Measurements of Residence Time Distribution for the Peroxide Degradation of Polypropylene in a Single-Screw Plasticating Extruder

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Synopsis

Measurements of the residence time distribution (RTD) in a single-screw plasticating extruder were carried out during experimental studies of the peroxide-initiated controlled chemical degradation of polypropylene (PP). A radioactive tracer method was employed, and the effect of screw speed, temperature, and reaction on the RTD was examined. An increase of the peroxide concentration resulted in a broader distribution whereas an increase of the extrusion temperature was found to result in a narrower distribution. Use of low screw speeds simply increased the time delay through the extruder without affecting considerably the breadth of distribution. Results obtained from the present experiments were compared with several theoretical models.

INTRODUCTION

During the flow through an extruder, fluid elements follow helical paths generated by the relative motion of the screw and barrel surfaces. As a result of this peculiar nonuniform velocity field, different fluid particles have different residence times and undergo different strain and thermal histories. Determination of the residence time distribution (RTD) of the polymer is very important when evaluating the performance of an extruder in areas where the time factor has a great impact on the product quality. RTD is a crucial parameter that can be used to analyze mixing and product uniformity especially when different additives are blended with polymers. When RTD is properly used in the design of screws used for the extrusion of temperature sensitive materials such as PVC, thermal degradation can be minimized and product quality can be improved. With the advent of reactive extrusion of polymers, screw extruders are increasingly being used as chemical reactors for either polymerization or chemical modification reactions. In this case, the RTD is a parameter that has to be determined so that screws are designed in such a way to provide sufficient time for the completion of the reaction without affecting other performance characteristics. Also, the molecular weight distribution (MWD) of the product is largely affected by the spread in residence times of the reacting material in the extruder.

The concept of the residence time distribution functions was initially used by Danckwerts[1] in the analysis of continuous flow systems for the calculation of the efficiencies of chemical reactors and blenders. Application of this concept to polymer extrusion dates back to the work of Mohr et al.[2] and McKelvey[3] but Pinto and Tadmor[4] were the first to derive expressions for the

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RTD function in a single-screw melt extruder. The derivation was based on a parallel plates flow model under isothermal and Newtonian flow assumptions. An extension of this work for power-law fluids was presented by Bigg and Middleman,[5] who verified their model with data from extrusion experiments of Newtonian and non-Newtonian liquids. In the area of plasticating extrusion, Lidor and Tadmor[6] calculated theoretically the RTD in a single-screw extruder by modeling the solids coveying, melting, and melt pumping mechanisms that occur in the extruder channel.

Generally, residence time distributions can be measured experimentally by means of a tracer technique. This is accomplished by introducing the tracer as a step or impulse function at the input of a system and by monitoring its concentration at the exit as a function of time. A good tracer must be easily detected and must not alter the flow characteristics of the process fluid. In the past, several tracer techniques have been employed in measurements of RTD in extruders. Wolf and White[7] were the first to develop such a technique using a radioactive tracer. They performed experiments under different processing conditions, and they verified Tadmor's RTD model for melt extrusion. Similar experiments have been done by Janssen et al.[8] in a twin-screw extruder. The same method was also used by Schott and Saleh.[9] Although this method is very accurate, especially at low tracer concentrations, other methods have also been used. Todd[10] has measured RTD with polybutenes using methylene blue as a tracer, and Todd and Irving[11] have done experiments with glucose solutions using KNO_3 and $NaNO_3$ as tracers. Werner and Eise[12] used iron powder as a tracer, and they monitored continuously the magnetic properties of the extrudate to determine the tracer concentration. Rauwendaal[13] used antimony oxide, Kemblowski and Sek[14] used sodium chloride, and Walk[15] used cadmium selemide as a tracer. Nichols et al.[16] employed a tracer consisting of a polymer–additive blend and determined its concentration at the exit of a twin-screw extruder by measuring on-line the capacitance of the extrudate. Stamato and Weiss[17] used an ionomer tracer to measure the RTD in a single-screw extruder during the extrusion of polystyrene.

Recently, Suwanda et al.[18] carried out RTD measurements in a single-screw extruder for the peroxide-initiated degradation of polypropylene. A radioactive tracer was used, and the effects of reaction and operating conditions were studied. The RTD measured was combined with their batch kinetics model for the prediction of the MWD changes due to the reaction.

In the present work, using a radioactive MnO_2 tracer, the effect of the presence of a reaction on the RTD in a single-screw plasticating extruder was studied. The reaction was peroxide-promoted degradation of polypropylene. In this process, PP was premixed with a peroxide, and it was extruded for the purpose of producing resins with narrow MWDs. During this reactive extrusion process, radicals produced from the peroxide decomposition initiate β-scission reactions. As a result, the molecular weight and the viscosity of the polymer melt reduces dramatically, depending on the peroxide concentration.[18-21] These changes of the viscosity largely affect the flow pattern and hence the RTD in the extruder. The purpose of this work was to demonstrate that the presence of a chemical reaction that alters the polymer viscosity affects significantly the RTD in a single-screw extruder. Experimental runs were carried out at various processing conditions, and the results were compared to predictions from several theoretical models.

