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A THERMO-OXIDATION, NON-ISOTHERMAL KINETIC STUDY OF THERMALLY AGED AND γ-IRRADIATION-AGED EVA COMPOUND SAMPLES

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ABSTRACT

The authors present the results of an attempt to evaluate the non-isothermal kinetic parameters for the oxidation accompanied by the release of volatile compounds undergone by non-aged, thermally aged and γ-irradiation-aged EVA compound samples. The differences between the kinetic behaviour of the samples according to their previous treatments are discussed.

INTRODUCTION

A previous paper [1] presented the results concerning the thermal stability of EVA (polyethylene with 17% vinyl polyacetate) subjected to thermally accelerated and γ-irradiation-induced ageings. It was shown that EVA aged both thermally and by γ-irradiation exhibits two kinds of thermo-oxidation processes, namely an initial exothermic process (at low temperatures) accompanied by a slight weight increase, followed, at higher temperatures, by exothermic processes accompanied by release of volatile compounds.

When heated in air, the thermally aged samples exhibit two thermo-oxidation processes with release of volatile compounds (denoted II and III) while the γ-irradiation-aged samples exhibit only one thermo-oxidation process (II) [1].

This paper is devoted to the evaluation of the non-isothermal kinetic parameters for process III of the thermally aged samples and process II of the γ-irradiation-aged samples.

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EXPERIMENTAL

The thermal curves were recorded on a Q-1500 D MOM Budapest Paulik–Paulik–Erdey-type derivatograph in a static air atmosphere, in the temperature range 20–500 °C, at a heating rate of 3.1 K min^{-1}. The rest of the experimental details, including the recording conditions, are given in our previous paper [1].

METHODS OF PROCESSING THE EXPERIMENTAL DATA

These methods were used to evaluate the non-isothermal kinetic parameters: the Coats–Redfern [2]; the Coats–Redfern modified by Urbanovici and Segal [3]; and the Flynn–Wall for constant heating rate [4]. The experimental data programs, in BASIC, [5,6] were run on a TIM S computer. A program to regenerate the thermogravimetric curve in (α, t °C) coordinates, using the values of the kinetic parameters determined by the Coats–Redfern method, was also used [7]; with this program, it can be seen whether or not the experimental points lie on the regenerated TG curve.

RESULTS AND DISCUSSION

Tables 1 and 2 list the values of the non-isothermal kinetic parameters for the previously mentioned thermo-oxidation processes. It can be seen that the values of the non-isothermal kinetic parameters of a given sample are in satisfactory agreement.

Although the thermo-oxidation processes of the thermally aged samples take place in practically the same temperature range, the reaction order and the rate equation depend on the ageing conditions. This statement is also valid for the γ-irradiation-aged samples at room temperature.

The highest value of the activation energy was obtained for the initial sample corresponding to the non-aged material. The lower activation energy values for the thermally aged and γ-irradiation-aged samples may be assigned to some thermally induced or γ-irradiation-induced intermediates (hydroperoxides, macromolecular radicals, ketonic groups) which are active in the thermo-oxidation with release of volatile compounds.

As shown in our previous paper [1], thermo-oxidative degradations with release of volatiles are preceded by an oxidation process accompanied by a slight weight increase. This process is attenuated for the γ-irradiated samples, probably because of a γ-irradiation-induced solid-state oxidation of the EVA at room temperature. This assumption is confirmed by the lower activation energy values found for process II with release of volatiles of the γ-irradiated samples.

TABLE 1

The values of the non-isothermal kinetic parameters of process III for non-aged and thermally aged samples of EVA compound using three different methods

T [a] (°C)	t [b] (h)	ΔT [c] (°C)	Methods											
			Coats–Redfern				Modified Coats–Redfern				Flynn–Wall, a = const.			
			E_A [d] (kcal mol^{-1})	n [a]	A [f] (s^{-1})	r [g]	E_A [d] (kcal mol^{-1})	n [e]	A [f] (s^{-1})	r [g]	E_A [d] (kcal mol^{-1})	n [e]	A [f] (s^{-1})	r [g]
(Initial sample)		284–332	77.4	1.4	2.88×10^{26}	0.996	77.2	1.3	2.37×10^{26}	0.996	75.8	1.4	7.5×10^{25}	0.996
130	1000	290–330	59.2	0.4	2.51×10^{19}	0.996	60.0	0.4	5.37×10^{19}	0.997	58.5	0.4	1.49×10^{19}	0.997
130	1500	278–325	64.3	0.5	2.78×10^{21}	0.994	63.8	0.4	1.75×10^{21}	0.994	61.8	0.4	3.41×10^{21}	0.994
130	2525	283–327	57.6	1.3	1.17×10^{19}	0.985	57.6	1.2	1.15×10^{19}	0.986	56.9	1.3	7.1×10^{18}	0.985
130	3800	285–327	54.6	0.3	4.85×10^{17}	0.986	53.8	0.2	2.33×10^{17}	0.988	54.1	0.3	3.34×10^{17}	0.987
145	228	271–341	63.5	0.9	4.92×10^{20}	0.992	63.3	0.8	4.41×10^{20}	0.992	62.6	0.9	2.62×10^{20}	0.993
180	30	258–327	36.7	0.9	1.19×10^{11}	0.988	36.6	0.8	1.16×10^{11}	0.988	37.0	0.9	1.27×10^{11}	0.989

