

## Variability of Ultimate Properties of Elastomers

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### Synopsis

The measurement of the ultimate properties of elastomers is characterized by variability in the data. For example, when a sufficient number of specimens is tested, distributions in the values of the stress-at-break, strain-at-break, and time-to-break are commonly obtained. It is pointed out that such variability can be rationalized on the basis of variations in both the degree of crosslinking and in the size of naturally occurring flaws present in the elastomer.

### INTRODUCTION

We have been interested in the relationship between chemical structure and ultimate properties of elastomers for some time. Three graphic representations of ultimate property data of interest to us are the failure envelope, the time dependence of the stress at break,  $\sigma_b$ , and the time dependence of the strain at break,  $\epsilon_b$ .<sup>1</sup> It is characteristic that while scatter in the failure envelope, i.e., a plot of  $\log(\sigma_b T_0/T)$  versus  $\log \epsilon_b$ , where  $T_0$  is an arbitrary reference temperature and  $T$  is the test temperature, is usually limited to about  $\pm 10\%$  from a mean curve, which can probably be attributed to small variations in the average network chain concentration  $\nu_e$ , the scatter in the time dependence of both  $\sigma_b$  and  $\epsilon_b$  is quite large. For example, it is not uncommon for the data to be scattered by plus or minus two decades from the mean on the time-to-break scale. Such scatter makes it difficult to test the applicability of time-temperature superposition to ultimate property data, as well as to use these time-to-break curves to predict long-term rupture.

There are at least two factors which can account for variability in ultimate property data, namely, variability in the degree of crosslinking and variability in the size of preexistent flaws or cracks. It is possible to discriminate between the relative contributions of these two factors, as will now be shown.

### RESULTS AND DISCUSSION

If a test specimen, subjected to uniaxial tension, contains a small edge crack, the condition for tearing to occur is given by<sup>2</sup>

$$\theta = 2KcU \quad (1)$$

where  $\theta$  is the tearing energy,  $K$  is a numerical factor and a slowly varying function of the strain,  $c$  is the length of the crack measured in the undeformed state, and  $U$  is the elastically stored energy density in the absence of a crack. It has

also been established, for elastomers which do not undergo strain-induced crystallization, that the rate of crack growth,  $dc/dt$ , increases with  $\theta$  according to<sup>3</sup>

$$\frac{dc}{dt} = A\theta^n \quad (2)$$

where  $A$  and  $n$  are constants. Combining eqs. (1) and (2) yields

$$\frac{dc}{dt} = A(2KcU)^n \quad (3)$$

For experiments carried out at constant strain rate,  $U$  may be expressed as<sup>4</sup>

$$U = B(rt)^p \quad (4)$$

where  $B$  and  $p$  are constants,  $r$  is the strain rate, and  $t$  is time. Substituting this expression for  $U$  into eq. (3) and integrating yields finally<sup>4</sup>

$$t_b = \frac{(pn + 1)}{A(n - 1)(2K)^n U_b^n c_0^{n-1}} \quad (5)$$

where  $c_0$  is the initial length of the crack. This expression shows that  $t_b$  is determined almost entirely by the very early stages of tearing. For example, with  $n = 5$ , a typical value for a noncrystallizing elastomer, over 90% of the breaking time will have elapsed before the crack doubles in length.

Greensmith<sup>4</sup> demonstrated that eq. (5) was applicable to his results for an SBR gum elastomer for both deliberately induced cuts of various sizes and for specimens with no introduced cuts. In the latter case, the value of  $c_0$  was of the order of  $10^{-2}$  cm. In order to demonstrate the importance of  $c_0$  in contributing to data scatter, it must be shown that eq. (5) is consistent with other experimental data.

From an examination of data in the literature, it has been found that the relationship between  $\theta$  and  $dc/dt$ , obtained at various temperatures and at different degrees of crosslinking for SBR elastomers, can be represented by<sup>5</sup>

$$a_T a_x \frac{dc}{dt} = A_0 \left( \frac{\theta T_0}{\nu_e T} \right)^n \quad (6)$$

where  $a_T$  is the time-temperature shift factor,  $A_0$  is a parameter which is independent of  $\nu_e$ , and  $a_x$  is a shift factor which takes into account the effect of differences in network chain concentration on the time scale. It is given by<sup>6</sup>

$$a_x = \left( \frac{m}{\nu_e} \right)^{7.7} \quad (7)$$

where  $m$  is a constant. Use of the  $a_x$  shift factor allows one to superpose time-dependent data obtained from elastomers which differ in network chain concentration, including the time dependence of the ultimate properties. Equation (6) thus permits one to predict the effect of both temperature and  $\nu_e$  on the rate of crack growth. It can be shown that  $U_b$  is related to  $\epsilon_b$  by

$$\frac{U_b T_0}{\nu_e T} = \frac{3RT_0 \epsilon_b^p}{p} \quad (8)$$

where  $T_0$  is an arbitrarily chosen reference temperature,  $R$  is the gas constant in the appropriate units, and  $p$  is a number close to 2. Hence, combining eqs. (1), (6), and (8) yields

$$\epsilon_b = \left[ \frac{p^n(pn + 1)}{(n - 1)c_0^{n-1}A_0(2K)^n(3RT_0)^n} \frac{a_T a_x}{t_b} \right]^{\frac{1}{pn}} \quad (9)$$

which can be rearranged to

$$\epsilon_b = k \left( \frac{t_b}{a_T a_x} \right)^{-\frac{1}{pn}} \quad (10)$$

where

$$k = \left[ \frac{p^n(pn + 1)}{(n - 1)c_0^{n-1}A_0(2K)^n(3RT_0)^n} \right]^{\frac{1}{pn}} \quad (11)$$

