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Viscoelastic Factors in the Strength of Elastomers Under Complex Stress by a Puncture Method*†

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INTRODUCTION

We became interested in penetration testing of rubber vulcanizates with an indentor about three years ago when a characteristic dip in the load-penetration curve was observed in the course of precise durometer hardness measurements for which an Instron testing machine was used to apply and record the force.[1] The force at first rises steeply as the indentor is applied, drops briefly in a characteristic way after penetration to a certain depth, and then rises again. Examination of the specimen shows that failure has occurred at this dip in the curve and that the rubber is permanently punctured because of the high stresses about the indentor. We have designated the point of maximum force before the dip in the curve as the puncture point, and its coordinates as the puncture strength and the puncture depth. Our interest in this type of measurement stemmed from its reproducibility, its obvious convenience as a possible strength criterion for rubber compounds, and the expectation that a strength test with such nonhomogeneous stress might be found to correlate better with service performance under certain condition. Vickers and Robison[2] have described this puncture phenomenon and have stated that there is a correlation between abrasion resistance and the resistance of rubber to penetration by a blunt needle.

A thorough study of a mechanical property of a viscoelastic material requires measurements of the effects of time and temperature. The interesting question arises as to how much may be seen in this way of the viscoelastic processes underlying the puncture measurement and whether a puncture test can be established by these viscoelastic procedures which will be a valid and reproducible method for securing a strength criterion for elastomers.

In recent years significant advances have been

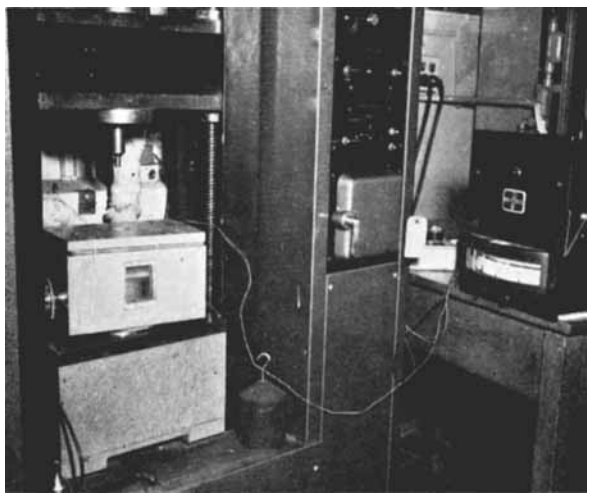

Fig. 1. Experimental arrangement for penetration testing.

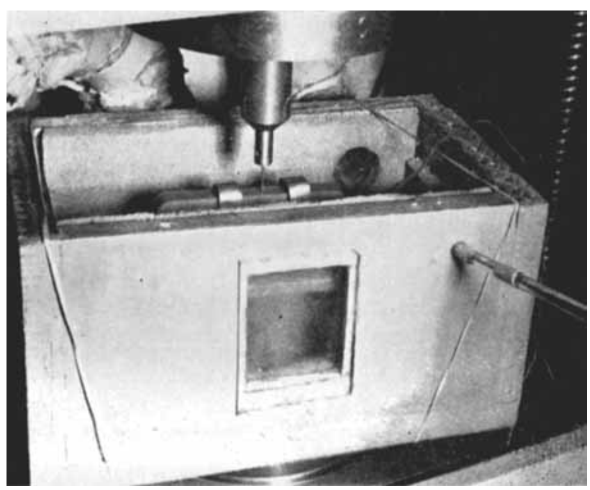

Fig. 2. Close-up of sample chamber with lid removed to show the specimen and the indentor.

