Measuring the Residence Time Distribution in a Twin Screw Extruder with the Use of NIR-Spectroscopy

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ABSTRACT: The mean residence time (MRT) and the residence time distribution (RTD) of polypropylene in a twin-screw extruder was determined directly in-line with the help of near infrared (NIR) spectroscopy and the use of an UV-absorber as tracer. Different experiment alignments such as screw speed, mass throughput, back pressure as well as tracer content and their influence on MRT and RTD have been investigated. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39919.

INTRODUCTION

The residence time is the (mean) amount of time that a polymeric material spends in a processing system (i.e., the time from entering to leaving the specific system). In our case, the residence time is referred to the time that a polymer particle needs from the hopper to the end of the die in a twin or single-screw extruder. For a homogenous material exposure, the residence time in an extruder barrel or in the extruder die should be uniform. However, in reality, there are a lot of circumstances leading to non-uniform residence time. In a twin-screw extruder, the developed residence time for every fluid element is non-uniform due to back mixing as well as wall adherence on the barrel wall or the screw surface. Therefore, a distribution of residence times is developed depending on different machine alignments as well as the polymer (formulation) itself.[1,2]

The residence time distribution (RTD) has a major influence on the final product quality as it represents the time of material exposure to temperature, pressure as well as mixing and shearing geometries. The RTD can influence the material both in a positive (homogenization) and in a negative (material degradation) way.[3,4] Therefore, several attempts to measure this time have been carried out. The most common way to measure this time is the use of a specific tracer material, which is given into the extruder feed. The concentration of this tracer at the exit stream is then determined. A wide variety of different tracer types and methods of detecting the concentration of the tracer have been investigated. A few examples of tracers that have been used are fluorescent tracers such as perylene,[5] NaCl,[6] TiO2,[7,8] iron powder,[9] a CaCO3 masterbatch,[10] NaNO3[11] as well as dif-

ferent color dyes.[12] Different methods, for the detection of the concentration are available in literature leading from offline methods,[6,9] where the extruded string is divided in parts and the concentration is measured, to on-line and in-line determination of the concentration like optical methods,[7,8] ultrasonic devices,[10,13] electrical methods,[11] Raman spectroscopy,[1,13] and even visual spectroscopy.[12,13]

All the above described in-line methods use a calibration method, which connects the spectral data or the electrical properties to the concentration value. This calibration method is very time consuming due to the fact that in most cases, if the matrix material is changed, the calibration needs to be redone. With our method, no calibration is needed and the RTD can be measured in-line and matrix independently as it detects the tracer (concentration) directly, in-line and in real-time by measuring the wave number and intensity of the specific UV-absorber peak at 6475 cm^{-1}. In this study, we varied the feed rate, screw speed, back pressure, tracer concentration, and determined the process settings influence on the minimum as well as mean residence time (MRT) and RTD.

EXPERIMENTAL

Materials

The isotactic Polypropylene (PP) homopolymer HC600TF (melt flow index (MFI) 2.8 g/10 min; 230°C/2.16 kg) was used for the investigations. It was supplied by Borealis, Linz, Austria. As tracer the UV-absorber Tinuvin 791 from BASF AG, Germany was used.
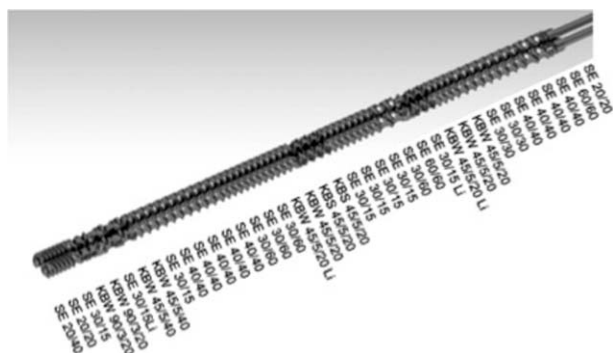
The investigations were carried out on an intermeshing, co-rotating twin-screw extruder Theysohn TSK30/40D (Theysohn

Table I. Experimental Settings as Well as Minimum and Mean Residence Time and Variance

