Material Behaviour

Correlating chemical and physical changes of photo-oxidized low-density polyethylene to the activation energy of water release

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Shiran Garnai Hirsch[a,b], Boris Barel[a], Dina Shpasser[c], Ester Segal[a,**], Oz M. Gazit[c,*]

[a] Department of Biotechnology and Food Engineering, Technion – Israel Institute of Technology, Haifa 3200003, Israel
[b] Netafim Ltd., D.N Hefer, 38845 Israel
[c] Department of Chemical Engineering, Technion – Israel Institute of Technology, Haifa 32000, Israel

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ABSTRACT

Understanding and quantifying the effect of degradation on the chemical and physical properties of LDPE films is crucial for maintaining high quality of recycled LDPE products. Thermal gravimetric analysis coupled with mass spectroscopy (TGA-MS), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry and electron microscopy combined with modulated TGA (MTGA) were used to evaluate LDPE films that sustained natural and accelerated weathering. Cross-referencing the chemical changes occurring to the LDPE samples during the weathering process with the dynamic results of MTGA provided a strong correlation between the release of caged water from the bulk of the LDPE and a specific energy value (E'), termed here as 'volitalization energy'. The E' value and the temperature at which it is measured are shown, for the first time, to be descriptors for the extent of photo-degradation. The data for accelerated- and naturally-induced degradation show a similar trend with respect to the effect of UVA radiation. A strong correlation is shown between the extent degradation determined by the traditional carbonyl index and the rate of water evaporation at the E' temperature.

1. Introduction

Exceptional thermal and chemical properties combined with excellent processability are what makes polyethylene (PE) one of the most extensively used synthetic polymers [1]. Unfortunately, the highly stable chemical structure of PE is also what makes it not biodegradable, resulting in the accumulation of huge amounts of post-usage waste [2]. The weathering of PE is known to have a strong damaging effect on its chemical and mechanical properties, leading in many cases to early application failure [3–5]. Hence, much emphasis is placed on mitigating these negative effects in an effort to extend the service life of PE-based products and substantially increase the use of recycled PE [6]. This has stimulated much research into the understanding and quantification of the governing photo-oxidative degradation processes and their effect on the micro and macro scale of PE[7].

Modulated thermal gravimetric analysis (MTGA), first introduced by Blaine and Hahn in 1998, was developed as a tool to obtain continuous kinetic information on the decomposition processes of polymers [8,9]. The technique is based on an oscillating temperature program superimposed on a linear heating profile, which produces a sine wave force function. In this method, the rate of mass change is continuously measured as a function of the oscillating temperature generating local maximum and minimum temperature values (termed as 'peaks' and 'valleys'). Using these values, the continuous activation energy curve is plotted according to equation (1) [7]:

$$E = \frac{RT_P T_V \ln(d\alpha_P/d\alpha_V)}{T_P - T_V} \tag{1}$$

where $d\alpha_P$ is the mass rate-of-change (% min^{-1}) at the temperature (T_P) where the peak is found and $d\alpha_V$ is the mass rate-of-change (% min^{-1}) at the temperature (T_V) where the valley is found. For more details regarding this equation please see Supporting Information, Equations S1-S2, and ASTM E2958 [10].

In traditional MTGA, multiple cycles of the sine wave are collected to plot the continuous activation energy curve, see Fig. 1. From the plateau region in the continuous energy curve we can calculate the activation energy for LDPE decomposition (E) [9]. As can be seen in Fig. 1, there are two sharp peaks at the onset and offset of the continuous activation energy curve. The most current claim is that these two sharp points are unrealistically high, and hence do not have any physical meaning [7,8].

Herein, we used the MTGA method to study the photo-degradation effect on low-density PE (LDPE) and evaluate the change in E values.

* Corresponding author.
** Corresponding author.
E-mail addresses: esegal@technion.ac.il (E. Segal), ozg@technion.ac.il (O.M. Gazit).
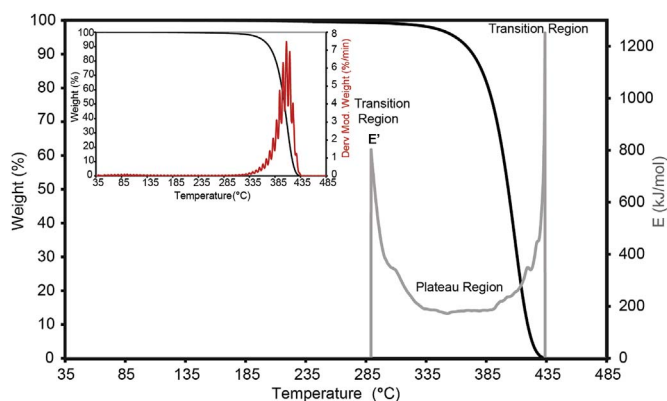
Fig. 1. Modulated thermogram (black trace) and the corresponding continuous activation energy curve (gray trace) for neat LDPE (un-weathered control sample). The inset depicts the corresponding modulated derivative.

Surprisingly, we find that the photo-degradation process has no effect on the traditionally calculated *E* values [11–17], neither under natural nor under accelerated weathering conditions. In contrast to what is currently perceived, we show here that the extent of LDPE photo-degradation is linearly correlated to the onset value associated with the measured activation energy curve. Analyzing the properties of LDPE using MTGA and TGA-mass spectrometry (TGA-MS) we show that this measured activation energy onset corresponds to the energy needed for the volatilization of water molecules locked within the polymer framework. We further show that the amount of water lost at a specific onset value is correlated with the value of the carbonyl index (CI), which is traditionally used to evaluate the extent of photo-degradation. We therefore term the energy value measured at the onset of the continuous activation energy curve as the E′, the energy of volatilization.

