

# A simple kinetic approach to fibre failure:

## 2. Lifetime distributions

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A simple kinetic theory of fibre failure has been developed that predicts not only the median lifetimes of fibre samples under constant load but also the distribution in these lifetimes based upon the distribution in the static breaking load of the fibre samples. The theory is applied to Kevlar fibres where data for lifetime under various loads are known.

(Keywords: fibres; kinetics; failure; Kevlar)

### INTRODUCTION

The ability to predict the lifetime of organic fibres under load is of critical importance in assigning reliability in many civilian and military applications. There are two kinds of lifetime predictions. The first is the prediction of the median lifetime for a collection of samples under identical loads and is characterized by certain average material properties. The second, and in many cases of more importance where high reliabilities are required, is the prediction of the lifetime distributions under reduced loads in a collection of samples. The origin of this distribution is undoubtedly traceable to the variation in material properties from one sample to the next. These variations can be characterized by the distribution of static breaking loads in the collection of samples. Even in production processes with a high degree of quality control, the variation in static breaking load will span several per cent or more of the median value, generally exhibiting Gaussian or Weibull behaviour. The task we will address here is how to convert this easily measured narrow distribution in static breaking load to the very broad and asymmetric distribution in lifetime behaviour<sup>1,2</sup>.

To demonstrate the situation we present in *Figure 1* data for the static breaking load, a measure of fibre strength, in pounds force (lbf) of 53 epoxy impregnated Kevlar strands<sup>3</sup>. We note here that the term 'strength' generally refers to a load per cross-sectional area. The fibres tested were all Du Pont Kevlar PRD-49-III fibres composed of 267 filaments and impregnated with Union Carbide ERL2258/ZZL0820 epoxy, (100/30) by weight. The fibre phase represented 71.5% of the total volume. Static tensile strength tests were performed on 25.4 cm fibres at 25°C at an elongation rate of 1.0 cm/min. Failure generally occurred at about 2.5% strain, about 40 s into the test. Work at other strain rates gave similar static strengths. Unfortunately no diameter measurements were made. We will assume equality of cross-sections and thus associate the distribution of the breaking loads with a distribution in static strength and use these terms interchangeably. It should also be noted that the samples tested for static breaking load and those tested for lifetime behaviour came not only from the same manufacturer's

batch, but also from the same spool. Further the samples tested for lifetime behaviour were loaded at the same rate as those tested for static tensile strength. In *Figure 1*, the spikes are associated with the ordinate on the right and represent the actual data. The solid curve is the best normalized Gaussian fit for the distribution, and is given by

$$g(s) = \frac{1}{\sqrt{2\pi b}} e^{-(s-\langle s \rangle)^2/2b} \quad (1)$$

where  $s$  is the breaking load with average  $\langle s \rangle = 22.05$  lbf and the variance,  $b$ , is given by

$$b = \sum_{i=1}^N (s_i - \langle s \rangle)^2 / (N - 1) = 0.2952 \text{ (lbf)}^2 \quad (2)$$

The broken curve is the best normalized Weibull fit and is given by

$$w(s) = \frac{m}{s_w} \left( \frac{s}{s_w} \right)^{m-1} \exp[-(s/s_w)^m] \quad (3)$$

where the shape parameter,  $m$ , and the scale parameter,  $s_w$ , were determined by the method of maximum likelihood to be 46.3 and 22.30 lbf, respectively<sup>2</sup>. The scale of the ordinate on the left is for the normalized Gaussian,  $g(s)$ , or Weibull,  $w(s)$ , and represents, for the curves, the probability density of breaking at a given strength. Note that the range of the data is only about  $\pm 6\%$  of the mean and that the differences between the Gaussian and Weibull fits are small. In *Figure 2* we plot lifetime behaviour for a collection of 100 fibres held at 80% of the breaking load. Note that the distribution of breaking times span nearly three decades, with the time for breakage of the first 50% of the fibres only about 15% of the total time required for breakage of all of the fibres. More important from the reliability viewpoint is the short time failure, 15% of the sample had failed in less than 50 h. The ability to understand and predict this broad, very asymmetric distribution from the relatively narrow and symmetric distribution of static strengths is what this paper is concerned with.

