

## Mullins Effect and Rubber-Filler Interaction\*

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### INTRODUCTION

A recent paper<sup>1</sup> from this laboratory has presented a molecular theory for the so-called "Mullins Effect." This effect consists of the fact that a rubber containing filler shows a higher tensile modulus on the first stretch than it does on succeeding stretches. The lower modulus persists in the material even though the material is allowed to relax for many days at room temperature. However, the rubber recovers its original high modulus if it is allowed to rest at temperatures near 100°C. The purpose of this report is to investigate the dependence of the Mullins softening effect upon the following variables: curing agent, filler, stretching temperature, and recovery temperature. Useful conclusions concerning the rubber-filler system will be derived from the observed data.

### THEORY

It has been shown<sup>1</sup> that the Mullins softening effect can be ascribed to the tearing loose or breaking of chains attached between filler particles. As pointed out previously, the distance between filler particles will deform in direct proportion to the overall deformation of the filled rubber. A polymer molecule bound to sites on each of two adjacent filler particles must stretch as the filler particles are separated during the deformation of the rubber. Since a chain is unable to stretch beyond its maximum length, there is a finite extension of the rubber for which any given chain between filler particles will break. The random nature of the equilibrium chain configurations insures that even a small elongation of a filled rubber will cause some of the chains to break. Also, since the stress needed to break a chain (or tear it loose from the filler) is usually many times larger than the stress in an average chain in the rubber, the load

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held by these highly stressed chains just before they break will often be quite large, even though the number of such chains is relatively small.

A typical stress-strain curve for a carbon black-filled rubber is shown in Figure 1. On the first stretch the rubber follows the curve OFC. After the rubber has been allowed to relax for a long time in the unstretched state, it now stretches along the curve OACD. On a third stretch it will follow curve OBEDG. If one assumes that the softening effect is the result of the breaking of chains (or, alternatively, tearing chains loose from the filler particle) in conformity with the above picture, one can derive<sup>1</sup> an approximate relation for  $\tau_1 - \tau_2$  as defined in the figure. It is

$$\tau_1 - \tau_2 = 4.75 \times 10^{-3} Q F_c (a/\sigma)^2 (a/b)^{1/2} (\gamma + 1)^{-1} \exp \{ 4.7 (a\alpha'_1/b)^{1/2} \} \quad (1)$$

where

$$Q = a' \ln \left[ \frac{\alpha'_2(1 + \gamma^{-1}) - \alpha'}{\alpha'_1(1 + \gamma^{-1}) - \alpha'} \right] - \ln \left[ \frac{\alpha'_2(1 + \gamma^{-1}) - 1}{\alpha'_1(1 + \gamma^{-1}) - 1} \right]$$

and

$$\gamma = \alpha F_c / kT$$

In these expressions it is assumed that a chain requires a force  $F_c$  to break or tear loose. The filler particle area per chain attachment is  $\sigma$  and the average separation of filler particle surfaces is  $b$ . It is assumed that the actual equilibrium molecular chain may be replaced in the usual fashion by a freely orienting chain with segment length  $a$ . The extension ratio of the chains,  $\alpha'$ , is related to the overall sample extension ratio through the equation

$$\alpha' = (\alpha - v_f^{1/3}) / (1 - v_f^{1/3})$$

where  $v_f$  is the volume fraction of filler.

The previous paper showed how eq. (1) could be used in conjunction with data such as are shown in

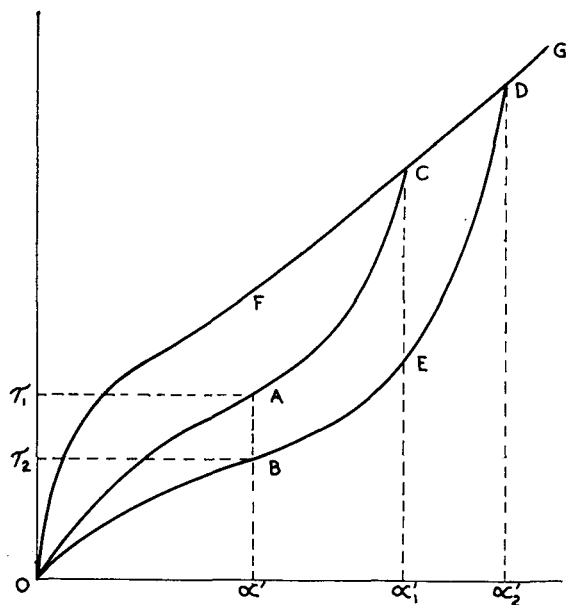


Fig. 1. Schematic diagram of softening during stressing.

Figure 1 to obtain the value of  $F_e$ ,  $b$ , and  $\sigma$ . This method was applied to some data of Mullins and Tobin, but apparently experimental difficulties associated with permanent set and relaxation effects made the derived values of  $F_e$ ,  $b$ , and  $\sigma$  rather uncertain. Later work by Wagner<sup>2</sup> on both carbon black- and silica-filled stocks showed that good agreement with theory is obtained in the case of carbon black stocks. However, some discrepancies appear in the silica stocks, presumably as a result of particle aggregation. In this paper we explore further the usefulness of eq. (1).

#### EXPERIMENTAL METHODS

All measurements were taken inside a constant temperature air chamber with standard tensile creep equipment. Mullins softening curves were obtained by use of the following procedure. Load increments of constant magnitude were added at constant time intervals (5 min. at 30°C. and 1 min. at 90°C.), readings of sample length being made at 4.5 and 0.75 min. after the load increment had been added. Before running a second stretch cycle the rubber was allowed to relax in the zero load state for a time period at least ten times longer than the time taken for the stretching cycle.

It was usually found that the carbon black stocks returned to within 5% of their original length after relaxing. Although swelling in benzene and drying of the relaxing samples will remove most of this discrepancy, such a procedure was not felt necessary

in this case. However, the silica-filled samples were often many per cent longer after relaxing than they were before stretching. These samples were always relaxed further by swelling in benzene. They then recovered to within about 4% of their original length.

When Pliolite S-6 (a butadiene-styrene copolymer of high styrene content) was used as filler, heating to about 90°C. for several minutes was sufficient to allow the rubber to return to approximately its original length. This latter procedure was not effective in the cases of the other two fillers. In all cases, the  $\alpha$  values were computed on the basis of the sample length just before a given stretch cycle was started.

