# Stress Softening in Elastomer Blends

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## Synopsis

Compressive stress softening (Mullins effect) in black-filled vulcanizates of the blended system natural:nitrile:brominated butyl rubber has been investigated. The results are expressed in terms of parameters derived from successive stress-strain cycles. The ratio of the work done on loading in the first and second cycles is called the load work ratio, $R_w$. A similar quantity, $R_h$, is defined for the loss or hysteresis work. Both load and loss work ratios show a compositional dependence similar to other properties of blends. The variation of $R_w$ and $R_h$ with composition agrees with the recent thesis of Mullins, Harwood, Payne and others that the Mullins effect is a property of the elastomer. Sudden variation of $R_h$ with elongation has been interpreted in light of recent results of R. W. Smith as indicative of vacuole formation.

## Introduction

Mechanical blending of elastomers to achieve desired properties is a well-established art. Renewed interest in recent years has been based on a desire to define quantitatively the effect of composition on the finished valcunizate.[1,2] Recent work by Mullins and co-workers[4] has characterized the stress softening of rubber as a property of the elastomer. R. W. Smith[5] has reported a new source of stress softening in vacuole formation under tension. The present paper reports the application of parameters based on the Mullins effect under compressive loading. The functional dependence of these parameters on composition below a certain level of strain supports the idea that the Mullins effect is a property of the elastomer.

## Experimental

### Elastomer Compound Preparation

The ternary system of natural rubber (pale crepe), nitrile rubber (Paracril BLT), and brominated butyl (Hycar 2202) with 50 phr HAF black (Philblack 0) was studied as the vulcanizates. The formulation was in parts by weight:

| | | |
|---|---|---|
| Gum blend | 100.0 | |
| HAF black | 50.0 | (Philblack 0) |

| 2,2'-methylene-bis(4-methyl- | | |
|---|---|---|
| 6-tert. butylphenol) | 1.0 | (Antioxidant 2246) |
| Stearic acid | 2.0 | |
| Zinc dimethyldithiocarbamate | 1.33 | (Methyl Zimate) |
| Zinc oxide, NBS | 15.0 | |
| Tetramethylthiuram disulfide | 1.0 | (Methyl Tuads) |
| Cab-O-Sil | 0.003 | |

Except as noted, elastomers were blended prior to the incorporation of additives. Blending and milling were done on a 6 × 12" roll mill with the slow roll at 24 rpm and a friction ratio of 1.5 at 120°F for 10 min as prescribed by Shundo, Imoto, and Minoura.[2]

A single curing system was used for the entire series of compositions. All compounds (except compounds numbered >40) were checked for completeness of cure using the Monsanto Oscillating Disk Rheometer and conventional physical properties. Generally, 15 min. at 300°F was sufficient to effect cure, but all specimens were cured for 30 min with many also cured at 15 min. No differences could be detected in the value of the work ratios even though some samples showed a slight increase in tensile strength at the 30-min level.

### Test Specimens and Procedure

To ensure plane strain conditions,[3] specimens were molded as toroidal rings (0-rings), 3.5 O.D. × 0.425" cross-sectional diameter. They were aged one week before testing. Specimens were stressed in compression between plates coated with fluorocarbon mold release to ensure slippage. The stress-strain curves were recorded on the Instron tester, two cycles of loading and unloading for each specimen with a 10 to 15-sec interval between cycles.

Crosshead speeds of 0.02, 0.1, 0.2, and 0.5 in./min were used at a maximum deformation of 0.1 in. Areas under the stress-strain curves were measured with a polar planimeter. Both loading and unloading curves were integrated.

### Calculation of Results

Ratios of the work (area) under the second cyclic stress-strain curve to the first cyclic stress-strain curve were computed for both the loading curves and the hysteresis loops. The mean values with the standard deviations are tabulated in Table I.

