

Stress Softening in Natural Rubber Vulcanizates. Part V. The Anomalous Tensile Behavior of Natural Rubber

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Synopsis

Stress-strain cycling of natural rubber to high strains produces greater softening than amorphous rubbers, but only if the force on the sample is relaxed below a certain value during the cycle. This phenomenon, attributed to crystallization shows why nonrelaxing tests give a longer fatigue life than relaxing tests.

INTRODUCTION

Previous publications¹⁻⁷ have described the stress softening phenomenon resulting from repeated strain cycling of unfilled and reinforced natural rubber (NR) vulcanizates and from reinforced styrene-butadiene rubber (SBR). Other publications^{8,9} have reported measurements of the energy loss, or hysteresis, in the first strain cycle of several rubbers, and this has been related to the energy density or work done in extending the rubber. This paper describes differences between the tensile behavior of NR vulcanizates and those of amorphous rubbers and discusses how these differences are reflected in strength and fatigue behavior.

EXPERIMENTAL

The tensile tests were performed on ring specimens cut from a sheet 0.25 cm. thick by means of a rotating cutter. The inner diameter of the rings was 2.75 cm. and the wall thickness was 0.15 cm. The samples were extended on an Instron tensile tester at 10 cm./min.—a strain rate of approximately 200%/min.

RESULTS

Tensile Cycling

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 smaller force. Most of the softening occurs during the first deformation cycle, and after a few stressing cycles a steady state is reached.

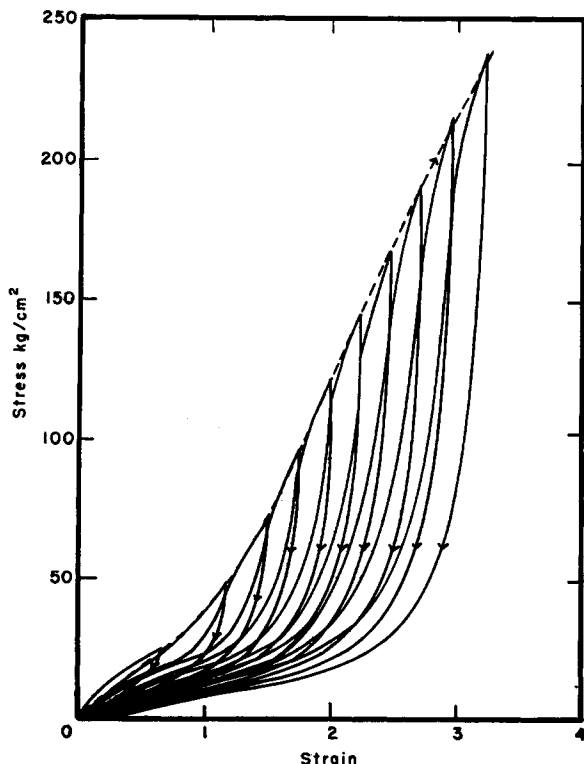


Fig. 1. Stress-strain loops for SBR + 60 phr ISAF carbon black. Dotted line, the stress-strain curve for a new sample.

In filled rubbers this phenomenon is termed "The Mullins Effects" and has been the subject of numerous investigations^{1-7,9-14} but Harwood, Mullins, and Payne^{3,4} have also shown that considerable softening occurs in gum vulcanizates as well as in black-loaded rubbers. Stress softening is now attributed to the non-affine deformation of network junctions or aggregates attached to highly extended short chains.

A feature of the "Mullins Effect" is that when the second and subsequent stressing cycles are examined above and below the maximum strain reached during the first extension, stress softening is observed only at elongations less than the previous maximum extension; at greater elongations the behavior of rubber is closely similar to that of rubber not previously extended. It has been assumed hitherto that when extensions exceed the previous maximum extension, the stress-extension curve coincides with that obtained from a fresh sample extended initially. This assumption is valid for an SBR vulcanizate containing filler such as 60 phr ISAF black, and for gum or filled NR vulcanizates at low extensions, but it is no longer valid at high extensions.

