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Long-Time Creep in a Pure-Gum Rubber Vulcanizate: Influence of Humidity and Atmospheric Oxygen *

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Long-time creep of natural rubber cured with a sulfur-accelerator recipe containing no filler can be conveniently represented by a plot of $(E-E_1)/E_1=\Delta E/E_1$ with a double-abscissa scale showing log t and t. E is the elongation at any time t, after application of the load, and E_1 its value at unit time. Experimental data conform to the equation

$$\Delta E/E_1=A\ \log t+B(t-1)$$

except for a more rapid rise preceding rupture. The constants A and B can be evaluated from only three observations—at the longest time (about 70 days), at one minute, and at an intermediate time. $\Delta E/E_1$ is approximately linear with log t when t is less than $0.1(A/B)$ and approximately linear with t when t is greater than $4.343(A/B)$. The observed modulus was about 1.4 MPa and A was about 2.4 percent/(unit log t) when the atmosphere was a vacuum, dry N_2, or dry air. The modulus was lowered very slightly and A became about 4 percent/(unit log t) when the air was saturated with water. B was raised from about 2×10^{-5} percent/min to about 20×10^{-5} percent/min when the vacuum or dry N_2 was replaced by dry air and to about 50×10^{-5} percent/min when the air was saturated with moisture. A is considered to be related to physical relaxation, while B corresponds to a chemical reaction, probably oxidative degradation.

Key words: Compliance of rubber; creep, long-time, in rubber; humidity, effect of, on creep of rubber; modulus of rubber, effect of humidity; oxygen, influence of, on creep of rubber; rubber, natural, creep; time, effect of, on compliance of rubber.

1. Introduction

Previous studies [1, 2][1] in the laboratories of the National Bureau of Standards have investigated the compliance of a typical pure-gum rubber compound vulcanized in a conventional sulfur-accelerator system. The range of temperature in those studies was from −60 to +100 °C, while the time at a given temperature in most cases ranged from 5 s to 10 min. The present work was undertaken in order to study the compliance at room temperature during time intervals from 1 min to about 100,000 min (about 70 days). The effect of ambient humidity and atmospheric oxygen on compliance and creep were given special attention in this study.

2. Experimental Arrangements

The recipe used was ASTM Formula 1A in Method 15–59T (formerly called ACS–1 Recipe) as follows: Natural rubber (NBS 385a) 100; Zinc Oxide (NBS 370a) 6; Sulfur (NBS 371b) 3.5; Stearic Acid (NBS 372c) 0.5; and Mercapto-benzothiazole (NBS 383) 0.5 parts by weight. From a flat sheet cured 60 min at 125 °C (257 °F) strips were cut with dimensions about 150 × 6.56 × 0.50 mm. A mass of 257.6 g was suspended, producing an initial stress of 0.770 MPa (7.85 kg/cm^2) on each specimen. The specimens were marked with gage marks 100 mm apart. A two-telescope cathetometer was used to measure elongations to the nearest 0.1 mm. Observations were begun 2 or 3 min after the application of the force and were continued to about 100,000 min—about 70 days. The temperature and relative humidity of the laboratory were held at 23.5 °C and 35 percent respectively.

The specimens were contained in glass tubes to permit the attainment of four different conditions as follows:

Specimen A—Conditioned 2 hours in dry nitrogen before test. Dry nitrogen passed through tube during test.

Specimen B—Conditioned 5 weeks in desiccator with $CaCl_2$ before test. Dry air passing over $CaCl_2$ during test.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Specimen C—Surrounded by laboratory air (35 percent relative humidity) before and during test. No circulation.

Specimen D—Conditioned 5 weeks over water before test. Air bubbled through water during test.

It should be noted that the thickness of the specimens was limited to only 0.50 mm in order to accentuate the effects of the atmosphere around the specimens and to eliminate diffusion limitations as much as possible.

3. One-Minute Elongation and Modulus

In view of the importance of an accurate value of E_1, the 1-min elongation, in the calculations, this value was determined by plotting the elongation against the logarithm of the time for all observations in the first hundred minutes. In all cases, straight lines were obtained in conformity with literature results (quoted later in this paper) extending to times of the order of milliseconds. Consequently a linear extrapolation of our observations was used to obtain the 1-min intercept, where $\log t = 0$.

