Kinetics of a Thermooxidative Degradation of Polyethylene: Fractal Analysis

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ABSTRACT: It is shown that kinetics of polyethylene thermooxidative degradation is influenced by both spatial and temporary (energetic) disorder of structure. Thus, the theorem of subordination is carried out (i.e., the multiplicative behavior of exponents describing these kinds of disorder is observed). As heat aging is usually carried out at rather high temperatures, this circumstance leads in an increase of contribution of temporary (energetic) disorder. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2348–2351, 2004

Key words: polyethylene; aging; thermal properties

INTRODUCTION

It is supposed[1] that the thermooxidative degradation in polyethylenes can be realized according to two modes: kinetic and diffusive. The first mode corresponds to thin samples; the second mode corresponds to a massive and separating boundary. Between these modes is a sample thickness of 1 mm. In the present article, a process of a thermooxidative degradation in film samples of high-density polyethylene (HDPE) and its compositions with an oxygen acceptor—highly dispersed Fe—FeO mixture (Z)—HDPE+Z theoretically will be studied. This analysis will be made within the framework of fractal models describing reactions in nonordered mediums.[2–5] The most relevant features of these models is the simultaneous influence on a thermooxidative degradation process of spatial and temporary (energetic) disorder described in the terms of the so-called subordination theorem.[5] The purpose of the present article was to clarify the factors influencing a thermooxidative degradation rate and to offer the quantitative description of this process as an example of HDPE and two compositions HDPE+Z.

EXPERIMENTAL

A gas-phased industrial HDPE specified by GOST (Russian state standard) 16338-85 as grade 276 was used. It has a weight-average molecular weight (M_w) of 1.5×10^5 and molecular weight distribution M_w/M_n of 14.2. The degree of crystallinity is determined by the density and is equal to 0.68. The compositions HDPE + Z with contents Z 0.05 and 0.10 wt % (notations HDPE + 0.05Z and HDPE + 0.10Z, respectively) are utilized. Samples of studied polyethylenes were compression molded as films by a thickness of 0.4 mm at a temperature of 463 K and a pressure of $\sim$ 5 MPa.[6]

The heat aging of long duration is carried out in climatrone with good ventilation of air at temperatures of aging 363 and 463 K. A kinetics of the oxidation of thin specimens HDPE and compositions HDPE+Z is examined by the assumulation of carbonyl groups [)C=O]. The IR spectrums are received by the spectrophotometer (Perkin–Elmer) at room temperature. The absorption band with frequency v = 1700–1750 cm^{-1} is used and corresponds to stretching vibrations of a carbonyl groups.[7]

RESULTS AND DISCUSSION

In Figures 1 and 2, dependences of carbonyl group concentrations C_{carb} on treating time t_{ag} at aging temperatures T_{ag} = 353 and 463 K are shown, respectively. As is possible to see, qualitative relationship $C_{carb}(t_{ag})$ for both utilized T_{ag} are identical and the distinction essentially consists of a scale t_{ag} or rate of thermooxidative degradation. Consider the possibility of the description of a thermooxidative degradation process within the framework of fractal models.[4,5] The trajectory of a oxygen molecule O_2 in these models is described as a trajectory of random walk, and amount reacted with O_2 of a macromolecule sites is described as number of sites $\langle s \rangle$ visited by this walk. Apparently, in such treatment, it is necessary to accept

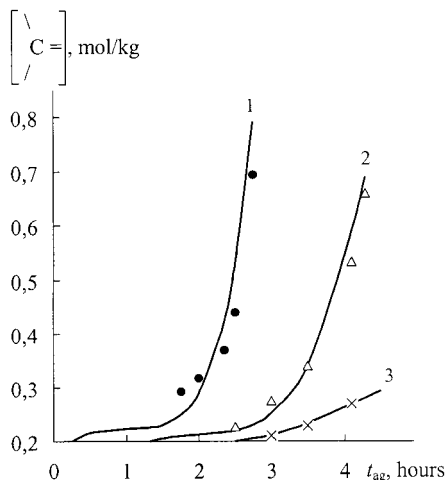$$C_{carb} \sim \langle s \rangle \tag{1}$$
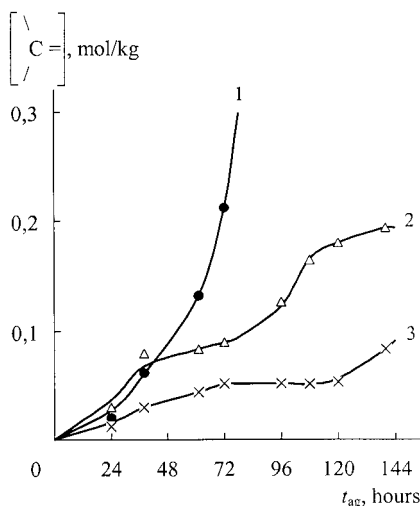
Figure 1 The dependences of carbonyl groups concentration c_{carb} on heat aging duration t_{ag} at $T_{ag} = 353$ K for HDPE (1) and compositions HDPE+0.05Z (2) and HDPE+0.10Z (3).