THEORY AND RESULTS

In a previous paper<sup>4</sup>, henceforth referred to as paper 1, we developed a kinetic approach<sup>5</sup> to predicting the median lifetimes of fibre samples. We considered a fibre to be made up of  $N$  interacting 'elements', the sum of which represents a measure of the fibre strength. It is tempting to associate the elements with either the filaments or perhaps individual polymer chains, however it is limiting to do so. It is best to simply consider the elements as a mathematical construction which represents the fibre strength. Our approach was then to model the stress-induced rate of degradation of the strength by an Arrhenius-like rate expression

$$\frac{dN}{dt} = -Ae^{-(E-\gamma\sigma/N^a)/RT} N^a \quad (4)$$

where  $A$  is interpreted as a stress related frequency factor and the stress related activation energy,  $E$ , is reduced by a

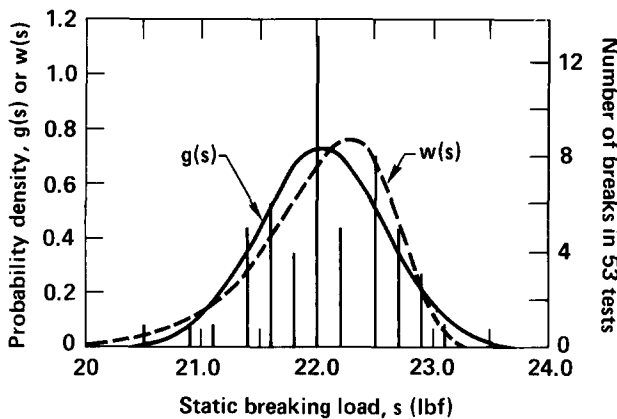


Figure 1 Static breaking loads of Kevlar fibres<sup>3</sup>. The solid curve represents the best normalized Gaussian fit to the data which is for 53 samples and is represented by the spikes. The broken curve is the best Weibull fit to the data

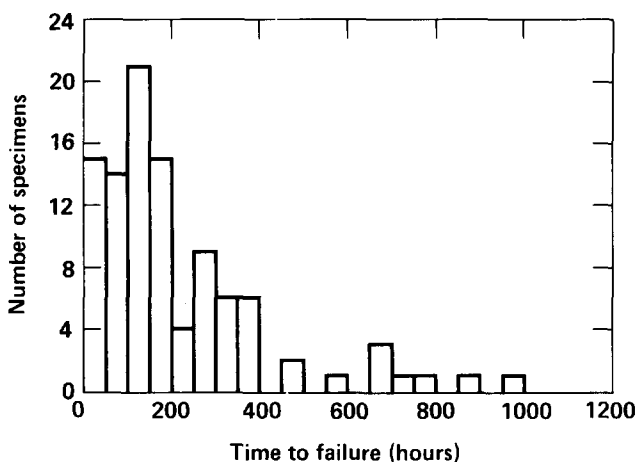


Figure 2 Lifetime data for 100 Kevlar fibres samples held at 80% of their breaking load<sup>3</sup>

Table 1 Additional terms  $Q(\alpha, a, x)$  to the modified Zhurkov expression, equation (8), for the time-to-break,  $t_B$ , of a fibre for various values of  $\alpha$  and  $a$ .  $x$  represents the term  $(\gamma\sigma/RTN_0^a)$ ,  $P(x)$  is defined in equation (10), and  $S(x)$  in equation (12). With  $N_0$  taken as unity the expressions are appropriate for the  $Q(\alpha, a, x)$  term in equation (5)