EXPERIMENTAL

Experiments were carried out in a Killion 38-mm single-screw extruder ($L/D = 24$) with a rod die. More information on the extruder and die specifications are given by Agur.[22,23] Experimental runs were performed at two different screw speeds (30 and 60 rpm), two temperature levels (220 and 230°C) and three peroxide concentrations (1, 0.02, and 0.05%). The polypropylene used was a KY6100 powder from Shell with MFI = 3 g/10 min, $\overline{M}_w = 3 \times 10^5$ and $\overline{M}_w/\overline{M}_n = 7.6$. The peroxide used was 2,5-dimethyl-2,5-di-*tert*-butylperoxy hexane (Trigonox-101) from Akzo Chemie.

Neutron activation analysis was used in the RTD measurements. This type of analysis is a versatile and sensitive technique that can be used to determine the chemical composition of material samples. It is based on the properties of the atomic nucleus rather than the electronic structure, and it is therefore a method of elemental analysis as opposed to molecular analysis.

The RTD was determined by injecting a pulse of tracer material in the feed of the extruder. The tracer was manganese dioxide (MnO_2), and the input pulse consisted of 2 g of PP–MnO_2 mixture 1% in MnO_2. Samples were collected from the extrudate at time intervals ranging from 5 to 20 s. The samples were irradiated in the McMaster nuclear reactor for 4 min, and the concentration of MnO_2 was determined from measurements of the induced radioactivity. For this purpose a Canberra Series 90 multichannel analyzer with an APTEC/NRD coaxial spectrometer was used for the detection of the γ-rays emitted by the Mn^{56} radioisotope. For every sample an energy spectrum was obtained in which a manganese peak was detected. A typical energy spectrum of two samples with different concentrations is presented in Figure 1. The surface area of the peak was computed, and, after correction for background radiation and varying counting and delay times, the number of counts was converted to manganese concentration using an atomic absorption standard solution calibration curve.

The age distribution of the fluid leaving the extruder was calculated as the $E(t)$ function:[24]

$$E(t) = \frac{C(t)}{\int_0^\infty C(t') \, dt'} \tag{1}$$

where $C(t)$ is the concentration of tracer in the sample collected at time t.

Data on the experimentally measured $C(t)$ will usually contain random errors and will be truncated at some finite time t. Data can be used in several ways:[25] Data are used directly; data are fitted to a model. In the present work, the data were used directly, and the integral in eq. (1), representing the area under the curve, was calculated numerically. When accurate calculation of this area is required, fitting a model with an exponential tail to the experimental data is usually appropriate. This is the case when experimentally measured RTD are used combined with batch kinetic models for the determination of species concentration at the exit of the continuous flow reactor.[18] The cumulative distribution function $F(t)$, which defines what fraction of the exiting fluid has a residence time of t or less, was calculated as

