

MODELING MOLECULAR WEIGHT DISTRIBUTION, VINYL CONTENT AND BRANCHING IN THE REACTIVE EXTRUSION OF HIGH DENSITY POLYETHYLENE

M. ASTEASUAIN, M.V. PÉREZ, C. SARMORIA and A. BRANDOLIN

Planta Piloto de Ingeniería Química (UNS-CONICET), CC 717, 8000 Bahía Blanca, Argentina.

abrandolin@plapiqui.edu.ar

Abstract— We study reactive modification of high density polyethylene by organic peroxides. We improve a previous model capable of describing average molecular weights and vinyl content to incorporate the calculation of long-chain branching and complete molecular weight distributions. We calculate average molecular weights and long-chain branching indexes for molecules with a given number of vinyls, by applying a double moment technique over those variables. No moment technique was applied to the vinyl content so the model has the capability of calculating those average quantities for every vinyl content. To calculate molecular weight distribution we apply probability generating function definitions with respect to the molecular size, to the mass balances of radical and polymer species of a given number of vinyls. We use two distinct definitions of probability generating functions, each one directly applicable either to the number or weight distributions. These probability generating functions are numerically inverted to obtain the corresponding calculated molecular weight distribution. Results give a deeper insight into the evolution of vinyl groups and branching points formation. MWD and vinyl content predictions are compared with qualitative experimental data showing the model capabilities.

Keywords— MWD, Mathematical modeling, pgf, Vinyl content, Long-chain branching.

I. INTRODUCTION

High density polyethylene (HDPE) is a versatile thermoplastic, for which product and market development continue to open new applications. It is produced either as a linear polymer or one with short-chain branches if a co-monomer is used. The specific properties of each HDPE grade result from the combination of several variables: density, molecular weight, molecular weight distributions (MWD), vinyl content and degree of branching (Ward and Hadley, 1993). Catalyst technology has made possible the improvement of the performance of the different grades of HDPE. Nevertheless, reactive modification is an established and economic post-reactor option to tailor molecular properties of HDPE in order to broaden its range of application.

Organic peroxides are used to generate primary radicals that will attack the polymer. It is generally accepted that primary radicals abstract hydrogen from the polymer molecule, which then undergoes mainly crosslinking. Depending on the operating conditions a certain degree of scission may be observed. Vinyl content plays an important role in the reactive modification. The concentration of terminal double bonds present in polyethylene decreases rapidly for increasing initial peroxide concentrations, indicating a strong selectivity towards their reaction. It has also been observed that the increase in molecular weight is higher for resins with higher vinyl content (Smedberg *et al.*, 1997; Suwanda and Balke, 1993a). As modification proceeds the initially linear polymer becomes increasingly branched, the branches having a size similar to that of the original polymer molecules. The creation of this type of branches leads to a drastic change in rheological and mechanical properties as discussed by Pérez *et al.* (2001).

Few mathematical models in the literature describe the specific process of modification of polyethylene. Some of them use a statistical approach as reviewed by Gloor *et al.* (1994), the main interest being the prediction of gel points and of average molecular weights and MWDs of the sol fractions. The statistical approach does not provide information as a function of time.

Suwanda and Balke (1993b) were the first to use a kinetic approach. They aimed at the prediction of molecular weight distributions, allowing molecules with either 1 or 0 vinyls. They calculated the distribution by discretizing it in up to 500 degree of polymerization points. They obtained good predictions of molecular weights for low density polyethylene and linear low density polyethylene, but not for HDPE. With respect to vinyl content they could not predict a drop as large as the one observed experimentally in all cases.

In a previous work we proposed a kinetic model (Pedernera *et al.*, 1999) that described the length of the polymer chain and the concentration of vinyl groups simultaneously. The resulting infinite system of mass balance equations was solved using a double moment technique. The model predicted average molecular weights and the average concentration of vinyl groups as functions of time. This model resulted in improved predictions of the experimental data over the previously

mentioned kinetic model of Suwanda and Balke.

In this work, we present a generalization of our previous model, which allows us to account for the entire molecular weight distribution, as well as the long-chain branching. We develop a deeper insight into the vinyl group distribution among the molecules given the operating conditions of the modification process. We focus on the modification taking place in a press at constant temperature, under conditions where scission is not measurable.

