

Heat Aging in Fluoroelastomers

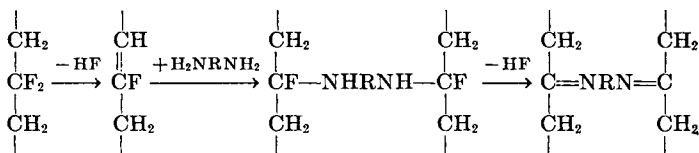
D. K. THOMAS, *Chemistry, Physics and Metallurgy Department, The Royal Aircraft Establishment, Farnborough, Hants., England*

Synopsis

Continuous and intermittent stress relaxation measurements have been made on a copolymer of vinylidene fluoride and hexafluoropropylene crosslinked with diamines or high energy radiation, and a study has been made of the effect of heat on the raw polymer. The results show that heat aging in diamine vulcanizates is the result of two simultaneous processes; one is a rapid oxidative reaction in and at the crosslinks resulting in the replacement of the primary crosslinks by a more thermally stable type, and the other is an oxidative reaction in the polymer main chain leading to a very slow breakdown of the rubber network. This second reaction is thought to be identical with that occurring in the unvulcanized polymer. The surprisingly poor resistance to compression set of diamine vulcanizates is consistent with the first process, and the good long-term aging properties are a result of the second one.

There is considerable interest in copolymers of vinylidene fluoride and hexafluoropropylene (VF-HFP) as elastomeric materials displaying outstanding chemical and thermal stability.¹ Of the purely organic rubbers which are available commercially these alone have a useful service life at temperatures of 200°C. and above; they eventually embrittle on aging, and it is known that aging proceeds more rapidly in air than in vacuum.

VF-HFP copolymers can be crosslinked successfully by means of organic peroxides, high energy radiation, and some polyfunctional amines, the method favored commercially being that employing amines. All three methods lead to elastomers having comparable physical properties, and the indications are that their resistance to high temperatures is similar. The nature of the crosslink introduced by diamines has been the subject of a number of investigations,¹⁻³ and recent work by Smith and Perkins³ on the crosslinking of VF-HFP copolymer by hexamethylenediamine carbamate (HMDA-C) shows in convincing manner that the reaction is a three-stage process involving (1) elimination of HF from the polymer chain to form double bonds, (2) reaction of the diamine with these double bonds to form crosslinks, and (3) an elimination of HF to form double bonds in the crosslinks:



where R is (CH₂)₆.

The crosslinks introduced by organic peroxides or high energy radiation probably result from the removal of fluorine and/or hydrogen atoms from the polymer and combination of the polymer radicals thus formed.

Physical tests made intermittently during the exposure of HMDA-C vulcanizates to air at 200°C. show them to be exceptionally stable by comparison with other organic elastomers; properties such as tensile strength, breaking elongation, and modulus remain virtually unchanged after a period of 56 days.⁴ The resistance to compression set, however, gives quite a different picture of vulcanizate stability; after being compressed for 28 days at 160°C. the rubber recovers only 25% of the imposed deformation, and this poor resistance to compression set persists even at 120°C. Clearly even at these relatively low temperatures changes are occurring in the three-dimensional rubber network which are important when long-term usage in constant compression or tension is envisaged.

In the work reported here the effect of heat on the raw polymer is considered together with the results of stress relaxation measurements on the crosslinked polymer, the object being to reconcile the outstanding thermal stability on exposure in an unstrained condition with the relatively poor resistance to compression set under much less severe conditions.

EXPERIMENTAL

Preparation of Vulcanizates

Three crosslinking agents were used: hexamethylene-diamine carbamate (HMDA-C), *p*-phenylenediamine, and γ -irradiation from a Co⁶⁰ source. In all cases 15 parts by weight of magnesia were incorporated into the VF-HFP copolymer.

Sheets of 0.010 in. thickness were made in a suitable mold. When diamines were used the crosslinking cycle was 1 hr. at 150°C. in a press at 1500 psi followed by 24 hr. at 200°C. in an air oven. In the case of γ -irradiation the 0.010-in. thick sheets were sealed in evacuated Pyrex vessels and irradiated to 15 Mrad; they were then heated for 24 hr. at 200°C. in vacuum.

