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Effect of Peroxide Concentration on the Modification of the LLDPE: Statistical Experimental Design and Thermal Properties

Valéria D. Ramos[1](✉), Helson M. da Costa[1], Anderson O. Pereira[1], Marisa C. G. Rocha[1], Aílton de S. Gomes[2]

[1]Instituto Politécnico - IPRJ, Universidade do Estado do Rio de Janeiro - UERJ, P.O. Box 97282, 28.601-970 Nova Friburgo, RJ, Brazil
[2]Instituto de Macromoléculas Professora Eloisa Mano -IMA, Universidade Federal doRio de Janeiro - UFRJ, P.O. Box 68525, 21.945-970 Rio de Janeiro, RJ, Brazil

E-mail: valramos@iprj.uerj.br, Fax: 55 021 (22) 2528-8536

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Summary

The effect of small concentrations of dicumyl peroxide (DCP) on the modification of a linear low density polyethylene (LLDPE) during a reactive extrusion process was investigated. The experiments were arranged in a two level factorial design in order to evaluate the effect of temperature zones (X_1), peroxide concentration (X_2) and screw rpm (X_3) on the modification of LLDPE. The melt flow index (MFI) was used as a response variable. It was verified that the thermal properties, crystalline melting temperature (T_m), the heat of fusion (ΔHmelt) and the crystallinity degree (X%) decrease with the increasing of the peroxide concentration. The crystallization temperature (T_c) increased up to 0.05% w/w peroxide, whereafter the level stays almost constant. The gel content of the samples however indicated that a three-dimensional network was negligible in the experimental conditions used.

Introduction

Modification polyethylene has become commonly used for a number of industrial applications which require withstanding high temperature environments. Examples of such applications include wire and cable coating, hot water tubing and steam resistant food packaging [1]. There are a variety of ways to achieve the modification of polyethylene. Polyethylene has no functional groups which can provide modification capability, such as the kin one finds in typical thermosetting resins like polyamides or polyurethanes. Hence the modification must be induced by the incorporation of another component [2]. Peroxide, radiation, and silane are the three main ways of modification employed industrially [3-5]. The modification of polyethylene by organic peroxides has received appreciable attention in the literature and becoming a more widely accepted and studied method of altering polymer structure and properties. The dicumyl peroxide, has been shown to be effective in the introduction of long-chain branches in otherwise linear polyethylenes [6], and at low concentrations, it favorably alters molecular weight distributions [7-9]. At higher peroxide concentrations, modification polyethylene is obtained [10-12]. Dicumyl peroxide is a popular choice because of its favorable decomposition rate at normal processing temperatures of polyethylene. The low levels of peroxide needed to effect substantial changes in molecular weights, for example, present a cost effective route to varying desired product properties and thus a method of tailoring the polymer properties [13-15]. The effect of low concentrations of peroxide initiators on polymer properties has not attracted significant interest until recently. However, reactive extrusion process with low levels of peroxides can offer a practical route for the modification of the extrudability of LLDPEs and there is a growing interest in this method to improve the balance of processability characteristics of polyolefins [16,17]. What is seen experimentally is that as the initiator concentration is increased, the polyethylene average molecular weight will increase up to a critical point at which insoluble gel will begin to form. Above this peroxide concentration, increasing amounts of gel will be formed until the polyethylene is almost completely gelled. Thus, the primary effect of peroxide-induced modification on the MWD of polyethylene is to broaden the distribution at the high molecular weight end. There is also evidence that some polymer degradation occurs, resulting in a broader distribution at the lower molecular weights [14,18]. Thus, the net effect is a broadening of the MWD. The present work addresses of the results of investigations of changes occurring on the molecular structure of linear low-density polyethylene (LLDPE) using small amounts of peroxides.

Experimental

Materials

The polymer used in this investigation was a comercial linear low-density polyethylene (RA-34 U3), generously supplied by Politeno Indústria e Comércio S. A., with a 1-butene comonomer (Mn = 46,500; Mw = 427,800). The resin was provided in powder form. The dicumyl peroxide (Perkadox BC FF) was kindly provided by Akzo Nobel Chemicals, with half-lifetime of 29 s at the experimental temperature of 180°C. All chemicals were used as received.

