ANALYZING & TESTING

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KINETICS AND TTT DIAGRAM FOR CURING OF EPOXY-AMINE SYSTEM

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Agenda

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1. Introduction
2. Dependence of Tg on the Degree of Cure (DSC, TM-DSC)
3. Reaction Kinetics
4. Gel Point determination (Rheology, Kinetics)
5. Construction of TTT Diagram
6. Validation of TTT diagram

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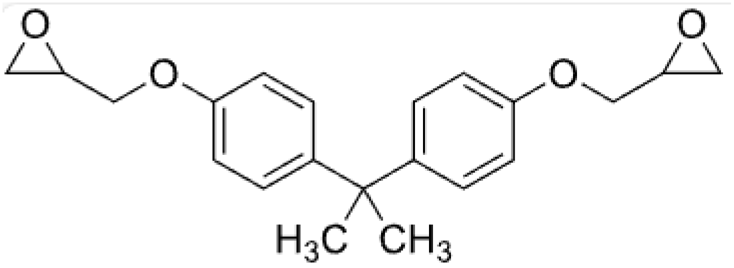
1 Introduction

Diglycidylether bisphenol A (DGEBA)-based epoxy resin.



a hardener (e.g., amine) is mixed to the epoxy monomer and this mixture is introduced into a mold containing (or not) a reinforcement.

Under the influence of temperature for thermally activated curing systems the hardener initiates ring opening of the epoxy group.

A crosslinking reaction follows, during which the epoxy and the hardener form a 3D network. During this, the material transforms from a processable liquid resin into a structural solid.

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Macromolecular Theory and Simulations

Research Article

Time–Temperature-Transformation (TTT) Cure Diagram of an Epoxy–Amine System

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Abstract

A time–temperature-transformation diagram is created for the curing reaction of a diglycidylether bisphenol A (DGEBA)-based epoxy resin. It results from a kinetic analysis performed by means of dynamical differential scanning calorimetry (DSC) measurements; a gelation curve determined with isothermal and dynamical rheological tests; and a vitrification curve obtained from temperature-modulated dynamic DSC measurements. The resulting diagram is validated by comparison of isothermal measurements with the corresponding calculated curves.

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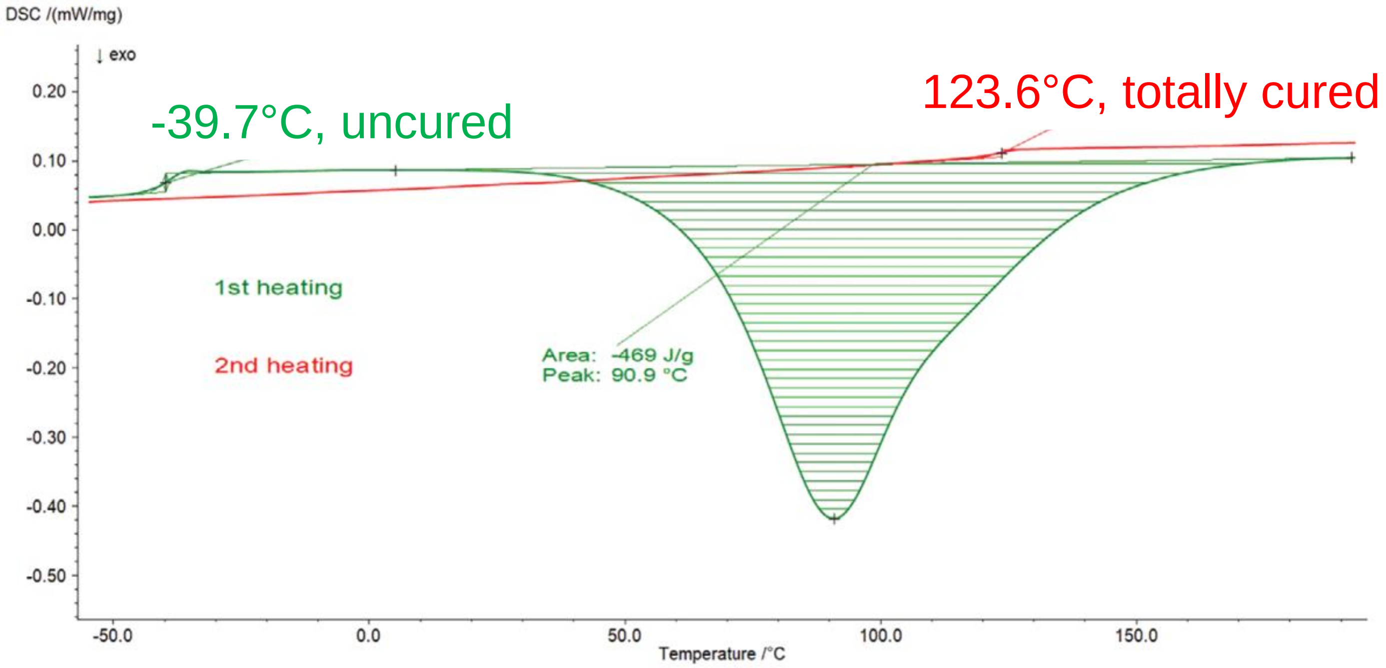
2 Dependence of Tg on the Degree of Cure (DSC, TM-DSC)

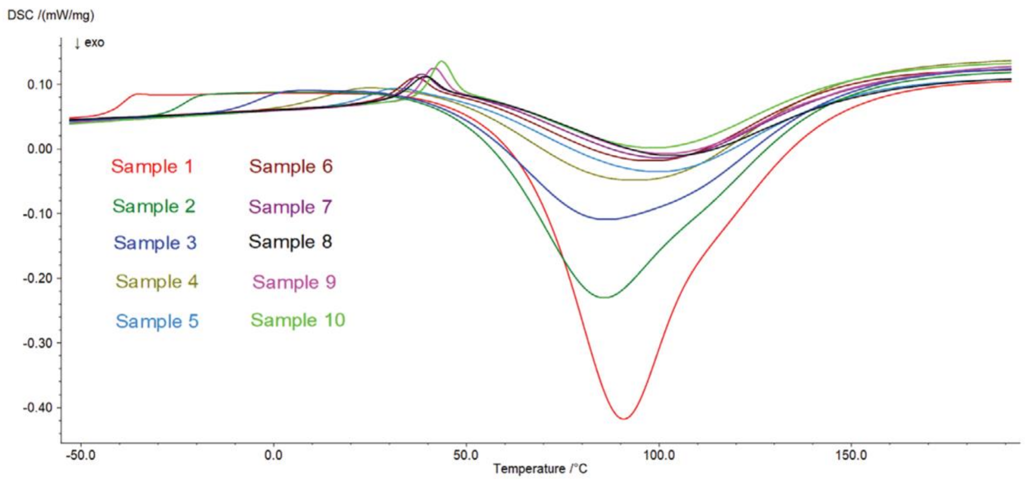
Moving of Tg during curing



Total heat flow of the modulated DSC measurement performed on sample 1 during the first and second heating

