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# A Modification of the Method of Intermittent Stress Relaxation Measurements on Rubber Vulcanizates

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## INTRODUCTION

The use of stress relaxation techniques in the study of scission and crosslinking reactions in rubbery high polymers was put on a theoretical basis by Tobolsky and co-workers in 1944–46.[1] Since then, the extensive use of this method on rubber vulcanizates has provided valuable information on the changes taking place in the molecular networks of such materials under the influence of heat, light, oxygen, etc. The decay of stress in the continuous stress relaxation measurements, where the rubber sample is maintained at a fixed elongation, is a measure of scission reactions, on the other hand, the change in stress observed by intermittent stress relaxation measurements, where the rubber sample is allowed to remain in an unstrained condition and then the stress required to attain a fixed elongation is measured occasionally, is the net effect of the crosslinking and scission reactions.

In a short note[2] the author has mentioned a useful modification of this procedure and applied it in a recent investigation of the stress relaxation of peroxide vulcanizates.[3] The modification consists simply in obtaining the intermittent relaxation values by determining, during the continuous stress relaxation experiment and on the same specimen, the change in apparent tangent modulus. This is done by subjecting the relaxing specimen to a small additional stress at various intervals and measuring quickly the corresponding increase in elongation. Since this method has been referred to in recent review articles and should be of general interest to those engaged in stress relaxation measurements, it may be justified to present it here in some detail.

## THEORETICAL

According to the statistical theory of rubber elasticity, the force associated with the remaining chains of the original network of a specimen relaxing continuously at the extension ratio $\alpha$ is given by

$$F_1 = A_0kT[\alpha - (1/\alpha^2)]N_{0,\,t} \quad (1)$$

where $A_0$ is the cross-sectional area measured in the original, unstrained state, and $N_{0,\,t}$ the number of original network chains (per unit volume) remaining at time $t$. By an infinitesimal increase $d\alpha$ in extension ratio, these chains contribute to the increase in force by the amount

$$dF_1 = A_0kT[1 + (2/\alpha^3)]N_{0,\,t}\,d\alpha \quad (2)$$

In addition, the force is also increased by an amount $dF_2$, as a result of the presence of a certain number $N_{c,\,t}$ of new chains per unit volume; these chains are formed by a concurrent crosslinking reaction. This new network has a cross-sectional area of $A_0/\alpha$ in its unstrained state, and thus their contribution to the increase in force is

$$dF_2 = (A_0/\alpha)kT\left\{1 + \frac{d\alpha}{\alpha} - \frac{1}{[1 + (d\alpha/\alpha)]^2}\right\} N_{c,\,t} \quad (3)$$

$$= A_0kT(3/\alpha^2)N_{c,\,t}\,d\alpha$$

Hence, the total increase in force is given by

$$dF = dF_1 + dF_2 = A_0kT\{[1 + (2/\alpha^3)]N_{0,\,t} + (3/\alpha^2)N_{c,\,t}\}d\alpha \quad (4)$$

which gives, for the case of extension ratios of 1.20 and 1.50,

$$(dF/d\alpha)_{1.20} = A_0kT(2.16\ N_{0,\,t} + 2.08\ N_{c,\,t}) \quad (5)$$

and

$$(dF/d\alpha)_{1.50} = A_0kT(1.59\ N_{0,\,t} + 1.33\ N_{c,\,t}) \quad (6)$$

respectively. The corresponding expressions for the force $F_t$ in the intermittent stress relaxation experiments are

$$F_{t_{1.20}} = A_0kT[\alpha - (1/\alpha^2)](N_{0,\,t} + N_{c,\,t}) \quad (7)$$
$$= A_0kT(0.51\ N_{0,\,t} + 0.51\ N_{c,\,t})$$

