Stress Softening in Natural Rubber Vulcanizates. Part IV. Unfilled Vulcanizates

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Synopsis

Stress softening (Mullins effect) is observed in gum natural rubber vulcanizates. The magnitude of this softening is similar to that in carbon black-filled vulcanizates. The amount of stress softening is slightly greater in vulcanizates cured to produce predominantly polysulfide crosslinks than in those containing monosulfide or carbon–carbon crosslinks. The total recovery of stress softening in the vulcanizates containing monosulfide or carbon–carbon crosslinks suggests that the phenomenon is attributable to a quasi-irreversible rearrangement of molecular networks due to localized nonaffine deformation resulting from short chains reaching the limit of their extensibility. This nonaffine deformation results in a displacement of the network junctions from their initial random state.

INTRODUCTION

Previous papers[1-3] have shown that the stress softening in unfilled vulcanizates of natural rubber is similar in magnitude to the stress softening observed in carbon black-loaded rubbers. This paper reports further studies of the stress softening in unfilled vulcanizates to throw light on the nature of the mechanisms responsible for the effect. A series of NR vulcanizates, differing in amount and type of crosslinking, were examined. The types of crosslink studied were polysulfide, monosulfide, and carbon–carbon.

EXPERIMENTAL RESULTS

The formulations of the rubber compounds used in this study are listed in the Appendix.

Figure 1 shows the stress–strain curves for an unfilled NR vulcanizate during the first and a number of subsequent cycles to the same extension. The rate of extension was 200%/min. The data presented in Figure 1 show that most of the stress softening occurs during the first cycle, but that there is some further softening even up to the eighth cycle, by which time the initial maximum stress of 90 kg./cm.^{2} has been reduced to 40 kg./cm.^{2}.

If stress softening is defined as the reduction in stress between the first and second stressings at the maximum extension, then Figure 2 shows that the stress softening increases with the maximum stress to which the rubber
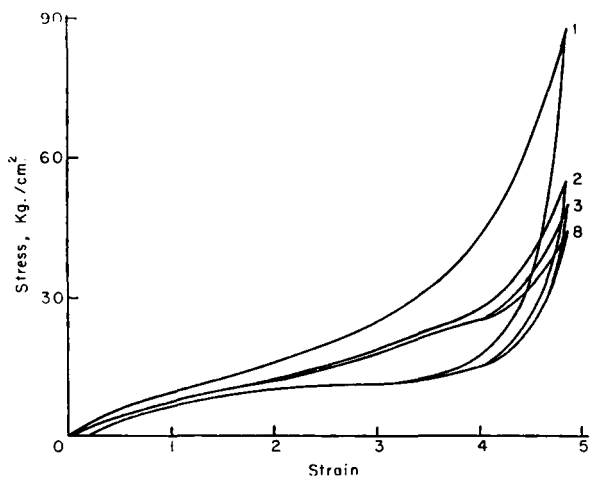
Fig. 1. Effect of successive stress–strain cycles on an unfilled NR vulcanizate. Cycles numbered on curve.
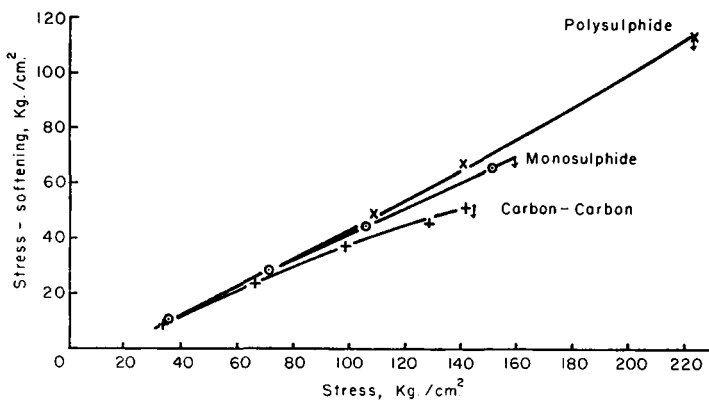

Fig. 2. Comparison of stress softening for vulcanizates: types A, B, and C with the same initial modulus of 9 kg./cm.^{2}.

was subjected before the rubber was retracted and subsequently re-extended. Figure 2 also shows that the amount of stress softening in three different types of vulcanizate crosslinked to possess the same Young's modulus as defined by the Martin, Roth, and Stiehler equation, is appreciable and similar in magnitude. However the polysulfide vulcanizate is stress-softened slightly more than the monosulfide while the carbon–carbon vulcanizate experiences the least, but still appreciable, degree of stress softening.

