

Characterization of a Vulcanizate of the Halogenated Butyl Rubber, MD-551. I. Gum Properties

M. BERGER

Esso Research and Engineering Company, Central Basic Research Laboratory, Linden, New Jersey

INTRODUCTION

MD-551 is a chlorinated copolymer of isobutylene and isoprene with an average unsaturation of 1 to 2%.¹ The vulcanizate differs from the vulcanizate of butyl rubber by virtue of the differences in the nature of the crosslinks which are possible and the resultant differences in the by-products of vulcanization. Thus, any differences between the properties of the MD-551 and the butyl vulcanizates are attributable to differences between their crosslinking and/or the effects of by-products of vulcanization. Because of this, it would appear that a characterization of MD-551 can best be made by a comparison with conventional butyl rubber under similar conditions.

CHARACTERIZATION OF SAMPLES

The polymers chosen for this work were MD-551 and Enjay Butyl 325. Both polymers have number-average molecular weights of about 197,000. The MD-551 has a chlorine content of 1.1 to 1.3 wt.-%.

The vulcanizates might be compared in a number of ways. The two comparisons that immediately suggest themselves are each polymer optimally cured, and the two polymers at equal densities of crosslinking. As a means of characterization, the former comparison introduces a number of problems. The optimum cure system for MD-551 is quite different from that for Enjay Butyl 325, and thus in order to understand any differences in properties, the effect of variations in crosslinking density would have to be taken into account. For this reason, it was decided to run all tests on polymers of equal densities of crosslinking. Hence, it should be borne in mind that the results in various tests reported here do not necessarily represent the optimum for each vulcanizate but rather values for strictly comparable vulcanizates.

Swelling Behavior

The formulations used are shown in Table I. A series of these compounds were cured for various

TABLE I
Formulations for Cure at 307°F.

	Enjay Butyl 325	MD-551
Enjay Butyl 325	200	—
MD-551	—	200
Stearic acid	2.0	2.0
Zinc oxide	10	10
Tetramethylthiuram disulfide	—	1.0
Tellurium diethyldithiocarbamate	1.5	—
Sulfur	3.0	—

lengths of time. The vulcanizates were then swollen in cyclohexane and the apparent molecular weight between crosslinks calculated by the Flory-Rehner expression:²

$$M'_c = \rho V_1 V_2^{1/3} [\ln(1 - V_2) + V_2 + \mu V_2^2] \quad (1)$$

Here M'_c is the apparent molecular weight between crosslinks, ρ is the density of polymer, V_1 the molar volume of solvent, V_2 the volume fraction of polymer in the swollen gel, and μ the liquid-polymer interaction coefficient. It is necessary to establish a value for μ by an independent method. This was done by the equilibrium stress method, as will be shown in a later section. From M'_c we can calculate the true molecular weight between crosslinks, M_c , according to Flory:³

$$1/M'_c = g(1/M_c - 2/M_n) \quad (2)$$

where M'_c is the apparent molecular weight between crosslinks, M_c the true molecular weight between crosslinks, M_n the number-average-molecular weight, and g is a variable factor which is 3.3 for butyl. It should be noted that the use of g at a value of 3.3 will give M_c values higher than those we normally see in the literature, where the value

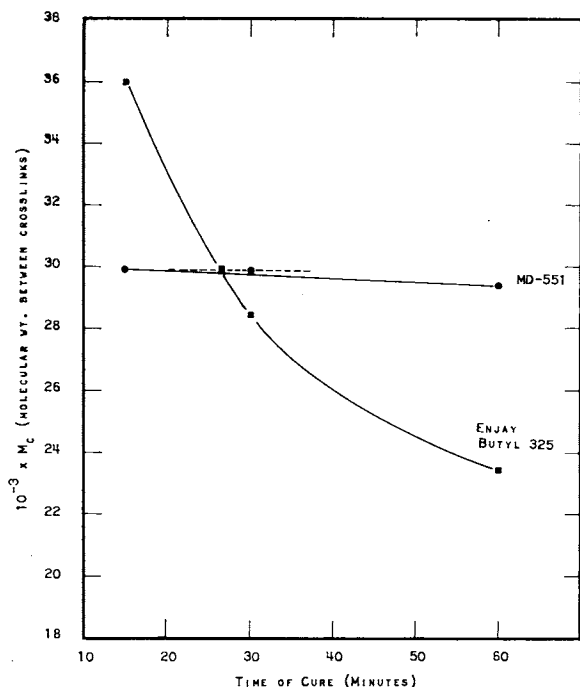


Fig. 1. Average molecular weight of chain between crosslinks (M_c) vs. cure time for MD-551 and Enjay Butyl 325.

is usually set at unity. The g factor is related only to the accuracy of the molecular weight M_c calculated. Any comparisons with previous published data should make allowance for the relative differences in the M_c values. Using eqs. (1) and (2), we have plotted M_c against time or cure, and the results are shown in Figure 1. In addition to indicating the points of equal crosslinking densities for the two polymers, Figure 1 shows the excellent and well-known cure characteristics of MD-551, i.e., the vulcanizate system reaches its equilibrium at an early cure time, promoting rapid curing, and then stabilizes at that value so that the danger of overcuring is avoided.