Referring to Figure 1, these ratios are defined as follows:

$$\text{Load work ratio} \quad R_w = \frac{W_2}{W_1}$$

$$\text{Loss work ratio} \quad R_n = \frac{h_2}{h_1}$$

$R_w$ is a direct measure of the Mullins stress softening effect since it in-

TABLE I
Summary of Work Ratios for Ternary Elastomer Blends

| No. | Composition PC:BLT: Hycar 2202 | No. of samples | Load Work Ratio ($R_w$) | | | | Loss Work Ratio ($R_h$) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Mean | Std. dev. | Low | High | Mean | Std. dev. | Low | High |
| 1 | 1:1:1 | 6 | 0.714 | 0.014 | 0.694 | 0.732 | 0.563 | 0.009 | 0.552 | 0.574 |
| 2 | 4:3:3 | 4 | 0.766 | 0.098 | 0.646 | 0.847 | 0.648 | 0.132 | 0.508 | 0.764 |
| 3 | 3:4:3 | 7 | 0.744 | 0.031 | 0.703 | 0.807 | 0.579 | 0.040 | 0.523 | 0.636 |
| 4 | 3:3:4 | 1 | 0.747 | — | — | — | 0.588 | — | — | — |
| 5 | 2:3:5 | 13 | 0.716 | 0.011 | 0.692 | 0.727 | 0.546 | 0.017 | 0.522 | 0.582 |
| 6 | 3:5:2 | 14 | 0.736 | 0.122 | 0.375 | 1.04 | 0.572 | 0.076 | 0.297 | 0.630 |
| 7 | 5:3:2 | 8 | 0.717 | 0.028 | 0.675 | 0.775 | 0.557 | 0.006 | 0.550 | 0.567 |
| 8 | 5:2:3 | 4 | 0.707 | 0.018 | 0.690 | 0.726 | 0.535 | 0.040 | 0.476 | 0.560 |
| 9 | 3:2:5 | 8 | 0.699 | 0.026 | 0.666 | 0.752 | 0.533 | 0.011 | 0.511 | 0.549 |
| 10 | 2:5:3 | 8 | 0.755 | 0.017 | 0.732 | 0.790 | 0.603 | 0.033 | 0.570 | 0.670 |
| 11 | 1:0:0 | 16 | 0.782 | 0.028 | 0.736 | 0.846 | 0.587 | 0.041 | 0.490 | 0.659 |
| 12 | 0:1:0 | 15 | 0.758 | 0.010 | 0.737 | 0.779 | 0.641 | 0.016 | 0.616 | 0.664 |
| 13 | 0:0:1 | 14 | 0.606 | 0.027 | 0.564 | 0.654 | 0.447 | 0.020 | 0.414 | 0.492 |
| 14 | 1:0:0 | 13 | 0.761 | 0.015 | 0.730 | 0.790 | 0.612 | 0.028 | 0.577 | 0.688 |
| 15 | 3:2:0 | 8 | 0.709 | 0.023 | 0.658 | 0.733 | 0.564 | 0.018 | 0.542 | 0.598 |
| 16 | 3:0:2 | 10 | 0.721 | 0.006 | 0.713 | 0.733 | 0.545 | 0.072 | 0.506 | 0.744 |
| 17 | 2:3:0 | 8 | 0.767 | 0.012 | 0.749 | 0.783 | 0.625 | 0.027 | 0.598 | 0.675 |
| 18 | 2:0:3 | 7 | 0.713 | 0.035 | 0.688 | 0.790 | 0.536 | 0.051 | 0.483 | 0.629 |
| 19 | 0:3:2 | 8 | 0.789 | 0.012 | 0.766 | 0.804 | 0.617 | 0.023 | 0.580 | 0.657 |
| 20 | 0:2:3 | 8 | 0.803 | 0.046 | 0.752 | 0.898 | 0.616 | 0.050 | 0.577 | 0.732 |
| 21 | 1:1:1 | 16 | 0.716 | 0.022 | 0.649 | 0.738 | 0.568 | 0.029 | 0.469 | 0.606 |
| 31 | 1:1:1 M | 4 | 0.752 | 0.009 | 0.746 | 0.764 | 0.590 | 0.010 | 0.576 | 0.598 |
| 32 | 8:0:2 | 6 | 0.700 | 0.012 | 0.686 | 0.715 | 0.520 | 0.012 | 0.506 | 0.539 |
| 33 | 0:2:8 | 5 | 0.719 | 0.006 | 0.712 | 0.726 | 0.542 | 0.010 | 0.529 | 0.554 |
| 34 | 0:3:7 | 6 | 0.741 | 0.007 | 0.734 | 0.752 | 0.560 | 0.006 | 0.554 | 0.571 |
| 35 | 1:7:2 | 6 | 0.745 | 0.009 | 0.734 | 0.755 | 0.605 | 0.006 | 0.598 | 0.611 |
| 36 | 1:0:1 | 6 | 0.722 | 0.005 | 0.717 | 0.732 | 0.512 | 0.006 | 0.504 | 0.519 |
| 37 | 1:5:4 | 6 | 0.756 | 0.012 | 0.746 | 0.779 | 0.588 | 0.008 | 0.575 | 0.599 |
| 42 | 2:7:1 | 6 | 0.723 | 0.006 | 0.718 | 0.732 | 0.583 | 0.011 | 0.566 | 0.593 |
| 43 | 1:4:5 | 6 | 0.749 | 0.003 | 0.747 | 0.754 | 0.571 | 0.010 | 0.561 | 0.591 |
| 38 | 3:0:7 | 6 | 0.711 | 0.009 | 0.699 | 0.722 | 0.504 | 0.004 | 0.499 | 0.509 |
| 39 | 3:1:1 | 6 | 0.677 | 0.006 | 0.668 | 0.682 | 0.523 | 0.008 | 0.515 | 0.531 |
| 40 | 3:2:0 | 6 | 0.656 | 0.012 | 0.639 | 0.669 | 0.532 | 0.006 | 0.524 | 0.540 |
| 41 | 0:1:1 | 6 | 0.756 | 0.006 | 0.747 | 0.762 | 0.590 | 0.019 | 0.563 | 0.616 |
| 40 | 3:2:0 M | 5 | 0.738 | 0.010 | 0.726 | 0.749 | 0.640 | 0.009 | 0.627 | 0.651 |
| 44 | 1:5:4 M | 4 | 0.792 | 0.002 | 0.789 | 0.795 | 0.598 | 0.012 | 0.585 | 0.610 |
| 45 | 4:5:0 M | 5 | 0.780 | 0.006 | 0.774 | 0.788 | 0.601 | 0.007 | 0.592 | 0.610 |
| 46 | 8:0:2 M | 4 | 0.756 | 0.010 | 0.750 | 0.771 | 0.517 | 0.011 | 0.504 | 0.531 |
| 47 | 2:5:3 M | 5 | 0.778 | 0.004 | 0.771 | 0.782 | 0.590 | 0.007 | 0.582 | 0.598 |