It is of interest to note that the strengths of the vulcanizates rank in the same order as the degree of stress softening experienced by the three types of vulcanizate, i.e., polysulfide is stronger than monosulfide which is stronger than the carbon–carbon crosslinked rubber.

Recovery of Stress Softening

It has been observed that prestressed natural rubber samples left relaxed at ambient temperature for several days regained very little of their reduced stress. However, as some recovery was evident, means of accelerating and increasing it were examined. This examination of possible recovery was undertaken to assess the stability of the softening effect and to throw light on the mechanisms responsible.

Recovery by Heating. Rubber samples from all three vulcanizing systems which had undergone two strain cycles to a high initial stress were heated *in vacuo* at 100°C. for 24 hr. and then subjected to two further complete stressing cycles. Figure 3 shows the initial and second stressing curves for two type C rubber vulcanizates of different crosslink density. The first stressing curves after heat treating the samples are given by the broken lines, and it is clear that almost complete recovery has occurred. In contrast, the polysulfide vulcanizates A, which suffered the largest stress softening, only partly recovered their initial moduli (Fig. 4). Vulcanizates B gave results intermediate to the other two vulcanizates, showing substantial but not complete recovery (Fig. 5).

Recovery by Swelling. Another method of determining whether stress softening is temporary or permanent in nature was to swell the stress-softened rubber in a convenient solvent (benzene), and, after equilibrium swelling had been reached, to evaporate off the solvent *in vacuo*. Figures 6a, 6b, and 6c show examples of the stress–strain curves for vulcanizates A, B, and C, respectively, both for the initial sequence of stressing curves (1d and 2d), and for the samples subjected to the solvent treatment (1r
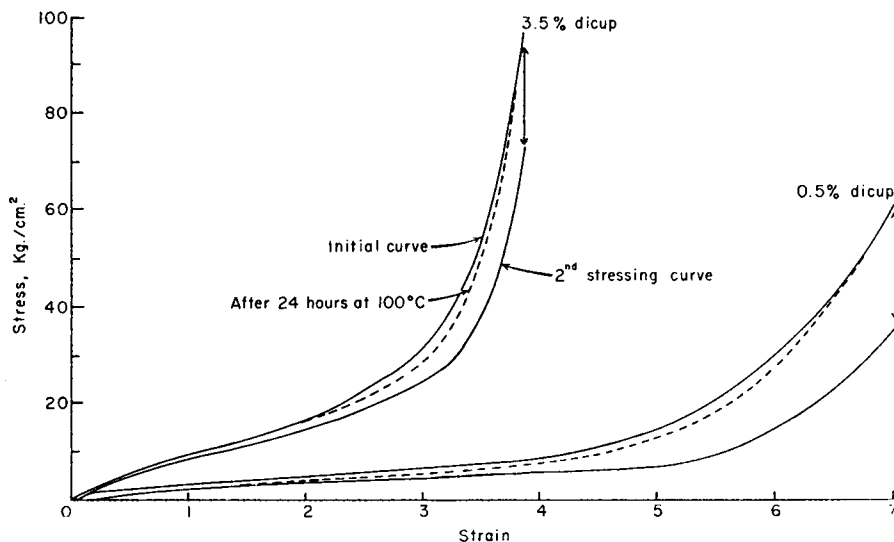

Fig. 3. Recovery of stress softening by heat treatment for type C vulcanizates.

