

4 FEB 1987

THE BRITISH SOCIETY OF RHEOLOGY

BULLETIN



1986, Vol. 29 No. 4

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ISSN-0045-3145

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1986/87

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EDITORIAL

In this issue we are pleased to publish a very substantial review paper by C.P. Buckley of the Polymer Engineering Division at UMIST. This work was presented at the Leeds conference on Deformation in Solid Polymers and I am sure it will prove to be a valuable reference for workers in this field.

The first of the Society's special lectures - the Treloar Memorial Lecture was given by Professor Sir Sam Edwards at UMIST in November. The lecture was well attended and well received. It will be repeated at Leeds on January 20th.

I would like to remind members of the society that I am always ready to receive short papers or articles for publication in the Bulletin. I would particularly like to continue the series started by Howard Barnes describing the work of various research groups. One or two pages is all that is required plus an optional photograph.

Finally, I would like to draw members attention to the following notice :-

1987 Annual Award

Society Members are invited to make nominations for the above award. Proposals should be sent to the Secretary as soon as possible.



Peter Townsend

DEFORMATION IN SOLID POLYMERS

A REVIEW

by

C P Buckley

Polymer Engineering Division,
Department of Mechanical Engineering,
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Introduction

The behaviour of solid polymers in deformation is remarkable, in the rich variety of effects they display. Young's moduli are found covering an enormous range: $1 - 10^5$ MPa. Extensions of more than 500% are often possible before fracture. Sometimes these huge strains are apparently permanent, sometimes almost totally recoverable. It is not surprising that over the last 40+ years many scientists have been inspired to research the deformation of these materials. The commercial thrust to optimise design and manufacture of polymer products has also been a powerful stimulus to the research, and has brought with it the interest and involvement of engineers.

Each researcher naturally approaches the subject with a different perspective. Here, though, I am going to assume that we share a common purpose; to seek as full an "understanding" as possible of the deformation of solid polymers, along whatever intellectual avenues such understanding is to be found. Furthermore, since in the real world stress and strain are almost invariably multiaxial, I shall assume that our goal is to understand the three-dimensional relation between deformation and applied loads.

I want to begin by sharing some thoughts on the philosophy of the subject. Then we shall embark on a brief tour of the chief landmarks as I see them.

Our subject is no different from other scientific endeavours, in that advances in understanding have come from the continual construction and refinement of theories and their test against experiment. In the study of deformation of solids, it is helpful to classify theories as belonging to one of two categories. A phenomenological theory is created by working out the logical consequences of "a priori" assumptions concerning the nature of the deformation. Further understanding then comes from mechanistic theories, based upon additional assumptions and hypotheses concerning the micromechanics of the material at the molecular or supramolecular level. In the young science with which we are concerned these two stages are far from complete, and I believe we must be alert to the possibility of further advances originating in either stage.

Some of the "a priori" assumptions we make are so familiar that we take them for granted. For example: it is the assumption that the material is a continuum that leads us to state that stresses are determined only by the tensor of deformation gradients $\underline{F}$, with elements defined

$$F_{ij} = \partial x_i / \partial X_j \quad (1)$$

(x_i are the new Cartesian co-ordinates of a point initially at X_j), and not by higher derivatives. It is on the further assumption that stresses are independent of the rigid body rotation component of $\underline{F}$ that we choose to define the finite strain tensor $\underline{E}$ in a way that is invariant under rigid body rotation:

$$\underline{E} = \frac{1}{2}(\underline{F}^T \underline{F} - \underline{I}) \quad (2)$$

(Superscript T denotes transpose, $\underline{I}$ is the unit matrix).

And it is on the basis of yet another assumption, that displacement gradients are small compared to unity, that we can sometimes approximate Eq (2) by its infinitesimal limit $\underline{\epsilon}$, with elements defined

$$\epsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial X_j} + \frac{\partial u_j}{\partial X_i} \right) \quad (3)$$

where the displacement vector is defined $u_i = x_i - X_i$.

Fortunately, further "a priori" assumptions are often appropriate, greatly simplifying the phenomenological framework. They are the assumptions that the constitutive relation (relation between stress and strain) exhibits one or more of:

linearity (valid for vanishingly small stress)

elasticity (uniqueness of stress-strain relation)

isotropy (or generally some specified symmetry).

These assumptions imply powerful restrictions on the form of the constitutive relation. Various combinations are possible. To express them compactly, let us briefly digress into the language of sets.

Let c be the constitutive relation for a given material in given circumstances. Let L , E , I and S be the sets of possible constitutive relations with the attributes linearity, elasticity, isotropy and some arbitrary specified symmetry respectively ($I \subseteq S$). Then the classes of behaviour I will consider here can all be expressed in terms of relations between c and L , E , I and S , as shown in Figure 1.

To conclude these opening comments, I want to reiterate a message that has long been known to some, but which has emerged with increasing force over the last 15 years or so. Polymer solids as often studied are in unstable structural states very far removed from thermodynamic equilibrium. Recognition of this fact must permeate all our attempts to understand the deformation of these materials. The issue is so fundamental to our interpretation of polymer deformation, I propose to split the remainder of this paper into two Parts, concerned respectively with equilibrium and non-equilibrium structural states.

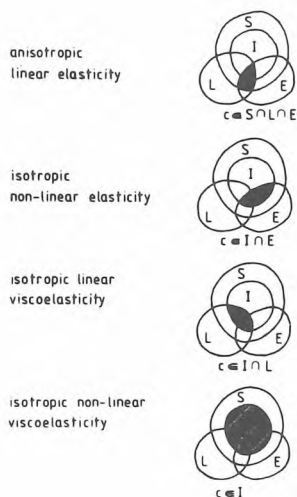


Figure 1 Pictorial representation of various classes of deformation behaviour encountered in solid polymers. c symbolises the constitutive relation; L , E , I and S symbolise the sets of all constitutive relations exhibiting the attributes linearity, elasticity, isotropy, or some arbitrary symmetry respectively.

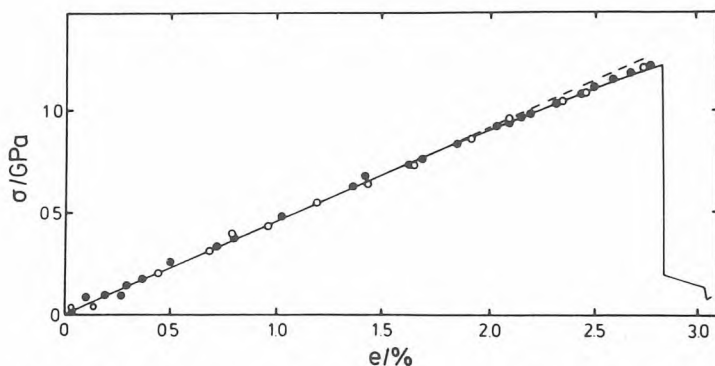


Figure 2 Tensile stress-strain curve for a polydiacetylene single crystal fibre. Filled and open points refer to loading and unloading respectively. Reproduced from Galiotis et al (3).

PART I: EQUILIBRIUM STRUCTURES

Crystals and Rubbers

Linear Elasticity of Polymer Crystals

At sufficiently low temperatures, the equilibrium state is the crystalline state. The deformation of polymer crystals seems a good place to begin.

It corresponds to the case where polymer molecular backbones are fully aligned. It is therefore the bench-mark against which to judge attempts to maximise stiffness and strength by achieving a high degree of molecular orientation in polymer solids. This topic now has real practical significance, since polymer fibres are being developed, and some indeed are already commercially available, with axial tensile modulus a significant fraction of that of the crystal. The Kevlar fibre (E.I. du Pont de Nemours trademark) - poly(paraphenylene terephthalamide) - has been available for some time with axial tensile modulus $E \sim 125$ GPa, while the crystal axial modulus of this polymer is believed to be only $E_c \sim 190$ GPa. As a result of extensive research by Professor Ward and others, a similar situation has now been reached with highly oriented polyolefines (1).

Experimental and theoretical effort has so far concentrated on the small strain, linear elastic response of polymer crystals. Thus the infinitesimal strain measure has been used, Eq (3), and the phenomenological framework has been that of anisotropic linear elasticity.

If stress and strain tensors $\bar{\sigma}$, $\bar{\epsilon}$ are expressed as column matrices σ_p , ϵ_q in the usual contracted notation ($p, q = 1 \dots 6$), they are then linearly related through the crystal stiffness matrix C_{pq}

$$\sigma_p = C_{pq} \epsilon_q \quad (4)$$

The assumption of elastic behaviour means we take C_{pq} to be a time-independent, symmetric matrix, with certain restrictions on the relative magnitudes of its elements to ensure the energy of deformation is positive-definite (2). The assumption of Neuman's Principle (2) means that C_{pq} must have at least the symmetry of the crystal structure. On this basis, all "a priori" assumptions are embodied in Eq (4), and it provides the phenomenological framework for expressing both experimental results and theoretical predictions.

I know of no polymer crystal for which the full matrix C_{pq} has yet been measured experimentally. Work has focused on measuring and interpreting the tensile moduli E_c , in particular the tensile modulus $E_{c||}$ parallel to the molecular axes.

The measurement of moduli of polymer crystals has proved a difficult task in itself. The small size of the crystals as they normally occur (major dimension $\sim 1 \mu\text{m}$) means they cannot be tested directly. A dramatic recent development, however, has been the successful preparation of macroscopic single crystals of polydiacetylenes by solid state polymerisation. These crystals can be grown as needles several centimetres in length, with molecular axes aligned along the axes of the needles, and it has been possible to

carry out tensile tests to determine $E_{c\parallel}$ directly (3). A typical axial tensile stress-strain curve obtained on one of these needles is shown in Figure 2. It is interesting to note that the needles were found to show no hysteresis or creep (3), and the curvature evident in Figure 2 is the manifestation of non-linear elasticity.

To be able to carry out mechanical tests on polymer crystals directly in this manner is highly unusual. The great majority of measurements of E for polymer crystals have been made using one of three indirect methods.

- (1) Wide-Angle X-ray Diffraction (WAXD)
- (2) Raman Spectroscopy (RS)
- (3) Inelastic Neutron Scattering Spectroscopy (INSS)

The WAXD method was pioneered by Dulmage and Contois (4) and exploited extensively by Sakurada and co-workers (5). It relies on the X-ray measurement of changes in lattice spacing in stressed specimens. In the spectroscopic methods RS and INSS, E_c is found from the velocity of sound v_s in crystals, determined from the frequency ν and wavelength λ of longitudinal acoustic waves in the lattice:

$$\frac{E_c}{\rho_c} = v_s^2 = \nu^2 \lambda^2 \quad (5)$$

where ρ_c is the crystal density. The RS method was pioneered by Shimanouchi and co-workers, who in fact obtained the first estimate of $E_{c\parallel}$ for a polymer by inferring the case of polyethylene from results obtained with n-alkanes (6).

