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Processing of composite structures

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Abstract - Chemoviscosity and chemorheology indicate the viscosity variations induced by chemical reactions and thus denote a scientific discipline studying viscoelastic behaviour of reacting systems. This article briefly resumes some of the theoretical and experimental aspects of the epoxy system chemorheology.

INTRODUCTION

The synthesis and processing of thermoplastics are distinct operations, as these polymeric materials, in fact, soften and flow on heating and return to the solid state when cooled. Thermosets, on the other hand, are polymerized and processed in a single irreversible operation which transforms a low molecular weight liquid into a cross-linked polymer. Although thermosets, as solid materials, should potentially have superior engineering properties, often they do not present a good reproducibility of their characteristics, in contradistinction to the thermoplastic polymers, due to the less controlled and more complex formation process. The cure of a reactive prepolymer involves the transformation of low molecular weight monomers or oligomers from liquid to rubber and solid state, as a result of the formation of a polymeric network by chemical reaction of the reactive groups in the system. Gelation and vitrification, which are two macroscopic phenomena encountered during this process, strongly alter the viscoelastic behaviour of the material.

Gelation, associated with a dramatic increase in viscosity, occurs at a degree of reaction calculable for each reacting system according to the theory first proposed by Flory (ref. 1). On a molecular level, the increase in viscosity corresponds to the increase in molecular weight and to the incipient formation of infinite branched molecules. While the growth and branching of the polymer chains occur in the liquid state, where the system is still soluble and fusible, infinite network is developed after the gel point by intramolecular reactions of the branched molecules, finally leading to an insoluble cross-linked solid.

Vitrification is the formation of a glass solid which usually follows gelation, occurring as a consequence of the network becoming denser through further cross-linking. Vitrification may prevent further reaction by reducing the mobility of unreacted functional groups. Although chemical control is the basic assumption of all statistical treatments of curing, in some cases, cure may also be controlled by physical factors, such as diffusion constraint in the glass transition region. The knowledge of structural parameters of the cured systems as a function of reactivity of the functional groups and their stoichiometric ratios is important for elucidation and control of the processing and application properties.

Viscosity control during the polymer processing is particularly critical for thermosetting systems, since viscosity may vary with temperature, flow condition and time, due to the chemical reactions occurring in the liquid state. Chemoviscosity and chemorheology indicate the viscosity variation induced by chemical reactions and represent a scientific discipline studying viscoelastic behaviour of the reacting system. This knowledge is very important in the fabrication of polymer composite parts, especially for aerospace applications, where precise resin cure control is required. The viscosity-time profiles must make possible the simultaneous bubbling-off of the trapped gas and sorbed moisture, fiber compaction, and resin flow before the resin has turned into gel ceasing to flow. The polymerization kinetics and chemoviscosity should therefore be controlled by an appropriate temperature programming.

The principal physical events occurring during a cure cycle are illustrated in Fig. 1. Thus, the viscosity initially decreases with time as the temperature is increased, but the reactions are still not activated. During this first stage, sorbed volatiles should start to diffuse out of the resin. When the viscosity reaches its minimum and then begins to increase, due to the occurrence of the thermosetting reactions, trapped bubbles must be allowed to leave the composite. Bubbles, in fact, become mobilized when the viscous flow forces are sufficiently large to overcome the surface tension forces (ref. 2). Pressure which drives the resin flow should be correctly applied in a limited range of viscosity in order to properly remove the excess resin and trapped bubbles, and to consolidate the plies. Figure 1 qualitatively shows the viscosity limits (A and B) that must be matched by the resin. The lower limit (B) is imposed by the flow characteristics of the system to avoid an excessive lost of resin from the composite and to ensure the flow forces necessary to mobilize the bubbles. A too highly viscous liquid, on the other hand, does not allow a sufficient flow of resin and compaction of the system. In this case too bubbles are not removed from the composite. Other important physical events, such as void nucleation and volatiles diffusion and desorption, must be considered.

