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Adaptive modelling of materials test results: tear energy in filled rubber networks

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We have elaborated a procedure for numerically modelling the behaviour of polymer-based materials as a function of two independent variables such as temperature and rate. The parameters of the model are chosen to have close physical significance, e.g. in terms of molecular theories or other measurements. The model may be adjusted to the data by a least-squares fit, yielding the optimal parameters provided the chi-squared test shows the fit to be acceptably good. Specimens may be compared by studying the dependence of individual fitted model parameters on preparation variables. Under certain conditions this procedure can be extended to result in the quantitative prediction of the ingredients and preparation needed to produce a material of desired properties. We describe the implementation of the procedure on a computer-graphics facility, and apply it to the study of the tear energy in filled vulcanizates.

1. Introduction

The preparation of materials having desired properties, often still the subject of trial and error augmented by a wealth of experience, is increasingly being put on a scientific basis. In the case of polymers this transition is far from complete; the understanding of materials properties conferred by modern molecular theories must be supplemented and extended by observed correlations [1]. Simple polymer systems greatly benefit in this regard from the attribute of thermorheological simplicity, i.e. the equivalence, firmly based on theoretical considerations [2], of changes in test rate and corresponding changes in temperature. The time–temperature superposition of the results of mechanical tests then produces a single master curve from whose interpolation the results of measurements at untested rate–temperature combinations are successfully predicted.

The dependence of the physical properties of viscoelastic materials on temperature and rate clearly points out the inadequacy of single-point testing procedures; thus a variation of the testing rate and/or temperature is indispensable for even the most elementary understanding of polymer behaviour. But it is the property of time–temperature superposability which facilitates the remedy: the two independent variables reduce to a single one. While the trade-off between rate and temperature is well understood theoretically [3], the shape of the master curve itself is only semi-quantitatively described; mathematical models for it [4, 5] must still be regarded as heuristic even when molecular theories are involved in their construction and parameterization, although this approach limits the accuracy of distant extrapolations of test results.

More complex, heterogeneous polymer materials often exhibit mechanical behaviours for which attempts at time–temperature superposition fail to produce a single master curve [6–8]. The question of whether this failure is in part attributable to artefacts of the testing procedure at certain time–temperature combinations is, of course, of great interest to the understanding of the material at the microscopic, molecular level. However, such considerations are largely irrelevant in a macroscopic description of the material under this test, assumed to be representative of conditions encountered in practical use. Thus a model description of mechanical tests as a function of temperature and rate must contain, in addition to the fully shiftable basic model, certain heuristic features which depart from time–temperature shiftability. A representation of the results thus necessitates the use of two independent variables [8], the model constituting a curved surface which may be viewed in projection from a convenient angle.

We have implemented such a description of materials behaviour on an engineering computer-graphics facility. Our model has certain desirable features in terms of its connection with molecular theories [9–11] and materials preparation variables, and any of its parameters may be automatically adjusted to produce the best fit to the data at hand. The resulting parameters may then be compared with those of an identical fit for a material of different constitution or preparation. This approach represents the initial stages of a procedure which envisions the prediction of materials and preparation required to produce polymer systems of desired physical properties. A preliminary account of this work has been presented [12]; the system is currently in use in several studies of tearing energy in filled polymer networks [13].

2. General approach

2.1. Modelling the test results

The results of any mechanical test may be expressed as z, a function of independent variables x and y. In our

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implementation, z represents the logarithm of the tear energy, x the absolute temperature and y the logarithm of the rate of tearing. The function $z(x, y)$ has one of several fixed forms, one of which is to be described in Section 3; it is driven by a set of up to 17 parameters. Some of these may be adjustable, others remain fixed, including those which have purely definitional status. If n of these parameters p_j are adjustable, then

$$z = F(x, y; p_1, \ldots, p_n) \quad (1)$$

The form of the function F is chosen to be able to represent a wide range of possible results for the test under consideration, provided some of the parameters are optimally adjusted. Considerable freedom exists in the choice of various additive contributions to F, and moreover, in the manner of parameterizing these. The mathematically desirable attributes of this parameterization are discussed elsewhere [14]; a brief review will suffice. The number of adjustable parameters must be appropriate: too few will not permit the data to be reproduced, while too many must result in ambiguities as well as being wasteful. Of course, the number of data points available should greatly exceed n. The parameters are chosen whenever possible to be approximately "orthogonal": each affects the function in a way not closely duplicated by any other. Of course, parameters whose main effect on the function occurs in a region of x and y devoid of data are immaterial and cannot be adjusted at all.