Sample	Feed rate (kg/h)	Screw speed (rpm)	Back pressure (bar)	Tracer concentration (g)	Minimum residence time (s)	Mean residence time (s)	Variance (s^2)
S01fr	6				170	242	610
S02fr	8				136	193	709
S03fr	10	200			111	159	540
S04fr	12				98	139	358
S05fr	14		0		86	126	421
S06ss		100			135	206	894
S07ss		150		10	124	173	542
S08ss		200			111	159	540
S09ss		250			101	147	462
S10ss		300			99	140	362
S11bp	10		30		108	170	738
S12bp			60		111	181	840
S13bp		200	90		120	194	1023
S14tc				5	110	145	248
S15tc			0	10	111	159	540
S16tc				20	109	178	950

Holding, Vienna, Austria). The feed rate was set from 6 kg/h to 14 kg/h in 2 kg/h steps. The tracer was added at the hopper in a single shot from 5 to 20 g/batch. The screw speed was varied from 100 to 300 rpm for a feed rate of 10 kg/h. The back pressure was generated and adjusted from 0 to 90 bar by using a melt pump in reverse mode as throttle right after the compounder. The melt temperature was set to 200°C. The different process settings can be seen in Table I. Figure 1 shows the screw design used for the investigations.
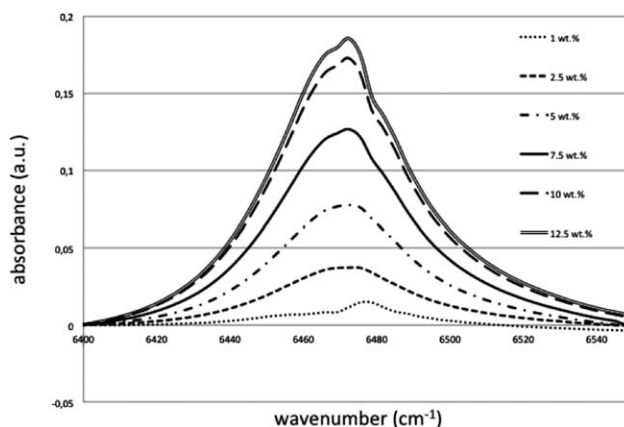
For in-line measurement a Fourier transform near infrared (FT-NIR) spectrometer from i-Red Infrared Systems (Linz, Austria) was used. The spectrometer works at a spectral range of 12000–3800 cm^{-1} (830–2630 nm) with a spectral resolution of 1.5 cm^{-1}. The probe was fixed in a $1/2''$ UNF pressure transducer bore in the center of the die. The used probe can withstand a temperature of 280°C and 200 bar and was connected to the spectrometer using fiber optics. The light coming from the probe is passing the polymer sample and then reflected by a mirror, which is mounted exactly opposite in another bore.

This combination of transmission and reflection is called transflection operation mode.

The spectral data was collected with near infrared process spectrometer software (NIPS).

For a simple determination of the RTD the measured spectra of the pure PP were taken as background at first. The RTD can then be measured by determining the wave number and intensity of the specific UV-absorber peak at 6475 cm^{-1}. To proof the direct link between the concentration of the tracer and the peak at 6475 cm^{-1}, a calibration curve was measured. We used 1–12.5 wt % of tracer (gravimetrically dosed) and measured the peak at 6475 cm^{-1}. The calibration curve (Figure 2) was measured at 200 rpm and a throughput rate of 10 kg/h. For a single spectrum 20 scans (10 scans/s) were averaged. As can be seen the higher the concentration the higher is the peak, which is consistent with Apruzze et al.[12] or Gendron et al.[14] Figure 3

Figure 1. Specific screw design for the measurements with conveying (SE) and kneading (KB) segments.

Figure 2. Calibration curve for different tracer contents at a screw speed of 200 rpm and a throughput rate of 10 kg/h.

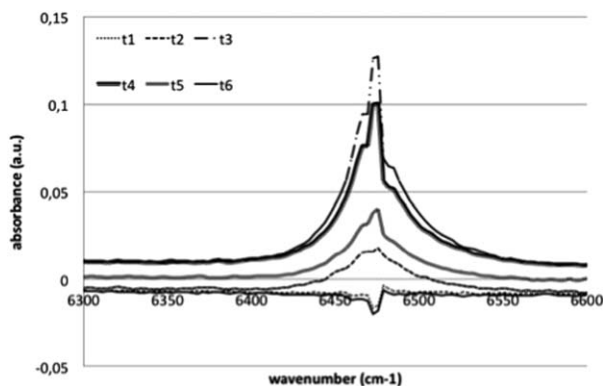**Figure 3.** Measurement of the specific UV-absorber peak of a single RTD curve for time fractions $t_1 < t_2 < t_3 < t_4 < t_5 < t_6$.

