NATIONAL CENTER for ADVANCED MATERIALS PERFORMANCE

Material Characterization for Processing: ACG MTM45-1

Material Model Development
Final Project Wrap-Up

Prepared by: A. Shahkarami and D. Van Ee
Reviewed by: D. Van Ee

Approved: A.Poursartip

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Version: 1.0

CONVERGENT MANUFACTURING TECHNOLOGIES

Project Definition

Material: ACG MTM45-1

Modeling performed for:

- Cure Kinetics
- Heat Capacity (Cp)
- Viscosity

Material Description

• **MTM45-1** is a variable cure temperature, medium toughness, high service temp modified epoxy system

• Material forms received from ACG are as follows:
  - Fabric Prepreg (HTS5630-145-32%RW, received Aug 22, 2006)
  - UD Prepreg (CFO 526A-36%RW, received Aug 22, 2006)

• Tests were done on UD prepreg and comparison drawn with fabric

• Manufacturer's recommended cure cycles are:

Pre-Cure

Autoclave	**Vacuum Bag**
1-3ºCpm	1-3ºCpm
20hr @ 80ºC or	20hr @ 82ºC or
4hr @ 120ºC	4hr @ 120ºC
2hr @ 130ºC	2hr @ 130ºC
2hr @ 180ºC	

Post-Cure

3ºCpm to initial cure temp
0.3ºCpm to post-cure temp
Hold at 180ºC -0/+5ºC for 2hr -0/+30 min
Cool at 2ºCpm to 70ºC

Material Description

Manufacturer's recommended cure cycles are:

PREPREG

Pre-Cure (at 3Cpm max)

Autoclave
20hr @ 80ºC or
4hr @ 120ºC
3hr @ 135ºC
2hr @ 180ºC

Post-Cure

2 hr at 200±2ºC (for max Tg)
2 hr at 180ºC (for 140C wet service T)
(max temp rate 20ºC per hr from 80ºC

RESIN

Pre-Cure

Autoclave
1-5ºCpm
20hr @ 82ºC or
4hr @ 120ºC
2hr @ 130ºC
2hr @ 180ºC

Vacuum Bag
1-5ºCpm
20hr @ 82ºC or
4hr @ 120ºC
2hr @ 130ºC

Post-Cure

3ºCpm to initial cure temp
0.3ºCpm to post-cure temp
Hold at 180ºC -0/+5ºC for 2hr -0/+30 min
Cool at 2ºCpm to 70ºC

Cure Kinetics Model

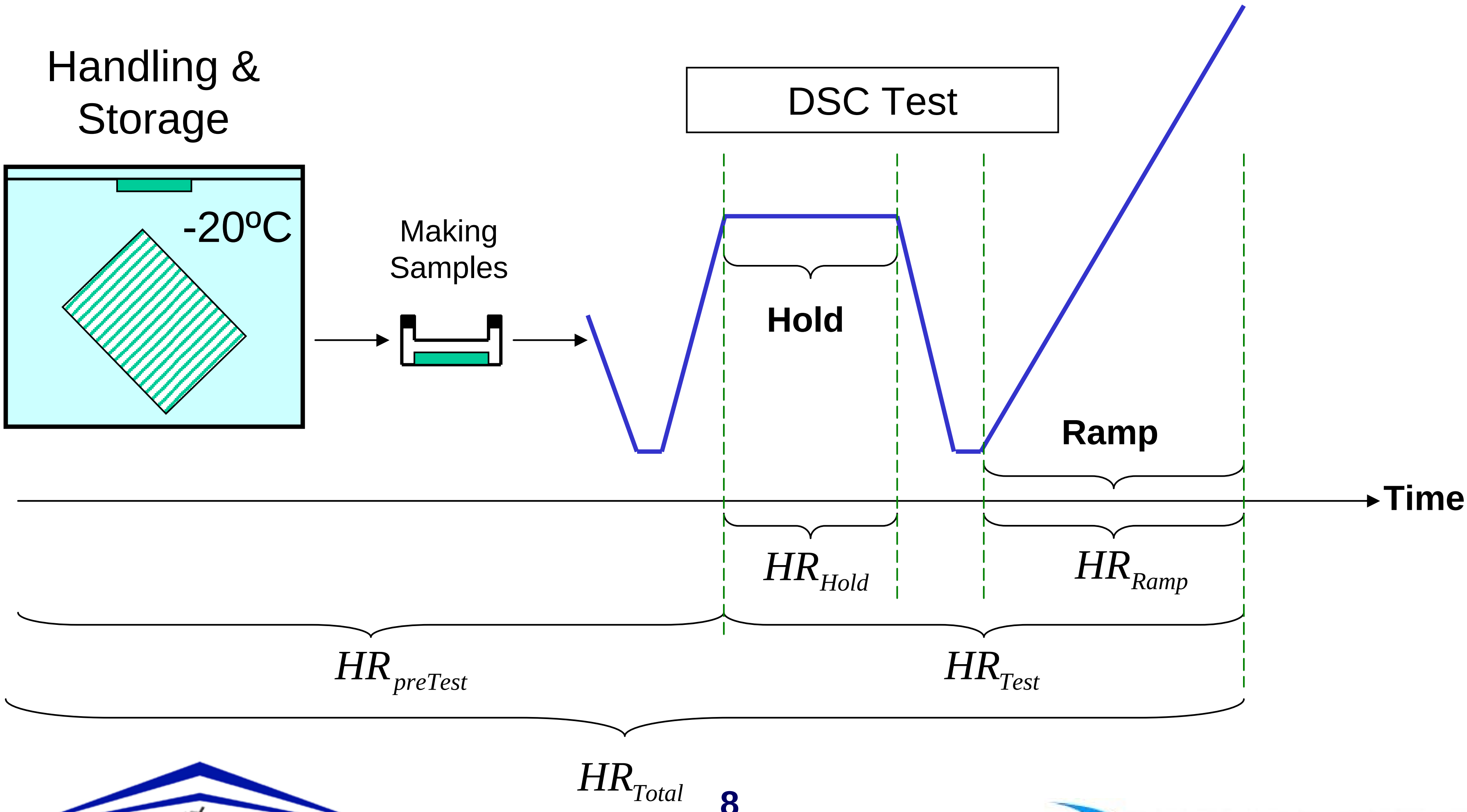
Nomenclature

Iso	or Isothermal: Conditioned isothermal DSC tests where the specimen is held at a constant temperature long enough so that the reaction slows down significantly due to diffusion
Int	or Interrupted: Isothermal tests where the hold segment terminates before the reaction stops due to diffusion
Dyn	or dynamic: DSC tests where the specimen temperature is increased at a constant rate until the reaction completes
RES	or Residual: Dynamic DSC tests performed after the hold segment of Iso and Int tests to complete the remainder of the chemical reaction
CC	or CureCycle: DSC tests designed to recreate the recommended cure cycles for the material, interrupted at certain points to investigate the cure advancement during the cure cycle
x	or DoC: Degree of Cure
x_{Hold}	Degree of cure at the end of the hold segment of isothermal tests
$\dot{x}$	or xdot: Cure Rate
T_g	Glass transition temperature

Nomenclature

HF	Heat Flow, measured in the DSC experiments (W)
HR_{Ramp}	The heat of reaction released during the ramp segment of the DSC tests (in dynamic tests and the residual ramps of the isothermal tests) (J/g)
HR_{Hold}	The heat of reaction released during the hold segment of the DSC tests (mostly in all variation of isothermal tests) (J/g)
$HR_{preTest}$	The heat of reaction released during the cure advancement in material before the start of the test (material handling, storing, etc.) (J/g)
HR_{Test}	The total heat of reaction measured through the two stages of the DSC test (J/g) $\left(= HR_{Hold} + HR_{Ramp}\right)$
HR_{Total}	The total heat of reaction of the material tested (J/g) $\left(= HR_{preTest} + HR_{Test}\right)$
HR_{Iso}^{avg}	The average of the total heat of reaction measured through the various stages of the isothermal DSC tests (J/g)
HR_{Dyn}^{avg}	The average of the total heat of reaction measured through the various stages of the dynamic DSC tests (J/g)
HR_{Total}^{avg}	The average of the total heat of reaction measured through the various stages of all the DSC tests (J/g)
HR_{Model}	Model heat of reaction; the nominal value of total heat of reaction used in the model (J/g)

HR Definition



Summary

• Differential Scanning Calorimetry (DSC) tests were performed to characterize the cure kinetics of ACG MTM45-1. A Q1000 TA Instrument DSC was used for this purpose.

• Normal pans were used to perform the DSC tests on unidirectional prepreg form.

• Characterization was performed on UD tape and comparison to fabric prepreg response was done.

DSC Test Procedure

Isothermal Tests

In isothermal tests, the sample is equilibrated at a very low temperature and then heated up to a predefined hold temperature at a very high rate. The sample is held at this temperature for a predetermined duration of time (i.e. until the reaction stops due to diffusion or full cure in the case of conditioned isothermal tests, or earlier as predefined for interrupted isothermal tests). The sample is then cooled down, followed by a residual ramp at a known rate (typically 1-4 cpm). The residual ramp ensures that the material is fully cured, and provides the material Tg at the end of hold, as well as the residual heat of reaction. A second ramp is also performed to determine the final (full cure) Tg.

Dynamic Tests

In dynamic tests, the sample is equilibrated at a very low temperature and then heated up at a predetermined rate. The goal is to fully cure the sample on the ramp. A second ramp follows to determine the final glass transition temperature (fully cured Tg).

DSC Tests Performed

The DSC tests were performed are summarized below:

- Dynamic tests: 19 tests @ 0.25 to 4ºCpm
- Isothermal tests: 43 tests 100ºC to 205ºC
- Interrupted Isothermal tests: 7 tests at 160ºC
- Other: 2 cure cycle tests, 2 dynamic on fabric

After careful examination of the results and investigation of the consistency of the data, the temperature range of interest was chosen to be 100ºC to 200ºC. However, a number of tests were dismissed due to anomalies and the remaining isothermal and dynamic tests (see table on next slide) were considered in the analysis.

DSC Test Matrix

Test	Mass (mg)	Rate (°C/min)	$Temp_{max}$ (°C)
MTM45-025cpm-02	14.5	0.25	280
MTM45-05cpm-02	12.9	0.5	250
MTM45-075-02	13	0.75	260
MTM45-1cpm-01	6.19	1	250
MTM45-1cpm-02	4.1	1	260
MTM45-1_5cpm-01	6.09	1.5	250
MTM45-1_5cpm-02	5.09	1.5	250
MTM45-1_5cpm-03	5.7	1.5	260
MTM45-2cpm-02	5.4	2	250
MTM45-3cpm-02	14.5	3	300
MTM45-4cpm-02	13.2	4	300

		Hold	
Test	Mass (mg)	Temp (°C)	Time (min)
MTM45-160C-INT10-01	4.00	160	10
MTM45-160C-INT20-01	6.10	160	20
MTM45-160C-INT30-01	5.70	160	30
MTM45-160C-INT35-01	5.10	160	35
MTM45-160C-INT40-01	5.80	160	40
MTM45-160C-INT45-01	6.40	160	45
MTM45-160C-INT50-01	5.30	160	50

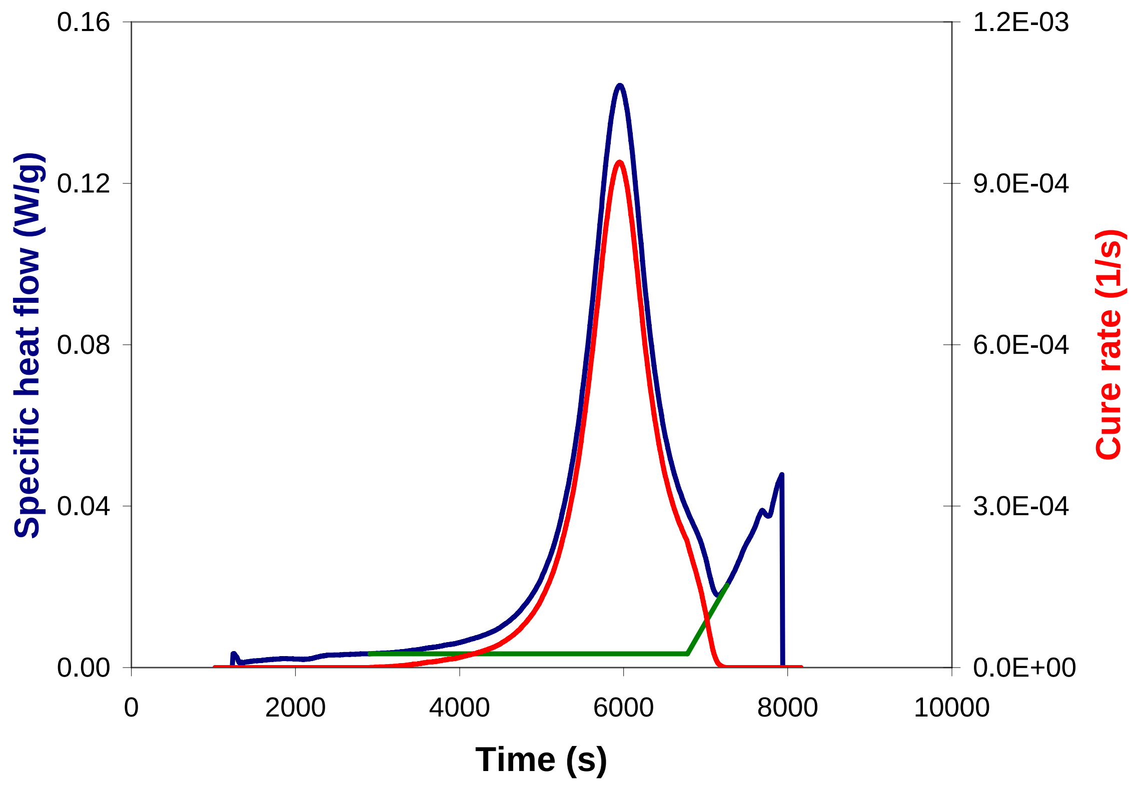
		Hold	
Test	Mass (mg)	Temp (°C)	Time (min)
MTM45-100-02	14.1	100	600
MTM45-110-03	13.3	110	600
MTM45-120-02	10.9	120	480
MTM45-130-02	11.7	130	420
MTM45-140-01	4.6	140	360
MTM45-150-03	14	150	360
MTM45-155-03	12.5	155	360
MTM45-160-03	13.7	160	360
MTM45-170-01	5.2	170	240
MTM45-175-02	3.8	175	240
MTM45-180-01	6.38	180	240
MTM45-180-04	14.6	180	240
MTM45-190-03	13.3	190	180
MTM45-200-02	18	200	180

Test	Mass (mg)
MTM45-CureCycle-S3-01	5.80
MTM45-CureCycle-S2-01	6.70

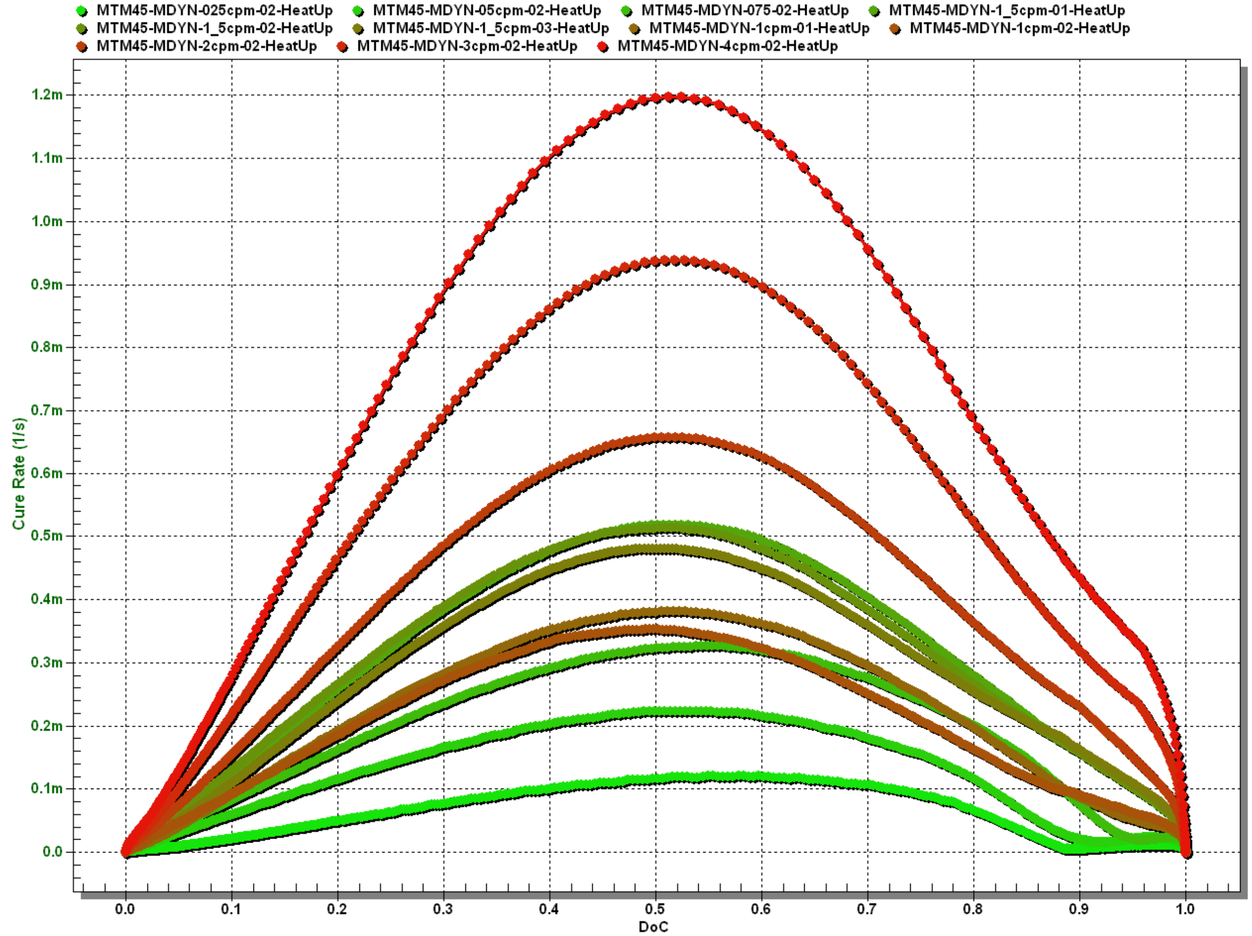
Degree of Cure Calculation

Raw DSC data was linearly sparsed and smoothed.

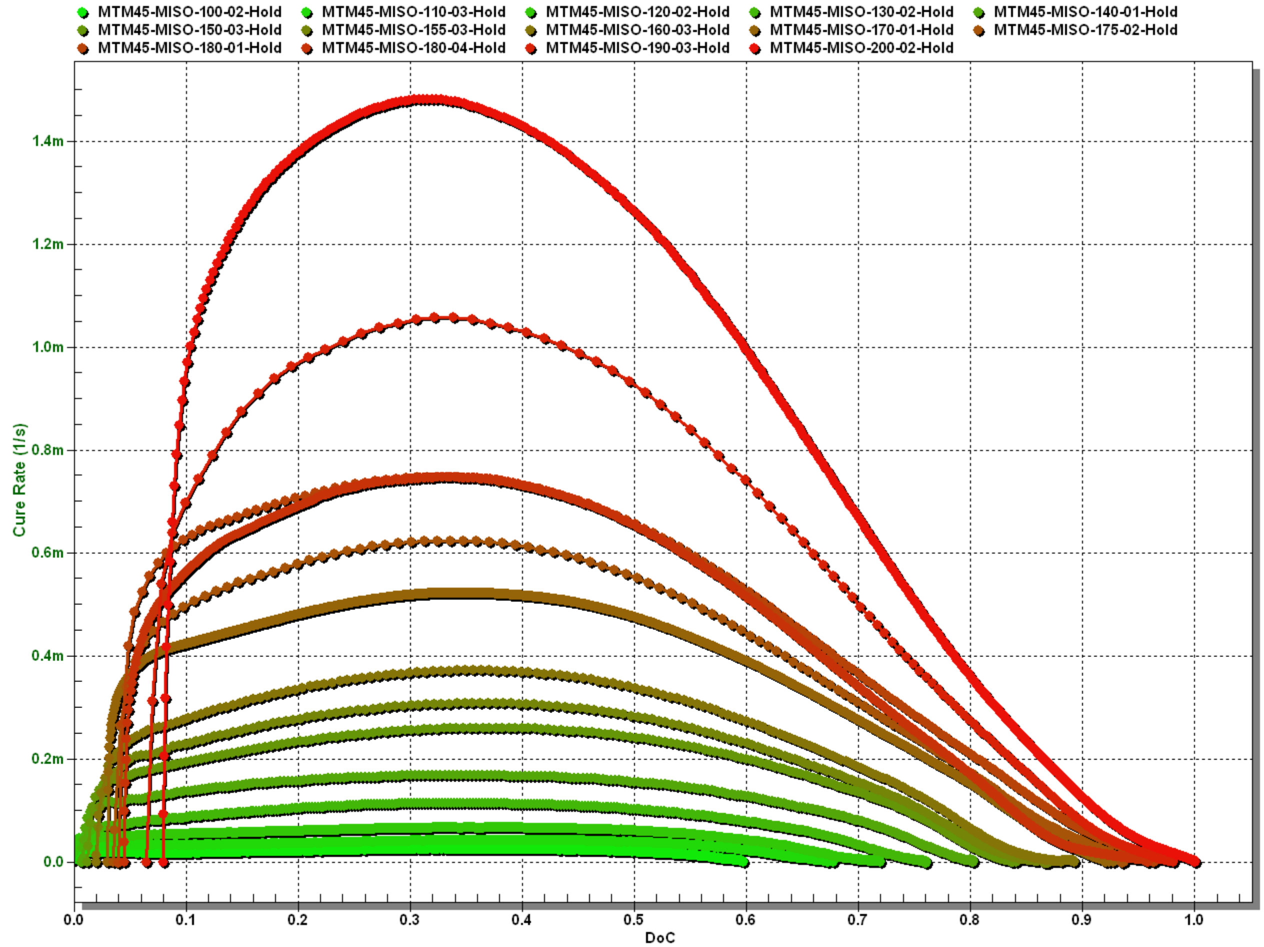
A bi-linear baseline was considered for dynamic tests in order to calculate the total heat of reaction and degree of cure.
Baselines fitted to Isothermal tests were chosen to be linear.



