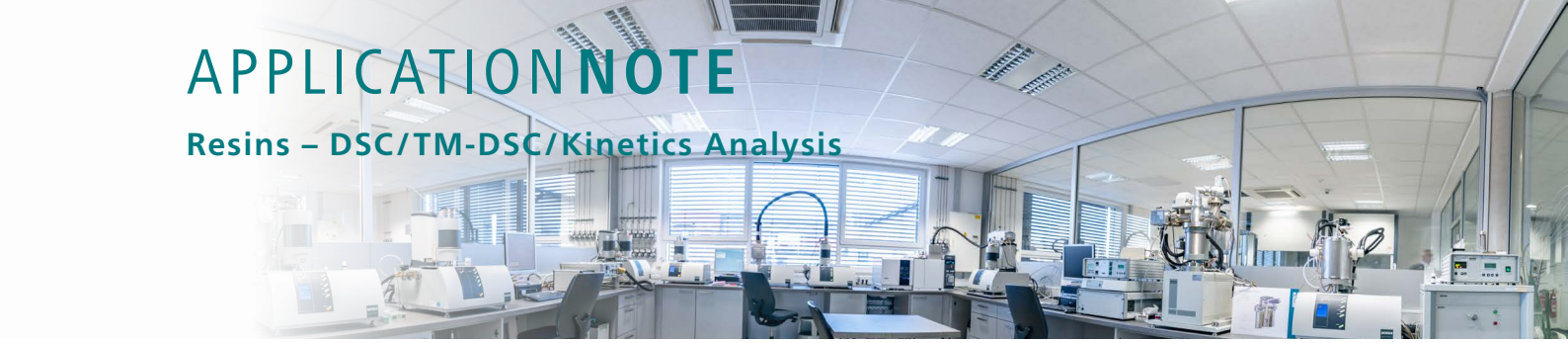


Time-Temperature-Transformation (TTT) Diagramm of Epoxy Resin

Claire Strasser, Dr. Elena Moukhina and Dr. Mohammed Bouzbib

Introduction

Epoxy resin is a highly versatile and durable material widely recognized for its exceptional mechanical, thermal, and adhesive properties. Since its discovery, it has become a cornerstone of innovation across various industries due to its ability to withstand extreme environmental conditions, resist chemical damage, and provide structural strength.

At the core of many epoxy resin formulations lies 2,2-bis(4-(2,3-epoxypropyl) phenyl) propane, commonly known as bisphenol A diglycidyl ether (formula in figure 1, BADGE). BADGE serves as a key component in the production of epoxy resins, offering excellent adhesive and anticorrosive properties.

Their production involves mixing an epoxy monomer with a hardener, which initiates a cross-linking reaction under controlled temperature, transforming the liquid resin into a solid 3D network.

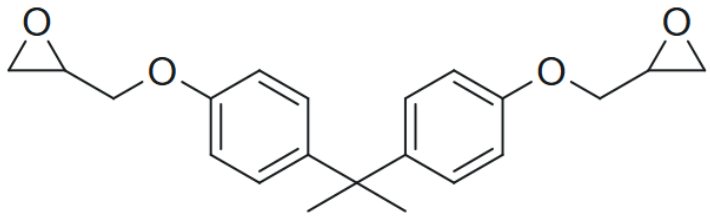
During curing, two key transitions occur: gelation and vitrification. Gelation marks the irreversible transformation of the resin into a viscoelastic gel, associated with increased viscosity and stiffness, typically occurring at a degree of cure between 55% and 80%. Vitrification happens when the resin reaches the glass transition temperature (T_g). At this point, the resin passes from a rubbery to a glassy state, yielding a slowdown or even a complete stop of the cure rate. Vitrification is reversible, and raising the temperature can restart the reaction. For these transitions, it is critical to ensure proper resin flow before gelation and to optimize the curing conditions for reaching a high degree of cure.

This study proposes a method of creating Time-Temperature-Transformation (TTT) diagrams for epoxy resin systems by analyzing curing kinetics through non-isothermal temperature-modulated DSC and rheological measurements. This approach uses a two-step kinetic model to develop a TTT diagram, mapping the timing of gelation and vitrification during isothermal curing and thus aiding in optimizing curing parameters and reducing energy costs.