By these means, $E_{c\parallel}$ has now been measured for many polymers. Values for 15 polymers were given in their 1971 review by Holliday and White (7), and others have been added since. Not surprisingly, perhaps, E_c for other crystal directions has received much less attention, but values are now available for several polymers.

A selection of those measured values of E_c for which theoretical derivations are also available in the literature are plotted in Figure 3, as $E_c(\text{exp})$ and $E_c(\text{theo})$ respectively. A pattern is discernible. The highest modulus is obtained when the strain energy density absorbed in C-C bond stretching is maximised: among the cases shown, $E_c(c \text{ axis})$ for polyethylene (PE). E_c is reduced by helicity of the chain - allowing C-C bond rotation to contribute to E_c - (e.g. PTFE, PP PEO); by side-groups - causing reduction of strain-energy density (e.g. PDA₁ and PDA₂); or by application of stress normal to the chain axis (e.g. $E_c(a \text{ axis})$ for PE).

As can also be seen from Figure 3, there is very reasonable agreement between measured values of E_c and values that have been predicted theoretically. The predictions were all based on more or less detailed hypotheses concerning the interatomic potentials, with force constants of the chemical bonds obtained from spectroscopy. The free energy of deformation W was calculated for the unit cell under a given strain, and minimised to find the various atomic equilibrium displacements. The equilibrium values of W under imposed strains then gave C_{pq} :

$$C_{pq} = \frac{\partial \sigma_p}{\partial \epsilon_q} = \frac{\partial^2 W}{\partial \epsilon_q \partial \epsilon_p} \quad (6)$$

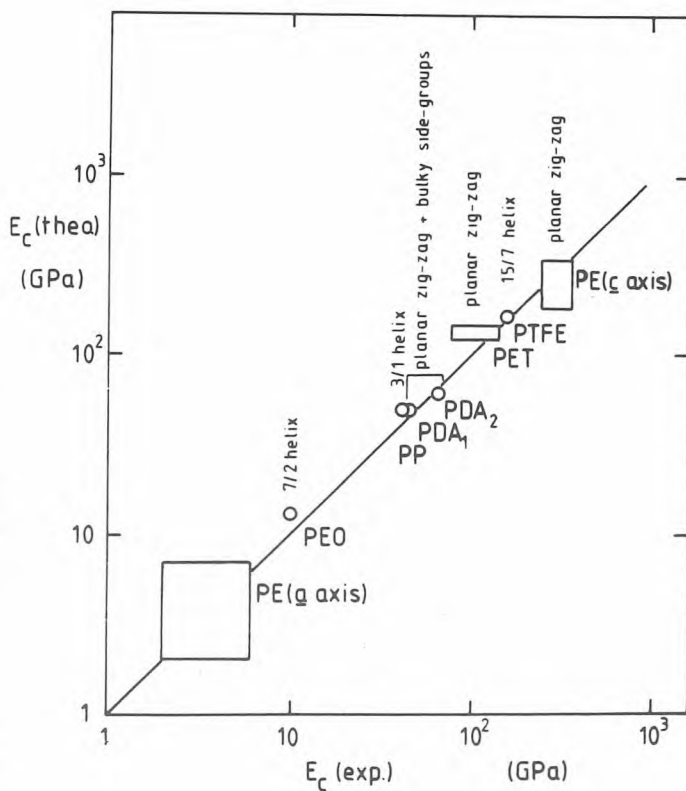


Figure 3 Collection of values of polymer crystal tensile moduli: theoretical E_c (theo) versus experimental E_c (exp). Rectangular boxes indicate the range of literature values.

Key: PE polyethylene; PEO poly(ethylene oxide); PP polypropylene; PDA₁, PDA₂ two substituted polydiacetylenes; PET poly(ethylene terephthalate); PTFE polytetrafluoroethylene.

Early calculations of this type considered only C-C stretching and C-C-C angle opening and therefore could yield only $E_{C||}$ (8). More recent refinements have included many more intra- and intermolecular interactions, and have yielded the entire C_{pq} matrix. This more complete analysis is exemplified by the work of Tashiro, Kobayashi and Tadokoro (9) for polyethylene and atactic poly(vinyl alcohol).

It would seem that the major features of measured crystal elastic constants can now be understood without difficulty in terms of known interatomic interactions. Discrepancies remain, but we can anticipate that these will be steadily eroded by refinements in knowledge of atomic arrangements within polymer crystals, and of the relevant interatomic potentials.

Elasticity of Rubbers

Let us turn now to the only other class of solid polymers where the structure can be assumed to be in a state of equilibrium: cross-linked amorphous polymers at temperatures above T_g , where they exhibit rubber elastic behaviour. In practice, of course, rubbery polymers are not perfectly elastic. Viscoelastic effects such as creep and stress relaxation occur. Nevertheless, given an adequate degree of crosslinking, it is reasonable to assume that a genuine equilibrium elastic response does exist for these materials under load, even though it may be impractical to reach it within the time-scale of a particular experiment. On this understanding, we can discuss the elastic response of rubbers.

To accommodate the very large deformations of which rubbers are capable, it is customary to express experimental data in a form which is not restricted to small deformations. Thus Eq (2) is preferred to Eq (3) as a definition of strain. The constitutive relation is assumed "a priori" to exhibit both elasticity and isotropy. The assumption of elasticity means we can postulate the existence of a unique free energy of deformation W , while the assumption of isotropy means that W is invariant under all possible symmetry operations.

A valid means of expressing the last point is to allow W to depend on strain only through three independent invariants of the finite strain tensor $\underline{\underline{E}}$. This type of approach was pioneered by Rivlin (10). He in fact used invariants of the closely related tensor (c.f. Eq (2)) $\underline{\underline{C}}$, where

$$\underline{\underline{C}} = \underline{\underline{E}}^T \underline{\underline{E}} = 2\underline{\underline{E}} + \underline{\underline{I}} \quad (7)$$

The invariants chosen were the three coefficients in the characteristic equation of this tensor. In terms of the principal extension ratios $\lambda_1, \lambda_2, \lambda_3$ they are given by

$$\begin{aligned} I_1 &= \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \\ I_2 &= \lambda_1^2 \lambda_2^2 + \lambda_2^2 \lambda_3^2 + \lambda_3^2 \lambda_1^2 \\ I_3 &= \lambda_1^2 \lambda_2^2 \lambda_3^2 \end{aligned} \quad (8)$$

In practice, rubbers are relatively incompressible compared to their compliance in other modes of deformation. The volume, therefore, can be assumed

approximately constant and we deduce

$$W = W(I_1, I_2), \quad I_3 = 1 \quad (9)$$

From the free energy function, nominal stresses are found by differentiation with respect to λ_1 . Because, however, we have used the assumption of incompressibility, the stresses can be found from W only to within an unknown hydrostatic stress. We therefore derive stress differences. For example, the difference between principal true stresses $\lambda_1 \sigma_1, \lambda_2 \sigma_2$ (σ_1 are principal nominal stresses) is given by (10)

$$\lambda_1 \sigma_1 - \lambda_2 \sigma_2 = 2(\lambda_1^2 - \lambda_2^2) \left[\frac{\partial W}{\partial I_1} + \lambda_3^2 \frac{\partial W}{\partial I_2} \right] \quad (10)$$

At this point we have exhausted all the simplifying consequences of "a priori" assumptions. To gain further understanding we must invoke theories of molecular deformation, to obtain restrictions on the form of the function $W(I_1, I_2)$.

Such a theory is available in the form of the well-known statistical theory of rubber elasticity, based on the entropy elasticity of a network of chains obeying Gaussian statistics. In its simplest form, it states that at absolute temperature T

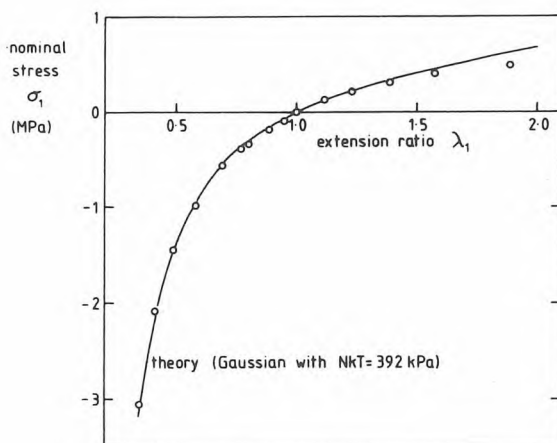
$$W = \frac{1}{2} G (I_1 - 3), \quad G = NkT \quad (11)$$

where G is the shear modulus, k is the Boltzmann constant and N the number of sub-chains (between crosslinks) per unit volume. The predictions of this theory can be fitted well to experimental data for extension ratios not too far from unity. For uniaxial extension or compression in the λ_1 direction, $\lambda_2 = \lambda_3 = \lambda_1^{-1/2}$ since $I_3 = 1$, and Eqs (10) and (11) together yield the following expression for the nominal stress

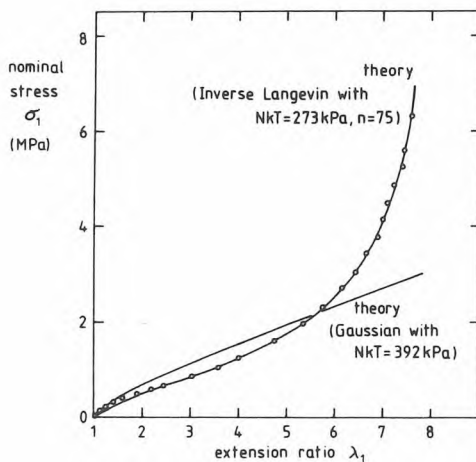
$$\sigma_1 = NkT \left(\lambda_1 - \frac{1}{\lambda_1^2} \right) \quad (12)$$

Eq (12) agrees well with experimental data obtained in compression over a wide range $\lambda_1 = 1 - 0.2$, but in extension it provides a tolerable fit to data over only a narrower range $\lambda_1 = 1 - 1.3$. At very large extensions, the theory fails completely. Typical results from the work of the late Professor Treloar (11) are shown in Figure 4a,b. Major departures from the predictions of the Gaussian statistical theory have also been seen in vulcanised natural rubber under biaxial states of stress (11). It would appear that Gaussian theory is a poor description of the deformation of rubbers in general.

