

## **ON THE CHANGE IN THE THERMAL BEHAVIOUR OF THE COMPOUND EVA OWING TO ACCELERATED THERMAL AND RADIATION-INDUCED AGEING**

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### **ABSTRACT**

A derivatographic investigation has allowed us to demonstrate the changes undergone by the compound EVA as a consequence of thermal and radiation-induced ageing. For samples thermally aged at 130, 145 and 180 °C, as well as for those aged through  $\gamma$ -irradiation with a dose rate of 0.1 MRad h<sup>-1</sup>, two kinds of thermo-oxidative degradation have been found, which occur on heating the samples in air: an initial exothermic effect accompanied by a slight weight increase and exothermic effects accompanied by loss of volatile compounds. Up to 340 °C, the thermally aged samples exhibit two successive exothermic effects accompanied by loss of weight, while the irradiated ones exhibit only one such exothermic effect. The thermally aged samples heated in air up to 340 °C exhibit a weight loss of 16–21% while the weight loss corresponding to the sample aged through irradiation is 28–30%.

The results obtained by thermal analysis have been correlated with the results concerning the relative elongation at break following accelerated thermal and irradiation-induced ageing.

### **INTRODUCTION**

The use of polymeric electroinsulating materials in nuclear powered generating stations requires a knowledge of their behaviour during heating and irradiation. In order to obtain this information, the samples are submitted to accelerated thermal and radiation-induced ageing and then their mechanical properties (elongation at break, traction and compression resistance, etc.) and electrical properties (dielectric strength, resistivity, etc.) are followed. From the results thus obtained, the lifetime of these materials under operating conditions can be determined [1]. In order to obtain the necessary information, thermogravimetric and thermodifferential analyses

are very useful methods as they can provide the ranges of thermal stability [2–8] as well as the changes undergone by the polymeric material as a consequence of accelerated ageing [3].

This work presents the results obtained for the determination of the thermal characteristics of the compound EVA (polyethylene + vinyl polyacetate) from derivatographic data following accelerated thermal and radiational ageing. The results are correlated with those obtained at the change of the relative elongation at break after accelerated ageing.

## EXPERIMENTAL

The EVA used (polyethylene and 17% vinyl polyacetate with self-oxidants and fireproofing) was produced by ICECHIM-Brazi.

The heating curves of the powdered samples of EVA were recorded on a Q-1500 D MOM, Budapest-type Paulik–Paulik–Erdey derivatograph in a static air atmosphere, in the temperature range 20–500°C at a heating rate of 3.1 K min<sup>-1</sup>.

The accelerated thermal ageing of the test specimens took place in a WSU-200 oven with forced air circulation in which the temperature was kept constant with an accuracy of ±2%.

The  $\gamma$ -irradiation of the test specimens was performed at room temperature using a <sup>60</sup>Co source.

The relative elongation at break of the initial test specimens as well as of those submitted to accelerated ageing was determined on a universal machine, MONSANTO T-lo/E, with an accuracy of ±1%.

The test specimens (dumb-bell test pieces) of EVA of 1 mm thickness were in agreement with ASTM D-412 requirements.

## RESULTS AND DISCUSSION

The thermal ageing of the compound EVA in the oven with forced air circulation was investigated under the following conditions:

- (i) at 130°C with ageing times: 1000, 1500, 2525 and 3800 h;
- (ii) at 145°C with ageing times: 228, 467, 610, 949 and 1909 h;
- (iii) at 180°C with ageing times: 30 and 150 h.

The ageing of the EVA with  $\gamma$ -irradiation was performed at a dose rate of 0.1 MRad h<sup>-1</sup> with ageing times of 20, 40, 60, 80, 100 and 120 h.

Derivatograms were recorded for the initial test samples as well as for the aged ones. The elongation at break was determined for the same test samples. Thus all the necessary information to investigate the effect of accelerated ageing on the mechanical and thermal properties of the EVA compound was obtained.

