

## Stress Relaxation and Hysteresis at Various Strain Rates

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### Synopsis

Applying the Boltzmann superposition principle on a generalized Maxwell model, an analysis of the relations between extension, relaxation, and hysteresis is presented, which shows that any one of these three can be calculated from the other two. It is shown that the relaxation modulus does not vary with strain rate when time is measured from the start of extension, except in the early period of relaxation. It is demonstrated that the first derivative of the ratio of extension stress-strain rate with respect to time is the limiting value of the relaxation modulus. The short-time end of relaxation modulus-time curve can be readily extended for several decades of logarithm of time without resorting to the temperature effect. The results obtained from the treatment of experimental data on polyisobutylene verify the theoretical deductions, which may also be considered as an additional explicit proof of the Boltzmann superposition principle.

### Introduction

Although stress relaxation and hysteresis have enjoyed important positions in the study of mechanical behavior of viscoelastic materials for many years, several important basic details remain to be elucidated with regard to the characteristics and the technique of the treatment of experimental data. For instance, experiments on stress relaxation and hysteresis are always carried out after a short duration of extension. However, the relationships between extension stress and relaxation stress and between extension stress and hysteresis stress are not explicitly defined. In some published stress relaxation work, the experiment time is measured from the point where the extension is stopped and the relaxation begins.<sup>1,2</sup> According to the superposition principle, the time should be measured from the beginning of the extension.<sup>3</sup> The small difference in the zero point of time affects little the data at long time, but it becomes significant in the short time region. What then is the proper way to measure the experiment time?

Another problem in this area is the effect of strain rate on the relaxation stress. The stress-time relation derived from a Maxwell model, which is generally accepted for the interpretation of stress relaxation, predicts that the relaxation stress is directly proportional to strain rate; yet this equation has not been used to treat relaxation curves obtained at different strain rates.

The purpose of the present investigation was, therefore, to study these points of question, namely, (1) the relationships between extension stress and relaxation stress and between extension stress and hysteresis stress; (2) the proper way to measure the experiment time; and (3) the effect of strain rate on relaxation stress and hysteresis stress.

### Experimental

The experimental data used in this work were obtained with specimens cut from compression molded polyisobutylene sheets, about two millimeters thick, made of a commercial polyisobutylene (Vistanex 120,  $M_v = 1.9 \times 10^6$ ). All runs were made under constant crosshead speed which was converted to strain rate by the use of an effective gage length calculated in the manner given in a previous work.<sup>4</sup>

All the specimens were conditioned at 23°C. and 50% relative humidity for three days, before testing, except those for various strain rates which were conditioned in the same atmosphere for three months. The low strain rate data were obtained with an Instron table model instrument with specimens of 1/2 in. width and 2 in. jaw separation. Data at higher strain rate were measured on a Plastechon dynamic tensile tester with jaw separation at 4 in. In the following discussion the true stress will be used throughout, which is calculated by applying a correction for the reduction of the cross sectional area, equal to  $1 + \gamma$ , where  $\gamma$  is the elongation based on the effective gage length.

### Extension

For a generalized Maxwellian model under extension at a constant strain rate  $v$ , the differential equation relating the stress, the relaxation time  $\tau$ , and the experiment time  $t$  is

$$\frac{ds}{dt} + \frac{s}{\tau} = vE$$

where  $s$  is the contribution to stress of the Maxwell element with relaxation times between  $\tau$  and  $\tau + d\tau$ . The relaxation time of an element is defined customarily as the ratio of the dashpot constant  $\eta$  to the spring constant  $E$ , i.e.,  $\tau = \eta/E$ . Integrating first over time  $t$ , and then over relaxation time  $\tau$ , after inserting the definition  $E = H(\tau)d\tau$ , the stress is

$$\begin{aligned} S_e &= v \int \tau H [1 - \exp\{-t/\tau\}] d\tau \\ &= v \int \tau H d\tau - v \int \tau H \exp\{-t/\tau\} d\tau \\ &= vf(t) \end{aligned} \quad (2)$$

where  $H(\tau)$  is a function of relaxation time  $\tau$  and generally called the spectrum of relaxation time. For convenience of discussion, the resulting total stress in extension over the whole mechanical model is designated by  $S_e$ , and further abbreviated to the form  $vf(t)$ . This equation has been

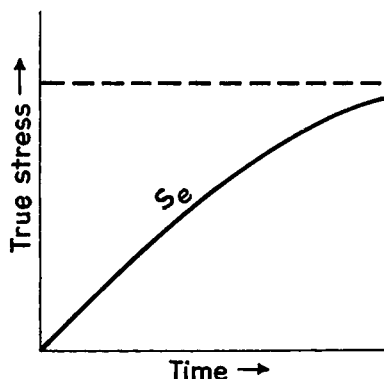


Fig. 1. A schematic extension stress-time curve.

