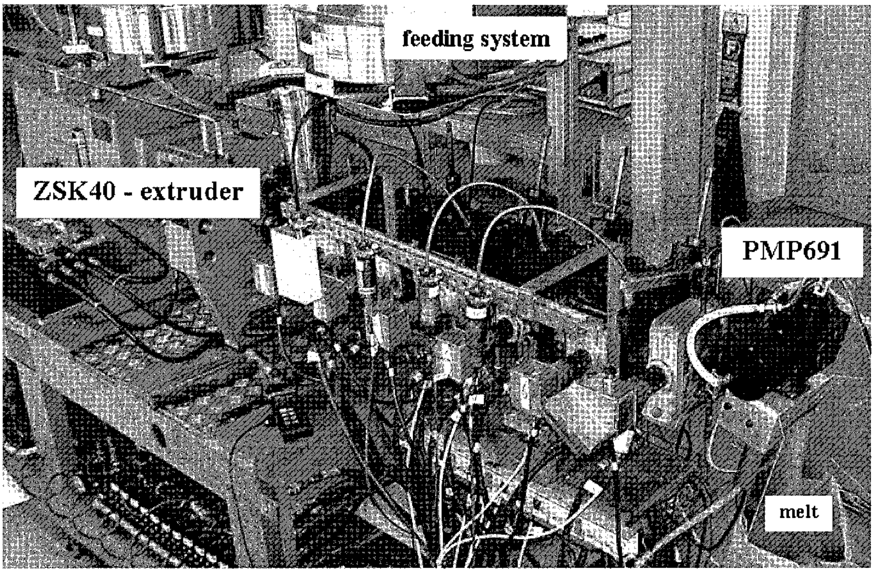


Figure 5. Adaptation of the Process-Micro-Photometer PMP691 to a ZSK40-extruder

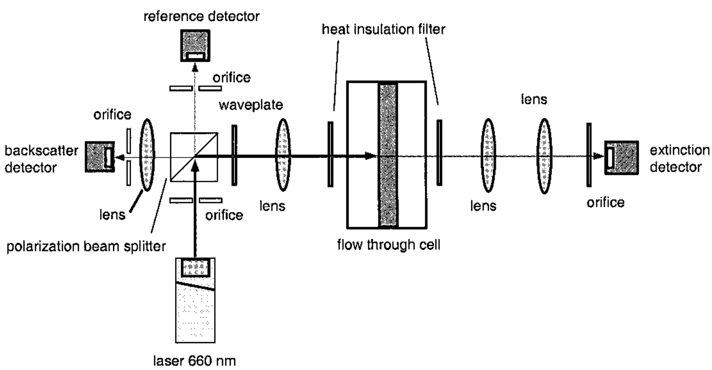


Figure 6. Optical setup of the Process-Micro-Photometer PMP691 [2]

the intensity of the incident laser light. By simultaneous registration of extinction and backscatter signals a maximum of information can be obtained from the particles. The temporal run of these two voltage signal is displayed exemplary in Figure 7. As a negative aspect of using the Process-Micro-Photometer PMP691 high pressure losses within the slit die has to be kept in mind. Maximum extrusion flow rates are limited by this fact. One way to avoid that kind of process restriction is taking the sensor out of the main polymer stream. For that reason a bypass type of the Process-Micro-Photometer has been developed (Figure 8). PMP692 was designed as a purity sensor by combining the optical setup of an extinction alignment with the signal processing unit of a single particle counter.

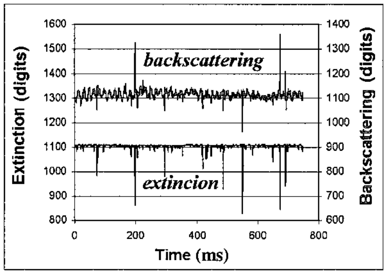
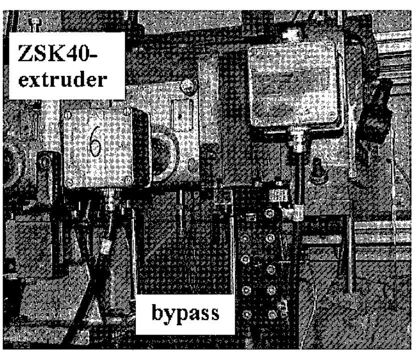