Solubility and Swelling Measurements

Known weights of polymer were immersed in a large excess of acetone at 28°C.; after a period of 72 hr. the swollen material was removed, surface dried, and weighed. The solvent was then driven off and the residual dry polymer weighed. The solubility was obtained from the initial and final dry weights; the volume fraction of polymer in the swollen material was calculated, values of 1.644 and 0.787 being used for the density of polymer and solvent, respectively.

Infrared Absorption Spectra

Films of raw polymer 0.004 in. thick were prepared in a laboratory press at 120°C. These proved adequate for a study of the relevant regions of the

infrared spectrum. An Infracord double-beam instrument was used with a rock salt prism.

Stress Relaxation Measurements

A pressure transducer has been modified for use in the automatic measurement of rates of continuous and intermittent stress relaxation in thin strips of rubber.⁵ These measurements are particularly well suited to studies of rubber network stability, and their application to this type of problem has been fully described.^{6,7} The virtue of the transducer used in this work is that it can be exposed to temperatures of up to 300°C. for prolonged periods without damage. The output in millivolts is directly proportional to applied load from room temperature to 300°C.

Strips of rubber 0.5 cm. wide were used, and these were usually extended by 20% of their original length.

Compression Set Measurements

Disks of rubber of thickness $\frac{1}{4}$ in. were compressed by 20% of their original thickness and were aged in this condition. After aging they were released from compression and allowed to recover for 10 min. at the aging temperature and 15 min. in cold water before being dried and measured. The set was then expressed as the percentage of deformation which was not recovered.

RESULTS

Solubility and Swelling Measurements

The effect upon solubility of heating the VF-HFP copolymer in air at 250°C. is shown by the results in Table I.

TABLE I
VF-HFP Copolymer Heated in Air at 250°C.

Time, hr.	Fraction soluble in acetone at 28°C.	Volume fraction of polymer in swollen gel fraction at equilibrium in acetone at 28°C.
3	0.78	Not determined
24	0.52	0.02 ₃
42	0.47	0.02 ₃
48	0.48	0.02 ₁
137	0.53	0.01 ₉

Heating the copolymer in vacuum at 250°C. produced a change in color but no measurable change in solubility.

Infrared Absorption Spectra

Changes occurring in the absorption spectrum of VF-HFP copolymer during heating at 250°C. are shown in Figure 1. New bands develop at

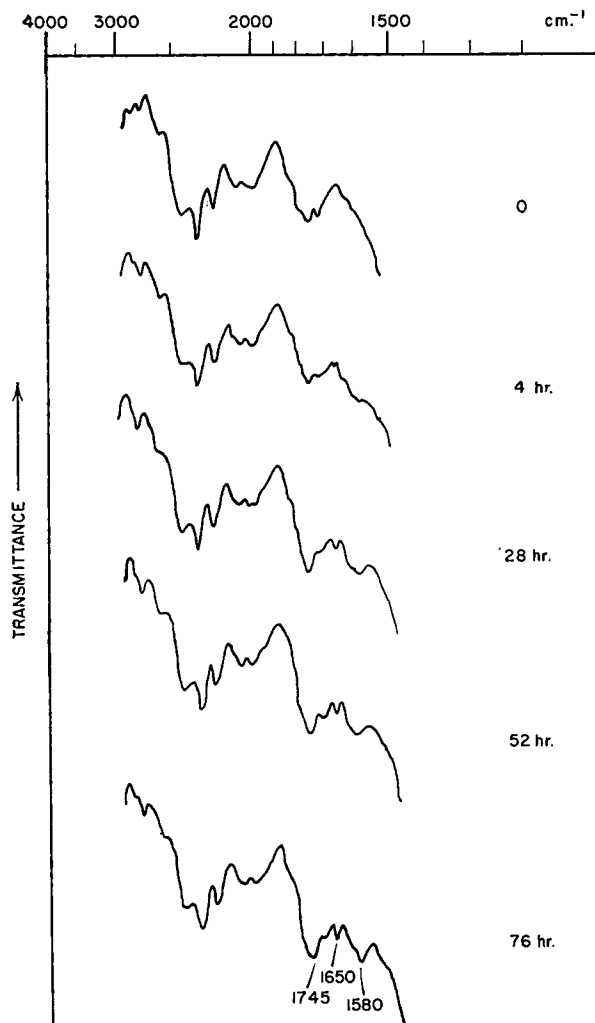


Fig. 1. Changes in the infrared absorption spectrum of raw VF-HEP on heating in air at 250°C.

