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Peroxide modification of polyethylene. Prediction of molecular weight distributions by probability generating functions

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Abstract

We present a mathematical model able to describe the complete molecular weight distributions of polyethylene during reactive modification by organic peroxides. The method is applicable to batch processes, such as modification in a press or a plug-flow extruder, and in its present form is valid up to the gel point. We apply probability generating function definitions to the mass balances of radical and polymer species in the reacting medium. Three different probability generating functions are applied, each one directly applicable either to the number, weight or chromatographic distributions. These generating functions are numerically inverted to obtain the corresponding calculated molecular weight distribution. Two different inversion methods are used, and their relative performances analyzed. Predictions are compared with qualitative experimental data obtained in a press. Model predictions on molecular weight distributions are in agreement with experimental trends. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Molecular weight distribution prediction; Mathematical modeling; Reactive modification

1. Introduction

In polyolefins, final properties depend directly on average molecular weight, molecular weight distribution and short and long chain branching indexes. Those characteristics may be changed either by manipulating operating and design conditions in the reactors or by treating the virgin resin with organic peroxides. The latter is becoming more popular in view of its lower cost. It is in principle possible, through reactive processing, to change relatively inexpensive commodity polymers into higher priced specialty polymers [1]. In general, a trial and error approach is used to establish the operating conditions that will produce a given polymer, since peroxide addition leads to a complex situation where several chemical reactions occur simultaneously. A theoretical understanding of the process would help to minimize the need of trial runs, with their associated expense. For example, a model to simulate and predict polymer properties given the operating conditions of the reactive modification would help in understanding how to tune the final properties of the modified resin. This would be an important aid in the design of new products, as well as in the outlining of optimization strategies prior to production at commercial scale.

Few mathematical models in the literature describe the specific process of modification of polyethylene [2]. Very useful reviews on modeling may be found in Hamielec et al. [2] and Suwanda and Balke [3]. Some of the models use a statistical approach [1,2,4–8], where the emphasis is on the prediction of molecular weight distributions and gel points. For example, Saito [6] and Hamielec et al. [7] presented a differential–integral equation that describes the complete molecular weight distribution when simultaneous scission and chain branching occur. The general solution of this equation is not yet available, but several authors [1,8] have found solutions for particular cases. The statistical approach allows the prediction of molecular weight distribution at a given extent of reaction; it does not provide information as a function of time. In order to be able to use those equations it is generally necessary to establish independently the values of the degree of scission and density of crosslinking.

Suwanda and Balke [3] were the first to use a kinetic approach to address this problem. They aimed at the prediction of molecular weight distributions of the modified polymers. Their model discriminated between molecules with and without terminal vinyl groups. They considered crosslinking, end-linking and chain extension in the reacting system, but neglected scission on the grounds that its effect

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Nomenclature

A	pre-exponential factor
C_i	chromatographic fraction of molecules in the *i*th fraction of the chromatogram
E	activation energy
f	initiator efficiency
I	peroxide initiator
k_{ct}	kinetic constant for chain transfer to polymer (L/mol s)
k_{d}	kinetic constant for peroxide decomposition (s^{-1})
k_{ha}	kinetic constant for hydrogen abstraction (L/mol s)
k_{s}	kinetic constant for scission reaction (s^{-1})
k_{t}	kinetic constant for termination by combination (L/mol s)
M_a	moment of order a of polymer
M_i	molecular weight
M_{mon}	monomer molecular weight
M_{n}	number-average molecular weight
M_{w}	weight-average molecular weight
MWD	molecular weight distribution
N	inversion method parameter
N_{exp}	number of experimental runs
Nz	number of points to be evaluated in z
ObjF	objective function
pgf	any of the probability generating functions
pgfc	probability generating function of the chromatographic molecular weight distribution
pgfn	probability generating function of number molecular weight distribution
pgfw	probability generating function of the weight molecular weight distribution.
$p_j(m)$	number ($j = n$), weight ($j = w$) or chromatographic probability ($j = c$) of radicals having a degree of polymerization equal to 'm'
$p_j^*(m)$	number ($j = n$), weight ($j = w$) or chromatographic probability ($j = c$) of polymer having a degree of polymerization equal to 'm'
P_n	polymer with n monomer units and j terminal vinyl groups
$P_n^{\cdot}$	macroradical with n monomer units and j terminal vinyl groups
r_i	Papoulis' parameter
$R_{\mathrm{c}}^{\cdot}$	initiation radical
RH	inert molecule
t	reaction time (s)
$w_{M_{\mathrm{n}}}$	weight factor of objective function
$w_{M_{\mathrm{w}}}$	weight factor of objective function
Y_a	moment of order a of radical
z	transformed variable in pgf functions

Greek symbols

$\phi_j(z)$	number ($j = n$), weight ($j = w$) or chromatographic ($j = c$) probability generating function for size distribution of radicals
$\psi_j(z)$	number ($j = n$), weight ($j = w$) or chromatographic ($j = c$) probability generating function for size distribution of polymer
$\phi_j'(z)$	first derivative of the number ($j = n$), weight ($j = w$) or chromatographic ($j = c$) probability generating function for size distribution of radicals
$\psi_j'(z)$	first derivative of the number ($j = n$), weight ($j = w$) or chromatographic ($j = c$) probability generating function for size distribution of polymer

Subscripts and superscripts

calc	calculated values
exp	experimental values

would be equivalent to a reduction in initiator efficiency. They solved differential equations for polymer molecules of length 'n' with and without terminal vinyl groups, choosing the overall link-density as the independent variable and assuming quasi-steady state for radicals of all lengths. They calculated the distribution for 300–500 degree of polymerization points. The model had two parameters (initiator efficiency, and the double bond reactivity ratio) which were used to fit the model to experimental data. For commercial samples of low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) the model makes a fairly good prediction of both M_{w} and molecular weight distribution (MWD). It also predicts a drop in vinyl content, although not as large as the experimentally observed one. It failed to predict MWD changes in high-density polyethylene (HDPE). If the model was simplified by neglecting terminal unsaturations, the capacity to predict MWD was lost for most polyethylenes except HDPE samples of low initial vinyl content.

