EPOXY POLYMERS: TEMPERATURE–TIME–TRANSFORMATION DIAGRAM BY MEANS OF DSC INVESTIGATIONS

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ABSTRACT

The aim of this work is to show that isothermal and non-isothermal DSC investigations allow the temperature–time–transformation diagram of a polymer system to be drawn. DSC data can be worked out according to a simple model which supports the interpretation of the gelation process in terms of viscosity. It is seen that the degree of cure attained at the gelation point depends on the temperature of cure and that this crucial process is similar to the formation of a glass phase from a melt.

INTRODUCTION

The phenomenological kinetics of polymerization of epoxy resins can be adequately assessed on the basis of non-isothermal DSC investigations [1,2]. The same approach allows one to recognize that fibres and elastomers can affect the kinetics of cure in composites and adhesives respectively [3,4].

This information does not, however, suggest the conditions for adequate technical preparation of these polymers i.e. the best temperature and time of cure. As remarked by Gillham [5], a very useful tool for this purpose is the temperature–time–transformation (TTT) diagram, which allows direct realization of the main events in the course of the cure process. The experimental technique employed by Gillham is torsional braid analysis (TBA) which gives a thermomechanical spectrum. However, the instrumental arrangement is quite complex and certainly not easily available in most laboratories. The approach to TTT diagrams by means of the more usual techniques of thermal analysis is therefore of some interest.

The aim of the present work was the definition of the TTT diagram of an epoxy adhesive, namely the HX-206, on the basic of DSC investigations. DSC data were also employed to assess the phenomenological cure kinetics at various temperatures, according to the procedure defined in previous work in this laboratory [1–4].

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EXPERIMENTAL

The composition of the adhesive HX-206 is reported in ref. 6 as 91.9wt.% components of the epoxy resin and 8.1wt.% liquid CTBN (carboxy terminated butadiene acrylonitrile). According to the same researchers [6], the epoxy resin contains 73wt.% DGEBA (diglycidyl ether of bisphenol A), 20wt.% bisphenol A, and 7 wt.% DICY (dicyandiamide).

Samples (20–30 mg) of the starting mixture, which was kindly supplied by the Laboratory of Experimental Technology of the aerospace firm G. Agusta (Italy), were examined with isothermal DSC at 323, 348, 373, 398 and 435 K to detect the time required to attain gelation (t_{gel}) and that to attain vitrification (t_{vit}). However, samples examined at 323 K did not give reproducible and reliable results; this failure is interpreted in the next section. Isothermal DSC traces obtained at 443 K did not allow reliable detection of t_{gel}. Other samples of the starting mixture were checked by DSC at a heating rate of 5, 10, 20, 30, 50 and 90 K min^{-1} to single out the respective onset and end temperature, T_{on} and T_{end}, of the exothermic peak of polymerization.

These data lie along the corresponding $T = T[\log(t)]$ curve in the TTT diagram (these diagrams require the use of the logarithmic scale for the time to represent a significant extension of each phase formed), i.e. $T = 298 + H_r \exp[\log(t)]$, where H_r is the corresponding heating rate and 298 K is the starting temperature of the scan.

The phenomenological kinetics of cure were determined at 323, 348, 373, 398 and 435 K, according to the procedure employed in previous work [1,2]. Samples (30 mg) were precured at these temperatures for different periods of time to attain different values of the degree of polymerization α.

The samples were then checked by DSC at a heating rate of 10 K min^{-1} to evaluate the heat supplied in exhaustive polymerization. The data were worked out according to refs. 1 and 2 to attain the α vs. t_{cure} trend at each temperature considered: in the present case, however, the fitting equations do also account for the corresponding t_{gel}, as described in a later section of the paper.

The instrumental apparatus employed was a Du Pont thermoanalyser model 1090.

RESULTS AND DISCUSSION

TTT diagram

The main features of a TTT diagram (temperature of cure T_c vs. time of cure t_c) of an epoxy resin are the curves which represent the "gelation" (i.e. the formation of a still soft network) of the low-viscosity mixture of epoxy components and hardeners, and the "vitrification" of the almost completely cured polymer (see Fig. 1).
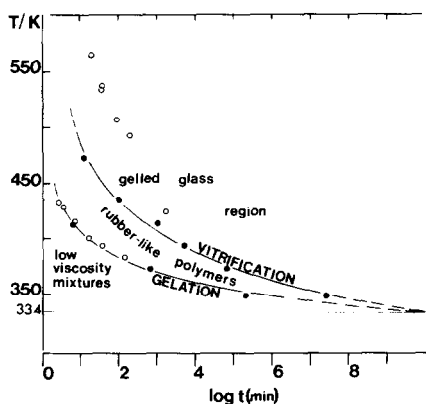
Fig. 1. TTT diagram of the epoxy adhesive HX-206. Filled and empty circles refer to isothermal and non-isothermal DSC investigations respectively. The lower and the upper group of empty circles correspond to the onset and to the end temperatures respectively of the exothermic peak in the DCS trace. They lie along the $T = T[\log(t)]$ curves (not reported in the figure) which represent the respective heating rates.