On the basis of these curves, it was decided to run all characterization studies at M_c of 29,800. This corresponds to cure times of 27 min. for the Enjay Butyl 325 and 30 min. for the MD-551. In this report, unless otherwise noted, all data refer to vulcanizates of this crosslink density.

Diffusion Behavior

The constants for diffusion of cyclohexane through the two polymers are identical and can be expressed by

$$D = 1.3 \times 10^{-8} \exp \{12.5V\} \quad (3)$$

where V is the concentration of solvent in the polymer and D is the diffusion constant. These measurements were carried out on the instrument developed by Buckley and Berger.⁴ As was pointed out in reference 4, such measurements can be interpreted in terms of the three-dimensional configuration of the polymer being tested. The fact that MD-551 and Enjay Butyl 325 have the same values of diffusion indicate that the molecular chain configurations of the polymers in the unstrained state are identical. Further, we would guess that in any situation in which only small changes from the unstressed state occur (as in small-amplitude dynamic testing, or low-extension testing), the two polymers would behave similarly.

Stress-Strain Behavior

Figures 2, 3, and 4 show the stress-strain behavior of the two gum vulcanizates at three different temperatures and at a variety of extension rates. For almost all conditions, at extensions below 500% the stress-strain behaviors of the MD-551 and the butyl are identical. This is shown clearly in Figure 5 which affords a detailed view of the early portion of the stress-strain curves for both polymers. The similarity of this behavior

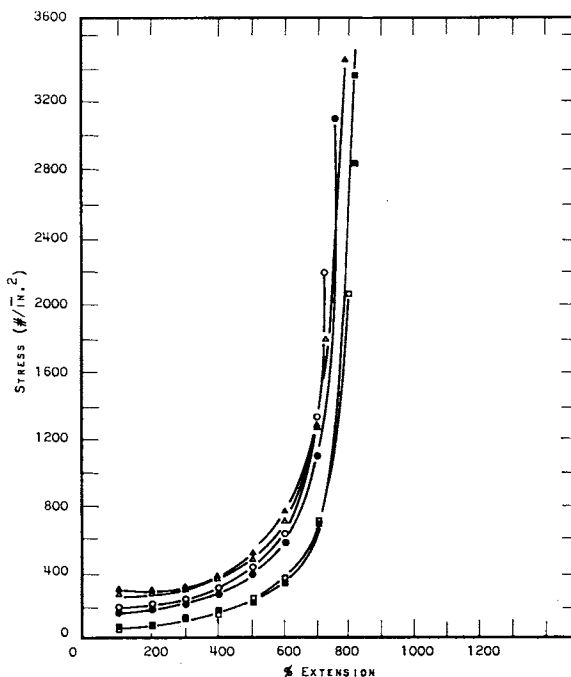


Fig. 2. Stress vs. strain at -30°F . for Enjay Butyl 325 extended at rates of (■) 52%/min., (●) 650%/min., (▲) 5000%/min., and for MD-551 extended at rates of (□) 50%/min., (○) 520%/min., (△) 5000%/min.

substantiates that of the swelling behavior discussed previously. At extensions above 500%, the polymers respond quite differently, the extent of the difference depending on the temperature of

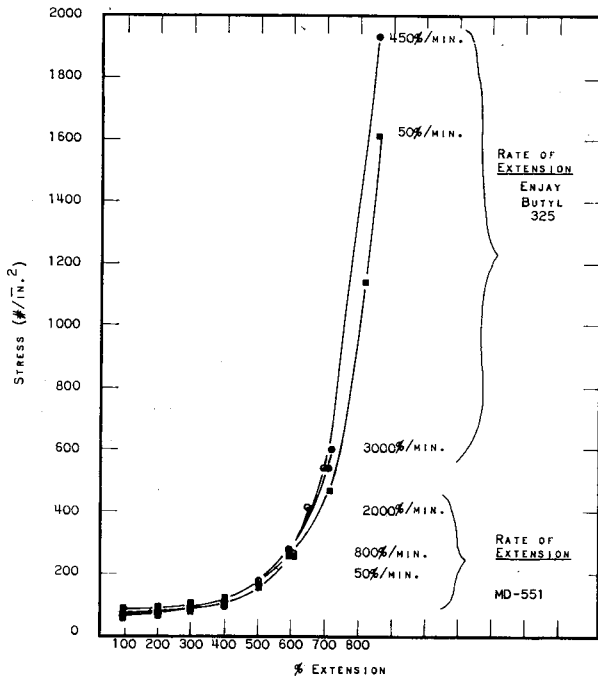


Fig. 3. Stress vs. strain at 72°F. for Enjay Butyl 325 and MD-551.

