Rise of Temperature on Fast Stretching of Butyl Rubber

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The rise of temperature on fast stretching of natural and synthetic rubber stocks was investigated recently by Dart, Anthony, and Guth (D.A.G.). Since then the experimental technique was considerably improved and the taking of data greatly simplified thereby. By D.A.G. emphasis was placed to record temperature rises of up to 15°C for extensions up to 700 percent by a fast galvanometer of moderate sensitivity. In the present work this high heat was investigated. In addition, however, a less fast but more sensitive galvanometer was employed to record changes of temperature as small as 0.001°C for 0–80 percent extension. In accordance with early work by Joule on natural gum (1859) it was found that also Butyl gum stocks show an initial cooling effect. This passes at a thermoelastic inversion point into a heating effect. In agreement with the recent theory by James and Guth the thermoelastic inversion point was found to depend solely upon the thermal expansion coefficient of the unstretched stock. The coefficient of thermal expansion was measured for Butyl stocks in the present work. Butyl tread stocks also show the thermoelastic inversion point. The work of D.A.G. showed that the rise in temperature on extension is a slowly rising function of the extension with a steep upward turn and almost linear continuation after the onset of crystallization. The samples were kept extended for a minute and then the cooling arising on retraction also measured. The negative of the cooling on retraction plotted against extension fall, according to the second law of thermodynamics as it should under the extension curve, but crosses it at the onset of crystallization. For Butyl gum stocks this crossing takes place at rather high (600 percent or more) extensions in agreement with x-ray work. More similarity was found between Butyl and Hevea tread stocks than between the corresponding gum stocks. Loading shifts the onset of crystallization to a range of smaller extensions. In addition to measuring the change of temperature on extension and retraction, the residual rise in temperature after an extension and immediate fast cycle retraction was also observed. This quantity is a measure of internal friction in Butyl rubber and is closely connected with rebound and free vibration tests. Summarizing, the method described has a twofold application for development work: 1. Changes of the temperature on extension and delayed retraction indicate in a simple manner the onset and progress of crystallization. 2. Changes of the temperature in a fast cycle give an estimate for internal friction. Both these applications will facilitate attempts to improve present synthetics.

INTRODUCTION

THE rise of temperature on fast stretching is one of the noteworthy characteristics of rubber stocks. If one stretches rapidly a Hevea gum band several hundred percent and applies it to the chin, one gets a direct sensory observation of the heat developed. This shows that the temperature must have been higher than that of the body, i.e., there must have been a temperature rise of 12–15°C. Surprisingly enough such a "high heat" was not observed, when the human lip was replaced by a supposedly more objective apparatus, namely, by a thermocouple in conjunction with a galvanometer. In addition, different authors reported different values for the heat rise—all much lower than at 15°C. Recent work in this laboratory by Dart, Anthony, and Guth[1] was done with a fast galvanometer. This work

showed that the use of slow galvanometers was one reason why previous investigators could not observe "high heat." In addition, a survey of various types of natural and synthetic gum and tread stocks showed that the heat generated depends sensibly upon the type of stock used. This accounts for the disagreement among earlier investigators.

The work of Dart, Anthony, and Guth[1] showed that for gum stocks, the rise in temperature on extension is a slowly rising function of the extension. This slow rise is owing to the heat into which the work of stretching is transformed. For stocks which crystallize on stretching, the rise in temperature takes a steep upward turn and continues almost linearly after the onset of crystallization. This was found to be the case for Hevea and Neoprene. Hycar OR, on the other hand, did not show the upward turn in agreement with x-ray data, which do not reveal any crystallization for this type of synthetic. Now, for the case of Butyl gum stocks, x-ray data show that they
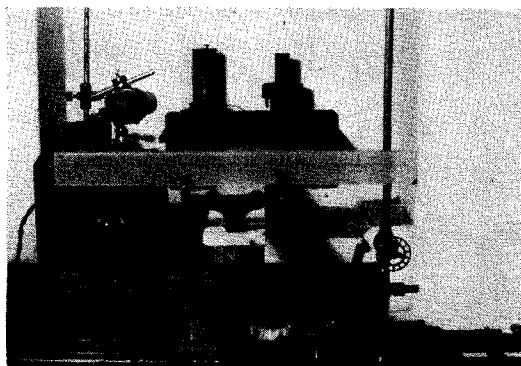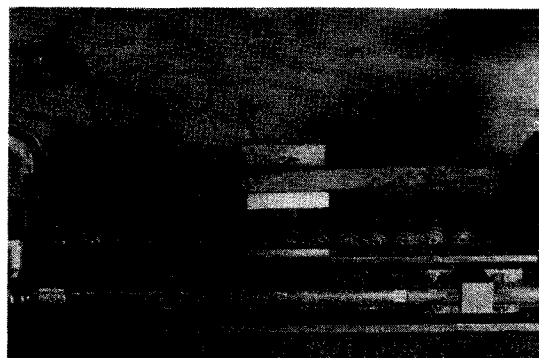

FIG. 1.

