Application of Raman Spectroscopy for Determining Residence Time Distributions in Extruder Reactors

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INTRODUCTION

The time that a polymeric material spends in the barrel of an extruder is known as its residence time. In an ideal plug flow reactor, all elements of the fluid travel at the same velocity, and the residence time of each fluid element is the same.[1] However, the velocity profile developed in twin-screw extruders is nonideal because of backmixing, as well as the slow exchange of bulk material to and from a polymer film on the barrel wall or screw surfaces. Consequently, a distribution of residence times is produced for the polymer, and this distribution is known as the exit age distribution or residence time distribution (RTD). The measurement of the RTD in an extruder usually involves a stimulus-response method.[2] The extrusion process is subjected to a pulse input of a tracer at the feed port. The concentration of the tracer in the extrudate is then recorded as a function of time. A graphical plot of the tracer concentration against extrusion time produces the RTD curve. Some tracers which have been employed in the literature and the relevant property measured are given in Table I.

The average residence time can be determined during the extrusion process by the addition of a pulse of carbon masterbatch (time, $t = 0$). The time when the extrudate changes color ($t = t_{min}$) and the time when the extrudate returns to its original color ($t = t_{max}$) are recorded. The average residence time (RT) may be calculated from Eq. 1:

$$RT = \frac{(t_{max} + t_{min})}{2}.$$ (1)

This equation is valid for the mean average value of RT only with the provision that the RTD is a normal distribution. However, the RTD from an extrusion process is a skewed normal distribution, with a longer tail at the high values of time (t), and therefore the value obtained for the residence time is the "median" and not the "mean" average. The "median" average is an overestimation of the "mean" average residence time in the current system. A second problem with this method is that the operator has to discern the point at which all of the tracer has disappeared (t_{max}), which in practice is difficult and can result in error.

A previous report by Hendra et al.[3] in the literature described the application of Raman spectroscopy to the in-line analysis of molten poly(ethylene terephthalate) using a specially constructed glass die. In this study, the effects in Raman spectra were interpreted in terms of changes in molecular shape caused by varying shear rate and melt temperature. However, no studies were made of the RTD in the system.

A novel technique for the determination of the RTD for an extrusion process has been explored and reported in the current study, where off-line Raman spectroscopic measurements were employed to determine the concentration of a tracer in high-density polyethylene (BP HD5050ea). It was necessary for the tracer to satisfy the following requirements:

- It must have an intense Raman signal close to a reference band in the base polymer.
- The Raman signal should not be masked by a band in the base polymer.
- Effective mixing with the base polymer has to occur.
- It must be nonreactive under extrusion conditions.
- It must be capable of being pulsed into the feed port.

It was found that titanium dioxide (TiO_2, BDH) mixed with polyethylene under the extrusion conditions and had strong Raman scattering at $\nu(TiO)$ 650 cm^{-1}.

EXPERIMENTAL

Powdered TiO_2 (2 g) was pressed into a small pellet with a ten-ton laboratory press, so that it could be added to the extruder as a pulse. The APV MP2030 co-rotating, 30-mm fully intermeshing, self-wiping, twin-screw extruder was operated at a mass flow rate of 4 kg/h, and the

APPLIED SPECTROSCOPY

TABLE I. Tracers used to determine RTDs in extruders.

Tracer	Property measured
$KNO_3/NaNO_3$	Electrical conductivity[a]
Carbon in LDPE	Color[b]
Antimony oxide	X-ray fluorescence[c]
Iron powder	Magnetism[d]
$Mn^{56}O_2$	Radioactivity[e]

[a] D. B. Todd and H. F. Irving, Chem. Eng. Prog. **65**, 1 (1969).
[b] T. Sakai, SPE ANTEC Tech. Papers **33**, (1987).
[c] C. J. Rauwendaal, Polym. Eng. Sci. **21**, 1092 (1981).
[d] J. P. Pauux and A. Ainser, Polymer Processing Society 9th Annual Meeting, Manchester, U.K. (1993).
[e] L. P. B. M. Janssen, R. W. Hollander, M. W. Spoor, and J. M. Smith, AIChE J. **25**, 351 (1979).

pellet of TiO_2 was introduced to the feed port. A sample of extrudate was collected at the die once every 10 s for subsequent Raman analysis. The Raman spectroscopic equipment comprised two main parts: a Spectra-Physics 2020-5 argon-ion laser with a nominal output power of 1.5 W at 488.0 nm, and a Spex Industries 1401 double monochromator with photon-counting detection accomplished with an EMI 9789 QA photomultiplier tube. Spectrometer control was carried out with a Nicolet 1180 computer. Raman spectra (1 scan) of the samples were obtained between 575 and 1175 cm^{-1} (Fig. 1). Relevant peak areas were calculated with the use of a PC software package.[4] The peak area at 650 cm^{-1} for TiO_2 was ratioed with the peak area at 1150 cm^{-1} for HDPE, so that the relative peak areas could be plotted against time to produce an RTD curve.

