

## Relaxation Processes in Vulcanized Rubber. II. Secondary Relaxation Due to Network Breakdown

A. N. GENT

*Natural Rubber Producers' Research Association, Welwyn Garden City, Herts., England\**

### I. INTRODUCTION

The relaxation of vulcanized rubbers at normal temperatures shows the following characteristic behavior. The stress under a constant deformation decays by an amount substantially proportional to the logarithm of the period in the deformed state. Similarly, the deformation under a constant load increases by an amount proportional to the logarithm of the period under load. This behavior will be denoted the primary relaxation to distinguish it from others to be described; it appears to reflect the physical rearrangement of molecular positions in the final stages of the approach to equilibrium.<sup>1</sup>

After long times at normal temperatures another relaxation process, denoted here the secondary relaxation, becomes evident and eventually dominant. An examination of this process in natural rubber vulcanizates is described below.

### II. EXPERIMENTAL

Thin strips of the vulcanized rubbers were subjected to constant tensile loads and the resulting extensions measured by means of a cathetometer. The application of load occupied a second or two, the first measurement being made 15 sec. later and subsequent ones at convenient intervals during the progress of relaxation. The strips were generally 10 cm. long, 0.75 cm. wide, and 0.075 cm. thick. They were suspended in test chambers held at a temperature of 23 or 60°C., a period of 1 hr. being allowed to attain the requisite temperature before the load was applied. In some instances the test chamber containing the test piece was evacuated by means of an oil pump to a pressure somewhat below  $10^{-2}$  mm. of mercury. The 1-hr. conditioning period then permitted thorough evacuation to be achieved also.

\* Present address: The Institute of Rubber Research, University of Akron, Akron, Ohio.

The mix formulations and vulcanization conditions employed in preparing the test pieces are given in the appendix to Part I,<sup>1</sup> with the exception of two peroxide vulcanizates. They had the following formulations in parts by weight:

J: natural rubber (smoked sheet) 100, dicumyl peroxide 3, phenyl- $\beta$ -naphthylamine 1.

K: deproteinized pale crepe 100, dicumyl peroxide 3.

They were vulcanized by heating for 50 min. at a temperature of 140°C.; material K was subsequently extracted with hot acetone before use.

### III. EXPERIMENTAL RESULTS

#### Appearance of a Second Creep Process

The increase in extension with time under a constant tensile load was measured for a number of different vulcanizates at two temperatures, 23 and 60°C. It was found to be substantially proportional to the logarithm of time under load for several decades of time and then a marked change in character appeared, reflecting the emergence of the secondary creep process. Some typical results are shown in Figure 1, where the increase in extension is plotted, as a fraction of the extension 0.1 min. after applying the load, for test pieces of a tetramethylthiuram disulfide vulcanizate before E and after D extraction with hot acetone.

The initial rates of increase in the fractional extension are seen to be lower for the extracted material D at both temperatures, and lower at 60°C. for both materials. However, the second creep process becomes dominant after times varying between  $10^2$  and  $10^5$  min., and ultimately the extracted material is worse than the unextracted, and the increase in extension at 60°C. is larger than that at 23°C. for both materials. The two conclusions reached from short-time observations, i.e., that the extracted material is superior and that the creep rates at 60°C. are lower, are thus seen to be inap-

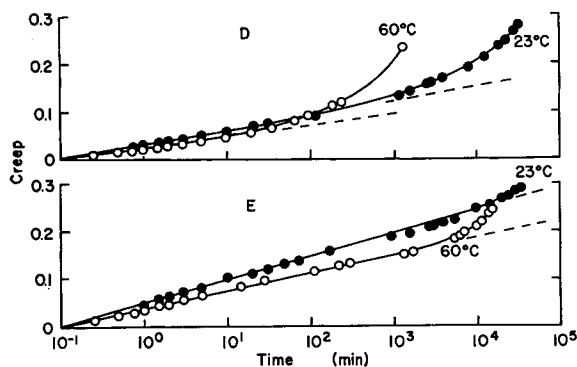


Fig. 1. Creep relations at 23 and 60°C. for a tetramethylthiuram disulfide vulcanizate before E and after D extraction with acetone. The increases in extension are expressed as fractions of the extension after 0.1 min. under load.

pliable after long times under load. It seems clear, therefore, that two processes are operative.