FIG. 2.

do crystallize on stretching, but start at very high extensions only (500 percent and higher). Therefore, it seemed to be of interest to study the onset and continuation of crystallization for Butyl stocks by means of "high heat" curves.

In addition the initial cooling effect at small extensions was studied by employing a sensitive but slower galvanometer. Changes of temperature as small as 0.001°C ("low heat") could be observed. The experimental technique for taking both high and low heat data was greatly improved and simplified compared to our earlier work referred to.[1] Moreover, besides taking extension and delayed retraction curves as in reference 1, the residual heat for extension and immediate retraction (fast cycle) was also observed.

I. EXPERIMENTAL METHOD

A compressed air driven machine was used to obtain rapid extensions and retractions. With this machine, extensions can be produced from 0 percent up to any elongation in 0.1 second. The machine can also be used for rapid extension-retraction oscillations up to frequencies as high as 600 per minute, and the gradual rise of temperature in the sample followed as a function of number of cycles, speed of cycles, and degree of elongation.

Temperatures were measured with a copper-constantan thermocouple sandwiched between two samples given a half-twist. For small temperature changes a galvanometer of longer period, about 8 sec., and a sensitivity of 4×10^{-9} amp. per millimeter was employed. This apparatus is shown in Figs. 1 and 2.

II. COMPOSITION OF THE STOCKS

The stocks were prepared for us by the Esso Laboratories. The ingredients of each vulcanizate are given in parts by weight in Table I. Numbers 1, 2, 4, and 5 were cured for 60 minutes at 307°F; number 3 (non-sulfur cure) for 45 minutes at 287°F. Slabs with dimensions $13.5 \times 13.5 \times 0.25$ were cured for 70 minutes.

III. PHYSICAL PROPERTIES OF THE RAW STOCKS AND TENSILE DATA FOR THE CURED STOCKS

The following data were communicated to us from the Esso Laboratories.

The Butyl A raw stock possessed about 0.95 mole percent (based on the C_4H_8 chain unit) of unsaturation according to the Kemp-Wijs method, the unsaturation figure for the Butyl B polymer is about 1.5 percent. Their intrinsic viscosities are about the same, 1.25 in di-iso-butylene at 20°C. The corresponding viscosity average molecular weight is 290,000.

Tensile data for the cured stocks are given in Table II.

IV. RESULTS ON HIGH AND LOW HEAT

High heat curves for stocks 1–5 are given in Figs. 3–7. All three curves (extension, retraction, fast cycle) were obtained using one single sample. Previous work in this laboratory[1] has shown that somewhat higher ΔT values could be obtained by using a different sample for each extension, the reason being that some temporary or permanent set was introduced at each extension. However, variations within the batch partially offset this
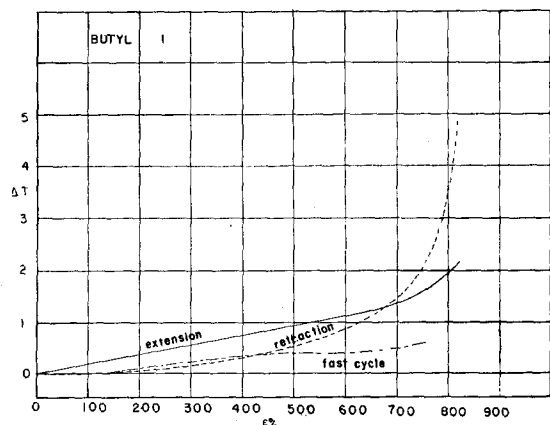
FIG. 3.

TABLE I.

Stock No.	1	2	3	4	5
Butyl A	100	100	—	—	—
Butyl B	—	—	—	100	100
Zinc oxide	5	5	—	5	5
Stearic acid	3	3	—	3	3
Sulfur	1.5	1.5	—	1.5	1.5
Calbot No. 9, Black	—	50	—	—	50
Treads	1	1	—	1	1
Captax	—	0.5	—	—	0.5

TABLE II.