Dependence of the Glass Transition Temperature on the Degree of Cure (DSC)

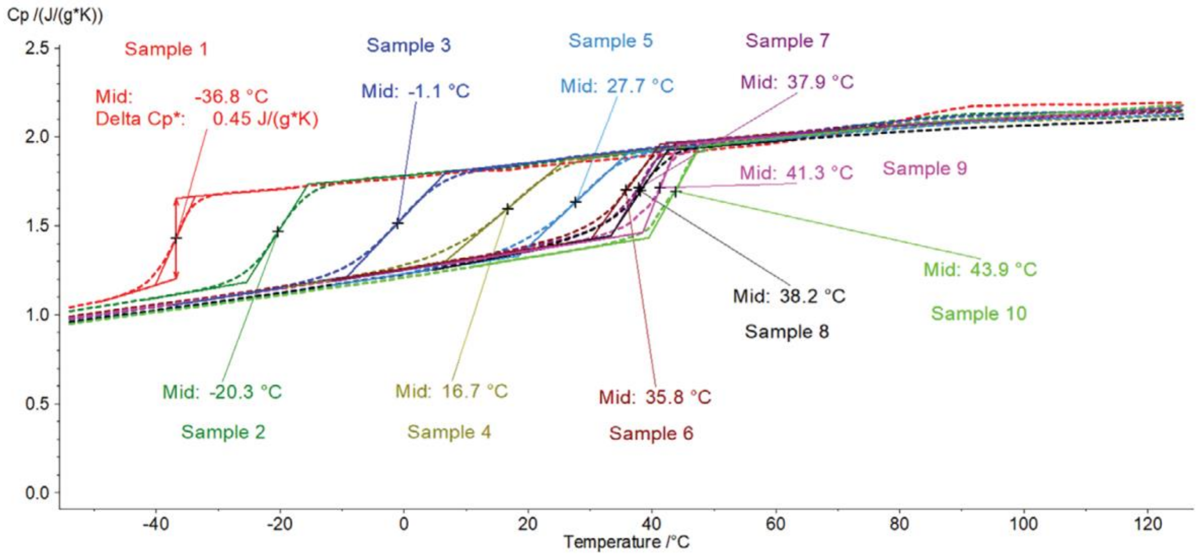
Tg can be measured by DSC only begin of curing process



Sample	Curing time at 20 °C [h]	Degree of cure [%]
1	0	0
2	2.38	20
3	4.75	39
4	7.13	53
5	9.51	60
6	11.89	67
7	14.27	67
8	16.65	70
9	19.03	69
10	21.41	71
1, 2nd heating	–	100

Total heat flow of the modulated DSC measurements at 3 K min−1 on samples 1–10 with different degrees of cure.

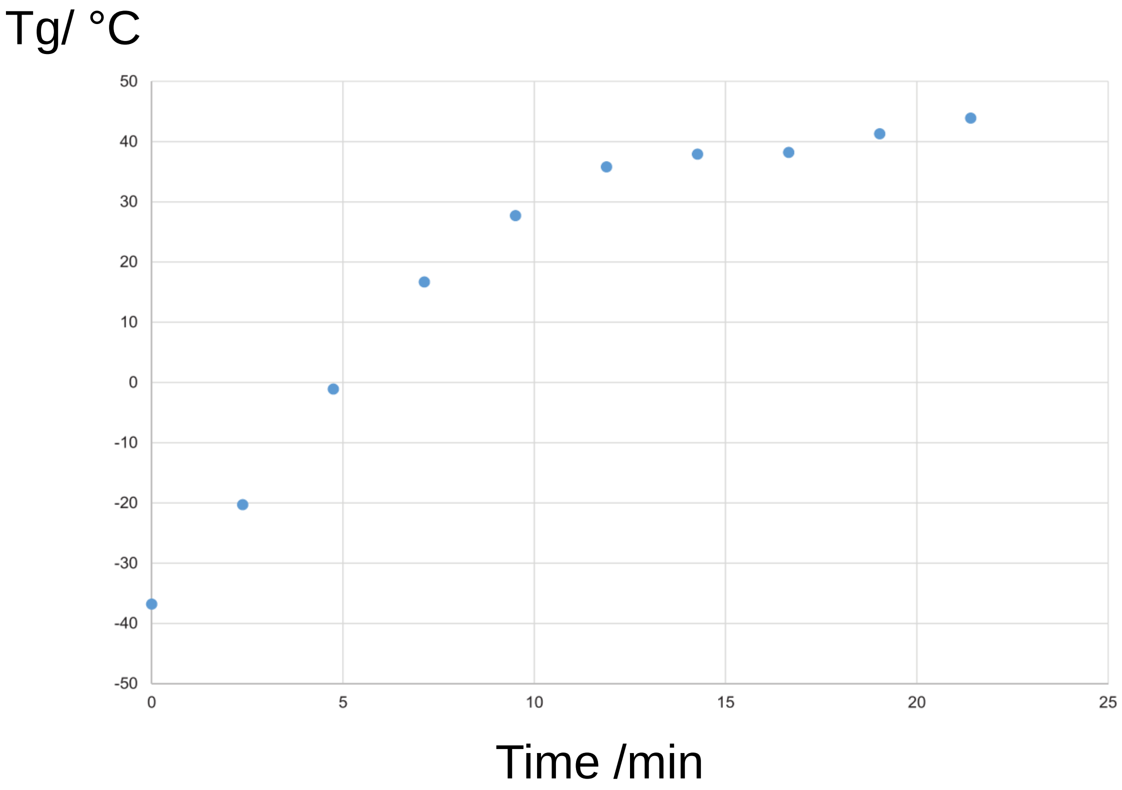
Dependence of the Glass Transition Temperature on the Degree of Cure (TM-DSC)



Sample	Glass transition temperature [°C]
1	−36.8
2	−20.3
3	−1.1
4	16.7
5	27.7
6	35.8
7	37.9
8	38.2
9	41.3
10	43.9
1, 2nd heating	126.1