M = Elastomers were mixed with HAF Black before blending.
PC = Pale crepe natural rubber.
BLT = Paracril BLT nitrile rubber.

volves only the loading curve. The hysteresis, due to the Mullins effect, the breakdown in the carbon black chains and viscoelastic behavior of the elastomer, is measured by the areas $h_1$ and $h_2$. Since the same amount and
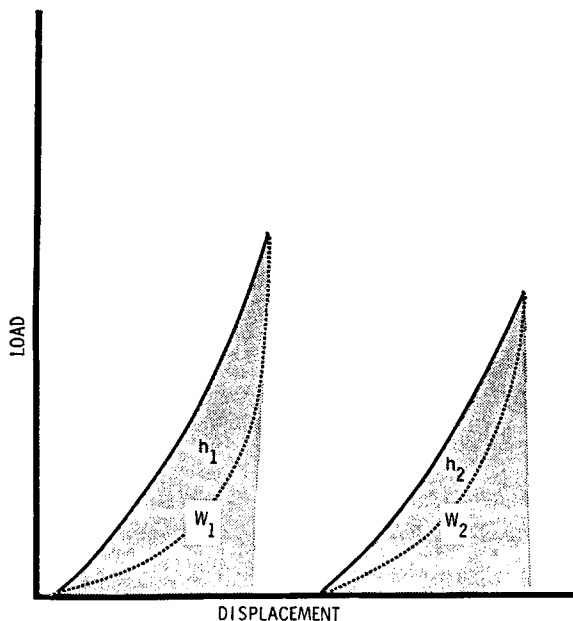
Fig. 1. Definition of load work and loss work ratios.

