

Stress Softening in Natural Rubber Vulcanizates. Part II. Stress Softening Effects in Pure Gum and Filler Loaded Rubbers

J. A. C. HARWOOD, L. MULLINS, and A. R. PAYNE, *Natural Rubber Producers' Research Association, Welwyn Garden City, Herts., England*

Synopsis

Considerable stress softening (Mullins effect) occurs in both gum and filler loaded vulcanizates of natural rubber and SBR. When compared at the same stress, the extent of softening is similar in both gum and filled vulcanizates. The stress softening is shown to be mainly due to changes in the rubber phase in the filled vulcanizate, and related to that of the gum vulcanizate by the use of the strain-amplification factor discussed in Part I of this series.

INTRODUCTION

When new samples of gum and carbon black-filled rubber vulcanizates are stretched and then allowed to retract, subsequent extensions to the same strain require a lower force. Most of this softening occurs during the first deformation, and after a few stretching cycles a steady state is reached. This phenomenon has been termed the Mullins effect¹⁻⁶ and has been the subject of several investigations. It has been suggested that in filled vulcanizates the magnitude of the effect is an important indication of the reinforcing potential of fillers, since this stress softening reflects hysteresis within the vulcanizate⁷ and thus the amount of work which the vulcanizate can absorb. Hitherto this behavior has been mainly attributed to the breakage of carbon black chains or agglomerates, or to the breakage of weak bonds between the rubber and the carbon black surface.³⁻⁵ This paper shows how the stress softening in carbon black-filled vulcanizates is determined by stress softening which occurs in gum vulcanizates when subjected to pre-stressing.

EXPERIMENTAL RESULTS

Figure 1 shows three sets of tensile stress-strain curves obtained on the following natural rubber vulcanizates: gum, gum with 20 phr HAF (high abrasion furnace) black, and with 80 phr HAF black. The three vulcanizates were stressed initially to the same load on an Instron tensile tester at a strain rate of 2 per minute and at room temperature. Also shown on the

figure are the first retraction (curves 2) and the second complete stressing cycles, (curves 3 and 4) for extensions up to the same strain as the initial strain. The samples were allowed to relax a few minutes between each stress cycle; after this period the rate of recovery was very slow. The compounding and vulcanizing details are given in the Appendix.

With each of the three vulcanizates, considerable softening has occurred between the first and second stressing cycles (curves 1 and 3). To compare the three sets of curves in Figure 1 more directly, it is convenient to plot values of the stress in curves 1, 2, and 3 as a function of the stress required

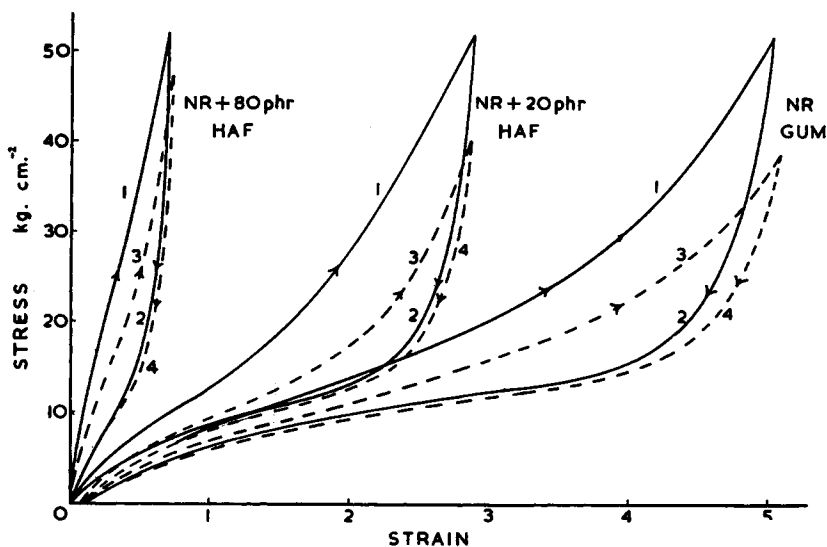


Fig. 1. Stress (referred to original cross-section) versus strain for (a) gum vulcanizate, (b) vulcanizate containing 20 phr HAF, and (c) vulcanizate containing 80 phr HAF: (1) initial stressing curve; (2) first retraction curve; (3) second stressing curve; (4) second retraction curve.