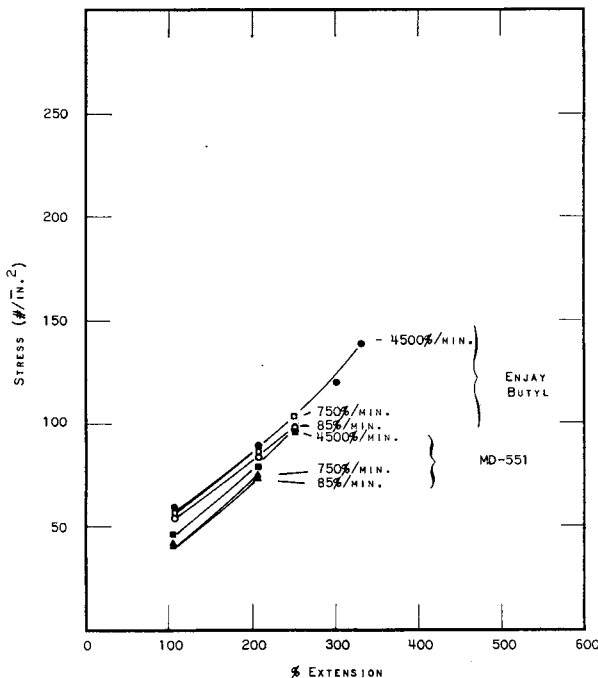


Fig. 4. Stress vs. strain at 212°F. for Enjay Butyl 325 and MD-551.

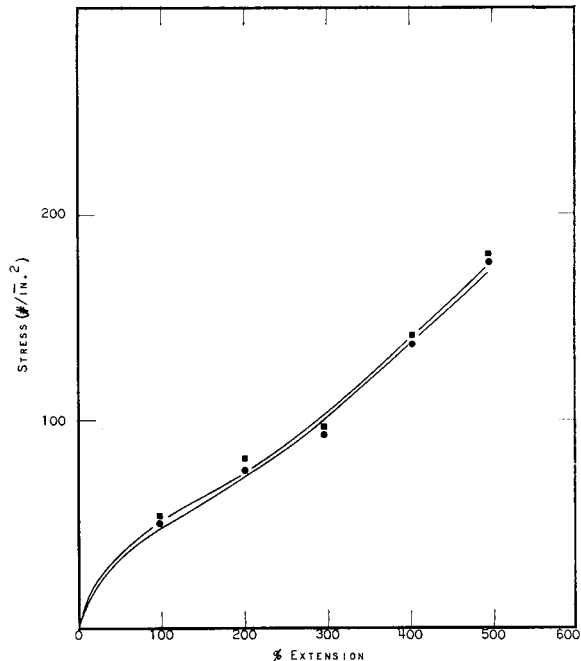


Fig. 5. Stress vs. strain at room temperature for (■) Enjay Butyl 325 of 1850 lb./in.² tensile strength and (●) MD-551 of 250 lb./in.² tensile strength, extended at 20 in./min.

the test. The stress at 72°F. in the case of MD-551 continues to increase moderately with strain until about 600% extension, and then the sample fails. On the other hand, the stress in the butyl increases very rapidly with strain and the sample fails at about 700 to 800% extension with a considerably higher stress than the MD-551. At low temperatures (-30°F.) the stress in both polymers increased rapidly with strain above 500%. The butyl, however, still has a higher tensile strength. At elevated temperature (212°F.) neither polymer shows rapid increase of stress with strain. Indeed, for most test conditions, the polymers do not reach 500% extension. The butyl, however, still has a slightly higher tensile strength. The tensile strengths of the vulcanizates versus rate of extension at various temperatures are shown in Figure 6. Three-dimensional plots for each polymer are shown in Figures 7 and 8.

From all the data, it appears that under high strain the molecular chains of the butyl vulcanizate are capable of "ordering" or crystallizing, while those of the MD-551 are not. This conclusion is based on a number of considerations. The high slope of the butyl stress-strain curve at 72° is generally attributed to crystallization. This effect is absent in MD-551. Examination of Figure 6