Figure 4. Influence of feed rate on the residence time distribution at a screw speed of 200 rpm and 10 g tracer.

shows the absorbance spectra for different points in time (t_1–t_6) during the measurement of one RTD curve. This curve stands for the evolution of the residence time during processing. At every time fraction, a specific peak intensity can be measured from zero to maximum and back to zero. With this information, the distribution curve $E(t)$ can be easily generated, with $C_T(t)$ standing for the concentration of the tracer or, as described before, for the intensity of the peak.[15,16]

$$E(t) = \frac{C_T(t)}{\int_0^\infty C_T(t)dt} \qquad (1)$$

Using the RTD concentration curves, the MRT of the curves can be calculated with[15,16]

$$\bar{t} = \int_0^\infty t \cdot E(t)dt \qquad (2)$$

and the width of the RTD curves can be calculated by the variance and is defined by the second moment centered on the mean[15,16]:

$$\sigma^2 = \int_0^\infty (t - \bar{t})^2 \cdot E(t)dt \qquad (3)$$

The minimum as well as the mean residence for the different feed rates can be seen in Table I.

Another possibility to describe the RTD is the cumulative distribution function. By definition this fraction of molecules that have spent a time t or less in the production line and can be calculated with[15,16]:

$$F(t) = \int_0^t E(t)dt \qquad (4)$$

The calculation of the cumulative residence time curves demonstrates at what time for example 50% of the particles have left the extruder.

RESULTS AND DISCUSSION

Figures 4 and 5 show the RTD and the cumulative distribution function for different feed rates. The amount of tracer was set to 10 g leading to a different maximum level of the curve for the different feed rates. As expected the minimum and mean RT is increasing with a decreasing feed rate, which corresponds
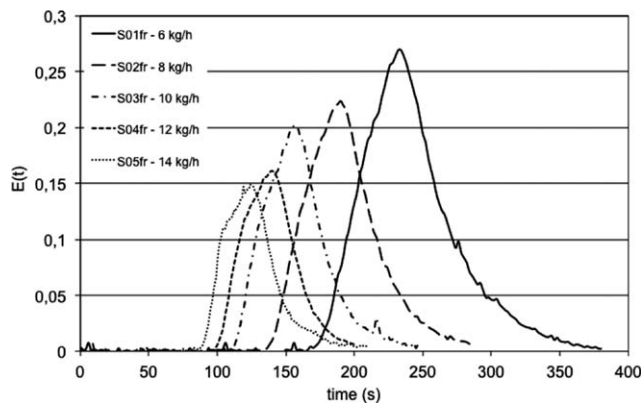
with the results of other researchers like De Ruyck,[6] Apruzze et al.,[12] Ilo et al.,[17] or Melo.[18] Furthermore, the results show that with increasing feed rate the width of the curves in Figure 4 is decreasing respectively the slope in Figure 5 is increasing. The difference of the peak intensity is due to the constant tracer content (10 g) and thus the decreasing tracer concentration with increasing feed rate. For a quantitative evaluation of the RDT the tracer concentration must be kept constant.

Figures 6 and 7 show the RTD and the cumulative distribution function for different screw speeds. It can be seen that the level gets lower and the width gets wider with decreasing screw speed. These results are correlating with similar measurements from Gendron et al.,[14] Hu et al.,[19] or Melo.[18] Regarding the curve slope in the cumulative distribution functions, the change is similar to Figure 5 as it is decreasing with decreasing screw speed. An exception in Figures 6 and 7 is the RTD curve for a screw speed of 100 rpm. The reason for the "scattering" curves is that the tracer might not be equally dispersed, which is leading to fluctuating concentration values for the tracer.

Figures 8 and 9 show the RTD and the cumulative distribution function for different back pressure settings. It can be clearly seen, that with higher back pressure the MRT is increasing and the RTD curves are shifted to higher values in time. Generally, every process setting (kneading elements,[18,20] feed rates, back pressure
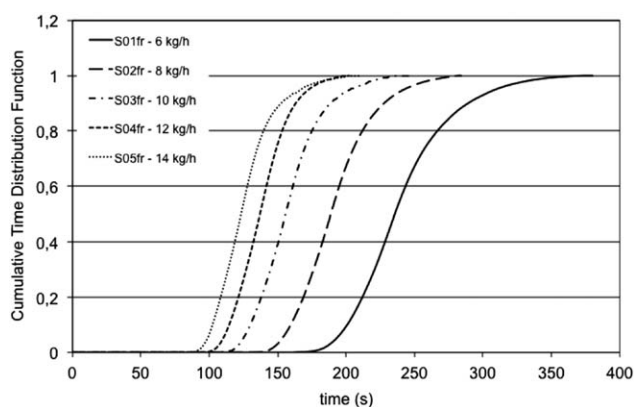