to produce the same strain during initial stressing (curve 1). It is apparent from this comparison (Fig. 2) that the magnitude of softening is essentially similar in all three vulcanizates. The softening process in the highly filled rubber (80 phr HAF) vulcanizate is therefore mainly due to changes in the rubber phase only, rather than to changes in the carbon black structure or agglomerates, or to the breakage of weak bonds between the rubber chains and the highly absorptive or reactive carbon black surface, as have been postulated previously as the basic mechanisms of stress softening.⁸

Figure 3 is plotted in the same manner as Figure 2 and shows stress versus initial stress curves obtained on the gum natural rubber vulcanizate, and on similar natural rubber vulcanizates containing 60 phr of different types of black. In order to avoid confusion, data for each separate vulcanizate

have been displaced horizontally. Again, the behavior of filler-loaded vulcanizates is substantially similar to that of the gum vulcanizate. Figure 4 gives data for some other more reinforcing types of black.

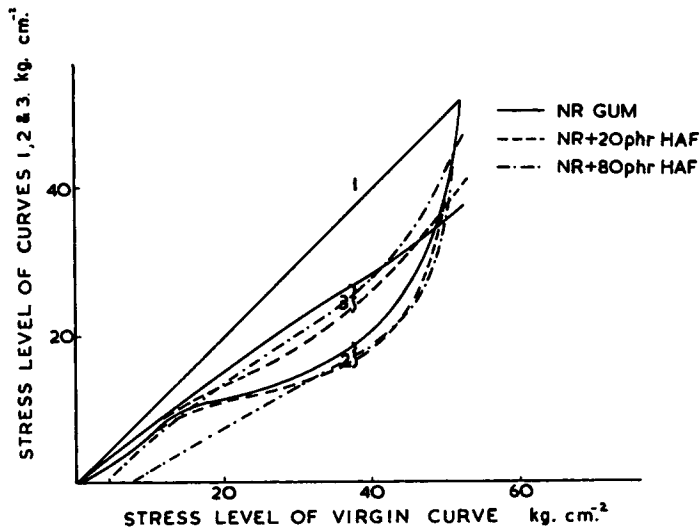


Fig. 2. Stress in curves (1), (2), and (3) of Fig. 1 vs. initial stress in curve (1).

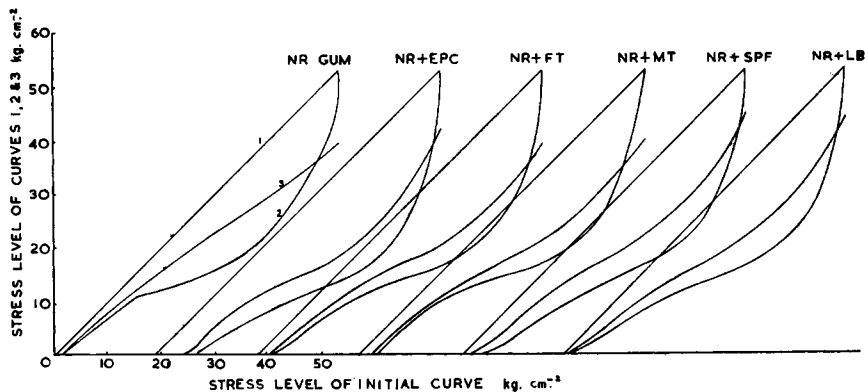


Fig. 3. Stress vs. initial stress plots of NR and range of blacks.

Figures 5 and 6 describe the behavior of SBR vulcanizates loaded with the same types of black as used in the NR series. Here, of course, no gum SBR results could be determined for comparison, as the gum vulcanizate was too weak to reach the stress levels involved in this study. There is a pronounced similarity between the results obtained on both rubbers especially in the degree of stress softening between the first and second extension

(curves 1 and 3). The size of the loop between the second extension and retraction (curves 3 and 4) varies with the nature of the black and this will be discussed later in this paper.