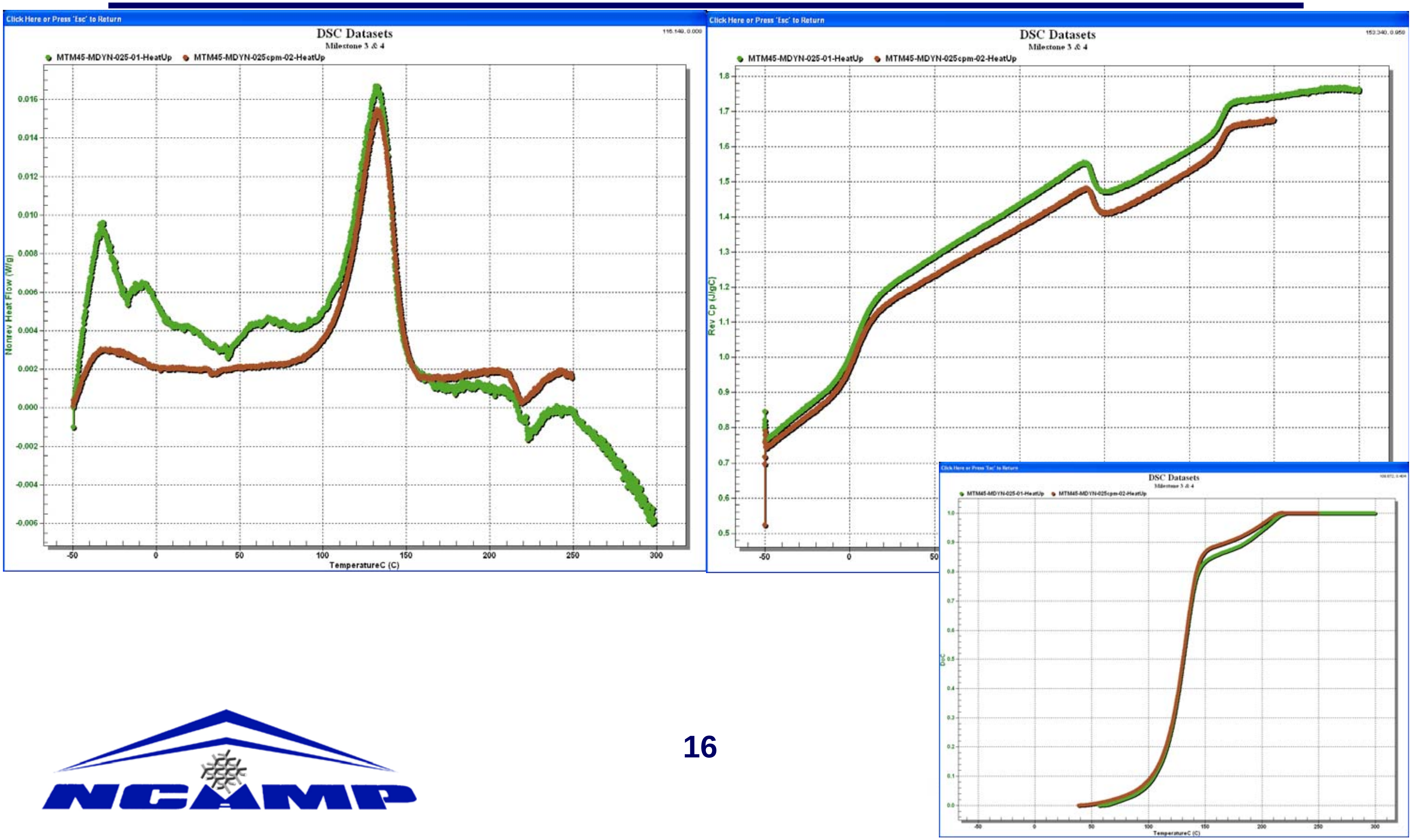
Cure Rate vs. DoC – Dyns



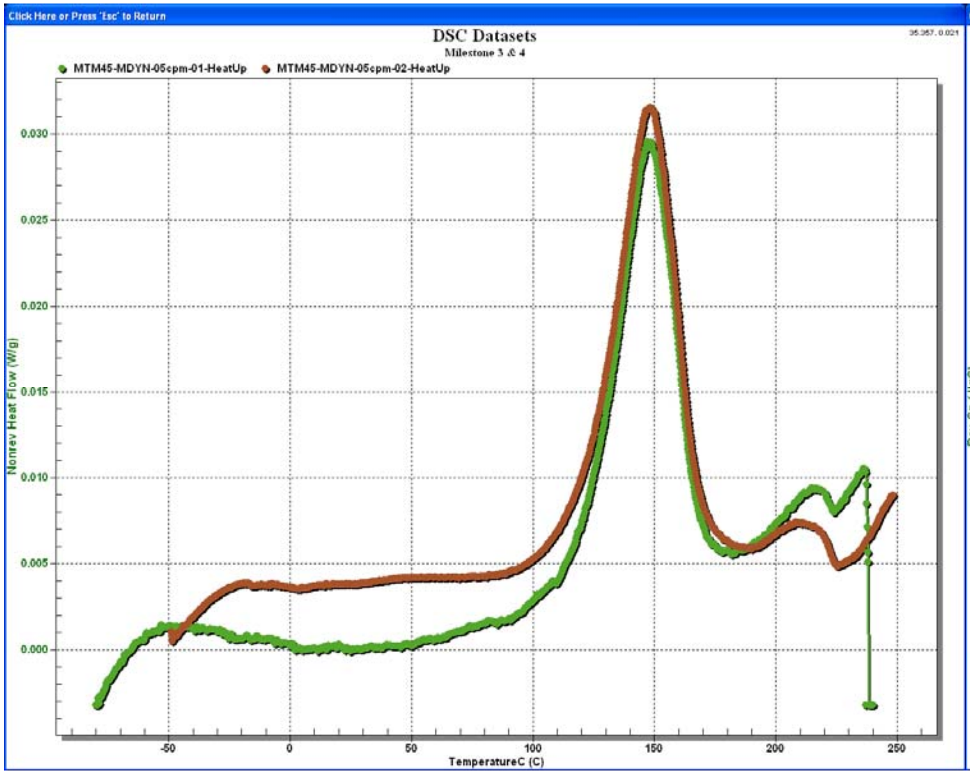
Cure Rate vs. DoC – Isos

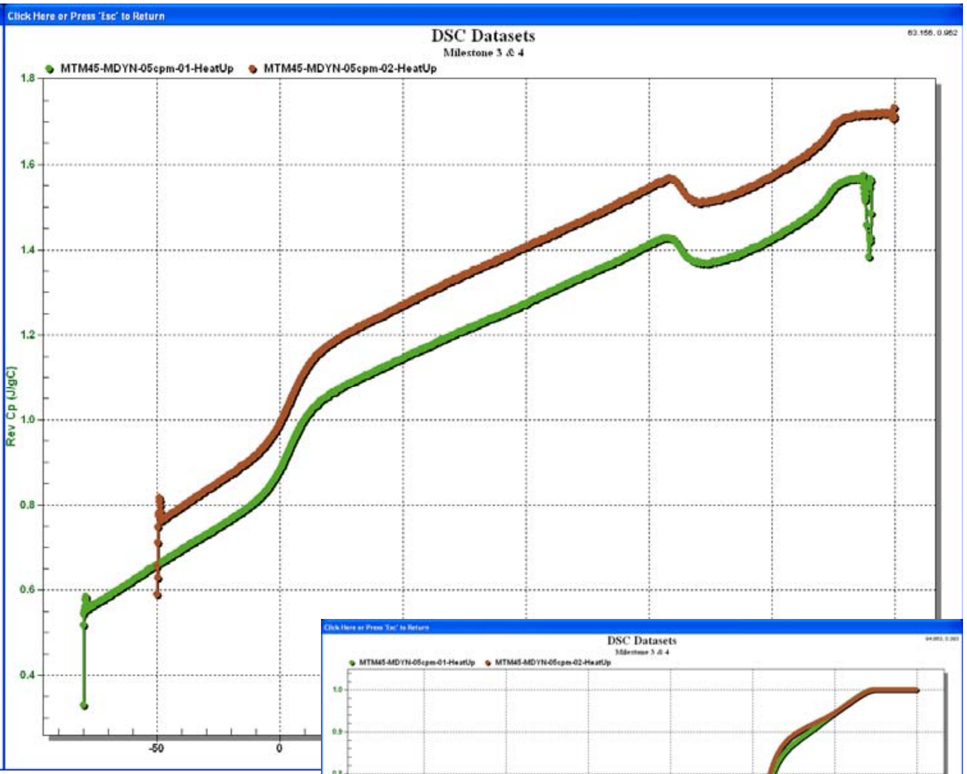


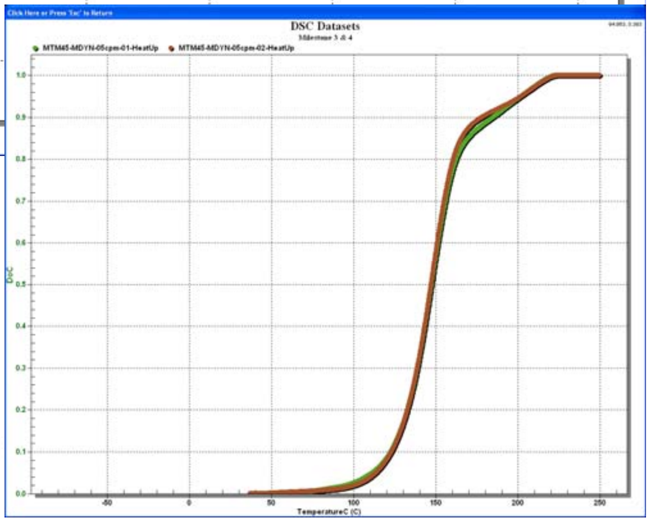
0.25 Cpm Tests



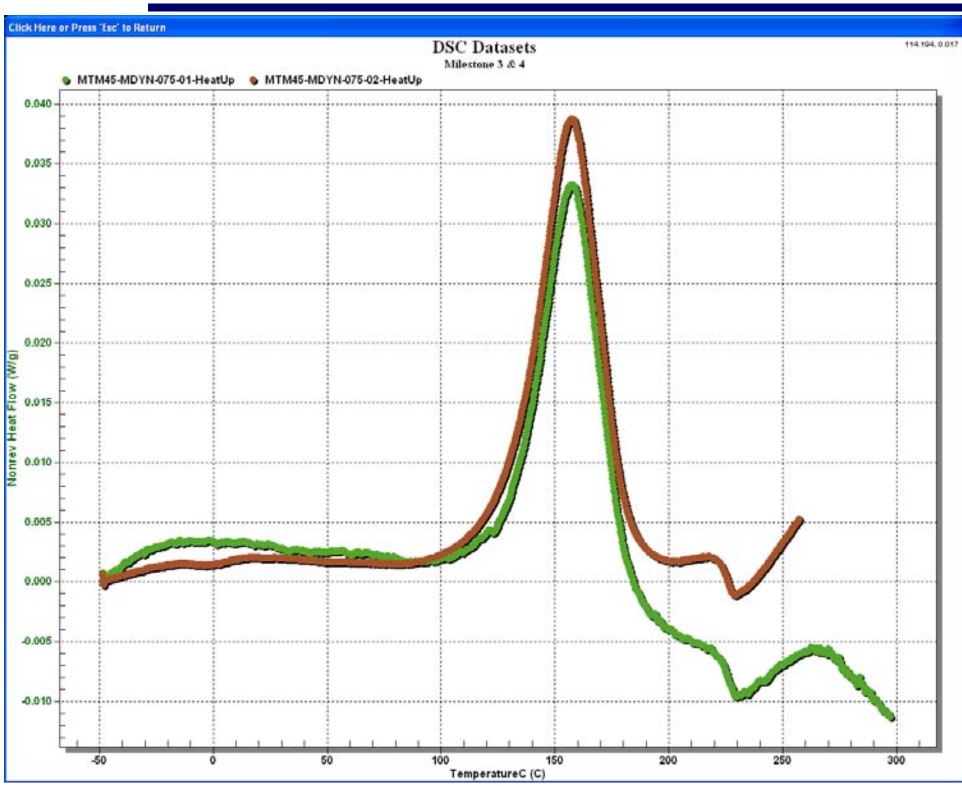
0.50 Cpm Tests

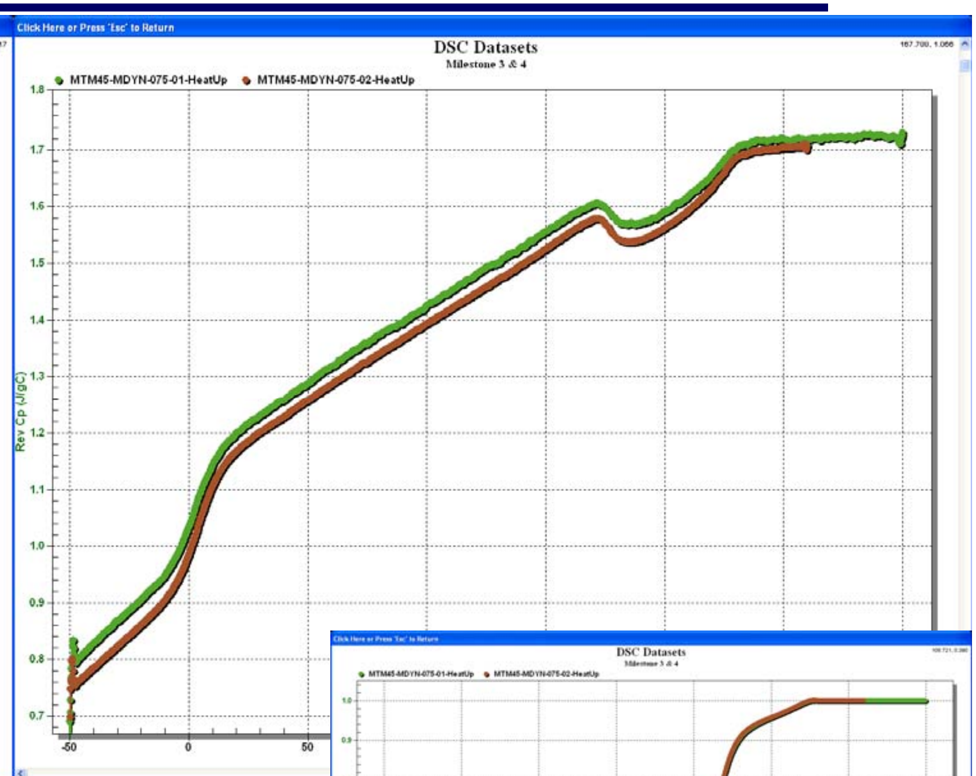


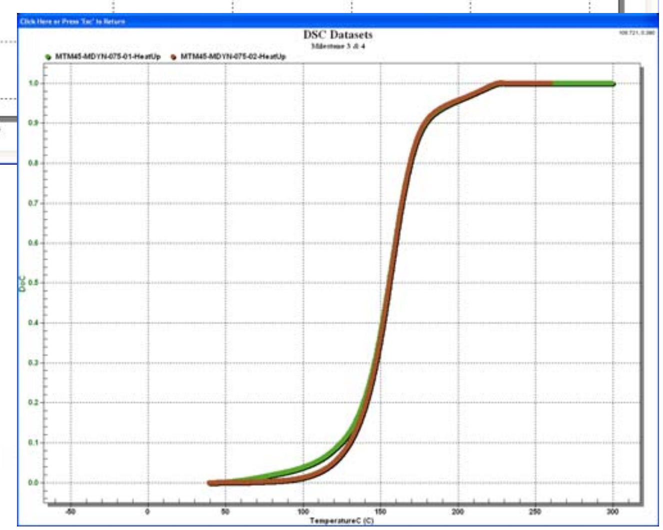




0.75 Cpm Tests

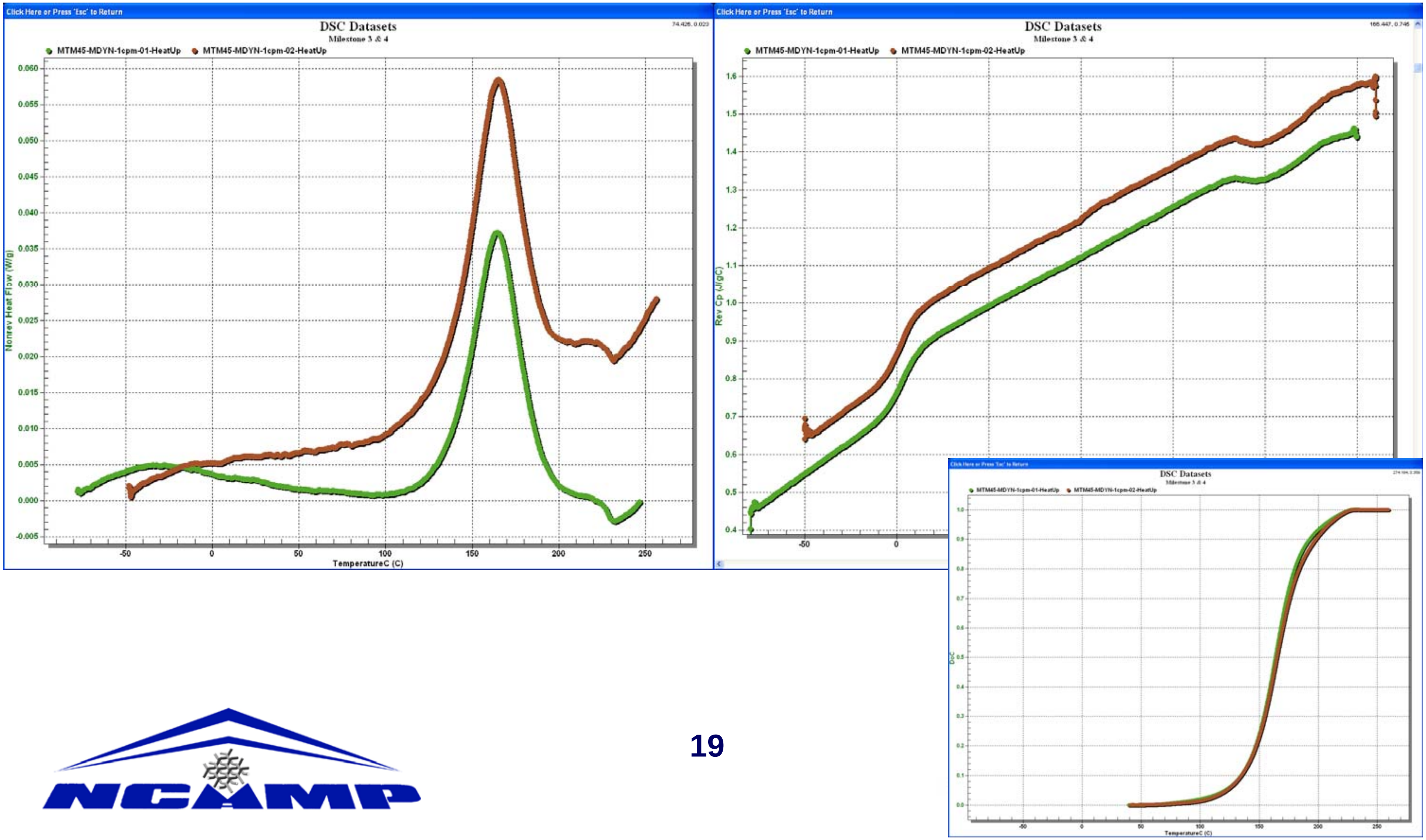






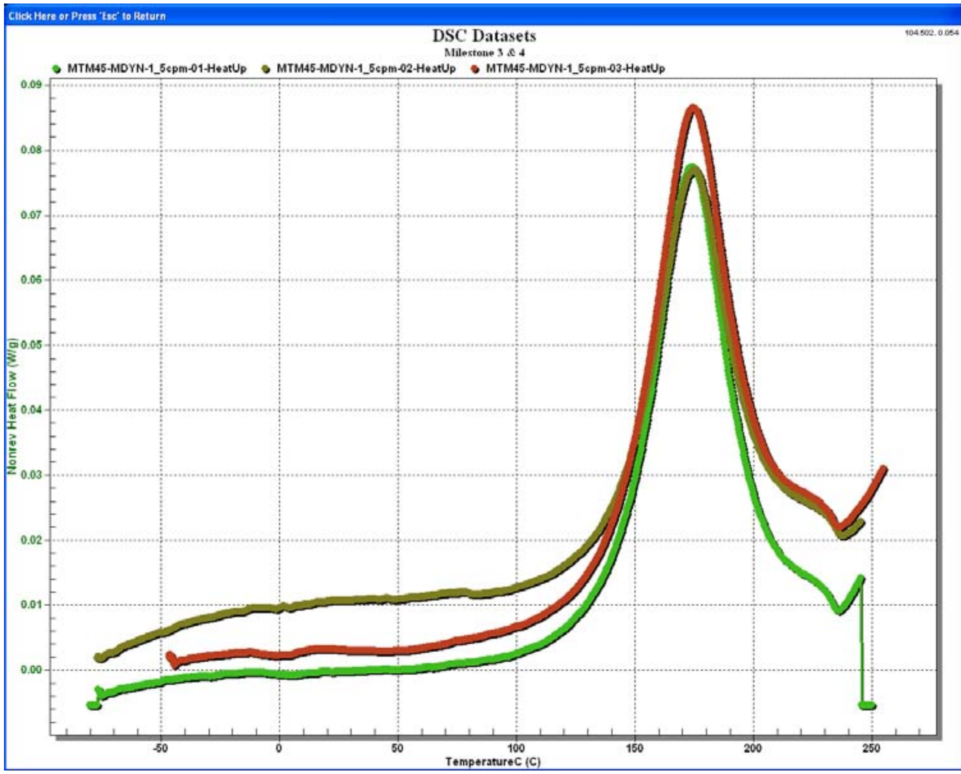
NCAMP

1 Cpm Tests



Click Here or Press 'Esc' to Return
DSC Datasets
Milestone 3 & 4
MTM45-MDYN-1cpm-01-HeatUp
MTM45-MDYN-1cpm-02-HeatUp
Nonrev Heat Flow (W/g)
TemperatureC (C)
Rev Cp (J/gC)
DoC

1.5 Cpm Tests



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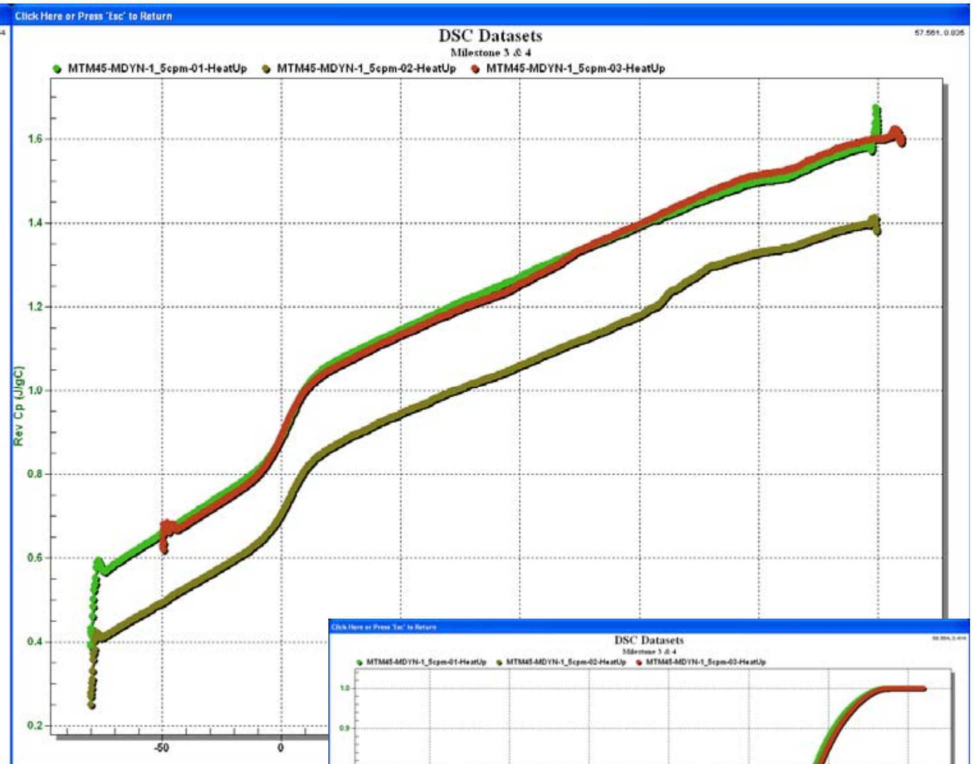
DSC Datasets
Milestone 3 & 4
MTM45-MDYN-1_5cpm-01-HeatUp
MTM45-MDYN-1_5cpm-02-HeatUp
MTM45-MDYN-1_5cpm-03-HeatUp
Nonrev Heat Flow (W/g)
TemperatureC (C)



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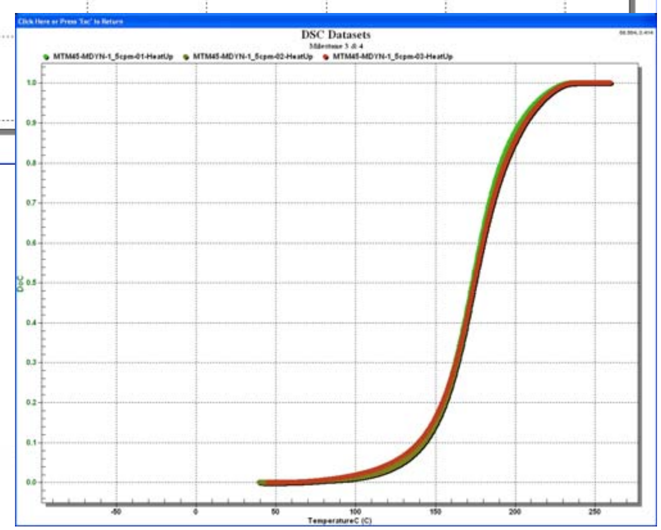
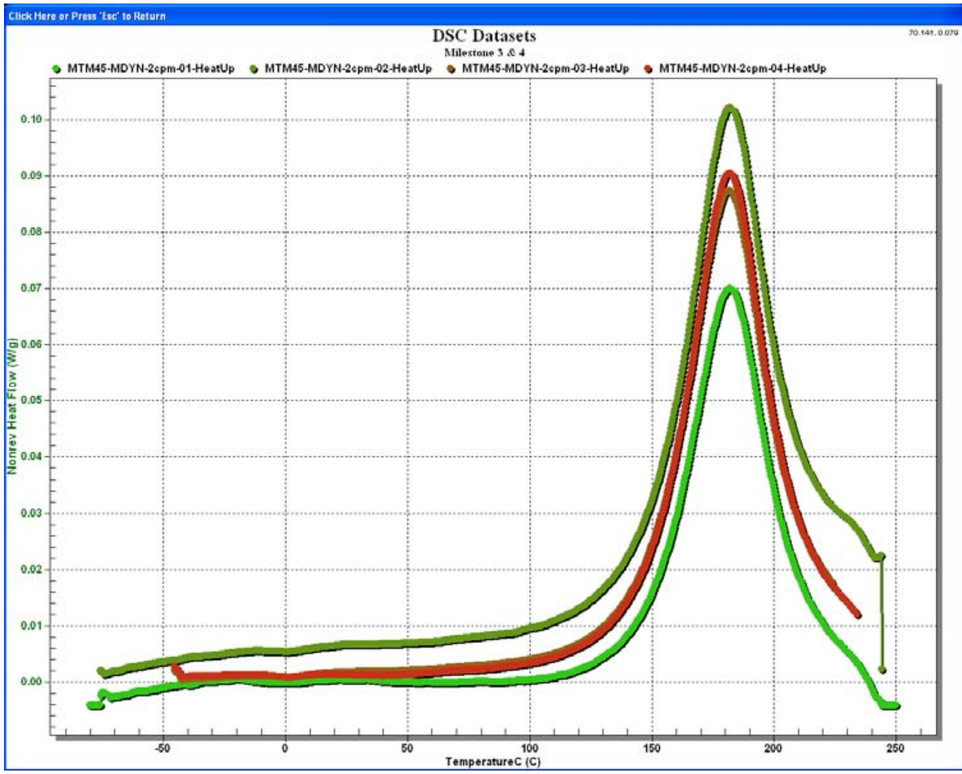
DSC Datasets
Milestone 3 & 4
MTM45-MDYN-1_5cpm-01-HeatUp
MTM45-MDYN-1_5cpm-02-HeatUp
MTM45-MDYN-1_5cpm-03-HeatUp
Rev Cp (J/gC)



DSC Datasets

2 Cpm Tests



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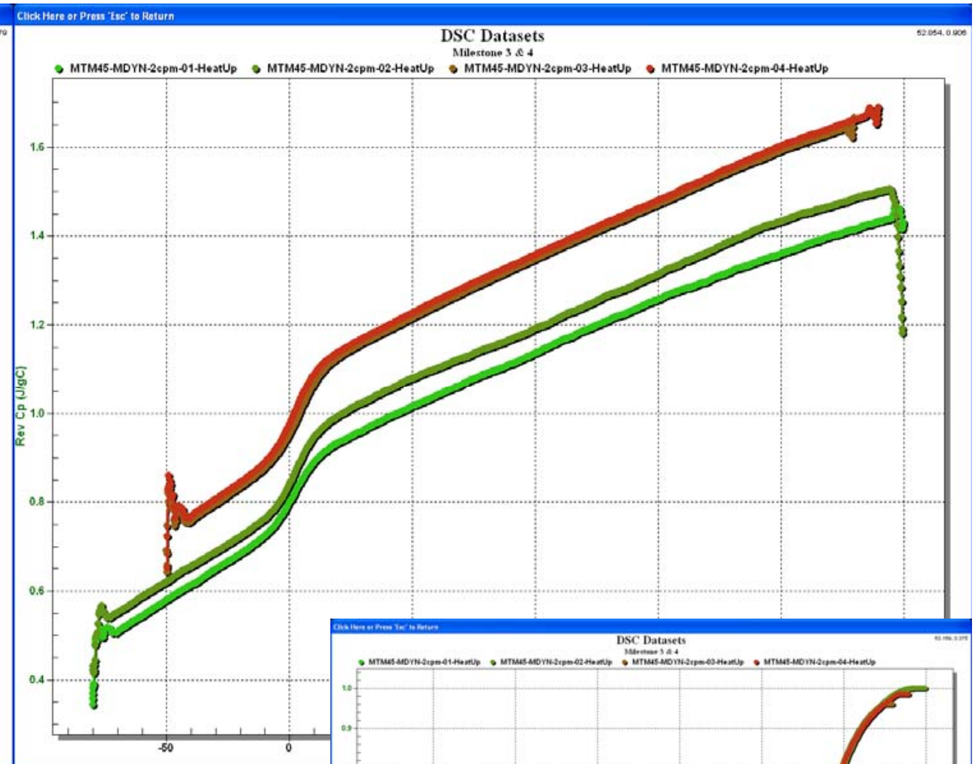
DSC Datasets
Milestone 3 & 4
MTM45-MDYN-2cpm-01-HeatUp
MTM45-MDYN-2cpm-02-HeatUp
MTM45-MDYN-2cpm-03-HeatUp
MTM45-MDYN-2cpm-04-HeatUp
Nonrev Heat Flow (W/g)
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
-50
0
50
100
150
200
250
TemperatureC (C)



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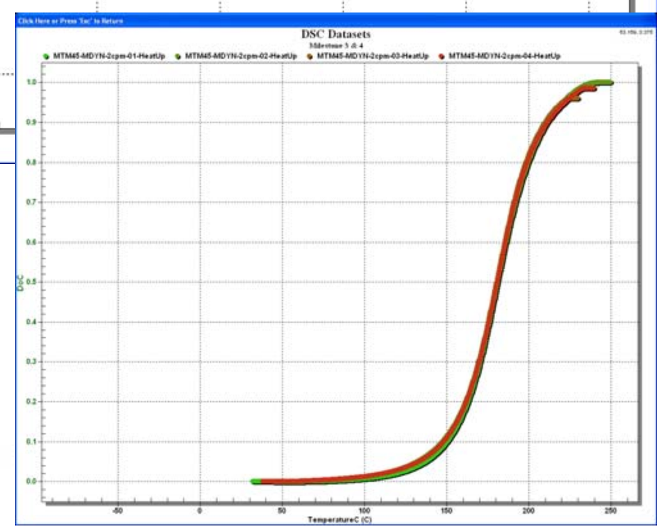
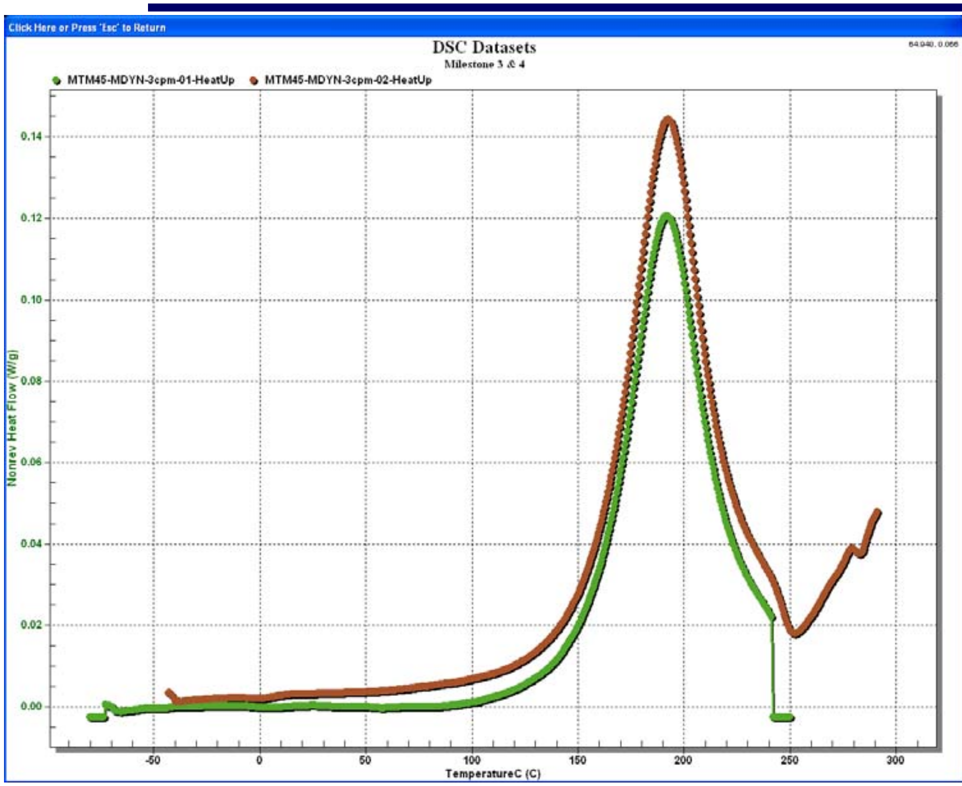
DSC Datasets
Milestone 3 & 4
MTM45-MDYN-2cpm-01-HeatUp
MTM45-MDYN-2cpm-02-HeatUp
MTM45-MDYN-2cpm-03-HeatUp
MTM45-MDYN-2cpm-04-HeatUp
Rev Cp (J/gC)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
-50
0



DSC Datasets
TemperatureC (C)

3 Cpm Tests



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DSC Datasets
Milestone 3 & 4
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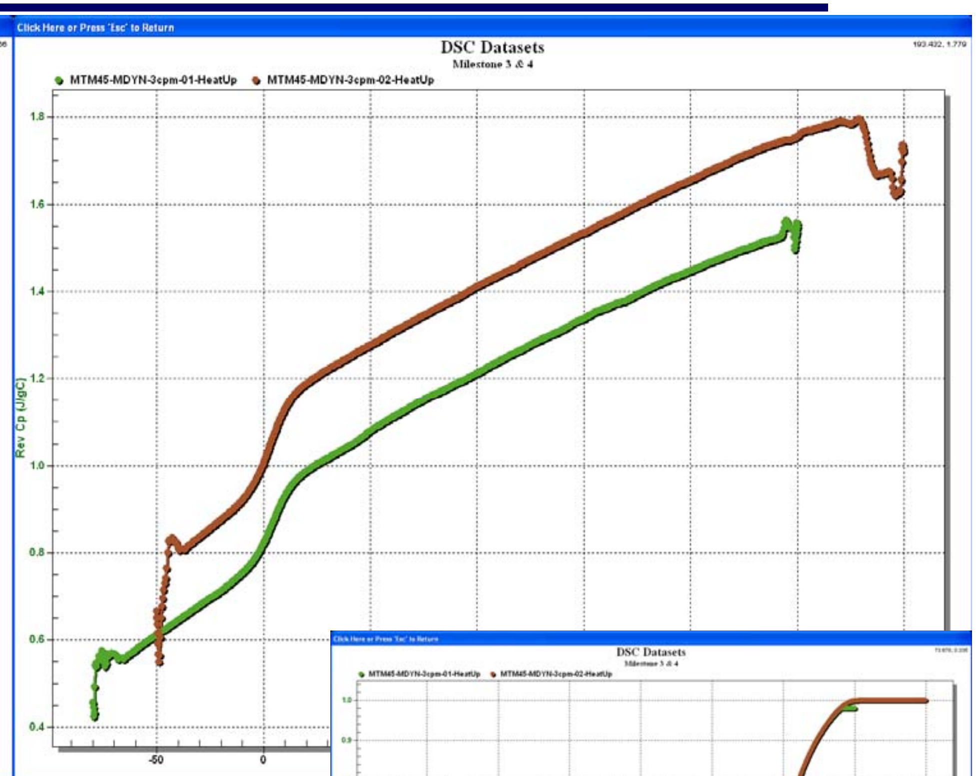
MTM45-MDYN-3cpm-02-HeatUp
Nonrev Heat Flow (W/g)
TemperatureC (C)



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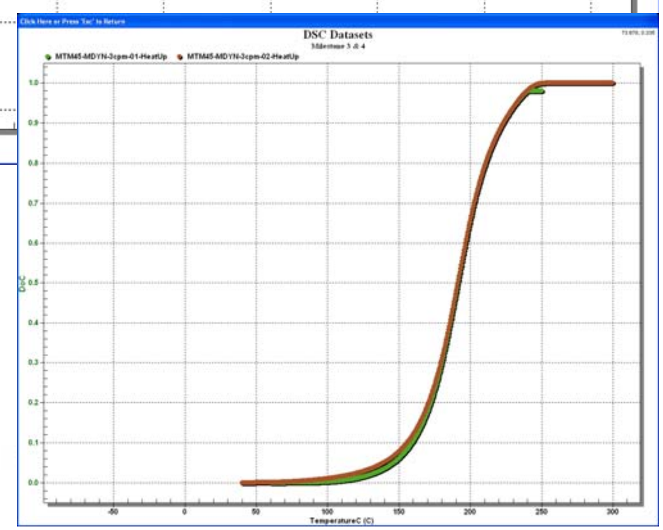
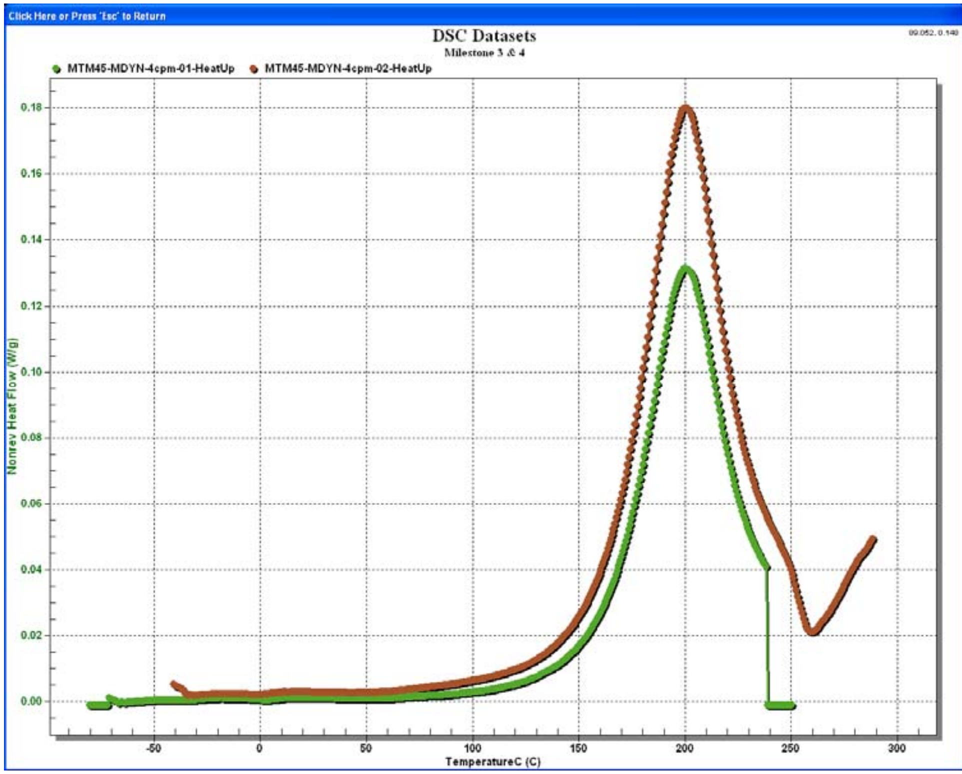
DSC Datasets
Milestone 3 & 4
MTM45-MDYN-3cpm-01-HeatUp
MTM45-MDYN-3cpm-02-HeatUp
Rev Cp (J/gC)



DSC Datasets
TemperatureC (C)

4 Cpm Tests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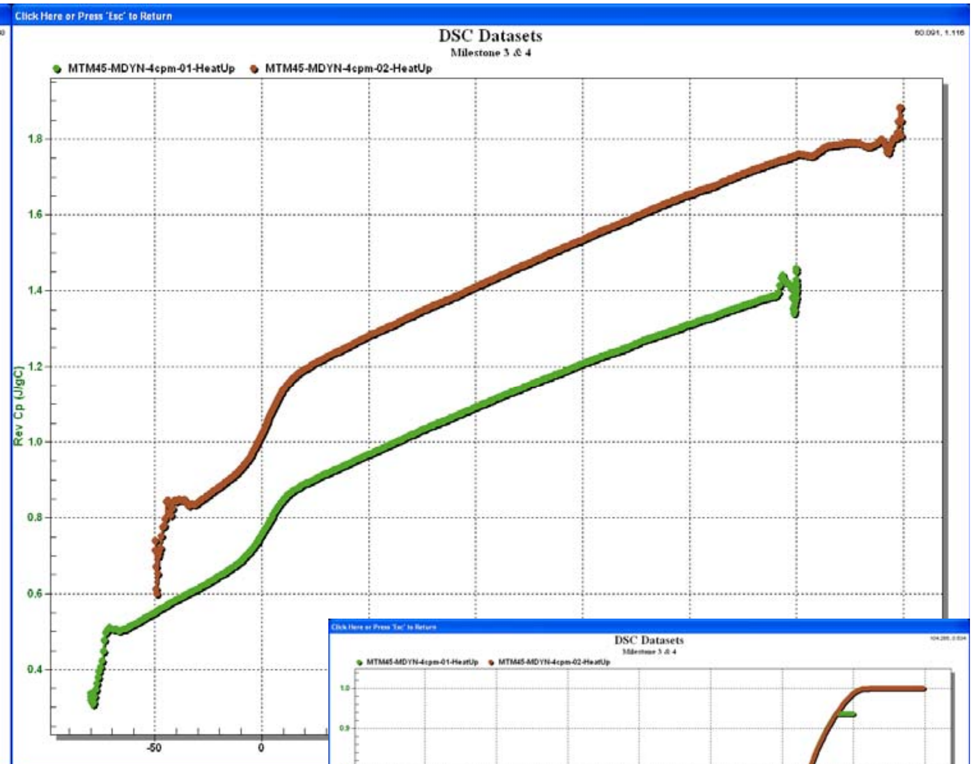
DSC Datasets
Milestone 3 & 4
MTM45-MDYN-4cpm-01-HeatUp
MTM45-MDYN-4cpm-02-HeatUp
Nonrev Heat Flow (W/g)
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-50
0
50
100
150
200
250
300
TemperatureC (C)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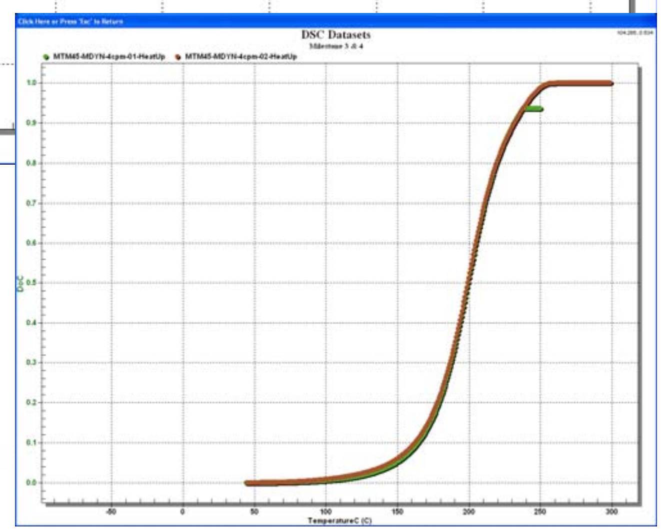
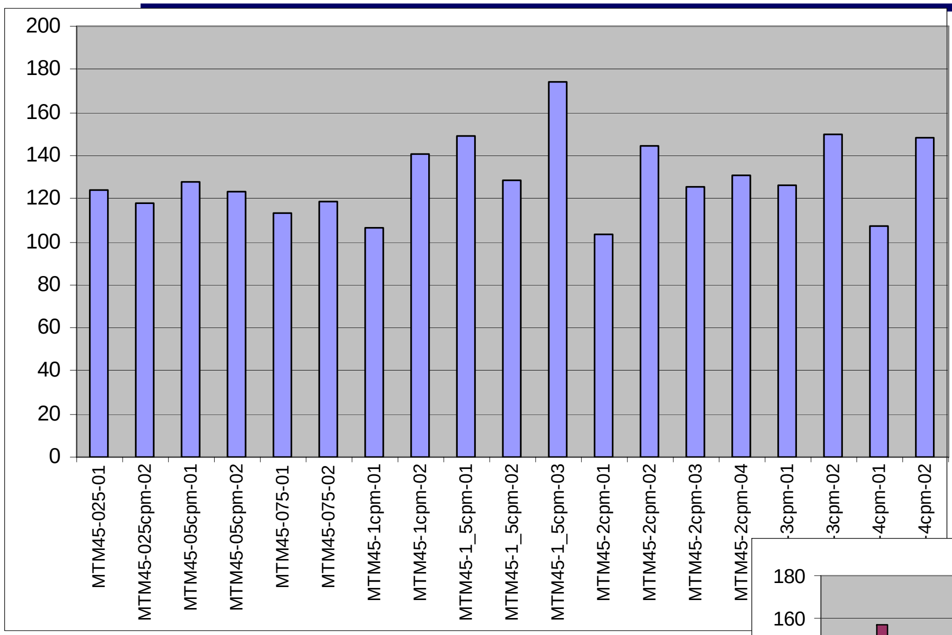
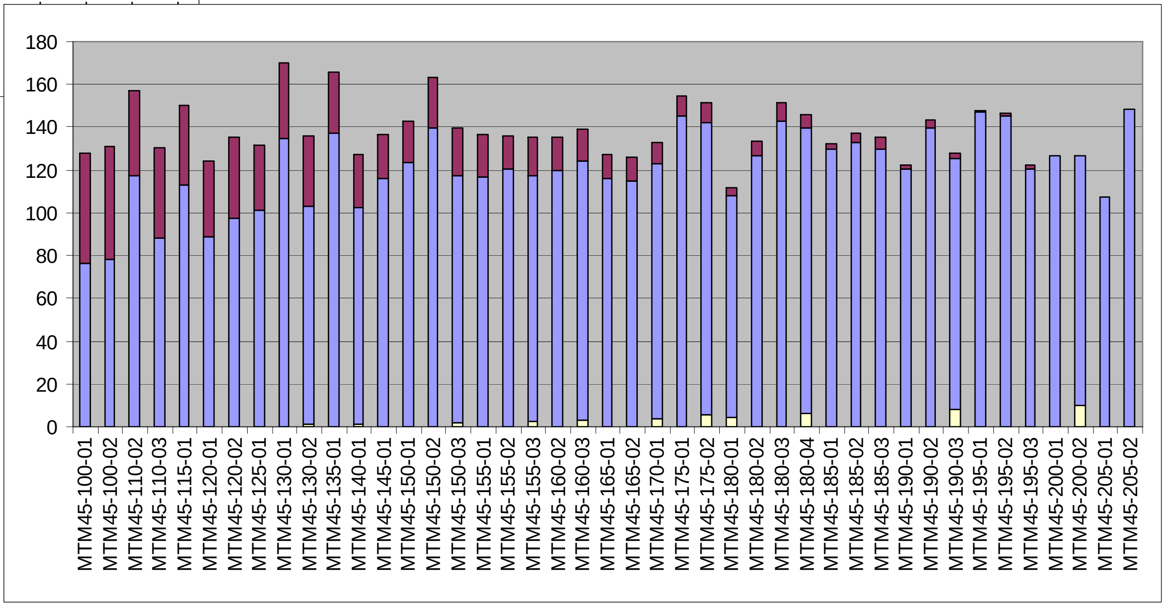
DSC Datasets
Milestone 3 & 4
MTM45-MDYN-4cpm-01-HeatUp
MTM45-MDYN-4cpm-02-HeatUp
Rev Cp (J/gC)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
-50
0