Stock	Load at 300% lb./in.²	T.S. lb./in.²	B.E. in %
1	—	1900	950
2	280	2500	790
3	950	2000	500
4	—	2900	1000
5	380	2675	780

advantage of using different samples. The ΔT values obtained give the curve denoted "extension." After the sample had been stretched (in about one-tenth of a second), it was kept extended for one minute and then the machine pushed it back (again in one-tenth of a second) to the unstretched state. The negative of the temperature change involved in this (forced) retraction process is plotted as "retraction." The curve designated "fast cycle" represents the residual ΔT value for an extension and immediate (forced) retraction. Again, extension and retraction took place in two tenths of a second.

Low heat curves for stocks 4 and 5 are given in Figs. 8 and 9. Extension, retraction, and fast cycle curves were obtained in the same way as for the case of high heat.
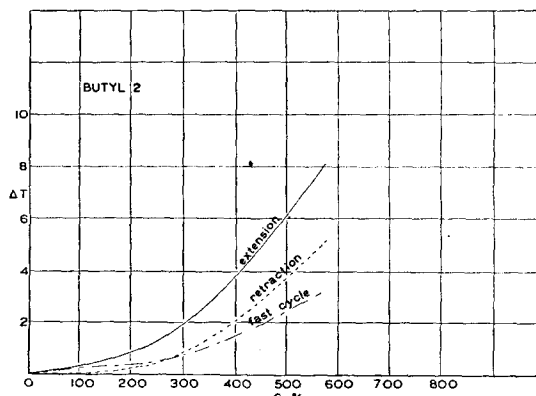

FIG. 4.

V. DISCUSSION OF THE RESULTS

The first question we have to answer is that concerning the basic physical significance of the extension, retraction, and fast cycle curves.

(a) Extension Curves

Thermodynamics (Kelvin, 1855) gives the formula for the change of temperature ΔT on adiabatic extension

$$\Delta T = \frac{T}{C_L} \int_1^L \left(\frac{\partial Z}{\partial T}\right)_L dL; \qquad (1)$$

where T is the absolute temperature, C_L the specific heat at constant length per cm³ (independent of L), L the relative length (extended length divided by original length, the original length taken at the initial temperature T), Z the stress (actual force per unit original cross section).

$$L = (\epsilon/100) + 1 \qquad (2).$$

expresses L in terms of the more familiar percentage extension ϵ. Formula (1) correlates the temperature coefficient of the stress at constant extension $(\partial Z/\partial T)_L$ with the change in heat $\Delta T \cdot C_L$ on adiabatic stretching. The change (rise) in temperature on adiabatic stretching is entirely similar to the rise in temperature on adiabatic compression of a gas. The physical meaning of formula (1) is clearer if we recognize that (cf. Anthony, Caston, and Guth[2] and James

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[2] Anthony, Caston, and Guth, J. Phys. Chem. **46**, 836 (1942); cf. also Peterson, Anthony, and Guth, Ind. Eng. Chem. **34**, 1349 (1942).
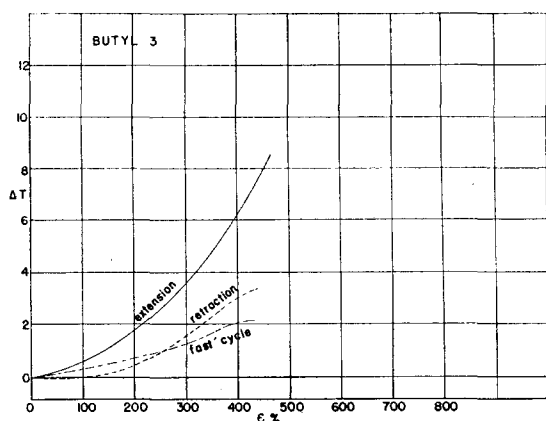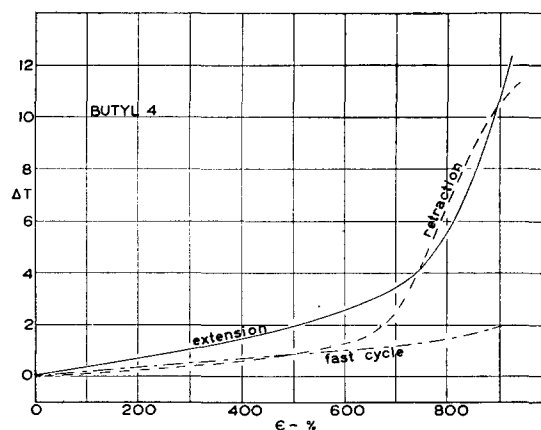
FIG. 5.