Sample Preparation

Initially LLDPE powder was pre-dried overnight at 70°C. The polymer was then mixed with a previously prepared acetone solution of peroxide. Acetone in the uniform slurry was removed by evaporating slurry in room temperature for 24 h. This mixture was used as the masterbatch. From masterbatch, samples were prepared using a variable concentration of the DCP (0.0 to 0.2 % w/w). This process of sample preparation has in the past been determined to be effective in providing uniform peroxide dispersion on the surface of the resin, along with negligible residual solvent concentration.

Reactive Extrusion

Reactions of DCP with LLDPE were performed in a single screw extruder (Wortex). The diameter of this screw is 30 mm and the ratio of length to diameter (L/D) is 32.

The extruder was operated at a speed of 10 rpm, and with a sequence of segment temperatures at 180, 190, 200, and 200°C from feeder to die. The die temperature was set at 210°C.

Statistical Experimental Design

The experiments were arranged in a two level factorial design in order to evaluate the effect of temperature zones (X_1), peroxide concentration (X_2), and screw rpm (X_3) on the modification of LLDPE (Table 1). Eight treatment combinations were carried out (Table 2) and two observations taken at that particular treatment combination for melt flow index (MFI) evaluation.

Table 1. Low and high levels for X_1, X_2 and X_3

Variable	Level	
	Low (-)	High (+)
X_1 (temperature zone)	Isothermal (all zones in 200°C)	Non-isothermal (180/190/200/200/210°C)
X_2 (DCP, % w/w)	0.02	0.07
X_3 (screw speed, rpm)	10	30

Table 2. Algebric signs for different experiments in the 2^3 design

Variable	E1	E2	E3	E4	E5	E6	E7	E8
X_1	-	+	-	+	-	+	-	+
X_2	-	-	+	+	-	-	+	+
X_3	-	-	-	-	+	+	+	+

Characterization Methods

Melt Flow Index (MFI)

The melt flow index (MFI) of the all reactive extrusion products were determined to obtain an indirect measurement of the changes in the average molecular weight (Mw) and the molecular weight distribution (MWD) of the LLDPE samples. The measurements of MFI were done with a Tinius-Olsen extrusion plastometer according to the ASTM D1238 method test condition 'L': 190°C; load 2160 g.

Differential Scanning Calorimetry (DSC)

The thermal behavior of virgin polymer and reactive extrusion products was characterized by differential scanning calorimeter on a Perkin-Elmer DSC-7 equipped with thermal analysis data acquisition software. Polymer samples of 4.5-6 mg were encapsulated in standard aluminum pans. An indium standard was used to calibrate the temperature scale and enthalpy of melting. The endotherms were measured at a heating rate of 20°C/min over a range of 30-250°C.

Gel Content Analysis

Gel contents were determined by a solvent extraction technique, whereby modified PE samples were immersed in refluxing Xylene. Previously weighed samples (cut into a number of small pieces) were allowed to swell and the soluble portions were extracted in Xylene at 120 ± 2°C for 24 h. The samples were then dried to a constant weight in a vacuum oven at 60 ± 1°C. The percentage of the weight remaining, with respect to the initial weight, gave the gel fraction.

Gel content (%) = [weight sample after extraction / initial weight sample] x 100 (1)

Results and Discussion

Statistical Experimental Design

By using the analysis of variance for 2^3 design, one may estimate the average effects and the variables which are most significant for the modification of LLDPE by DCP using the melt flow index as the control variable. Montgomery [20] cites the calculation methodology and Table 3 summarizes the effects of the variables X_1, X_2 and X_3 upon MFI. From Table 3, it can be observed that peroxide concentration (X_2) is the most important variable, as expected. On the other hand, the extrusion conditions are important variables only when combined (X_1X_3 or X_2X_3) since, from variance analysis, X_1 and X_3 alone are not considerable.

Table 3. Analysis of variance for MFI

Variable	Average effect	Sum of squares (SS_i)	Df	Mean square	F-ratio
X_1	-0.073	0.021	1	0.021	9.57
X_2	-1.053	4.435	1	4.435	1992.61
X_3	0.128	0.065	1	0.065	29.43
X_1X_2	-0.018	0.001	1	0.001	0.58
X_1X_3	0.198	0.157	1	0.157	70.44
X_2X_3	-0.182	0.132	1	0.132	59.56
$X_1X_2X_3$	-0.057	0.013	1	0.013	5.85
Error		0.018	8	0.002	
Total error		4.843	15		

Eq. 2 can be used for a correlation between the results and the variables investigated.