Further, it is possible to write the common relationship connected $\langle s \rangle$ with time t:[8]

$$\langle s \rangle \sim t^{d_s/2} \qquad (2)$$

where d_s is the spectral (fraction) dimension of a structure.

With allowance for relationships (1) and (2), it is possible to plot dependences c_{carb} on t_{ag} in double log–log coordinates and on their slope to determine the value d_s. In Figure 3, such dependences for HDPE, HDPE + 0.05Z, and HDPE + 0.10Z at $T_{ag} = 463$ K are

Figure 2 The dependences of carbonyl groups concentration c_{carb} on heat aging duration t_{ag} at $T_{ag} = 463$ K for HDPE (1) and compositions HDPE+0.05Z (2) and HDPE+0.10Z (3). Lines, experimental dependences; points, calculation on eq. (15).
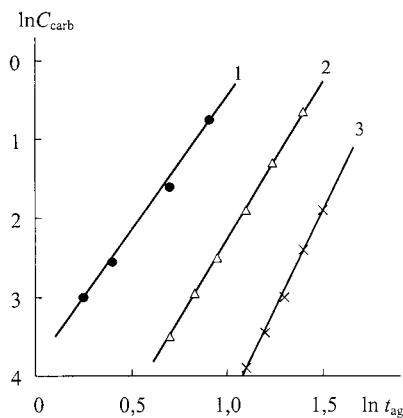
Figure 3 The dependences of carbonyl groups concentration c_{carb} on heat aging duration t_{ag} at $T_{ag} = 463$ K in double log–log coordinates for HDPE (1) and compositions HDPE+0.05Z (2) and HDPE+0.10Z (3).

shown. As is possible to see, the expected linear correlations allowing the determination of the values d_s are obtained, which appeared to equal 4.79–7.85. As is known,[9] value d_s alone can vary only within the limits of $1 \leq d_s \leq 2$ and that fact, determined from the graph's slope of a Figure 3 value $d_s > 2$ means that the so-called effective values d_s' are obtained, as[5]

$$d_s' = \gamma \, d_s, \qquad (3)$$

where the exponent γ characterizes a degree of temporary and, possibly energetic disorder of structure, whereas d_s alone characterizes its spatial disorder.

To determine the value d_s, it is possible from the equation[10]

$$d_s = 2d_f/d_w \qquad (4)$$

where d_f is a fractal dimension of a structure, and d_w is a dimension of a random walk trajectory on fractal.

As shown in ref. 11, the polyethylene structure can be simulated within the framework of a Witten–Sander irreversible aggregation model. In turn, for aggregates of Witten–Sander, the Aharony–Stauffer rule is well executed, according to which one value d_w is determined, so[10]

$$d_w = d_f + 1 \qquad (5)$$

The values d_f for studied polyethylenes are accepted according to the data of ref. 1. The calculation d_s according to eqs. (4) and (5) gives its average value ~ 1.46 for all studied polyethylenes. Then, it is possible to calculate the value of a exponent γ for both T_{ag} according to eq. (3). The value γ is varied within the limits 3.65–7.85. An exponent γ has physical sense. The probability $\psi(t)$, that some following event will

happen in time t after previous event, can be written as[5]

$$\psi(t) = c/(t^{1+\gamma}) \qquad (6)$$

where c is some constant.

Supposing, in the context of the present article, that the event is the reaction of O_2 with the reactive center of a polyethylene macromolecule and accepting arbitrary $c = 10^4$, we acknowledge, that for $\gamma = 3.65$, the interval between two adjacent events is equal to 7.25 units of time, and for $\gamma = 7.85–2.83$ units of time. Thus, the above-mentioned variation γ leads to a decreasing temporary interval between carbonyl groups formation $\sim$ 2.5 times. As indicated above, estimations of the value $\psi(t) = 1$ (i.e., is equal to absolute probability of event). The relationship (6) demonstrates an existence of temporary scaling for a function $\psi(t)$ (i.e., its fractal in time nature[5]. It means that the trajectory O_2 on polyethylenes structure should be described not by random walk (RW), and random walk with continuous time (RWCT), the model which on is based the introduction of the fractal set of events time.[5]

Consider the structural aspects of increase γ or amplification of temporary (energetic) disorder. The algebraic damping $\phi(t)$ generally can be described as[5]

$$\Phi(t) \sim (t/\tau)^{-\gamma}, \quad \gamma > 0, \quad t > \tau \qquad (7)$$

where t is reaction duration, and τ is relaxation time.

