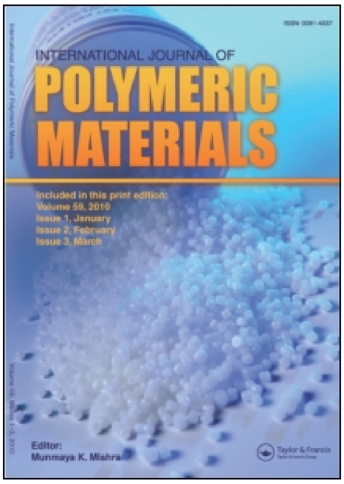

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Structure-Property Relationships in a Polymer

E. H. Andrews[a]
[a] Department of Materials, Queen Mary College, London, E1, England

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Structure–Property Relationships in a Polymer†

E. H. ANDREWS

Department of Materials, Queen Mary College, London E1, England

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The way in which polymer molecular structure controls structure on higher levels of organization in a solid polymer is briefly reviewed, as is also the way in which structure, on all levels, controls physical properties. The "line of descent" from molecular structure to physical properties is then illustrated at length in the case of one particular polymer, *cis*-polyisoprene (natural rubber). It is shown how the crystalline-amorphous morphology in the solid is controlled both by the chemical microstructure of the polymer and by the physical conditions (temperature, time, strain) under which solidification occurs. By changing these "processing conditions" great changes can be effected in the morphology.

The mechanical properties of the solid are then examined as a function of morphology and shown to depend strongly on the various morphological parameters, such as the amount and orientation of the crystalline phase and the orientation and state (rubber or glass) of the amorphous phase.

1 THE ROLE OF MOLECULAR STRUCTURE

This paper is not primarily concerned with molecular structure, but it is impossible to discuss "structure–property" relationships without beginning at this point. One of the main ideas behind this paper is that the molecular structure of a polymer does not uniquely define its solid-state properties and that the latter often depend much more strongly on the higher levels of structure ("morphology"). It must never be forgotten, however, that the morphology of a solid polymer, itself derives from the "interaction" of the molecular characteristics with the conditions under which the morphology is formed. We have only to remember that polymers as materials are what they are because they possess a characteristic molecular structure, namely that of a long chain.

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†Lecture at the Scientific Symposium at the occasion of the Dedication of Midland Macromolecular Institute, September 29, 1972.

The proper perspective in structure–property relationships can best be given diagrammatically. In Figure 1 is shown a kind of "family tree" or line of descent, tracing the properties of polymers back to their molecular structure. To avoid over complicating the diagram, I have restricted it to the thermomechanical category of properties and omitted the electro-magnetic and chemical property categories. Clearly, however, these aspects could be included in a similar manner.

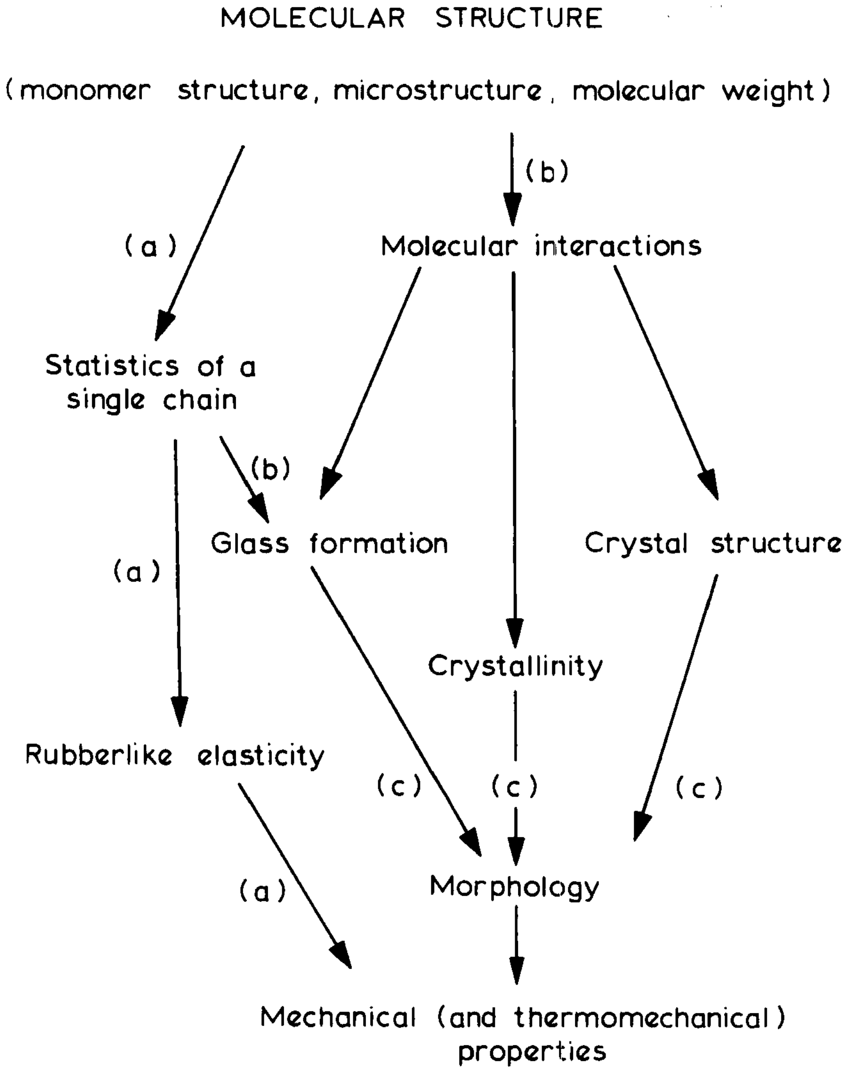

FIGURE 1 Property–structure lines of descent.

Reference to Figure 1 reveals immediately the very complicated nature of the dependence of mechanical properties (including thermomechanical properties) upon molecular structure. This is why many early attempts to relate properties directly to molecular structure met with only limited success. (My personal experience bears this out, since one of my first tasks as a newly qualified scientist in an industrial laboratory was to evaluate a series of aromatic esters for their fibre properties with a view to selecting the molecular structure which gave the best result. At that time very little was known about the physical structure or morphology of fibres.)

There is one property, that of rubberlike elasticity, which is largely dependent upon the independent behaviour of single molecules (route (a) in Figure 1). This behaviour is found at temperatures sufficiently high that the kinetic motion of the molecules swamps the constraint of molecular interactions. The material then behaves to a first approximation, as an assembly of non-interacting chains.

All other mechanical properties, however, depend strongly on molecular interaction. Indeed the temperature range over which rubberlike behaviour is observed is itself limited by the phenomenon of glass formation where molecular interactions predominate.

The role of interaction is indicated by routes (b) in Figure 1. According to the molecular structure, interactions result in the establishment of structures of a higher order, namely glasslike and crystal structures. Which of these two structures will form as a polymer is cooled from the melt or precipitated from solution depends both on the inherent capacity to crystallize and on the relative rates of cooling (or precipitation) and crystallization. Both capacity and kinetics are controlled by the molecular microstructure as well as by the more obvious thermodynamic parameters. Commonly both crystalline and amorphous regions occur in the solid polymer and their relative amounts and arrangements (size, shape, orientation, organization) depend not only upon the factors mentioned above but also on mechanical parameters such as stress or strain obtaining in the system during the formation of the morphology ((c) in Figure 1).