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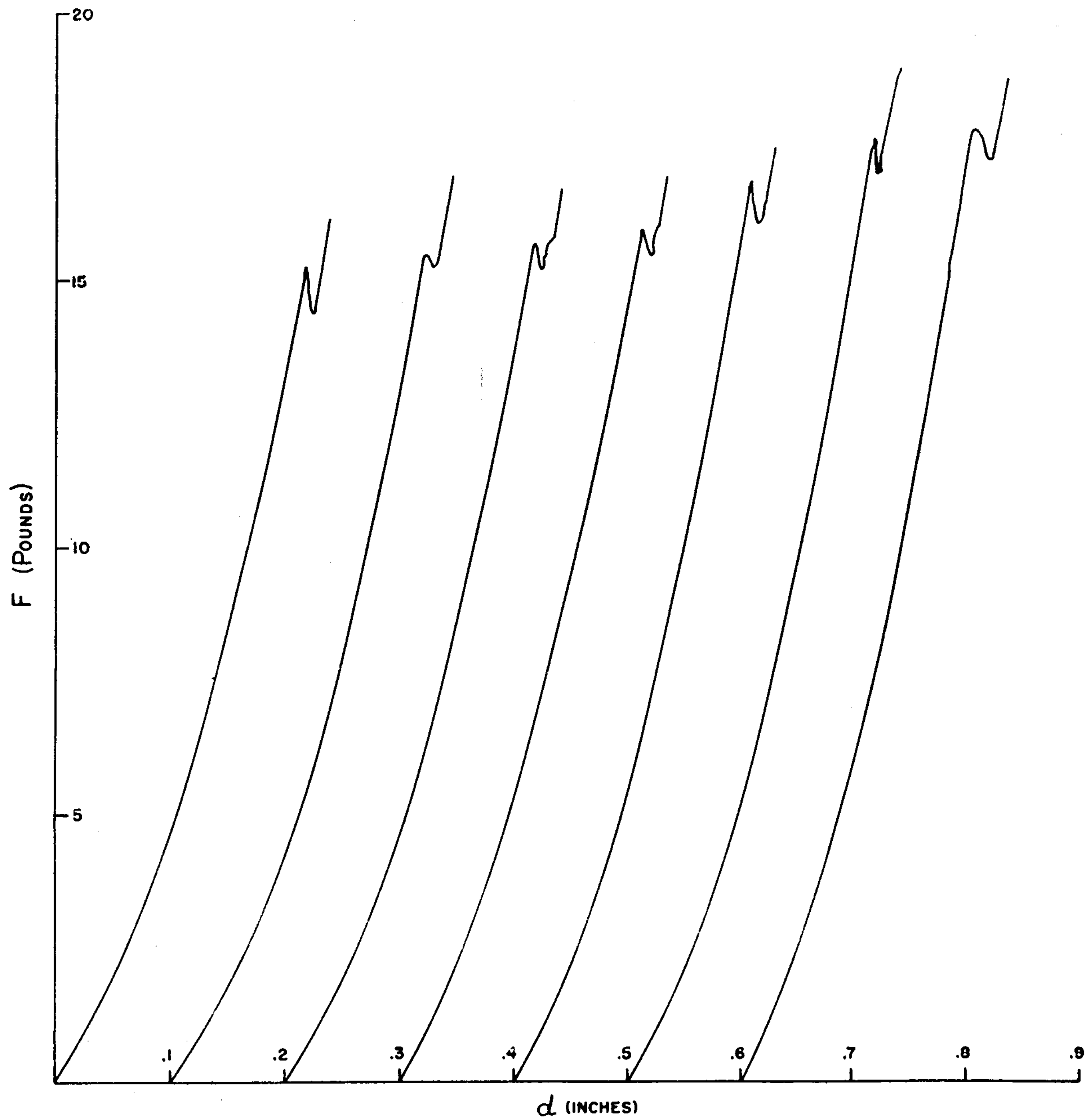

Fig. 3. Reproduction of recorded curves of force vs. penetration depth for different rates of penetration at 10°C. for Compound C: (left to right) 0.05, 0.1, 0.2, 0.5, 1, 2, and 5 in./min.

made in putting the time and temperature dependence of stress–strain properties on a common footing. Viscoelastic relations obtained in simpler experiments[3,4] have been found to apply also in some degree to behavior under large strains[5,6] and for the ultimate strength and elongation.[7–9] These fundamental investigations have usually been made under conditions of homogeneous stress and often by dynamic methods. A basic question still to be resolved experimentally is to what extent one can apply these results to more complex geometries of deformation and nonhomogeneous stresses. The puncture phenomenon appeared to provide a suitable basis for an investigation from this point of view.

EXPERIMENTAL

Figure 1 shows the apparatus used for studying puncture strength as a function of rate of penetration and of temperature. The temperature-controlled chamber in which the specimens were conditioned and tested rested on the compression load cell beneath the crosshead of an Instron testing machine. The indentor was mounted on the crosshead. The air circulating in the test chamber was fed from a rear chamber where it could be either heated electrically or cooled with liquid nitrogen in such a way as to control the temperature in the test chamber. The experiments were performed at several temperatures, and at each temperature at several rates of penetration usually varying over a range of one hundredfold, that is, from 0.05 to 5 in./min.

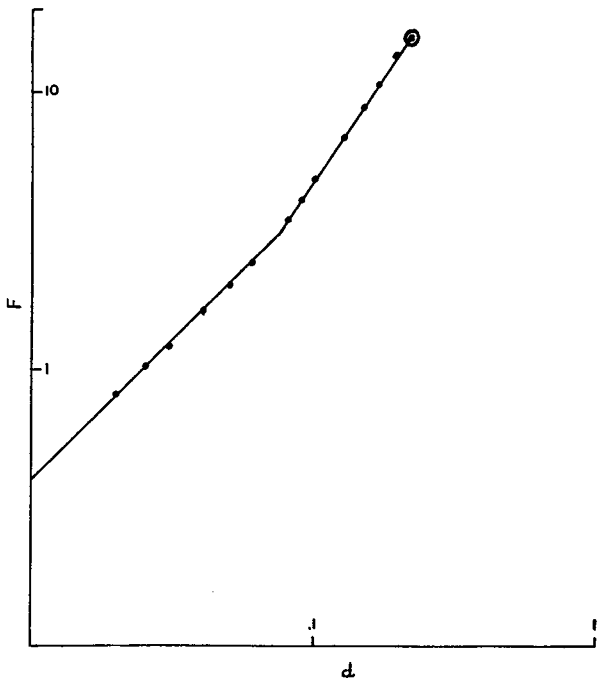

Fig. 4. Logarithmic plot of force vs. penetration for Compound C at 10°C. and a rate of 0.05 in./min.

