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Stress-Strain Behavior of Irradiated Polyurethane Elastomers*

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INTRODUCTION

The empirical equation developed by Martin and co-workers[1] has been found to describe, in a remarkably successful manner, the equilibrium stress-strain behavior of many elastomeric materials up to extension ratios of $\alpha \leq 3$.

According to this (MRS) relationship, the force developed by a rubber sample per unit of undeformed cross section is given by:

$$f = E_0 (\alpha^{-1} - \alpha^{-2}) \exp \{K(\alpha - \alpha^{-1})\} \quad (1)$$

where E_0 = tangent modulus at $\alpha = 1$, and K = material constant.

This expression has recently been used by several investigators to determine the elastic modulus as a function of mechanical degradation and chemically induced scission and crosslinking processes. The MRS relationship was found to be applicable to a wide variety of vulcanizates. It was found to be less successful in describing the stress-strain behavior of vulcanizates containing carbon black and other fillers.

The idea suggested itself that if the MRS relationship were applicable to irradiated elastomers, its use might contribute substantially to a systematization of experimental data since, in this manner, the stress-strain behavior can be characterized simply by two parameters, E_0 and K. If, moreover, the dose dependence of these parameters could be determined, it would be possible to arrive at predictive relationships of more general utility which in turn might furnish valuable clues to the underlying molecular processes.

The MRS relationship, eq. (1), was rearranged in logarithmic form such that:

$$\ln [f(D)\alpha^2/(\alpha - 1)] = K(D)[\alpha^{-1} (\alpha^2 - 1)] + \ln E_0 (D) \quad (2)$$

where D indicates the radiation dose dependence of the various parameters. Thus, by plotting the quantity $\ln [f(D)\alpha^2/(\alpha - 1)]$ as a function of $[\alpha^{-1} (\alpha^2 - 1)]$, a straight line is obtained. The parameter $K(D)$ is then equal to the slope of the straight line and $\ln E_0(D)$ is its intercept with the ordinate.

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TABLE I
Irradiation Data and Calculated Values of ln E_0 and K

Sample description	Run no.	γ, erg/g.(C)	Neutron dose, n/cm.^{2}	Irrad. temp., °F.	ln E_0	K
1. Du Pont Adriprene L,	1	0	0	80	5.25	0.400
100 pts.; MOCA, 12 pts.;	2	0	0	260	5.76	0.114
Cure 3 hrs. at 100°C.	3	2×10^9	1.25×10^{15}	80	5.97	0.049
	4	5.4×10^9	1.8×10^{15}	260	5.04	0.350
2. Du Pont L-167, 100 pts.;	1	0	0	80	5.47	0.528
MOCA, 18 pts.; cure	2	0	0	260	5.79	0.382
1 hr. at 100°C.	3	2×10^9	1.25×10^{15}	80	5.60	0.500
	4	5.4×10^9	1.8×10^{15}	260	5.79	0.280
3. Du Pont L-167, 100 pts.;	1	0	0	80	3.44	0.472
1,4-butanediol, 5.8 pts.;	2	0	0	260	3.44	0.413
trimethylolpropane, 1.0 pt.;	3	2×10^9	1.25×10^{15}	80	3.76	0.310
cure 4 hrs. at 140°C.	4	5.4×10^9	1.8×10^{15}	260	3.27	0.263
4. Genthane S-1	1	0	0	80	3.33	0.820
	2	0	0	260	2.88	1.00
	3	1.3×10^{10}	5.3×10^{15}	−65	2.54	1.02
	4	1.5×10^{10}	6.7×10^{15}	80	3.39	0.836
	5	1.9×10^{10}	8.5×10^{15}	260	1.39	1.91
5. Genthane S-2	1	0	0	80	2.81	1.015
	2	0	0	260	2.28	1.255
	3	1.3×10^{10}	5.3×10^{15}	−65	2.89	1.02
	4	1.5×10^{10}	6.7×10^{15}	80	2.44	1.265
	5	1.9×10^{10}	8.5×10^{15}	260	1.96	1.68