II. MATHEMATICAL MODEL

We develop a set of mass balances for the reacting species where the different lengths, number of vinyls and number of branching points are taken into account. A triple moment technique was used to calculate number and weight average molecular weights as well as average number of branching points for species having j vinyls, $j=0, 1, 2 \dots$. To calculate molecular weight distributions we apply another transform technique that makes use of probability generating function (pgf) definitions applied to the number and weight MWD, following the general technique illustrated in Asteasuain *et al.* (2002b). Equations are set for the pgfs of each species, from which in principle it would be possible to calculate MWDs for species having distinct number of vinyls. The moments of the distributions are needed as input, so they must be calculated as functions of residence time simultaneously with the pgf. The pgf transforms considered in this work are defined for discrete distributions, as those found in polymer science, and their transformed variable is real and bounded. This makes them attractive to be used in a simulation involving polymeric species, such as the one in this work. In the present process it must be considered that we start from polymer, and there exists a nonzero pgf curve from the beginning. In consequence this pgf must be estimated from the MWD of the virgin resin. In this work we calculate pgf for the global molecular weight distribution. The calculated pgfs are numerically inverted using two inversion methods (Papoulis, 1956; Stehfest, 1970). This allows recovery of MWD.

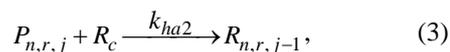
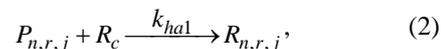
The modification process is postulated to occur isothermally in a perfectly stirred batch process, and the usual assumption of quasi-steady state of radicals is not employed. We focus on the pregel region only. The model accounts for the existence of vinyl groups in the polymer molecules. No restriction is imposed on the maximum number of vinyl groups per molecule. Molecules with no vinyls are also allowed. We also take into consideration the presence of long-chain branches. Radicals and macroradicals are assumed to contain only one active site since the model has been implemented to perform calculations in the pregel region. The proposed mechanism is shown below (Eqns. 1 – 6). This mechanism is an extension of the one we previously reported (Pedernera *et al.*, 1999). In this work we add a counter to keep track of the number of branches and we do not include the scission reaction since the degree of scission

appears to be negligible at the operating conditions for which the experimental data used for comparison were obtained.

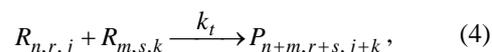
Initiation



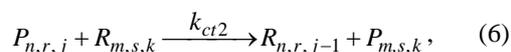
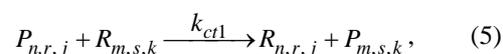
Hydrogen Abstraction



Termination by Combination



Chain Transfer to Polymer



In these equations I is the initiator, R_c is the initiation radical produced by thermal decomposition of the peroxide initiator (Eqn. 1), P are polymer molecules and R are macroradicals, where the first index indicates the number of monomeric units, the second index indicates the number of branches and the third one the number of vinyls. The first and second indexes may vary between 1 and infinity, and the third one between zero and a maximum related to the number of monomers.

Every time a hydrogen abstraction occurs in the backbone of the molecule (Eqn. 2) a polymer molecule is converted to a macroradical of the same size, number of vinyls, and long-chain branching points. Equation 3 represents a hydrogen abstraction that consumes a vinyl group, then in this case the resulting macroradical has the same size and number of branching points but one vinyl less. As the kinetic constants for these reactions are given per unit of reactive site, when performing mass balances they must be multiplied by the number of reactive sites involved. Termination is assumed to occur by combination (Eqn. 4), where the resulting polymer molecule has a length, number of vinyl groups and number of branching points equal to the sum of the respective quantities in the reacting radicals. If a macroradical attacks a hydrogen anywhere on a polymer molecule a chain transfer to polymer occurs (Eqns. 5 and 6). The situation is similar to the hydrogen abstraction by an initiation radical.

Mass balances are established for all of the species involved in the reaction mechanism as follows (Eqns. 7-10).

Peroxide Initiator

$$\frac{d[I]}{dt} = -k_{di}[I], \quad (7)$$

Primary Radical

$$\begin{aligned} \frac{d[R_c]}{dt} &= 4k_{di}f_i [I] \\ &- [R_c]k_{ha1} \sum_{n=1}^{\infty} \sum_{r=1}^{r_n} \sum_{j=0}^{j_n} [P_{n,r,j}] (2n-3j) \\ &- k_{ha2} [R_c] \sum_{n=1}^{\infty} \sum_{r=0}^{r_n} \sum_{j=0}^{j_n} 3j [P_{n,r,j}] \end{aligned} \quad (8)$$