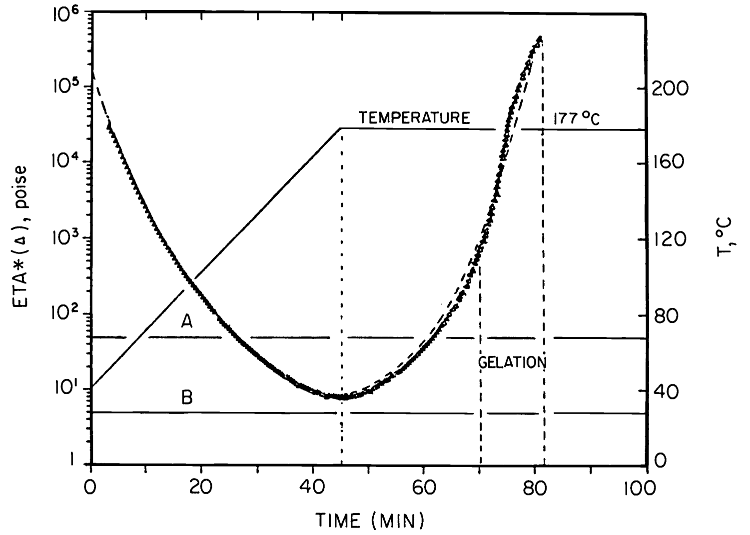

Fig. 1. Viscosity profiles during a cure cycle. Gelation (----) and viscosity (——) limits.

THEORETICAL AND EXPERIMENTAL DETERMINATION OF THE GELATION LIMITS

Successful processing of the thermosetting resins requires an understanding of the relationships involving the rheological behaviour, curing kinetics, and changes in the molecular weight distribution.

In order to determine the conditions of formation of an infinitely large branched structure, Flory (ref. 1) introduced a convenient quantity, viz., the branching coefficient α, defined as the probability that a given functional group of a branched unit of functionality greater than two leads, via a chain of bifunctional units, to another branched molecule. In the case of the tetrafunctional TGDDM and difunctional DDS, if we denote with P_a and P_e, respectively, the fractions of primary amine and epoxy groups which have reacted, the branching coefficient is

$$\alpha = P_a P_e = r P_a^2 = P_e^2/r \qquad (1)$$

where r is the ratio of amine (m_a) and epoxy (m_e) groups initially present in the reactive mixture,

$$r = m_a/m_e = g M_a/f M_e \qquad (2)$$

with f and g being the functionalities of the M_e and M_a moles of TGDDM and DDS molecules.

A convenient critical condition announcing incipient formation of an infinite network is given in terms of the branching coefficient by

$$\alpha_c = 1/(f-1) \qquad (3)$$

and therefore as a function of the mixture composition and epoxy conversion

$$P_{ec}^2 = r/(f-1) = M_a g/(M_e f(f-1)) \tag{4}$$

In particular, for the system presented here, $\alpha = P_e^2/0.320$, $\alpha_c = 0.33$ and $P_{ec} = 0.315$ (ref. 3).

Generally, the molecular constitution of the products of condensation of f-functional and bifunctional units is described by the complexity distribution and by the average number of bifunctional unit per chain. As the reaction progresses, larger species are formed at the expense of the smaller ones. The theoretical concentration of monomers, which is always greater than all the other species, decreases continuously, leading to the formation of dimers, trimers, etc.; this concentration reaches its maximum and then decreases. The curves of the weight fraction of various species continue through the gel point without discontinuity. Flory first derived (ref. 1) the size distribution relationships for trifunctional and tetrafunctional branching units that were subsequently generalized by Stockmayer (ref. 4) for f-functional units. The weight distribution function of x-mers in a poly-f-condensation is,

$$W_x = [(1-\alpha)/\alpha][(f\,x-x)!\,f]/[(x-1)!\,(f\,x-2x+2)!]\beta^x \tag{5}$$

where $\beta = \alpha(1-\alpha)^{f-2}$.