The empirical stress-strain equation of Martin, Roth, and Stiehler [3]

$$F/M = (L^{-1} - L^{-2}) \exp A(L - L^{-1})$$

was used to calculate the ratio of F (force divided by the cross-sectional area of the unstretched specimen) to Young's Modulus M, the slope of the stress-elongation curve at zero stress. $L = E + 1$ is the ratio of stressed length to unstressed length, where E is the elongation. The constant A is 0.38. The 1-min. modulus M_1 was then calculated from the ratio F/M and $F = 0.770$ MPa (7.85 kg/cm^2) obtained from the force and the cross-sectional area of the unstretched specimen. The results are given in table 1. It is concluded that the oxygen content of the atmosphere surrounding the specimens has very little effect on the 1-min modulus. The modulus appears to be lowered slightly at the highest humidity but the change is small.

TABLE 1

Specimen	A	B	C	D
Atmosphere	N_2	Air	Air	Air
Relative Humidity %...	very low	very low	35	100
E_1.....................%...	144.7	144.7	146.2	153.6
F/M........................	0.5243	0.5243	0.5272	0.5386
M_1.................MPa...	1.469	1.469	1.461	1.430

The decrease in modulus at 100 percent relative humidity was somewhat less than the 3.5 percent decrease reported by Derham [4] as the relative humidity was increased from 20 to 80 percent.

In the present work, it has been found convenient to express the results in terms of the fractional creep $\Delta E/E_1$ where E_1 is the elongation at 1-min, E the elongation at a later time, and $\Delta E = E - E_1$. The modulus or compliance at any time can be calculated, if desired, from the elongation and the stress by the method just used to calculate the 1-min modulus.

4. Results of Creep Experiments

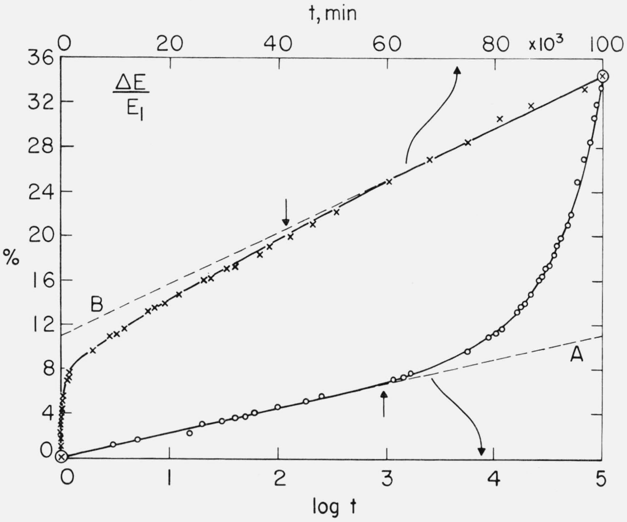

FIGURE 1.—*Double-abscissa plot of experimental values of fractional change in elongation of specimen B (dry air atmosphere) as a function of log* t *(lower curve, lower scale) and also as a function of* t *(upper curve, upper abscissa scale).*

Scales coincide at $t = 1$ and $t = 100{,}000$ min. Both curves represent the equation

$$\Delta E/E_1 = 2.239 \log t + 23.59 \times 10^{-5}(t-1)$$

where t is in minutes and $\Delta E/E_1$ in percent. Lower dashed straight line has the slope $A = 2.239$ percent/(unit log t). Upper dashed straight line has the slope $B = 23.59 \times 10^{-5}$ percent/min. Vertical arrows mark the limits of approximate linearity given in table 2.

It is convenient to present the creep results in the form of a double-abscissa plot like figure 1. Here t is the time during which the load is applied, and the fractional change in elongation $\Delta E/E_1$ is given as a function of log t (lower curve, lower abscissa scale) and also as a function of t (upper curve, upper abscissa scale). A comparison of the two scales is made by noting the two abscissa values corresponding to any given ordinate. In figure 1 the scales are made to coincide at $t = 1$ min ($\log t = 0$) and at $t = 100{,}000$ min ($\log t = 5$). Consequently the two curves must intersect at these points whatever the nature of the function $\Delta E/E_1$.

It can be seen in figure 1 that in dry air the creep, measured as the observed fractional change in elongation $\Delta E/E_1$, is linear with log t over an extended region up to about 1000 min and linear with t beyond about 40,000 min. In the intermediate region both lines are curved.