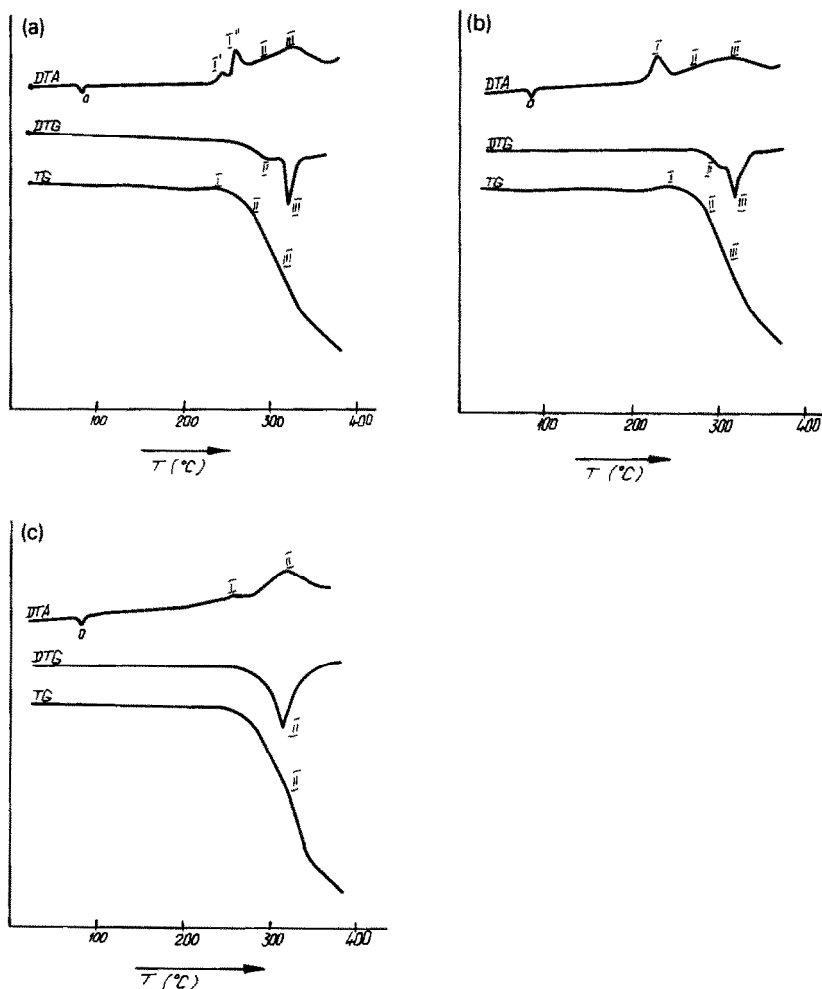


Fig. 1. Derivatograms corresponding to the thermal degradations of EVA: a, initial sample (non-aged); b, sample thermally aged at 130°C for 1000 h; c, sample aged by  $\gamma$ -irradiation at a dose rate of 0.1 MRad h<sup>-1</sup> for 40 h.

Figure 1 shows the derivatogram of the non-aged EVA, the so-called initial compound (a), of the same compound thermally aged at 130°C for 1000 h (b) and of the same compound aged by  $\gamma$ -irradiation for 40 h (c). All the other derivatograms corresponding to thermally and radiationally aged test specimens are of the form given in Fig. 1, b and c.

All the samples exhibit a phase transition of the first-order at 78–82°C (the peaks marked with “0”) which corresponds to the soaking of the polymer material.

Figure 1a shows that the non-aged EVA compound exhibits two oxidative degradation processes, I' and I'', located at 243 and 252°C with a slight weight increase, and two other oxidation processes which occur with weight loss, II and III, located just after the I'' oxidation peak.

TABLE 1  
The parameters of the thermo-oxidative degradation of the unaged and thermally aged EVA compound<sup>a</sup>

Ageing conditions		Process I			Process II			Process III			% $m_1$	
$T$ ( $^{\circ}\text{C}$ )	$t$ (h)	$T_i$ ( $^{\circ}\text{C}$ )	$T_{\max}$ ( $^{\circ}\text{C}$ )	$T_f$ ( $^{\circ}\text{C}$ )	$T_i$ ( $^{\circ}\text{C}$ )	$T_{\max}$ ( $^{\circ}\text{C}$ )	$T_f$ ( $^{\circ}\text{C}$ )	$T_i$ ( $^{\circ}\text{C}$ )	$T_{\min}$ ( $^{\circ}\text{C}$ )	$T_f$ ( $^{\circ}\text{C}$ )	% $m_2$	% $m_3$
Initial sample		231 <sup>b</sup>	243 <sup>b</sup>	252	284	332	317	18.3	23.2			
		245 <sup>c</sup>	252 <sup>c</sup>									
130	1000	210	230	237	290	330	317	11.5	17.3			
130	1500	210	223	245	278	325	318	12.7	18.7			
130	2525	199	215	225	283	327	320	12.9	18.2			
130	3800	185	208	235	285	327	320	11.5	15.8			
145	228	221	240	250	271	342	327	14.3	18.7			
145	467	215	230	235	270	328	319	13.3	16.7			
145	610	208	225	255	275	327	318	13.0	16.5			
145	946	207	222	235	262	332	318	14.7	18.2			
145	1909	186	219	224	276	330	321	17.0	22.3			
180	30	205	227	230	258	327	320	15.7	20.1			
180	150	180	210	216	275	327	320	14.0	19.7			