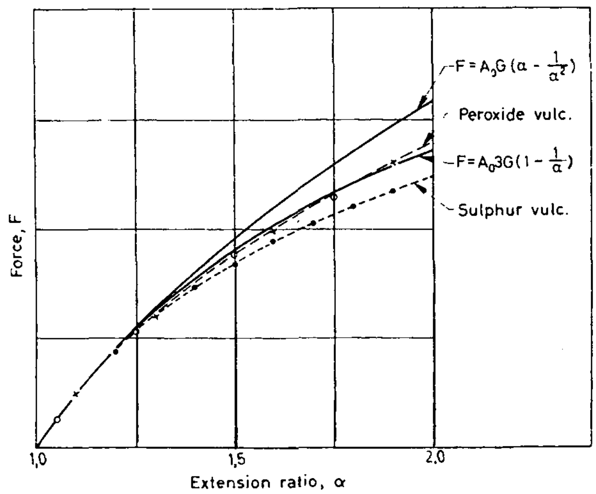


Fig. 1. Comparison between theoretical and experimental force-extension curves.

and

$$F_{i_{1.50}} = A_0kT(1.06\ N_{0,\ t} + 1.06\ N_{c,\ t}) \quad (8)$$

respectively.

It appears from eqs. (5)–(8) that, whereas the two types of chain contribute with equal weight (per chain) to the value of $F_i$, this is, theoretically, not so in the case of $dF/d\alpha$. At an extension ratio as low as 1.20, however, every new chain formed in the crosslinking reaction contributes, on the average, only about 4% less to the value of $dF/d\alpha$ than does one of the original chains. At $\alpha = 1.50$, the difference is, theoretically, of the order of 20%.

The behavior of actual rubbers, however, agrees only to a first approximation with eq. (1). In Figure 1 the general shapes of the force-extension curves at relatively small strains of ordinary soft pure gum sulfur vulcanizates are shown, together with the theoretical curve on the basis of eq. (1), all adjusted to the same modulus at very small extensions. It is seen that, although the discrepancies between the theoretical and the experimental curves are almost negligible up to 25% extension, from then on the experimental curves begin to fall markedly below the theoretical. It is also noticed that the effect is a little less pronounced in the case of the peroxide vulcanizate.

The consequence of these deviations from the theoretical eq. (1) is that the $N_{0,\ t}$ term in eqs. (5) and (6) should be reduced according to the relative difference between the slopes of the theoretical and the experimental stress-strain curves at the particular extension ratio considered. This correction is seen to be of such an order of magnitude that the numerical factor in the two terms may well be expected to become almost equal, or, in other words, that the two types of chain contribute equally (per chain) to the value of $dF/d\alpha$. Mathematically, this would be true if the experimental curves could be represented by the simple equation

$$F = A_0 3G(1 - 1/\alpha) \quad (9)$$

where $3G$ is equal to the Young's modulus at infinitesimally small strains. This is actually one[4] of the many equations which have been suggested to describe the stress-strain behavior of actual rubbers. It corresponds to Hooke's Law for stress on the cross-sectional area in the deformed state. As shown in Figure 1, it fits the initial part of the experimental curves much better than does the theoretical eq. (1). The fit is particularly good in the case of peroxide vulcanizates. It was expected, therefore, that at moderate extensions the intermittently measured values of $dF/d\alpha$ would be very nearly proportional to the values of the secant modulus as obtained by conventional intermittent stress relaxation measurements. Since $\alpha$ and $d\alpha$ in the method described here always refer to the original length of the specimen in the unstressed state (before this length has been increased by the introduction of new crosslinks in the strained specimen), $[(\alpha/A_0)\ (dF/d\alpha)]$ may be termed the apparent tangent modulus.

Below, the approximate proportionality between intermittent stress (secant modulus) and apparent tangent modulus values has been demonstrated experimentally.