The inferior performance of the extracted vulcanizate at long times is suggestive of an aging process, since this material is particularly susceptible to oxidative attack.<sup>2,3</sup> The higher creep rates at 60°C. are also in accord with this hypothesis, since the rate of attack of atmospheric oxygen is increased by a rise in temperature.

### Characterization of Secondary Creep

In an attempt to characterize the secondary creep process numerically, the amount of secondary creep was estimated by subtracting the primary contribution from the observed creep. The primary contribution was obtained by extrapolating the linear portion of the creep curve, represented by the broken lines in Figure 1. The secondary contribution determined in this way was found to be approximately proportional to the period under load for the majority of materials (Fig. 2). A rate  $C'$  could therefore be assigned to the process; the values obtained are given in Table I.

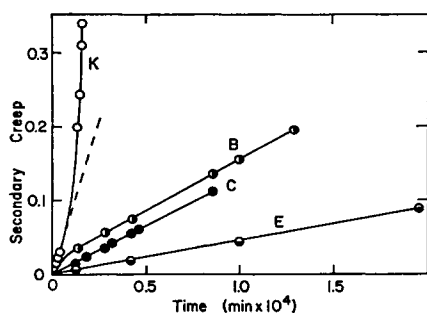


Fig. 2. Secondary creep at 60°C. for four vulcanizates.

TABLE I  
Rates  $C'$  of Secondary Creep and Times  $T'$  at which 1% Departure from Primary Creep Relation Appears, at 60°C.

Vulcanizate	$C'$ , % per week	$T'$ , hr.
B	14.5	12
B (at 23°C.)	—	170
C	13	17
C (at 23°C.)	—	600
D	100	1
D (at 23°C.)	4	18
E	4.3	53
J	1	150
K	100 <sup>a</sup>	3

<sup>a</sup> Continuously increasing rate.

For the peroxide vulcanizate K the secondary creep accelerated continuously (Fig. 2), presumably reflecting the autocatalytic nature of oxidation in this material.<sup>4</sup> The value given in Table I for the rate  $C'$  merely provides an indication of the magnitude of the changes taking place.

Another measure of the secondary creep process is given by the time  $T'$  at which a significant departure from the semilogarithmic primary creep relation could be discerned. A value of 1% of the extension at 0.1 min. under load was arbitrarily chosen to represent a significant departure; the corresponding times are listed in Table I. They are seen to be inversely related to the rates of secondary creep, as would be expected.

### Effect of Test Temperature and Vulcanizate Composition

The rates of secondary creep given in Table I are in accord with the susceptibility to oxidative deterioration of the vulcanizates, as measured by stress relaxation at elevated temperatures.<sup>4,5</sup> It thus appears that this process is simply the consequence of oxidative scission, taking place slowly at normal temperatures and more rapidly at 60°C. To test this conclusion, some experiments were conducted at 60°C. in air and in vacuo. The results are described in the following two sections.

#### Experiments in Vacuo

(a) Peroxide and tetramethylthiuram disulfide vulcanizates. The creep of test pieces of a tetramethylthiuram disulfide vulcanizate before E and after D extraction with hot acetone is shown in Figure 3. The rate of secondary creep for the extracted material D in vacuo is only about one-hundredth of that in air. For the unextracted material E the rate is already quite small in air, and

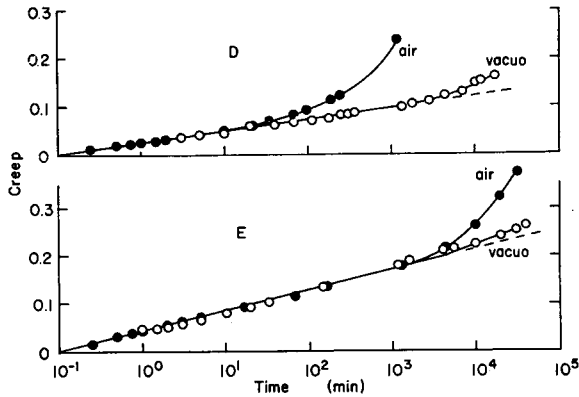


Fig. 3. Creep at 60°C. in air and *in vacuo* for vulcanizates D and E.