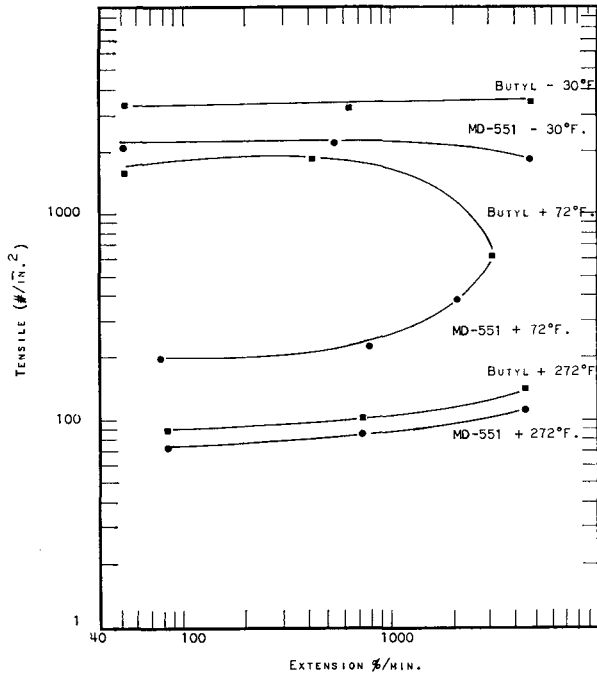


Fig. 6. Tensile strength vs. rate of extension for Enjay Butyl and MD-551 at various temperatures.

shows that the tensile strength of the butyl at 72°F. *decreases*, while that of the MD-551 *increases*, with increasing rate of extension. It has been pointed out in the literature^{5,6} that a decrease in tensile strength with increasing rate of extension is indicative of a structure characterized by crystallization at high extensions. This decrease occurs because a finite time is required in order for crystallization to take place, and as the sample is strained at faster and faster rates, there is less and less time available. Hence, the sample loses strength. An amorphous polymer, on the other hand, gains strength at rapid rates of extension, owing to the fact that steric entanglements do not have time to break during the time of the test, and thus act as additional crosslinks. It is important to note that at high temperatures, where crystallization is impossible, the two polymers have very similar tensile strengths. At very low temperatures, where the majority of effective crosslinks are steric ones and the chemical crosslinks in the two polymers become ineffectual, the tensile strengths are again quite similar.

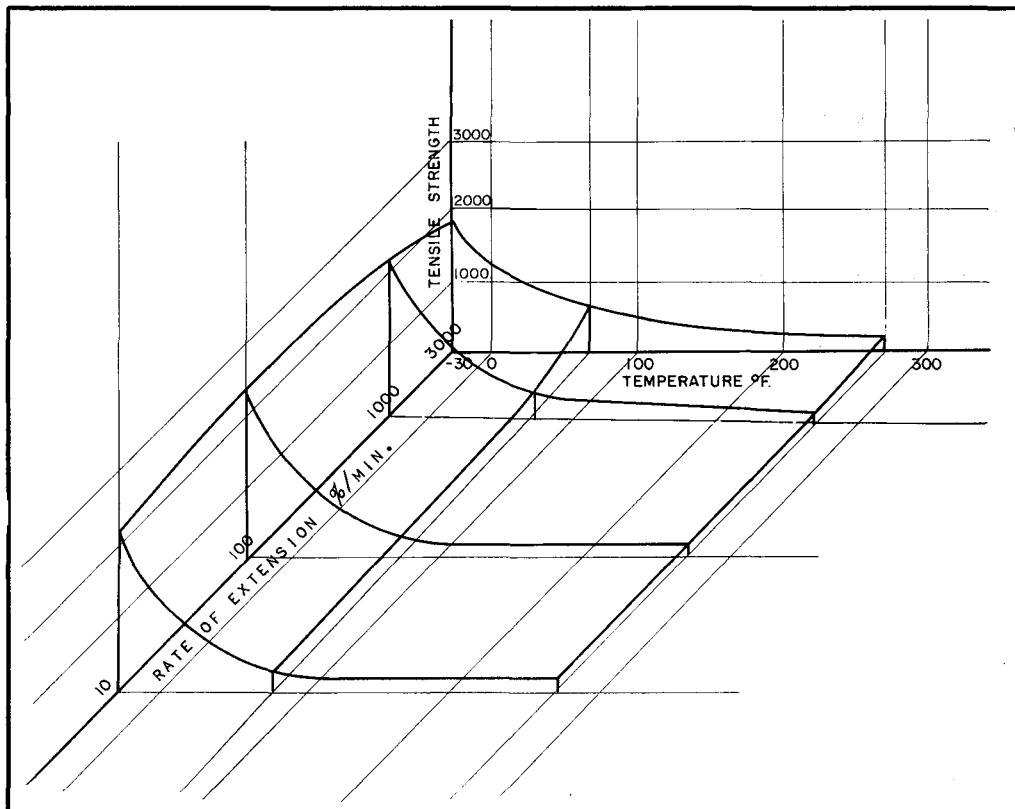


Fig. 7. Tensile strength vs. temperature and rate of extension for MD-551.