1580 and 1650 cm^{-1} , and the band at 1745 cm^{-1} in the original spectrum sharpens and increases in intensity with time of heating.

Stress Relaxation Measurements

The rates of stress relaxation were found to be independent of strain over the range used in this work. The rates of continuous stress relaxation are shown in Figures 2-7 and those of intermittent stress relaxation in Figures 8 and 9. It has previously been shown that in a diamine vulcanizate of the copolymer used in this work the force f required to produce a moderate extension is directly proportional to the concentration of effective net-

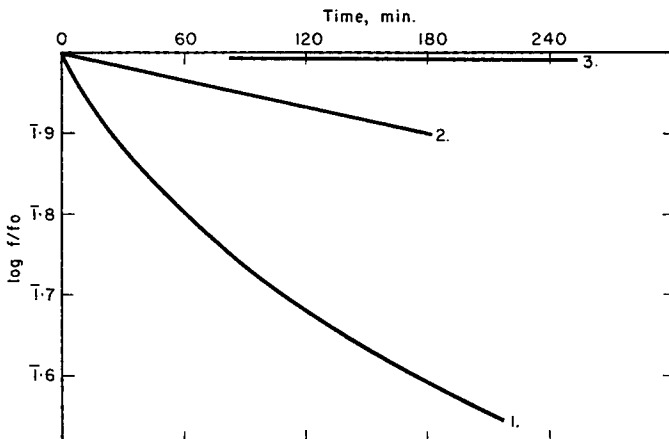


Fig. 2. Continuous stress relaxation of VF-HFD vulcanizate at 250°C.: (1) in air at 1 atm.; (2) in nitrogen at 1 atm.; (3) *in vacuo* (10^{-4} cm. Hg).

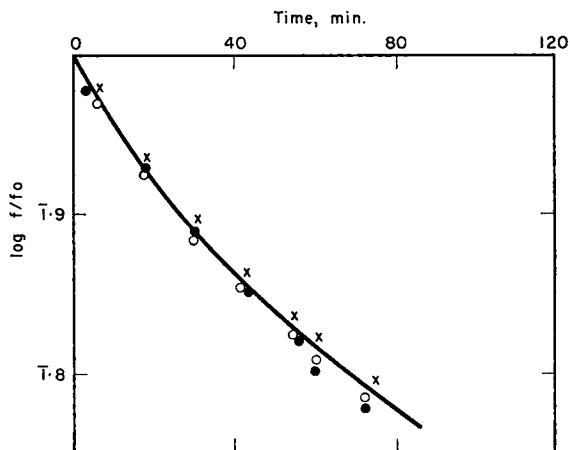


Fig. 3. Continuous stress relaxation of VF-HFP vulcanizates at 250°C.: in air: (O) 2.0% HMDA-C; (+) 1.5% HMDA-C; (●) 1.0% HMDA-C.

work chains in the material, or in other words, to the crosslink density. The results of stress relaxation measurements are then interpreted in the way described by Tobolsky.⁶

Compression Set Measurements

The resistance to compression set of VF-HFP copolymer crosslinked with HMDA-C is shown in Table II. Values are quoted at 250°C. and 160°C. for vulcanizates processed in the conventional way, and for the same materials which had been conditioned for 24 hr. at 250°C. in a relaxed condition.

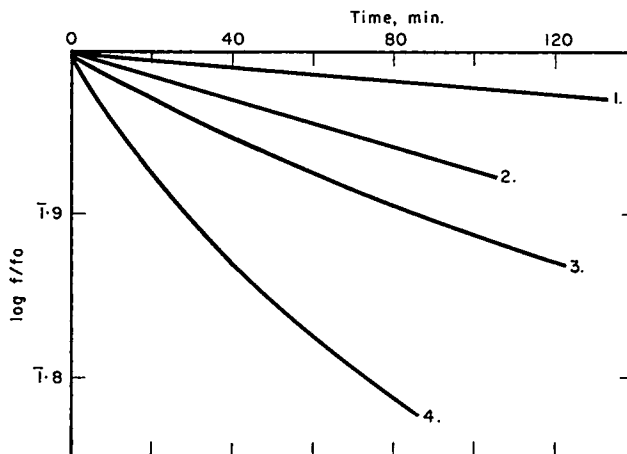


Fig. 4. Continuous stress relaxation of a VF-HFP vulcanizate in air: (1) at 200°C.; (2) at 215°C.; (3) at 225°C.; (4) at 250°C.