FIG. 6.

FIG. 7.

and 'Guth[3] for the use of this concept)

$$T(\partial Z/\partial T)_L = T(\partial S/\partial L)_T = Z_{(S)}. \qquad (3)$$

S is the entropy as a function of L and T, and $Z_{(S)}$ designates the entropy part of the stress. Then:

$$\Delta T = \frac{T}{C_L} \int_1^L Z_{(S)} dL \qquad (4)$$

or

$$(d/dL)(C_L \Delta T) = Z_{(S)}; \qquad (4')$$

i.e., differentiation of the ΔT vs. L curve yields $Z_{(S)}$ if C_L is known. If C_L is not known, (4') will still yield $Z_{(S)}$ except for the numerical factor C_L.

The foregoing makes clear the physical significance of the ΔT vs. L curves for extension. Formula (4) is established first for a single phase. If a (more or less slow) crystallization process occurs in a certain L range, formula (4) holds also through crystallization.

The general behavior of $Z_{(S)}$ is known from references 2 and 3. There a relaxation method [described in reference 2] was applied to obtain $Z_{(S)}$. The range of crystallization was investigated by Wiegand and Snyder,[4] Meyer and Ferri,[5] Caston, Anthony, and Guth[6] and recently, more accurately by Wood and Roth.[7] From these investi-

[3] H. James and E. Guth, J. Chem. Phys. **11**, 455 (1943); cf. also E. Guth, *Surface Chemistry*, pub. No. 21, A.A.A.S. (1943), p. 103; E. Guth, Alexander's *Colloid Chemistry*, (Reinhold Publishing Corporation, New York, 1944), Vol. V, p. 286.

[4] Wiegand and Snyder, Rubber Chem. Tech. **8**, 151 (1935).

[5] Meyer and Ferri, Helv. Chim. Acta. **18**, 570 (1935).

[6] Caston, Anthony, and Guth, unpublished material.

[7] L. A. Wood and F. A. Roth, J. App. Phys. **15**, 781 (1944). We are indebted to Dr. Wood and Mr. Roth for discussions of their work prior to its publication.
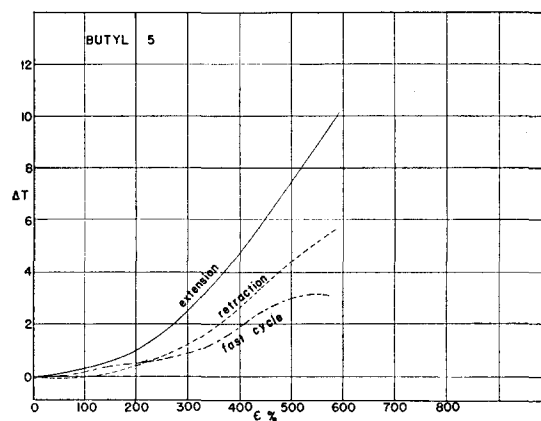
gations, it follows that the $Z_{(S)}$ vs. L curve looks schematically as drawn in Fig. 10. (a) is drawn to a larger scale than (b) in order to show clearly the thermoelastic inversion. Here we plotted, besides $Z_{(S)}$, the total stress Z and the internal energy component

$$Z_{(U)} = Z - Z_{(S)}. \qquad (5)$$

The integral of $Z_{(S)}$ as derived from Fig. 10 will appear as shown in Fig. 11 (assuming $C_L \cong 0.4$), i.e., the change in temperature is first negative, passes through a minimum, given by $(\partial Z/\partial T)_L = 0$, goes to zero and becomes positive.

$$(\partial Z/\partial T)_L = 0 \qquad (6)$$

defines the isometric (=isotonic) thermoelastic inversion point because, at the extension L_i, given by the root of (6), the sign of the slope of the isometrics (Z-T curves at constant L)

changes.

$$\Delta T = 0 \tag{7}$$

defines the adiabatic thermoelastic inversion point, L_a. Both L_i and L_a are indicated in Fig. 10(a).