Equally important are the physical significance and intuitive meaning of the parameters. When possible, parameters are easily relatable to materials properties and/or theoretical constructs (molecular theories; free-volume theory, etc.) applicable to the test results. For practical reasons, initial guesses for the adjustable parameters need to be obtainable from a cursory inspection of the data: baseline levels as well as positions, heights and widths of the features to be described, are much preferable to higher coefficients of polynomials (which tend, in any case, to be obscure in their significance). Parameters representing the results of independent measurements (thermal expansivity, etc.), or reference temperatures, etc., may enter the model but are never adjusted.

Both the test itself as well as the model describing its results avoid reference to extensive, design-related dimensionality, and concentrate on intensive materials properties. Critical times or temperatures, asymptotic or extremal responses or their derivatives, are useful candidates as parameters, whether these describe response properties or ultimate, failure, attributes.

2.2. Comparing model and data; fitting

To permit comparing model and data, the latter must include experimental uncertainties, e.g. standard deviations of the results of repeated identical tests: the measurements report $z \pm \Delta z$ at a given (x, y). The basis for the comparison is the reduced chi-square statistical measure of goodness of fit [15]:

$$\chi_\nu^2 = \frac{1}{N - n} \sum_{i=1}^{N} \left(\frac{F(x_i, y_i; p_1, \ldots, p_n) - z_i}{\Delta z_i} \right)^2 \quad (2)$$

with N denoting the number of data points, ν being the number of degrees of freedom, $N - n$. When this index greatly exceeds unity, the fit is not acceptable, either because the parameters p_j have incorrect values or else because the model itself is inappropriate; this latter eventuality is revealed only after the parameters have been optimized. Because for a given comparison or fit the data are fixed, reduced chi-square may be regarded as a function solely of the adjustable parameters; optimization of these parameters is achieved by requiring the partial derivatives to vanish:

$$\partial \chi_\nu^2 / \partial p_j = 0 \qquad j = 1, \ldots, n \quad (3)$$

Because the form of F must be selectable without extraneous mathematical constraints, these secular equations are in general not linear with regard to p_j, and thus cannot be solved by standard methods. (The subject of non-linear curve-fitting is discussed in detail in the literature [15].) In order not to prejudice the range of convergence by locally linearizing chi-square or the model function, we have chosen the fully non-linear Davidon (or Fletcher–Powell) variable metric minimization algorithm [16, 17] with a modification permitting the derivatives in Equation 3 to be evaluated numerically [14, 18]. This avoids the need for incorporating codes for all analytic derivatives $\partial F / \partial p_j$ into the program, and thereby facilitates experimentation to obtain the optimal forms for the contributions to F. Like all non-linear fitting routines, ours requires initial guesses for all adjustable parameters to be supplied; sometimes the program is able to converge starting from a standard set of parameters contained within the program. The algorithm also checks that the obtained solution represents a minimum rather than a local maximum in chi-square, and attempts to establish that the minimum is universal rather than local.

After a successful fit, all significant information about the data is contained in the optimized set of parameters; together with the chosen form of the model they constitute a complete and highly distilled description of the data irrespective of the number, coordinates and precision of the data points. Thus except for the graphic presentation the original data have no further part in the analysis. It is this functional representation of the data which makes possible the extensive comparison among data sets, i.e. on the basis of variations in constitution or preparation, to be described below.

The output of the fitting program includes reduced chi-square, the optimized parameters p_j^*, and the statistical uncertainties of the latter, Δp_j^*. These uncertainties [15] are important in deciding whether a given parameter changes significantly with specimen preparation, particularly large values indicating insensitivity of the model to that parameter given the available data. Fits producing excessive chi-square values are rejected; those with acceptable values (for a desired confidence level [15]) are associated with the data set and the model until they are replaced by the results of a better fit of the same model.

The program contains two (or more) models, each of which is fitted to each set of data. A successful fit implies no unique status for the model in question;

more than one model may adequately represent the data. Our experience shows that for well-constructed models a clear decision as to superior fit is not usually possible, particularly when several sets of data are included in the comparison. Addition of further data to a set necessitates refitting, the principal changes typically being a reduction in the uncertainties Δp_j^*, and slight adjustments to the values of p_j^* themselves.

2.3. Comparison among specimens

As outlined thus far, the modelling is useful mainly as an aid to interpolation, i.e. prediction of the behaviour at values of x and y for which no test data have yet been taken. Of greater interest is prediction of the behaviour of similar material differing in one or more aspects of constitution, preparation, or thermal and mechanical history. These attributes will be collectively referred to as preparation variables; each sample (or in cases where the testing procedure is destructive, each batch of identical samples) is characterized by a set of preparation variables, whose numerical values are stored with the test data. Many preparation variables may take a continuous range of values (concentration of an ingredient, crosslink density, ageing time, etc.), while others have essentially integer, often binary, character (presence or absence of a trace ingredient, choice between two or more crosslinking agents, etc.). Even these may usually be transformed into other, molecular, variables having a continuous range.