The epoxy conversion, and hence the branching coefficient present in the above expression, is usually derived from experimental techniques, such as IR spectroscopy, thermal analysis or liquid chromatography. Differential scanning calorimetry (DSC) is often used for the indirect determination of the progress in the cure of thermosetting systems, with the assumption that the heat evolved is proportional to the extent of reaction. The DSC traces as obtained in complex cure cycles (upper part of Fig. 2) may therefore be used to determine the actual epoxy conversion kinetics (lower part of Fig. 2), leading to a theoretical determination of the molecular composition according to eqs(1-5).

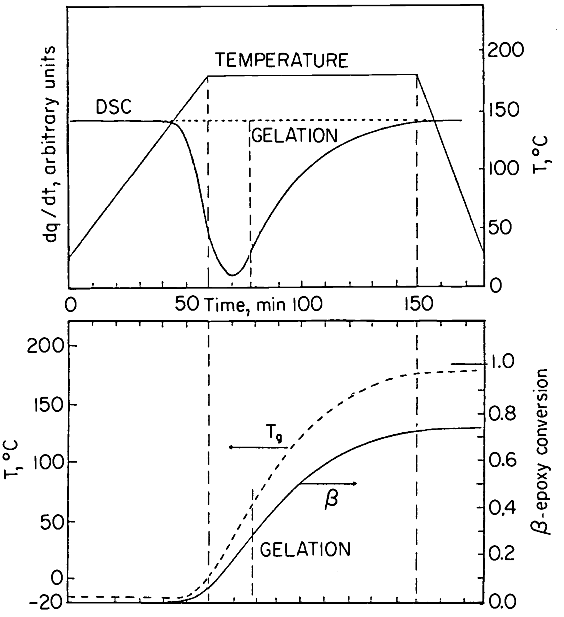

Fig. 2. DSC traces during a cure cycle (upper part); measured kinetics of epoxy conversion and T_g changes (lower part).

RHEOLOGY OF THERMOSETTING REACTIONS

The processing and final properties of thermosets depend on their composition as well as on details of the network structure generated below the gel point. Viscosity, as indicated before, reflects the molecular distribution and complexity in the thermosetting material, and is one of the most important properties of the polymer. An accurate predictability of the material properties, such as the polymerization kinetics and related changes in viscosities, implies the knowledge of the basic phenomena occurring during the overall process.

As previously discussed, the formation of macromolecular species and subsequently of the polymer network is accompanied by a significant rise in the initial viscosity and glass transition temperature of the system.

The increase in molecular weight as a consequence of the cure reaction causes as increase in viscosity which initially varies linearly with time (Fig. 3). However, while the polymerization proceeds, branching of the linear products occurs, leading to complex intermolecular interactions, such as entanglements, which further increase the viscosity of the system. An upturn is then observed before the occurrence of gelation, where the viscosity measured under the steady shear reaches an infinite value. The weight average degree of polymerization

$$\bar{X}_w = (1 + \alpha)/(1 - (f - 1)\alpha) \tag{6}$$

increases rapidly as the reaction proceeds, reaching 'infinity' at the gel point. The progressive increase in viscosity of the liquid reacting system up to an 'infinite' value as the gel point is approached is explained by its dependence on the weight average molecular weight.

Although the liquid state can be characterized by steady-state viscosity measurements, dynamic mechanical techniques are preferred for thermosets due to the extreme rheological changes occurring during the conversion of the liquid prepolymer into a solid crosslinked polymer that cannot be monitored by a single mechanical test. Several dynamic-mechanical techniques have been proposed to study the reactive system through the thermosetting liquid to a solid change in state (ref. 5).