RESULTS AND DISCUSSION

The mean residence time in these processes, $\bar{t}$, is given by Wolf et al.:[5]

$$\bar{t} = \frac{\sum\limits_{0}^{\infty} t \cdot C(t) \cdot \Delta t}{\sum\limits_{0}^{\infty} C(t) \cdot \Delta t} \qquad (2)$$

where $C(t)$ is the tracer concentration, relative to polyethylene, and Δt represents the time interval between the samples. Thus, the mean residence times for the extrusion process at 4 and 8 kg/h were calculated to be 175 (see Table II) and 118 s, respectively.

The residence times (t) can be normalized to the mean residence time ($\bar{t}$):

$$\theta = \frac{t}{\bar{t}} \qquad (3)$$

where θ is the normalized time, t is the residence-time, and $\bar{t}$ is the mean residence time. Similarly, the tracer concentration at time equal to t can be normalized to the total tracer concentration:

$$E(t) = \frac{C(t)}{\sum\limits_{0}^{\infty} C(t)\Delta t} \qquad (4)$$

in which $E(t)$ is the normalized tracer concentration, $C(t)$ is the tracer concentration, and Δt is the time interval
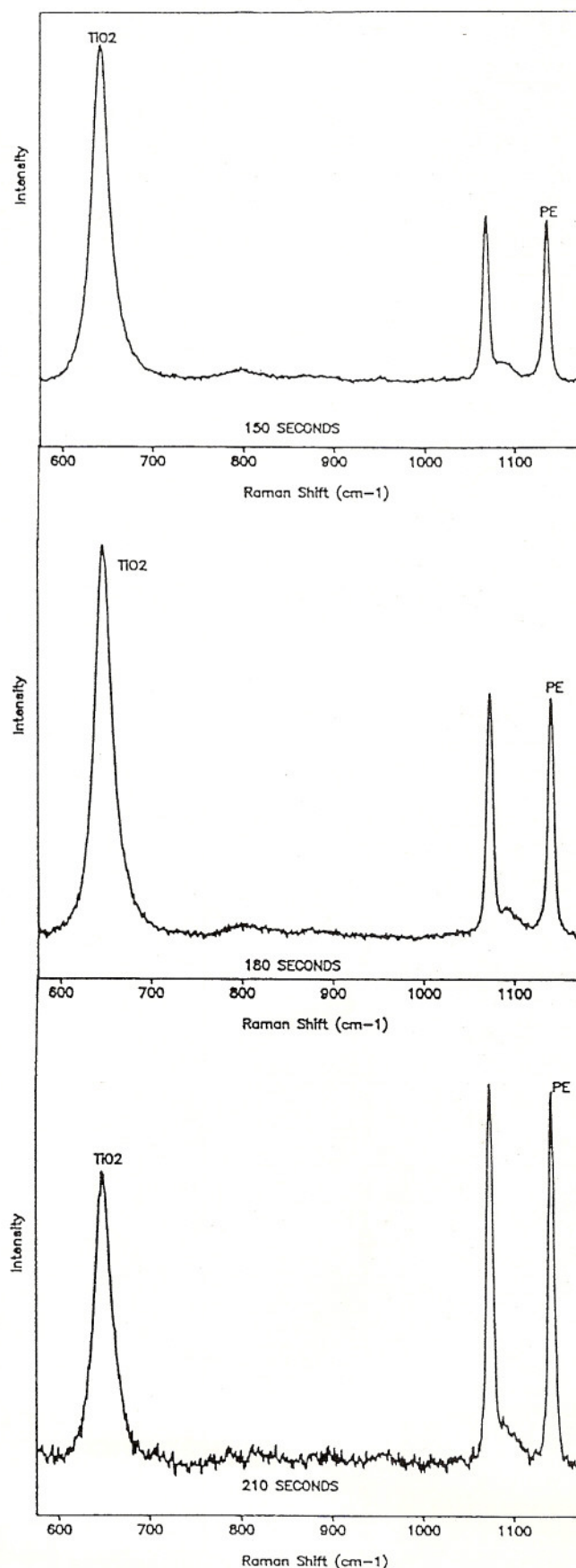

FIG. 1. Raman spectra of high-density polyethylene with varying levels of TiO_2 incorporated at $t = 150$, 180, and 210 s.