As yet, however, no significant improvement on the Gaussian theory has been found in this respect, that is expressed in the form of Eq (9). Studies have been made of the dependence of W on I_1 and I_2 , but have been of a purely empirical nature. Thus, assuming W to be a continuous function of I_1 and I_2 , we may always express W as an infinite polynomial in these invariants:



(a)



(b)

Figure 4 Stress-strain curves for cross-linked natural rubber in uniaxial tension or compression. Solid lines show fitted curves according to the "Gaussian" or "Inverse Langevin" formulations of the statistical theory of rubber elasticity. Data points from Treloar (11).

$$W = \sum_{r,s=0}^{\infty} C_{rs} [I_1 - 3]^r [I_2 - 3]^s \quad (13)$$

where $C_{00} = 0$. When Eq (13) is expanded in increasing powers of λ_i , it is clear that Eqs (11) correspond to taking the first term only, if we identify $NkT/2$ with C_{10} . Naturally, greater accuracy is obtained by including more terms. For example, the free energy function suggested by Mooney, which provides an excellent fit to stress-strain data in uniaxial extension over the wider range $\lambda_1 = 1 - 3$, corresponds to taking two terms.

$$W = C_{10} [I_1 - 3] + C_{01} [I_2 - 3] \quad (14)$$

To obtain an improved fit to stress-strain data over a wider range of stress states, uniaxial and biaxial, it is necessary to employ yet more higher order terms in the polynomial. For example, Rivlin and Saunders (12) subjected a sheet of natural rubber vulcanizate to biaxial extensions in which I_1 and I_2 were varied systematically. Then, from the measured stresses (e.g. Eq (10)) $\partial W / \partial I_1$ and $\partial W / \partial I_2$ were determined separately. In this way they showed that W took the form

$$W = C_{10} [I_1 - 3] + f(I_2 - 3) \quad (15)$$

where f is a (decreasing) function of $I_2 - 3$. Since the work of Rivlin and Saunders, however, other biaxial test results have suggested that even Eq (15) is not always adequate. This approach no longer appears to have the promise that was once thought.

In recent years, a more profitable expression of the phenomenological framework for rubbers has come to the fore. The same "a priori" assumptions are made, but the isotropy requirement is now expressed directly in terms of principal extension ratios, thus

$$W = W(\lambda_1, \lambda_2, \lambda_3) \quad (16)$$

where W is understood to be a symmetric function of its arguments. Work by Treloar and Riding (13) illustrates the potential of this approach. They applied to biaxial stress states the "inverse Langevin" non-Gaussian statistical molecular theory proposed by Kuhn and Grun and previously applied to uniaxial extension. The predictions of this theory can be deduced accurately only by numerical integration, but it leads to results equivalent to expressing W as a symmetric function of λ_i , exactly in the manner of Eq (16). The great advantage of this non-Gaussian theory is that it accounts well for the overall form of stress-strain curves, including the upturn in stress at high extensions, arising from the finite extensibility of the network (ignored in the Gaussian theory). In the case of uniaxial extension, it predicts (in the approximate analytical form due to James and Guth)

$$\sigma_1 = \frac{1}{2} NkTn^{\frac{1}{2}} \left[L^{-1}(\lambda_1 n^{-\frac{1}{2}}) - \lambda_1^{-\frac{3}{2}} L^{-1}(\lambda_1^{-\frac{1}{2}} n^{-\frac{1}{2}}) \right] \quad (17)$$

where L^{-1} indicates the inverse Langevin function ($L(y) = \coth y - \frac{1}{y}$) and n is the number of statistical segments between crosslinks. Figure 4(b) shows that with a suitable choice of n and N it can replicate extremely well the shape of the stress-strain curve at large extensions. Note, however,

that it is not possible to fit simultaneously both high λ_1 and low λ_1 portions of the curve. Similarly, in the more recent application of the theory to biaxial stress states by Treloar and Riding, it was found to be highly successful in predicting the overall shape of stress-strain curves (13). But again it was not possible to fit quantitatively an entire curve with the same values of adjustable parameters n and N .

A better fit to experimental stress-extension data can be obtained if necessary by empirical application of symmetric functions W of λ_1 , λ_2 and λ_3 . Particularly successful has been the form of function suggested by Ogden (14).

$$W = \sum_j \frac{\mu_j}{\alpha_j} (\lambda_1^{\alpha_j} + \lambda_2^{\alpha_j} + \lambda_3^{\alpha_j} - 3) \quad (18)$$

There is no restriction here on the values of the exponents α_j . Indeed, the proposition that W can be expressed directly in terms of λ_1^2 (eq (16)) rests on the recognition that W is not restricted to functions of even powers of λ_i , in contrast to the earlier Rivlin formulation. It seems highly likely that the new approach will prove the more fruitful in the search for improved molecular theories of the deformation of rubbers.

That there is a need for further development of the molecular theories is demonstrated by more than just the imperfect fit of predicted and experimental stress-strain curves. It has long been known that there is an internal energy contribution to the free energy of deformation, whereas the statistical theory is cast in terms of configurational entropy alone. The precise magnitude of the internal energy contribution is in dispute, for the reason that its measurement is sensitive to error from various sources. The problems involved, and progress up to a few years ago, were reviewed by Price (15). Further refinements to the molecular theory of rubber elasticity must accommodate the internal energy contribution to W , and also improve the fit of stress-strain predictions to experiment.

My discussion of rubbers has assumed that they exist in an equilibrium amorphous state. For most rubbers at small to moderate extensions this assumption is valid. It is well-known, however, that some rubbers show crystallisation under large strains. For example, the vulcanised natural rubber specimen of Figure 4 was found to crystallise beyond $\lambda_1 \sim 5$. This is a consequence of increasing alignment of network sub-chains causing an increase in melting-point (through reduction in entropy of fusion) and an increase in nucleation density. Crystallisation can be presumed to cause distortion of the stress-strain curve, and so leads to doubt when comparing theory and experiment at large deformations. The major up-turn in stress, however, is without doubt primarily due to finite network extensibility, as it is clearly apparent even in rubbers which are known not to crystallise (11).

PART II: NON-EQUILIBRIUM STRUCTURES

Semicrystalline Polymers and Amorphous Polymers at $T \leq T_g$ Linear Viscoelasticity

I want to move on now to the more usual case of non-equilibrium polymer structures. Here great care is needed in design of experiments, to ensure that measurements refer to the same structural state as was intended.

Let us consider small deformations of a polymer behaving as an isotropic linear viscoelastic solid. The constitutive relation then exhibits both linearity and isotropy. It follows that the infinitesimal strain tensor at time t , $\underline{\epsilon}(t)$, is related to the history of the stress tensor $\underline{\sigma}(u)$ through the Boltzmann Superposition Principal (BSP) in the form

$$\underline{\epsilon}(t) = \frac{1}{3} \int_{-\infty}^t B(t-u) \dot{\underline{\sigma}}_m du + \frac{1}{2} \int_{-\infty}^t J(t-u) \dot{\underline{\sigma}}' du \quad (19)$$

where $\underline{\sigma}' = \underline{\sigma} - \frac{1}{3} \underline{\sigma}_m$, $\underline{\sigma}_m = \frac{1}{3} \text{tr} \underline{\sigma}$

which are the deviatoric stress and mean stress respectively. B and J are the creep compressibility and shear creep compliance respectively. When written in this way, Eq (19) shows that viscoelastic effects such as creep have two components arising from time-dependences of the two functions B and J respectively.

There have not been many studies of creep in polymers where B and J were measured separately. A notable exception, however, is the recent work by Read and Dean (16) on isotropic, glassy poly(methyl methacrylate) (PMMA). Their experiments consisted of tensile creep and oscillatory tests, in which both the tensile creep compliance D and the lateral contraction ratio ν were measured. The BSP was invoked to deduce creep data from dynamic responses. As can be shown from Eq (19)

$$D = \frac{B}{9} + \frac{J}{3}, \quad \nu = \frac{\frac{3}{2}J - B}{3J - B} \quad (20)$$

and hence B and J were obtained. The time-dependences of both J and B are shown in Figure 5 for the β -relaxation of PMMA at 23°C. It is clear that the relaxation is manifest in both quantities, with the centre of relaxation located in the same region of the time-scale (~ 0.1 s in this case). Thus two common assumptions about the creep deformation of polymers are seen to be false. The contribution of compressibility cannot be ignored, neither can its time-dependence.

The creep process shown in Figure 5 is only one of a family of relaxations exhibited by PMMA in different regions of the time-scale. Combining data from several sources, I have estimated the form of the entire curve of $\tan \delta$ versus frequency (for oscillatory loading in shear) for this polymer at 20°C. This is shown in Figure 6. The pattern is typical of what would be obtained with other polymers. One sees a series of relaxation processes. The frequencies at which they appear tend to decrease with increasing physical size of the group of atoms which is relaxing.

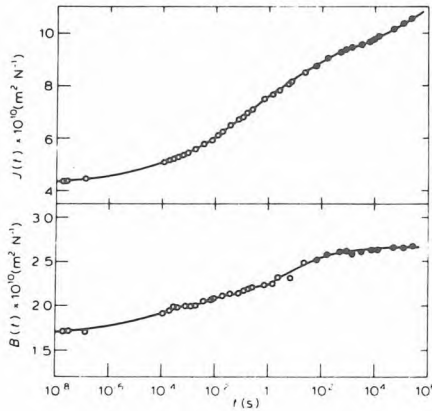


Figure 5 Small strain shear creep compliance $J(t)$ and creep compressibility $B(t)$ of PMMA at 23°C. Reproduced from Read and Dean (16).

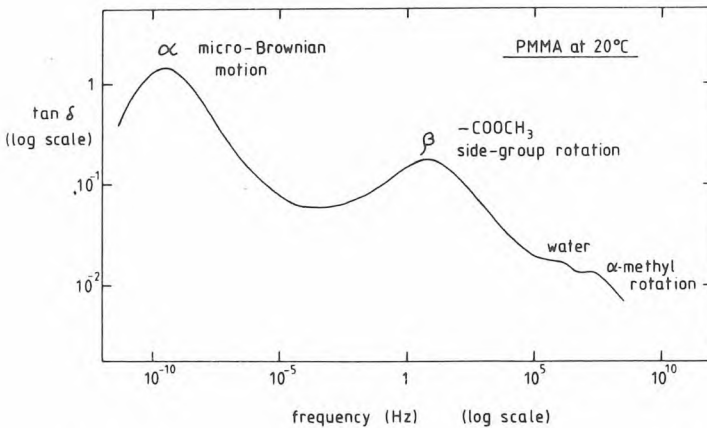


Figure 6 Estimated plot of $\tan \delta$ versus frequency for shear deformation of PMMA at 20°C.