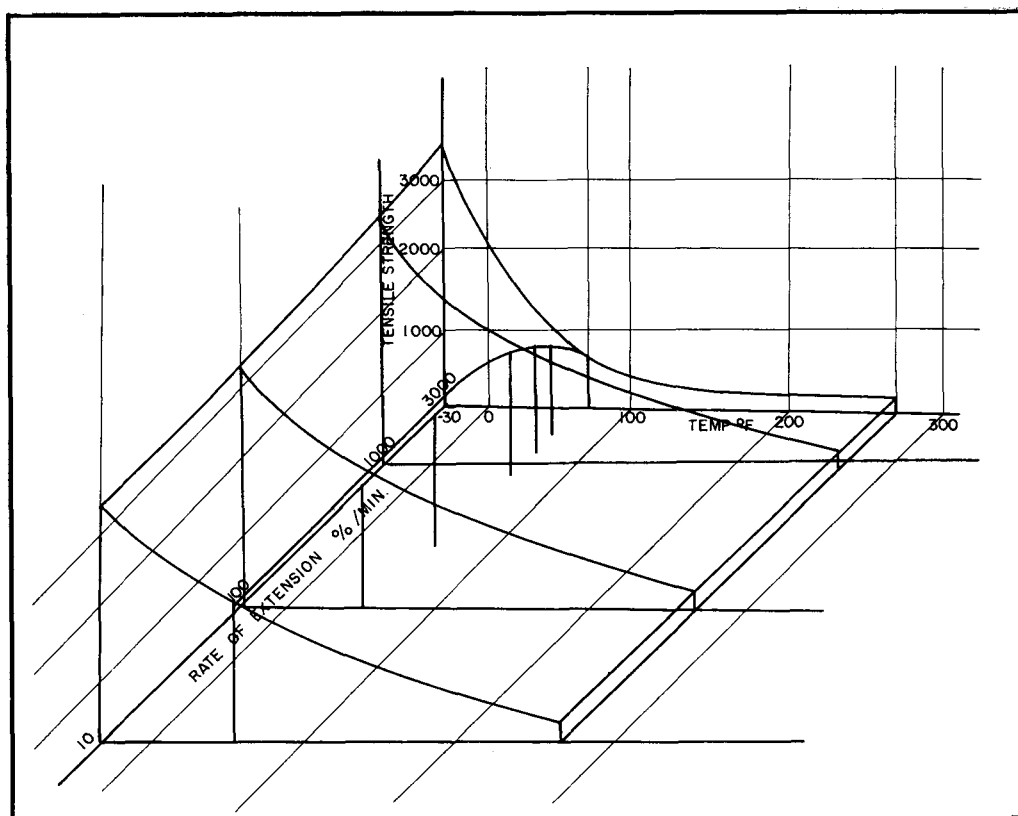


Fig. 8. Tensile strength vs. temperature and rate of extension for Enjay Butyl 325.

A possible explanation for the difference between the behaviors of the two polymers is found in the nature of their crosslinks. The Enjay Butyl 325 has sulfur crosslinks. Under high extension, it is possible for these crosslinks to break and then reform in a fashion more amenable to alignment. The nature of the MD-551 crosslink is not too clearly understood (this will be gone into in more detail in a later section). However, the assumption here is that it is mechanically more stable than the sulfur crosslink. Hence, under high strain conditions, the crosslink will not adjust rapidly enough to permit chain alignment to occur, and hence crystallization will not take place. If this concept is correct, one would expect that crystallization could take place in MD-551 if the polymer were stretched very, very slowly. Figure 9 shows the x-ray patterns of butyl and MD-551 for various degrees of extension. The butyl photographs were taken shortly after the sample was stretched. It appears that crystallization, as evidenced by the layer line spots in the x-ray photographs, occurs rapidly. The MD-551, on the other hand, cannot be extended to the degree necessary for crystallization unless the stretch occurs very slowly. In this

case, the sample was stretched from 500 to 650% over a period of 216 hr. and crystallization did occur, as shown by the patterns in Figure 9.

This is not the first time it has been observed that the nature of the crosslink influences crystallization. This was previously found with resin-cured butyl⁷ which, much like an MD-551 vulcanizate, did not crystallize on being stretched except under very slow stretching.

Stress Relaxation

The polymers were further examined by means of stress relaxation measurements. Polymers were extended and held for long periods of time at 50% elongation, and the stress developed was continuously recorded. This was done at temperatures of 212, 167, 122, and 77°F. The data are shown in Figures 10, 11, 12, and 13. Figure 13, giving the stress relaxation at 212°F., is an excellent illustration of the well-known high temperature stability of MD-551.