The intermediate region between these curves corresponds to rubbery states of the system. Here the formation of cross-links reaches exhaustion and the so-called "reticulation" occurs. When the system is isothermally cured, it goes from a state of low viscosity and poor polymerization (the region on the left of the gelation curve) to the rubbery state, and finally, to a gelled glass state (beyond the vitrification curve), where any further progress of the cure is practically quenched owing to the very high viscosity.

Once gelation has occurred, the progress of the cure will yield a peculiar final polymer with mechanical and thermomechanical properties different from those of a polymer obtained by curing the same initial mixture at another temperature [5].

In the present work, these events are singled out as follows from the isothermal DSC trace: the onset of the exothermic peak refers to the start of gelation; the time range spanned by the DSC peak refers to the extension of the rubbery region at the temperature considered; the end of the peak, i.e. the exhaustion of the heat supply, refers to the attainment of vitrification.

The process of segregation of the elastomeric phase cannot be observed with this approach because of its poor thermal effect which cannot give a significant signal in the DSC trace. Provided that the record of the DSC trace allows the onset time and the end time of the exothermic peak of polymerization to be properly singled out, the DSC approach to the TTT diagram gives directly, at every T_c considered, the time required for gelation, t_{gel}, and that required for vitrification, t_{vit}. This was indeed the case for T_c lower than 440 K, i.e. when t_{gel} is greater than 1.5 min. For a higher T_c, t_{gel} becomes too small to be singled out with reasonable accuracy. However, t_{vit} can always be singled out with satisfactory confidence.

Analogous results can also be obtained from non-isothermal DSC traces recorded at different heating rates. In this case the experimental data are in the form of temperatures, namely, the onset and the end temperatures, T_{on} and T_{end}, of the exothermic peak. In the TTT diagram these points lie along the respective $T = T(t)$ curves (see experimental section). It is readily apparent (see Fig. 1) that the t_{gel} data drawn in this way (i.e. from T_{on}) are in agreement with those obtained from isothermal DSC traces, whereas this is not the case for T_{end} data.

This difference can be well justified by the fact that the attainment of gelation occurs in either case following a thermal history in the low-viscosity region of the TTT diagram. Within this region, the difference between the isothermal and non-isothermal treatment is indeed negligible, since the system is still in the state of mixture of "free and small" molecules whose molecular weight grows equally either with the increase in T or with the elapse of time, and no extended branching and cross-linking occurs.

The T_{end} of the non-isothermal DSC peak cannot be matched with the exhaustion of the isothermal DSC peak of the system with the same t_{gel}.

In spite of the fact that in either case the gelation process should have defined [5] the same main features of the polymer network, the system which undergoes a non-isothermal treatment will profit from the slower increase in viscosity (owing to the rise in T) to enhance its degree of cure with respect to the isothermally treated system.

The experimental data reported in the TTT diagram of Fig. 1 are in line with analogous results found by Peng and Gillham [7] for similar systems of epoxy adhesives with the TBA approach.

Viscosity and gelation

The statement that gelation may be defined as an isoviscous event [5] was reconsidered here on the basis of a naive model proposed in previous work [8]. According to this model (see Appendix), a general expression for the viscosity of a polymer undergoing cure would be

$$\log[\eta/\eta(\alpha = 1)] = 1 - \exp(-kt) \tag{1}$$

where $\eta(\alpha = 1)$ is the viscosity of the polymer, fully cured ($\alpha = 1$) and assumed to be in a rubbery state and k is the kinetic constant of the cure process at the temperature considered. A polymer system which undergoes isothermal gelation at a given T would therefore have a viscosity which obeys the following relationship:

$$\log\left[\eta_{gel}/\eta(\alpha = 1)\right] = 1 - \exp\left(-kt_{gel}\right) \tag{2}$$