Such data have been widely used to characterise relaxation processes in polymers. This field was very active in the two decades 1950-1970 during and following the first production of most of the now common synthetic polymers. In fact, much of what is known today of polymer relaxation behaviour was reviewed as early as 20 years ago in the book by McCrum, Read and Williams (17). Yet progress has been painfully slow. There is still today very little precision in our knowledge of molecular motions involved. The major hurdle has been uncertainty of microstructure at the molecular level. The environment of a relaxing molecular segment in most cases is simply not known.

Several routes have been taken in seeking the physical origins of relaxations in polymers. I will mention here just three and illustrate them with reference to polyethylene. This exhibits three processes α , β , γ , in order of decreasing relaxation time (or temperature).

(i) Chemical modification. This approach has made two pivotal contributions for polyethylene. Kline, Sauer and Woodward (18) measured mechanical damping in samples of polyethylene with varying degrees of side-branching, expressed as the number of methyl groups per 1000 carbon atoms (since each branch is capped by a methyl group). Results are shown in Figure 7. They suggest strongly that the β -relaxation is associated with motion of the branch-points. In another classic study during the 50's, Schneider and Wolf (19) showed by chlorinating polyethylenes and so destroying crystallinity that the α -process depends for its existence on the presence of crystals.

(ii) Systematic variation of crystallinity. Gray and McCrum (20) examined the dependence of the γ -relaxation magnitude on the volume fraction degree of crystallinity, which they varied by means of varying thermal treatment, see Figure 8. The three measures of relaxation magnitude yielded by the torsion pendulum experiment - the maxima in J'' , Δ (logarithmic decrement) and G'' - showed contradictory trends. The mechanics of isotropic two-phase solids tells us, however, that of the three Δ is most likely to be linear in the degree of crystallinity (20). Figure 9 then shows conclusively that the γ -relaxation occurs predominantly in the amorphous fraction.

(iii) Preparation of model structures. McCrum and I prepared drawn and annealed sheets of linear polyethylene (LPE) with a simple, pseudo-single-crystal texture (21). Lattice vectors a , b , c were well aligned almost in the three principal directions of the sheets, but we managed to vary the preferred orientation of lamellar crystal surfaces (Figure 9). The anisotropy of tensile creep in the α -region then led us to conclude unambiguously that the α -process occurs by interlamellar shear (Figure 10). This view concurred with that of Ward and co-workers (22) using a similar approach but with different orientation procedures.

These and other pieces of the jigsaw tell us for polyethylene: the γ -process involves local mode motion of amorphous CH_2 sequences, several carbon atoms long; the β -process behaves as if the glass transition of regions of the chain around branch-points; the α -process occurs by shearing of the interlamellar amorphous layers, probably triggered by chain rotation and displacement in the crystals.

I want to turn now to the strong influence that temperature has on viscoelastic processes. It has long been known that at temperatures in the region above T_g , changing temperature has the primary effect of uniformly expanding or contracting the time-scale of viscoelastic response functions. So when these functions are plotted against a logarithmic time-base, they

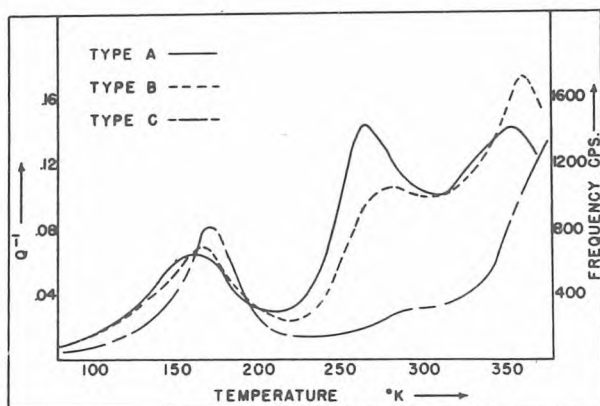


Figure 7 Mechanical damping in polyethylene, showing the effects of varying the degree of side-branching. Types A, B and C refer to polyethylenes with 32, 16 and 1 methyl groups per 1000 carbon atoms respectively. The central peak (β relaxation) increases strongly with increasing branching. Reproduced from Kline, Sauer and Woodward (18).

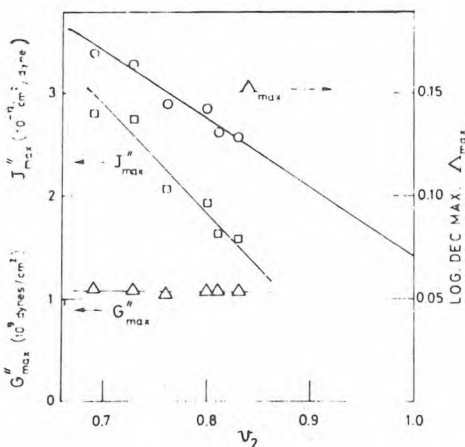


Figure 8 Magnitude of the γ -relaxation in linear polyethylene: variation with volume fraction degree of crystallinity v_2 . Three measures of relaxation magnitude are shown. Reproduction from Gray and McCrum (20).

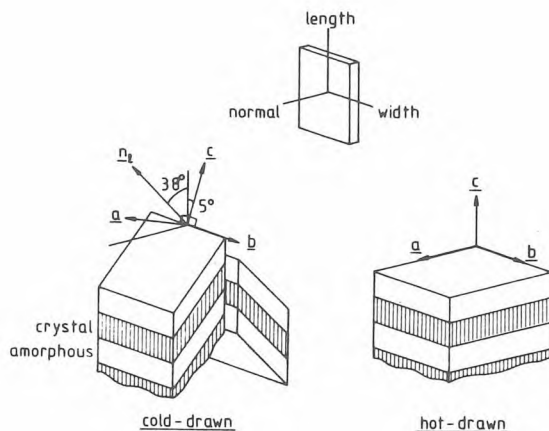


Figure 9 Schematic diagram of crystallographic and lamellar orientation in oriented sheets of linear polyethylene, prepared by drawing at constant width, followed by annealing (21).

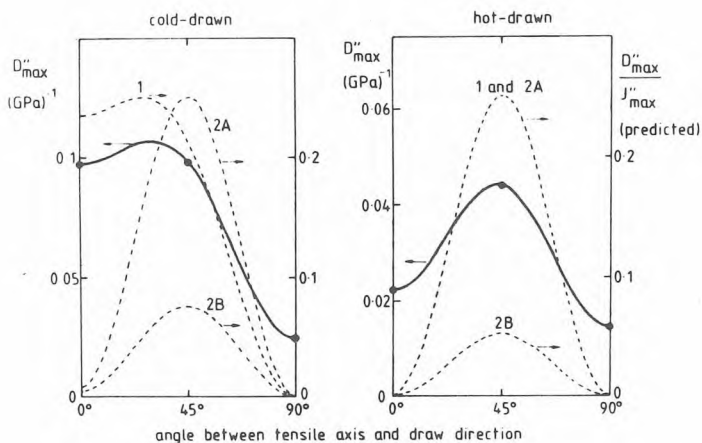


Figure 10 Anisotropy of the α -relaxation in linear polyethylene with biaxial orientation as shown in Figure 9 (21). Dashed lines show anisotropy expected in each case if there were no spread in lamellar orientation, according to three hypotheses for the α -relaxation process: interlamellar shear (1), (hk0) intracrystalline shear (2A), (h00) intracrystalline shear (2B).

shift without change of shape to left or right with rise or fall in temperature. From the many reports of this in the literature, I have chosen Plazek's shear creep data for a polystyrene fraction ($M\eta = 46900$) to illustrate the point (23), see Figure 11. T_g for this fraction was 98°C .

The quantity plotted here is the reduced shear compliance J_p , obtained from J and the density ρ , absolute temperature T and their values ρ_0 , T_0 at a reference temperature (in this case 100°C)

$$J_p(t) = \left(\frac{\rho T}{\rho_0 T_0} \right) J(t) \quad (21)$$

The compliance is plotted in this way to allow for a secondary effect of temperature. The limiting compliance on the rubber plateau (second inflection in Figure 11) is proportional to $(\rho T)^{-1}$ (see Eq (11)). The compliance in the short time (glassy) limit also varies with temperature, but the effect of this here is negligible (17). Plazek then removed the contribution of viscous flow by re-plotting as the recoverable component of compliance. Finally he shifted the curves horizontally to obtain superposition, generating the so-called "Master Curve" for $T_0 = 100^\circ\text{C}$, Figure 12. The point to note from this composite curve is the extraordinary accuracy with which the separate curves superpose. If the breadth of the time-scale of response is ascribed to a distribution of retardation times, then all retardation times must be modified by the same factor a_T on change of temperature.

The shift factors derived from this data are plotted in Figure 13. The points agree well with the WLF equation (24), drawn as the full line in this Figure,

$$\ln a_T = \frac{-C_1(T - T_0)}{C_2 + T - T_0} \quad (22)$$

where C_1 , C_2 are constants. This equation has been probably the most influential in the history of polymer deformation studies. It applies to very many polymers (25), and indeed to other glass-forming liquids (24), at temperatures in the range above T_g . Its physical basis is the attribution of changes in relaxation times solely to changes in free volume (24).

Although the data in Figure 11 were gathered at temperatures not far above T_g , (as determined dilatometrically) careful experiment design by Plazek ensured that the polystyrene was in structural equilibrium throughout each creep test. At lower temperatures this is impractical, and the situation is far more confused. We return to this question shortly.

In the regions of secondary relaxations, evidence for accurate time-temperature superposition is much less convincing. On the contrary, evidence is mounting that here the relaxation spectra change shape on change of temperature. A good example is from the work of Read (26) on the β -process in PMMA. The normalised tensile relaxation spectrum ϕ_T was estimated at several temperatures, from dynamic tests covering a wide span of frequency. The spectrum was found to show pronounced narrowing with increasing temperature, Figure 14. Now, in terms of the Arrhenius equation, a relaxation time τ_i associated with an activation enthalpy ΔH_i is given by

$$\ln \tau_i = \ln \tau_{0i} + \Delta H_i / RT \quad (23)$$

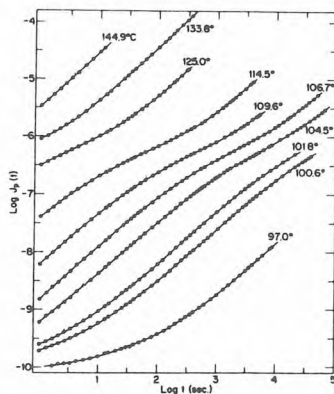


Figure 11 Small strain shear creep of a polystyrene fraction in the region of T_g . J_p is the reduced shear compliance (see text). Reproduced from Plazek (23).

