QUALITY CONTROL OF THE CURE PROCESS OF THERMOSETTING RESINS BY MEANS OF DIFFERENTIAL SCANNING CALORIMETRY

A. Apicella, C. A. Beretta, M. A. Castiglione-Morelli, E. Martuscelli*, L. Nicolais, and *M. R. Nobile**

DEPARTMENT OF MATERIALS AND PRODUCTION ENGINEERING, UNIVERSITY OF NAPLES,
PIAZZALE TECCHIO, 80125, NAPLES, ITALY
*CONSIGLIO NAZIONALE DELLE RICERCHE (CNR), ISTITUTO DI RICERCHE SU TECNOLOGIA DEI POLIMERI E REOLOGIA,
VIA TOIANO 6, 80772 ARCO FELICE, NAPLES, ITALY

Calorimetric and rheological characterizations of thermosetting resin formulations containing a novalac epoxy resin hardened with 60 to 120 parts per hundred of methylated maleic acid adduct anhydride are described. The calorimetrically determined epoxy conversion has been related to the gelation limits theoretically calculated from Flory's non-linear copolymerization theory and experimentally verified in rheological tests.

Epoxy resins are commonly used as thermosetting matrices in the preparation of prepregs consisting of glass or carbon fibres immersed in formulated matrices. The resin formulations are complex mixtures of epoxy resins, hardeners, catalysts and diluents. Further, the resin may be "staged" (partially reacted) during the manufacture in order for it to satisfy rheological and process specifications or undergo further compositional changes during transport and storage, due to its reactivity. Since the processability and properties of polymer composites depend on the chemical composition of the prepreg material, quality control is required to guarantee their consistency from batch to batch. In fact, while the synthesis and processing of thermoplastics are distinct operations (these polymers soften and flow on heating and they return to the solid state once cooled), thermosets are polymerized and processed in a single operation, which transforms a low molecular weight liquid into a cross-linked polymer. Although thermosets should potentially have superior engineering properties as solid materials, they often do not exhibit good reproducibility of their characteristics, as is the case with thermoplastic polymers, owing to their less well-controlled and complex transformation process. The cure of a reactive prepolymer involves the transformation of low molecular weight monomers or oligomers from liquid to rubber and solid states as a result of the

formation of a polymeric network by chemical reaction of the reactive groups in the system. Gelation and vitrification, 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 from the theory first proposed by Flory [1]. At a molecular level, the increase in viscosity corresponds to an increase in molecular weight and to the incipient formation of infinite branched molecules.

Growth and branching of the polymer chains occur in the liquid state, where the system is still soluble and fusible; an infinite network is developed after the gel point, through 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. A knowledge of the structural parameters of cured systems as a function of the reactivity of the functional groups and their stoichiometric ratios is important for elucidation of the curing reaction, and the control of processing and application properties. Chemical control is the basic assumption of all statistical treatments of curing, but in some cases, cure may also be controlled by physical factors, such as diffusion in the glass transition region, which lead to the formation of inhomogeneous structures, thereby, sometimes indirectly, affecting the physical properties and durability of cured epoxy resins [2]. The processing and the final properties of thermosets depend on their composition and on the details of the network structure generated below the gel point. Viscosity control during polymer processing is particularly critical for thermosetting systems, since the viscosity may vary with the temperature, flow conditions and time, due to the chemical reactions occurring in the liquid state. Accurate predictability of the material properties, such as the kinetics of polymerization and the related changes in the viscosities, implies a knowledge of the basic phenomena occurring during the overall process.

There is therefore a need for chemo-rheological characterization, using analytical techniques able to identify not only the composition of the thermosetting matrices, but also their behaviour when stored, handled and processed.

Experimental

The samples used in this study were mixtures of tetrafunctional novalac resin (supplied by S.I.R.) and methylated maleic acid adduct of phthalic anhydride (MNA) accelerated by 2-ethyl-4-methylimidazole. The compositions utilizing 2.5 parts of accelerator and 60 to 120 parts of MNA per hundred parts of epoxy resin

were investigated. Samples were prepared by heating the resin at 70° for about 30 min in order to soften it and to better mix the MNA. Finally, the accelerator was added at room temperature. A Mettler DSC 30 was used to scan the resin mixtures at 5 deg/min from $-40°$ to   250°. The curve $\Delta H/\Delta H_T(P_e)$ vs. temperature was