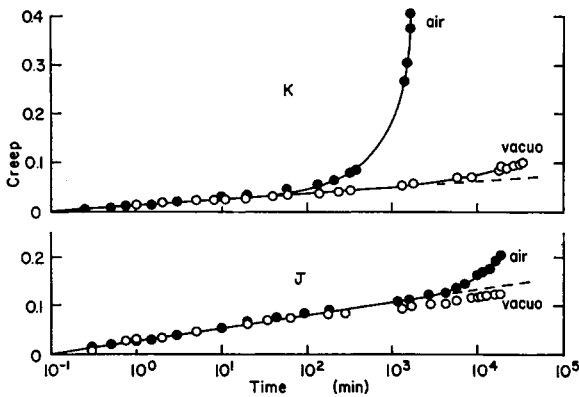


Fig. 4. Creep at 60°C. in air and *in vacuo* for vulcanizates J and K.

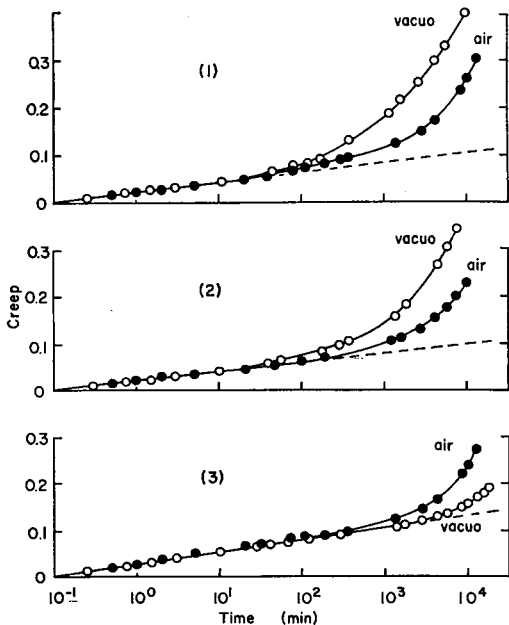


Fig. 5. Creep at 60°C. in air and *in vacuo* for sulfur vulcanizate B; vulcanization times at 140°C.: (1) 15 min., (2) 30 min., (3) 120 min.

*in vacuo* the secondary creep was much slower so that it did not reach a sufficient amount to make an accurate comparison of rates possible.

The occurrence of any appreciable amount of secondary creep in *in vacuo* is presumably due to oxygen present at the modest degree of evacuation achieved in these experiments. This is supported by the observation that greater amounts of creep occur in *in vacuo* for the materials more susceptible to oxidation (the extracted material in Fig. 3, for example).

Closely similar results were obtained for peroxide vulcanizates, as shown in Figure 4. The extracted material in this case is particularly susceptible to oxidation, and the secondary creep is about 200 times as fast in air as in *in vacuo*.

These results are concordant with the hypothesis that secondary creep reflects oxidative scission of the network structure. For a sulfur vulcanizate, however, a striking anomaly was found as described below.

(b) *An accelerated-sulfur vulcanizate.* The secondary creep of vulcanizate B was found to be faster in *in vacuo* than in air, as shown in Figure 5. This surprising result indicates that the process cannot be entirely attributed to a simple oxidation mechanism, for this vulcanizate. Figure 5 shows that the relaxation in air is not greatly affected by increasing the vulcanization time, whereas the relaxation in *in vacuo* becomes greatly retarded until it is considerably slower than that in air. The change in vulcanization time from 15 min. to 2 hrs. does not cause an appreciable change in the *degree* of crosslinking, and the extension under a given stress does not alter significantly. It appears, therefore, that the large and rapid relaxation in *in vacuo* is a consequence of the failure of specific crosslink structures,<sup>6</sup> which are replaced by more stable forms on continued vulcanization. Other

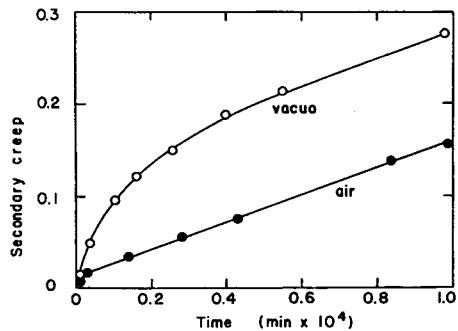


Fig. 6. Secondary creep at 60°C. for vulcanizate B (vulcanized 15 min. at 140°C.).

work<sup>7,8</sup> shows that continued vulcanization of similar materials is accompanied by a rearrangement of the sulfur crosslinks (in some cases without substantial alteration in number) to yield shorter, and presumably more stable, forms.