The rubbers used in this study were compounded according to the recipes given in Table I. In all cases the base stock was SBR-1500. Vulcanization was carried out in a laboratory press at a temperature of 150°C. Cure times were chosen such that essentially all of the curing agent had been used up in the vulcanization process. This precludes the possibility of any appreciable cure during the course of the measurements.

TABLE I  
Weights of Ingredients in Curing Recipes

	Recipe				
	A	B	C	D	E
SBR-1500	100	100	100	100	100
HAF black	30	30	30	30	
Hi Sil-233				50	
Pliolite S-6					50
Sulfur	1.75			3	2
Peroxide (dicumyl)		1.0	0.5		
ZnO	5.0			4	5
Stearic acid	2.0				2
D.P.G.	0.25				
Anax	1.0				
Nobs	0.75				
PBNA			2.0		
MBT				2	
Triethanolamine				1	
Altax					1.5
Methyl tuads					0.1

#### RESULTS: CARBON BLACK

##### Parameters from Softening Curves

Typical Mullins softening curves for SBR-1500 containing 30 parts HAF black (Recipe A) are shown in Figures 2 and 3. These data may be analyzed by means of eq. (1) in the manner outlined previously. If one assumes  $a = 4.3 A.$ , as was

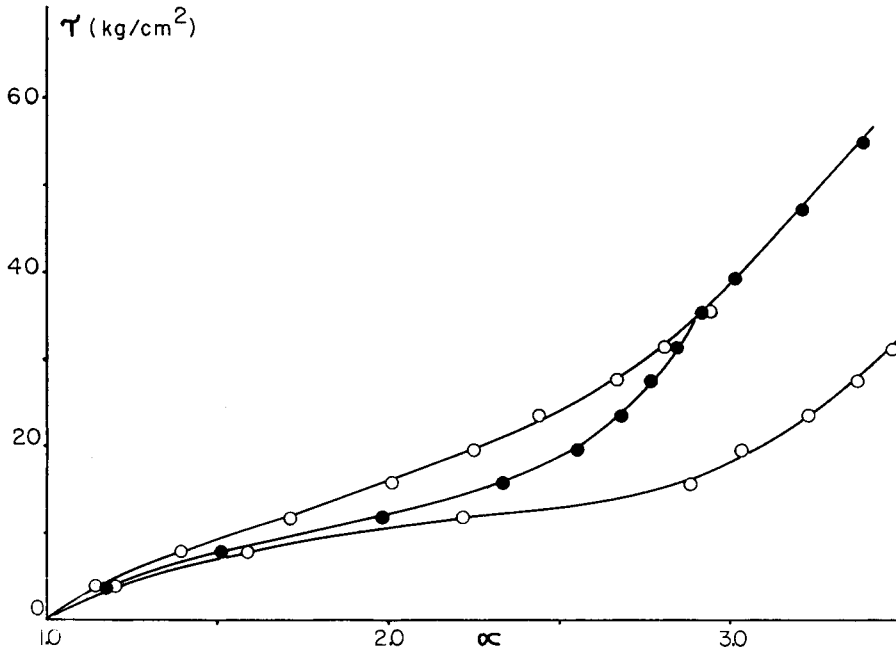


Fig. 2. Softening curves at 30°C. for SBR + 30 HAF black. The value of  $\alpha_2$  was 4.00.

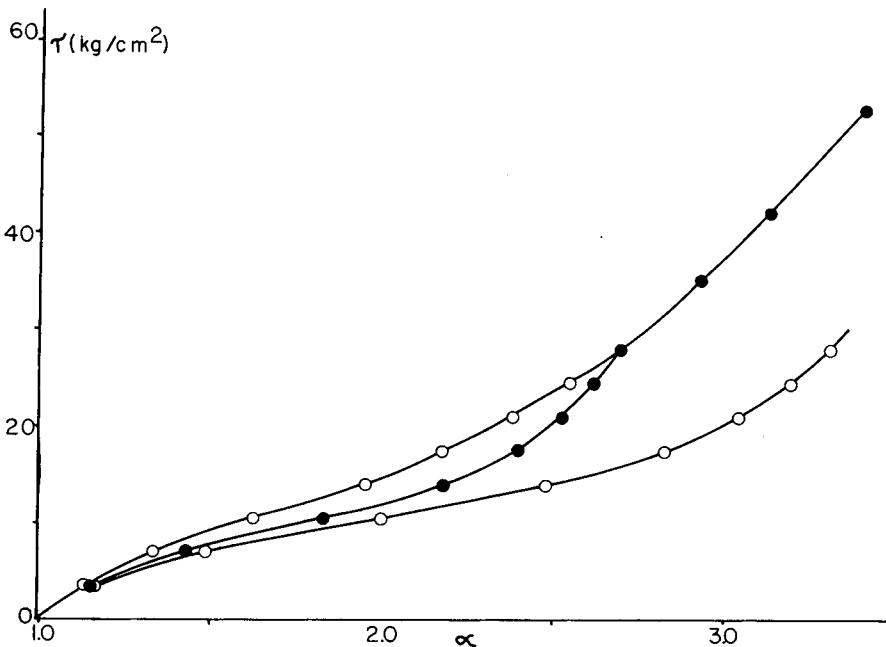


Fig. 3. Softening curves at 30°C. for SBR + 30 HAF black. The value of  $\alpha_2$  was 3.79.

found in the previous paper,<sup>1</sup> one obtains the values of  $\gamma$ ,  $b$ , and  $\sigma$  found in Table II. The theoretical and experimental plots for determining  $\gamma$  are shown in Figure 4. Some leeway is possible, but  $\gamma$  is apparently close to 50.