Finally, the mechanical properties are dependent directly on the morphology, since the response of the solid to stress or strain is the averaged sum of the responses of the individual components in the morphology. If the polymer is a homogeneous glass, the "morphology" must be construed in terms of appropriate concepts such as free-volume, close-range order and mean molecular orientation. If the polymer is a "composite" of crystalline and amorphous phases the situation is more complex, involving the totality of structural characteristics in both phases together with specific phase interactions (e.g. tie molecules anchored by the crystalline phase but extending through the amorphous phase).

It is clearly impossible to deal with the whole area defined by Figure 1 in a single paper. In what follows, the kinds of dependence discussed above will be illustrated mainly by examples drawn from our experience over some years of a single polymer—*cis*-polyisoprene or natural rubber.

Apart from the importance of this material in the history of polymer science, there are additional advantages of working with polyisoprene. It can be readily and quantitatively isomerized to change its microstructure; it crystallizes sufficiently slowly to allow control of the morphology; it can be obtained in a wholly amorphous condition for comparison with semi-crystalline specimens and, finally, the amorphous phase can be changed from glassy to rubberlike by passage through the glass transition temperature at the reasonably convenient temperature of −70°C, without changing the crystalline phase in any way.

The examples chosen below to illustrate structure property relationships are as follows. Firstly, the effect of small microstructural changes on the morphology and kinetics of crystallization. Secondly, the effect of strain on morphology, strain being regarded as a "processing variable", and thirdly, the effect of morphology upon some high-strain mechanical properties such as modulus, yield stress and fracture stress. The work is discussed here in review form only and further details will be found in the references. Acknowledgements are due to several co-workers, namely Drs. P. J. Owen, P. E. Reed, A. Singh and Ingrid Voigt-Martin.

2 THE EFFECT OF MOLECULAR MICROSTRUCTURE ON CRYSTALLINE MORPHOLOGY AND KINETICS

Final properties, we have asserted, depend on morphology and this, in turn, depends upon those kinetic processes which give rise to it. It follows that crystallization kinetics, interacting with the "processing conditions" (thermal history, for example) are of central importance to the subject. Andrews, Owen and Singh[1] have investigated the effect of small changes in molecular microstructure upon the crystallization kinetics of *cis*-polyisoprene. The changes were of two kinds, namely small amounts (up to 10 %) of isomerization of the initially *cis*-polymer and chemical cross-linking by peroxide decomposition involving equally small numbers of monomer units.

The linear growth rates of lamellar crystals (grown in very thin films of the melt) were measured directly using electron microscopy and an osmium tetroxide staining technique which arrests crystal growth after any chosen period of time. The dramatic results are shown in Figure 2. At a given temperature (−26°C) the linear growth rate, G, of the crystals is reduced one-thousandfold by the random introduction of one isomerized unit in ten homopolymer units (10% isomerization). There is a linear dependence of log *G* upon the fraction *β* of isomerized material. A similar effect is produced by cross-linking although this appears to be only half as effective as isomerization in suppressing the crystal growth rate.

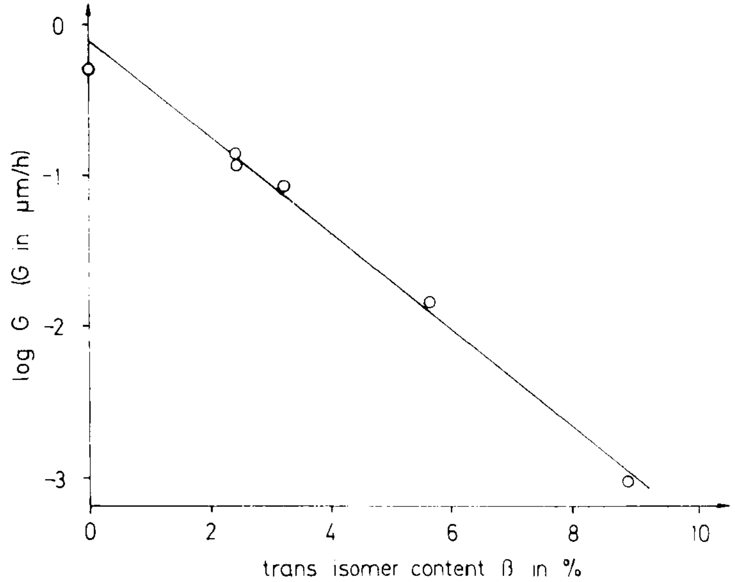

FIGURE 2 Single crystal growth rate *G* at −26°C, as a function of the fraction *β* of isomerized material in *cis*-polyisoprene [after Andrews, Owen and Singh;[1] used by permission of the Royal Society.]

Since the temperature dependence of *G* was unaffected by isomerization or cross-linking, it was concluded that the reduction in *G* could not be due to changes in the thermodynamic parameters (heat of fusion, melting temperature, interfacial energies) which appear in the classical equations[2] for growth by secondary nucleation. Instead, the authors explained their result in terms of a novel "exclusion" mechanism, as follows.

Continuous growth of a polymer crystal occurs by a modification of the classical "secondary nucleation" process. In this process, the slowest (and thus the rate controlling) step is the deposition of a new block of solid material on to a smooth growth surface (Figure 3). Once this block (the "secondary nucleus") has been deposited, a new monolayer is rapidly completed because atoms or molecules crystallize readily at any step on the surface. In polymer crystallization the process is probably more complex, involving the secondary nucleation of each separate molecule on to the growth surface. In either case, however, it is necessary to establish a secondary nucleus which is large enough to be thermodynamically stable. This "critical size" requirement suggested that an uninterrupted sequence of homopolymer units, sufficient in number to form a critical size nucleus, was a requirement for the attachment of a new molecule to the growth surface. Andrews *et al.* were able to show theoretically that the crystal growth rate G would be affected by the fraction β of randomly distributed "foreign" units according to the equation,

$$\ln(G/G_0) = -(N-1)\beta \tag{1}$$

where G_0 is the growth rate for the homopolymer and N is the number of monomer units required in uninterrupted sequence. Not only does Eq. (1) describe exactly the relationship found in Figure 2, but the value deduced for N gave a width for the secondary nucleus of 1.98 nm compared with an independent thermodynamic estimate of 1.94 nm.

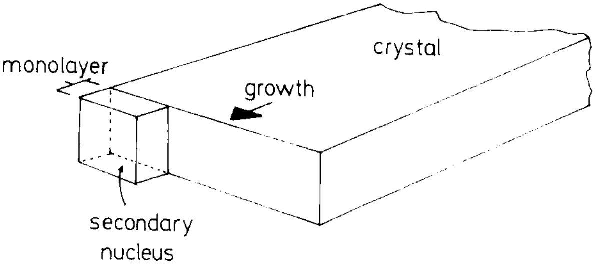

FIGURE 3 Crystal growth by secondary nucleation.