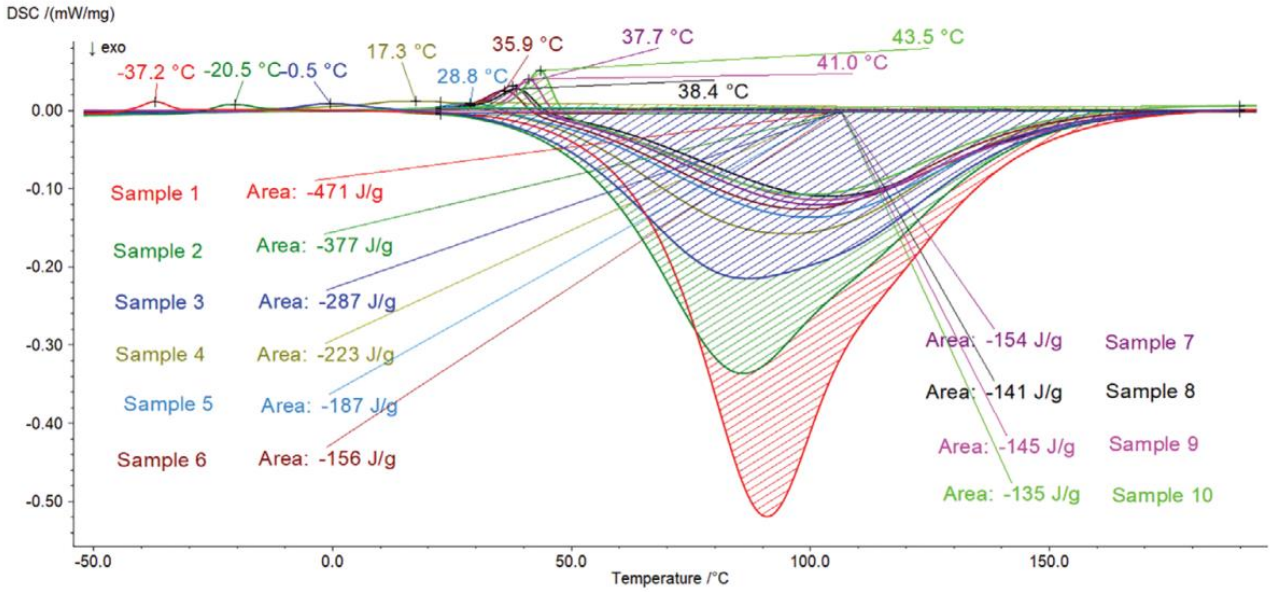
Reversing Cp (specific heat capacity) for the samples with different degrees of cure

Glass transition temperature vs time at 20°C



Progression of the glass transition temperature (midpoint) as a function of the curing time at 20 °C

Dependence of the rest Enthalpy on the Degree of Cure (DSC)



Sample	Peak enthalpy [J g^{-1}]
1	471
2	377
3	287
4	223
5	187
6	156
7	154
8	141
9	145
10	136
1, 2nd heating	0

Nonreversing heat flow for the samples with different degrees of cure

Results of TM-DSC

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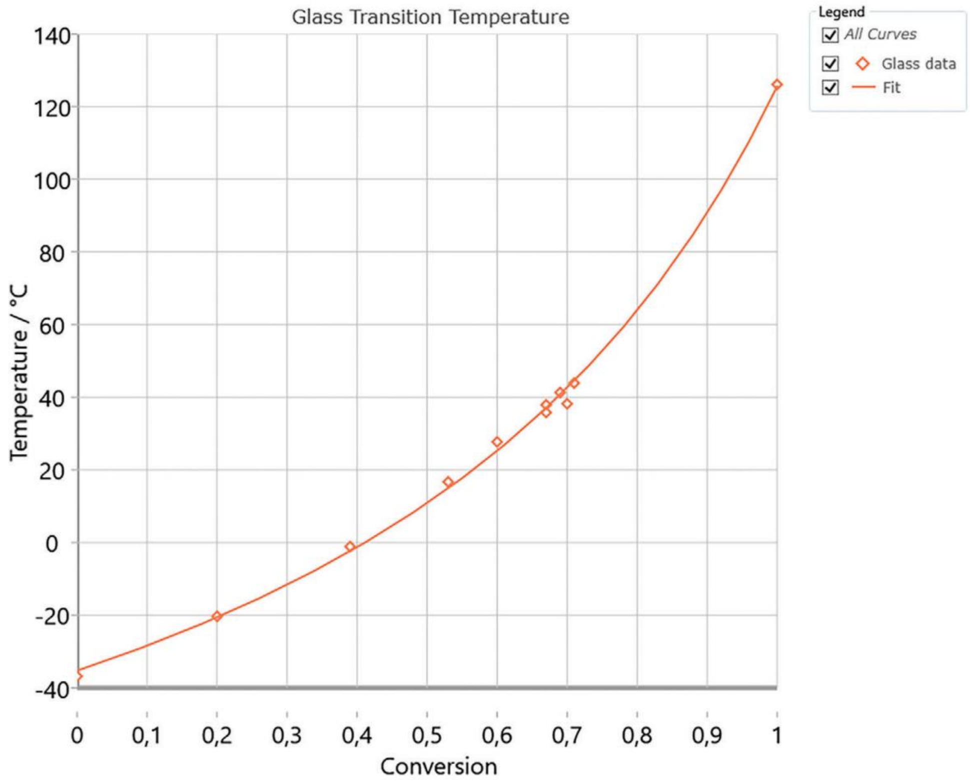
Table 1. Results of the temperature-modulated DSC measurements.

Sample	Curing time at 20 °C [h]	Glass transition temperature [°C]	Peak enthalpy [J g^{-1}]	Degree of cure [%]
1	0	−36.8	471	0
2	2.38	−20.3	377	20
3	4.75	−1.1	287	39
4	7.13	16.7	223	53
5	9.51	27.7	187	60
6	11.89	35.8	156	67
7	14.27	37.9	154	67
8	16.65	38.2	141	70
9	19.03	41.3	145	69
10	21.41	43.9	136	71
1, 2nd heating	–	126.1	0	100

Glass transition Temperature depends on Conversion



Di Benedetto equation

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

$$\lambda = \frac{\Delta C_p\,(\text{fully cured material})}{\Delta C_p\,(\text{fully uncured material})} = 0.4$$

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3 Reaction Kinetics

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Chemical rate

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha)$$

$$f(\alpha) = (1 - \alpha)^n$$

Kamal-Sourour

$$\frac{d\alpha}{dt} = (1-\alpha)^n \cdot \left[A_1 \cdot \exp\left(-\frac{E_{a1}}{RT}\right) + A_2 \cdot \alpha^m \cdot \exp\left(-\frac{E_{a2}}{RT}\right)\right]$$

Diffusion rate

$$k(T) = A \cdot \exp\left(-\frac{E}{RT}\right)$$

$$\frac{1}{k} = \frac{1}{k_D} + \frac{1}{k_{chem}}$$

$$k(T) = k_{chem} = A \cdot \exp\left(-\frac{E}{RT}\right)$$

William-Landels-Ferry:

$$k_D(\alpha, T) = D_0 \exp\left[\frac{C_1 (T - T_g(\alpha))}{C_2 + T - T_g(\alpha)}\right]$$