Polymer molecules with n monomer units, r branching points and j vinyls ($n=1 \dots \infty$, $r=0 \dots r_n$, $j=0 \dots j_n$)

$$\begin{aligned} \frac{d[P_{n,r,j}]}{dt} &= -k_{ha1} [R_c] (2n-3j) [P_{n,r,j}] \\ &- k_{ha2} [R_c] 3j [P_{n,r,j}] \\ &+ 0.5k_t \sum_{k=0}^j \sum_{s=0}^r \sum_{t=1}^{n-1} [R_{n-t,r-s,j-k}] [R_{t,s,k}] \\ &- k_{ct1} (2n-3j) [P_{n,r,j}] \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} \sum_{s=0}^{s_m} [R_{m,s,k}] \\ &+ k_{ct1} [R_{n,r,j}] \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} \sum_{s=0}^{s_m} (2m-3k) [P_{m,s,k}] \\ &- 3jk_{ct2} [P_{n,r,j}] \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} \sum_{s=0}^{s_m} [R_{m,s,k}] \\ &+ 3k_{ct2} [R_{n,r,j}] \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} \sum_{s=0}^{s_m} k [P_{m,s,k}] \end{aligned} \quad (9)$$

Radical molecules with n monomer units, r branching points and j vinyls ($n=1 \dots \infty$, $r=0 \dots r_n$, $j=0 \dots j_n$)

$$\begin{aligned} \frac{d[R_{n,r,j}]}{dt} &= k_{ha1} [R_c] (2n-3j) [P_{n,r-1,j}] \\ &+ 3k_{ha2} [R_c] (j+1) [P_{n,r,j+1}] \\ &- k_t [R_{n,r,j}] \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} \sum_{s=0}^{s_m} [R_{m,s,k}] \\ &+ k_{ct1} (2n-3j) [P_{n,r,j}] \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} \sum_{s=0}^{s_m} [R_{m,s,k}] \\ &- k_{ct1} [R_{n,r,j}] \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} \sum_{s=0}^{s_m} (2m-3k) [P_{m,s,k}] \\ &+ 3k_{ct2} [P_{n,r,j+1}] (j+1) \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} \sum_{s=0}^{s_m} [R_{m,s,k}] \\ &- 3k_{ct2} [R_{n,r,j}] \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} \sum_{s=0}^{s_m} k [P_{m,s,k}] \end{aligned} \quad (10)$$

The mass balance equations are infinite in number. In this work, we employ two transform techniques to be able to calculate polymer properties, the pgf and the moment techniques. A double moment technique is adequate to calculate average molecular properties such as molecular weights, long-chain branching points per

monomeric unit and vinyl content. The pgf transforms are well suited for the recovery of the complete MWD after appropriate inversion.

By applying the moment definitions to the length and number of branches we obtain double moments for each population of molecules with a given number of vinyl groups. This allows us to calculate average properties for molecules with different number of vinyl groups:

a th, b th order moment for polymer with j vinyls

$$M_{a,b,j} = \sum_{n=1}^{\infty} \sum_{r=0}^{r_n} n^a r^b P_{n,r,j}, \quad (11)$$

$a = 0,1,2 \dots; b = 0,1 \dots; j = 0,1,2 \dots$

a th, b th order moment for radicals with j vinyls

$$Y_{a,b,j} = \sum_{n=1}^{\infty} \sum_{r=0}^{r_n} n^a r^b R_{n,r,j}, \quad (12)$$

$a = 0,1,2 \dots; b = 0,1 \dots; j = 0,1,2 \dots$

To transform mass balances, Eqns. 9 and 10 must be multiplied by $n^a r^b$, and then added up for all polymer lengths and branches. The resulting moment balances are shown in Eqns. (13) and (14). It should be noted that when solving the a th moment, the $(a+1)$ th order moments appear in these equations. These are estimated using a log-normal approximation as in Pedernera *et al.* (1999).

Equations 7, 8, 13 and 14 must be solved simultaneously. In order to implement the computer program, the sums in Eqn. 8 must be replaced by the moments they represent. The system of $2+6 \times (J_{\max}+1)$ stiff ordinary differential equations may be solved numerically (Gear, 1971). J_{\max} is chosen so that results are reproducible.

$$\begin{aligned} \frac{dM_{a,b,j}}{dt} &= -k_{ha1} [R_c] (2M_{a+1,b,j} - 3jM_{a,b,j}) \\ &- k_{ha2} [R_c] 3jM_{a,b,j} \\ &+ 0.5k_t \sum_{k=0}^j \sum_{s=0}^r \sum_{r=0}^a \binom{a}{r} \binom{b}{s} Y_{a-r,b-s,j-k} Y_{r,s,k} \\ &- k_{ct1} \left[(2M_{a+1,b,j} - 3jM_{a,b,j}) \sum_{k=0}^{\infty} Y_{0,0,k} \right. \\ &\quad \left. - Y_{a,b,j} \sum_{k=0}^{\infty} (2M_{1,0,k} - 3kM_{0,0,k}) \right] \\ &+ 3k_{ct2} \left[Y_{a,b,j} \sum_{k=0}^{\infty} kM_{0,0,k} \right. \\ &\quad \left. - jM_{a,b,j} \sum_{k=0}^{\infty} Y_{0,0,k} \right] \end{aligned} \quad (13)$$