Epoxidised novolak resin

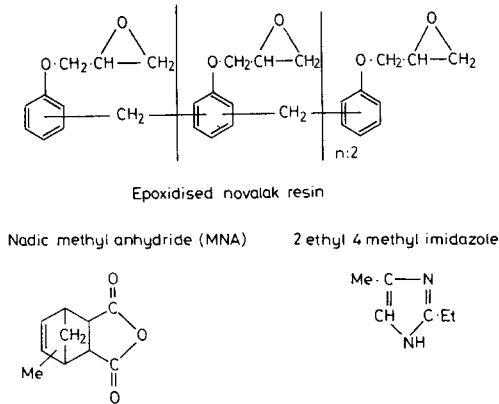Nadic methyl anhydride (MNA)   2 ethyl 4 methyl imidazole

Fig. 1 Structures of the components used in the thermosetting formulations

evaluated with a specific DSC computer program. Dynamic viscosity measurements of the reaction mixtures were made with a Rheometric Dynamic Viscosimeter, equipped with disposable parallel plates 5 cm in diameter, operating at 1 Hz. Samples were heated at 5 deg/min from 30° to 150°. The component formulae are reported in Fig. 1.

Results and discussion

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 the glass transition temperature. Several dynamic mechanical techniques have been proposed [3–5] for study of reactive systems throughout the thermosetting liquid to solid state change. A general Time-Temperature-Transformation diagram (TTT), proposed by Gillham et al. [6], can be obtained from dynamic-mechanical characterization. These useful plots describe the state of a curing thermoset as a function of temperature and time. In these TTT diagrams several different zones and characteristic temperatures and times, associated with different chemorheological behaviour, can be observed. The rheological behaviour of a reacting system is mainly governed by two effects, one related to the structural

10*

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 [7]:

$$\ln{(\eta/\eta_r)} = -C_1(T - T_g)/(C_2 + T - T_g) + C_1(T_r - T_g)/(C_2 + T_r - T_g) \quad (1)$$

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 the system passes to reach the critical stage and gelation. Statistical theory has been used to describe the curing of epoxy resins. The results, however, were somewhat invalidated by the too simplified reaction schemes used. The importance of deviation from the ideal network structure in the cured epoxies, due to the stoichiometric imbalance or to incomplete reaction, is recognized in the literature [8]. The development of modern statistical theories of the branching processes, employing cascade substitution and the formalism of the probability generating functions or conditional probability, deals with the complex problem of network formation [9. 10]. For non-linear condensation, the growth of the macromolecule, which is not restricted in only two directions, increases its functionality, continuing the building of the structure to yield finally, at a molecular level, an essentially infinite network. A rather sudeen transformation from a viscous to an infinitely viscous gel characterizes the incipient formation of the spatial network.

In order to determine the conditions of formation of an infinitely large branched structure, Flory [11] introduced a convenient quantity, 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 our case, if we denote by P_a and P_e, respectively, the fractions of anhydride and epoxy groups which have reacted, the branching coefficient is:

$$\alpha = P_a P_e = rP_a^2 = P_e^2/r \quad (2)$$

where r is the ratio of anhydride (m_a) to epoxy (m_e) groups initially present in the reaction mixture:

$$r = m_a/m_e = gM_a/fM_e \quad (3)$$

with f and g the functionalities of the M_e and M_a moles of epoxy resin and anhydride molecules. A convenient critical condition for the incipient formation of an infinite network is given in terms of the branching coefficient by

$$\alpha_c = 1/(f-1) \quad (4)$$

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

$$P_{ec} = (r/(f-1))^{1/2} = (M_a g/M_e f(f-1))^{1/2} \tag{5}$$

Thermal analysis can provide information about the chemical and physical events occurring in the system during a thermal screen. A DSC thermal scan performed on a resin formulation containing 90 parts per hundred of anhydride is illustrated in Fig. 2. The steep gradient of the material heat capacity characterizes
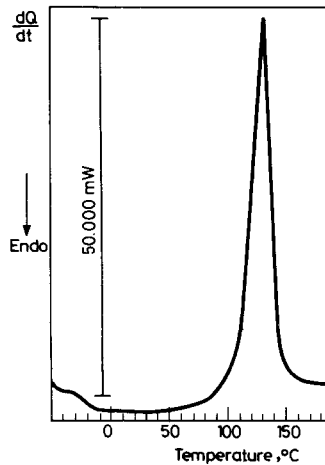
Fig. 2 DSC curve of the reactive mixture

the increased mobility of the polymer segments occurring when the still unreacted resin overcomes its glass transition at $-28°$. The complex reactive mixture presents a unique curve, characterized by exothermal peaks of fixed intensities, whose area defines the heat of reaction of the system.

The functionalities of the epoxy and anhydride molecules should be carefully considered in order to calculate correctly the critical epoxy conversion at the gel point from the theoretical considerations previously discussed. In particular, the single epoxide group may be considered either monofunctional or bifunctional, depending on the reaction mechanism assumed for the polymerization reactions with the hardener molecules. According to the mechanism discussed later, the epoxides are described as reacting directly not with the anhydrides, but with the acid formed by their reaction with a hydroxyl group. If the epoxide rings are opened by the diacid formed when the anhydride interacts with a water molecule present as sorbed moisture, chain extension will occur and the group should be considered monofunctional (the overall novalac epoxide molecule is tetrafunctional).