and 2r).   In the case of the efficient vulcanization systems, B, which produce predominantly monosulfide crosslinks, and the peroxide system, C, producing carbon–carbon crosslinks, complete recovery of the stress-softening effects has been brought about by swelling.   In contrast, only partial recovery is observed in the polysulfide-crosslinked rubbers (Fig. 6a).
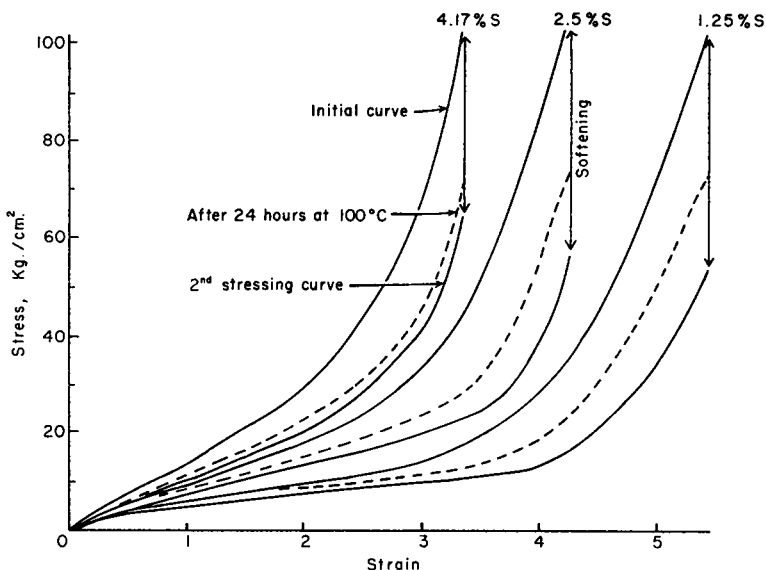

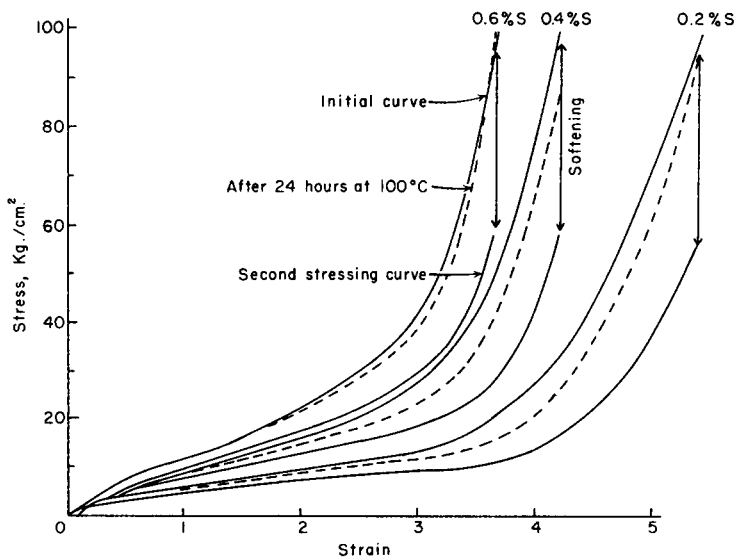Fig. 4. Partial recovery of stress softening by heat treatment for type A vulcanizates.

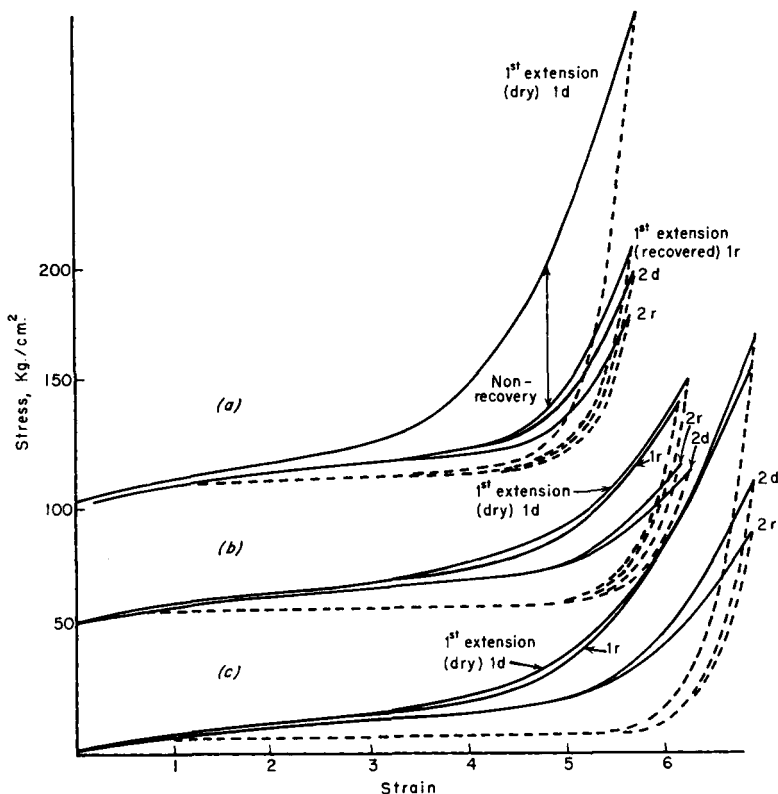Fig. 5. Partial recovery of stress softening by heat treatment for type B vulcanizates.

