A mechanical model for creep, recovery and stress relaxation in polymeric materials

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A mechanical model is presented, in which viscoelastic response is described by the action of time-dependent latch elements. The model represents viscoelastic changes occurring through incremental jumps as opposed to continuous motion. This is supported by the observation that polymeric creep, recovery and stress relaxation can be correlated with stretched exponential functions, i.e. Weibull and Kohlrausch-Williams-Watts, since (i) the former is also used in reliability engineering to represent the failure of discrete elements and (ii) there is evidence of the latter being an approximation to the Eyring potential energy barrier relationship, which describes motion in terms of molecular jumps.

For polymeric materials, the ability to model viscoelastic response underpins our understanding of deformation mechanisms and facilitates solutions to long-term load-bearing design problems. Mechanical models are common, the simplest being the Maxwell (spring and dashpot in series) and Voigt (spring and dashpot in parallel) models; the former can be used for representing stress relaxation, the latter for creep and recovery conditions.

More complex models involve 3 or 4 elements, such as the Zener and combined Maxwell-Voigt models: both of these can represent creep, recovery and stress relaxation [1]. It is said however, that real materials in general are not describable by models containing a small number of springs and dashpots, i.e. they often lack sufficient accuracy for quantitative prediction [2, 3]. This may be attributed to the restricted timescales that these models can represent. Broad timescales require models that provide a distribution of retardation or relaxation times; this can be resolved by representing creep and recovery with a 'generalized Voigt model', consisting of Voigt elements connected in series, and stress relaxation by a 'generalized Maxwell model', using Maxwell elements connected in parallel [3]. A more elegant solution lies with a single model for creep, recovery and stress relaxation. This is afforded by the Zener model, since it can be generalized into a series of Voigt elements (for broad timescales) and a series spring (representing instantaneous elastic deformation) [4].

According to Rosen [3], some authorities object strongly to mechanical models, since real materials are not made of springs and dashpots. Nevertheless, as Rosen suggests, these materials are not made of equations either, and the visualization of deformation is facilitated by these models. Unfortunately, improving quantitative accuracy by using a generalized model with many elements could increase mathematical complexity to the point where the number of parameters may be impractically large, and (potentially complex) methods of approximation are needed [3, 4].

A common factor in these models is that viscoelastic deformation is considered to vary smoothly, i.e. a material undergoing creep, recovery or stress relaxation does so continuously with time. This letter considers an alternative approach, in which viscoelastic changes are suggested to occur through incremental jumps. On a molecular level, the phenomenon could be envisaged as segments of molecules jumping between positions of relative stability. The approach was first evaluated by the author, when it was found that polymeric creep and recovery could be accurately represented by equations based on the Weibull distribution function [5]. Thus for creep under an applied load, the total strain is:

$$\varepsilon_{\mathrm{ctot}}(t) = \varepsilon_{\mathrm{i}} + \varepsilon_{\mathrm{c}}\left[1 - \exp\left(-\left(\frac{t}{\eta_{\mathrm{c}}}\right)^{\beta_{\mathrm{c}}}\right)\right] \qquad (1)$$

where ε_{i} is the initial instantaneous strain from application of the load and the ε_{c} function represents creep strain, which is determined by the characteristic life (η_{c}) and shape (β_{c}) parameters as a function of load duration, t. When the load is removed, there may be some instantaneous (elastic) strain recovery, which is then followed by time-dependent recovery strain:

$$\varepsilon_{\mathrm{rvis}}(t) = \varepsilon_{\mathrm{r}}\left[\exp\left(-\left(\frac{t}{\eta_{\mathrm{r}}}\right)^{\beta_{\mathrm{r}}}\right)\right] + \varepsilon_{\mathrm{f}} \qquad (2)$$

where the ε_{r} function, for viscoelastic strain recovery, is determined by parameters synonymous with