Figure 7 shows the effect of increasing volume concentration of HAF black. To a first approximation all of the curves are similar, although at

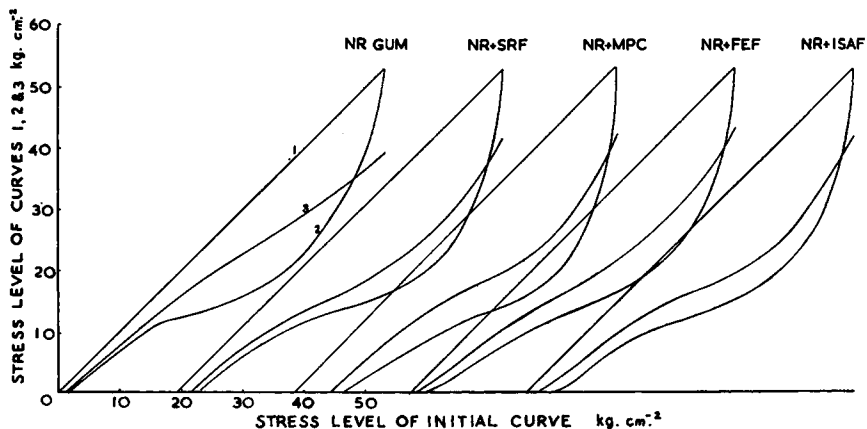


Fig. 4. Stress vs. initial stress plots of NR and range of blacks.

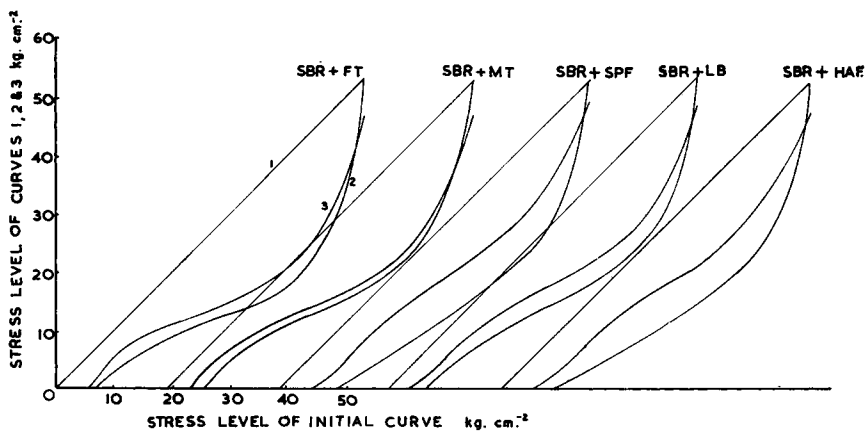


Fig. 5. Stress vs. initial stress plots of SBR and range of blacks.

very low stresses increase in concentration of black results in an increase in the difference between curves 1 and 2. This is to be expected, as it is now well established that at low stresses there is a contribution to hysteresis due to the breakdown of carbon black chain networks or agglomerates⁹

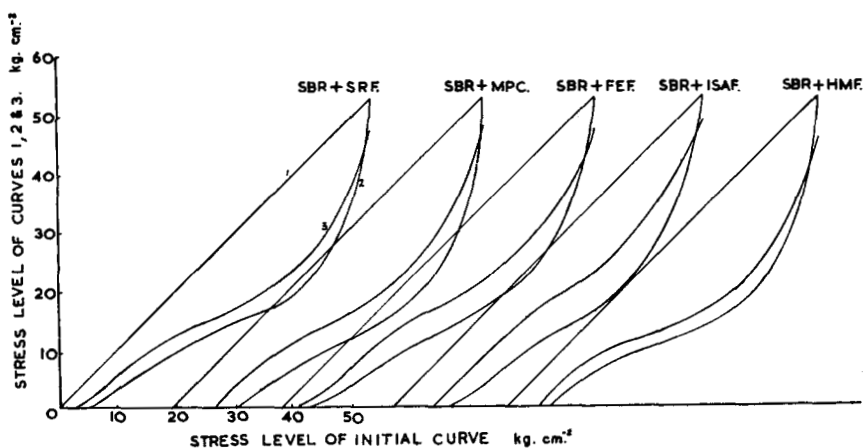


Fig. 6. Stress vs. initial stress plots of SBR and size of blacks.