Figure 1 is a plot of repeated stress versus strain cycles for a SBR + 60 phr ISAF vulcanizate, each succeeding stress-strain cycle being stressed to

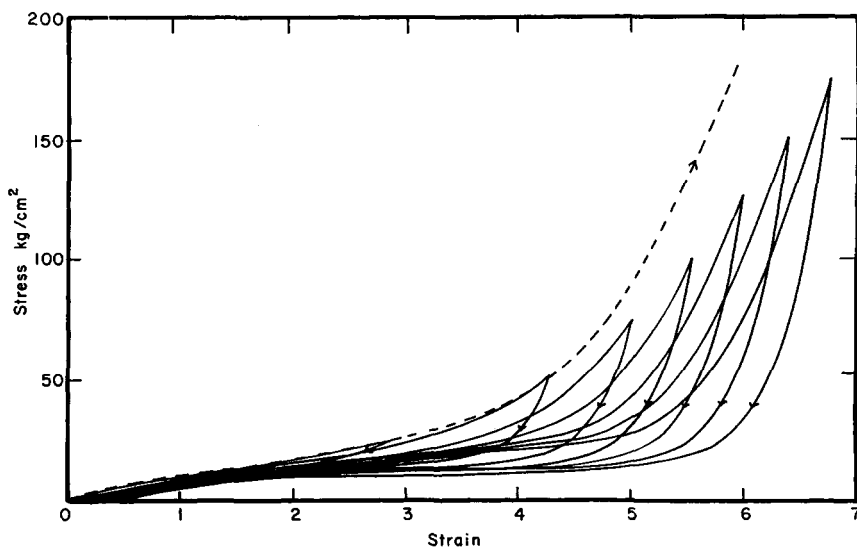


Fig. 2. Stress-strain loops for NR gum vulcanizate. Dotted line, the stress-strain curve for a new sample.

a higher level in incremental steps. Also plotted as the dashed line on Figure 1 is the stress-strain curve of a fresh sample extended to break on initial stressing. The coincidence of the maximum of the loops with that of the original curve is excellent, and the assumptions underlying this feature of the Mullins Effect is justified for this system.

Figure 2 shows the stress-strain loops of gum NR subjected to the same stressing program as the SBR + 60 ISAF vulcanizate discussed above. This time there is no coincidence between the maximum portions of the loops and the original stress-strain curves above about 400% extension. Figure 3 shows the results for a 60 phr ISAF filled NR vulcanizate and the lack of agreement above 200% extension is again apparent.

To illustrate the difference in behavior between NR and SBR in another way, a stressing sequence was carried out in which the rubber was reversed at a moderate stress, retracted to zero stress and then subsequently re-extended to break. This sequence of stress-strain cycling was then compared with the stress-strain curve obtained from a fresh sample of rubber, Figure 4c, which shows the result for an SBR + 60 ISAF vulcanizate and illustrates how closely the upper portions of the curves agree. In contrast, the results for an NR gum, and a 60 phr ISAF NR vulcanizate are shown in Figures 4a and b; it can be seen that no coincidence of the previously unstretched and the cycled data occurs.

Partially Retracted Cycling

Differences in the tensile behavior of NR and SBR have been ascribed mainly to the ability of NR to crystallize when strained. The influence of