kind of black is present, the change in $R_h$ can be attributed to the elastomers. The effect of changes in crosshead speed was small over the range covered, hardly more than the experimental error at one of the given speeds.

Bicyclic tensile stressing at various percents elongation was carried out on 0.075 in. thick ASTM tensile strips for compounds containing the three single elastomers. Crosshead speeds were 0.1 and 5 in./min. $1/R_h$ has been used previously by Smith[5] who asserted it to be a measure of vacuole formation in binary blends of SBR and butadiene rubber.

## Discussion

The object of this investigation was to determine the compositional dependence of the stress-softening and hysteresis. Black-filled ternary blends of elastomers as the vulcanizates were investigated under compressive loading. In view of the work at Harwood, Mullins, and Payne,[4] in which comparison of succeeding tensile stress-strain cycle was used as a measure of stress softening, it did not seem too great a departure to apply a related comparison to stress-strain cycles in the compressive mode. However, it appeared advisable to compare the values of $R_h$ obtained in both tensile and compressive deformations.

The compositional dependence of $R_w$ and $R_h$ is shown in Figures 2 and 3. The graph is not meant to imply a functional significance but was drawn in the manner shown for visual clarity. The line represents the values calculated from the $R_w$ or $R_h$ for the pure elastomers assuming a simple additive dependence on the volume fraction. These values were then arranged in
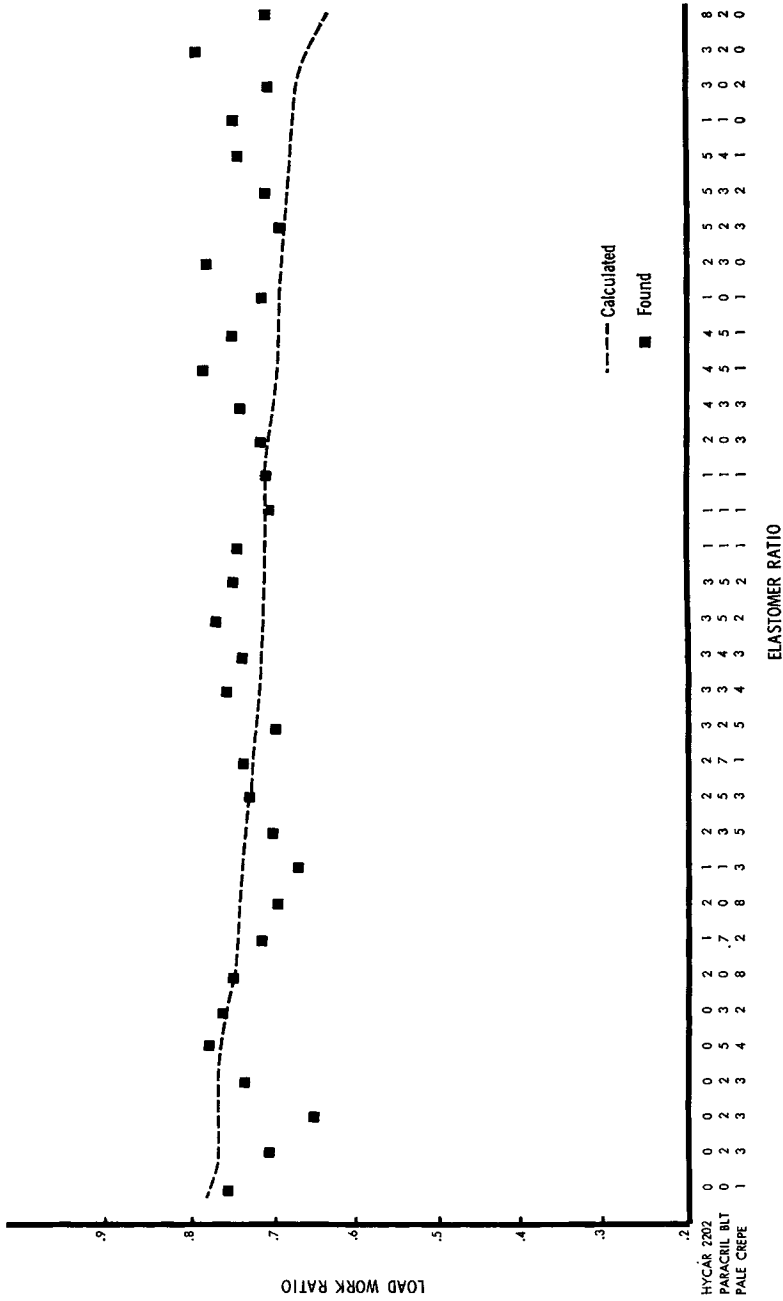
Fig. 2.   Load work ratio versus composition.