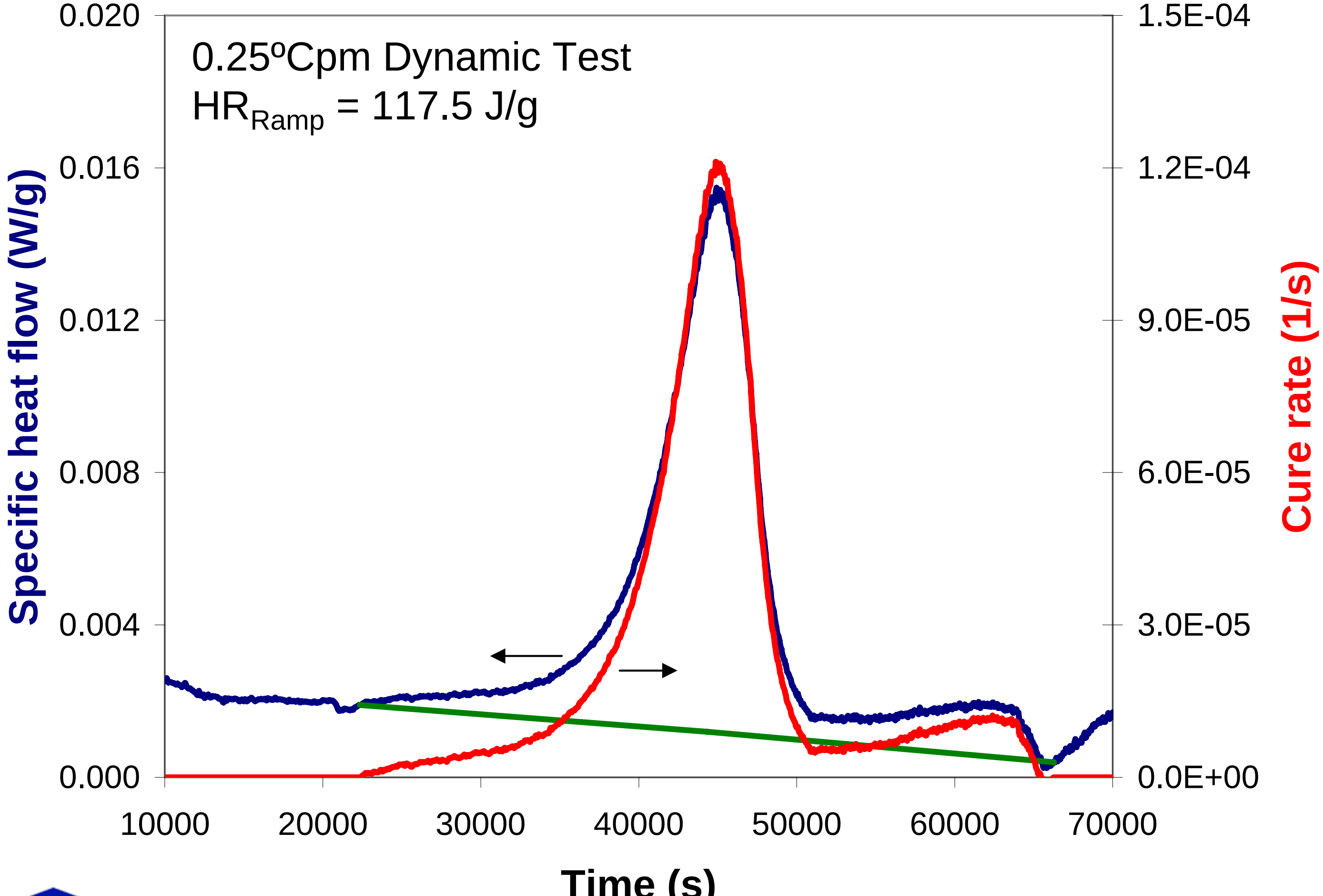

DSC Datasets

HR – All Dynamics

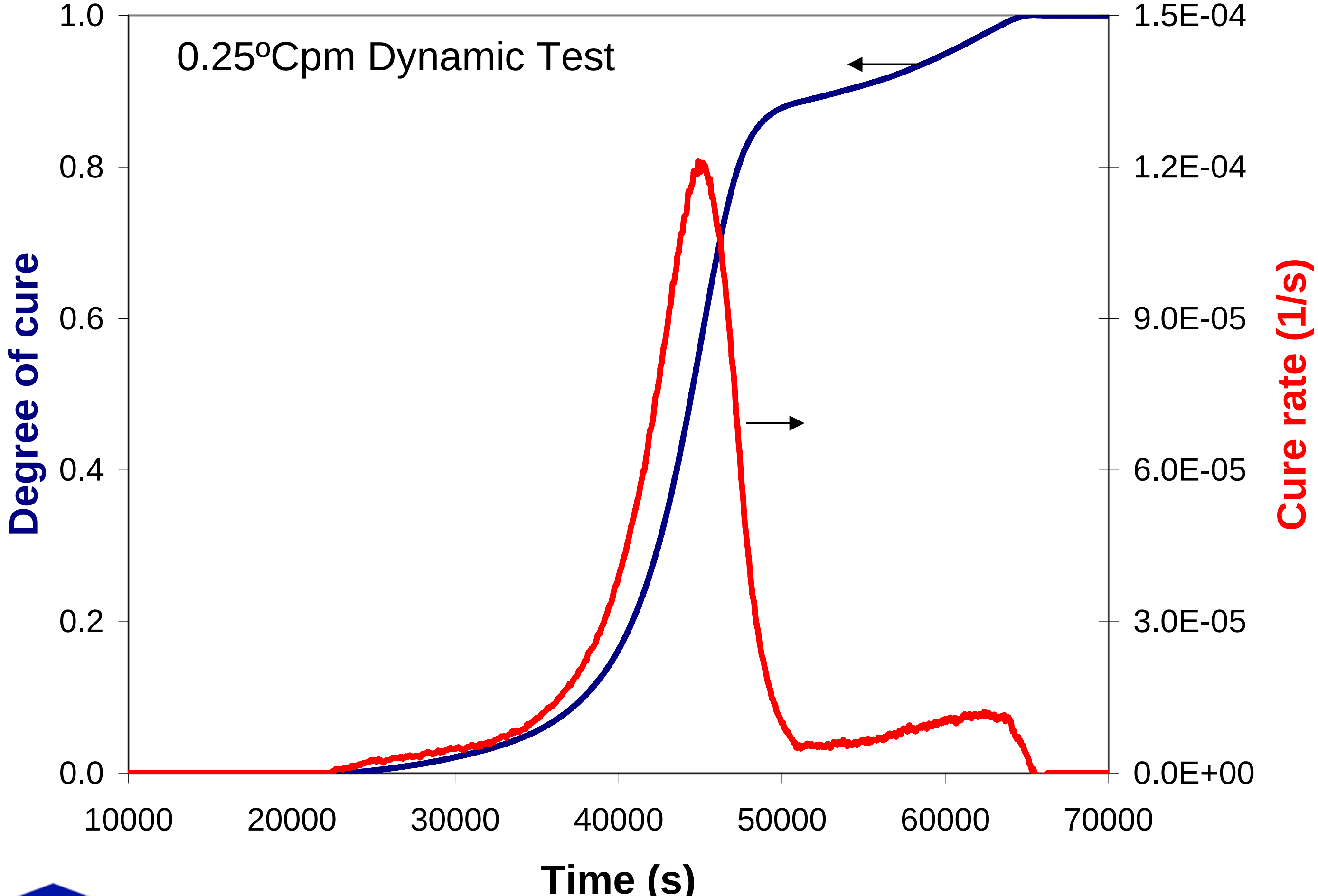




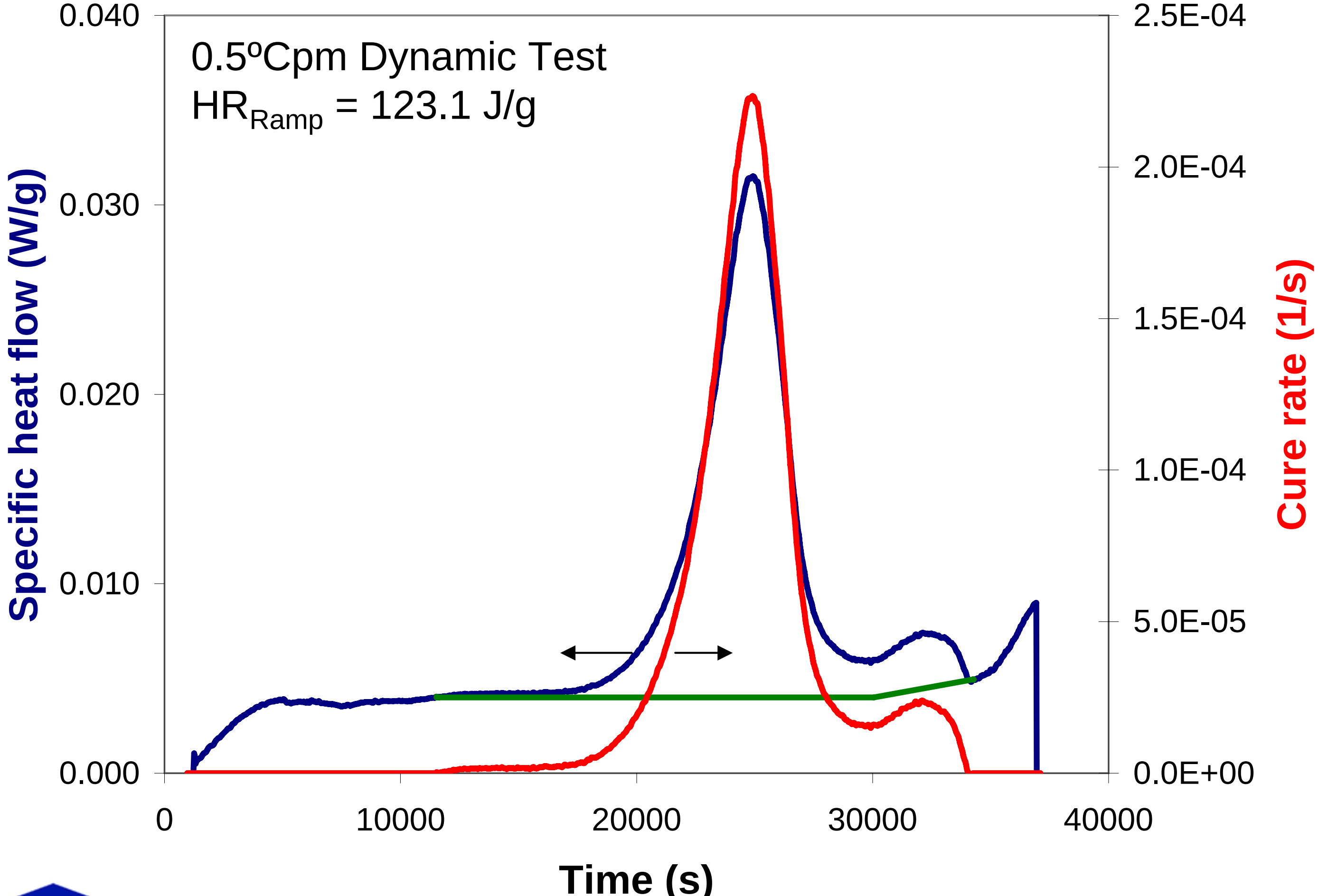
Heat Flow Response – 0.25cpm



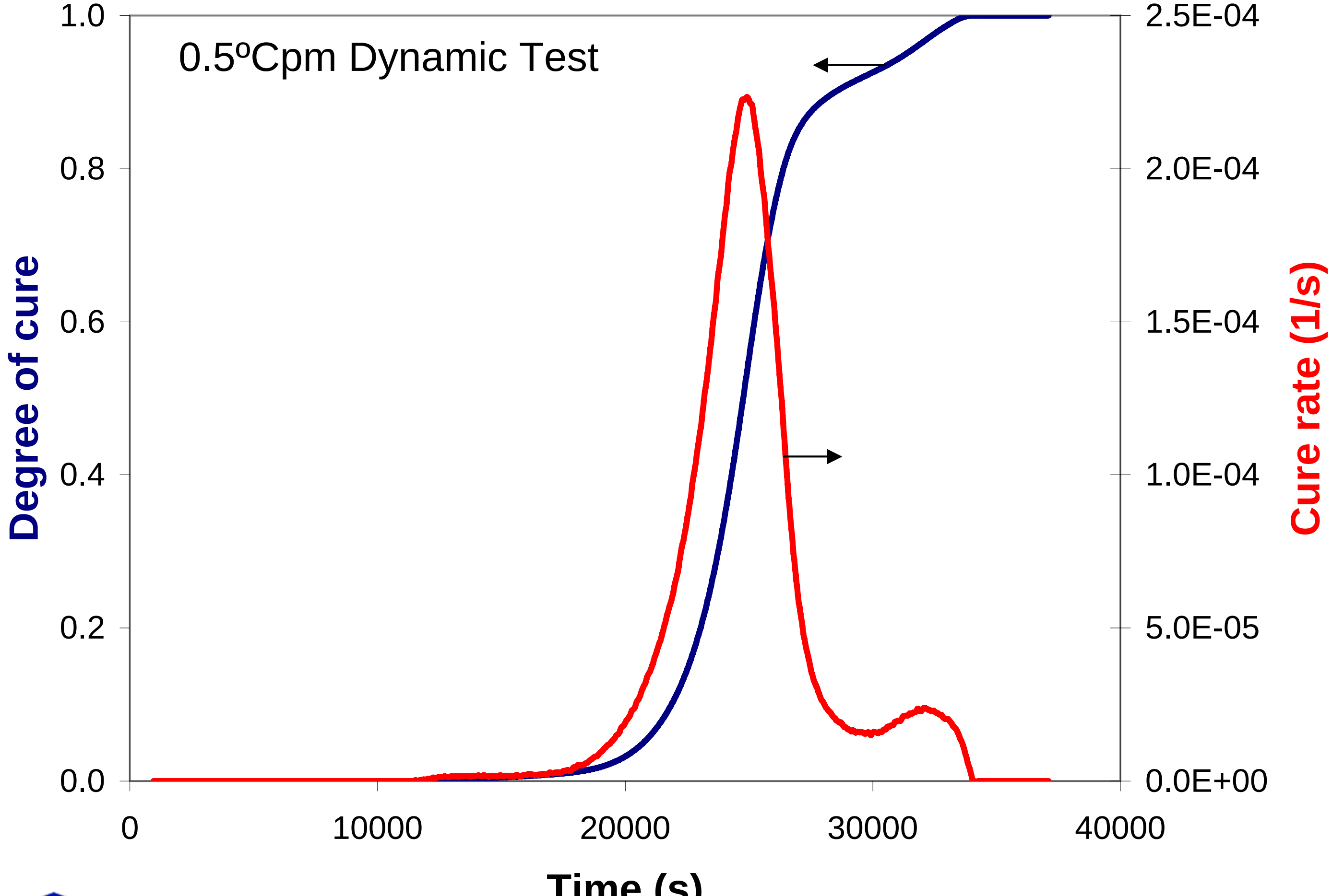
DoC and Cure Rate – 0.25cpm



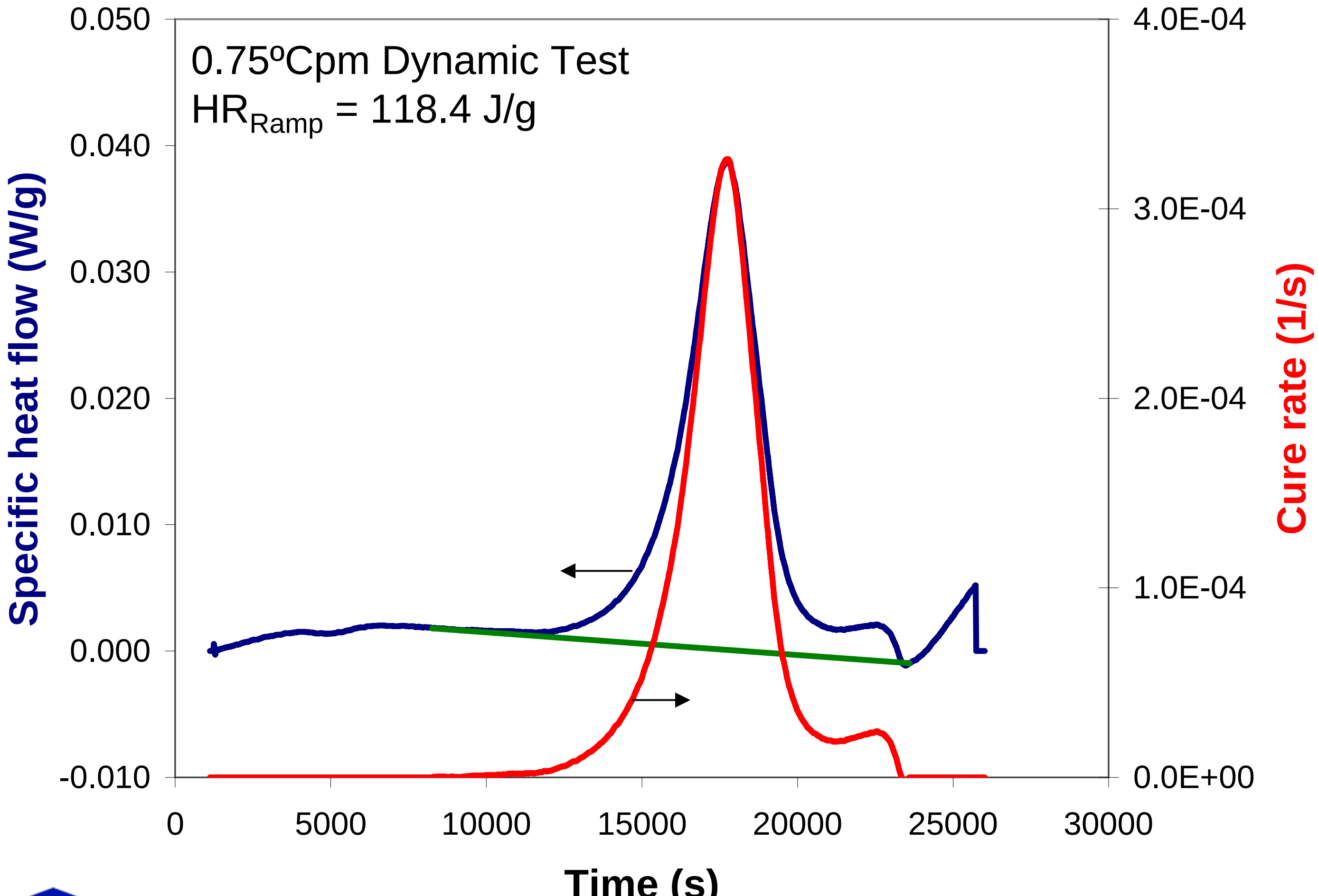
Heat Flow Response – 0.5cpm



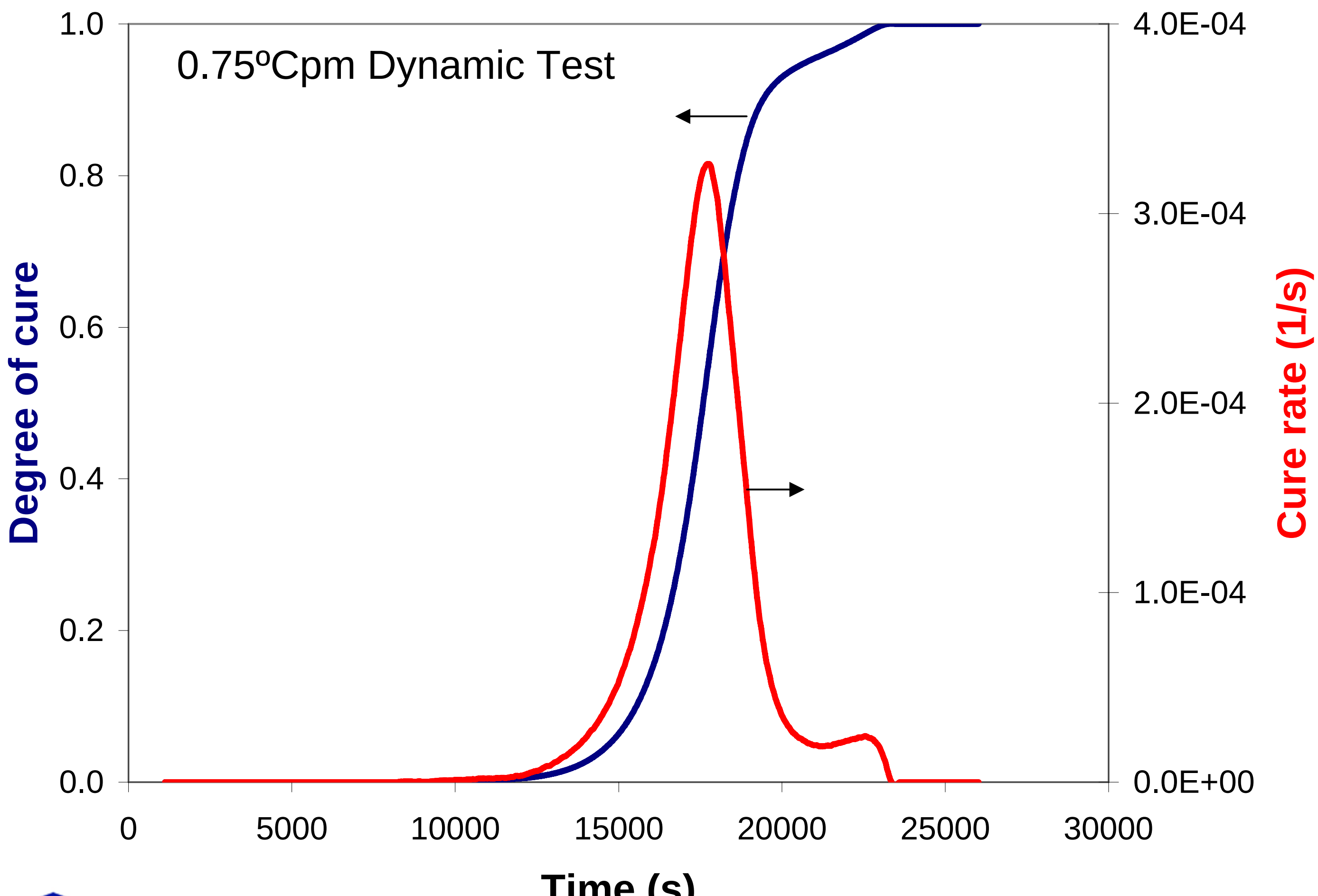
DoC and Cure Rate – 0.5cpm



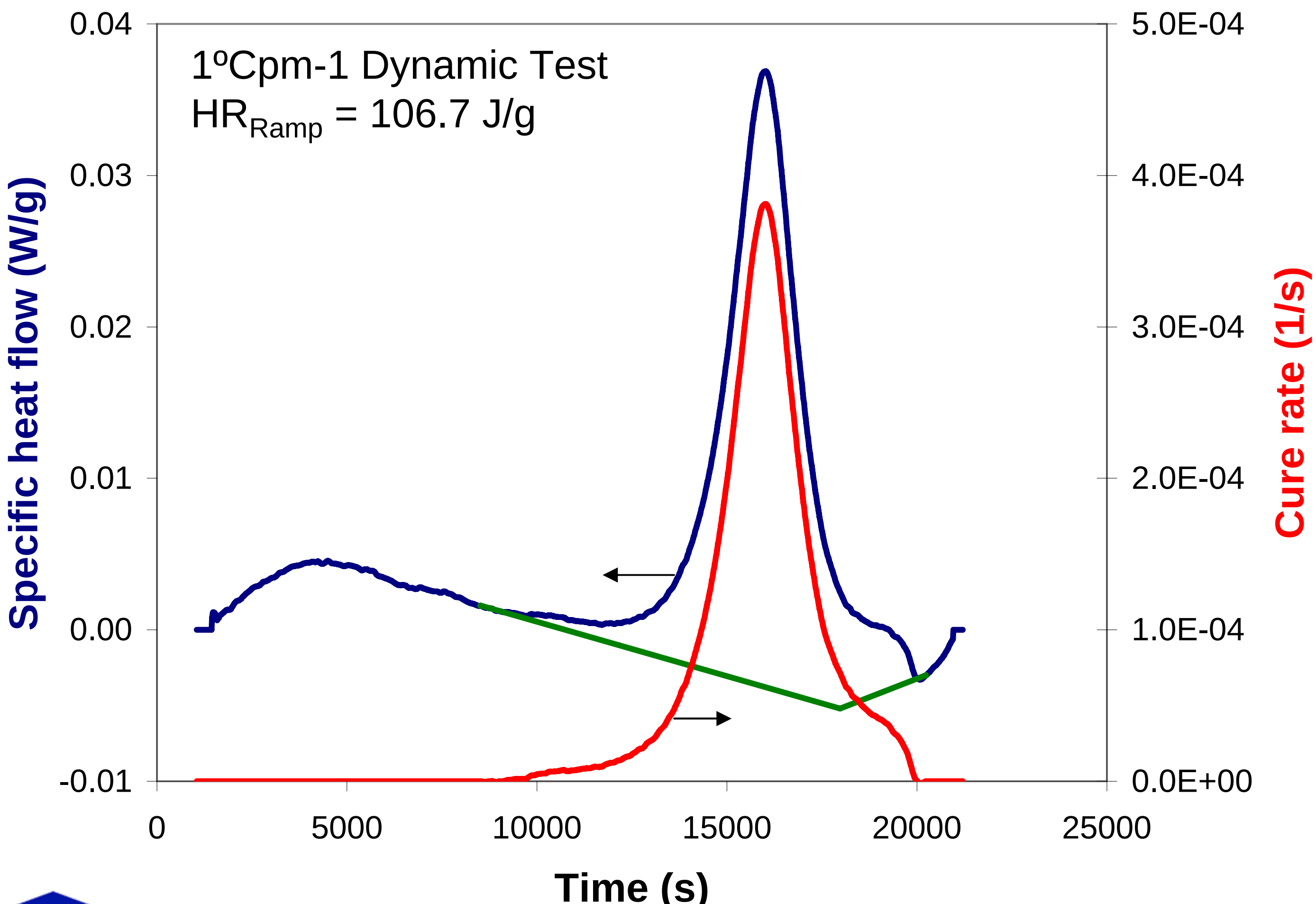
Heat Flow Response – 0.75cpm



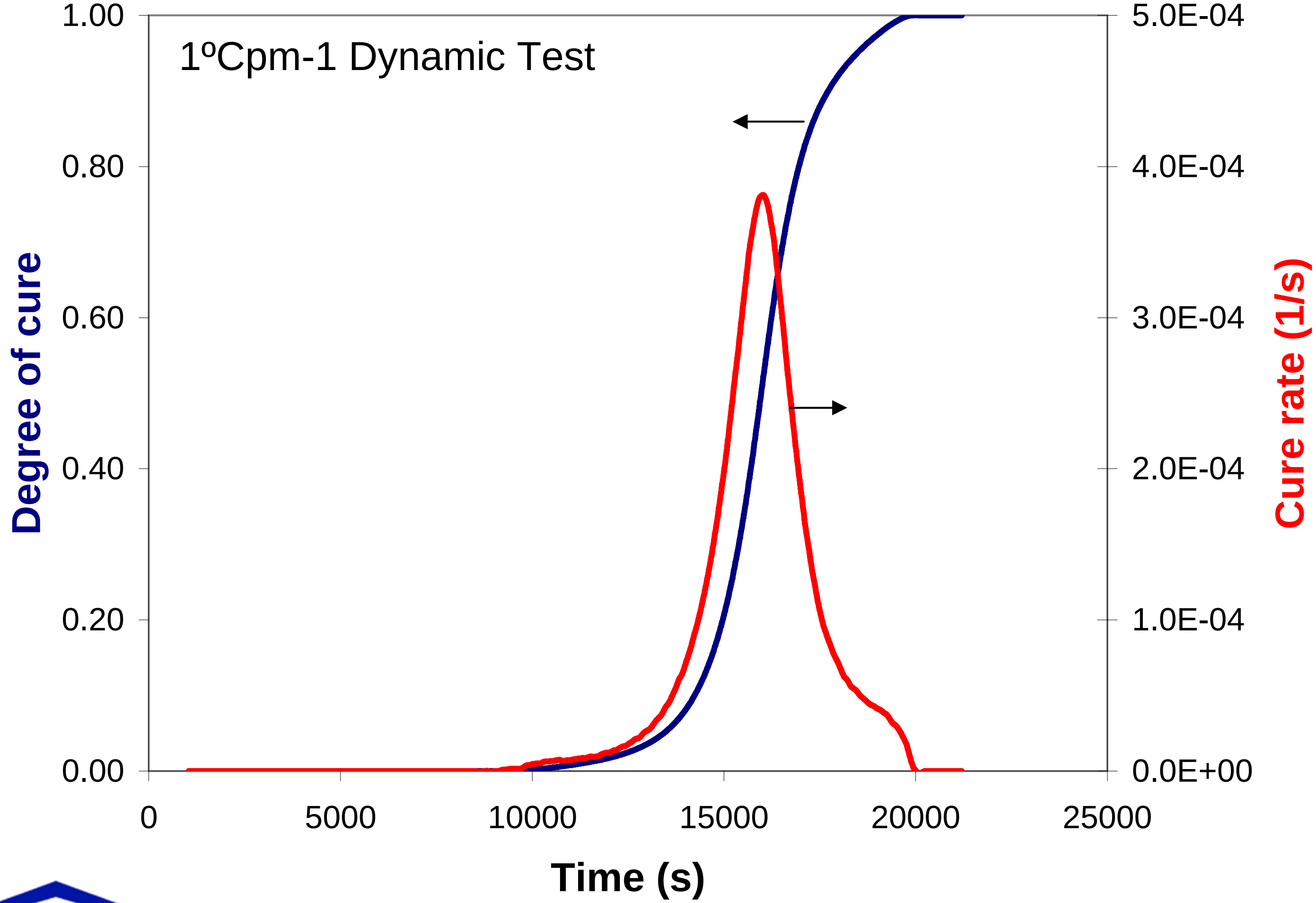
DoC and Cure Rate – 0.75cpm



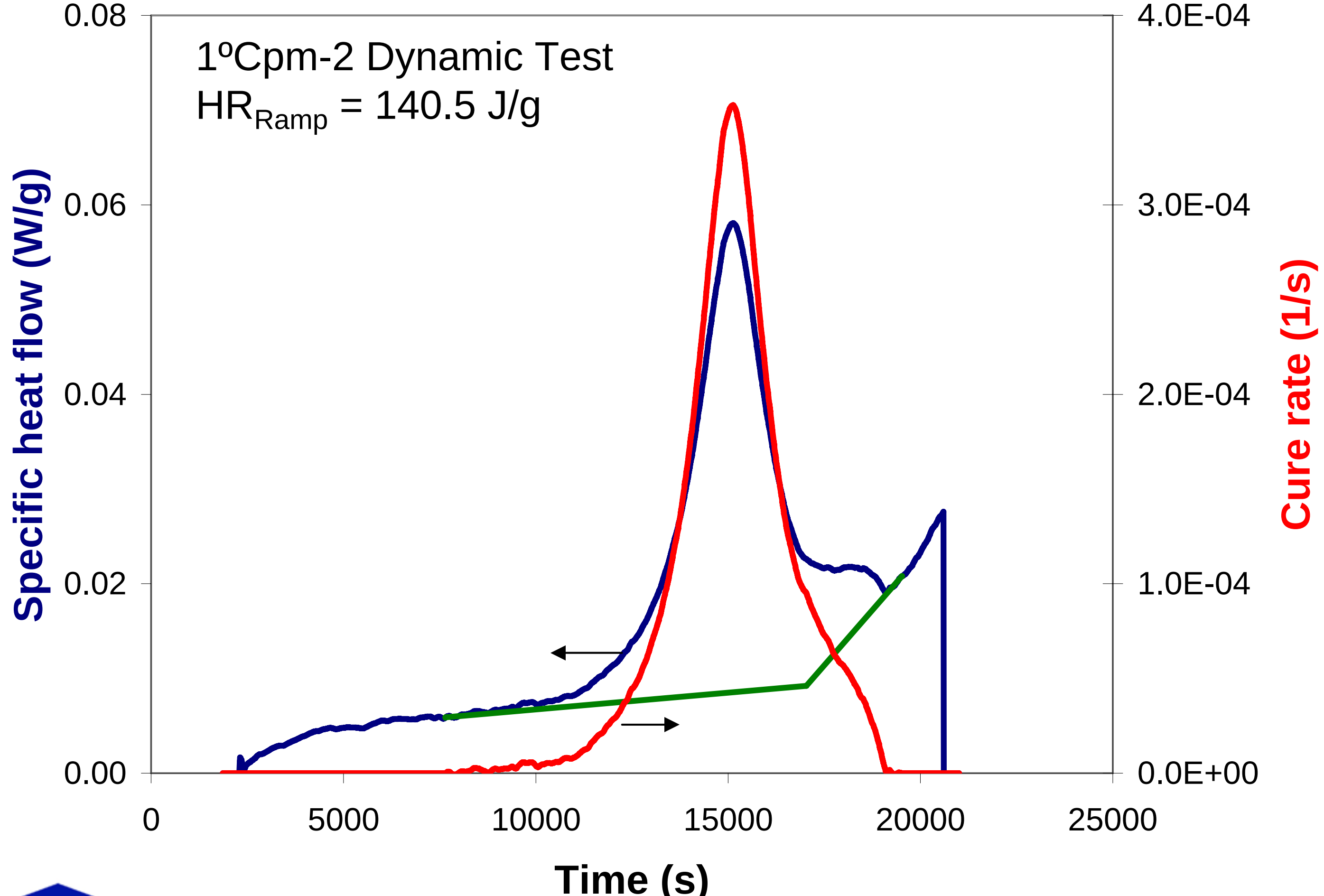
Heat Flow Response – 1cpm-1



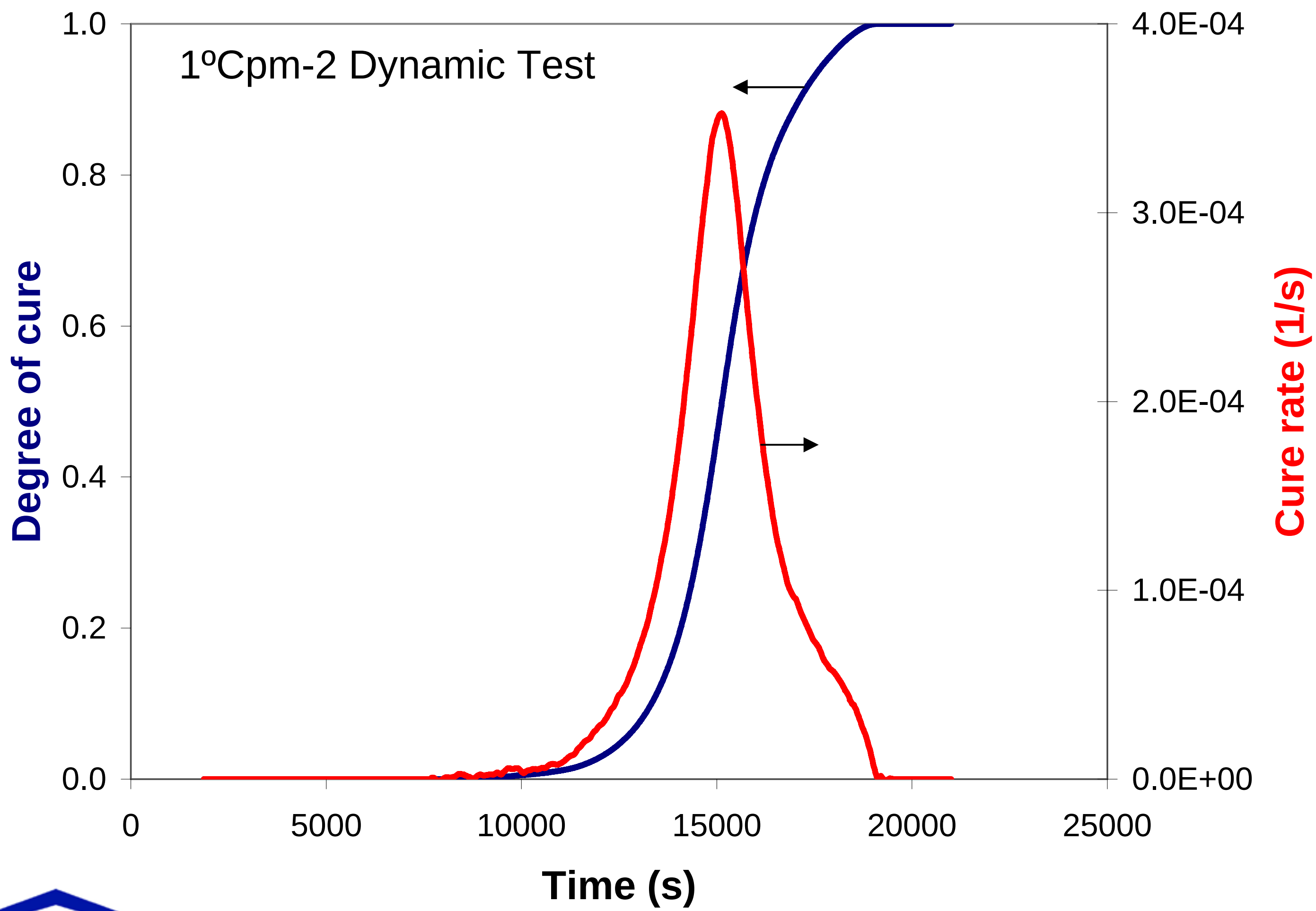
DoC and Cure Rate – 1cpm-1



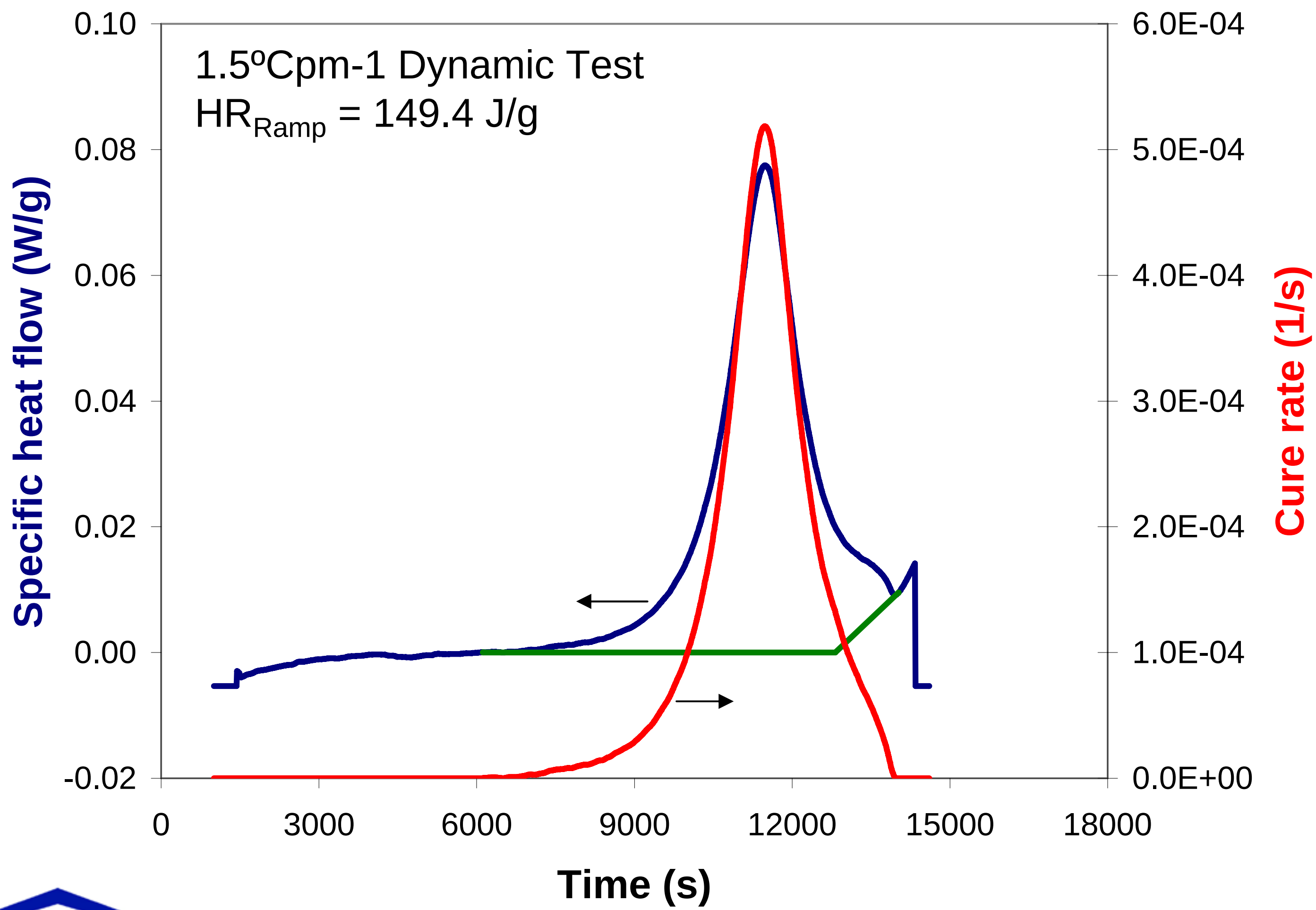
Heat Flow Response – 1cpm-2