Materials: Epoxy Resin Composition and Mixing Ratio

The measurements were conducted on a commercial epoxy resin (Resoltech 1040T), composed of DGEBA (resin) and two diamines, 4,4'-methylenebis(cyclohexy lamine) and 3-aminomethyl-3,5,5-trimethylcyclohexyl-amine (hardener).

An epoxy mixture with a 1000:300 w/w resin-to-hardener ratio was studied.



1 Bisphenol A diglycidyl ether

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Instruments, Methods and Workflow

- **Dependence of Glass Transition Temperature, T_g, on the Degree of Cure:** Tests for partially cured samples: Temperature-Modulated DSC (TM-DSC), analytical dependence; Di Benedetto's equation: Kinetics Neo
- **Kinetic Analysis and Kinetic Model:** Tests at different heating rates: Differential Scanning Calorimetry (DSC). Kinetic modelling based on DSC tests and T_g dependence on the degree of cure: Kinetics Neo
- **Determination of Gel Point:** Isothermal Tests (Rheology)
- **Construction of Time-Temperature-Transformation (TTT) Digram:** Kinetics Neo

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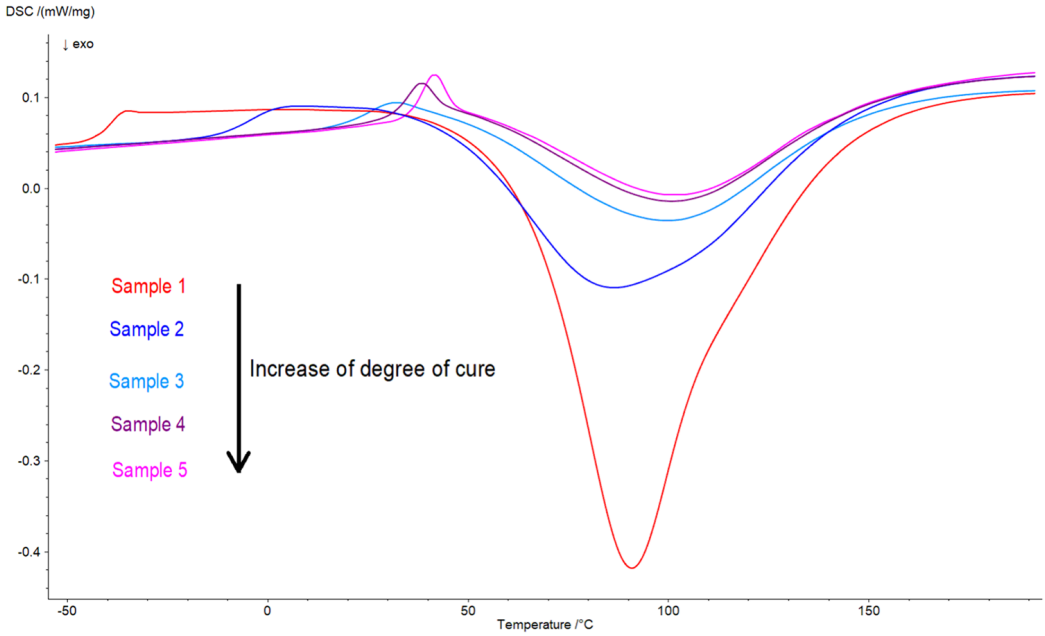
Dependence of Glass Transition Temperature, T_g, on the Degree of Cure

The dependence of the glass transition on the degree of cure was investigated using the temperature-modulated DSC (NETZSCH DSC 214 with Autosampler).

Five samples were prepared in aluminum crucibles with a pierced lid and then partially cured at 20°C for different times to have different degrees of cure. These partially cured samples were tested by temperature-modulated DSC to separate the glass transition effect from the enthalpy relaxation and the remaining curing.

TM-DSC tests were performed from -60°C to 200°C at a heating rate of 3 K/min with a 60 s modulation period and a 0.8 K temperature amplitude under nitrogen flow (40 ml/min).