To study the effect of changes in a given preparation variable on the test results, a series of samples differing systematically in (only or mainly) that the variable is tested and the results are subjected to the model fit. Our computerized procedure provides plots of any desired p_j for a given model as a function of any selected preparation variable, the data base including all specimens in the series of interest. This search, conducted interactively, reveals the parameters which are particularly sensitive to that preparation variable. To quantify that sensitivity, a low-order polynomial fit is automatically invoked and its parameters are used as an aid in predicting p_j for as-yet unexamined values of that preparation variable. This quantification is repeated, under operator direction, for all p_j significantly sensitive to that preparation variable. Later, the entire examination may be repeated for other preparation variables of interest.

The distant goal envisioned for this methodology is the prediction of the preparation variables required to produce a material of the desired properties, at least for materials within narrowly defined constraints. The attainment of this goal will depend on the successful solution of three problems:

(a) Dealing with the simultaneous variation of more than one preparation variable. The correlations thus engendered among the various p_j terms should be amenable to treatment by the interaction matrix method along the lines described by Kelley and Williams [1].

(b) Relating the p_j values to macroscopic properties of interest. The success of this step depends on a felicitous choice of model and its parameterization, and may involve simple combinations of the p_j values in the derivation of a given physical property.

(c) Inverting the forward correlations developed in (a) and (b) to predict properties from preparation variables. While this problem is purely mathematical rather than conceptual, ambiguities will arise if the forward correlations are non-monotonic. In such cases the inverting algorithm must be able to produce more than one set of preparation values resulting in the desired properties, leaving the final choice of preparation to be made on the basis of other criteria such as availability, expense, etc.

3. Implementation

3.1. General

The procedures described have been implemented on the Engineering Computer Graphics Facility at the University of Akron, based on a Prime 850 time-sharing computer system. The resulting program is designed to be used interactively from a high-resolution monochrome graphics terminal, but also produces optional output and plots on a line printer capable of a graphics mode, as well as one of several incremental pen plotters. Except for system calls, certain device drivers, and low-level graphics routines, all code is written in standard Fortran 77, and includes its own data-base management facilities as well as extensive data checking and error recovery. The length of the source file is some 17 000 lines, over one-third of which is documentation and user directions.

After optionally entering new test data or modifying (e.g. adding to) selected existing data, the user enters commands directing the analysis: manual or automatic curve-fitting, comparison of model surfaces or model parameters (including automatic polynomial fits) among selected data sets, and generating plots, with viewing angles of three-dimensional plots under user control. The curve-fitting stage permits the selection of the model to be applied, the setting and manual changing of model parameter values, the selection of the parameters which are to be optimized, and the multi-parameter non-linear optimization. The checking for uniqueness and reliability of the chi-square minimum is divided between automatic (random step) and manually directed features.

Association of optimal parameter combinations for that model with the data set is mandatory and automatic: a superior parameter combination (as evidenced by the lowest chi-square obtained so far), however obtained, supplants the previous best set. To help decide whether the inclusion of a particular feature of the model is "cost-effective" for the data set under consideration, the Gauss criterion may be applied [15]; for identical data, comparisons between fits of the same model with more or fewer parameters adjustable are made on the basis of reduced rather than standard chi-square.

3.2. Standard model

The present implementation of the procedure contains two models, of which the one to be described is regarded as preferable for the representation of tear

energy. Recalling that $z = F(x, y)$, with F denoting the logarithm of the tear energy in $J\,m^{-2}$, x being temperature (K) and y being the logarithm of the tear rate in m sec^{-1}, the first requirement is to generate the time–temperature-superposable part F' of the function

$$F'(x, y) = f(x_r, y') - \log\left(\frac{x}{x_r[1 + \alpha(x - x_r)]}\right) \quad (4)$$