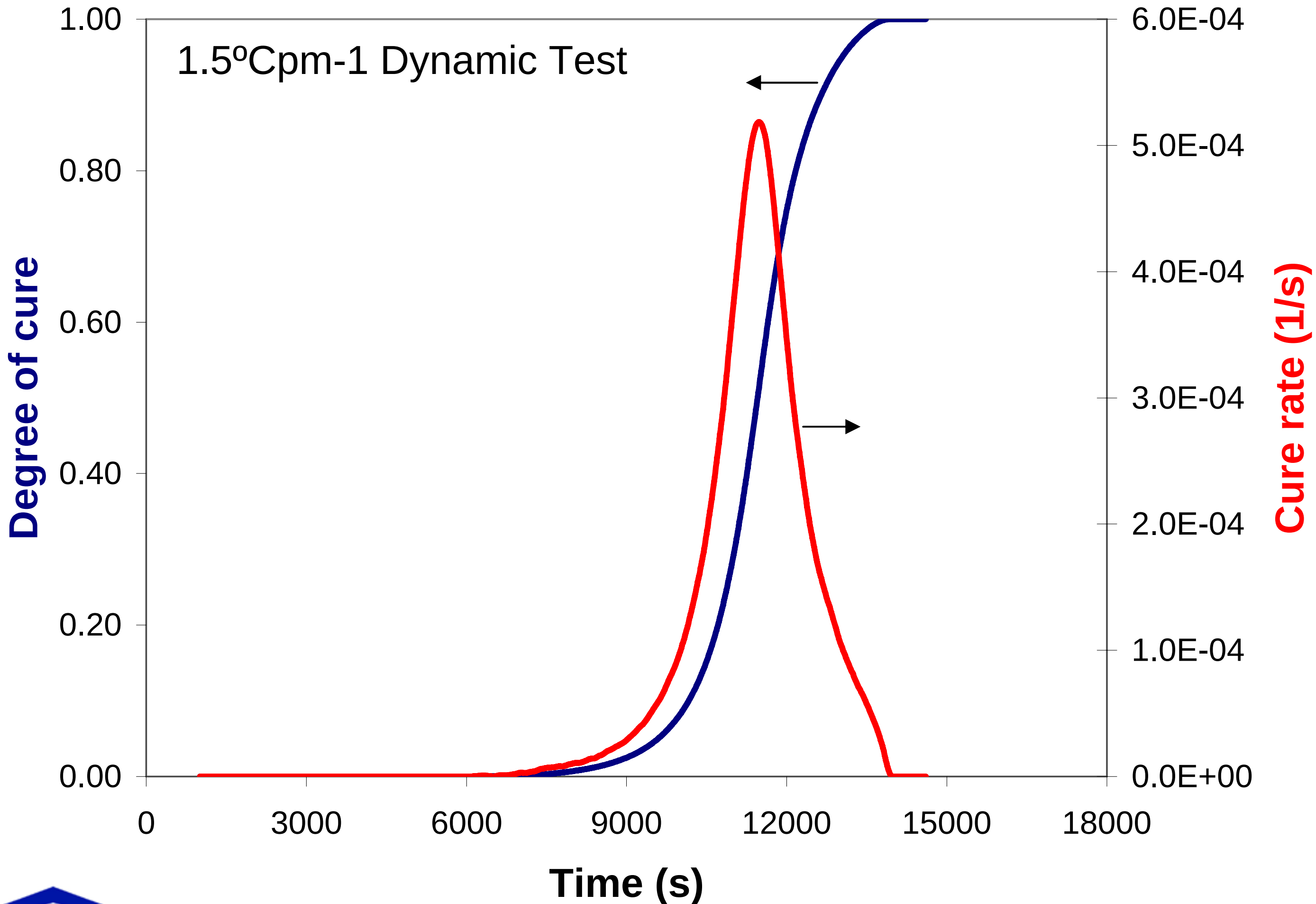
DoC and Cure Rate – 1cpm-2



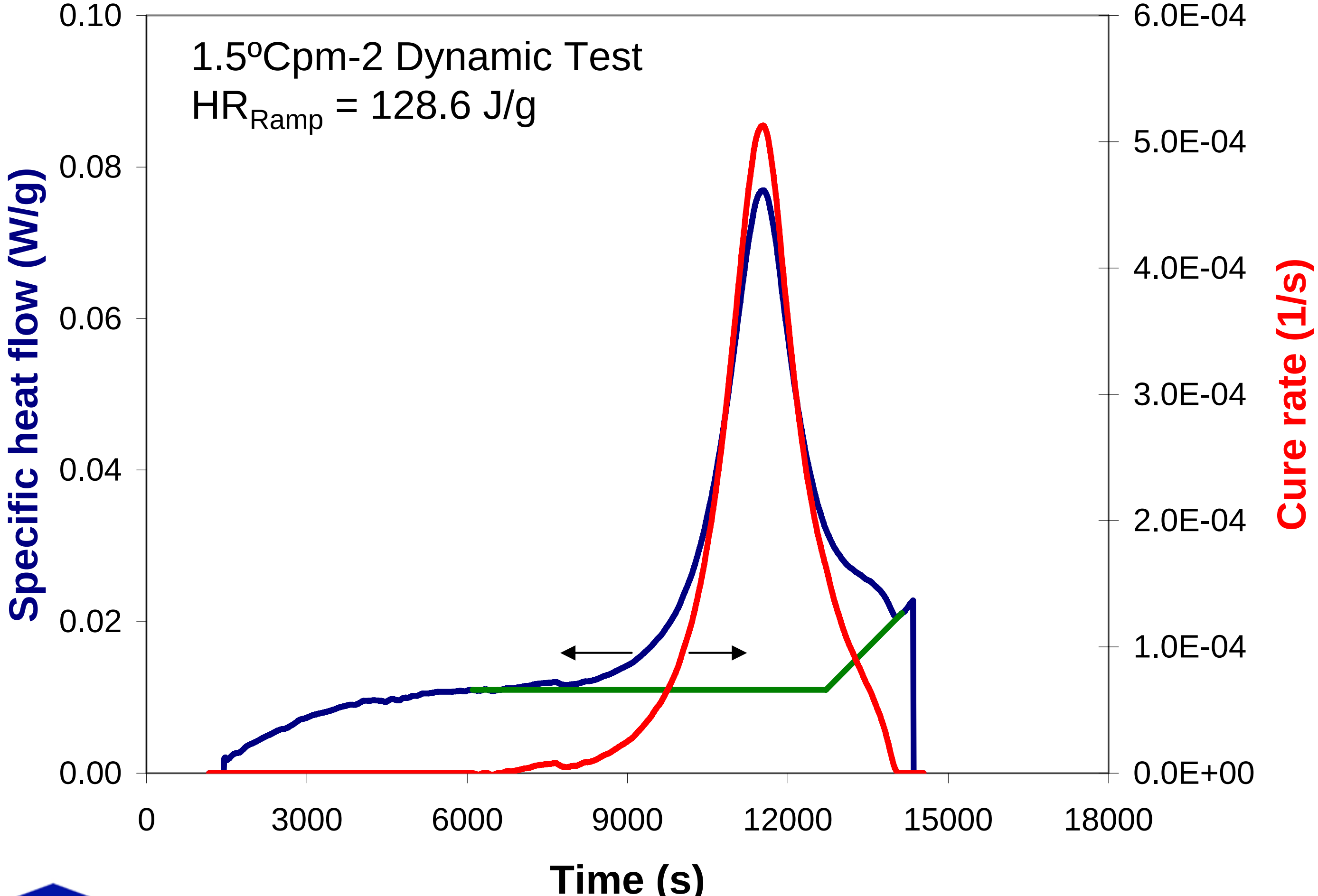
Heat Flow Response – 1.5cpm-1



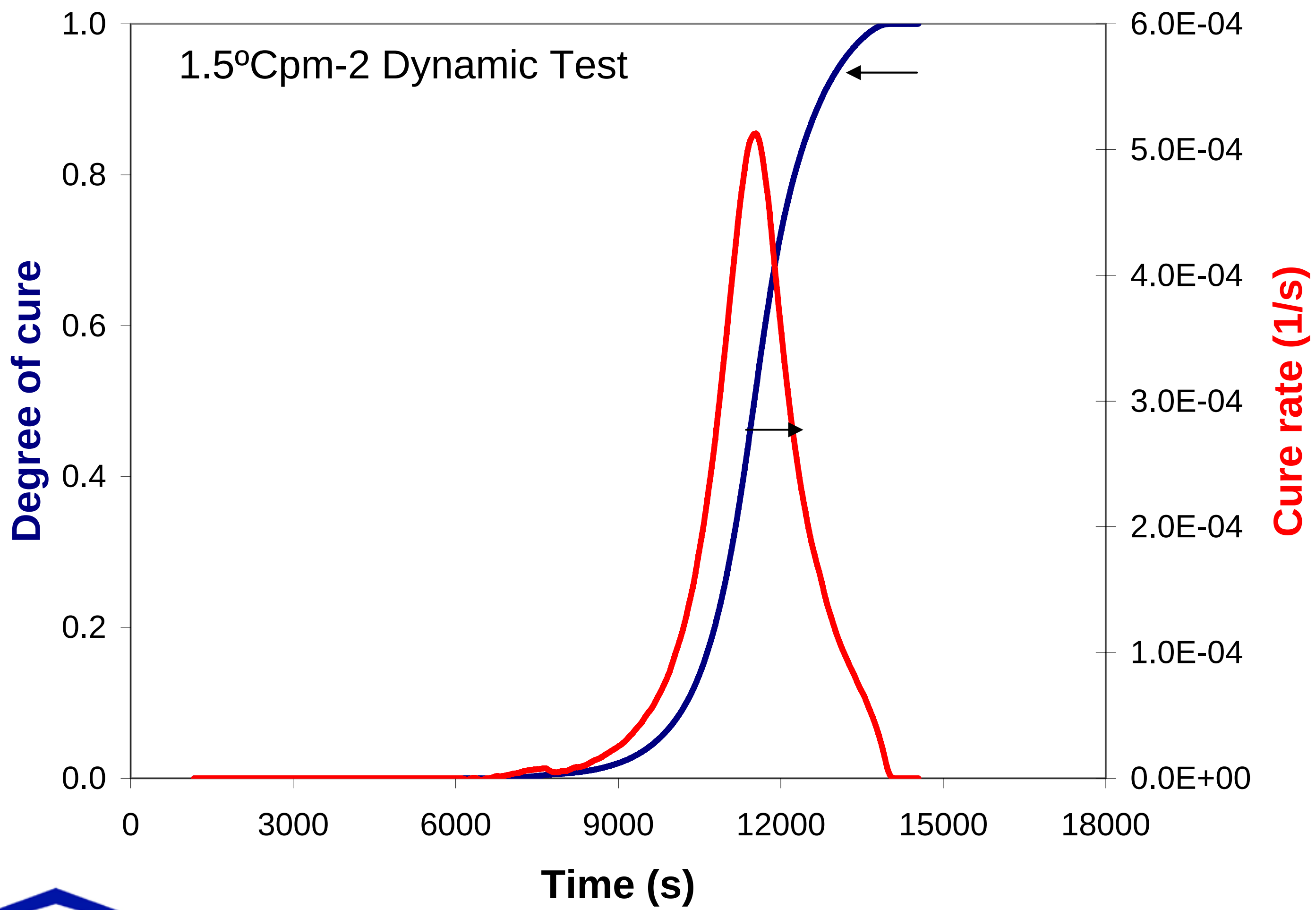
DoC and Cure Rate – 1.5cpm-1



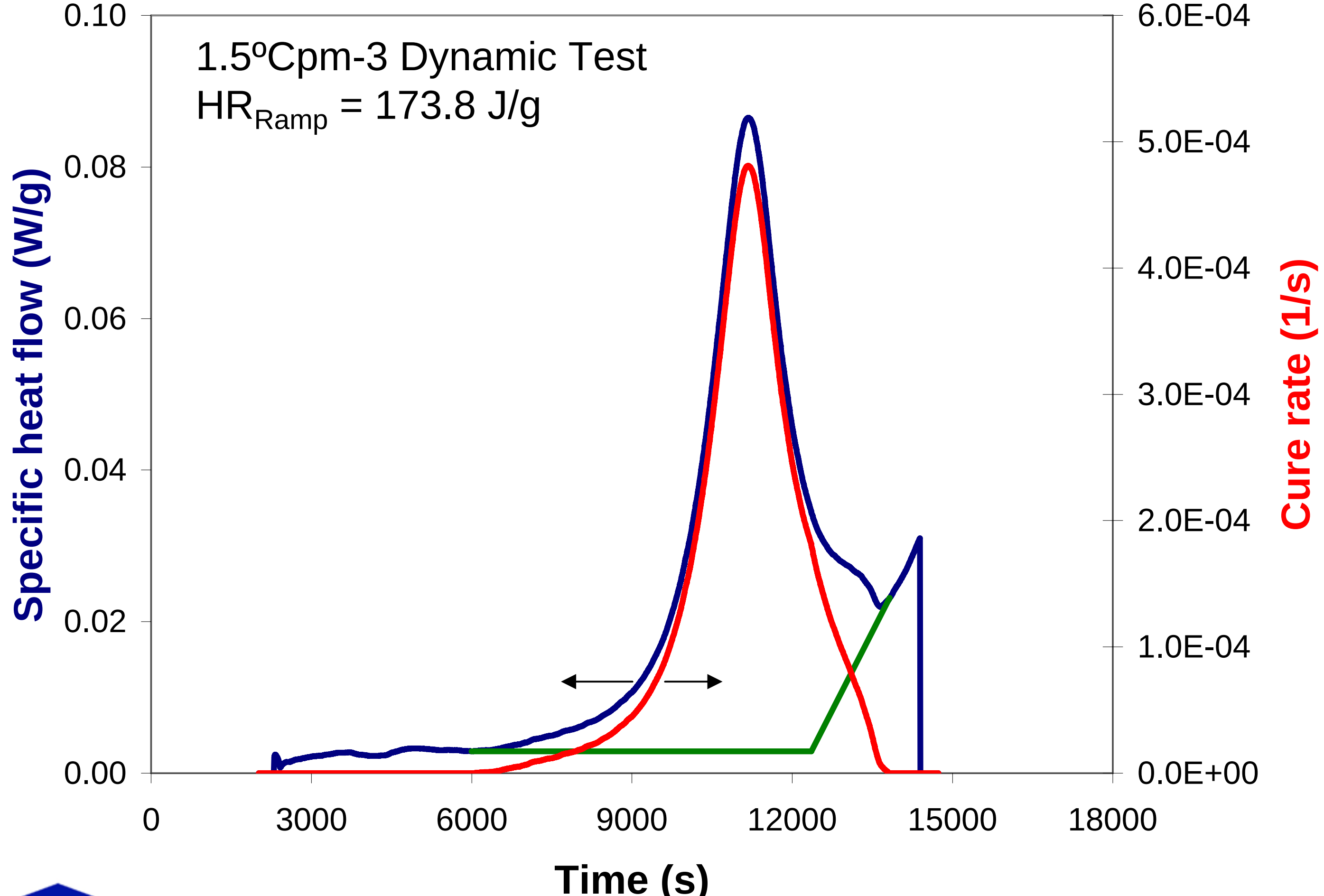
Heat Flow Response – 1.5cpm-2



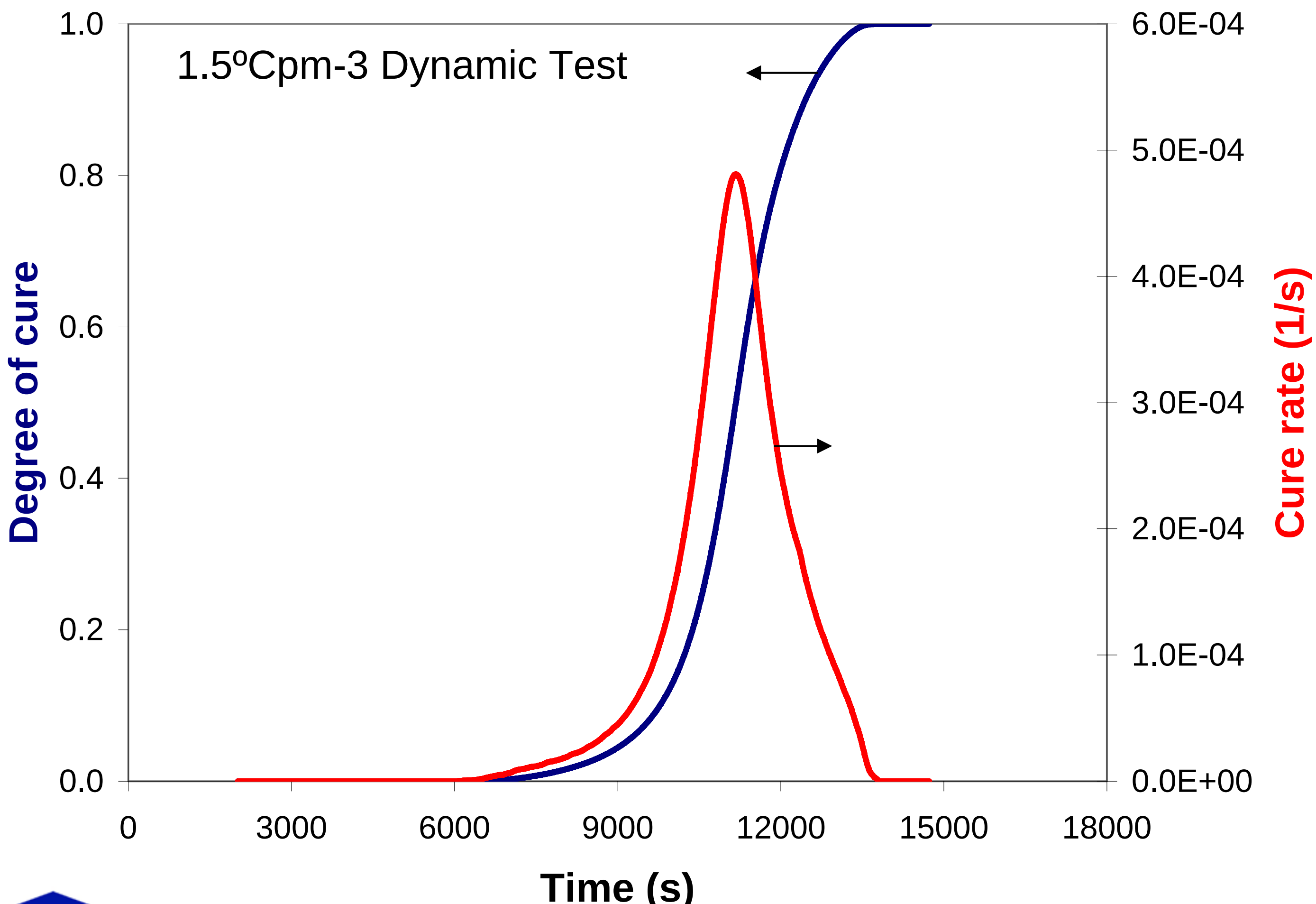
DoC and Cure Rate – 1.5cpm-2



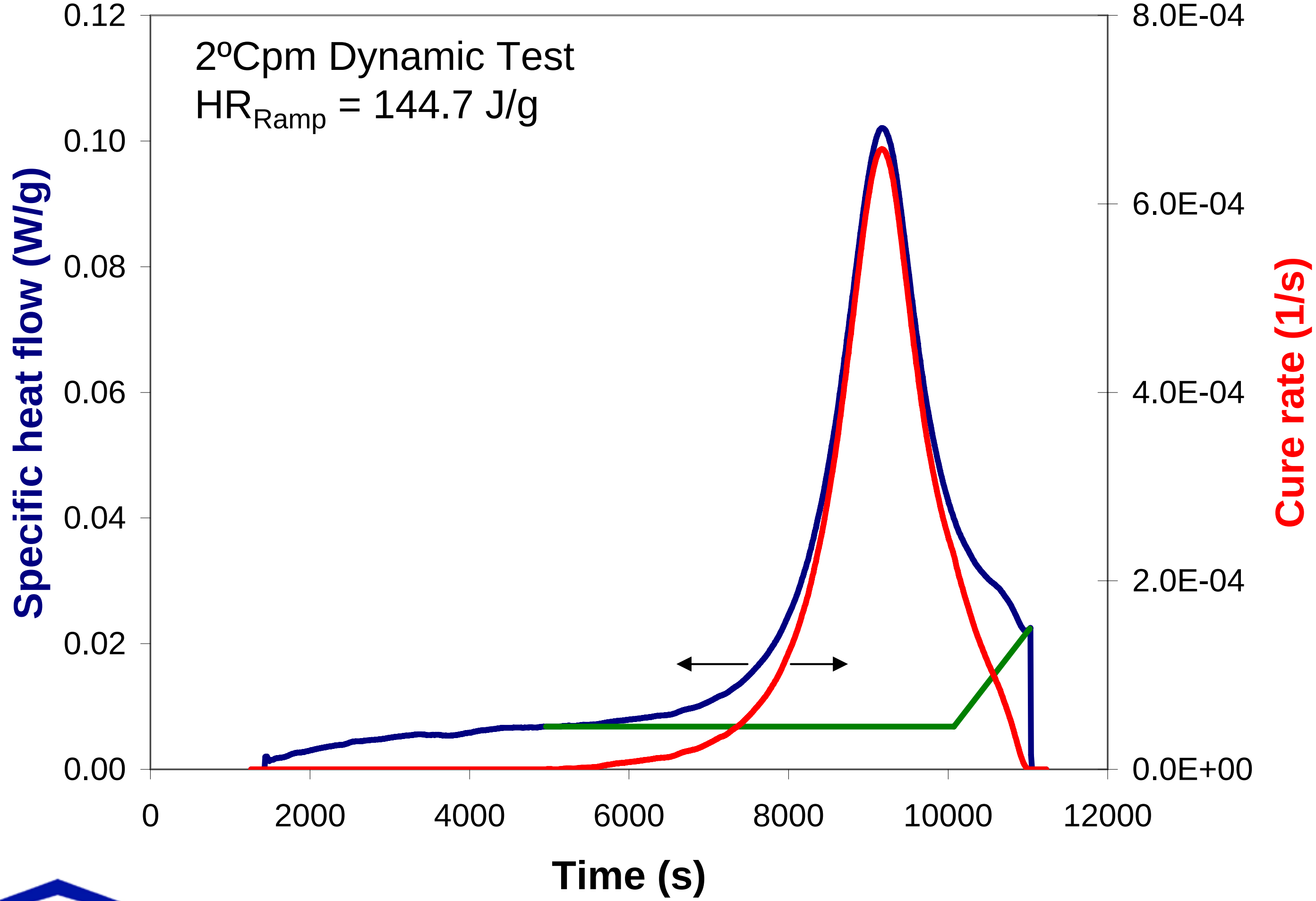
Heat Flow Response – 1.5cpm-3



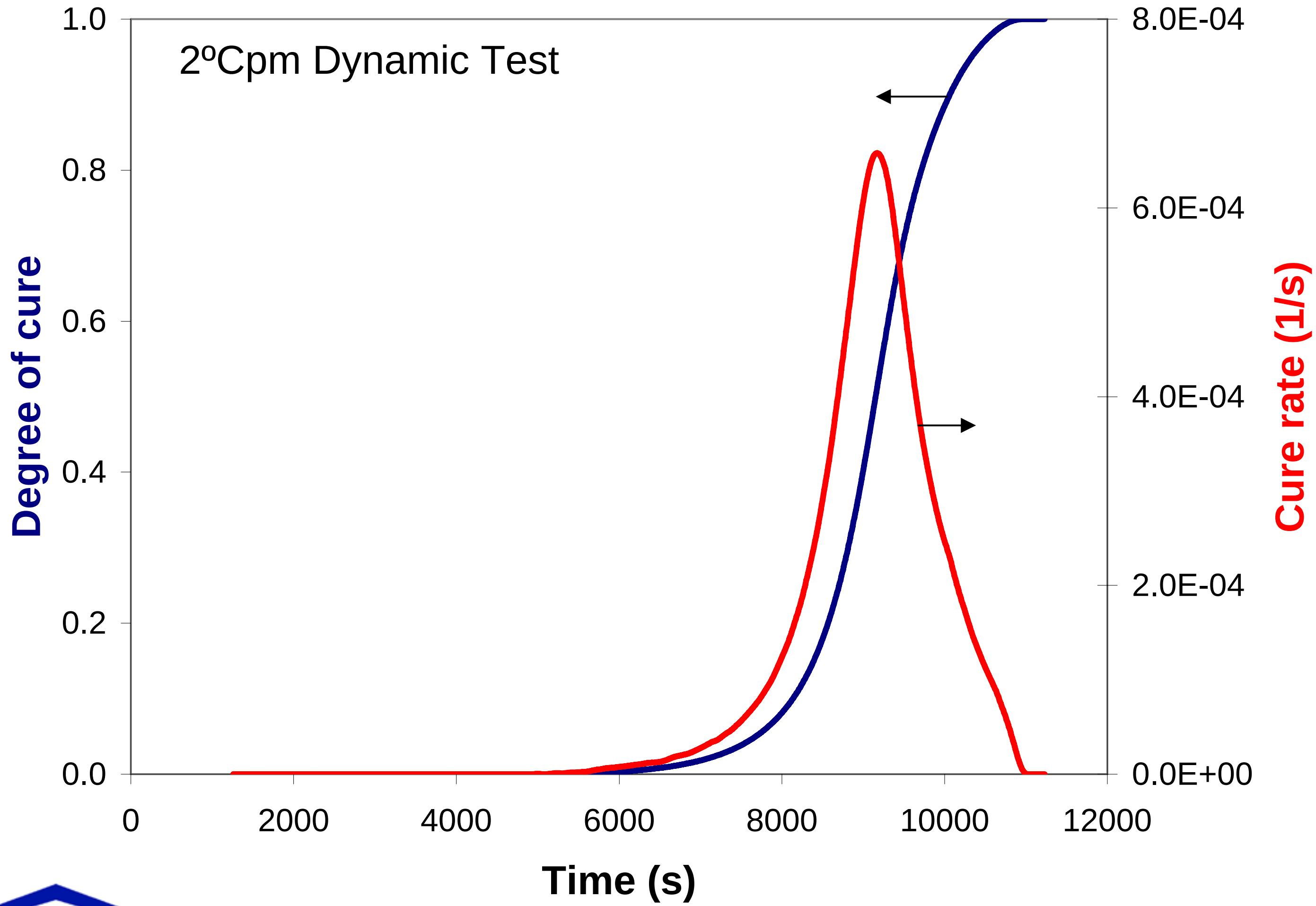
DoC and Cure Rate – 1.5cpm-3



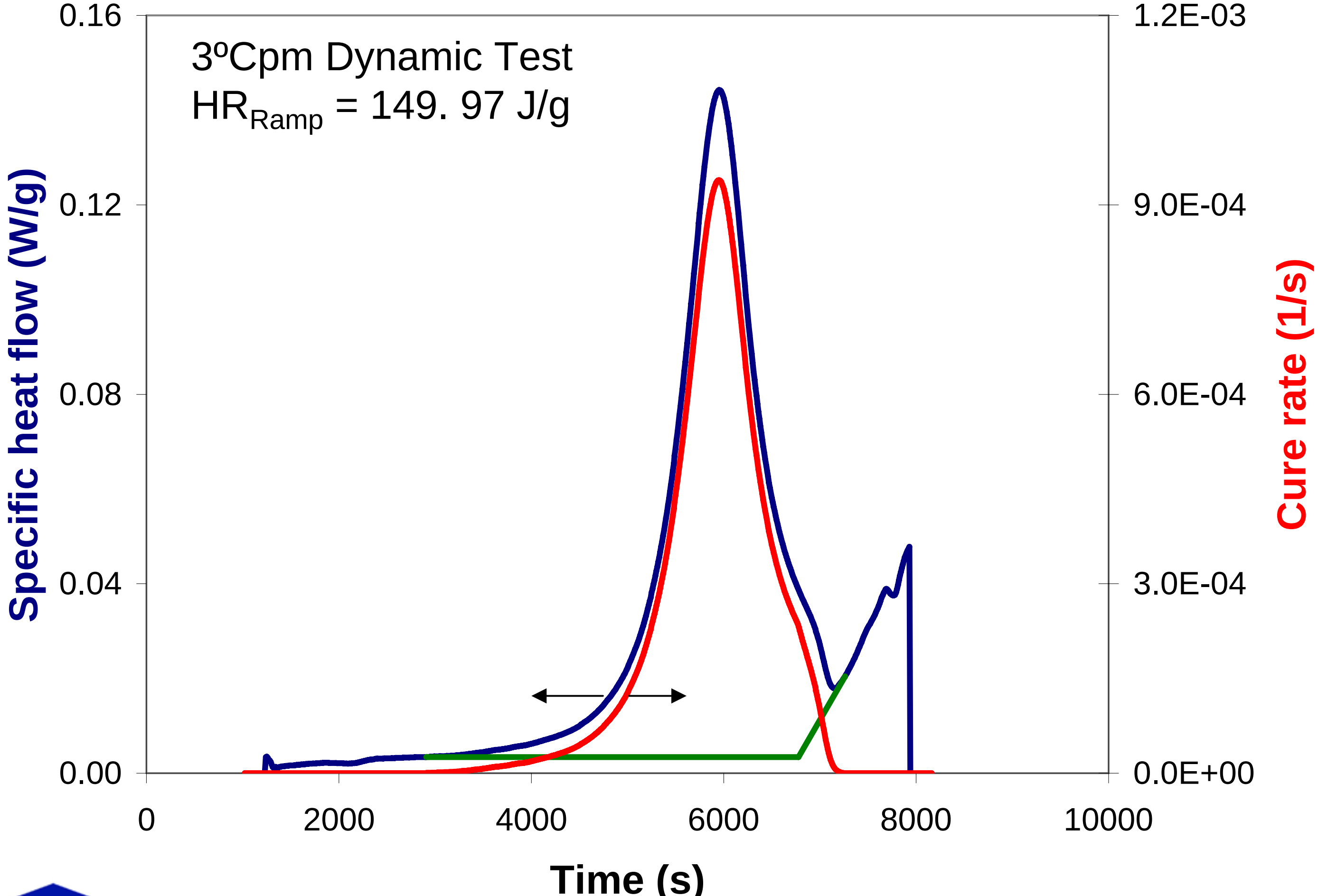
Heat Flow Response – 2cpm-2



DoC and Cure Rate – 2cpm-2



Heat Flow Response – 3cpm



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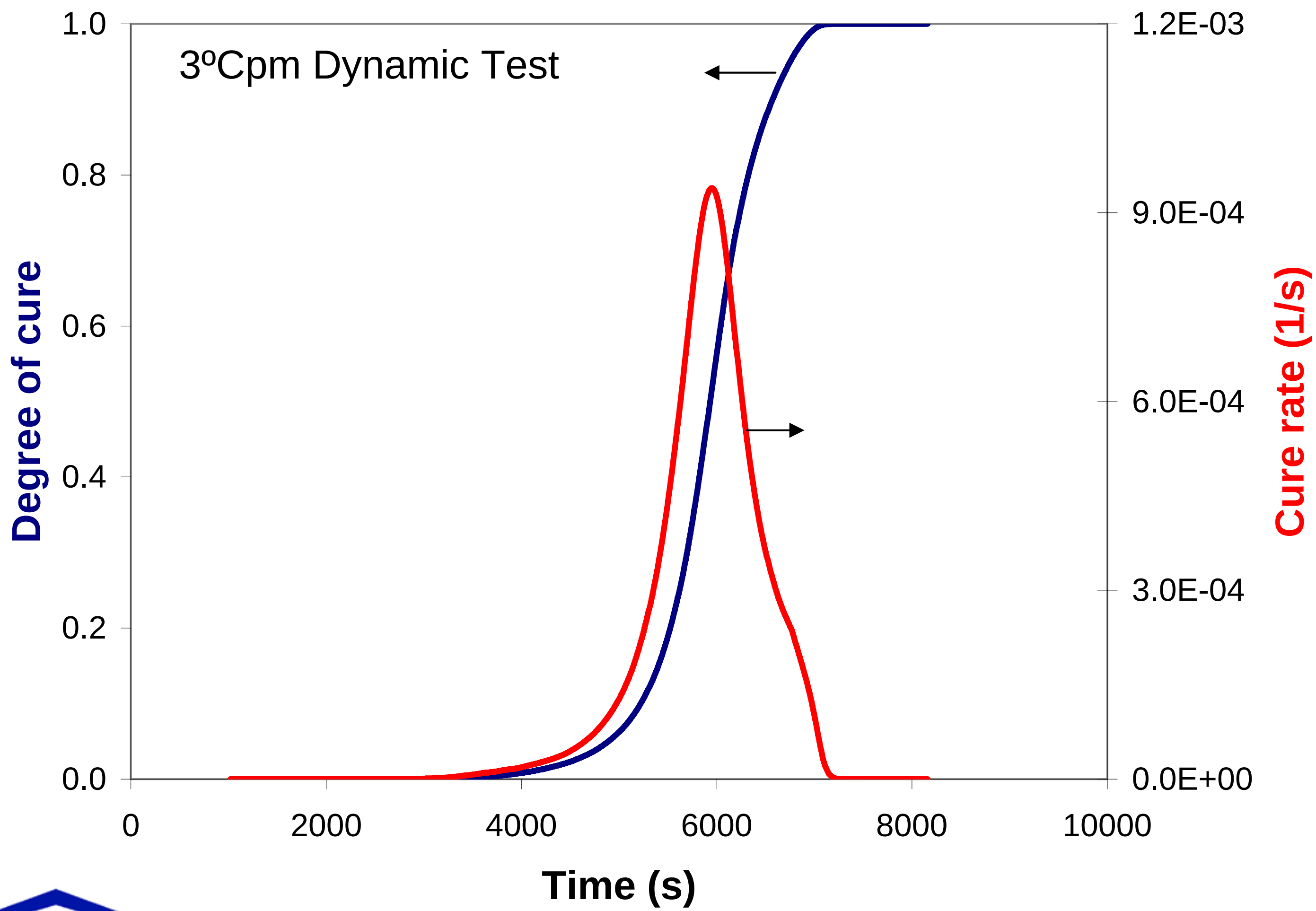
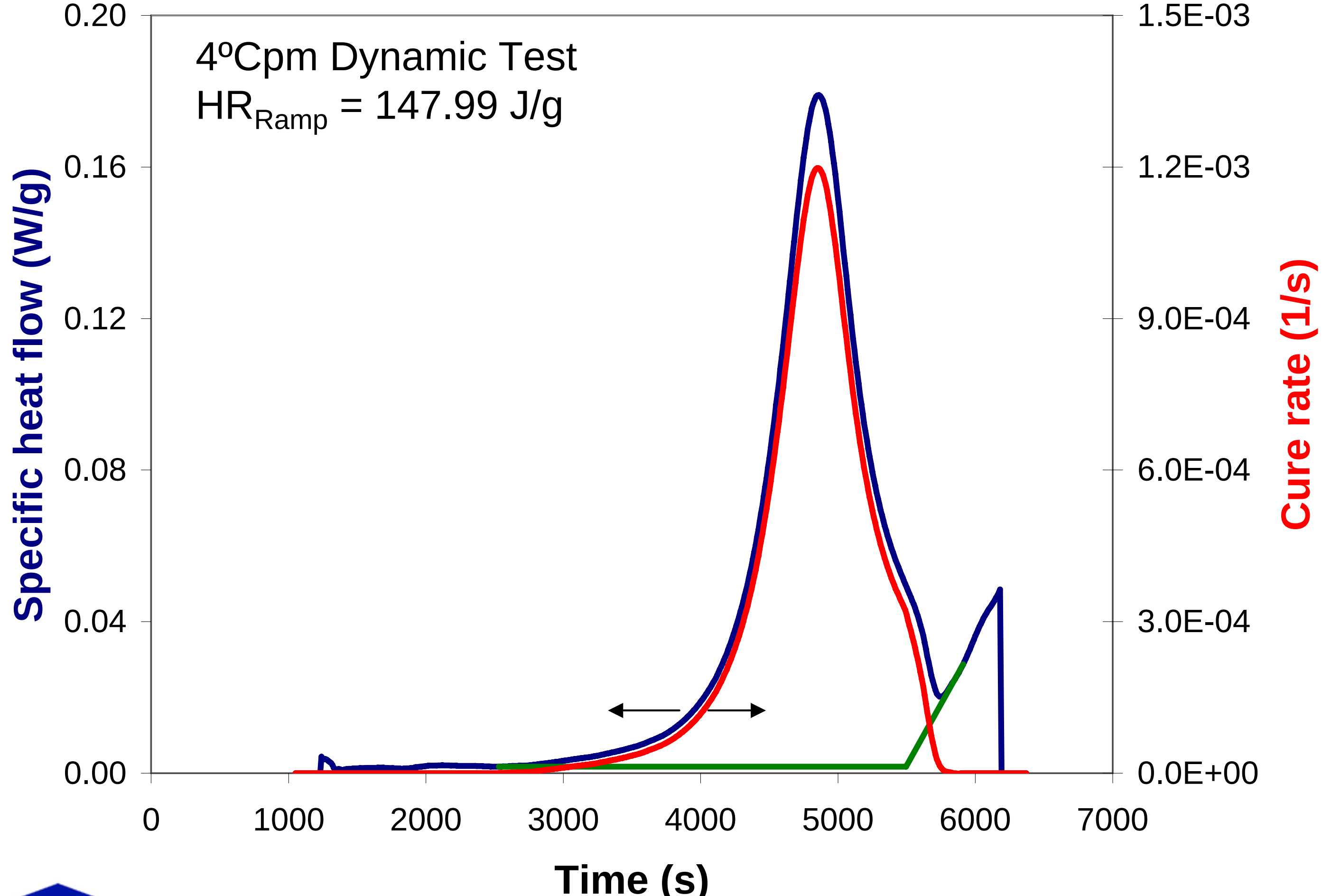
