The Theoretical Estimation of Effective Spectral Dimension for Polymer Melts

G. V. Kozlov, I. V. Dolbin, G. E. Zaikov

Kabardino-Balkarian State University, Chernishevsky st., 173, 360004, Nalchik KBR, Russia
Institute of Biochemical Physics Russian Academy of Sciences, Kosygin st. 4, 119991, Moscow, Russia

ABSTRACT: The theoretical technique of an effective spectral dimension estimation for polymer melts is offered. The comparison of experimental and theoretical values of this parameter has shown their good correspondence. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1353–1356, 2004

INTRODUCTION

It has become clear that polymers in the majority of their states and at different structural levels are fractals.[1,2] This fundamental rule basically has changed views on a kinetics of processes, which passing at heat aging of polymeric materials. The author[3] was shown that for fractal (self-similar) space the decrease of reaction rate k with the increase of its duration t is observed, that analytically written as follows:

$$k \sim t^{-h}, \qquad (1)$$

where h is the heterogeneity exponent ($0 \leq h \leq 1$), which will be equal to zero only for homogeneous samples; in this case, the behavior becomes classic (Euclidean): $k = $ const.

In its turn, exponent h is connected to effective spectral dimension d_s' of medium by the following simple relationship[3]:

$$d_s' = 2(1 - h). \qquad (2)$$

The experimental studies of heat aging processes of a number of polymers have confirmed the correctness of this approach[3] in general and the equations (1) and (2) in particular.[4,5] Besides, it was shown[6] that the main structural factor controlling a thermopoxidative degradation process of polymer melts is just d_s'. Therefore, the purpose of the present article is the working out of a technique for theoretical estimation of d_s' as

well as verification of it on an example of melts of two polymers: polyarylate (PAr) and polyarylatearylene-sulphonoxide (PAASO).

EXPERIMENTAL

PAr on a basis of dichloroanhydride 1,1-dichloro-2,2-di(n-carboxiphenil) ethylene and bisphenol A is used, which has the following constitution:
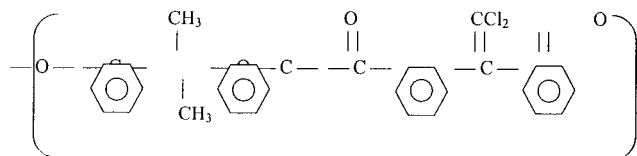
Block copolymer PAASO, synthesized from diane, mixture of (1:1) dichloroanhydrides of tere- and isophalic acids, dihydroxil-containing olygoarylenesulfonoxide on the basis of diane and 4,4'-dichlorodiphenylsulfone with molecular weight 4600 is also used, which has the following constitution:
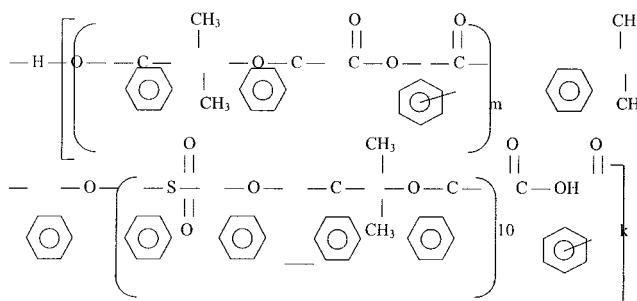
The average molecular weight $\overline{M_w}$ is determined by method of approaching to equilibrium (Archibald method) in ultracentrifuge 3170 of the corporation MOM (Budapest, Hungary).

Correspondence to: G. E. Zaikov (chembio@sky.chph.ras.rv).

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TABLE I
Basic Properties of Studied Polymers and Their Thermooxidative Degradation

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Polymer	Method of polycondensation	Notation	T_g, K	$\overline{M_w} \times 10^{-3}$	$k_d \times 10^{-4}$, s^{-1*}
PAr	Interphase	—	462	69	0.17
	Low-temperature	PAASO-1	472	76	0.19
PAASO	High-temperature	PAASO-2	474	64	0.24

* At $T = 623$ K.