Here x_r represents the reference temperature, which enters the shifted function f as well as the second term, the entropy–density correction [2]; the latter also involves the thermal expansivity α. The shifted rate is related to the original rate in the conventional way [2] by

$$y' = y + \log a_T \quad (5)$$

with a_T calculated either from the Williams–Landel–Ferry (WLF) theory [3] using

$$\ln a_T = -\frac{c_1^0(x - x_r)}{c_2^0 + x - x_r} \quad (6a)$$

where c_1^0 and c_2^0 are constants, or else from an Arrhenius-like expression

$$\ln a_T = A[(x - x_0)^{-1} - (x_r - x_0)^{-1}] \quad (6b)$$

where A is a constant, with the choice between these determined by a binary parameter which is not fitted. The function f itself consists of a baseline z_0 plus a broadened edge feature which terminates in a higher plateau of level z_p. (The modelling of a two-stage approach to an upper plateau is described by Plazek *et al.* [4] and, in more detail, by Su [5].) If the approach to this plateau is more complex, a second, similar feature of height h may be optionally interposed [19]. Combining these, we write

$$f(x_r, y') = z_0 + \frac{z_p - z_0 - h}{1 + \exp[2(y' - y_a)/w_a]} + \frac{h}{1 + \exp[2(y' - y_b)/w_b]} \quad (7)$$

The midpoints along y of the edge features are given as y_a and y_b, while their y-widths are w_a and w_b, respectively. The shiftable part of F now being complete, a single non-shiftable Gaussian peak of height H, centred at coordinates x_c and y_c, with full widths at half height w_x and w_y in the respective directions, may be added:

$$F(x, y) = F'(x, y) + H \exp(-br^2) \quad (8)$$

where $b = 4 \ln 2$ and

$$r^2 = \left(\frac{x - x_c}{w_x}\right)^2 + \left(\frac{y - y_c}{w_y}\right)^2$$

If h or H is set to zero, the respective expressions are not evaluated in order to save computational effort. In these cases, the other parameters contained in only these expressions become irrelevant and cannot be adjusted. The complete function may be seen to involve as many as 17 parameters, three of which are never fitted. The simplest cases call for $h = H = 0$, so that only four parameters (z_0, z_p, y_a, w_a) are subject to adjustment when the shift constants are known. A list of all parameters with some explanation is given in Table I. The parameters have immediate physical significance, either by way of definition (x_r and the WLF–Arrhenius choice of shift mechanism), or as the results of other experiments (α as well as the shift constants), or else as quantities easily estimated by inspection of the data. The chosen form of F assures a reasonable degree of orthogonality among the parameters, provided that the available data suffice to determine all adjustable parameters.

TABLE I Description of parameters for tear-energy model

Parameter	Symbol*	Explanation and comments
p_1	z_0	Baseline, log of threshold tearing energy
p_2	z_p	Upper plateau level of log (tearing energy)
p_3	y_a	y-midpoint of principal edge feature
p_4	w_a	y-width of principal edge
p_5	h	z-height of secondary edge feature
p_6	y_b	y-midpoint of secondary edge
p_7	w_b	y-width of secondary edge
p_8	c_1^0 or A	First time–temperature shift constant
p_9	c_2^0 or x_0	Second shift constant; see Parameter No. 17
p_{10}	x_c	x-position of centroid of peak feature
p_{11}	y_c	y-position of peak centroid
p_{12}	w_x	x-width of peak (full width at half height)
p_{13}	w_y	y-width of peak
p_{14}	H	z-height of peak
p_{15}†	α	Thermal expansivity
p_{16}†	x_r	Reference temperature (K)
p_{17}†	0 or <0	Choice: WLF (0) or Arrhenius (<0) shifting

*Symbols refer to those used in Equations 4 to 8.
†Parameter is not fitted.

3.3. Graphic representation

The graphics routine concerned with representing the data as a function of x and y, together with the model, first establishes a reference frame in the form of a rectangular box whose transparent surfaces represent the extremal values of x, y and z; its edges are shown as lines. Axes drawn parallel to the three frontal edges are labelled and supplied with marks and corresponding numbers. The data points are represented as symbols viewed frontally; error bars are represented as vertical lines whenever they exceed the size of the parent symbol.

The model function using the current parameters is evaluated at the corners of a 30 × 30 regular rectangular grid in the x–y plane, whose outer edges are coincident with the vertical planes of the box. Each point in this grid is connected by a straight line to its four nearest neighbours. The systems graphics routine which draws this surface permits the selection of a hidden-line algorithm; our experience shows that its use generally results in a less informative presentation than a surface fully transparent to the data points (but opaque to itself), provided that the user selects the most advantageous viewing angles.