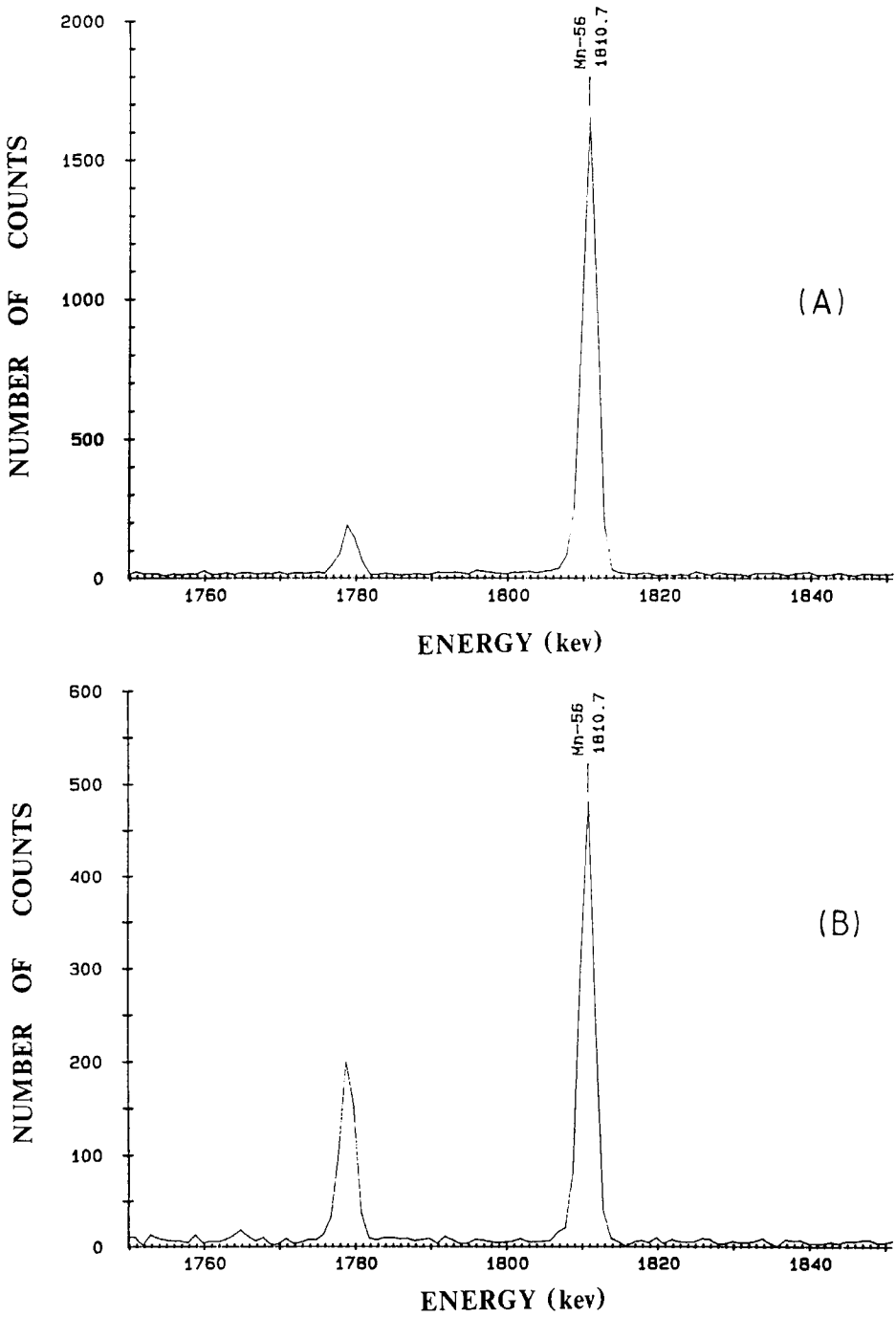$$F(t) = \int_0^t E(t') \, dt \tag{2}$$

Fig. 1. Energy spectrum of samples with (A) a high concentration of MnO_2 and (B) a low concentration of MnO_2.

The mean residence time and the variance were calculated by the equations

$$\bar{t} = \int_0^\infty tE(t)\, dt \tag{3}$$

$$\sigma^2 = \int_0^\infty t^2 E(t)\, dt - \bar{t}^2 \tag{4}$$

THEORETICAL MODELS

The data obtained from the present experiments were compared to predictions from several theoretical models. The first model was that of Pinto and Tadmor,[4] according to which

$$t = \frac{L}{3V_b \sin(\omega)\cdot\cos(\omega)(1+\Phi)} \cdot \frac{3a - 1 + 3\sqrt{1 + 2a - 3a^2}}{a\left[1 - a + \sqrt{1 + 2a - 3a^2}\right]} \cdot \frac{H + h}{2H} \tag{5}$$

$$E(t) = \frac{9}{2} \frac{V_b \sin(\omega)\cos(\omega)(1+\Phi)}{L} \cdot \frac{a^3\left[1 - a + \sqrt{1 + 2a - 3a^2}\right]^3}{(6a^2 - 4a - 1)\sqrt{1 + 2a - 3a^2} + 3a - 1} \tag{6}$$

$$F(t) = \tfrac{1}{2}\left[3a^2 - 1 + (a - 1)\sqrt{1 + 2a - 3a^2}\right] \tag{7}$$

where a is the normalized depth in the extrusion channel and

$$1 + \Phi = 2Q/WHV_z \tag{8}$$

For more details the reader is referred to the original paper. This model describes the RTD in a single-screw melt extruder with a constant depth channel. The ratio $(H + h)/2H$ in eq. (5) is the correction factor for the tapered channel as suggested by Wolf and White.[7]

The other models used were the following:

Dispersion model[24]:

$$E(\theta) = \frac{1}{2\sqrt{\pi\theta\xi}}\exp\left[-\frac{(1 - \theta)^2}{4\theta\xi}\right] \tag{9}$$

where

$$\theta = t/\bar{t} \tag{10}$$

Here, the parameter ξ describes the degree of axial dispersion or the deviation from the ideal plug flow.

Tanks-in-series model[24]:

$$E(\theta) = \frac{N(N\theta)^{N-1}}{(N - 1)!}\exp(-N\theta) \tag{11}$$

where N is the number of perfectly mixed stirred tanks in the model.

