

Microphotometric Inline Determination of Polymer Blend Morphologies during Extrusion Processing

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Received 19 January 2006; accepted 1 August 2006

DOI 10.1002/app.25235

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

ABSTRACT: A novel inline method using microphotometric measuring principle is able to determine mean particle sizes of polymer blends directly during extrusion processing. This process-micro-photometer (PMP) is adapted on a special slit die at the extruder head. Refractive indices needed for particle size calculation have been measured by an inline refractometer for all the involved polymers at molten state. For investigation, blends have been made from polystyrene (PS), polypropylene (PP), polyamide (PA6), and polymethylmethacrylate (PMMA); and the resulting blend morphologies

are found to be smaller than 1 μm in all cases. Sensor calculations show good correlation to microscopic reference measurements. Because of multiple scattering effects at larger particle number concentrations an exact particle size calculation is limited to low volume concentrations of that polymer blends because of the small blend particle sizes. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 258–262, 2007

Key words: blends; extrusion; particle size; refractive index; inline sensor

INTRODUCTION

To achieve tailor-made product qualities it is a common technique to mix various basic polymers as polymer blends. This operation is usually done on twin-screw extruders because of its special mixing characteristics. Incompatibility of most of these polymer partners results in a multiphase system with disperse droplets of the minor phase distributed in a matrix of the major phase. Blend morphology is strongly depending on process parameters during extrusion. By optimizing these parameters, product properties can be improved step by step. In general, a fine and homogenous phase morphology gives the best product performance. This extruder parameter optimization is usually done empirically, because there are no reliable models to be used for calculation up to now.

From the current state of the art blend morphologies are usually characterized by offline analysis in terms of microscopy followed by an image analysis. This procedure is quite time consuming. A sample taken from the running process has to be quenched, a cut has to be made by a microtome, and then the sample has to be etched in a specific solvent. After that the blend morphology can be characterized from the images generated by SEM or light microscopy with the help of an image analysis software. This procedure usually takes

a whole day, and so there is a very large lag of time between taking the sample and getting a result. Even though there are some methods for optimizing the sampling by using special extruder sandwich plates or a sliding barrel technique this lag of time for analysis will remain. For melt observation directly in the screw channel during the extrusion process, an extruder has been equipped with a special sapphire window.¹ This on-line visualization was used for observation of the melting phenomena of polystyrene (PS) and polypropylene (PP). A quantitative morphology characterization is not possible with this method. For laboratory use a so called “on-line morphology flow cell” is connected to a single screw extruder via a special slit die.² It consists of an optical window, a traveling microscope, and certain video equipment. As one example, PP/polyamide (PA6)-blends have been investigated by this method. Other on-line techniques using dielectric spectroscopy,³ ultrasonics,⁴ and light scattering^{5–7} are described in literature. Some of these methods are limited on very special applications. If needed input parameters are not exactly known, blend particle sizes can be determined only qualitatively. Because of their complex assembly and calculation algorithm, these techniques are often used at laboratory equipment. In many cases they are not suitable for industrial inline process measurements with its harsh conditions. From that state of the art development of a simple designed but robust process sensor for quantitative and exact inline calculation of polymer blend particle sizes for application at industrial production lines was claimed to be the objective.

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TABLE I
Selected Properties of the Used Polymers

Polymer	Grade	Producer	Crystallinity	Density (g/cm ³)	MFR (cm ³ /10 min)	Glass-transition temperature (°C)	Melting temperature (°C)
Polystyrene	PS 143E	Basf AG	Amorphous	1.05	10 (200°C, 5 kg)	85	–
Polypropylene	PP Novolen 1100N	Targor	Semicrystalline	0.91	16 (230°C, 2.16 kg)	–	163
Polyamide	PA 6 Ultramid B3	Basf AG	Semicrystalline	1.13	130 (275°C, 5 kg)	60	220
Polymethylmethacrylate	PMMA Altuglas V044	Arkema	Amorphous	1.19	2.1 (230°C, 3.8 kg)	Not specified	–

EXPERIMENTAL

Materials

For the experiments various polymer blends from PS, PP, PA6, and polymethylmethacrylate (PMMA) have been extruded with volume concentrations in a range from 0.25 to 50 vol %. Detailed information on some selected properties of the used polymers is given in Table I.

