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Stress Softening in Natural Rubber Vulcanizates. Part III. Carbon Black-Filled Vulcanizates

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Synopsis

Stress softening (Mullins effect) occurs in rubber vulcanizates during the first and subsequent deformations. This paper shows the similarity of the degree of stress softening in both unfilled and carbon black-filled vulcanizates of natural rubber when stressed almost to break. This confirms the earlier investigations which were confined to moderate stresses. A simple interpretation of the tensile stress–strain results for filled rubbers is that the strain in the rubber is increased by the presence of the filler, so that the ratio of the average strain in the rubber to the measured overall strain is given by a strain amplification factor. The usefulness of this concept is confirmed by showing the similarity of the stress-softened curves after normalizing the strains, provided the vulcanizates of both gum and filled vulcanizates were subjected to the same initial stress.

INTRODUCTION

When new samples of gum and black-filled rubbers are stretched to a given elongation and then retracted, subsequent extension to the same strain requires a lower force. Most of this softening occurs during the first deformation, and after a few stressing cycles a steady state is reached. This phenomenon has been termed the Mullins effect and has been the subject of numerous investigations.[1–4] Earlier papers by Harwood, Mullins, and Payne[5,6] have shown that considerable softening can occur in pure gum vulcanizates as well as in black-loaded rubbers. These earlier studies were confined to moderate stresses. It is the purpose of this paper to extend the work described earlier to stresses similar to those required to break the rubber.

The compounds used in this investigation were natural rubber vulcanizates containing 60 phr of a wide range of different types of commercially available carbon blacks and a series of NR vulcanizates containing 0, 20, 40, 60, and 80 phr HAF (high abrasion furnace) black. The compounding recipe was: 100 parts natural rubber (RSS1), 3.5 phr ZnO, 2.5 phr stearic acid, 1 phr PBN, 2.5 phr sulfur, 0.6 phr accelerator CBS, and 5 phr Dutrex R; Also 60 phr SRF or MPC, FEF, ISAF, HAF, EPC, FT, MT, SPF, LB. The vulcanizing time was 40 min. at 140°C.

EXPERIMENTAL RESULTS

Figure 1 shows two sets of load–extension curves obtained on a pure gum natural rubber and a natural rubber containing 60 phr HAF black.

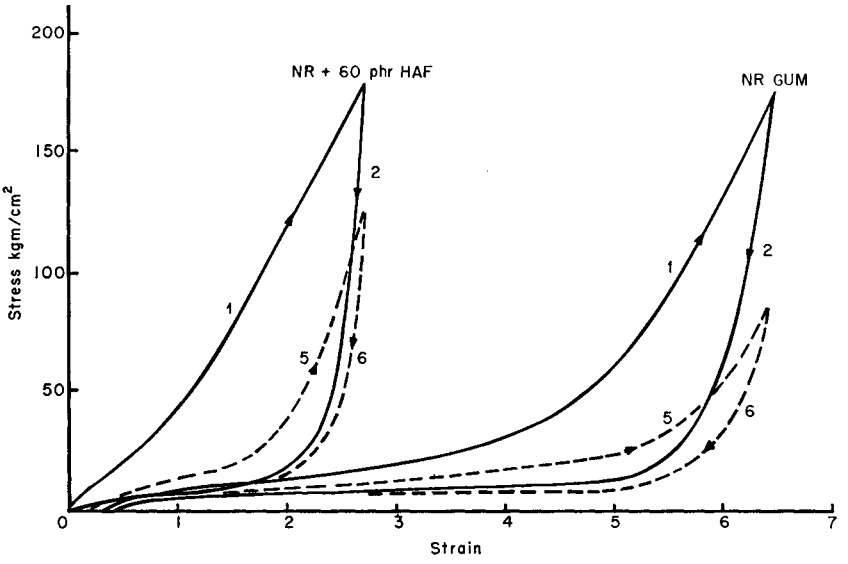

Fig. 1. Stress softening of NR vulcanizates: (left) containing 60 phr HAF carbon black; (right) unfilled; (*1*, *2*) first cycle; (*5*, *6*) third cycle shown as broken lines.

The two vulcanizates were stressed initially to the same load (near breaking load) on an Instron tensile tester at a strain rate of 2/min. and at room temperature. Also shown on the figure are the first retraction curves, (curves *2*) and the curves for the third complete stressing cycle (curves *5* and *6*) to the same maximum extension as the first cycle. It is apparent that considerable stress softening has occurred in both vulcanizates between the first and third extensions, (compare curves *1* and *5* in Fig. 1).