The statistical theory by James and Guth[3] gives an expression for $(\partial Z/\partial T)_L$ containing only one adjustable parameter K and the measurable cubic thermal expansion coefficient α of the unstretched sample (T_0: room temperature 300°K)

$$\left(\frac{\partial Z}{\partial T}\right)_L = K\left[L - \frac{1 + \alpha T_0}{L^2}\right], \tag{8}$$

valid for the range of extension of Figs. 10(a) and 11(a). Inserting into (1) we obtain

$$\Delta T = (KT/2C_L)[L^2 + L - 2(1 + \alpha T_0)]$$
$$\times [(L-1)/L]. \tag{9}$$

From (8) and (6) we have

$$L_i = 1 + (\alpha/3)T_0; \tag{10}$$

from (9) and (7) it follows that

$$L_{ad} = 1 + (2\alpha/3)T_0. \tag{11}$$

We have measured α both for the gum and the tread stock and obtained

$$\alpha\text{-gum} = 1.74 \times 10^{-4}, \tag{12}$$
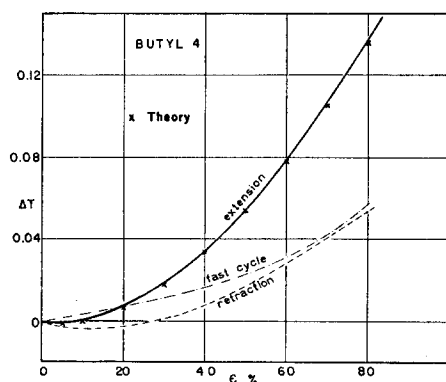
$$\alpha\text{-tread} = 1.17 \times 10^{-4}. \tag{13}$$

The value of α-gum looked somewhat low in view of the fact that for many Hevea and synthetic gum stocks $\alpha \cong 2.1 \times 10^{-4}$. However, a glance at Fig. 8 shows that experimentally

$$\begin{aligned} L_i &= 1.05, \\ L_a &= 1.10, \end{aligned} \tag{14}$$

which are just exactly the theoretical values according to (10) and (11) if we substitute (12). The crosses in Fig. 8 indicate the theoretical values for ΔT using again (12). The agreement with experiment is rather good.
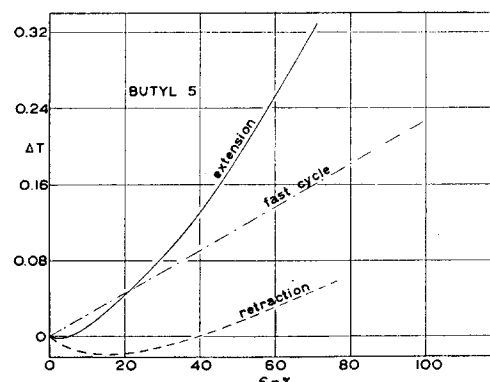

FIG. 9.

For extensions up to 700 percent the ΔT vs. L curves rise slowly. This whole range is covered by the statistical theory of James and Guth;[3] we just have to replace (8) by its generalization involving the inverse Langevin function.

Physically, in this range 0–700 percent the work done on stretching transforms practically completely into heat, $C_L \cdot \Delta T$.

For extensions above 700 percent, however, crystallization sets in. The $C_L \cdot \Delta T$ corresponding to the steep upward turn of the high heat curve represents the latent heat of crystallization. The above interpretation holds for gum stocks, i.e., Figs. 3 and 6. The tread stocks, Figs. 4 and 7 and the non-sulfur cure, Fig. 5, show different behavior. Here the high heat curve starts its upward turn much earlier. The early upward turn for tread stocks is partly owing to an earlier onset of crystallization as a consequence of carbon black reinforcement. Partly, however, it is owing to frictional heat between the rubber matrix and carbon black.

This interpretation for gum stocks is supported by considering the retraction curve.

(b) Retraction

The retraction curve is more arbitrary than the extension curve, since the one-minute delay could be replaced by a shorter or longer waiting

period, thereby changing the retraction curve. Below the range of crystallization the retraction curve is always below the extension curve in accordance with the second law of thermodynamics.

At the onset of crystallization the retraction curve crosses the extension curve, owing to the fact that additional crystallization took place during the waiting time of one minute. It was shown in reference 1 that the crystallization process takes time. After completion of crystallization, we have again one phase, and retraction recrosses the extension and is again below it. This may be seen in Fig. 6.

An estimate of the latent heat of crystallization may be obtained by taking the difference in ΔT between the two crossings. The difference in ΔT between the two crossings, multiplied by C_L, measures the heat of crystallization. We see from the steepness of rise of the extension and retraction curves that the heat of fusion is very considerable (cf. Fig. 6).