Double-abscissa plots for specimens A and D were qualitatively similar to that shown in figure 1 for

Specimen B. The plot for Specimen C in room air at 35 percent humidity was similar in all respects except that it showed much larger values of $\Delta E/E_1$ at all times with an increasing deviation from the linear relation for values of t above about 50,000 min. At 86,658 min the observed value of $\Delta E/E_1$ was about 154 percent as contrasted with 125 percent obtained by linear extrapolation. In contrast with the other specimens also, Specimen C broke after being stretched for about 90,000 min whereas the other three specimens were still intact when they were unloaded at about 100,000 min.

5. Equation for Representing Creep as a Function of Time

All the data obtained in the present studies, except for the anomalous increase in the creep of Specimen C after 50,000 min, could be well represented by an equation of the following form:

$$\Delta E/E_1 = A \log t + B(t-1) \qquad (5.1)$$

where A and B are independent of time. The two solid curves in figure 1 are drawn to represent this equation, with the constants $A=2.239$ percent/(unit $\log t$) and $B=23.59\times 10^{-5}$ percent/min. The observed values of $\Delta E/E_1$ lie close to those given by the equation, as can be seen from the experimental points plotted in figure 1 and similar plots for the other specimens. The only serious deviation is that already mentioned for Specimen C just before it broke.

The predicted slopes of the two curves are obtained by differentiation of eq (5.1)

$$\frac{\partial}{\partial \log t}\left(\frac{\Delta E}{E_1}\right) = A + Bt \qquad (5.2)$$

$$\frac{\partial}{\partial t}\left(\frac{\Delta E}{E_1}\right) = 0.4343A/t + B \qquad (5.3)$$

It can be seen that the values given by eq (5.2) approach the constant A as t is reduced, while those given by eq (5.3) approach the constant B as t is increased. This behavior is apparent in figure 1, which includes straight lines drawn with these slopes.

In quantitative terms, as t increased, $\frac{\partial}{\partial \log t}\left(\frac{\Delta E}{E_1}\right)$ is equal to A initially and becomes 10 percent greater than A when

$$t = 0.1\ (A/B) \qquad (5.4)$$

On further increase of $t\,\frac{\partial}{\partial t}\left(\frac{\Delta E}{E_1}\right)$ decreases to a value only 10 percent greater than B when

$$t = 4.343\ (A/B) \qquad (5.5)$$

Beyond this point the slope approaches B asymptotically.

The two constants A and B in eq (5.1) can be evaluated by solving two simultaneous equations obtained from two of the observations. In our work the constants have been obtained from only two observed values of $\Delta E/E_1$, one where $\log t$ was about 5 and the other where it was about 3. Thus in future work, unless the validity of the form of eq (5.1) is doubted, only two observations need be made, in addition to the 1-min value. It would seem best of course to make use of the creep at the longest time for one observation. The constants obtained in the present study depended very little on which intermediate time was chosen for the second observation.

The numerical results obtained in our work are given in table 2. After the constants A and B had been evaluated, the curves were drawn to represent eq (5.1). The ratio (A/B) was then used in eqs (5.4) and (5.5) to determine the remaining quantities in table 2. This procedure is regarded as more precise and accurate than a determination of these quantities directly from the graphs. The quantities in the last three lines of table 2 indicate the approximate boundaries of the linear relations. For example, for Specimen B the lower curve in figure 1 is regarded as approximately linear up to the point where $\log t = 2.98$ (namely where $t=949$ min) and the upper curve becomes approximately linear after a time $t=41{,}200$ min. These abscissas are marked with vertical arrows in figure 1. In the intermediate region both lines are curved. It can be noted that variations in the ratio A/B are chiefly due to variations in B, and that large values of B lead to small values of time marking the boundary regions.

6. Discussion

An examination of the data in tables 1 and 2 shows that the substitution of nitrogen for air (with the elimination of oxygen) in the atmosphere caused no change in the 1-min modulus and very little change in the value of the constant A. Essentially the same value of this quantity was found in an independent experiment in which the glass tube was evacuated instead of being filled with nitrogen.

On the other hand the slope of the curve in the long-time region, where it is nearly linear with time, was increased tenfold by the presence of air.