Extruders

For the experiments two twin-screw extruders (ZSK40-Coperion, Micro27-Leistritz) with characteristic L/D ratios from 31 to 48 have been used. Both extruders were equipped with standard screw configurations. The throughput varied within a range from 5 to 20 kg/h at screw speeds from 50 to 400 rpm. Barrel temperature was set to 240°C.

Process-micro-photometer sensor

The process-micro-photometer (PMP) is coupled to a slit die which is connected to the extruder head by a special adapter (Figs. 1 and 2). Sensor is based on microphotometric measuring principle. A laser light beam is emitted by a laser source, and it is directed by the beam splitter to the sapphire window equipped slit die. If any particles interact with that incident laser beam they will cause a light attenuation (= extinction) which means a change of the integral signal on the extinction detector. Additional backscatter signals are recorded, for instance, if any strongly reflecting gas bubbles are within the melt. To avoid multiple scattered light a highly focused laser and a small layer thickness of the slit die (1 mm) were chosen. All experiments described in this article have been carried out with the sensor shown in Figure 1. This sensor works up to 1000 bar and 300°C. As a further development, this sensor type is followed by a smaller version which allows much more flexible extruder access because it is using 1/2 in. 20 UNF standard ports.

Particle size calculation

Calculation of particle sizes of particle collectives from photometric sensor signals is based on Lambert-Beers law:

$$E = -\ln(T) = c_V A_V L \quad (1)$$

Light extinction E (T = transmission) is depending on the volume concentration of the particles c_V , the optical path length L , and the volume-specific extinction cross section A_V .

Mie theory gives the correlation of this parameter with the refractive indices of the minor and the major

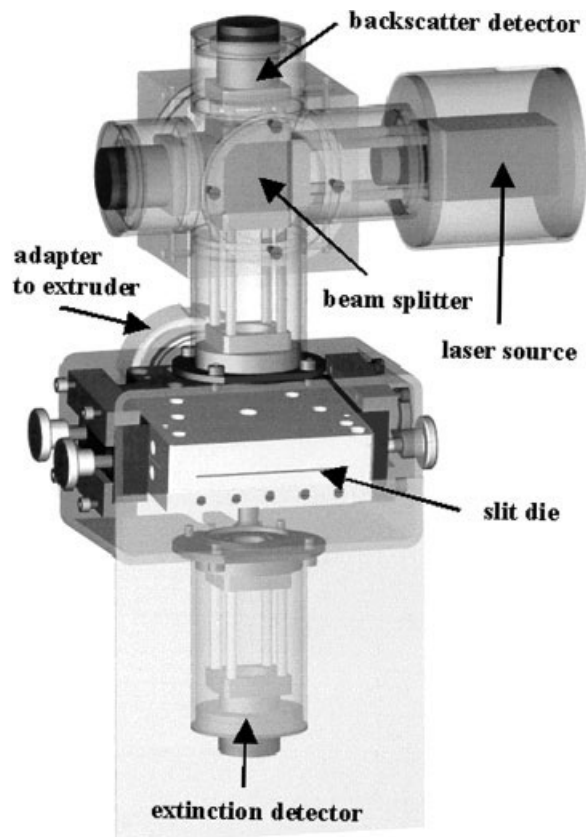


Figure 1 Process-micro-photometer (PMP), optical sensor setup.