Figure 5. Cumulative distribution of the of feed rate influence on the residence time distribution at a screw speed of 200 rpm and 10 g tracer.
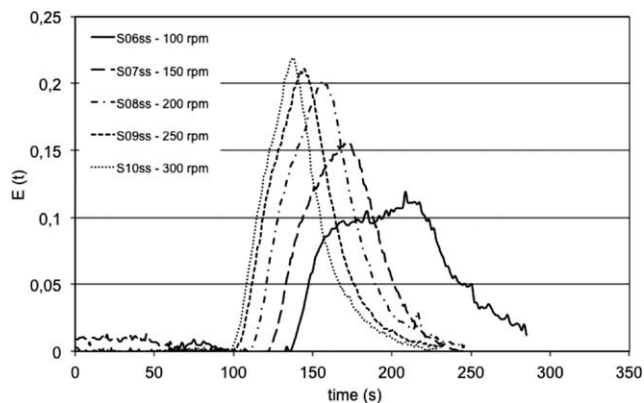
Figure 6. Influence of screw speed on the residence time distribution at a feed rate of 10 kg/h and 10 g tracer.

Figure 7. Cumulative distribution of the of the screw speed influence on the residence time distribution at a feed rate of 10 kg/h and 10 g tracer.
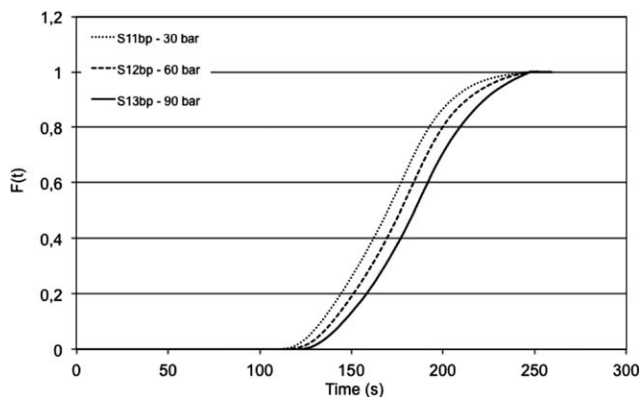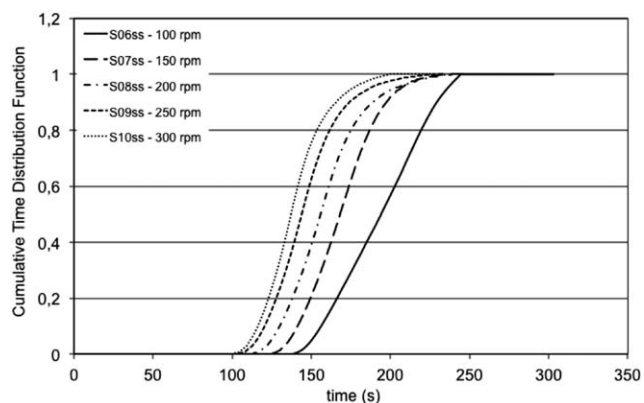

Figure 9. Cumulative distribution of the back pressure influence on the residence time distribution at a feed rate of 10 kg/h and 200 rpm screw speed.
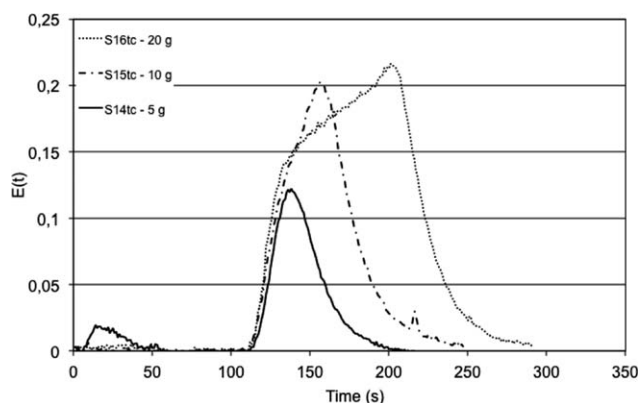

Figure 10. Influence of tracer content on the residence time distribution at a feed rate of 10 kg/h and 200 rpm screw speed.

etc.) or material parameter (viscosity,[19,21] cross-linking[22] etc.) leading to a higher machine resistance of being flown through by a polymeric particle leads to a higher residence time.