An increase of humidity in the air produced a slight progressive decrease in 1-min modulus and a moderate progressive increase in the value of the constant A. The value of the constant B, the slope of the curve in the long-time region increased considerably with increase of humidity. Specimen C—where the relative humidity was 35 percent and there was no circulation of air around the specimen—was anomalous in several respects. The constant B was even larger than that

TABLE 2

Specimen		A	B	C	D
Atmosphere	Unit	Dry N_2	Dry Air	Air 35%RH	Air 100%RH
A	%/(unit log t)	2.590	2.239	2.874	3.961
B	10^{-5}%/min.	2.349	23.59	125.1	54.22
A/B	min.	110,300	9,491	2,297	7,305
$\Delta E/E_1$ at $t=10^5$	%	15.3	34.9	[a] (190) [b] (140)	74.0
log t where $\frac{\partial}{\partial \log t}\left(\frac{\Delta E}{E_1}\right)=1.10A$		4.04	2.98	2.36	2.86
t where $\frac{\partial}{\partial \log t}\left(\frac{\Delta E}{E_1}\right)=1.10A$	min.	11,030	949	230	730
t where $\frac{\partial}{\partial t}\left(\frac{\Delta E}{E_1}\right)=1.10B$	min.	479,000	41,200	[c] 9,980	31,700

[a] Extrapolated from observed values.
[b] Extrapolated from linear relation.
[c] Linear relation not followed beyond $t=50{,}000$ min.

for Specimen D, where the air was bubbled through water to produce a relative humidity of 100 percent. Furthermore the linear relation for Specimen C was followed only from about 10,000 to 50,000 min and the specimen broke after about 90,000 min.

Further work would be desirable to ascertain the cause of this anomalous behavior. It is quite likely that the stagnant air surrounding Specimen C contained substances capable of accelerating the degradation of the rubber. These might be products of the degradation reaction exerting an autocatalytic effect on the reaction, or they might include ozone from the air of the room, which was illuminated by fluorescent lamps. On the other hand, with Specimens A, B, and D, which were surrounded by an atmosphere of nitrogen or air which had been passed over $CaCl_2$ or bubbled through water, the forced circulation removed the accelerating substances from contact with the specimens.

The form of eq (5.1) indicates that there are two different processes leading to creep. The first is predominant at short times, is fully recoverable, and is characterized by the value of the constant A. The second is predominant at long times, may be only partially recoverable, and is characterized by the value of the constant B.

Both processes are effective throughout the whole range of time, and the boundaries of the regions of predominance are characterized by the values of the ratio A/B as can be seen from eqs (5.4) and (5.5). It can be seen from the values given in table 2 that there is an extensive intermediate region where neither process predominates. Here one arbitrarily defines the boundaries of the region as those where the respective slopes differ by more than 10 percent from their limiting values. With this definition, one finds that the time increases by a factor of 43.43 in this region. The experimental values of $\Delta E/E_1$ are in good agreement with the equation throughout this region as well as in the regions where one process or the other is predominant. The existence of this intermediate region has not been explicitly recognized in previous work.

7. Comparison With Previous Investigations

The form of creep relation shown by eq (5.1) is apparently very general. It has been applied to many amorphous and polycrystalline solids of widely different molecular structures. Lyons [5] has claimed that it is representative of all normal creep (except at high stresses near the breaking load). He gives a comprehensive historical summary of its use for many materials and in his own work applied it to the creep of tire cords. However, Findley [6, 7] considers that the creep of plastics is better represented in terms of an equation containing the time raised to a positive fractional power.

The application of eq (5.1) to rubber has been quite limited. Derham, Lake, and Thomas [8] have found it applicable to a rubber vulcanizate at 70 °C. They consider the parameter A to represent the physical component of the creep and the parameter B to represent the chemical component. The values they reported were $A=1.82$ percent/(unit log t) and $B=346\times10^{-5}$ percent/min.

In many instances the time of observation of the creep in rubber has been so short that the only region noted has been the "primary creep" region, in which the fractional creep is proportional to the logarithm of the time [9–15]. In other work [3, 16, 17] the rise above the line has been noted at the longer times, especially at 70 °C or higher temperatures. It has usually been denoted as "secondary creep," without any quantitative evaluation, such as that which we have given here in terms of the constant B. A striking advance in this respect was made by Gent [18]. In a comprehensive study, he obtained values of the secondary creep by subtracting the primary creep from the observed creep. He reported observations extending up to 15,000 min showing that the secondary creep in most cases was linear with time. This is in accordance with eq (5.1) and yielded values of B ranging from 50×10^{-5} to 140×10^{-5} percent/min at 60 °C.