It appears, then, that the growth kinetics are extremely sensitive to molecular inperfections of whatever kind, the effects being far more marked than those of molecular weight variation,[3] for example. The amount and perfection of crystallinity achieved in a polymer subjected to a given processing history is thus likely to be equally sensitive unless care is taken to anneal the material.

The influence of small amounts of isomerization upon the ultimate (i.e. well annealed) morphology is negligible. Thus, provided time is given for the crystals to grow to their full extent, the results are wholly similar. In normal polymer conversion processes, however, such as extension, fibre spinning, blow moulding, etc., morphology may be strongly affected by changes in crystal growth kinetics. For example, regions which crystallize under high shear stress will have a very different morphology from regions which crystallize after the shear stress has relaxed. Rapidly crystallizing species may thus have a "high shear" morphology due to transient shear stresses whilst slowly crystallizing species may reveal little or no "memory" of the time spent by the melt under shear.

Cross-linked specimens of *cis*-polyisoprene, unlike isomerized material, *do* exhibit important morphological differences from the uncross-linked case.[4] These differences are illustrated in Figures 4 and 5. Figure 4a shows a spherulite grown in an uncross-linked thin film and Figure 4b one grown in a cross-linked film. In the latter, the lamellae are relatively short and discontinuous by comparison with the former. This may be due either to the physical impedance of growth by localized regions of high cross-linking or by an increased tendency for nucleation of lamellae resulting in a large population of "young" (and thus short) crystals. Figures 5a and 5b show a similar contrast for crystallization in a strained film (see next section). The long row-nucleated structures, often up to 10–20 μm, typical of uncross-linked rubber are strongly suppressed by cross-linking. Row nuclei still occur in cross-linked specimens, but are typically only a fraction of a micron in length, though much more numerous. The explanation of this may at first appear to be a physical blockage of row-nucleus growth, but is more likely to arise from the increased elasticity of the melt (which opposes the shape change involved in the formation of a long cylindrical nucleus).

3 THE EFFECT OF MECHANICAL CONSTRAINT ON MORPHOLOGY

3.1 Strain in the melt

During polymer conversion the melt is normally subject to deformation, either by shear in the die or mould, or by subsequent drawing or blowing processes. The degree to which these processes affect polymer morphology depends on the time, temperature and the severity of the deformation. If the stresses relax before crystallization is initiated, the latter occurs isotropically, but if stresses are present during even the early stages of solidification the effect on morphology can be profound.

Natural rubber films have a sufficiently high molecular weight to sustain applied stress in their melt condition even in the absence of cross-linking. They therefore afford a model thermoplastic system in which the effects of melt stress can be studied by the application of *static* strain (not possible in most polymer melts).

The results of this study are already well-documented,[5] and Figures 4a and 5a have already been given to show the morphological differences between a film crystallized unstrained and one crystallized from a strained (200%) melt. Kinetic evidence[1] reveals that the stress relaxes rapidly in the strained (uncross-linked) film, so that most of the crystallinity develops in a relaxed film. The *initial* crystallization, however, consisting of a row nucleus, forms rapidly under stress and governs the subsequent growth morphology even after the stresses have relaxed.

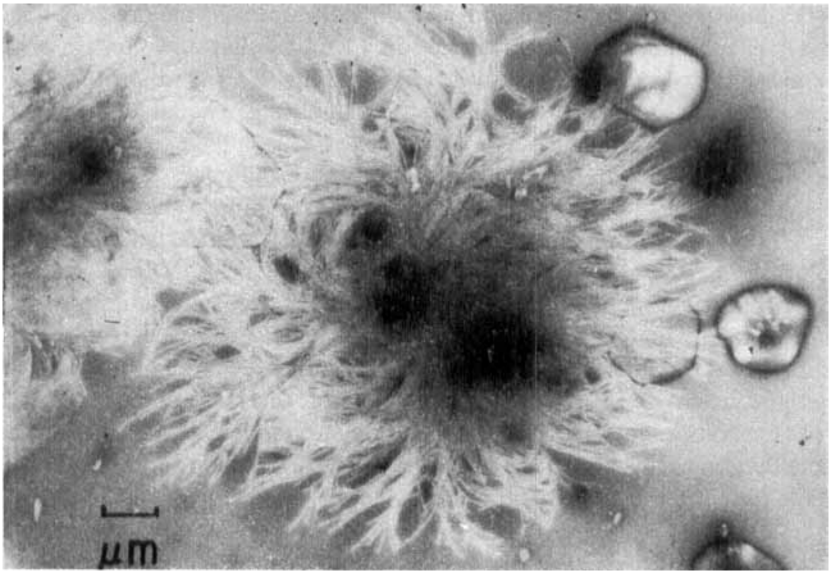

FIGURE 4a Spherulite grown in a thin film of natural rubber (all micrographs stained with OsO_4). [Reprinted by permission of the Royal Society.]

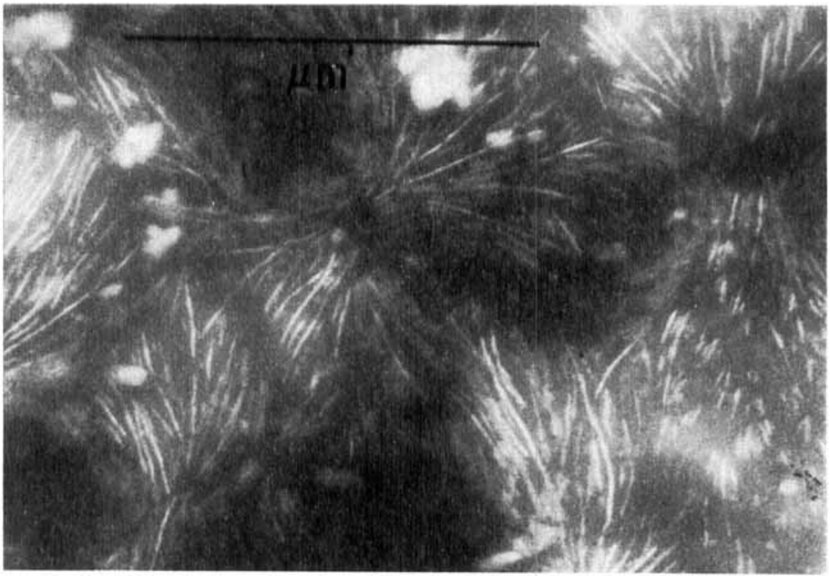

FIGURE 4b As Figure 4a, but in a film cross-linked by exposure to sulphur chloride vapour (after Owen[4]).

