A STOCHASTIC MODEL FOR THE PREDICTION OF THE MOLECULAR WEIGHT DISTRIBUTION OF (CONTROLLED RHEOLOGY) PEROXIDE DEGRADED POLYPROPYLENE

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Optional Course / Track Number - 70

Abstracts

A model based on empirical observations and on the random nature of the reaction between peroxide radicals and tertiary hydrogens of polypropylene resins was developed to predict changes in the molecular weight distribution (MWD) when controlled rheology (CR) resins are produced. The model was succesfully applied to production scale and bench trial resins. Predicted and modeled MWD compare reasonably well.

Introduction

Peroxide induced degradation of polypropylene (PP), described by Rado in 1960 (1), is a post-reactor operation with the purpose of lowering the average molecular weight and narrowing the molecular weight distribution (MWD). Figure 1 depicts the mechanism for the degradation, known as beta-scission. Since the rupture of the chains reduces the viscosity of the resin, the degradation is also called a vis-breaking process, and the resulting products are called polypropylene controlled rheology (CRPP) resins.

Modeling of the degradation, based on kinetics and processing variables, was done by Balke et al (1-4), Tzoganakis et al (5-9) and Ryu et al (10) . More recently, Triacca et al. (11) used a mathematical model, originally developed for irradiated polymers, to describe the changes in MWD by random scission as a function of the initial MWD and the peroxide level. The peroxide reacts in one step and produces a random scission.

In a later study Pabedinskas (12) developed a model based on a melting mechanism. In this model, it is assumed that the peroxide concentration available for degradation follows the same profile the melt does in an extruder: as the resin melts the peroxide reacts. The profile concentration is incorporated into the kinetic model developed by Balke and the entire MWD predicted.

The present paper presents a random scission model developed from binomial probability concepts, in which, based on empirical observations, the peroxide is allowed to follow a half-life decay pattern. This approach combines concepts of random scission as shown by Triacca and a peroxide profile as considered by Pabedinskas but without using a kinetic approach.

Calculations are performed with a standard spread-sheet, and requires just 3 minutes to obtain the results on a 486 CPU, DX2 66 Mhz personal computer . The model has been successfully applied to laboratory and bench trials.

Model Description

Input

Peroxide data:

a) grams of peroxide,
b) molecular weight,
c) functionality.

Starting Material:

a) Discretized MWD.

Output

Modeled Resin

a) Discretized MWD.
b) Calculates the molecular weight parameters (MWP): Mn, Mw, Mz, Mz+1.
c) Plots MWD

Considerations:

1) The model assumes that the starting material is composed of chains of different sizes as given by the discretized MWD obtained by GPC.
2) The concentration of the chains is obtained from the GPC data as shown in Table 1.
3) The melt is assumed to react with the peroxide in eight succesive steps in which different peroxide amounts are added. The peroxide added at a given step follows an inverse geometric decay pattern as indicated in Figure 2. In each step the MWD of the resin is modified depending on the amount of peroxide added to that step.
4) Calculations are based on 100 gr. of resin.

Calculations

The procedure is as follows:

A) User must specify a peroxide efficiency(f) between 0 and 1. Start with 0 .6

B) Calculate the peroxide concentration to be used in the model (Co) as follows:

$$Co = Pa * f \quad (1)$$

where Pa is the peroxide concentration actually added to the resin to be modeled.

C) Calculate the concentration of peroxide to be added in each step (k), ***as indicated in Figure 2***:

$$C_k = Co / (2^k) \quad (2)$$

1) Calculate the total probability (alfa) of scission in the bulk polymer for the kth "step":

$$\alpha = \frac{\text{number of tertiary carbons in resin...}}{\text{number of peroxide radicals added}} \quad (3)$$

2) Calculate the probability of scission and no scission for a given chain assuming that the attack experienced by each of the polymer chains is governed by a Poisson probability function:

$$P(x,m) = \frac{m^x \exp(-m)}{x!} \quad (4)$$

where:

m is the *average number* of scissions in a given chain:

$$m = \alpha * N , \quad (5)$$

N is the number of tertiary carbons in a given chain, and

x is the number of scissions a chain can experience, e.g.: one, two, three, etc.

3) Determine the molecular weight of the new chains .