$$\begin{aligned} \frac{dY_{a,b,j}}{dt} = & k_{ha1}[R_c](2M_{a+1,b,j} - 3jM_{a,b,j}) \\ & + 3k_{ha2}[R_c](j+1)M_{a,b,j+1} \\ & - k_t Y_{a,b,j} \sum_{k=0}^{\infty} Y_{0,0,k} \\ & + k_{ct1} \left[\begin{aligned} & (2M_{a+1,b,j} - 3jM_{a,b,j}) \sum_{k=0}^{\infty} Y_{0,0,k} \\ & - Y_{a,b,j} \sum_{k=0}^{\infty} (2kM_{1,0,j} - 3kM_{0,0,k}) \end{aligned} \right] \\ & + 3k_{ct2}(j+1)M_{a,b,j+1} \sum_{k=0}^{\infty} Y_{0,0,k} \\ & - 3k_{ct2} Y_{a,b,j} \sum_{j=0}^{\infty} jM_{0,0,k} \end{aligned} \quad , \quad (14)$$

The following useful polymer properties are calculated from moment results:

Number-average molecular weight for molecules with j vinyls

$$Mn(j) = 28 \frac{M_{1,0,j} + Y_{1,0,j}}{M_{0,0,j} + Y_{0,0,j}} \quad , \quad (15)$$

Weight-average molecular weight for molecules with j vinyls

$$Mw(j) = 28 \frac{M_{2,j} + Y_{2,j}}{M_{1,0,j} + Y_{1,0,j}} \quad , \quad (16)$$

Number of branching points per monomeric unit

$$Xb(j) = \frac{M_{0,1,j} + Y_{0,1,j}}{M_{1,0,j} + Y_{1,0,j}} \quad , \quad (17)$$

Weight percent of molecules with j vinyls

$$Wvi(j) = 2800 \sum_{j=0}^{\infty} M_{1,0,j} \quad , \quad (18)$$

Global properties (Mn_{calc} , Mw_{calc} , Xb_{calc}) are obtained by summing each term in the equations through all possible values of j . For example, for the global number average molecular weight the following expression is used:

$$Mn_{calc} = 28 \frac{\sum_{j=0}^{\infty} (M_{1,0,j} + Y_{1,0,j})}{\sum_{j=0}^{\infty} (M_{0,0,j} + Y_{0,0,j})} \quad , \quad (19)$$

To describe molecular weight distributions, we use different definitions of pgf transforms for number or weight distribution. For details on the application of the technique the reader is referred to Asteauain *et al.* (2002b). Briefly, those two distributions have associated probabilities related to the number and weight fractions, respectively. In each case, the probability that certain fractions of radical or polymer molecules with j vinyls have a length “ n ” is symbolized by $P_a^\oplus(N = n, J = j)$, where $a=0$ indicates a number distribution and $a=1$ indicates a weight distribution. The probability generating functions are defined as (Miller and Macosko, 1988):

$$\Phi_{a,j}(z) = \sum_{n=0}^{\infty} z^n P_a^\oplus(N = n, J = j), \quad a = 0,1 \quad , \quad (20)$$

Table 1: Balance terms and their corresponding pgf transforms for MWD

Balance term, $n \geq 0$	Pgf transform
$\frac{d \left\{ \sum_{r=0}^{r_n} [T_{n,r,j}] \right\}}{dt}$	$\frac{d(U_{a,0,G} \Phi_{a,j}(z))}{dt} \quad j=0,1,2,\dots$
$\alpha \sum_{r=0}^{r_n} [T_{n,r,j}]$	$\alpha U_{a,0,G} \Phi_{a,j}(z) \quad j=0,1,2,\dots$
$\alpha j \sum_{r=0}^{r_n} [T_{n,r,j}]$	$\alpha j U_{a,0,G} \Phi_{a,j}(z) \quad j=0,1,2,\dots$
$\alpha n \sum_{r=0}^{r_n} [T_{n,r,j}]$	$\alpha \left[z \frac{\partial (U_{a,G} \Phi_{a,0,j}(z))}{\partial z} \right]$
$\alpha \sum_{m=1}^{n-1} \sum_{r=0}^{r_{n-m}} [T_{n-m,r,k}] \sum_{t=0}^{t_m} [T_{m,t,l}]$	$\alpha tct(a)_{k,l} = \alpha \sum_{t=0}^a \binom{a}{t} (U_{t,0,G} \Phi_{t,k}(z)) (U_{a-t,0,G} \Phi_{a-t,l}(z))$

where $\Phi_{a,j}(z) = \psi_{a,j}(z)$ when dealing with polymer molecules and $\Phi_{a,j}(z) = \phi_{a,j}(z)$ in the case of radical molecules. $P_a^\oplus(N = n, J = j)$ is calculated as follows