<sup>a</sup>  $T$ , Temperature at which the accelerated ageing occurred;  $t$ , ageing time;  $T_i$ ,  $T_{\max}$ ,  $T_f$ , the initial, maximum and final temperatures of the process;  $T_{\min}$ , temperature corresponding to the minimum of the DTG curve for process III; %  $m_1$ , %  $m_2$  and %  $m_3$ , the weight losses which occur before the beginning of process I and after processes II and III; %  $m_1$ , total weight loss.

<sup>b</sup> Corresponding to peak I' on the DTA curve (Fig. 1a).

<sup>c</sup> Corresponding to peak I'' on the DTA curve (Fig. 1a).

TABLE 2

The parameters of the thermo-oxidative degradation of the EVA acceleratively aged by  $\gamma$ -irradiation at a dose rate of 0.1 MRad h<sup>-1</sup> <sup>a</sup>

<i>t</i> (h)	Process I	Process II		$T_{\min}$ (°C)	% $m_t$
	$T_{\max}$ (°C)	$T_i$ (°C)	$T_f$ (°C)		
20	251	260	340	324	30.5
40	248	255	340	317	29.0
60	249	262	338	320	31.5
80	248	250	336	325	27.3
100	—	260	340	323	28.4
120	—	255	340	325	28.4

<sup>a</sup> The notation is the same as in Table 1.

The derivatogram of the thermally aged samples (Fig. 1b) exhibits the same phenomena of thermo-oxidative degradation with the only difference being that there is only one exothermic peak, I, corresponding to the oxidation with weight increase.

For the samples aged by  $\gamma$ -irradiation (Fig. 1c), their derivatogram exhibits an exothermic oxidation process, I, without weight loss, and an exothermic process, II, corresponding to an oxidation with weight loss. The peak I is quite weak in comparison with the peaks in Fig. 1a and 1b and appears only for irradiation times of less than 100 h. In contrast with the TG and DTG curves for the non-aged and thermally aged samples, the TG and DTG curves for the irradiated samples exhibit only one oxidation process with release of volatile compounds.

Such a thermo-oxidative degradation characterised by two kinds of oxidation (one accompanied by weight increase and the other accompanied by release of volatile compounds) is typical for other materials such as polyethylene and polypropylene [9], polyacetylene [10] and also elastomers [11].

Tables 1 and 2 list the parameters of the thermo-oxidative degradation.

For the initial sample as well as for the thermally aged ones (Table 1), the weight losses which precede process I (%  $m_1$ ) are negligible or relatively unimportant, the weight losses with release of volatiles being more pronounced for process III (%  $m_3$ ). For non-aged EVA, the total loss of weight (%  $m_t$ ) is 23.2%, while for the same compound thermally aged, the %  $m_t$  changes are between 16% and 20%. Taking into account the experimental errors inherent in such measurements, it follows that for the samples acceleratively aged at 130, 145 and 180°C, the total loss of weight is practically the same.

From Table 1, one can see that for the same ageing temperature, the temperature of the start of process I ( $T_i$ ) as well as the temperature corresponding to the maximum of the DTA curve ( $T_{\max}$ ) decreases with the increase in the thermal ageing time. Thus, for the thermal ageing at 130°C,

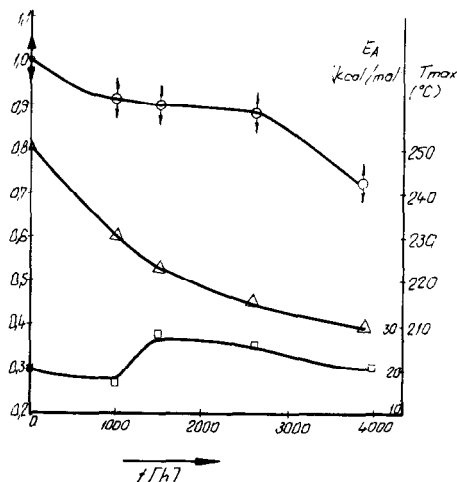


Fig. 2. Changes with ageing time in the relative elongation at break ( $k_e$ ), the temperature corresponding to the peak of the DTA curve ( $T_{max}$ ) and the activation energy of process I ( $E_A$ ) for EVA aged at 130°C: ○,  $k_e$ ; △,  $T_{max}$ ; □,  $E_A$ .

