

The Physics of Macromolecules*

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Abstract

The long, flexible, chain-like macromolecules play a major role in our existence. As carbohydrates they are the central link in the food chain of all living things; as rubbers they enable the world's transport system to function; as textiles they clothe us, whilst as plastics they serve us in a thousand ways. Above all, perhaps, as biopolymers they constitute most of the interesting parts of ourselves. Physical interest in these varied materials ranges from the shape and size of individual molecules to properties such as the strength, elasticity or dielectric behaviour of amorphous and paracrystalline polymers. Mechanical behaviour is examined in relation to four separate states of polymers: rubberlike, glassy, viscoelastic and partially crystalline. Examples of biopolymers and synthetic polymers are described and the role of viscoelasticity in the performance of motor car tyres is discussed.

1. Introduction

Relating the physical properties of a material to its atomic structure has been a favourite occupation of physicists for over a century. They have been very successful with elementary substances such as platinum, helium or silicon, and even with small molecular materials such as water, salt or quartz. The largest of these 'ordinary' molecules are things like sucrose or heroin with molecular masses up to 400 or so. Beyond this there is a gap until we reach the relatively enormous molecules called *macromolecules*, with masses from several thousand up to several million. The importance of these macromolecular materials can be gathered from a short selection of them: silk, leather, wool, eggs, meat, wood, rubbers, waxes, nylon, polythene, proteins, nucleic acids, and in fact most of the material that we ourselves are made of, except for the bones and the water.

Although important, these materials presented great initial difficulties to the physicists. Their physical properties did not fit neatly into the accepted categories. Moreover their molecular constitution was unknown so that it was impossible to relate their physical properties—even if they could be measured—to the atomic structure. Characteristically the problems were ignored. Physical measurements of these materials were left to lesser breeds without the law—such as industrial chemists—and for many years the substances themselves received no mention whatsoever in the physics textbooks.

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But during the 1930s the establishment of the long chain molecule concept by Herman Staudinger, in the teeth of strenuous opposition, led directly to such discoveries as nylon and it could no longer be ignored. A polymer molecule was recognized as a long, flexible chain comprising hundreds or thousands of small molecular groups—the monomers—joined end to end like a necklace of beads. In World War II, the great contributions of synthetic rubber and of plastics such as polythene led to a situation where at least the industrial scientists were well aware of the significance and nature of the problem. In the U.S.A., the U.S.S.R. and Japan, polymer institutions have since been created for both basic and applied studies of macromolecular materials. In England and Australia, however, the subject is still relatively languishing.

This paper briefly reviews several aspects of macromolecular physics, illustrating them by reference to four polymeric states of particular practical interest: elastomeric (rubberlike), glassy, viscoelastic and partly crystalline. These four categories include both natural and synthetic polymers, organic and inorganic, including the polymeric materials of which living things are made.

2. Shapes of Individual Molecules

The key to the physical properties of these materials lies in the shape and packing of their individual macromolecules. The shapes of macromolecules can easily be visualized by taking as a molecular model a piece of wool about 15 m long. At one extreme the molecule may be in a completely disordered condition—the so-called random coil—when it is represented by a loose, tangled ball of wool, perhaps some 50 cm across. At the other extreme the molecule may be fully extended, as represented by the fully stretched 15 m length of the piece of wool.

In biological macromolecules, where intramolecular bonds make a significant contribution to the free energy, a common extended form is the helix. This is simply the curve generated in three dimensions by a succession of regularly repeating identical units, corresponding to a straight line in one dimension or a circle in two.

A typical helix can be modelled by winding the wool helically round a straight, stiff wire some 5 m long. These extreme shapes of individual macromolecules can be measured quite precisely in a dilute solution using optical methods such as light-scattering or rotary polarization.

In a suitable solvent the segments of a macromolecule are subject to rapid Brownian motion correlated only at short range with the movements of their neighbours. The whole molecule passes through a gamut of configurations but its time-average form is that of a roughly spherical random coil. A classic electron micrograph by Richardson (1964) of a gold-shadowed specimen prepared from a very dilute solution of polystyrene supported this concept by showing the individual molecules in their compact, spherical form. But it is more pressing here to consider how molecular configurations determine the physical properties of the materials in bulk.