CONVERGENT MANUFACTURING TECHNOLOGIES

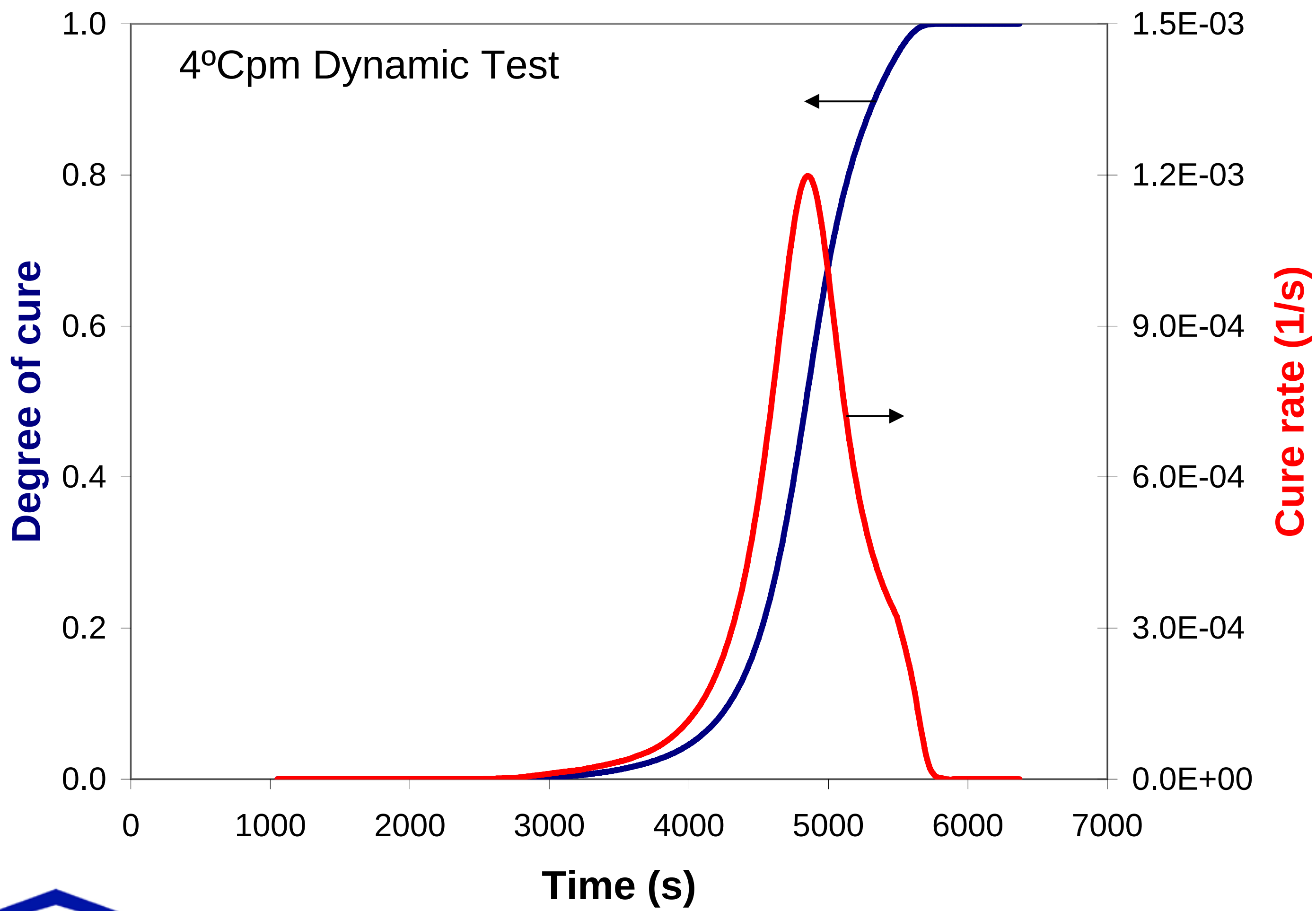
DoC and Cure Rate – 3cpm



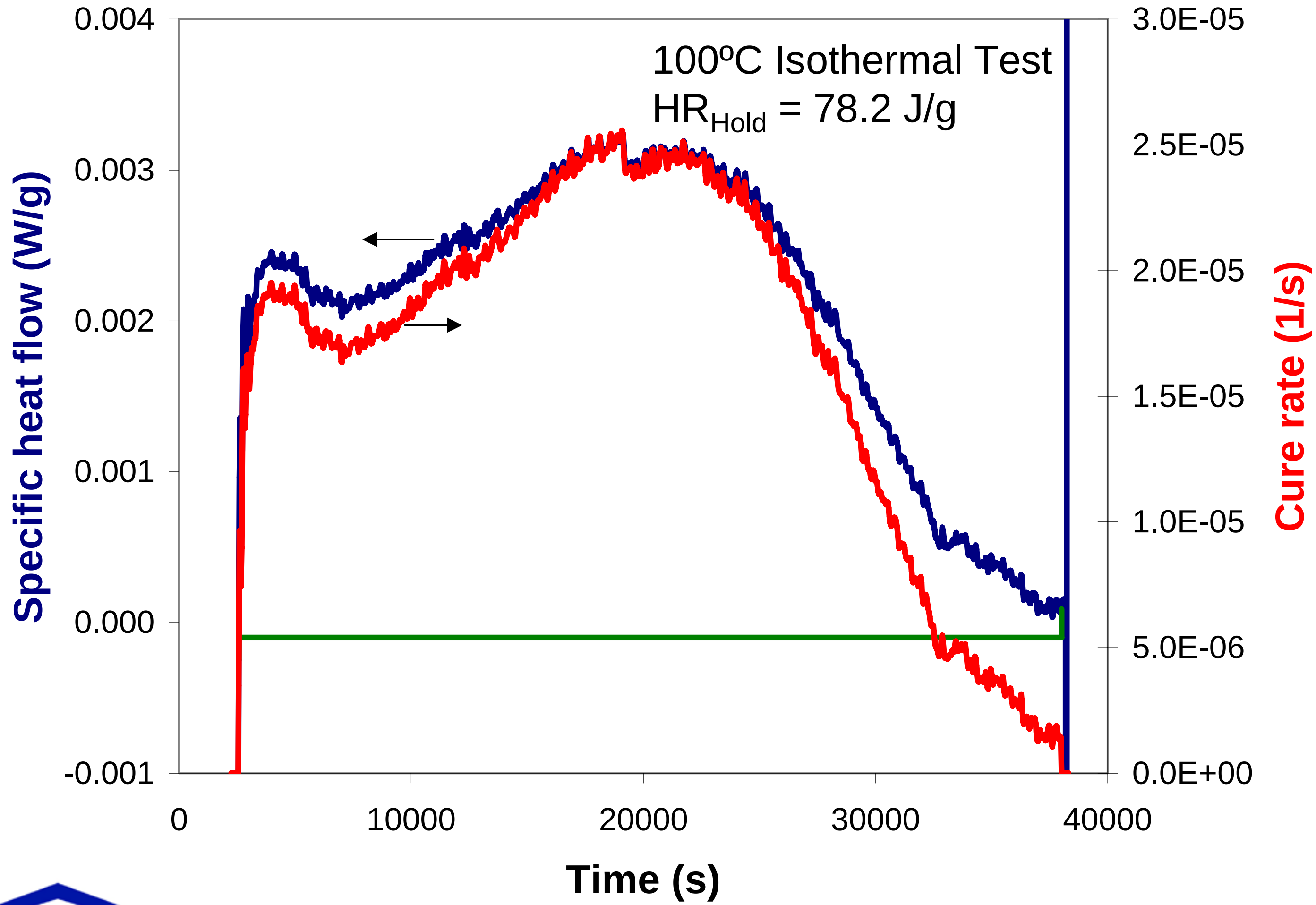
Heat Flow Response – 4cpm



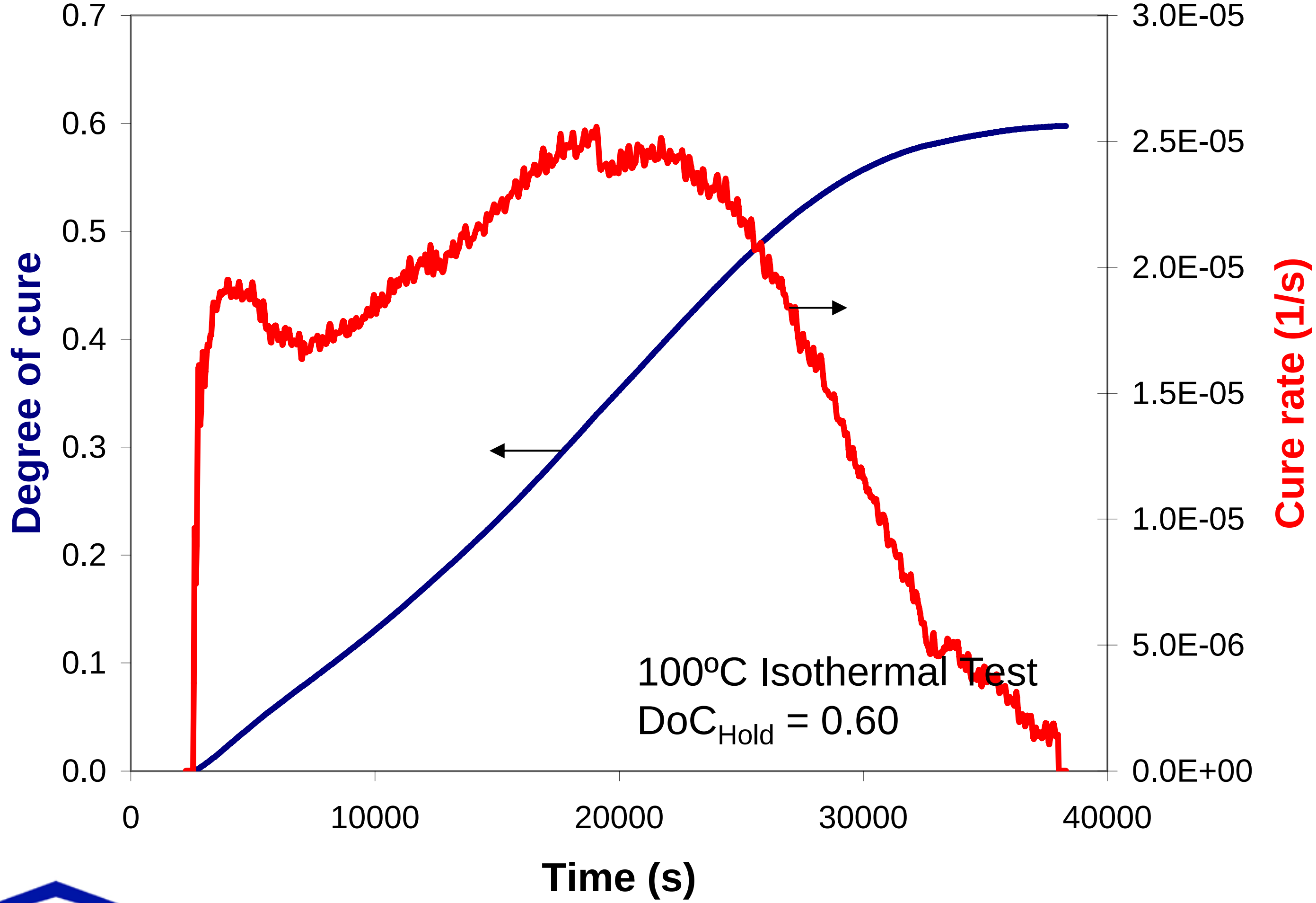
DoC and Cure Rate – 4cpm



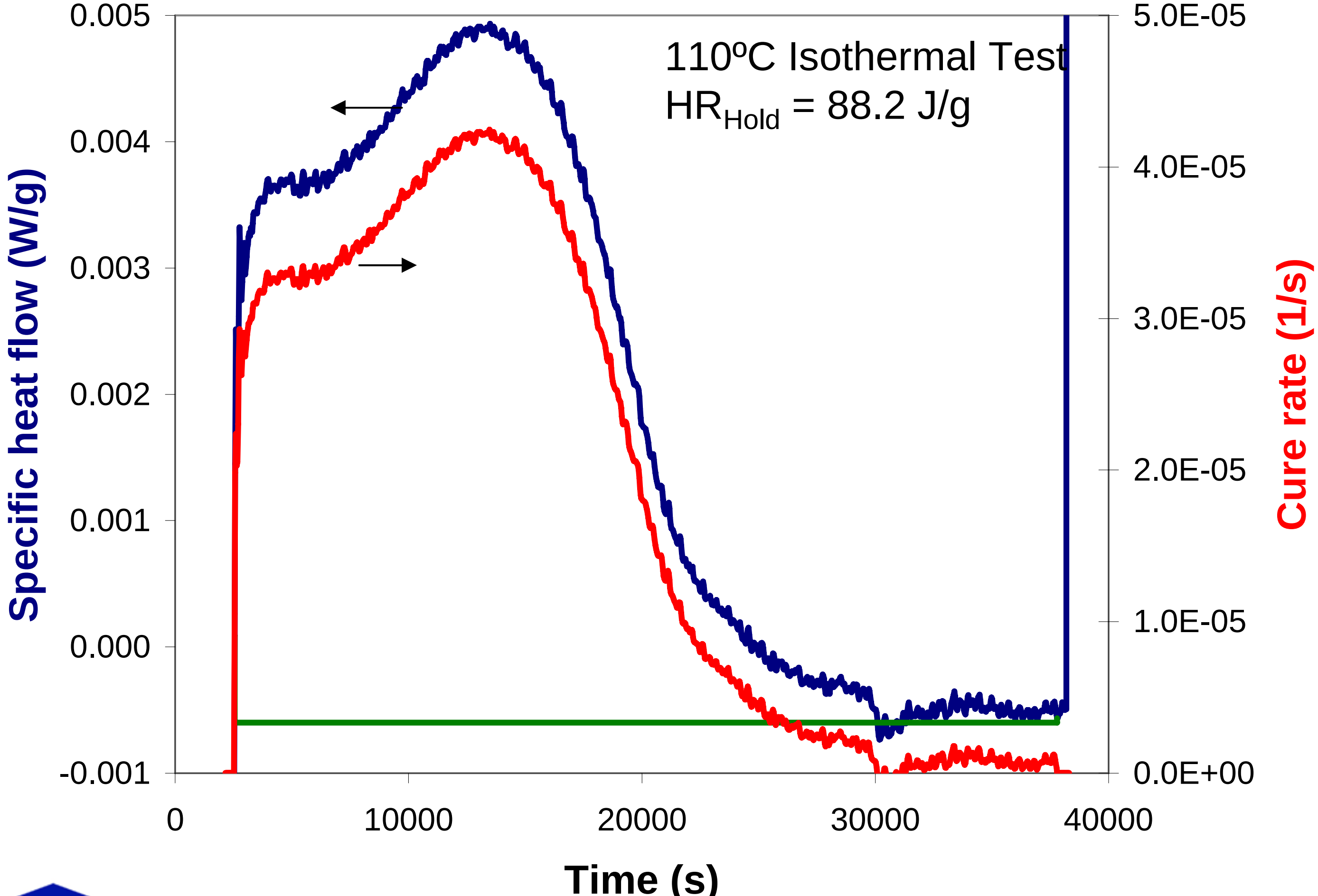
Heat Flow Response – 100ºC



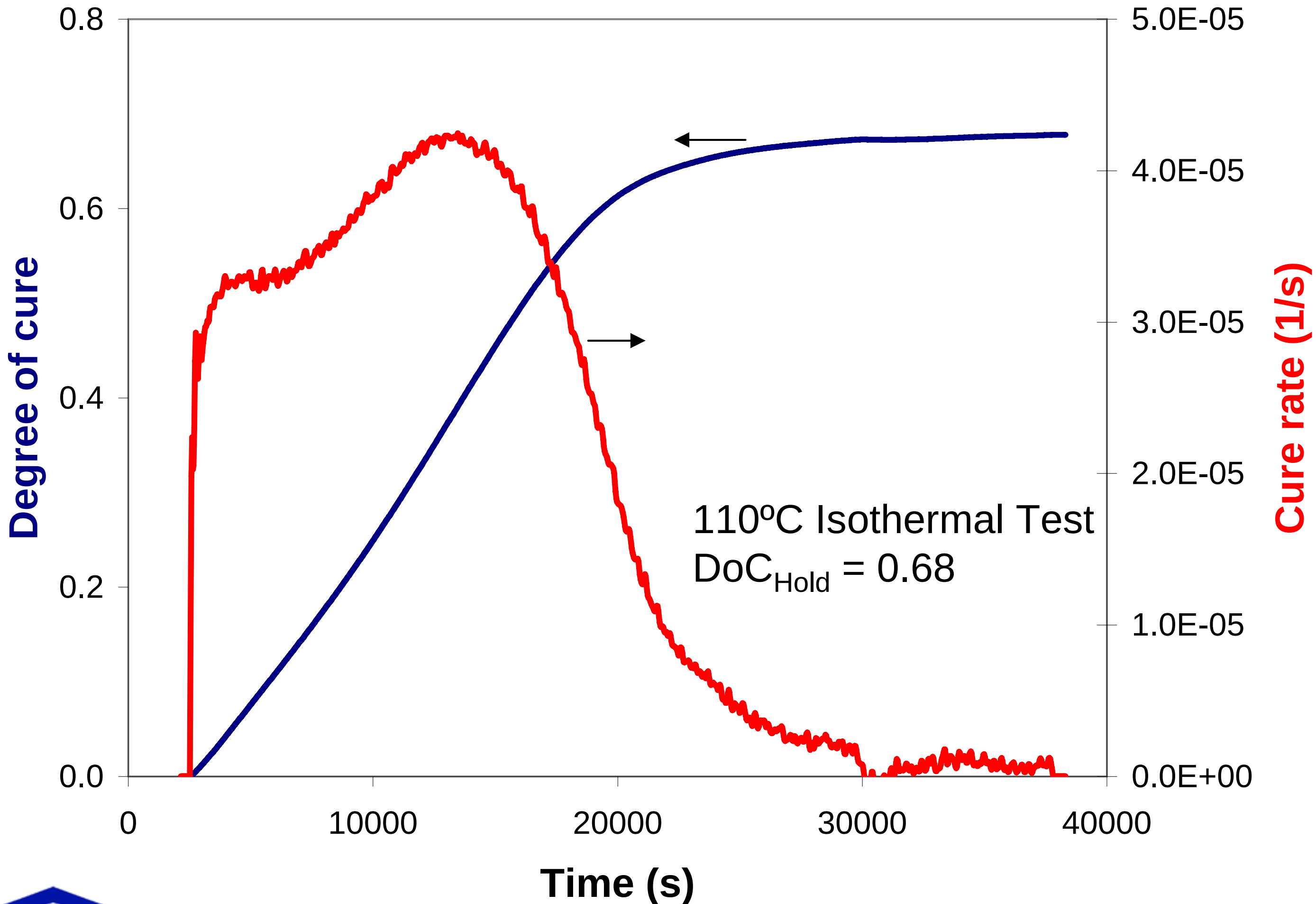
DoC and Cure Rate – 100ºC



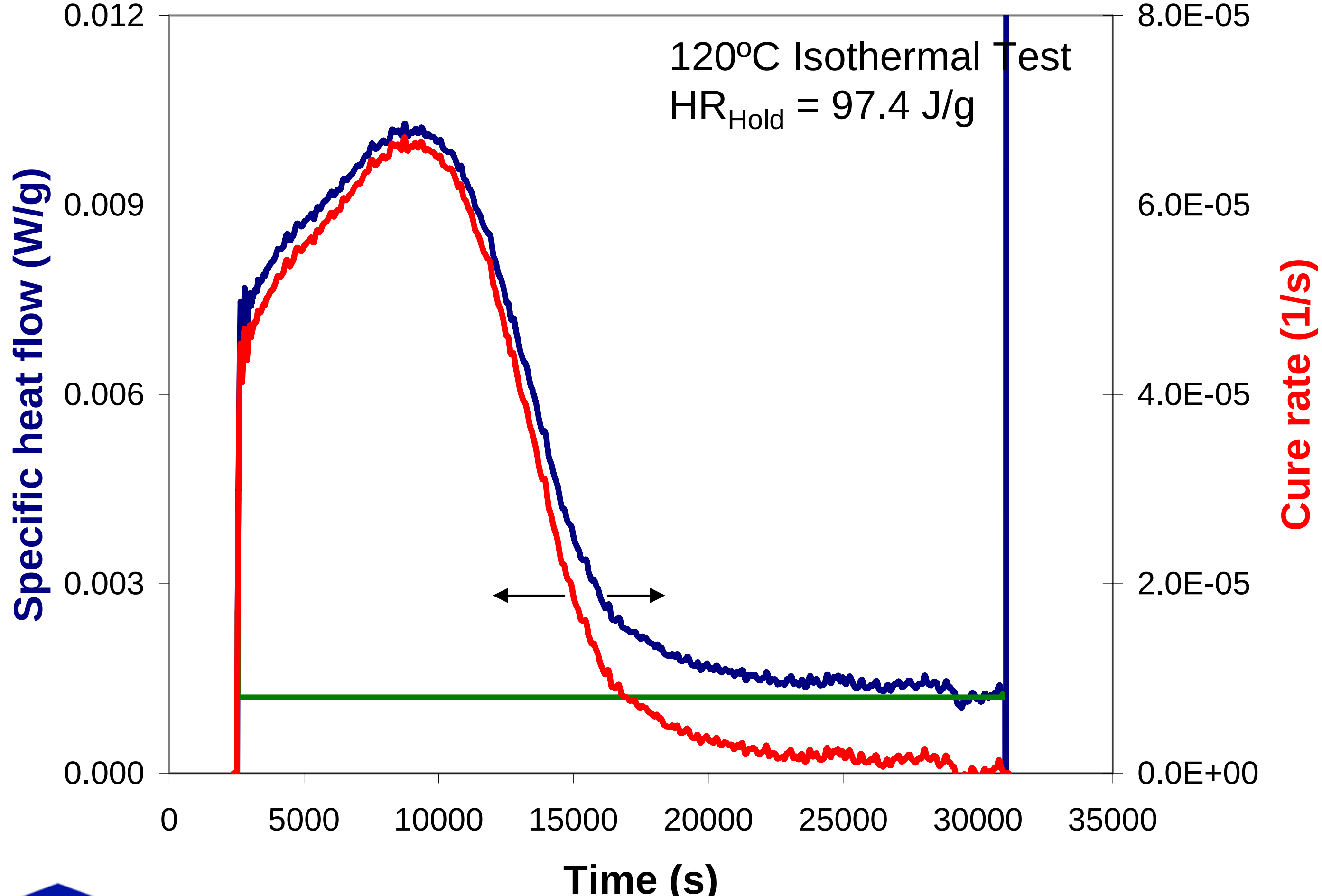
Heat Flow Response – 110ºC



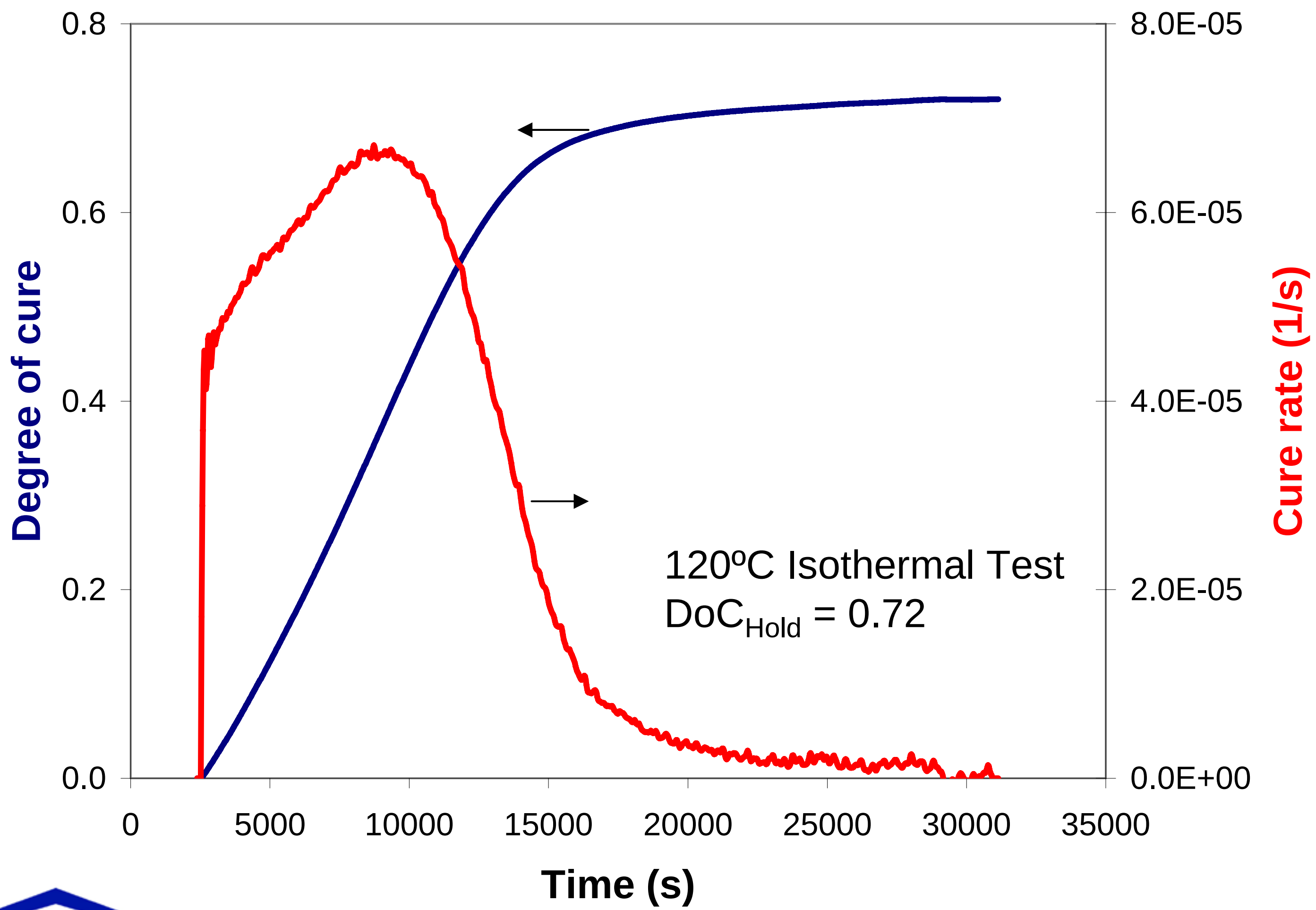
DoC and Cure Rate – 110ºC



Heat Flow Response – 120ºC-1



DoC and Cure Rate – 120ºC-1



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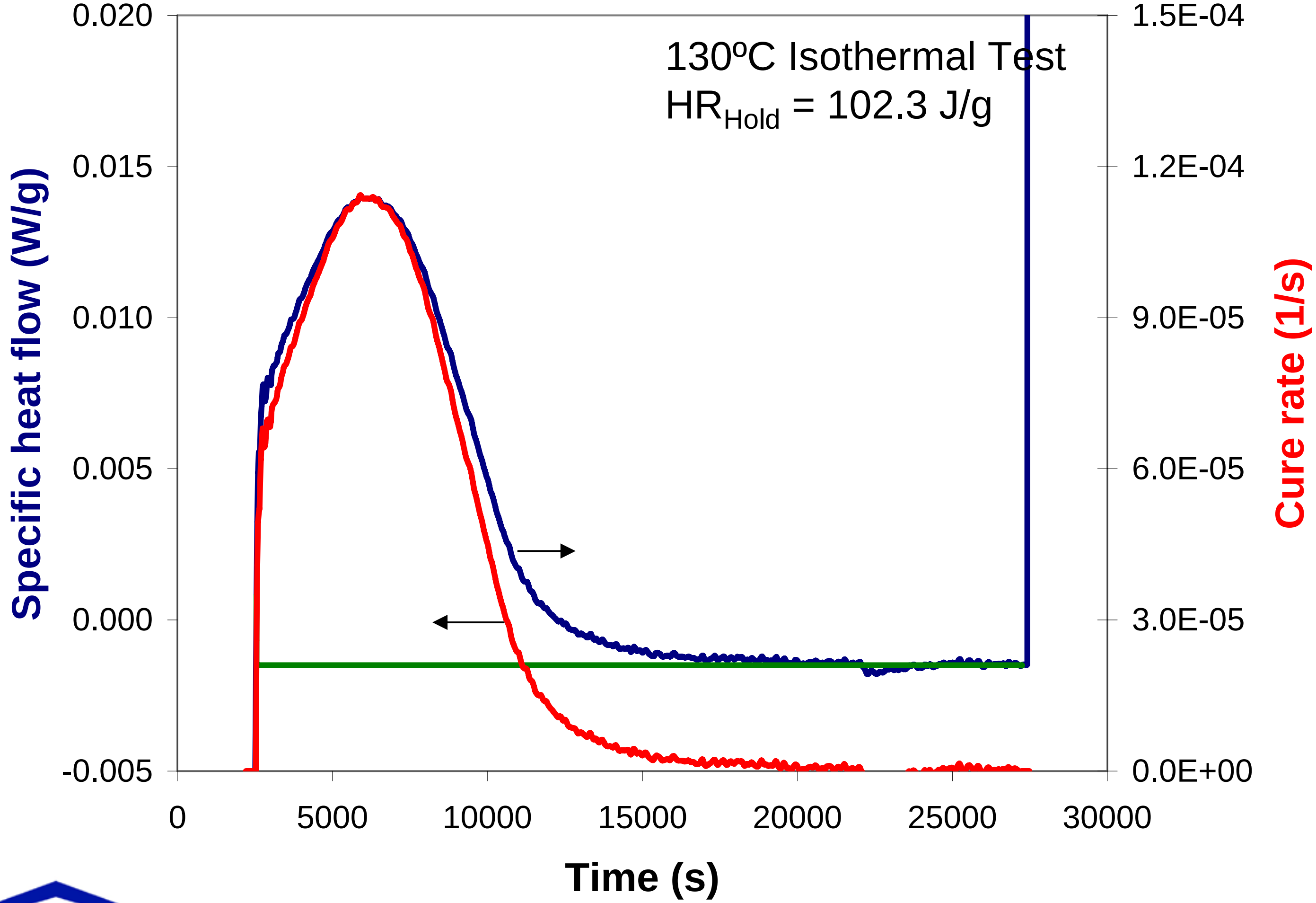
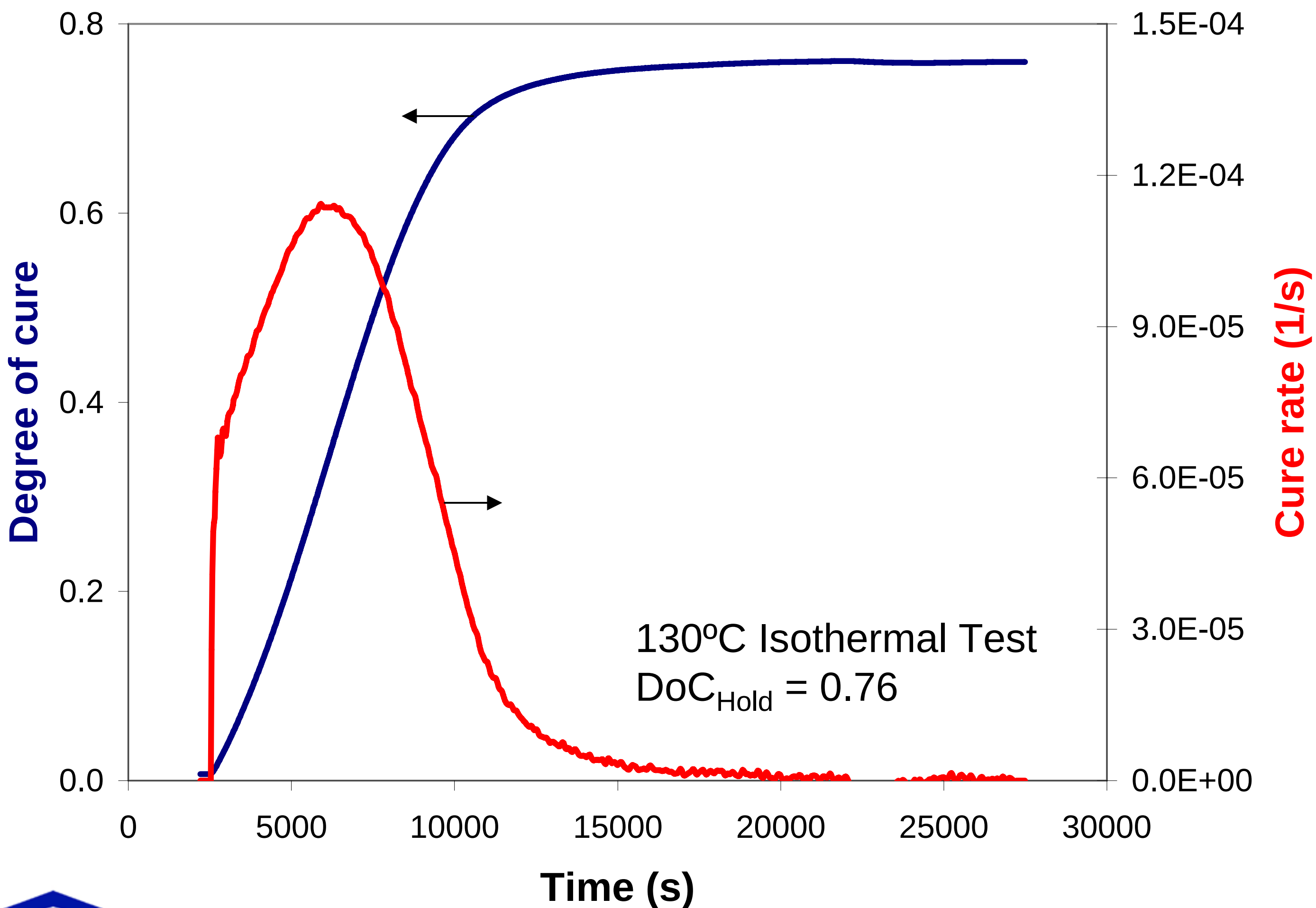
CONVERGENT MANUFACTURING TECHNOLOGIES