Fig. 6. Recovery of stress softening by swelling treatment: (a) type A, (b) type B, (c) type C vulcanizates. Curves (a) and (b) displaced vertically for convenience of presentation.

Set Measurements

Stress softening is accompanied by tension set, the measurement of which affords additional information on the mechanisms involved. Figure 7, for instance, shows a three-dimensional plot of the percentage set (24 hr. after stressing) for polysulfide-crosslinked vulcanizates (A) against the initial stress and the modulus of the vulcanizate. For low modulus rubbers the amount of set is extremely large due to plastic flow. In the rubbers with the higher degrees of crosslinking, the set varies little with modulus but increases substantially with stress level. Figures 8 and 9 show similar results for vulcanizates B and C. Here the degree of set is considerably smaller at comparable stress and modulus levels than for the polysulfide-crosslinked vulcanizates (A).

After prestressing, the vulcanizates were swollen in benzene for 24 hr. and subsequently dried. Then the sets remaining in the rubbers after this treatment were measured, and the results are shown in Figure 10 for the polysulfide vulcanizates A. An appreciable amount of set persisted in these
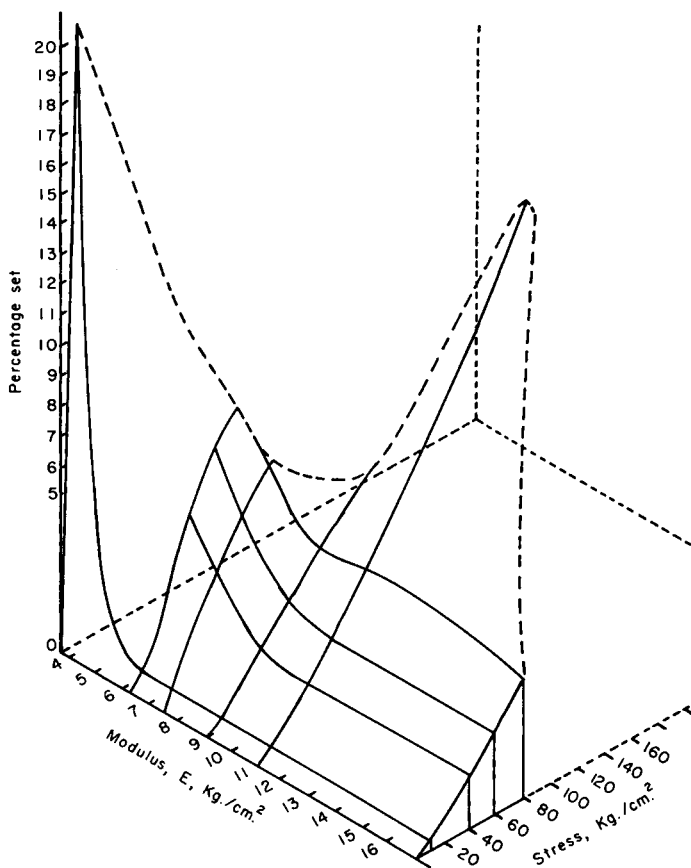
Fig. 7. Three-dimensional plot of percentage set against initial stress and modulus for type A vulcanizates.

rubbers, whereas with vulcanizates B and C, the swelling treatment reduced the set to zero. This behavior parallels the stress-softening effects discussed above.

CONCLUSIONS

The experimental data presented in this paper confirm that unfilled vulcanizates of natural rubber can be stress-softened in a similar manner to that well-documented phenomenon in filler-loaded vulcanizates known as the Mullins effect.[4] The amount of stress softening is slightly greater in the vulcanizates cured to produce predominantly polysulfide crosslinks than in those containing monosulfide or carbon–carbon crosslinks, but the amount of stress softening in all three vulcanizate types is appreciable. The stress softening in monosulfide- and carbon–carbon-crosslinked rubbers can be completely recovered by swelling in benzene liquid and then drying, but only partial recovery of these effects was obtained in the polysulfide-crosslinked vulcanizates. The stress-softening mechanism is attributed to