(a) *Rubberlike State*

The most obvious characteristic that distinguishes polymeric materials from 'ordinary' solids is the ability to be stretched reversibly by many hundred per cent, whereas ordinary solids usually cannot withstand an extension of even one per cent.

This reversible high elasticity is a direct consequence of the randomly coiled configurations of the long chain molecules of which the substance is made. It is also necessary that the long chains should be flexible and that the intermolecular forces should be low. The rubberlike condition is thus a state of matter and not just the property of a particular chemical substance. For example reversible highly elastic behaviour is shown by plastic sulfur, ordinary natural rubber (*cis*-polyisoprene) or synthetic rubbers, bouncing putty (polydimethylsiloxane), or by elastin, the protein which gives the elasticity to veins and arteries.

Clearly there is a fundamental difference between the high elasticity of rubberlike materials and the elasticity of normal solids such as glass or steel. The difference can be traced to the behaviour of the long-chain rubber molecule. A randomly coiling long-chain molecule has the surprising property of behaving like a linear spring. Thus if one end is fixed and the other is pulled away from it, there is a restoring force directly proportional to the distance between the ends. The origin of this force is purely entropic, just like the pressure in an ideal gas.

The problem resembles Rayleigh's treatment of the flight of a seagull, an example of a three-dimensional random walk. If we idealize the molecule as a freely jointed chain with n links, each of length L , the probability of finding one end at a distance r in a particular direction from the other end turns out to be proportional to $\exp(-3r^2/2nL^2)$. All configurations of the freely jointed molecule are equally likely, so that this probability is simply a measure of the number of configurations available at the end-to-end separation of r .

According to Boltzmann the entropy is k times the logarithm of this number, so that

$$S = -3kr^2/2nL^2. \quad (1)$$

If the molecule is slowly stretched to its full extent the entropy decreases continuously to zero (there is then only one possible configuration). The increase in free energy for a small stretch dr is equal to $f dr$, the work done by the elastic restoring force f . As there is no internal energy component in this ideal rubber we can set $f dr$ equal to $-T dS$, where T is the absolute temperature. It follows from equation (1) that

$$f = (3kT/nL^2)r, \quad (2)$$

showing that the long-chain molecule does indeed behave like a linear spring. This equation is analogous to the equation of state for an ideal gas

$$p = NkT/V. \quad (3)$$

In both rubber and gas the elasticity is purely entropic so that the elastic restoring force is directly proportional to the temperature.

A calculation for a crosslinked *network* of macromolecular chains (e.g. a rubber band) shows that the force needed to extend a strip to λ times its initial length should be equal to

$$F = KXT(\lambda - \lambda^{-2}), \quad (4)$$

where X is the crosslink density and K is a constant. An actual experiment shows good agreement with this theory up to extensions of 200–300% (Fig. 1), remarkably