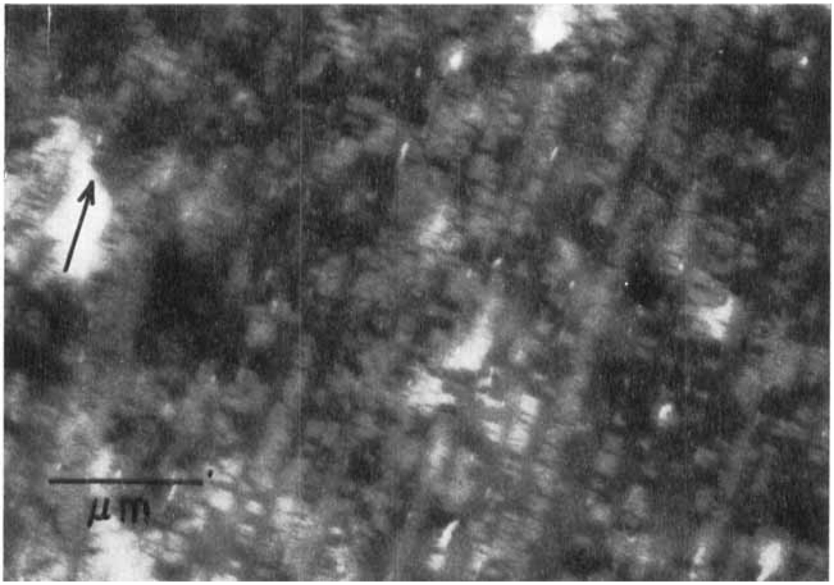

FIGURE 5a Row nucleation in a thin film of natural rubber crystallized at 300% strain (after Owen[4]).

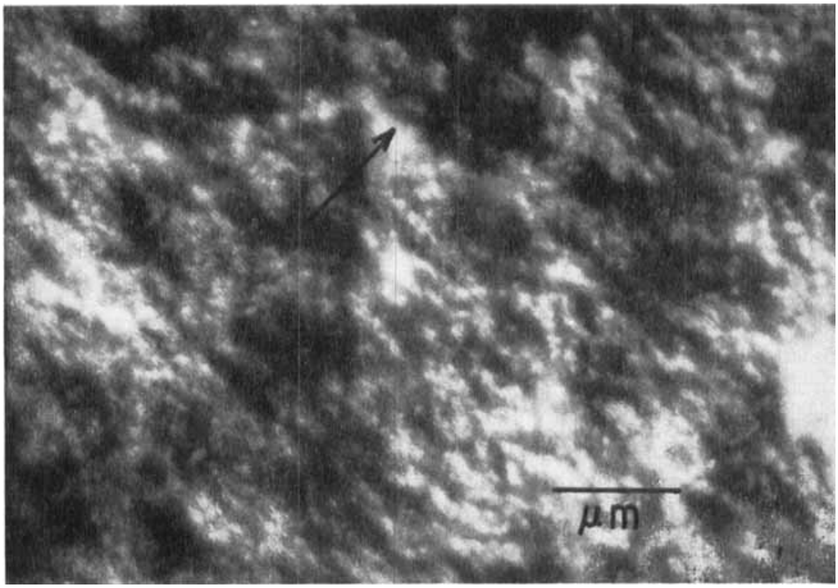

FIGURE 5b As Figure 5a, but in a cross-linked film (after Owen[4]).

At higher melt strains the density of row-nucleation increases, and the crystal melting temperature is elevated until spontaneous crystallization occurs at room temperature in a form described by Andrews[5] as γ-filaments (Figure 6). Alongside the obvious morphological changes associated with crystallization from a strained melt must be included the hidden morphological variable of molecular orientation in the amorphous phase.

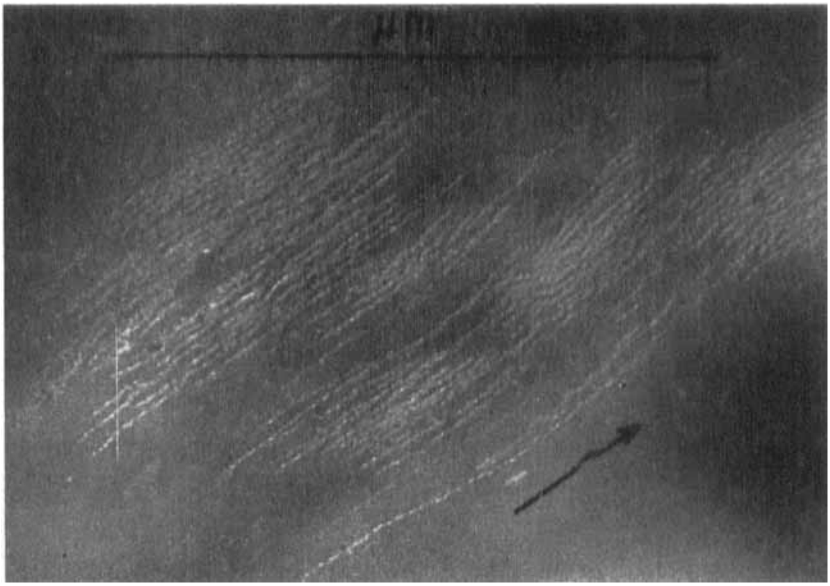

FIGURE 6 γ-filaments in thin film of natural rubber crystallized at 400% strain.

Figure 7 summarizes schematically the morphological effects of melt strain in natural rubber. In all cases the molecular chain axis is normal to the plane of lamellar crystals but lies parallel to the length of row nuclei and γ-filaments. This encourages the view that the lamellae are essentially similar to the folded-chain single crystals obtained by precipitation from dilute solution, and the variation in their thickness with crystallization temperature[2] reinforces this view. In the same way, row nuclei and γ-filaments are probably highly imperfect extended chain crystals as sketched in Figure 8. The row nuclei formed at intermediate strains (Figure 9 shows the early stages) are often very cleanly defined filaments of diameter as little as 3 nm. By contrast, γ-filaments are always particulate along their length[5,6] (Figure 6). This difference may well arise because the γ-filaments form very rapidly (almost spontaneously) whereas the rate of growth of row-nuclei at lower strains (although greater than that of lamellar crystals by a factor of 10^2) is still measurable[4] at some 100 μm/h. The degree of perfection is thus much lower in the γ-filaments.

The qualitative features outlined in Figure 7 are not restricted to *cis*-polyisoprene, but appear to be quite general for the melt crystallization of thermoplastics. Thus, almost identical patterns of behaviour have been found for isotactic PMMA, polycarbonate,[7] *trans*-polyisoprene,[8] *trans*-polychloroprene, isotactic polystyrene[9,10] and polyethylene.[9]

The quantitative aspects of row-nucleated morphology depend, of course, upon the amount of row nucleated material formed, since the row-nucleation density increases with time to a certain level and then remains constant. The final row nucleation density has been measured[4] for *cis*-polyisoprene as

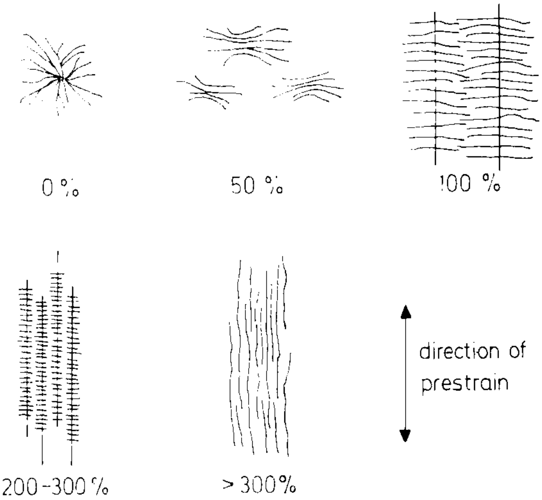

FIGURE 7 Morphological effects of melt strain in crystallized natural rubber (schematic).