Double-step kinetic model with vitrification

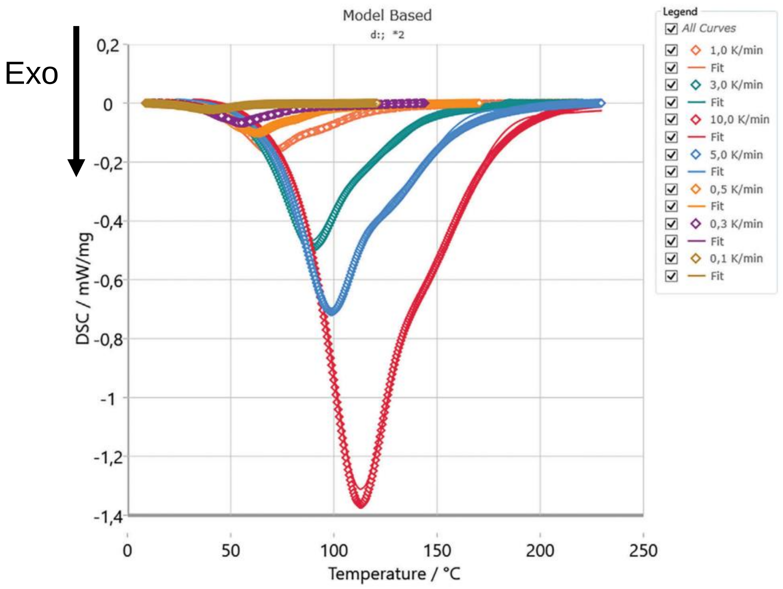


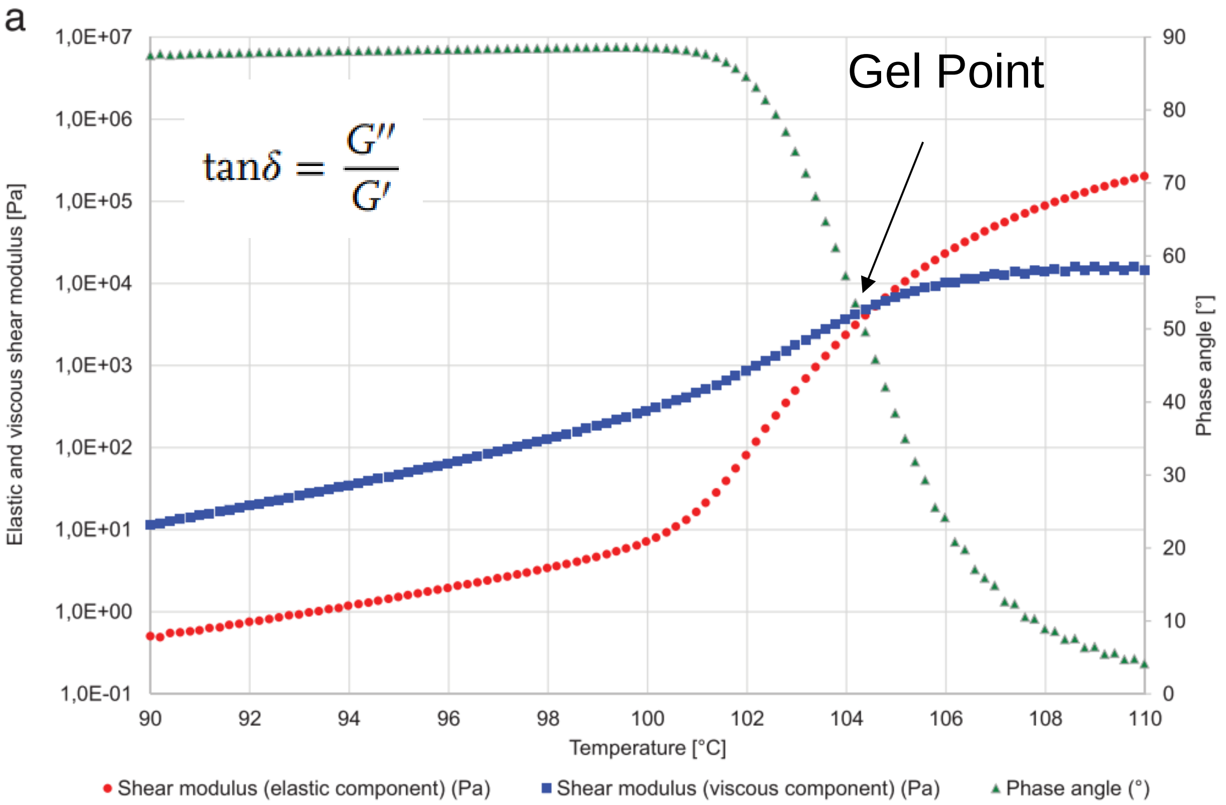
Table 2. Result for the kinetic parameters, obtained by means of the non-linear regression.

Parameter	Result of the nonlinear regression	
	First step	Second step
Activation energy	51.081 kJ mol^{-1}	54.83 kJ mol^{-1}
Log(PreExp)	4.31Log(1/s)	4.73Log(1/s)
ReactOrder *n*	1.74	1.02
Log(AutocatPreExp)	0.96Log(1/s)	–
Log(*K*(diff))	–	−3.68
C1(diff)	–	42.00
C2(diff)	–	50.00 K
Contribution	0.73	0.27

Description of the curing DSC curves by means of the kinetic model (2-step reaction; 1st step according to Equation (7), 2nd step according to Equation (6), diffusion-controlled reaction according to Equation (10) for T < Tg).

4 Gel Point determination (Rheology, Kinetics)

Gel Point Determination over shear modulus



$$\tan\delta = \frac{G''}{G'}$$

Gel Point Determination

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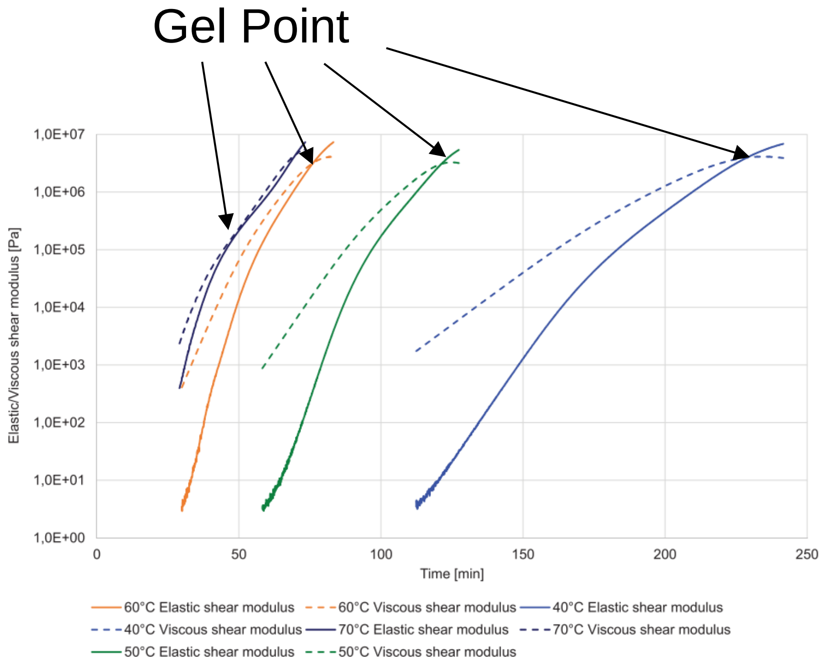