To emphasize the similarity of the stress-softening effects in pure gum and filled-loaded rubbers, it is convenient to plot the values of the stress in curves 2–6 at any strain as a function of the initial stress given by curve *1*. By this means we can compare directly the initial curve *1* with the retraction curve *2* and with the subsequent stressing and retraction curves. It is apparent from this comparison of the data in Figure 2 that the magnitude of softening is large, although that for the gum rubber is not quite as large as for the black filled vulcanizates. Nevertheless, in the third complete extension and retraction cycle (curves *5* and *6*), the degree of softening for the pure gum vulcanizate approaches in magnitude the stress softening experienced by the carbon black-filled vulcanizates, especially at the higher stress levels.

The curves *3* (second extensions) for the black-loaded vulcanizates have been separately labeled to draw attention to the fact that reinforcing blacks, such as HAF, SRF, and ISAF, produce a lower degree of stress softening at the maximum strain than the less reinforcing blacks such as fine thermal black (FT). This behavior is associated with the amount of set which results from the initial stressing process and will be discussed later in this paper.

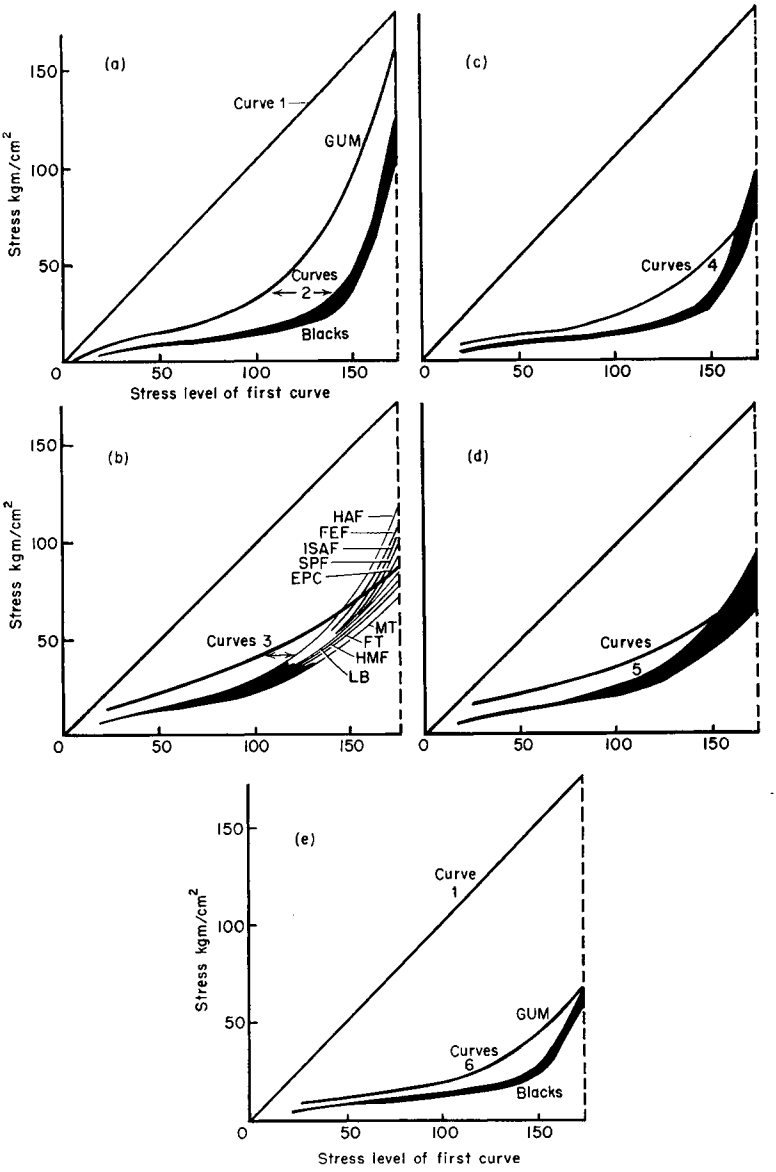

Fig. 2. Stress normalization plots illustrating effect of type of filler and successive cycling on stress softening: (*a*) first cycle; (*b*), (*c*) second cycle; (*d*), (*e*) third cycle. Stress versus stress level of the first stressing curve of NR gum shown as a single line; NR + 60 phr black results shown as a continuous band on all plots.