6. General Tire polyurethane Type R	1	0	0	80	3.19	0.838
	2	0	0	260	2.56	1.075
	3	1.3×10^{10}	5.3×10^{15}	−65	2.50	0.919
	4	1.5×10^{10}	6.7×10^{15}	80	6.32	−0.467
	5	1.9×10^{10}	8.5×10^{15}	260	3.11	1.28
7. Disogrin 1 DSA6865	1	0	0	80	4.46	0.523
	2	0	0	260	4.26	0.605
	3	1.3×10^{10}	5.3×10^{15}	−65	5.0	0.326
	4	1.5×10^{10}	6.7×10^{15}	80	4.34	0.955
	5	1.9×10^{10}	8.5×10^{15}	260	3.99	0.605
8. Disogrin 1 DSA9250	1	0	0	80	5.74	0.333
	2	0	0	260	5.73	0.325
	3	1.3×10^{10}	5.3×10^{15}	−65	5.75	0.263
	4	1.9×10^{10}	8.5×10^{15}	260	5.68	0.362
9. Disogrin 2 DSA9840	1	0	0	80	5.41	0.389
	2	0	0	260	5.41	0.389
	3	1.3×10^{10}	5.3×10^{15}	−65	6.03	0.060
	4	1.5×10^{10}	6.7×10^{15}	80	5.9	0.208
	5	1.9×10^{10}	8.5×10^{15}	260	6.0	0.016
10. Disogrin 2 DSA7560	1	0	0	80	4.26	0.486
	2	0	0	600	3.97	0.575
	3	1.3×10^{10}	5.3×10^{15}	−65	4.60	0.394
	4	1.5×10^{10}	6.7×10^{15}	80	4.64	0.570

EXPERIMENTAL

The experimental data treated here were taken from recent work carried out at our laboratory.[2] The test specimens consisted of various

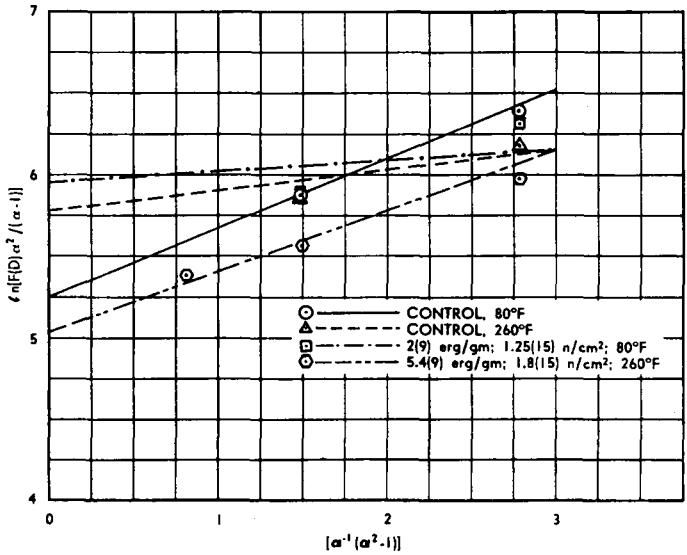

Fig. 1. Stress-strain behavior of irradiated polyurethane elastomers. Sample 1: Du Pont Adiprene L, 100 parts; Moca, 12 parts; cure 3 hrs. at 100°C.