The presence of air appears to stabilize the "weak" crosslinks, at least to a considerable degree, as the relaxation is then appreciably slower and of the order of that for vulcanizates of quite different crosslink structures, where the relaxation is primarily due to oxidative scission. The relaxation in air cannot be attributed entirely to oxidation, however, as the measurements of recovery described in the following section show.

The course of secondary creep in vacuo differed appreciably from that in air. In Figure 6 the secondary contribution is plotted against time under load on a linear scale; in air it increases approximately linearly with time, but in vacuo the relation is far from linear. Initially, the rate of creep is high but it decreases continuously to reach a value of the same order as the (constant) rate in air.

The relaxing structures in vacuo thus appear to diminish in number with the passage of time, as would be expected if they are associated with specific crosslink forms. In air, the chief cause of relaxation appears to be oxidative scission of the network chains and progressive elimination of reactive units would not become apparent, at least in the present relaxation range.

Measurements were also carried out of the relaxation of the rubber vulcanized for 15 min., after extraction with hot acetone. The relaxation in air was much faster due to the removal of antioxidant, while that in vacuo was somewhat slower than for the unextracted material. Presumably the extraction process caused some reduction of the unstable crosslinks. These changes in the rates of relaxation caused a reversal of the previous positions, shown in Figure 5, the relaxation in air being evident after 50 min. while that in vacuo did not become apparent until 300 min. after loading. Thus anomalously rapid relaxation in vacuo did not appear in the extracted material.

Previous measurements on similar accelerated-sulfur vulcanizates have revealed considerable relaxation in vacuo, but it has not hitherto been found to approach that in air, still less exceed it. This discrepancy with the present findings may be attributed to the use of long vulcanization periods,<sup>9,10</sup> or the absence of antioxidant<sup>11,12</sup> in the materials examined. The former would lead to a predominance of stable crosslink structures and the

latter to a particularly rapid relaxation in air, as described above. Also, the test temperatures were generally much higher than that employed in the present work, and this might alter the relative positions if oxidative scission and crosslink failure have different temperature dependences.

### Recovery of Secondary Creep

Measurements were made of the recovered deformation when the load was removed after a substantial amount of secondary creep had occurred. The results are shown in Figure 7 for a peroxide vulcanizate K and a conventional sulfur vulcanizate containing antioxidant C. The creep measurements are represented by circles and the recovery measurements, plotted against time from the removal of load, by crosses.

For complete recovery, the recovered deformation will attain the value of the extension immediately before the load was removed. This appears to be substantially the case for the peroxide vulcanizate K after a recovery period similar to the time under load, and for this material the major part of the secondary creep, in addition, of course, to the primary creep, is recoverable.

It appears that the loss of a large proportion of network chains due to oxidative scission does not impede the return to the undeformed state. Virtually complete recovery is, in fact, to be expected for this material where oxidative scission is not accompanied by crosslink formation in the stretched state.<sup>4</sup>

For the sulfur vulcanizate, oxidative scission is known to be accompanied by substantial amounts of crosslinking formation, and it was found that the

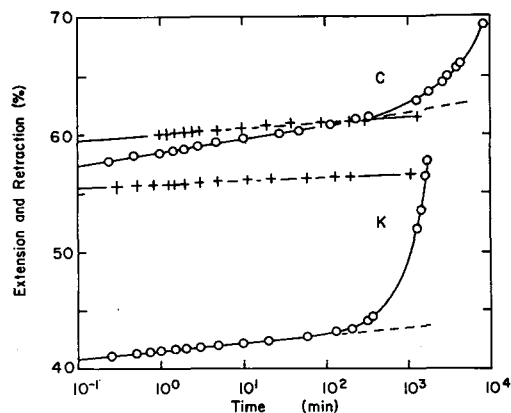


Fig. 7. Creep (O) and recovery (+) relations at 60°C. for vulcanizates C and K. The measured displacements are referred to the original unstrained lengths.

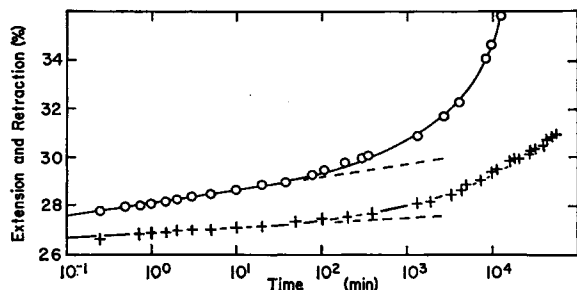


Fig. 8. Creep (O) and recovery (+) relations at 60°C. for vulcanizate B (vulcanized 15 min. at 140°C.)

material did not recover a significant amount of the secondary creep which had taken place (Fig. 7), suggesting that about as many new chains are introduced by crosslink formation as are lost by oxidative attack.