Normalization of Data

In Part I, Mullins and Tobin[7] have shown that the stress–strain behavior of a black-loaded rubber vulcanizate can be described in terms of the stress–strain behavior of the gum base vulcanizate if it is assumed that the average strain present in the rubber phase is increased by the presence of

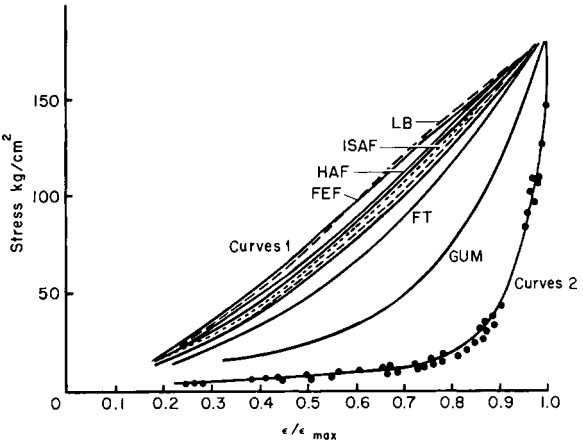

Fig. 3. Strain normalization of the first stressing cycle showing the effect of filler. Points refer to the retraction curves for both gum and filled vulcanizates. ϵ/ϵ_{max} is the strain normalizing factor. All rubbers stressed to same initial stress.

the filler by a factor X. This strain amplification factor describes the ratio of the average strain in the rubber phase to the measured overall strain, and in the case of thermal black which consists of spherical particles, is given by the relation

$$X = 1 + 2.5c + 14.1c^2$$

which is similar to the Guth-Einstein expression for the viscosity of suspensions of solid spherical particles. For asymmetrically shaped particles, X becomes

$$X = 1 + 0.07\,fc + 1.62\,f^2c^2$$

where f is the shape factor (length to diameter) of the particle.

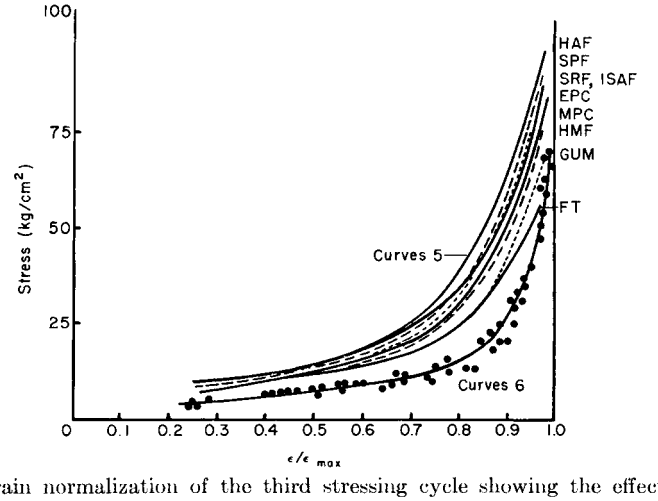

Fig. 4. Strain normalization of the third stressing cycle showing the effect of filler. Notation as in Fig. 3.

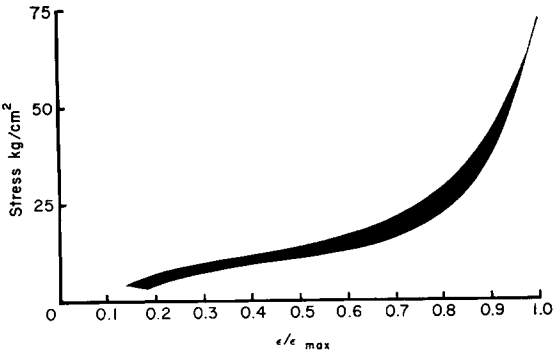

Fig. 5. Strain normalization of the second stressing curve for gum and filled vulcanizates when stressed to 75 kg./cm.^{2}. The results are shown as a band.

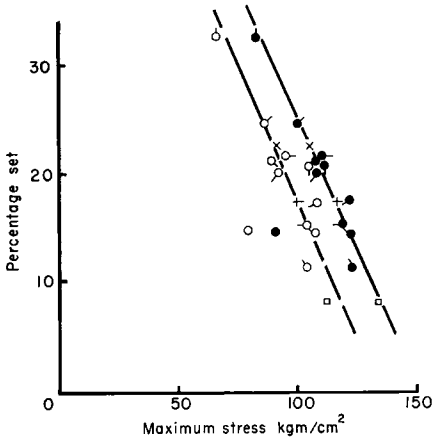

Fig. 6. Percentage set versus maximum stress in the (O) second and (●) third stressing cycles: (O, ●) unfilled NR; (◇ , ◆) clockwise flag, 60 phr FT (upright), HMF, SRF, EPC, MPC, LB, FEF, ISAF, HAF, SPF, respectively; × 20 phr HAF; (+) 40 phr HAF; (□) 80 phr HAF.