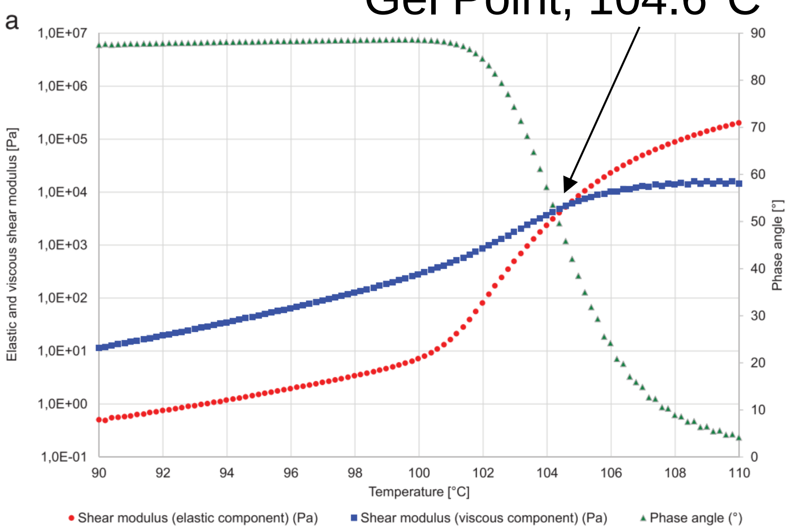
Table 3. Gel point time obtained for the different isothermal tests.

Temperature [°C]	Gel point time [min]	Degree of cure [%]
40	224.8	63
50	117.3	63
60	72.1	66
70	46.5	68

Curves of the elastic (solid line) and viscous (dashed line) shear moduli for isothermal conditions at 40, 50, 60, and 70 °C

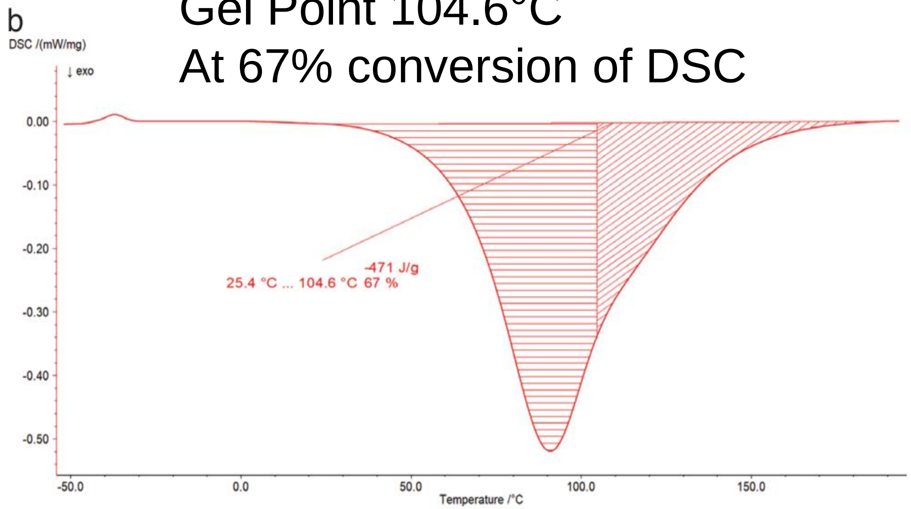
Construction of TTT Diagram: gel point

Gel Point, 104.6°C



Gel Point 104.6°C

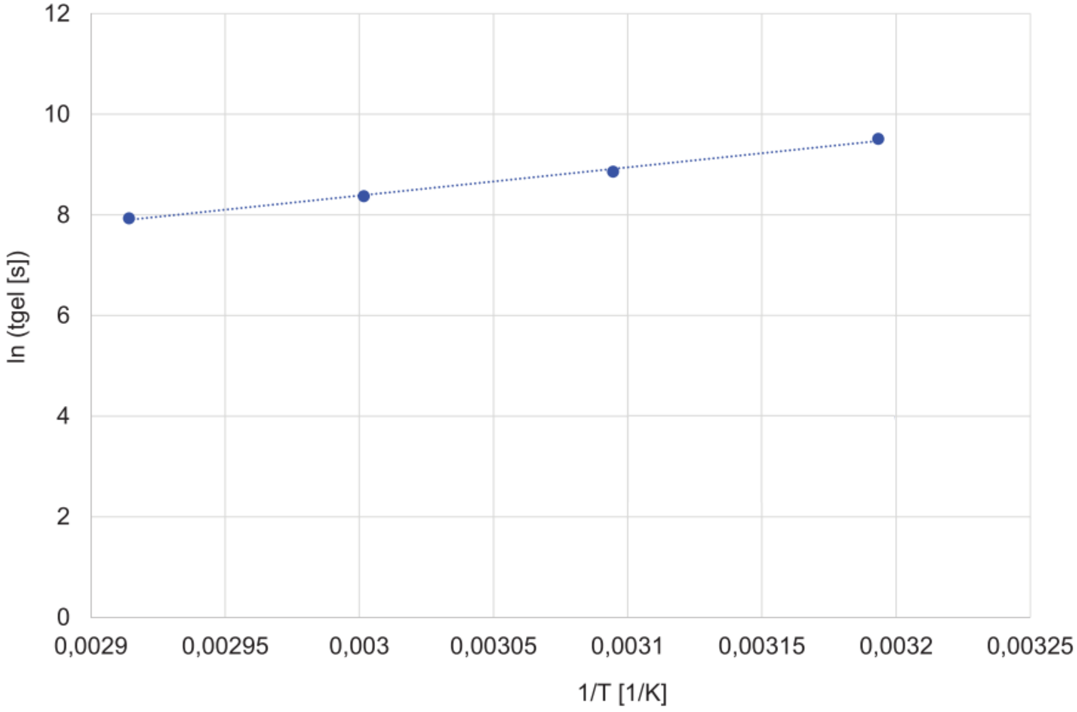
At 67% conversion of DSC



a) Elastic and viscous shear moduli, phase angle measured during the temperature ramp at 3 K min−1

b) Heat flow measured during the temperature ramp at 3 K min−1

Gel Point Determination



Gel time versus 1/T.