In a previous work [9] we proposed a generalized kinetic model that takes into account not only combination reactions but also transfer to polymer and scission. The model describes the length of the polymer chain and the concentration of vinyl groups simultaneously. Any number of vinyl groups per molecule is allowed. The resulting infinite system of mass balance equations is solved using a double moment technique. The model predicts number, weight and z-average molecular weights and the concentration of vinyl groups as functions of time. The kinetic constants and the initiation efficiency were estimated through a nonlinear regression using experimental data in the pregel region. This model resulted in improved predictions of the experimental data over previous kinetic modeling [3], since it gives good estimates of both average molecular weights and vinyl content.

In this work we extend our previous mathematical model in order to be able to predict the complete molecular weight distribution of polyethylene during the modification process given its operating conditions. We focus on the modification taking place in a press at isothermal conditions. To this purpose we establish a simplified set of mass balances for the reacting species that does not include the usual quasi-steady state approximation. We assume that each radical molecule contains only one active site. The effect of the number of active sites per molecule has been investigated by Zhu and Hamielec [10], who concluded that for the case of polymerizations with crosslinking, polyradicals may be present in significant amounts only near the gel point, depending on the relative values of the kinetic constants. The presence of polyradicals should no doubt be considered in a model that attempts to predict gel points and sol fractions, but it seems reasonable to preserve the monoradical assumption when dealing with polyethylene modification in the pregel region. We also assume that reactions are not diffusionally controlled. Zhu [5] showed that including diffusion control could affect model results. As we show in Section 5, our model gives reasonable results without taking diffusion into account.

Once the model is set up, we apply a transform technique. The chosen transform is the probability generating function (pgf). Three different pgfs were defined, to describe the number, weight and chromatographic distributions, respectively. Pgfs are calculated as functions of residence time, and are numerically inverted to allow recovery of the molecular weight distributions [11,12]. We previously used this approach to solve the complete molecular weight distribution of the polyethylene and EVA copolymers produced in industrial autoclave reactors obtaining very interesting results [13]. In that case, the initial values of the pgfs are zero, since polymer and radicals are not fed to the reactor. In the present process we start from polymer, so there exists a nonzero pgf curve from the beginning. In consequence this pgf must be estimated from MWD of the virgin resin. As the only available MWD is that of the polymer as a whole, for the present purpose we lump polymer molecules with and without vinyl groups, considering them as a single species.

2. MWD Model

We used a simplification of our previously proposed kinetic mechanism [9] for the modification of polyethylene by peroxides at low concentration. The simplification consists in averaging the number of terminal unsaturated bonds over all polymer molecules. The remaining characteristics of the proposed kinetic mechanism remain unchanged from the original one [9]: it applies to an isothermal modification process, radicals and macroradicals are assumed to contain a single active site, and the usual assumption of quasi-steady state of radicals is not used. This model has been implemented to work in the pregel region.

The simplified mechanism includes radical generation by initiator decomposition (Eq. (1)), hydrogen abstraction (Eq. (2)), termination by combination (Eq. (3)), chain transfer to polymer (Eq. (4)) and scission (Eq. (5)):

Initiation

$$I \xrightarrow{k_d} 4R_c^{\cdot} \tag{1}$$

Hydrogen abstraction

$$P_m + R_c^{\cdot} \xrightarrow{k_{ha}} P_m^{\cdot} + \mathrm{RH} \tag{2}$$

Termination by combination

$$P_m^{\cdot} + P_r^{\cdot} \xrightarrow{k_t} P_{m+r} \tag{3}$$

Chain transfer to polymer

$$P_m + P_r^{\cdot} \xrightarrow{k_{ct}} P_m^{\cdot} + P_r \tag{4}$$

Chain scission

$$P_m^{\cdot} \xrightarrow{k_s} P_r + P_{m-r}^{\cdot} \tag{5}$$

In these equations I is the initiator (2,5-dimethyl-2,5-bis(tert-butyl-peroxy)-hexane (DBHP)), $R_c^{\cdot}$ is the initiation radical, P_n and $P_n^{\cdot}$ are polymer molecules and macroradicals with n monomer units, respectively, and RH is an inert molecule.

The next step in modeling this process is setting up mass balances for all the species involved in the kinetic mechanism. If the modification takes place in a press, the independent variable is the reaction time. The same equations can be applied to the modification process that uses an extruder, provided plug flow is present. In that case, the independent variable is residence time.

Mass balances for all the species present during the process are shown in Eqs. (6)–(9):

Initiator

$$\frac{\mathrm{d}[I]}{\mathrm{d}t} = -k_d[I] \tag{6}$$

Initiation radical

$$\frac{\mathrm{d}[R_c^{\cdot}]}{\mathrm{d}t} = 4k_d f[I] - k_{ha}[R_c^{\cdot}]\sum_{m=1}^{\infty} 2m[P_m] \tag{7}$$

Polymer molecule P_m ($m = 1, 2, \ldots, \infty$)

$$\frac{\mathrm{d}[P_m]}{\mathrm{d}t} = -k_{\mathrm{ha}}[R_{\mathrm{c}}^{\bullet}]2m[P_m] - k_{\mathrm{ct}}2m[P_m]\sum_{r=1}^{\infty}[P_r^{\bullet}] + k_{ct}[P_m^{\bullet}]\sum_{r=1}^{\infty}2r[P_r] + \frac{k_{\mathrm{t}}}{2}(1-\delta_{m,1})\sum_{r=1}^{m-1}[P_{m-r}^{\bullet}][P_r^{\bullet}] + k_{\mathrm{s}}\sum_{r=m+1}^{\infty}[P_r^{\bullet}] \tag{8}$$

Macroradical $P_m^{\bullet}$ ($m = 1, 2, \ldots\infty$)

$$\frac{\mathrm{d}[P_m^{\bullet}]}{\mathrm{d}t} = k_{\mathrm{ha}}[R_{\mathrm{c}}^{\bullet}]2m[P_m] + k_{\mathrm{ct}}2m[P_m]\sum_{r=1}^{\infty}[P_r^{\bullet}] - k_{\mathrm{ct}}[P_m^{\bullet}]\sum_{r=1}^{\infty}2r[P_r] + k_{\mathrm{t}}[P_m^{\bullet}]\sum_{r=1}^{\infty}[P_r^{\bullet}] - k_{\mathrm{s}}(m-1)[P_m^{\bullet}] + k_{\mathrm{s}}\sum_{r=m+1}^{\infty}[P_r^{\bullet}] \tag{9}$$

For this work, we assume that the smallest radical and polymer molecules have length one. Since both radical and polymer molecules may have, theoretically, any length between one and infinity, the resulting mass balance equations are infinite in number. Several techniques may be applied to allow their solution. Some of them are useful for calculating the average molecular properties and others for solving the complete molecular weight distribution. In this work, we employ the well-known moment technique [14,15] to obtain average properties, and pgf transforms to deal with MWD calculations.