Figure 5 shows the plot used to determine  $b/a$  and  $\sigma$ . The data are well represented by a straight

line as theory predicts. One obtains  $b/a$  from the slope of the line,<sup>1</sup> and  $\sigma$  can be obtained from the intercept of the line.<sup>2</sup> These values are given in Table II and are seen to be in fair agreement with the values found by Wagner<sup>2</sup> in a different stock. Comparison of the values given by Wagner for milled and unmilled stocks indicates that the rub-

TABLE II  
Interaction Parameters

Material	$\gamma$	$b, \text{A.}$	$\sigma, \text{A.}^2$
HAF Black			
This work <sup>a</sup>	50	26	140
Wagner <sup>b</sup>	50	34	124
Wagner <sup>c</sup>	50	98	28
Hi Sil-233			
This work <sup>a</sup>	50	390	23
Wagner <sup>b</sup>	10	62	19
Wagner <sup>c</sup>	10	1720	6

<sup>a</sup> 30 parts by weight, milled.

<sup>b</sup> 50 parts by weight, milled.

<sup>c</sup> 50 parts by weight, not milled.

ber used in this investigation had been milled somewhat more than was true in Wagner's case.

The change in the value of  $b$  with milling is in the expected direction.<sup>2</sup> As the rubber is milled, the filler aggregates will break up. Consequently, the surface area of filler will increase greatly, and the average separation of surfaces must decrease. For this reason, the value of  $b$  is a measure of particle dispersion. It will be smaller for a better dispersed mixture.

It is not as clear why  $\sigma$ , the surface area per attachment, should increase with milling. This could possibly reflect the fact that rather weak rubber-filler attachments are broken during the milling operation. If this were the case, it is hard to understand why these bonds are not reformed during the vulcanization process. Probably a more reasonable interpretation for the variation of  $\sigma$  is the following.

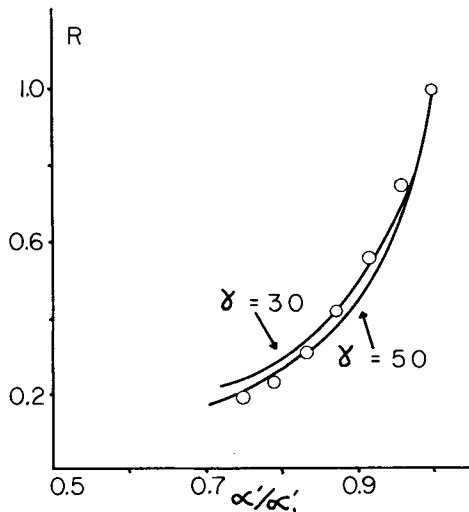


Fig. 4. Curves used for determining  $\gamma$  for SBR + 30 HAF black.

As the rubber is milled, a great deal of chain breaking occurs. This reduces greatly the average length of the rubber chains. Since only those chains which are continuous between filler particles can be effective in producing the Mullins effect, each new chain end introduced into the sample will decrease the possible number of chains contributing to the Mullins effect. This chain end effect will tend to make the computed value of  $\sigma$  too large. Whether or not this factor can account for the magnitude of the change in  $\sigma$  is not obvious and will be investigated further at a later time.

### Temperature Dependence

If the rubber-filler bond is weak enough, one would expect the rubber to approach its softened state even on the first stretch provided the temperature is high. This follows from the fact that at high temperatures many of the rubber-filler bonds would be expected to be broken even before the load is applied. Consequently, the rubber would be in its softer state even before stretching. The data of Figure 6 show the first stretch behavior for the rubber of recipe A at two temperatures, 34 and 89°C. It is seen that the rubber is not softer at the higher temperature. In fact, the well known temperature variation of the modulus of a network consisting of Gaussian chains causes the rubber to appear softer at the lower temperature. We therefore conclude that the rubber-filler bonds are strong enough to remain essentially intact even at 89°C. Evaluation of  $\gamma$  for the rubber at this higher temperature indicates that  $F_c$  is constant within experimental error over the range 39–89°C.

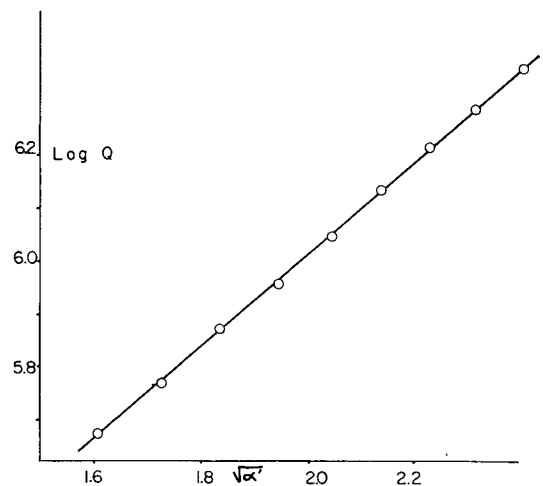


Fig. 5. Experimental plot used to determine  $b$  and  $\sigma$  for SBR + 30 HAF black.

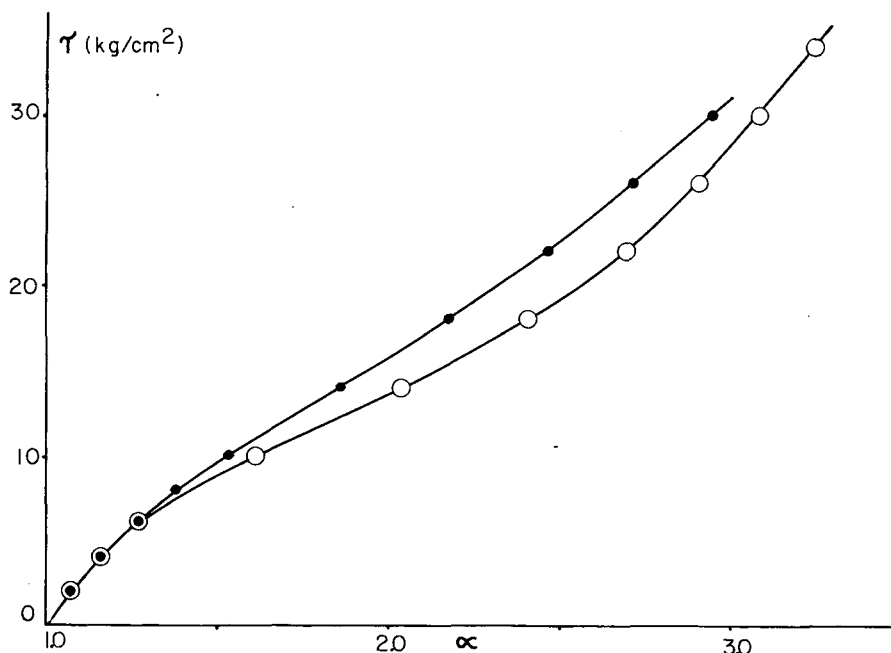


Fig. 6. Stress-strain behavior on the first stretch for SBR + 30 HAF black at two temperatures; (O) 34°C.; (●) 89°C.