TABLE II. Calculations for the determination of the $F(\theta)$ plot (Fig. 2). Mass flow rate 4 kg/h.[a]

Time, t (min)	$C(t)$[b]	$C(t) \times \Delta t$	$\theta = t/\bar{t}$	$c(t) \times \Delta t$	$E(t) = \dfrac{C(t)}{\Sigma_0^{\infty} C(t)\cdot\Delta t}$	$E(\theta) = \bar{t} \times E(t)$	$E(\theta) \times \Delta\theta$	$F(\theta)$
0.00	0.00	0.00	0.00	0.000	0.000	0.000	0.000	0.000
1.67	0.10	0.18	0.57	0.017	0.011	0.033	0.002	0.002
1.84	0.90	1.73	0.63	0.150	0.101	0.293	0.017	0.019
2.00	2.00	4.17	0.69	0.334	0.224	0.652	0.037	0.056
2.17	6.10	13.75	0.74	1.019	0.682	1.988	0.113	0.170
2.34	5.20	12.60	0.80	0.868	0.581	1.695	0.097	0.267
2.50	7.50	19.38	0.86	1.253	0.839	2.444	0.139	0.407
2.67	5.75	15.83	0.92	0.960	0.643	1.874	0.107	0.514
2.84	4.80	14.03	0.97	0.802	0.537	1.564	0.089	0.604
3.00	5.60	17.27	1.03	0.935	0.626	1.825	0.104	0.709
3.17	3.20	10.41	1.09	0.534	0.358	1.043	0.059	0.768
3.34	4.00	13.69	1.15	0.668	0.447	1.304	0.074	0.843
3.50	2.75	9.85	1.20	0.460	0.308	0.896	0.051	0.894
3.67	1.70	6.38	1.26	0.284	0.190	0.554	0.032	0.926
3.84	0.80	3.14	1.32	0.134	0.089	0.261	0.015	0.941
4.00	0.80	3.27	1.38	0.134	0.089	0.261	0.015	0.956
4.17	0.95	4.04	1.43	0.159	0.106	0.310	0.018	0.974
4.34	0.60	2.65	1.49	0.100	0.067	0.196	0.011	0.985
4.50	0.60	2.75	1.55	0.100	0.067	0.196	0.011	0.996
4.67	0.20	0.95	1.60	0.033	0.022	0.065	0.004	1.000
4.83	0.00	0.00	0.00	0.000	0.000	0.000	0.000	1.000
	Sum = 53.55	Sum = 156.07		Sum = 8.94				

[a] Mean residence time, $\bar{t}$ = 156.07/53.55 = 2.91 min (175 s).
[b] Raman peak areas (TiO$_2$/polyethylene).

between the samples. $E(t)$ can also be normalized to the mean residence time:

$$E(\theta) = \bar{t}E(t). \tag{5}$$

The cumulative normalized tracer concentration, $F(\theta)$, may then be obtained:[5]