2. Experimental section

2.1. Preparation of LDPE films

LDPE samples (Ipethene 4203 by Carmel Olefins Ltd. Haifa, Israel), without stabilizing additives, with a MFI of 0.2 g/10 min and a density of 0.92 g cm^{-1} were used in this study. Thin films (50 $\pm$ 2 μm thick) were produced using a 30 mm single-screw extruder (L/D ratio of 30:1 with a screw speed of 120 rpm) equipped with a film blowing line (Labtech Engineering, Thailand). The die temperature was adjusted to 210 °C and the blown ratio was 2.5.

2.2. Weathering conditions

The LDPE films were weathered under natural and accelerated conditions. For natural weathering (NW), the films were exposed on the roof of our laboratory at Kibbutz Magal, Israel, for a period of four months (March–July 2015). Specimens were fixed in a custom-built setup, in which the films were positioned facing south at an angle of 45° with respect to the ground. The temperature, relative humidity and total irradiance were continuously recorded during exposure. Accelerated weathering (Acc) was conducted in a QUV tester (Q-Lab, USA) and the films were exposed to UVA irradiance (1.55 W m^{-2}) at 60 °C with natural humidity created by the presence of an open water bath. No humidity cycles were performed. The weathered films were removed at designated time intervals for subsequent characterization.

2.3. Characterization

2.3.1. Modulated thermal gravimetric analysis (MTGA)

MTGA analysis was carried out using a TGA Q5000 IR (TA Instruments, USA) according to ASTM E2958-14 [10]. For each

measurement, a sample of 3.8 $\pm$ 0.3 mg, consisting of 6 small circular films (50 $\pm$ 2 μm thick and 5 mm in diameter), was placed in a "flower shape" arrangement within a platinum pan to obtain optimal heat transfer. The sample was first conditioned at 35 °C under nitrogen atmosphere (99.999%) for 30 min at a flow rate of 25 mL min^{-1} and subsequently heated from 35 °C up to 500 °C at a rate of 2 °C min^{-1} under nitrogen. The temperature modulation amplitude was ± 5 °C for a period of 200 s. To reduce statistical error, three independent measurements were carried out for each sample. Following each test the TGA pan was cleaned by heating under air. The activation energy (*E*) and pre-exponential factor (log *Z*) were calculated using the TA universal analysis software. Notably, the specific set of parameters used here for the MTGA analysis were obtained following an optimization process conducted using the method described by Blaine and Hahn, for more details see Refs. [9,18]. The interested reader is referred to section 2 and Fig. S3 in the SI for more details on the parameter selection for the LDPE sample used here.

2.3.2. Thermal gravimetric analysis-coupled with mass spectrometry (TGA-MS)

TGA-MS experiments were carried out using a LABSYS Evo TGA (Setaram, France) coupled to a QGA mass spectrometer (Hiden Analytical, England), monitoring molecular species with 1–200 m/z. The QGA was equipped with two detectors; Faraday cup and SEM (secondary electron multiplier). Samples (12 $\pm$ 2 mg) were first conditioned at 35 °C under argon atmosphere (99.999%) for 30 min at a flow rate of 25 mL min^{-1}, and subsequently heated from 35 °C to 500 °C at a rate of 2 °C min^{-1} under argon. The discharge gas was transferred to the QGA through a capillary gas connection heated to 210 °C by applying a vacuum of 10^{-6} torr. TGA data was analyzed using Calisto thermal analysis software and the MS data was analyzed using the MASsoft 7.

2.3.3. Fourier transform infrared - attenuated total reflectance (FTIR-ATR)

Samples were measured on a Thermo 6700 FTIR instrument equipped with a DTGS-detector and a diamond ATR device (Smart iTR). Spectra were collected at a range of 500–4000 cm^{-1} and the instrument resolution was set to 4 cm^{-1} with 16 scans per spectrum. For each sample, at least 5 independent measurements were collected.

2.3.4. Differential scanning calorimetery (DSC)

DSC measurements were performed using a Mettler-Toledo DSC-1 instrument equipped with HSS7 - High Sensitivity Sensor. For analysis, LDPE samples (5.2 $\pm$ 0.3 mg) were placed in 40 μl sealed aluminum pans and measured under nitrogen atmosphere at a flow rate of 25 mL min^{-1}. Measurements consisted of the following four sequential steps: (1) heating from −10 °C to 160 °C, (2) sample maintained at 160 °C for 3 min, (3) cooling to −10 °C and (4) heating to 160 °C. All steps were carried out a constant rate of 10 °C min^{-1}. The degree of crystallinity (X_c) was calculated using the following equation:

$$X_c = \frac{\Delta H_m}{f_P \Delta H_m^0} \tag{2}$$

where, ΔH_m is the latent fusion heat, f_P is the LDPE weight fraction, and ΔH_m^0 is the theoretical latent heat of fusion for 100% crystalline LDPE (293 J g^{-1}) [19].

2.3.5. High resolution scanning electron microscopy (HRSEM)

The morphology of the films was studied using a Zeiss Ultra-Plus Schottky field emission gun SEM (FEG-SEM) system operated at 1 keV. For cross-section analysis the films were cryogenically fractured in liquid nitrogen. To minimize charging effects samples were gold sputtered (Polaron sputter coater E5150) prior to imaging.