Stress relaxation at 212°F. occurs principally because of oxidative scission.⁸ The energy of activation for this scission can be calculated as

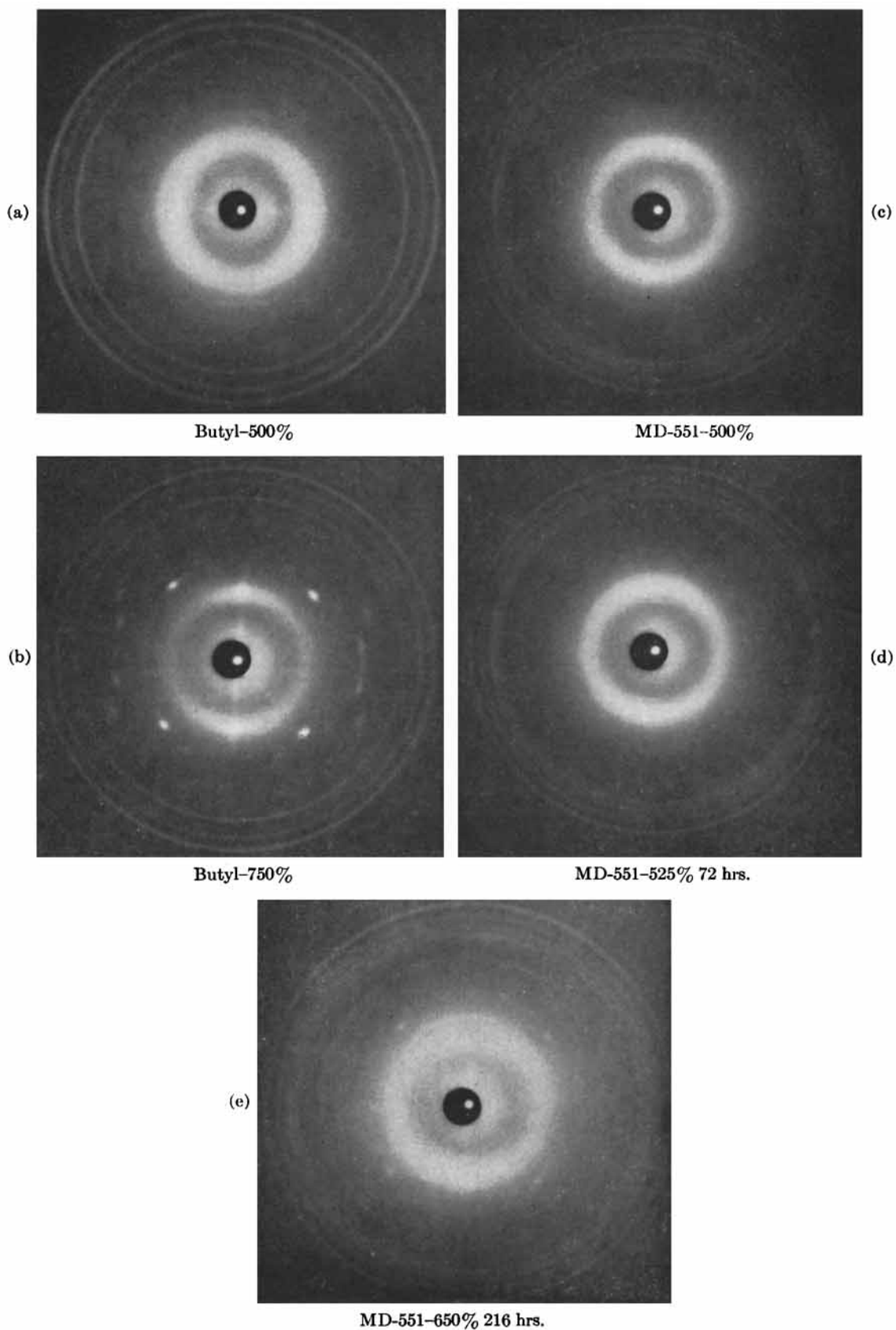


Fig. 9. X-ray patterns of Enjay Butyl 325 and MD-551 under extension.

follows from the theory of absolute reactions.⁸ The reaction rate constant K is given by

$$K = (kT/h) \exp \{ -\Delta F/RT \} \quad (4)$$

where k is Boltzmann's constant, h is Plank's

constant, R is the gas constant, ΔF is the free energy of activation per mole, and T the absolute temperature. To a good approximation, the stress decay is given by

$$\tau = \tau_0 \exp \{ -kt \} \quad (5)$$

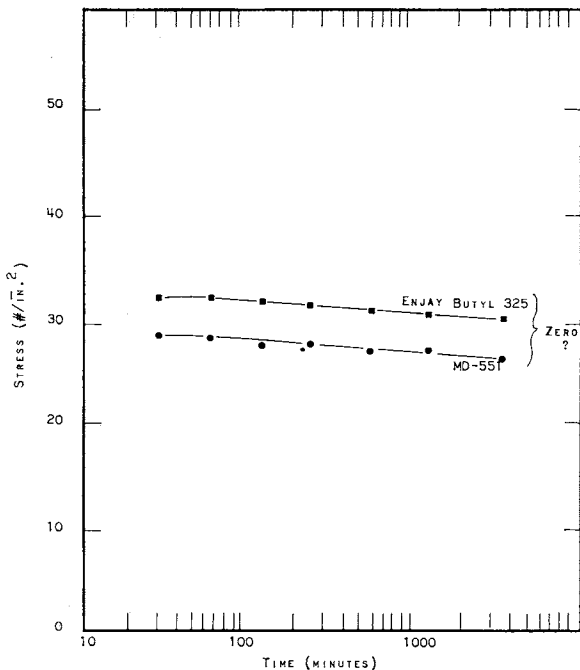


Fig. 10. Relaxation of stress in Enjay Butyl 325 and MD-551 extended 50%, at 77°F.

