

EXPANSION COEFFICIENTS OF FLUORINATED ELASTOMERS

A. CUCCURU

Laboratorio di Radioprotezione—Camen, 56010 San Piero a Grado, Pisa (Italy)

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ABSTRACT

An analysis of the behaviour of five fluoroelastomers in the temperature range -120 to $+150^{\circ}\text{C}$ has been carried out by thermomechanical analysis; the linear expansion coefficient of crude and of gamma-irradiated fluoroelastomers has been evaluated. Finally the influence of the thermal history of the sample has been examined.

INTRODUCTION

Although thermal properties of fluoroelastomers have been widely studied, dimensional changes occurring on heating these materials have been often neglected.

Since thermomechanical analysis data correlated well with expansion coefficients and phase transitions, they provide a valid method for meaningful investigations into the physical properties and mechanical behaviour of materials.

This report describes the change in linear expansion coefficients of five fluorinated elastomers, and the examination of the influence of thermal history and of gamma-irradiation on linear expansion.

EXPERIMENTAL

Materials

The elastomers examined were: Viton A, Viton B, Tecnoflon 3A, Tecnoflon SL, Tecnoflon T and their compositions are reported in Table 1.

Instrumentation

The instrumentation used was a DuPont 941 thermomechanical analyzer (T.M.A.), a plug-in module for 990 thermal analysis system. Maximum sensitivity of the instrument is $1.5 \cdot 10^{-4}$ in. of probe displacement per inch of chart paper in a temperature range from -120 to 500°C .

Heating was done by means of a cylindrical heater containing a control thermocouple and surrounding the probe tube containing the sample. The instrument was calibrated and checked for linearity by measuring the coefficient of linear expansion of aluminum, whose expansion coefficient values vs. temperature are well

TABLE 1

COMPOSITION OF THE FLUROELASTOMERS EXAMINED

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

<i>Elastomer</i>	<i>HFP</i> (%)	<i>PFP</i> (%)	<i>ETF</i> (%)	<i>VF</i> (%)	<i>VA</i> (%)
Viton A	≈ 20			≈ 80	
Viton B	≈ 20		≈ 20	≈ 60	
Tecnoflon 3A		≈ 20		≈ 80	
Tecnoflon SL		≈ 20		≈ 80	≈ 3
Tecnoflon		≈ 20	≈ 20	≈ 60	

known. The linear expansion coefficients of the samples have been determined by the following equation:

$$\alpha_T = \frac{S \times \text{slope}_T}{h}$$

where α_T = linear expansion coefficient at temperature T ($^{\circ}\text{C}^{-1}$); S = sensitivity of instrument for a given Y-axis scale deflection (mils deflection per in. of chart paper); h = height of sample (mils; 1 mil = 0.001 in.); slope_T = slope of expansion profile at temperature T (in. of chart paper per $^{\circ}\text{C}$).

The experimental conditions were as follows: sample height in the range 60–120 mils depending on the furnished raw material; heating rate: $10^{\circ}\text{C min}^{-1}$; sample atmosphere: oxygen-free nitrogen, to avoid oxidation of the sample, at a flow-rate of 10 ml min^{-1} ; temperature range examined: -120 to $+150^{\circ}\text{C}$; freezing was carried out by dipping the cylindrical heater surrounding the tube containing the sample in liquid air; a nitrogen flux was maintained in the sample tube to remove any humidity trace to avoid ice formation on the sample. The sample was maintained at -120°C for half an hour before carrying out the experiment.

RESULTS

In Fig. 1 are reported the expansion profiles of the five fluoroelastomers examined and in Table 2 the linear expansion values obtained by the reported profiles. They compare favorably with some linear expansion data of similar products reported in literature¹⁻⁴.

Each profile can be divided into three zones: the first one, in the temperature range -120 to -25°C characterized by a constant linear expansion coefficient value; the second characterized by a sudden inversion of the expansion sense, and the third marked by an abrupt increase of the linear expansion. The change in slope in the second region of the profile cannot be clearly explained: it may be attributed to

