Thermochimica Acta, 15 (1976) 253–256

Note

Thermal stability in air of gamma irradiated fluoroelastomers

A. CUCCURU AND F. SODI
Laboratorio di Radioprotezione, Camen, 56010 San Piero a Grado, Pisa (Italy)
(Received 15 September 1975)

In previous papers the characterization, the linear expansion coefficients, the thermal stability in inert atmosphere of five hydrofluoroelastomers (Viton A, Viton B, Tecnoflon 3A, Tecnoflon SL, Tecnoflon T) irradiated up to 50 Mrads have been reported[1–3].

In this note the exothermic thermal degradation of the elastomers irradiated up to 25 Mrads, and kinetic data such as overall activation energy (E_A), order of reaction (n), pre-exponential factor ($\log A$) and the rate constant for the oxidative degradation are reported. The kinetic analysis was carried out by the Flynn and Wall[4] and the Rogers and Smith[5] relations which are thought to be sufficiently valid for the purpose of the present investigation.

EXPERIMENTAL

Materials, TG and DSC apparatus, experimental conditions and gamma irradiation technique are the same as previously described[2,3].

RESULTS

The elastomers were irradiated and examined after 5, 13, and 25 Mrads. The irradiation treatment gives rise to a noteworthy change in the fluoroelastomers properties: as shown in Table 1 the initiation temperatures for the oxidative degradation of the irradiated specimens are greatly decreased with increase in radiation dose; the rate of weight loss is also affected: as shown in Figs. 1 and 2 samples irradiated to a greater degree all show a definite decrease in the maximum values of the weight-loss rate; these curves also indicate that the greater the radiation dose, the greater the initial weight losses.

The kinetic parameters measured are summarized in Table 2 and clearly indicate a variation in the oxidative mechanism of the irradiated elastomers: generally the ones of the irradiated samples decrease if compared to those of unirradiated specimens; only Viton A and Viton B show an anomalous behaviour when irradiated at 13 Mrads, evidencing a surprising increase of the kinetic parameter values.

TABLE 1
THERMOGRAVIMETRIC RESULTS FOR IRRADIATED FLUOROELASTOMERS
T_{max} = temperature at which the degradation rate has a maximum.

Elastomer	*Radiation dose (Mrads)*	*Degradation temp. range (°C)*	T_{max} *(°C)*
Viton A	0	320–560	490
	5	290–540	490
	13	260–530	490
	25	250–510	470
Viton B	0	380–495	480
	5	370–485	475
	13	360–470	450
	25	270–470	455
Tecnoflon 3A	0	380–580	490
	5	370–560	480
	13	320–540	480
	25	280–530	470
Tecnoflon SL	0	380–560	480
	5	360–540	480
	13	280–530	480
	25	260–530	480
Tecnoflon T	0	400–550	510
	5	370–530	500
	13	350–510	490
	25	270–490	480

TABLE 2
KINETIC PARAMETERS FOR THE OXIDATIVE DEGRADATION OF THE FLUOROELASTOMERS EXAMINED

Elastomer	*Radiation dose (Mrad)*	*Overall activation energy (kcal mol^{-1})*	*Reaction order, n*	*log A*	*K (min^{-1})*
Viton A	0	66.50	0.20	18.86	0.58
	5	62.50	0.20	17.70	0.54
	13	78.70	0.90	22.45	0.68
	25	64.20	0.30	18.70	0.59
Viton B	0	88.40	0.40	25.63	0.78
	5	82.65	0.40	23.60	0.73
	13	103.14	0.60	31.27	0.99
	25	70.57	1.00	20.94	0.66
Tecnoflon 3A	0	82.56	1.10	23.57	0.72
	5	68.27	0.60	19.78	0.61
	13	59.50	0.80	17.16	0.53
	25	51.22	0.60	14.88	0.47
Tecnoflon SL	0	59.10	0.40	16.96	0.53
	5	51.30	0.40	14.21	0.42
	13	48.87	0.60	13.90	0.44
	25	40.70	0.30	11.40	0.36
Tecnoflon T	0	62.50	0.50	17.20	0.51
	5	51.27	0.30	14.20	0.43
	13	47.57	0.30	13.30	0.41
	25	35.66	0.20	9.75	0.31