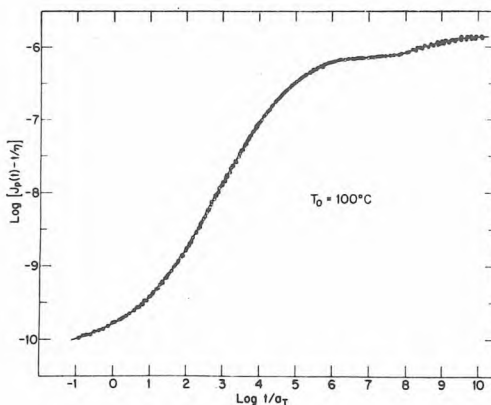


Figure 12 "Master curve" for the recoverable shear compliance of polystyrene, obtained by horizontal shifting of creep curves shown in Figure 11. Reproduced from Plazek (23).

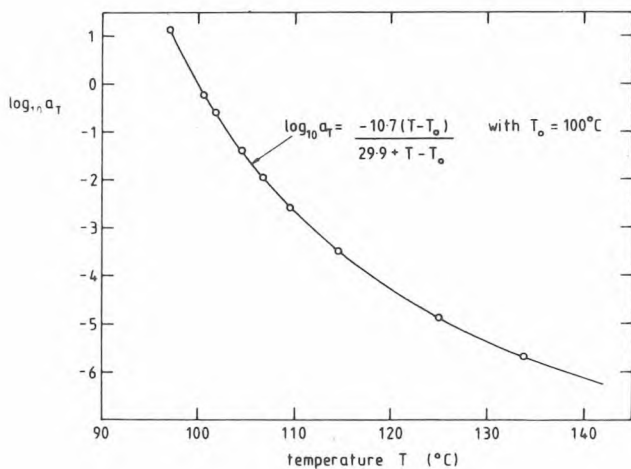


Figure 13 Shift factors used in generating the "master curve" of Figure 12, showing agreement with the WLF equation. Re-drawn from Plazek (23).

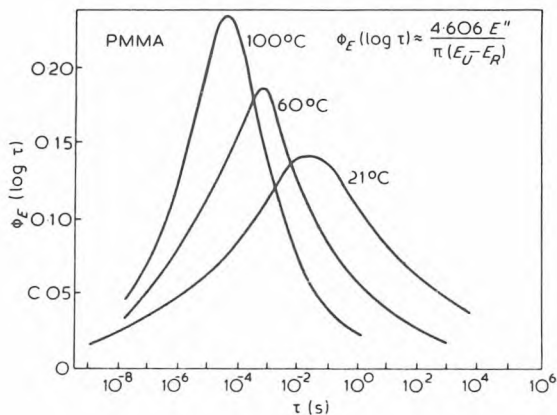


Figure 14 Normalised tensile relaxation spectra estimated for the β -process in PMMA, showing narrowing with increasing temperature. Reproduced from Read (26).

The narrowing of ϕ_E that we see in Figure 14 is thus indicative of longer relaxation times τ_i having higher activation energies ΔH_i . The same effect was recently confirmed and accurately quantified by McCrum (27) for the α and β -processes in polypropylene. Note that it challenges a fundamental tenet of polymer viscoelastic analysis until now: that relaxation spectra arise from distributions of τ_0 , with only a single ΔH applying to each process. It is certain to cause a minor revolution in our thinking.

We have acknowledged already the non-equilibrium structural state in which polymers usually exist. Now it happens that the linear viscoelastic response functions are particularly sensitive to structural state. Consequently, when structural evolution takes place as is to be expected, there are pronounced time-dependent changes in these functions. There have been scattered references to such effects since the earliest days of the subject, and they were the subject of a careful study long ago by Kovacs, Stratton and Ferry (28). Nevertheless, the instability of polymer viscoelastic properties was substantially overlooked, until the publication by Struik of the results of a major programme of research devoted to this problem (29). He coined the term "physical ageing", to describe the thermoreversible effects observed and to distinguish them from effects due to chemical degradation.

I have chosen a single graph to illustrate Struik's findings. Figure 15 shows a set of tensile creep curves for amorphous PVC, obtained after isothermal ageing for time t_e at 20°C , following a quench from 90°C . In this polymer $T_g \approx 70^\circ\text{C}$. It is clear that during physical ageing at $T < T_g$ retardation times steadily increase with elapsed time from the moment of the quench. In fact, to a first approximation the creep curves merely shift to the right along the logarithmic time-base without change of shape. In cases such as this, Struik found the shift to correlate well with concurrent changes in volume, and formed the hypothesis that retardation times are determined uniquely by the free volume, even in these non-equilibrium states. This remains the best unifying explanation for events, but its general validity is far from certain. There does exist conflicting evidence, suggesting thermoelastic stresses as the cause of some ageing effects in crystalline polymers (30).

Non-Linear Viscoelasticity

Finally, we arrive at what is perhaps the most challenging facet of polymer deformation: non-linear viscoelasticity. The nonlinear viscoelastic regime begins at strains of at most $\sim 0.5\%$ in semicrystalline polymers and amorphous polymers at $T \leq T_g$. The precise figure depends in part on the resolution of strain measurement. Under these conditions, displacement gradients are so small that the approximation for strain given by Eq (3) can be used, without fear of confusing geometrical non-linearity with genuine non-linearity of the constitutive relation. My comments here will be confined to such cases.

In framing our phenomenological theory we must now jettison the assumption of linearity as well as that of elasticity. Of the three "a priori" assumptions of Figure 1, we are left with just the symmetry of the material. Here I will discuss only isotropic materials. Furthermore, there is not space here to deal with the phenomenological theory for general loading of such a material; a theory due in particular to Green and Rivlin. It is well reviewed in the books by Lockett (31) and by Findley, Lai and Onaran (32). Instead, I will use the rather different approach which Green and I suggested, in which stress histories are expressed as sums of proportional

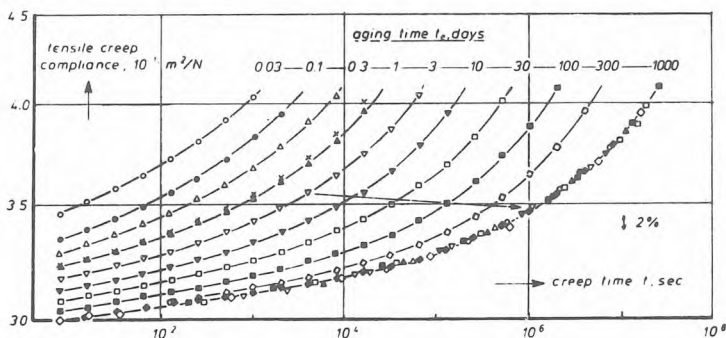


Figure 15 Tensile creep of PVC, initiated at various times t_a following a quench from 90 to 20°C, showing physical ageing. Reproduced from Struik (29).

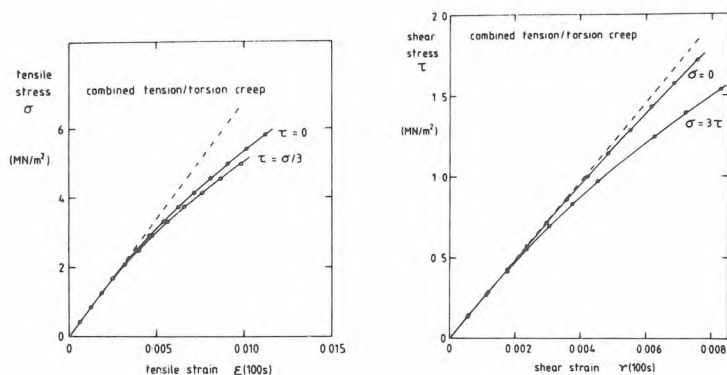


Figure 16 Isochronous stress-strain curves for polypropylene at 65°C obtained from creep in combined tension/torsion (open points), compared with curves obtained in pure tension or pure torsion (filled points).

loading histories (33). In particular, I want to proceed straight to single proportional loading histories, because here some very useful simplifications apply. The beauty of proportional loadings is that they can be expressed in terms of just a single constant stress tensor, say $\underline{\sigma}_0$, and a single scalar function of time, say $f(u)$: the stress history is then given by

$$\underline{\sigma}(u) = \underline{\sigma}_0 f(u) \quad (24)$$

It follows that the strain tensor at time t can always be expressed, for any isotropic material

$$\underline{\varepsilon}(t) = \alpha_0 \underline{I} + \alpha_1 \underline{\sigma}_0 + \alpha_2 \underline{\sigma}_0^2 \quad (25)$$

where α_i are functions of any three independent invariants of $\underline{\sigma}_0$ and are functionals of $f(u)$. Now the available experimental data on non-linear viscoelasticity of polymers is almost entirely confined to cases of plane stress. The in-plane strain is then given in terms of the stress by the even simpler equation (33)

$$\underline{\varepsilon}(t) = \phi_0 \underline{I} + \phi_1 \underline{\sigma}_0 \quad (2D) \quad (26)$$

where we use (2D) to signify that here the tensors have 2 dimensions only. The two response functions ϕ_0 , ϕ_1 depend on the stress time-sequence $f(u)$ (for $-\infty < u < t$) and two invariants of the stress. Following the usual practice in plasticity, we will use the first invariant I_1 of the three dimensional stress and the second invariant I_2' of its deviatoric component:

$$I_1 = \text{tr } \underline{\sigma}_0, \quad I_2' = \frac{1}{2} \text{tr}(\underline{\sigma}_0')^2 \quad (27)$$

These characterise the hydrostatic and deviatoric components of the stress. Now it is interesting to compare Eq (26) with Eq (19) for the linear case. Consider a creep stress history. Then we find they have the same form, with

$$\frac{\phi_0}{I_1} = \frac{B}{9} - \frac{J}{6}, \quad \phi_1 = \frac{J}{2} \quad (28)$$

Thus, in-plane response to plane stress proportional loadings can be described conveniently by simply considering B and J to be generalised compliances, depending on stress through the invariants I_1 , I_2' , and being functionals of $f(u)$.