The total heat flow from the temperature-modulated DSC tests is depicted in figure 2. The results show the residual curing for these samples. The glass transition temperature of the fully uncured sample 1 has the lowest value. The higher the initial degree of cure, the lower the enthalpy of the exothermal peak of residual curing. As long as the reaction progresses, the glass transition temperature increases, leading to its overlapping with the exothermal curing peak for higher degrees of cure.



2 Total heat flow of the modulated DSC measurements at 3 K/min on samples 1 to 5 with different degrees of cure

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The glass transition temperature, T_g, from the reversing heat flow and the curing enthalpy from the non-reversing heat flow for each sample are detailed in table 1 along with the curing time as 20°C and the degree of cure, calculated from the residual enthalpy. The fully uncured sample 1 was completely cured during the first heating, where it has a glass transition temperature T_{g0} [1]. Then it was heated a second time in order to determine the glass transition temperature ($T_{g\infty}$) for the totally cured material (last line in table 1).

The degree of cure of the samples 2 to 5 was determined by comparing the enthalpy of the curing peak to the enthalpy of the fully uncured sample.

Based on the measured values, summarized in table 1, a plot of the glass transition temperature versus degree of cure can be created by applying the DiBenedetto equation (2).

$$(T_g - T_{g0}) / (T_{g\infty} - T_{g0}) = \lambda\alpha / (1 - (1 - \lambda)\,\alpha) \quad (2)$$

T_{g0}: glass transition temperature of the uncured resin
$T_{g\infty}$: glass transition temperature of the fully cured resin
α: degree of cure
λ: fitting constant

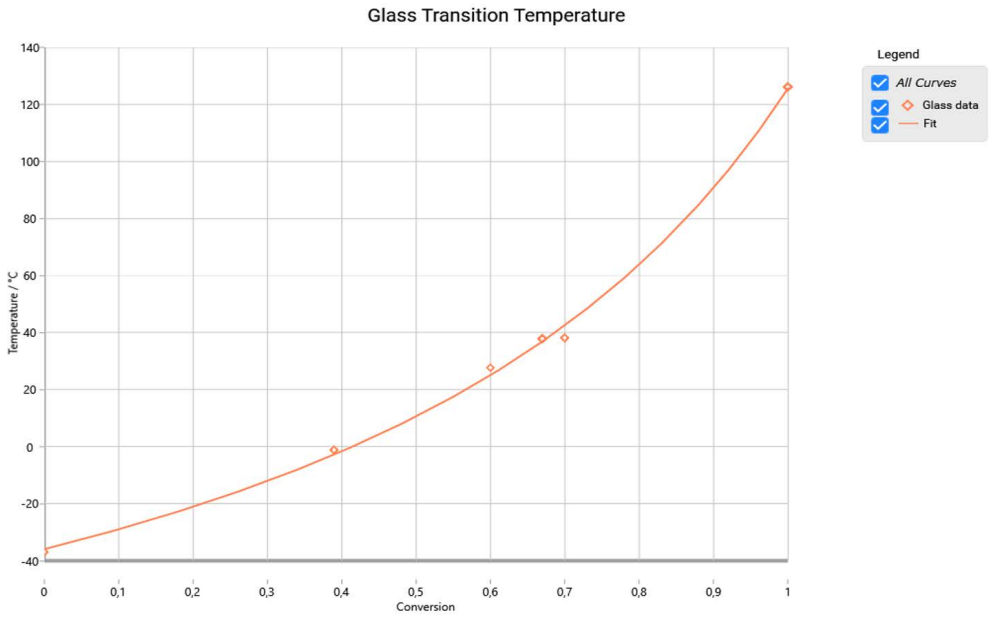
Table 1 Results of the temperature-modulated DSC measurements

Sample	Curing time at 20°C [h]	Glass transition temperature [°C]	Enthalpy of rest curing [Jg^{-1}]	Degree of cure [%]
1	0	-36.8	471	0
2	4.75	-1.1	287	39
3	9.51	27.7	187	60
4	14.27	37.9	154	67
5	19.03	41.3	145	69
1st, 2nd heating	-	126.1	0	100

Figure 3 depicts the glass transition temperatures as a function of the degree of cure gathered experimentally as well as the DiBenedetto fit in the Kinetics Neo software.