$$t_{gel} = C \cdot \exp\left(\frac{E}{RT}\right)$$

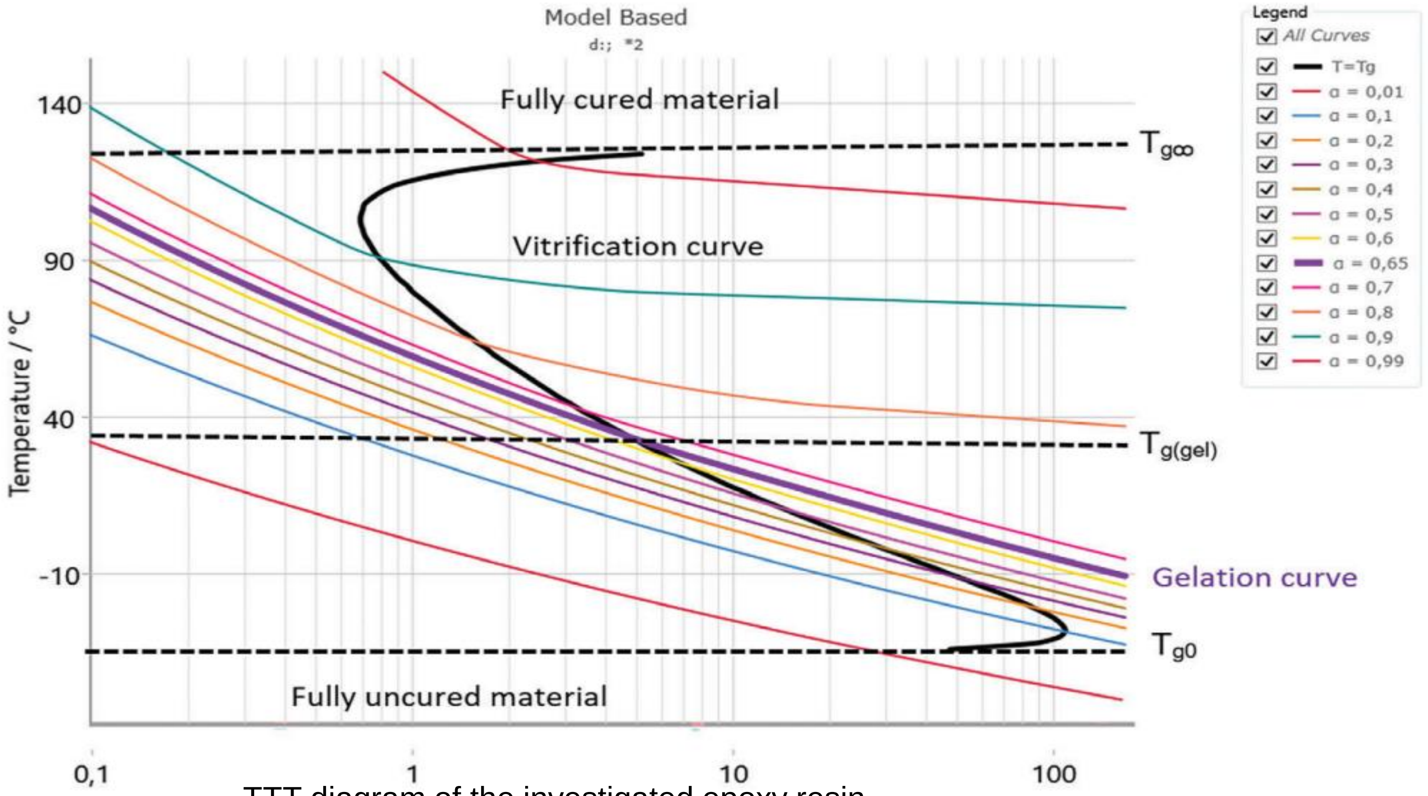
t_{gel}: gel time [s], C: constant dependent on temperature [s], E: activation energy [kJ mol^{-1}] for the reaction up to the gel point, T: temperature of isotherm [K], R: gas constant.

Table 4. Kinetic parameters calculated from the linear fit of the relationship between the gel time and temperature and the corresponding degree of cure (uncertainties calculated according to ref. [22]).

Kinetic parameter	Experimental value
Activation energy	47 +/− 2 kJ mol^{-1}
C	−8.5 +/− 0.9Ln(1/s)
Degree of cure	65 +/− 2%

5 Construction of TTT Diagram

Time-Temperature-Transformation diagram based on DSC data



TTT diagram of the investigated epoxy resin

Time-Temperature-Transformation diagram based on DSC data

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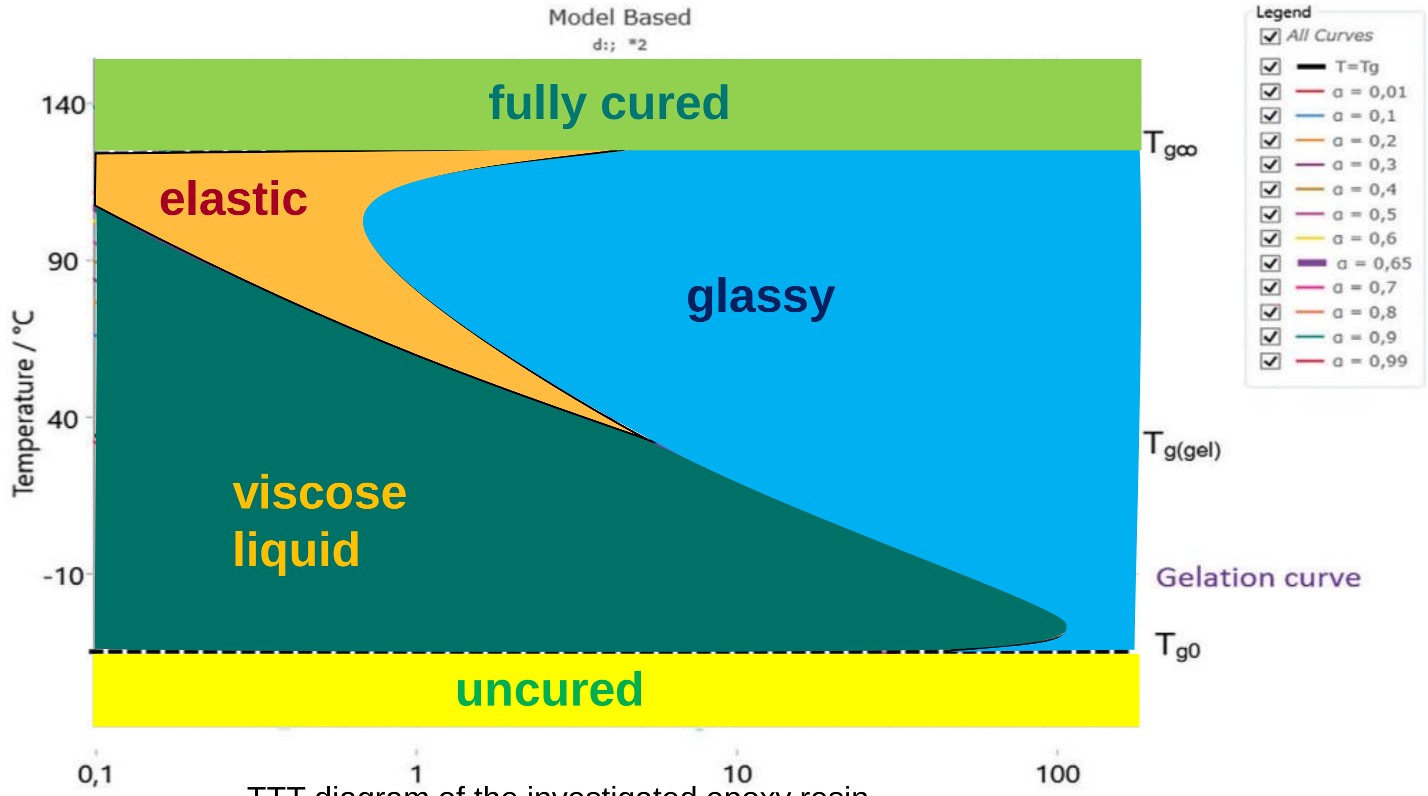

