3 The kinetics of cure and network formation

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3.1 Cure of epoxy resins

Although the cure of an epoxy resin involves reaction between epoxy and hardener reactive groups, as discussed in chapter 2, the full characterization of the cure process involves many other factors. During cure, a liquid or fluid resin–hardener mixture is converted to a solid (chapter 1, section 1.1 and Figure 1.1). Critical features are gelation and the onset of vitrification. The latter effect occurs as the glass transition temperature, \( T_g \), approaches the cure temperature, \( T_c \). The determination and alternative definitions of \( T_g \) will be considered later (section 3.2). However, it should be noted that the glass transition temperature is a function of the extent of reaction, \( X_e \),

\[
X_e = \frac{E_o - E(t_c)}{E_o}
\]

with \( E_o \) and \( E(t_c) \) being the concentrations of epoxy groups present initially and at cure time \( t_c \) and has been used as a measure of the extent of reaction (Wisanrakkit and Gillham, 1990). When the difference between the cure temperature and the glass transition temperature becomes ‘small’, that is, \( \Delta T = T_c - T_g(X_e) \) is small, curing reactions become diffusion controlled because molecular mobility is rapidly reduced as \( \Delta T \to 0 \). Cure may continue very slowly even when \( \Delta T \) becomes negative. Then the glass transition temperature exceeds the cure temperature.

Initially when \( T_c > T_g(0) \) the rates of the curing reactions are chemically kinetically controlled, and the rate expressions which have been proposed for the early stages of cure will be discussed in section 3.4. With the formation of larger more highly branched molecules, a critical point is reached, the gel point, and then there is the formation of an infinite three-dimensional network. If \( T_c \) is too low, vitrification may occur before gelation and then further reaction may be inhibited. An elevated temperature may be used to reduce the viscosity so that the hardener can be mixed into the resin and then the curing reactions can be quenched by rapidly cooling the mixture to a storage temperature below \( T_g(0) \), the glass transition temperature of the ‘compounded’ resin. However, it is necessary to ensure that mixing is complete before gelation, since the viscosity rises rapidly at the gel point and the resin will not flow after formation of an incipient network. Thus, information on gelation and vitrification is required to
characterize an epoxy resin cure system and to specify an efficient cure programme to ensure that the properties of the cured resin are optimized for a specific application.

For the technological application of epoxy resins it is essential that mixing of resin with the hardener and any other components should be complete before the onset of gelation. The origin of some of the morphological features that have been observed in cured resins may well be due to incomplete mixing, so that there are regions rich in hardener and hence vice versa. When the stoichiometry of the resin and hardener is considered, such heterogeneity will limit the extent of chemical conversion and hence the attainment of optimum physical and mechanical properties.

The 'pot-life' of the mixed resin and hardener is the time after mixing that the resin can be processed for such applications as impregnation, casting or other operations which involve 'flow'. Such operations have to be completed before the viscosity of the resin starts to increase as the gel point is approached. The viscosity could obviously be reduced by increasing the temperature, but then curing reactions can occur and hence the pot life-time will be reduced. For some applications diluents are added to reduce the viscosity so that processing can be completed expeditiously. The pot-life may be determined by use of so-called 'gel-timers'; commercial instruments with a probe which 'prods' the resin periodically. When penetration is prevented by gelation the time is recorded. Such measurements can be sensitive to the sample size since the heat evolved in an exothermic reaction causes the temperature to rise and hence the reaction proceeds more rapidly and the curing resin may exhibit an 'exotherm'. For similar reasons the pot-life will depend on the batch size, since the heat evolved will depend on the volume which increases more rapidly than the surface area from which heat can be lost.

In the cure schedule it is usual to specify a cure time $t_c$ and a cure temperature $T_c$. However, the resin temperature may not ever be constant at $T_c$ due to its low thermal conductivity and subsequently to an exothermic heat of reaction (Amdouni et al., 1990). With a resin sample of finite thickness there will be a time-lag before the whole sample attains this impressed temperature, $T_c$. The time required for the centre of the resin to attain $T_c$ will depend on the thermal diffusivity of the resin/hardener, the product thickness and the heat transfer coefficient between for example a metal mould and the initially liquid resin. This heat transfer coefficient may change during cure because of shrinkage of the resin away from the metal mould surfaces. For the cure of thicker sections the temperature of the centre of the moulding may well exceed that of the mould surfaces, because of the heat of reaction. To avoid excessive exotherms it is often necessary to cure the resin at a relatively low cure temperature, e.g. 100°C for BADGE + DDM, with a subsequent increase in the temperature for a post-cure of up to maybe 180°C.