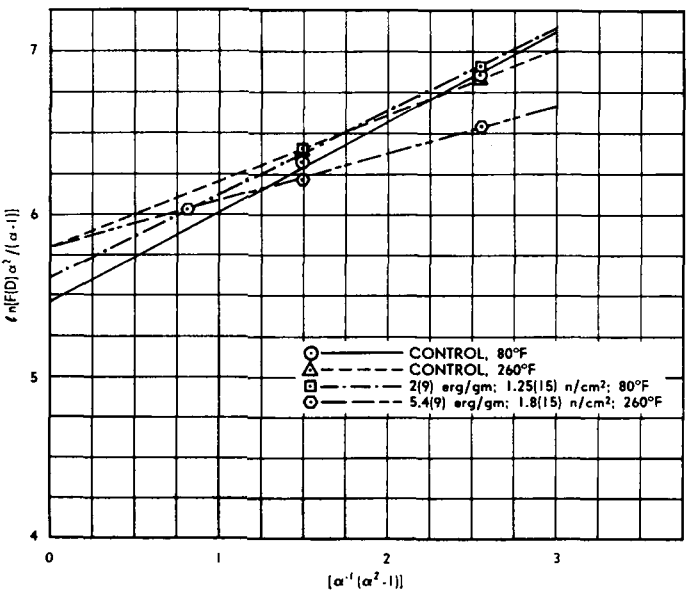

Fig. 2. Stress-strain behavior of irradiated polyurethane elastomers. Sample 2: Du Pont L-167, 100 parts; Moca, 18 parts; cure 1 hr. at 100°C.

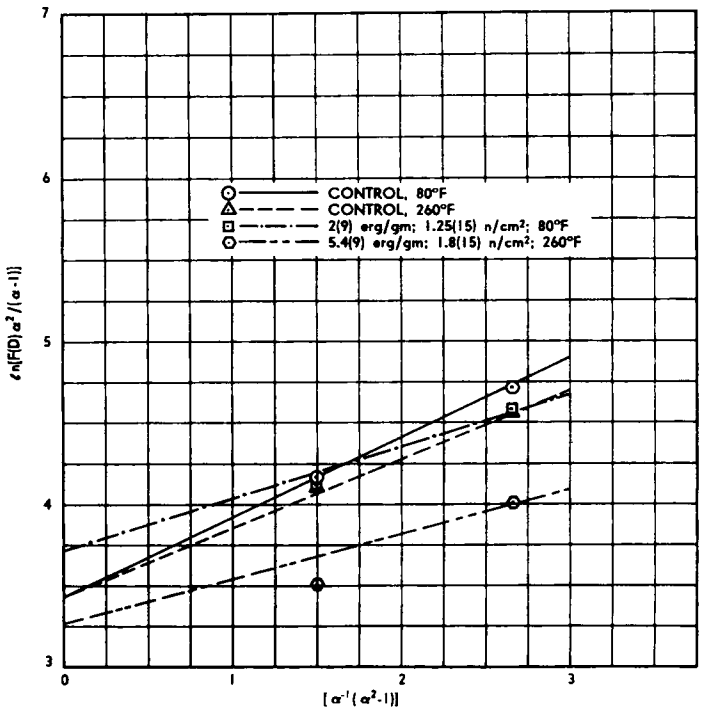

Fig. 3. Stress-strain behavior of irradiated polyurethane elastomers. Sample 3: Du Pont L-167, 100 parts; 1,4-butanediol, 5.8 parts; trimethylolpropane, 1 part; cure 4 hrs. at 140°C.

types of polyurethane elastomers (see Table I). The specimens were prepared according to the procedure prescribed for tensile specimens in the ASTM standards (ASTM-D 412-51T, Die C). Measurements of stress-strain values (per cent modulus) and ultimate tensile strength were also carried out in accordance with this procedure for the controls as well as the irradiated specimens. The latter were irradiated in the unstressed state in the General Dynamics Ground Test Reactor. The irradiation was conducted at three different temperatures, -65, 80, and 260°F. The control specimens were subjected to the same temperature regimen except that no controls were run at -65°F. The specified temperature was maintained from 1 hr. before irradiation until 1 hr. after termination of irradiation. Thereafter, all specimens were stored at room temperature for approximately thirty days prior to the stress-strain measurements. These were performed at approximately 80°F.

Specimens were irradiated at various dose levels in the range of 2×10^9 to 1.9×10^{10} ergs/g.(C) (γ-dose) plus the dose imparted by the associated neutron flux (see Table I). A set of five tensile specimens was irradiated for each set of dose, irradiation temperature, and extension ratio (or tensile strength measurement).