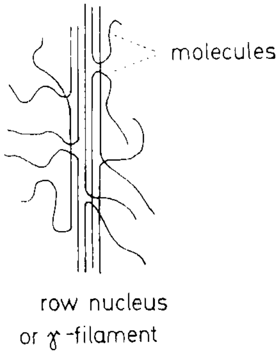

FIGURE 8 Possible structure of row nuclei and γ-filaments (schematic).

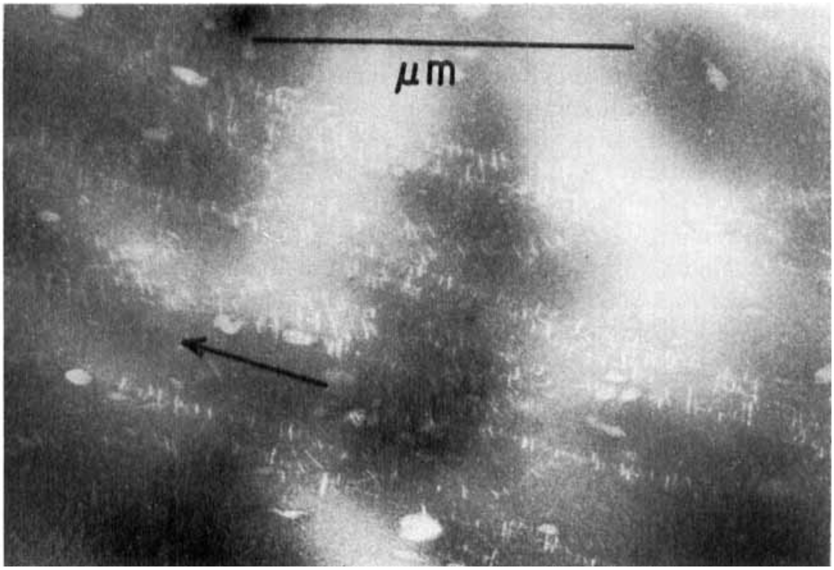

FIGURE 9 Early stages of row-nucleated crystallization showing row-nucleus.

a function of strain and temperature and is shown in Figure 10. The effect of strain is self-evident, but the effect of temperature is very interesting. As the melt becomes warmer the row nucleation density first decreases to a minimum around −12°C and then rises again. At high strains this rise is dramatic and clearly foreshadows the spontaneous γ-crystallization observed at slightly higher strains and temperatures.

3.2 Hydrostatic pressure

Finally in this section we refer to a different mechanical constraint which can be imposed upon the melt during crystallization, namely that of hydrostatic pressure. It has been established that, in linear polyethylene, crystallization under high pressure gives rise to a thickening of the normal folded-chain lamellae from a few hundred Angstroms to several microns.[11,12] The thickening at sufficiently high pressures and temperatures is such that the molecules unfold completely into an extended chain form. Material in this condition is extremely friable, i.e. has no mechanical strength, emphasizing the importance of inter-crystalline amorphous material in imparting the toughness usually associated with polyethylene.

Some preliminary experiments[13] have been carried out on the crystallization of thin films of natural rubber under gas pressures of up to 5 kbar. The most

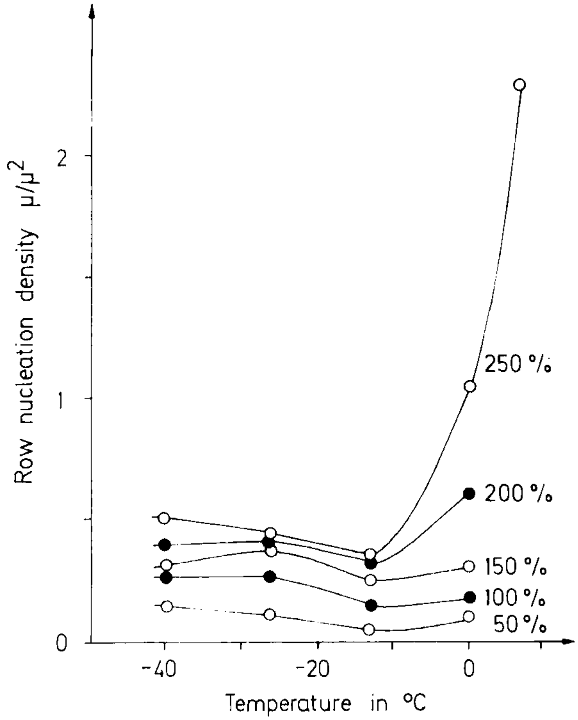

FIGURE 10 Final row nucleation density for *cis*-polyisoprene as a function of strain and temperature (after Owen[4]).

obvious effects are that the nucleation density is vastly increased so that unstrained films no longer exhibit a spherulitic habit but, instead, show a high concentration of separate single crystal zones shaped like oblate spheroids. Since there is good evidence[14,15] that the "aspect ratio" (length-to-thickness ratio) of lamellae in a bulk polymer strongly affect its elastic modulus, the destruction of the spherulitic habit by pressure could significantly affect mechanical properties. Needless to say, many polymer forming processes involve the application of hydrostatic pressure as well as shear stress.

4 MORPHOLOGY AND MECHANICAL PROPERTIES IN NATURAL RUBBER

4.1 The investigations

The investigations[16] detailed in this section, and carried out by Dr. P. E. Reed, were based on the thin film studies described in the previous section. Bulk

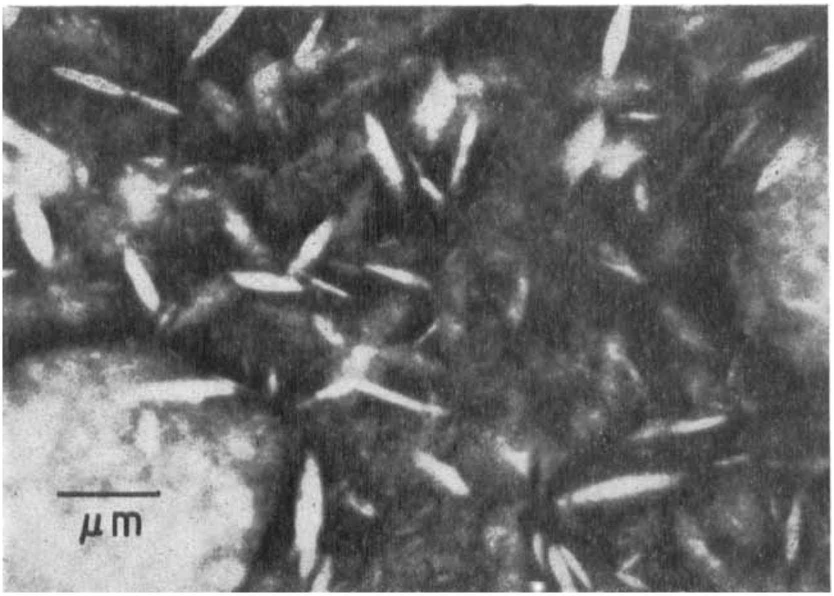

FIGURE 11 Thin film of natural rubber crystallized at 20°C at 4 kbar pressure. [After Andrews and Phillips.[13] Reprinted by permission of Wiley-Interscience.]

specimens of lightly cross-linked natural rubber were crystallized at −26°C under tensile strains ranging from 0 to 6 to develop the whole range of morphologies revealed by the thin film work. Crystallization was taken to completion in all cases giving a crystalline fraction of 0.3 ± 0.05 for all samples, and tensile tests were carried out at temperatures below −26°C covering both the rubber-like and glassy regions of the amorphous polymer (above and below −70°C respectively). From the stress–strain curves, mechanical parameters such as initial modulus, yield stress, fracture stress and fracture strain could be obtained.