applied successfully to the extension data on various viscoelastic materials.<sup>5</sup>

It can be readily verified that the first integral is the sum of all the dashpot constants in the model and that the first term, which is independent of time  $t$ , is the stress at constant strain rate  $v$  as if the springs were not present. This asymptotic Newtonian behavior of the viscoelastic material is depicted as the horizontal broken line in Figure 1 to compare with the extension stress shown as the solid line. This situation can be realized when the Maxwellian material is extended to very long time where the ratio  $t/\tau$  is large enough for every value of  $\tau$  to make the second term vanish. This is the steady state of the viscoelastic material, at which all the dashpots are moving at the prescribed strain rate. This steady state is similar to the completely relaxed state attained in a stress relaxation process in that all the elastic springs are relaxed. The similarity, however, ends here. In the steady state of extension with all the dashpots moving at the prevailing strain rate, the strain increases with the increase of time, while in the latter case, the strain being constant, the time rate of motion of all the dashpots is zero. For all practical purposes,  $\exp\{-t/\tau\}$  is negligible at the neighborhood of  $t/\tau = 10$ . Since the relaxation time spectrum of a viscoelastic material generally covers a range of many decades of logarithm of relaxation time, at any time  $t$  which is practically attainable, there will be some elements in the model with relaxation times smaller than or equal to  $t/10$ , so that they are at their steady state. Therefore, during the extension of a viscoelastic material, due to its very nature of viscoelasticity, more and more elements are reaching the steady state as the experiment time increases. It will be shown later that the time rate of approaching the steady state is the limiting case of stress relaxation.

### Relaxation

The stress relaxation experiment is carried out by stretching the viscoelastic material at a constant strain rate to a predetermined strain and then

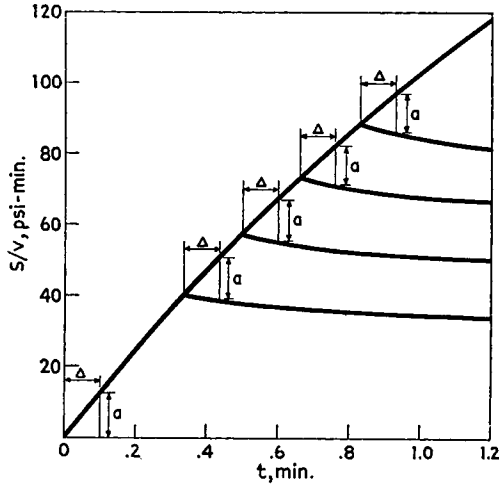


Fig. 2. Extension and relaxation stress-time curves of polyisobutylene.

the decaying stress is measured as a function of time while the strain is kept at the specified level. This process can be considered as subjecting the material to a constant strain rate to a certain time  $t_0$  and then a strain rate of the same magnitude but opposite in sign is applied so that the net strain rate is zero. According to the Boltzmann superposition principle, when the stress during the extension at strain rate  $v$  is given by eq. (1) then, the relaxation stress  $S_r$  after time  $t_0$  during relaxation will be

$$S_r = vf(t) - vf(t - t_0) \quad (2)$$

because the negative strain rate is applied at time  $t_0$ . Subtracting eq. (2) from eq. (1), we have

$$S_e - S_r = vf(t - t_0) \quad (3)$$

This function is of the same form as that of eq. (1) except that the origin of time axis is shifted to  $t_0$ , i.e.,

$$(S_e - S_r)_{t=t_0+\Delta} = S_{e,t=\Delta} = vf(\Delta) \quad (4)$$

This expression states that if the behavior of the viscoelastic material follows eq. (1) and the superposition principle is applicable to this material, the difference between the extension stress  $S_e$  and the relaxation stress  $S_r$  at a certain time after the extension is stopped is equal to the extension stress at the same interval of time from the moment when the extension was started.

In order to verify this equality, a series of relaxation determinations were made on polyisobutylene specimens at a single strain rate of  $1.0 \text{ min.}^{-1}$ . The extension in individual runs was stopped at 20, 30, 40, and 50 sec., respectively. The resulting curves are reproduced in Figure 2 along with the extension stress-time curve obtained separately. For the uni-

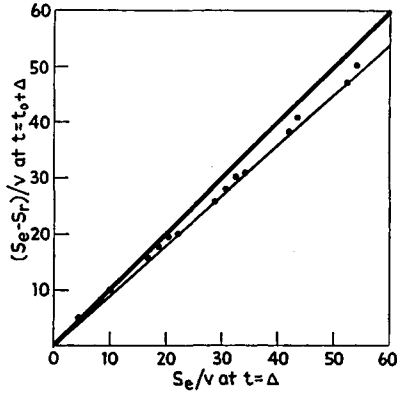


Fig. 3. A comparison of  $(S_e - S_r)/v$  with  $S_e/v$ : (●) Experimental data; (heavy —) theoretical line; (light —) line of 10% deviation.