$$F(\theta) = \sum_0^t E(\theta)\cdot\Delta\theta. \tag{6}$$

A plot of the cumulative normalized tracer concentration [$F(\theta)$] against normalized time (θ), the $F(\theta)$ distribution, may be used to calculate the proportion of ma-
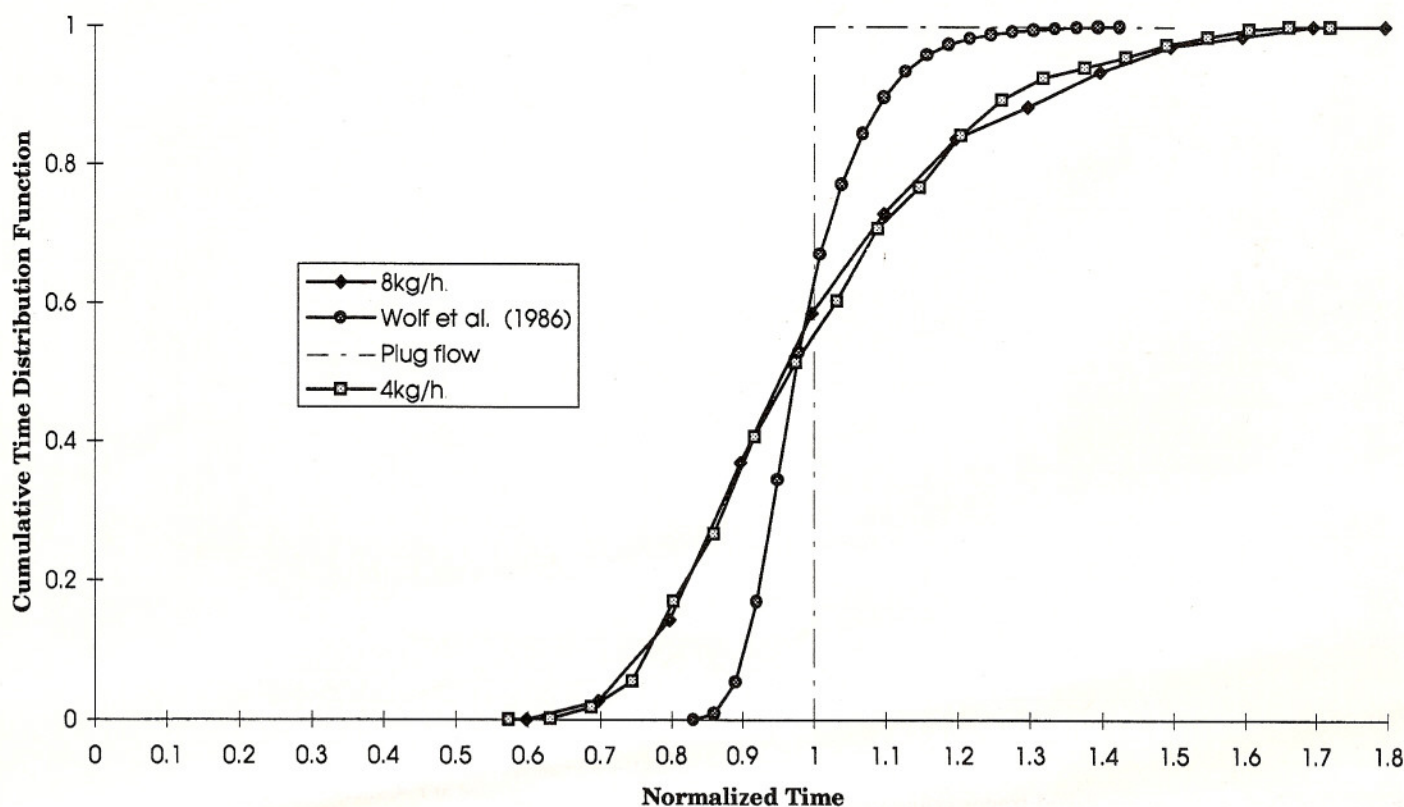

FIG. 2. $F(\theta)$ functions for a co-rotating twin-screw extruder (current work), counter-rotating twin-screw extruder, and plug flow.

terial which spends a given percentage of the mean residence time in the barrel (Fig. 2). It is apparent that the normalized distributions with polyethylene flow rates of 4 and 8 kg/h overlay each other. The plots show that the material spends at least 60% of the mean residence time in the extruder, and all the material has exited before 180% of the mean residence time has been reached.

The distributions in the current work in Fig. 2 have been superimposed with two other residence time distributions. Simple plug flow is indicated, where all the material spends the mean residence time in the system, and a vertical line passing through $\theta = 1$ is produced. Therefore, the $F(\theta)$ plot can highlight the process deviation from a plug flow residence time distribution, and different configurations or operating conditions can be compared. For comparison with the current work, a set of data from Wolf et al.[5] is also provided. Wolf et al. used a 90-mm counter-rotating twin-screw extruder operating at 62 kg/h at a screw speed of 30 rpm. The counter-rotating extruder has a narrower distribution than the co-rotating twin-screw used in the present work. All the material spends at least 85% of the mean residence time in the counter-rotating twin-screw extruder, compared with 60% in the current work.

CONCLUSION

The potential of measuring residence time distributions by Raman spectroscopy has been demonstrated in the current work, and further studies are in progress which extend the work to in-line analysis.

1. O. Levenspeil, *Chemical Reaction Engineering* (Wiley, New York 1972), 2nd ed.
2. D. B. Todd, Intern.Polym.Process. **8,** 1 (1993).
3. P. J. Hendra, D. B. Morris, R. D. Sang, and H. A. Willis, Polymer **9,** 23 (1982).
4. LabCalc, commercial software (Galactic Industries, Salem, New Hampshire, 1990).
5. D. Wolf, N. Holin, and D. H. White, Polym. Eng. Sci. **26,** 640 (1986).