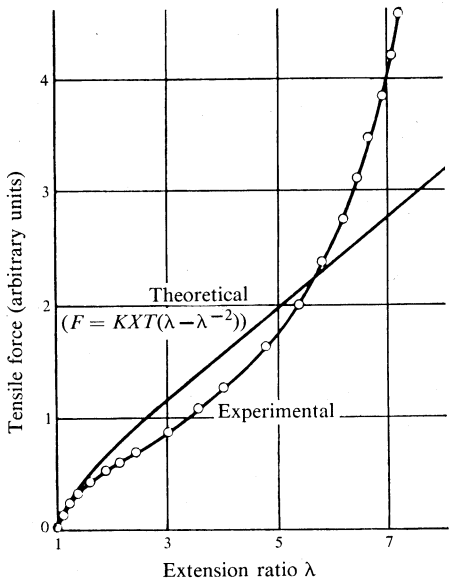
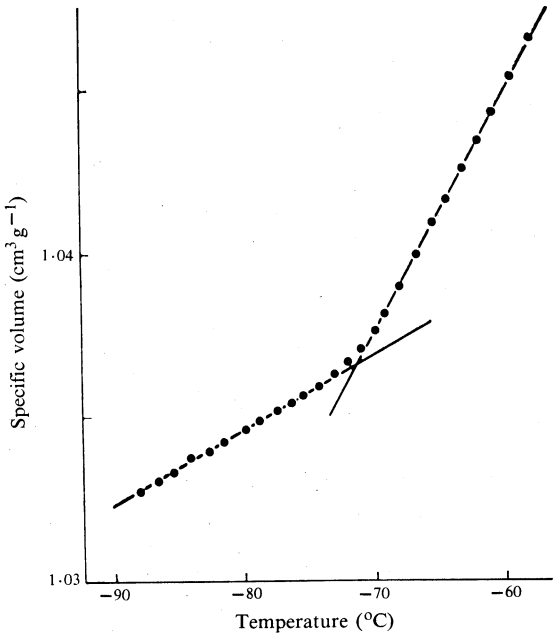


Fig. 1. Tensile force-extension curves for a strip of natural rubber.

Fig. 2. Specific volume-temperature relationships for natural rubber, showing the inflexion at the glass-transition temperature.



good agreement, in fact, for a relation that accounts for such large strains in terms of only one adjustable parameter, namely X , the degree of crosslinking.

The progressive departure from the theoretical curve at extensions above about 300% is due in large part to crystallization. I shall consider the implications of crystallization after discussing the other two states of amorphous polymers, the glassy state and the viscoelastic state.

(b) Glassy State

When a rubberlike polymer becomes sufficiently cold, the relative rotations of molecular chain segments are inhibited so that the basis of the rubberlike state is lost. The material is then a hard, relatively brittle solid, resembling an organic glass made from small organic molecules, and its Young's modulus rises by a factor of more than a thousand. If it is cooled steadily at a rate of say 1°C every few minutes, properties such as the thermal expansivity change fairly abruptly from those appropriate to a liquid to those typical of a glass (Fig. 2).

As this is a kinetic process, the same transition from liquid to glass can in principle be obtained by keeping the temperature constant and testing at a very high rate of strain, e.g. by firing a bullet through a specimen.

As seen in Fig. 2, the change from liquid to glass is smeared out over a small temperature range, but a point within this range is taken as the glass-transition temperature T_g . Evidently an amorphous polymer will appear to be rubberlike if its glass transition is well below room temperature; or glassy if its glass transition is well above room temperature. Thus we normally experience natural rubber as a rubber ($T_g = -68^{\circ}\text{C}$) and polystyrene as a hard, brittle glass ($T_g = 100^{\circ}\text{C}$).

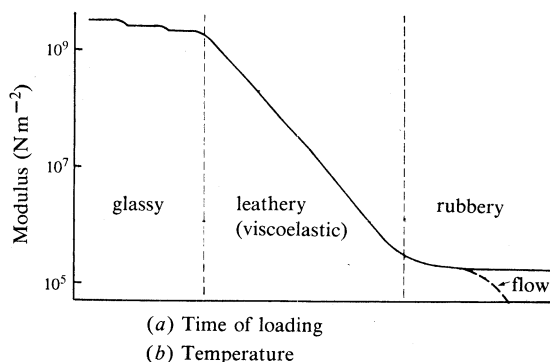


Fig. 3. Identical curves for shear modulus of a polymer as a function of (a) time of loading at constant temperature; (b) temperature at constant time of loading.

(c) Viscoelastic State

For a polymer in the rubberlike state at a constant temperature the physical properties are independent of time. In the glassy state there is not a true thermodynamic equilibrium, but the viscosity is so high ($>10^{13}$ P) that the physical properties are again essentially time independent. These states are, of course, idealized extremes, and real polymers show behaviour somewhere inside the enormous range bridging the gap between the glassy and rubberlike states, the precise values depending upon the relevant conditions of temperature and time. Fig. 3a gives a typical representation of how an elastic modulus of a polymer varies with the time of loading at constant temperature. Fig. 3b is the *identical* curve and it shows, with a suitable choice of scale, how the modulus measured after a constant time of loading varies with temperature.