Our own previous studies [2, 19] of compliance, as measured by indentation, showed a region of linearity of compliance at 25 °C with $\log t$ over a range of about 6 decades of $\log t$—3 of them below 1 min and 3 of them above. At the shortest times, the values fell below the line because of the approach to the glass transition. At the longest times, the values rose higher and higher above the line. The slope of the line corresponded to a change of 2 percent/(unit $\log t$) in reasonable agreement with the values of A given in table 2. Our previous work involved time-temperature equivalence of course, unlike the present constant temperature studies, which involved no observations at times of less than 1 min. However Wildschut [20] and Brenschede [9] have reported the results of direct recovery measurements at room temperature indicating a linearity of recovery with $\log t$ to times as short as about 6 ms—at which point inertial effects appeared. Brenschede's results showed linearity with $\log t$ to values as high as 10,000 s, a range of about 6 decades of logarithmic time.

We have noted only three instances [21–23] in the literature where the creep near room temperature has been plotted with time as the abscissa for times longer than 10,000 min, so that B could be evaluated. In all three cases there was a range over which B was approximately constant.

The work of Braun [21] on stretched rubber bands at 27 °C showed the expected initial linearity of creep with $\log t$ with a slope of 3–4 percent/(unit $\log t$). When plotted against t, the creep showed the expected region of rapid rise followed by a region of approximate linearity with time. Here for elongations in the range 220 to 280 percent with fractional creep values of 27–55 percent a value of B of about 15×10^{-5} percent/min could be calculated. Finally Braun found a region of more rapid rise beginning at 120–200 days (depending on the tension) and terminating in rupture in about 240 days.

Our present work extending to about 70 days included only one case of rupture, namely Specimen C, which broke in about 63 days (90,000 min), following a pre-rupture rapid increase of creep.

The second long-time creep study was that of Mooney, Wolstenholme, and Villars [22] who followed the compression creep of several thick rubber vulcanizates for 3000 days (4.3×10^{6} min). After the initial rise, the compression creep at 35°C showed linearity with time with a slope corresponding in one instance to a value of $B = 4. \times 10^{-5}$ percent/min.

Linnig, Parks, and Stiehler [23] followed the creep of a stretched pure-gum rubber vulcanizate for about 56,000 min. The only previous workers to present their results in a double-abscissa plot like figure 1, they show data from which one can calculate that $A = 2.12$ percent/(unit $\log t$) and $B = 306 \times 10^{-5}$ percent/min at 50 °C. They state that the change from linearity on a log-time scale to linearity on a uniform time scale occurred at about 1500 min at 50 °C, sooner at 70 °C, and later at 24 °C. Their results were not given in sufficient detail to make obvious the intermediate region where neither plot is linear, as already noted in the present studies.

The increase of the constant A with humidity would be anticipated from the results of Derham and coworkers [4, 8, 24] who found that the stress relaxation at 25 °C was almost linear with $\log t$. The slope increased from about 1.6 percent/(unit $\log t$) when the relative humidity was 15 percent to about 2.5 percent/(unit $\log t$) at 92 percent relative humidity [8]. In other work [4] it increased from 2 percent/unit $\log t$ at 15 percent relative humidity to 3.4 percent/unit $\log t$ at 100 percent humidity. These values may be compared with those obtained for the constant A in the present work.

Derham and co-workers [8, 24] have reported values of a quantity corresponding to the constant B (denoted as the "chemical creep rate") at temperatures of 50, 60, 70, and 80 °C. The observed values of B ranged from near 10×10^{-5} percent/min at 50 °C to more than 1000×10^{-5} percent/min at 80 °C. When $\log B$ is plotted against T^{-1}, the reciprocal of the temperature in kelvins, straight lines are obtained, corresponding to activation energies of 20–30 kcal/mol (85–125 kJ/mol), the values depending on the vulcanizing system, particularly the amount of antioxidant. It is considered significant that an activation energy of 30 kcal/mol corresponding to oxidative chain scission has been previously reported, as calculated from the observations of stress relaxation of a natural rubber vulcanizate at 100 to 130 °C by Tobolsky, Dillon, and Prettyman [25–27].

We have not found values for the change of the constant A with temperature. The change is certainly small [24] and is probably a decrease with increase of temperature. Gent [18] has reported observations indicating that A is slightly smaller at 60 °C than at 23 °C. The same behavior can be noted in results for GR-I (Butyl rubber) given by Martin, Roth, and Stiehler [3].