TABLE I
Compound Recipes

	A	B	C	D
Cold SBR	100		100	
OE-SBR (25 parts oil)		100		
Butyl rubber				100
Sulfur	1.75	1.75	1.75	1.75
Zinc oxide	3	3	3	3
Stearic acid	2	2	2	2
Morpholinothio-2-benzothiazole	1.1	0.9	1	
Mercaptobenzothiazole				0.5
Tetramethylthiuram disulfide				1.0
HAF black			50	50
Cure, min./°F.	60/290	60/290	45/290	45/290

Figure 2 gives a close-up view of the test chamber and shows the specimen about to be punctured. The specimen was a vulcanized strip having a square cross section, 0.5 × 0.5 in., with the strip fitting loosely in a track so that it could be ad-

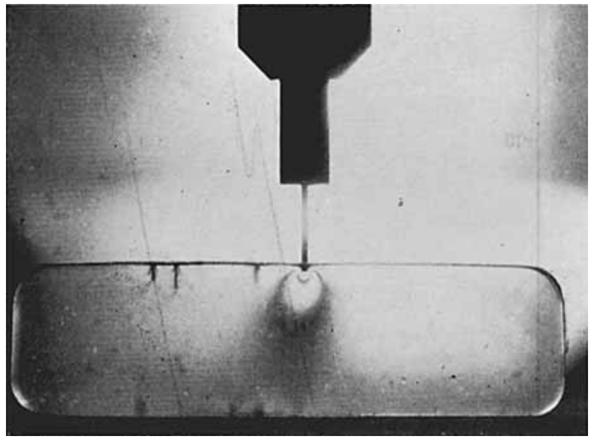

Fig. 5. Photoelastic pattern showing isochromatics for Region I for a model PVC compound.

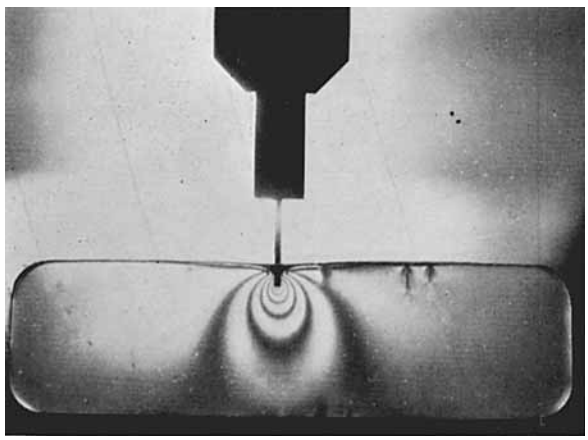

Fig. 6. Photoelastic pattern for Region II.