(c) Fast Cycle Curves

These curves give actually the hysteresis loop between the extension and retraction branch of stress-strain curves taken in 0.2 second. For, that loop is simply given by

$$\text{Loop} = C_L \cdot \Delta T. \tag{15}$$

This loop (of Fig. 12) corresponds to the dynamic hysteresis loop for extensional free or forced vibrations around a static strain of $\epsilon^*/2$ and with a constant dynamic amplitude of $\epsilon^*/2$, and a
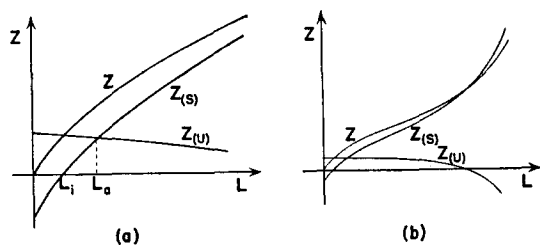

FIG. 10.

frequency of 5 cycles per second. It does correspond more closely to the first cycle of a free or a forced vibration. A comparison with sustained forced vibrations is possible, of course, by observing ΔT for repeated fast cycles. The relation

of the fast cycle curves to rebound data is the same as that of the corresponding free vibrations. Of course, the static strains and amplitudes employed in forced or free vibrations are of the order of 10–30 percent, whereas the amplitudes
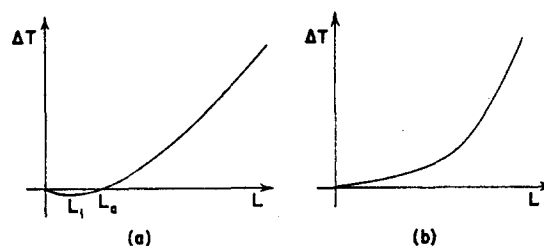

FIG. 11.

for high heat measurements may go right up to the breaking elongation, i.e., up to 1000 percent.

It should be pointed out that the impact resilience as measured by the rebound of a ball or of a pendulum depends *both* upon the dynamic hysteresis loop and upon the dynamic modulus, i.e., stiffness of the stock. Roughly, we may consider the rebound as a half free vibration. For the percentage resilience R we obtain then

$$R = (h_R/h) = \exp\,(-H_A/A^2E),$$

where h_R is the height of rebound, h is the height of fall, H_A is the energy loss per cycle for vibrations with constant amplitude A, and E is the dynamic modulus.*

We wish to point out that the hysteresis loops corresponding to fast cycles (0.2 sec.) are presumable solely or mostly owing to internal friction.

"Static" hysteresis loops, obtained with comparatively slow speed stretching (for instance, with the usual 20 inches per minute), are owing to stress relaxation. There is a correlation between the two types of hysteresis loops, but probably not a simple one. We shall discuss this correlation in another place.

The fast cycle curves are *not* the difference between extension and retraction. Particularly for the gum stocks the fast cycle curves increase much slower with the elongation than the extension and retraction curves. For small elongations, Fig. 8 shows the fast cycle to rise almost linearly in the beginning and then approach the retraction branch.

* Cf. for instance Dillon, Prettyman, and Hall, J. App. Phys. **15**, 309 (1944), see p. 320.

VI. GENERAL DISCUSSION

(a) Gum Stocks

1. Low Heat

The low heat curve for Butyl gum (compound 4) may be compared with that of a Hevea gum, cf. Fig. 5 of James and Guth.[3] The extension curves are about the same, both for Butyl and for Hevea. Since Butyl at the same elongation has a lower stress value than Hevea (i.e., the value of K is smaller for the former) the value of C_L must also be smaller for Butyl than for Hevea. This conclusion will be checked by direct measurement of C_L. The smaller value of the thermal expansion coefficient will also tend to raise ΔT, but this influence acts only in the neighborhood of the thermoelastic inversion point.

The retraction and fast cycle curves (the last not given in Fig. 5 of James and Guth[3]) differ greatly for Hevea and Butyl. Since Butyl shows less stress relaxation than Hevea, this difference must be owing to the considerably greater internal friction of Butyl.

2. High Heat

The extension curves for stocks in Figs. 3 and 6 have roughly the same form up to about 400 percent. It should be pointed out that the accuracy of high heat curves increases with the elongation because of the better contact between the rubber and the thermocouple. Above 400 percent the curve rises faster for stock 4 than for stock 1. This behavior is in keeping with the higher tensile strength and somewhat higher breaking elongation of stock 4 in contrast to stock 1. It is to be expected that between 800 and 1000 percent a further steep rise of ΔT occurs, in view of the steep rise of the stress-strain curves in this region. Experiments are underway to check this conclusion.