Note that we have so far made no assumption, other than isotropy, about the nature of the viscoelastic behaviour. The next question is: what form do the non-linearities take in practice, when expressed in this framework? For illustration, I have selected data for isotropic polypropylene in the region of room temperature and above.

I begin with some results from my own study of combined tension/torsion creep of a few years ago. Figure 16 shows isochronous stress-strain curves for shear and tension respectively, obtained from creep tests in pure torsion, pure tension and combined tension/torsion. There are two manifestations of non-linearity (departures from predictions of Eq (19)). First, the isochronous

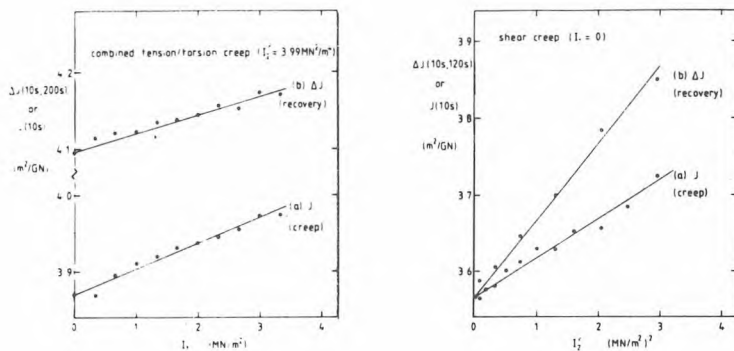


Figure 17 Isochronous shear compliance obtained from creep $J(t)$ or recovery $\Delta J(t-t_R, t_R)$ of polypropylene at 65°C, versus stress invariants I_1 and I_2' .

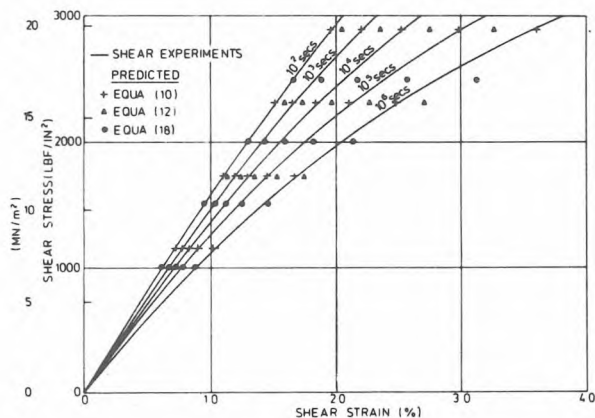


Figure 18 Measured isochronous stress-strain curves for PMMA in shear at 20°C (Full lines), compared with predictions from tension/compression creep response according to various empirical equations. Reproduced from Benham (34). Equation numbers refer to Benham's paper: his Eq (10) corresponds to Eq (29) of the present text.

plots are not linear, always bending towards the strain axis. Second, there is pronounced synergism between tension and shear (shear stress increases tensile creep, tensile stress increases shear creep). Both effects are encompassed by the phenomenological theory. J was found to increase with both I_1 and I_2' , for creep and recovery. Results are shown in Figure 17. By contrast, β was found to be independent of stress over the range covered (33).

I must mention here what seemed to me at the time an extraordinarily successful empirical correlation reported by Benham (34). He found that by combining axial strain ϵ_a and transverse strain ϵ_t for creep in tension or compression under stress σ , say, he could predict the shear strain γ for creep under a shear stress τ

$$\gamma(\tau, t) = \frac{1}{\sqrt{3}} \{ [\epsilon_a(\sigma, t) - \epsilon_t(\sigma, t)] - [\epsilon_a(-\sigma, t) - \epsilon_t(-\sigma, t)] \} \quad (29)$$

where $\tau = \sigma/\sqrt{3}$. I reproduce one of his graphs in Figure 18. Eq (29) corresponds to Benham's equation (10). The prediction is accurate well out into the non-linear region. Intrigued by this, Green and I delved a little and found (33) that in fact Eq (29) results directly from the phenomenological Eq (26), requiring only that the dependence of ϕ_1 on invariants I_1, I_2' has the slightly restricted form

$$\phi_1(I_1, I_2') = \phi_1(0, I_2') + \Delta\phi_1(I_1, I_2') \quad (30)$$

where $\Delta\phi_1$ is an odd function of I_1

$$\Delta\phi_1(I_1, I_2') = -\Delta\phi_1(-I_1, I_2') \quad (31)$$

The effects of varying stress time-sequence $f(u)$ are illustrated well by Turner's measurements of the response of polypropylene at 20°C to complex tensile stress histories (35). Consider the two cases sketched in Figure 19: creep stress doubling at time t_d , and creep recovery at time t_r . In the stress doubling experiment, linear viscoelasticity (Eq (19)) would predict the additional axial tensile strain $\Delta\epsilon_d$ at time t to be

$$\Delta\epsilon_d(t) = \epsilon_c(t-t_d) \quad (32)$$

Figure 20 shows this additional strain measured for two stress levels σ at $t = t_d + 100$ s. The bar marked A shows what was obtained when both stress steps were applied together (i.e. $t_d + 0$). The bar marked B is the prediction based on superposition (i.e. Eq (19)). Note that more additional strain is produced than predicted, $\Delta\epsilon_d(t) > \epsilon_c(t-t_d)$, indicating non-adherence to linear superposition. But note also that the error $\Delta\epsilon_d(t) - \epsilon_c(t-t_d)$ diminishes as t_d increases.

In the creep recovery experiment, linear viscoelasticity would predict the recovery strain $\Delta\epsilon_r$ at time t to be

$$\Delta\epsilon_r(t) = \epsilon_c(t-t_r) \quad (33)$$

Turner used this equation to predict the residual strain during recovery,

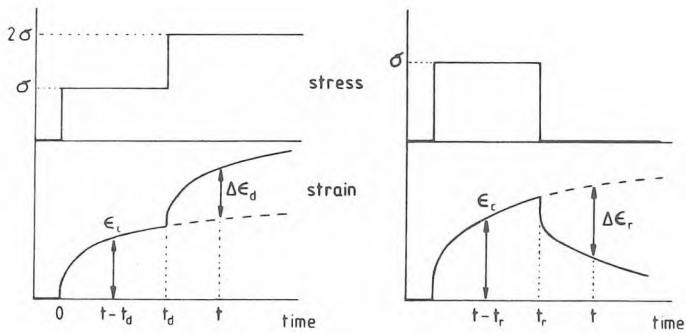


Figure 19 Schematic diagram showing creep stress doubling and creep recovery.

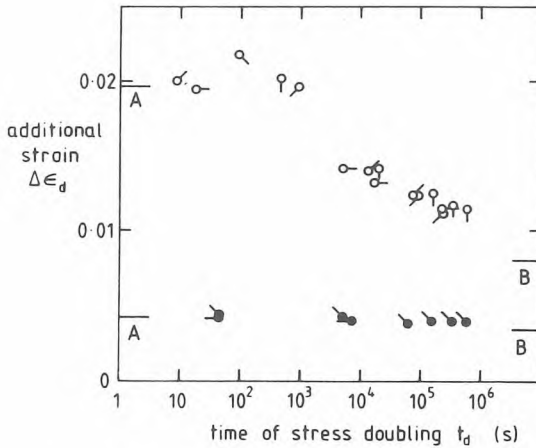


Figure 20 Additional strain measured at time $t = t_d + 100 \text{ s}$ in tensile creep stress doubling experiments on polypropylene at 20°C . For meanings of bars A and B see text. Stresses were $\sigma = 5 \text{ MN/m}^2$ (filled symbols) and $\sigma = 10 \text{ MN/m}^2$ (open symbols). Different symbols refer to different specimens. Re-drawn from Turner (35).

and then made comparisons with measured recovery. Figure 21 shows that soon after unloading, when $t - t_R \leq t_R$, recovery is faster than predicted; $\Delta \epsilon_R(t) > \epsilon_C(t - t_R)$. But near $t - t_R = t_R$ there is a cross-over and from then on recovery is more sluggish than predicted $\Delta \epsilon_R(t) < \epsilon_C(t - t_R)$.

Now the really remarkable feature of these results of Turner is their generality. Not long before Turner's work, Ward and Onat had made a detailed study of creep and recovery in oriented polypropylene fibres, and observed precisely the same effects (36). Over the years since then, many polymers have been studied, with similar results. There is now little doubt that these effects are characteristic of the non-linear viscoelastic behaviour of solid polymers. At the phenomenological level, they can be described in terms of the Green-Rivlin infinite series of multiple integrals, for expressing ϵ as a functional of $\sigma(u)$

$$\begin{aligned} \epsilon(t) = & \int_{-\infty}^t J_1(t-u_1) \frac{d\sigma}{du_1} du_1 + \int_{-\infty}^t \int_{-\infty}^t J_2(t-u_1, t-u_2) \frac{d\sigma}{du_1} \frac{d\sigma}{du_2} du_1 du_2 \\ & + \int_{-\infty}^t \int_{-\infty}^t \int_{-\infty}^t J_3(t-u_1, t-u_2, t-u_3) \frac{d\sigma}{du_1} \frac{d\sigma}{du_2} \frac{d\sigma}{du_3} du_1 du_2 du_3 \\ & + \dots \end{aligned} \quad (34)$$

There have been many suggestions that this series can be truncated at the third term, to within acceptable accuracy (32,37). If this be so, the departures from linear superposition I have mentioned reflect the relative magnitudes of the various kernels since Eq (34) then gives

$$\begin{aligned} \Delta \epsilon_d(t) - \epsilon_C(t - t_d) = & 2J_2(t, t - t_d)\sigma^2 \\ & + 3[J_3(t, t, t - t_d) + J_3(t, t - t_d, t - t_d)]\sigma^3 \end{aligned} \quad (35a)$$

$$\begin{aligned} \Delta \epsilon_R(t) - \epsilon_C(t - t_R) = & 2[J_2(t, t - t_R) - J_2(t - t_R, t - t_R)]\sigma^2 \\ & + 3[J_3(t, t, t - t_R) - J_3(t, t - t_R, t - t_R)]\sigma^3 \end{aligned} \quad (35b)$$

There is at present no mechanistic theory to account for these intriguing non-linearities. But evidence is accumulating that they are linked to the non-equilibrium nature of the structural state. Since the structure is in a state of continuous evolution, it is to be expected that application of a finite stress will affect the rate, and perhaps even the course, of the evolution of structure and properties. The way in which this occurs is conveniently studied by linear perturbation experiments. The linear response is measured to small perturbations in stress, superimposed on a large stress. To avoid ambiguity in interpretation, the main stress and perturbing stress should be applied in noninteracting modes (e.g. tension and shear) (38).