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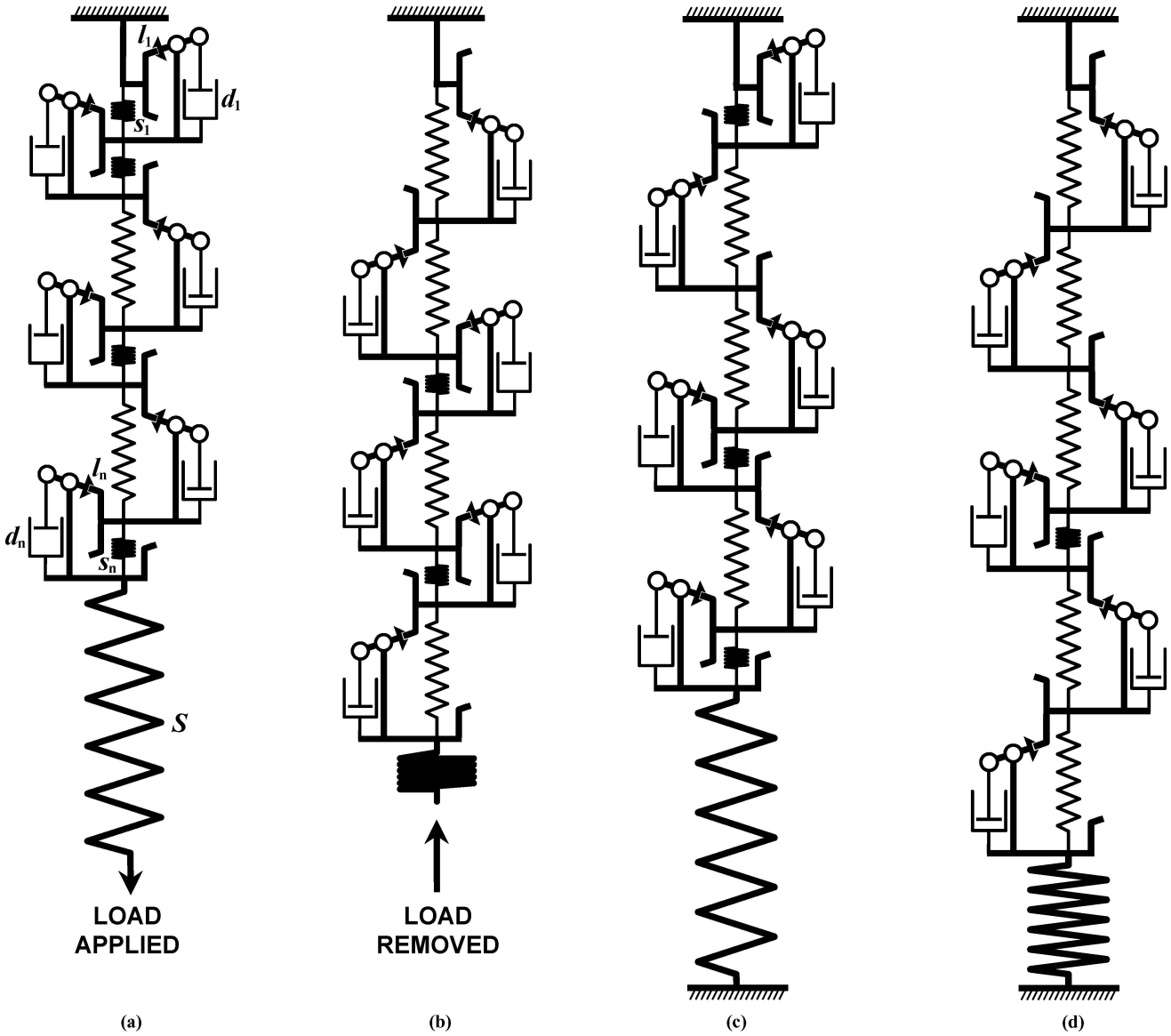

Figure 1 A spring-dashpot latch model to represent time-dependent deformation in polymeric materials: (a) Creep, (b) Recovery, (c) Stress relaxation at time t, and (d) Stress relaxation at time $t + \Delta t$, showing an increase in the number of latch elements triggered into their extended positions. In a real polymeric material, these deformation processes would need to be represented by many latch elements to give a broad distribution of trigger times.

those of Equation 1 over recovery time t, and ε_f is the permanent strain from viscous flow. These equations correlated very well with experimental data from semi-crystalline polymers, enabling both time-dependent and time-independent strain to be predicted [5]. Since the Weibull function is used in reliability engineering, it was suggested in Ref. [5] that, like the failure of elements in a system, viscoelastic recovery could be modelled as a population of time-dependent mechanical latches; each latch would be considered to have 'failed' once it had been triggered, thereby making recovery proceed by one incremental step.

