Some Physical-chemical Transitions in Fibre Structure*

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Fibres are partially crystalline, partially oriented linear polymer materials, which can exist in a variety of metastable states. This, and the diversity of possible structural forms, is the reason why there are many transitions, which often have interesting features. The structural complexity arises from the many forms which give partial crystallinity, ranging from a uniform intermediate state to a mixture of crystalline regions of particular shapes, separated by and linked with and through chain segments in non-crystalline regions. The diversity of structure has been reviewed by HEARLE and GREER[1].

This paper will comment on several transitions which are both of scientific interest and of technological importance.

The dependence of mechanical properties of wool on a crystal lattice transition

Wool, as part of an immense complexity of structure at all levels from the chemical composition of the proteins to the gross features of the fibre, is thought to contain

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crystalline microfibrils, about 7.5 nm in diameter, spaced at intervals of about 10 nm in a matrix which can be regarded as a rubber so highly cross-linked that it contains about two random links between network points.

In the unstrained state, the crystal lattice in the fibrils is a slightly distorted α-helix, with hydrogen bonding between the chains of the helix, but under axial stress it transforms into an extended chain lattice with hydrogen bonding between chains. Except for the fact that it is initiated by a directional stress, this is like any other crystalline phase transition and will be characterised by an equilibrium stress at which the two forms exist together, as described by Ciferri[2], and a critical stress for the nucleation of the new lattice. In current work, we have found, as would be expected, that the equilibrium stress is temperature dependent, but is substantially independent of rate, and the critical stress is both temperature and rate dependent.

In an isolated fibre, the stress would drop from the critical value to the equilibrium value once the transition had started, and a single zone of the extended chain lattice would grow as extension proceeded further. But in the fibre system as a whole, Hearle and Chapman[3,4,5,6] have shown that stress transfer from the fibril to the matrix limits the size of zone which can grow without forcing the stress to rise above the value for fresh nucleation elsewhere. The transition thus proceeds in separate zones along the fibril. The elucidation of this behaviour, which explains the observed mechanical properties of wool and replaces some older, rather artificial theories, demonstrates the need for combining realistic study of the physical-chemical behaviour of the structural elements of fibres with realistic study of the mechanics of composite systems. The stress-strain curves of the structural elements, of the whole system, and of an actual fibre are shown in figure 1.

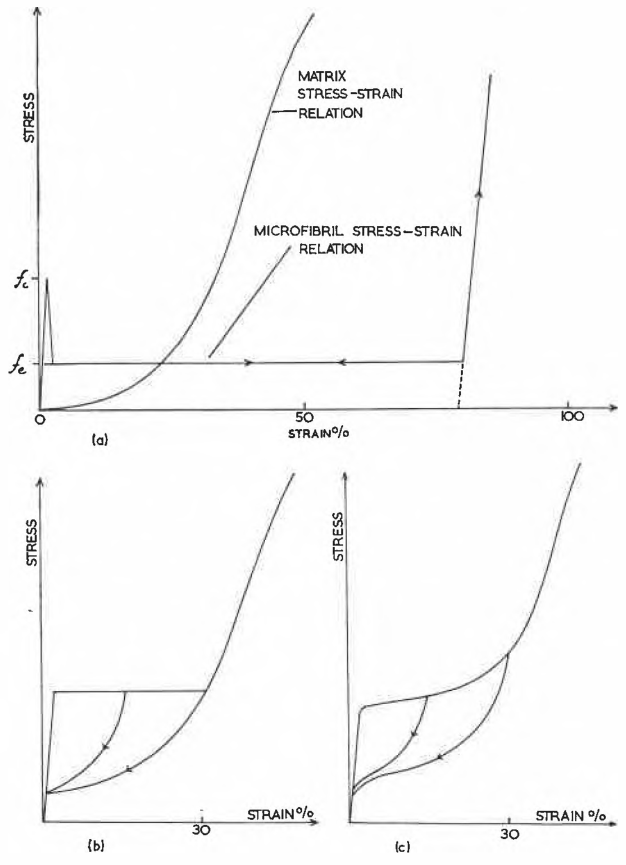

Figure 1. (a) Stress-strain properties of individual structural elements of wool. (b) Stress-strain curve predicted by model. (c) Typical stress-strain curve of wool fibre: some of the differences from the predicted curve are due to fibre irregularity

"Second-order transitions" in synthetic fibres

In simple amorphous polymers there is a well defined glass-to-rubber transition, which occurs without change of structure, but reflects a change in response of the system from rigid to flexible. The thermodynamic nature of this transition is debatable. Fundamentally, it seems possible to postulate a sharp second-order transition for an isolated chain which occurs when there is a catastrophic mutual failure of barriers to rotation all along the chain. This demonstrates indeed a weakness of the rotational isomerism model of Volkinstein[7], in that the barriers which define the separate isomeric states are no longer present when there are appreciable jumps between the isomeric positions.

However, in real solid polymers, there is a variable local environment and so the transition is less sharp. In practice it is a time-dependent phenomenon, reflecting the situation when there is sufficient mobility in the system to be apparent at the time-scale of any particular experiment.