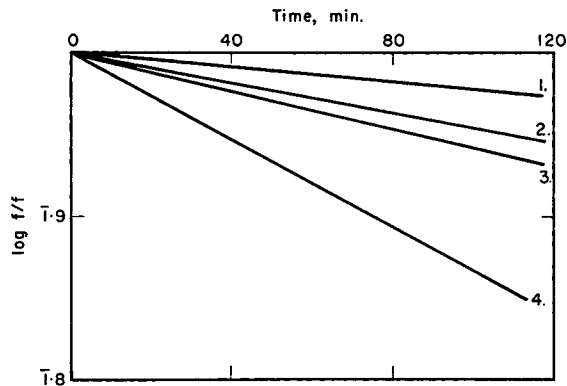


Fig. 5. Continuous stress relaxation of VF-HFP vulcanized with *p*-phenylenediamine: (1) at 203°C.; (2) at 220°C.; (3) at 228°C.; (4) at 250°C.

TABLE II
Resistance to Compression Set of VF-HFP Copolymer Crosslinked with Diamine

Temperature, °C.	Time, days	Compression set, %	
		Conventional vulcanizate	Conditioned vulcanizate (heated for 24 hr. at 250°C.)
250	1	91	47
	2	100	67
160	2	25	16
	4	39	26
	8	53	31
	28	76	47

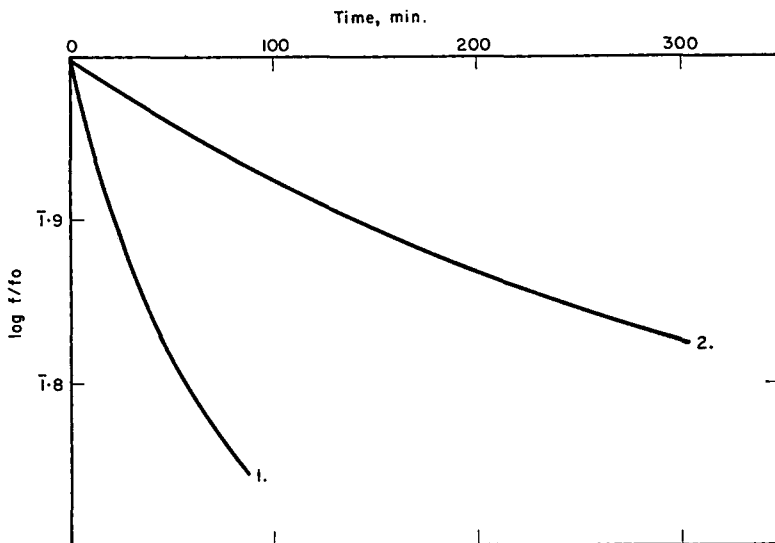


Fig. 6. Continuous stress relaxation in air at 250°C: (1) first network; (2) second network.

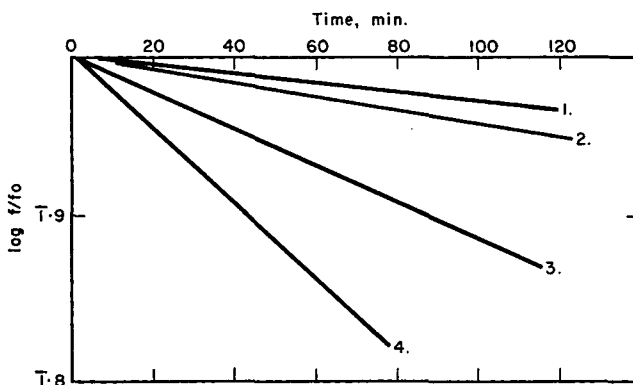


Fig. 7. Continuous stress relaxation of VF-HFP vulcanized by γ -irradiation: (1) at 200°C.; (2) at 210°C.; (3) at 228°C.; (4) at 240°C.