In the interpretation of the results to follow, the $E(t)$ curve rather than the $F(t)$ curve is used since it is more sensitive to slight differences of the RTD.
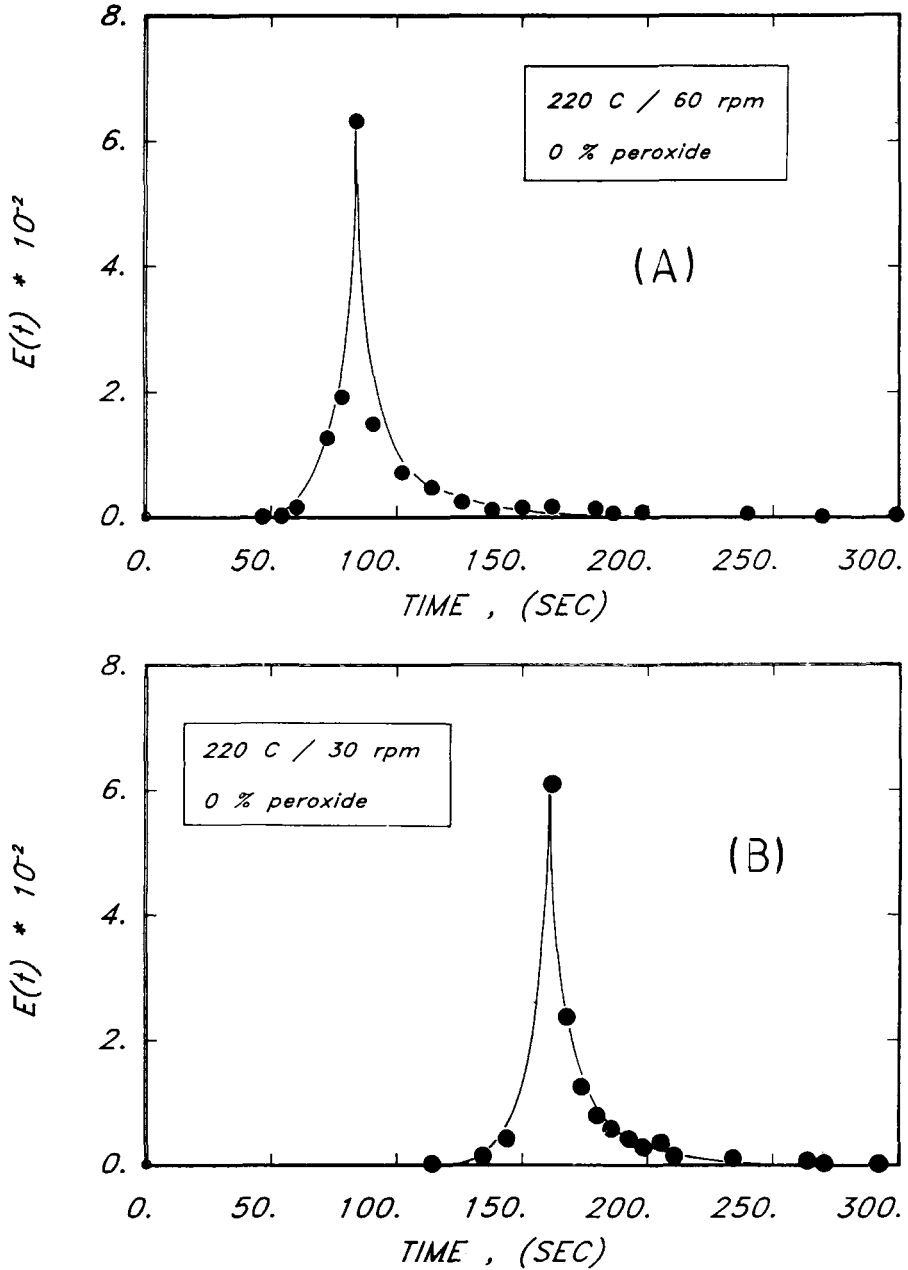
Fig. 2.   Effect of screw speed on the residence time distribution: (A) 60 rpm; (B) 30 rpm. 220°C; 0% peroxide.

RESULTS AND DISCUSSION

Residence time distribution measurements were first carried out without any peroxide present in