Soon after World War II new polymers were being produced in profusion, but assessment of their properties was inhibited by the vast quantity of data that could be generated for each polymer simply by testing over a wide range of

temperatures and times (or frequencies). Williams, Landel and Ferry (WLF)* brought order out of the chaos by referring all dynamic measurements, whether mechanical or electrical, to the glass-transition temperature of the individual polymer. They then showed that an equation of surprising universality could be used to transform all the measurements on a particular polymer so as to yield a single curve displaying the behaviour of that polymer at any chosen temperature over many orders of magnitude of time or frequency. The transformation was accomplished essentially by multiplying the time (or frequency) of any observation at a temperature T by a factor a_T given by

$$\log a_T = 17.44(T - T_g)/(51.6 + T - T_g). \quad (5)$$

(The strange numerical constants are, in fact, universal. They are related to the difference in thermal expansivities above and below the glass-transition temperature and to the so-called 'free volume' at the glass-transition temperature.)

The WLF equation had an immediate practical application. It could be used to predict the values of physical properties of a polymer under conditions very different from those under which it had been tested. In particular a laboratory experiment carried out over a wide temperature range but taking only a few hours to complete could be used to predict the properties of a polymer over weeks, months, or even years.

Equation (5) was at first received with scepticism and even hostility. Its enormous practical success largely silenced the opposition but theoretical enquiries into the question of just why it works so well have been a fruitful source for investigations of the molecular mechanics of polymer behaviour.

(d) *Partially Crystalline State*

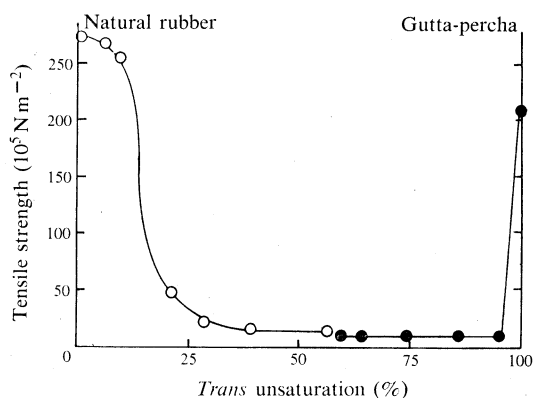
It seems surprising that a tangled mass of long thread-like molecules could ever achieve sufficient order to become even partially crystalline. But in fact the tangling is maintained only by the thermal energy of the molecules themselves. If the temperature is reduced gradually, i.e. without quenching the system by plunging it abruptly below its glass-transition temperature, minimum free energy requirements will ensure that many neighbouring segments pack closely and regularly together into microcrystallites. The polymer has thus become effectively a composite material consisting of a rubberlike matrix packed round the small, hard crystallites. This clearly has a major effect upon the physical properties, generally improving the strength and wearing qualities of the material.

Even without lowering the temperature, many polymers can be crystallized simply by stretching. This orders the molecular chains and promotes the formation of crystallites oriented in the direction of stretch. Even partial crystallinity can be of crucial importance in many applications—synthetic fibres, for instance, or automobile tyres. But in the supreme example of the design of materials made from macromolecules, the proteins and tissues of living creatures, we find that many systems are almost completely crystalline.

* A useful general reference for polymer viscoelasticity, particularly the derivation and use of the WLF equation, is Ferry (1970).

The dramatic effects of both forms of crystallization upon the strength of a polymer are illustrated in Fig. 4. Natural rubber is *cis*-polyisoprene. It has a high tensile strength because its chains are stereoregular and fit together neatly, thereby developing a high degree of crystallization as it is stretched. Calculated on the actual cross section at break, a strip of rubber may show a tensile strength of 100 MN m^{-2} , approaching the strength of mild steel.

Fig. 4. Tensile strength of isomerized polyisoprenes. [Cuneen and Higgins (1959).]