formity of the figures in this work  $S/v$  is plotted as ordinate, instead of  $S$ . When the strain rate is the same for all runs, this change amounts only to a change of scale, and will not have any effect to the discussion. The extension part of each relaxation curve has been made to almost coincide with the extension curve by comparing several points. The average of the several ratios of the stresses at the corresponding experiment times was applied to the respective relaxation curve. The adjustment factor ranges from 0.96 to 1.04 in value, which is reasonable considering the experimental error involved in the measurement of specimen width and thickness. According to eq. (4), all the distances marked as  $a$  in Figure 2, which represent either  $S_e/v$  at  $t = \Delta$  or  $(S_e/v - S_r/v)$  at  $t = t_0 + \Delta$ , should be equal, and so should be the other corresponding distances for other values of  $\Delta$ . The fact that it is the case can be seen from Figure 3, in which the difference  $(S_e/v - S_r/v)$  at  $t = t_0 + \Delta$  is plotted against  $S_e/v$  at  $t = \Delta$ . For clarity only some sample points are shown as solid circles, while the heavy line is the predicted curve with the light line showing the limit of 10% deviation from the predicted value. It is evident that the experimental results are within this limit, which is generally taken as the magnitude of experimental error for this type of determination. Therefore, eq. (4) is verified.

### Hysteresis

The conventional hysteresis experiment is to extend the specimen to a certain elongation, say 100%, at constant crosshead speed and then let the specimen retract to zero stress by reversing the motion of the crosshead. The ascending branch and the descending branch form a loop with the elongation axis when the data are plotted as a stress-strain curve. A stress-time plot can be obtained by turning around the descending branch about a vertical axis at 100% elongation and changing the elongation axis into time scale. The result will bear the resemblance to a stress

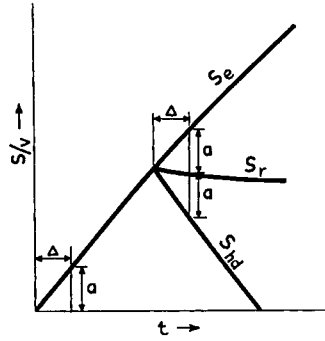


Fig. 4. Relations between extension, relaxation and hysteresis stresses.

relaxation curve, except the descending branch is much steeper than the relaxation curve. Hence, the phenomenon of hysteresis is nothing but a variation of a stress relaxation process, in which the magnitude of the negative strain rate is twice that of the extension strain rate instead of being equal to the extension strain rate as in the case of relaxation. The stress  $S_{hd}$  on the descending branch of a hysteresis loop is described by the following equation:

$$S_{hd} = vf(t) - 2vf(t - t_0) \quad (5)$$

where all symbols have the same meaning as before. A comparison of eqs. (5) with eqs. (1) and (2) reveals that

$$S_e/v - S_r/v = S_r/v - S_{hd}/v \quad (6)$$

or

$$(S_e/v - S_{hd}/v)_{t=t_0+\Delta} = 2(S_e/v)_{t=\Delta} \quad (7)$$

That is to say, the difference between the extension stress and the relaxation stress at  $t = t_0 + \Delta$  is equal to the difference between the relaxation stress and the stress on the descending branch of the hysteresis loop at the same experiment time, which is, in turn, equal to the extension stress at  $t = \Delta$ , as shown previously. Or, the difference between the extension stress and the stress on the descending branch of the hysteresis loop at time  $t = t_0 + \Delta$  is twice as much as the extension stress at  $t = \Delta$ . This statement is diagrammed in Figure 4, in which all distances marked  $a$  should be equal. The equations for the hysteresis loops after the first are readily to be derived by further application of the superposition principle. The equations for the second loop, for instance, are

$$S_{ha} = vf(t) - 2vf(t - t_0) + 2vf(t - t_1) \quad (8)$$

$$S_{hd} = vf(t) - 2vf(t - t_0) + 2vf(t - t_1) - 2vf(t - t_2) \quad (9)$$

For the third loop, for  $S_{ha}$  one term of  $2vf(t - t_1)$  is added to the expression for  $S_{ha}$  of previous loop and for  $S_{hd}$  the difference  $2vf(t - t_2) - 2vf(t - t_3)$  is