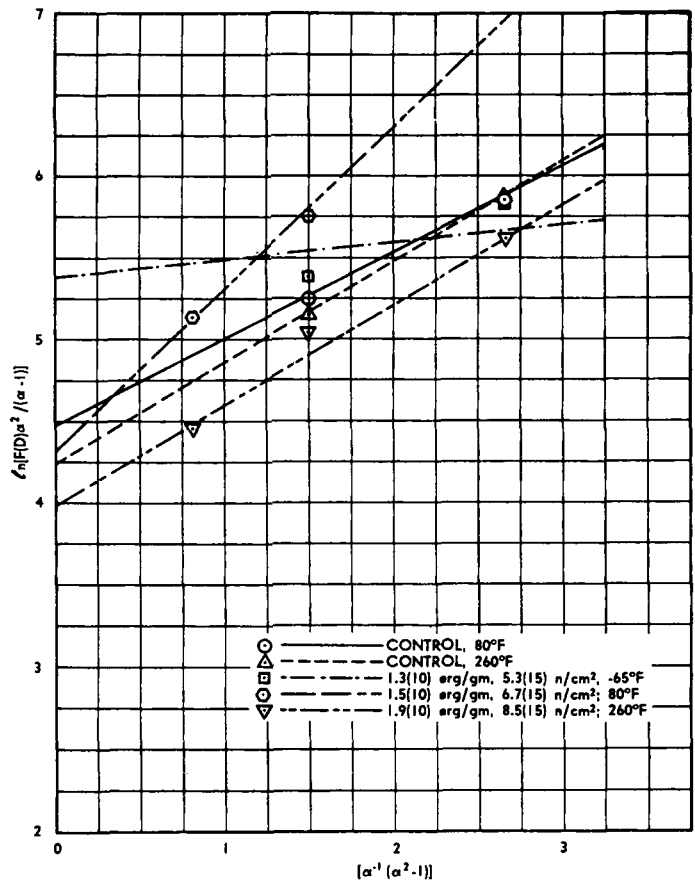

Fig. 4. Stress-strain behavior of irradiated polyurethane elastomers. Sample 4 (Genthane S-1).

Dosimetric measurements of the dose absorbed from the gamma-ray component of the reactor radiation were conducted with nitrous oxide and tetrachloroethylene dosimeters, while the associated neutron fluxes were measured by means of aluminum foils and sulfur pellets. Whenever this type of gamma-ray dosimetry was not feasible on account of irradiation temperature, gamma-ray doses were obtained from neutron doses by the use of known neutron-to-gamma ratios.

Neutron fluxes were modified to include all neutrons of energy $E > 0.33$ mev by the use of appropriate factors derived from the Ground Test Reactor neutron spectrum.[3,4]

DISCUSSION OF RESULTS

In Figures 1–10 the experimental data on the various polyurethane elastomers are plotted according to the procedure outlined above; i.e., the