Figure 7. Extinction and backscatter signals of the Process-Micro-Photometer PMP691

This enables the PMP692 to determine particle concentration and classify those particles into different size classes. One non-negligible disadvantage of this sensor solution is its online property, its not working inline. Some time always passes by until a melt sample reaches the measuring volume of the sensor from the actual process. So realtime character of a measurement is damped down. There are additional problems like a large required space for installing the sensor to the extruder and arising waste.



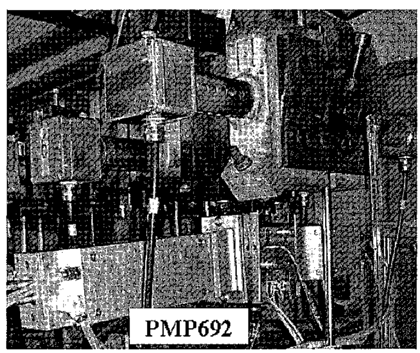
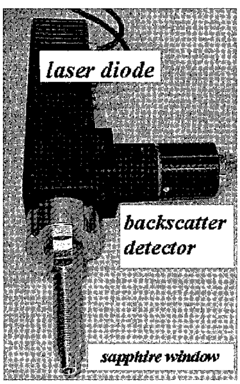


Figure 8. Adaptation of the bypass Process-Micro-Photometer PMP692 to a ZSK40

The third sensor to be introduced challenges these issues. The PMP693 is designed as a screw-in microphotometer as it is shown in Figure 9. It works inline and is compatible to all standard dynisco threaded holes which are usually used for temperature or pressure sensors. So a high degree flexibility and a minimum process impairment was achieved. As illustrated in Figure 9 the screw-in microphotometer PMP693 is adapted to the same sandwich plate as the bypass version via a standard dynisco threaded hole. Its measuring mode is predefined by its design to a backscattering measurement. A laser light beam is emitted by a diode and focussed by several optical elements into the polymer melt close to the sapphire window. If there are any reflecting particles within the melt the amount of light which is scattered at 180° will be registered by a detector. In comparison to an extinction setup backscattering is not as sensitive to very small particles. That points to the main disadvantage of this sensor type.



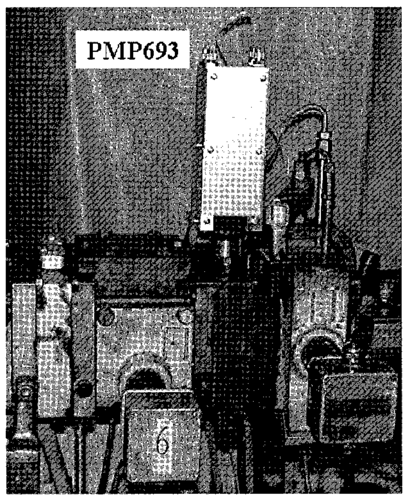


Figure 9. Adaptation of the screw-in Process-Micro-Photometer PMP693 to a ZSK40

Results and Discussion

Transparency control

As it has been mentioned already it is possible to perform a classical turbidimetry by applying the integral signal processing mode of the microphotometric sensors. Pure polymers are completely transparent in molten state no matter if they are amorphous or semi-crystalline in solid state. If there are small amounts of a second polymer remaining inside the extruder for instance from processing before there will be a certain turbidity of the extruded melt. For that reason the Process-Micro-Photometer can be utilised to control if a polymer which is processed by extrusion is pure or kind of a polymer blend. In Figure 10 two extruded polymer melts with differing turbidity and their belonging transmission diagrams of the Process-Micro-Photometer are shown. A turbid melt results in a decreased transmission level because a certain amount of light is scattered by lots of small blend particles. Additional to this turbidimetry integral signal analysis is useful to control the concentration of multi-polymer melts during blend processing. Corresponding to blend composition a certain turbidity appears. Any changes of turbidity mean changes of blend concentration. Such changes result for instance from an inaccurate feeding system as it is