It is therefore concluded that the rubber-carbon attachments are high energy bonds, most probably chemical in nature.

### Recovery from Softening

The above temperature behavior of the Mullins effect is in sharp contrast to the fact that recovery of the original hardness of the rubber occurs fairly rapidly at 89°C. Measurements have been carried out on the rubber of recipe A to ascertain how the rubber recovers as a function of time.

If one stretches a rubber to an extension ratio  $\alpha_m > \alpha_0$  and if a stress  $\tau_1$  is needed to stretch the rubber to  $\alpha_0$  on the first stretch and  $\tau_2$  is needed to stretch the rubber to  $\alpha_0$  on the second stretch, then  $\tau_1 - \tau_2$  is a measure of the chains broken or torn loose during the elongation from  $\alpha_0$  to  $\alpha_m$ . Suppose the rubber is now allowed to rest in the relaxed state at a high temperature. Then  $\tau_3$ , the stress needed to elongate the rubber to  $\alpha_0$  at some later time, will lie intermediate between  $\tau_1$  and  $\tau_2$ . The ratio  $(\tau_1 - \tau_3)/(\tau_1 - \tau_2)$  is a measure of the softening still remaining at that time.

If one assumes that  $(\tau_1 - \tau_3)/(\tau_1 - \tau_2)$  is proportional to the number of chains which were broken during the extension from  $\alpha_0$  to  $\alpha_m$  and which have not been reformed or replaced by equivalent chains, one can readily derive an ex-

pression for the variation of this quantity with time. This is done in the Appendix. One finds that

$$\log [(\tau_1 - \tau_3)/(\tau_1 - \tau_2)] = -gKt \quad (2)$$

where  $K$  is a rate constant and  $g$  is the number of possible cross-link sites in an average chain connecting two filler particles.

To test the above relation, the experimental data for recovery at various temperatures have been plotted as suggested by eq. (2) so as to obtain a series of straight lines. These plots are shown in Figure 7. Within the rather large experimental error, straight lines do result when the data are plotted in this way.

Furthermore, the slopes of the straight lines of Figure 7, being equal to  $-gK$ , can be plotted in the usual way to obtain an activation energy for this process. This plot is shown in Figure 8. The activation energy computed from the straight line of this plot is 22 kcal./mole.

In an effort to ascertain the molecular basis for the recovery process, experiments were also carried out with dicumyl peroxide cured stocks as given in recipes B and C. Even after aging the samples at 80°C. for 15 hr. before beginning experimental work with them, these stocks showed no tendency for recovery at 80°C. Instead, the materials continued to become progressively softer. Apparently

this is a result of the unstable character of peroxide cured stocks in general.

Recovery experiments with a silica filled stock (Recipe D) showed the same behavior as the black stocks. Some of these data are also shown in Figure 7. It will be noticed that the recovery

is slower for the silica stocks than for the carbon black stocks.

Finally, permanent set measurements were carried out with the stock of recipe A. These consisted of elongating the rubber of original length  $L_0$  to a fixed length  $L_m$  and maintaining it there for a

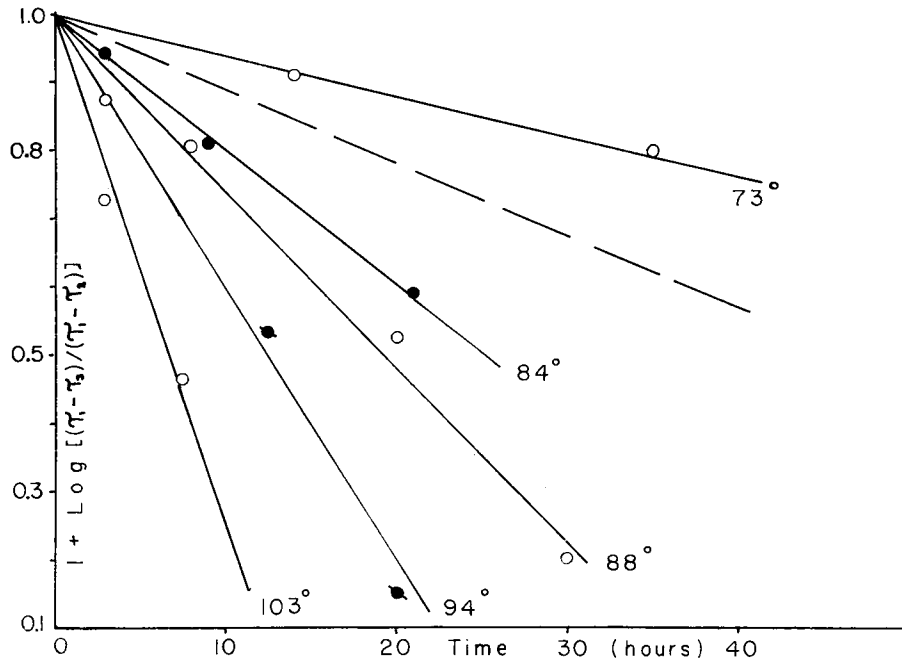


Fig. 7. The recovery of hardness for SBR + 30 HAF black at the temperatures indicated. The broken line is for SBR + 50 Hi Sil-233 at 88°C.