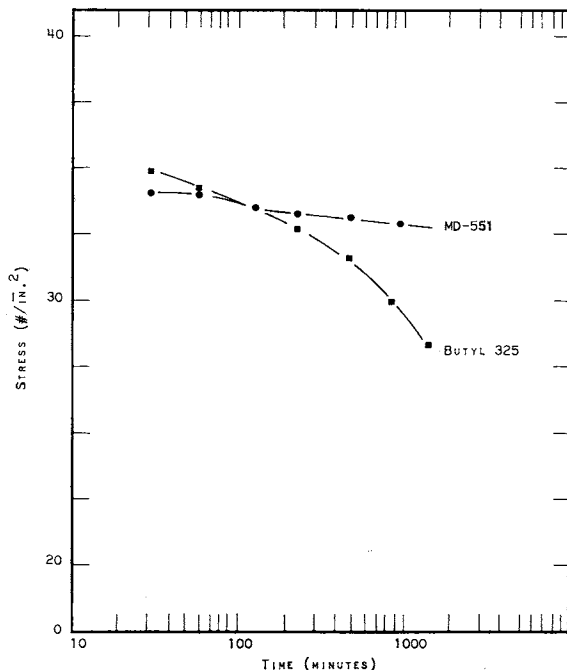


Fig. 12. Relaxation of stress in Enjay Butyl 325 and MD-551 extended 50%, at 167°F.

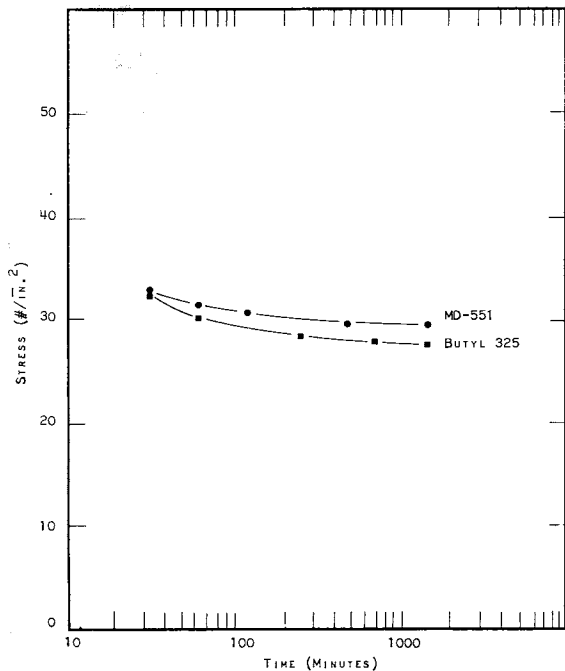


Fig. 11. Relaxation of stress in Enjay Butyl 325 and MD-551 extended 50%, at 122°F.

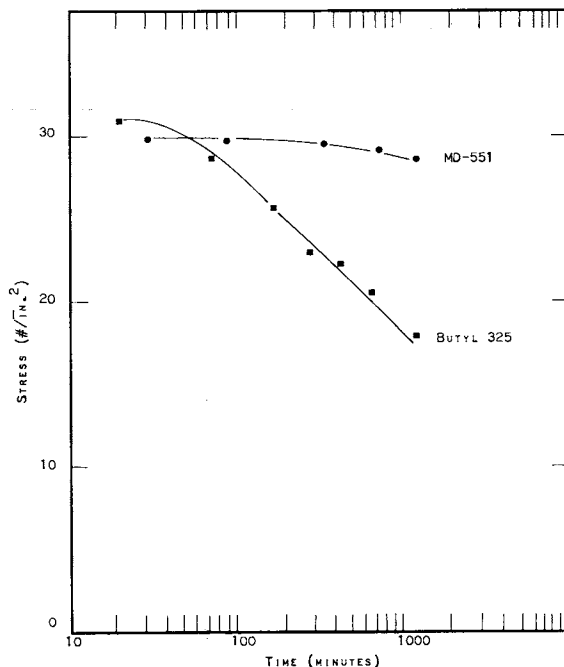


Fig. 13. Relaxation of stress in MD-551 and Enjay Butyl 325 extended 50%, at 212°F.