$$P_a^\oplus(N = n, J = j) = \frac{n^a \sum_{r=0}^{r_n} [T_{n,r,j}]}{\sum_{n=1}^{\infty} \sum_{j=0}^{j_n} \sum_{r=0}^{r_n} n^a [T_{n,r,j}]}, \quad (21)$$

$$= \frac{n^a \sum_{r=0}^{r_n} [T_{n,r,j}]}{U_{a,0,G}}, \quad \text{for } a = 0,1$$

where $T_{n,r,j}$ represents polymer or radical molecules with n monomeric units, r branching points, and j vinyl groups, $U_{a,0,G}$ is the a th, 0th global moment for radical or polymer. In order to transform the mass balance equations (Eq. 9 and 10) must be multiplied by $n^a z^n$ and added for all possible values of n and r . Table 1 shows the results of the transformation for various terms in the mass balance equations. The resulting pgf balances are shown in Eqns. 22 and 23.

pgf balance for polymer molecules

$$\begin{aligned} \frac{d(M_{a,0,G}\Psi_{a,j}(z))}{dt} = & -k_{ha1}[R_c] \left\{ 2z \frac{\partial(M_{a,0,G}\Psi_{a,j}(z))}{\partial z} \right. \\ & \left. - 3j(M_{a,0,G}\Psi_{a,j}(z)) \right\} \\ & - k_{ha2}[R_c] 3j(M_{a,0,G}\Psi_{a,j}(z)) \\ & - k_{ct1} \left\{ 2z \frac{\partial(M_{a,0,G}\Psi_{a,j}(z))}{\partial z} \right\} \sum_{k=0}^{\infty} Y_{0,0,k} \\ & + k_{ct1}(Y_{a,0,G}\phi_{a,j}(z)) \sum_{k=0}^{\infty} (2M_{1,0,k} - 3kM_{0,0,k}) \\ & + 3k_{ct2}(Y_{a,0,G}\phi_{a,j}(z)) \sum_{k=0}^{\infty} kM_{0,0,k} \\ & - 3jk_{ct2}(M_{a,0,G}\Psi_{a,j}(z)) \sum_{k=0}^{\infty} Y_{0,0,k} + k_t \sum_{k=0}^j tct(a)_{k,j-k} \end{aligned}, \quad (22)$$

pgf balance for radical molecules

$$\begin{aligned} \frac{d(Y_{a,0,G}\phi_{a,j}(z))}{dt} = & k_{ha1}[R_c] \left\{ 2z \frac{\partial(M_{a,0,G}\Psi_{a,j}(z))}{\partial z} \right. \\ & \left. - 3j(M_{a,0,G}\Psi_{a,j}(z)) \right\} \\ & + 3k_{ha2}[R_c](j+1)(M_{a,0,G}\Psi_{a,j+1}(z)) \\ & + k_{ct1} \left\{ 2z \frac{\partial(M_{a,0,G}\Psi_{a,j}(z))}{\partial z} \right\} \sum_{k=0}^{\infty} Y_{0,0,k} \\ & - k_{ct1}(Y_{a,0,G}\phi_{a,j}(z)) \sum_{k=0}^{\infty} (2M_{1,0,k} - 3kM_{0,0,k}) \\ & + 3k_{ct2}(j+1)(M_{a,0,G}\Psi_{a,j+1}(z)) \sum_{k=0}^{\infty} Y_{0,0,k} \\ & - 3k_{ct2}(Y_{a,0,G}\phi_{a,j}(z)) \sum_{k=0}^{\infty} kM_{0,0,k} \\ & - k_t(Y_{a,0,G}\phi_{a,j}(z)) \sum_{k=0}^{\infty} Y_{0,0,k} \end{aligned}, \quad (23)$$

The final system to be solved is composed of $2+6 \times (J_{\max}+1)+4 \times (J_{\max}+1) \times Nz$ balances. Nz is the number of values of z where each pgf must be evaluated. This value is about 350, depending on the selected inversion method and the number of points to be recovered on each MWD.

As input data, the model requires the mass of polymer to be modified, molecular weight of monomer, MWD of the virgin resin, together with its number average (Mn) and weight average (Mw) molecular weights, vinyl content, peroxide concentration, peroxide molecular weight, operating temperature and residence time. The two pgfs of the virgin resin are also needed; it may be necessary to calculate them from the experimental MWD, as detailed elsewhere (Brandolin *et al.*, 2001). We use the kinetic parameters reported elsewhere (Pedernera *et al.*, 1999). The complete system of equations is solved by means of the same algorithm for stiff systems used for the moment model (Gear, 1971). Unlike what was done with the moment equations, we do not solve the pgf equations for every possible value of j . Instead we calculate the pgf for the global polymer by lumping all j values. The output of the pgf model consists of the two types of pgf as functions of residence time and z . These quantities are then fed to the inversion algorithms.