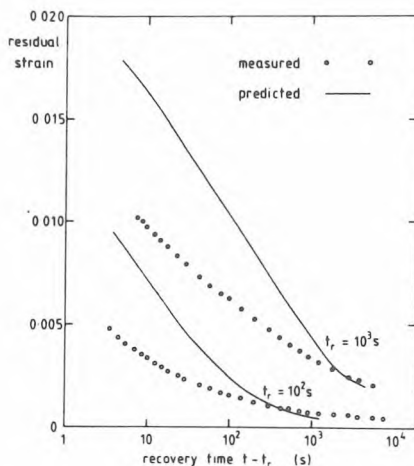
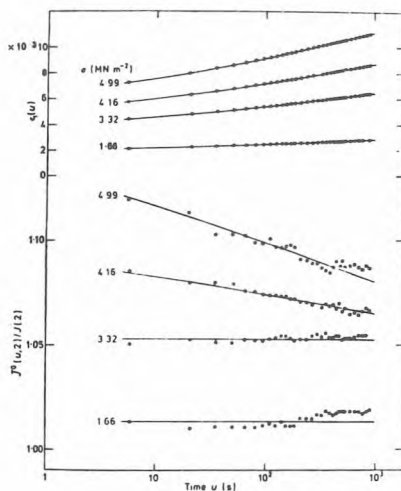


Figure 21 Residual strain measured during tensile creep recovery of polypropylene at 20°C, with creep stress $\sigma = 20 \text{ MN/m}^2$. Full lines show predictions based on linear viscoelasticity. Re-drawn from Turner (35).



(a)

Figure 22 Small strain, 2s isochronous shear compliance obtained in linear perturbation experiments superimposed on (a) tensile creep and (b) recovery ($v_1 \equiv t_r = 930 \text{ s}$) of polypropylene at 65°C. u is time elapsed since start of tensile creep. Compliance is normalised with respect to its value at the start of tensile creep. Also shown is the concurrent axial tensile strain ϵ_2 . Reproduced from Buckley (38).

Figure 22 shows some typical results from my experiments of this type (large tension + small shear) carried out on polypropylene at 65°C (38). Figure 22 shows the 2 second isochronal shear compliance, normalized with respect to its initial value, repeatedly probed during tensile creep and recovery. Note the pattern: when the tensile stress changes, J jumps to a new value (higher than its initial value) and then decays. More recently, several groups have reported similar findings. Of particular note is the observation by Smith and others (39) that application of even a large compressive strain produces similar effects.

The clear implication from all these results is that a change of stress (even removal of a tensile stress or addition of a compressive stress) causes some "rejuvenation" of the structural state, followed by renewed physical ageing. This was Struik's conclusion, based on his observation of interactions between stress and physical ageing (29,40). However, there is inadequate evidence at present to go further and support Struik's contention that mechanical relaxation times are determined solely by free volume. An alternative view is more consistent with the data for polypropylene, that the evolution of compliance reflects the evolution of microstress within the heterogeneous solid (38). I suspect that neither is completely correct. A fully convincing physical picture of events still evades us.

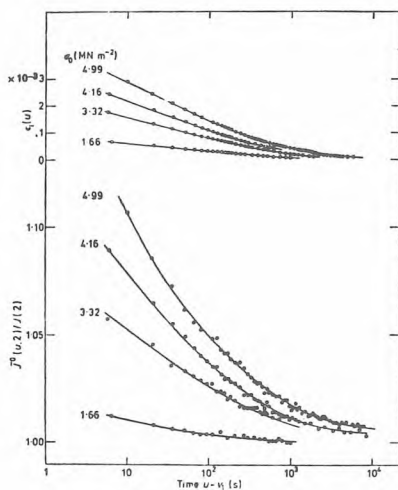
Conclusions

This has been a brief survey of a large subject. Many important topics have been squeezed out. I have chosen to discuss only the four major themes which seem to me to lie at the core of the subject.

In closing, I want to underline two conclusions which can be drawn from this review. Firstly, progress has come only through the combined inputs of researchers with quite different perspectives. The peculiar character of polymer deformation - often involving large strains, often non-linear, often inelastic, often anisotropic - has presented researchers with formidable problems. It has required considerable development of phenomenological theory, alongside mechanistic physics. To make further progress, we must expect to have to exploit both lines of attack together. We cannot afford the luxury of treating them as alternatives.

The second conclusion is that the evolving, non-equilibrium, nature of most polymer structures plays a critical role in determining their properties. A finite stress, applied to such a structure, contributes to its thermo-mechanical history and hence influences the course of its evolution, in addition to causing a strain directly. Unravelling such complexity is going to be difficult. Perhaps progress will come from the application of non-linear irreversible thermodynamics to polymer structures, as suggested by Lindenmeyer (41).

Clearly, there are exciting challenges ahead.



(b)

Figure 22 (continued)

Acknowledgements

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Butterworth Scientific Ltd: Figures 5 and 14.

Elsevier Science Publishers BV: Figure 15.

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BRITISH SOCIETY OF RHEOLOGY

BALANCE SHEET as at 30th JUNE 1986

<u>ASSETS</u>	<u>1986</u>	<u>1985</u>	
<u>Fixed Assets</u>			
Microcomputer at cost	2174	2174	
Less: Depreciation to date	<u>1738</u>	<u>1302</u>	872
<u>Investments</u>			
Redbridge 9 3/4% Bond	-	2500	
Trustee Savings Account	<u>-</u>	<u>2409</u>	4909
<u>Current Assets</u>			
Cash at Lloyds Bank :-			
Special Deposit Account	14146	-	
Deposit Accounts	3176	13911	
Current Account	<u>2332</u>	<u>1840</u>	15751
Sundry Debtors		4183	316
		<u>24273</u>	<u>21848</u>
<u>LIABILITIES</u>			
<u>Current Liabilities</u>			
Sundry Creditors		325	138
<u>Net Assets</u>	<u>£23948</u>	<u>£21710</u>	
Represented by :-			
General Fund as at 1st July 1984	21710	19392	
Add: Trustee Savings Bank Interest	188	131	
	<u>21898</u>	<u>19523</u>	
Add: Excess of Income over Expenditure	2050	2187	
	<u>£23948</u>	<u>£21710</u>	

ANTHONY EVANS
..... Hon. Treasurer

We have examined the books of account of the British Society of Rheology and report that to the best of our knowledge the above Balance Sheet and Revenue Account are in agreement therewith.

Chancery House
3 Hatchlands Road,
Redhill, RH1 6AA
28th November, 1986

ALFRED SIMMONS & COMPANY
Chartered Accountants

BRITISH SOCIETY OF RHEOLOGY

REVENUE ACCOUNT for the year ended 30th JUNE 1986

<u>Expenditure</u>	<u>1986</u>	<u>1985</u>
Council Expenses	1773	1556
Bulletin Production Costs	1458	1184
Expenditure by Officers :-		
President	-	35
Secretary	45	54
Treasurer	7	53
Membership Secretary & Circulation	<u>923</u> 975	<u>639</u> 781
Professional Fees	150	138
Insurance	39	45
Annual Awards	305	300
Miscellaneous	1830	372
Depreciation :-		
Microcomputer	<u>436</u>	<u>434</u>
	6966	4810
Excess of Income over Expenditure	<u>2050</u>	<u>2187</u>
	<u>£9016</u>	<u>£6997</u>
<u>Income</u>		
Annual Subscription and Entrance Fees	2755	2584
Publisher -Rheology Abstracts	3573	2650
Advertising Revenue	260	93
Bulletin Subscriptions	20	135
Investment Income :-		
Bank Deposit Account Interests	1465	926
Redbridge Bond	113	171
Inland Revenue (Tax Repayments)	<u>49</u> 1627	<u>72</u> 1169
Conferences : Net Surplus per account	781	366
	<u>£9016</u>	<u>£6997</u>
<u>Conference Account</u>		
Surplus :		
Birmingham Conference less expenses	-	230
London Conference less expenses	-	(5)
Aberystwyth Conference less expenses	-	141
Reading Conference less expenses	1181	-
Leeds Conference less expenses	(200)	-
Norwich Conference less expenses	(200)	-
	<u>£781</u>	<u>£366</u>

MEMBERSHIP NEWS

The following applications for Membership of the British Society of Rheology were approved at the Council Meeting on the 9th September 1986.

Mr. Christopher ANTON,
Department of Chemical Engineering,
University of Cambridge,
Pembroke Street,
Cambridge CB2 3RA

B.A. M.I. Chem.Eng.

feta BDGH

Dr. Christopher Paul BUCKLEY
Department of Mechanical Engineering,
UMIST,
Manchester M60 1QD

MA., D.Phil., F.P.R.I.

fetsa BC

Mrs. L.M. CHENG,
Department of Food Machinery,
HeiLongjiang Commercial College,
Harbin, CHINA

Diploma in Food Techn.

fetsa FL

M. Hilary DAVIES,
Department of Mathematical Sciences,
University of Alaska,
3211 Providence Drive,
Anchorage,
AK 99508, U.S.A.

B.Sc., Ph.D.

fetsa N

Dr. Mohd Halim b. MOHD SHARIFF
Department of Mathematics,
University of Brunei,
BRUNEI Darussalam

Ph.D.

petsa ACN

Mr. Brendan O'DONNELL,
Polymer Laboratory,
Department of Metallurgy and
Engineering Materials,
University of Newcastle-upon-Tyne,
Haymarket Lane,
Newcastle-upon-Tyne NE1 7RU

B.Sc.

peta ABCDIN

Mr. Mark W.A. PATERSON,
Polymer Laboratory,
Department of Metallurgy and
Engineering Materials,
University of Newcastle-upon-Tyne,
Haymarket Lane,
Newcastle-upon-Tyne NE1 7RU

B.Sc. (Hons)

peta BCDIN

Mr. Samad Bin SOLBAI,
Department of Chemical Engineering,
University of Cambridge,
Pembroke Street,
Cambridge CB2 3RA

B.Eng.(Mech), M.Eng.Sc.
fetsa BCD

Mr. Ken THOMAS,
Division of Materials Applications,
National Physical Laboratory,
Teddington,
Middlesex.