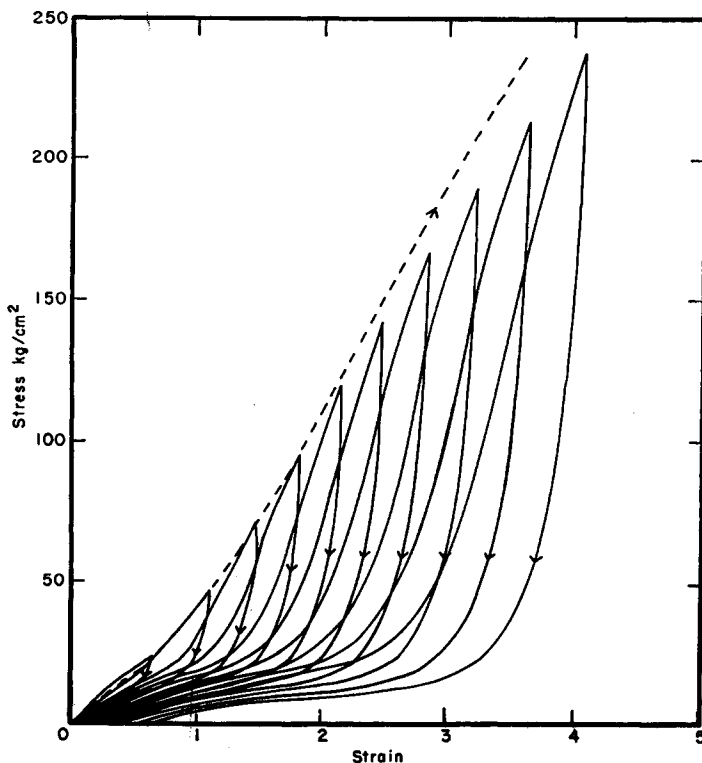


Fig. 3. Stress-strain loops for NR + 60 phr ISAF carbon black. Dotted line, the stress-strain curve for a new sample.

crystallinity on stress softening can be illustrated by the nature of the stress-strain loops when the retraction curve is not returned to zero stress, but cycled between the previous maximum stress and some lower stress. Figure 5 gives results of experiments carried out on NR + 60 ISAF black vulcanizate. Figure 5a shows that, for a small reduction in stress from the maximum, only a very small increase in maximum extension and an extremely small hysteresis loop was produced on reextension to the maximum stress. In Figure 5b, the increase in extension after an 85% reduction in stress is still very small, but when the rubber is retracted to only about 5% of the original stress, Figure 5c, the next stressing produces a marked increase in the maximum extension of the rubber and a large hysteresis loop.

A direct comparison of the behavior of three rubbers is illustrated in Figure 6 where the increase in extension divided by initial extension, $\Delta L/L$, is plotted against the reduction in stress divided by initial maximum stress, $\Delta S/S$, for the series of the curves shown in Figure 5. (ΔS and ΔL are defined in Figure 5c.) The SBR black vulcanizate shows a small linear increase of $\Delta L/L$ with $\Delta S/S$ over the whole range of stress cycling

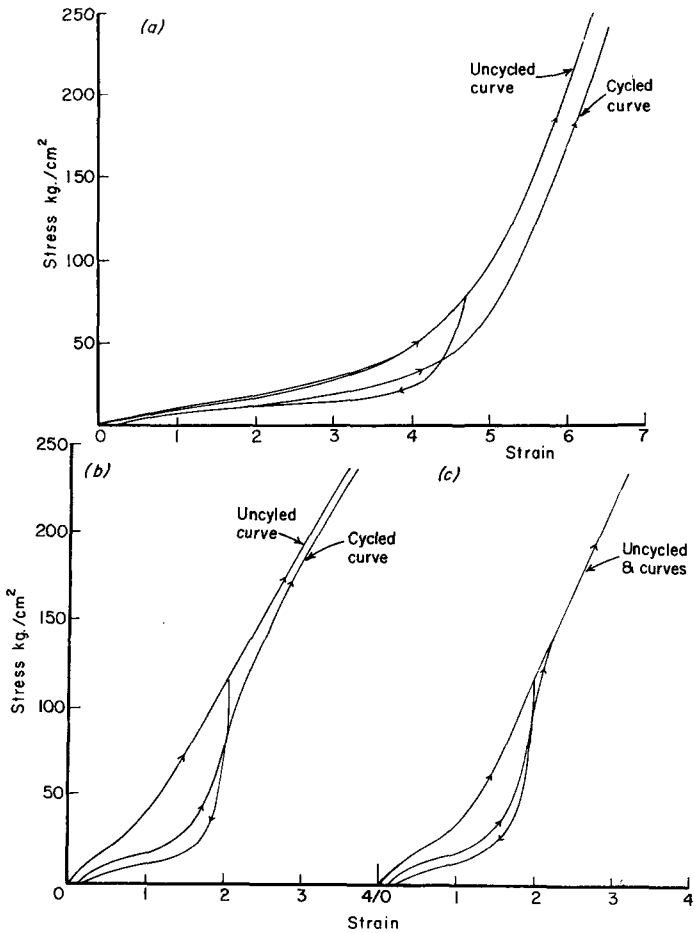


Fig. 4. Stress-strain curves for uncycled and cycled samples of: (a) NR gum vulcanizate; (b) NR + 60 phr ISAF; and (c) SBR + 60 phr ISAF carbon black.

amplitude; this reflects the viscoelastic creep of the polymer. The curves for the NR gum and black vulcanizates show a very large increase in $\Delta L/L$ when $\Delta S/S$ is above 0.9. This large increase in $\Delta L/L$ for NR reflects the effect of crystallites melting when $\Delta S/S$ is greater than 0.9 and the reformation of the crystallites in a *stress-softened* rubber as the stress is again increased.