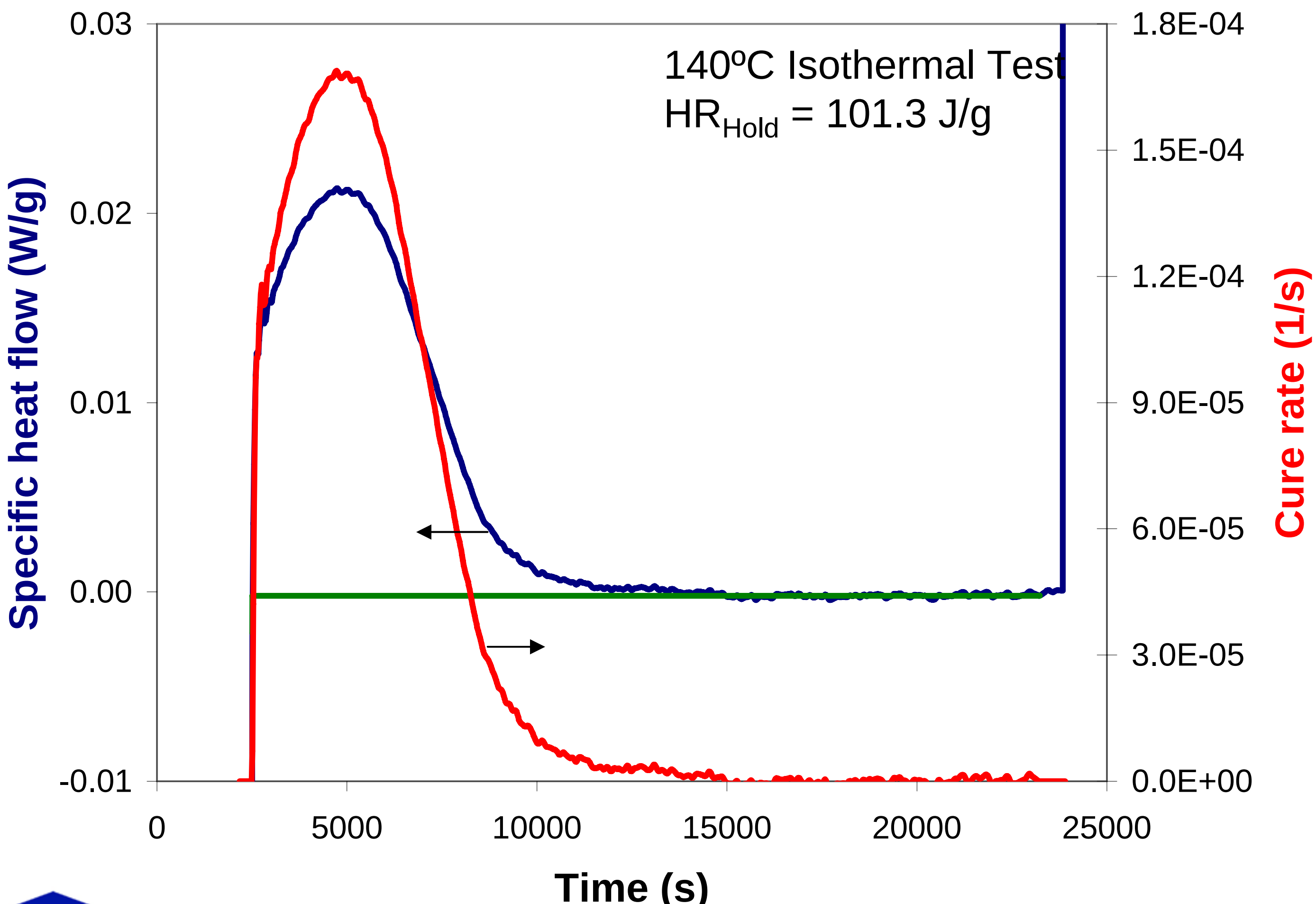
Heat Flow Response – 130ºC



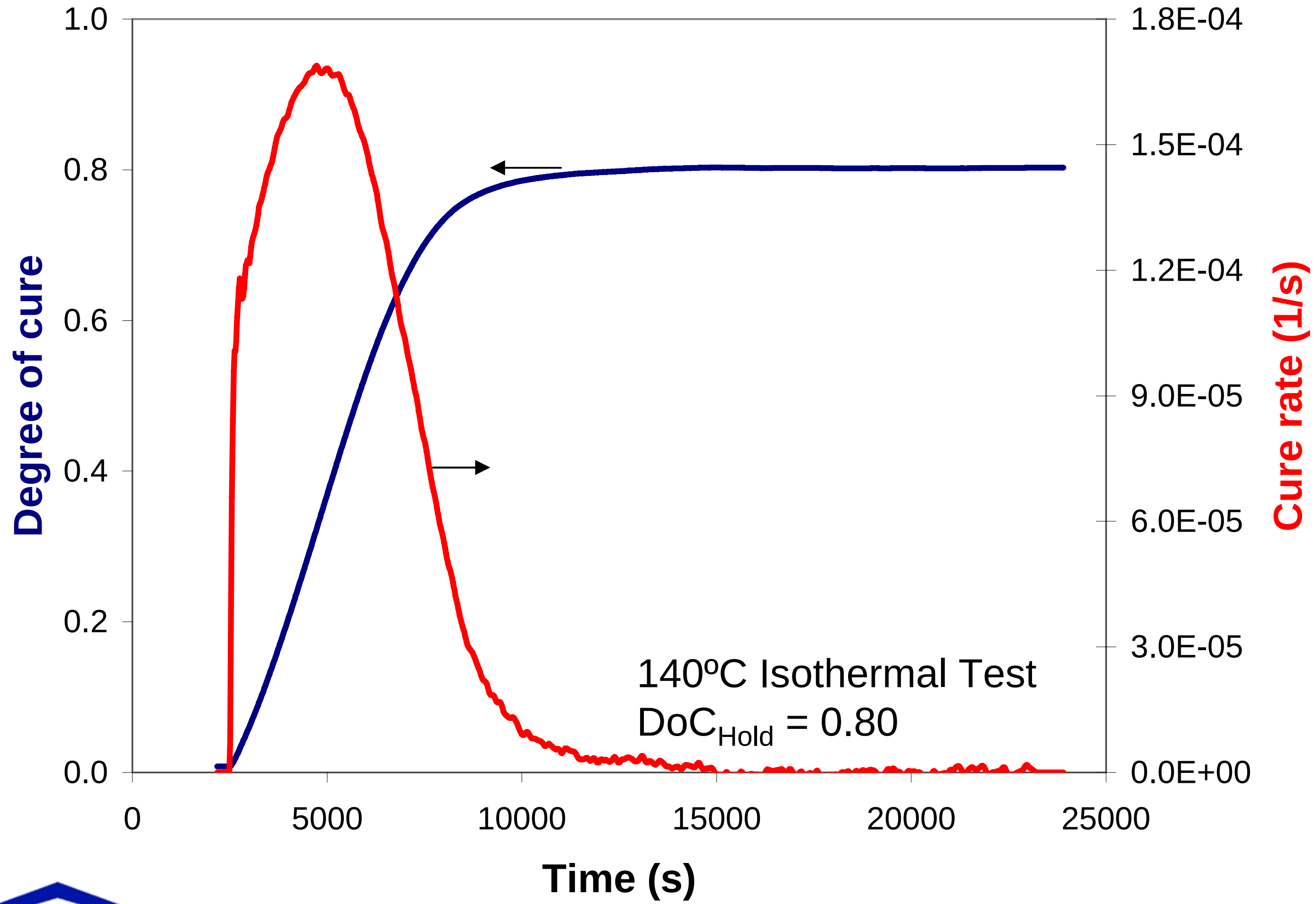
DoC and Cure Rate – 130ºC



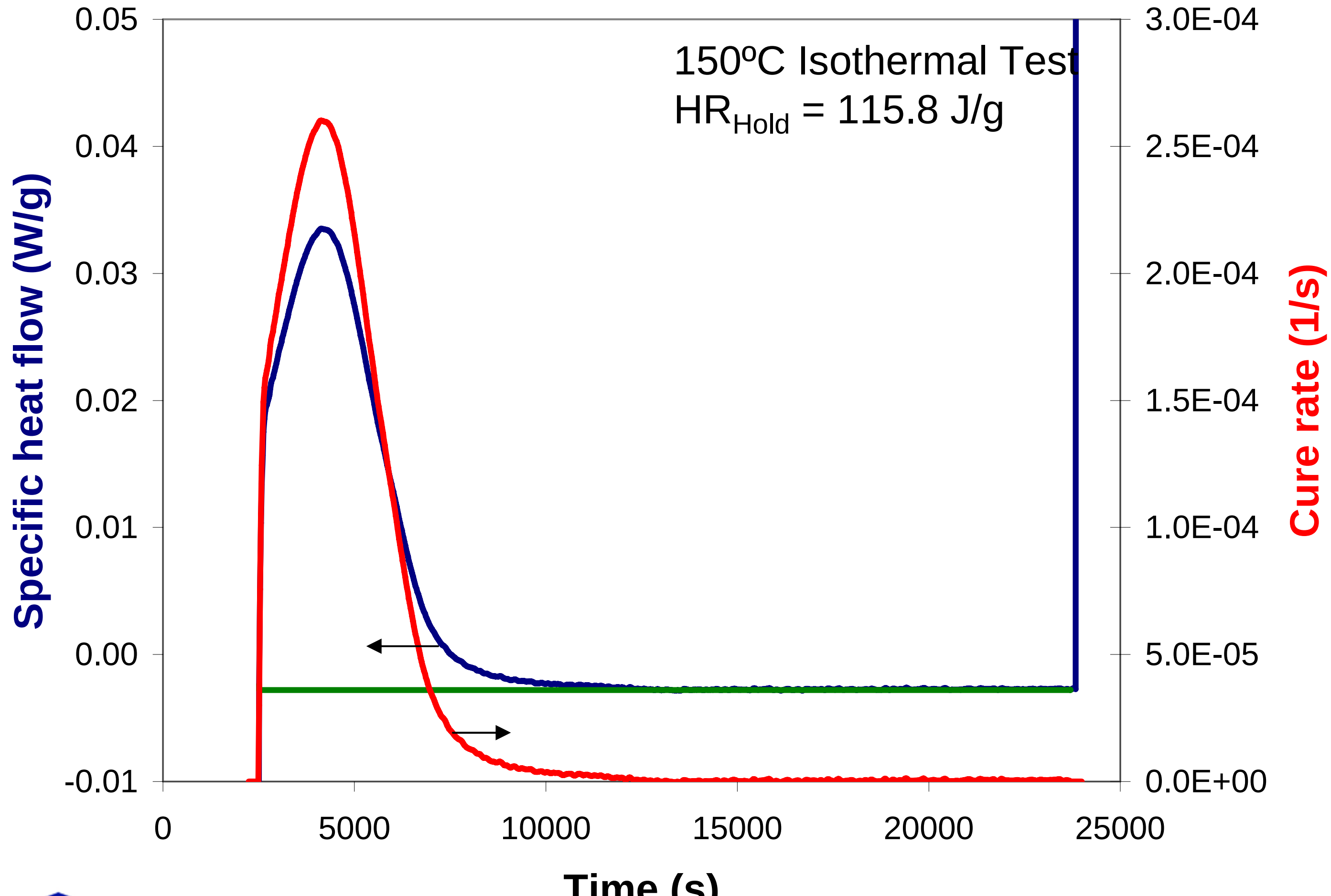
Heat Flow Response – 140ºC



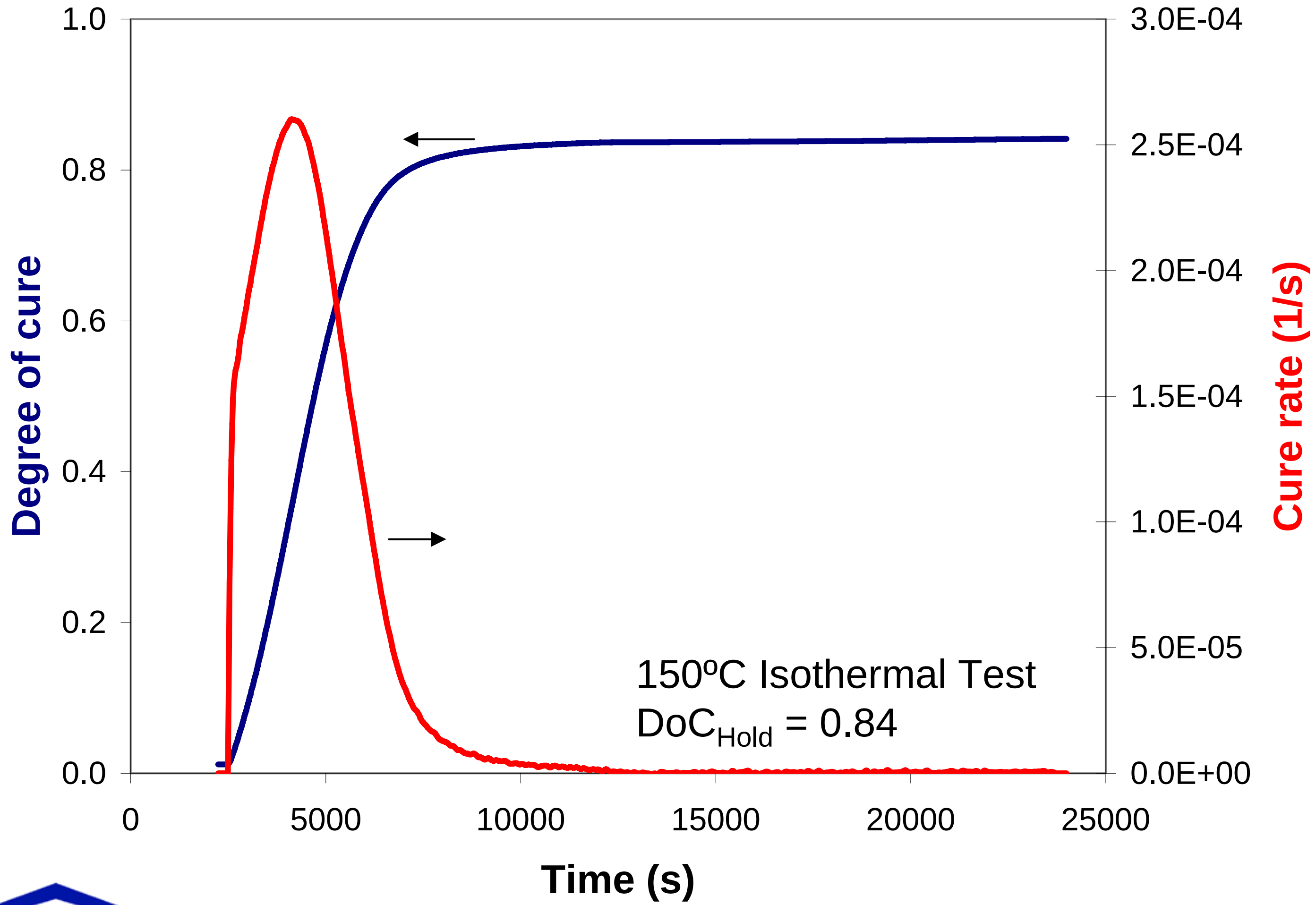
DoC and Cure Rate – 140ºC



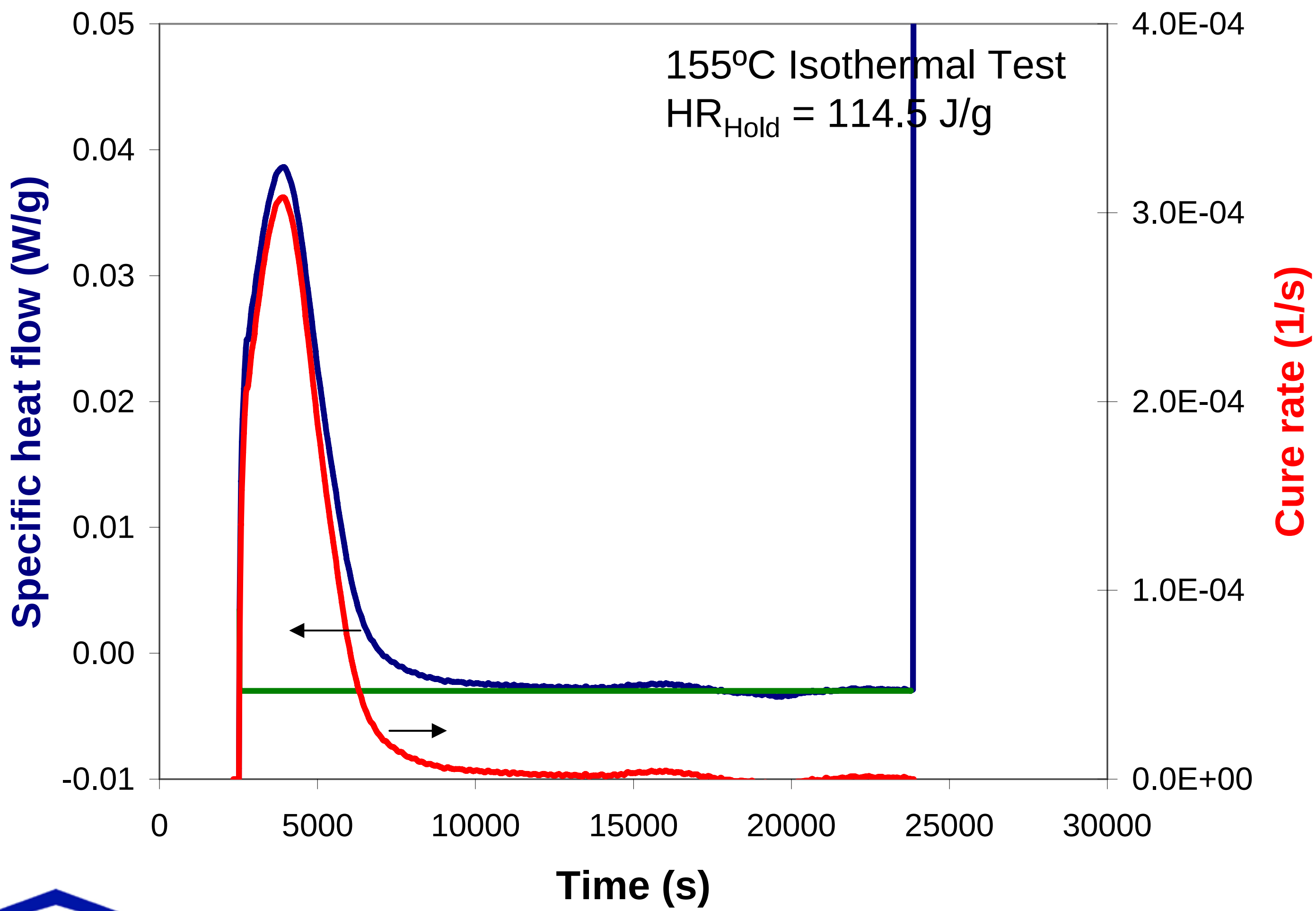
Heat Flow Response – 150ºC



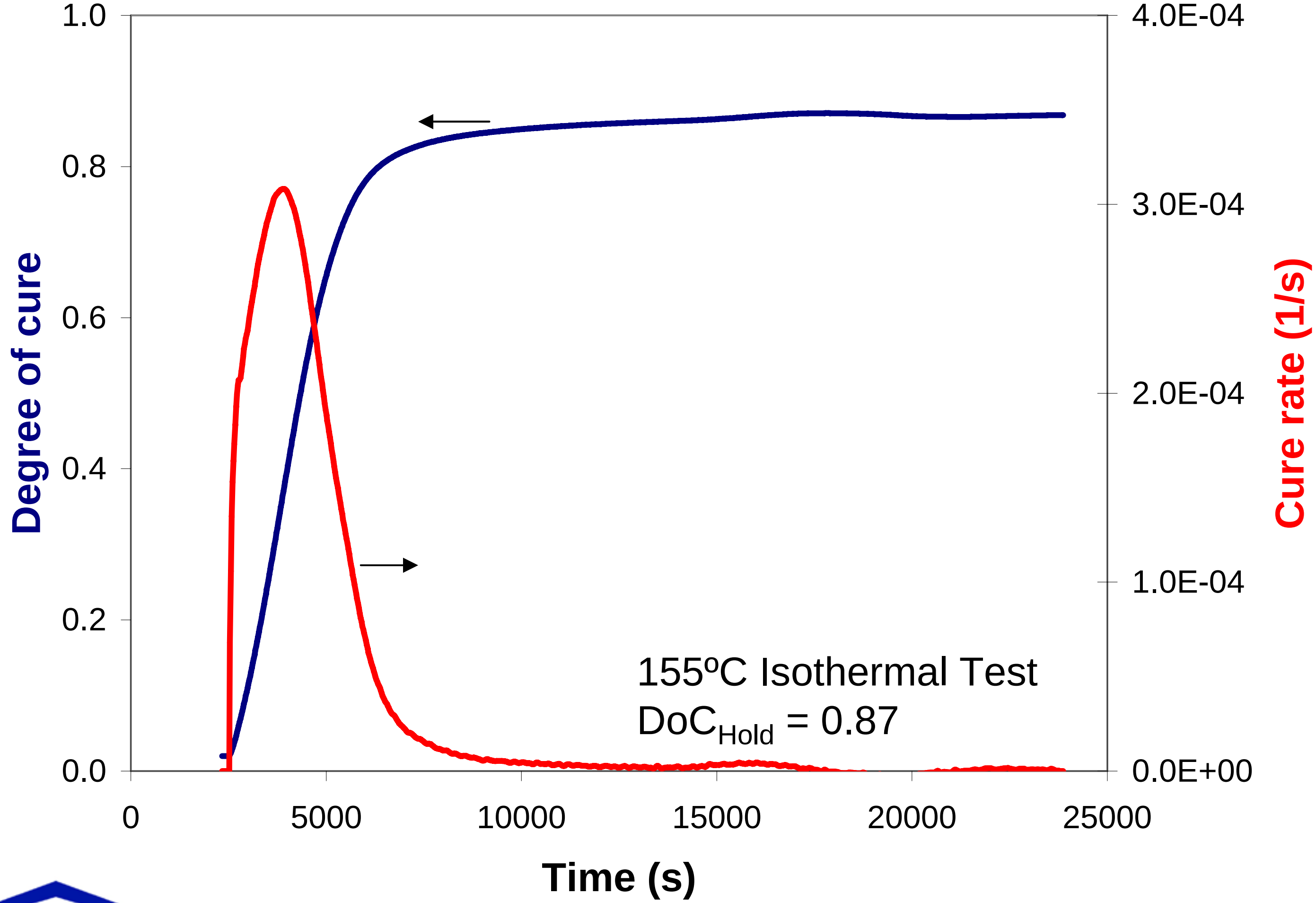
DoC and Cure Rate – 150ºC



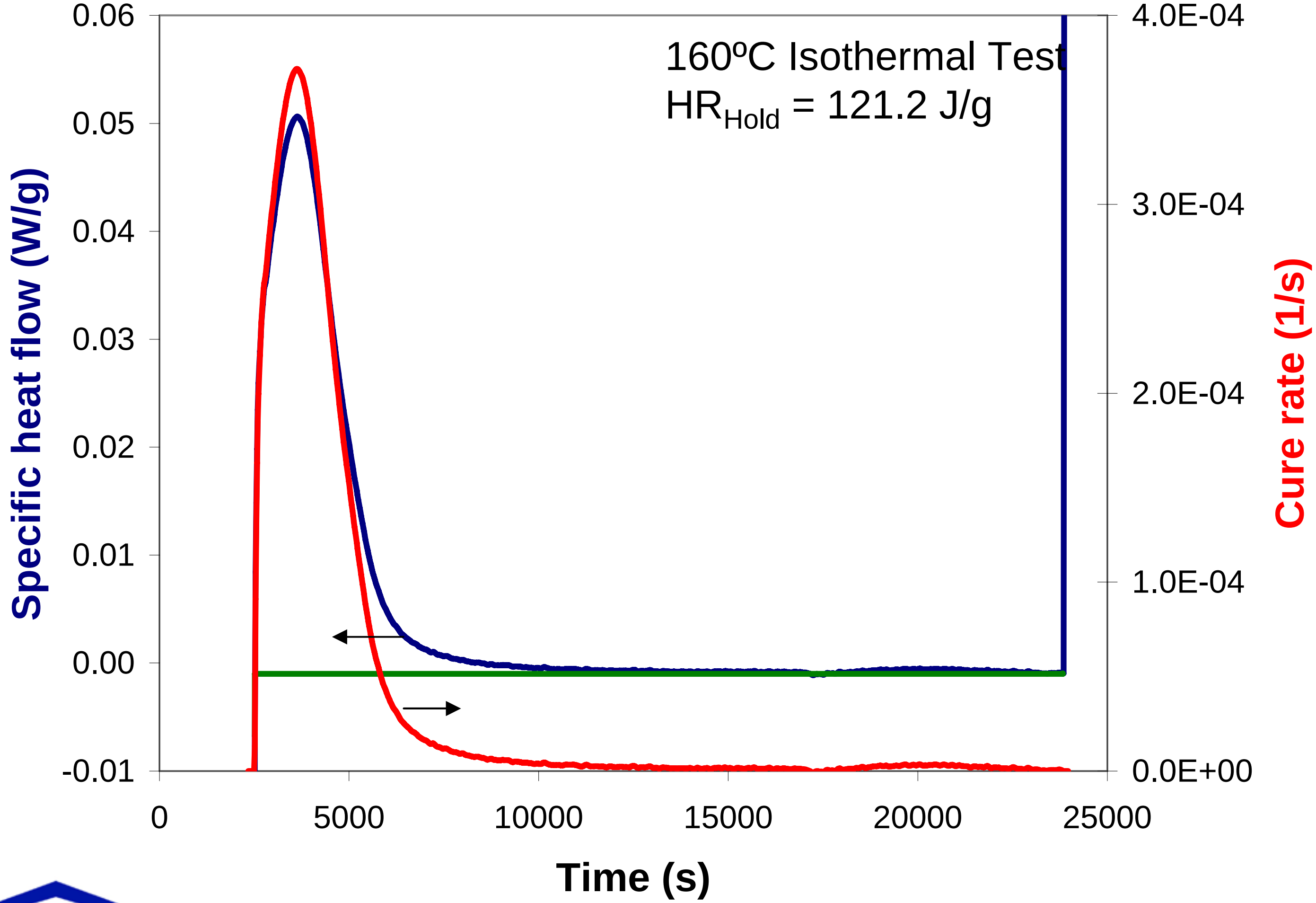
Heat Flow Response – 155ºC



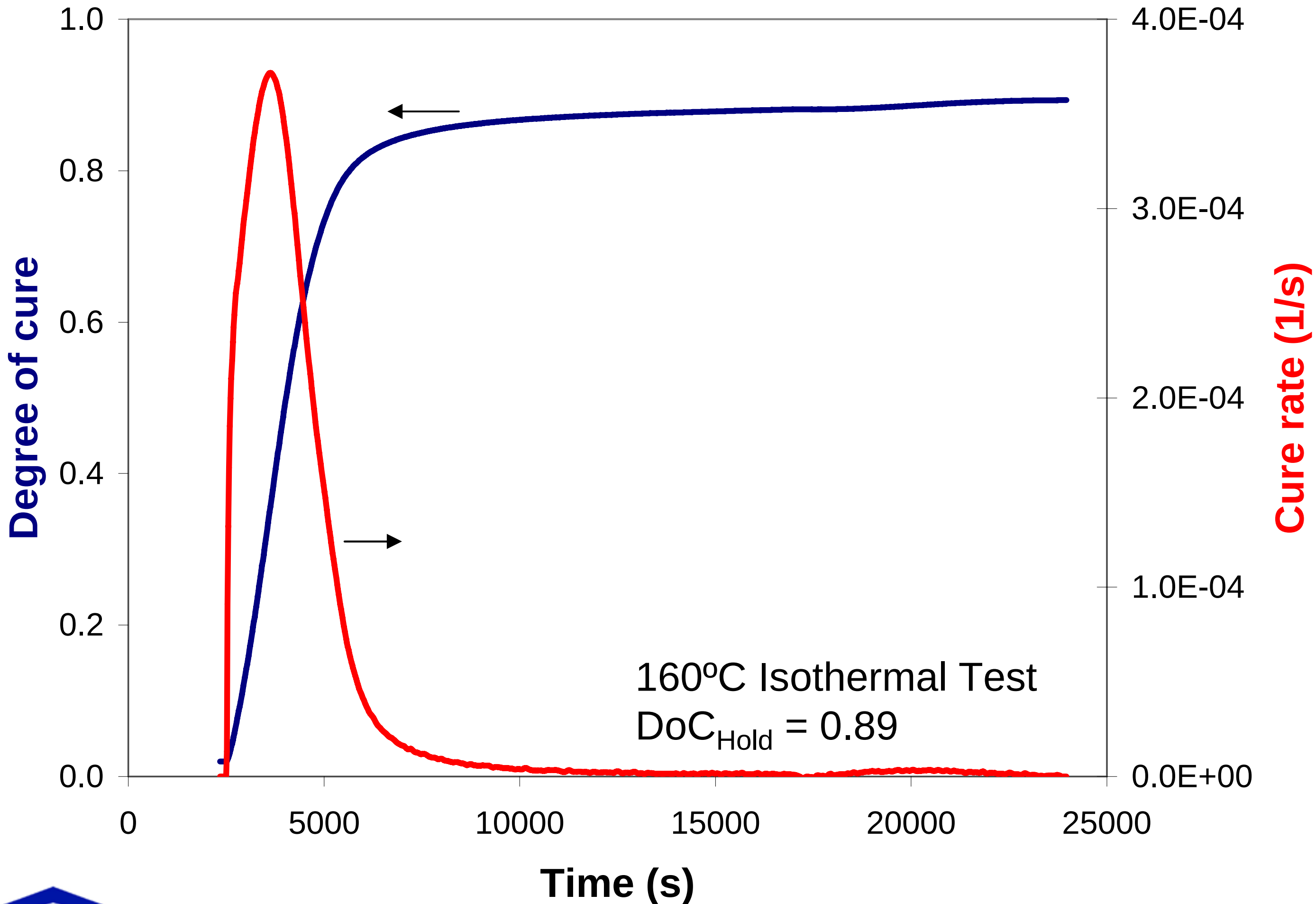
DoC and Cure Rate – 155ºC



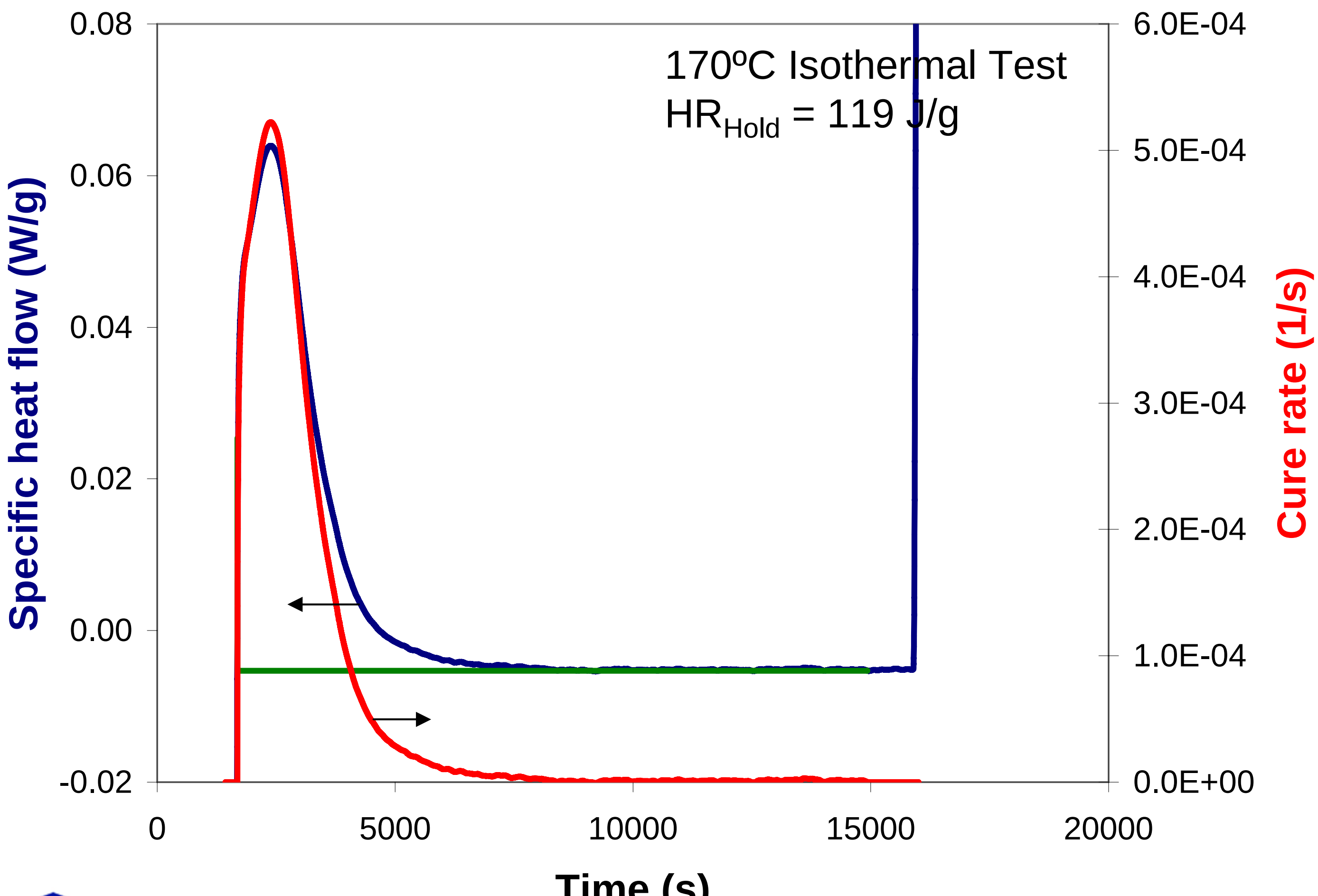
Heat Flow Response – 160ºC



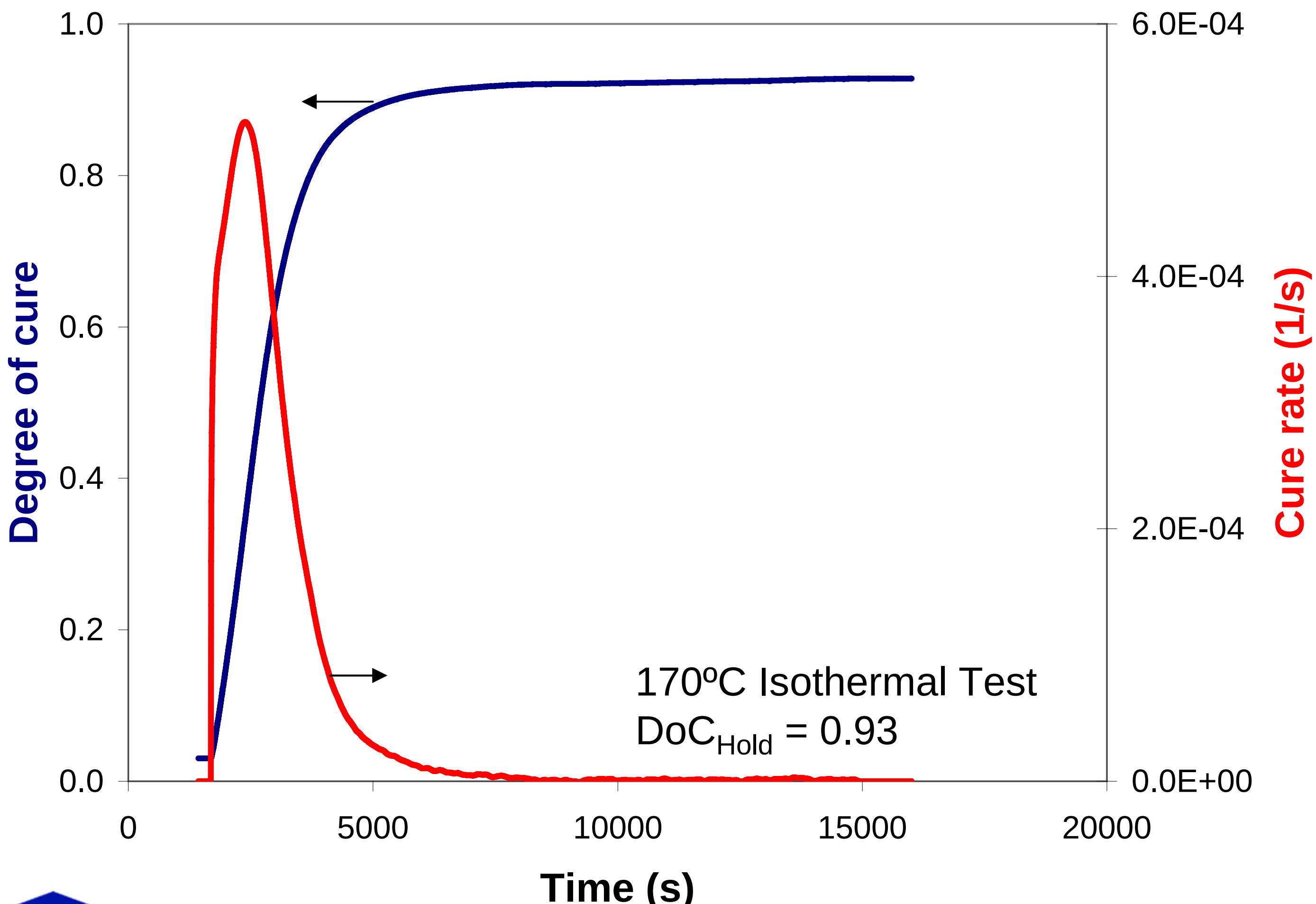
DoC and Cure Rate – 160ºC



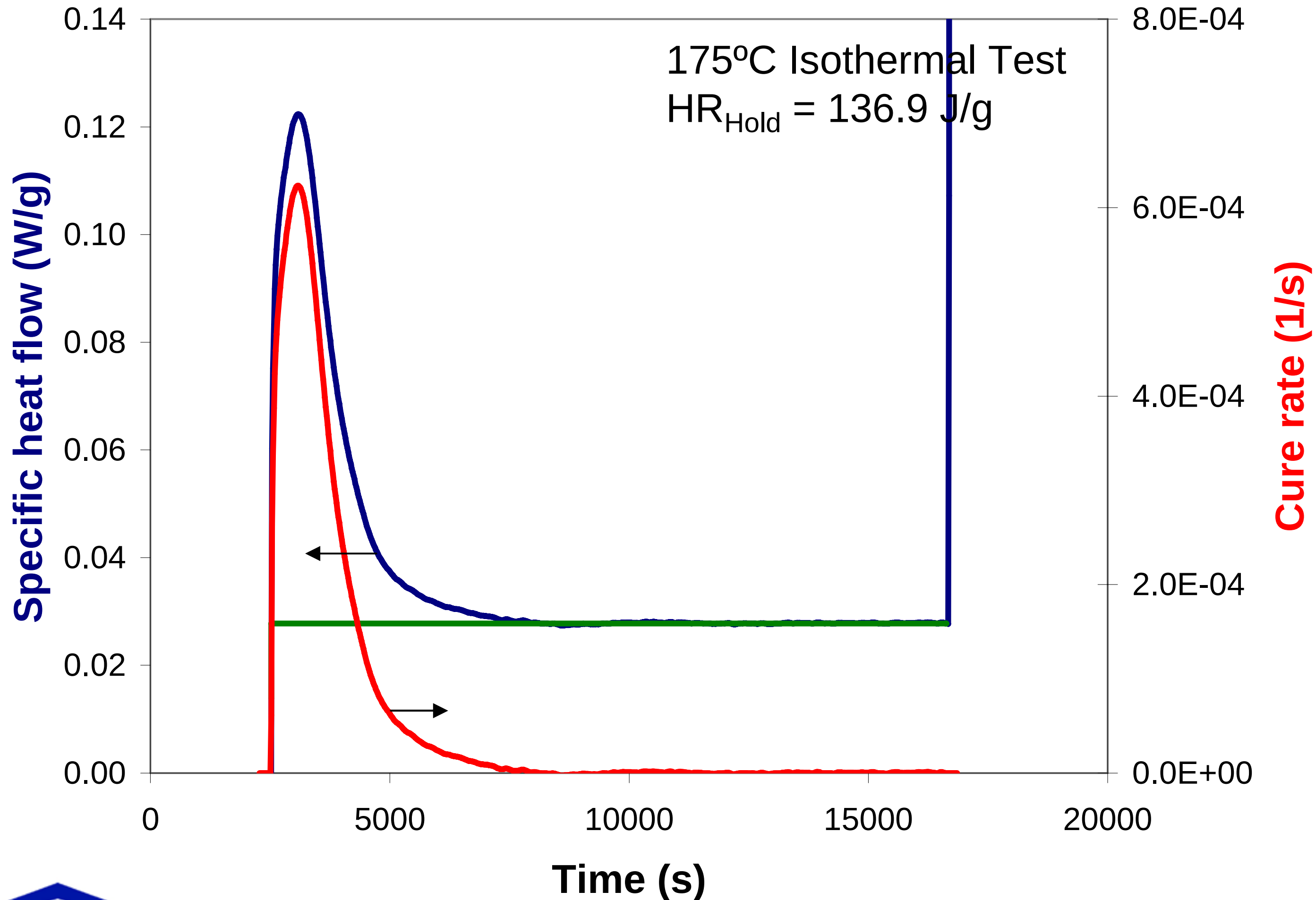