It is easy to verify that η_{gel} would be independent of T (i.e. gelation would be an isoviscous event) only when the "activation energy" of the cure rate is
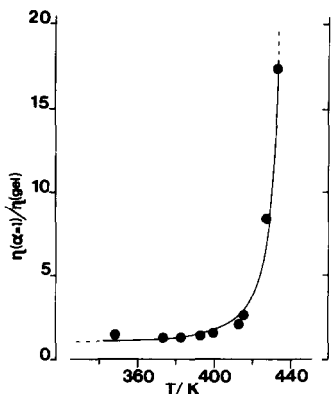
Fig. 2. Ratio between the viscosity of the fictitious fully cured and rubber-like polymer, $\eta(\alpha = 1)$, and that of the mixture of the reactants at the gelation point, η_{gel}, according to the model reported in the Appendix.

equal to that of t_{gel} and when η ($\alpha = 1$) may be assumed as independent of T.

Figure 2 shows the results of our computations according to eqn. (2), when the corresponding k values at various T are employed (see below). The fit of the experimental trend can be obtained with the function.

$$\eta(\alpha = 1)/\eta_{gel} = 0.57 \exp\left[-56.5/(T - 450)\right]$$

which has the form of the well-known equation of Vogel–Tamman–Fulcher for the viscosity. Here the temperature, $T = 450$ K, would represent the condition where the system passes directly from the liquid-like state of the starting mixture to the fully cured state without modifying its viscosity, which remains very low. Such a process is expected when the temperature of cure is close to the highest glass transition temperature $T_{g\infty}$.

Phenomenological kinetics of cure

The kinetics of the cure process at various temperatures was assessed via the procedure proposed in previous work [1,2], i.e. by working out the values of the heat amounts delivered by samples, partially cured at the same T, when they undergo non-isothermal DSC. It may be recalled that the degree of cure α, which is considered in our computations, directly represents the fraction of bonds actually formed in the isothermal cure [2]. Hence α reflects the progress of the cure in the molecular sense.

The phenomenological order of the kinetics which allows the best fit of the experimental data is indistinguishable from unity. Therefore, the adequate form of the equation which can describe such kinetics at a given T is
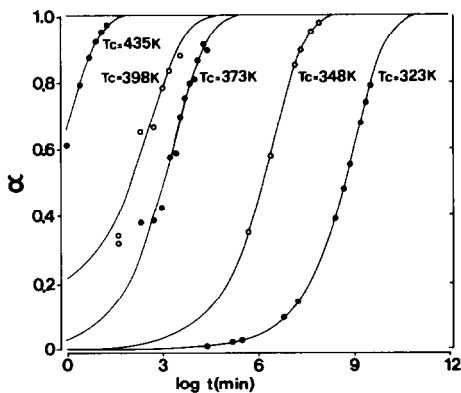
$$1 - \alpha = \exp(-kt)$$

Fig. 3. The degree of cure vs. the time of cure (on a logarithmic scale) at various temperatures.

where k is the kinetic constant. This equation should, however, be modified to take into account the fact that the onset of the exothermic peak in the DSC trace occurs when some bonds among the molecules of epoxies and hardeners are already formed, i.e. when α is already over zero. This "shift" may indeed be negligible in many cases and accordingly was not considered in previous work [1,2].

In the present case, however, for the sake of matching the kinetics of cure with the information given in the TTT diagram, the non-simplified equation was used:

$$1 - \alpha = \left(1 - \alpha_{gel}\right) \exp\left[-k\left(t - t_{gel}\right)\right] \qquad (3)$$

which also allows the α_{gel} values to be computed. Figure 3 shows the α vs. t trends at various temperatures. The very large differences among the respective cure rates required the use of a logarithmic scale for the abscissa. Table 1 reports the k and the t_{gel} values at each temperature. The formal activation energy found for the cure rate is about 94 kJ mol^{-1}, which is close

TABLE 1

The phenomenological kinetic constant k and the time required to attain gelation, t_{gel}, for various temperatures of isothermal cure

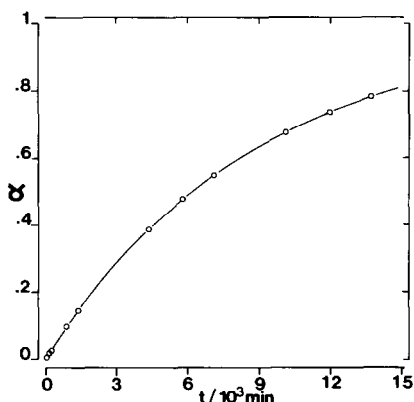| T (K)	k (min^{-1})	t_{gel} (min)
323	1.13×10^{-4}	
348	1.43×10^{-3}	440
373	3.19×10^{-2}	14.9
398	6.60×10^{-2}	3.5
435	9.73×10^{-1}	1.6
443	1.62	less than 1.5