Fig. 3.  Loss work ratio versus composition.

decreasing order to determine the order of plotting the experimental values. Each composition is shown along the abscissa as the weight ratio of the elastomers. The oscillatory behavior of the experimental points is believed to be a coincidence. Reviewing the experimental procedure revealed that the "bincure" or time between milling and curing of samples was also oscillatory if ordered in the same way. Neglecting this artifact, the experimental values of $R_w$ and $R_h$ for these ternary blends are a simple additive function of the volume fraction of the elastomers. This finding agrees with the assertion of Harwood, Mullins, and Payne[4] that the Mullins effect is a function of the elastomer.

A plot of $1/R_h$ vs. % elongation, in the manner of Smith,[5] shown in Figure 4, reveals that each elastomer assumes a very similar value for $1/R_h$ up to about 100% elongation. Then there is a divergence for each elastomer. In the neighborhood of 300% elongation, an abrupt increase in slope occurs, after which an erratic leveling takes place. The sudden change in slope can be conveniently explained by the results of Smith[5] who observed vacuole formation in SBR at 300% elongation accompanied by a large increase in $1/R_h$.

Besides the structural failure seen through the electron microscopic detection of vacuoles, there is every reason to suppose that, prior to this drastic failure, there are lesser failures which give rise to smaller, optically undetectable, free volume defects. It is postulated that the continuous increase in these lesser defects accounts for the change in slope of $1/R_h$ vs. elongation for different elastomers between 100 and 300% elongation.

On the other hand, no sharp break in the curve of $1/R_h$ vs. deformation was observed up to an average of 45% compressive strain. The values of $1/R_h$ vs. deformation for different elastomers given in Table II remain sensibly constant and distinct. Thus, if vacuole formation is occurring in compression. it must happen only at very severe compressive strains.

Natural rubber gave somewhat more erratic results in general than did the two synthetic elastomers. This is believed to be due to crystallization

TABLE II
Reciprocal Loss Work Ratio Vs. Deformation
for 3.5″ × 0.425″ Rubber O-Rings

