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Thermo-oxidative degradation study of melt-processed polyethylene and its blend with polyamide using time-resolved rheometry

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ABSTRACT

Time-resolved mechanical spectroscopy (TRMS) was conducted to study the thermo-oxidative degradation of linear low density polyethylene (LLDPE) samples with different thermal histories and their blends with a polyamide (PA6) in the melt state. Neat LLDPE was first melt-processed at 180, 220, 250, and 260 °C in an extruder and then pre-processed LLDPE samples were further extruded with PA6 at 260 °C to form various LLDPE/PA6 blends. TRMS measurements were conducted under an air atmosphere at 0.5% strain and a constant frequency of 0.1 rad/s for LLDPE samples and at a range of frequencies between 0.1 and 60 rad/s for LLDPE/PA blend samples, over a 1 h period. In the case of LLDPE samples, time-sweep experiments were carried out at 190, 220, and 240 °C, whereas the temperature was fixed at 240 °C for the LLDPE/PA blend samples. The observed rheological behaviors revealed that the degradation resulted in an increase in the elastic moduli of the LLDPE and LLDPE/PA blends regardless of the thermal history. LLDPE processed at different processing temperatures produced different viscoelastic behaviors in cases where the LLDPE samples were processed at lower temperatures (180 and 220 °C) where a rapid increase in the modulus over a short period was seen. On the other hand, a change in the pre-processing temperature of the LLDPE had no effect on the rheological property of the corresponding LLDPE/PA6 blends. Cross-linking reactions during measurements under an air atmosphere could be the main reason for the growth in the modulus as a result of thermo-oxidative degradation. It was found that degradation was only a function of the temperature and exposure time, not the frequency. The most important result of this study was that collecting data on the isochronal moduli at different scanning frequencies was a more accurate way to understand the degree of cross-linking compared to running conventional frequency sweep tests, where the molecular structure of the material was unstable as a result of rapid degradation.

1. Introduction

Polyethylenes (PEs) are commodity polymers that are frequently used as packaging materials even though they exhibit poor barrier properties against certain chemical components. One way to overcome this drawback is blending with another polymer with good barrier properties along with superior mechanical strength such as a polyamide (PA) [1,2]. It is well documented that both polymers are prone to thermal degradation when certain conditions are met, e.g., specific temperature ranges, oxygen content, and shear intensities [3–6]. During their degradation, polymers may undergo chain scission, crosslinking, or both simultaneously as competitive reactions, depending on the conditions and extent of the process [4,7–9]. In such a scenario, the oxidation of the PE is initiated by carbon radical production (chain scission), which is followed by the recombination of these radicals (alkyl radicals) and their addition to carbon-carbon double bonds ($CH_2{=}CH{-}$vinyl groups), causing cross-linking [10]. On the other hand, the oxidation of PA6 leads to the formation of alkoxy radicals containing amide and carboxylic groups from the decomposition of hydroperoxides during the chain scission process, whereas further oxidation leads to a cross-linking reaction between amine groups ($-NH_2$) and other reactive groups such as aldehydes and amides [6,11]. Alternatively, the degree of degradation (chain scission or cross-linking) could affect physical properties such as the viscosity

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and final thermal stability of the products. From another perspective, thermo-oxidative degradation can be used to initiate the biodegradation process by reducing the molecular weight to the point where biodegradation can proceed [8,12]. Therefore, it is important to study the effect of the thermo-oxidation process for polymers to develop materials with superior performance under optimized processing conditions.

Different techniques have been used to study the thermo-oxidative degradation of polymers, including thermogravimetric analysis (TGA) [7,12,13], differential scanning calorimetry (DSC) [7], Fourier transform infrared spectroscopy (FTIR) [5,13,14], size exclusion chromatography (SEC) [1], gas chromatography (GC) [7], oxygen uptake [6], chemiluminescence [6], and UV spectroscopy [5,6]. One of the most reliable techniques to study the mechanisms of the degradation process is the melt-rheological methods because it is very sensitive to any small microstructural changes from chain scission to crosslinking [4,15,16]. Conventional frequency sweep tests are very common to study the dynamic of polymers with respect to their molecular structures and morphologies as they probe polymers within their linear viscoelastic regions where molecular structures do not change during the tests. Low frequency results are richer in information as they are associated with longer relaxation times related to the larger portions of the materials. However, the longer required experimental time related to the low frequency regions could surpass the degradation time of some of testing materials (e.g., transient polymers). Thus, the long relaxation time associated to the structure of the polymer might not be accurate as degradation has already interfered with the structure and hence the properties. It has been shown that for materials undergoing fast degradation, conventional frequency sweep tests may not be informative because the degradation can occur within a few seconds during the course of frequency sweep tests. Alternatively, Mours and Winter [17] proposed the use of Time-resolved mechanical spectroscopy (TRMS) as a convenient technique to monitor the properties, e.g., the elastic and loss moduli, of transient materials at a single frequency. TRMS is a technique to sequentially acquiring the frequency dependencies of materials by probing the dynamic mechanical properties of such materials within their linear viscoelastic regions (constant strain amplitude) over a specific measuring time and at a fixed frequency [9,17–19].