For this purpose we use the following moment equations (Eqs. (10) and (11)).

*a*th moment of chain length distribution of polymer molecules

$$M_a = \sum_{m=1}^{\infty} m^a P_m \quad a = 0, 1, 2, \ldots \tag{10}$$

*a*th moment of chain length distribution of radicals

$$Y_a = \sum_{m=1}^{\infty} m^a P_m^{\bullet} \quad a = 0, 1, 2, \ldots \tag{11}$$

To obtain the moment balance equations for polymer or radical, both sides of Eqs. (8) and (9) must be multiplied by the *a*th power of its chain length m (m^a), then a summation over all possible values of m in the reacting system ($m = 1, \ldots\infty$) is performed. After some laborious algebraic steps, Eqs. (12)–(14) result:

*a*th moment of polymer

$$\frac{\mathrm{d}M_a}{\mathrm{d}t} = -k_{\mathrm{ha}}[R_{\mathrm{c}}^{\bullet}]2M_{a+1} - k_{\mathrm{ct}}2M_{a+1}Y_0 + k_{\mathrm{ct}}2Y_aM_1 + 0.5k_{\mathrm{t}}\sum_{r=0}^{a}\binom{a}{r}Y_{a-r}Y_r + k_{\mathrm{s}}\sum_{m=2}^{\infty}[P_m^{\bullet}]\sum_{r=1}^{m-1}r^a \tag{12}$$

*a*th moment of radicals

$$\frac{\mathrm{d}Y_a}{\mathrm{d}t} = k_{\mathrm{ha}}[R_{\mathrm{c}}^{\bullet}]2M_{a+1} + k_{\mathrm{ct}}Y_0 2M_{a+1} - k_{\mathrm{ct}}Y_a 2M_1 - k_{\mathrm{t}}Y_aY_0 - k_{\mathrm{s}}(Y_{a+1} - Y_a) + k_{\mathrm{s}}\sum_{m=2}^{\infty}[P_m^{\bullet}]\sum_{r=1}^{m-1}r^a \tag{13}$$

where

$$\sum_{m=2}^{\infty}[P_m^{\bullet}]\sum_{r=1}^{m-1}r^a = \begin{cases} Y_1 - Y_0 & \text{if } a = 0 \\ \frac{1}{2}Y_2 - \frac{1}{2}Y_1 & \text{if } a = 1 \\ \frac{1}{3}Y_3 - \frac{1}{2}Y_2 + \frac{1}{6}Y_1 & \text{if } a = 2 \end{cases} \tag{14}$$

Eqs. (12)–(14) must be solved together with Eq. (7), which in terms of moments becomes:

$$\frac{\mathrm{d}[R_{\mathrm{c}}^{\bullet}]}{\mathrm{d}t} = 4k_{\mathrm{d}}f[I] - 2k_{\mathrm{ha}}[R_{\mathrm{c}}^{\bullet}]M_1 \tag{15}$$

It should be noted that M_{a+1} and Y_{a+1} appear in the balance of M_a and Y_a, respectively. A closure problem arises. It is common practice to employ a function of the moments that are solved through balances to estimate the highest order moments [15,16]. This can be done exactly when the distribution type is known. In any other case, the obtained values are approximated by assuming a distribution type. When solving up to the second moment through balance equations, Eqs. (16) and (17) are used to estimate the polymer and radical 3rd moments as in our previous work [9]. It is well-known that predictions of number-average molecular weights, where zero and first order moments are used, are not affected by this approximation but second order moment and weight average molecular weight results are affected. In view of this, it is very important to select the type of distribution correctly. For this system, this selection was done according to the procedure outlined in Zabisky et al. [16], by which the type of the curve is selected by comparing calculated and experimental z-average molecular weights.

$$M_3 = \left(\frac{M_2}{M_1}\right)^3 M_0, \tag{16}$$

$$Y_3 = \left(\frac{Y_2}{Y_1}\right)^3 Y_0, \tag{17}$$

As we explain later, the 0th, 1st and 2nd moments are necessary for the pgf calculations. Eqs. (6), (12)–(17) must be solved simultaneously with the pgf equations.

2.1. Probability generating functions

When calculating the complete MWD, we apply the concept of pgf to the mass balance equations. The radical and polymer length distributions may be described in several different forms. In this work, we consider distributions in number, weight or chromatography basis. Those three distributions have associated probabilities. If molecules are chosen randomly using a number (n) probability, all molecules have an equal chance of being chosen. If the random selection is made using a weight (w) probability, all units of mass are equally likely to be chosen. If a chromatographic (c) probability is used, the quantities with equal probabilities are those with equal value of the product of mass times the molecular weight. In each case, the probability that a certain fraction of radical molecules has a length 'm' is symbolized by $p_j(m)$, $j = n$, w or c. Given a discrete distribution of probabilities $p_j(m)$, the probability generating function associated with it is defined as shown in Eq. (18) [15]:

$$\phi_j(z) = \sum_{m=0}^{\infty} p_j(m) z^m \quad j = n, w, c \tag{18}$$

If the probability distributions for polymers are symbolized by $p_j^*(x)$, we can also define pgfs for polymer length distributions, as indicated in Eq. (19):

$$\psi_j(z) = \sum_{n=0}^{\infty} p_j^*(m) z^m \quad j = n, w, c \tag{19}$$

The transformed variable is 'z'. Even though z could be complex, for this work we have only used real z, which in that case must verify $0 \le z \le 1$. Then, the pgf is a real, continuous, convex, increasing function of z that may take values between 0 and 1 [17]. Other useful definitions related to pgf derivatives are shown in Appendix A. In order to define the various pgfs, it is necessary to calculate several different probabilities. This can be done in terms of concentrations of radical and polymer species, and the different moments of the distributions as shown in Appendix A. As an example we show how to calculate the number probabilities, $p_n(m)$ and $p_n^*(m)$, using Eqs. (20) and (21):

$$\text{Radicals :} \qquad p_n(m) = \frac{[P^{\cdot}_m]}{\sum_{m=1}^{\infty} [P^{\cdot}_m]} = \frac{[P^{\cdot}_m]}{Y_0} \tag{20}$$

$$\text{Polymer :} \qquad p_n^*(m) = \frac{[P_m]}{\sum_{m=0}^{\infty} [P_m]} = \frac{[P_m]}{M_0} \tag{21}$$

where $[P^{\cdot}_m]$ and $[P_m]$ are the molar concentrations of radicals and polymer of length 'm', respectively. The weight and chromatographic probabilities are calculated as shown in Appendix A.