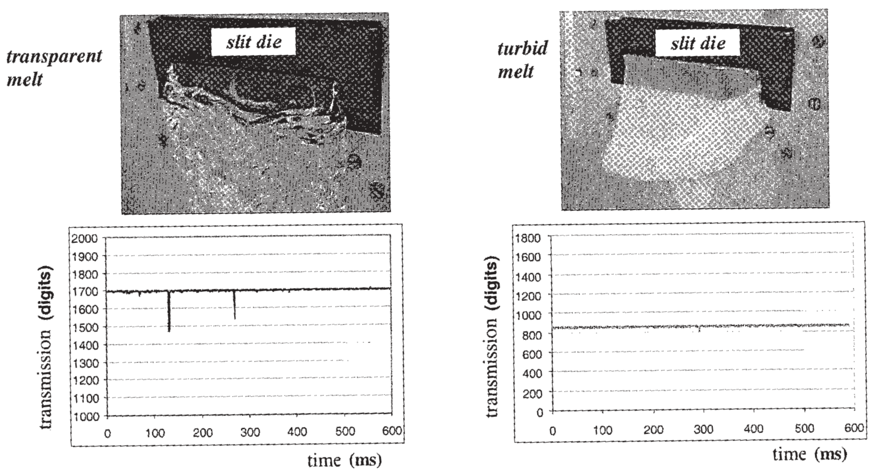


Figure 10. Static transmission signals of a transparent and a turbid polymer melt

shown in Figure 11. In this case a two component polymer blend has been extruded. During processing some technical problems with one of the two feeders appeared. As a result of this blend concentration fluctuated periodically. Figure 11 illustrates clearly that these fluctuations are transferred to the transmission signal of the microphotometric sensor.

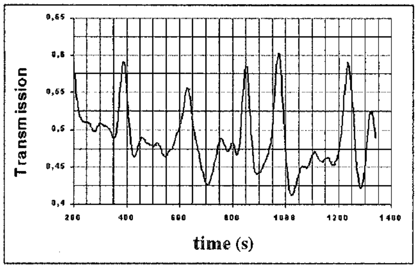


Figure 11. Periodic fluctuations of the transmission signal corresponding to concentration-fluctuations of the extruded polymer blend caused by technical feeding problems

Particle size calculation of low concentrated polymer blends

This calculation was done as described one section before. It is restricted to low blend concentrations (about 5 wt.%) because of multiple scattering effects for higher concentrated blends. At this time there are no adequate estimations in literature to eliminate these effects. With knowledge of the optical properties of both blend components and its volume concentration particle sizes can be calculated from measured microphotometer transmission values with the help of *Lambert/Beer's* – Law [3] in combination with the theory of *Mie.*[4] Volume concentrations are known from extruder feeding system and the refractive indices of both blend partners as dominating optical properties have been determined at process temperature by using a special inline refractometer. [7]

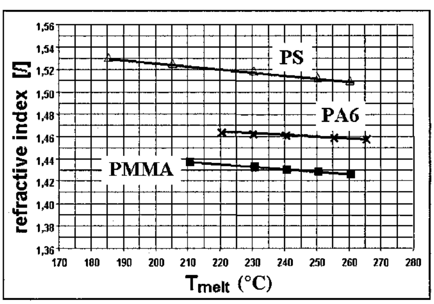


Figure 12. Temperature dependence of refractive index of PS, PA6 and PMMA measured by an inline refractometer

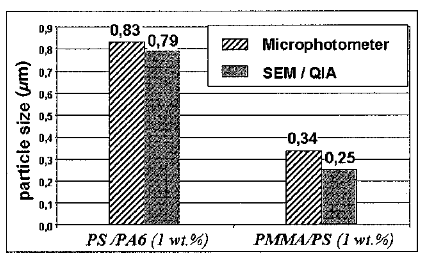


Figure 13. Calculated particle sizes from microphotometric measurements and SEM + Quantitative Image Analysis (QIA) for two low concentrated blends [8]