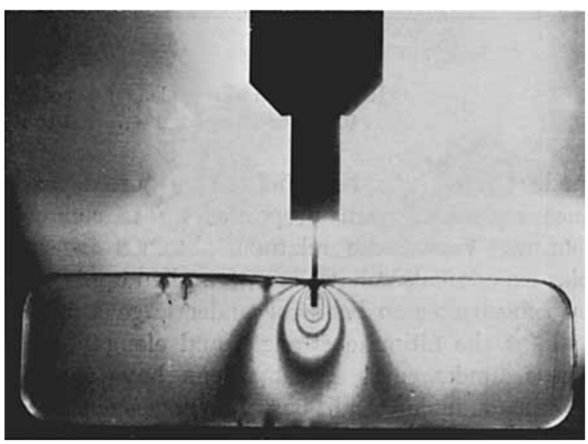

Fig. 7. Photoelastic pattern immediately after puncture

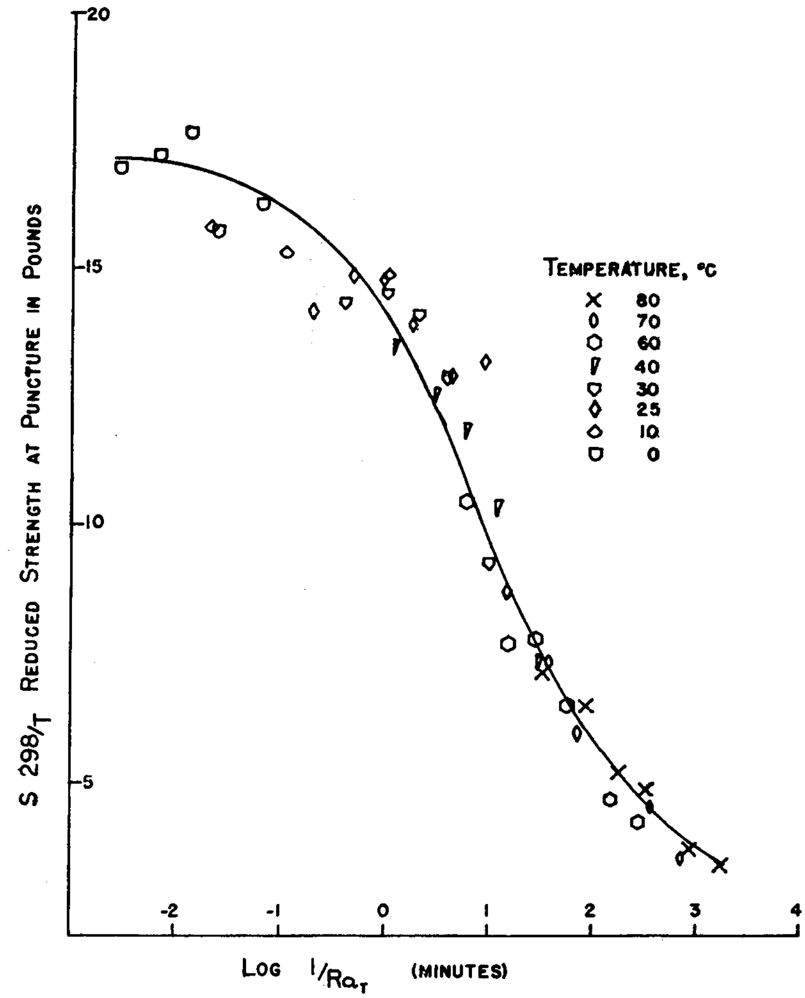

Fig. 8. Master curve for Compound A (SBR gum compound). Puncture strength reduced to 25°C. vs. log reciprocal reduced rate.

vanced to a new position for each puncture. Stops were provided to hold the strip down when the indentor was withdrawn. The indentor was lubricated with silicone grease before each puncture as this was found to give better reproducibility. The average of two values was used for each puncture strength determination. All the strips for one experimental series were prepared at the same time and were kept in the chamber throughout the run in order to ensure a controlled thermal history. The experimental scatter of the results was reduced by these procedures. Four vulcanizates were studied: gum compounds of SBR and of oil-extended SBR, and tread-type compounds of SBR and of butyl rubber. The compound recipes are given in Table I.

The indentors were made from steel drill rod, 0.047 in. in diameter unless otherwise stated. Indentors of two forms were tested. One of these had a flat end, and the other had a truncated-conical point corresponding to the standard point used for durometer hardness measurements.[10]

In Figure 3 are presented some typical load-penetration recordings obtained for different rates of penetration. The curves are displaced from the origin so that each can be seen clearly. With the tapered form of indentor point the type of curve shown in Figure 3 was obtained, even at lower temperatures, where the curves obtained with the flat-ended indentor showed plateaus at the puncture point rather than dips. The flat-ended indentor, however, gave more reliable results, the precision being about ±10%. Since the beginning of the plateau was easily distinguishable, this form of the indentor was chosen for the experimental work.

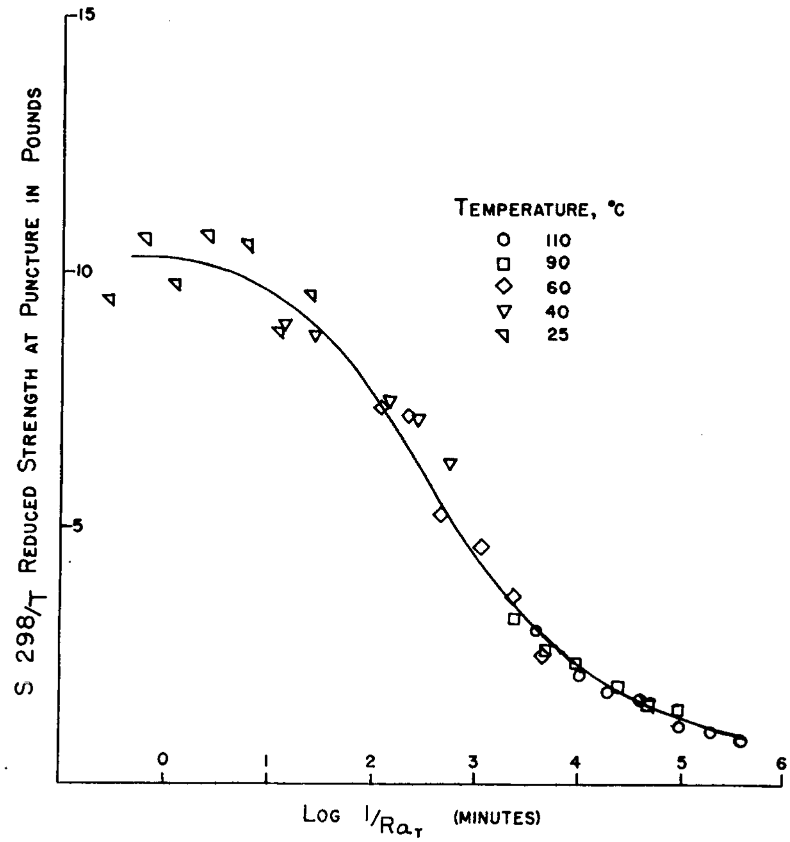

Fig. 9. Master curve for Compound B (oil-extended SBR gum compound).

RESULTS AND DISCUSSION

The recorded load–penetration curves may be analyzed conveniently by plotting both the force and the penetration on logarithmic scales as shown in Figure 4, which is such a plot for data obtained with Compound C at 10°C, and a rate of indentation of 0.05 in./min. The plot terminates at the puncture point. Typically, two regions of penetration behavior are evident, as the curve may be represented approximately by two intersecting straight lines. There is some doubt about the lowest points, which could not be determined very accurately.

