

EFFECTS OF TEMPERATURE, PEROXIDE CONCENTRATION, AND PEROXIDE ADDITION TECHNIQUE ON THE MOLECULAR WEIGHT DISTRIBUTION OF CONTROLLED RHEOLOGY POLYPROPYLENE RESINS

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Abstracts

A series of controlled rheology resins were made in an intensive-shear mixer. Experiments were conducted at 200 and 230°C. Two peroxide levels and three different peroxide incorporation techniques (PIT) were used. Changes in the molecular weight distribution (MWD) curves were measured and peroxide efficiency (PE) calculated by using a stochastic model (1). The results indicate a higher efficiency at 200°C, a PE independent of concentration, and the effect of the PIT on peroxide efficiency and on MWD shape.

Introduction

Controlled rheology polypropylene (CRPP) resin properties depend strongly on processing conditions as well as on the molecular weight distribution (MWD) of the starting material. Comprehensive investigations of peroxide effects on the MWD of polypropylene resins have been presented by Balke et al. (2-5), Tzgonakis et al. (6-10) and Ryu et al. (11,12)

Triacca et al. (13) presented a study in which a peroxide was incorporated into the non-degraded resin from solution. The solvent was carefully evaporated and the degradation was carried out on a differential scanning calorimeter (DSC). These authors applied a random scission model, originally developed for irradiated polymers, and obtained a better prediction of the MWD than the studies mentioned above. When Triacca et. al. applied the model to different data available in the literature, they concluded that the overall efficiency is strongly affected by processing conditions. Therefore, they pointed out the need for a study to determine the effects of processing conditions on the overall efficiency of the degradation process.

It is the purpose of this paper to follow the suggestions made by Triacca et. al. and explore the effects of some of the processing conditions, as Ryu et al. (11, 12) did it but adding the peroxide directly into the melt.

The effects will be determined by measuring efficiency of the degradation process, MFI, and MWD. The efficiency will be obtained by using a stochastic

model developed by the authors of this article (see paper # 70).

This study will explore the following processing variables: temperature, peroxide concentration level, peroxide addition technique.

Materials and Equipment.

The starting material is a polypropylene reactor grade resin MFI of 4.6. The peroxide used was 2,5-Dimethyl-2,5-di-(t-butyl peroxy) hexane (Lupersol 101, provided by Elf-Atochem). BHT was added as stabilizer after degradation was completed. The degradation was carried out in a 60 ml. capacity roller blade style mixer. Molecular weight distributions were determined by using a Waters Model 150 C Gel Permeation Chromatograph..

Experimental.

Parameters studied.

Vis-breaking was carried out in a Brabender mixer at constant temperature, during 10 minutes at 100 rpm. Temperature effects on degradation efficiency were determined by reacting the starting resin with 723 ppm of peroxide at 200 and 230°C. In order to determine the contribution of shear-work to the degradation process, the starting resin was run with no peroxide at each of these temperatures. Concentration effects were determined at 200 °C by using two peroxide levels, 362 and 723 ppm. The peroxide addition mode was evaluated by using three different techniques to incorporate the peroxide into the resin. Nitrogen blanketing was present in every experiment. Temperature variations were ± 3 °C. Each combination of temperature, peroxide level and addition mode was identified as a Case as follows:

CASE A: Direct injection of peroxide into the melt. Two consecutive injections (no more than 20 seconds apart, and each injection required no more than 5 seconds) in different zones of the melt, without mixing in between (*Method 1*), at 200 °C.

723 ppm of peroxide, T=200 C.

CASE B: Four consecutive injections of 181 ppm (each injection was made in less than 5 seconds), with mixing between injections until torque reached a steady state value (*Method 2*), at 200 °C
723 ppm of peroxide, T=200 C.

CASE C: Direct injection of peroxide into the melt. One injection (made in less than 5 seconds) (*Method 3*), at 200 °C.
723 ppm of peroxide, T=200 C.

CASE D: Method 1, injected at 200°C.
362 ppm of peroxide, T=200 C.

CASE E: Method 1, injected at 230 °C.
723 ppm, T=230 C.

CASE F: No peroxide added.
0 ppm, T =200 C.

CASE G: No peroxide added.
0 ppm, T =230 C.

It should be noted that:

- 1) peroxide injections were made with a micro-syringe.
- 2) triplicates were run for each of the cases.
- 3) mixing efficiency was tested by adding a dye to the resin. The time needed for homogeneity was about 3 minutes.
- 4) experiments were carried out for at least 10 minutes, or two and a half times the time required for peroxide level to drop down to 1 % , whichever was higher. The time required for peroxide concentration to decay to 1% of its original concentration was provided by Elf-Atochem.