To invert the pgf, we used an adaptation of the methods originally developed by Papoulis (1956) and Stehfest (1970) for Laplace transforms. Stehfest's method belongs to a group of methods that compute a sample while Papoulis's method uses a series expansion of the original function, as explained in an extensive review (Davies and Martin, 1979). In brief, both of them make use of weighted sums of values of the trans-

formed function at certain points of the transform variable to recover the original function at a given point of its independent variable. Each method requires the user to fix the value of one or two parameters, whose optimum values depend on the type of function being inverted. In the original works both methods were tested using functions very different from the MWD to be obtained here. For our purposes, then, we must not only adapt the methods to be used with pgf transforms (instead of Laplace transforms), but we must also find the optimum values of the parameters associated to each method when recovering functions that behave like MWDs do. We have previously shown (Brandolin *et al.*, 2001) that the Laplace transform and the pgf transform are equivalent at specific values of their independent variables, found as $e^{-s} = z$. Making use of this equivalence, we have adapted several numerical inversion methods proposed for Laplace transforms for the inversion of pgf transforms (Asteasuain *et al.*, 2002a; Brandolin *et al.*, 2001), and developed criteria for choosing the method's parameters. We use that equivalence and those criteria for the inversion methods studied in the present work.

The computational effort required by each method may be estimated by the number of times the pgf must be calculated for a given number of molecular weight

points, as explained in our previous works (Asteasuain *et al.*, 2002a; Brandolin *et al.*, 2001) These quantities depend also on the values of method's parameters.

III. RESULTS AND DISCUSSION

To validate the model, experimental data were obtained in our laboratory (Cassano *et al.*, 1997). A commercial linear high density polyethylene, provided by Oxy Petrochemical ($M_n = 21,700$; $M_w = 53,200$), was chemically modified with 2,5-Dimethyl-2,5-Bis(Ter-Butyl-Peroxi)-Hexane. 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 wt%. Each mixture was treated at 170°C in a press for twenty minutes to ensure complete reaction. Samples were analyzed for vinyl content by Fourier Transform Infrared Spectroscopy. MWD of product samples were analyzed by size exclusion chromatography (SEC) in a Waters-150-C ALC-GPC, with a set of Polymer Laboratories gel columns with nominal pore size of 10^6 , 10^4 and 500 Å and a refractive index detector. 1,2,4-trichlorobenzene at 140° C was used as solvent and a flow rate of 1 ml/min was employed. Since data of modified resins were analyzed ignoring the presence of branches, they should be considered qualitative. Figure 1 presents the MWD of the virgin and modified resins.

Table 2. Average properties for different initial peroxide concentrations

	Virgin Resin	0.025	0.05	0.075	0.1	0.2
<i>Mn</i> (0)	0	21,700	21,700	21,800	21,900	21,300
<i>Mn</i> (1)	21,700	22,100	23,100	24,400	25,800	30,200
<i>Mn</i> (2)	0	109,900	119,900	132,900	147,600	190,000
<i>Mn</i> (3)	0	241,700	265,000	296,500	331,800	428,900
<i>Mn</i>_{calc}	-----	22,500	23,400	24,400	25,400	30,700
<i>Mn</i>_{exp}	21,700	24,700	28,600	25,800	31,350	29,400
<i>Mw</i> (0)	0	52,900	54,300	56,200	58,200	60,300
<i>Mw</i> (1)	53,200	57,100	65,600	73,300	88,000	117,500
<i>Mw</i> (2)	0	191,800	217,600	261,100	287,800	377,100
<i>Mw</i> (3)	0	362,500	403,700	458,600	518,900	662,500
<i>Mw</i>_{calc}	-----	60,600	71,200	86,833	111,900	785,720
<i>Mw</i>_{exp}	53,200	70,300	78,000	98,700	130,000	157,300
<i>Wvi</i> (0)	0	40.0	48.7	53.0	55.0	52.3
<i>Wvi</i> (1)	100.0	56.7	46.0	39.7	35.3	23.0
<i>Wvi</i> (2)	0	2.9	4.2	5.1	5.7	5.5
<i>Wvi</i> (3)	0	0.3	0.8	1.4	2.0	2.7
% <i>Vi</i>_{exp}/<i>Vi</i>_{expvirg}	100.0	70.0	47.0	39.0	31.0	10.0
<i>Xb</i> (0)	0	3.65x10 ⁵	7.33x10 ⁻⁵	9.64x10 ⁻⁵	1.21x10 ⁻⁴	1.73x10 ⁻⁴
<i>Xbi</i> (1)	0	378x10 ⁵	8.71x10 ⁻⁵	1.39x10 ⁻⁴	1.95x10 ⁻⁴	3.69x10 ⁻⁴
<i>Xb</i> (2)	0	1.51x10 ⁻³	3.58x10 ⁻⁴	2.22x10 ⁻³	2.662x10 ⁻³	4.12x10 ⁻³
<i>Xb</i> (3)	0	3.11x10 ⁻³	3.44x10 ⁻⁴	4.83x10 ⁻³	5.89x10 ⁻³	9.49x10 ⁻³
<i>Xb</i>_{calc}	-----	4.73x10 ⁻⁵	9.45x10 ⁻⁵	1.42x10 ⁻⁴	1.89x10 ⁻⁴	3.78 x10 ⁻⁴