In the first region, at the beginning of the penetration, the slope of the line is approximately unity, and the force is proportional to the depth of penetration. In the second region, the slope of the line on the logarithmic plot is close to $^3/_2$.

The dependence of the force on the radius of the indentor can be obtained from plots of the type shown in Figure 4 for a series of indentors of differing radii. The lines of Region I and II are extrapolated to unit depth. The logarithms of these force intercepts are then plotted for each region against the logarithms of the radii, and the slope of this line gives the radius power.

Preliminary data obtained with a series of indentors on one vulcanizate gave the following empirical expressions for the force-depth relation:

For Region I

$$F = C_1 rd \tag{1}$$

For Region II

$$F = C_2 r^{1/2} d^{3/2} \tag{2}$$

Here F is the force, r is the radius of the indentor, and d is the depth of penetration. The classical relation for penetration of an ideally elastic, semi-infinite body by a cylindrical indentor is[11]

$$F = 2.67Erd \tag{3}$$

where E is Young's modulus. The normal compressive stress on the face of the indentor for the above case is given by:

$$p = F/2\pi r(r^2 - x^2)^{1/2}$$

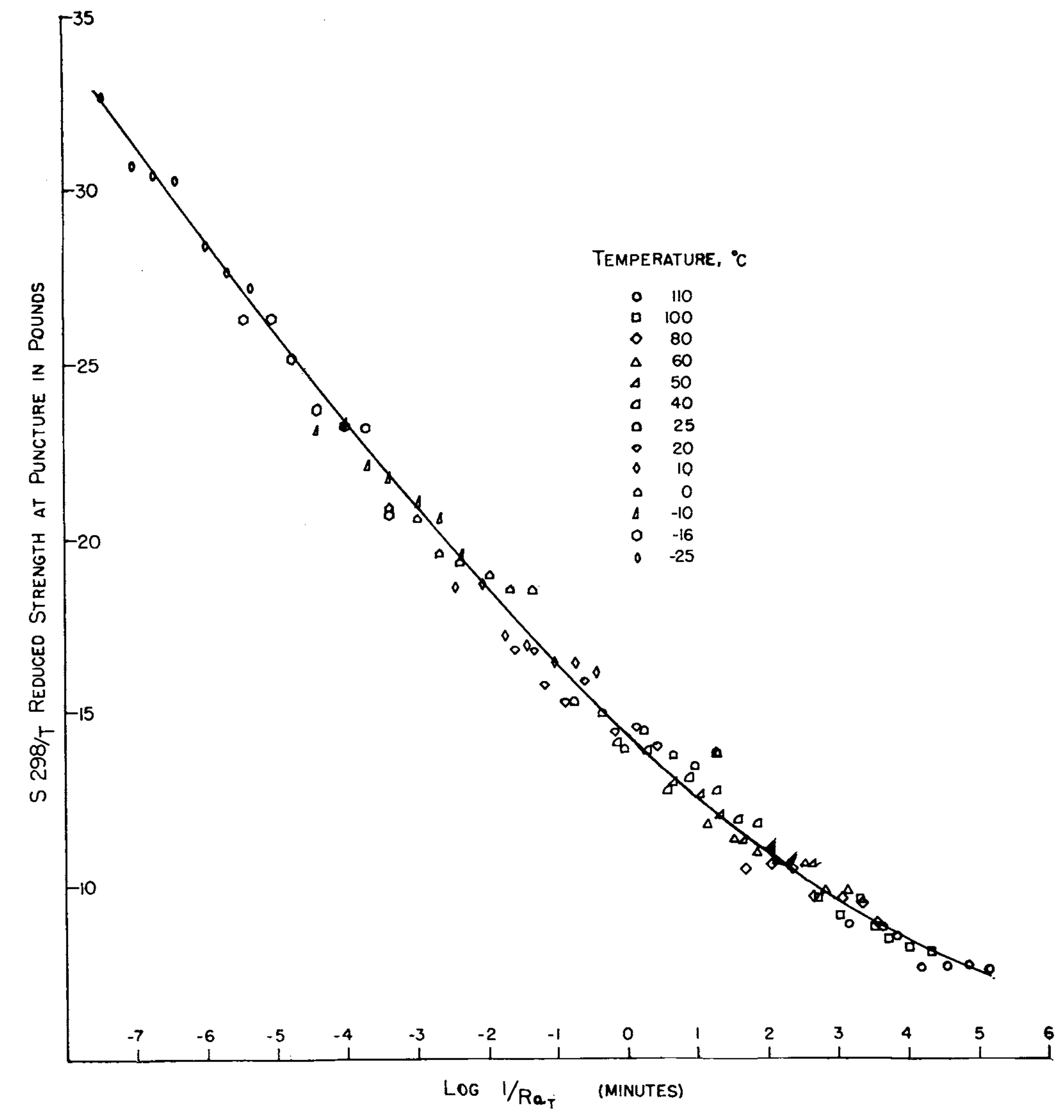

Fig. 10. Master curve for Compound C (SBR, tread-type compound).

where x is the distance from the center. It is apparent that this stress, in the ideal case, becomes infinite at the edge of the indentor, and in an actual case high stress concentrations will occur. At the center of the indentor, the compressive stress is inversely proportional to r^2.