2.2. pgf Balances

In order to obtain the pgf balances, it is necessary to multiply both sides of the mass balance equation for a molecule of chain length m by an appropriate factor. For instance to obtain the pgf balance of the number distribution, we multiply by the mth power of z (z^m), then sum for all possible values of m ($m = 0, \ldots, \infty$), finally rearrange the resulting equation in terms of the distribution moments, the number pgf (pgfn) and pgf derivatives. To obtain the weight pgf (pgfw) or the chromatographic pgf (pgfc) balance equations, the mass balance equations are multiplied by mz^m and m^2z^m, respectively, and the same procedure is followed.

When Eqs. (8) and (9) are transformed in this manner, Eqs. (22)–(27) are obtained. Applying the pgf transform to Eq. (8) results in pgf balances of the polymer chain length distribution, and its application to Eq. (9), in pgf balances of the radical distribution. More detailed information about this transformation process may be found elsewhere [18].

Balance of pgfn for the radical number-distribution

$$\begin{aligned}\frac{\mathrm{d}\{Y_0 \phi_n(z)\}}{\mathrm{d}t} ={}& k_{\mathrm{ha}}[R^{\cdot}_{\mathrm{c}}]2M_0 z\psi'_n(z) + k_{\mathrm{ct}}2Y_0 z\psi'(z)M_0 \\ & - k_{\mathrm{ct}}\phi_n(z)2Y_0M_1 - k_{\mathrm{t}}\phi_n(z)Y_0^2 - k_{\mathrm{s}}(z\phi'_n(z) \\ & - \phi_n(z))Y_0 + \frac{k_{\mathrm{s}}}{z-1}Y_0(\phi_n(z) - 1)\end{aligned} \tag{22}$$

Balance of pgfn for the polymer number-distribution

$$\begin{aligned}\frac{\mathrm{d}\{M_0 \psi_n(z)\}}{\mathrm{d}t} ={}& -k_{\mathrm{ha}}[R^{\cdot}_{\mathrm{c}}]2z\psi'_n(z)M_0 - k_{\mathrm{ct}}2z\psi'_n(z)M_0Y_0 \\ & + k_{\mathrm{ct}}\phi_n(z)2Y_0M_1 + \frac{k_{\mathrm{t}}}{2}Y_0^2\phi_n(z)^2 \\ & + \frac{k_{\mathrm{s}}}{z-1}Y_0(\phi_n(z) - 1)\end{aligned} \tag{23}$$

Balance of pgfw for the radical weight-distribution

$$\begin{aligned}\frac{\mathrm{d}\{Y_1\phi_w(z)\}}{\mathrm{d}t} &= k_{\mathrm{ha}}[R^{\cdot}_{\mathrm{c}}]2z\psi'_w(z)M_1 + k_{\mathrm{ct}}z\psi'_w(z)2M_1Y_0 \\ &\quad - k_{\mathrm{ct}}\phi_w(z)2Y_1M_1 - k_{\mathrm{t}}\phi_w(z)Y_1Y_0 \\ &\quad - k_{\mathrm{s}}Y_1(z\phi'_w(z) - \phi_w(z)) \\ &\quad + \frac{k_{\mathrm{s}}}{(z-1)^2}[\phi_w(z)Y_1(z-1) \\ &\quad + zY_0(1-\phi_n(z))] \qquad (24)\end{aligned}$$

Balance of pgfw for the polymer weight- distribution

$$\begin{aligned}\frac{\mathrm{d}\{M_1\psi_w(z)\}}{\mathrm{d}t} &= -k_{\mathrm{ha}}[R^{\cdot}_{\mathrm{c}}]2M_1z\psi'_w(z) - k_{\mathrm{ct}}2M_1z\psi'_w(z)Y_0 \\ &\quad + k_{\mathrm{ct}}Y_1\phi_w(z)2M_1 + k_{\mathrm{t}}Y_0\phi_n(z)Y_1\phi_w(z) \\ &\quad + \frac{k_{\mathrm{s}}}{(z-1)^2}[\phi_w(z)Y_1(z-1) \\ &\quad + zY_0(1-\phi_n(z))] \qquad (25)\end{aligned}$$

Balance of pgfc for the radical chromatographic-distribution

$$\begin{aligned}\frac{\mathrm{d}\{Y_2\phi_{\mathrm{c}}(z)\}}{\mathrm{d}t} &= k_{\mathrm{ha}}[R^{\cdot}_{\mathrm{c}}]2zM_2\psi'_{\mathrm{c}}(z) + k_{\mathrm{ct}}2zM_2\psi'_{\mathrm{c}}(z)Y_0 \\ &\quad - k_{\mathrm{ct}}Y_2\phi_{\mathrm{c}}(z)2M_1 - k_{\mathrm{t}}Y_2\phi_{\mathrm{c}}(z)Y_0 \\ &\quad - k_{\mathrm{s}}Y_2(z\phi'_{\mathrm{c}}(z) - \phi_{\mathrm{c}}(z)) \\ &\quad + \frac{k_{\mathrm{s}}}{(z-1)^3}[(z-z^2)2Y_1\phi_w(z) \\ &\quad + (z^2+z)Y_0\phi_n(z) \\ &\quad + (z^2-2z+1)Y_2\phi_{\mathrm{c}}(z) - (z^2+z)Y_0] \\ &\qquad (26)\end{aligned}$$