Equation (10) is precisely the form we obtained for the dependence of  $\epsilon_b$  on the time to break.<sup>7</sup> Further, since the factor  $k$  contains a contribution from  $c_0$ , the initial size of the flaw, we have demonstrated that variations in the initial flaw size do contribute to scatter in experimental data.

Following the same type of argument, the dependence of the stress at break on time to break can be written as

$$\frac{\sigma_b T_0}{\nu_e T} = 3RT_0 k \left( \frac{t_b}{a_T a_x} \right)^{-\frac{1}{2n}} \quad (12)$$

which indicates that the  $\log(\sigma_b T_0 / \nu_e T)$ ,  $\log t_b$  and  $\log \epsilon_b$ ,  $\log t_b$  plots have the same slope at a given value of  $t_b$  but with intercepts which differ by the factor  $3RT_0$ .

Since eqs. (10) and (12) were derived using the relationship given by eq. (8), they will be valid generally only for test conditions such that the failure data fall on the master failure envelope, i.e., for long reduced times.

Considering the expression for the constant  $k$  and assuming  $p = 2$  and  $n = 5$ , which are reasonable values for these parameters, then  $k$  and hence both  $\sigma_b$  and  $\epsilon_b$  are proportional to  $c_0^{-0.4}$  which is a relatively weak dependence on the initial flaw size. In order to account for the scatter in the time-to-break plots,  $c_0$  would have to vary by some ten orders of magnitude, and this is unlikely. The other variable,  $\nu_e$ , occurs implicitly in both eqs. (10) and (12) through  $a_x$ . Again assuming that  $p = 2$  and  $n = 5$ ,  $\sigma_b$  and  $\epsilon_b$  become proportional to  $\nu_e^{-0.77}$ ; and again this is not a very strong dependence. In order for variations in  $\nu_e$  to account for four decades of scatter on the time scale,  $\nu_e$  would have to vary by about five orders of magnitude, which again is not plausible.

It is very unlikely that the crosslinks are distributed uniformly throughout the network. Rather, it seems more likely that the crosslinks occur in groups especially when one considers the process used for the insertion of crosslinks. For example, in sulfur vulcanization, zinc oxide, fatty acid, sulfur, and an accelerator are employed. The zinc oxide, though finely divided, still has particles which are finite in size. In addition, most of the common accelerators do not melt at the vulcanization temperature, and they, too, although finely divided still are characterized by particles of finite size.

Thus, at least in the initial stages of vulcanization, it would seem that the chemical reactions involved occur on the surfaces of particles; and hence it seems reasonable to assume that the crosslinks which are introduced at this stage are likely to do so at polymer sites in contact with the particle surface. This is a process which could lead to a vulcanizate having a wide distribution in the number of crosslinks per primary network chain. Other considerations in conjunction with eq. (7) suggest furthermore that the high crosslink density regions should act as flaws and are in fact sites where fracture may be initiated.

Thus, in our view, it is both the size of the flaw,  $c_0$ , and the inhomogeneous nature of the crosslinking process which produce regions of various sizes and of differing degrees of crosslinking, which are in competition as sites for the initiation of failure. If  $c_0$  is of such a size, i.e., an intentionally introduced cut, then it will control fracture initiation. On the other hand, if  $c_0$  is small and a region exists wherein  $\nu_e$  is very high, then  $\nu_e$  will control fracture initiation. Thus, it is likely that combined variations in both  $c_0$  and  $\nu_e$  produce the large scatter observed in the time-to-break plots. Incidentally, it is our experience that the scatter in both the  $\sigma_b, t_b$  and  $\epsilon_b, t_b$  plots is about the same, and this too is expected since as eqs. (10) and (12) show, the dependence on  $c_0$  and  $\nu_e$  is the same for both.

Finally, it should be mentioned that  $c_0$  and variations in  $\nu_e$  over various regions of the vulcanizate would not be expected to have any appreciable effect on the shape of the stress-strain curve or on the failure envelope. As mentioned above, over 90% of the breaking time will have elapsed before the crack doubles in length. Furthermore, since  $c_0$  is presumably small relative to the cross-sectional area of the test piece, the effect of  $c_0$  in reducing the effective cross-sectional areas will be negligible. The existence of a small number of regions in which the crosslink density is very high will likewise not have an appreciable effect on the stress-strain curve or the failure envelope because they would function as filler particles and the presence of a small number of inclusions will not affect either the shape of the stress-strain curve or failure envelope. These considerations offer an explanation for the relative absence of scatter in failure envelope plots.

This paper represents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100, sponsored by the National Aeronautics and Space Administration.

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Received August 17, 1973

Revised July 29, 1974