Temperature dependence of these indices is shown in Figure 12 exemplary for some basic polymers. Figure 13 shows some results for calculated blend particle sizes. Calculations have been carried out for a Polystyrene/Polyamide6 (PS/PA6) and a Polymethylmethacrylate/Polystyrene (PMMA/PS) blend with a concentration of 1 wt.% in each case. It can be seen from these calculations that blend particles are nano-scaled. Additional particle dimensions have been examined by Scanning Electron Microscopy (SEM) followed by a Quantitative Image Analysis (QIA). Figure 13 illustrates a good agreement with microphotometric calculations. Application of this procedure to low concentrated droplet forming additives is possible too.

Detection of model particles

All applications mentioned before are using the integral signal analysis of the Process-Micro-Photometer. This evaluation mode is characterised by a low time resolution to get information on nano-scaled high concentrated blend particles from a static transmission level. On the other hand single particle detection to perform a purity control is quite an important field of application. Larger particles (micro-scaled) have to be detected at very low concentrations which requires a different evaluation algorithm. Therefore stochastical signal processing of the Process-Micro-Photometer can be utilised. Isolation of single particle impulses is done by a high time resolution. Information on particle situation is achievable by fluctuations of the microphotometric signals. To proof sensitivity of the Process-Micro-Photometer iron- and limestone- model particles in lower micrometer range have been added to a PS/PMMA blend. Figure 14 demonstrates clearly that model particles cause fluctuations of the transmission signal. It has to be kept in mind that the PS/PMMA

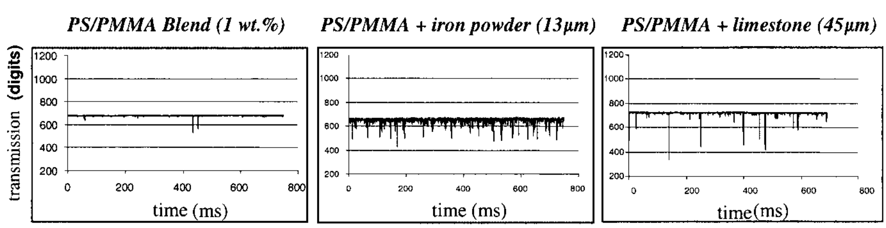


Figure 14. Microphotometric transmission signals of model particles (iron powder 13μm, limestone 45μm) added to a PS/PMMA blend (1 wt.%)

blend is already a disperse system. A large number of nano-sized PMMA particles is well distributed in a PS matrix. In contrast to a decrease of the signal level by these nano-scaled particles connected to a certain turbidity micro-scaled particles show single impulses. By applying different modes of signal evaluation Process-Micro-Photometer enables its user to watch on nano- and micro-scaled particles separately.

Monitoring of extrusion start-ups

By means of single particle measurements this sensor can be applied to control extrusion start-ups. This phase of extrusion processing is characterised by a large number of impurities within the polymer melt. Small amounts of a different polymer extruded before are still remaining inside the extruder in most of the cases. A well known problem of start-ups are so called black spots. These melt impurities result from thermal polymer degradation during extrusion stagnation. In Figure 15 microphotometric monitoring of an extrusion start-up is demonstrated. Impurities within the melt have been counted per minute by a special trigger concept. From that realtime monitoring it can be concluded at which time of an extrusion start-up process melt-quality is constantly adequate. In this special case start-up time is about one hour. Figure 16 shows the reason for that high counting rate during the first minutes of extrusion processing. Single impulses in transmission signal represent black spot impurities.