It was shown in an earlier study that the strain data can be normalized by the use of the factor ϵ/ϵ_{max} where ϵ is the measured extension and ϵ_{max} is the maximum strain during the first extension. The same technique of normalization has been used to analyze the present data. Figure 3, for instance, plots stress versus ϵ/ϵ_{max} for the pure gum and filler-loaded natural rubber vulcanizates. It can be seen from the figure that during the first extension (curves *1*) the most reinforcing blacks give the highest stress levels of all the vulcanizates studied whereas the pure gum vulcanizate gives the lowest. On the other hand, Figure 3 also shows that the retraction data (for curve *2*) for all the vulcanizates are very similar.

Figure 4 shows similar data for the stressing curves *5* and the subsequent retraction curves *6*. As expected, at $\epsilon/\epsilon_{max} = 1.0$, compounds containing the most reinforcing blacks have been less stress-softened than the gum

and the rubber filled with fine thermal black, even though these maximum stresses are now only about half the values of the initial stress (180 kg./cm.^{2}) to which the vulcanizates had been subjected.

If during the second stressing, all the vulcanizates are extended to the same stress instead of being stressed to the original extension, then all the normalized extension data, both for loaded compounds and for the gum, become very similar, as shown in Figure 5. The basic idea that the main differences in stress softening can be attributed to differences in the X factor seems to be justified, provided we compare the data at the same stress levels.

Tension Set

Figure 6 shows a linear relationship between the percentage set after the third stressing and the maximum stress. The higher the structure of black the smaller is the amount of set and the higher is the maximum stress level. Increasing the amounts of carbon black also reduces the set and increases the maximum stress values.

Figure 7 shows the percentage set against the initial strain to which all the rubbers were subjected under a stressing load of 180 kg./cm.^{2}, and an excellent linear relationship for the black-loaded rubbers is apparent. The positive intercept on the strain axis suggests that a strain of just under 100% extension is required before set becomes apparent. When the stressed samples were swollen in benzene vapor for 24 hr. and the vapor subsequently evaporated off *in vacuo*, the amount of set was reduced by a similar amount in all the vulcanizates including the gum. With a subsequent more drastic treatment of swelling in liquid benzene, a further reduction in set was observed after drying. The reduction in set appears

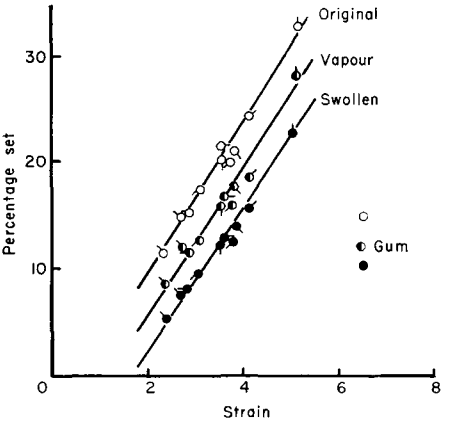

Fig. 7. Percentage set vs. maximum strain in cycle showing the effect of recovery of set by solvent vapor and liquid swelling treatment; (○) original set data; (◐) set after vapor swelling treatment; (●) set after liquid swelling treatment; flag notation as in Figure 6.

to be independent of the type of black, and even of the presence of the black.[8]

Empirical Stress–Strain Relationships

Martin, Roth, and Stiehler[9] have developed an empirical equation to describe isochronal stress–strain data obtained from creep curves, viz.:

$$S = M\ [(1/\lambda) - (1/\lambda^2)]\ \exp\ \{A[\lambda - (1/\lambda)]\}$$

where M is Young's modulus, S the stress, and λ the strain ratio. A is an empirical constant. Rearranging this equation gives:

$$\log\ [S\lambda^2/(\lambda - 1)] = \log M + 0.434A\ [\lambda - (1/\lambda)]$$

Smith[10] found that in experiments on gum SBR vulcanizates, the Martin-Roth-Stiehler equation adequately described the whole stress–strain curve right up to the breaking strain. Landel and Stedry[11] found a similar result when examining a polyurethene rubber at low strain rates and high temperatures. Harwood and Payne[8] have shown that the Martin-Roth-Stiehler equation is applicable up to high strains for natural rubber vulcanizates with varying amounts and types of crosslinking.