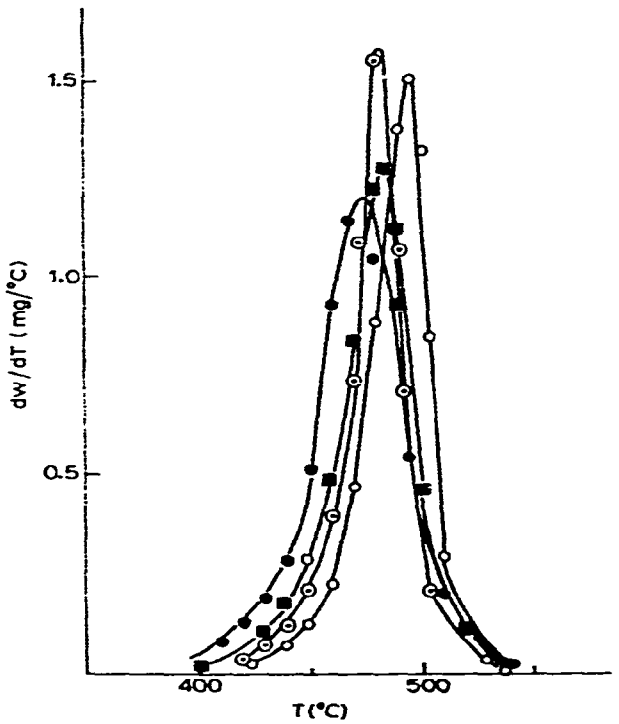

Fig. 1. Weight-loss rate for the oxidative degradation of Tecnoflon 3A irradiated at: (○) 0 Mrads, (⊙) 5 Mrads, (■) 13 Mrads, (●) 25 Mrads. Similar curves were obtained for the other elastomers examined.

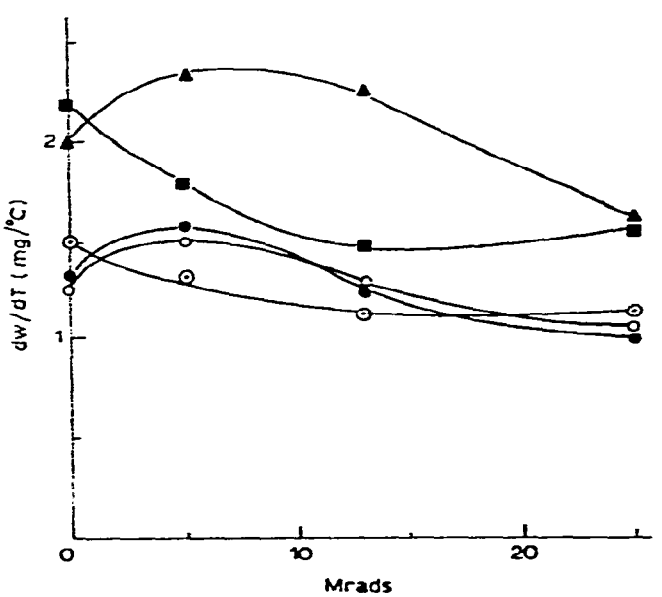

Fig. 2. Maximum weight-loss rates for the oxidative degradation of: (●) Viton A, (▲) Viton B, (■) Tecnoflon 3A, (⊙) Tecnoflon SL and (○) Tecnoflon T, irradiated in the range 0–25 Mrads.

REFERENCES

1 A. Cuccuru, P. Banditelli, S. Manfredini and L. Argiero, *Chim. Ind.*, 55 (1973) 6.
2 A. Cuccuru, *Thermochim. Acta*, 12 (1975) 135.
3 A. Cuccuru and F. Sodi, *Thermochim. Acta*, 12 (1975) 281.
4 J. H. Flynn and L. A. Wall, *J. Res. NBS*, 70 A (1966) 6.
5 R. N. Rogers and L. C. Smith, *Anal. Chem.*, 35 (1952) 1024.