$a$	$\alpha=1/2$	1	2
0	$\ln[N_0] + \ln[1 - x + xP(x)]$	$\ln[N_0] + \ln[1 - P(x)]$	$\ln[N_0] + \ln[S(x)]$
1	$-\ln[x/2] + \ln[P(x)]$	$-\ln[x] + \ln[P(x)]$	$-\ln[2x] + \ln[P(x)]$
2	$-\ln[xN_0/2] + \ln[1 + 1/x]$	$-\ln[xN_0]$	$-\ln[2xN_0] + \ln[1 - S(x)]$

term which is linear in the applied stress,  $\sigma$ .  $N$  is the number of surviving elements, a measure of remaining strength, at time  $t$ . The coefficient of  $\sigma$ , comprised of a constant  $\gamma$  divided by  $N^a$  recognizes that since  $\sigma$  is the constant applied stress, as the strength, or number of elements diminishes, the effective stress on those remaining increases. For  $\alpha=1$  we are modelling equal load-sharing among all elements, values of  $\alpha$  less than unity correspond to more local load-sharing. We note here that the residual strength is proportional to  $N^a$ . The rate expression is written as being to order  $a$ . As will be discussed later, the results are very insensitive to values of  $a$  from 0 to 2. Simple integration of a scaled dimensionless value of  $N$  from one to zero yields the fibre lifetime,  $t_B$ , as

$$\ln t_B = \frac{E-\gamma\sigma}{RT} - \ln A + Q\left(\alpha, a, \frac{\gamma\sigma}{RT}\right) \quad (5)$$

where the form of the function  $Q$  depends upon the values of  $\alpha$  and  $a$  chosen and is given in Table 1. A discussion of this formula and its application to the median lifetimes of Kevlar fibres was the topic of paper 1. We will now rework the theory slightly to allow for a distribution of initial fibre strengths.

To do this we will integrate equation (4) from  $N_0$  to 0, where  $N_0$  is the effective number of elements before load is applied and is thus related to the static breaking load. Concurrent integration of  $t$  from 0 to  $t_B$ , the time to break, gives us

$$t_B = - \int_{N_0}^0 A^{-1} N^{-a} e^{+(E-\gamma\sigma/N^a)/RT} dN \quad (6)$$

which with rearrangement (let  $x = \gamma\sigma/RTN_0^a$ ) yields for  $\alpha \neq 0$

$$t_B = \left(\frac{\gamma\sigma}{RT}\right)^{\frac{1-a}{a}} \frac{e^{E/RT}}{\alpha A} \int_{\frac{\gamma\sigma}{RTN_0^a}}^{\infty} x^{\frac{a-1}{a}} e^{-x} dx \quad (7)$$

or

$$\ln t_B = \frac{E-\gamma\sigma/N_0^a}{RT} - \ln A + Q\left(\alpha, a, \frac{\gamma\sigma}{RTN_0^a}\right) \quad (8)$$

Note that with  $\alpha$  and  $a$  equal to zero,  $Q$  is also zero and we have the simple Zhurkov relationship<sup>6</sup>. The functions  $Q(\alpha, a, x)$  are given in Table 1 for various values of  $\alpha$  and  $a$ .  $P(x)$  comes from an approximate expression for the exponential integral<sup>7</sup>

$$\int_x^{\infty} e^{-t} t^{-1} dt = x^{-1} e^{-x} P(x) \quad (9)$$

where  $P(x)$  is given by

$$P(x) = \frac{x^2 + a_1x + a_2}{x^2 + b_1x + b_2} \quad (10)$$

$$a_1 = 2.334733 \quad b_1 = 3.330657$$

$$a_2 = 0.250621 \quad b_2 = 1.681534$$

The approximation has an error of less than 0.00005.  $S(x)$  comes from an asymptotic expression for the incomplete gamma function<sup>8</sup>,

$$\Gamma(\frac{1}{2}, x) = \int_x^\infty e^{-t} t^{-1/2} dt = x^{-1/2} e^{-x} (1 - S(x)) \quad (11)$$

where

$$S(x) = \sum_{i=1}^\infty \frac{(2i-1)!(-1)^{i+1}}{(2x)^i} \quad (12)$$

We can now calculate the distribution in the lifetime based on the distribution in the static strength. Let us scale  $N_0$  such that  $N_0 = 1$  represents the mean static strength. For the Gaussian fit of the Kevlar data displayed in Figure 1 this results in