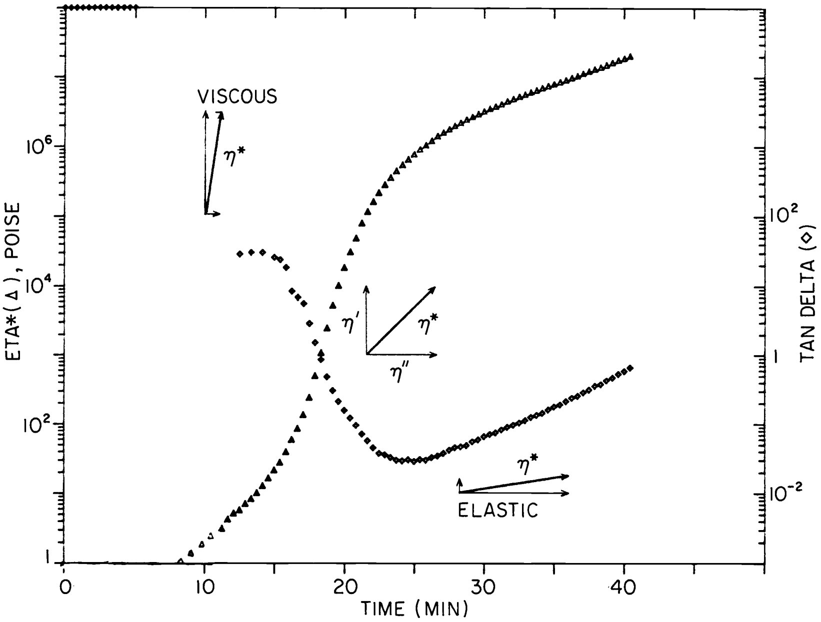

Fig. 3. Complex viscosity and tangent loss in an isothermal cure

The complex viscosity and the ratio of the two components of the complex shear modulus measured in an isothermal cure at 180°C are reported in Fig. 3. The viscous component of the complex viscosity is initially much higher than the elastic one (see vectors in Fig. 3), and the system behaves as a liquid. However, as its viscosity increases, molecular branching becomes significant, increasing the elastic character of the mixture. The first inflection on the viscosity curve is then observed. Loss factor tan δ which initially assumed high values suddenly decreases, as the polymerization and branching proceed beyond the critical point, where its value is unity. A second inflection of the complex viscosity occurring when tan δ reaches its minimum announces the formation of an infinite elastic network (gel point). The elastic component of viscosity is, in fact, maximum at this point.

Theoretical approaches which explicitly consider the molecular and temperature dependence of viscosity have been presented recently (refs. 6,7). The rheological behaviour of a reacting system is, in fact, basically governed by two effects, one related to the structural changes caused by the cure reactions (chemical aspect), and the other due to the variation in molecular mobility induced by the temperature variations (physical aspect). The dependence of viscosity on temperature may be described by using the William, Landel and Ferry (WLF) equation:

$$\ln(\eta/\eta_r) = -C_1(T - T_g)/((C_2 + T - T_g)) + C_1(T_r - T_g)/(C_2 + T_r - T_g) \qquad (7)$$

where η_r is the viscosity at the reference temperature T_r, C_1 and C_2 are constants and T_g is the glass transition temperature of the unreacted system or of any of the intermediate states which the system passes to reach the critical stage and gelation.

Figure 4 reports the prediction capability of the WLF equation for a TGDDM-DDS unreacting system at different degrees of polymerization.

