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Modelling and simulation of fluorescence in polymer melt strands of polyester resin and polypropylene

Gregor Gerstorfer *, Bernhard G. Zagar

Institute for Measurement Technology, Johannes Kepler University, Altenbergerstrasse 69, 4040 Linz, Austria

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A B S T R A C T

To expand the knowledge of the extrusion process in co-rotating twin-screw extruders, an optical measurement system was previously introduced (Gerstorfer et al., 2013) [1] to acquire residence time density functions. One of the key problems, occurring with the measurement setup, is investigated in this contribution: the penetration depth of the exciting light and the fluorescence intensity at the melt strand surface was previously unknown. Simulations based on Beer–Lambert's law in combination with experimentally acquired optical parameters of the processed material result in useful assertions. In this paper, the comparison of simulation results for different kinds of material allow to interpret future measurement results more properly.

1. Introduction

In polymer extrusion, the comprehension of the extrusion process, which is influenced by mixing mechanisms, the developed flow pattern, and reaction and heat transfer processes, has to be deepened. Therefore, comparable characteristics of extruders are defined; one of them is the residence time density function. Its shape can give an impression of the longitudinal mixing behaviour, and its first and second order statistical moments (mean residence time and variance) are quantitative numbers which can be used for comparison. The residence time density function changes significantly with changes in mass throughput and screw speed, which are externally controlled, and also with changes of screw configurations. Since screws can be modularly configured (at least at the investigated types of extruders), the influence of increasing or decreasing the number and intensity of kneading elements can be quantified with the residence time density function. An example of a residence time density and distribution function is shown in Fig. 1. To obtain the residence time density function, a measurement setup was developed, which was introduced in previous works [2,1]. A small concentration—small enough to not influence the steady state of the extrusion process—of tracer (a batch of 20% daylight fluorescent pigment Swada HMP Lunar Yellow 27 and 80% polyester resin) is injected at the intake zone of an extruder, and the time dependent tracer concentration is acquired at the extruder exit. For that purpose, a UV-light source illuminates evenly the melt strand at the extruder exit and a spectrometer (Hamamatsu MiniSpectrometer C10082CAH) is used to measure the fluorescence intensity of the melt. Since the polymer melt itself fluoresces in a different part of the spectrum (visible blue) than the used pigment ($\lambda_{\mathrm{fluor}} = 527$ nm), the intensity of the fluorescence of the pigment is a measure for the tracer concentration. Fig. 2 shows a schematic of the measurement setup. Hence, the residence time density function can be taken as an impulse response of the extruder, which is, by analogy to systems theory, a linear, time invariant system. Linearity in this approach is referred to the tracer input. This means, that a steady extrusion process is regarded as the system

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* Corresponding author. Tel.: +43 732 2468 1345; fax: +43 732 2468 9233.

E-mail address: gregor.gerstorfer@jku.at (G. Gerstorfer).

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which is impulsively excited. So the proof of linearity has to be taken out with regard to tracer. Accordingly, Fig. 3 shows the measurement results of a series of measurements using different amounts of tracer. Due to gain variations during the measurement, the result is not exact; nevertheless it shows that the shape of all resulting curves is the same. This is verified by the included subplot, which shows that all measurement results lie on top of each other after normalization. So we assume that the system behaves linearly in the observed range.

The modelling of the illumination of the melt strand using a UV light source, which is in the setup mentioned above a high power UV LED spot operating at $\lambda_{\text{in}} = 375$ nm in combination with a collimating lens, is presented in the next section. With the resulting simulation model, the influence of an inhomogeneity of the melt strand's pigment distribution on the fluorescence distribution is investigated. Results are discussed in the subsequent conclusion.

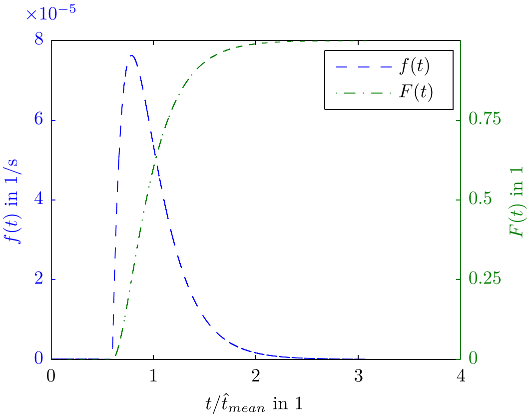

Fig. 1. Shape of the residence time density function $f(t)$ and the residence time distribution function $F(t)$. The time axis is normalized by the mean residence time $\hat{t}_{\text{mean}}$.