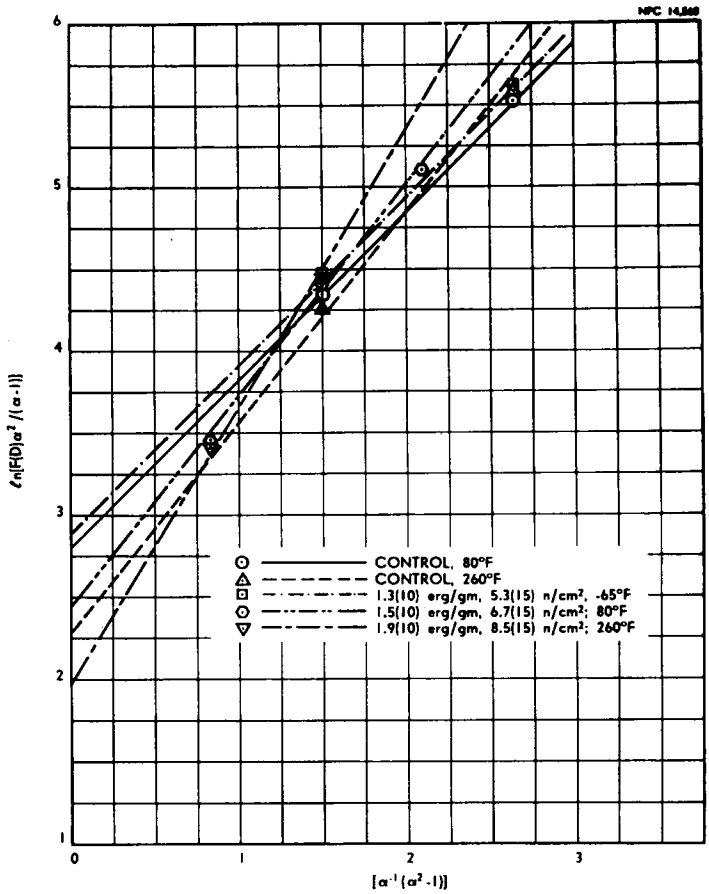

Fig. 5. Stress-strain behavior of irradiated polyurethane elastomers. Sample 5 (Genthane S-2).

quantity $\ln f(D)\alpha^2/(\alpha - 1)$ is represented as a function of $\alpha^{-1}(\alpha^2 - 1)$. The resultant straight lines were fitted to their appertaining experimental points by a least-square analysis.

On the whole, the data are in surprisingly good agreement with the behavior predicted by the MRS relationship, despite the fact that, for the first four polyurethane compounds, extension ratios beyond 3 (i.e., beyond the accepted upper limit of validity of the MRS relationship) were included in the least-square analysis. The values of ultimate tensile strength and elongation were not considered in this investigation. This was so because the measurement of tensile strength involves rheological processes to a significantly greater extent than in simple tensile quasi-equilibrium stress-strain measurements. Moreover, the numerical values, in most instances, exceeded the range of applicability of the MRS equation.

No systematic correlation between dose and the two parameters E_0 and K could be established, although there is significant internal consistency in

stress-strain behavior for each level of dose and irradiation temperature, with the exception of one case (Fig. 6: dose level 1.5×10^{10} ergs/g.(C), 80°F.). In the majority of cases it was noted that whenever ln E_0 increased with dose, K decreased, and vice versa. For the specimens irradiated at 80°F. the predominant trend for ln E_0 was to increase with dose, whereas in the case of the 260°F. irradiations the predominant trend for ln E_0 was to