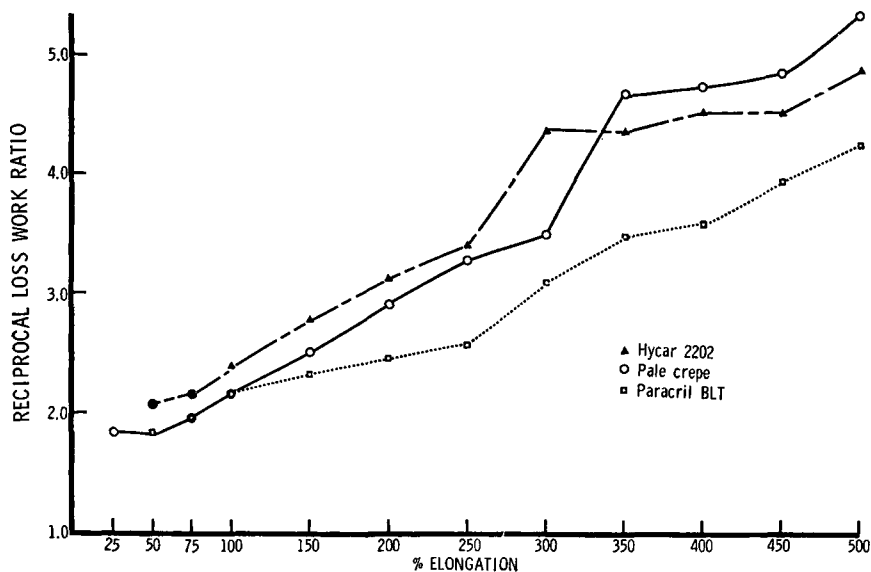| Deformation (in.) | $R_h$ | | |
|---|---|---|---|
| | Natural | Paracril BLT | Hycar 2202 |
| 0.02 | 1.57 | 1.62 | 2.12 |
| 0.05 | 1.68 | 1.55 | 2.12 |
| 0.075 | — | 1.52 | 2.12 |
| 0.10 | 1.82 | 1.56 | 2.24 |
| 0.15 | 1.80 | 1.58 | 1.95 |
| 0.18 | — | — | 1.85 |
| 0.184 | — | 1.61 | — |
| 0.20 | 1.88 | — | — |
| 0.218 | 1.78 | — | — |

Fig. 4. Reciprocal loss work ratio versus elongation.

of natural rubber on deformation. Anomalies in the behavior of natural rubber at high strains have been attributed to crystallization in a recent paper by Harwood and Schallamach.[6]

The order of mixing of elastomer blends with the carbon black was chosen such that the elastomers were blended first, and the HAF black was then compounded with the blend. Since Marsh, Voet, and Price[7] found no evidence for migration of black between rubber phases, it can be assumed that black milled into a blend is incorporated in a random manner among the elastomer components. In the present work, several compositions were duplicated using master batches of the individual elastomers with 50 phr HAF black. This change in the order of mixing produced a detectable, but not startling, increase in $R_w$ and $R_h$. However, work by Hess, Scott, and Callan[10] showed that in a blend of 50/50 polybutadiene and pale crepe rubber the black was incorporated preferentially into the softer polybutadiene phase. This might explain the variation in $R_w$ and $R_h$ as a result of the different mixing procedures. From an exhaustive study on binary rubber blends of natural, SBR, and NBR elastomers, Komskaya and Slonimskii[8] concluded that the properties of combined stocks are governed primarily by the behavior of the mixed rubbers themselves and not by the ingredients incorporated into the stocks. They found that, while the level of the properties could be changed by additives, the relative change in properties for the mixture depends on the elastomer composition.

The system studied was chosen because it offered, at once, an opportunity to observe the effects of mixing elastomers with both low and high affinities for each other. Natural rubber is a nonpolar hydrocarbon elastomer.

Brominated butyl is largely hydrocarbon but has some polar character; and nitrile rubber is strongly polar. This combination was thought to give a system wherein blending and nonblending effects could be detected with stress softening as the response variable.

It has been shown by deDecker and Sabatine[1] and by Fujino and co-workers[9] that the mechanical properties of blends of polymers are the properties of the outer or matrix phase. Significant changes in a property with composition occur at phase inversions, i.e., at compositions where there is an exchange of outer and inner phases. Thus, blends of polyvinyl acetate and poly(methyl-methacrylate) show an inversion at 70% PMMA as determined by glass temperatures. A similar change seems to occur in the composition vs. $1/R_h$ curve presented by Smith.[5] What could be interpreted as a phase inversion occurs at about 33% butadiene rubber.