TABLE II
Activation Energies of MD-551, Enjay Butyl 325, Hevea Gum, and SBR gum

	ΔF , kcal./mole
MD-551	32.275
Enjay Butyl 325	30.242
Hevea gum ^a	30.37
SBR gum ^a	31.84

^a Data of Tobolsky.⁸

where τ is the stress and τ_0 the initial stress. Tobolsky points out that even if eq. (5) does not hold strictly, K can be calculated roughly by finding the time in which the stress reaches 36.8% (or $1/\epsilon$) of its original value. Using these expressions, we have calculated the activation energies for the MD-551 and Enjay Butyl 325. The results are shown in Table II, along with activation energies of SBR and natural rubber gums which were measured by Tobolsky. The higher the activation energy, the more resistant is the polymer to oxidative scission. In looking at Table II, one should keep in mind that a small difference in activation energy represents a major difference in heat stability. These data show clearly the superiority of MD-551 for high temperature stability. Unfortunately, because of difficulty of zeroing the stress relaxation apparatus, the absolute level of the stress could not be ascertained to better than $\pm 5\%$ accuracy. However, the shapes of the curves are correct to much higher precision. From Figure 10 we see that at low temperatures (25°) the MD-551 and the Enjay Butyl 325 vulcanizates are very similar. This is substantiation of our earlier observation that the molecular structures of the polymers (at least for low extensions) are similar. From these curves, using the method of Fletcher et al.,⁹ we can calculate the apparent molecular weights between crosslinks. This result used in conjunction with swelling data yields interaction coefficients. Fletcher uses the relationship

$$f = (\rho RT/M'_c)(\alpha - \alpha^{-2})$$

where f is the equilibrium stress, R the gas constant, T absolute temperature, α the extension ratio, ρ the polymer density, and M'_c the apparent molecular weight. Substituting the M'_c values into eq. (1) then yields μ , the interaction coefficients of these polymers with cyclohexane. For MD-551 $\mu = 0.415$ and for Butyl 325 $\mu = 0.392$. This agrees well with the values of μ found in the literature.¹⁰

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Synopsis

We have found that vulcanizates of MD-551 and butyl rubber at identical crosslink densities have similar properties in low deformation tests at room temperatures. At high extension, the butyl has considerably higher tensile strength which we have associated with crystallization. The MD-551, on the other hand, shows heat stability far superior to that of butyl. It is postulated here that both these differences follow from the nature of the crosslinks in each polymer. The crosslinks in the MD-551 are thought to be both mechanically and chemically more stable than those in butyl. This prevents crystallization on stretching and enhances high temperature stability. Thus far, we have been concerned only with the gum properties of the MD-551. From our previous work, we would expect carbon black to improve the tensile properties of MD-551. Future work will therefore be concerned with properties of reinforced MD-551. In addition, studies will be made in order to learn more about the crosslinks and how they affect vulcanizate performance.

Résumé

On a trouvé que le MD-551 et le butyle, ayant la même densité de ponts ont les mêmes propriétés aux tests de faible déformation à température de chambre. A des extensions plus élevées on remarque pour le butyle une augmentation de la force de tension, qui a été associée à la cristallisation. Le MD-551 d'autre part possède des propriétés de stabilité à la chaleur plus élevées que le butyle. Nous avons proposé que ces deux différences sont dues à la nature de la liaison de pontage dans chaque polymère. Nous croyons que la liaison de pontage du MD-551 est mécaniquement et chimiquement plus stable que celle du butyle. Ceci empêche la cristallisation à l'étirement et augmente la stabilité à des températures plus élevées. Jusqu'à présent nous avons seulement étudié les propriétés du MD-551 comme gomme. Mais de ce travail nous pouvons déduire que l'addition de noir de carbone peut améliorer la force de tension du MD-551. Un travail ultérieur sera consacré aux propriétés de renforcement. Nos études permettront d'avoir des renseignements sur les liaisons de pontage et sur la manière dont elles se comportent à la vulcanisation.

Zusammenfassung

Es wurde gefunden, dass MD-551 und Butyl mit gleichem Vernetzungsgrad bei Tests mit geringer Verformung bei Zimmertemperatur ähnliche Eigenschaften haben. Bei starker Dehnung besitzt butyl eine wesentlich höhere Zugfestigkeit, was, wie festgestellt wurde, auf Kristallisation zurückzuführen ist. Andererseits zeigt MD-551 wesentlich bessere Hitzebeständigkeit als Butyl. Es wird hier angenommen, dass diese Unterschiede auf die Natur der Vernetzungsstellen in den Polymeren zurückzuführen sind. Die

Vernetzung von MD-551 wird mechanisch und chemisch für stabiler gehalten als bei Butyl. Dies verhindert Kristallisation beim Dehnen und steigert die Beständigkeit gegen hohe Temperatur. Bisher wurden nur die Eigenschaften von ungefülltem Gummi MD-551 untersucht. Frühere Arbeiten würden eine Verbesserung der Zugeigenschaften von MD-551 durch Russ erwarten lassen. Zukünftige Arbeiten werden sich mit den Verstärkungseigenschaften befassen. Weiters werden Untersuchungen zum besseren Verständnis der Natur der Vernetzungsstellen und deren Einfluss auf das Verhalten der Vulkanisate durchgeführt werden.