DISCUSSION

Action of Heat on the Raw Polymer

Heating the raw polymer at temperatures in excess of 200°C. for 1 hr. or more produces one obvious change; the polymer develops a light brown color which deepens somewhat on further heating. The occurrence of important structural changes is shown by the change in solubility which accompanies heating in air (see Table I). There is an initial rapid fall in solubility, the value reaches a minimum after about 40 hr. heating and then proceeds to rise slowly. The values for the volume fraction of polymer in

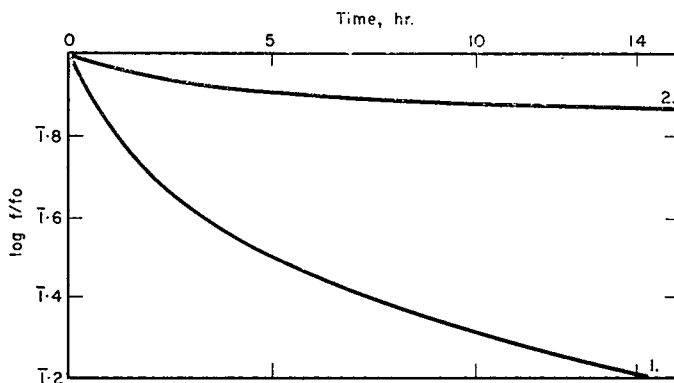


Fig. 8. Stress-relaxation of VF-HFP vulcanizate in air at 250°C.; (1) continuous; (2) intermittent.

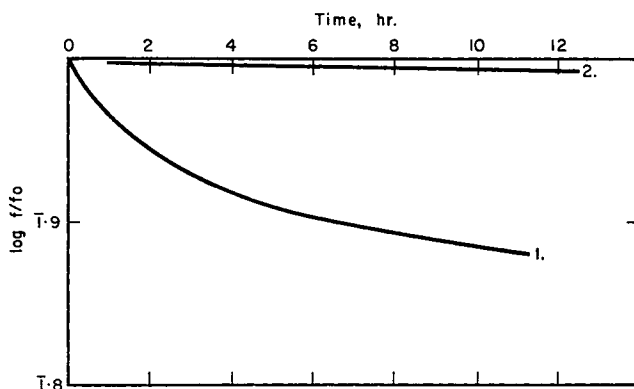


Fig. 9. Intermittent stress relaxation of VF-HFP vulcanizate in air at 250°C.: (1) first network; (2) second network.

the swollen gel are too low to be accurate, but the trend is toward lower values as the time of heating goes beyond 24 hr. This type of variation of solubility, together with the formation of swollen gel, indicates the simultaneous occurrence of crosslinking and chain scission in the polymer, with chain scission predominating. If crosslinking only were occurring, the soluble fraction would fall continuously to zero. The important role of oxygen in these reactions is shown by the fact that heating at 250°C. in vacuum produced the same color change but with no change in solubility.

The infrared spectra throw further light upon the effects of heat on the polymer; the new band at 1580 cm^{-1} is assigned to conjugated C=C bonds, and the absence of a shift to longer wavelength as heating continues suggests that the length of conjugation is constant.⁸ The weak band at 1650 cm^{-1} could be due to isolated double bonds $-\text{CH}=\text{CF}-$ formed by the elimination of HF from the polymer chain.⁹ The band at 1745 cm^{-1} in the unheated polymer is assigned to $-\text{CH}=\text{CF}_2$ end-groups;⁹ the changes observed in this band could be due to an increased concentration of this group, to the formation of an oxygenated group such as $\text{HC}=\text{O}$, or to both.

The formation of such groups could be seen as the result of an oxidative scission reaction.

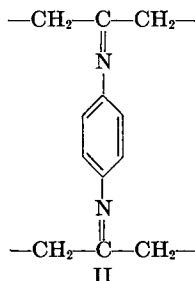
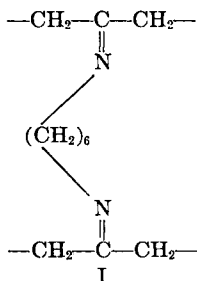
These results lead to the following conclusions regarding the effect of heat on the unvulcanized VF-HFP polymer. The primary effect of heat is to produce unsaturation in the polymer, presumably by elimination of HF. The color changes produced *in vacuo* and in air are due to the formation of conjugated C=C bonds. In the presence of air, oxidative reactions occur which lead to crosslinking and scission of the polymer, with the latter predominating. The initial attack by oxygen presumably occurs at methylene groups in positions alpha to double bonds.

