

A BRIEF DESCRIPTION TO THE AVRAMI THEORY

The kinetics of crystallisation in bulk systems is important for the science and engineering of materials, namely crystalline polymers. Suppose that a crystalline body, either a single-crystal or an assembly of crystallites such as spherulite or cylindrite, is nucleated and grows in a free space. The volume of crystal, V can be simply given by:

$$V = a(kt)^n \quad (1)$$

where, a is the shape parameter of the growing body, k is the linear growth rate and n is the integer constant which takes 1, 2 and 3 for one- two- and three- dimensional growths, respectively. The parameter k is, for instance, $(4/3)\pi$ for a sphere, $\sqrt{2}/3$ for an octahedron, etc.

What happens when more than two crystalline bodies grow in a space? Soon or later, they will collide with each other and for each growing body Eq.(1) will no longer hold. This problem was studied since 1930s by Avrami and others, leading to a mathematical formula. One approach is as follows.

Let us assume that crystalline bodies are distributed randomly in a system. Even though the growing fronts exist only on the surface of the bodies, the place to find a growth point of infinite size, dV , in the space is regarded also random. Then, at the moment when the extent of the transformation is X ,

$$dV / dX = 1 / (1 - X) \quad (2)$$

By integrating Eq.(2), setting $V=0$ at $X=0$, and introducing the relationship of Eq.(1),

$$1 - X = \exp(-Kt^n) \quad (3)$$

or $\log \{-\ln(1 - X)\} = n \log(t) + \log(K) \quad (4)$

where, K is the product of a , k and the number of nuclei. “ n ” is called the Avrami-exponent. The expression of Eq(4) is conveniently used to fit experimental data and obtain the values of n and K .

The above assumes the ‘predetermined’ nucleation in which the embryos of nuclei exist in the system and they are activated simultaneously at time zero. This condition applies, at least at a first approximation, to many crystalline polymers. In fact, a trace of impurities such as those from polymerisation catalysts act as nuclei and, on occasion, nucleating agents are deliberately added to

facilitate the nucleation. When the system is pure, time-dependent ‘sporadic’ nucleation becomes significant and, for such a case, some theory predicts that Avrami-exponent increases by unity.

One interesting property of Eq(3) pointed out by the present author is that, at the maximum of dX / dt , X takes a unique value which is dependent only on n but is independent of K .

By differentiating Eq.(3) twice,

$$dX / dt = Knt^{n-1} \exp(-Kt) \quad (5)$$

$$d^2 X / dt^2 = Kt^{n-2} \cdot \exp(-Kt) \cdot \{(n-1) - Knt\} \quad (6)$$

By setting $d^2 X / dt^2 = 0$,

$$Kt = (n-1) / n \quad (7)$$

By introducing the relationship of Eq.(7) into Eq.(3),

$$X = 1 - \exp\{-(n-1) / n\} \quad (8)$$

Thus, $X = 0.39346$ and 0.48658 for $n = 2$ and 3 , respectively.

For polymers, common growth morphology is spherulite. A cylindrite formation is realised only when a needle-shaped nucleus exists and epitaxial growth takes place. An example was the case when the nucleus was polyoxymethylene whisker and the matrix was polyacetal resin (polyoxymethylene). Similar overgrowth crystallisation is observed also in systems in which graphite fibre is embedded in polypropylene or high-density polyethylene.

EXPERIMENTAL METHODS TO FOLLOW THE CRYSTALLISATION PROCESS

For polymers, dilatometry was traditionally used to trace the volume shrinkage (or expansion in rare cases) that occurs during crystallisation. The use of DSC (differential scanning calorimeter) for measuring the exotherm became common since late 1960s. In either method, the system is first brought above the specimen's melting temperature and then moved fast to a certain temperature below the melting temperature so as the crystallisation takes place isothermally at a constant linear growth rate. The temperature dependence of the growth rate is a matter of interest but not discussed here. Visually, the growth of polymer crystals can be observed under the polarising microscope equipped with a heat-control device. Generally, a birefringent crystal is observed in bright white colour when its main axis is set parallel to the axis of cross-nicol. As the setting angle deviates, the object turns dark and is completely unseen when the angular difference is 45 degrees. Thus, a spherulite which is presumed to consist of numerous crystallites shows a 'Maltese-Cross'. If a retardation plate is inserted in the light path between the polariser and analyser, the field is coloured and the polarity of birefringence can be determined from the colour change of the object.