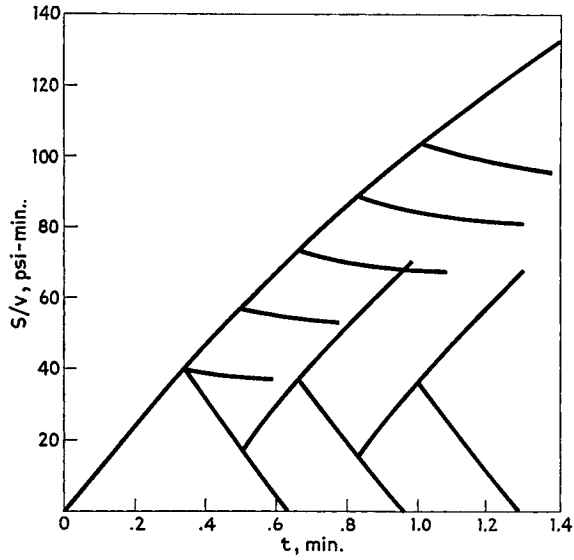


Fig. 5. Extension, relaxation and hysteresis curves of polyisobutylene

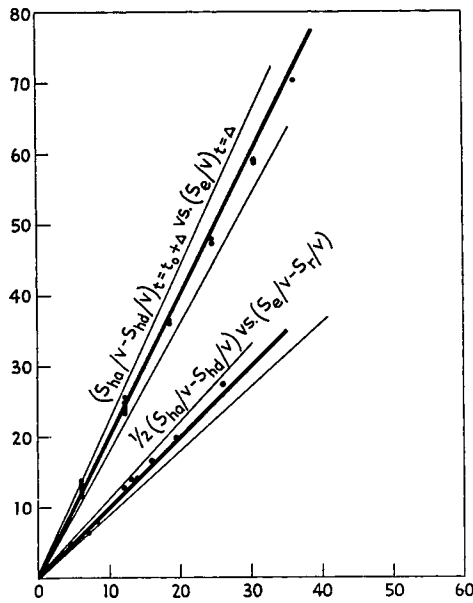


Figure 6.

added, and so on. The difference between  $S_{na}$  and  $S_{nd}$  on any two adjacent branches is

$$S_{na} - S_{nd} = 2vf(t - t_j)$$

where  $t_j$  is the time at which these two branches are joined together. For the purpose of testing this deduction, a hysteresis experiment with

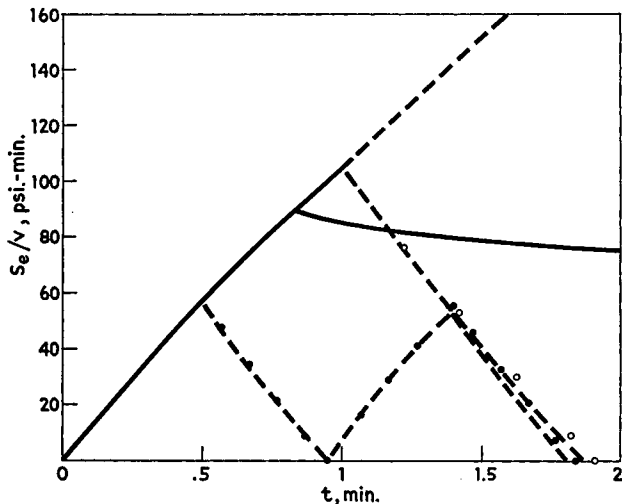


Fig. 7. Prediction of extension and hysteresis stresses (---); from experimental extension and relaxation stresses (—); (●, ○) experimental hysteresis stresses.

polyisobutylene specimens was made by extending the specimens for 20 sec. and reversing the crosshead motion at this moment and 10 sec. thereafter, so that the resulting data can be compared with the relaxation data shown in Figure 2. Both sets of data are shown together in Figure 5. The waves at the lower part of the figure are the successive hysteresis loops. The validity of eqs. (6) and (7) are shown in Figure 6 by plotting the differences on the left side of the equations against that on the right side as points. The heavy lines are the theoretical curves, while the light lines are the limits of 10% error. The fact that no points are beyond the limits of 10% error is considered as a satisfactory proof for the equations derived. As a further proof of all the equations derived so far, the extension part of a relaxation curve with  $t_0 = 50$  sec. was extended to experimental time beyond 50 sec. by use of the rewritten form of eq. (4).

$$S_{e,t=t_0+\Delta} = S_{e,t=t_0} + S_{r,t=t_0+\Delta}$$

The result is reproduced in Figure 7 as broken line with the relaxation curve itself being shown as solid line. From this calculated extension curve the descending branches of two hysteresis curves were calculated by means of eq. (7), one for  $t_0 = 0.5$  min., and the other for  $t_0 = 1.0$  min., corresponding to 50 and 100% nominal elongation, respectively. The descending branches were allowed to go below the time axis, i.e., the stress was allowed to assume negative values. Although it is not very realistic, theoretically it is sound. The point at which the descending curve intercepted the time axis was the end of the descending branch as  $S_{hd} = 0$  at this point. The ascending branch of the second hysteresis loop of 50% elongation was calculated from this point on by means of eq. (8). The duration of the ascending branch of the second loop was taken as equal to



that of the descending branch of the first loop. The reason for this is that since the crosshead was set to return at a specific elongation, the amount of retraction occurring in the descending branch of the first loop had to be made up in the ascending branch of the second loop before the crosshead started to return. The second descending branch was calculated in the same manner as the first was obtained. The resulting curves are reproduced in Figure 7, in which the points indicate the comparable experimental data determined in separate runs. The agreement is fairly good.