Stress Relaxation Measurements

The results of continuous stress relaxation experiments give the rate at which the three-dimensional rubber network is breaking down, it being assumed that any new crosslinks formed in the strained rubber do not contribute to the tension. Figures 2, 3, and 4 show the results of continuous stress relaxation measurements made on VF-HFP crosslinked with a diamine (HMDA-C) and they show that (a) the reaction leading to network scission is an oxidative one, (b) it is not an autocatalytic reaction, the rate eventually falls below that required by a first-order scission reaction, (c) the rate of stress relaxation is independent of crosslink density over the range studied.

The decrease in rate of stress relaxation to below that expected for a first-order process becomes apparent when about 30% of the initial rubber network (henceforth called the first network) has broken down. This may be due to the formation of new crosslinks which, at this stage begin to make a significant contribution to the tension in the rubber. It will be recalled that this type of relaxation curve was obtained with sulfur-vulcanized natural rubber in which simultaneous scission and crosslinking is occurring, whereas in peroxide vulcanizates, where scission only is occurring, the rate increases with time.¹⁰ A rate of relaxation which is independent of crosslink density is consistent with the occurrence of scission in or at the crosslink.⁷ The energy of activation for the scission process (as determined from the linear regions of the relaxation curves) is 23.3 kcal./mole, and this is of the same order as that found for the oxidative scission of hydrocarbon rubbers.¹¹

The work of Smith and Perkins³ has shown that the crosslink in VF-HFP vulcanized with HMDA-C has structure I.



To ascertain whether scission occurred both in and at the crosslinks the HMDA-C was replaced by *p*-phenylenediamine to give a crosslink of structure II. The most readily oxidizable groups in these structures are the methylene groups in positions alpha to the C=N bond. Structure I has six such groups, two in the crosslink and four at the crosslink; structure II has four, all at the crosslink. If scission were occurring only at the crosslinks, the rates of stress relaxation would be the same for both vulcanizates. Reference to Figures 4 and 5 shows that this is not so, the rate of scission being significantly less in structure II. The activation energy for scission is, to within the limits of experimental error, the same in both vulcanizates, and hence the difference in rate is due to a difference in concentration of reactive sites rather than to a difference in reactivity of methylene groups situated in or at the crosslinks.

A prolonged continuous stress relaxation measurement on the first network at 250°C. showed it to be virtually completely destroyed in 24 hr. An intermittent stress relaxation measurement under the same conditions showed that scission was accompanied by a substantial amount of crosslinking (see Fig. 8). Application of Tobolsky's two-network theory⁶ showed that for every 100 network chains broken in the first network about 80 new ones are formed as a result of this crosslinking reaction. Therefore after 24 hr. at 250°C. the "first network" has been replaced by a "second network" having a slightly lower concentration of network chains. If the crosslinks in the second network are identical with those in the first, then, according to the results shown in Figure 3, the rate of continuous stress relaxation should be the same in both cases. This is not so; Figure 6 shows the second network to be the more stable, the energy of activation for the scission reaction is 27.5 kcal./mole, which is significantly greater than the value of 23 kcal./mole for the first network.

In a VF-HFP polymer crosslinked by γ -irradiation, the crosslinks are presumably formed directly between the carbon atoms of adjacent polymer chains. Continuous stress relaxation measurements for such a vulcanizate are shown in Figure 7, and they reveal a surprisingly high rate of network scission. The energy of activation for this process is 28 kcal./mole, a value close to that obtained for the second network in a HMDA-C vulcanizate. A probable explanation for the high rate of network scission is that a large number of isolated C=C bonds are formed in the polymer during irradiation, and these render the vulcanizate more susceptible to oxidative attack in the main chain.

The rate of intermittent stress relaxation in the second network is compared with that of the first network in Figure 9; variation of rate with temperature in the second network leads to a value of 50.4 kcal./mole for the energy of activation. The expression relating relaxation rate constant k with temperature is:

$$k = 5.2 \times 10^{18} \exp \{ -50,400/RT \} \quad (1)$$

and

$$k = -\frac{1}{t} \ln (f_t/f_0) \quad (2)$$

where t is expressed in hours and f_t and f_0 are the forces required to produce the same extension in the rubber at time t and zero time, respectively.