The glass transition temperature T_g of the studied copolymers is defined by the dielectric method. The studies are carried out by quantometer BM-560 "Tesla" (Prague, Czechia) at frequency 1 MHz.[7]

For studies of the thermooxidative degradation processes in the air, the ampullary technique is used. The working volume of ampoules is equal to 3×10^{-5} l. The average initial contents of oxygen make up the value 2.5–3.0 mol. O_2/mole of polymer. The kinetic curve oxygen consumption $N_{O_2}(t)$ is obtained within temperature range 573–723 K.[7]

The plotting of logarithmic anamorphoses of kinetic curves $N_{O_2}(t)$ allows determining the constant of the reaction rate k_d for thermooxidative degradation. The methods of polycondensations by which the examined polymers are synthesized, and also their basis characteristics, are given in Table I.

RESULTS AND DISCUSSION

As is shown by Klymko & Kopelman,[8] at studies of chemical reactions on fractal objects the corrections on existence in the system of small clusters are necessary. Such corrections require usage in theoretical estimations not commonly accepted spectral (fracton) dimension d_s,[9] but its effective value d_s' that is due to energetic and temporal disorder of reactive space.[3] For percolation systems two cases are possible:[10]

a) The random walk is placed on the largest percolation cluster of the system characterized by dimension d_s.

b) The random walk can get on any cluster, including the cluster of a small size. The set of such clusters is characterized by a parameter d_s'.

Let's consider which of the two above-mentioned cases is applicable to a polymers melt. As shown by Kozlov and colleagues,[11] the amorphous polymer structure in a glassy state represents a percolation cluster, the percolation threshold of which on a temperature scale coincides with the glass transition temperature T_g of a polymer. The formation of such percolation cluster is determined by existence of local order domains in polymers at temperatures $T \leq T_g$. At $T > T_g$ the system of such domains is disintegrated[12] and the polymer structure is not a percolation system

any more. There is a problem of parameters describing a polymer melt structure. The studies of thermooxidative degradation processes of PAr and PAASO are made in temperature range $T = 573–723$ K, and the temperature range of glass transition temperatures of these polymers makes 462–474 K (Table I). As it is stated by Bershtein and Egorov,[13] the temperature of the so-called transition "liquid 1–liquid 2" T_{ll} can be estimated as follows:

$$T_{ll} \approx (1.20 \pm 0.05)T_g. \tag{3}$$

From (eq. 3) and the data of Table I the condition follows: $T > T_{ll}$. At T_{ll} there is transition of a polymeric melt from "liquid with the fixed structure" (where the residual structural ordering is observed[13]) to the true liquid state or "the unstructured liquid."[14] Nevertheless, "absence of structure" of a melt at $T > T_{ll}$ concerns the absence of the supermolecular structure, but the macromolecular coil structure in a melt remains the important structural factor (in essence, the only structural factor at $T > T_{ll}$). Thus, the structure of polymer melts in conditions of the present studies can be considered as a set of a large number of separate clusters (macromolecular coils), and trajectory of a molecula (atom) of oxygen on such structure is simulated by random walk. In this case, for an estimation d_s', the equation obtained by Argyrakis[10] is applicable:

$$d_s' = d_s\left(2 - \frac{d}{d - \beta/\nu}\right), \tag{4}$$

where d is the dimension of Euclidean space in which fractal is considered, and β and ν are static percolation indexes.