In polyamides, which are typical synthetic fibre materials, and also in polyesters, the situation is more complicated first because the transition is only in the non-crystalline part of the whole fibre (and there may be other transition in the crystal) and secondly because transition gets split into two parts as shown in figure 2. The first loosening of the very low temperature rigidity occurs below room temperature in two minor transitions when the $-CH_2$-chain sequences develop freedom of bond rotation. The more severe loosening comes when the hydrogen bonds between the $-CO \cdot NH-$ groups cease to hold and go into a state of dynamic equilibrium. The latter transition is not very cooperative—the bonds can break individually—and so gives a broad transition region, akin to a dissociation phenomenon.

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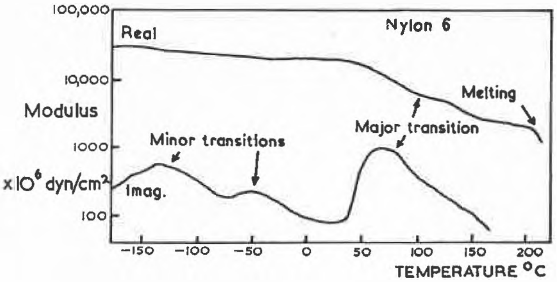

Figure 2. Transitions in nylon 6 as observed by Takayanagi[10]

Transitions of this sort are important in fibre technology. The freedom of movement at room temperature gives toughness, without too much softness, to the structure. Any transition also gives possibilities of setting, either advantageously or as a nuisance since the structure will lock into a deformed position if it is cooled down through a transition zone into a rigid state. Since there is no change in basic structure, the set is reversible and temporary.

Melting behaviour

Permanent setting is brought about by changes in the crystal size and morphology within the fibres. The small, imperfect crystals forced by rapid quenching or drawing can be melted at lower temperatures, with growth of larger and better crystals. This is the annealing process. Treatment at successively higher temperatures, melting gradually larger, more perfect crystals, can be used where several setting processes are needed in a complete manufacturing sequence.

As would be expected the melting (setting) temperature is highly dependent on the moisture content of the fibre. There is also an effect of directional stress, due to the influence of an additional term in the entropy change. In the ordinary way, one writes an expression for melting temperature T_m as:

$$T_m = \Delta U / \Delta S,$$

where ΔU is the internal energy change and ΔS is the entropy change for material going from crystal to melt.

But in the polymer system we have the situation indicated in figure 3. The entropy change must be taken as:

$$\Delta S = \Delta S_1 + \Delta S_2,$$

where ΔS_1 is the entropy change for the actual material going from crystal to melt, and ΔS_2 is the entropy change of the linked chain proceeding to another crystalline region, and able to take up a more disordered conformation.

The term ΔS_2 will be dependent on the stress-strain state of the material.

There have been many reports of two different forms of polyamide and other polymer structures, dependent on their heat treatment. The experimental evidence, based on the work of Bell[8], is reviewed by Hearle and Greer[1]. Briefly, rapid quenching yields form I, while slow cooling or annealing yields form II. Form I has a single temperature (256 °C in nylon 66) at which a melting endotherm appears, but the endotherm for form II, which might be expected to be more stable, occurs at a lower temperature (234 °C or less), although prolonged annealing causes it to rise eventually to a value higher than for form I.

The results have recently been criticised as being due to recrystallisation in the differential scanning calorimeter[9], but there are, without doubt, very distinct differences between the forms.

Figure 3

There is also controversy over interpretation. Hearle and Greer[1] have pointed out that the observed transitions in different circumstances would be explained by a free energy diagram as shown in figure 4, with the rider that there was a large barrier to be surmounted before form II could be obtained, but only a low barrier between the melt and form I.

The different lines for form II represent the usual effect of changing size and perfection of crystals, and it is suggested that form II is a fairly typical assembly of separate crystalline regions.

The suggestion for form I is that it is a more uniform structure in which many individual chain segments are in crystallographic register with neighbours, but there are no separate crystalline regions. Viewed in terms of formation from the melt, it would be seen as a lowering of internal energy, by chain segments "grabbing" their neighbours without long-range movement. Viewed in terms of formation from form II, as can occur on annealing above the form II melting-point, it might be seen as a "shuffling" of chains past one another as thermal

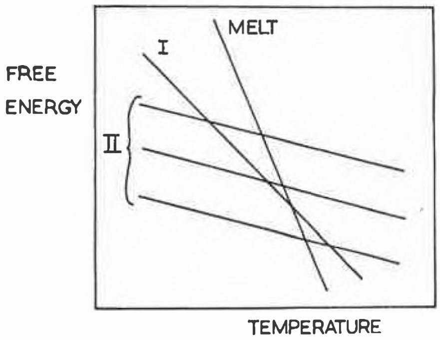

Figure 4

Figure 5

vibrations increase, with some preferred increase in entropy, but without too much loss of internal energy. The situation may be compared to a line of separate packs of cards as in figure 5 (a): there would be little loss of surface contact, but considerable increase in disorder, if the layers of cards were randomly translated with respect to one another, as in figure 5 (b).

Whatever explanations emerge in future, and whatever new experiments show up, the melting behaviour of fibrous polymers like the other transitions, is certainly a matter of interest and complexity.

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