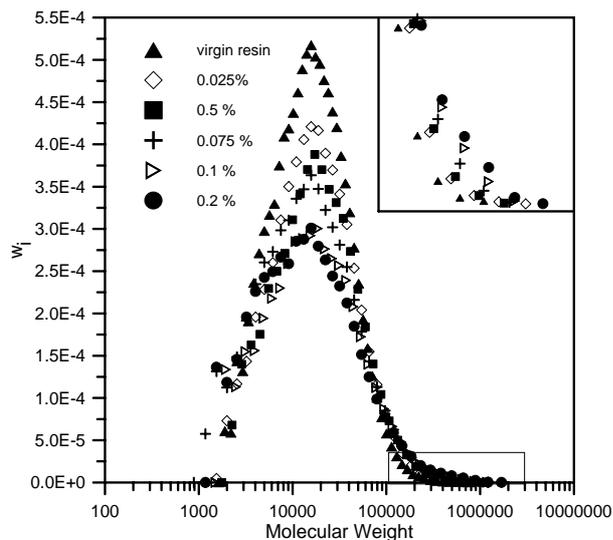


Fig. 1. Measured weight MWDs for virgin resin and modified products (Parameter: Initial peroxide concentration)

Table 2 shows some of the model results with respect to average molecular parameters. Results are discriminated by number of vinyls (j). Please note that there are molecules with a greater number of vinyls than those shown; we have only presented the most relevant ones. $Mn(j)$ and $Mw(j)$ generally increase with increasing peroxide concentration for all j values. The average values for the entire sample are very close to those of molecules with zero and one vinyl groups, which represent the highest proportion in the sample. Molecules with the larger vinyl content have higher molecular weights and lower polydispersities, consistent with a small number of large molecules produced by the crosslinking reactions. The differences between experimental and calculated values are more evident at the highest initial peroxide concentrations, where the polymer is getting closer to the gel point and experimental results are more error-prone. Weight distributions of polymers with given numbers of vinyl groups are shown in Table 2 and Fig. 2. The latter shows the evolution of the distributions as a function of residence time for an initial peroxide content of 0.1% w/w. Because of the particular synthesis process used to produce our HDPE, it is reasonable to assume that the untreated polymer contains only molecules with one vinyl group. As the reaction proceeds, most vinyl groups are consumed, producing molecules with no vinyls. There also appear molecules with more than one vinyl due to the crosslinking reactions. The distribution of vinyl content of the polymers treated with all the initial peroxide concentrations are shown in Table 2. It may be observed that for all peroxide concentrations about half the mass consists of molecules without vinyls. As peroxide concentration increases, the fraction of mass that contains high-vinyl molecules tends to increase, as expected. The experimental data on vinyl content are close to the calculated values for molecules with one vinyl.