Fig. 1 extends these principles, to present a generalized phenomenological model which depicts creep, recovery and stress relaxation in terms of the mechanical latch approach. The model consists of latches, the triggering time of each latch (l_1, l_2,... l_n) being dependent on the stiffness of the corresponding spring (s_1, s_2,... s_n) and viscosity of the dashpot (d_1, d_2,... d_n). Under creep conditions (Fig. 1a), triggering times would be reduced as creep load is increased, thereby increasing the strain rate. In recovery (Fig. 1b) however, these times would be expected to be greater, since there is no externally applied load; thus recovery strain rates become lower than those from creep. A proportion of the latch units, with triggering times that approach infinity on recovery, could be considered to represent viscous flow effects. Instantaneous (elastic) deformation within the material is represented by the large spring, S. The model is also consistent with stress relaxation conditions (Fig. 1c, d), in that S contracts as the latch units progressively extend with time. Stress relaxation rates will clearly be faster for a polymer in which S has high stiffness.

In addition to the link with failure of elements in a system, the incremental step argument is supported by considering the following. The Kohlrausch-Williams-Watts (KWW) function has been used to represent time-dependent phenomena, principally for relaxation in amorphous materials [6]. Although the function originated from the nineteenth century (Kohlrausch), its modern usage follows from the work of Williams and

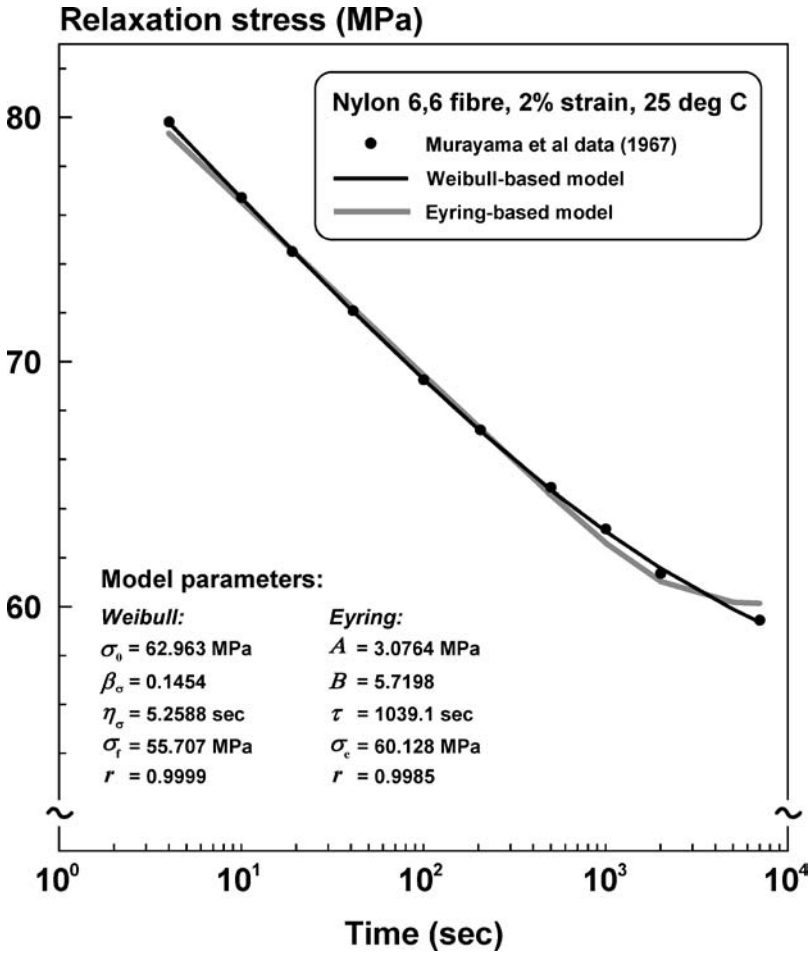

Figure 2 Analysis of stress relaxation data from Murayama et al. [14] for nylon 6,6 fiber, using Equation 3 (Weibull-based model) and Equation 4 (Eyring-based model). The quality of fit between measured and equation-predicted stress values is indicated by the correlation coefficient, *r*.

Watts for dielectric decay [7]. The KWW function is in fact identical in form to that proposed by Weibull [8], i.e. an empirical 'stretched exponential' function, which leads (for example) to equations comparable with Equation 1 being used to characterize creep in amorphous polymers [9–11]. Of importance here is a link that has been proposed [12] between the KWW function and the potential energy barrier relationship as developed by Eyring *et al*. [13], since the latter relates the motion of matter to molecular jumps. In Ref. [12], the KWW function is shown to be an approximation to the potential energy barrier model by comparing corresponding curves plotted with arbitrary values. Fig. 2 takes this further by taking stress relaxation data for a semi-crystalline polymer (nylon 6,6 fiber) [14] and fitting equations corresponding to (i) the KWW/Weibull function and (ii) the potential energy barrier model, using *CurveExpert 1.3* software. For (i), the stress relaxation is:

$$\sigma_{\mathrm{rel}}(t) = \sigma_0\left[\exp\left(-\left(\frac{t}{\eta_\sigma}\right)^{\beta_\sigma}\right)\right] + \sigma_{\mathrm{f}} \qquad (3)$$

where the σ_0 function represents time-dependent stress and σ_{f} is the final stress as t approaches infinity. Thus σ_{f} is represented by the elastic contribution from S in Fig. 1d that remains once all contributing latch units have triggered in response to the stress relaxation conditions. For (ii), the Eyring-based model adapted from Ref. [12] is used:

$$\sigma_{\mathrm{rel}}(t) = A\,\mathrm{atanh}\left[\tanh(B)\exp\left(-\frac{t}{\tau}\right)\right] + \sigma_{\mathrm{e}} \qquad (4)$$

where A and B are constants and τ is the relaxation time. The parameter σ_{e} is introduced here as an addition to the equation from Ref. [12], and is synonymous with σ_{f} in Equation 3.

Fig. 2 indicates good agreement between the two models and with the experimental data, although the Weibull-based model shows improved correlation at longer relaxation times. Using stress relaxation data from ultra-high modulus polyethylene monofilament [15], these trends are also indicated in Fig. 3; however, the broader timescale appears to exacerbate the limitations of the Eyring-based model. It is nevertheless encouraging that σ_{f} and σ_{e} have comparable values, as in Fig. 2.

Also shown in Fig. 3 is the model described by Wilding and Ward [15] fitted to their own data. Although this model appears to be a poorer fit than those of Equations 3 and 4, it has theoretical justification: stress relaxation is described as two thermally activated processes operating in parallel, each process being a Maxwell element incorporating an Eyring (instead of a conventional) dashpot. Thus, like Equation 4, the Wilding-Ward model is founded on the Eyring potential energy barrier relationship. From Ref. [12], $A =$

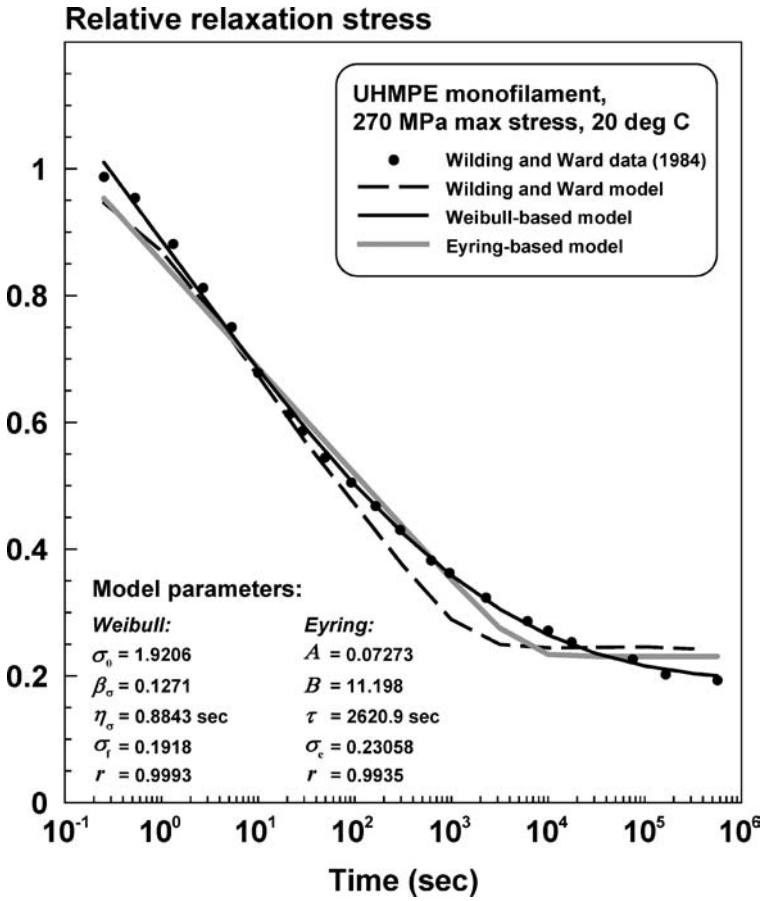

Figure 3 Analysis of stress relaxation data (relative to an initial stress value) from Wilding and Ward [15] for ultra-high modulus polyethylene monofilament, as described for Fig. 2. Also shown is the Wilding-Ward model plotted from Ref. [15].