However, the hydroxyls formed in the epoxide ring opening may further interact with other anhydride molecules, forming monoacids capable of epoxide ring opening. In such a case, each epoxide group is cross-linked with two anhydride molecules and is therefore acting as a bifunctional unit (the overall novalac will
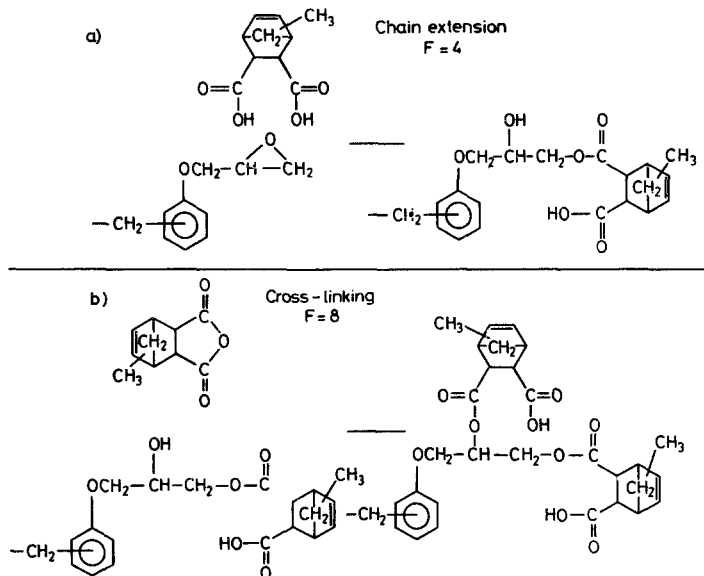

Fig. 3 Reaction schemes of the possible anhydride-epoxy reaction; a) Reaction of the epoxide with a diacid (chain extension). b) Anhydride opening and esterificatin (cross-linking)

have a functionality of eight). The anhydride in both cases behaves as bifunctional. Hence, the critical epoxide conversion, calculated from Eq. 5 for a system presenting a stoichiometric ratio $r = 1.47$, is 0.70 if the epoxide molecule is tetrafunctional or 0.46 if its functionality is eight (Fig. 3).

DSC is often used for the indirect determination of the advancement and kinetics of the cure of epoxy systems, with the assumption that the heat evolved is proportional to the extent of reaction [12, 13]. These models assume simple nth-order kinetics with the temperature-dependent rate constant given by an Arrhenius expression, although epoxy reactions are often characterized by multiple reactions and autocatalytic behaviour. When organic acids, or most commonly their anhydrides, are used as hardeners for the epoxide, chain extension and cross-linking are due to their catalytic action towards homopolymerization, or to their reaction to form polyesters with the epoxides or hydroxyls formed therefrom. The fact that the optimum properties of the resin are often achieved by using less than

stoichiometric quantities confirms that catalysis is an important part of this reaction. Since the organic acid is directly involved in the reaction with the epoxide, multiple reactions should occur during the anhydride cure of an epoxy resin, namely:

a) the formation of a monoester containing a free carboxyl group from the reaction of the anhydride with a hydroxyl (initially presents as an impurity introduced with promoting agents);

b) the main reaction of the carboxyl formed in the previous step with the epoxide to form a diester and a hydroxyl;

c) the polyetherification of the epoxides induced by the reaction with the hydroxyls. Since the ring opening by a hydroxyl results in the formation of a new hydroxyl, this reaction does not alter their concentration in the system.

DSC analysis, however, may be successfully applied to such complex systems when the kinetics and heats of reaction of the single steps are independently determined [14]. In order to assign characteristic heats of reaction to the epoxide ring opering in different reaction mechanisms, the values determined in DSC tests should be referred no to the overall weight of the mixture, but only to the weight of the epoxy component. The variation of ΔH (J/g resin) vs. parts per hundred of MNA Fig. 4 allows determination of the stoichiometric quantity of the anhydride. The cure behaviour of the epoxy resin-MNA-accelerator mixture was analyzed by
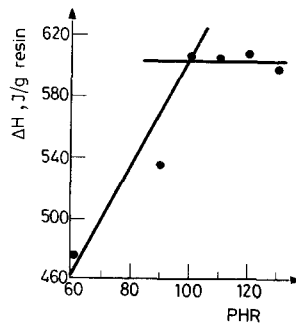