quasi-irreversible rearrangement of molecular networks due to localized nonaffine deformation resulting from short chains reaching the limit of their extensibility. This nonaffine deformation results in a displacement of the network junctions from their initial random state.
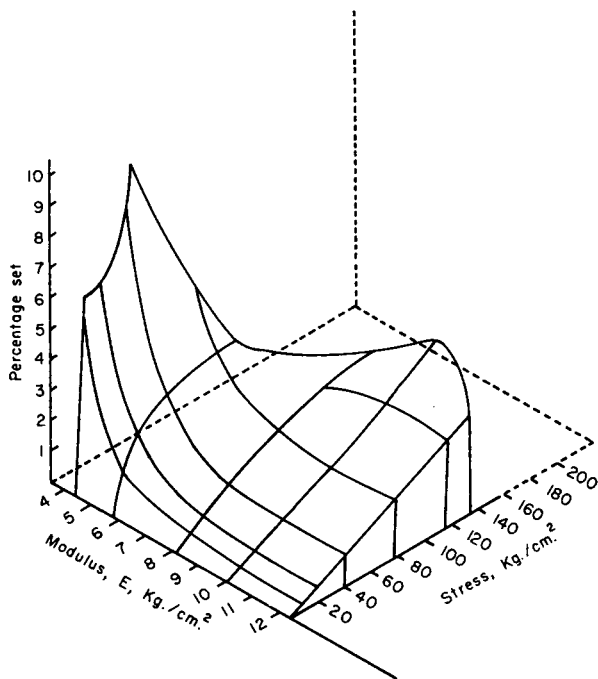

Fig. 8. Three-dimensional plot of percentage set against initial stress and modulus for type B vulcanizates.
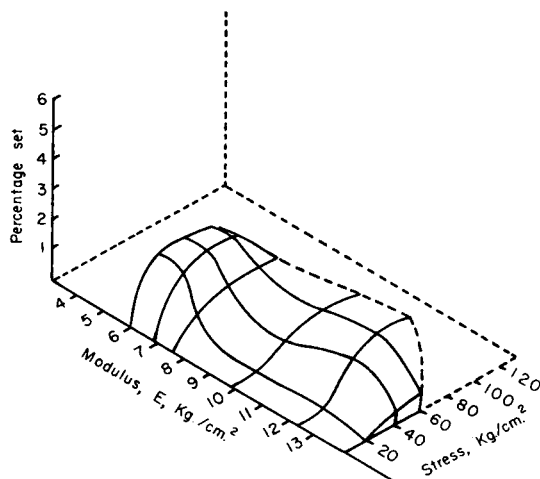

Fig. 9. Three-dimensional plot of percentage set against initial stress and modulus for type C vulcanizates.
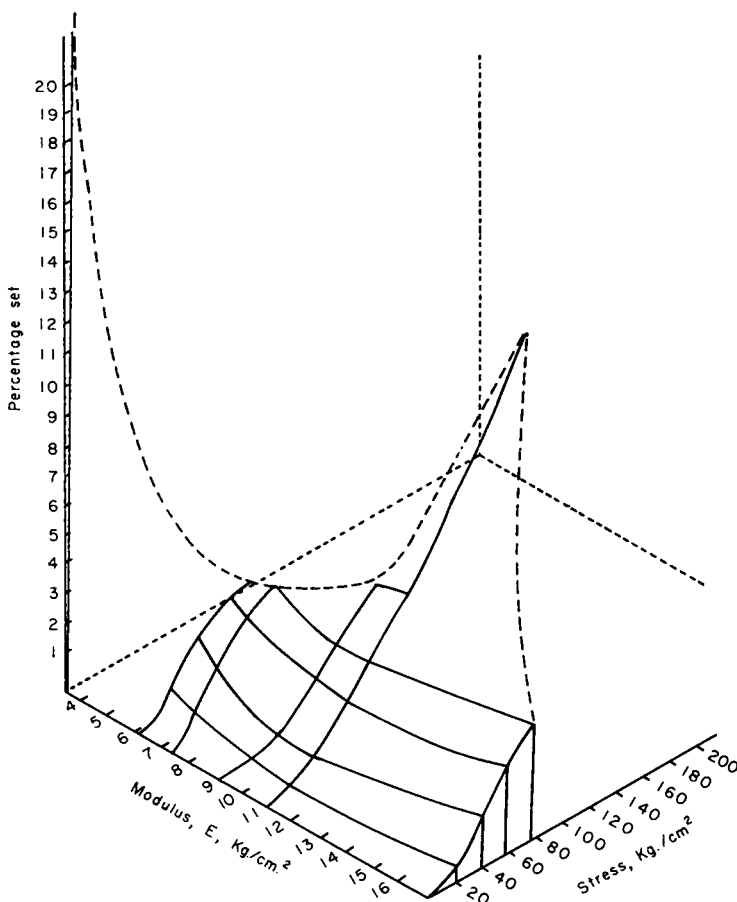
Fig. 10. Residual set after solvent treatment for type A vulcanizates.