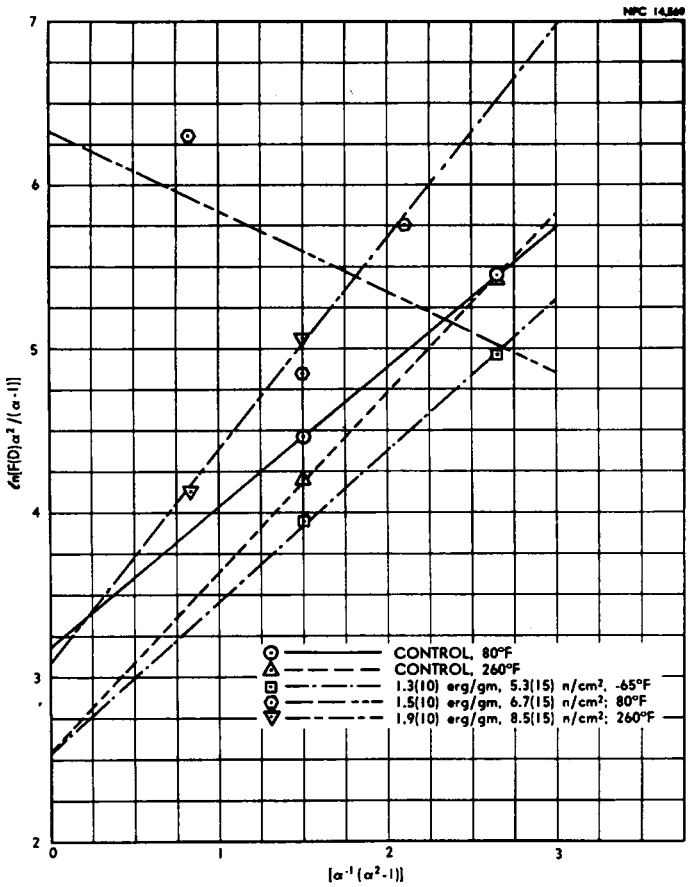

Fig. 6. Stress-strain behavior of irradiated polyurethane elastomers. Sample 6 (General Tire polyurethane Type R).

decrease with dose. It appears that, in general, the parameter K is a slowly varying function of dose while the initial tangent modulus varies exponentially with dose.

Since the experimental data used here were not designed specifically with this analysis in mind, certain inadequacies and errors are encountered that can be substantially eliminated in future experiments. However, since

there is an indubitable internal consistency in each set of tests, the applicability of the MRS relationship to the irradiated polyurethane vulcanizates examined can be held to have been conclusively demonstrated. Two major sources of error are conjectured to be at least partially responsible for the apparent lack of systematicity in the behavior of the parameters E_0

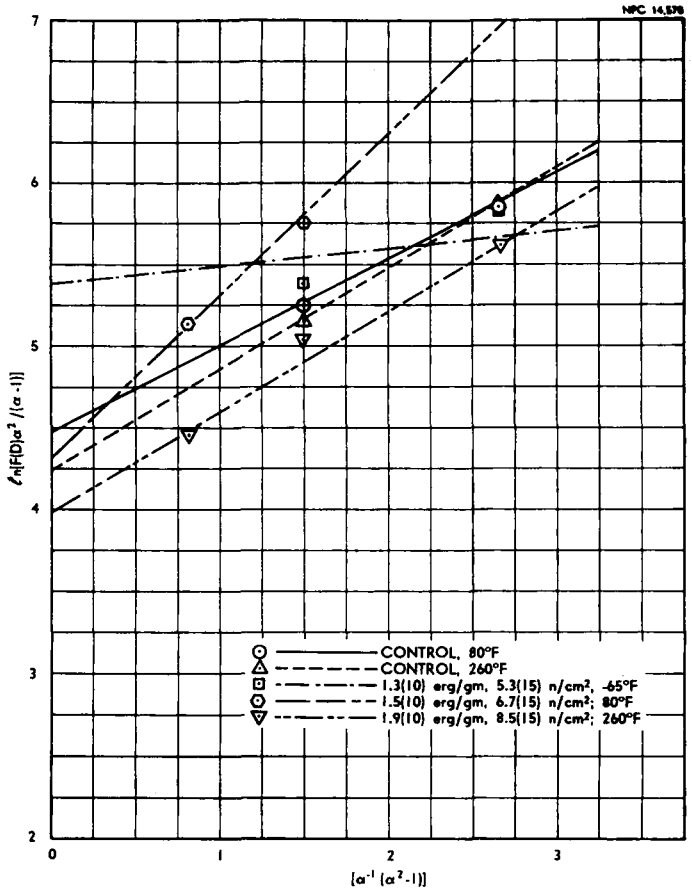

Fig. 7. Stress-strain behavior of irradiated polyurethane elastomers. Sample 7 (Disogrin L DSA 6865).

and K as a function of dose: (*a*) dosimetric inaccuracies and (*b*) irregularities in the temperature history of the specimens. For example, very little could be ascertained about the exact course of the temperature treatment, particularly during the period between withdrawal from the reactor and time of measurement. Finally, other uncontrolled environmental factors such as ozone generation in the reactor may have adversely influenced the results.