[a] T, Temperature of ageing.
[b] t, Ageing time.
[c] ΔT, Temperature range of the thermo-oxidation process.
[d] E_A, activation energy.
[e] n, Apparent reaction order.
[f] A, Pre-exponential factor.
[g] r, Correlation coefficient of linear regression.

TABLE 2

The values of the non-isothermal kinetic parameters of process II (thermo-oxidation) for the EVA compound radiationally aged at a dose rate of 0.1 MRad h^{-1} [a]

t (h)	ΔT (°C)	Method											
		Coats–Redfern				Modified Coats–Redfern				Flynn–Wall, a = const.			
		E_A (kcal mol^{-1})	n	A (s^{-1})	r	E_A (kcal mol^{-1})	n	A (s^{-1})	r	E_A (kcal (mol^{-1})	n	A (s^{-1})	r
20	260–340	30.0	0.2	1.68×10^{8}	0.998	30.6	0.2	2.8×10^{8}	0.998	30.7	0.2	3.49×10^{8}	0.999
40	255–340	41.1	0.5	3.44×10^{12}	0.998	41.6	0.5	5.50×10^{12}	0.999	41.2	0.5	3.92×10^{12}	0.999
80	248–325	42.1	1.1	1.31×10^{13}	0.997	42.6	1.1	2.17×10^{13}	0.998	42.1	1.1	1.41×10^{13}	0.998
100	260–340	38.4	0.8	3.5×10^{11}	0.999	38.9	0.8	5.79×10^{11}	0.999	38.1	0.7	2.56×10^{11}	0.999
120	255–325	28.2	0	2.79×10^{7}	0.999	28.8	0	4.65×10^{7}	0.999	29.0	0	6.64×10^{7}	0.999

[a] Same notation as in Table 1.

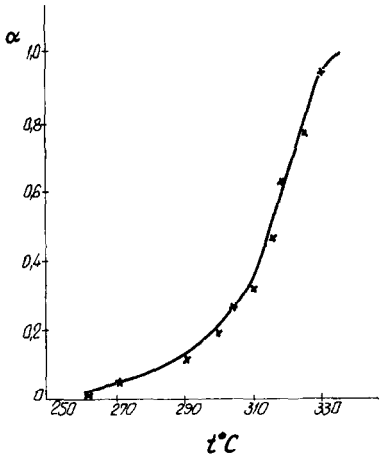

Fig. 1. Regenerated TG curve in (α, t °C) coordinates for EVA γ-irradiation-aged at a dose rate of 0.1 MRad h^{-1}, irradiation time = 40 h: ———, calculated curve; ×, experimental points.

For thermally aged samples as well as for those aged by γ-irradiation, some values of the pre-exponential factor, corresponding to reaction order values close to unity, equal those values predicted by the transition state theory [8,9], thus suggesting that a true monomolecular decomposition occurs. The reaction order values less than unity may be due to a mixed regime (kinetic and diffusional) controlling the decomposition [9,10]. Reaction order values above unity which characterise the non-aged EVA can be ascribed to the decomposition of structural units consisting of more than one molecule which coexist with the monomolecular ones.

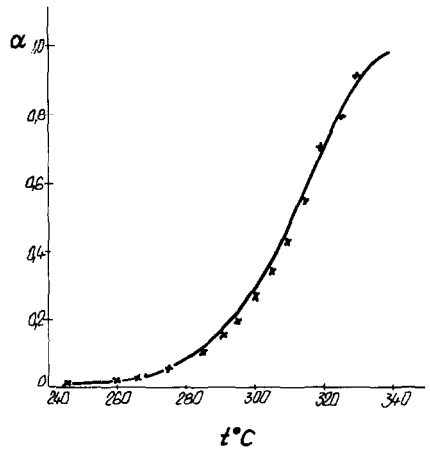

Fig. 2. Regenerated TG curve in (α, t °C) coordinates for EVA γ-irradiation-aged at a dose rate of 0.1 Mrad h^{-1}, irradiation time = 80 h: ———, calculated curve; ×, experimental points.

Figures 1 and 2, show two TG curves regenerated using the Coats–Redfern values of the kinetic parameters. The experimental points lie virtually on the regenerated curve thus indicating the validity of the non-isothermal kinetic parameter values.

CONCLUSIONS

The kinetic parameters of the non-isothermal thermo-oxidation of EVA compound, non-aged, thermally aged and γ-irradiation-aged, evaluated using three methods, show that the reaction mechanism depends on the ageing conditions.

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