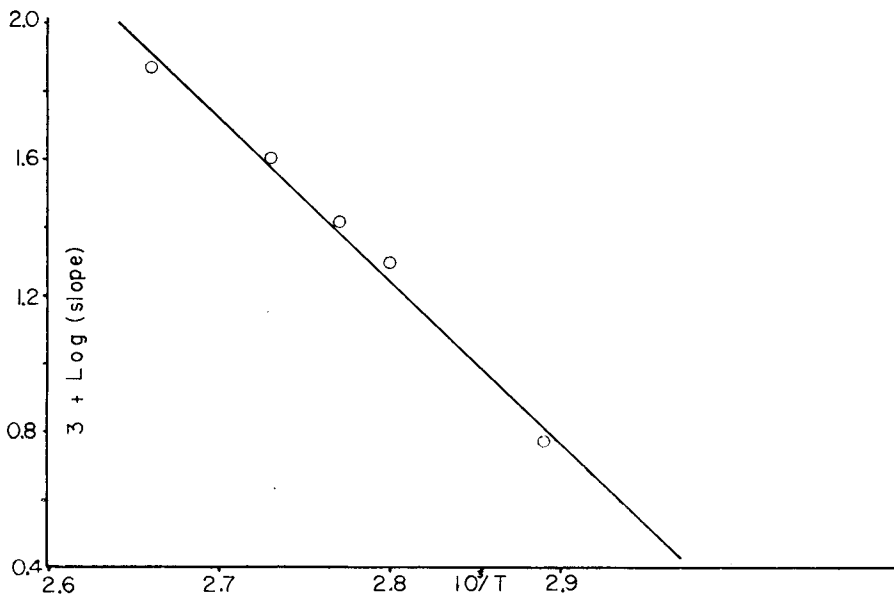


Fig. 8. A plot used to obtain an activation energy from the data shown in Figure 7.

fixed period of time at a given temperature. The rubber was then allowed to retract to its new equilibrium value  $L_f$ . If one assumes that a second network having  $\nu_1$  chains was formed in the sample at the higher temperature while elongated, one can write the following equation for the force balance between the two networks now present:

$$\begin{aligned} & -\nu_1 kT \left\{ (L_m - L_f)/L_m - [(L_m - L_f)/L_m]^{-2} \right\} \\ & = \nu_0 kT \left\{ (L_f - L_0)/L_0 - [(L_f - L_0)/L_0]^{-2} \right\} \quad (3) \end{aligned}$$

where it is assumed that  $\nu_0$  did not change much during the heating period.

It is possible to use eq. (3) to determine how fast a network develops in the polymer as a result of thermal action under the conditions of our experiment. The ratio  $(\nu_1/\nu_0)$  involves easily measured quantities and is readily obtained. For example, the value of  $(\nu_1/\nu_0)$  after 14 hr. at 94°C. was found to be 0.13.

It is also possible to compute the quantity  $(\nu_1/\nu_0)$  in terms of a crosslinking rate constant as is shown in the Appendix. One finds

$$\nu_1/\nu_0 = 1 - \exp \{-g'Kt\} \quad (4)$$

The rate constant  $K$  is the same as that used in eq. (2) but  $g' \neq g$  since  $g'$  is the number of possible crosslink sites in a chain between filler particles. The latter quantity will ordinarily be larger than the former since the number of attachments to the filler particles is usually only a small fraction of the total number of crosslinks.

From Figure 7 one sees that the recovery from softening at 94°C. is such that  $gKt = 0.6$  after 14 hr. This is to be compared with a value of about 0.12 for  $g'Kt$ . For this to be true,  $g$  must be five times as large as  $g'$ . Such a value appears reasonable in view of the above discussion.

It would therefore appear that the process involved in the recovery of SBR from the Mullins softening effect is the same as that which gives rise to permanent set in this material. Since it is generally agreed that the breaking of old and formation of new network chains under thermal action is the cause of the permanent set discussed here, it appears that this process is the cause of the recovery effect as well. The activation energy found for the recovery process is in the expected range for such an explanation.

## RESULTS: OTHER FILLERS

### Hi Sil-233

This material was formulated in recipe D. Although Wagner<sup>2</sup> has investigated this material rather extensively as far as the Mullins softening curves are concerned, it was felt that some extension of his work to other temperatures would be of value. The Mullins recovery of this material was discussed in the previous section and shown to be somewhat slower than for a carbon black stock at the same temperature. It is not known whether this difference is the result of differences in the  $g$  factor in the two instances or whether it indicates that

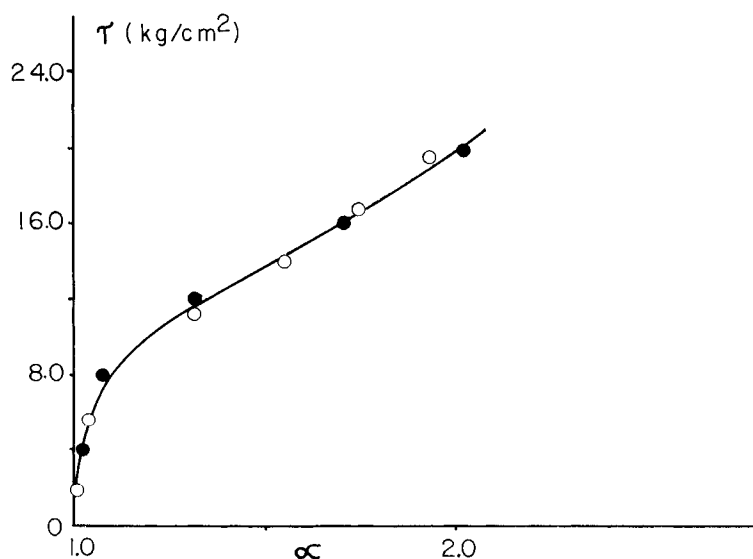


Fig. 9. Stress-strain behavior on the first stretch for SBR + 50 Hi Sil-233 at two temperatures: (○) 34°C.; (●) 80°C.

the scission-recombination reaction is less efficient in this case. Either explanation is possible.