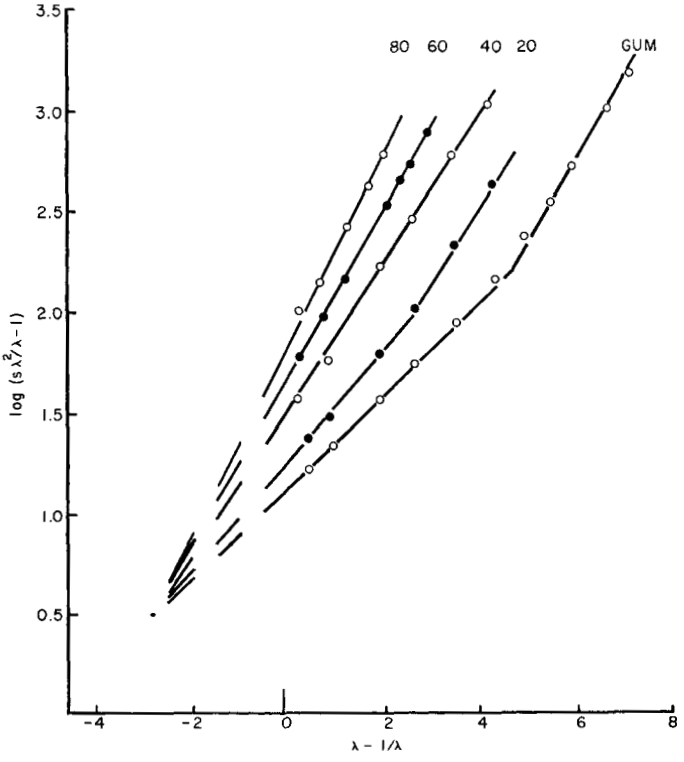

Fig. 8. Log $[S\lambda^2/(\lambda - 1)]$ vs. $[\lambda - (1/\lambda)]$ for gum NR and 20, 40, 60, 80 phr HAF.

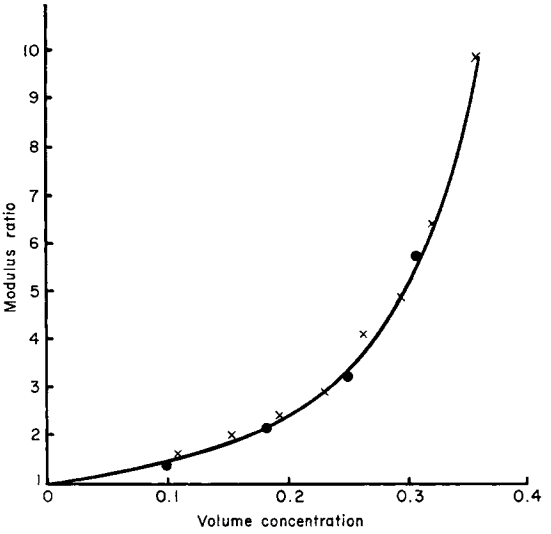

Fig. 9. Modulus ratio versus volume concentration of filler, (HAF black in NR): (×) dynamic results, (●) tensile results.

Figure 8 shows plots of log $[S\lambda^2/(\lambda - 1)]$ versus $\lambda - (1/\lambda)$ for gum and HAF vulcanizates containing 20, 40, 60, and 80 phr black. The Martin-Roth-Stiehler equation describes the data for these rubbers quite adequately at low and moderate extensions. The interesting feature of these plots is that all the data extrapolate back to a single point. The discontinuity at high extensions of the curves for the pure gum and the 20 phr black vulcanizate is typical of natural rubber and is presumably associated with the onset of crystallization.

Payne[12] has shown, using dynamic mechanical oscillations to strain the rubber, that the dynamic shear modulus of black-loaded rubbers tends to fall to an asymptotic value, G'_∞, with increasing dynamic strain amplitudes. These strain amplitudes, however, are small compared with the maximum strain applied in this work. The modulus G'_∞ was shown to be a function of the concentration of the black and the modulus of the pure gum rubber phase and to result from the hydrodynamic effect of the asymmetrically shaped filler particle. Figure 9 plots the ratio $G'_{\infty\text{black}}/G'_{\infty\text{pure gum}}$ versus the concentration of the carbon black. Also plotted in the same figure are the values of the ratio $M_{\text{black}}/M_{\text{pure gum}}$, where M_{black} and $M_{\text{pure gum}}$ are the moduli of the black and the pure gum rubbers obtained from the Martin-Roth-Stiehler plots. The two sets of modulus ratio values are identical.