$$Y = \text{Average} + a * X_1 + b * X_2 + c * X_3 + ab * X_1X_2 + ac * X_1X_3 + bc * X_2X_3 + abc * X_1X_2X_3 \quad (2)$$

where Y is the control variable (MFI); X_1, X_2 and X_3 are variables; a, b, c are constants that are related with the influence of the variables; ab, ac, bc and abc are constants that are related with interactions between the variables. After the analysis of variance for 2^3 design, a final equation (Eq.3) for the study of DCP-modified LLDPE samples is:

$$Y = 0.6935 - 0.5265 * X_2 + 0.0990 * X_1X_3 - 0.0910 * X_2X_3 \quad (3)$$

where the better conditions for LLDPE modification by DCP, in the single-screw extruder, are low screw speed (10 rpm) and non-isothermal operation.

Melt Flow Index (MFI)

Measurement of melt flow index (MFI) was performed on the virgin polymer sample and all samples to which 0.02 a 0.2 % w/w DCP was added. The expected increase in Mw as a result of peroxide modification was observed. Fig. 1 shows that MFI is descreasing rapidly with peroxide concentration up to 0.1% w/w and then starts to approach zero. However, the analysis of gel content indicated that the amount of insoluble material is negligible in all reactive extrusion products. Similar behavior was observed by Wong and Varrall [2] in postextruded polyethylene samples containing 0.1 % w/w DCP.

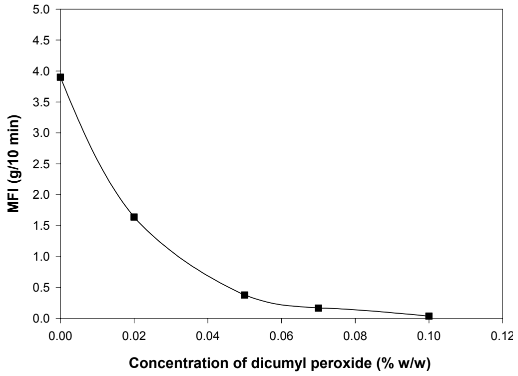

Figure 1. Plot of MFI vs concentration of dicumyl peroxide (DCP)

Thermal Properties

Crystalline melting temperature (T_m), crystallization temperature (T_c), crystallinity degree (X%) and the heat of fusion (ΔHmelt) of all samples PE are presented in Table 4. The results show that the T_m decreases with the increasing of the peroxide concentration. T_c increased up to 0.05% w/w peroxide, whereafter the level stays almost constant. The crystallinity degree decreases whith the increasing of the peroxide concentration. Sajkiewicz and Phillips [21] reported that crystallinity decreases with the increasing molecular weight and branching content. Therefore, the determination of the crystallinity degree can be used as qualitative indication of the branching content from measurements of crystallinity. It has been verified that even at low peroxide concentration it is possible to detect an increasing of chains irregularities

Table 4. Plot of T_m, T_c, crystallinity degree and ΔH_{melt} of samples containing different concentrations of DCP

DCP (% w/w)	T_m(°C)	T_c(°C)	X%	ΔH_{melt}(J/g)
0.00	123.4	103.2	48.67	131.2
0.02	123.7	104.6	50.89	137.2
0.05	123.6	105.7	47.39	127.8
0.07	123.8	106.4	44.89	121.0
0.10	123.1	106.7	46.05	124.1
0.20	121.5	106.3	41.12	110.8

by the decreasing of the crystallinity degree. As expected, ΔHmelt increases at 0.02% w/w peroxide and begins to drop at 0.05% w/w. This result can be an indication that there was an increasing chains irregularity in a polymer chain upon peroxide treatment.

Conclusions

It is known that in modification LLDPE with organic peroxides the extrusion process conditions must be controlled, since peroxide incorporation and the processing of the peroxide mixture should take place without premature modification (scorching). The absence of microgel as indicated by the gel content analysis of all extrudates demonstrates that the extrusion process conditions used, as well as the method of dispersing the peroxide, were reasonably successful in generating homogeneous products. It was verified that the thermal properties, crystalline melting temperature (T_m), the heat of fusion (ΔH_{melt}) and the crystallinity degree (X%) decrease with the increasing of the peroxide concentration. The crystallization temperature (T_c) increased up to 0.05% w/w peroxide, whereafter the level stays almost constant. This result can be an indication that there was an increasing chains irregularities in a polymer chain upon peroxide treatment. In the condition adapted in this work however there was no formation significant of a three-dimensional network.

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