The present discussion has been limited to natural rubber cured with conventional sulfur-accelerator recipes. The creep behavior of natural rubber crosslinked by peroxides has not been considered. In the latter case the studies of Thirion and Chasset [28–30] over about 4 decades of log time have shown that the rate of stress relaxation at temperatures below 65 °C decreases with increase of time. This was confirmed by Steiner and Tobolsky [31], but the range of only 2 decades in our own work [32] with peroxide-cross-linked rubbers was not sufficiently extended to show a decrease. In terms of the quantities used here, this is equivalent to a decrease of A with time. For conventional vulcanizates however, at temperatures well above the glass transition temperature we have found no evidence of such a decrease in our work [2, 19] or in the literature.

8. Conclusions

The long-time creep of natural rubber cured with a conventional sulfur-accelerator recipe containing no filler can be conveniently shown near room temperature by a plot of $\Delta E/E_1$ with a double-abscissa scale—one marked in units of log t and the other in units of t. When experimental data from the present work and from previous studies reported in the literature are plotted in this manner it is noted that invariably the first scale yields a linear relation at short times and the second a linear relation at long times.

The limiting linear relations just mentioned suggest the two-constant equation

$$\Delta E/E_1 = A \log t + B\ (t-1)$$

already proposed as a general creep equation for many materials. In the case of rubber the range of values of t investigated is from about 10 ms as studied by previous investigators to about 70 days in our work and other studies. Any significant deviations from the equation can be noted by inspection of the double-abscissa plot. We found that the equation furnished an excellent representation of almost all our experimental data up to the longest times. In one instance in our work and in a few other cases there was a pre-rupture increase of $\Delta E/E_1$ above the values given by the equation. This behavior can reduce somewhat the upper limit of validity of the general equation.

The constants A and B can be evaluated from experimental observations of $\Delta E/E_1$ by solving two simultaneous equations obtained from values at the longest time, at one minute, and at an intermediate time.

In the present work, the constant A was essentially the same [about 2.4 percent/(unit log t)] when the atmosphere surrounding the specimen was a vacuum, dry nitrogen, or dry air. The value was raised when the atmosphere was room air at 35 percent relative humidity and became about 4 percent/(unit log t) when the air was saturated with water.

The constant B was raised tenfold when the atmosphere was dry air instead of dry nitrogen. It was further increased by a factor of about 2, when the air was saturated. The value of B for the specimen in an atmosphere of stagnant room air was still greater than this by another factor of more than 2. It is possible that this atmosphere contained autocatalytic degradation products or other constituents which were removed when the air was bubbled through water or passed over $CaCl_2$.

The approximate boundaries of three different regions of time are determinable from the ratios A/B. In the first region where t is less than 0.1 (A/B) $\Delta E/E_1$ is approximately linear with log t. In the second region, where t is between 0.1 (A/B) and 4.343 (A/B), $\Delta E/E_1$ is not linear with either log t or t. In the third region, where t is greater than 4.343 (A/B), $\Delta E/E_1$ is approximately linear with t. A fourth region of anomalous increase preceding rupture is sometimes found, especially when B is large.

The creep process characterized by the constant A appears to be a physical process [14] continuing indefinitely but becoming of diminishing importance relative to the creep process characterized by the constant B. For most conventional pure-gum natural rubber vulcanizates A has a value of 2–4 percent/(unit log t). The process characterized by B is effective from the beginning but its relative importance increases until it finally predominates. It is probably associated with a chemical change, presumably oxidative degradation of the rubber network [18]. However any process which is proportional to the time under stress would be included. The values of B ranged from 2×10^{-5} to 125×10^{-5} percent/min in our work. The values were increased considerably by the presence of oxygen and water in the atmosphere surrounding the stretched specimen. The work of others [24, 26] has shown that the change of B with temperature corresponds to an activation energy of 20–30 kcal/mol (85–125 kJ/mol). The value of A probably decreases slightly with increase of temperature [3, 18].

There are many interesting possibilities for the application of this type of analysis to a study of the effect of other variables on long-time creep. One of these would involve the effect of temperature on the constants A and B. Another study could well be an investigation of the anomalous pre-rupture creep already mentioned. The long-time creep of rubber cross-linked with dicumyl peroxide might well be studied to determine the behavior of the constant B as the constant A is made smaller and smaller by increased cross-linking [32]. Finally it would be of interest to evaluate A and B for various types of synthetic rubber.

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