The marked decrease in the fatigue life of a rubber sample which is allowed to retract to zero stress or strain has been recorded many times in the literature and has been the subject of close study in fatigue and cut growth measurement by Lindley, Thomas, Lake, and co-workers.¹⁵⁻¹⁷ The improvement of fatigue life by cycling under nonrelaxing conditions is far more marked for natural rubbers than for other noncrystallizing rubbers. The behavior of NR is illustrated in Figure 7, which shows that about 100

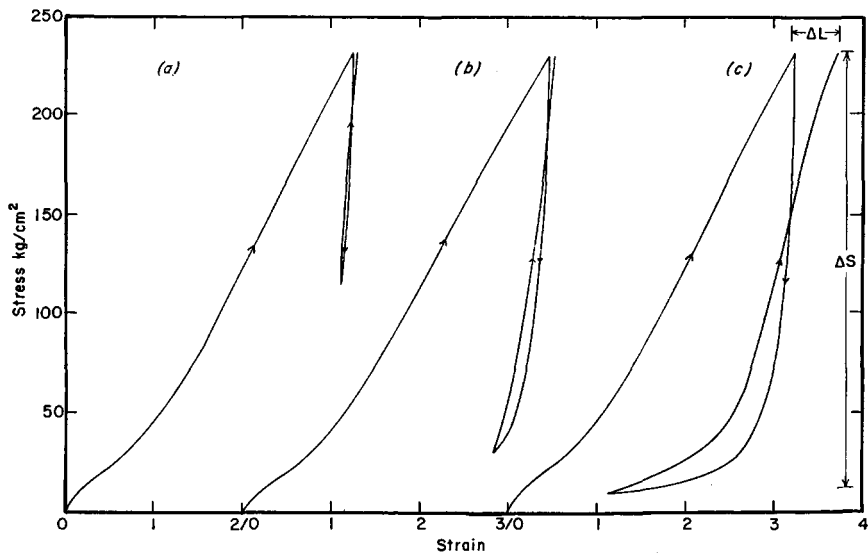


Fig. 5. Stress-strain loops demonstrating the pattern of experiments for NR + 60 phr ISAF carbon black.

cycles are required to bring about failure in NR gum when $\Delta S/S$ is 0.5. (All of the cycles have not been shown in the figure as the hysteresis loop is small and the curves cannot be differentiated.) In marked contrast, Figure 7b shows that failure in the rubber subjected to the same maximum stress occurred in the second cycle when $\Delta S/S = 1$ even though a high mean stress was maintained on the rubber which was not cycled to zero stress.

Energy Measurements at Break

Grosch, Harwood, and Payne^{8,9} have demonstrated that for amorphous polymers the energy density at break (E_b) is related to the hysteresis at break (H) by the general relationship

$$E_b = KH^{2/3} \quad (1)$$

This is illustrated in Figure 8 which shows E_b against H for a noncrystallizing isomerized natural rubber (INR) at several temperatures on a double logarithmic scale and the straight-line relationship is shown. Also plotted on the same graph are the results for an NR gum vulcanizate; these do not obey eq. (1) except at very high temperatures ($>140^\circ\text{C}$.) and temperatures below about 60°C .

This anomalous behavior is due to the ability of NR to crystallize at high strains. Between 60 and 140°C . the bulk of the NR remains nearly amorphous, but the highly strained region around the inherent flaws in the sample gives rise to crystallinity, thus causing the NR to show less hysteresis at break than would be expected. Outside this temperature