Conclusions

The relevance of these results to the aging of VF-HFP vulcanized with HMDA-C can now be considered.

The comparatively poor resistance of VF-HFP to compression set can be explained in terms of the rapid oxidative scission of the first network and simultaneous formation of a second network. Stress relaxation measurements show that the first network can be completely removed by heating for 24 hr. at 250°C.; they also show that it is largely replaced by a more thermally stable second network. It follows that heating the conventional HMDA-C vulcanizate for 24 hr. at 250°C. should lead to a material possessing a better resistance to compression set. This prediction is verified in a striking way by the results shown in Table II.

The energy of activation for scission in the second network is the same as that for a γ -vulcanizate; it is likely that the crosslinks in the latter are stable at 250°C. and that scission in this case is occurring in the polymer main chain. The same may be true of the second network. Evidence obtained from heating the unvulcanized polymer shows a slow oxidative reaction to be occurring in the main chain, the net effect of which is a slow breakdown of the polymer. If this were occurring in a vulcanizate containing stable crosslinks it would eventually become brittle. Intermittent stress relaxation measurements on the second network lead to a relationship between rate of network breakdown and temperature [see eqs. (1) and (2)]. It is instructive to compare the damage suffered by the rubber network in a given time, as calculated from these equations, with the change in physical properties as observed in long term aging tests at the same temperature. Such a comparison is made in Table III, and it can be seen that the results are consistent, in that the time required to produce a significant change in modulus (M_{100}) and network chain concentration (ν/ν_0) is much the same.

TABLE III
Values of 100% Modulus M_{100} from Long-Term Aging at 200°C. and ν/ν_0 from Stress Relaxation Data Extrapolated to 200°C.

Time, days	M_{100}^a , psi	ν/ν_0
0	330	1
8	377	1
30	354	0.98
79	320	0.95
160	300	0.91
331	255	0.83

^a Data of Sinnott.⁴

On these grounds it is proposed that the good long-term aging of VF-HFP vulcanizates is a result of slow oxidative scission of the main chain in the second network, and that this reaction is identical with that occurring in the raw polymer.

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Résumé

On a étudié les propriétés du copolymère de fluorure de vinylidène et d'hexafluoropropylène ponté soit par des diamines soit par des radiations de haute énergie. On s'est intéressé également à l'effet de la chaleur sur les propriétés du copolymère brut. Les résultats permettent de conclure que le processus de vieillissement par la chaleur dans les élastomères vulcanisés par les diamines est causé par deux réactions simultanées. On constate en premier lieu une oxydation rapide aux endroits de pontage du au remplacement du pont primitif par un autre qui est plus stable thermiquement. L'autre réaction est une oxydation lente de la chaîne polymérique principale d'où résulte une rupture très lente du réseau caoutchouteux. On pense que cette réaction est similaire à celle qui se produit dans le caoutchouc non-vulcanisé. Le premier mécanisme serait consistant avec la très faible résistance à la compression présentée de manière inattendue par les élastomères vulcanisés par les diamines et l'excellente résistance au vieillissement serait le résultat du second processus.

Zusammenfassung

An einem mittels Diaminen oder durch energiereiche Strahlung vernetzten Vinylidenfluorid-Hexafluorpropylen-Copolymeren wurden kontinuierliche und intermittierende Spannungsrelaxationsmessungen durchgeführt und der Einfluss von Hitze auf das Rohpolymere untersucht. Wie die experimentellen Ergebnisse zeigen, geht die Hitzealterung in Diamin vulkanisaten auf zwei gleichzeitig ablaufende Prozesse zurück, nämlich eine rasche Oxydation in und an den Vernetzungen, die zum Ersatz der primären Vernetzung

durch einen thermisch stabileren Typ führt, und eine Oxydation in der Polymerhauptkette, die einen sehr langsamen Abbau des Kautschuknetzwerkes verursacht. Man nimmt an, dass diese zweite Reaktion mit der im unvulkanisierten Polymeren ablaufenden identisch ist. Die überraschend geringe Kompressionsbeständigkeit von Diamin-vulkanisaten steht mit dem ersten Prozess in Einklang und die guten Langzeitalterungseigenschaften beruhen auf dem zweiten Prozess.

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