4) Calculate, for each of the new chains, the moles produced:

5) Repeat steps 1, 2, 3 and 4 for each of the "chains" of the discretized MWD.

6) Compute the new MWD.

7) Repeat steps 1 through 5 for each of the "instantaneous steps"; in each case the initial MWD is the final MWD of the previous step.

8) Results:
   a) Calculate Mn, Mw, Mz, Mz+1.(MWP)
   b) Plot the MWD.

D) Evaluation:
   a) Compare the modeled MWP with the MWP measured by GPC and if the error for the average molecular is less than 5% **,**
   b) Plot the modeled and the actual MWD curves and if they overlap reasonably well,
   c) go to step E, otherwise
   d) go to step A and change the efficiency and start the process all over again until modeled MWP and MWD curves compare reasonably well with the measured (by GPC) MWP and MWD curve.

E) Final Report:
   a) Peroxide efficiency used by the model.
   b) Percentage of error of the modeled MWP with respect to the MWP obtained by GPC.
   c) Table with the discretized modeled MWD.
   d) Plot the MWD curves of the starting material, modeled resin and actual resin.

Figure 3 shows the model architecture and depicts other options such as selecting the peroxide decay pattern and dosing (Z). The Z value should be specified as an integer and can be used when in an actual process the peroxide is dosed in Z equal amounts.

Model Applications

Figure 4 shows GPC curves of the starting material and the CRPP resin (Final), and the results of the model predictions for several peroxide efficiencies. Experimentally, the starting material was reacted with 723 ppm of peroxide, which produced the "Final" PPCR (actual) resin. The amount of peroxide the model needed to match the MWD of the Final resin was 470 ppm, which corresponds to a peroxide efficiency of 65%. This efficiency is similar to the 58 % reported by Tzoganakis (7) . Most of the resins studied with the model showed an efficiency between 50 and 60 %.

Figure 5 shows the results as a percentage of error of the modeled MWD parameters with respect to the actual GPC data, for a resin obtained by reacting the starting material with 362 ppm. A peroxide efficiency of 60% gives the minimum error between actual and modeled MWD parameters.

The model was applied to a series of resins obtained from different starting resins, for which the peroxide efficiency was between 50 and 60%. The modeled molecular weight distributions compare reasonably well with the GPC data and the percentages of error between experimental and calculated values are shown in Table II.

Conclusions.

The model predicts reasonably well the final MWD of a resin, as long as the MWD of the starting resin is provided and the peroxide concentration is known.

Not only are the efficiencies calculated by the model are in good agreement with the value reported by Tzoganakis (7) , but the model has also been used successfully in plant trials.

This model can be used as a reliable tool for the prediction of the final MWD of controlled rheology resins. Efforts are continuing to determine the usefulness of the model in the study of processing conditions affecting peroxide efficiency .

Since some resins showed variations of the Mz and Mz+1 values larger than 10%, further model improvements are recommended to determine if the variations are statistically significant.

Acknowledgments

The authors gratefully thank Fina Oil and Chemical Co. for providing financial support, materials and equipment for this study.

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TABLE I. Typical GPC data.

chain	Mwi	grams
j	5 040 720	0.04
(j+1) th	4 736 774	0.05
(j+2) th	4 450 968	0.06
(j+3) th	4 182 501	0.07
:	:	:
(j+n) th	1452	0.03