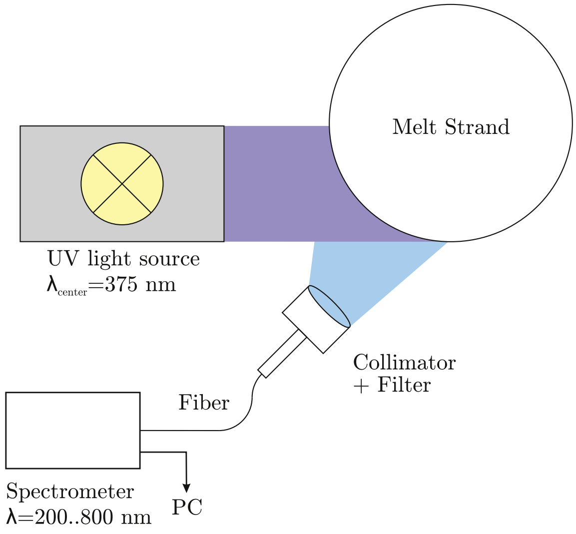

Fig. 2. Schematic of the measurement setup. The UV light source illuminates the melt strand, the spectrometers acquires via a collimating lens and a filter, which blocks the excitation wavelength, the fluorescence of the daylight fluorescent pigments contained in the polymer melt.

2. Modelling

The beam is modelled as a collimated light source impinging onto the melt strand in radial direction. Boundary effects as reflection when entering the melt strand are neglected in this consideration. Furthermore, the melt strand is modelled as a cylinder with radius R containing homogeneously distributed fluorescent pigments. The polymer attenuates the luminous flux of the impinging light according to Beer–Lambert's law

$$I(x) = I_0 e^{-\alpha(\lambda_{\text{in}})x}, \tag{1}$$

with x – penetration depth, I_0 – incident intensity at surface, $I(x)$ – penetration depth dependent intensity, and $\alpha(\lambda_{\text{in}})$ – absorption coefficient of the polymer melt at the wavelength of the incident light. So parts of the incident UV light are absorbed by the material, which are either transformed into heat or emitted as fluorescence light. The probability of emitting fluorescence light when a pigment absorbs UV light is given by the quantum efficiency QE. Since only UV light absorbed by pigments inside a volume element can excite fluorescence, the fluorescence flux of the distributed source can be calculated as

$$\Phi_{\text{fluor}} = \iiint_{V_{\text{illum}}} C \cdot QE \cdot \frac{dI_{\text{absorb}}(x)}{dx} dxdydz \tag{2}$$

with C – concentration of pigments, $I_{\text{absorb}}(x) = I_0 e^{\alpha(\lambda_{\text{in}})x} (1 - e^{-\alpha_{\text{Pigment}}(\lambda_{\text{in}})x})$ – by pigments absorbed flux and $\alpha_{\text{Pigment}}(\lambda_{\text{in}})$ – absorption coefficient of the used pigment. The integration border is given as the illuminated volume of the polymer V_{illum} which forms the distributed light source. The derivative of the absorbed flux with respect to the penetration depth is due to the above mentioned absorption of UV light in an infinitesimally small volume element. Furthermore, the fluorescence of the tracer particles is the measurand, so its concentration C as well as its quantum efficiency QE appear in Eq. (2).

Fluorescence is a stochastic process, hence its emission is isotropic [3] and each point of excitation becomes a point source (hence the denominator $4\pi r^2$ in Eq. (3)). Subsequently, the fluorescence intensity transmitted to the surface of the melt strand can be calculated using again Beer–Lambert's law (see Eq. (1)) and the absorption coefficient $\alpha(\lambda_{\text{fluor}})$ of the polymer melt at the fluorescence wavelength by integrating over the penetration depth dependent distributed light source:

$$I_{\text{fluor,out}}(R, z, \varphi) = \iiint_{V_{\text{illum}}} K \cdot \frac{e^{-\alpha(\lambda_{\text{in}})x - \alpha(\lambda_{\text{fluor}}) r(x,R,z,\varphi)}}{4\pi (r(x,R,z,\varphi))^2} dxdydz,$$
$$\text{with } K = C\,QE\,I_0\,\alpha(\lambda_{\text{in}}). \tag{3}$$

The attenuation of impinging light by pigments is neglected in Eq. (3) since it is scaled by its concentration and therefore negligible. The above introduced illuminated volume is modelled along the radial direction of the melt