the melt. The effect of screw speed on the RTD is shown in Figure 2. the temperature was kept constant at 220°C. Increasing the speed from 30 to 60 rpm resulted in a decrease of the mean residence time from 176 to 98 s. However, the shape of the distribution remained almost the
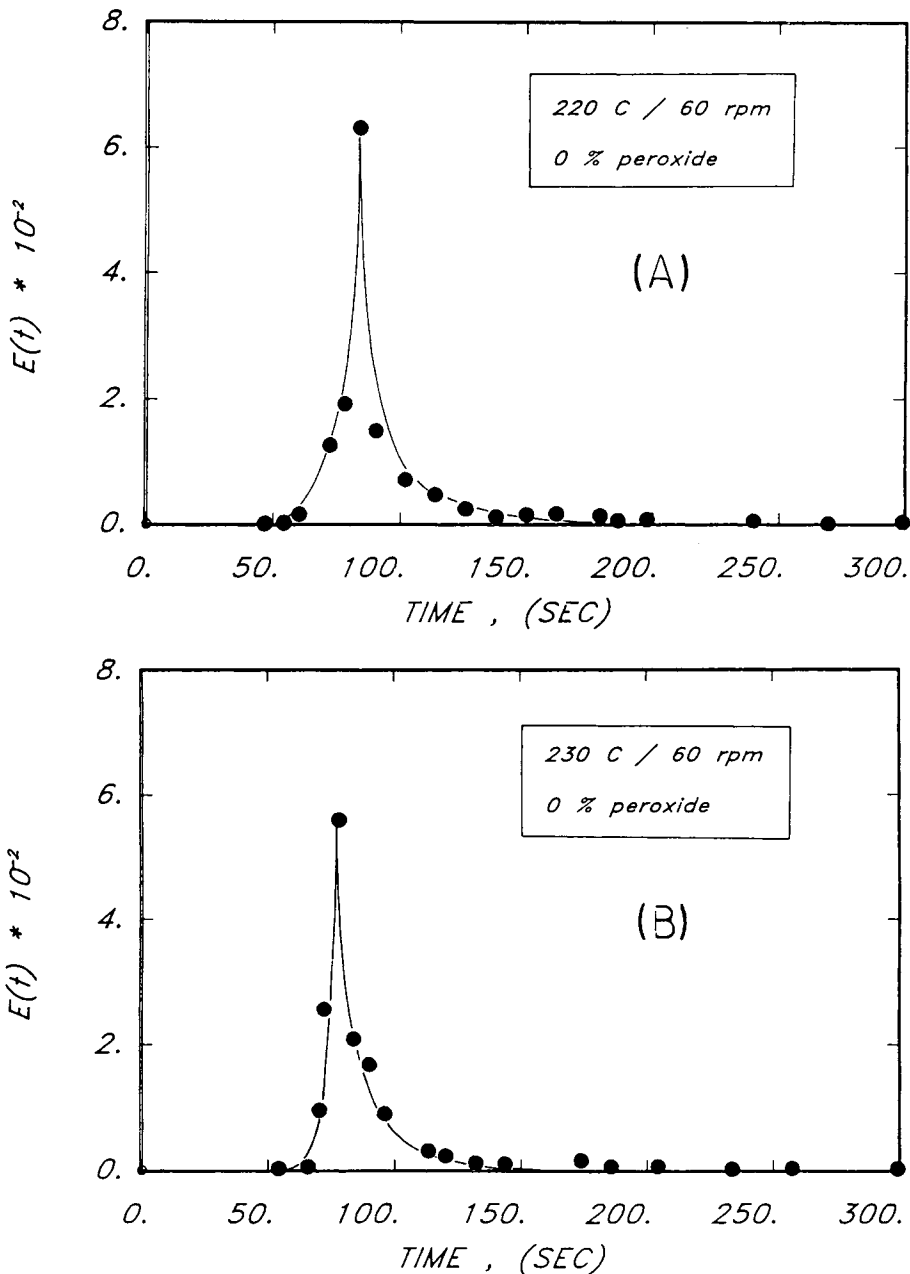
Fig. 3. Effect of extrusion temperature on the residence distribution: (A) 220°C; (B) 230°C. 60 rpm; 0% peroxide.