It should be remembered that, when the crystallisation is conducted between glass plates, under the microscope, the growth directing perpendicular to the glass planes is restricted and accordingly the actual growing bodies are two-dimensional, the basic forms being a disc and a rectangle plate, for spherulite and cylindrite, respectively. The demonstration programme applies to this case.

REFERENCES

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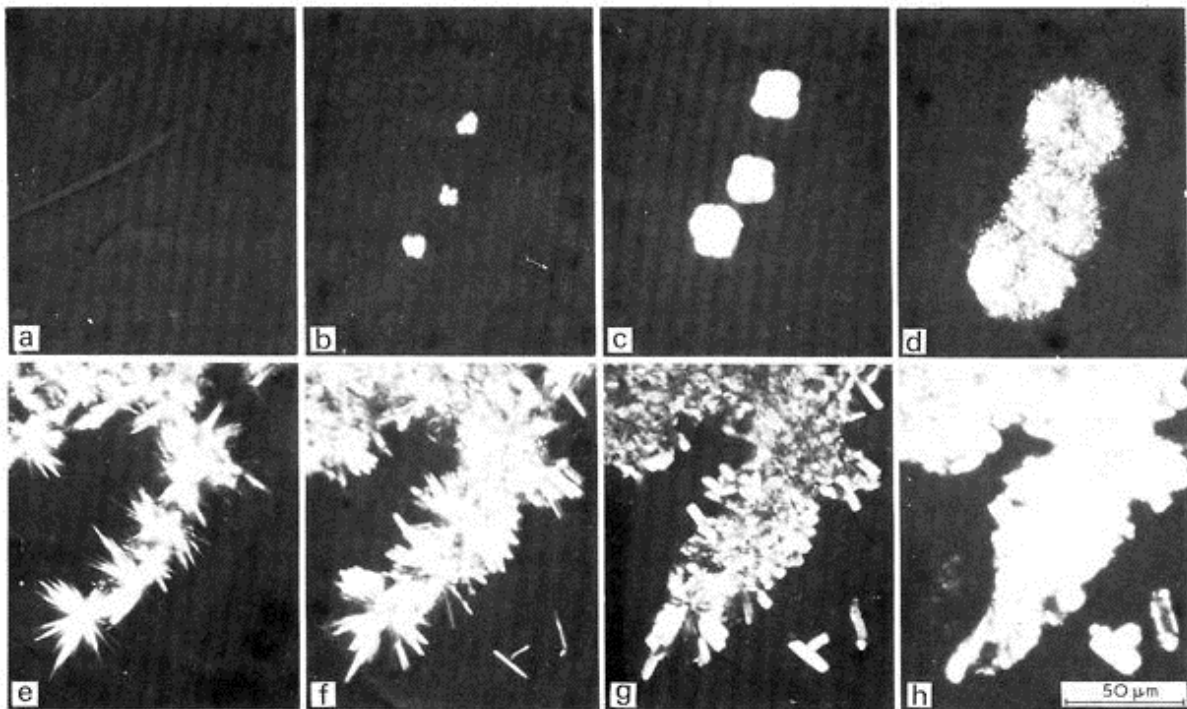


Figure 1 Polarized micrographs of Delrin crystallizing in isothermal conditions, (a)–(d) without needle shaped crystals at 432.5K and (e)–(h) with needles at 435K. (a) 0 min; (b) 5 min; (c) 8 min; (d) 12 min; (e) 0 min; (f) 2 min; (g) 4 min; (h) 6 min