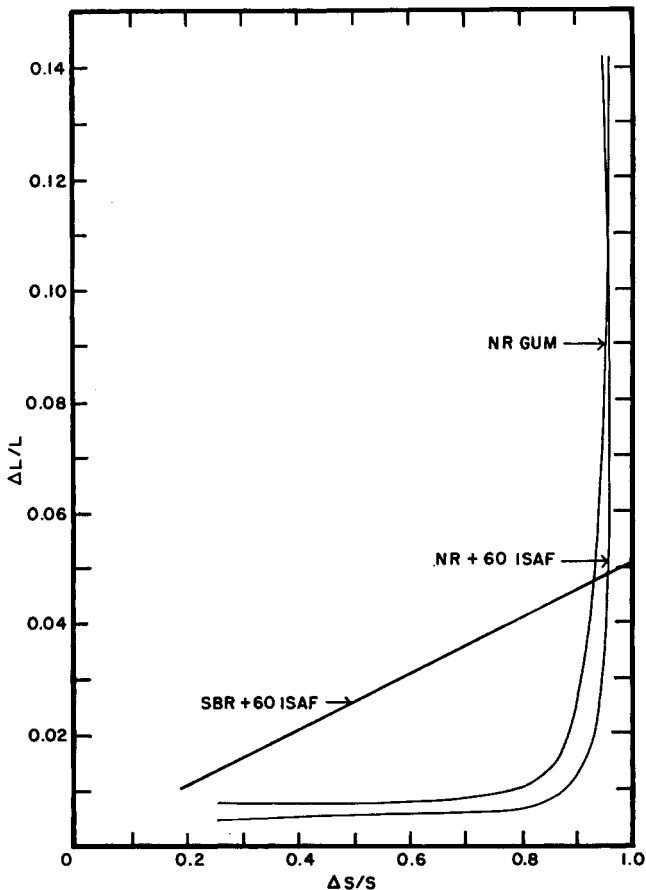


Fig. 6. $\Delta L/L$ vs. $\Delta S/S$ for NR gum, NR + 60 phr ISAF, and SBR + 60 phr ISAF carbon black.

range the rubber is either predominantly crystalline (lower temperature) or predominantly amorphous (higher temperature).

Figure 9 shows a typical set of tensile results for the NR vulcanizate tested at 100°C ., a temperature at which the energy density at break values departed seriously from those observed for the amorphous rubbers. On fresh samples, stressed to break, the tensile stress was about 44 kg./cm.^2 . However, with new samples stressed almost to break, retracted and subsequently stressed to failure, the tensile stress at break increased to 70 kg./cm.^2 , a value more than 50% higher. This behavior was only observed at temperatures between 60 and 140°C . These results illustrate that the failure conditions in a crystallizing rubber are not easily or simply related to the stored energy and hysteresis conditions in the bulk rubber. It is known that higher extensions around the flaws can give rise to local crystallinity at overall extensions insufficient for crystallinity to occur in the bulk of the rubber.

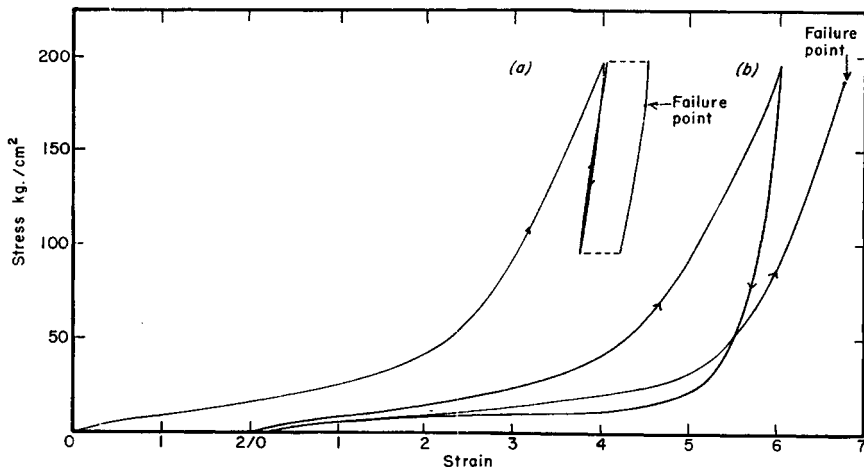


Fig. 7. Fatigue stress-strain loops for NR gum vulcanizate: (a) $\Delta S/S = 0.5$, and 100 cycles to failure; (b) $\Delta S/S = 1.0$, failure occurs on the second extension cycle.