Balance of pgfc for the polymer chromatographic-distribution

$$\begin{aligned}\frac{\mathrm{d}\{M_2\psi_{\mathrm{c}}(z)\}}{\mathrm{d}t} &= -k_{\mathrm{ha}}[R^{\cdot}_{\mathrm{c}}]2zM_2\psi'_{\mathrm{c}}(z) - k_{\mathrm{ct}}2zM_2\psi'_{\mathrm{c}}(z)Y_0 \\ &\quad + k_{\mathrm{ct}}Y_2\phi_{\mathrm{c}}(z)2M_1 + k_{\mathrm{t}}Y_0\phi_n(z)(Y_2\phi_{\mathrm{c}}(z) \\ &\quad + Y_1\phi_w(z)) + \frac{k_{\mathrm{s}}}{(z-1)^3}[(z-z^2)2Y_1\phi_w(z) \\ &\quad + (z^2+z)Y_0\phi_n(z) + (z^2-2z+1)Y_2\phi_{\mathrm{c}}(z) \\ &\quad - (z^2+z)Y_0] \qquad (27)\end{aligned}$$

Through convenient inversion of each one of the pgf the corresponding MWDs can be obtained, as detailed in the sections that follow.

2.3. Pgf model resolution

A very large differential equation system (Eqs. (6), (12)–(15), (22)–(27)) must be solved to obtain the number, weight and chromatographic pgf. The total number of equations is 8 + 6 Nz, where Nz are the number of values of z where each pgf must be evaluated as required by the selected inversion method, in our case Papoulis [19,20] or Stehfest's algorithm [21,22], which will be described in Section 3. Other z values may be incorporated in the calculations in order to improve the accuracy in the numerical estimation of pgf first derivatives, which appear in all the pgf equations. These derivatives are calculated by backward finite differences.

The model requires as input data the mass of polymer to be modified; molecular weight of monomer; number- and weight-average molecular weights as well as molecular weight distribution of the virgin resin; peroxide concentration and molecular weight; operating temperature and residence time.

The pgfs are dependent variables of the system so it is necessary to extract their initial values from the MWD of the virgin resin. First, the experimental data is converted to number fraction (n), weight fraction (w), and chromatographic fraction (c) as functions of degree of polymerization, as thoroughly detailed elsewhere [11]. To accomplish the summations indicated in the pgf definitions it is necessary to evaluate the distribution beginning at the lowest available degree of polymerization (DP_1) and perform the summation with unit steps. Cubic splines [23] are applied to the experimental data to obtain all the information needed to calculate Eq. (18). We consider that no radicals are present in the virgin resin so the corresponding pgfs are null at the beginning of the modification reaction.

Kinetic parameters are also necessary. The ones used in this work are presented in Table 1. They are the same as the ones employed to obtain average molecular weights in our previous work [9], except for the pre-exponential factor of the termination by combination reaction. Since the presence of vinyl groups was not explicitly considered in the present model (but was considered in the previously reported one), the modification of the mentioned pre-exponential factor was necessary so that calculated and experimental average

Table 1
Kinetic parameters

Kinetic constant	A (L mol s)	E (J mol)
Hydrogen abstraction, k_{ha}	5.00×10^8	6.28×10^4
Chain transfer to polymer k_{ct}	1.25×10^8	6.28×10^4
Termination by combination, k_{t}	1.20×10^{10}	6.70×10^4
Chain scission, k_{s}	1.00×10^4	1.09×10^5
Initiator decomposition, k_{d}	1.98×10^{12}	1.24×10^5
Efficiency, $f = 0.98$		

molecular weights matched. An algorithm for least-squares estimation of nonlinear parameters [24] is used to obtain the best parameter estimation. The initial guess for the parameter was taken from our previous work [9]. The generic objective function employed was:

$$\mathrm{ObjF} = \sum_{i=1}^{N_{\mathrm{exp}}} \left\{ w_{M_{\mathrm{n}}} \left| 1 - \frac{M_{\mathrm{n}_i}^{\mathrm{calc}}}{M_{\mathrm{n}_i}^{\mathrm{exp}}} \right| + w_{M_{\mathrm{w}}} \left| 1 - \frac{M_{\mathrm{w}i}^{\mathrm{calc}}}{M_{\mathrm{w}i}^{\mathrm{exp}}} \right| \right\} \tag{28}$$

where the superscripts ‘exp’ and ‘calc’ correspond to experimental and calculated values, respectively.

The complete system of equations is solved by means of Gear’s method [25] for stiff systems. The output of the pgf model consists of pgfn, pgfw and pgfc as functions of residence time and z. These quantities serve as data for the inversion algorithms [11,12]. When inverting pgfn, the number molecular weight distribution is obtained directly. Inversion of pgfw and pgfc results in weight and chromatographic molecular weight distributions, respectively. Emphasis is placed on the chromatographic MWD of the final modified product, since this is the only material for which experimental information is available for comparison.

3. pgf Inversion algorithms

We use in this work the inversion formulas proposed by Papoulis [19,20] and by Stehfest [21,22] as adapted for the inversion of pgf transforms. Full details may be found in Brandolin et al. [11] and Asteasuain et al. [12].

Eq. (29) shows Papoulis’ expression:

$$f\left(\frac{M_i}{M_{\mathrm{mon}}}\right) = \sum_{n=0}^{N} a_{n,i} P_{2n}\left(\exp\left(-r_i \frac{M_i}{M_{\mathrm{mon}}}\right)\right) \tag{29}$$

In this equation $P_{2n}(x)$ are Legendre polynomials that can be calculated from the recursive formula: $P_0(x) = 1$, $P_1(x) = x$, $(n+1)P_{n+1}(x) = (2n+1)xP_n(x) - nP_{n-1}(x)$. This method has two parameters,r_i and N [12]. For the present problem we found that suitable values for r_i may be calculated from $r_i = \ln(2)M_{\mathrm{mon}}/M_i$, that is, a new value for each molecular weight point where the distribution is to be calculated. The set of coefficients $a_{n,i}$ $(n = 0,\dots,N)$ are calculated for each value of r_i by solving the system of equations presented in condensed form in Eq. (30):

$$r_i \mathrm{pgf}(e^{-(2k+1)r_i}) = \sum_{m=0}^{k} \frac{(k-m+1)_m}{2(k+1/2)_{m+1}} a_{m,i} \quad k = 0,1,2,\dots,N \tag{30}$$

Here, the factors between parentheses in the right hand side may be expressed generically as $(j)_l$ and calculated by means of Eq. (31):

$$(j)_l = \begin{cases} 1 & l = 0 \\ j(j+1)\dots(j+l-1) & l > 0. \end{cases} \tag{31}$$

With this method, $f(M_i/M_{\mathrm{mon}})$ may be calculated at any value of M_i/M_{mon} from the value of the real part of the transform in a series of equidistant points, defined by the parameter r_i.