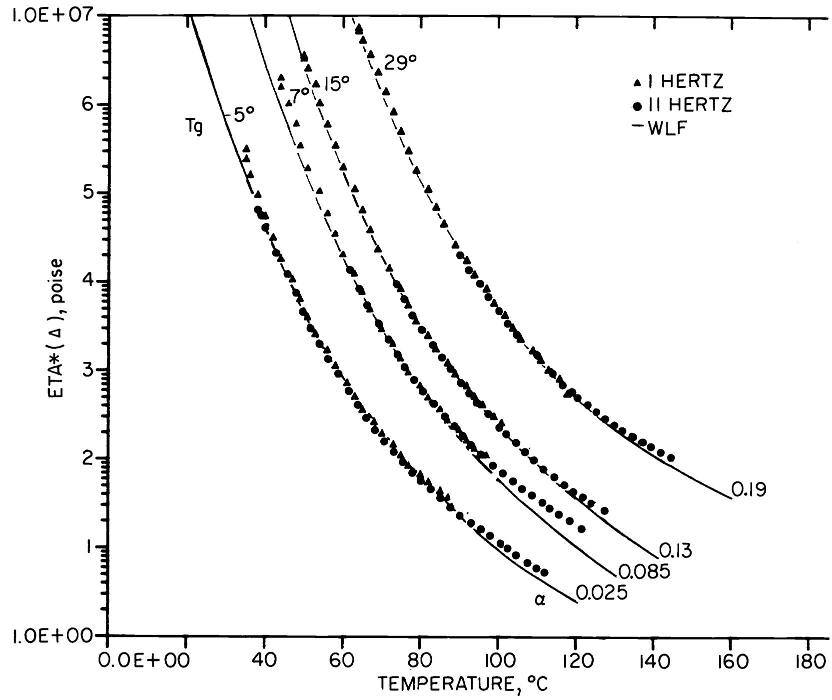

Fig. 4. Experimental (●▲) and theoretical (WLF) viscosities

On the other hand, the variation in viscosity is determined, at a fixed temperature, by changes of the molecular characteristics, and may be derived under the following assumptions. For a linear polymer, the viscosity is related to the molecular weight by (ref. 8),

$$\eta = K M_w^a \qquad (8)$$

where $1 < a < 2.5$ for M_w lower than a critical value and equal to 3.4 for M_w higher than the critical value. A similar relationship has been proposed by Valles and Macosko (ref. 8) for a nonlinear copolymerization such as that considered here,

$$\eta = k(g\ M_w)^a \qquad (9)$$

with $a = 3.4$ and g, the ratio of the square of the gyration radii of a branched to a linear chain of the same molecular weight, defined as (ref. 8),

$$g = [(1 - \alpha(f-1)/2\alpha] \ln[(1 - \alpha)/(1 - \alpha(f-1)] \qquad (10)$$

If we normalize the viscosity to its initial value at $\alpha = 0$,

$$\eta(\alpha)/\eta_o = (g\, M_w(\alpha)/M_{wo})^a = (g\, \bar{X}_w)^a \qquad (11)$$

where $\bar{X}_w$ is the degree of polymerization previously defined (eq. 6).

A combination of the previous expression leads to

$$\eta(\alpha) = \eta_o \left| \frac{1-\alpha}{2\,\alpha} \ln \frac{1-\alpha}{1-\alpha(f-1)} \right|^{3.4} \qquad (12)$$

The experimental viscosity profile in an isothermal test carried out at 180°C is adequately described by eq. 12 (ref. 7).

The viscosity changes in a reactive system continuously heated up to the final cure temperature should be predicted by combining expressions containing the temperature (eq. 7) and molecular dependence (eq. 12),

$$\eta(T,\alpha) = \eta_{or} \left| \frac{1-\alpha}{2\,\alpha} \ln \frac{1-\alpha}{1-\alpha(f-1)} \right|^{3.4} \exp \frac{C_1(T_r-T_{go})/(C_2+T_r-T_{go})}{C_2(T-T_g(\alpha))/(C_2+T-T_g(\alpha))} \qquad (13)$$

where η_{ro} is the viscosity of the unreacted system at a reference temperature and T_{go} is its glass transition temperature.

The rate of variation of the glass transition temperature with the degree of cure determined by differential scanning calorimetry, as illustrated in Fig. 2 (lower part), are used in eq. (13). The predictability of eq. (13) is also successfully tested in Fig. 1.

CONCLUSIONS

The topology of crosslinked network generated in a thermosetting epoxy resin by the cure reaction strongly depends on the cure thermal history and on the initial composition system. An approach to structure-property relationships needs the investigation of the system chemorheology and thermokinetics, and a correlation of the properties of the cured materials with the variation in composition and initial state of the prepolymer.

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