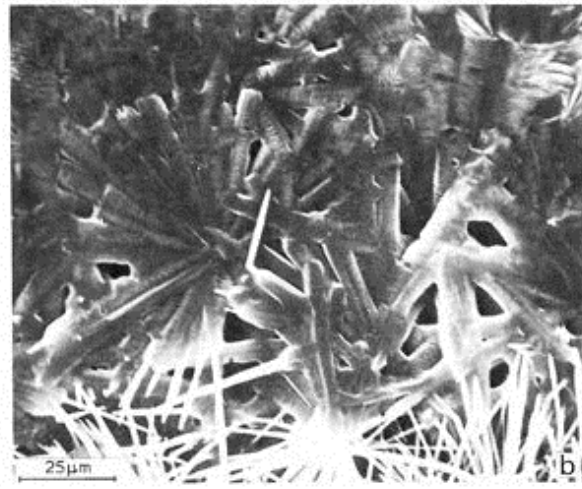
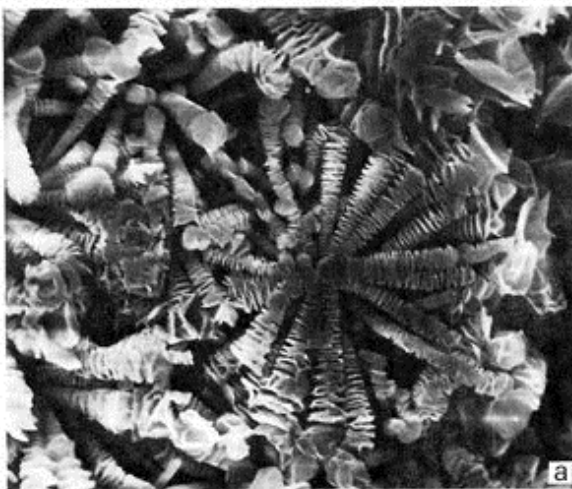


Figure 2 Scanning electron micrographs of: (a) 'shish-kebab' structures formed from 0.1% bromobenzene solution of Delrin on needle shaped crystals; (b) Delrin melt crystallized at ~436K over needles

Source: Ref.1

Original needle-like crystals formed an assembly radiating many pieces together from a centre. They were isolated and dispersed in a polymer matrix for kinetic experiments.

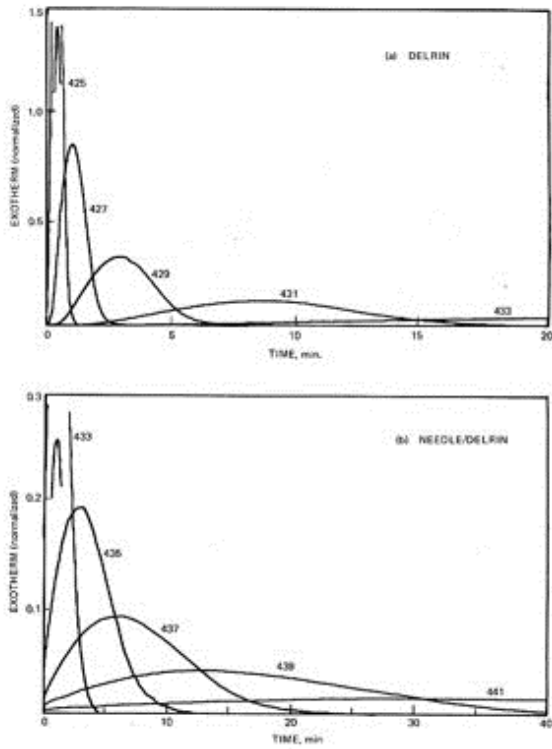


Fig.1 DSC crystallisation isotherms of Delrin at various temperatures, (a) without needle-like crystals and (b) with 1% needles embedded. The curves have been normalised to the unit area. The figures denote crystallisation temperatures (K).

Source: Ref.2

Embedding polyoxymethylene whiskers of in the molten Delrin (chemically the same polymer) was possible as the melting temperature of the former was much higher by virtue of its crystalline perfection.