$$g'(N_0) = \frac{1}{\sqrt{2\pi b'}} e^{-(N_0 - 1)^2/2b'} \quad (13)$$

where  $g'(N_0)$  is the normalized Gaussian probability that a strand has strength  $N_0$  and  $b' = 6.07 \times 10^{-4}$ . Equation (8) can now be evaluated for values of  $N_0^i$  where  $i$  is the decimal per cent of fibres that have a strength less than  $N_0^i$  and is given by

$$i = \int_{-\infty}^{N_0^i} g'(N_0) dN_0 = \frac{1}{2} \left[ 1 + \operatorname{erf} \left( \frac{N_0^i - 1}{\sqrt{2b'}} \right) \right] \quad (14)$$

where

$$\operatorname{erf}(y) = -\operatorname{erf}(-y) = \frac{2}{\sqrt{\pi}} \int_0^y \exp(-x^2) dx \quad (15)$$

The equivalent expression for the Weibull distribution is

$$i = 1 - \exp[-(N_0^i/s'_w)^m] \quad (16)$$

where  $s'_w = s_w / \langle s \rangle = 1.012$ .

The results are displayed in Figures 3 and 4 for the 90% and 80% load levels. The per cent failure is plotted versus the fibre lifetime. The smooth solid and broken lines for the Gaussian and Weibull distributions of static strengths correspond to values of  $\alpha$  equal to 1/2, 1 and 2 as shown, and the choppy line is from the experimental data. As noted earlier, the results are extremely insensitive to the value of  $a$ . The differences for values of  $a$  between 0 and 2 are greatest at high per cents of failure, but even here represent only a few per cent of the difference between the different  $\alpha$  values. The data shown is for  $a = 1$ . In order to facilitate comparison we have selected values of  $E$  and  $\gamma$  so

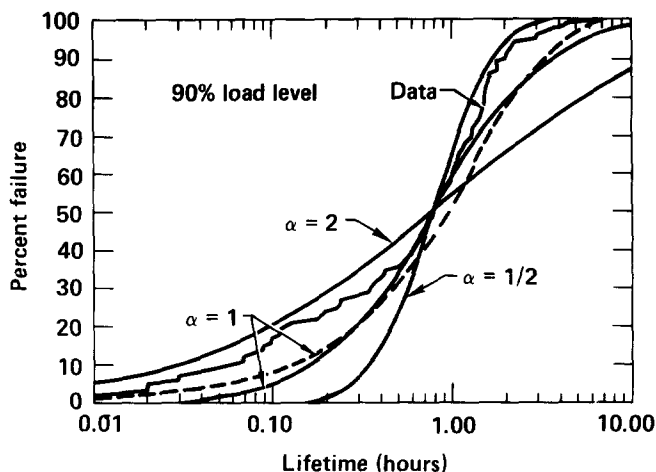


Figure 3 Lifetime data for Kevlar fibres held at 90% of their breaking load. The cumulative per cent failure is plotted versus the lifetime. The choppy line is the raw data<sup>3</sup> and the smooth curves are the theory for values of  $\alpha$  as shown. Solid lines are from the Gaussian fit of the static strengths and broken line for  $\alpha = 1$  is from the Weibull fit. Energetic parameters were chosen to force agreement of the lines from the Gaussian fits at 50% failure to facilitate comparison

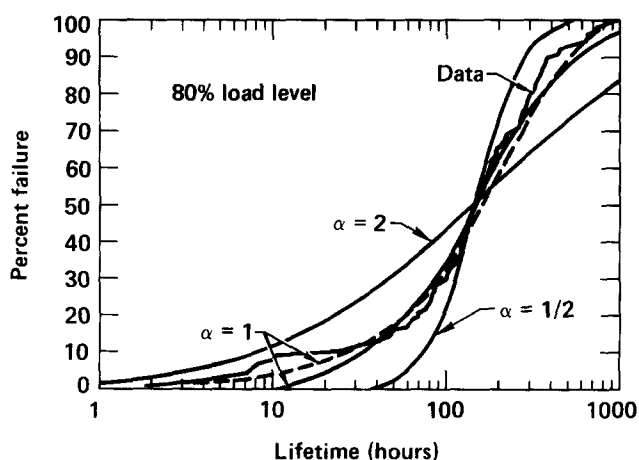


Figure 4 Lifetime data for Kevlar fibres held at 80% of their breaking load. Their cumulative per cent failure is plotted versus the lifetime. The choppy line is the raw data<sup>3</sup> and the smooth curves are the theory for values of  $\alpha$  as shown. Solid lines are from the Gaussian fit of the static strengths and broken line for  $\alpha = 1$  is from the Weibull fit. Energetic parameters were chosen to force agreement of the lines from the Gaussian fits at 50% failure to facilitate comparison