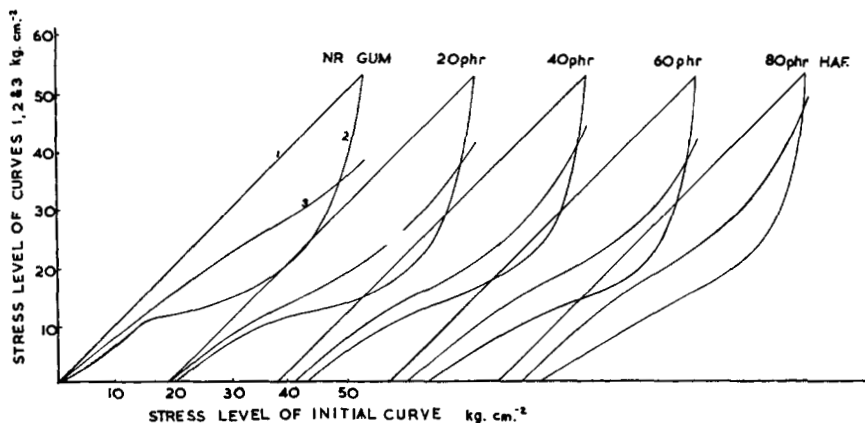


Fig. 7. Stress vs. initial stress plots of NR and HAF blacks.

ANALYSIS OF RESULTS

Normalization of Data

In Part I, Mullins and Tobin¹⁰ have shown that the stress-strain behavior of black-loaded rubber vulcanizates can be described in terms of the stress-strain behavior of the pure gum base vulcanizate, if it is assumed that the average strain present in the rubber phase is increased by the presence of filler, by a certain factor. This strain-amplification factor X describes the ratio of the average strain in the rubber phase to the measured overall strain, and in the case of thermal black 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.

The use of this strain-amplification factor involves the assumption that the effective strain in the rubber phase of a filled vulcanizate at any stress is equal to the strain in the base vulcanizate without filler at the same stress. In the present study all the vulcanizates were subjected to the same initial

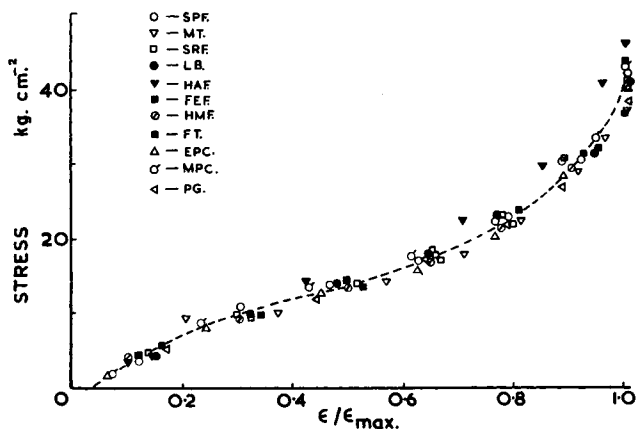


Fig. 8. Stress vs. normalized strain (ϵ/ϵ_{\max}) for NR second extension (curves 3).

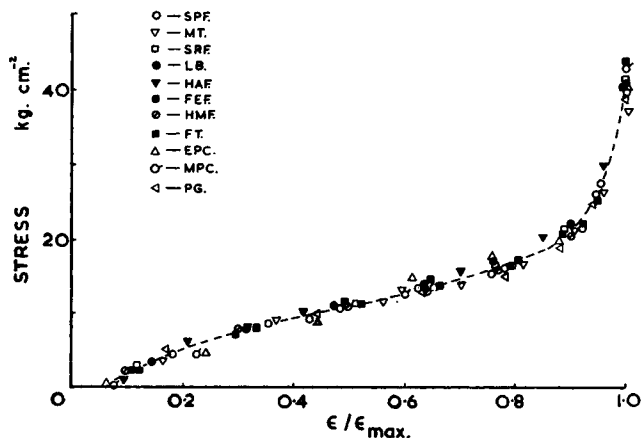


Fig. 9. Stress vs. normalized strain (ϵ/ϵ_{\max}) for NR second retraction curve (curves 4).

maximum stress and therefore to the same effective maximum strain. It should therefore be possible to normalize the strain data obtained on both gum and filler-loaded vulcanizates by the use of the factor ϵ/ϵ_{\max} , where ϵ is the measured extension and ϵ_{\max} is the maximum extension corresponding to the same initial maximum stress.