Basic to this work is the assumption that the morphology in bulk is essentially similar to that in thin films for equivalent melt strains, apart from the "three-dimensional" character of the former. Thus, at zero melt strain we expect a spherulitic structure, at 50–100% spherulites flattened to bring their lamellar plane normals (molecular axis) towards the strain axis, at 100–400% cylindrical row-nucleated "shish-kebab" structures and at strains greater than 400%, γ-filaments. Because both lamellae and row nuclei are such small structures, thin sectioning of the bulk fails to reveal anything but a loss of spherulitic morphology with increasing strain. However, both light scattering[17] and X-ray[6] studies (of polychloroprene) provide strong indirect evidence that bulk morphologies correspond closely to their thin film counterparts at equivalent melt strain.

Reed's collected data for the mechanical properties of crystalline natural rubber is shown in a series of three-dimensional graphs, Figures 12 to 16. Each diagram shows one mechanical property (e.g. fracture stress) plotted vertically as a function of pre-strain (i.e. melt strain, the "morphological variable") and of the temperature of testing. The results will be discussed separately.

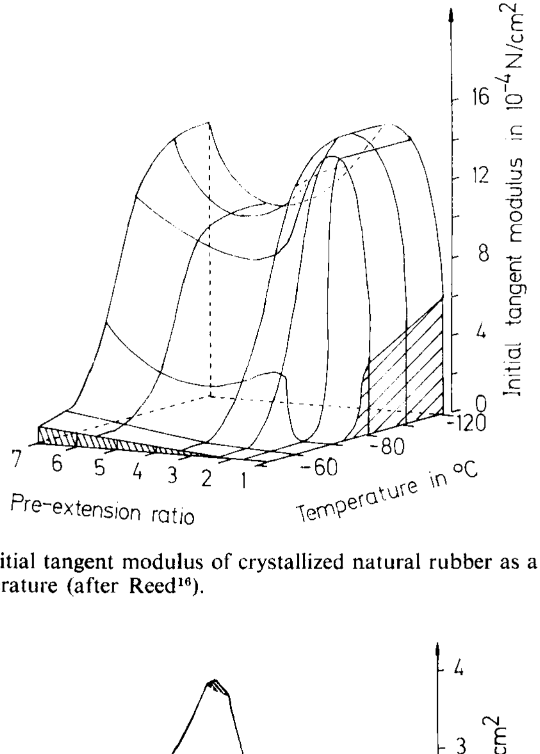

FIGURE 12 Initial tangent modulus of crystallized natural rubber as a function of pre-strain and temperature (after Reed[16]).

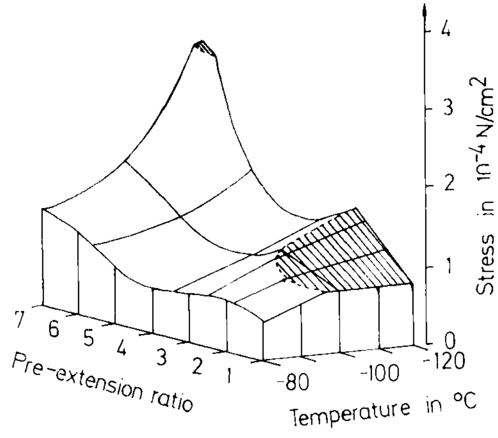

FIGURE 13 As Figure 12, but for yield and brittle fracture stresses of crystallized material (after Reed[16]). Yield surface shown plain, brittle fracture surface shaded.

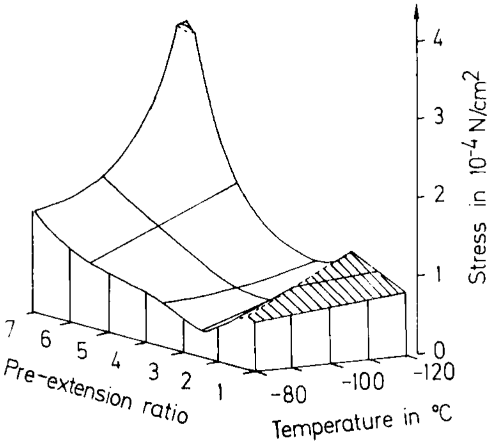

FIGURE 14 As Figure 13, but for amorphous material (after Reed[16]). Yield surface shown plain, brittle fracture surface shown shaded.

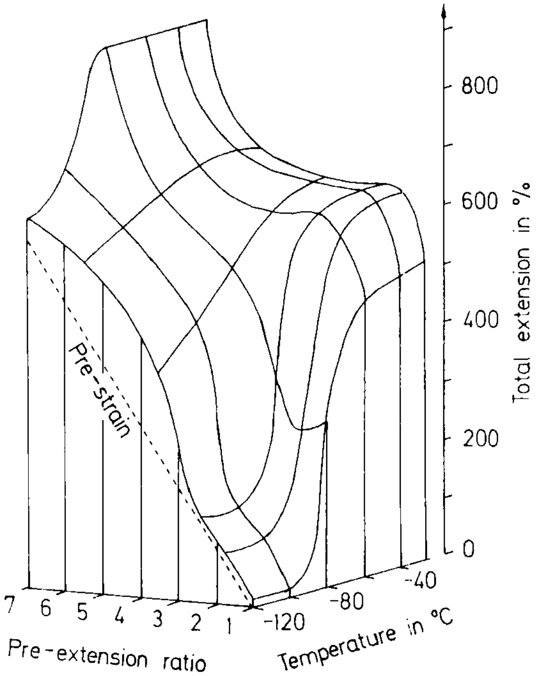

FIGURE 15 As Figure 12, but for total breaking strain (after Reed[16]).

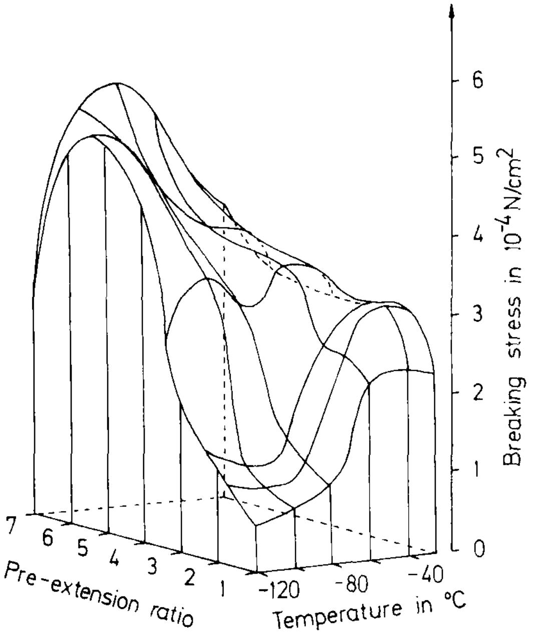

FIGURE 16 As Figure 12, but for true breaking stress (after Reed[16]).