Procedure

Sample Preparation

The procedure is outlined as follows:

- 1) Mix fluff with antioxidant package.
- 2) Weigh 45 gr. samples.
- 3) Set mixer at desired temperature. Turn on Nitrogen.
- 4) Load sample into Brabender, mixing at 40 rpm.
- 5) Increase velocity to 100 rpm and wait for temperature to get back to the set point.
- 6) Monitor torque (torque will increase once the resin melts). Once the temperature is at set point and torque indicates melt condition,
- 7) slow the velocity to 40 rpm, open the chamber, stop the mixing and add the peroxide.,
- 8) Close chamber and increase velocity to 100 rpm. Start recording temperature, time and torque every minute.
- 9) At the end of 8 minutes , reduce velocity to 40 rpm, open gate and add stabilizer (to get 1000 ppm of BHT).

- 10) Mix stabilizer for 1 minute at 100 rpm.
- 11) Turn off motor. Turn off Nitrogen.
- 12) Open chamber, quench melt resin with compressed air.
- 13) Scrape polymer from chamber.
- 14) Cool down the sample.
- 15) Grind sample.
- 16) Measure MWD.

Notes:

From steps 3 to 11, a nitrogen stream is blown over the chamber gate.

Criteria for Efficiency

Efficiency is determined by using a stochastic model developed by the authors of this article and presented in this conference (#71). The method is as follows:

- 1) Input the discretized GPC data of the non-degraded resin to the model.
- 2) Make predictions of molecular weight parameters (MWP) by using several peroxide levels in the model.
- 3) Calculate the percentage of error for the MWP for each of the predictions with respect to the GPC molecular weight parameters (Mn, Mw, Mz and Mz+1) of the degraded resin, i.e.:

$$\% \text{ Error for Mz} = \frac{100 * (\text{modeled Mz} - \text{measured Mz})}{\text{measured Mz}}$$

- 5) Select the MWD curves for which the percentage of error in the parameters is below 15 % for Mn and less than 5 % for the average molecular weight.
- 6) Choose the predicted MWD with the lowest percentage of error on the MWP.
- 7) Look for the peroxide level needed for the chosen MWD.
- 8) Calculate the efficiency by dividing the model peroxide level by the peroxide level actually used for the CR resin under analysis.

Results

Table I shows the peroxide efficiency, MFI, and the MWD parameters for each of the cases.

Table II shows the percentages of error for each resin when the model was applied to each case.

Figures 2 through 6 show the effects of temperature, concentration level and peroxide addition technique on the measured MWD

Discussion of Results

Temperature effects. (Cases A and E).

Changing the temperature from 200 to 230°C (Cases A and E) causes a 40 % decrease in the peroxide efficiency and a change in MFI: from 4.6 to 16, compared to 4.6 to 36. The MWD parameters are given in Table I and are compared in Figure 1. Such changes are better observed by looking at Figure 2.

Concentration effects (Cases A and D).

Concentration changes do not affect the efficiency of the peroxide. The differences are observed in the MFI (36 vs. 16) and in the MW parameters (see Table I) are clearly observed in Figures 3 and 4. An interesting result is that both resins have about the same polydispersity index (PI) : 5.2 and 5.6.

Addition effects (Cases A, B, C).

The three methods used to add the peroxide gave different MFI's and peroxide efficiencies, even though the polydispersity indexes are very similar (see Table II and Figure 5). Case A and C give very similar results, with just a slight difference in PI observed. Case B seems to be the less efficient way to incorporate the peroxide into the resin since the high molecular weight content is higher compared to Cases A and C, see Figure 6.

Shear-work effects. (Cases F and G)

The shear work effects are observed by inspection of Table II, the percentage of change is evident at 230°C but not at 200°C.

Comparisons based on the efficiencies and amounts of peroxide actually added to the resins of Cases D and E indicate that about the same amount of peroxide was consumed. Table II also shows a difference of about ten percent in the MWP between the two cases, which indicates that, even though the peroxide used up by the resins is the same, the scission events produced different MWD curves. Their relative positions (given by the average molecular weight) and their high molecular weight contents are different, see Table II.

Conclusions

This study showed that the efficiency of the degradation process is higher at 200°C than at 230°C. Addition of the peroxide at high temperature and directly into the melt might produce self-decomposition of the peroxide prior to full dispersion. The higher the temperature, the higher the amount of peroxide radicals before full dispersion and therefore the higher the self-decomposition and/or reaction with chain radicals.

This study also indicated that the efficiency is practically independent of peroxide concentration but dependent on the method used to incorporate the peroxide into the resin. The best method, based on both the MFI and the narrowing of the MWD, is when the peroxide is injected in one step; the second best is when

the peroxide is injected in two regions of the melt; and the worst method is when the peroxide is injected in four equal amounts with mixing in between.

