Theoretical Evaluation and the Effect of Thermal Degradation on the Time–Temperature–Transformation (TTT) Diagram of Bisphenol A Epoxies

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ABSTRACT: A brief discussion about the Time–Temperature–Transformation (TTT) diagram is presented. Using diamino diphenylsulfone-cured diglycidyl bisphenol A as a representative example, its TTT diagram is completed by including the thermal degradation. The theoretical diagram as obtained from the kinetics of curing and thermal degradation is compared with experimental data. The agreement is good, slight deviations are observed only in the time to vitrify above 150°C and the maximum available glass temperature, which is due to side reactions and onset of thermal degradation during curing. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3894–3896, 2003

Key words: epoxies; TTT diagram; cure kinetics; thermal degradation; side reactions

INTRODUCTION

From its original development, the Time–Temperature–Transformation (TTT) diagram has become a valuable tool in education to characterize the changes and transitions during curing of thermosets from liquid to rubber up to the final glass.[1–3] In some cases, attempts were also made to include the thermal degradation[4,5] and to introduce theoretical models.[6–8] However, all these suffer from the limited data base, because due to experimental restrictions only data at intermediate temperatures are available, but not from both the high and low temperature regions.

So, since appropriate theoretical models for both the kinetics of curing[9–11] and thermal degradation[12] are available, it seems more promising to calculate all data, i.e., the times to gel and to vitrify, and that of devitrification, from an independent basis, and to compare them with experimental data.

THEORY

All theoretical background is discussed in detail in the literature, so it may be outlined here in short.

Curing of epoxies by amines proceeds via an autocatalyzed second-order mechanism. The increasing glass temperature must be accounted for by introducing a mobility term,[9,10] so the reaction rate is obtained by

$$\frac{dp}{dt} = (k_1 + k_2 p)(1 - p)^2 e^{\{(E_s/RT)[(1/T-T_0)-(1/T-T_0^i)]\}} \quad (1)$$

where k_1 and k_2 are temperature-dependent rate constants that follow Arrhenius kinetics by

$$k_1 = k_1^0 e^{-(E_{A1}/RT)} \quad (2)$$

and

$$k_2 = k_2^0 e^{-(E_{A2}/RT)} \quad (3)$$

where k_1^0 and k_2^0 are the pre-exponential factors and E_{A1} and E_{A2} are the corresponding activation energies.

The p is the cure conversion and E_s is the segment activation energy that characterizes the segmental mobility. T is the absolute temperature and $T_0 = T_g - 45$ a reference temperature below T_g, where all mobility ceases. T_0^i accounts for the degree of advancement at the beginning of the reaction.

The increasing glass temperature during curing can be characterized by[11]

$$T_g = [T_g^\infty - K_1(1 - p)]\left(1 + K_2\frac{X_c}{1 - X_c}\right) \quad (4)$$

where T_g is the actual glass temperature, T_g^∞ is the backbone glass temperature, and K_1 and K_2 are constants characterizing the influences of end groups and crosslinks on the glass temperature.

X_c is the crosslink density defined as the mole fraction of structural units present as crosslinks dependent on cure conversion. For the system discussed

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here (difunctional resin and tetrafunctional curing agent at stoichiometric equivalence), it is obtained from statistics by

$$X_c = \frac{1}{3}[2p^3(1 - p) + p^4] \qquad (5)$$

Finally, according to ref. 12, the thermal degradation can be considered as a reversal of curing, its kinetics proceeds via a first-order mechanism and can be characterized by

$$p_t = p_i e^{-k_d t} \qquad (6)$$

where p_t is the actual glass temperature after some degradation time t and p_i is the initial degree of cure as obtained from eqs. (1)–(3). The rate constant k_d again follows Arrhenius kinetics by

$$k_d = k_d^0 e^{-(E_{A(d)}/RT)} \qquad (7)$$

So all theoretical relations are available that are necessary to calculate the time to gel, the time to vitrify and also that for devitrification after long exposure times at high temperatures and thus to complete the TTT diagram on a proper theoretical basis.
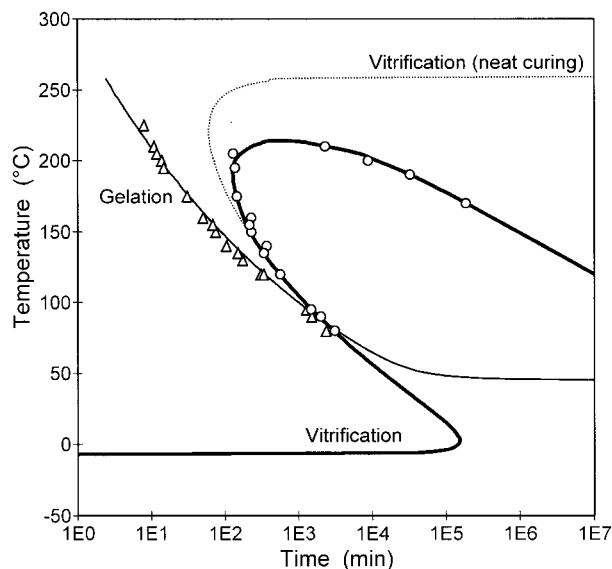
THE TTT DIAGRAM

A TTT diagram is a plot of the time to gel (t_{gel}) and the time to vitrify (t_{vit}) for isothermal cure over a wide temperature range, usually between the glass temperature of the unreacted monomer mixture and that of the fully cured resin.