Gutta percha is isomeric with natural rubber. It is polyisoprene in the *trans* form rather than the *cis*, and as the *trans* configurations pack together more easily, gutta percha is already a crystalline solid at room temperature. It also has a high tensile strength. When either material is partly isomerized, by treatment with hot sulfur dioxide for instance, the crystallinity is reduced or destroyed. As Fig. 4 shows, the tensile strength is thereby reduced to less than 10% of that of the pure isomers.

3. Some Illustrations and Applications

The rubberlike and crystalline states are exquisitely illustrated by the fibrous proteins of living systems. A protein is a long-chain molecule, a polymer in which each monomer unit is a particular amino acid, selected from a pool of about 20 different amino acids. The protein *elastin* contains a number of amino acids which prevent any regular, crystalline order from developing. The molecules thus take the form of random coils, so that fibres of elastin are rubberlike and confer the required elasticity upon tissues such as arteries or veins. The strength and stiffness of these blood vessels, however, is conferred by another protein, *collagen*, which is the most versatile and widespread protein in the animal world. Fine collagen fibres form the basic framework of the skin, the tendons that transmit the muscular force of the limbs, the cartilage in joints, the cornea which protects and acts as a transparent window for the eye, and most of the so-called connective tissues. They also fill the space between the mineral crystals in bone.

Each collagen molecule has the form of a long, narrow rod 1.4 nm in diameter and 300 nm long (half of the wavelength of orange light and so marginally long enough to become visible!). The rod itself is formed from three helical molecular chains twisted together and held in this extended state by a system of hydrogen bonds between the chains. If the collagen becomes too hot the thermal energy of the molecules overcomes the stabilizing influence of the hydrogen bonds and the rodlike

molecule collapses into a random coil; the fibrous tissue is thus transformed into a rubbery solid. This is a commonplace experience, small pieces of tendon or cartilage in raw meat transforming into rubbery chunks of gristle during the production of the everyday meat pie.

It should be remarked that as the melting of collagen is a cooperative process the melting point is sharply defined, even though a protein by its nature is somewhat heterogeneous. Thus wet skin, tendon or other collagenous tissue from a mammal will start to melt at one or two degrees below 60°C and be fully melted by one or two degrees above.

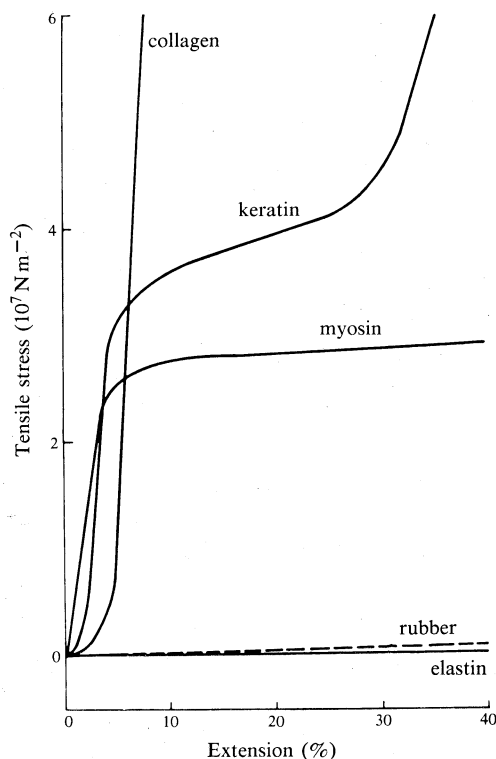


Fig. 5. Tensile stress-strain behaviour of fibrous proteins (natural rubber included for comparison).

The morphology of the 'fibrous proteins' thus determines whether they are soft and extensible, like elastin, or inextensible (although, because they are long and thin, flexible) like collagen. The force-extension curves in Fig. 5 show the wide range of mechanical behaviour that can be obtained. The α -keratin protein of hair and the myosin of muscle both display highly nonlinear behaviour. In the native form their molecules take the form of a helix with a relatively low pitch—the so-called α -helix. After an extension of 1 or 2% the system of hydrogen bonds supporting the helix breaks down cooperatively so that, with the application of just a little more tension, the helical turns open out into a fully-extended zig-zag form known as the β -conformation.