### Effect of Strain Rate

It has been shown in the previous sections by comparing relaxation stress and extension stress at the same strain rate that the difference between these two stresses is a function of  $(t - t_0)$ , instead of either  $t$  or  $t_0$  alone, as described by eq. (3). This equation also shows that the function  $(S_e/v - S_r/v) = f(t - t_0)$  is independent of strain rate  $v$ . This is shown to

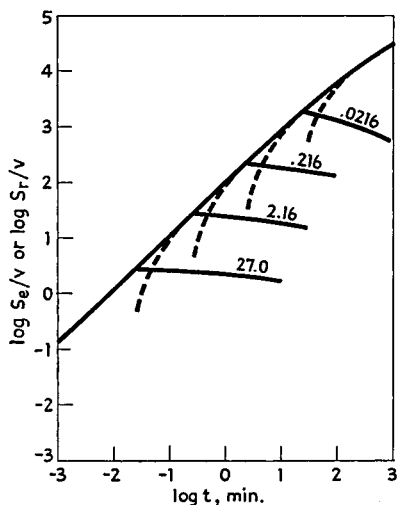


Fig. 8. Extension and relaxation curves of polyisobutylene at various strain rates: (—) Experimental data; (---)  $S_e/v - S_r/v$  calculated.

be indeed the case with the data shown in Figure 8, in which a composite  $S_e/v$ -versus- $t$  curve obtained on polyisobutylene at several strain rates ranging from 0.0216 to 27  $\text{min.}^{-1}$  is shown along with the  $S_r/v$ -versus- $t$  curves at strain rates of 0.0216, 0.216, 2.16, and 27  $\text{min.}^{-1}$  as indicated. As it would not be possible with a linear scale to cover the very wide experimental range without losing detail, these curves are presented in log-log scale. The extension of all relaxation runs was stopped at 50% nominal elongation. The difference curves  $S_e/v - S_r/v$  calculated from this set of data are superimposing as broken lines on the respective relaxation curves and replotted against  $(t - t_0)$  as solid circles in Figure 9 to compare with

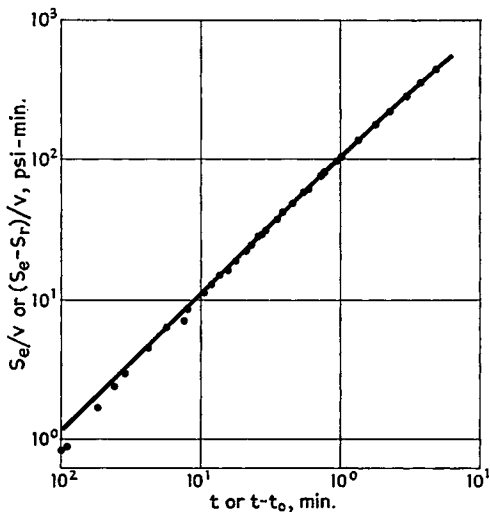


Fig. 9. Comparison of  $(S_e - S_r)/v$  (●) with  $S_e/v$  at various strain rates.

the extension curve shown as solid line. The excellent agreement between the points and the curve proves that eqs. (3) and (4) are obeyed not only by experimental data at the same strain rate, but also by the relaxation stress of polyisobutylene at various strain rates.

A natural conclusion from this result would be that the experiment time in a relaxation experiment should be measured with  $t = t_0$  as the origin of the time axis, i.e., from the moment the extension is stopped. However, with the use of this convention, the difference between extension stress and relaxation stress would have to be used and the result would be exactly the  $S_e/v$ -versus- $t$  curve. If the latter curve is available to start with, there is no advantage to using the relaxation data to get the same curve again. In the next section it will be shown that relaxation data can be put to more profitable use when the experiment time is measured from the point  $t = 0$ .

For cases of variable strain rate, it can be readily derived that eq. (3) still holds, except that  $v$  is the strain rate at  $t = t_0$  and that the relaxation modulus curve can be obtained by differentiating the resulting  $(S_e/v - S_r/v)$ -versus- $(t - t_0)$  curve.