same. This result is fully in agreement with the measurements of Wolf and White[7] for low density polyethylene. However, Suwanda et al.[18] reported that an increase of screw speed results in a broader distribution.

Figure 3 shows the effect of the extrusion temperature on the RTD. An increase of the barrel temperature by 10°C resulted in a slightly narrower distribution. It seems that the reduction of the melt viscosity due to tempera-
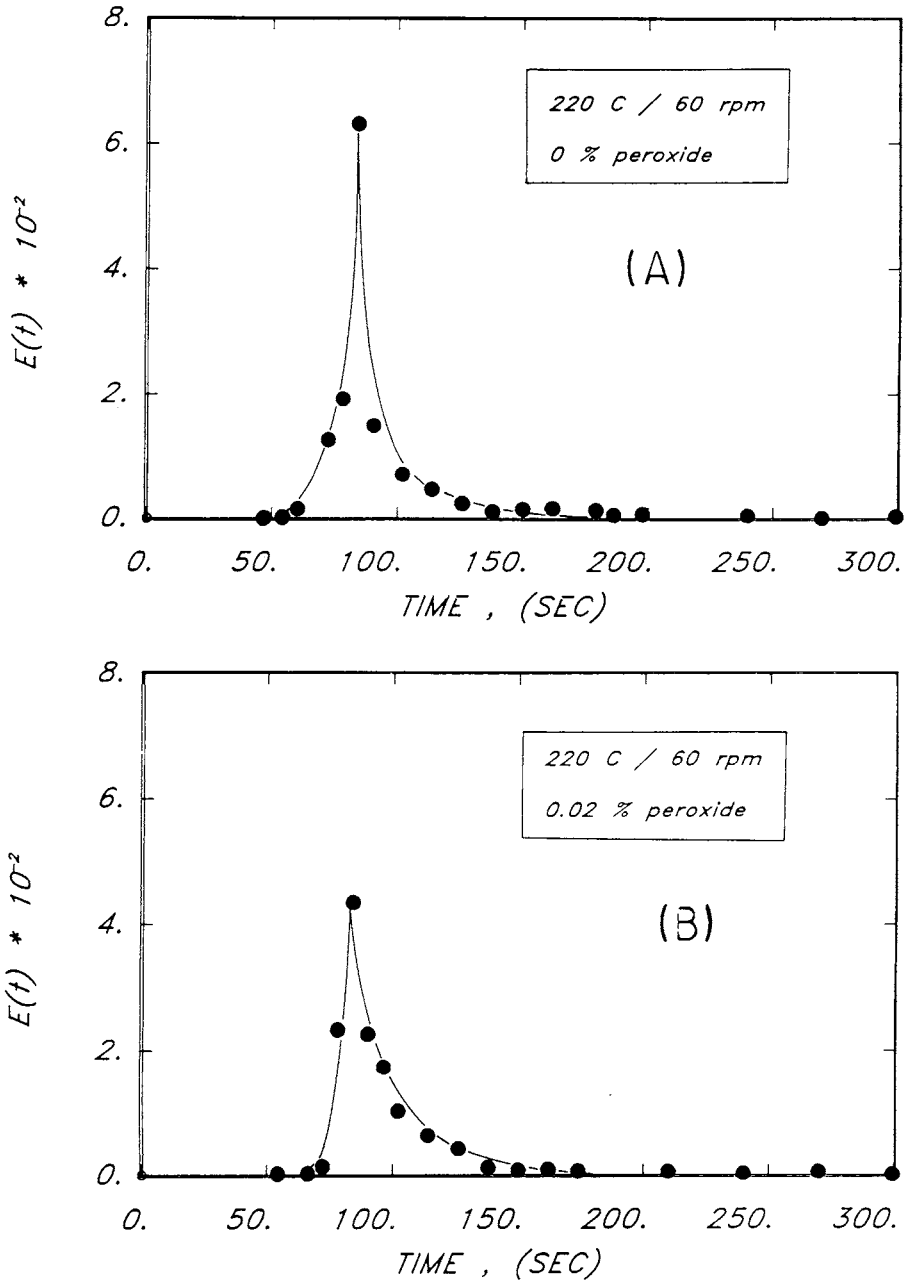
Fig. 4.   Effect of peroxide concentration on the residence time distribution: (A) 0% peroxide;
(B) 0.02% peroxide; (C) 0.05% peroxide. 220°C; 60 rpm.
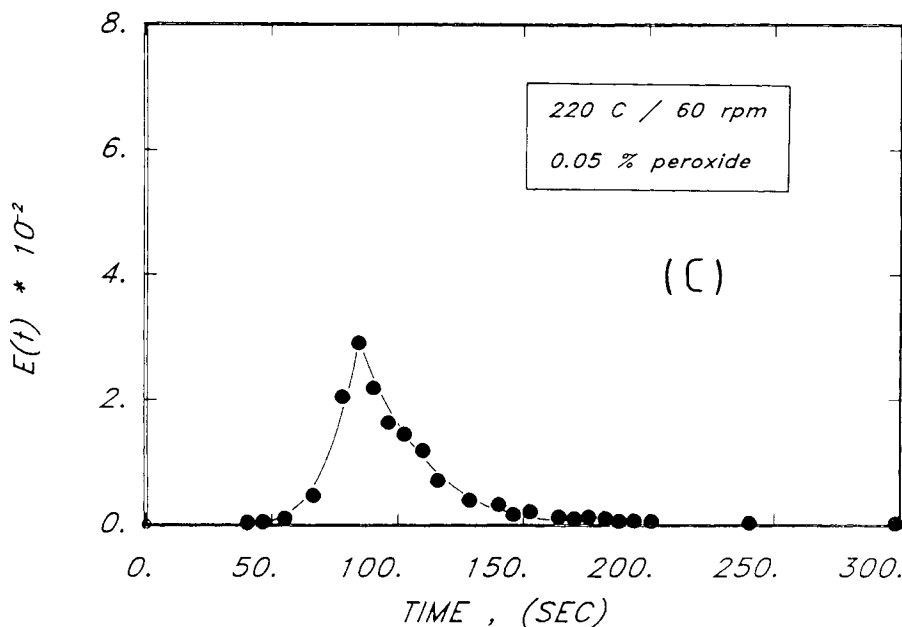
Fig. 4. (*Continued from the previous page.*)