The fact that more stress softening and less recovery was observed in polysulfide-crosslinked vulcanizates than in the rubbers with the shorter crosslinks can be confidently explained by the labile nature of the poly-sulfide links, which break under tension and then reform in the stretched condition, resulting in a permanent deformation of the vulcanizate.

APPENDIX

Compounding Details

Type A Vulcanizates (Polysulfide Crosslinks). These were compounded of natural rubber (NR RSS1) (100 parts), ZnO (5 phr), lauric acid (1 phr), together with Accelerator CBS (0.048, 0.12, 0.18, 0.24, 0.4, 0.6, or 1.0 phr), and sulfur (0.2, 0.5, 0.75. 1.0, 1.65, 2.5, or 4.17 phr, respectively). They were cured for 30 min. at 140°C.

Type B Vulcanizates (Monosulfide Crosslinks). These were compounded of NR RSS1 (100 parts), ZnO (5 phr), lauric acid (1 phr), together with Accelerator CBS (1.28, 2.25, 4.5. 6.0, or 9.0 phr) and sulfur (0.08, 0.15, 0.3, 0.4, or 0.6 phr, respectively). They were cured for 120 min. at 140°C.

Type C Vulcanizates (Carbon–Carbon Crosslinks). These were compounded of NR RSS1 (100 parts), ZnO (5 phr), lauric acid (1 phr), together with dicumyl peroxide (0.5, 0.7, 1.0, 1.5, 2.5, 3.5, or 4.5 phr). They were cured for 60 min. at 140°C.

References

1. L. Mullins, J. A. C. Harwood, and A. R. Payne, *J. Polymer Sci. B*, **3**, 199 (1965).

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Résumé

Le ramollissement sous tension (effet Mullins) a été observé pour des vulcanisats de caoutchouc de gomme naturelle. L'importance de ce ramollissement est semblable à celle des vulcanisats chargés avec du noir de carbone. Cette importance du ramollissement sous tension est faiblement plus élevée dans les vulcanisats traitüs et contenant principalement des ponts polysulfures que dans ceux contenant des ponts monosulfurés ou carbone–carbone. Le recourement total de ce ramollissement sous tension au sein de ces vulcanisats contenant des ponts monosulfures ou carbone–carbone suggère que le phénomène est attribuable au réarrangement quasi-irréversible des réseaux moléculaire dû à la déformation locale résultant de ce que certaines chaînes courtes atteignent leur limite d'extensibilité. Cette déformation résulte de déplacements des points de jonctions du réseau au départ de leur état initial statistique.

Zusammenfassung

Die Spannungserweichung (Mullinseffekt) in ungefüllten Naturkautschukvulkanisaten wird untersucht. Die Grösse der Erweichung ist derjenigen in russgefüllten Vulkanisaten ähnlich. Der Betrag der Spannungserweichung ist bei Vulkanisaten, welche vorwiegend unter Bildung von Polysulfidvernetzungen vulkanisiert wurden, etwas grösser als in Vulkanisaten mit Monosulfid- oder Kohlenstoff–Kohlenstoffvernetzungen. Die vollständige Rückbildung der Spannungserweichung bei Vulkanisaten mit Monosulfid- oder Kohlenstoff–Kohlenstoffvernetzung zeigt, dass diese Erscheinung auf eine quasi-irreversible Umlagerung des Molekülnetzwerks durch eine lokalisierte, nichtaffine, durch die Erreichung der Dehnungsgrenze kurzer Ketten bedingte Deformation zurückzuführen ist. Diese nicht- affine Deformation führt zu einer Verschiebungs- der Vernetzungsstellen aus ihren statistischen Anfangslagen.