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THERMAL STABILITY OF γ-IRRADIATED FLUOROELASTOMERS

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

The thermal stability of five hydrofluoroelastomers, irradiated up to 50 Mrad by γ-rays in the hot cell of the reactor "G. Galilei", has been investigated by thermogravimetric analysis. The apparent activation energy and the order of reaction for the degradation were evaluated by the Flynn and Wall method. The results show a noteworthy decrease in the thermal stability of the irradiated elastomers.

INTRODUCTION

It is well known that radiation has a marked effect on the physical properties of fluoroelastomers. Many investigations of the chemical nature of changes occurring upon irradiation were performed by electron spin resonance, nuclear spin resonance, infrared analysis, dynamic mechanical methods, and specific volumes studies[1–4,7].

Only a few tentative investigations have been reported on the effects of radiation on fluoroelastomers by means of thermal methods. It is the purpose of this paper to report and discuss the changes occurring in the thermal properties of some hydrofluoroelastomers subjected to a γ-radiation dose up to 50 Mrad.

EXPERIMENTAL

Materials

The elastomers examined were Viton A. Viton B, Tecnoflon 3A, Tecnoflon SL, Tecnoflon T and their composition is reported in Table 1.

Apparatus

A thermobalance Du Pont 950 was used to investigate the thermal stability of the fluoroelastomers examined. The temperatures were sensed by a chromel–alumel thermocouple with its junction in contact with the sample pan, and recorded by the recording apparatus of the Du Pont 900 consolle. The experimental conditions were: sample weight, 50 mg of comminuted elastomer; sample support, an open platinum pan; sample atmosphere, oxygen-free argon at a flow-rate of 30 ml min^{-1}; heating rate, 10°C min^{-1}.

TABLE 1

COMPOSITION OF THE FLUOROELASTOMERS EXAMINED

HFP = hexafluoropropylene; PFP = 1,2,3,3,3-pentafluoropropylene; ETF = ethylene tetrafluoride; VF = vinylidene fluoride; VA = vulcanizing agent.

Elastomer	*HFP* (%)	*PFP* (%)	*ETF* (%)	*VF* (%)	*VA* (%)
Viton A	$\simeq 20$			$\simeq 80$	
Viton B	$\simeq 20$		$\simeq 20$	$\simeq 60$	
Tecnoflon 3A		$\simeq 20$		$\simeq 80$	
Tecnoflon SL		$\simeq 20$		$\simeq 80$	$\simeq 3$
Tecnoflon T		$\simeq 20$	$\simeq 20$	$\simeq 60$	

Irradiation

Samples were irradiated in the hot cell of the reactor "G. Galilei" in air, at room temperature, using spent fuel elements γ-rays to a dosage up to 50 Mrad at a dose rate in the range $1.28 \div 0.33$ Mrad h^{-1}.

RESULTS

The fluoroelastomers were irradiated and examined after 5, 13, 25 and 50 Mrad. The γ-irradiation treatment gives rise to a noteworthy change in fluoroelastomers properties: as shown in Table 2, the initiation temperature for the thermal degradation of the irradiated specimens is greatly decreased with increase in radiation dose. Also the rate of weight loss in greatly effected: 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 rate curves also indicate that the greater the radiation dose, the greater the initial losses. Furthermore the temperature, at which the weight loss-rate has a maximum, shifts towards lower values as shown in Fig. 2.

In other words then, the irradiation treatment has weakened the elastomer to the extent that fragments are eliminated at lower temperatures than previously. Again the amount of char, residue to the thermal degradation, increases with the radiation dose.

In order to investigate the thermal stability of the irradiated samples, the apparent activation energy, E_A, and the order of reaction, n, were evaluated from the TG curves by the method of Flynn and Wall[5] using the following equation:

$$\ln \frac{\mathrm{d}w/\mathrm{d}T}{(w_0 - w_T)^n} = \ln \frac{A}{B} - \frac{E_A}{RT}$$

where $\mathrm{d}w/\mathrm{d}T$ is the rate of change in weight, w_0 is the initial weight of reactant, w_T is the weight of reactant at the absolute temperature T, n is the order of reaction, E_A is the apparent activation energy, and R is the gas constant.

TABLE 2

THERMOGRAVIMETRIC RESULTS FOR IRRADIATED FLUOROELASTOMERS

Fluoroelastomer	*Radiation dose (Mrad)*	*Temp. range of degradation (°C)*	*Max. rate of degradation (°C)*	*Residue (%)*
Viton A	0	390–510	480	2.8
	5	370–505	475	5.7
	13	310–505	475	6.6
	25	280–505	473	5.4
	50	260–510	470	1.0
Viton B	0	410–525	500	1.2
	5	380–525	497	1.4
	13	355–520	495	1.9
	25	340–515	490	2.3
	50	310–515	490	3.2
Tecnoflon 3A	0	360–515	495	4.2
	5	350–515	495	6.5
	13	330–515	490	7.1
	25	300–510	485	10.1
	50	270–505	480	11.7
Tecnoflon SL	0	380–525	500	1.8
	5	380–525	495	2.2
	13	370–520	485	9.0
	25	300–515	480	4.5
	50	290–515	480	5.5
Tecnoflon T	0	410–525	500	1.4
	5	390–525	500	2.5
	13	350–525	495	3.0
	25	320–520	490	3.2
	50	310–520	485	1.1

Trial values of n between 0 and 2, consistent with the order of reaction usually reported for thermal degradation of elastomers, were used in an Arrhenius plot until a straight line was obtained, from which the value of E_A was evaluated. The value of n which satisfies the above condition is assumed to be the reaction order. The values of E_A and n thus obtained are listed in Table 3 and clearly indicate a variation in the degradation mechanism of the irradiated elastomers: generally the apparent activation energies and the order of reaction for the degradation of the irradiated samples decrease compared with those of unirradiated ones; only Viton A and Tecnoflon SL show, at low radiation doses, an increase of these two parameters.