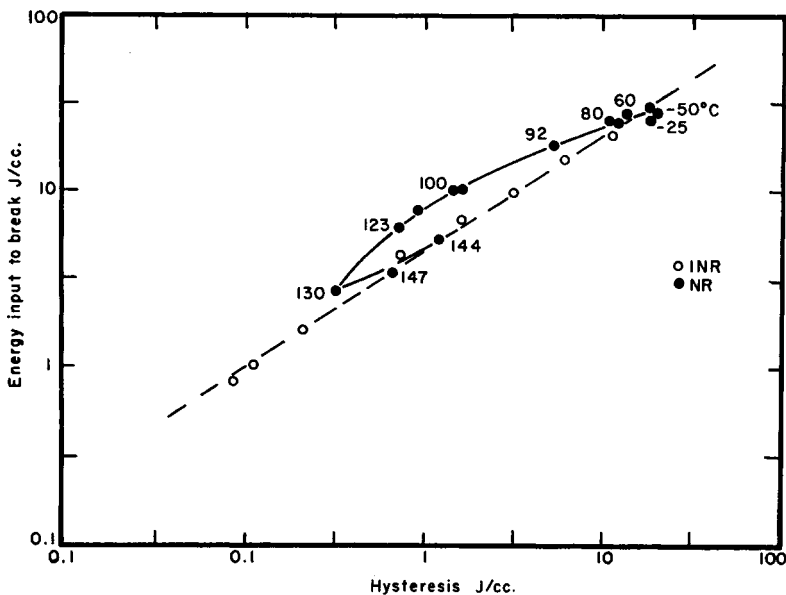


Fig. 8. Energy input to break E_b vs. hysteresis H for: (○) INR and (●) NR, over a temperature range of -50 to $+150^\circ\text{C}$.

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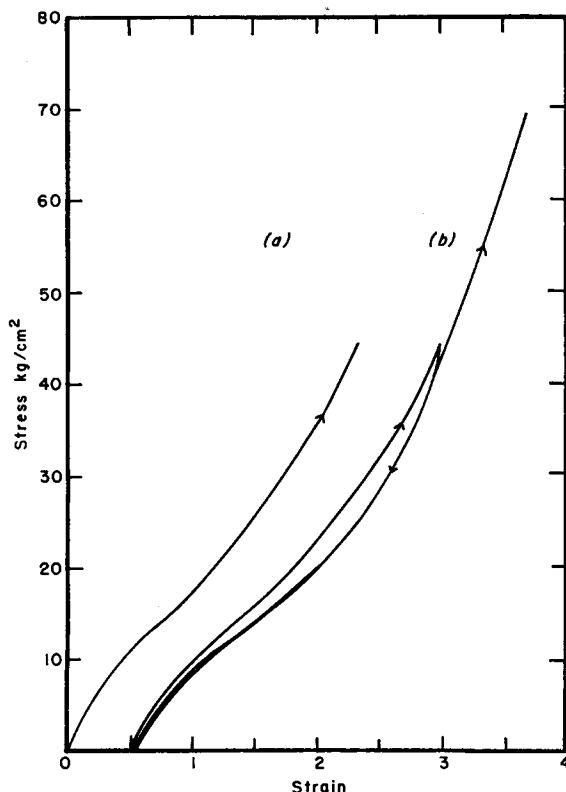


Fig. 9. Stress-strain curves for NR gum vulcanizate at 100°C.: (a) a new sample extended to near break, then retracted and subsequently extended to break.

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Résumé

Les cycles tension-étirement du caoutchouc naturel soumis à de fortes tensions produisent un ramollissement plus élevé que celui de caoutchoucs amorphes, mais uniquement si la force exercée sur l'échantillon est relaxée endessous d'une certaine valeur au cours du cycle. Ce phénomène attribué à la cristallisation montre pourquoi des tests effectués en absence de relaxation donnent une durée de fatigue plus longue que les tests avec relaxation. Un autre résultat de la cristallisation en cours de cycle est une amélioration de la force de tension.

Zusammenfassung

Beim Durchlaufen eines Spannungs-Dehnungszyklus zu hohen Verformungen tritt bei Naturkautschuk eine grössere Erweichung auf als bei amorphen Kautschukarten, aber nur dann, wenn während des Zyklus eine Relaxation der auf die Probe wirkenden Kraft unterhalb eines bestimmten Wertes eintritt. Diese, einer Kristallisation zugeschriebene Erscheinung zeigt, warum Tests ohne Relaxation eine höhere Ermüdungsdauer liefern als Tests mit Relaxation. Eine weitere Folge der Kristallisation während des Zyklus ist eine Erhöhung der Zugfestigkeit.

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