Fig. 4. The degree of cure vs. the time of cure at 323 K. At this temperature the system does not undergo gelation. The curve starts from the origin and no time shift (i.e. t_{gel}) is observable.

to that computable for t_{gel} from the slope of the straight line fit of log t_{gel} vs. $1/T$ [7]. In this computation the data concerning samples cured at 323 K have not been included, since no gelation actually occurs at this temperature (see Fig. 1). In fact, the system held at 323 K remains below the horizontal straight line which passes through the intersection between the gelation and the vitrification curve in the TTT diagram, i.e. at $T = 334$ K. Under these conditions the system undergoes vitrification without any previous gelation process; therefore it has no definite long-range network and probably cannot be properly matched with the polymers obtained at higher temperatures. It is indeed possible to realize that the α vs. t trend observed for $T = 323$ K (see Fig. 4) does actually pass through the origin, i.e. no shift is observed which may account for the time required for the gelation. Nevertheless, the phenomenological kinetic order is close to unity also at this temperature and the corresponding k value is in line with those computed for the other temperatures. As a final consideration, it may be of some interest to recognize directly that the degree of cure attained at the gelation point and at the vitrification point does significantly depend on the temperature of cure.

In Fig. 5, for the sake of analogy with the TTT diagram, the temperature of cure, T_c, has been plotted against α. The curve concerning α_{gel} has the trend expected for a process where forces driving the attainment of equilibrium conditions (i.e. a perfectly ordered lattice) are in competition with the hindering effect of the growing network, just as in the case of glass formation from melts [9]. The trend observed for α_{vit} can be represented by a straight line which intersects the branches of the curve drawn for α_{gel} at about 335 K and 445 K respectively. The whole plot is therefore a representation of the TTT diagram reported in Fig. 1, where the time of cure has been replaced by the degree of cure in the abscissa.
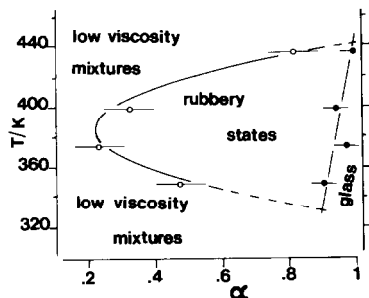
Fig. 5. Temperature of cure T_c vs. the degree of cure α_{gel} and α_{vit} at the gelation and vitrification point respectively. For comments see the text.

It is apparent that isothermal cure cannot yield fully cured polymers if the cure temperature is below 445 K, whereas a mixture of reactants held at 450 K should be able to attain the condition $\alpha = 1$ without previous gelation. The $T_{g\infty}$ of this system should therefore be close to 450 K. For $T_c < 335$ K, the system would escape gelation and undergo vitrification at $\alpha < 0.9$.

CONCLUSIONS

Isothermal and non-isothermal DSC investigations allow the TTT diagram of a polymer system to be drawn.

The simple model proposed in the Appendix suggests an interpretation of the process of gelation in terms of viscosity. It is possible to recognize that the degree of cure attained at the gelation point depends on the temperature of cure and that this crucial process is similar to the formation of a glass phase from a melt.

APPENDIX

In previous work [8] devoted to the correlation between the glass transition temperature T_g and the degree of cure α, the following relationship was suggested between the viscosity η and α:

$$d\eta = \gamma\eta \, d\alpha \tag{A1}$$

where

$$\gamma = \log[\eta(\alpha = 1)/\eta(\alpha = 0)]$$

In the case of a cure process (beyond the gelation) with phenomenological kinetics of the first order, i.e.

$$1 - \alpha = (1 - \alpha_{gel}) \exp[-k(t - t_{gel})] \tag{A2}$$

the following expressions can be derived from eqn. (A1):

$$\log[\eta/\eta(\alpha = 0)] = \gamma(1 - \alpha_{gel}) \exp(kt_{gel})[1 - \exp(-kt)]$$

and

$$\log[\eta(\alpha = 1)/\eta(\alpha = 0)] = \gamma(1 - \alpha_{gel}) \exp(kt_{gel})$$

These give directly the following equation:

$$\log[\eta_{gel}/\eta(\alpha = 1)] = 1 - \exp(-kt_{gel}) \tag{A3}$$

Accordingly, t_{gel} and k data at various temperatures allow the plot shown in Fig. 2 to be drawn.

ACKNOWLEDGEMENT

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