It is evident then, that γ-irradiation of the elastomers examined here, exerts a noteworthy effect on their chemical structure and on their thermal degradation behaviour. Yet, the overall effects are complex and apparently in contrast. In fact, the increase, with radiation dose, of char residue of the irradiated fluoroelastomers seems to indicate crosslinking, but the progressive changes in the rate curves of Fig. 2 are more characteristic of degradation.

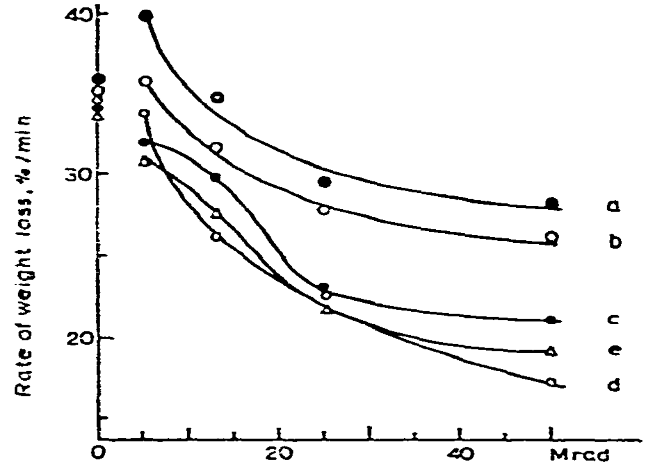

Fig. 1. Variation with radiation dose in the maximum values of the weight-loss rate for: Viton A (a), Viton B (b), Tecnoflon T (c); Tecnoflon 3A (d), Tecnoflon SL (e).

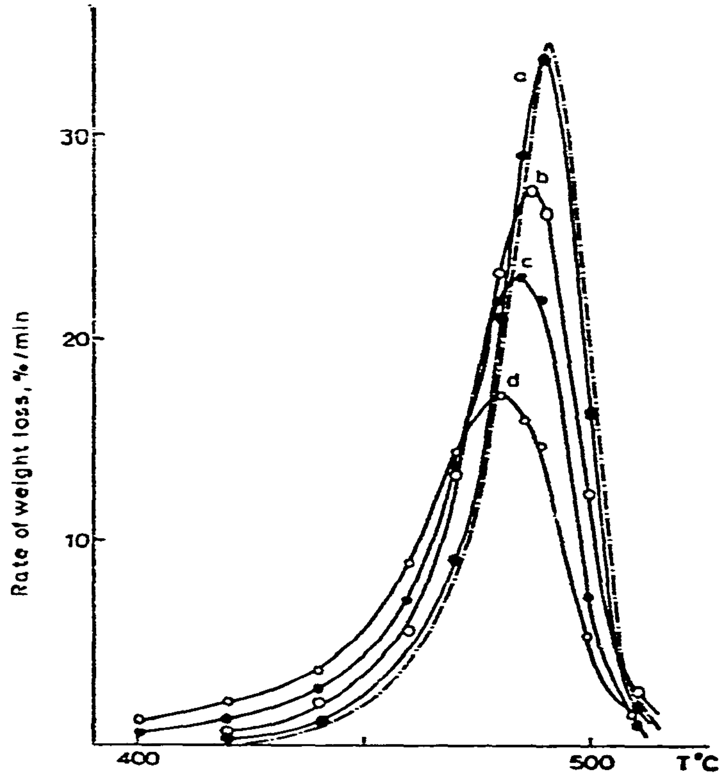

Fig. 2. Rate of weight-loss curves for Tecnoflon 3A irradiated at: 0 Mrad (dotted curve), 5 Mrad (a), 13 Mrad (b), 25 Mrad (c), and 50 Mrad (d). Similar curves were obtained for the other elastomers examined.

TABLE 3

ACTIVATION ENERGY AND ORDER OF REACTION OF IRRADIATED FLUOROELASTOMERS

Data evaluated by TG curves.

Fluoroelastomer	*Radiation dose (Mrad)*	*Activation energy (kcal mol^{-1})*	*Reaction order*
Viton A	0	83.5	1
	5	103.7	1.3
	13	73.0	1.4
	25	47.9	0.7
	50	37.5	0.8
Viton B	0	87.6	1
	5	74.3	0.7
	13	51.8	0.3
	25	41.4	0.3
	50	33.9	0.4
Tecnoflon 3A	0	84.1	1
	5	80.3	0.8
	13	72.1	1.3
	25	44.2	0.6
	50	30.9	0.5
Tecnoflon SL	0	79.8	1
	5	68.2	0.6
	13	79.2	1.7
	25	48.3	0.8
	50	27.4	0.2
Tecnoflon T	0	66.6	0.7
	5	62.9	0.7
	13	53.9	0.7
	25	38.9	0.4
	50	30.7	0.4

As suggested[6] the thermal degradation of hydrofluoroelastomers can be discussed in terms of two competing reactions: the one involving decomposition by rupture of chain bonds, and the other involving the splitting off of a hydrogen atom adjacent to a fluorine atom as hydrogen fluoride, with formation of a double bond. If the first reaction occurs then no residue would be formed, while if the fluoroelastomer decomposes by the second process the formation of a finite residue is possible. It is very likely that the elastomers examined here, degrade normally by both mechanisms, and γ-radiation enhances crosslinking even if chain scission occurs to an appreciable extent and remains the main phenomenon. This is plausible because the bonds on the carbon atom adjacent to the double bond are weaker than normal, as are those of the carbons forming crosslinking.

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