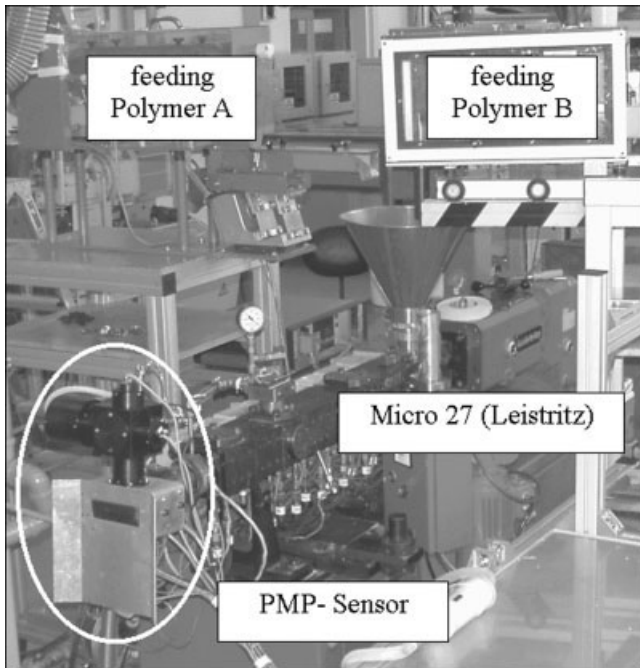


Figure 2 Polymer blend extrusion on a twin-screw extruder (Micro27-Leistritz) combined with an inline PMP sensor.

blend partner (m_{PolymerA} , m_{PolymerB}), the wavelength of the laser light λ , and with the polymer blend particle size x .

$$A_V = f(m_{\text{PolymerA}}, m_{\text{PolymerB}}, \lambda, x) \quad (2)$$

If all these parameters are known, blend particle size can be calculated from a measured light extinction. Volume concentration of the extruded polymer blend is given by the feeding ratio. Wavelength is defined from the used laser source, optical path length by the slit die height. An exact particle size cal-

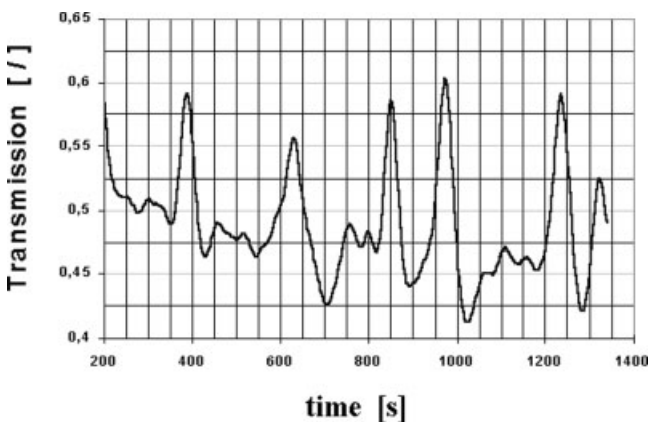


Figure 3 Periodic fluctuations of the light transmission signal caused by periodic fluctuations of polymer blend concentration.

ulation is strongly depending on exact input values for refractive indices of both blend partners at processing temperature. For that purpose no data can be found in literature. Therefore, a tailor-made inline refractometer from ABBE-type was used to determine refractive indices for all analyzed polymers at various melt temperatures.

Morphology analysis is limited on low concentrated blend systems. If particle concentration is too large, multiple scattering effects prevent exact particle size calculation, because there is no more linear correlation between extinction E and volume particle concentration c_V in terms of Lambert–Beers law.

RESULTS AND DISCUSSION

Control of blend concentration

First of all, described particle sensors can be used for inline control of stability of polymer blend concentration. Feeding systems are not working exactly constantly in some cases, especially, if they are operated outside of their working range. This leads to fluctuations of blend concentration and thus to unwanted changes in blend morphology. Because of that fluctuations, melt turbidity is changing slightly, which can be observed by light transmission measurements (Fig. 3). The transmission signal is shifting periodically by a changing number of scattering particles within the active measuring cross section because of the periodical changes in volume concentration caused by an irregular operating feeding system.