## EXPERIMENTAL

In the relaxometer used in the present investigation, the force was measured by means of a balance mounted above the thermostatted chamber in which the specimen was relaxing, the upper specimen clamp being connected with the balance through a thin wire. The apparatus was constructed for continuous as well as intermittent stress relaxation measurements. The apparent tangent modulus was measured during continuous stress relaxation by placing a small additional weight on the scale intermittently, thereby increasing the tensile force on the specimen by an amount $\Delta F$. The corresponding increase $\Delta\alpha$ in extension ratio was then determined by measuring very accurately the increase in length of the specimen by means of a microscope. In the present experiments the additional load $\Delta F$ was so chosen as

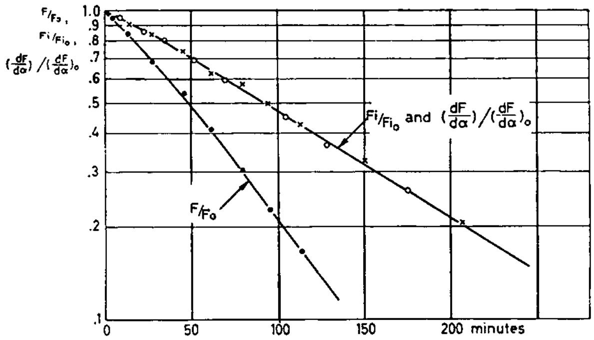


Fig. 2. Relaxation curves by (O) intermittent tangent modulus, (X) conventional intermittent stress and (●) continuous stress for an acetone-extracted sulfur vulcanizate relaxing in air at 110°C.

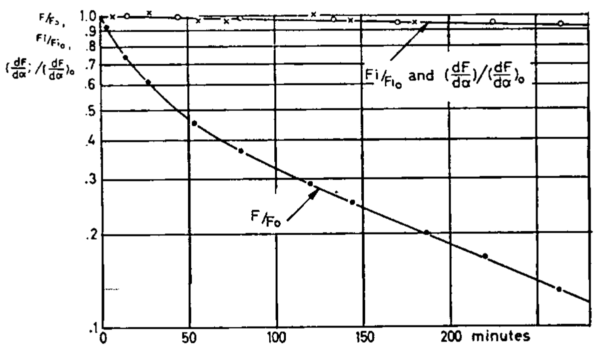


Fig. 3. Relaxation curves by (O) intermittent tangent modulus, (X) conventional intermittent stress, and (●) continuous stress for an unextracted sulfur vulcanizate relaxing in air at 110°C.

to give an increase in length of about one-tenth of the original elongation.

Typical results of measurements on an ordinary type of acetone-extracted sulfur vulcanizate relaxing in air at 110°C. and at an extension ratio of only 1.20, comprising continuous and intermittent stress and tangent modulus relaxation measurements, are presented in Figure 2. The specimens were prepared from 100 parts first grade pale crepe, 3 parts sulfur, 3 parts zinc oxide, 0.5 part stearic acid, 1.0 part mercaptobenzothiazole, and 5 parts carbon black (MPC) 5 and cured for 30 min. at 141°C. It appears clearly that during the whole experiment there is no measurable difference between $F_t/F_{t_0}$ and $(\Delta F/\Delta\alpha)/(\Delta F/\Delta\alpha)_0$, where $F_{t_0}$ and $(\Delta F/\Delta\alpha)_0$ are the values at time $t = 0$. Figure 3 shows typical relaxation curves at an extension ratio of 1.50 on the same sulfur vulcanizate (except for the omission of the MPC) which was not subjected to extraction with acetone. Again, there is excellent agreement between the two types of modulus curves. It may be noted that in this

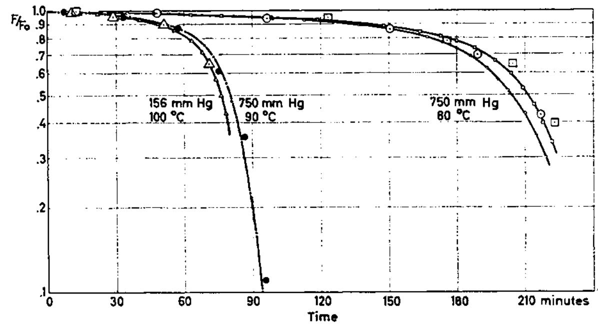


Fig. 4. Intermittent tangent modulus values (large experimental points) and continuous stress relaxation curves (small points) for peroxide vulcanizates of purified rubber at different temperatures and oxygen pressures.

particular case, where surplus vulcanizing agents are not removed by extraction, the rate of scission is practically equal to the rate at which new chains are formed in the crosslinking reaction.