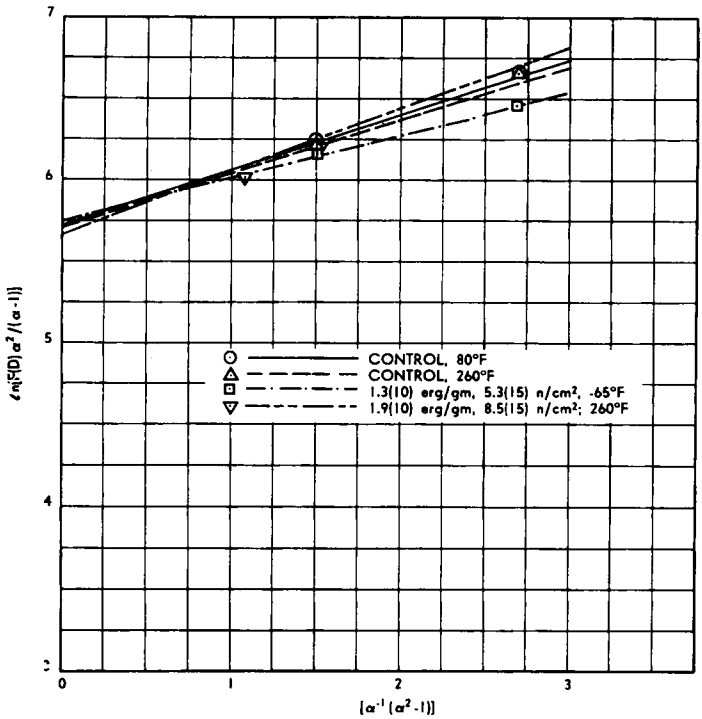

Fig. 8. Stress-strain behavior of irradiated polyurethane elastomers. Sample 8 (Disogrin 1 DSA 9250).

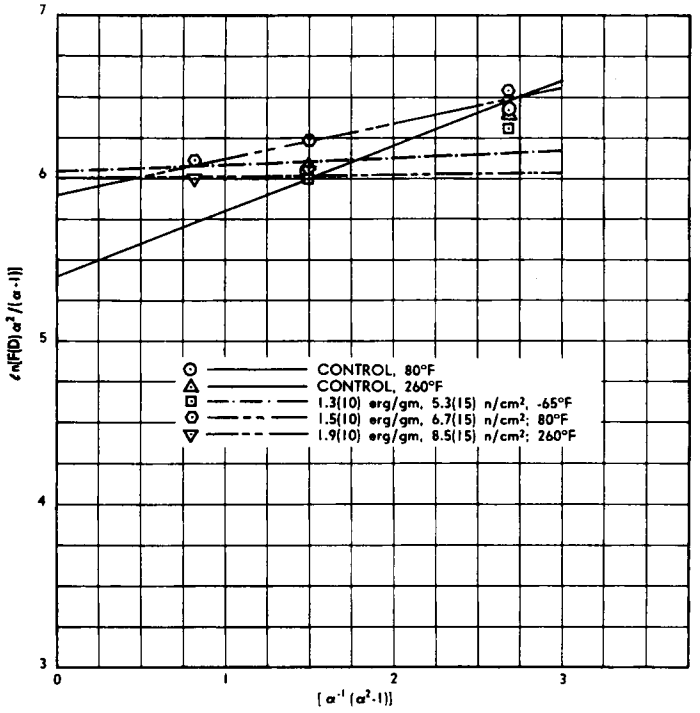

Fig. 9. Stress-strain behavior of irradiated polyurethane elastomers. Sample 9 (Disogrin 2 DSA 9840).