The retraction curves coincide for the two stocks up to about 600 percent elongation. From there on the curve for stock 4 rises steeper than that for stock 1.

The fast cycle curves rise very slowly for both stocks. The investigation of the range above 800 percent will be interesting.

Comparison of the Butyl high heat curves of Figs. 3 and 6, with the high heat curve of a Hevea

gum stock (cf. Fig. 4 of Dart, Anthony, and Guth[1]) is quite revealing. That particular Hevea gum stock crystallizes at about 250 percent elongation, as the first crossing of the extension and retraction curves indicates. Actually the retraction branch is somewhat lower than the extension branch below 250 percent, as more accurate experiments have shown. However, the difference between extension and retraction is smaller for Hevea than for Butyl. The characteristic difference between Hevea and Butyl is, of course, the late and more abrupt crystallization of Butyl in contrast to the earlier and more gradual crystallization of Hevea. This is indicated in the schematic Fig. 13 where the solid curve represents extension and the dashed curve retraction. The first crossing indicates the onset of crystallization.

The correlation of stress-strain curves (and hysteresis loops) with x-ray data is somewhat complicated by the fact that x-ray diagrams are taken over a period of hours during which the rubber samples are kept at constant extension and suffer stress relaxation. No such difficulty enters into the discussion of crystallization using high heat data. As a matter of fact, high heat data may be helpful in establishing the correct relationship between x-ray and stress-strain data.

(b) Tread Stocks[8]

1. Low Heat

Figure 9 for stock 5 shows a thermoelastic inversion point and a much steeper rise of the low
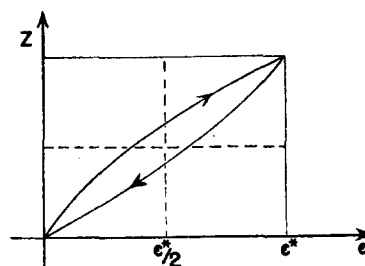

FIG. 12.

heat curve than Fig. 8 for the gum stocks. This steeper rise is, of course, caused by the stiffening

[8] For a theory of filler reinforcement cf. J. Rehner, Jr., J. App. Phys. 14, 638 (1943). This aspect of the problem is discussed more fully by E. Guth, J. App. Phys. 16, 20 (1945).

of the stock by carbon black reinforcement. The difference between extension and retraction branch is also much bigger for the tread than for the gum stocks. Butyl tread shows a low heat curve essentially similar to Hevea tread, the
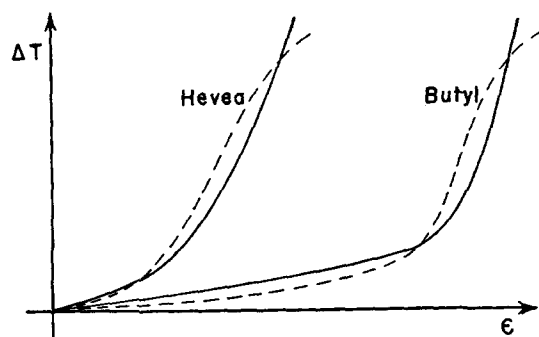

FIG. 13.

separation between extension and retraction branches being larger for Butyl than for Hevea.

2. High Heat

Figures 4 and 7 show the data for the stocks 2 and 5, respectively. Figure 5, the non-sulfur cure, shows essentially the behavior of a very stiff tread stock. For tread stocks, the retraction branch is always below the extension branch without any crossing. Conclusions about the onset of crystallization may be drawn only from the steepness of the curves. Therefrom one would conclude that crystallization starts between 200 and 300 percent. Figure 14 compares high heat curves for Hevea and Butyl tread. The cross on the curves indicates the onset of crystallization. The Hevea curve is taken from Fig. 7 of Dart, Anthony, and Guth.[1] Comparison of Figs. 13 and 14 shows that the carbon black induces both for Hevea and Butyl an earlier crystallization. Consequently stronger forces will act between the chains of a tread than for a gum stock. In order to get a correct view of carbon black reinforcement in Butyl rubber, it seems necessary to consider the whole stress-strain curve and the whole high heat curve, not just tensile strength. It was pointed out already by Turner, Haworth, Smith, and Zapp,[9] that on the basis of tensile strength alone, carbon blacks do not reinforce Butyl, but they enhance other

physical properties, as for instance modulus and tear resistance. Figure 15 shows the stress-strain curves for stocks 4 and 5.