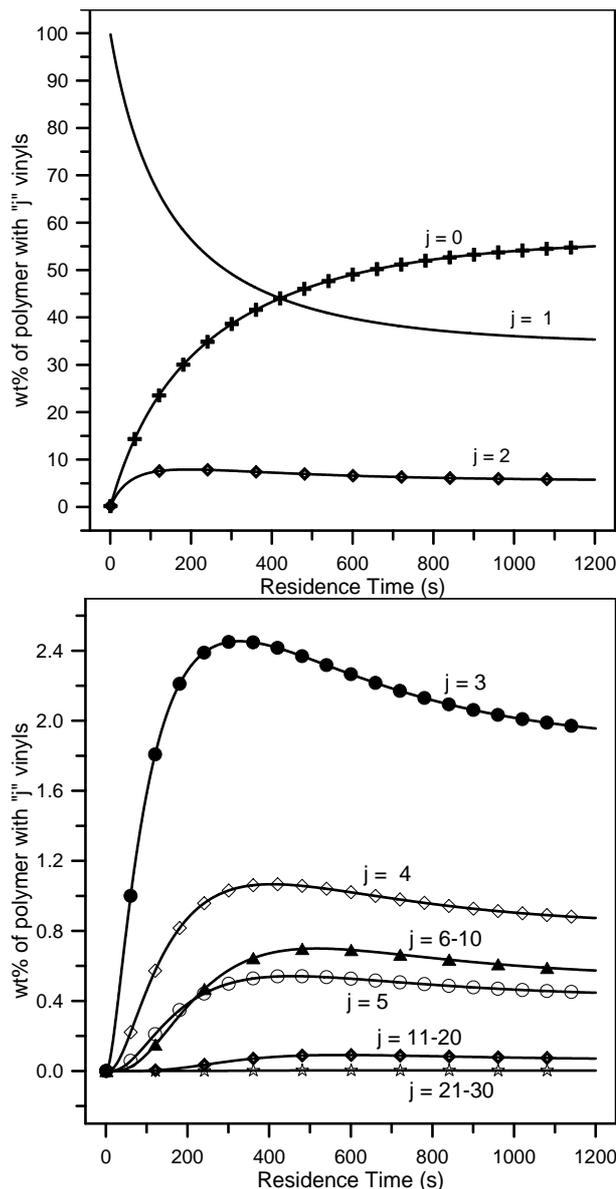


Fig. 2. Mass composition of molecules with a given number of vinyl groups (j).

With respect to crosslinking, the molecules with higher vinyl content are the most branched ones. The average number of branching points increases with increasing peroxide concentration, a result consistent with the rest of our findings.

The calculated weight distributions obtained using the algorithm by Papoulis at the end of the process, for different initial peroxide concentrations, is shown in Fig. 3. The corresponding virgin resin MWD is also shown for comparison. A broadening is predicted as the initial peroxide concentration increases. This is due to the higher initiation radical concentration that results, which favors crosslinking reactions. MWD curves cross the one for the virgin resin at high molecular weights. A shoulder appears at 0.1 wt% and finally a bimodal trend is evident for 0.2 wt%. The predicted MWDs for all peroxide concentrations are very similar to the ex-

perimental ones shown in Fig. 1. It must be noted that no parameter adjustment was done using data of complete MWD.

Similar results were found when using either Stehfest's or Papoulis' method, when using the corresponding optimum parameters, the computational effort being similar in both methods. It should be noted that pgf balances are solved for a set of z values determined by the expected range of the MWD. Both inversion methods may predict small negative or positive values for a given molecular weight if there are very few molecules of that size. In the case of Fig. 3, the range is wider than the actual MWD, resulting in the observed small negative values.

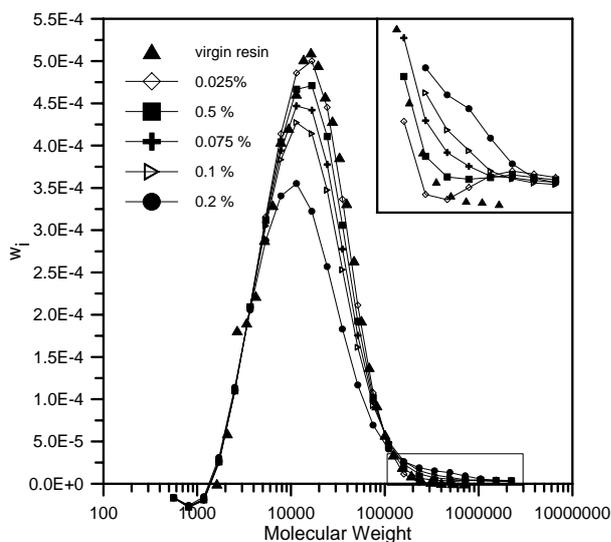


Fig. 3. Calculated weight MWDs for different initial peroxide concentration by Papoulis's method and measured MWD for the virgin resin.

IV. CONCLUSIONS

In this paper we propose an enhanced model for the reactive modification of high-density polyethylene. We have solved a system of transformed mass balance equations for the batch process, considering the size, number of branches and number of vinyl groups of all the molecules. In its present form, the model is valid up to the gel point. We have applied pgf transforms to the mass balance equations thus allowing the description of the number and weight MWD of the modified polymers. Numerical inversion of the transformed variables has allowed a very good recovery of the entire molecular weight distribution, as compared to the experimental distributions measured by SEC. The two numerical inversion methods used gave results of comparable quality at a similar computational cost. The model has also provided predictions of vinyl contents and branching points that may help in the understanding of the modification process.

Overall, our model at its present stage of development constitutes a viable alternative to pilot plant or

industrial scale trial-and-error experiments, with economic and safety advantages. It is a tool that has potential in optimization studies of industrial reactors and in the development of new polymer grades.

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