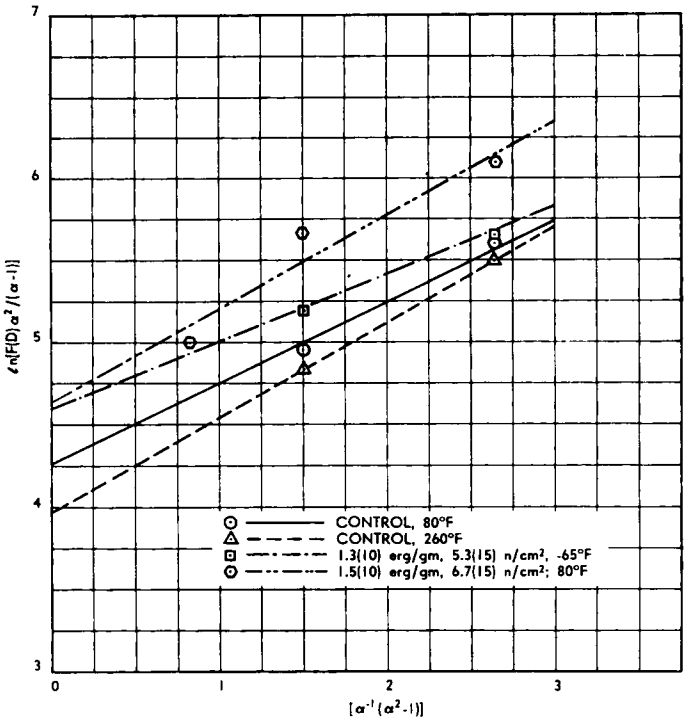

Fig. 10. Stress-strain behavior of irradiated polyurethane elastomers. Sample 10 (Disogrin 2 DSA 7560).

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Synopsis

The applicability of the Martin-Roth-Stiehler stress-strain relationship to a number of reactor-irradiated (gamma-ray dose range 0–1.9 × 10^{10} ergs/g. in carbon) polyurethane elastomers has been demonstrated. For each level of dose and irradiation temperature, the stress-strain values showed remarkably good agreement with the behavior predicted by this relationship, thus permitting a realistic characterization of the stress-strain curves up to extension ratios of 3 by two parameters: the tangent modulus E_0 and a coefficient K. While the available data did not justify conclusive inferences regarding the explicit nature of the functions $E_0(D)$ and $K(D)$, it appears from this analysis that E_0 varies exponentially with dose D and that K is a slowly varying function of dose.

Résumé

On a démontré que la relation entre la force et la tension de Martin-Roth-Stiehler est d'application pour un certain nombre d'élastomères de polyuréthanne irradiés dans un réacteur (domaine de la dose de rayons gamma 0–1.9 $\times$ 10^{10} ergs/gr calculé en carbone). Les valeurs force-tension, pour chaque dose et chaque température d'irradiation, montrent un accord remarquable avec le comportement prévu par cette relation, ce qui permet une réelle caractérisation des courbes force-tension jusqu'à une extension du rapport égale à 3 au moyen des deux paramètres: le module tangent E_0 et le coefficient K. Tandis que les données utilisables ne justifient pas des conclusions concernant la nature explicite des fonctions $E_0(D)$ et $K(D)$, il semble, à partir de cette analyse, que E_0 varie exponentiellement avec la dose D et que K est une fonction qui varie faiblement avec D.

Zusammenfassung

Es wird gezeigt, dass die durch Martin, Roth und Stiehler entwickelte Spannungs–Dehnungs-Beziehung auf eine Anzahl in einem Kernreaktor bestrahlte (Gammadosisgebiet: 0–1.9 $\times$ 10^{10} erg/gramm (in Kohlenstoff) Polyurethankautschuke anwendbar ist. Die Spannungs–Dehnungs-Werte zeigen für jede Dosisstufe und Bestrahlungstemperatur recht gute Übereinstimmung mit dem durch diese Beziehung verausgesagten Verhalten. Die Spannungs–Dehnungs-Kurven können somit bis zum Dehnungsverhältnis 3 durch zwei Parameter charakterisiert werden: den Tangentialmodul E_0 und einen Koeffizienten K. Obwohl die verfügbaren Beobachtungen noch keine bestimmten Schlüsse hinsichtlich der genauen Art der Funktionen $E_0(D)$ und $K(D)$ gerechtfertigen, scheint diese Analyse doch zu zeigen, das E_0 sich exponentiell mit der Dosis D ändert und dass K eine sich mit der Dosis langsam variierende Funktion darstellt.

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