Comparison of eqs. (1) and (3) seems to indicate that at the start of the pentration the functional relationship between the variables in the actual case approximates that for the ideal case. Indeed, eq. (3) has been verified for the Shore indentor which has a truncated-conical end.[12]

For greater depths of penetration, the classical relationship of eq. (3) is no longer followed. One way of looking at this is that a shape factor comes into play.[13] Thus, eq. (2) may be written

$$F = C_2rd(d/r)^{1/2} \tag{5}$$

and $(d/r)^{1/2}$ may be looked upon as a shape factor.

Figures 5, 6, and 7 are photographs from a photoelastic study of the penetration of specimens of a model polyvinyl chloride compound. Figure 5 shows the isochromatic fringes in Region I at the start of the penetration obtained by use of a polariscope with circularly polarized light. The isochromatics are lines of maximum shear stress. The picture serves to indicate the complex nature of the stress. The stress lines emerge from the face of the indentor in accord with the classical solution. Figure 6 is a similar photograph taken in Region II.

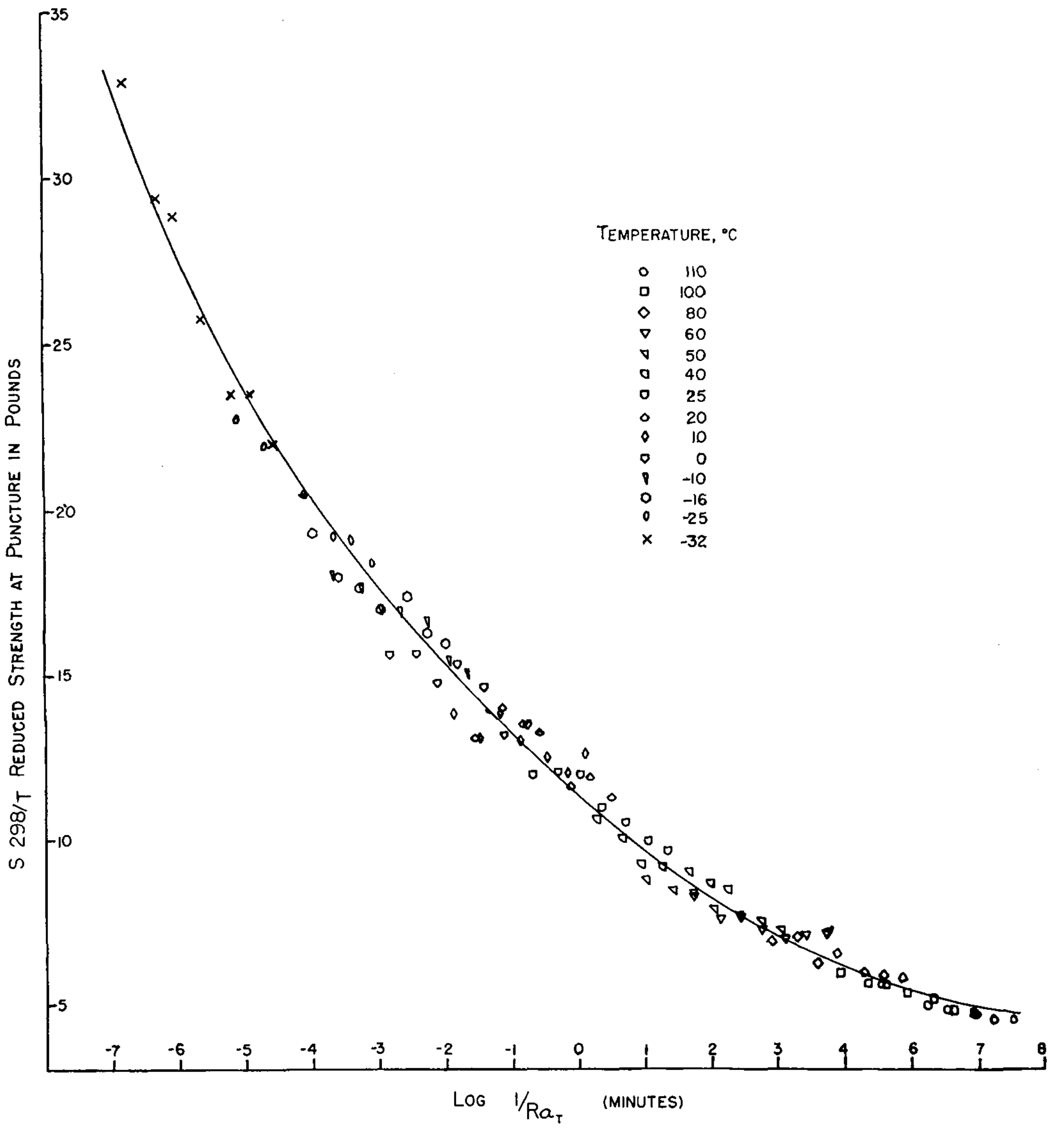

Fig. 11. Master curve for Compound D (Butyl, tread-type compound).

The stress lines now appear to be emerging also all along the deformed boundary, and a considerable stress gradient occurs along the deformed boundary in contact with the indentor.