B.Sc., C.Eng.,C.Phys.,FIM, F.Inst.P,FPRI
fetsa DG

Prof. Yuri G. YANOVSKY,
Institute of Petrochemical Synthesis,
USSR Academy of Sciences,
Leninsky Prospekt 29,
Moscow GSP-1, 117912,
USSR

D.Sc.
fetsa DN

THE INSTITUTE OF CERAMICS

Press Release

The Institute of Ceramics is in the process of forming a **Cement and Concrete Group** which, in addition to providing a forum for papers of high scientific quality, will seek to co-operate with other bodies in promoting the application of science in cement and concrete technology. Non-members of the Institute of Ceramics who are interested, and who would like to receive further information, are invited to write to **Dr. G.H. Tattersall at 174 Millhouses Lane, Sheffield, S7 2HE.**

Seminar Report

Rheology of Cementitious Materials

An invited seminar was held at Liverpool University on October 17th 1986 in honour of the visit to the United Kingdom of Dr Lech Rudzinski of the Technical University of Kielce, Poland. The rheology of cement based mixes is of considerable technological importance in view of the fact that if the material cannot flow into the corners of a mould, or be spread evenly by hand the long term properties of the hardened product will be impaired. However, in spite of the enormous quantities of cement and concrete used throughout the world the research community in the field of rheology is quite small.

Dr Rudzinski has many publications on both fluid rheology of fresh cement mixes and solid rheology of the hardened products, and was visiting Liverpool for detailed discussions. It seemed a good opportunity to get the U.K. research community together for an all day exchange of ideas. It is believed that this was the first meeting in the U.K. devoted solely to the fluid rheology of cementitious materials and all agreed that there should be more.

Eight papers were presented and discussed. Due to illness Dr Ashley Hibbert (BP Research Centre) was unable to speak about industrial rheological methods used for oil well cement slurries, and the meeting instead opened with Abid Haimoni (Bradford University) who described the rheology and gelling properties of a particular slurry formulation. The slurry has to be capable of being pumped through the annulus between the oil well casing and the surrounding strata, displacing the drilling mud and filling the space before setting and hardening. Next Dr Stephan Jefferis (Kings College London) described acoustic wave methods for rheological investigations. Both shear and compressive wave propagation have been used for cement and concrete and the problems associated with each were described.

Compressive wave propagation at ultrasonic frequency is the only technique able to cover both fresh and hardened material, but careful deaeration is necessary in the former case. In the last paper of the morning Dr Rudzinski described the rheology of non-shrinking cement pastes. These cements contain calcium sulphoaluminate which expands and counteracts the shrinkage occurring in ordinary portland cement.

After lunch in the pleasant surroundings of Staff House the meeting heard from Dr. Geoff Tattersall about the behaviour of fresh concrete under vibration. Concrete conforms well to the Bingham model but upon vibration the yield value is overcome and the material flows under its own weight. Elegant experiments on the rate of efflux under vibration using such inexpensive apparatus as a four-inch plastic pipe and a carpenter's tape measure were described. Next Don Winpenny (Sheffield City Polytechnic) discussed methods of reducing the slight operator sensitivity in the only commercially available apparatus for measuring the rheology of fresh concrete by improved torque measurement. Then it was back to cement pastes as Prof. John Raffle (Loughborough University) described the volume changes and sedimentation behaviour of cement suspensions, a matter important in the development of structure within the system. Harry Thurairatnam (University College London)

described rheological and other properties of structural grouts for repairs to offshore structures and the meeting concluded with a summary of the rheology of high alumina cement pastes by Dr Phil Banfill (Liverpool).

Discussion was lively throughout and we look forward to the next meeting. Any offers for a venue?

Dr P F G Banfill
School of Architecture & Building Engineering
University of Liverpool
P O Box 147
Liverpool
L69 3BX



Left to right: Dr. S.J. Jefferis, Dr. G.H. Tattersall, C. Ellis, Dr. T. Gregory, Dr. A. Waterhouse, D. Wimpenny, Sue Gill, Prof. J.F. Raffle, Dr. L.S. Rudzinski, H. Thurairatnam, Dr. P.F.G. Banfill, A. Haimoni

RHEOLOGY OF SUSPENSIONS AND PARTICULATE SOLIDS

Preliminary Programme

A joint meeting of The British Society of Rheology and the Colloid and Interface Science Group of the Faraday Division of the Royal Society of Chemistry, to be held at the University of Bath on Thursday and Friday, 9th-10th April 1987.

PROGRAMME

Thursday, 9th April 1987

From 10.00 a.m. Registration

12.00 noon LUNCH

First Scientific Session

1.30 p.m. Extrusion of Wet Powder Masses

J.M. Newton
School of Pharmacy, London

2.10 p.m. Creaming in Oil-in-Water Emulsions

P. Richmond
Institute of Food Research, Norwich

2.50 p.m. Present Experimental Problems with the Rheology of Cement Pastes

P.F.G. Banfill
University of Liverpool

3.30 p.m. TEA

4.00 p.m. Fractals and Flocculation

R. Ball,
University of Cambridge

4.40 p.m. Rheology of Strongly Flocculated Dispersions

R. Buscall
ICI Corporate Colloid Science Group, Runcorn

5.30 p.m. END OF SESSION

7.00 p.m. Sherry Reception

7.30 p.m. DINNER

Overnight

There will be an instrument exhibition in the room adjacent to the Lecture Theatre

Friday, 10th April 1987

8.00 a.m.

BREAKFAST

Second Scientific Session

9.00 a.m.

Viscosity of Concentrated Suspensions in the Vicinity of the Glass Transition

W. van Megen

Royal Melbourne Institute of Technology

9.40 a.m.

Ab Initio Rheology from Colloidal Dynamics
Particulate Computer Simulation

D.M. Heyes

Royal Holloway and Bedford New College

10.30 a.m.

COFFEE

11.00 a.m.

Viscoelastic Properties of Hard Sphere Dispersions

C.G. de Kruif

Van't Hoff Laboratorium, Utrecht

11.40 a.m.

Viscoelastic Properties of Concentrated Dispersions of Charged Particles

J.W. Goodwin, S. Keeping and C. Zukoski

University of Bristol

12.30 p.m.

LUNCH

Third Scientific Session

1.40 p.m.

Rheological Properties of High Concentration Non-Aqueous Dispersions

T. Strivens

ICI Paints Division, Slough

2.20 p.m.

Dynamic Moduli of Nonaqueous Model Suspensions

J. Mewis, W.J. Frith and T.A. Strivens

Katholieke Universiteit, Leuven

3.00 p.m.

TEA

3.30 p.m.

Viscoelastic Properties and Structure of Clay and Oxide Colloidal Dispersions

J. Ramsay

AERE, Harwell

4.10 p.m.

Stress Relaxation in Non-Aqueous Colloidal Dispersions

P.A. Reynolds

International Paint

4.50 p.m.

Shear Thickening in Concentrated Stable Dispersions

H. Barnes

Unilever Research, Port Sunlight

5.20 p.m.

END OF SESSION

CALL FOR PAPERS

"Flow Processes in Composite Materials"

Conference to be held in April 1988

The objective of this conference is to explore the flow processes observed in the whole range of composite materials in order to identify common underlying themes, where those themes differ from the rheology of single phase materials, and how they can be exploited in order to achieve novel effects. Both theoretical and practical papers would be welcomed particularly in the fields of:

	densely packed particulate systems
	pastes
and	fibre reinforced plastics
including	structural composite materials

Offers of papers should be addressed to:-

F.N. Cogswell
ICI plc
The Materials Centre
P.O. Box No.90
Wilton Centre
Middlesbrough
Cleveland TS6 8JE

Early notification of intention to submit a paper would be appreciated. Abstracts will be required by 1st September 1987.

PhD Ambitions?

Brunel - Raychem CASE Studentship

A 3-year CASE Studentship, supported by the Science and Engineering Research Council*, is available NOW for the following project:-

Advanced Thermoplastic Fibre Composites

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- o The candidate will be based at Brunel University, Department of Materials Technology under the supervision of Dr. M.J. Folkes.
- o During the course of the research programme, the candidate will have the opportunity of using a wide range of sophisticated techniques both at Brunel and at the Raychem research laboratories, based at Swindon.
- o Raychem is a materials science based company pioneering new materials for the Electronics, Telecommunication, Aerospace and other high technology markets and is particularly strong in the field of exploiting novel polymeric systems for a wide range of applications.

If you have a degree (1 or 2(1)) in physics, materials science, polymer technology (or related discipline) and would be interested in applying for the Studentship, please write to

Dr. M.J. Folkes
Department of Materials Technology
Brunel University
Uxbridge
Middlesex

Tel: (0895) 74000 Ext 2378 or 2972

enclosing a detailed curriculum vitae before February 23rd 1987.

* The normal conditions of eligibility for SERC Studentships will apply.

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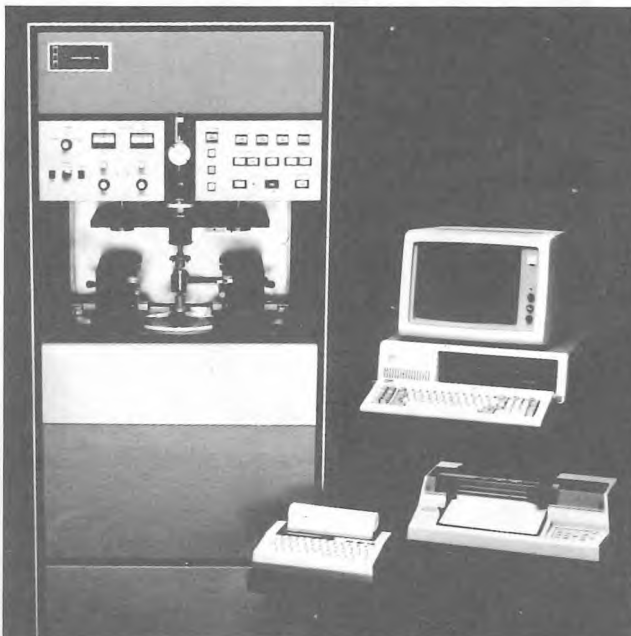
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INTEREST IN RHEOLOGY BE THEY INDUSTRIALISTS,
LABORATORY TECHNICIANS OR ACADEMICS.**

For further details or an application form please contact :-

Dr J.Ferguson
University of Strathclyde
Dept. of Pure and Applied Chemistry
Thomas Graham Building
295 Cathedral Street
Glasgow G1 1XL

Telephone 041-552-4400

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