Determination of refractive indices

For calculation of mean blend particle dimensions, refractive indices of both involved polymers are needed at processing conditions. These values can be found in literature only at room temperature. Figure 4 dem-

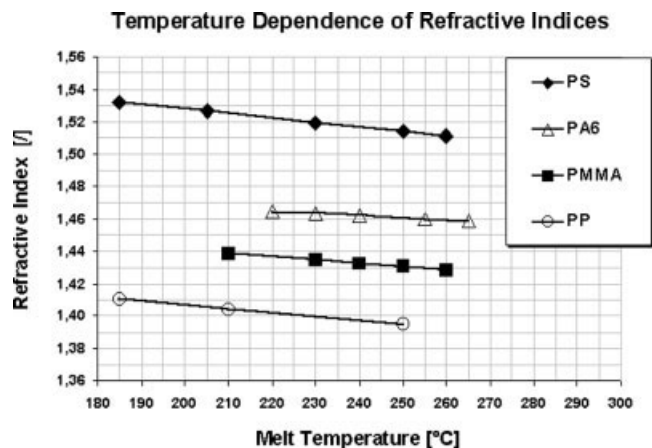


Figure 4 Refractive indices of four basic polymers at various melt temperatures.

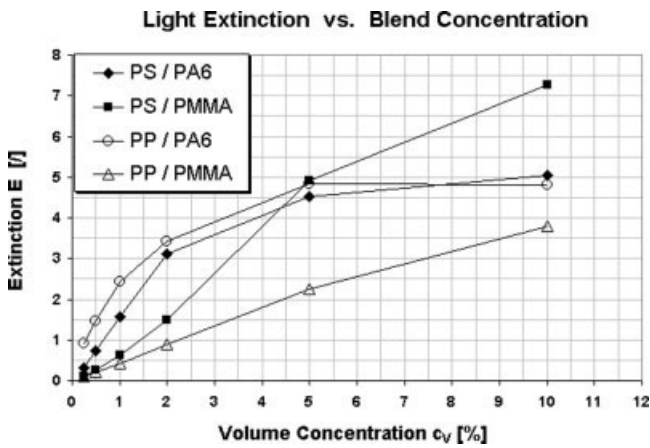


Figure 5 Light extinction measured by the PMP-sensors for different blend concentrations.

onstrates a strong linear temperature dependence of refractive indices for all the used polymers determined by an inline-melt-refractometer. Optical properties of a blend system are described by the relative refractive index calculated from the value of the disperse phase divided by the value of the matrix phase. A strong extinction effect by a strong light scattering can be expected for blends with strongly differing refractive indices at melt temperature.

Determination of polymer blend particle sizes

Figure 5 shows the measured light extinction over blend volume concentration. These values are depending on blend particle size as well as optical blend properties which means refractive indices of both blend partners. Curves for PS/PMMA and PP/PMMA are nearly linear up to 10 vol %. For PS/PA6 and PP/PA6 curves discontinue linearity already at about

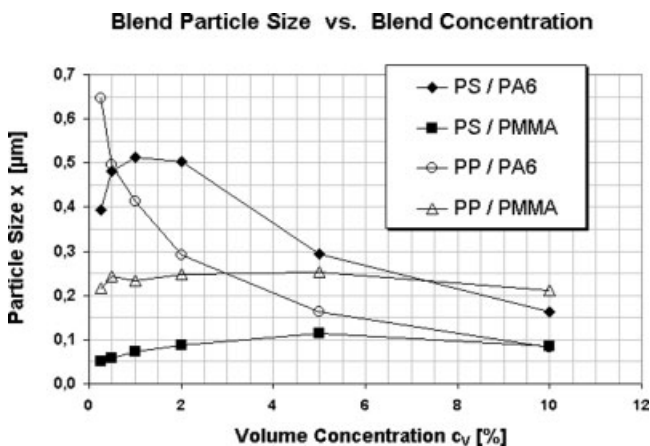


Figure 6 Calculated particle size from measured light extinctions for four blends at various concentrations.