This fit was obtained with the following parameters:

T_{g0} = -35.8°C
$T_{g\infty}$ = 125.7°C
λ = 0.40



3 Glass transition temperature versus degree of cure with fit according to the DiBenedetto equation.

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Kinetic Analysis and Kinetic Model

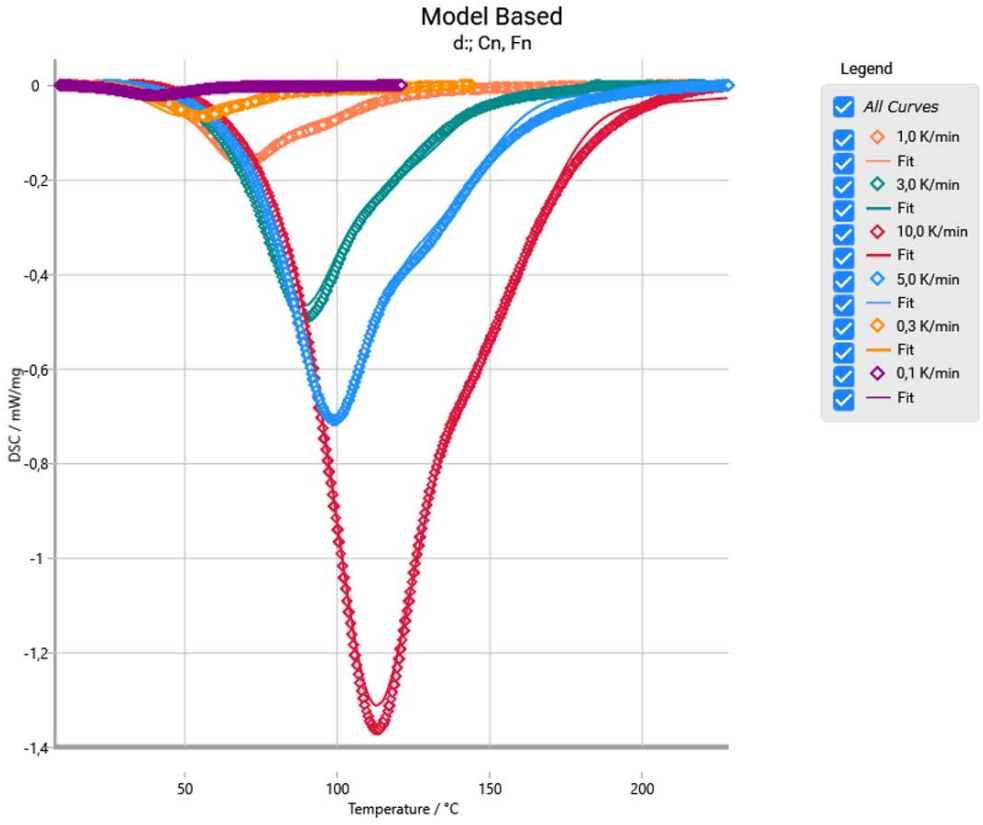
A second set of tests used varying heating rates (0.1 to 10 K/min) to study reaction kinetics. For this, new mixtures were prepared, weighed, and immediately measured (samples 6 to 11).

Figure 4 shows the measured experimental data (points) along with the curves (solid) calculated with the kinetics parameters optimized in the NETZSCH Kinetics Neo software, based on six DSC measurements at different heating rates of 0.1 to 10 K min^{-1}. A model with two successive steps was selected to characterize the reaction kinetics because the shoulder detected in the exothermal curing peak along with the peak minimum indicated a 2-step reaction.

This model included an autocatalysis reaction for the first step (simplified Kamal-Sourour equation) and an n^{th} order reaction for the second step. Additionally, diffusion control above the glass transition temperature (see DiBenedetto results from TM-DSC tests) was considered for the second step. A non-linear regression was performed to optimize the kinetics parameters (pre-exponential factors, activation energy and reaction order); see table 2.