When the alpha form has all been extended into the beta form, the crystalline fibre once more becomes stiff and relatively inextensible. The plateau region, where the length and proportions of the alpha and beta forms vary enormously for only

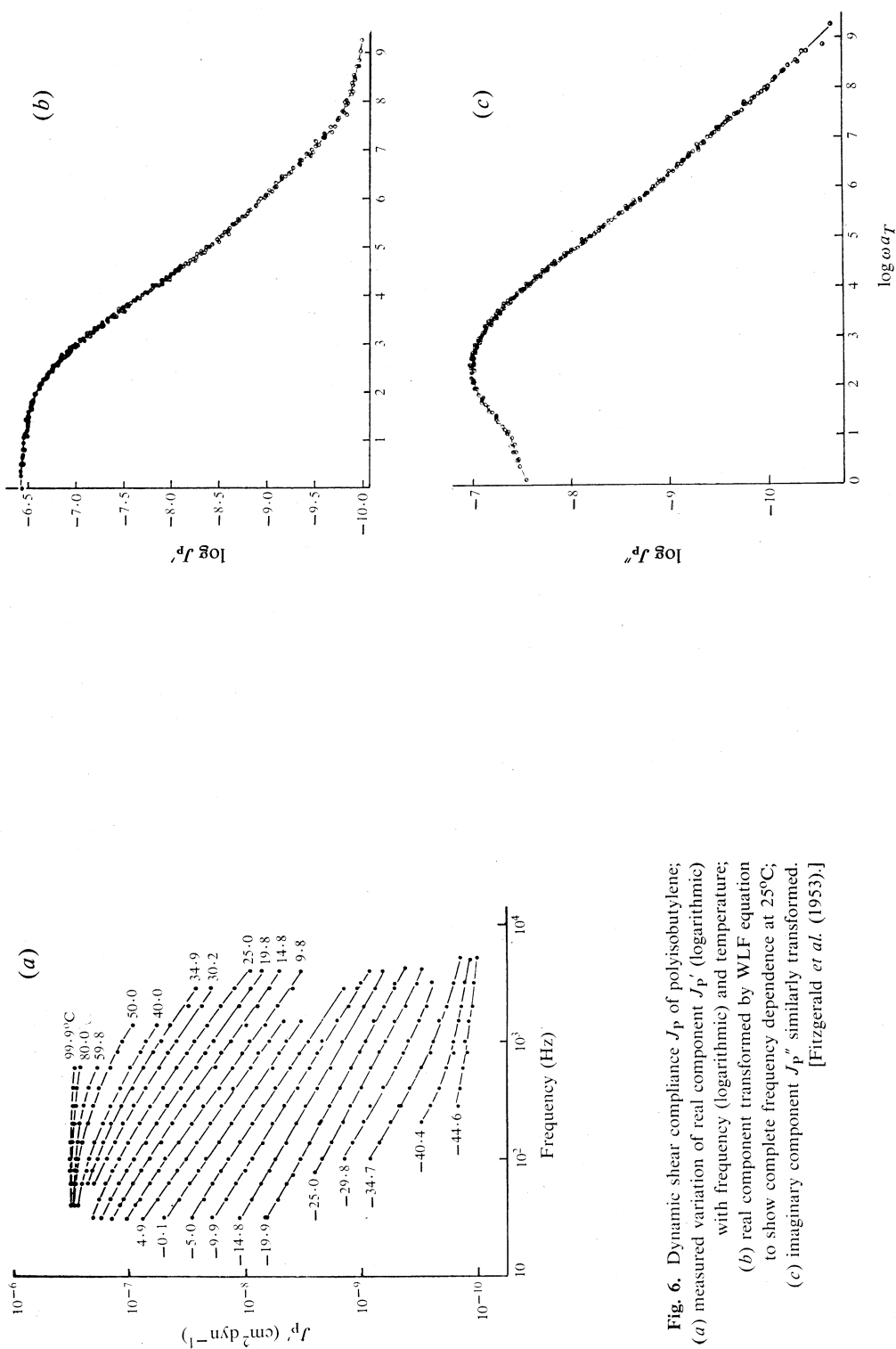


Fig. 6. Dynamic shear compliance J_p' of polyisobutylene; (a) measured variation of real component J_p' (logarithmic) with frequency (logarithmic) and temperature; (b) real component transformed by WLF equation to show complete frequency dependence at 25°C; (c) imaginary component J_p'' similarly transformed. [Fitzgerald *et al.* (1953).]

a small increment of force, represents a phase transition. It is an impressive phenomenon, but it is not clear whether it has ever found any function in nature. Certainly human beings have not yet discovered any significant application (except, perhaps, indirectly in the permanent waving of hair!).

A more immediately practical question is that of the strength of polymers. Crystallinity is an obvious method of obtaining a strong material, but the amorphous, glassy polymers turned out to be much stronger than they ought to be in relation to the conventional inorganic glasses. Investigation of that question has directed attention to the role of crack-stopping in composite materials, and led to such developments as polystyrene toughened by blending with a small proportion of rubber. Another example is the incorporation of finely-divided carbon black in synthetic rubber tyres, not merely to save rubber but to provide a dramatic increase in wear resistance.

Within the limitations of space, however, I shall only consider the further question of the role of viscoelasticity, a subject which pervades virtually the whole of polymer science.

First it should be noted how well the WLF equation (5) governs the dynamic behaviour of polymers. Fig. 6 shows how measurements of the complex shear compliance, carried out over two decades of frequency and a range of nearly 150°C, are transformed.

