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Material Properties

Study of different peroxide types on the modification of LLDPE. Part 1. Factorial experimental design and thermal properties

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Abstract

A commercial-grade linear low-density polyethylene (LLDPE) resin was modified using different peroxide types. The effect of two peroxides types (Trigonox 101 and Perkadox 14-40B-PD) on the molecular weight of LLDPE during a reactive extrusion process was studied. The influence of the peroxide type and the processing conditions were investigated using a factorial experimental design. The dependent variable studied was melt flow index (MFI). Preliminary results showed that the most significant processing variables were screw speed rate (30 rpm) and peroxide type, 0.07% w/w (Trigonox 101). The more important observation of this work was that peroxides with similar half-lifetimes and the same ultimate active free-radical species can exhibit very different behavior in the same polymer system. The choice of the best peroxide for a particular application should not be made entirely on the basis of the peroxide degradation rate at a specified temperature. In addition, Trigonox 101-treated samples exhibited crystalline melting temperature (T_m), heat of fusion (ΔH_{melt}) and degree of crystallinity ($X\%$) decreasing with the increase of the peroxide concentration, while the crystallization temperature (T_c) increased up to 0.05% w/w peroxide.

Keywords: LLDPE; Bifunctional peroxides; Thermal properties; Reactive extrusion

1. Introduction

Polyethylene insulation is modified in wire and cable applications in order to enhance its dimensional stability at elevated temperatures. Organic peroxides have become increasingly important as initiators of free-radical degradation mechanisms in polyethylene (PE) in order to modify the polymer structure and properties. There are a variety of peroxides available for reaction with polyolefins and investigations of their relative efficiencies have been reported [1–4].

Dicumyl peroxide, has been shown to be effective in the introduction of long-chain branches in otherwise linear polyethylenes [4], and at low concentrations it favorably alters molecular weight distribution [5–7]. At higher peroxide concentrations, cross-linked polyethylene is obtained [8–10]. Dicumyl peroxide is a popular choice because of its favorable decomposition rate at normal processing temperatures of polyethylene.

The different peroxide decomposition rates are perhaps the primary factor in choosing a particular peroxide for an intended application. Bifunctional peroxide decomposition occurs through a two-step process, involving formation of an intermediate alkoxy radical species. The lifetime of this strongly abstracting species will alter the peroxides overall efficiency rating

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significantly, and therefore, the peroxides studied in the above study could be expected to behave somewhat differently in terms of curing rates [7,10].

Since, the whole process is carried out to improve high-temperature dimensional stability, it is also important that the modified polymer does not exhibit excessive hot creep, as measured under specified conditions and at equivalent gel contents.

The present article describes the results of investigations of changes occurring in the molecular structure of linear low-density polyethylene (LLDPE). The aim of this work is to compare the relative efficiencies of two different bifunctional peroxides in their ability to modify a PE resin. The effect of temperature zones (X_1), peroxide type (X_2), and screw rpm (X_3) on melt flow index (MFI) of the LLDPE samples are reported. The 2^3 design was used to verify which peroxide type and processing conditions are favorable for peroxide modification of LLDPE when a single-screw extruder is employed.

2. Experimental

2.1. Materials

The LLDPE in powder form used in this investigation was (RA-34 U3), generously supplied by Politeno Indústria e Comércio SA, with a 1-butene comonomer (M_n=46,500; M_w=427,800). Specifications of this LLDPE are detailed in Table 1. All peroxides used were kindly provided by Akzo Nobel Chemicals, with decomposition rates summarized in Table 2. Fig. 1 shows the structures of the different peroxides types. All chemicals were used as received.

2.2. Experimental design

In this work, the experiments were arranged in a two level factorial design in order to evaluate the effect of temperature zones (X_1), peroxide type (X_2) and screw speed rpm (X_3) on the modification of LLDPE (Table 3). Eight treatment combinations were carried out (Table 4) and the mean of two samples taken at each particular treatment combination for melt flow index (MFI) evaluation.

Table 1
Resin specifications of LLDPE (RA-34 U3)

Mechanical properties	ASTM method	Values
Melt index	D 1238	4.2 (g/10 min)
Density	D 792	0.935 (g/cm^3)
Flexural strength	D 747	450 (MPa)
DSC peak melting	DSC[a]	123.4 (°C)
Tensile strength at break	D 638[b]	22 (Mpa)
Elongation at break	D 638[b]	1080(%)
Impact strength (Izod)	D 256	180 (J/m)

[a] Speed test = 10 °C/min.
[b] Speed test = 50 mm/min.

Table 2
Peroxides used and half-lifetimes in an EPDM compound

Peroxide	Sample code	Half-life (s)		
		at 118 °C	at 147 °C	at 171 °C
2,5-Dimethyl-2,5-di(*tert*-butyl peroxy)hexane	Trigonox 101	36,000	3600	360
Di(*tert*-butyl peroxyisopropyl) benzene	Perkadox 14-40B-PD	36,000	3600	360

Half-lifetimes are shown only for peroxide/polymer mixtures used in this study.

The factorial experimental design helps to verify whether or not there is a synergistic effect of the preparation conditions on the final properties of the polymer. Experimental design has been frequently used in different research experiments because it provides the best information regarding the effects of independent variables and their interactions on model parameters with the minimal number of runs. Runs must be randomized in order to minimize noise interference on final results. The empirical correlations obtained make it possible to optimize the system responses according to each property evaluated [11].

2.3. Sample preparation

Initially, LLDPE powder was pre-dried overnight at 70 °C. The polymer was then mixed with a previously prepared solution of peroxide in acetone. Acetone in the homogeneous slurry was removed by evaporating the slurry at room temperature for 24 h. This mixture was used as the masterbatch. From the masterbatch, samples were prepared using a variable concentration of the Trigonox 101 (0.0–0.2% 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.

2.4. Single-screw extrusion system

Trigonox 101 treated samples were produced in a single screw extruder (Wortex). The diameter of the screw was 30 mm and the ratio of length to diameter