Eqs. (32) and (33) show Stehfest’s extrapolation formulas, where the method parameter is N:

$$f\left(\frac{M_i}{M_{\mathrm{mon}}}\right) \approx \frac{M_{\mathrm{mon}} \ln(2)}{M_i} \sum_{n=1}^{N} K_n \mathrm{pgf}\left(\exp\left(-n\frac{M_{\mathrm{mon}} \ln(2)}{M_i}\right)\right) \tag{32}$$

$$K_n = (-1)^{n+N/2} \times \sum_{k=[(n+1)/2]}^{\min(n,N/2)} \frac{k^{N/2}(2k)!}{(N/2-k)!k!(k-1)!(n-k)!(2k-n)!} \tag{33}$$

Each method has optimum parameter values (N and r for Papoulis or N for Stehfest) that may vary with the particular problem studied. The evaluation of r (in our case r_i) has been shown earlier. The optimum value of N, for both methods, was selected according to the SSQ1 criterion [11,12]. This criterion indicates that the optimum value of the parameter is the one that minimizes the sum of squares of the differences between curves calculated with two successive values of N.

As for computational effort, both methods require about N_{max} evaluations of pgf per molecular weight point, where N_{max} is the largest value of the method parameter used when applying the SSQ1 criterion.

4. Experimental validation

Table 2 shows the experimental data used for model validation. The data were obtained in our laboratory

Table 2
Experimental data at temperature = 170 °C and final time = 20 min [26,27]

DBHP concentration (w/w%)	Molecular weights	
	M_{n}	M_{w}
0.000	21,700	53,200
0.025	24,700	70,300
0.050	28,600	78,000
0.075	25,800	98,700
0.100	31,350	130,000
0.200	29,400	157,300

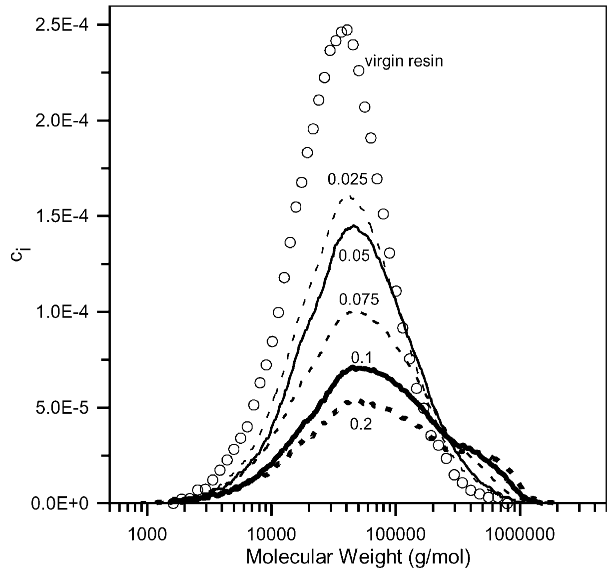

Fig. 1. Measured chromatographic MWDs (c_i) for virgin resin and modified products.

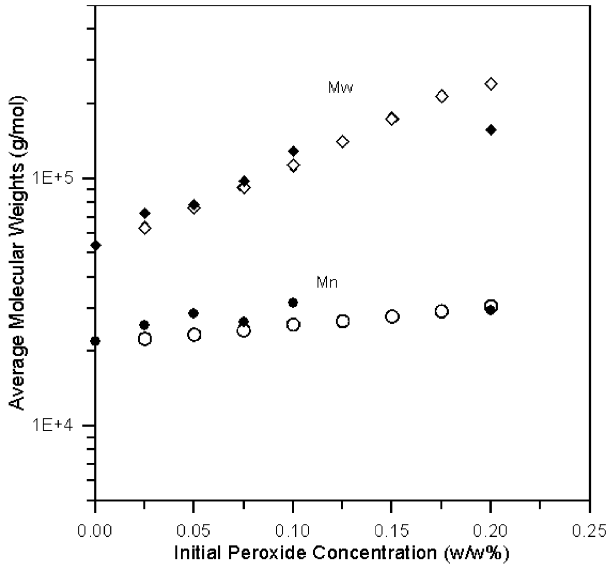

Fig. 2. Effect of initial peroxide concentration on average molecular weights of resins treated at the operating conditions given in Table 2. Hollow symbols: calculated values; filled symbols: experimental measurements.

[26,27]. A commercial linear high-density polyethylene, from Oxy Petrochemical ($M_n = 21,700$; $M_w = 53,200$), was chemically modified with DBHP. A powder of the virgin resin was impregnated with a peroxide solution to obtain five different peroxide concentrations: 0.025, 0.05, 0.075, 0.1 and 0.2 w/w%. Each mixture was treated at 170 °C in a press for 20 min to ensure complete reaction. MWD of product samples were analyzed by size exclusion chromatography (SEC) in a Waters-150-C ALC-GPC. The measured data for the virgin resin and modified samples were analyzed as if they all were linear polyethylenes. For the modified resins, the experimental MWD curves obtained by these means are only indicative of the modification effect on MWD. As result of the branching produced by the treatment, actual weight average molecular weights are expected to be higher than those measured by SEC. This effect must result more evident as the initial peroxide concentration increases. As the virgin resin is a linear polyethylene the measured MWD can be taken as valid input data for the model. Fig. 1 presents the MWD of the virgin and modified resins.

5. Results and discussion

The model predicts an increase of the average molecular weights with reaction time for a given initial peroxide concentration, as expected at this temperature where termination by combination is the main reaction [26]. This is in accordance with our previously reported results for this particular set of data [9]. We have compared model predictions at final reaction time with experimental results obtained with all the initial peroxide concentrations shown in Table 2. In particular, in Fig. 2 we show number and weight average molecular weights as functions of the initial peroxide concentration. Each calculated point (hollow symbols) is obtained from a different simulation run. Filled symbols indicate experimental values. As the peroxide concentration increases, the weight average molecular weight of the modified resin increases significantly. The number average molecular weight remains close to that of the virgin resin, indicating that scission reactions are less important than crosslinking reactions. The model follows all these changes adequately. In general, the differences between calculated and experimental data are of the same order of magnitude of the inherent errors of the experimental measurements. The largest difference appears for the weight average molecular weight obtained at the highest peroxide concentration employed (0.2 w/w%). This is to be expected because the material is approaching the gel point. It must also be remembered that the presence of branches was not considered when analyzing experimental SEC data.