Table 2 Kinetics parameters results

Parameter	1st step	2nd Step
Activation energy (kJ/mol)	51.1	54.8
Log (PreExp) (1/s)	4.3	4.7
ReactOrder n	1.7	1
Contribution	0.7	0.3



4 Description of the curing DSC curves using the Kinetics Neo software R2 coefficient of determination > 0.99.

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Determination of the Gel Point

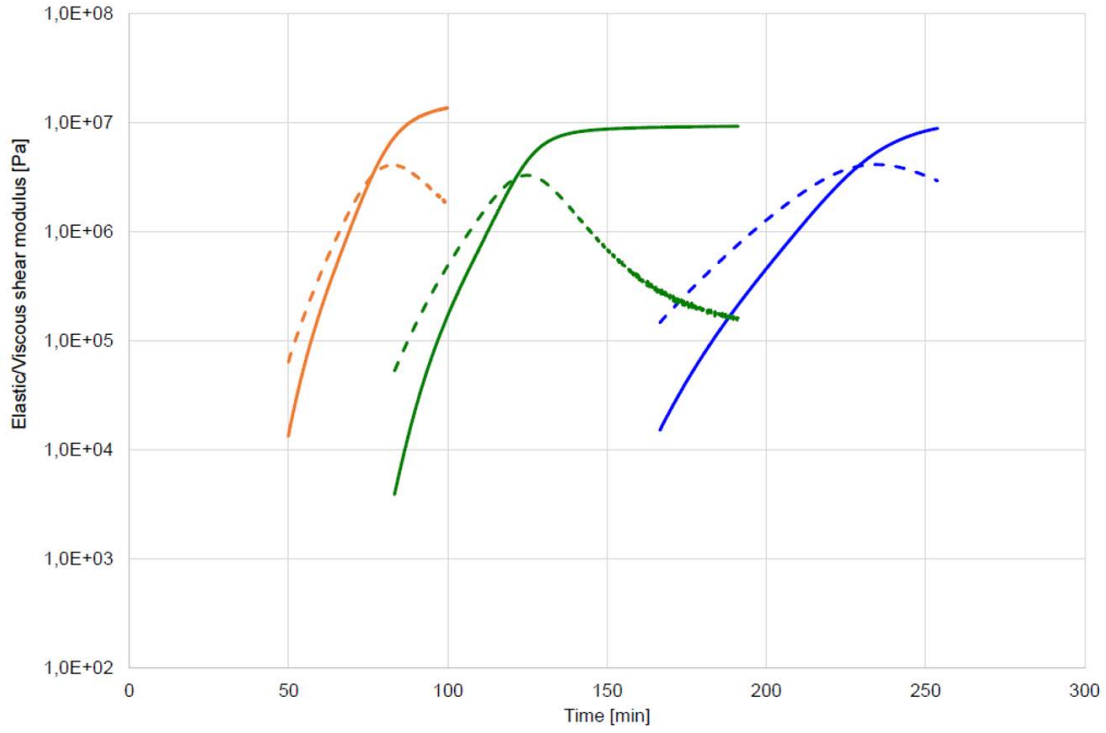
Rheological tests for gel point determination were conducted using a NETZSCH Kinexus Prime rheometer: For that, isothermal tests were performed from 40°C to 60°C with 0.1% strain at 1 Hz.

Figure 5 depicts the curves of the elastic (G') and viscous (G'') shear moduli during the three isothermal measurements at 40°C, 50°C and 60°C. They show a crossover of G´ and G´ indicating the gel point, above which the material is no longer able to flow for the frequency applied. The higher the temperature, the faster the reaction and the lower the time elapsed up to gel point.

Table 3 presents a summary of the results. The cure degree achieved at each temperature was determined using the gel point time from the conversion curve as a function of temperature or time predicted by the kinetics analysis.