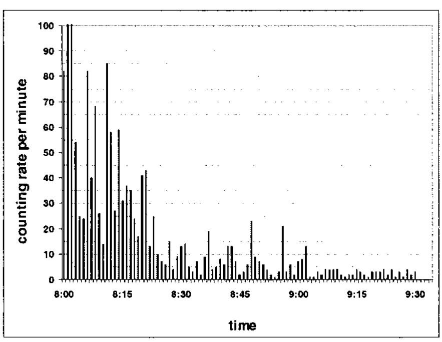


Figure 15. Microphotometric monitoring of extrusion start-up by counting impurities

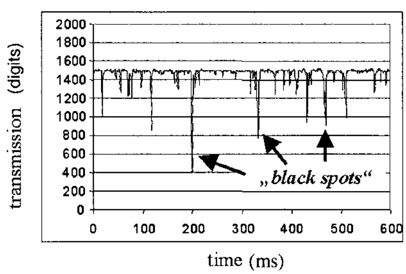


Figure 16. Single transmission impulses caused by black spots

Monitored optimising of melting process

Melting of a basic polymer as the first step before various kinds of additives are added into it is one of the most cost causing procedures in extrusion. For this reason there is a high potential of optimisation at this step. At first one main parameter to optimise melting process is configuration and length of the melting zone and with that length of the whole extruder (L/D ratio). Every centimetre of extruder length causes a lot of investment costs and therefore it has to be minimised. Secondly there is an opportunity to save running energy costs by optimising the melting zones temperature profile and extruder screw speed as well. Therefore extrusion process has to be operated at minimum temperatures and screw speeds but still assuring a homogenous melt without unmolten granules. Figure 17 demonstrates such an optimising of a melting process. As kind of a model system high melting PA granules have been added to a low melting PS matrix. Screw speed has been changed as a variable extrusion parameter. Pictures of Figure 17 illustrate the state of melting for screw speeds increased from 50min^{-1} up to 200min^{-1}. Whereas PS melt contains large granules of PA at 50min^{-1}, these particles are getting smaller with 100min^{-1} because of a larger mechanical stress connected to an increasing of melt temperature. At 200min^{-1} there are no unmolten granules left in the polymer matrix. Transmission signals correlate to this. Reduced fluctuations of the signal caused by unmolten PA particles can be observed with an increasing screw speed. As a quantitative value relative standard

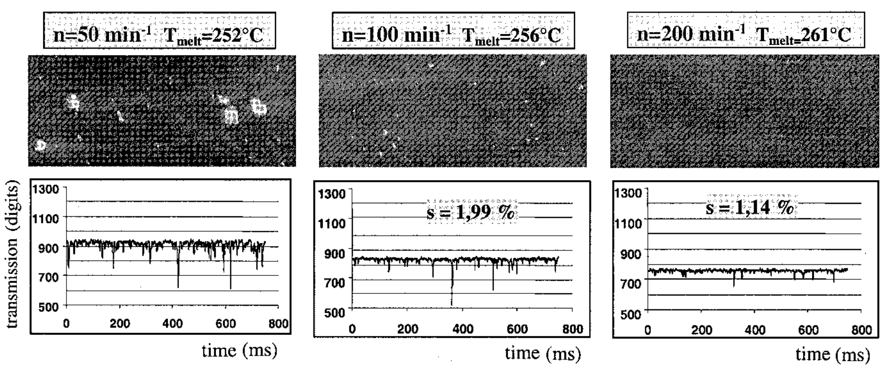


Figure 17. Melting process of PA granules in a PS matrix with different screw speeds (50, 100, 200min^{-1}), photos and microphotometric transmission signals (*s – standard deviation*)

deviation s can be used. Additional to that transmission level decreases by increasing turbidity caused by a large number of nano-scaled PA particles. In that special case 200min^{-1} seems to be the optimal extrusion screw speed.

Conclusions

From a large number of testing series the Process-Micro-Photometer (PMP) proved its suitability for applying it to extrusion processing under appropriate harsh conditions. By utilising different modes of signal evaluation a large range of particulate ingredients within a flowing polymer melt can be analysed in realtime. Integral transmission measurements provide information on concentration and size of nano-scaled blend particles whereas maximum blend concentration is limited to 5 wt.%. By observing microphotometric signals with high time resolution single particle analysis to perform an impurity detection can be applied by the user. Sensors have been used successfully for detection of black spots, gels, gas bubbles and unmolten resins. As a result of these examinations the Process-Micro-Photometer contributes to an improved quality control and process optimisation in extrusion processing because of its realtime character. At present there are three different versions of the Process-Micro-Photometer available but to get best possible measuring results each sensor has to be optimised for its special application.

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