In what follows, the calculated MWD curves were obtained by inversion of the corresponding pgf as explained earlier, using the optimum value of Papoulis' parameter N. This value was found to be $N = 4$. Results of comparable quality were obtained when using Stehfest's method. In this case the optimum parameter is also $N = 4$. In order to find those optimum parameters, the values of N_{max} were 15 for Papoulis's method and 18 for Stehfest's (Papoulis's solutions degraded badly for values of $N_{max} > 15$). For our implementation, then, Papoulis's algorithm was computationally less expensive, since, as explained earlier, the expense is directly proportional to N_{max}.

Figs. 3 and 4 show calculated results for the resin modified with 0.2 w/w% peroxide. We show the calculated

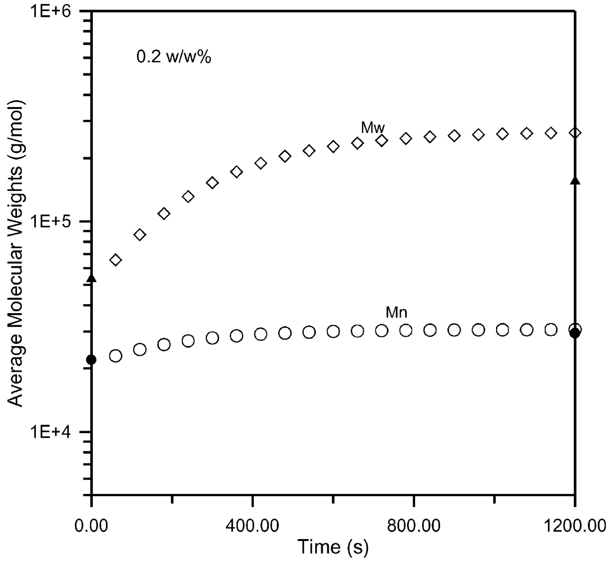

Fig. 3. Evolution with time of average molecular weights for material treated at the operating conditions given in Table 2 and initial peroxide concentration = 0.2 w/w%. Hollow symbols: calculated values; filled symbols: experimental measurements.

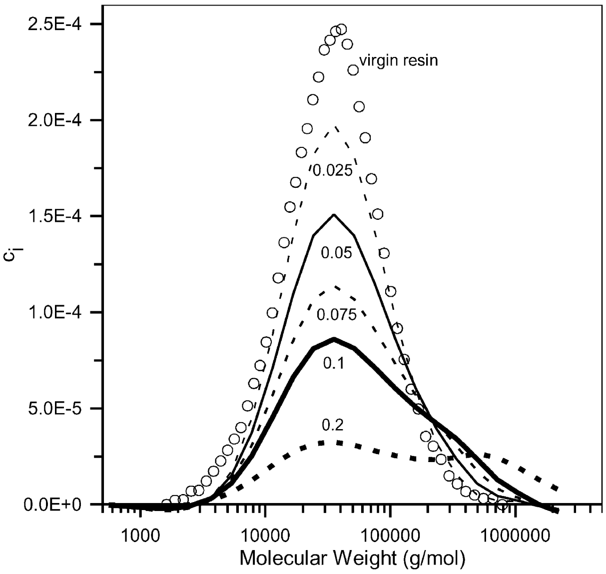

Fig. 5. Calculated chromatographic MWDs (c_i) for different initial peroxide concentrations measured in weight percentage, and for the operating conditions given in Table 2.

evolution of average molecular weights with time in Fig. 3, and of chromatographic MWD in Fig. 4. As the reaction proceeds average molecular weights increase, particularly the weight average molecular weight (see Fig. 3). The MWD broadens accordingly, as shown in Fig. 4. It is also apparent from this figure that there is a period, up to about one third of the total reaction time, where the MWD curves remain unimodal. Then a shoulder begins to appear and grow, until the final product presents a bimodal MWD curve. This may be attributed to crosslinking reactions that become more important as the molecules grow larger.

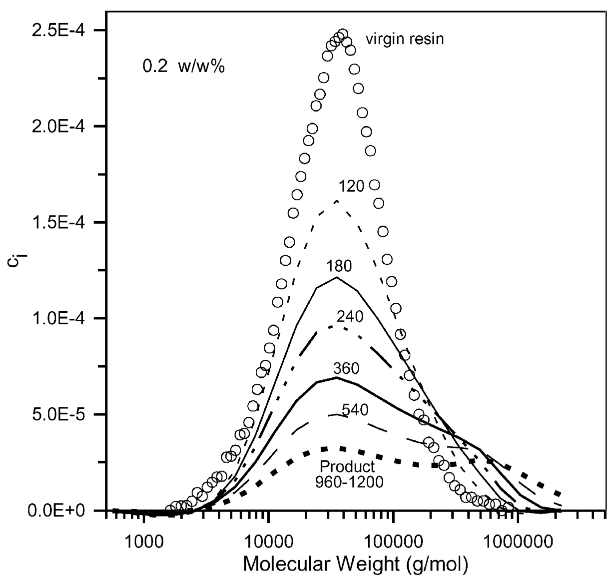

Fig. 4. Calculated chromatographic MWDs (c_i) at different reaction times measured in seconds, for 0.2 w/w% DBHP and the operating conditions given in Table 2.

The calculated chromatographic distribution obtained at the end of the process for different initial peroxide concentrations is shown in Fig. 5. The corresponding virgin resin MWD is also shown in the figure for comparison. A broadening in the distribution is predicted as the initial peroxide concentration increases. This may be explained as a consequence of the larger number of initiation radicals present when using higher peroxide concentrations, something that favors crosslinking reactions. MWD curves show an increase of the high molecular weight tail with respect to the one for the virgin resin. A shoulder appears at 0.1 w/w% and finally a bimodal curve is obtained for 0.2 w/w%.