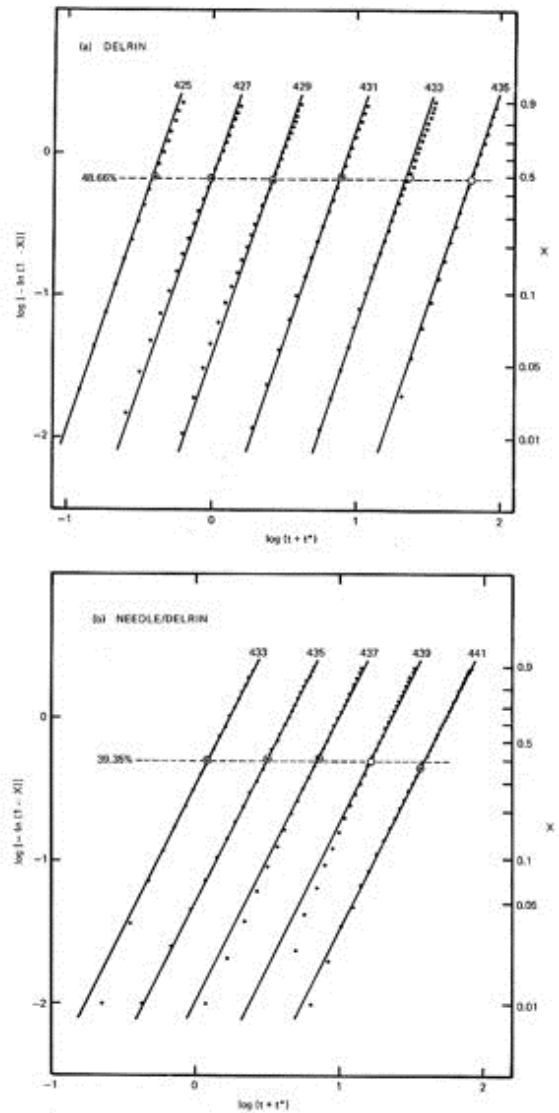
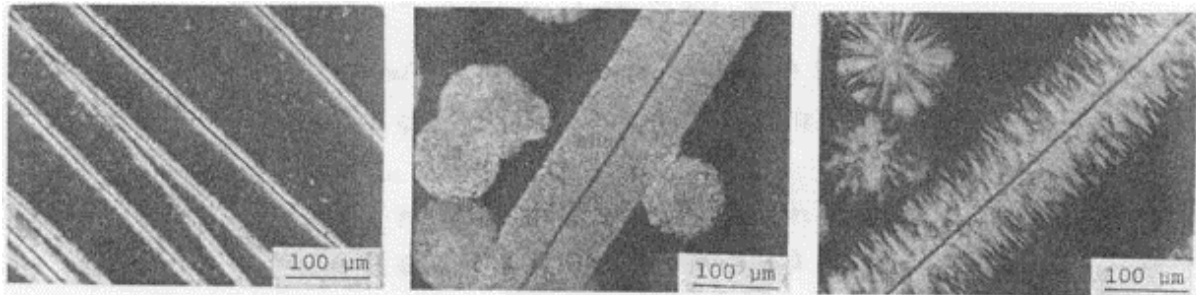


Fig.2 Double-logarithm plots for the crystallisation of Delrin, (a) without needle-like crystals forming spherulites and (b) with needles embedded forming cylindrites. The lines have been drawn with slopes 3 and 2, in (a) and (b), respectively.



(a)

(b)

(c)

Figure 1. Polarized micrographs of cylindrical growth around carbon fibers in isothermal conditions,
(a) polyethylene, 126°C, (b) polyoxymethylene, 165°C, (c) polypropylene, 130°C.

Source: Ref. 3

In (b) and (c), scenes in which both cylindrites and spherulites had appeared were chosen and photographed, although the former type growth were predominant in the presence of carbon fibres, especially at those rather high temperatures.