ture increase favors the drag flow more than the pressure flow component, and it causes less back mixing in the extruder channel. Similar temperature effects were observed by Suwanda et al.[18] The concentration of peroxide was found to have an opposite effect. This is shown in Figure 4. The experimental age distributions $[E(t)]$ presented here correspond to three different peroxide concentration levels (0, 0.02, and 0.05%). With all three concentrations the screw speed was 60 rpm, and the temperature on the barrel and the die was kept constant at 220°C. It is obvious that increasing the peroxide level reduces the peak of the distribution while it increases its breadth.

Calculated values of mean and the variance of these distributions are given in Table I. Similar results have been reported by Suwanda et al.[18] The changes of the residence time distribution are due to the viscosity reduction caused by the degradation reaction that decreases the molecular weight of the polymer. In the presence of the reaction, the reduced melt viscosity seems to favor the pressure driven back flow component. This can explain the broader

TABLE I
Mean Residence Time and Variance Values

Peroxide (wt %)	Temp (°C)	Screw speed (rpm)	$\bar{t}$ (s)	σ^2 (s)
0	230	60	95	668
0	220	30	176	698
0	220	60	98	714
0.02	220	60	104	760
0.05	220	60	107	785

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distributions at higher peroxide concentrations. One must point out that since the extruder used in the present study is a small one with a swallow channel, the effect of the reaction is expected to be even more pronounced in larger extruders where back-mixing effects are more important. Comparison between experimental data and predictions from Tadmor's melt extrusion model is given in Figure 5. It is clear that the presence of the reaction worsens the agreement between theory and present experimental results. This was ex-
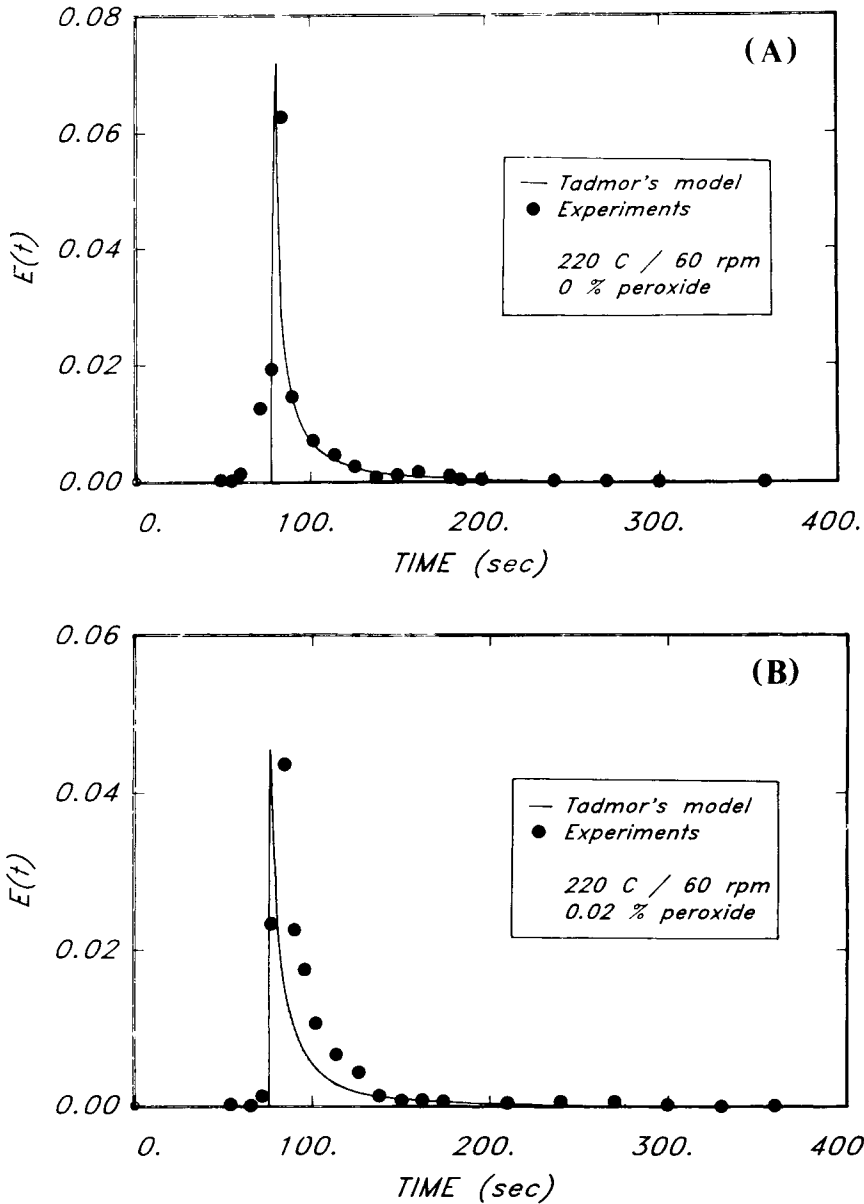
Fig. 5. Comparison between experimental measurements (●) and prediction from Tadmor's melt extrusion model (—) for three peroxide concentrations: (A) 0% peroxide; (b) 0.02% peroxide; (C) 0.05% peroxide. 220°C; 60 rpm.
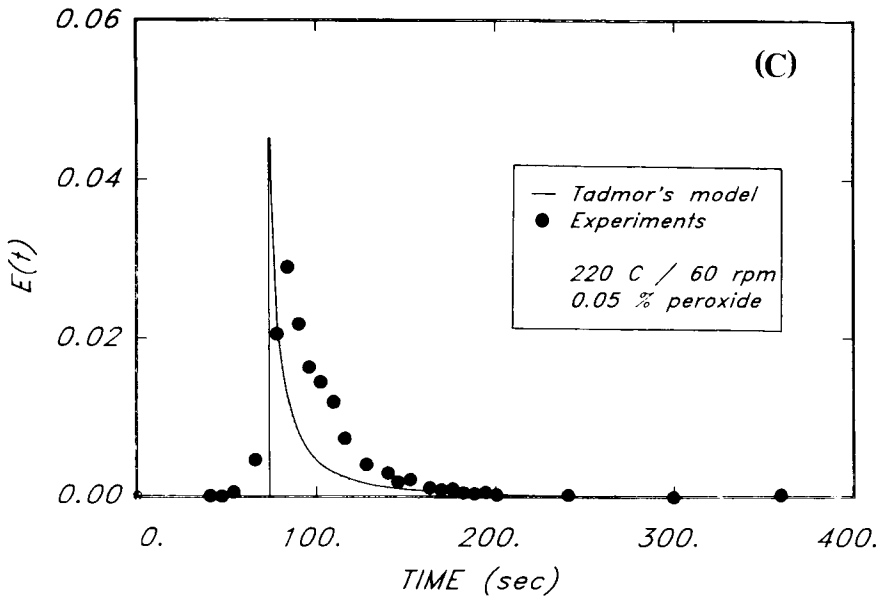
Fig. 5. *(Continued from the previous page.)*