Ternary systems are not so well documented. While it is tempting to say that the areas in Figure 5 represent matrix compositions, there are some incongruities which preclude this conclusion. For example, all components are well above their glass-transition temperatures; hence, to speak of a "higher melting" component is meaningless. Consequently, the stress softening contributed by each component need not depend on whether it is matrix or island phase. A contribution to $R_h$ depends only on whether there is a permanent or, at least, long-time deformation in the component after it has been strained.

Referring to Figure 5, the appearance of three areas could, in part, be a matter of insufficient resolution but not entirely so. Manifestly, the $R_h$ of pale crepe rubber is affected far more seriously by the addition of small amounts of brominated butyl than is nitrile rubber. This has some obvious practical consequences when other properties are retained. The fact that the $R_h$ of brominated-butyl rubber is not masked by natural rubber but is masked by Paracril BLT is probably due to the expected polar interaction between the brominated butyl and nitrile rubber.

The blend has not been examined in the presence of various curing systems to see how these areas would be affected. However, the fact that $R_w$ and $R_h$ are simple functions of the volume fraction of the elastomers, and the results of Komskaya and Slonimskii,[3] indicate that the curing system has little effect on the relative values of $R_w$ and $R_h$.

## Summary

1. The ratio of work under the first two successive stress-strain cycles is a parameter which relates stress softening to elastomer composition.

2. Results from the ternary blend natural:nitrile:brominated-butyl rubber, as the black-filled vulcanizates, indicate that the more polar elastomers exert the greater influence on the $R_h$ of the blend.

3. For the system natural:nitrile rubber:brominated butyl, the Mullins effect in compression is an additive function of the volume fraction of the elastomers.

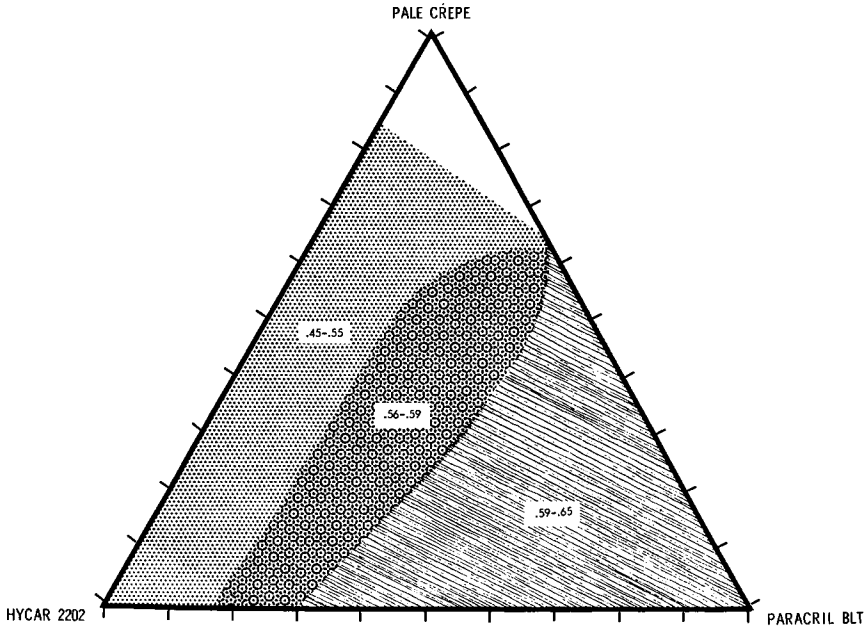4. Vacuole formation can be used to explain sudden changes in loss work

Fig. 5.   Loss work ratio versus composition.   A ternary rubber blend containing 50
PHR HAF black.

ratio with elongation.   Compressive loading does not produce a corre-
sponding response up to 45% strain.   Differences in loss work ratio for
different elastomers are thus attributed to the elastomer.

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