Similar results were obtained with the tetramethylthiuram disulfide vulcanizate E, less than one-third of the secondary creep being recovered after a period equal to the time under load. Thus, a substantial proportion of the chains lost by oxidation are replaced by crosslinking. In the extracted vulcanizate D, however, more than three-quarters of the secondary creep was recovered, so that little crosslinking had taken place. This difference between the extracted and unextracted materials is in accord with the conclusions of oxidation studies carried out at higher temperatures.<sup>13</sup>

The recovery of the accelerated sulfur vulcanizate B (in air) is shown in Figure 8, together with the original creep measurements. Initially the amount of recovery was small, the unrecovered deformation being larger than the total secondary creep. This indicates that a substantial amount of crosslinking had taken place in the stretched state. After a time similar to that for secondary creep to become evident, the recovery process accelerated markedly on a log time plot so that after long periods the unrecovered deformation was only about one-half of that estimated from the early recovery measurements. This change in the recovery process suggests that the crosslinks formed in the stretched state are themselves subject to failure. Since they presumably resemble the original crosslinks, it seems likely that some part of the secondary creep in air is also due to crosslink failure, although oxidative scission appears to predominate.

Secondary recovery in vacuo was generally slower than the secondary creep and far from complete even after long times, so that the new network

formed in the stretched state appears to be somewhat more stable than the original.

### Effect of Degree of Deformation

The creep in vacuo is shown in Figure 9 for test pieces of vulcanizate B under widely different tensile loads. The amount of creep, expressed as a fraction of the extension 0.1 min. after applying the load, is not independent of the degree of deformation but increases with increasing load. Similar behavior was described for the primary creep process in Part I,<sup>1</sup> and was shown to arise from the non-linear relation between load and deformation in simple extension, the rate of stress relaxation being substantially independent of the deformation level. Numerical factors were derived from a simple theoretical treatment to transform the observed creep under a given load to the corresponding stress relaxation at a constant extension, and good agreement with experiment was obtained.

Reduction factors were therefore calculated as described in Part I, from the values of the extension 0.1 min. after applying the load, for the creep relations shown in Figure 9. The reduced creep results are plotted in Figure 9 also, and are seen to superimpose accurately both in the primary and secondary regions.

It appears, therefore, that the secondary creep

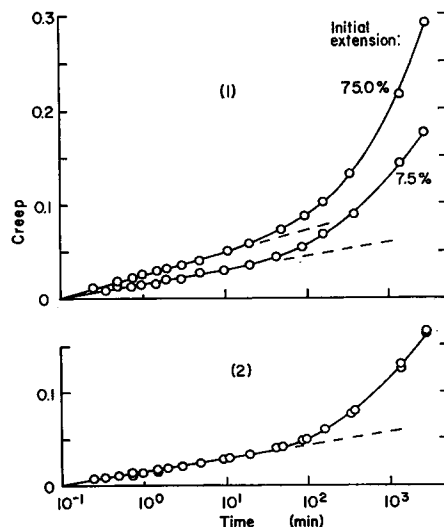


Fig. 9. Creep relations at 60°C. in vacuo for vulcanizate B (vulcanized 15 min. at 140°C.): (1) applied tensile stresses, referred to the unstrained cross-sectional area, of 7.5 and 1.0 kg./cm.<sup>2</sup>; the increases in extension are expressed as fractions of the extension after 0.1 min. under load; (2) results in upper figure reduced by calculated factors to yield the fractional stress relaxations.

process, as well as the primary one, reflects a fractional stress relaxation which is independent of the degree of deformation in the present range. The mechanism is thus not stress-activated but takes place equally rapidly and to equivalent extents over a wide range of deformation.

Similar agreement was obtained on reducing the measurements of creep in air under small and large tensile loads. The mechanism of secondary creep is quite different in this case, being chiefly due to oxidative scission, but again the reaction is not influenced by the degree of deformation, as Tobolsky, Prettyman, and Dillon<sup>9</sup> have shown.