$T_i$  decreases from 245°C (non-aged sample) to 185°C (3800 h aged sample); similarly  $T_{max}$  decreases from 252 to 208°C.

The values of the activation energy for process I have been calculated from the DTA curves using the method of Piloyan et al. [12].

Figures 2–4 show the changes in the relative elongation at break ( $k_e$ ), in  $T_{max}$  for process I and in the activation energy of the same process ( $E_A$ ) with the ageing times. For the samples aged at 130 and 180°C,  $T_{max}$  decreases with a decrease in  $k_e$ . For the samples aged at 145°C, the curve of  $k_e$  versus ageing time exhibits a maximum at  $\approx 650$  h. For the same temperature, a maximum in the activation energy is recorded at the same ageing time as the maximum in  $k_e$ . This particular behaviour of the polymer aged at 145°C can be ascribed to a slow reticulation of the material at this temperature. The reticulated polymer interacts with oxygen, the oxidation process occurring with higher activation energy values. At 145°C for ageing times higher than 650 h, the scission and thermo-oxidation of the polymer occur with activation energy values lower than 40 kcal mol<sup>-1</sup>.

Process I, which occurs with a slight weight increase, is generally assigned to the generation of hydroperoxides and ketonic groups [11,13] which are relatively stable in polymers. The products thus generated undergo thermo-oxidation reactions at higher temperatures with the release of volatile products (processes II and III on Fig. 1a and 1b). As seen from Table 1, for processes II and III for thermally aged samples, the parameters for the thermo-oxidative degradation are within the limit of experimental error.

From Fig. 1 and Tables 1 and 2 one can see that the EVA aged by  $\gamma$ -irradiation has a quite different thermal behaviour compared to the same

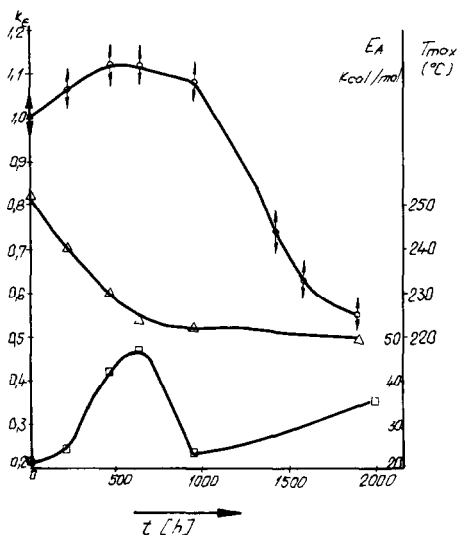


Fig. 3. Changes with ageing time in the relative elongation at break ( $k_e$ ), the temperature corresponding to the peak of the DTA curve ( $T_{max}$ ) and the activation energy of process I ( $E_A$ ) for EVA aged at 145°C:  $\circ$ ,  $k_e$ ;  $\Delta$ ,  $T_{max}$ ;  $\square$ ,  $E_A$ .

compound unaged or thermally aged. As previously shown, the DTA peak corresponding to process I is drastically diminished and totally disappears for samples irradiated for 100 and 120 h. In addition, the release of volatile

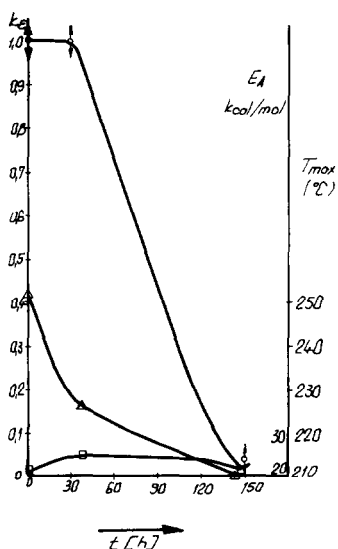


Fig. 4. Changes with ageing time in the relative elongation at break ( $k_e$ ), the temperature corresponding to the peak of the DTA curve ( $T_{max}$ ) and the activation energy of process I ( $E_A$ ) for EVA aged at 180°C:  $\circ$ ,  $k_e$ ;  $\Delta$ ,  $T_{max}$ ;  $\square$ ,  $E_A$ .

