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Thermorheological behavior of peroxide-induced long chain branches linear low density polyethylene

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ABSTRACT

In this article, the correlation between thermorheological behavior and molecular structure of linear low density polyethylene upon peroxide modification was explored. For this purpose, a commercial grade LLDPE (Exxon MobileTM LL4004EL) was reacted with different amounts of dicumyl peroxide (DCP) and their viscoelastic behavior were studied. Moreover, the samples were analyzed by size-exclusion chromatography coupled with a light scattering detector. Increasing the DCP content at roughly constant molar mass led to broadening of molecular weight distribution as well as increasing the number of long-chain branches. The latter consequently resulted in enhanced activation energy and delayed relaxation times of the LLDPE. The thermorheological behavior of peroxide modified samples was investigated and the results showed that the induced long chain branching changes the thermorheological behavior from simple to complex. The plotted results (activation energy versus phase angle) showed constant activation energy at low peroxide level (i.e., increasing the long chain branching) (up to 125 ppm) and a distinct variation from low to high phase angle with increasing the peroxide level. The theromorheological complexity threshold could be determined using these plots. The potential of thermorheological approach as an alternative powerful tool for analyzing LCB issue in peroxide modified LLDPE could be highlighted.

1. Introduction

A glance at the current literature witnesses that modification of polyolefins (PE) has been the subject of many investigations due to its importance from economical and processing viewpoints. In principle, modification of PE with organic peroxide is associated with an insoluble molecular network or gel, which affects the level of chain-linking. There exist only limited publications on the modification of PE using peroxide concentrations below the critical gel formation concentration. In such situation, the modified PE still behaves like a thermoplastic. However, the molecular structure of the PE changes in such a manner that the average molecular weight follows an ascending trends, at the same time its distribution becomes slightly broader, altering its properties in the molten and solid states [1–8].

Rheological investigation is a key in achieving useful information about events at molecular level. Accordingly, determination of degree of long chain branching (LCB) of polymers is essential for understanding their rheological response and optimizing their processing behavior [9–16].

Typically, a very low level of LCB has a significant impact on the processability of polymers, especially their melt strength. As a result, different authors have tried to exploit this rheological effect to characterize LCB [17]. The correlations established between degree of LCB and rheological response can be expressed as a fast and robust method for monitoring the microstructural changes during reactive processing of linear low density polyethylene (LLDPE).

In general, the rheological response of PEs is influenced by the type, content, and structure of branches. So far, diverse rheological methods have been examined and revealed that LCB-mPEs feature a higher temperature dependence than linear ones, but the introduction of LCBs also leads to the failure of the time temperature superposition principle, i.e., to a thermorheological complexity. For LCB-PEs, a drop in the activation energy (E_a) together with an increase in the storage modulus is characteristic of thermorheological complexity [18,19].

One way to distinguish the complex thermorheological behavior from the simple behavior would be determination of

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E_a. In the case that E_a shows no dependency on frequency, the modulus and phase angle of master curve can be explained in view of shifting in viscoelastic properties at different temperatures. This is a sign of simple thermorheological behavior, which is the case seen for linear PE. Increase of long-chain branching in linear PEs caused by dependency of E_a on frequency, modulus, and phase angle establishment of master curve seems impossible.

The activation energy of linear PEs takes the minimum value and will be affected by the long or short chain branches (SCBs). The activation energy of high density PE (HDPE) in the melt is estimated to be around 26–28 kJ/mol, while it is slightly higher (30–34 kJ/mol) for linear PEs containing SCBs. For LLDPE, the E_a takes the value of 34 kJ/mol. An increase in the LCB content possesses stronger effects on the activation energy, rather than the increase in the SCB content. The maximum activation energy of about 65 kJ/mol has been reported for LDPE, which has a great amount of LCBs. In general, the activation energy is independent of molecular weight (M_w) and molecular weight distribution (MWD), therefore the higher activation energy values of LDPE can be attributed to the presence of more LCBs that slow down the segmental motions [20–22].

For linear polyethylene, a simple thermorheological behavior was found, which means E_a is constant. Accordingly, E_a is independent of frequency or modulus, shear rate and relaxation time and therefore the determined viscoelastic properties in different temperatures can be shifted toward each other to obtain a master curve [23–25].