TTT diagram of the investigated epoxy resin

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6 Validation of TTT diagram

Comparison of measured and simulated data
Tg after different time durations at 20°C

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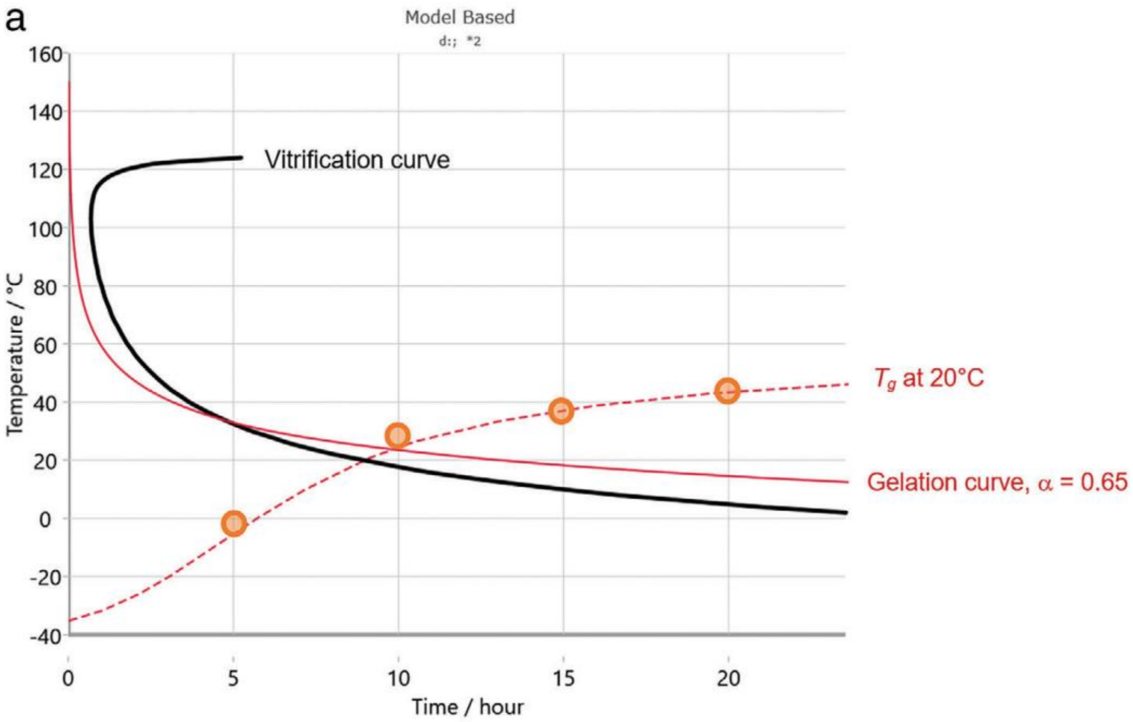
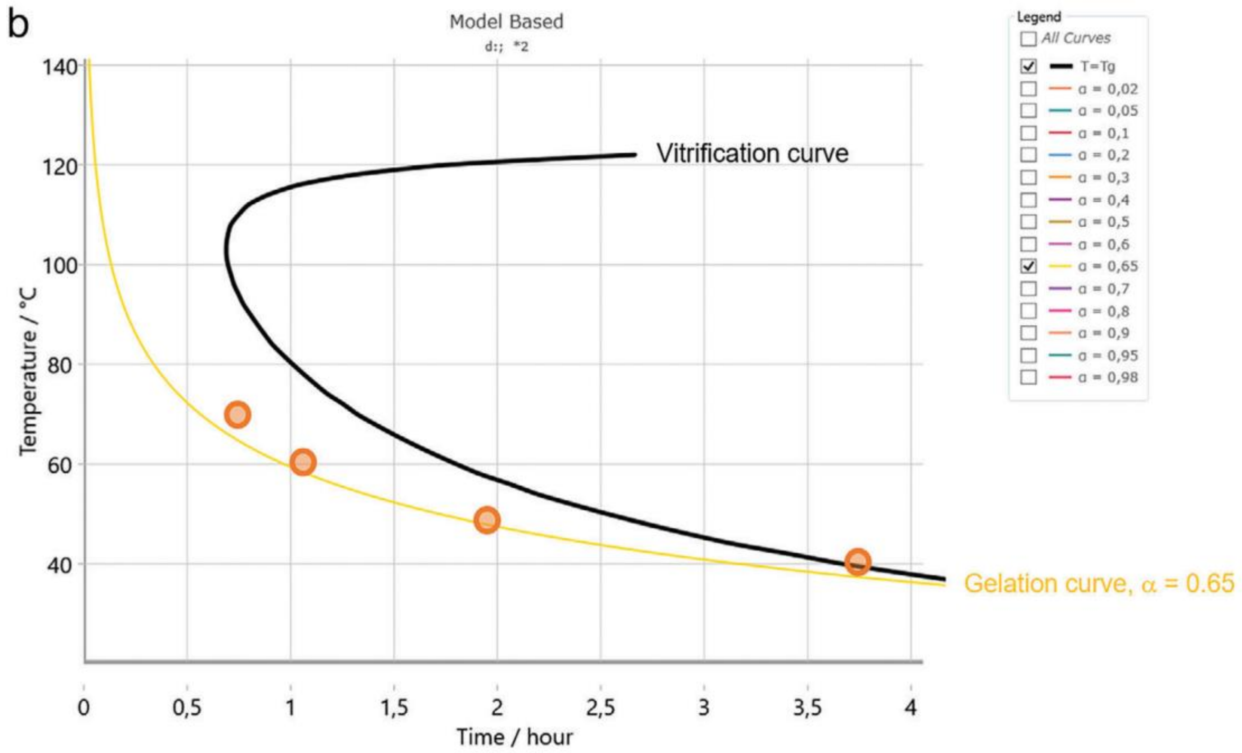


a) Prediction of the glass transition temperature (dashed, red)
‘and measured glass transition temperatures (orange circles) after 5, 10, 15, and 20 h at 20 °C

Comparison of measured and simulated data: Gel Points at different temperatures



b) Prediction of the gelation curve (yellow) and measured gel point times at 40, 50, 60, and 70 °C (orange circles)