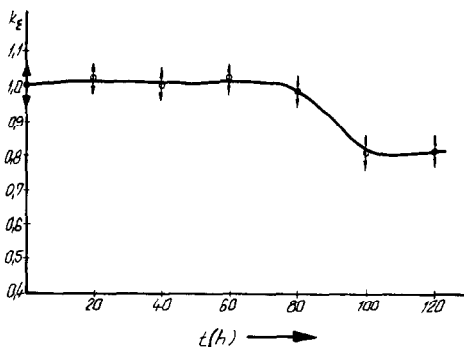


Fig. 5. Change in the relative elongation at break ( $k_e$ ) for EVA aged by  $\gamma$ -irradiation at a dose rate of  $0.1 \text{ MRad h}^{-1}$ .

products occurs during only one thermo-oxidation process whose maximum rate is recorded at  $317\text{--}325^\circ\text{C}$ , the same temperature range as for the thermally aged samples. The total loss of weight of the radiationally aged polymer is 10% higher than for the thermally aged polymer. The curve of mechanical degradation of the  $\gamma$ -irradiated polymer (Fig. 5) differs from that of the thermally aged polymers. The relative elongation at break is constant up to 80 h of ageing. At higher values of ageing time, the relative elongation at break decreases from 1 to 0.8. These results show that process I, oxidation without important changes of weight, occurs even at room temperature with completion at irradiation times higher than 100 h.

As for thermal ageing, ageing by irradiation generates macro-radicals, peroxy radicals, hydroperoxides and ketonic compounds [14,15]. At higher temperatures, these compounds interact with oxygen from the air giving rise to volatile products. As the amount of volatile products is higher than in the case of thermal ageing, it follows that the polymer EVA is characterised by a higher susceptibility to oxidation in the solid-state induced by  $\gamma$ -irradiation.

## CONCLUSIONS

The results concerning the changes of the thermal characteristics of the compound EVA as a consequence of thermal and radiational ageing have been presented.

For the thermally aged samples, the thermo-oxidative degradation consists of three successive processes, the first (process I) being accompanied by a slight increase of weight. For this process, the results obtained show that a change in the temperature corresponding to the peak on the DTA curve corresponds to a change in the elongation at break. Thus the periodic thermal analyses of test samples for thermal ageing could indicate the moment at which the specimens should be removed before a real change in the mechanical properties occurs.



The test specimens aged through  $\gamma$ -irradiation exhibit a higher loss in weight due to a more pronounced solid-state oxidation. For these samples, the disappearance of the DTA peak corresponding to process I coincides with the decrease in the relative elongation at break.

## REFERENCES

- 1 IEEE 383, Standard for Type Test of Class 1E Electric Cables Field Splices and Connections for Nuclear Power Generating Stations, 1974.
- 2 S.L. Madorsky, *Thermal Degradation of Organic Polymers*, Interscience, New York, 1964.
- 3 O. Vogl, I. Ivansung, H.C. Miller and H.W. Williams, *J. Macromol. Sci. A*, 2 (1968) 175.
- 4 V.V. Korshak, S.V. Viragradova, G.V. Danilov, L.A. Beribze and S.N. Salazkin, *Vısokomol. Soedin.*, 12 (1970) 129.
- 5 A.A. Berlin, B.G. Gherasimov and A.A. Ivanov, *J. Polym. Sci., C*, 41 (1973) 183.
- 6 T.J. Gademer, *J. Macromol. Sci. A*, 8 (1974) 15, 105.
- 7 S. Ciutacu, D. Fătu and E. Segal, *Thermochim. Acta*, 131 (1988) 279.
- 8 D. Fătu, Gabriela Geambaş, P. Budrugaec, S. Ciutacu and E. Segal, *Thermochim. Acta*, 149 (1989) 181.
- 9 M. Iring, Z.H. Laszlo, T. Kelen and F. Tüdos, in E. Buzagh (Ed.), *Proc. 4th International Conference on Thermal Analysis Vol. 2*, Budapest, 1975, Acad. Kiado, p. 127.
- 10 F.G. Will and D.W. McKee, *J. Polym. Sci., Polym. Chem. Ed.*, 21 (1983) 3479.
- 11 L. Slusarski, *J. Therm. Anal.*, 29 (1984) 905.
- 12 F.O. Piloyan, I.O. Ryabchikov and O.S. Novikova, *Nature*, 212 (1966) 1299.
- 13 V.T. Kagiya, K. Takemoto and M. Hagiwara, *J. Appl. Polym. Symp.*, 35 (1979) 95.
- 14 Y. Kemiya and E. Niki, in A.H. Jellinek (Ed.), *Aspects of Degradation and Stabilization of Polymers*, Elsevier, Amsterdam, 1978, Chap. III, p. 79.
- 15 V. Schnabell, *J. Radioanal. Nucl. Chem.*, 101 (1986) 413.