Fig. 4 The variation of ΔH (J/g resin) vs. parts of hardener (MNA) per hundred parts of epoxy resin

means of DSC and dynamic viscosity measurements. The gelation theory is combined with the WLF equation in order to describe the viscosity profiles during a thermal scan. The viscosity profile and the loss tangent (tan δ) values as functions of temperature are shown in Fig. 5. The initial viscosity decrease, due to the increase of the temperature, is adequately described by the WLF equation (continuous line). As can be seen from the figure, the experimental values are in good agreement with the theoretical profile calculated by using in Eq. 1 the constants $C_1 = 36$ and

$C_2 = 52°$, and the T_g value $(-28°)$ for the unreacted system measured in a DSC scan. An upturn is then observed before the occurrence of gelation, where a theoretically infinite molecular weight is reached. The progressive increase of the viscosity of the liquid reacting system up to an infinite value as the gel point is approached is explained by its dependency on the weight average molecular weight.
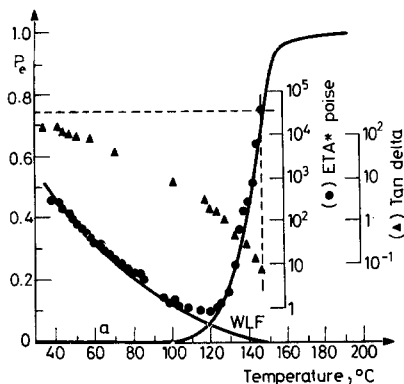

Fig. 5 Viscosity (η^*) and tan δ profiles and conversion of the epoxides (curve a) vs. temperature (heating rate 5 deg/min)

The minimum in the tan δ values (where the elastic component of the viscosity is maximum) is used to estimate experimentally the occurrence of gelation. The same Figure shows the curve for the conversion of the epoxy groups (continuous line a), obtained calorimetrically by DSC.

An experimental estimate of the epoxy conversion at the gel point may therefore be obtained from a comparison of the DSC and rheological curve profiles. The experimental value of the conversion is located between the theoretical values calculated assuming a tetrafunctional epoxy $(P_e = 0.70)$ and a molecule with a functionality of eight $(P_e = 0.46)$.

In conclusion, a critical and suitable use of DSC techniques associated with rheological characterization may be appropriate in the determination of the actual reaction kinetics and modelling of the cure viscosity, once the unreacted or partially reacted resin glass transition temperature and epoxy conversion during the cure are correctly determined.

* * *

References

1 P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, N.Y., 1953.

2 A. Apicella and Nicolais, I. & C.R.D., 23 (1984) 288.

3 A. F. Lewis and J. K. Gillham, J. Appl. Polym. Sci., 6 (1962) 422.

4 J. K. Gillham, CRC Critical Reviews in Macromolecular Sci., 11 (1974) 295.

5 M. Gordon and B. M. Grieveson, J. Polym. Sci., 29 (1958) 9.

6 J. K. Gillham, J. A. Benci and A. Noshay, J. Polym. Sci., C 46 (1974) 279.

7 M. L. William, R. F. Landel and J. D. Ferry, J. Am. Chem. Soc., 77 (1955) 3701.

8 J. P. Bell, J. Polym. Sci., A2 (1970) 417.

9 K. Dusek, Macromol. Chem. Suppl., 2 (1979) 35.

10 M. Gordon, Proc. Roy. Soc., A268 (1962) 240.

11 P. J. Flory, J. Am. Chem. Soc., 63 (1941) 3091.

12 R. B. Prime, Polym. Eng. Sci., 13 (1973) 365.

13 R. N. Roger and L. C. Smith, Therm. Acta, 1 (1970) 1.

14 A. Apicella, L. Nicolais, M. Iannone and Passerini, J. Appl. Polym. Sci., 29 (1984) 2083.

Zusammenfassung — Die kalorimetrische und rheologische Charakterisierung der Ansätze von hitzhärtbarem Harz wird beschrieben. Die Ansätze enthalten ein mit 60–120% methyliertem Maleinsäure-Adduktanhydrid gehärtetes Novolackepoxidharz. Die kalorimetrisch bestimmte Epoxidkonversion wurde auf die theoretisch aus der nicht-linearen Flory'schen Kopolymerisationstheorie berechneten und experimentell durch rheologische Tests bestätigten Erstarrungsgrenzen bezogen.

Резюме — Описаны калориметрические и реологические характеристики термореактивных резин, содержащих новолак-эпокси резину совместно с ангидридом метилированной малеиновой кислоты в качестве отвердителя. Превращение эпокси-резины, определенное калориметрическим методом, взаимосвязано с пределами гелеобразования, вычисленных по теории Флори для нелинейной кополимеризации и экспериментально подтвержденных в реологических испытаниях.