The box and its contents are displayed in an orthographic projection, which lacks a vanishing point; it

was felt that the modest reduction in visual ambiguity achieved by true perspective is not worth the extra computing effort. The operator needs to select only two viewing angles, the elevation above the base plane and the azimuth. Because the graphics terminals in use have two screen buffers, a view from another set of pre-programmed angles may be computed and transmitted to the terminal's undisplayed screen while the current display is being studied, until the new display is completely drawn. At that time the screens are logically interchanged, and the process is repeated for another set of viewing angles, thus simulating a rudimentary form of animation. When only two displays are to be studied (e.g. comparing two surfaces), these may be kept entirely in the terminal's display buffers and repeatedly and rapidly interchanged under program control without any transmission delay, permitting the convenient detection of small differences between the displays.

Model surfaces may be displayed with or without the corresponding data. Early experience with the system showed that considerable spatial ambiguity was possible in the presence of data, disguising the relative location of data points with respect to the surface. Experimentation showed that a vertical connection between each data point and the model surface above or below it (same x and y coordinates) effectively removed this ambiguity. This connection was implemented as a slender wire-frame pyramid with a small square base coincident with the surface and sharing its slope, the apex located at the centre of the data symbol. It is suppressed when the data point is within an error bar of the surface, leaving more distant points clearly referred to the surface.

A related set of routines shows two model surfaces simultaneously, usually with the hidden-line algorithm enabled; a display of the solid enclosed between the two surfaces is also possible. The hidden-line attribute is usually suppressed when the colour-pen plotter is used for hard-copy, where different colours or different line thicknesses can identify the surfaces. This advantage is denied to the line printer in its graphics mode, which closely resembles the terminal display. A conventional x–y display of selected model parameters as functions of an arbitrary preparation variable, together with a polynomial fit, is also available.

4. Example: filled polybutadiene networks

As a simple illustration of the computerized data analysis procedure described above, we show excerpts of the modelling of a series of tear tests on a simulated solid rocket propellant, an industrial polybutadiene (PB) matrix (Arco R–45M or 45HT) crosslinked and highly filled (70 vol %) with glassy polystyrene beads of 30 μm average diameter. In the data to be shown the beads were without surface reactivity, and hence were not chemically linked to the matrix network. Tear energies were extracted from tear tests conducted on specimens in the trouser geometry, with results corrected for the energy required for bending. The results were not further corrected for any small deviation of the tear path from linearity. Sample preparation and

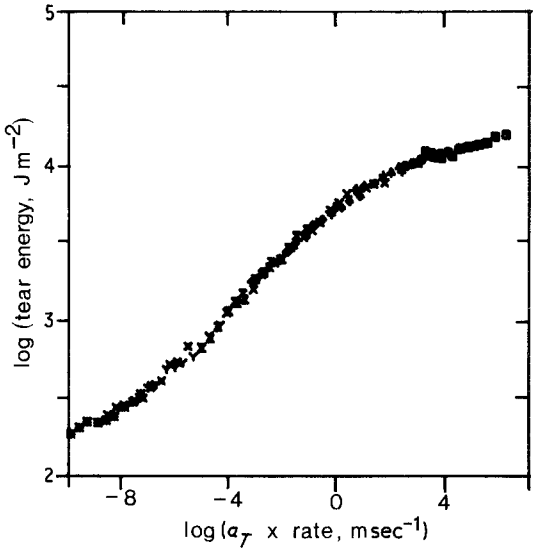

Figure 1 Rate-dependence of the tear energy (log–log) in a filled polybutadiene network (sample PS–L–HC), represented as a master curve in which data taken at twelve temperatures between −60 and +100° C are empirically shifted to a reference temperature of 25° C.

details of the tear test, including data reduction and correction, are described elsewhere [19].

Fig. 1 shows the tear energies in one such set of specimens, PS–L–HC, having a molecular weight between crosslinks $M_c \approx 4100$. The display is in the familiar form of a master curve, in which rate-dependences measured at twelve temperatures between −60 and +100° C are shifted empirically [2] to a reference temperature of 25° C. The computer program which performed this shifting then compared the extracted values of $\log a_T$ against $(x - x_r)$ with Equation 6a, adjusting c_1^0 and c_2^0 to obtain the best fit. Since the shifting resulted in an acceptable master curve and was consistent with the WLF hypothesis, our three-dimensional treatment was expected to replicate these findings.

Fig. 2 redisplays the same set of data as an explicit function of both independent variables, together with a fitted model surface employing WLF shifting. Examination of Fig. 1 suggested that the shape of the master curve is sufficiently simple to be successfully and economically described by a single broadened edge feature. Indeed, while the addition of the secondary edge slightly improved the fit, the three extra adjustable parameters actually raised the value of chi-square per degree of freedom. Given that unshiftable features were not necessary, p_5 and p_{14} were set to zero, making p_6, p_7, p_{10}, p_{11}, p_{12} and p_{13} irrelevant. With $p_{17} = 0$, $p_{16} = 298$ K and $p_{15} \approx 4.8 \times 10^{-4}$ K^{-1}, the only adjustable parameters were p_1, p_2, p_3, p_4, p_8 and p_9.