The aim of this study was to observe the effect of the thermal history on the kinetics of the thermo-oxidative degradation of linear low density polyethylene (LLDPE) samples and their corresponding blends with PA via a time-resolved rheology technique. Different LLDPE samples were processed at different temperatures from 180 °C to 260 °C in an extruder. Then, in the next step, these differently processed LLDPE samples passed through another extrusion to be blended with PA at 260 °C. This research may help us to understand the degradation kinetics of blends in the melt state.

2. Experimental

2.1. Materials

The polymers used in this study were commercial products. LLDPE, designated as HF120, was purchased from Sasol, South Africa. According to the supplier, it has a melt flow index (190 °C/2.16 kg) = 1.0 g/10 min, density = 0.920 g/m^3, and recommended melt-processing temperature of 190 °C. Nylon 6 (PA6), which was designated as UBE nylon 1030B, was purchased from UBE industries, Ltd. According to the supplier, it has a density = 1.14 g/m^3 and melt range temperature = 215–225 °C. Its measured melt flow index (250 °C/2.16 kg) was found to be 4.56 g/10 min.

2.1.1. Sample preparation

Neat LLDPE and 80 wt% pre-processed LLDPE/20 wt% neat PA6 blends were processed using a TE-30 co-rotating twin screw extruder (Nanjing ONLY Extrusion Machinery Co. Ltd), with an L/D of 40. Four neat LLDPE samples were processed at different temperatures:

(i) Processed at 180 °C; the following zone temperatures were used: 120, 160, 180, 180, 180, 180, 180, 180, and 180 °C; the die temperature was 180 °C; and the screw speed was 200 rpm.
(ii) Processed at 220 °C; the following zone temperatures were used: 120, 180, 220, 220, 220, 220, 220, 220, and 220 °C; the die temperature was 220 °C; and the screw speed was 200 rpm.
(iii) Processed at 250 °C; the following zone temperatures were used: 120, 220, 250, 250, 250, 250, 250, 250, and 250 °C; the die temperature was 250 °C; and the screw speed was 200 rpm.
(iv) Processed at 260 °C; the following zone temperatures were used: 120, 220, 260, 260, 260, 260, 260, 260, and 260 °C; die temperature was 260 °C; and the screw speed was 200 rpm.

It is interesting to note that the residence time for LLDPE's processed at 180 and 220 °C was about 1.10 min and it increased to 1.30 min for polymers processed at 250 and 260 °C.

Blends of 80 wt% pre-processed LLDPE samples and neat 20 wt% neat PA were processed using the following zone temperatures: 120, 200, 260, 260, 260, 260, 250, 250, and 245 °C, with a die temperature of 240 °C and screw speed of 200 rpm. During processing we did not find any change in residence time and color of the blend samples.

The extrudate was further molded using an injection molding machine (model: ENGEL, e-mac 50) to produce samples for rheological measurements. The following temperature zones were used: 220, 230, 235, 240, and 36 °C (mold temperature).

2.2. Characterization

2.2.1. Rheological analyses

Rheological analyses were conducted using a Physica MCR501 rheometer (Anton Paar Austria) equipped with 25 mm parallel plates. Time resolved mechanical spectroscopy (TRMS) measurements were carried out under an air atmosphere and a strain amplitude of 0.5% (linear region) within a 1 h period. The selected frequency for the melt-processed LLDPE samples was 0.1 rad/s, whereas various LLDPE/PA blend samples were probed at different frequencies of 0.1, 0.3, 1, 3, 6.28, 10, 30, and 60 rad/s to cover the low, intermediate, and high frequency regions. The time evolution rheological properties of the LLDPE were determined at different temperatures of 190, 220, and 240 °C, whereas the temperature was fixed at 240 °C for the LLDPE/PA blends, which was equal to their mixing temperature during injection molding. Frequency sweep tests were performed under an air atmosphere and a strain amplitude of 0.5%, with frequencies varying from 0.1 to 100 rad/s.

2.2.2. Morphology

A Carl Zeiss (Germany) Auriga FE-SEM with a GEMINI column was used to image the cryo-fractured (using liquid nitrogen) surfaces of neat LLDPE/PA blends. The surfaces were coated by an Au/Pd alloy and viewed using an acceleration voltage of 3 kV.