4.2 The initial modulus

The initial tangent modulus to the stress–strain curve is shown for crystallized specimens in Figure 12. Spherulitic material (corresponding to pre-extension of 0% strain or extension ratio of unity) deforms in an essentially rubberlike manner above −60°C, although its modulus is an order of magnitude greater than that of non-crystalline material. (On the scale of Figure 12 both these moduli are of negligible magnitude). There is evidence from other sources[15] that the moduli of spherulitic polymers is strongly affected by detailed spherulite structure such as the lamellar aspect-ratio referred to earlier. The morphological evidence (Figure 4b) thus suggests that cross-linked rubber, with discontinuous lamellae, should have a significantly lower modulus in the spherulitic form than uncross-linked material. This accords with the observation that raw rubber increases its stiffness by at least two orders of magnitude when crystallized spherulitically compared with the tenfold change found here.

As the pre-extension increases, the morphology changes from spherulitic to row-nucleated and finally to γ-filaments, but the progressive rise in initial modulus above −40°C can be attributed almost wholly to the increased orientation of the amorphous phase.

At an intermediate temperature of, say −60°C, the effect of changing morphology is more dramatic, the modulus rising very sharply on the establishment of row-nucleated structures in place of spherulites, but thereafter remaining fairly constant. It is suggested[18] that this is due to a "fibre reinforcement" mechanism in which the "shish-kebabs" act like oriented stiff fibres embedded in soft matrix. The effect fails to manifest itself at higher temperatures because the amorphous matrix is too soft, and fails to transmit significant shear stress from one "fibre" to another (this stress transmission is important because the fibres are discontinuous). At −60°C the amorphous material is entering its glass transition range and losing its rubbery character.

Once the amorphous phase is fully glass-like (below −80°C), the dependence of modulus on morphology follows a pattern which is not greatly affected by further reduction in temperature. The glassy state modulus of spherulitic polymer increases only twofold as the morphology is transformed to a row-nucleated form. That this increase can be attributed wholly to amorphous orientation has been convincingly demonstrated by studies on polychloroprene.[6] Clearly the elastic constants of the glassy and crystalline phases are now sufficiently alike for no "fibre reinforcement" to be observed. What is observed, however, is a wholly unexpected *decrease* in modulus with the establishment of the row-nucleated morphology above 100% pre-strain. This could be due to any of three causes.

Firstly, Reed[16] has shown that crystallization, under constant strain, into a row-nucleated morphology results in a relaxation of molecular orientation in the amorphous regions between lamellae. The *amorphous* orientation thus actually decreases with increasing pre-strain during the establishment of row-nucleated morphologies. This would reverse the trend observed for small pre-orientations, but would not really explain the persistence of the downturn in modulus up to high pre-extensions.

Secondly, the lamellar orientation having now become uniformly transverse to the direction of testing, it could be argued that fibre reinforcement effects are minimized. Reed[16] found, however, that specimens tested at different angles to the direction of pre-extension showed very little difference in modulus at −120°C, even when the angle was 90°. This shows that no "fibre reinforcement" occurs with lamellae in a glassy matrix as already proposed above.

Thirdly, it is possible that the mutually aligned lamellae in row-nucleated structures are able to deform co-operatively by crystallographic mechanisms (e.g. [001] slip) to increase the compliance of the bulk. Until mutual alignment is achieved such deformations are relatively ineffective (e.g. in the randomness of the spherulite), but a stack of parallel crystals can deform "as one". Since the lamellae are reasonably extensive at intermediate pre-extensions they effectively separate the glassy matrix into "slices" perpendicular to the tensile axis, so that the matrix has relatively little ability to constrain the deforming crystals. As the row nuclei become more closely spaced with increasing pre-extension the horizontal continuity of the lamellar array diminishes and the matrix exerts a more effective constraint. This, together with the continuing rise in amorphous orientation, eventually causes the modulus to rise again at high pre-extensions.

This explanation of the dependence of modulus on morphology, although qualitative, is in reasonable accord with our present understanding of strengthening mechanisms in two-phase systems and opens the way to more quantitative investigations.

4.3 Yield and brittle fracture stresses

In the glassy region, below −80°C, the stress–strain curves of both crystallized and amorphous natural rubber exhibit either brittle fracture or yield followed by strain hardening, according to the temperature and pre-orientation. Reed's data[16] for crystallized and amorphous rubber respectively are given in Figures 13 and 14. For pre-extensions above 300%, where spontaneous crystallization occurs during pre-extension, the data for the amorphous glass have been extrapolated algebraically. The regions of morphology and test temperature over which brittle fracture occurred are shown shaded. The testing rate was held constant throughout.

The differences between Figures 13 and 14 are not great, indicating that brittle fracture, yield and strain hardening are all strongly affected by amorphous orientation in low crystallinity polymers. This is further borne out by studies[6] on polychloroprene at 18% crystallinity. At higher crystalline content, we have shown elsewhere[18] (for polyethylenes) that inter-lamellar attachments play a much stronger part in determining yield behaviour.

Closer inspection of Figures 13 and 14 naturally reveals differences between the crystalline and amorphous cases. At low pre-extensions the brittle-ductile transition temperature is suppressed by the presence of crystallinity from −80°C to about −95°C. This is almost certainly due to the contribution of some low-stress ductility by the crystals. The second difference is that the shallow minimum which occurs in the yield stress as pre-extension increases, falls at a pre-extension ratio of 4 for the crystallized material but at 2.5 to 3.5 for the oriented amorphous specimens. This may again be explicable in terms of amorphous orientation since, as pointed out earlier, the local orientation in the amorphous phase of row-nucleated crystalline structures relaxes to a condition appropriate to a lower-than-nominal pre-extension.

If λ_s is the pre-extension ratio, Reed[16] calculated that the residual amorphous orientation in a row-nucleated specimen after crystallization would be,

$$\lambda_{AR} = 4.41\lambda_s/(6.3\text{–}0.3\lambda_s)$$

which gives $\lambda_{AR} = 3.5$ for $\lambda_s = 4.0$ in good agreement with the shift of the minimum, at least at the lower temperatures. The occurrence of a minimum in yield stress thus appears to relate solely to amorphous orientation.

The third difference between amorphous and crystallized material is the rise in yield stress in the latter at large pre-extensions and low temperatures. This is perhaps directly attributable to the γ-filaments which we have suggested contain a large proportion of extended chain material. Whilst we have seen that crystals in a glassy matrix provide no reinforcement of modulus (because the elastic constants of the two phases are too similar), the γ-filaments *can* provide considerable strengthening when the glassy matrix begins to flow, providing of course, the γ-filament itself does not yield. This reinforcement-against-yield will be greater with γ-filaments than with lamellar structures because (a) [001] or chain-axis slip will be easier in the latter and (b) because gross tensile deformation causes buckling of lamellae and rapidly brings the [001] direction into the plane of maximum shear stress; in contrast, γ-filaments will not tend to re-orient as a consequence of matrix flow.