As stated by Sokolov,[15] the fractal (Hausdorff) dimension Δ_f can be expressed like this:

$$\Delta_f = d - \frac{\beta}{\nu}. \tag{5}$$

Vilgis has shown[16] that for polymer melts the value Δ_f is determined as follows:

$$\Delta_f = \frac{d_s(d + 2)}{2}. \tag{6}$$

The combination of the equations (4)–(6) allows receiving the final formula supposed calculation d'_s on known values Δ_f:

$$d'_s = \frac{2(2\Delta_f - d)}{d + 2}.\qquad(7)$$

Let's consider some characteristic values Δ_f at $d = 3$, and values d'_s corresponding to them. At transition from fractal objects to Euclidean ($\Delta_f = d$) value $d'_s = 1.2$. As stated by Rammel & Toulouse,[17] for the last objects $d_s = 3$, that is, at the indicated transition the discontinuous change d_s is observed. For linear polymers minimal value $d_s = 1$[9] and from the equation (6), we shall receive $\Delta_f = 2.5$. In this case $d'_s = 0.8$. And at last, at $\Delta_f = 1.5$ (transparent macromolecular coils[18]) $d'_s = 0$.

The precalculation of fractal dimension Δ_f of macromolecular coil in a melt is necessary for calculation of values d'_s on the equation (7). The estimation of value Δ_f can be made as follows.[19] The formal kinetics of chemical reactions can be described by the following equation:

$$\frac{dQ}{dt} = k_d(1 - Q),\qquad(8)$$

where Q is a reaction degree of conversion, t is its duration, and k_d is a reaction rate constant.

The general fractal relationship also used for the description of the kinetics of chemical reactions has the following form[2]:

$$Q \sim t^{(3-\Delta_f)/2}.\qquad(9)$$

Differentiating a relationship (Equation 9) about time t and equating the derivative dQ/dt to the similar derivative in the equation (8), we shall receive[19]:

$$t^{(\Delta_f - 1)/2} = \frac{C_1}{k_d(1 - Q)},\qquad(10)$$

where C_1 is a constant, which can be estimated from the boundary conditions,[19] and the values k_d are accepted according to the data of Batyrova.[7] The value Q is defined as ratio $N_{O_2}/N_{O_2}^\infty$, where N_{O_2} is the amount of consumed oxygen in an arbitrary moment of time t, and $N_{O_2}^\infty$ is the amount of oxygen required for full oxidation of aliphatic and aromatic groups of studied polymers ($N_{O_2}^\infty \approx 25$ moles O_2/basis mole[20]).

The experimental values of a heterogeneity exponent h were calculated on kinetic curves $N_{O_2}(t)$. The value k_i, corresponding to time t_i, was determined from the equation [5]:
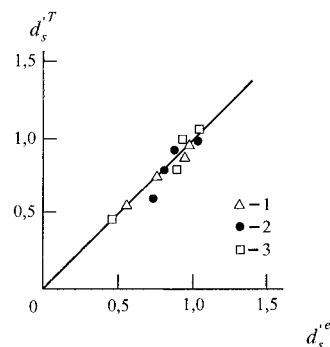

Figure 1 Relationship between experimental d''_s and calculated on the equation (7) d'^T_s values of effective spectral dimension for PAASO-1 (1), PAASO-2 (2), and PAr (3). The straight line gives a ratio 1:1.

$$k_i = \frac{N_{O_2}^{i+1} - N_{O_2}^i}{t_{i+1} - t_i}.\qquad(11)$$

Then, by plotting of dependences $k_i(t_i)$ in double log-log coordinates, it is possible from their slope to determine the value h and from the equation (2) to calculate experimental values of effective spectral dimension d''_s. In Figure 1 the comparison of theoretical values $d'_s(d'^T_s)$, calculated according to the equation (7), and experimental values d''_s, estimated according to the method described above, is shown. As it is possible to see, good correspondence of the theory and experiment is obtained (average divergence d'^T_s and d''_s equal ~4.5% and maximal −9.3%).

CONCLUSION

Thus, the theoretical technique of the estimation of effective spectral dimension d'_s for melts of polymers is offered. The comparison of experimental and theoretical values of this parameter has shown their good correspondence. The theoretical estimation d'_s is the first step to offering a computer predicting technique of thermooxidative degradation processes of polymer melts.

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