Figure 8 shows stress-strain curves obtained during second extension cycles plotted with this normalized strain axis for both gum and filler-

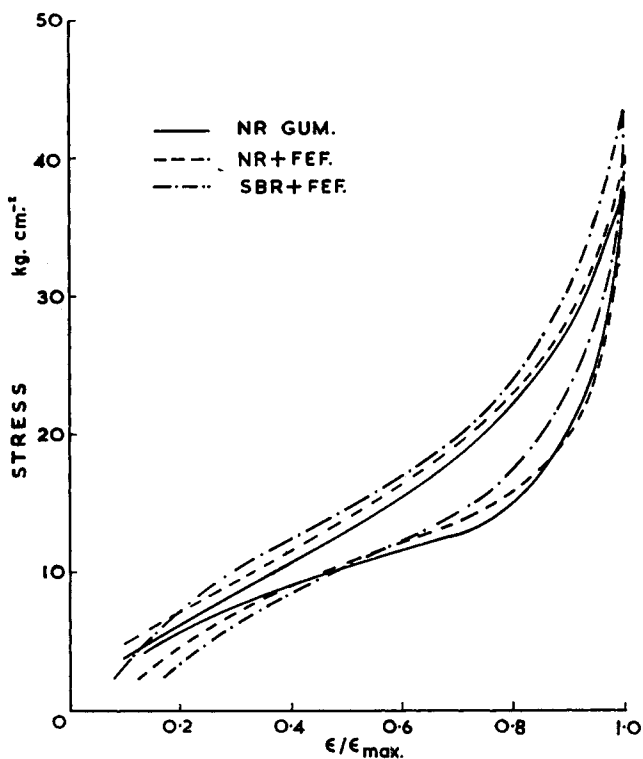


Fig. 10. Stress vs. normalized strain (ϵ/ϵ_{\max}), showing comparisons between NR gum, NR + FEF (60 phr) and SBR + FEF (60 phr) (FEF = fast extrusion furnace black).

loaded natural rubber vulcanizates. It can be seen that the curves are very similar for all the vulcanizates studied and the results confirm the general applicability of the use of a strain-amplification factor to describe the stress-strain behavior of filler-loaded vulcanizates. Figure 9 shows normalized plots obtained during retraction (curve 4), and again a single curve described the behavior of all the vulcanizates.

Similar results were obtained with SBR filler-loaded vulcanizates, and showed a close resemblance to those obtained with NR and given in Figures 8 and 9. The NR and SBR hysteresis loops are compared more directly in Figure 10, which plots the second hysteresis cycle (stress versus normalized extension, curves 3 and 4) for the gum NR and for both the FEF-filled NR and SBR vulcanizates. The similarity of these three hysteresis loops indicates that the second hysteresis loop of a rubber containing 60 phr of a reinforcing black is similar in shape to the hysteresis loop of a gum natural rubber, and that at these moderate extensions the presence of black does not increase the hysteresis above that of the gum rubber.

With less reinforcing fillers, the hysteresis loop in SBR is smaller than that of both the NR gum vulcanizates and the SBR vulcanizates containing

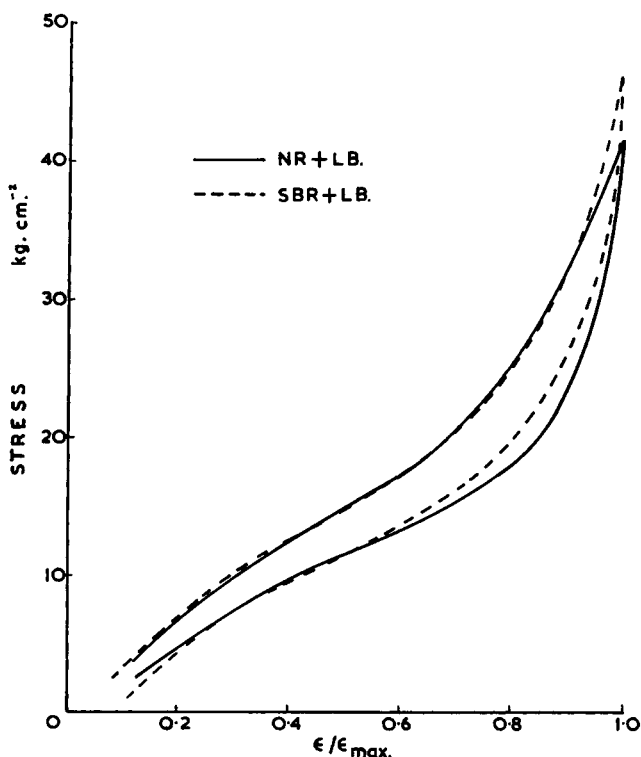


Fig. 11. Stress vs. normalized strain (ϵ/ϵ_{\max}), showing comparisons between NR + lampblack (60 phr) and SBR + lampblack (60 phr).

reinforcing fillers. This is illustrated in Figure 11, which compares hysteresis loops obtained for 60 phr lampblack in NR and SBR vulcanizates, and which shows a smaller loop area for the SBR vulcanizate. No explanation for this is offered in this investigation except to point out that the reinforcing filler in SBR introduces a hysteresis similar in magnitude to that of a pure gum NR vulcanizate.