The results of this study show that a variety of peroxide efficiency levels occur depending on the conditions under which the resins were mixed and reacted in the Brabender. On the other hand different efficiency levels can lead to similar MFI and similar MWD parameters and/or MWD curves.

Model predictions suggest that the amount of peroxide consumed in Cases D and E are about the same (Table II). Also, the MFI and PI values indicate that the amount of degradation in these cases was practically the same, but the position of the MWD curves with respect to the starting resin is different.

The question now is how relevant are these changes in efficiency, MFI and/or MWD with respect to the processing conditions of the resultant resins, and whether resins with similar molecular weight parameters and MFI (cases A and C, D and E, F and starting material) can be differentiated by other analytical techniques.

The objective of future studies, will include a look at their rheological behavior and how these properties depend upon the MWD parameters and peroxide treatment.

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TABLE I. Characteristic resins parameters .

Case	PE	MFI	Mn x 10 ⁻³	Mw x 10 ⁻³	Mz x 10 ⁻³	Mz+1 x 10 ⁻³	PI
Init.	---	4.6	41.7	325	1135	2128	7.8
A	65	36	26.7	138	368	710	5.2
B	25	25	30.9	162	409	737	5.2
C	55	41	30.4	145	367	710	4.8
D	60	16	36.7	205	599	1189	5.6
E	25	16	33.1	192	534	999	5.8
F	1	4.5	38.8	324	1093	2005	8.4
G	1	4.7	34.7	296	951	1682	8.5

PE Peroxide efficiency.

MFI Melt flow index.

PI polydispersity index: Mw/Mn

TABLE II. Percentage of difference of the MWD parameters of each resin with respect to the starting material.

	Mn	Mw	Mz	Mz+1	PI
Case A	36	57	68	67	34
Case B	26	50	64	65	33
Case C	27	55	68	67	39
Case D	12	37	47	44	28
Case E	21	41	53	53	26
Case F	7	0	4	6	-7
Case G	17	9	16	21	-9

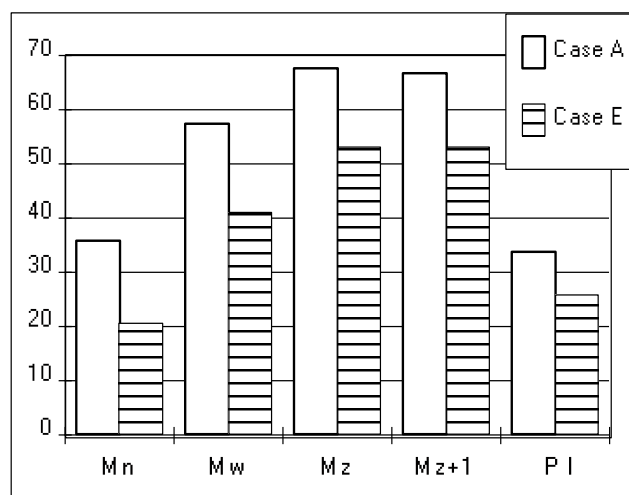


Figure 1. Temperature Effects.

Percentage of difference with respect to the starting material as given in table II. Cases A (200 C) and E (230 C).

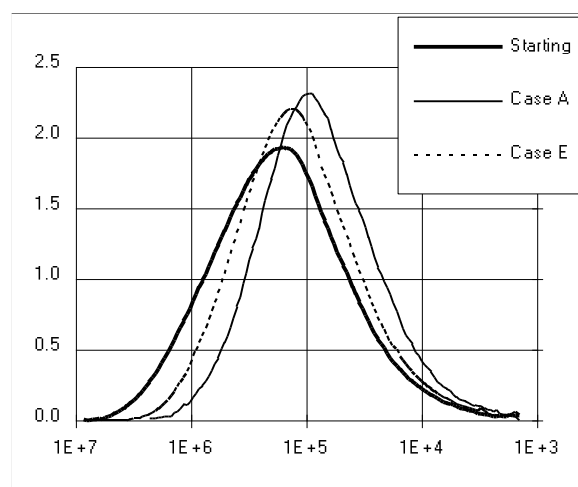


Figure 2. Temperature Effects.