Except for the shifting parameters, for which the results of the master curve analysis were substituted, the initial parameter guesses needed as input for the automatic curve-fitting routine were arrived at in a brief visual inspection of the data displayed with the model surface generated from the current parameter estimates. The reliability of the optimized parameters was found to be enhanced if the six parameters were fitted in two groups: alternately the edge feature (p_1 to

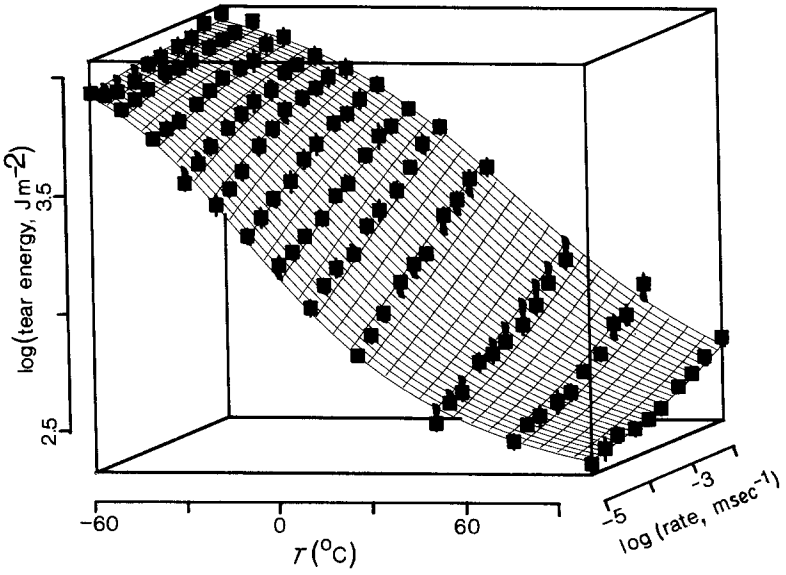

Figure 2 Data of Fig. 1 replotted as an explicit function of rate and temperature. The model surface incorporates a simple broadened edge between a threshold and an upper plateau in the rate-dependence, and is WLF-shifted in temperature. The plot shows experimental uncertainties in the data, and, where appropriate, a vertical connection between data points and surface.

p_4) and the shift constants (p_8 and p_9), repeating once or twice before completing the process using the full six-parameter fit. This strategy minimized the possibility of being detained in a local chi-square minimum, and reduced the effort required to untangle the inevitable non-orthogonality (parameter correlation) between p_4 and p_8. The optimum obtained by the fitting routine was tested and slightly refined in five automatic random parameter-displacements, each followed by refitting. The value of reduced chi-square ($=1.28$) characterizes the final fit as adequate. The values of the final fitted parameters for Fig. 2 are given in Table II.

The experiment was repeated using another set of specimens, PS–L–LC, identical to the earlier ones with the exception of its lower crosslink density ($M_c \approx 15\,000$). The model was fitted to the data from this experiment in a form and manner identical to the earlier case; the fit obtained was again satisfactory. The model surface obtained had a similar appearance, with many of the fitted parameters retaining their previous values within their combined respective uncertainties. Comparison between the surfaces, however, reveals significant differences as well. Fig. 3 shows both surfaces displayed together, without the data.

Examination of the numerical results of the fit reveals that the parameters p_1 and p_2 underwent the most significant changes as a result of the decrease in matrix crosslink density. The M_c-dependence of the tear energy asymptote p_1 is statistically significant, and admits of a direct molecular interpretation in terms of a concept proposed by Lake and Thomas [9]. The latter calls for a non-linear (square-root) dependence of p_1 on M_c, a fact not discernible here in the absence of data for three or more values of M_c. The application of the Lake–Thomas theory to tear data in unfilled specimens has been described elsewhere [4, 5].

The M_c-dependence of the plateau tear energy as expressed by p_2 is less precisely captured by the fit because fewer data points were available in the plateau region. Experience with these as well as various other materials has suggested that p_2 and p_1 tend to scale together, perhaps because the height of the plateau above the threshold tearing energy is affected by molecular and morphological variables separate from those which determine the threshold. In that case the current parameterization is inappropriate in this respect (as well as undesirably "non-orthogonal" in the sense discussed above), and p_2 should instead express the logarithm of the ratio of plateau to threshold tear energy, analogous to other features whose vertical extents are referred to the baseline asymptote. This change in parameterization is currently being considered.