that all the calculated Gaussian curves coincide with the experimental data at 50% failure. The differences between the values of  $E$  and  $\gamma$  for each line are small and vary from their mean by no more than 3%. The same parameters are used in the Weibull generated line which differs only slightly, as do the Weibull generated lines for  $\alpha = 1/2$  and 2 which are not shown.

## DISCUSSION

The first feature to note is that the basic premise, that the narrow distribution of static strengths leads to the broad asymmetric distribution of lifetimes, is supported by the theory, which appears at least qualitatively to deal correctly with the functionality. The essential aspect of equation (4) is the division of  $\sigma$  by  $N^2$ . This can be seen especially clearly by considering the simple Zhurkov expression, where both  $a$  and  $\alpha$  are zero, which erroneously predicts a Gaussian distribution in lifetime from a Gaussian distribution in static strength.

It should also be emphasized that the theory does not depend in any direct way on the functional form used to fit the static strength data. In most situations it is convenient to fit this data with some appropriate mathematical form. However it is the distribution of the data itself, when fed into equation (8), and not the mathematical form, that gives rise to the asymmetric lifetime behaviour. One could easily apply the theory to the raw data and bypass any functional form fits, which simply serve to smooth out the roughness of a limited data set.

It is interesting to note that for the Gaussian data at small fractions of failure a value of  $\alpha = 2$  seems to fit the data at both load levels best, while at larger fractions of failure values of  $\alpha$  between 1 and 0.5 work best. Without placing too much significance on the actual values we might interpret this trend from a high to a lower  $\alpha$  as follows. Considering equation (4) we can see that a small decrease in  $N$  increases the magnitude of the term  $\gamma\sigma/N^\alpha$ , which reduces the effective activation energy ( $E - \gamma\sigma/N^\alpha$ ), thus increasing the rate of degradation. Larger values of  $\alpha$  will accelerate this effect relative to smaller ones. Thus it is not surprising that the fibres which fail early are characterized by larger  $\alpha$  values. For the longer lived fibres the value of  $\alpha$  is less than unity, the value for equal load-sharing, reflecting the ability of the material to deal more locally with the degradation of strength, thus extending fibre life.

Though we have formulated the theory for fibrous materials, the basic formalism is general enough to be applicable to amorphous polymeric materials. The variable  $N$ , which represents the number of 'fibre elements' or strength can just as easily be associated with amorphous or network systems. This is particularly true in the latter case where the failure of a network system must be directly related to the failure of individual chains between crosslinking junctions.

Lastly, let us look at what is necessary to apply the theoretical procedures outlined here as a predictive tool. After all, a theory which predicts only what we already know is of limited utility. Basically we need two types of information. First we need to know what the distribution in static strength for the sample in question is. This is fairly easily and quickly done by standard mechanical test methods. Secondly we need to be able to evaluate the energetic parameters  $E$  and  $\gamma$ . This is best done by time-to-fail tests at high loads. The median data can be fit to the modified Zhurkov expression, equation (5), and even with  $Q$  taken as zero we will get reliable estimates of  $E$  and  $\gamma$ . The theory can then give estimates of both median lifetime and lifetime distribution at lower stress levels.

As discussed extensively in paper 1, at lower stress levels other modes of degradation may predominate.

Examples include chemical action by impurities, moisture or an environmental source, or exposure to light or other high energy radiation. Measuring the effects of these actions is difficult since they do not manifest themselves in short-time high-load lifetime tests. If estimates of the kinetic and energetic factors can be made they can be included in the model as was shown previously in paper 1 for median lifetimes. Extension of that work to calculation of lifetime distribution follows directly from what we have done for stress-induced failure.

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