Fig. 6a shows raw measurements of J'_p , the real (elastic) component of the compliance of polyisobutylene, taken from a classic paper by Fitzgerald *et al.* (1953). In Fig. 6b each curve has been displaced along the frequency axis by an amount calculated from the WLF equation to 'reduce' its values to the arbitrarily chosen reference temperature of 25°C. This procedure yields a smooth, well-defined curve from which the value of J'_p at 25°C can be read off for any frequency over a range of nine decades. Exactly the same equation, with the same constants, also reduces the measurements of J''_p , the imaginary part of the compliance, to a single, smooth curve as shown in Fig. 6c.

The imaginary component of the compliance is responsible for the energy loss in cyclic deformation, as in the tyres of a moving motor car for example. It controls the *rolling* friction of the tyres and is thus a significant factor in determining the fuel consumption of a rubber-tyred vehicle. However, it also influences the *sliding* friction of the tyre so that there is a conflicting requirement for a *higher* value of J''_p in order to improve the road-holding of the vehicle, especially in wet conditions.

Still more surprising, perhaps, is the fact that for non-crystallizing polymers the fracture process also is controlled by the viscoelastic properties. Smith (1958) first demonstrated how the tensile strength and the breaking elongation of a styrene-butadiene rubber, measured over a wide range of temperatures and rates of extension, follow exactly the same WLF equation. Corresponding to the real and imaginary compliances, smooth composite curves are obtained for tensile strength and for breaking elongation over strain rates ranging from 0.004 to 1000 s⁻¹ and temperatures from -70 to 100°C.

A motor car tyre is not, of course, worn out by a single stretch to break in a tensile testing machine. But it does wear out by a series of repeated high extensions at the tips of microcracks as the tread pulls away from the surface of the road. Synthetic rubber treads are loaded with carbon black to oppose this wearing process, but natural rubber has an intriguing built-in protection. At the very tip of the crack

there is a tensile stress *at right angles* to the direction in which the crack is propagating. The extension produces immediate crystallization, with the fibrous crystals oriented across the path of the crack, blocking any further stress concentration and providing an ideal crack-stopping mechanism. It seems that the Almighty intended us to ride in motor cars, for why else would we have been given rubber trees?

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