### Relaxation Modulus

The relaxation modulus  $E_r$  is customarily defined<sup>6,7</sup> as the ratio of relaxation stress to the elongation at which the relaxation is carried out, under the restriction that the extension time is small, although it has not been specifically stated how small the extension time should be. On the other hand, the specification of small extension time, combined with the limit of linearity of the material, dictates the use of relatively high strain rate. This definition for relaxation modulus presumably comes from

the approximate form of eq. (2) for the relaxation stress. Equation (2), without abbreviation, is of the form

$$\begin{aligned} \frac{S_r}{v} &= \int \tau H \left[ \exp \left\{ -\frac{t-t_0}{\tau} \right\} - \exp \left\{ -\frac{t}{\tau} \right\} \right] d\tau \\ &= \int \tau H \exp \left\{ -t/\tau \right\} [\exp \{ t_0/\tau \} - 1] d\tau \end{aligned}$$

When  $\exp \{ t_0/\tau \}$  is expanded and the terms higher than the first power are ignored, then

$$E_r = \frac{S_r}{\gamma_0} = \frac{S_r}{vt_0} \doteq \int H \exp \left\{ -t/\tau \right\} d\tau \quad (10)$$

The neglecting of the second power term requires for, say, 5% precision in the value of relaxation modulus that the value of  $t_0/\tau$  is smaller than 0.1, i.e., the relaxation time  $\tau$  must be greater than  $10t_0$ . Hence, the approximate form of the equation can be used only when the mechanisms that have relaxation times not ten times greater than  $t_0$  are relaxed. It can be readily proved that a mechanism is relaxed and contributes nothing to the relaxation stress when the experiment time is about ten times as large as its relaxation time. The approximate form, therefore, is applicable only when the experiment time is about one hundred times greater than the time at which the extension is stopped. For example, if the extension part in a relaxation determination lasts for 10 sec., the relaxation moduli calculated from the data at the time from 1000 sec. on will be reliable. Physically speaking, at time  $t_0$  the mechanisms with short relaxation times are relaxed. The application of the negative strain rate puts these mechanisms into action again. In order to eliminate the contributions of these mechanisms to the relaxation modulus and restore the true state of matter, time must be allowed for these mechanisms to relax. In this sense, the general practice of ignoring the first few moments of the relaxation curve is correct. This investigation, however, goes one step further by indicating how long this initial part should be ignored.

With this restriction applied, according to eq. (10), the relaxation moduli obtained at various strain rates should be equal when they are measured at same value of experiment time  $t$ . This is clearly demonstrated in Figure 10 by the relaxation moduli of polyisobutylene calculated from the relaxation data shown in Figure 8. The initial parts of these curves spread out like a fan, but at experiment time about one hundred times greater than  $t_0$ , which is marked by an arrow on the individual curve, the curves coincide, although they were obtained at various strain rates. Consequently, this result indicates that no special treatment is needed for relaxation data at various strain rates, if they are expressed in relaxation modulus, and that the extension time does not have to be short and any convenient strain rate can be used with equal benefit. It is obvious from this result that the experiment time should be measured from the start of extension. If  $t = t_0$  is taken as the origin of the time axis, the short time

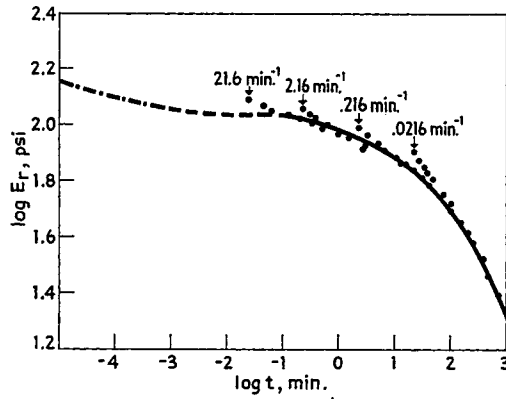


Fig. 10. Relaxation modulus curves of polyisobutylene (●) at various strain rates and derivative of stress-strain curve at low strain rate (---) and at high strain rate (-.-).

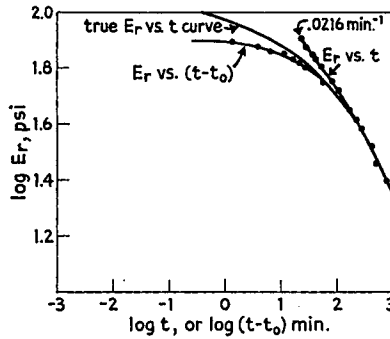


Fig. 11.

end of the relaxation modulus curve would be badly distorted. An extreme case is shown in Figure 11.

### Time Derivative of Stress

Equation (3) can be considered as a difference equation when  $t_0$  is very small and considered as an increment of  $t$ . When the increment approaches zero, the right side is the familiar form of a derivative.

$$\frac{df(t)}{dt} = \lim_{t_0 \rightarrow 0} \left[ \frac{f(t) - f(t - t_0)}{t_0} \right]$$

By definition,  $f(t)$  is equal to  $S_e/v$ . The left side is

$$\lim_{t_0 \rightarrow 0} \left( \frac{S_r}{vt_0} \right) = E_{r, t_0 \rightarrow 0}$$