Having taken the logarithm relationship (7), we acknowledge the reciprocal value γ in proportion to $\ln \tau$. In turn, the Doolittle equation gives interconnection of $\ln \tau$ and free volume of polymer f_g[12]

$$\ln \tau = B/f_g \qquad (8)$$

where B is constant.

The value f_g for $T_{ag} = 353$ K can be estimated from[13]

$$f_g \cong 0.017(1 + \nu)/(1 - 2\nu) \qquad (9)$$

where ν is Poisson's ratio, which can be determined from known values d_f according to[14]

$$d_f = 2(1 + \nu) \qquad (10)$$

For a HDPE melt ($T_{ag} = 463$ K), the value $f_g = 0.113$ is accepted,[15] and for compositions HDPE+Z, the value f_g for a melt is calculated from the formula[12]

$$f_g \cong (\ln(\eta/A))^{-1} \qquad (11)$$

where η is melt viscosity, accepted to equal the reciprocal value of the melt flow index (MFI),[6] and the constant A is determined from the known data $f_g = 0.113$ and MFI for HDPE.
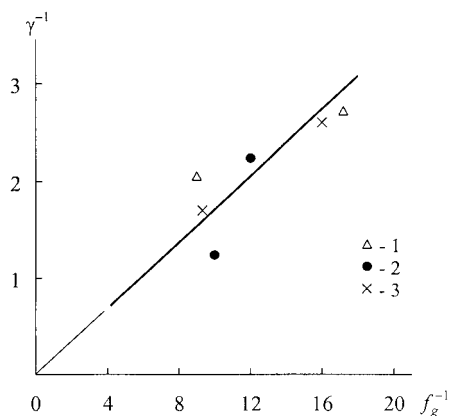
Figure 4 The relationship between reciprocal values of exponent γ and relative fraction of free volume f_g for HDPE (1) and compositions HDPE+0.05Z (2) and HDPE+0.10Z (3).

Thus, from combination of the eqs. (7)–(11), a linear correlation of reciprocal values γ and f_g follows. This rule confirms the data of Figure 4, which demonstrates the existence of the indicated correlation. This fact can be treated not only from positions of the free-volume theory, but also from positions of the fractal analysis. The increase of γ at an increase of T_{ag} means an amplification of a structure energetic disorder.[3] As is known[16] from degree of energetic excitation of polymer structure, to be exact, its loose-packed regions, it is possible to describe with the help of the extra energy localization regions dimension D_f. The value D_f is determined from[14]:

$$D_f = 2(1 - \nu)/(1 - 2\nu) \qquad (12)$$

The combination of eqs. (9) and (12) allows us to receive the following relationship between D_f and f_g

$$D_f \cong 117.6(1 - \nu)/(1 + \nu)f_g \qquad (13)$$

Thus, as shown in Figure 4, the interconnection between γ and f_g, and also relationship (13), it is necessary to expect the interconnection between γ and D_f. The data of Figure 5 confirm this supposition, analytically expressed as

$$\gamma \cong D_f \qquad (14)$$

Then, with reference to the thermooxidative degradation of polyethylenes, relationship (2) can be written as

$$c_{carb} = K(t_{in} + t_{ag}^{D_f d_s/2}) \qquad (15)$$

where K is constant, and t_{in} is duration induction period.
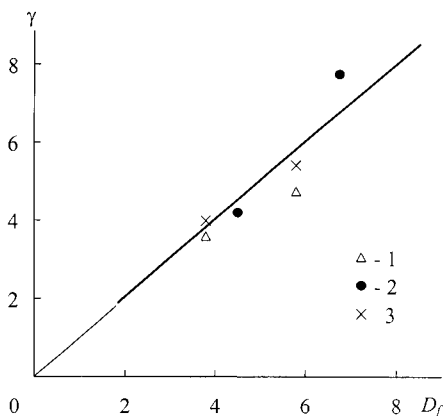
Figure 5 The relationship between exponent γ and extra energy localization regions dimension D_f for HDPE (1) and compositions HDPE+0.05Z (2) and HDPE+0.10Z (3).

In Figure 2, the comparison of experimental and calculated relationship (15) (the constant K in this relationship is determined by an adjustment method) dependence $c_{carb}(t_{ag})$ is shown. As is possible to see, for all three studied polyethylenes, the good correspondence of experiment and theory is obtained that the application of the considered fractal model for the description of a kinetics of a polyethylenes thermooxidative degradation allows.

CONCLUSION

Thus, the results of the present article have shown that on kinetics of polyethylenes, thermooxidative degradation is influenced by both spatial and temporary (energetic) disorder of structure. Thus, the theorem of subordination is correct [i.e., the multiplicative behavior of exponents d_s and γ (or D_f), describing these kinds of disorder is observed]. As heat aging is usually

carried out at rather high temperatures, this circumstance leads to an increase of contribution of temporary (energetic) disorder. The structural characteristics that determine the value γ in detail are considered.

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