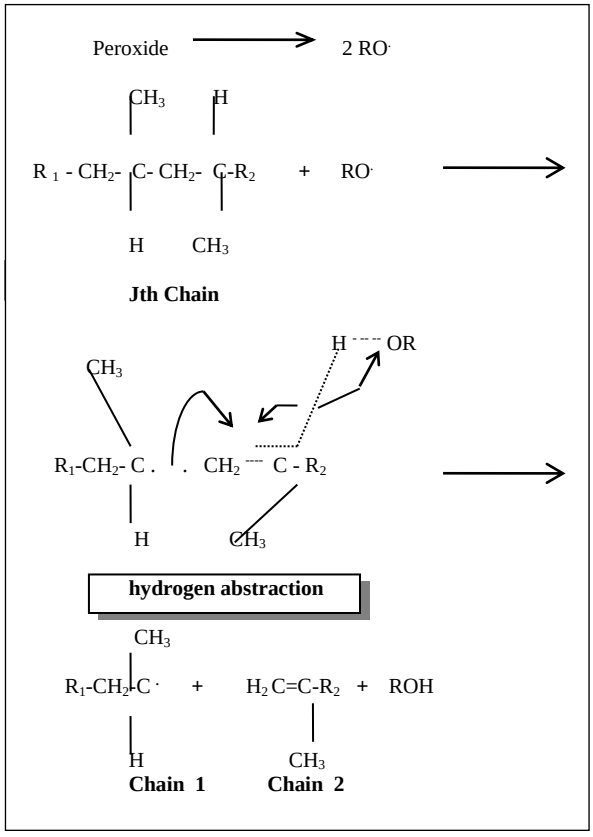
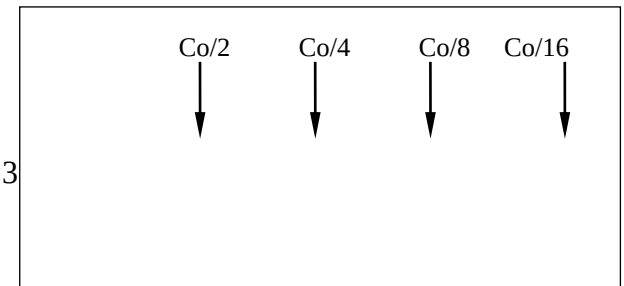
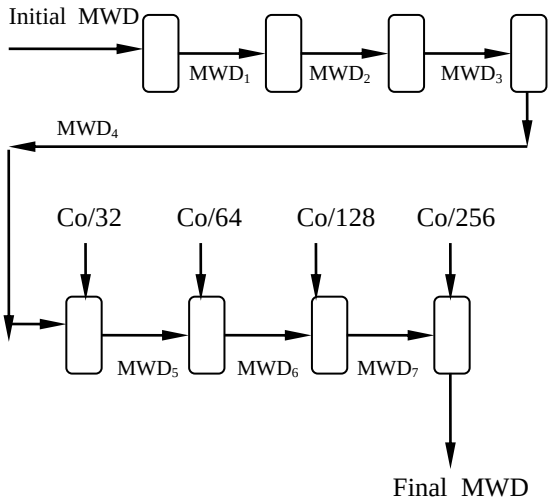


Figure 1. Reaction between a peroxide radical and a polymer chain.





Co is defined by equation 1.

Figure 2. Peroxide usage and MWD modification applied in the model.

TABLE II. Percentage of error for resins obtained with different peroxide levels and in different equipments. Efficiency range 50-65%.

	peroxide (ppm)	Mn	Mw	Mz	Mz+ 1
1	145	4.93	-1.9	-3.5	0.7
2	235	4.7	-6.8	-1.8	-4.8
3	284	4.7	6.8	0.1	0.6
4	323	4.2	12.7	6.6	4.6
5	363	2.6	4.9	-3.3	-5.8
6	398	8.8	2.45	-1.9	-3.4
7	470	-0.8	-0.04	7.9	14.2
8	615	-3.5	-0.8	2.6	2.1