So,

$$E_{r,t_0 \rightarrow 0} = \frac{df(t)}{dt} = \frac{dS_e}{vdt}$$

This shows that the time derivative of the ratio of extension stress  $S_e$  to the strain rate  $v$  is the value of relaxation modulus with  $t_0 \rightarrow 0$ . That is to say, the time derivative is the limiting value of the quantity designated as relaxation modulus. This derivative is the slope of the stress-strain curve which is generally called tangent modulus. Differentiation of extension stress  $S_e$  (eq. (1)) with respect to time  $t$  gives us

$$\frac{dS_e}{vdt} = \int H \exp \{-t/\tau\} d\tau \quad (11)$$

which is identical to the right side of eq. (10). Therefore, the so-called relaxation modulus is an approximation of this time derivative. Within the ordinary experimental error, these two quantities, namely, the modulus derived from the relaxation data and the tangent modulus calculated from the extension curve, can be used synonymously. This opens up a possibility of obtaining relaxation modulus from extension stress data. The advantage would be the extension of time range of relaxation modulus to the short time region without encountering the difficulty of doing the relaxation experiment at very short time. With the help of the high speed instrument available on the market, the time range of relaxation modulus curve can be extended to the microseconds without even running the relaxation determination. This is demonstrated by the broken line in Figure 10, which is the time derivative of the extension stress curve shown in Figure 8. The broken line at the left shown as dash and dot is the time derivative of the extension stress curve at a high strain rate of 3100 min.<sup>-1</sup> Thus, the relaxation modulus-versus-time curve is readily extended to cover many decades of logarithm of experiment time. A curve of this wide range would be a great help in the construction of master curve.

By the definition of the generalized Maxwell model, the slope of the  $S_e/v$ -versus- $t$  curve at  $t = 0$  is the Young's modulus of the viscoelastic material, which is the sum of all the spring constants in the model. In order to avoid the ambiguity in the determination of the slope of a curve at its initial part, the slope can be taken from both the extension part and the relaxation part of a relaxation run at the neighborhood of  $t_0$ , and the slopes at  $t_0$  are obtained by extrapolation, since it can be readily shown by differentiating eq. (3) that

$$\frac{dS_e}{vdt} - \frac{dS_r}{vdt} = \int H \exp \left\{ -\frac{t-t_0}{\tau} \right\} d\tau \quad (12)$$

and that at  $t=t_0$  the difference of these two slopes is equal to the Young's modulus at its strictest sense. The values determined from the relaxation data at strain rates of 0.0216, 0.216, 2.16, and 27 min.<sup>-1</sup> are 110, 105, 118,

and 110 psi, respectively, which are way below what should be as given by the published master curves of the same material of different molecular weight. This is attributed to the slow response of the instrument used for the determination, as before any load is recorded, some of the mechanisms are relaxed already. Nevertheless, eq. (12) may prove to be a better means than the conventional method to determine Young's modulus for practical use.

### Discussion

Since the Boltzmann superposition principle has been assumed to be valid in the theoretical derivations of this work, the agreement between predictions and experimental results can be considered as an additional explicit proof, by evidence under constant strain rate, to the applicability of this principle to the tensile behavior of viscoelastic materials.

It should be pointed out here that true stress is used in this work and that with regard to the distribution of relaxation time the above discussion is rather general in nature since the spectrum  $H(\tau)$  has been in no way limited to any particular form. The results obtained may, therefore, be applied to any kind of distribution, continuous or discrete. (For discrete distribution, of course, the integrations in the equations will be replaced by summations.)

It has been indicated in this investigation that any one of the three types of stress, namely, extension, relaxation and hysteresis stresses, can be calculated from the other two. When the initial part of a relaxation curve and the ascending branch of the first hysteresis loop are considered as part of the respective curve, all three then are fixed if one of them is known. To be more specific, relaxation and hysteresis curves can be obtained from extension curve directly. The extension part of relaxation curve or the ascending branch of the first hysteresis loop can be extended to longer time by the use of the respective relaxation part and hysteresis part. Theoretically speaking, the operation of addition or subtraction in eqs. (4), (6), and (7) can be repeated indefinitely and curves of many decades of logarithm of experiment time can be obtained when one curve is known for a wide range of time. However, the time increment in each operation is limited by the value of  $t_0$ , which is usually not very large. Although the technique can be applied advantageously for a short range of time, as has been done in this work, it might be very tedious for the purpose of obtaining a curve of wide range of time. For instance, with a relaxation curve with  $t_0 = 1$  min., it would not be practical to calculate the extension curve into the region of thousands of minutes. In this case, eq. (11) may prove to be more convenient to use. That is to say, the relaxation modulus curve can be obtained by differentiating the extension curve, and reversely, extension curve can be calculated from the relaxation modulus curve by integration.