### Evaluation of Measurements of Secondary Creep and Set

The amount of residual deformation or set, relative to the amount of secondary creep that had occurred prior to recovery, is a measure of the ratio of network chains newly introduced by crosslinking to those lost by scission. It is not, however, a *direct* measure of this ratio due to the nonlinear elastic behavior in simple extension. Andrews, Tobolsky, and Hanson<sup>14</sup> have proposed a relation between the set and the additional crosslinking for the particularly simple case of a material obeying the kinetic theory relationship between tensile stress and elongation. Such a treatment gives quantitative estimates of crosslinking and scission from the observations of secondary creep and set described in a previous section, but the analysis is not pursued further here as it lies outside the scope of the present investigation.

## IV. CONCLUSIONS

The following conclusions are reached:

(1) Because the early creep process, denoted here primary creep, is eventually superseded by a second process of completely different character, short-term tests at normal temperatures cannot be extrapolated to predict long-term behavior.

(2) The secondary creep process in simple vulcanizates appears to be oxidative scission of the molecular network. It is reduced by incorporating oxidation inhibitors, and by reducing the test temperature, while in vacuo it is virtually absent.

(3) In some sulfur vulcanizates, however, crosslink failure occurs quite rapidly in vacuo, i.e., in the absence of oxidative attack, and leads to extensive relaxation. In air the crosslinks are apparently

stabilized to some degree so that oxidative scission becomes the main cause of relaxation, but some contribution from crosslink failure may still be inferred.

(4) Both crosslink failure and oxidative network scission appear to be independent of the applied stress in the present range (1 to 10 kg./cm.<sup>2</sup>).

(5) Virtually complete recovery takes place, even when extensive network scission has occurred, provided no new crosslinks are formed in the stretched state. The "set," or incomplete recovery, when crosslinking takes place affords a measure of the extent of crosslinking. It is substantial for the sulfur vulcanizates examined but decreases after long times, probably due to failure of the new crosslinks.

The effect of the test temperature needs further examination; it may well be different for the two secondary creep processes. Also, the oxidation reaction is probably diffusion-controlled at certain temperatures. Attempts to study long-term creep behavior by accelerated tests on small samples therefore need careful study to avoid false conclusions.

It is interesting to note that in the absence of other processes the primary creep may continue for periods of 10<sup>5</sup> min. or more. As described in Part I<sup>1</sup> it appears to reflect physical rearrangement of molecular positions; clearly, these movements can be very protracted.

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### Synopsis

An experimental study is described of a "secondary" relaxation process in stretched vulcanizates, which becomes dominant after long periods at normal temperatures. It is shown to be affected markedly by the temperature, the atmosphere in which the test is conducted, and the presence of oxidation inhibitors. It is therefore attributed to oxidative deterioration of the molecular structure. In some vulcanizates, however, a similar or even greater relaxation is found to occur in vacuo, and this is attributed to the failure of specific crosslink structures. The extent of recovery on releasing the extended test pieces has also been investigated for a number of natural rubber vulcanizates.

### Résumé

On décrit une étude expérimentale d'un processus de relaxation secondaire dans les produits vulcanisés étirés, qui devient prédominant après un temps assez long, à des températures normales. On a mis en évidence l'effet considérable de la température, de l'atmosphère dans lequel le test est effectué, et de la présence d'inhibiteurs d'oxydation.

Par conséquent on attribue ce phénomène à des changements de structure moléculaire par suite d'une oxydation. Dans certains produits vulcanisés, une relaxation similaire ou même plus grande a été constatée sous vide, et cela est attribué à l'absence de structures pontées spécifiques. Le taux de recouvrement quand on relâche la pièce étirée a été étudié sur une série de caoutchoucs naturels vulcanisés.

### Zusammenfassung

Es wird eine Untersuchung eines "sekundären" Relaxationsprozesses in gedehnten Vulkanisaten beschrieben, der nach langer Versuchsdauer bei normalen Temperaturen vorherrschend wird. Es wird gezeigt, dass die Temperatur, die Atmosphäre, in der der Test verläuft, und die Gegenwart von Oxydationsinhibitoren einen merklichen Einfluss ausüben. Der Relaxationsprozess wird daher auf den oxydativen Abbau der molekularen Struktur zurückgeführt. Bei einigen Vulkanisaten wird jedoch im Vakuum eine ähnliche oder sogar grössere Relaxation gefunden, was auf das Fehlen von spezifischen Vernetzungsstrukturen zurückzuführen ist. Das Ausmass der Rückbildung beim Entspannen gedehnter Prüfstücke wurde ebenfalls für mehrere Naturkautschukvulkanisate untersucht.

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