Repeated Stress-Extension Cycling on Gum Rubber

Although most of the stress softening occurs during the first cycle of stressing, further stress softening occurs during repeated cycling, and Figure 12 shows the change in the stress levels at a particular strain during repeated cycling. For instance, the maximum stress drops from an initial value of 90 to 44 kg./cm.² when strained repeatedly to 480% extension.

Hysteresis

Hysteresis is known to play an important role in tear, heat build up, and in tensile and abrasion properties, and it has often been claimed that one of

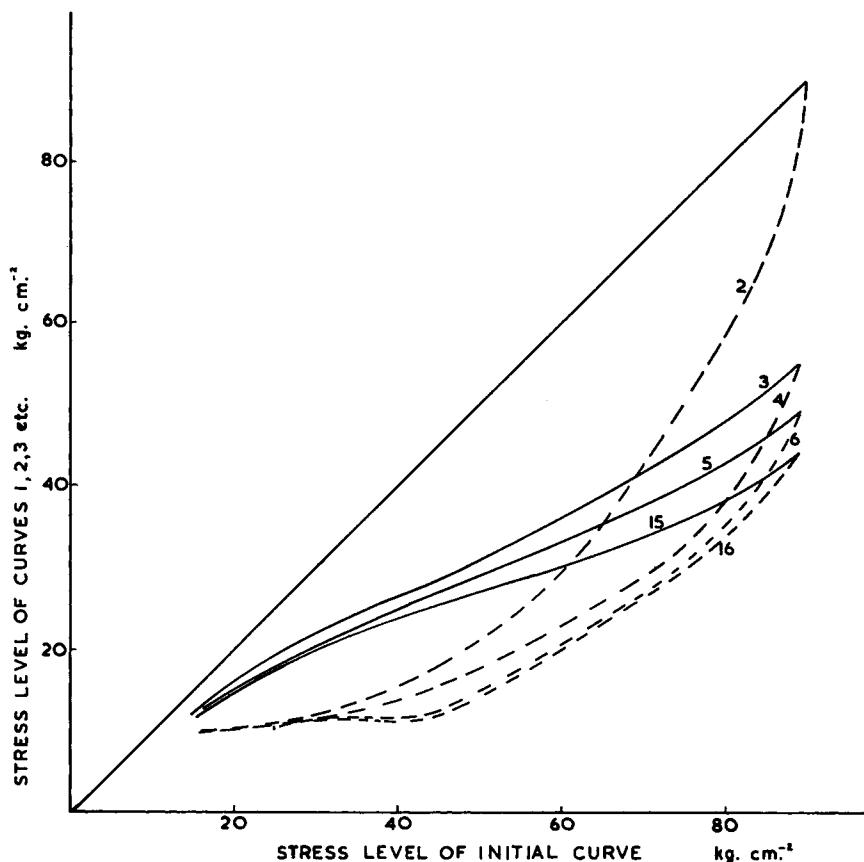


Fig. 12. Comparison of stress levels for repeated cycling of gum NR vulcanizate.

the major effects of carbon black in rubber is to introduce hysteresis. This present study and the earlier studies by Payne⁹ on dynamic properties indicate that although different carbon black may introduce very different amounts of hysteresis at small deformations, these differences largely disappear at moderate or large deformations when comparisons are made under conditions of constant stress. It is now possible to distinguish four main types of hysteresis in the stress-strain behavior of filled vulcanizates as follows:

(1) Hysteresis due to breakdown of carbon black chains, agglomerates of chains, and carbon black aggregates: hysteresis due to this cause is only apparent at low stresses.

(2) Hysteresis due to stress softening of pure gum vulcanizates: this is also present in filled vulcanizates and is known as the Mullins effect. It has been shown in this investigation that the behavior of both gum and filled vulcanizates show similar behavior in this respect.

(3) Hysteresis at large extensions associated with orientation and closer association of the rubber chains: with natural rubber this is pronounced and shows itself as crystallization.

(4) Hysteresis due to the viscoelastic behavior of rubber.

The results of this study show that after an initial stressing there is little additional contribution to stress-strain hysteresis introduced by carbon black.