This investigation shows also a convenient method to determine hysteresis loss directly from the extension stress-time curve. Hysteresis loss is

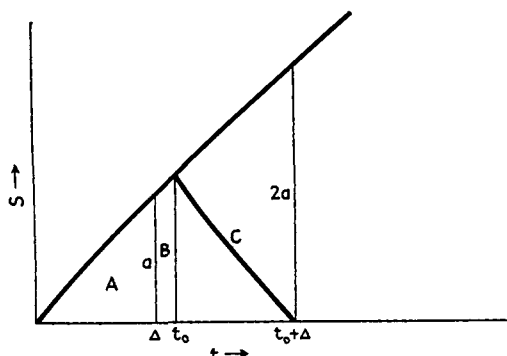


Fig. 12. Graphical calculation of hysteresis loss from extension curve.

generally defined as the percentage of energy lost as heat. On a stress-strain diagram it is the ratio of the area of the hysteresis loop to the area under the ascending branch. In terms of stress and time, the hysteresis loss  $w$  is

$$\begin{aligned}
 w &= \frac{v \int S_e dt - v \int S_{nd} dt}{v \int S_e dt} \\
 &= 1 - \frac{\int_{t_0}^{t_0+\Delta} [f(t) dt - 2 f(t - t_0)] dt}{\int_0^{t_0} f(t) dt} \\
 &= 1 - \frac{[\int_{t_0}^{t_0+\Delta} f(t) dt - 2 \int_0^{\Delta} f(t) dt]}{[\int_0^{\Delta} f(t) dt + \int_{t_0}^{t_0+\Delta} f(t) dt]} \\
 &= 1 - (C - 2A)/(A+B)
 \end{aligned}$$

where  $A$ ,  $B$ , and  $C$  designate the areas on a stress-time diagram, representing the corresponding integrals, as shown in Figure 12. The value of  $t_0$  is predetermined. The value of  $t + \Delta$  is determined by the point on the time axis where the stress is twice as much as that at  $t_0$ , found by trial and error. Applying this technique to the stress time curve shown in Figure 7, the hysteresis loss of polyisobutylene at a strain rate of  $1.0 \text{ min.}^{-1}$  and 100% elongation is found to be 18.0%, compared to the experimentally determined value of 18.2%. The agreement is good enough for all practical purposes.

### Summary

(1) An additional explicit proof of the applicability of the Boltzmann superposition principle to the tensile behavior of viscoelastic materials has been obtained by means of constant strain rate experiments.

(2) It has been demonstrated that any one parameter—relaxation stress, hysteresis stress, or extension stress—can be calculated from any other.

(3) The relaxation modulus curve determined at various strain rates is essentially the same unique and characteristic curve for each viscoelastic material.

(4) It has been shown that it is most satisfactory to choose the point at which extension starts as the origin of the time axis of a relaxation modulus curve.

(5) The tangent modulus obtained from a stress-strain curve is the limiting value of relaxation modulus. In practice, the time derivative of extension stress can be used to extend the relaxation curve at the short-time end.

(6) A technique has been developed for calculating hysteresis loss from the extension stress-time curve.

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### Résumé

En appliquant le principe de superposition de Boltzmann à un modèle de Maxwell généralisé, on présente une analyse des relations entre extension, relaxation, et hystérésis. Cette analyse montre que chacune de ces propriétés peut être calculée à partir des deux autres. On montre que le module de relaxation ne varie pas avec la vitesse d'élongation lorsque le temps est mesuré à partir de commencement de l'extension, excepté dans la première période de relaxation. On démontre que la dérivé première par rapport au temps, du rapport force d'extension-vitesse d'élongation est la valeur limite du module de relaxation. La brusque fin de la courbe module de relaxation-temps peut être facilement étendue sur plusieurs décades de logarithme du temps sans recourir à l'effet de température. Les résultats obtenus à partir due traitement des données expérimentales obtenues pour le polyisobutylène vérifient les déductions théoriques, ce qui peut également être considéré comme une preuve explicite supplémentaire du principe de superposition de Boltzmann.

### Zusammenfassung

Unter Anwendung des Boltzmannschen Superpositionsprinzips auf ein verallgemeinertes Maxwellmodell wird eine Analyse der Beziehung zwischen Dehnung, Relaxation und Hysterese gegeben, die zeigt, dass jede dieser drei Größen aus den anderen zwei berechnet werden kann. Es wird gezeigt, dass sich der Relaxationsmodul mit der Verformungsgeschwindigkeit, bis auf die Anfangsperiode der Relaxation, nicht ändert, wenn die Zeit vom Beginn der Dehnung an gemessen wird. Es wird gezeigt, dass die erste Ableitung des Verhältnisses Dehnungsspannung: Verformungsgeschwindigkeit nach der Zeit den Grenzwert des Relaxationsmoduls bildet. Das Kurzzeitende der Relaxationsmodul-Zeitkurve kann im logarithmischen Massstab leicht auf einige Größenordnungen der Zeit ohne Rücksicht auf den Temperatureffekt extrapoliert werden. Die bei der Behandlung der Versuchsdaten an Polyisobutylen erhaltenen Ergebnisse bestätigen die theoretischen Ableitungen, was auch als ein zusätzlicher expliziter Beweis des Boltzmannschen Superpositionsprinzips betrachtet werden kann.