Table 3 Gel point time obtained for the different isothermal tests

Temperature [°C]	Gel point time [min]	Degree of cure [%]
40	224.8	63
50	117.3	53
60	72.1	66



4 Thermal conductivity versus temperature

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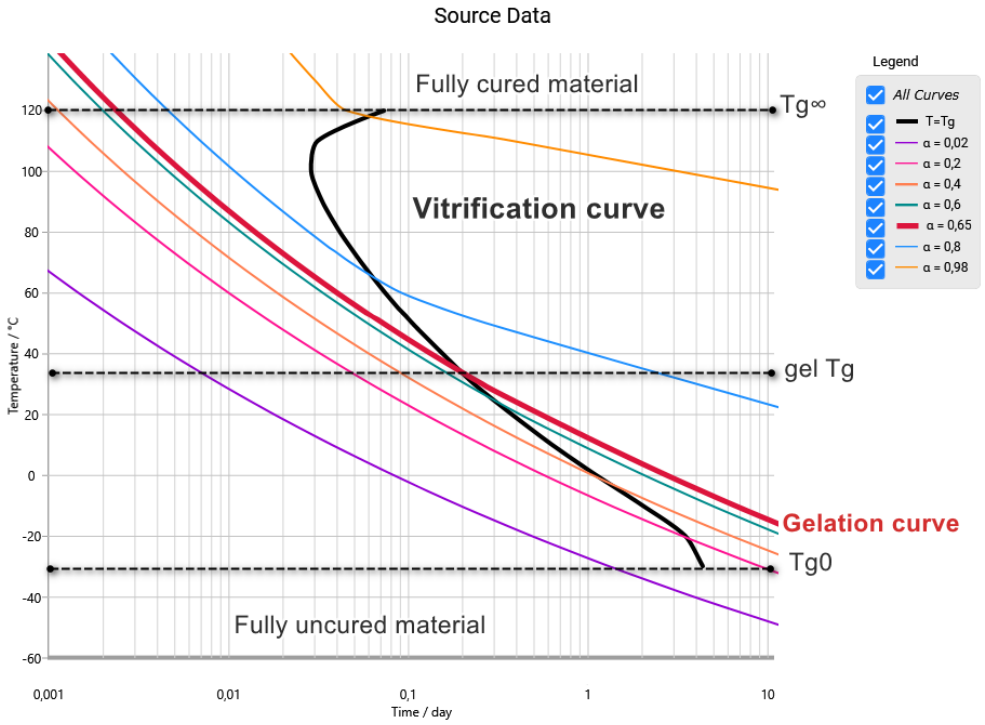

6 Time-Temperature-Transformation diagram of the examined epoxy resin.

Construction of Time-Temperature-Transformation (TTT) Diagram

The NETZSCH Kinetics Neo software was used for kinetics analysis and TTT diagram simulation.

The TTT diagram in figure 6 illustrates the material's cure state under isothermal conditions. Below -36.8°C, the monomers remain glassy, with a very slow curing rate, reaching 1% cure in at least 12 hours. Between -36.8°C (T_{g0}) and 126.1°C ($T_{g\infty}$), curing behavior varies with temperature. If the temperature stays below $T_{g(gel)}$ (crossing of the gelation and vitrification curves), vitrification occurs before gelation. Above ${}_{gel}T_g$, the material reaches the gel point before diffusion slows the reaction.

Conclusion

The use of Kinetics Neo software for calculating Time-Temperature-Transformation (TTT) diagrams offers a more advanced and predictive approach to analyzing the curing behavior. By leveraging kinetics analysis, it accurately identifies vitrification and gelation points, enabling precise control over material curing and more efficient process optimization.

Benefits of Kinetics Analysis

Reduced Costs & Waste: Optimized curing time lowers energy use and material waste, cutting costs and enhancing sustainability.

Accurate Cure Prediction: Provides precise modeling of the epoxy resin curing process, helping predict gelation and vitrification behavior under different temperature conditions.

Reduced Experimental Time: By using the NETZSCH DSC, rheological measurements and the Kinetics Neo software, this approach eliminates the need for long-term tests by avoiding trial-and-error experimentation while speeding up material development.

References

[1] Strasser, C., Moukhina, E., & Hartmann, J. (2024). Time-Temperature-Transformation (TTT) Cure Diagram of an Epoxy–Amine System. Macromolecular Theory and Simulations. https://doi.org/10.1002/mats.202400039

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