Minor but significant differences in the shifting parameters were found between the surfaces of Fig. 3; it was not possible to assign their origin unambiguously to the change in M_c. Differences in the shifting constants between Figs 1 and 2, i.e. for identical data reduced in different ways, are attributable to the difference in data treatment. Whereas in Fig. 1 the shifting was empirical, with a_T later fitted to the WLF temperature-dependence, in the treatment of Fig. 2 not only is the WLF shift directly imposed on all data simultaneously, but it is also intimately correlated with the functional form of the rate dependence and its appropriateness in describing the data. Since the differences in shifting constants between the two treatments were only some two combined statistical uncertainties in the respective fitted parameters, the disagreement is regarded as relatively modest.

An illustration of the effect of artefacts of either the measurement or the initial data reduction is given in Fig. 4. Here the model surfaces, as described above, are fitted to the same set of initial data (for another, similar, filled PB network) without and with

TABLE II Fitted model parameters for sample PS–H–HC

Parameter*	Symbol†	Fitted value	Units
p_1	z_0	2.378 ± 0.010	log (J m^{-2})
p_2	z_p	3.921 ± 0.015	log (J m^{-2})
p_3	y_a	-3.361 ± 0.03	log (m sec^{-1})
p_4	w_a	3.992 ± 0.008	log (m sec^{-1})
p_8	c_1^0	46.5 ± 3.8	–
p_9	c_2^0	335 ± 26	K

*See Table I.
†See Equations 4 to 8.

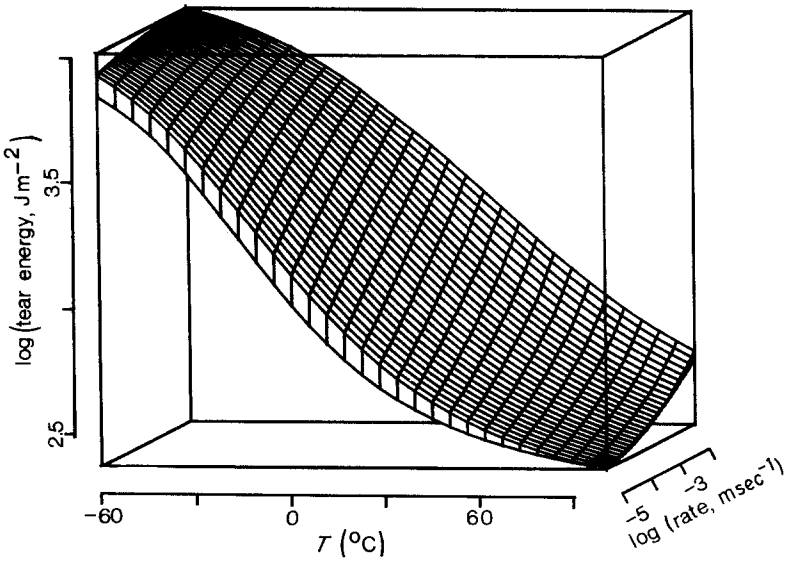

Figure 3 Comparison of the model surface of Fig. 2 (top) with an identical fit to data in a set of similar specimens (sample PS–L–LC) with lower crosslink density (see text). To reduce visual ambiguity (Moiré pattern), the surfaces are opaque and connected at the edges, simulating a solid object in projection.

a correction to the tearing energy for the work required to bend the trouser test specimen during tearing. The differences are highly significant and call for two observations. Firstly, the bending corrction is larger in magnitude than the effects of sizeable changes in sample constitution (see Fig. 3). Our experience shows that the domination of test artefacts over the usual differences in preparation variables is a general phenomenon, so that in extracting true materials properties the corrections for these artefacts must themselves be accurate to a high order.

Secondly, since bending energy is viscoelastic in nature, any correction for it must depend on rate and temperature. Hence the differences between the two surfaces in Fig. 4 are non-trivial, i.e. not limited to a simple decrement of p_1 and p_2 by equal amounts. Comparisons of the fitted parameters reveal significant changes to all four shape parameters p_1 to p_4, but essentially no changes to the shift constants.

To establish whether the WLF shift was indeed superior to the Arrhenius shift in these cases, we set $p_{17} = -1.0$ and $p_9 = 0$ K. The fit of p_8 jointly with p_1 to p_4 resulted in a distinctly inferior chi-square, although additional (simultaneous) adjustment of p_9 provided some improvement, resulting in a substantially negative (absolute) characteristic temperature x_0. For specimens in which the polystyrene filler beads were chemically attached to the binder network, the Arrhenius shift became approximately as successful as the WLF shift (two parameters adjusted in both cases). For these specimens, examination of the temperature-dependence of $\log a_T$ obtained from empirical shifting showed significant deviations of the results from both shifting schemes.