SUMMARY

Considerable stress softening occurs in both gum and filler loaded vulcanizates and when compared at the same stress the extent of softening is similar in both gum and filled vulcanizates. It thus appears that the softening process is mainly due to the rubber phase alone. Apparent differences between the stress-strain hysteresis loops of gum and filler-loaded vulcanizates are traced to an increase in the effective strain in the rubber phase resulting from the presence of black. This is discussed in Part I of this series.¹⁰

The mechanism of stress softening in gum vulcanizates is not well understood. Possible sources include (1) breaking and remaking of crosslinks during extension, (2) residual local orientation of network chains persisting after recovery, and (3) breaking of network chains.

APPENDIX

Compounding Details and Vulcanizing Conditions

Natural rubber: RSS1 100; ZnO 3.5; St. A 2.5; PBN 1; sulfur 2.5; CBS 0.6; Dutrex R 5; with 60 parts of one of the following carbon blacks, SRF, MPC, FEF, ISAF, HAF, EPC, FT, MT, SPF, LB, or with HAF 20, HAF 40, HAF 60, HAF 80. Vulcanized for 40 min. at 140°C.

SBR: Krylene NS, 100; ZnO 3.5; St. A 2.5; PBN 1; sulfur 2; CBS 1.1; Dutrex R 5; with 60 parts of one of the following carbon blacks, SRF, MPC, FEF, ISAF, HAF, EPC, FT, MT, SPF, LB, HAF. Vulcanized for 40 min. at 140°C.

The authors wish to acknowledge the assistance of Mr. R. Whittaker in obtaining and analyzing the experimental measurements. This work forms part of the program of research of the Natural Rubber Producers' Research Association.

References

1. Mullins, L., *J. Rubber Res.*, **16**, 275 (1947).
2. Mullins, L., *J. Phys. Colloid Chem.*, **54**, 239 (1950).
3. Blanchard, A. F., and D. Parkinson, *Ind. Eng. Chem.*, **44**, 799 (1952).
4. Blanchard, A. F., and D. Parkinson, *Proc. 2nd. Rubber Technol. Conf. (London)*, **414** (1948).
5. Bueche, F., *J. Polymer Sci.*, **4**, 107 (1960); *ibid.*, **5**, 271 (1962).
6. Harwood, J. A. C., L. Mullins, and A. R. Payne, *J. Polymer Sci.*, **B3**, 119 (1965).

7. Brennan, J. J., T. E. Jermyn, and M. F. Perdigas, paper presented at Division of Rubber Chemistry, American Chemical Society, Detroit, Michigan, April 1964.

8. Mullins, L., in *The Chemistry and Physics of Rubber-Like Substances*, L. Bateman, Ed., Maclaren, 1963, Chap. 11.

9. Payne, A. R., *Trans. Inst. Rubber Ind.*, **40**, T135 (1964); *J. Appl. Polymer Sci.*, **7**, 873 (1963); *J. Appl. Polymer Sci.*, **57**, 368 (1962).

10. Mullins, L., and N. Tobin, *J. Appl. Polymer Sci.*, **9**, 2993 (1965).

Résumé

Une considérable diminution de tension effect Mullins se présente tant dans la gomme que dans les vulcanisats de caoutchouc naturel et de SBR. Lorsque la gomme et les vulcanisats chargés sont soumis à la même force, l'importance du ramollissement est identique. On montre que cette diminution de tension est essentiellement due à des changements de la phase caoutchouteuse dans le vulcanisat chargé; on relie cette diminution à celle du vulcanisat gommeux par l'intermédiaire du facteur d'amplification de tension discuté dans la première partie par Mullins et Tobin.

Zusammenfassung

Eine beträchtliche Spannungserweichung (Mullins-Effekt) tritt sowohl bei gefüllten als auch bei ungefüllten Naturkautschuk- und SBR-Vulkanisaten auf. Bei gleicher Spannung ist das Ausmass der Erweichung bei gefüllten und ungefüllten Vulkanisaten ähnlich. Die Spannungserweichung wird hauptsächlich durch Veränderungen der Kautschukphase bei gefüllten Vulkanisaten hervorgerufen und kann zu derjenigen von ungefüllten Vulkanisaten mittels des in Teil 1 von Mullins und Tobin diskutierten Dehnungsverstärkungsfaktors in Beziehung gesetzt werden.

Received April 9, 1965