Heat Flow Response – 170ºC



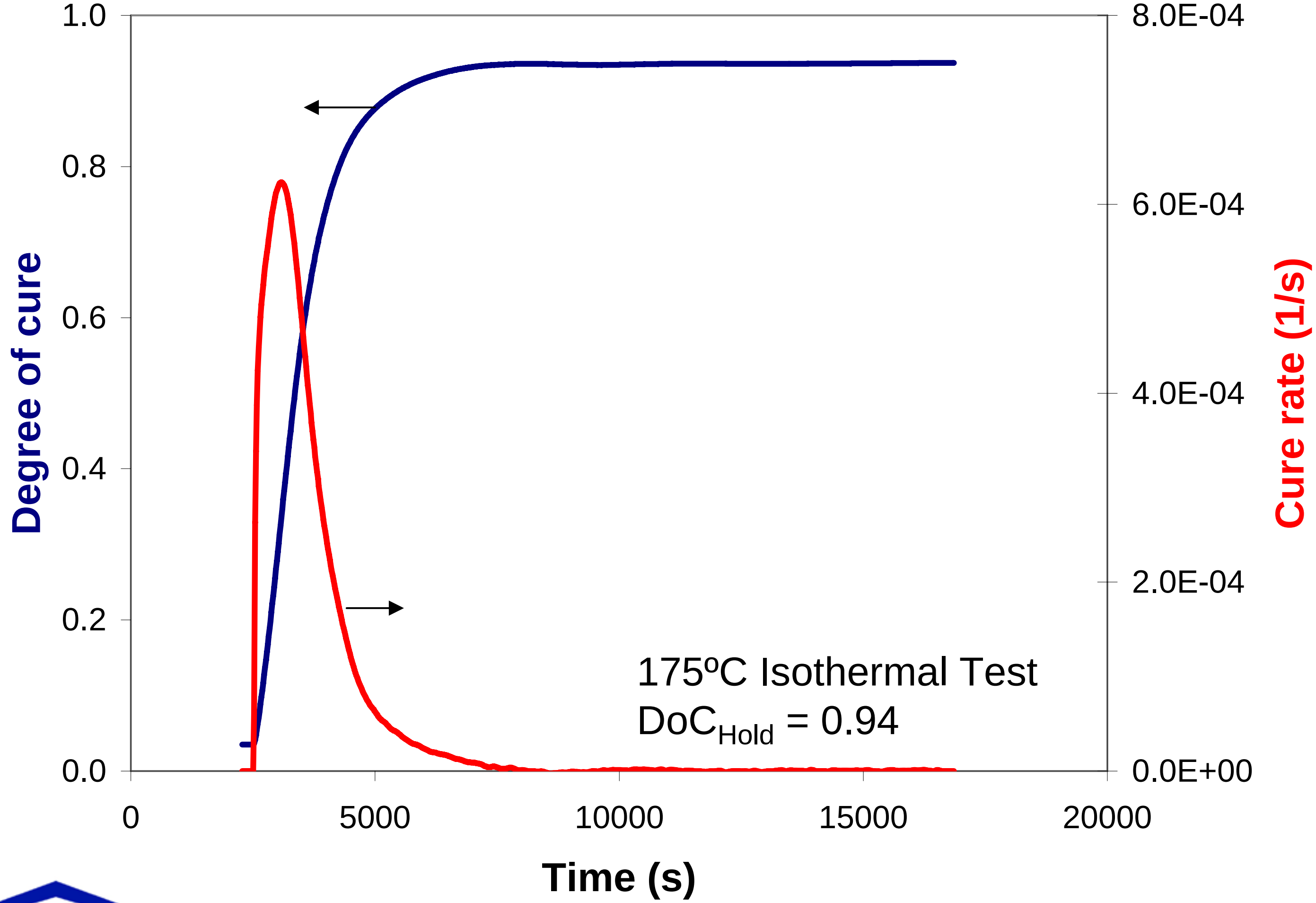
DoC and Cure Rate – 170ºC



Heat Flow Response – 175ºC



DoC and Cure Rate – 175ºC



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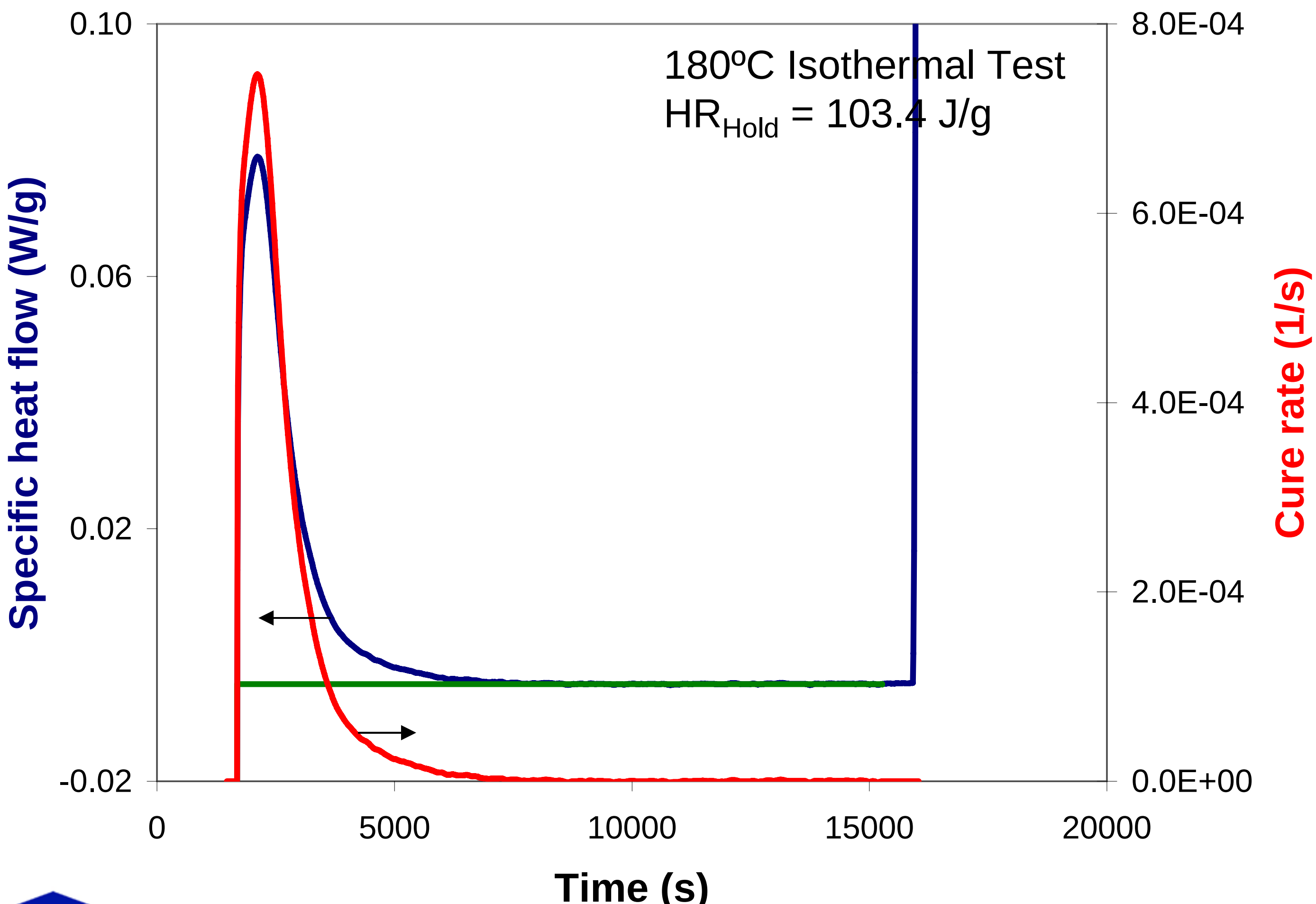
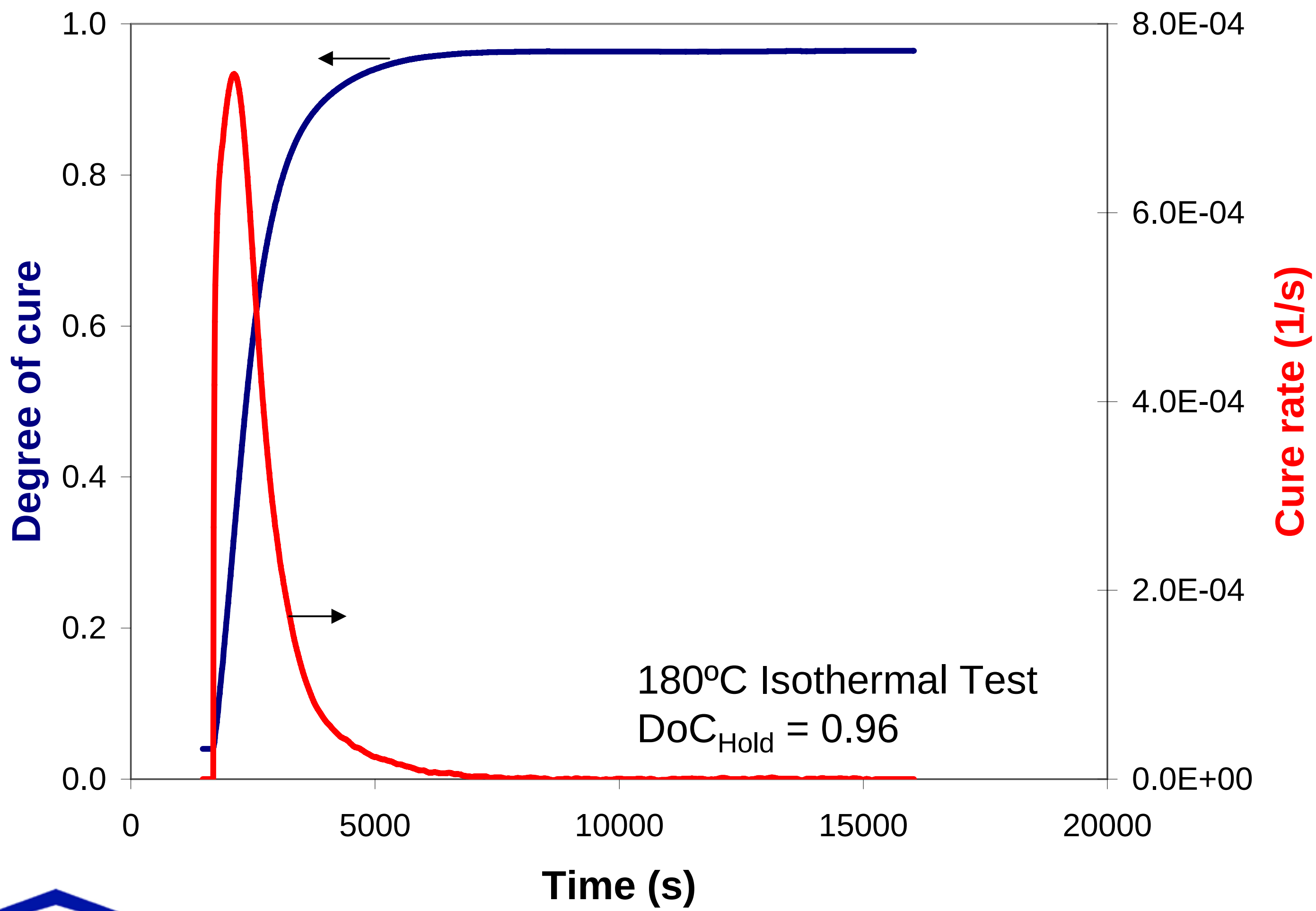
CONVERGENT MANUFACTURING TECHNOLOGIES

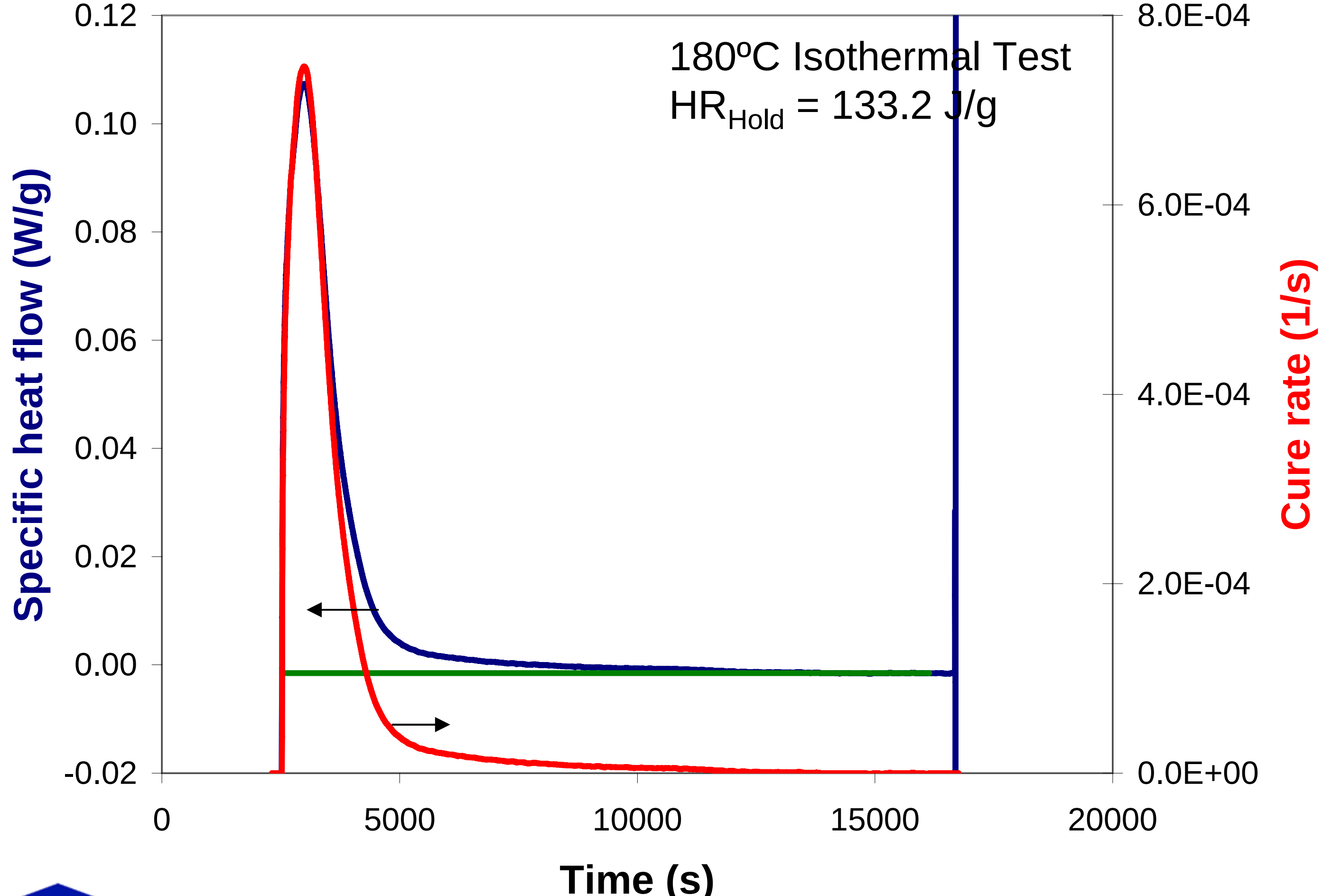
Heat Flow Response – 180-1ºC



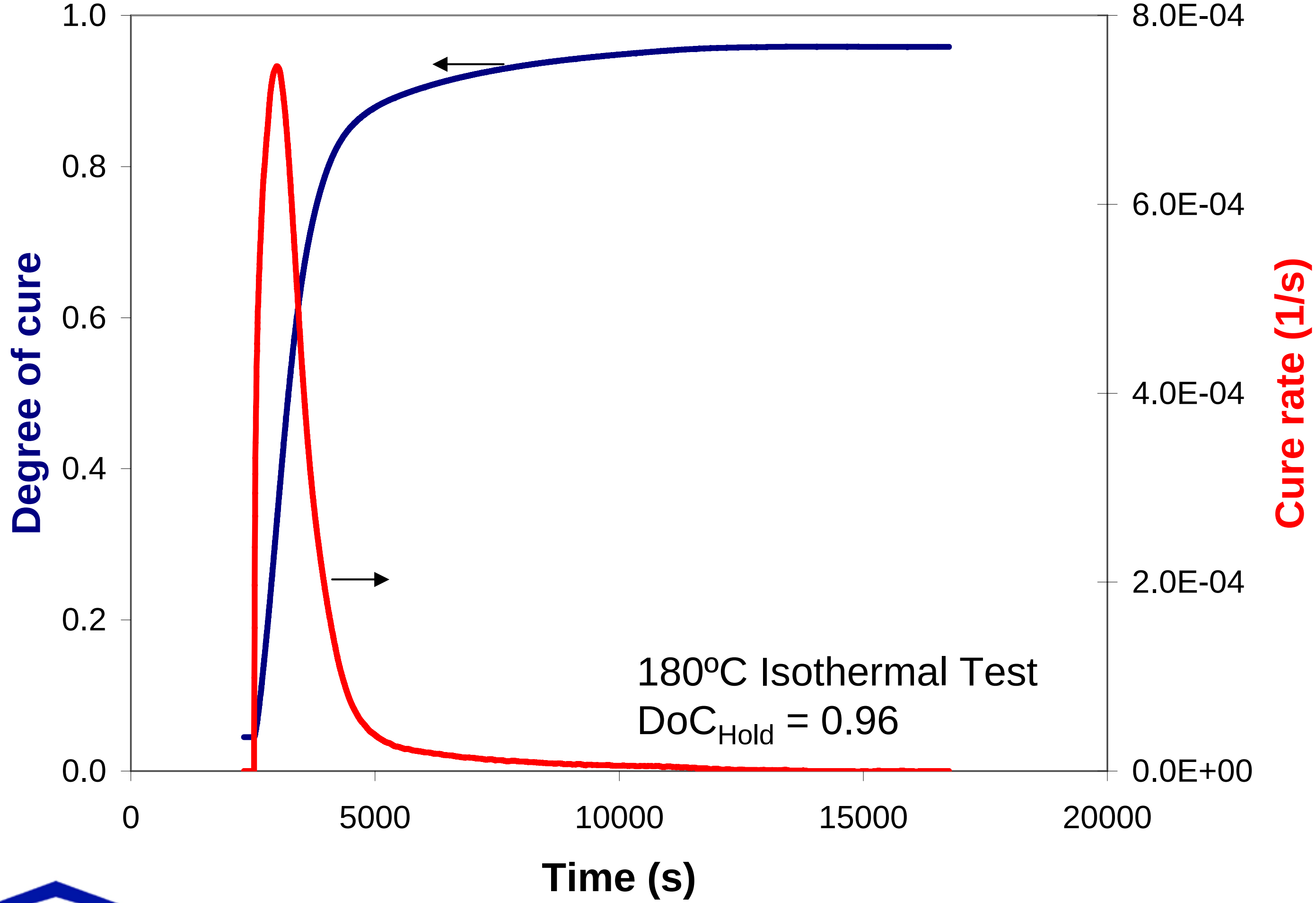
DoC and Cure Rate – 180-1ºC



Heat Flow Response – 180ºC-4



DoC and Cure Rate – 180ºC-4



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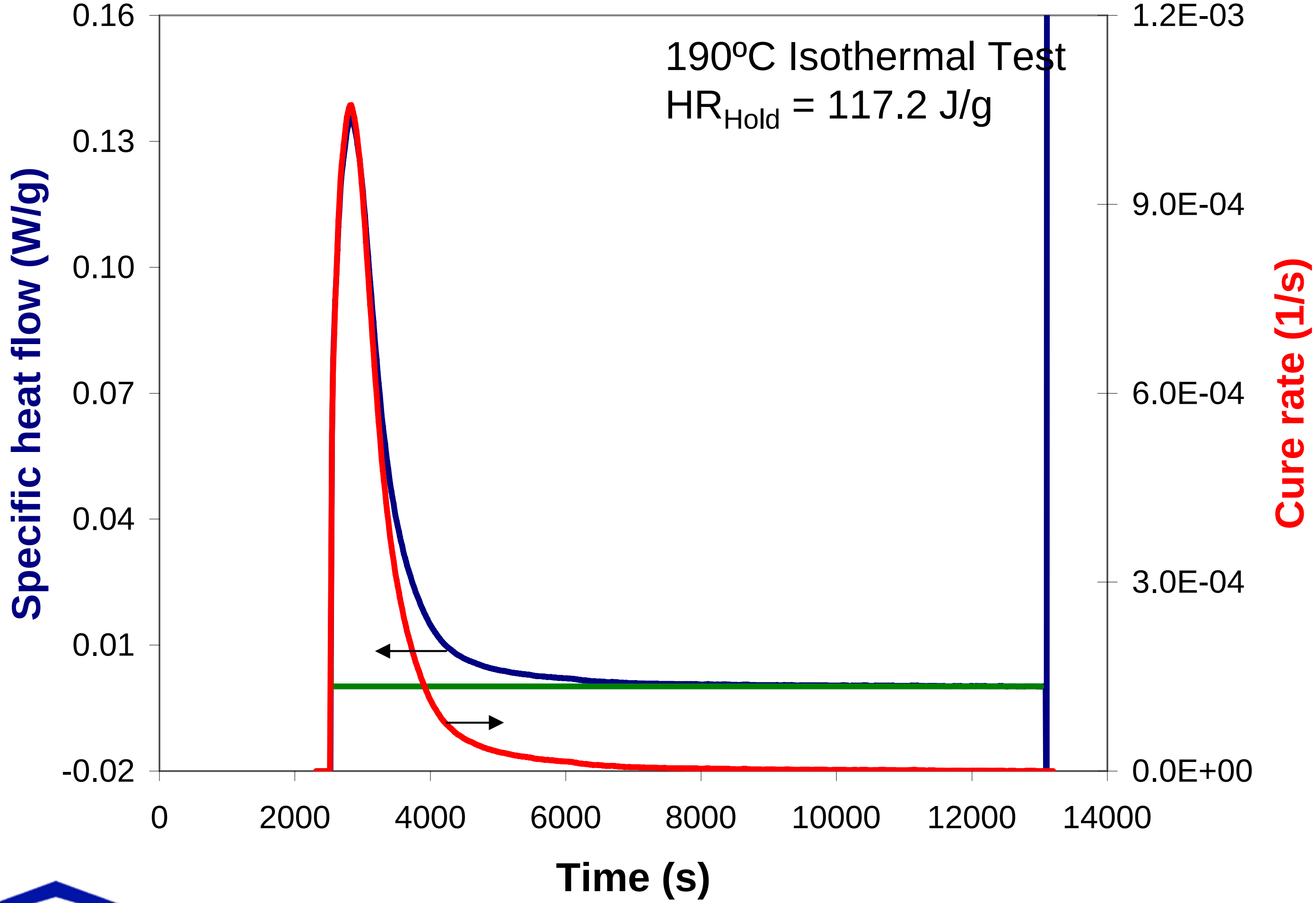
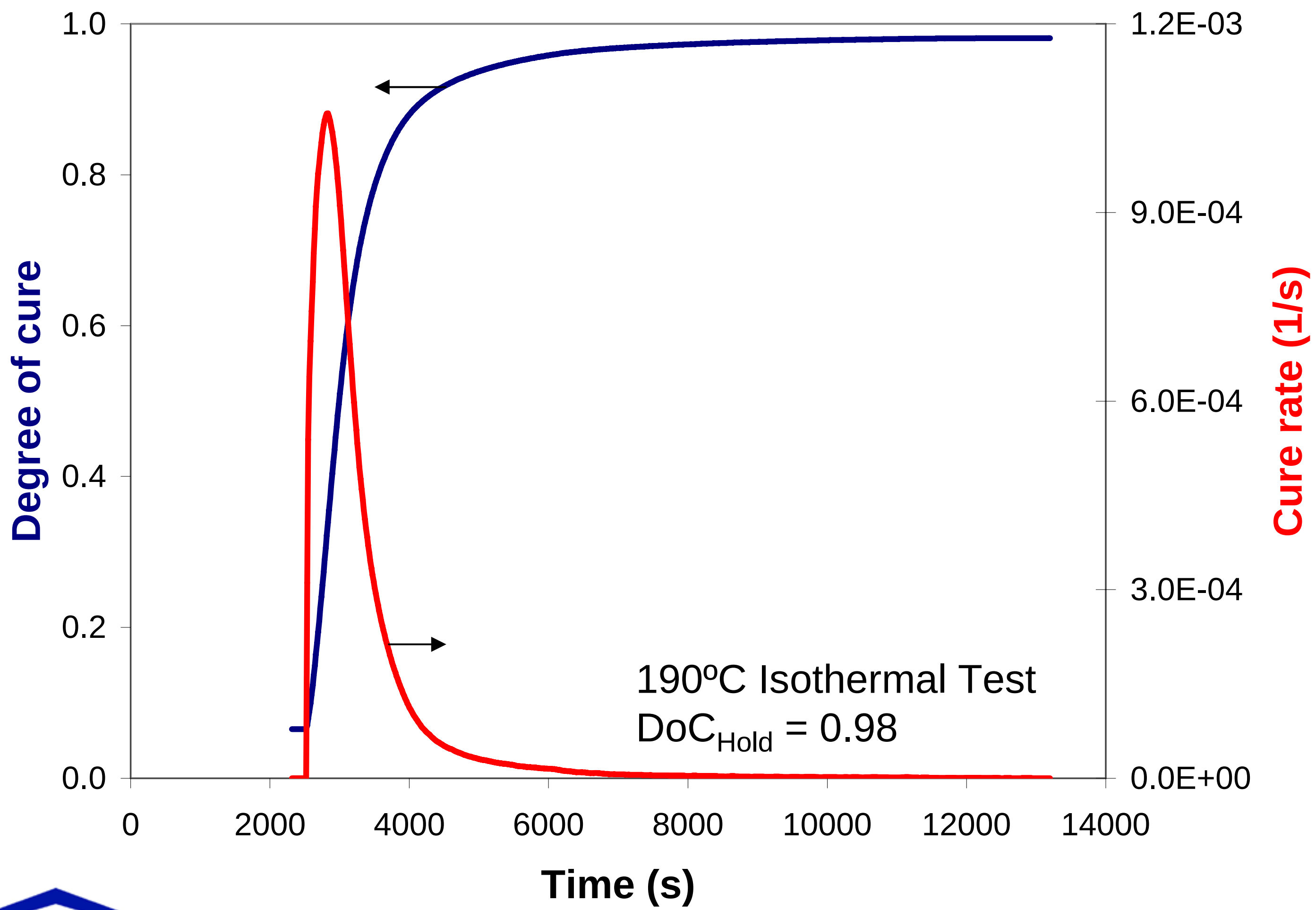
CONVERGENT MANUFACTURING TECHNOLOGIES