To determine whether the silica-rubber bond was weaker than that for carbon black, the data shown in Figure 9 were obtained. These data show how

the elongation during the first stretch depends upon the applied stress at two temperatures, 34 and 80°C. Although the stress needed to produce a given large elongation appears to be very slightly less at the high temperature than at the lower tem-

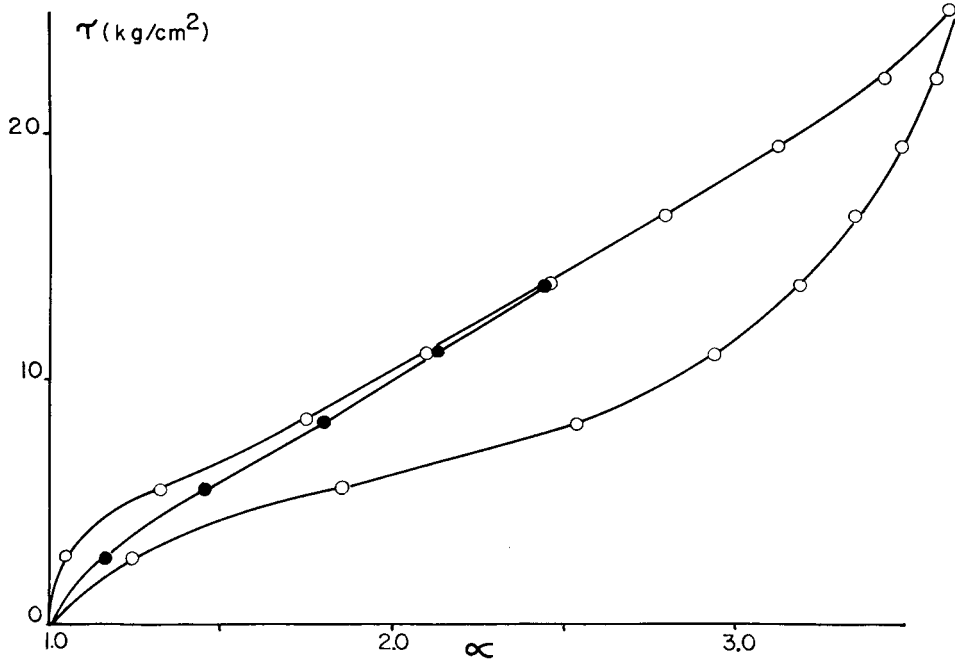


Fig. 10. Softening curves at 34°C. for SBR + Hi Sil-233: (●) data for the material after it had recovered 20 hr. at 115°C.

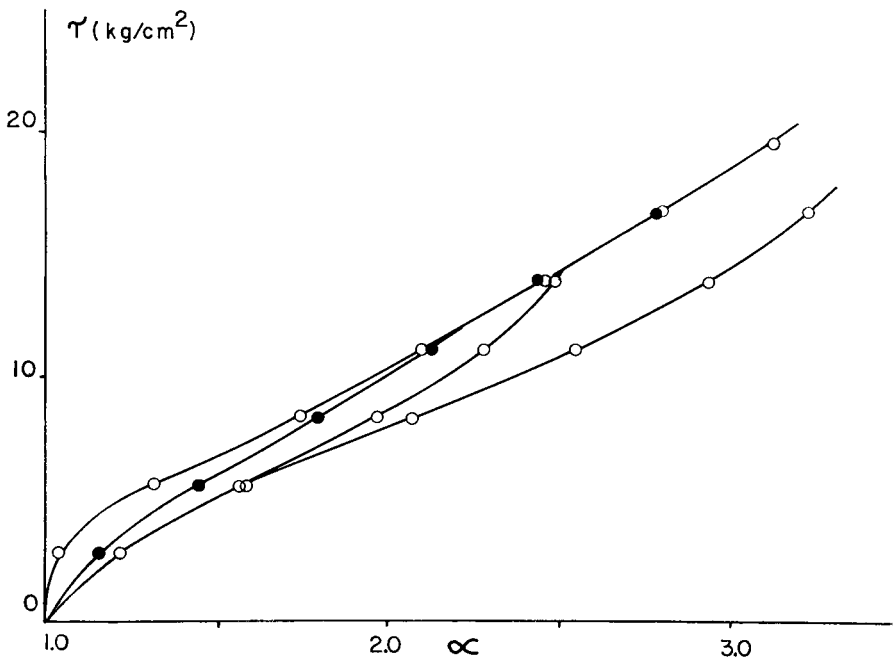


Fig. 11. Softening curves at 34°C. for SBR + Hi Sil-233: (●) data for the material after it had recovered 20 hr. at 115°C.



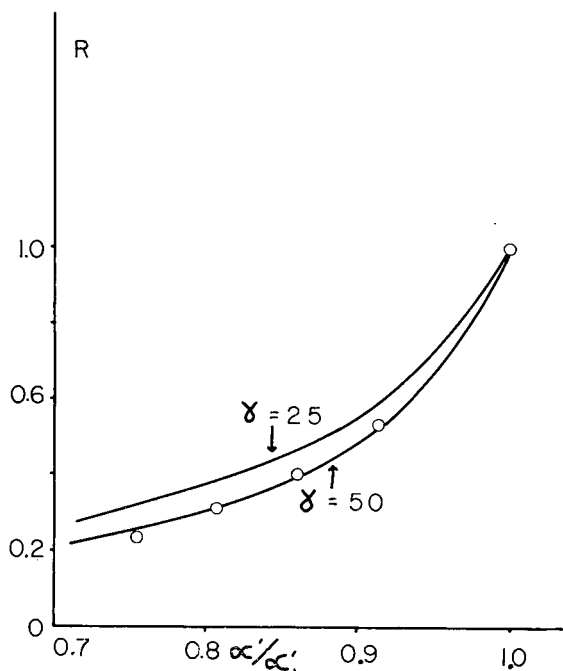


Fig. 12. Curves used in determining  $\gamma$  for SBR + 50 Hi Sil-233.

perature, this variation, even after the kinetic theory temperature correction has been applied, is near the limit of reproducibility of measurements with this stock and is therefore perhaps not significant. In any case, the bond between this silica and rubber is essentially stable for these purposes up to this temperature.

Typical softening curves for this material are shown in Figure 10. It will be noticed that the first stretch data show that the rubber appears abnormally hard for small loads. At a load of about 4 kg./cm.<sup>2</sup> the material actually behaves somewhat as though it had reached a yield point. Near this load the material does not approach an equilibrium elongation during the time interval of the measurements. This abnormal behavior appears to be associated with filler-filler structures in the material.

An instructive result is obtained if one examines the prestretched rubber used in Figure 10 after it has been allowed to recover for 20 hr. at 115°C. The initial stretch of this conditioned rubber follows the curve shown by the full circles in Figure 10. Notice that the initial anomalous portion of the curve is missing and is replaced by a more normal behavior. The upper portion of the curve coincides with the curve for the original rubber.