Validation of the TTT Diagram

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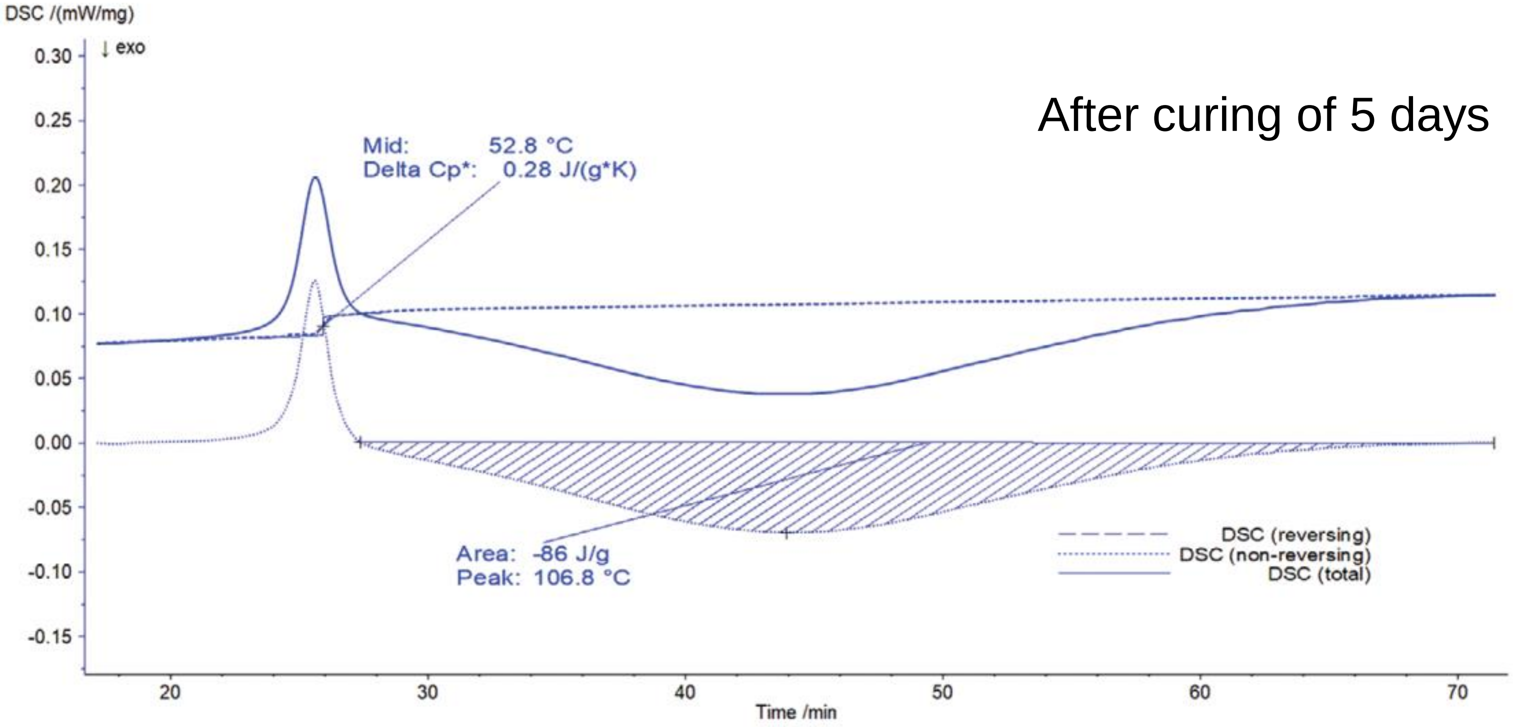
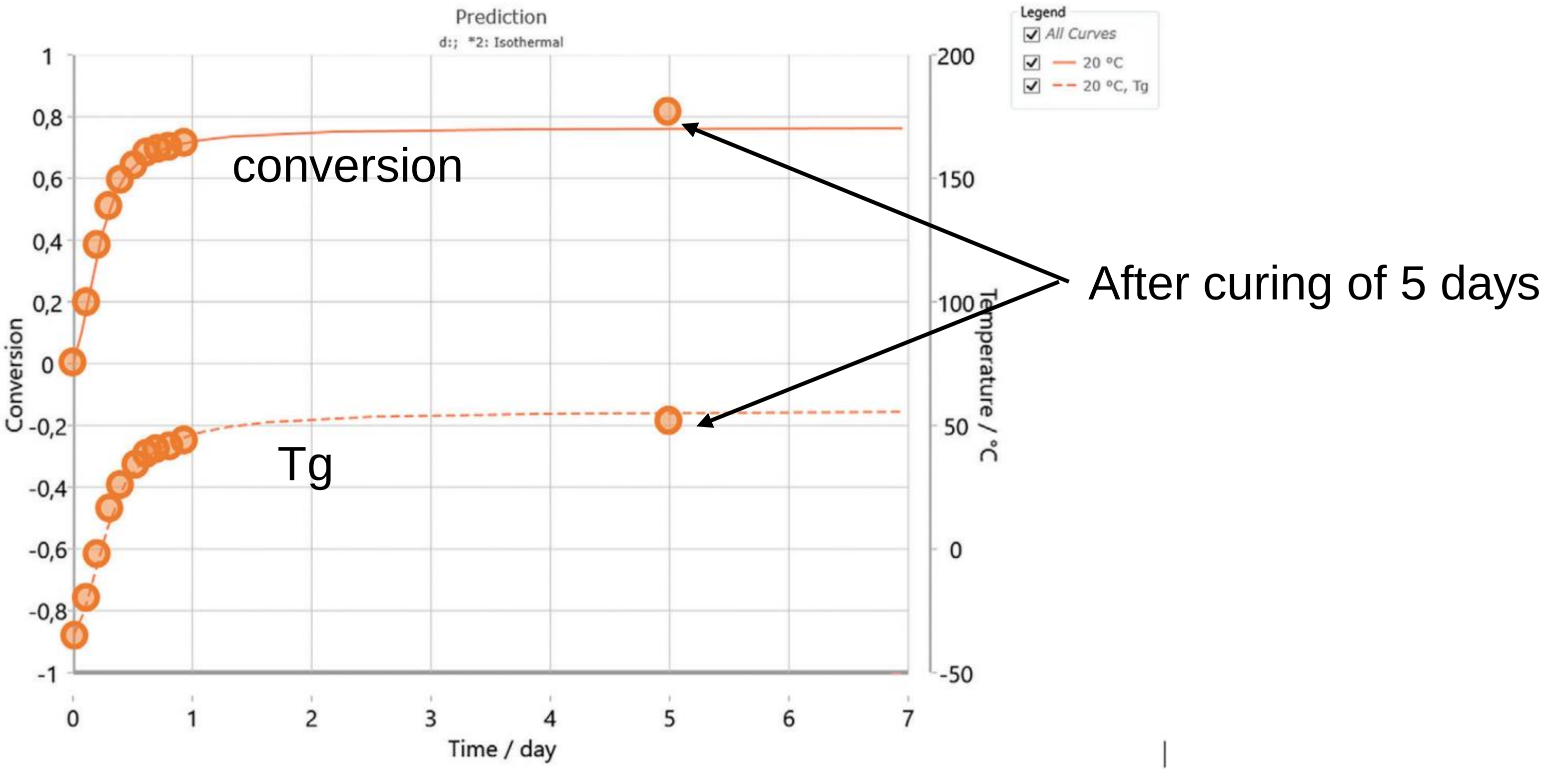


After curing of 5 days

Total, reversing, and nonreversing heat flows of a mixture cured at room temperature during the course of five days

Comparison of measured and simulated data of Tg



Prediction of Kinetics Neo for curing at room temperature

Summary

Time-Temperature-Tranformation Diagram for curing process can be calculated, including the glass transition and gel point

Data for analysis: DSC, TM-DSC, Shear viscosity

Software: Kinetics Neo

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