It was apparent that, with the model PVC compound, if the indentor was withdrawn just prior to puncture, no residual stress pattern was observed. After the material was punctured there was a persistent residual stress. This can be seen in Figure 7 on the left edge of the specimen, in two punctures made on the previous day. Figure 7 shows the situation immediately after puncture, and it appears that a new stress pattern is emerging from the face of the indentor which is superposed upon the residual stress pattern which has not yet relaxed after the puncture.

The puncture strength data for the four vulcanizates were reduced to values for 25°C. by multiplying by the ratio of the absolute temperatures in the usual way; they were then plotted against the logarithm of the reciprocal of the rate of penetration. The curves so obtained were shifted to correspond on a master time scale. The composite master curves are shown in Figures 8, 9, 10, and 11. The fit is considered satisfactory for this type of experiment. The master curves for the gum vulcanizates show a flat region at the start. For these data the penetration depth had become an excessive fraction of the sample thickness.[14]

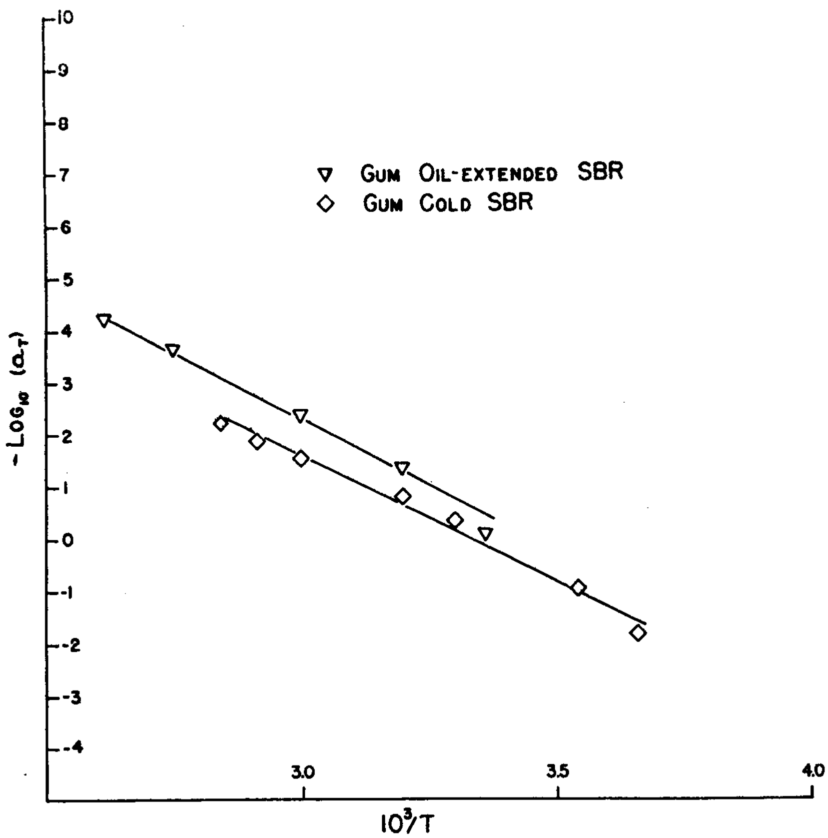

Fig. 12. Arrhenius plot of superposition factors for (◇) Compound A and (▽) Compound B.

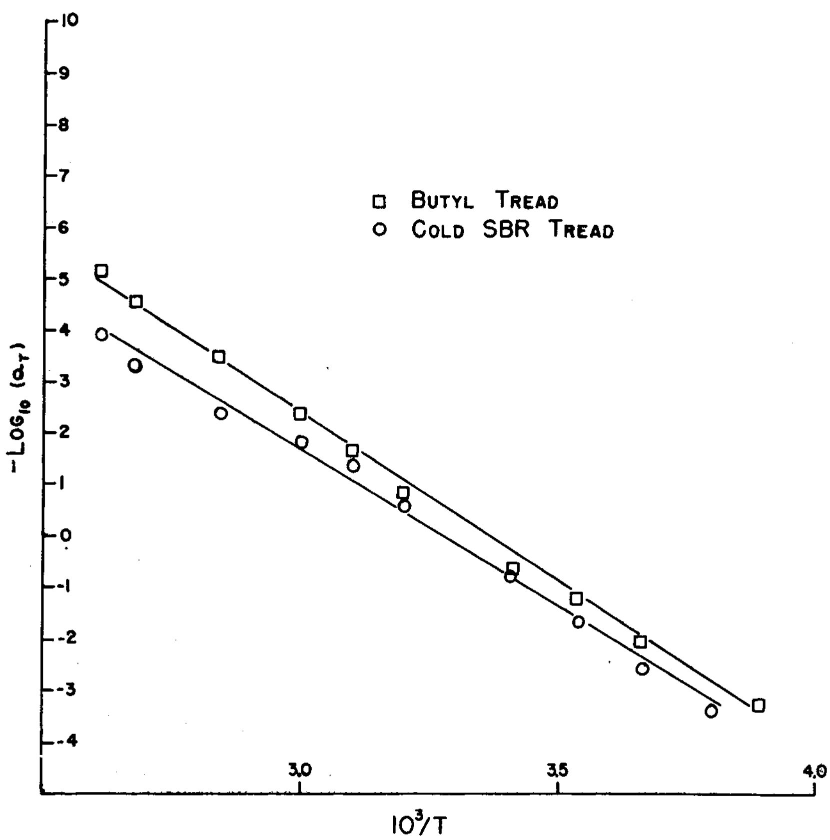

Fig. 13. Arrhenius plot of superposition factors for (○) Compound C and (□) Compound D.