We interpret this behavior as follows. The original rubber contained a loose agglomerate filler

structure. It was impossible to break up these aggregates to any large extent until a stress of about 4 kg./cm.<sup>2</sup> was reached. Above this stress the aggregates break apart and give rise to the pseudo-yield phenomena. Apparently the attachments originally present in these agglomerates do not reform at temperatures below 115°C. It would be instructive to study under what conditions they would re-form so that one could say why they are present in the original vulcanized rubber.

Although Wagner<sup>2</sup> computed the parameters  $\gamma$ ,  $b$ , and  $\sigma$  for a similar silica-filled stock, he had difficulty in obtaining a good fit to the theoretical curves because of the anomalous early portion of the first stretch curve. It was necessary for him to arbitrarily neglect data taken at low loads. The above results indicate that such a procedure was justified since the original portion of the curve is never recovered. To test this idea we have analyzed the data of Figure 11 in order to obtain the parameters  $\gamma$ ,  $b$ , and  $\sigma$ . Instead of using the original first stretch curve for the rubber, we have replaced it by the recovered stretch curve. The curves used for calculating  $\gamma$ ,  $b$ , and  $\sigma$  are shown in Figure 12 and 13. The values so obtained, along with those of Wagner,<sup>2</sup> are given in Table II.

It is seen that the present method of treating the data gives relatively good agreement between the theoretical and experimental curves as shown in Figures 12 and 13. A somewhat better fit to the theoretical curves is obtained by this method than

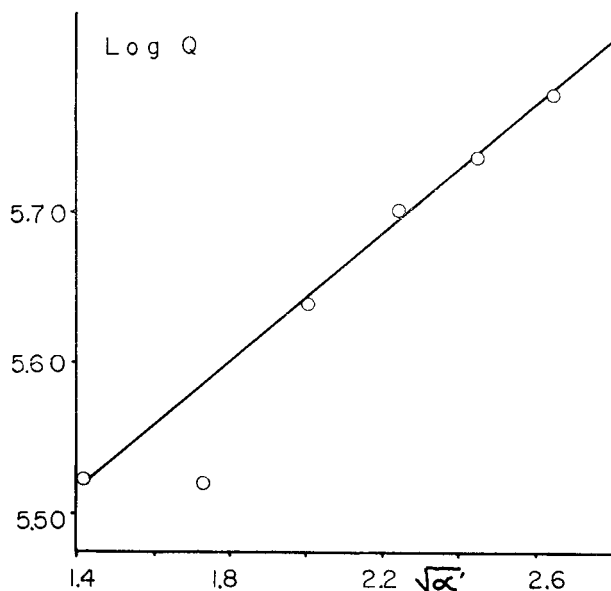


Fig. 13. Experimental plot used to determine  $b$  and  $\sigma$  for SBR + 50 Hi Sil-233.

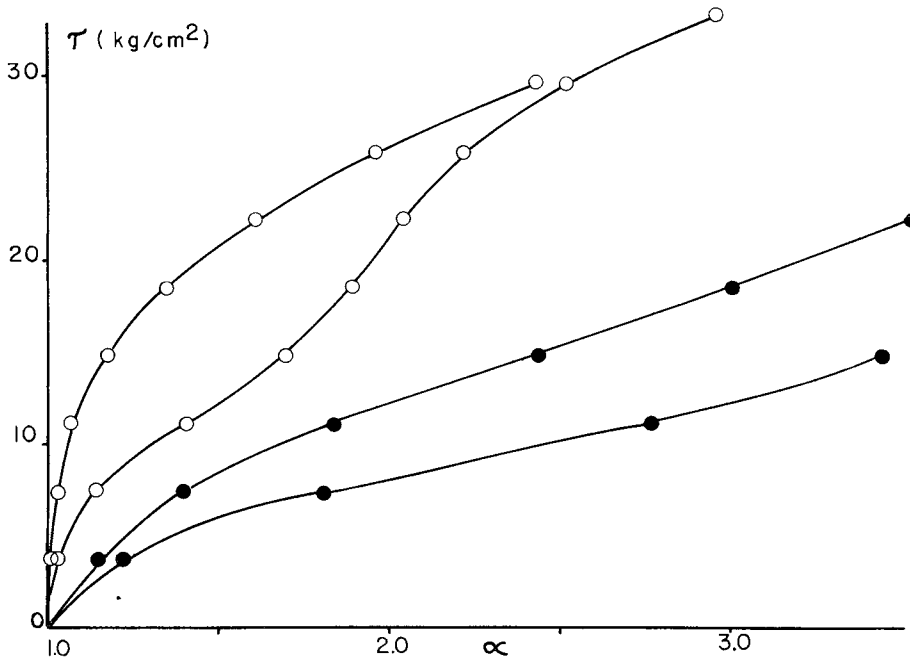


Fig. 14. Softening curves for a Pliolite S-6 filled SBR at (O) 33°C.; (●) 53°C.

Wagner<sup>2</sup> found using the original first stretch curve for analysis.

The value which we find for  $\gamma$  is much higher than the value found by Wagner. One would not expect the use of the recovered sample stretch curve to influence this computation to any great extent since the portion of the first stretch curve used is not in the region where the two curves differ much. The fact that Wagner used a much faster testing rate (change in  $\alpha$  was about one per minute) than used in the present work could cause a significant difference in results. This is a result of the fact that creep under a load increment is quite large for about the first minute after the load is applied, especially at high elongations. It should be noted in this respect that Wagner's computations for  $\gamma$  were made at somewhat higher  $\alpha$  values than used here. Another complicating feature in this regard is the fact that the compounding recipe used by Wagner contained only rubber, filler, and sulfur whereas the present recipe (D) was somewhat more complicated.

The values found for  $b$  and  $\sigma$  in this work are somewhat different from Wagner's. These differences could easily be the result of the fact that he used the original first stretch curve for the computations. In any case, both his and our data indicate that the dispersion of Hi Sil-233 is not as good as HAF black.

### Pliolite S-6

This material is a styrene-butadiene copolymer having a softening temperature near 60°C. It was compounded into the rubber on a mill according to recipe E. The Mullins softening curves for this material are shown for two temperatures, 33 and 53°C., in Figure 14. Since it is known that the adhesion of this material to rubber decreases rapidly at high temperatures, the large lowering in modulus at the higher temperatures is not unexpected. No computations were carried out on the basis of these data because the rubber seemed to be far from equilibrium during the measuring process. The rubber did not approach an equilibrium elongation under any of the load increments, and so the curves shown will depend severely upon the rate of measurement.