It is likely that the yield phenomena discussed here are all associated with shear yielding. At lower temperatures Reed and Natarajan[19] have shown that a new mechanism of yielding (that of crazing) comes into play in natural rubber, and the competitive nature of these two yielding mechanisms has been widely recognized in glassy polymers.[20]

4.4 Breaking stress and strain

Figures 15 and 16 show the breaking strain and stress respectively as functions of the usual variables for crystallized material. In the experiments, specimens are deformed in two stages, namely pre-extension to produce variable morphology and deformation during test. The variable of real significance is, of course, the total strain accommodated by the specimen before fracture and in Figure 15, therefore, is plotted this total strain given as the pre-extension plus the deformation during testing.

Plotted in this way it can be clearly seen that the fracture strain has a "plateau" value of some 600% over most of the experimental range except for two regions. The first of these is the region of brittle behaviour already noted at low temperatures and low pre-extensions. Here very little extension occurs during test, the total strain deriving almost wholly from the room-temperature pre-extension. The second exception occurs at high pre-extension and temperatures above T_g where total extensions up to 900% are consistently recorded. This improvement in extensibility occurs with a morphology of γ-filaments in a rubberlike matrix and almost certainly results from a fibre strengthening mechanism which inhibits crack propagation normal to the fibre (γ-filament) axis. This mechanism is familiar in materials such as wood and arises from the relative weakness of inter-fibrillar bond which encourages longitudinal fibrillation and blunts transverse cracks.[21] Reed[16] obtained striking fibrillation effects in specimens with very high pre-orientations.

Whilst the total extensibility of non-brittle specimens does not vary by a factor of more than 1.5 (and then only at high pre-extensions), the associated fracture stresses display drastic variations with morphological changes. This can be seen from Figure 16, where the load-bearing capacity nearly doubles at large pre-extensions as the temperature falls from −26°C to −120°C, and, at low temperatures, increases tenfold as the morphology changes from spherulitic to γ-filamentous. The breaking stress in Figure 16 is in all cases corrected for changes in specimen cross-section, i.e. it is the true load-bearing capacity of the material at the point of fracture.

At temperatures well above T_g, the breaking stress is fairly independent of pre-extension. Here the stress–strain curves are rubberlike and the morphology must undergo severe deformation before fracture. Since the actual fracture stress is independent of starting morphology, it is probably governed entirely by the amorphous matrix.

At low pre-extensions (up to $\lambda_s = 3$), the effect of reducing temperature through T_g is to produce embrittlement. Fracture here occurs in relatively poorly aligned material and the ultimate load-bearing capacity is understandably low. As pre-orientation increases, however, there is a rapid increase in the low temperature strength until (at $\lambda_s > 5$) reductions in temperature actually *increase* the strength of the material to a maximum before embrittlement once again causes a reduction. In the high strength region of Figure 16 the stress–strain curve, typically, exhibits yield and immediate, rapid strain hardening. As strain hardening becomes increasingly severe (with further reduction in temperature or increase in λ_s) the break in the stress–strain curve at yield is eliminated and brittleness again supervenes (Figure 17). This rapid strain hardening is typical of crystallized material and is not found in oriented amorphous polymers. It is thus attributable directly to the crystalline morphology.

The strength rise at −120°C with initial pre-orientation is apparently associated with a rise in yield stress (see Figure 17). Incipient yield appears to lead directly to fracture, and earlier these fractures were classified as brittle because there is no post-yield extension. Such a rise in yield stress can be attributed to amorphous orientation alone, although parallel tests on non-crystalline specimens showed that the latter always yielded at lower stress than the crystallized ones. Once yield is fully established, with significant post-yield deformation, the high breaking stress of the crystallized material is obviously a direct result of strain hardening (Figure 17) which occurs far less rapidly in amorphous material. What is the cause of this strain hardening?

It has already been suggested that yield in the crystalline phase is progressively suppressed as lamellar or "shish-kebab" structures give way to

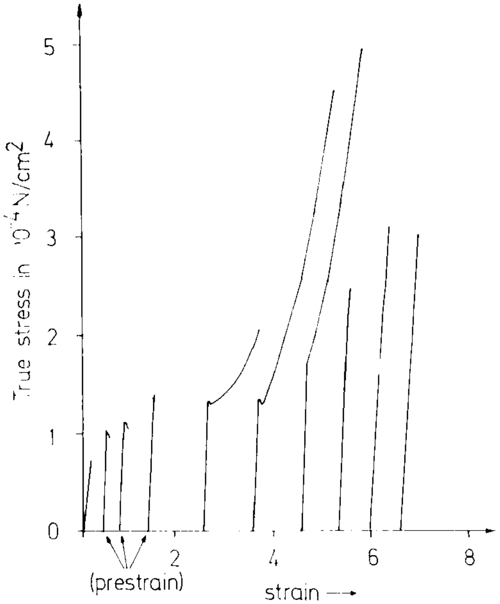

FIGURE 17 Stress–strain curves for pre-oriented and crystallized natural rubber tested at −120°C (after Reed[16]).

extended-chain or γ-filament fibrillar morphologies. Since the yield stresses for amorphous and crystalline specimens are not very different in the intermediate range of pre-extensions, it seems likely that here, at low temperatures, the onset of yield is controlled by the glassy phase. As significant plastic deformation accumulates, however, the glassy phase can only continue to deform if the attached crystalline material also deforms to accommodate the change of shape. Whilst this is relatively easy for lamellar crystals, it becomes progressively more difficult as the crystalline phase assumes a fibrillar character. This mechanism has already been invoked to explain the rise in yield stress at high pre-extensions and extends naturally to the post-yield region. A further factor may be the increased amount of inter-fibrillar connection as the γ-filaments become more closely packed with increasing pre-extension.

Eventually the strain-hardening mechanism is self-defeating; the material becomes so inextensible that it becomes prey to weakening by flaws, lacking any plastic flow to blunt incipient cracks. A new brittle condition is thus established and the strength falls drastically at $\lambda_s > 6$.

5 CONCLUSION

The detailed discussion of *cis*-polyisoprene has illustrated the validity of the original proposition, namely that the properties of polymeric solids depend upon their structure *at all levels* and not solely upon their molecular structure. The complexity of the data given in Figures 12–16 underlines the difficulty of providing simple rules in this area of structure–property relationships. Appeal has to be made to the anisotropic responses of both crystalline and amorphous phases to stress and, additionally, to specific mechanical interactions between the phases. It is in this latter area, for example, that molecular weight probably exercises a profound influence on mechanical behaviour.

The work reported here, then, represents just a fraction of the painstaking task of "mapping" properties in the multi-dimensional reference frame of structure. It is only as we continue this mapping that a rational and consistent picture will emerge.

One particular feature of the present paper is the necessity to appeal frequently to the concepts of composite material theory in seeking to explain the effects of morphology upon properties.

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