MWD obtained by GPC measurements. Cases A (200 C) and E (230 C)

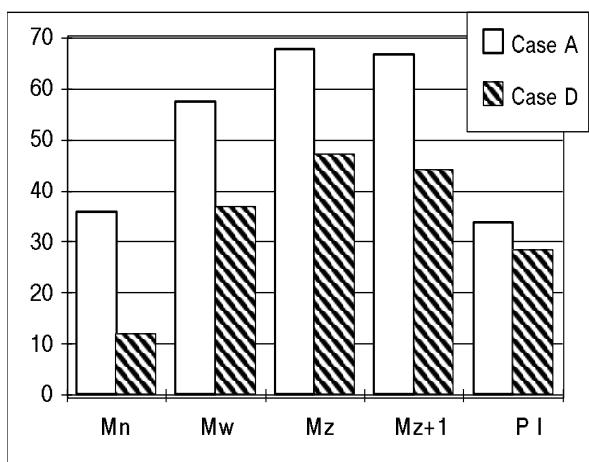


Figure 3. Concentration Effects.

Percentage of difference with respect to the starting material as given in table II. Cases A (723 ppm) and D (362 ppm)

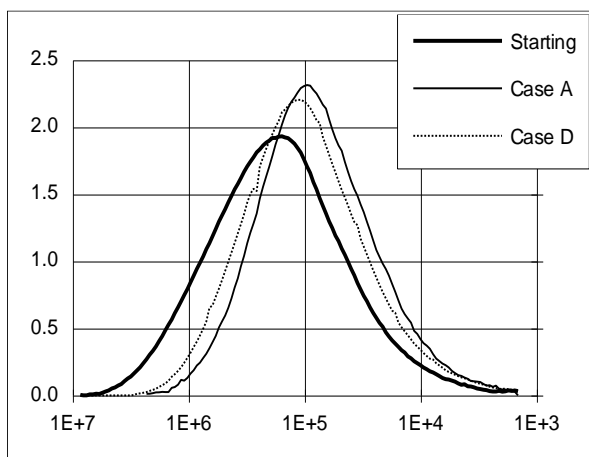


Figure 4. Concentration Effects.

MWD obtained by GPC measurements for the starting material and cases A (723 ppm) and D (362 ppm).

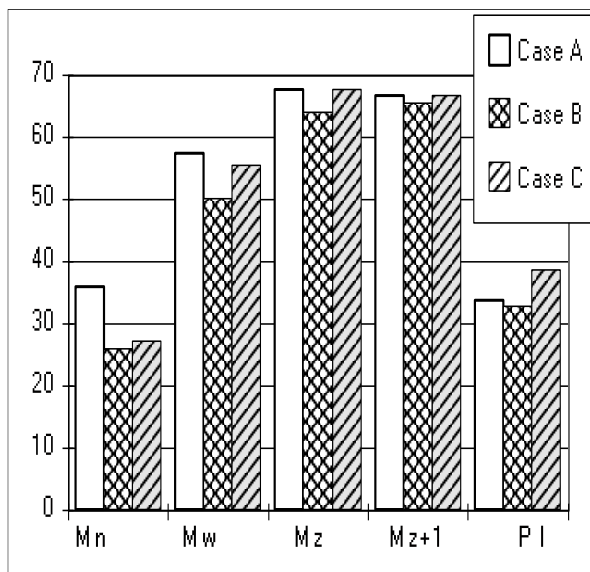


Figure 5. Method Effects.

Percentage of difference with respect to the starting material as given in table II. Cases A (Method 1), B (Method 2) and C (Method 3).

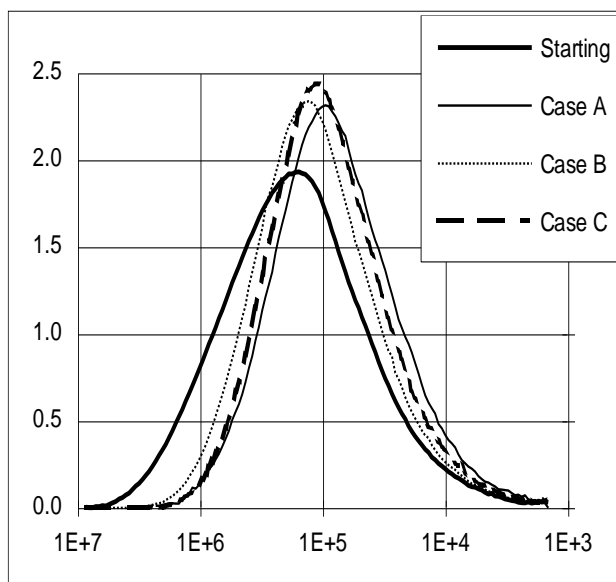


Figure 6. Method Effects.

MWD obtained by GPC measurements for the starting material and Cases A (Method 1), B (Method 2) and C (Method 3).

Key Word/Key Phrase

Controlled rheology polypropylene resins (CRPP), processing conditions, efficiency, molecular weight distribution of CRPP resins.