pected because this particular model does not include the effect of viscosity changes on $E(t)$. Predictions from the dispersion model are given in Figure 6 for several values of the dispersion parameter (ξ) while predictions from the tanks-in-series model are shown in Figure 7. Since the effect of the reaction is expected to be more important in large extruders, more complete mathematical models are required for the prediction of RTD in the case of reactive
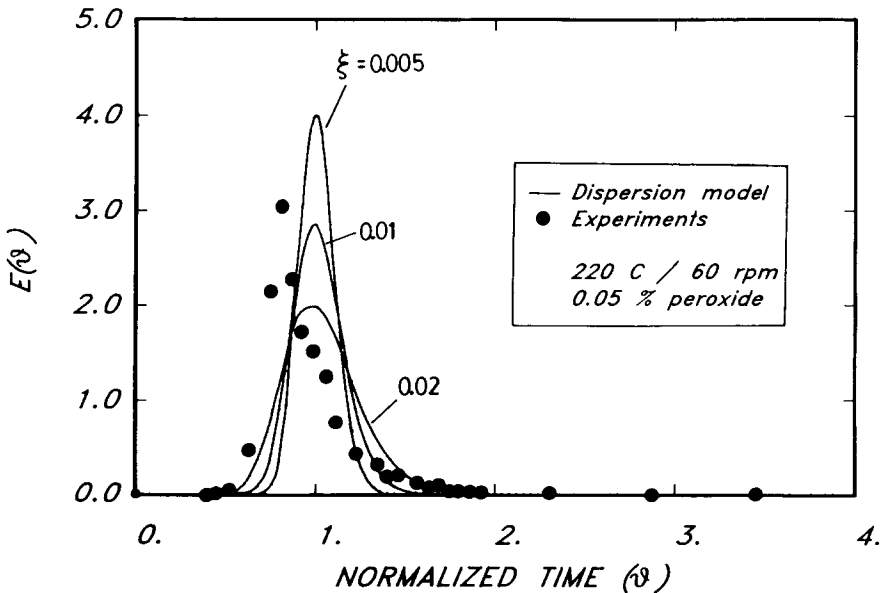

Fig. 6.   Comparison between experimental measurements (●) and predictions from the dispersion model (—): 220°C; 60 rpm; 0.05% peroxide.
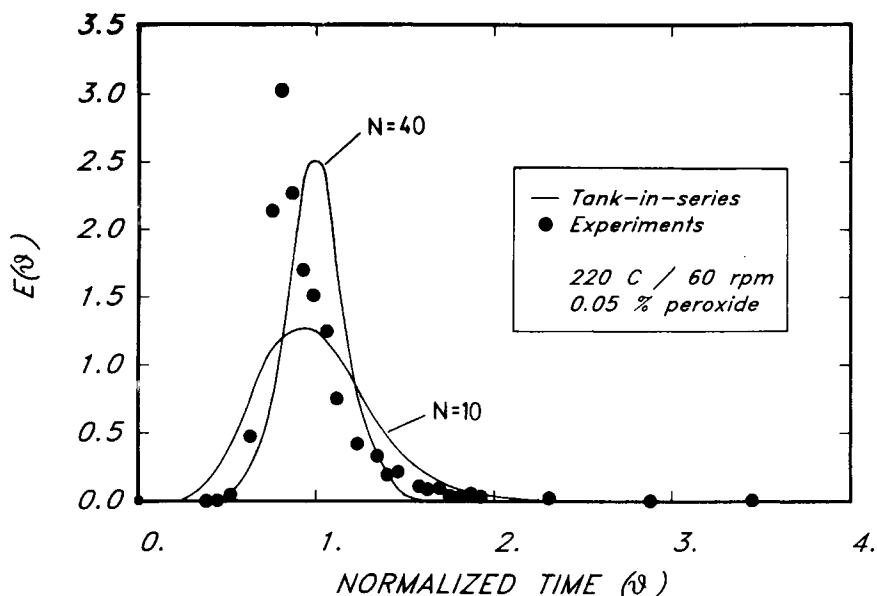
Fig. 7. Comparison between experimental measurements (●) and predictions from the tank-in-series model (—): 220°C; 60 rpm; 0.05% peroxide.

extrusion of polymers. Such models should be carefully used in the design of screws for reactive extrusion systems.

CONCLUSIONS

Measurements of the RTD have been carried out for the peroxide-promoted degradation of polypropylene in a single-screw plasticating extruder. Significant effects of the degradation reaction on the RTD were observed, and it was found that increasing the peroxide concentration level resulted in broader distributions. This behavior was attributed to the reduction of the melt viscosity which was caused by the reaction. An increase in the extrusion temperature was found to result in narrower distributions while the screw speed affected significantly the mean residence time but not the breadth of the RTD.

APPENDIX: NOMENCLATURE

a normalized depth in the extruder channel
$C(t)$ concentration of tracer in sample collected at time t (ppm)
$E(t)$ dimensionless age distribution
$F(t)$ dimensionless cummulative age distribution

H	channel depth at the beginning of the tapered section (m)
h	channel depth at the end of the tapered section (m)
L	channel length (m)
N	number of perfectly stirred tanks in eq. (11)
Q	volumetric flow rate (m^3/s)
t	time (s)
$\bar{t}$	mean residence time (s)
V_b	barrel velocity (m/s)
V_z	z-component of barrel velocity (m/s)
W	channel width (m)

Greek Symbols

θ	normalized time
ξ	dispersion parameter in eq. (9)
σ^2	variance of the distribution
Φ	parameter in eqs. (5)–(8)
ω	helix angle

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