This method of intermittent apparent tangent modulus measurements has also proved particularly useful in the case of natural rubber vulcanized with di-*tert*-butyl peroxide, the poor hot strength of which makes complete conventional intermittent stress relaxation measurements very difficult to carry through, due to a sudden breakage of the specimen after one or quite few extensions from the completely unstrained state. In Figure 4 the values obtained from apparent tangent modulus measurements on such peroxide vulcanizates of purified rubber (0.03% nitrogen content) are plotted, together with the continuous stress relaxation curves. There seems to be no measurable crosslinking at 90–100°C., whereas at 80°C. a small amount of crosslinking is indicated.

## CONCLUSIONS

The experimental relaxation curves presented here represent but a few of a large number of tests, all of which confirm the applicability of intermittent tangent modulus measurements at moderate extension ratios as a substitute for conventional intermittent stress relaxation measurements. The new method halves the time of experiment and reduces to some extent errors due to possible sample variations. It is particularly valuable in testing samples of low hot strength, as the danger of premature rupture when the specimen is stretched repeatedly from the unstrained state is eliminated.

## References

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## Synopsis

The method of continuous and intermittent stress relaxation measurements on rubber vulcanizates developed by Tobolsky and co-workers has been modified by the introduction of intermittent tangent modulus measurements during the continuous relaxation experiments. This allows rate of scission and crosslinking to be determined simultaneously and on the same specimen. The method is based on the use of small or moderate extension ratios $\alpha$ and on the fact that in this case the stress $f$ in actual rubbers is represented more closely by the empirical relationship $f = 3G(1 - 1/\alpha)$ than by the theoretical $f = G[\alpha - (1/\alpha^2)]$, where $3G$ denotes Young's modulus at infinitesimally small strains.

## Résumé

La méthode de mesures de tension-rélaxation continuelles et intermittents telle qu'elle a été développée dans le cas des vulcanisats de caoutchouc par Tobolsky et autres, a été modifiée en introduisant des mesures du module tangent intermittent au cours de l'expérience de rélaxation continue. Ceci permet de déterminer simultanément et sur un même échantillon la vitesse de rupture et la vitesse de pontage. La méthode est basée sur l'utilisation de rapports d'extension ($\alpha$) faibles ou modérés et sur le fait que dans ce cas la tension $f$ dans les caoutchoucs est représentés le mieux par l'équation empirique $f = 3G(1 - 1/\alpha)$ au lieu de l'équation théorique $f = G[\alpha - (1/\alpha^2)]$, dans laquelle $3G$ est équivalent au module de Young sous des tensions infiniment faibles.

## Zusammenfassung

Eine Abänderung der von Tobolsky und Mitarbeitern entwickelten Methode der kontinuierlichen und intertierenden Spannungsrelaxationsmessung an Kautschukvulkanisaten durch die Einführung von intermittierenden Tangentenmodul-Messungen während eines kontinuierlichen Relaxationsversuches wird angegeben. Dadurch wird die gleichzeitige Bestimmung der Kettenspaltungs- und Vernetzungsgeschwindigkeit an einer Probe ermöglicht. Das Verfahren beruht darauf, dass für den Fall der Anwendung kleiner oder doch mässiger Dehnungsverhältnisse ($\alpha$) die Spannung $f$ bei realen Kautschukproben sich mit besserer Annäherung durch die empirische Beziehung $f = 3G(1 - 1/\alpha)$ als durch die theoretisch abgeleitete $f = G[\alpha - (1/\alpha^2)]$ darstellen lässt, wo $3G$ dem Youngmodul für unendlich kleine Verformung äquivalent ist.

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