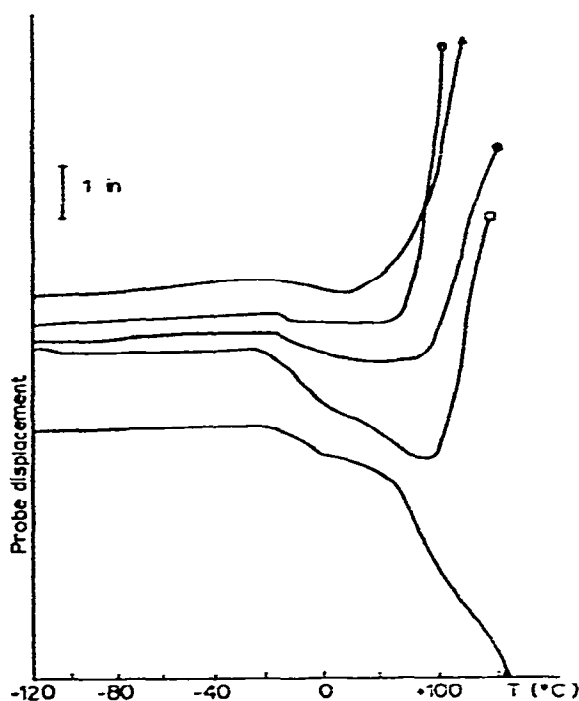


Fig. 1. Linear expansion profiles of: Viton A (\circ , $h = 100$ mils); Viton B (\triangle , $h = 120$ mils); Tecnoflon 3A (\bullet , $h = 63$ mils); Tecnoflon SL (\square , $h = 55$ mils); Tecnoflon T (\blacktriangle , $h = 70$ mils). h = sample height.

TABLE 2

LINEAR EXPANSION COEFFICIENTS OF THE EXAMINED FLUOROELASTOMERS

Negative values indicate contraction.

Compound	Temp. at which polymer contracts ($^{\circ}\text{C}$)	$\alpha_T \cdot 10^5$ ($^{\circ}\text{C}^{-1}$)								
		T ($^{\circ}\text{C}$)	-120	-25	-15	+20	+40	+75	+100	+120
Viton A	-22	+0.86	-5.7	-1.2	-1.5	+18.3	+69	+118		
Viton B	-20	+0.90	-8.2	+1.3	+6.8	+45	+115	+134		
Tecnoflon SL	-18	+0.54	-25	-5.4	n.d.	-9.1	+25.5	+55		
Tecnoflon 3A	-18	+0.77	-10.4	-6.7	-0.5	+4.5	+19	+38		
Tecnoflon T	-16	+0.56	-19.2	-0.6	-7.6	-14	-21	n.d.		

releasing of the strain in the sample or to a rapid increase of crystallinity degree as observed in other polymeric materials⁵⁻⁷. It is interesting to compare the behaviour of the elastomers examined here; as largely accepted a lower expansion coefficient indicates a higher degree of crystallinity or a more complete cure, whereas a higher linear coefficient of expansion illustrates incomplete cure or less crystallinity. Indeed

the introduction of a curing substance in Tecnoflon 3A gives an elastomer (Tecnoflon SL) with a lower expansion coefficient; furthermore by substituting hexafluoropropylene with 1,2,3,3,3-pentafluoropropylene, elastomers are obtained (Tecnoflon series) with a higher degree of cristallinity: the α_T values of Tecnoflon 3A, Tecnoflon SL and Tecnoflon T being lower than those of Viton A and Viton B. On the other hand, the introduction of ethylene tetrafluoride in Viton A and in Tecnoflon 3A to obtain a terpolymer (Viton B and Tecnoflon T, respectively) seems to give contrasting results. By comparing Viton A and Viton B expansion profiles in this manner we come to the conclusion that introduction of tetrafluoroethylene gives rise to an elastomer with a lower cristallinity degree; but comparing Tecnoflon 3A and Tecnoflon T does not confirm the above datum, viz. that the Tecnoflon T expansion profile is extremely anomalous.

A set of experiments has been carried out to ascertain the influence of thermal history on expansion characteristics. An example is reported in Fig. 2 where the expansion profiles of a sample of Viton B freezed as described above are shown and

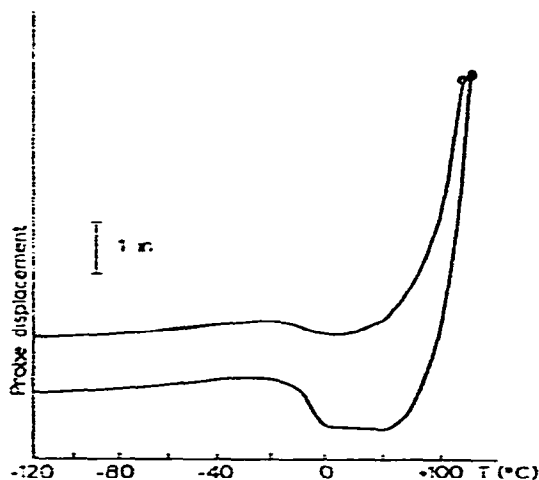


Fig. 2. Influence of thermal history on the linear expansion profile of a sample of Viton B: ○ sample freezed at -120°C ; ● sample freezed at -170°C and maintained for 2 h. Height of the samples: 120 mils.

a sample of Viton B freezed at -170°C , maintained at that temperature for 2 h and then slowly heated ($5^{\circ}\text{C min}^{-1}$) to 130°C . Comparing the two profiles shows a wide enlargement of the second zone and a sharply increasing rate of the expansion in the third zone of the profile of the sample freezed at -170°C . The different behaviour of the two samples may be attributed to a different degree of equilibrium achieved during the freezing process. In order to determine if the differences shown in Fig. 2 are artifacts of the particular thermal histories, it would be useful to obtain expansion data for samples cooled at extremely slow rates, but this is not possible with the present unit. However, such a behaviour was also observed for the other elastomers.