5. Concluding remarks

We have described a procedure which permits the accurate description of mechanical test results as a function of two independent variables, and the comparison of these results among specimens with different ingredients or preparation. The procedure requires a computer graphics system with facilities for maintaining substantial data bases. The latter contain not only the results of the measurements, but also the parameters of the current best description in terms of one or more models proposed for the data.

The models themselves are subject to several requirements and desiderata. They must, of course, be able to represent data from a given test on an entire family of materials under consideration, over the full range of

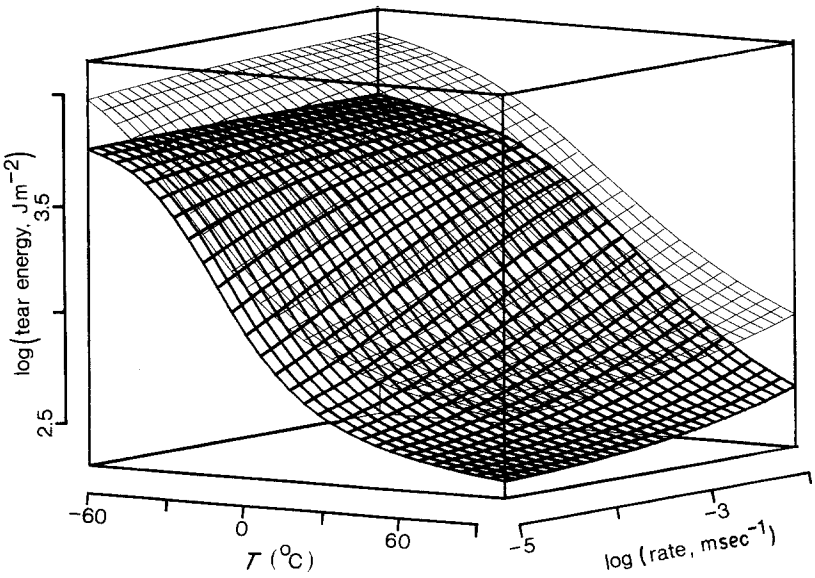

Figure 4 Comparison of two model surfaces fitted to the same set of measurements on a filled PB network. The top surface (transparent; fainter lines) represents a fit of the model to the raw data for sample R–45M–2; the lower surface describes a similar fit to the data corrected for the bending energy. The two surfaces are not simply related.

both variables (e.g. temperature and rate) of interest. The models must also incorporate as much physical significance and theoretical insight as possible, both with respect to the form of the function as well as to its parameterization. Finally, the parameterization must permit the fitting procedure to obtain an unambiguous separation of the effects of the various adjustable parameters on the model function. While these requirements severely limit the choices available in constructing the model, the success of any model is no assurance of its uniqueness as a valid description of the test data, and the final choice of the model to be used is likely to be made on practical or aesthetic grounds.

The immediate goal in the development of this facility is the comparison of specimens differing in some aspect of preparation. While semi-quantitative comparisons are possible simply through a visual examination of the fitted models, quantitative comparisons need to concentrate on the fitted parameters. From a study of the correlations of the parameters with the preparation variables it is possible to predict test results for rates and temperatures not yet explored. More important for the longer term, a methodology of this general nature is likely to be the basis of any sophisticated prediction of the ingredients and preparation necessary to produce polymeric materials with desired properties. In the interim, the procedure described here is a very useful tool in the systematic quantification of structure–property relations in the context of academic materials science.

It should be pointed out that the methods described here are sufficiently general for application in a wide range of fields. The tested specimens need not be based on polymers, the tests are not restricted to the mechanical or viscoelastic variety, the number of independent variables may be one, two, or greater (with increasing difficulty of presenting a suitable visualization of the model), and the variables themselves need not include temperature or rate.

Alternately, this methodology may be diverted from the examination of the effects of preparation and be turned instead to the study of testing procedures and data reduction. In several current efforts to measure tear energy in filled vulcanizates we are examining the effects of test specimen geometry and tear path constraint, as well as measures to prevent or correct for elastic or plastic specimen distortion during tearing. In these cases specimens are prepared in identical sets, and the comparisons between the results of different testing and data reduction procedures serve mainly to quantify the artefacts of each procedure, with a view to their reduction or elimination, or at least their standardization. Since the nature of the tear varies strongly with temperature and tear rate, variations in testing procedures will in general introduce non-trivial alterations into the data and the fitted model.

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