$kT/2v$ in Equation 4, where k is the Boltzmann constant, T is the absolute temperature and v is the Eyring activation volume. Using parameter values from Figs 2 and 3, v is 0.67 nm^3 and 0.1 nm^3 for the nylon 6,6 and polyethylene data respectively. It is encouraging to note that the magnitude of these values is comparable to activation volumes generally associated with polymer deformation, i.e. ∼0.05–1 nm^3 [16]. For the polyethylene data in Fig. 3, v is calculated from the assumption that for A, initial and maximum stress values are equal (270 MPa); however, if the initial stress was less, this may explain the lower value (0.1 nm^3) compared with those determined in Ref. [15] from the Wilding-Ward model (0.162 and 0.456 nm^3).

It is evident from Figs 2 and 3, that the applicability of models with just one or two Eyring dashpots (or activation volumes) will tend to be limited to restricted timescales. Thus, as with conventional, generalized spring-dashpot models, to represent accurately the viscoelastic response over many decades of time would require an Eyring-based model with numbers of elements that could increase mathematical complexity to the point of impracticality. Conversely, the stretched exponential approach provides excellent correlation with experimental data, even over broad timescales [5]. An example of the latter has been applied to the development of prestressed polymeric matrix composites using viscoelastically strained nylon 6,6 fiber [17]: Equation 2 was fitted to fiber recovery strain data taken over 6 decades of time to ∼1.5 years. Curves extrapolated from Equation 2 have predicted strain values that are in good agreement with measured strain after ∼4 years of recovery [18]. Neverthless, the stretched exponential approach cannot be entirely satisfactory, since it has no real theoretical basis.

To summarize, the mechanical latch-based model in Fig. 1 is presented to suggest that viscoelastic changes may occur through incremental jumps. The observation that creep, recovery and stress relaxation in polymeric materials correlate well with stretched exponential (KWW/Weibull) functions provides two supportive arguments. First, the Weibull distribution function is used in reliability engineering to represent the failure of (discrete) elements in systems. Second, the Eyring potential energy barrier relationship describes the motion of matter in terms of molecular jumps [13]. For stress relaxation, the KWW function (hence the Weibull model) is considered to be an approximation to this [12], which is supported by evidence from Figs 2 and 3.

References

1. R. J. CRAWFORD, "Plastics Engineering," 3rd edn., (Butterworth-Heinemann, Oxford, 1998) p. 84.
2. R. S. LAKES, "Viscoelastic Solids," CRC Mechanical Engineering Series (CRC Press, USA, 1999) p. 23.
3. S. L. ROSEN, "Fundamental Principles of Polymeric Materials," 2nd edn., (Wiley, New York, 1993) p. 299.
4. N. G. MCCRUM, C. P. BUCKLEY and C. B. BUCKNALL, "Principles of Polymer Engineering," (Oxford University Press, Oxford, 1988) p. 130.

5. K. S. FANCEY, *J. Polymer Eng.* **21** (2001) 489.
6. R. G. PALMER, D. L. STEIN, E. ABRAHAMS and P. W. ANDERSON, *Phys. Rev. Lett.* **53** (1984) 958.
7. G. WILLIAMS and D. C. WATTS, *Trans. Faraday Soc.* **66** (1970) 80.
8. W. WEIBULL, *J. App. Mech.* **18** (1951) 293.
9. R. WIMBERGER-FRIEDL and J. G. DE BRUIN, *Rheol. Acta.* **30** (1991) 419.
10. J. M. CHERIERE, L. BELEC and J. L. GACOUGNOLLE, *Polymer Eng. Sci.* **37** (1997) 1664.
11. C. MARIAS and G. VILLOUTREIX, *J. Appl. Polymer Sci.* **69** (1998) 1983.
12. A. DOBREVA, I. GUTZOW and J. SCHMELZER, *J. Non-Cryst. Solids* **209** (1997) 257.
13. S. GLASSTONE, K. J. LAIDLER and H. EYRING, "The Theory of Rate Processes" (McGraw-Hill, New York, 1941) p. 480.
14. T. MURAYAMA, J. H. DUMBLETON and M. L. WILLIAMS, *J. Macromol. Sci. (Phys.)* **B1** (1967) 1.
15. M. A. WILDING and I. M. WARD, *J. Mater. Sci.* **19** (1984) 629.
16. I. M. WARD and D. W. HADLEY, "An Introduction to the Mechanical Properties of Solid Polymers" (Wiley, Chichester, 1993) p. 210.
17. K. S. FANCEY, *J. Reinf. Plast. Comp.* **19** (2000) 1251.
18. K. S. FANCEY, *J. Adv. Mater.* **37** (2005).

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