In other words, the accuracy of time–temperature superposition represents the simple thermorheological behavior [25]. In some cases, the effect of temperature cannot be described by a single time-shift factor and different shift factor is required corresponding to times. As a result, the time-temperature superposition is no longer applicable. This kind of materials is called thermorheologically complex. The materials containing LCBs often shows the simple/complexity theromorheological behavior [26].

In recent years, lots of attentions were focused on the influence of branching on the rheological and thermorheological properties of PE and its blends. Investigations on the PEs reveal that LCBs have stronger effects on the rheological properties and more rheological temperature dependency as compared to SCBs. Rheological response of PEs depends on the type, content, and structure of branches. For LCB-PEs, a decrease in activation energy (E_a) with an increase in storage modulus was reported which is considered as a sign for thermorheological complexity [27–35].

Dordinejad et al. [36] performed different analytical approaches based on rheological measurements on two grades of neat m-LLDPE samples to define thermorheological behavior for the assigned system. In the other work [37], they focused on some model blend systems based on PE in order to examine the applicability and ability of diverse analytical techniques in defining thermorheological behavior of the blends and their relation with branching structure. Elsewhere [38], they qualitatively assessed long chain branching content in the LLDPE, LDPE and their blends via thermorheological analysis.

Golriz et al. [39], proposed a correlation between reactive modification conditions and degree of LCB in chemically-modified LLDPE. Moreover, by the use of a response surface method, correlations between the processing parameters and degree of LCB was established. In continuation [40], the Monte Carlo (MC) simulation could successfully monitor the microstructural changes due to the induced LCB, decreased terminal double bonds, and increased trans vinyl bonds in LLDPE during peroxide modification. Elsewhere [41], they studied the rtheological assessment of variable molecular chain structures of LLDPE under reactive modification. By the use of a simple rheological method that uses melt rheology, and is reasonable and consistent with estimations on the degree of LCB (x) and the volume fraction of the various molecular species produced during peroxide modification of LLDPE.

The main objective of the current work is to investigate and define thermorheological behavior of peroxide modified LLDPE and degree of imposed LCB, which is one of the most important characteristics of polyethylene reflecting changes in molecular chain structure upon peroxide modification. In particular, we report on the potential of thermorheological approach as an alternative powerful tool for analyzing LCB in the peroxide modified LLDPE.

2. Experimental

2.1. Materials

A commercial LLDPE (LL4004EL), with a melt flow index of 3.6 g/10 min (190 °C,2.16 kg) and a density of 0.924 g/cm^3 (20 °C), was purchased from ExxonMobil Chemical. The average molecular weight (M_w) of this grade of LLDPE was about 95,000 g/mol. DCP (molecular weight 270 g/mol) and xylene (a mixture of *o*-, *m*-, and *p*-xylene with boiling point of 140 °C and density of 0.87 g/cm^3 at 20 °C) were chemically pure and were obtained from Aldrich Chemical Co.

2.2. Modification procedure

LLDPE was melt compounded with various amounts of peroxide i.e., 0, 15, 125, 500, 700, 1000 (ppm) using a DACA twin-screw Microcompounder (DACA Instruments, Goleta, CA, USA) with a screw speed of 100 rpm and temperature of 185 °C within various residence times. The preparation conditions are shown in Table 1.

2.3. Gel analysis

The most highly modified LLDPE samples i.e., the samples treated with high concentarations of DCP were examined for content of gel according to ASTM 2765. Based on this standard the extraction in boiling xylene was the basis of all the analyses.

2.4. Size exclusion chromatography (SEC)

Average molecular weights and molecular weight distributions (MWDs) were determined by high-temperature SEC coupled with a multi angle laser light scattering (MALLS) detector and a refractive index (RI) detector. The polymer molecules are fractionated in the SEC by their hydrodynamic volume, which depends on the density in the dissolved state, molar mass and degree of LCD. Therefore, the conventional SEC using linear polymer standards for the calibration is not suitable for investigations of the molar mass of branched polymer structures due to the fact that the calculated molar mass averages would be lower than the true values [42]. By coupling SEC with MALLS, the

Table 1
Preparation conditions of peroxide modified LLDPE at various residence times and peroxide contents.

Sample code	Peroxide concentration (ppm)	Mixing time (min)
LL/0	0	3
LL/15	15	3
LL/125	125	3
LL/500	500	3
LL/700	700	3
LL/1000	1000	3
LL/700/7.5	700	7.5