Attempts to fit the Williams-Landel-Ferry (WLF) equation[4] by plotting the log of the shift factors necessary to bring the curves into correspondence against the absolute temperature and shifting this curve to correspond with a plot of log a_T against $(T - T_g)$ from the Williams-Landel-Ferry equation were not generally successful. Only for Compound A, the SBR gum compound, did the glass temperature thus determined agree with a value estimated from the Gehman low-temperature stiffness test,[15] but this was based on only a few data. Plots of $-\log a_T$ versus reciprocal absolute temperature are shown in Figures 12 and 13. It is evident that an Arrhenius relation describes the behavior with reasonable accuracy over the entire range.

From these results it can be said that the puncture process, which involves complex stresses, is amenable to viscoelastic treatment to establish its rate and temperature dependence, although the time–temperature relation may not necessarily be described by the WLF equation.

We wish to express our thanks to H. J. Osterhof and the Goodyear Tire & Rubber Company for permission to publish this work.

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Synopsis

Investigations of the viscoelastic aspects of the mechanical behavior of polymers have been limited almost exclusively to relatively simple conditions of homogeneous stress, that is, to tension or shear loadings. In the present work a study has been made from the viscoelastic standpoint of the response of several elastomers to a much more complex type of stress distribution arising from penetration up to failure by a cylindrical indentor for a range of temperatures and rates of penetration. The failure or "puncture point" was determined by a dip in the recorded curve of load versus depth of penetration. The puncture strength values were reduced to 25°C. by applying the ratio of absolute temperatures and plotted against the logarithm of the reciprocal of the rate of penetration. These curves were then shifted on the time scale to give a master curve after the manner of Tobolsky and of Ferry. The logarithms of the shift factors thus obtained were related to the reciprocal of the absolute temperature over the range studied. The results indicate a broader generality for the viscoelastic principle of time–temperature equivalence than has usually been supposed.

Résumé

Les recherches sur le comportement mécanique viscoélastique des polymères ont été limitées quasi exclusivement à des conditions relativement simples de tension homogène, c.à.d. à une tension ou étirement sous l'effet d'un poids. Dans le présent travail, on étudie la réponse viscoélastique de nombreux élastomères à un type beaucoup plus complexe de distribution de tensions, résultant de la pénétration jusqu'à l'apparition d'un défaut par une pointe cylindrique sur toute une gamme de températures et de vitesses de pénétration. L'apparition d'un défaut ou "point de ponction" était déterminé par un minimum dans la courbe de la charge en fonction de la profondeur de pénétration. Les valeurs de la force de ponction étaient ramenées à 25°C en appliquant le rapport des températures absolues, et portées en fonction du logarithme de l'inverse de la vitesse de pénétration. Ces courbes ont alors été déplacées le long de l'échelle des temps afin d'obtenir une courbe maîtresse suivant le procédé de Tobolsky et de Ferry. Les logarithmes des facteurs de décalage ainsi obtenus étaient reliés à l'inverse de la température absolue dans le domaine étudié. Les résultats indiquent une généralité plus grande pour le principe visco-élastique de l'équivalence temps-température que supposé habituellement jusqu'ici.

Zusammenfassung

Untersuchungen des viskoelastischen Verhaltens bei der mechanischen Beanspruchung von Polymeren haben sich fast ausschliesslich auf die verhältnismässig einfache Bedingung einer homogenen Spannung, d.h. auf Zugoder Scherbeanspruchung beschränkt. In der vorliegenden Arbeit wurde das Verhalten einiger Elastomerer unter dem Einfluss einer viel komplexeren Spannungsverteilung, die durch das Eindringen eines zylindrischen Körpers bis zum Bruch hervorgerufen wird, in einem gewissen Temperaturund Eindringgeschwindigkeitsbereich vom Standpunkt der Viskoelastizität aus untersucht. Der Bruch oder "Lochpunkt" wurde durch eine Vertiefung in der aufgenommenen Belastungs-Eindringtiefekurve bestimmt. Die Werte für die Lochungsfestigkeit wurden durch Bildung des Verhältnisses der absoluten Temperaturen auf 25°C reduziert und gegen den Logarithmus des Reziprokwertes der Eindeinggeschwindigkeit aufgetragen. Diese Kurven wurden dann in der von Tobolsky und von Ferry angegebenen Weise auf der Zeitskala verschoben und konnten zu einer gemeinsamen Kurve vereinigt werden. Die Logarithmen der so erhaltenen Verschiebungsfaktoren wurden im untersuchten Bereich als Funktion der reziproken, absoluten Temperatur dargestellt. Die Ergebnisse sprechen für eine breitere Anwendbarkeit des viskoelastischen Prinzips der Zeit-Temperaturäquivalenz, als üblicherweise angenommen wird.

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