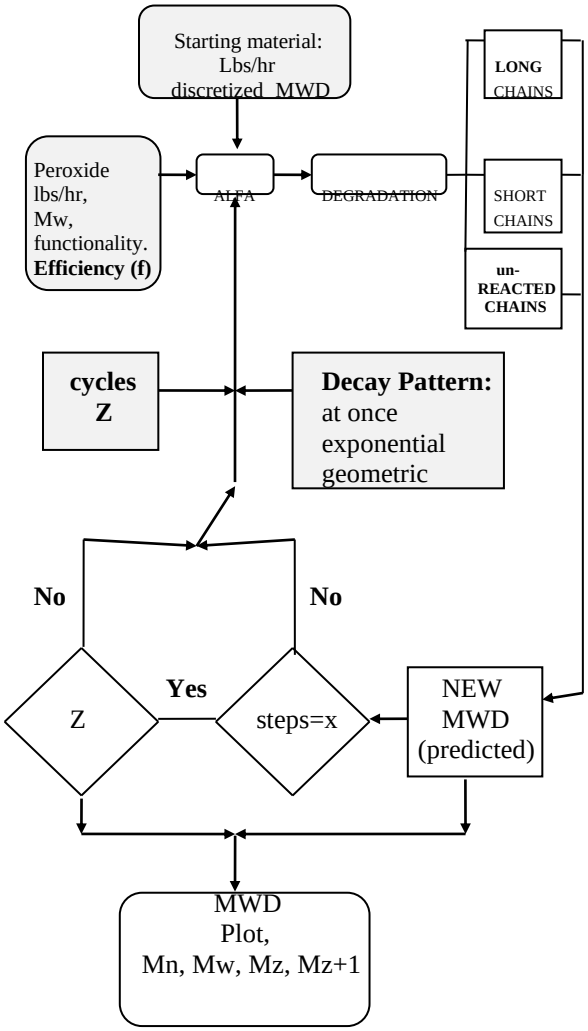


Figure 3. Model Architecture.

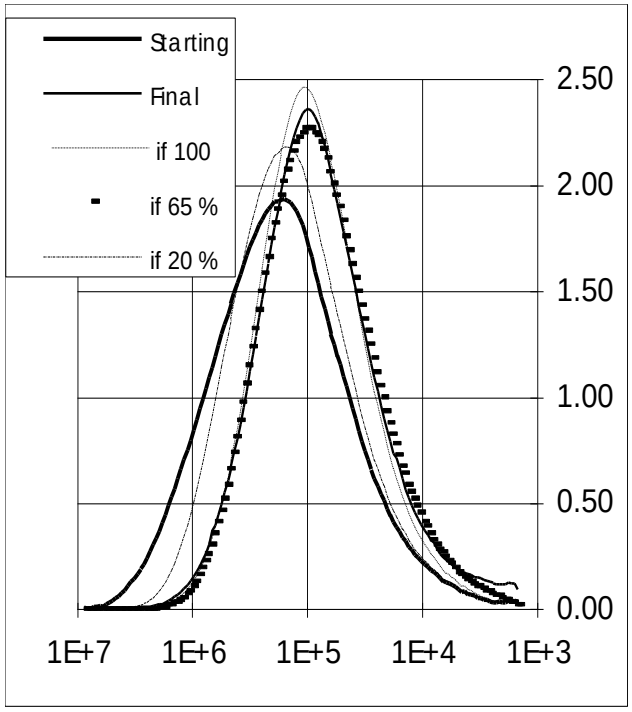


Figure 4. Typical model predictions. Final obtained by reacting Starting with 723 ppm. Three efficiency levels showed.

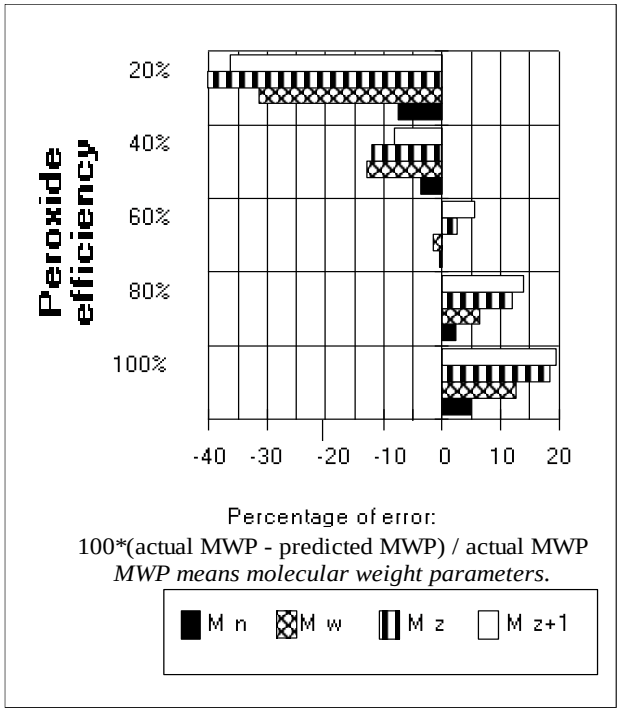


Figure 5. Percentage of error of modeled MWD parameters with respect to GPC data for several peroxide efficiencies for a resin reacted with 362 ppm of peroxide.

Key word/Key phrases

Controlled rheology polypropylene, molecular weight distribution, model for peroxide degraded polypropylene.