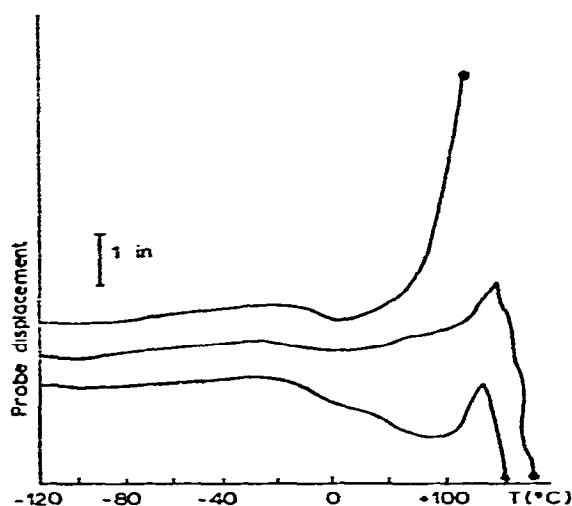


Fig. 3. Linear expansion profiles of gamma-irradiated Viton B: ● sample unirradiated; ○ sample irradiated at 13 Mrad; △ sample irradiated at 25 Mrad. Height of the samples: 120 mils.

TABLE 3

LINEAR EXPANSION COEFFICIENT OF IRRADIATED FLUROELASTOMERS

Negative values indicate contraction. T_1 = temperature at which elastomer begins contraction.

Elastomer	Radiation dose (Mrad)	T_1 (°C)	$\alpha_T \cdot 10^5$ (°C ⁻¹)						
			T (°C)						
			-120/-30	-15	+20	+40	+75	+100	+120
Viton A	0	-22	+0.86	-5.7	-1.2	-1.5	+18.3	+69	+118
	13	-25	+0.63	-7.2	-2.8	-3.2	-3.1	-7.2	n.d.
	25	-27	+0.83	-21.2	-6.3	-4.3	-4.9	-11.7	n.d.
Viton B	0	-20	+0.90	-8.2	+1.3	+6.8	+45	+115	+134
	13	-21	+0.85	-2.8	+1.1	+1.7	+3.8	+7.5	+8.7
	25	-23	+0.75	-1.6	-5.5	-3.8	-0.2	+0.3	+21
Teflon SL	0	-18	+0.54	-2.5	-5.4	n.d.	-9.1	+25.5	+55
	13	-18	+0.71	-12	-7.1	n.d.	-6	-2.3	+9.4
	25	-22	+0.54	-24	-4.6	n.d.	+2.5	+2.8	+13.5
Teflon 3A	0	-18	+0.77	-10.4	-0.7	-0.5	+4.5	+19	+38
	13	-20	+0.73	-17	-9.9	-5	-2.8	-2.5	-2.4
	25	-26	+0.97	-18	-3.5	+3.2	+6.8	+6.5	+6.3
Teflon T	0	-16	+0.56	-19.2	-0.6	-7.9	-14	-21	n.d.
	13	-18	+0.63	-6.8	-8.8	-13.6	-7.3	-8.2	n.d.
	25	-21	+0.96	-8.3	-17	-3.1	-4.8	-5.3	n.d.

Finally the influence of gamma-radiation on the expansion profiles of the elastomers has been examined.

Samples were irradiated in the hot cell of the reactor "G. Galilei" in air, at room temperature, using spent fuel element gamma-rays to a dosage up to 25 Mrads, at a dose rate in the range $1.28 \div 0.33 \text{ Mrad h}^{-1}$.

As shown in Fig. 3 and in Table 3, gamma-irradiation largely affects the expansion profiles and the linear expansion coefficient values of the elastomers, decreasing the α_T values with increasing radiation dose. As widely reported in literature, the fluoroelastomers are known to be susceptible to radiation-induced chain scission and to an increase in their crystalline content. The observed decrease of the expansion coefficients with radiation dose is consistent with an increase in crystallinity since the expansion of the amorphous region of polymers is generally greater than that of the crystalline region.

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