Figures 10 and 11 show the RTD and the cumulative distribution function for different tracer amounts. A higher tracer content has no influence on the minimum RT but on MRT and RTD. The variance and the total measured concentration peak are increasing with increasing tracer amount, which is covered by literature.[14,23] Another

important fact is that the curve with the highest content has much more scattering leading to an asymmetric RTD. This draws the conclusion, that there is an optimal tracer/polymer ratio (compromise between peak clarity and change in material behavior), which must be considered when setting up RTD measurements.

Table I shows that the minimum residence time is increasing from 86 s for a feed rate of 14 kg/h to 170 s for a feed rate of
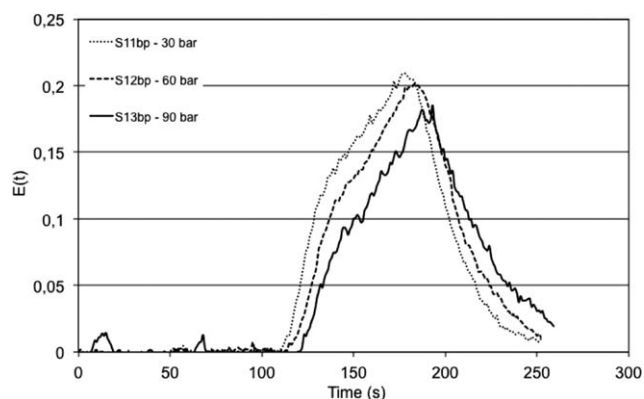

Figure 8. Influence of back pressure on the residence time distribution at a feed rate of 10 kg/h and 200 rpm screw speed.
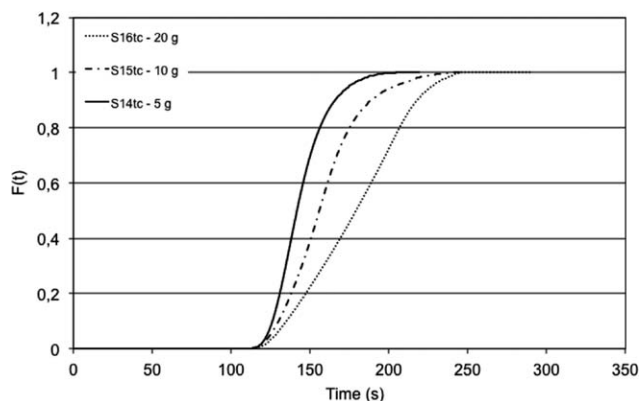

Figure 11. Cumulative distribution of the tracer content influence on the residence time distribution at a feed rate of 10 kg/h and 200 rpm screw speed.

6 kg/h. As far as the different screw speeds are regarded the minimum residence time increases from 99 s for a screw speed of 300 rpm to 135 s for a screw speed of 100 rpm. An increasing back pressure leads to increasing minimum residence time (from 108 to 120 s), MRT (from 170 to 194 s) and Variance (from 738 to 1023 s^2). The different tracer concentrations result in almost no change in minimum residence time (110, 111, and 109 s), slight increase in MRT (from 145 to 178 s), and significant increase in variance (from 248 to 950 s^2).

This means that the feed rate has a bigger influence on the minimum residence time. The MRT is nearly halved if the feed rate is set from 6 kg/h to 14 kg/h. A decrease of about a minute can be seen if the screw speed is set from 100 rpm to 300 rpm. As expected the width of the RTD curve figured by the variance ratio from Table I is getting lower with increasing screw speed. Regarding the feed rate a trend can be seen that a lower feed rate is leading to a higher variance. A direct comparison cannot be achieved due to the fact that the amount of tracer was always 10 g, which was leading to different concentration for the different feed rates and therefore to different variance values. The back pressure results show an expected dependency of the RTD and the back pressure and the tracer content must be set to an optimal level.

CONCLUSIONS

In this article, we demonstrated the great potential of measuring RTD in-line with the use of near infrared spectroscopy directly without the need for calibration. Our method offers a simple to use tool for measuring RTD curves as well as cumulative residence time curves. The investigations have been carried out on a co-rotating twin-screw extruder and with just one polypropylene but can be easily used with every other material filled or unfilled and in every extrusion process.

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