Since the gel point is constant and dependent only on functionality and stoichiometry—for diglycidyl bisphenol A (DGBA) and 4,4'-diamino diphenylsulfone (DDS) at stoichiometric equivalence it is $p_{gel}=0.577$—and since T_g known from eqs. (4) and (5), these data can be calculated from cure kinetics and completed by including the data of thermal degradation. This was already used to establish a preliminary TTT diagram from kinetics[9]; it is now completed by the thermal degradation and new experimental data. The data for thermal degradation were obtained following the procedure reported in ref. 12.

All data used for calculation are reported elsewhere[9,12]; they are as follows:

$k_1^0 = 6.7E5$ (min^{-1})
$E_{A1} = 64$ (kJ/mol)
$k_2^0 = 4.7E5$ (min^{-1})
$E_{A2} = 59$ (kJ/mol)
$E_s = 0.3$ (kJ/mol)
$T_g^\infty = 383$ (K)
$K_1 = 117$ (K)

Figure 1 Completed TTT diagram of a DGBA/DDS epoxy as obtained from the kinetics of curing and thermal degradation and its comparison to experimental data (experimental data from the literature[3,13] and this laboratory).

$K_2 = .777$
$k_d^0 = 6.89E9$ (min^{-1})
$E_{A(d)} = 138$ (kJ/mol)

The TTT diagram thus obtained is shown in Figure 1. As already outlined in ref. 9, good agreement is found for gelation, although TBA detects not true gelation, but an isoviscous state somewhat prior to gelation.[13] However, the deviation is not severe and also partially hidden by the logarithmic time scale.

The dotted line is the theoretical vitrification curve considering only neat curing without thermal degradation, the solid line below 150°C also the theoretical line. Above 150°C up to the maximum it is a fit to the data. The experimental data are collected partially from the literature[3,13] and this laboratory, where initial vitrification data were obtained by torsional braid analysis (TBA) and the degradation data by differential scanning calorimetry (DSC).

The vitrification curves exhibit the characteristic S-shaped appearence with a maximum at low and a minimum a high temperatures as known from the literature.[1–7] The maximum of the time to vitrify at low temperatures is found from kinetics 10°C above the glass temperature of the unreacted monomer mixture at a cure time of about 1.5E5 min. Due to the slow reaction, this maximum cannot be detected by experiment. From theory, the minimum of the time to vitrify is found at 220°C after 61 min cure time, then the time diverges due to the vanishing cure reaction.

Good agreement between experimental data and theory is found in the low temperature region. Then, beginning from ~150°C, a delay in the experimental

vitrification times from theory is observed and the glass temperature exhibits a maximum around ~210–215°C. Maximum glass temperatures of 210–212°C for this resin are also reported in the literature.[14,15]

Beyond that glass temperature maximum, during devitrification, the system is governed only by thermal degradation, since all epoxy groups are consumed meanwhile either by curing or side reactions. Here again good agreement is obtained between the experimental data and the theoretical line for degradation, which was calculated for a 212°C glass temperature maximum.

The deviation of the experimental data from theory above 150°C and the lower maximum glass temperature are due to side reactions and onset of thermal degradation that occur during curing.

The highly reactive epoxy groups undergo many side reactions when exposed to high temperatures, which cause loss of functional groups and therefore loss of potential network bonds.[16–19] Thus, a higher degree of cure is required to compensate for that loss, which leads to a corresponding delay in the time to vitrify and simultaneously to a decrease of the highest available glass temperature.

This is especially true for the usual mode of evaluating a TTT diagram, since here the unreacted samples are transferred to the preheated instrument, such that they are exposed immediately to high temperatures, where they are prone to side reactions.

Therefore the TTT diagram is affected also to some extent by the actual curing conditions, especially the heating rate. So, for a 210°C cure the final glass temperature for this resin was found to increase to 218°C by decreasing the heating rate to 0.1°C/min.[20] It seems, that near the maximum of the vitrification curve, side reactions and thermal degradation may account for an almost equal loss of the glass temperature from the theoretical value for neat curing down to the 210–218°C observed in practice. Their extent can be estimated to be around 3–4% each, since a glass temperature of 210°C corresponds to a degree of cure $p=0.92$.

It seems that degradation is governed primarily by the stability of the resin itself and its effective degree of cure, but not by the cure mechanism. Some data on cationically cured DGBA epoxies,[21] which parallel the degradation line obtained here, support this assumption.

CONCLUSIONS

The TTT diagram of a DGBA resin (Epikote® 828) and DDS was established from the kinetics of curing and thermal degradation and compared to experimental data using TBA.

Good agreement was found for the time to gel, although the method does not detect true molecular gelation, but an isoviscous state somewhat prior to gelation. However, the deviation is only marginal.

The time to vitrify exhibits a maximum at 1.5E5 min cure time ~10°C above the glass temperature of the unreacted monomer mixture. It is not accessible by experiment.

Good agreement between theory and experiment was found for the time to vitrify up to ~150°C, then a delay is observed, which is due to side reactions of the epoxy groups, that occur during curing. At long exposure times, when degradation becomes prominent, the experimental data again follow the theoretical curve based on the 210°C glass temperature maximum.

Due to side reactions and thermal degradation, the highest available glass temperature decreases to ~210–218°C depending on cure conditions. Both parameters are responsible for that decrease by approximately equal amounts.

It seems that degradation is primarily governed by the inherent resin stability and its effective degree of cure, but not dependent on the cure mechanism.

Thus, the curing of thermosets is represented by a competition between curing, side reactions, and thermal degradation.

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