One sees that in the range 0–750 percent a reinforcement of the same degree takes place as for GR-S; actually, it is smaller for Butyl than for GR-S. This range is characterized by the absence of crystallization. It seems that a certain irregularity, suppressible by crystallization, is necessary for a specifically large reinforcement by carbon black. The fact that Butyl gum does crystallize appreciably beyond 750 percent, as evidenced by the abrupt rise in the high heat curve and in the stress-strain curve itself, does not count, so to say, since the black stock breaks at 780 percent. In Hevea, blacks also cause a decrease in the breaking elongation, but since the crystallization is more gradual, crystallization and carbon black add up, roughly speaking, in the reinforcement. Now for Hevea, the reinforcing effect is relatively larger for an undercure, than for the optimum cure (determined by maximum tensile), and relatively smaller for an overcure. The probable reason is that for an undercure the breaking elongation is higher and so crystallization and carbon black have a larger region to add up for reinforcement. From this point of view, it would be interesting to see how far an undercured Butyl stock may be reinforced by blacks. Although the undercured Butyl gum has a lower tensile than the optimally cured, the corresponding black stocks may reverse in the order, particularly, if the breaking elongation of the black stock could be extended, say over 900 percent. It should be pointed out, however, that the work of Turner, Haworth, Smith, and Zapp[9] (cf. their Figs. 5 and 6) does not indicate such a reversal.

Another possibility, to obtain higher black tensiles would be a shift of the range of crystallization to lower extension or to make it start earlier so that it would be more gradual and less abrupt.* The experimental methods described in this paper could be very helpful in such attempts to improve on Butyl.

VII. CONCLUSIONS

Study of the rise in temperature on fast stretching of Butyl gum and tread stocks throws

[9] Turner, Haworth, Smith, and Zapp, Ind. Eng. Chem. 35, 958 (1943).

* Cf. Sturgis and Trepagner, Rubber Age 54, 325 (1944).
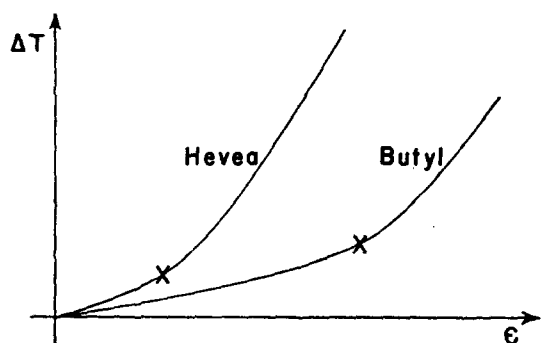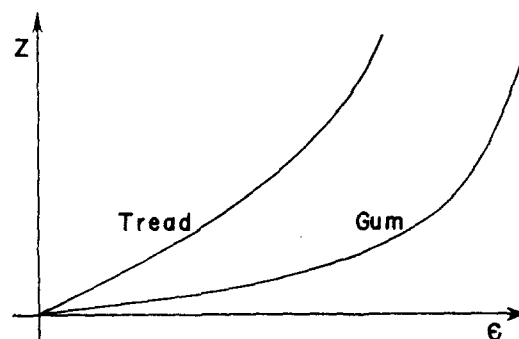
FIG. 14.

FIG. 15.

considerable light on crystallization, internal friction, and carbon black reinforcement as functions of elongation and other possible variables. For low elongations the low heat curves show the occurrence of thermoelastic inversion. They also show that internal friction is much larger for Butyl than for Hevea. For high elongations the high heat curves enable one to follow the late and abrupt crystallization, so characteristic for Butyl stocks. The carbon black reinforcement of Butyl is followed for the whole range of elongations up to the breaking point. Specific carbon black reinforcement takes place in the range of elongations before crystallization of the gum stock, but the shortening of the breaking elongation by the black excludes to a large extent the added reinforcement through crystallization.

Physical measurements of the type reported in this paper serve a manifold purpose. They enable one to establish a correlation between physical properties and chemical structure. Such a correlation is simpler for fundamental physical properties, as the ΔT vs. ϵ curve, than for the more complicated physical tests, as data from flexometer, which were designed to approach service conditions. Comparing different gum stocks with Butyl polymers, among themselves and with Hevea or other synthetics, these measurements may guide the development of better Butyl polymers. Finally, comparing tread with gum stocks they may help to recognize the nature of reinforcing by carbon blacks and the action of other compounding ingredients.

ACKNOWLEDGMENT