We have found [11,12] that the most dependable prediction is that of weight MWD. This may be attributed to the fact that it does not stress either the low molecular weights, as the number distribution does, or the very high molecular weight tail, as the chromatographic distribution. Even so, the predicted chromatographic MWDs for all peroxide concentrations show similar shapes and trends as the experimental ones, as a comparison between Figs. 1 and 5 shows. It must be noted that no parameter adjustment was performed using data of a complete MWD.

As an example of other capabilities of the model presented in this work, we calculate the effect of temperature on the modification of high-density polyethylene. The results may be observed in Figs. 6 and 7, where the calculated average molecular weights and MWDs are presented as functions of operating temperature for 0.2 w/w% initial peroxide concentration. The decomposition constant of the peroxide, DBPH, was calculated as a function of

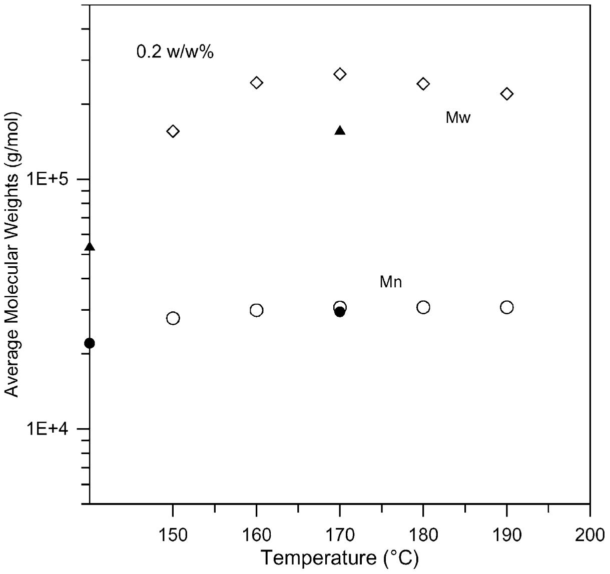

Fig. 6. Effect of temperature on average molecular weights for a resin modified with 0.2 w/w% DBHP. Hollow symbols: calculated values; filled symbols: experimental values.

temperature using the data in Table 1. It may be observed in Fig. 6 that in all cases the modified resins have higher average molecular weights than the virgin resin. The figure also shows that the maximum average weights are obtained when performing the modification at 170 °C. As the treatment temperature increases, the degree of modification becomes less important. This may be attributed to an increasing importance of the scission reaction with temperature. Again, the MWD results follow well this trend, as may be observed in Fig. 7.

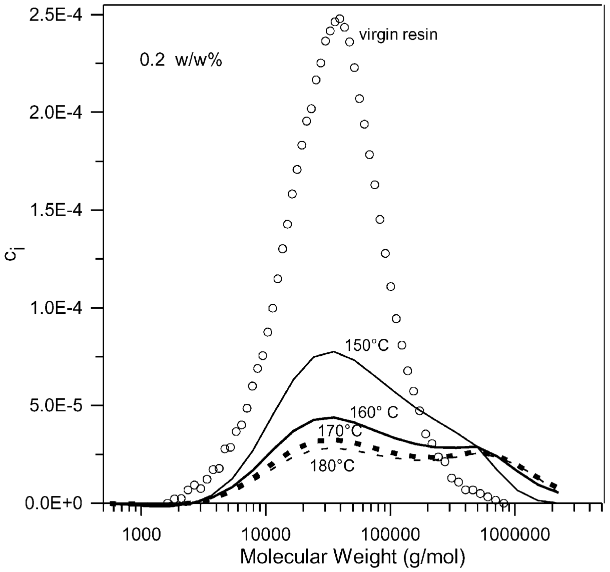

Fig. 7. Effect of temperature on final chromatographic MWD for a resin modified with 0.2 w/w% DBHP. Papoulis' method was used in the inversion.

6. Conclusions

In this paper we propose a model for the reactive modification of polyethylene aiming at developing a practical tool for prediction of molecular weight distributions. We have solved a system of transformed mass balance equations that describes the peroxide modification of polyethylene in a batch process at the pregel region. We have shown that the application of pgf transforms to the mass balance equations allows the description of the MWD of the modified polymers. Numerical inversion of the transformed variables has allowed a very good recovery of the entire molecular weight distribution, showing similar trends as the ones shown by the experimental distributions measured by SEC. The two numerical inversion methods used gave results of comparable quality.

Even though model validation was done using data from material modified in a press, the kinetic mechanism should also be valid for modification in an extruder with plug flow. Work is under way to predict MWD of polymer molecules with and without vinyl groups using the pgf technique.

Acknowledgements

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Appendix A

A.1. Useful relationships for the pgf equations

Derivatives of the pgf functions appear in all the balances. They may be evaluated as [17,28]:

$$\phi_j'(z) = \sum_{m=1}^{\infty} m p_j(m) z^{m-1} \qquad \psi_j'(z) = \sum_{m=1}^{\infty} m p_j^*(m) z^{m-1} \quad \text{(A1)}$$

A.2. Relationships between moments, concentrations and probabilities

The weight probabilities are calculated using Eqs. (A2) and (A3):

$$\text{Radicals :} \qquad p_w(m) = \frac{m[P_m^{\cdot}]}{\sum_{m=1}^{\infty} m[P_m^{\cdot}]} = \frac{m[P_m^{\cdot}]}{Y_1} \quad \text{(A2)}$$

$$\text{Polymer :} \qquad p_w^*(m) = \frac{m[P_m]}{\sum_{m=1}^{\infty} m[P_m]} = \frac{m[P_m]}{M_1} \quad \text{(A3)}$$

If the focus is on the pgf of the chromatographic distribution (pgfc), the corresponding probabilities are given by Eqs. (A4) and (A5).

$$\text{Radicals :} \quad p_c(m) = \frac{m^2[P_m^{\cdot}]}{\sum_{m=1}^{\infty} m^2[P_m^{\cdot}]} = \frac{m^2[P_m^{\cdot}]}{Y_2} \tag{A4}$$

$$\text{Polymer :} \quad p_c^*(m) = \frac{m^2[P_m]}{\sum_{m=1}^{\infty} m^2[P_m]} = \frac{m^2[P_m]}{M_2} \tag{A5}$$

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