### Appendix

Suppose  $n$  chains remain broken or not replaced by equivalent chains at time  $t$ . Suppose further that chains are being reformed in the sample as a whole at a constant number per second given by  $NK$  where  $K$  is a rate constant and  $N$  is the number of possible crosslink sites in the sample. Then if  $g$  is the number of possible crosslink sites in a chain

$$(dn/dt) = -(NK)(ng/N)$$

since  $(gn/N)$  is the chance that a newly re-formed chain will act to replace one of the  $n$  chains still unreplaced. This gives

$$n = n_0 \exp \{-gKt\}$$

If one assumes the softening effect to be proportional to  $n$ , one has

$$(\tau_1 - \tau_3)/(\tau_1 - \tau_2) = \exp \{-gKt\}$$

which leads directly to eq. (2) of the text.

This treatment may also be used to compute the growth of a second network in a stretched rubber. Intermittent stress relaxation measurements allow one to assume that the total number of chains remains essentially constant in SBR during the time of these experiments. Therefore, the rate of new chain formation is

$$(dv/dt) = -(v_0 - v)Kg'$$

from which  $(v/v_0) = 1 - \exp \{-g'Kt\}$ .

The author is indebted to Dr. Melvin Wagner for helpful discussions during the progress of this work. Dr. Wagner also furnished the silica-filled rubber. The other rubber compounds were kindly furnished to us by Dr. S. D. Gehman.

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## Synopsis

A previously reported theory for the Mullins softening effect has been used to interpret various new data for the behavior of filled SBR rubber under tensile load. The strength of the filler-rubber bond, the filler surface area per polymer molecule attachment, and the average filler surface separation have been determined for two fillers, HAF black and Hi Sil-233 (a silica). A styrene-butadiene type filler (Pliolite S-6) has also been investigated. The temperature dependence of the filler-rubber bond has been measured; results lead to the conclusion that the bonds to carbon black and silica are high energy bonds, probably chemical in nature. It is shown that the recovery of hardness in prestretched, filled SBR is a rate process having an activation energy of about 22 kcal/mole. It is inferred from this and from permanent set data that the recovery is the result of the chemical breaking and reforming of the rubber chain network at the higher temperatures where recovery occurs. Silica-filled rubbers are shown to possess a pseudoyield stress which gives rise to an anomalous shape for the stress-strain curve of this material when it is stretched for the first time. A prestretched, silica-filled rubber recovers its hardness when left at 115°C. for 20 hr., but the anomalous portion of the curve is replaced by more normal behavior. Possible interpretations of the observed results are given.

## Résumé

La théorie précédemment exposée pour l'effet de ramollissement de Mullins a été utilisée pour interpréter diverses nouvelles données concernant le comportement du caoutchouc SBR avec charge sous tension. La force du lien charge-caoutchouc, la liaison de la surface de la charge par molécule polymérique et la séparation moyenne de la surface de la charge ont été déterminées pour deux charges, le noir HAF et le Hi-Sil-233 (une silice). Une charge type des copolymères styrène-butadiène (Pliolite S-6) a également été étudiée. La dépendance thermique du lien charge-caoutchouc a été mesurée et amène à la conclusion que les liens avec le noir de carbone et la silice sont des liens d'énergie élevée, probablement de nature chimique. On montre que le recouvrement de la dureté du SBR soumis à extension préalable est un processus de vitesse ayant une énergie d'activation d'environ 22 kcal/mole. De tout cela on conclut que le recouvrement est le résultat de la rupture et reformation chimiques du réseau de chaînes de caoutchouc à des températures plus élevées où le recouvrement se passe. Les caoutchoucs chargés de silice manifestent un rendement apparent à la tension qui donne lieu à une forme anormale des courbes tension-élongation de ce matériau lorsqu'il est étiré pour la première fois. Un caoutchouc avec charge à la silice et soumis à extension préalable recouvre sa dureté s'il est abandonné à 115°C. durant 20 heures, mais la partie anormale de la courbe est remplacée par un comportement beaucoup plus normal. Des interprétations possibles pour ces résultats sont indiquées.

## Zusammenfassung

Eine früher entwickelte Theorie des Mullins-Erweichungseffektes wurde zur Erklärung verschiedener neuer Ergebnisse für das Verhalten von gefüllten SBR-Kautschuk unter Zugbeanspruchung herangezogen. Für zwei Füllstoffe, HAF-Russ und Hi Sil-233 (eine Kieselsäure), wurde die Festigkeit der Füllstoff-Kautschukbindung, die Füllstoffoberflächenbeanspruchung pro gebundenes Polymermolekül und der mittlere Abstand der Füllstoffoberfläche bestimmt. Auch ein Füllstoff vom Styrol-Butadienotyp (Pliolite S-6) wurde untersucht. Die Temperaturabhängigkeit der Füllstoff-Kautschukbindung wurde gemessen; sie führt zu dem Schluss, dass die Bindungen zum Russ und zur Kieselsäure hochenergetische Bindungen, wahrscheinlich von chemischer Natur, sind. Es wird gezeigt, dass die Härterückbildung bei vorgestrecktem, gefülltem SBR ein Prozess mit einer Aktivierungsenergie von etwa 22 kcal/Mol ist. Daraus und aus Ergebnissen über bleibende Verformung wird geschlossen, dass die Rückbildung das Ergebnis einer chemischen Spaltung und Neubildung des Kautschukmolekülnetzwerks bei den erhöhten Erholungstemperaturen ist. Kieselsäuregefüllter Kautschuk zeigt eine Pseudofliessgrenze, welche Anlass zu einer anomalen Gestalt der Spannungs-Dehnungskurve dieses Materials bei der erstmaligen Dehnung gibt. Ein vorgestreckter, kieselsäuregefüllter Kautschuk erhält seine ursprüngliche Härte bei 115° nach 20 Stunden wieder, der anomale Teil der Kurve wird dann aber durch ein normales Verhalten ersetzt. Erklärungsversuche für die erhaltenen Ergebnisse werden gegeben.

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