

Theoretical Equation for Rate of Crystallization - I. M. Hodge

The recent problem with cyan crystallization in donors has focussed attention on crystallization kinetics and the factors that affect them. This has been a concern of metallurgists and glass scientists for a century or more, and some theoretical results are available. An equation due to Turnbull is usually referred to as the "classical" expression for crystallization kinetics, and has provided qualitative insight into the cyan crystallization problem. We discuss the results given in a 1969 review by Turnbull[1].

The rate of crystallization I , in $\text{cm}^{-3} \text{sec}^{-1}$, is given by

$$I = nK \exp\left(\frac{-b\alpha^3\beta}{T_r \Delta T^2}\right) \quad (1)$$

where n is the number of molecules per unit volume in the sample (typically 10^{21}cm^{-3}), k is the frequency at which a molecule jumps across the liquid-crystal interface (a function of temperature, see below), b is a geometric constant ($16\pi/3$ for spheres), $T_r = \frac{T}{T_m}$, $\Delta T_r = \frac{T_m - T}{T_m}$, $\alpha = \frac{(NV^2)^{1/3}\sigma}{\Delta H_m}$, $\beta = \frac{\Delta H_m}{RT_m} = \frac{\Delta S_m}{R}$, (T_m , ΔH_m and ΔS_m are respectively the temperature, enthalpy and entropy of melting), V is the molar volume of the crystal, N is Avogadro's number, and σ is the liquid-crystal interfacial tension. The quantity α corresponds to the number of monolayers per unit area of crystal melted at T_m by an energy equal to σ , and is generally assumed (with direct experimental support for some metals) to lie between 0 and 1. Eq. (1) passes through a broad maximum for values of $T_r = T/T_m$ near 0.3, with the breadth and magnitude of the maximum strongly dependent on $\alpha\beta^{1/3}$.

Two major inferences can be drawn from this equation. (1) The degree of supercooling, $\Delta T_m = 1 - \frac{T}{T_m}$, is a very important thermodynamic driving force for crystallization, and draws attention to the melting or liquidus temperatures. This is the origin of the well known fact that lower melting crystals or eutectics are less susceptible to crystallization. (2) the interfacial tension, σ , between liquid and solid is also an important thermodynamic variable. The crystallization rate is proportional to $\exp(-\sigma^3)$, so that a lower interfacial tension will increase the rate of crystallization. If surfactants are drawn to this interface (not necessarily always the case, because of the identical chemical nature of the liquid and crystal), the interfacial tension could be lowered, and this may explain the longstanding observation that surfactants are potent accelerators of crystallization (although plasticization, discussed next, may also be involved).

For polymers and amorphous materials near but above T_g , the kinetic aspects of crystallization that are contained in the pre-exponential term k can be expected to adhere to the Fulcher or WLF equation:

$$k = k_0 \exp\left(\frac{B}{T-T_0}\right) = k_0 \exp\left(\frac{B}{T-T_g+C_2}\right) \quad (2)$$

where C_2 is typically 50K and B is typically 500 to 1000K. This rate has an effective activation energy

$$\frac{E_a}{R} = \left(\frac{B}{\left(1 - \left(\frac{T_g - C_2}{T_g}\right)\right)^2} \right) \quad (T > T_g) \quad (3)$$

and is well known to be very large when T is close to T_g . Thus if T is close to T_g , small changes in either T or T_g (e.g. by small amounts of potent plasticizers such as residual solvent or surfactants) can influence k , and therefore the rate of crystallization, very strongly. Below T_g , k is given by an Arrhenius equation with effective activation energy

$$\frac{E_a}{R} = \left(\frac{B}{\left(1 - \left(\frac{T_g - C_2}{T_g}\right)\right)} \right) \quad (T < T_g) \quad (4)$$

that can also be rather high (hundreds of kilojoules per mole). Thus the rate of crystallization can be significantly temperature dependent even in the glassy state below T_g . The transition from Fulcher to Arrhenius behavior, as the temperature decreases through the glass transition temperature range, is a complex function of thermal history (see ref. [2] for example), and this makes it extremely difficult to extrapolate from keeping temperatures near T_g to room temperature (virtually impossible in practice for product development purposes).

References

- [1] D. Turnbull, *Contemporary Physics* 10 473 (1969)
- [2] I. M. Hodge, *Macromolecules* 15 762 (1982); 16 898 (1983); 20 2897 (1987)