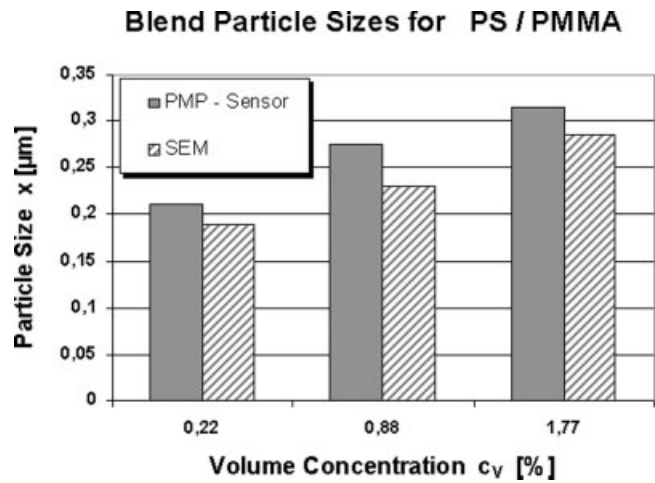


Figure 7 Correlation of PMP-sensor results to SEM measurements for a low concentrated PS/PMMA blend.

2 vol % which means leaving of the Lambert-Beer's range. From that point there will be increasing errors in particle size calculation with increasing blend concentration because of multiple scattering effects.

In Figure 6 calculated particle sizes for all examined blends are displayed for various concentrations. At first blends of PMMA with PS and PP show fine morphologies of about 0.1 µm for the PS/PMMA and 0.25 µm for the PP/PMMA blend. There is a slight increase of blend particle size with increasing blend concentration because of coalescence effects. Blends of PA6 with PS and PP form larger particles of about 0.5 µm for concentrations less than 2 vol %. The indicated decrease of particle size with increasing concentration is not corresponding to real morphology changes. As mentioned earlier this is due to errors in size calculation for concentrations larger than 2 vol % because of multiple scattering effects when Lambert-Beer's range is left.

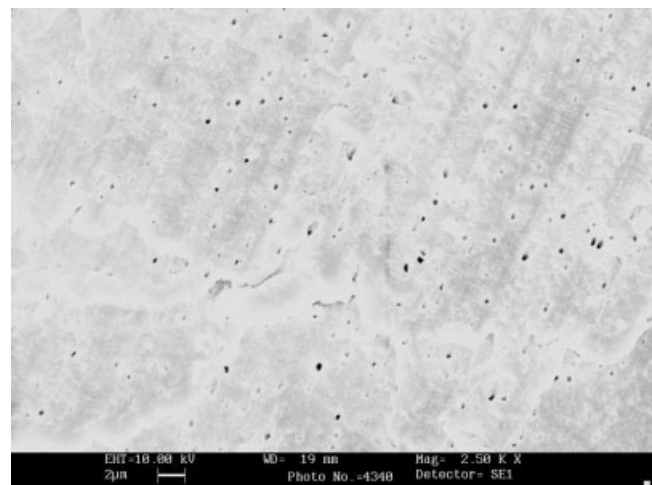


Figure 8 SEM image of a PS/PMMA blend at 1.77 vol %.

In conclusion blend morphology of the completely amorphous PS/PMMA blend is the finest followed by PP/PMMA with its one low-melting semicrystalline partner. High-melting PA6 results in larger blend particles in combination with PS and PP. Nevertheless, all morphologies show particles smaller than 1 μm . This leads to enormous particle number concentrations even at low blend volume concentrations, which is the reason for calculation disturbing multiple scattering.

Correlation to reference measurements

Blend morphology results of the PMP-sensor have been compared with classical morphology characterization method using SEM followed by quantitative image analysis (Fig. 7). Results are shown exemplary for a PS/PMMA blend at low blend concentrations where no multiple scattering will occur. With this graph good correlation between microphotometric and reference measurements is proofed. Furthermore, the already mentioned slight increase of blend particle size with an increasing blend concentration because of particle coalescence effects is demonstrated.

In comparison with this diagram a SEM-picture of this polymer blend at 1.77 vol % is shown in Figure 8 to give an illustration of the present blend morphology.

CONCLUSIONS

Described inline PMP-sensors can be applied to characterize blend morphologies in real-time during extrusion process. Results show that blend particles are less than 1 μm for the four examined blends. This is the reason for enormous particle number concentrations, which limits maximum blend volume concentrations for accurate particle size calculation on 2.10 vol % depending on particle size and optical blend properties in terms of refractive indices of both blend partners. For higher concentrations, only qualitative changes in particle situation can be observed.

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