The observed agreement between the two modulus ratios indicates that the stiffening effect of black in tensile tests at low or moderate strains is due to the hydrodynamic effect of broken-down carbon black networks. These degenerated networks remain after the breakdown of "structure" which occurs at very low strains and which is reflected by decrease in dynamic shear modulus to G'_∞. The ratio $M_{\text{black}}/M_{\text{pure gum}}$ obtained at

low extensions can be identified with the X factor. However at high extensions the ratio $\epsilon_{\text{max black}}/\epsilon_{\text{max pure gum}}$ will depend on the maximum stress to which the rubber has been subjected as the modulus of pure gum rubber is itself stress dependent. Thus under these conditions the X factor will no longer be identical to the ratio $M_{\text{black}}/M_{\text{pure gum}}$.

DISCUSSION

This paper has confirmed the conclusions of the previous paper[6] that the stress softening (Mullins effect) of a black-loaded vulcanizate is similar in magnitude to the stress softening of a gum rubber if the two vulcanizates are stretched initially to the same stress. The initial stress used in the present work was 180 kg./cm.^{2}, which is very near to the breaking stress of these vulcanizates.

The similarity of the normalized stress–strain curves for all the vulcanizates, both gum and loaded with 60 phr of different types of black, suggests that the main difference between the stress–strain characteristics of a filled and a pure gum rubber, after the initial stressing cycle, can be accounted for by the strain amplification factor X. The more reinforcing blacks possess the higher X factors, i.e., they stiffen the rubber more than, for example, a fine thermal black. It is concluded that the black is acting mainly in a stiffening capacity due to the hydrodynamic effects of the degenerate carbon black networks.

For sulfur-crosslinked pure gum vulcanizates, in which the crosslinks are polysulfidic, the stress softening is partly associated with the breakage of polysulfide linkages. These reform in the extended condition and produce a real permanent set, but the major stress softening is attributed to the incomplete recovery of the crosslinked network to its initial random state due to network junctions or similar associations being displaced in a nonaffine way during extension. For example, junctions at the ends of chains which become fully extended at relatively low extensions will be displaced in this way. Thus when the rubber is subsequently strained, the network is already in a preferred disposition.[8]

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Résumé

Un ramollissement sous tension se passe au sein de vulcanisats de caoutchouc au cours des premières déformations subséquentes. Cet article montre la similitude du degré de ramollissement sous tension à la fois dans des vulcanisats de caoutchouc naturel ne contenant pas de charges et contenant du noir de fumée lorsque il est étiré jusqu'à rupture. Ceci confirme les études antérieures qui avaient été limitées à des tensions modérées. Une interprétation simple des résultats d'élongation sous tension pour les caoutchoucs chargés consiste à admettre que la tension au sein du caoutchouc est accrue par la présence de la charge de telle sorte que le rapport de la tension moyenne au sein du caoutchouc à la tension globale mesurée est donné par un facteur d'amplification. L'utilité de cette notion est confirmée par la similitude des courbes de ramollissement sous tension après normalisation des tension pourvu que les vulcanisats à base de gomme et les vulcanisats chargés aient été soumis à une tension initiale identique.

Zusammenfassung

Spannungserweichung (Mullins-Effekt) tritt bei Kautschukvulkanisaten während der ersten und darauffolgenden Deformationen auf. In der vorliegenden Arbeit wird die Ähnlichkeit des Spannungserweichungsgrades bei ungefüllten und russgefüllten Naturkautschukvulkanisaten bei einer Spannung fast bis zum Reissen gezeigt. Dadurch werden früherer Untersuchungen bei mässigen Spannungen bestätigt. Eine einfache Interpretation der Zugspannungs-Verformungsergebnisse an gefülltem Kautschuk besteht darin, dass die Verformung in Kautschuk durch die Anwesenheit des Füllstoffs erhöht wird, sodass das Verhältnis von mittlerer Verformung im Kautschuk zur gemessenen Bruttoverformung durch einen Verformungsverstärkungsfaktor gegeben ist. Die Brauchbarkeit dieses Konzenpts wird durch die Ähnlichkeit der Spannungserweichungskurve nach einer Verformungsnormalisierung bestätigt, vorausgesetzt, dass sowohl die Vulkanisate von ungefülltem, als auch gefülltem Kautschuk der gleichen Anfangsspannung unterworfen wurden.

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