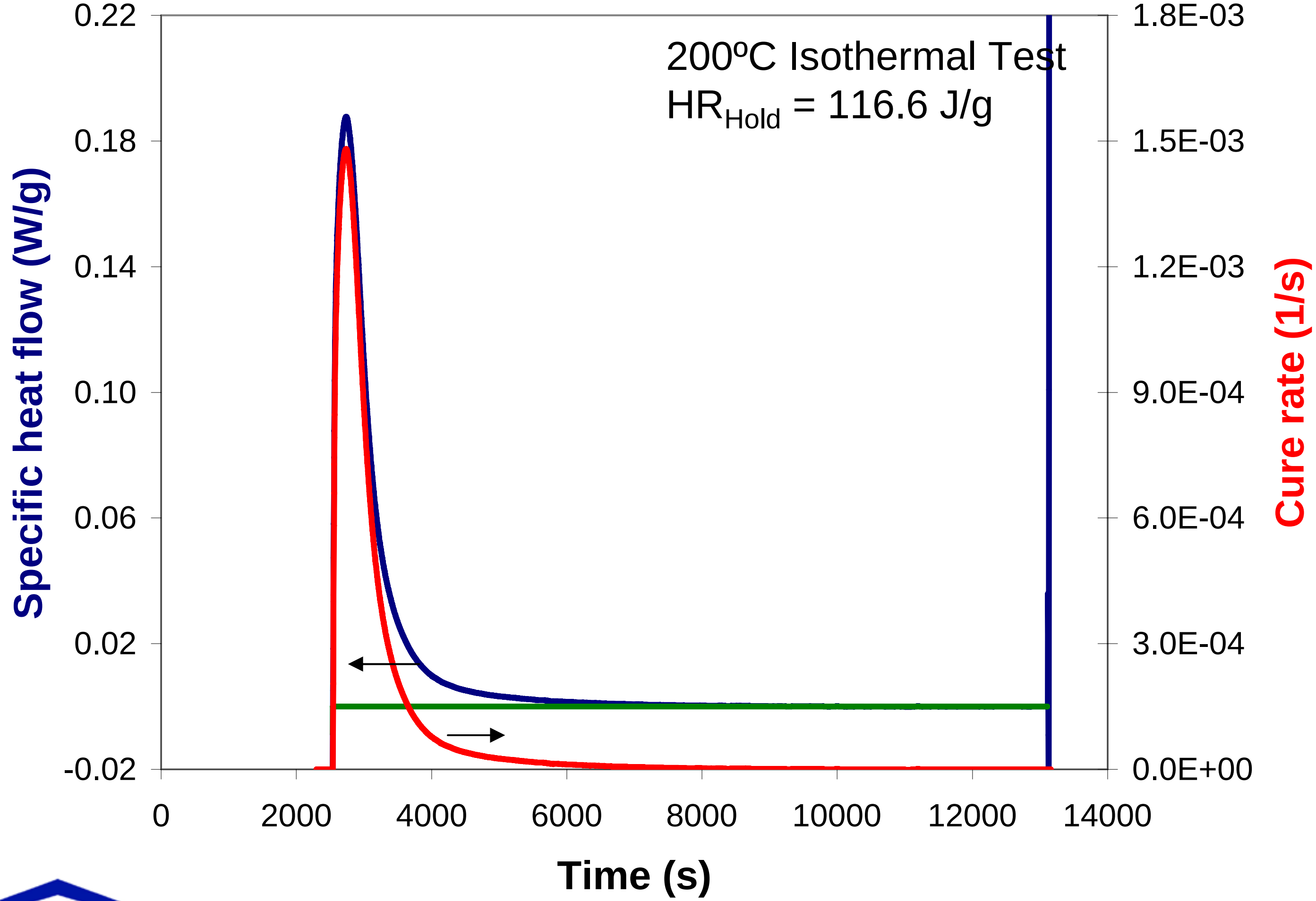
Heat Flow Response – 190ºC



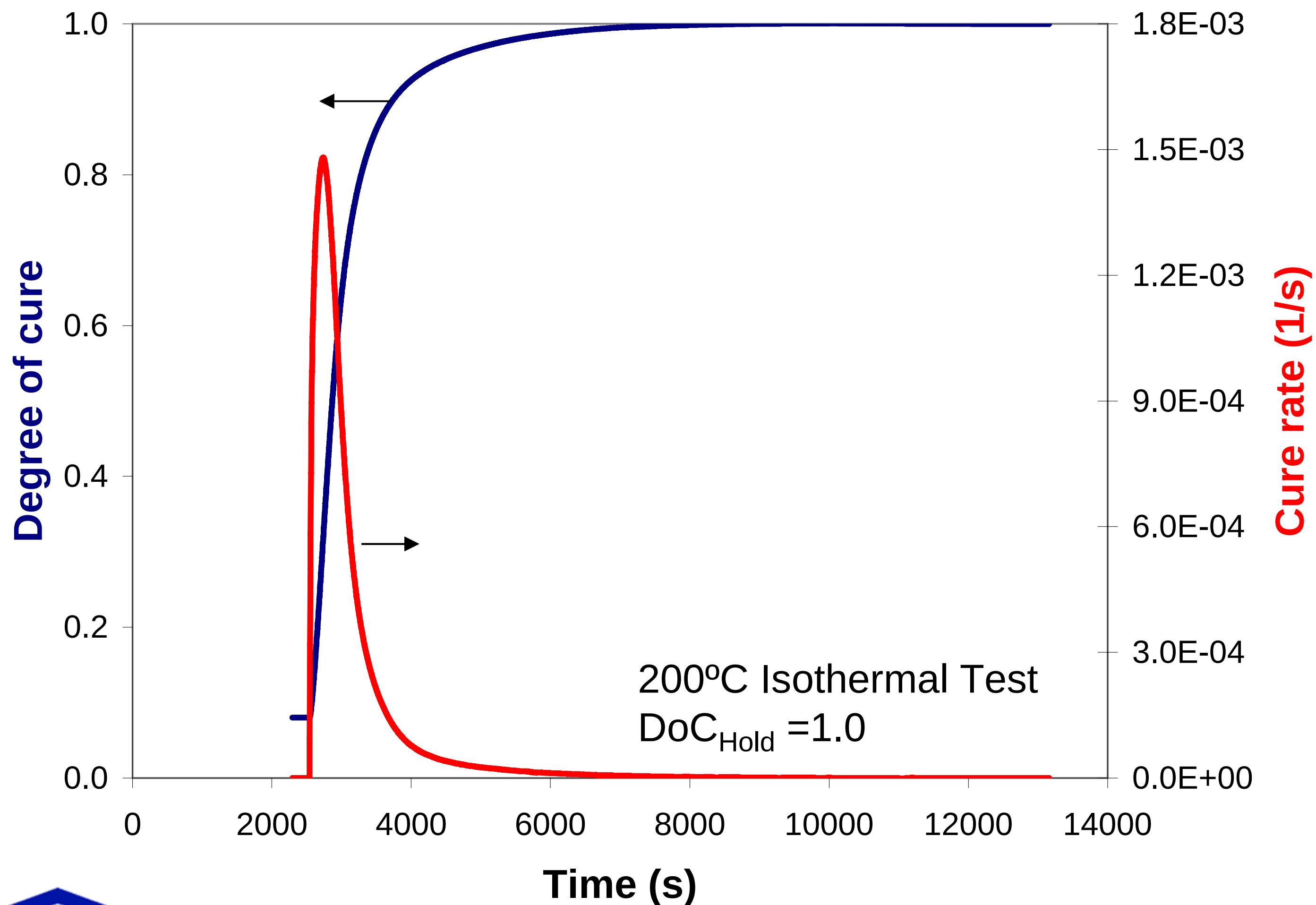
DoC and Cure Rate – 190ºC



Heat Flow Response – 200ºC



DoC and Cure Rate – 200ºC

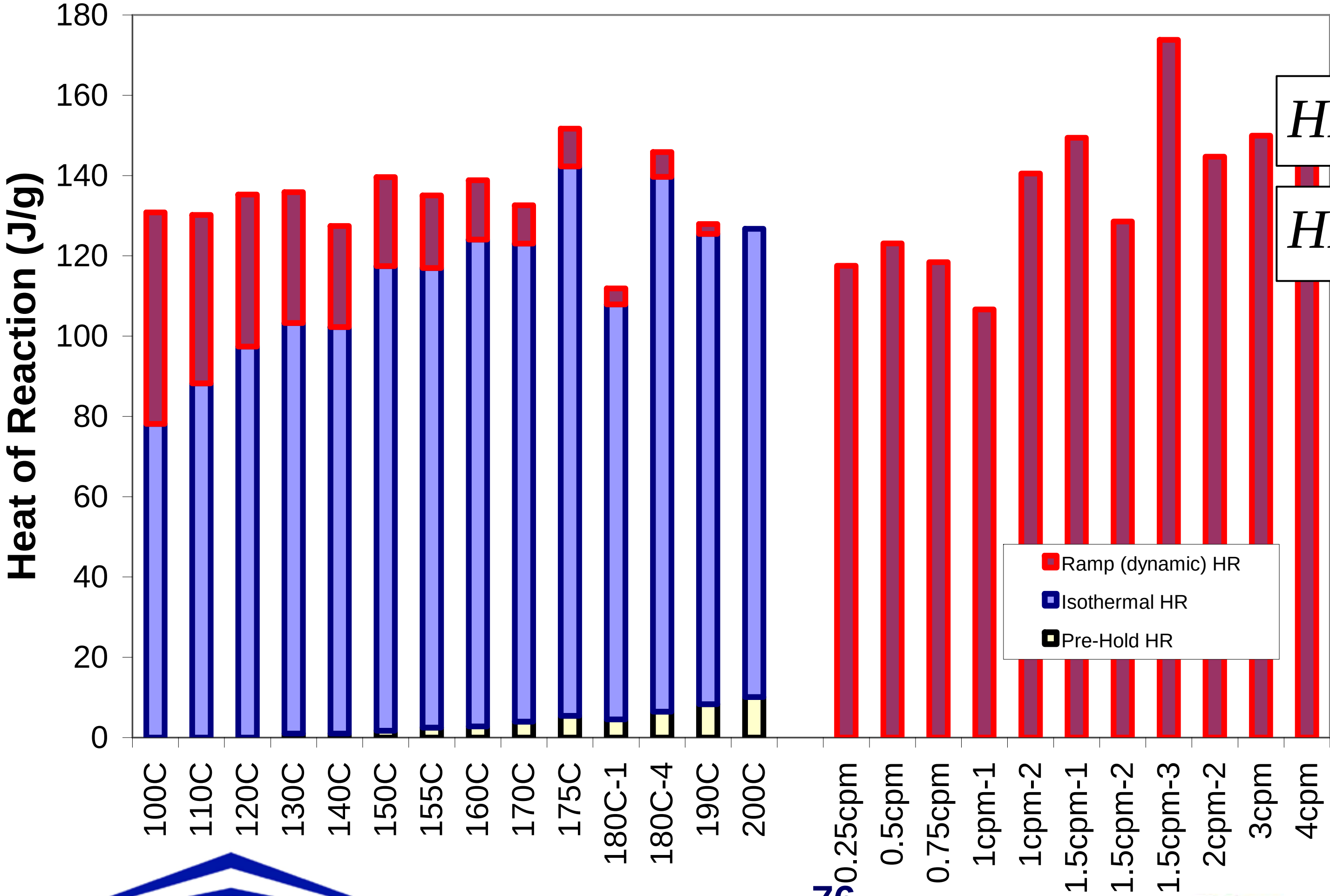


Heat of Reaction Tables

Test	Heat of Reaction (J/g)		
	Pre-Test	Ramp	Total
MTM45-025cpm-02	0	117.5	117.5
MTM45-05cpm-02	0	123.1	123.1
MTM45-075-02	0	118.4	118.4
MTM45-1cpm-01	0	106.7	106.7
MTM45-1cpm-02	0	140.5	140.5
MTM45-1_5cpm-01	0	149.4	149.4
MTM45-1_5cpm-02	0	128.6	128.6
MTM45-1_5cpm-03	0	173.8	173.8
MTM45-2cpm-02	0	144.7	144.7
MTM45-3cpm-02	0	150.0	150.0
MTM45-4cpm-02	0	148.0	148.0

Test	Heat of Reaction (J/g)			
	Iso-Ramp	Hold	Ramp	Total
MTM45-100-02	0.0	78.2	52.6	130.8
MTM45-110-03	0.0	88.2	41.9	130.2
MTM45-120-02	0.0	97.4	37.9	135.3
MTM45-130-02	1.0	102.3	32.6	135.9
MTM45-140-01	1.0	101.3	25.1	127.4
MTM45-150-03	1.7	115.8	22.1	139.6
MTM45-155-03	2.5	114.5	18.0	135.0
MTM45-160-03	2.8	121.2	14.8	138.9
MTM45-170-01	4.0	119.1	9.5	132.6
MTM45-175-02	5.4	136.9	9.4	151.7
MTM45-180-01	4.5	103.4	4.0	111.9
MTM45-180-04	6.5	133.2	6.2	145.9
MTM45-190-03	8.3	117.2	2.4	127.9
MTM45-200-02	10.1	116.6	0.0	126.7

Total Heat of Reaction



$$HR_{Iso}^{avg} = 133.6 \text{ J/g}$$

$$HR_{Dyn}^{avg} = 136.4 \text{ J/g}$$

Heat of Reaction - Model

For uni prepreg:

$$HR_{Iso}^{avg} = 133.6 \text{ J/g}$$

$$HR_{Dyn}^{avg} = 136.4 \text{ J/g}$$

→

$$HR_{Total}^{Avg} = 140 \text{ J/g}$$

(for prepreg)

Heat of reaction of neat resin:

Resin content (uni prepreg): 32% (wt)

$$HR_{Model} = 140/0.32 = 437.5 \text{ J/g}$$

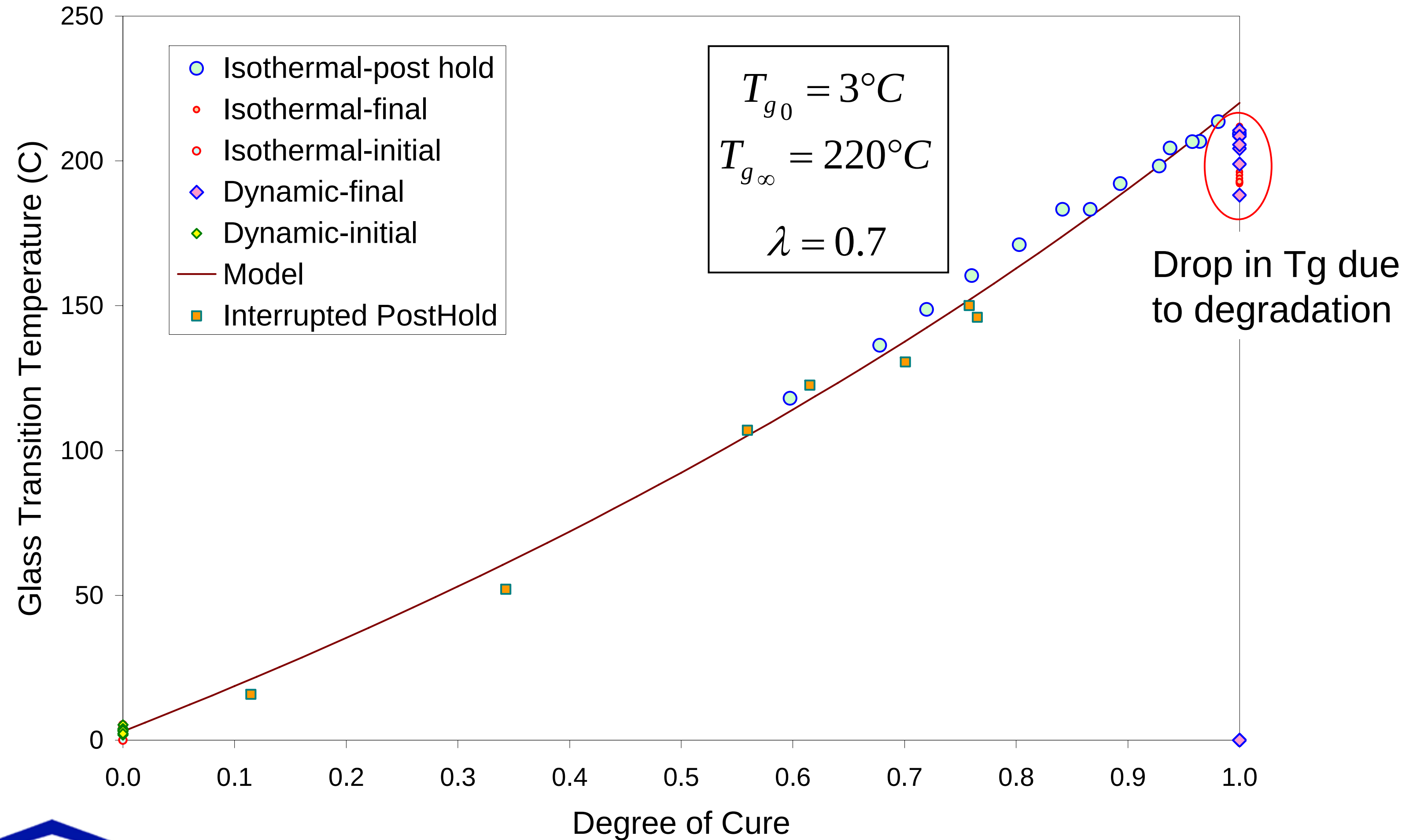
Tg Tables

Test	Initial		Final	
	DoC	Tg (ºC)	DoC	Tg (ºC)
MTM45-025cpm-02	0	3.3	1	-
MTM45-05cpm-02	0	5.3	1	198.9
MTM45-075-02	0	3.7	1	188.2
MTM45-1cpm-01	0	3.1	1	204.3
MTM45-1cpm-02	0	3.2	1	-
MTM45-1_5cpm-01	0	3.8	1	210.5
MTM45-1_5cpm-02	0	4.0	1	208.5
MTM45-1_5cpm-03	0	1.8	1	-
MTM45-2cpm-02	0	2.3	1	205.7
MTM45-3cpm-02	0	3.3	1	-
MTM45-4cpm-02	0	2.2	1	-

Test	Post-Hold Tg (ºC)	
	Test	Model
MTM45-160C-INT10-01	15.8	23.7
MTM45-160C-INT20-01	52.1	61.1
MTM45-160C-INT30-01	107.0	102.5
MTM45-160C-INT35-01	122.6	120.3
MTM45-160C-INT40-01	130.6	134.8
MTM45-160C-INT45-01	146.0	146.2
MTM45-160C-INT50-01	150.1	155.0

Test	Initial		Post-Hold	
	DoC	Tg (ºC)	DoC	Tg (ºC)
MTM45-100-02	0	3.0	0.60	118.0
MTM45-110-03	0	2.6	0.68	136.4
MTM45-120-02	0	2.9	0.72	148.7
MTM45-130-02	0	3.5	0.76	160.4
MTM45-140-01	0	4.9	0.80	171.1
MTM45-150-03	0	3.4	0.84	183.3
MTM45-155-03	0	3.4	0.87	183.3
MTM45-160-03	0	2.9	0.89	192.2
MTM45-170-01	0	-	0.93	198.2
MTM45-175-02	0	3.7	0.94	204.5
MTM45-180-01	0	-	0.96	206.7
MTM45-180-04	0	4.2	0.96	206.6
MTM45-190-03	0	4.5	0.98	213.6
MTM45-200-02	0	5.3	1.00	209.3

Glass Transition Temperature



Cure Kinetics Model

Cure kinetics model (CK13): $$\frac{dx}{dt} = \dot{x}_1 + \dot{x}_2 = \sum_{i=1}^{2} k_{eff\,i} (1-x)^{l_i} \left(\frac{1}{r_i} - x \right)^{m_i} \left(x^{n_{2i}} + b_i \right)^{n_i}$$

where $$\frac{1}{k_{eff}} = \frac{1}{k_k} + \frac{1}{k_d}$$

Kinetics model $$k_k = k_{k0} e^{-\left(\frac{E_a}{RT}\right)}$$

Diffusion model $$k_d = k_{d_0} e^{-\left(\frac{B}{f}\right)}$$

where $$f = a\left(T - T_g\right) + b$$

[1]If f<small then f=small (=1E-30 see CMT_vars2.f90)

Cure Kinetics Model

and $$a = \begin{cases} a_1 & T_g < T_{g\,a1} \\ S_a T_g + C_a & T_{g\,a1} < T_g < T_{g\,a2} \\ a_2 & T_{g\,a2} < T_g \end{cases}$$ with $$\begin{cases} S_a = \dfrac{a_2 - a_1}{T_{g\,a2} - T_{g\,a1}} \\ C_a = a_1 - S_a T_{g\,a1} \end{cases}$$

and $$b = \begin{cases} b_1 & T_g < T_{g\,b1} \\ S_b T_g + C_b & T_{g\,b1} < T_g < T_{g\,b2} \\ b_2 & T_{g\,b2} < T_g \end{cases}$$ with $$\begin{cases} S_b = \dfrac{b_2 - b_1}{T_{g\,b2} - T_{g\,b1}} \\ C_b = b_1 - S_b T_{g\,b1} \end{cases}$$

and the DeBenedetto equation: $$T_g = T_{g\,0} + \frac{\lambda x}{1 - (1 - \lambda) x} \left(T_{g\,\infty} - T_{g\,0} \right)$$

Cure Kinetics Model

$$\dot{x}_1 = k_{eff\,1}\left(\frac{1}{1.105} - x\right)^{1.892} x^{1.8}$$

$$k_{k1} = 8506e^{-\left(\frac{52938}{RT}\right)}$$

$$k_{d1} = 2000e^{-\left(\frac{0.35}{f}\right)}$$

$$f = a\left(T - T_g\right) + b$$

$$a = 4.8 \times 10^{-4}$$

$$b = \begin{cases} 0.025 & T_g < 70°C \\ \text{Linear bw } 0.025 \text{ and } 0.030 & 70°C < T_g < 140°C \\ 0.030 & T_g > 140°C \end{cases}$$

[1] If f<small then f=small (=1E-30 see CMT_vars2.f90)

Cure Kinetics Model

$$\dot{x}_2 = k_{eff}(1-x)^{0.757}\left(\frac{1}{0.193}-x\right)^{5.627} x^{0.171}$$

$$k_{k2} = 4.115e^{-\left(\frac{65946}{RT}\right)}$$

$$k_{d2} = 7\times10^{-3} e^{-\left(\frac{0.34}{f}\right)}$$

$$f = a\left(T - T_g\right) + b$$

$$a = 4.8\times10^{-4}$$

$$b = \begin{cases} 0.025 & T_g < 100°C \\ \text{Linear bw } 0.025 \text{ and } 0.040 & 100°C < T_g < 220°C \\ 0.040 & T_g > 220°C \end{cases}$$

[1]If f<small then f=small (=1E-30 see CMT_vars2.f90)

Cure Kinetics Model

Total Heat of Reaction (Prepreg):

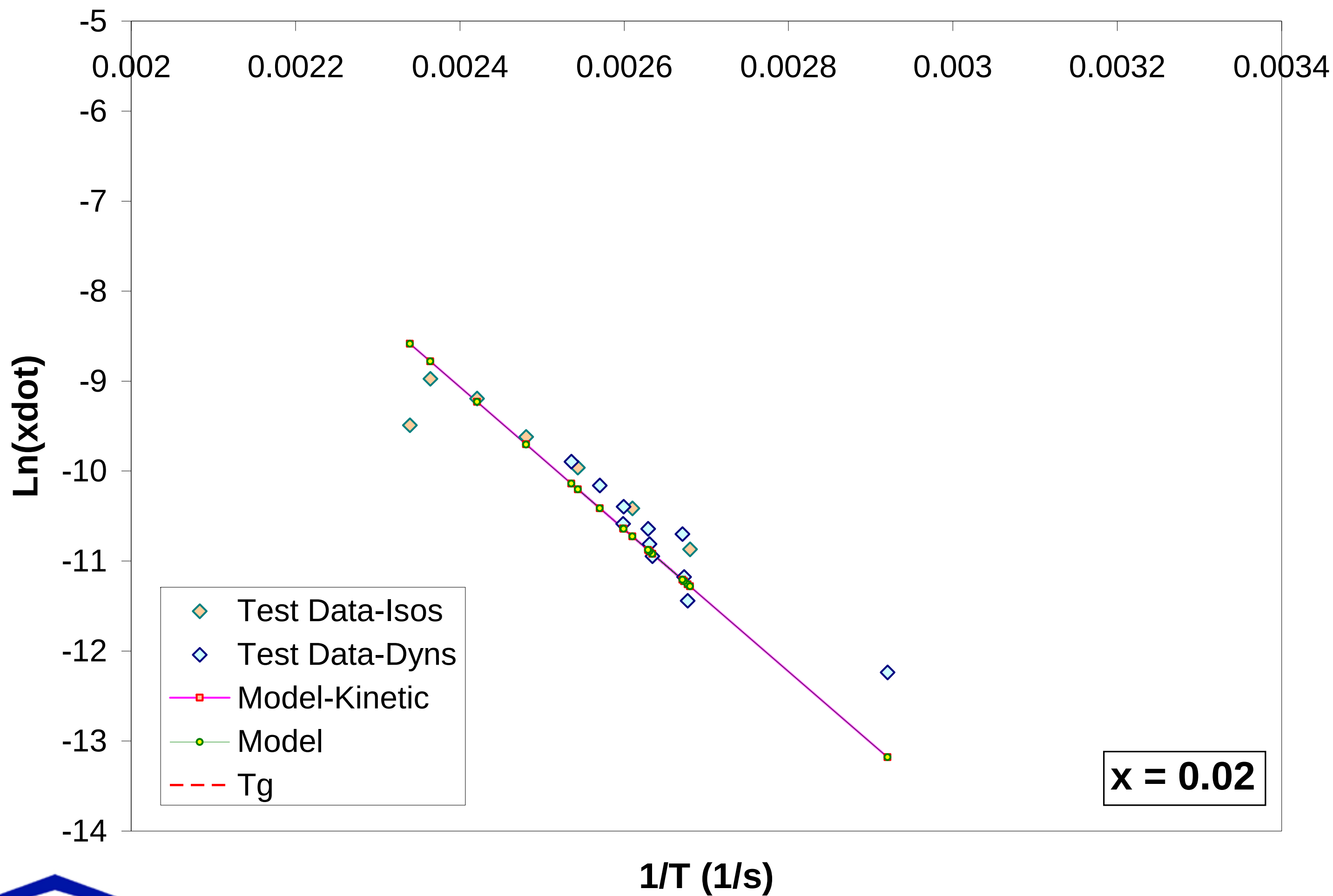
$$HR_{Total}^{Avg} = 140 \text{ J/g}$$

$$HR_{Model} = 437.5 \text{ J/g}$$

Glass Transition (Tg) Model (DeBenedetto):

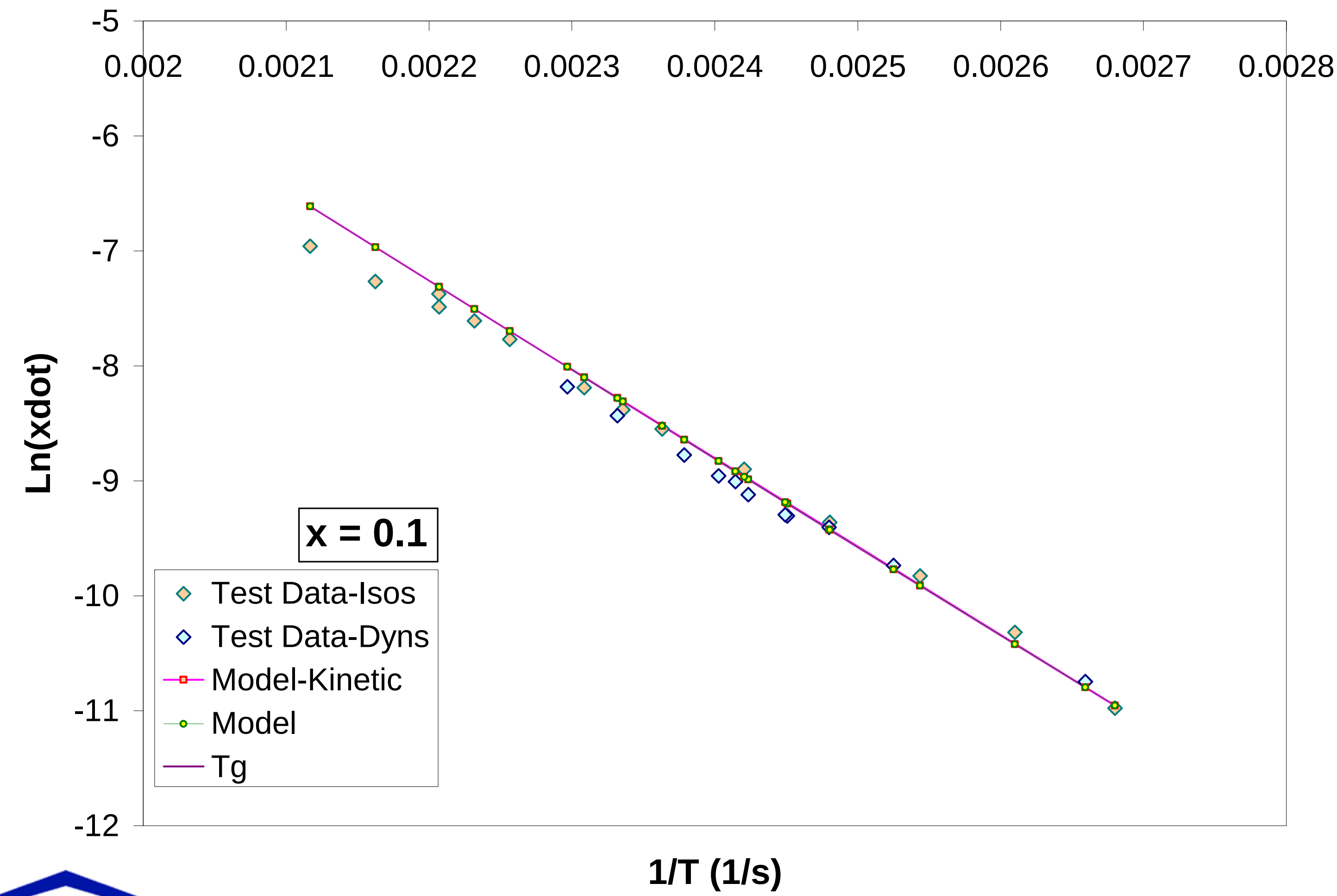
$$T_{g0} = 3°\text{C} \qquad T_{g\infty} = 220°\text{C} \qquad \lambda = 0.7$$

Ln(xdot)-1/T



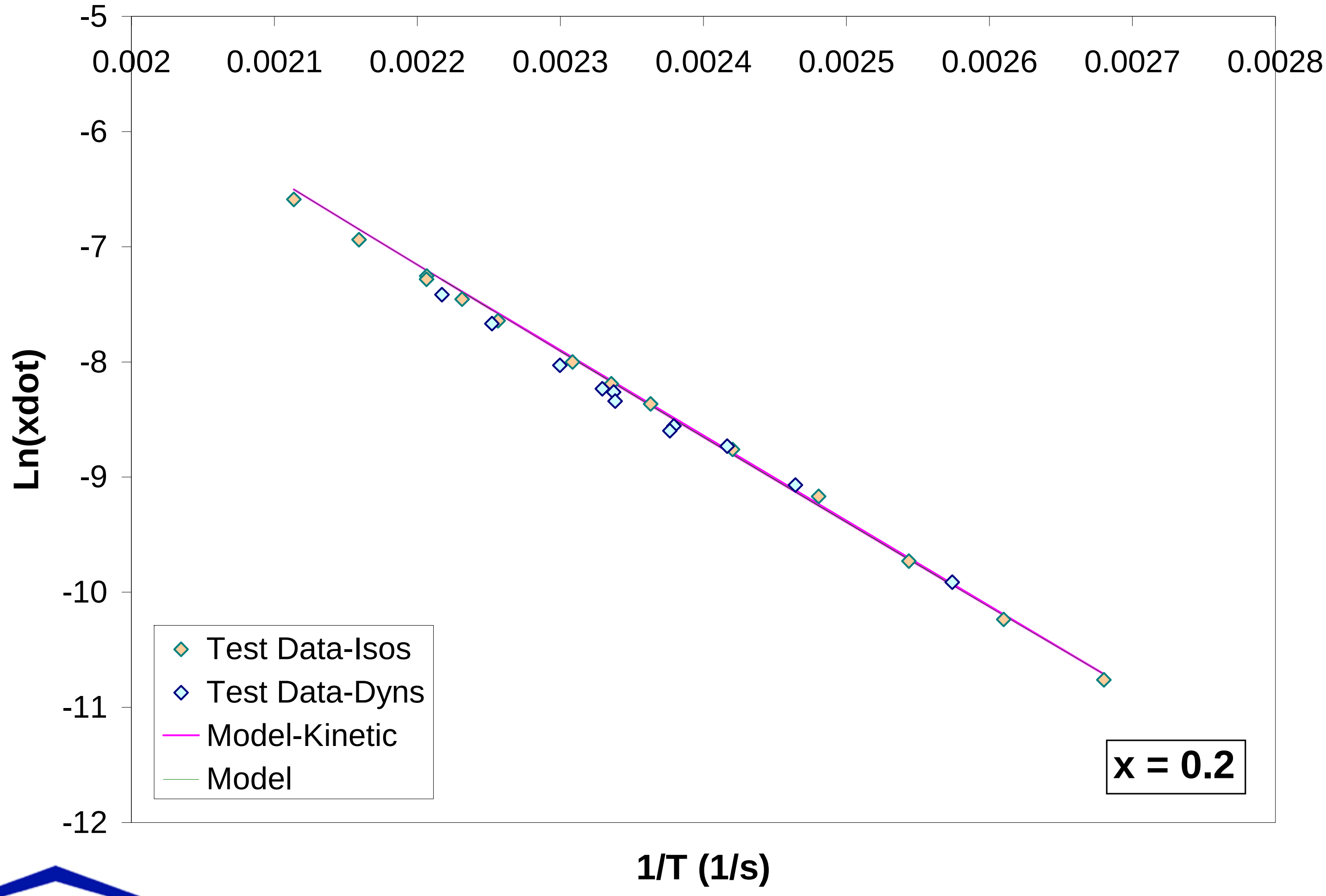
Ln(xdot)
1/T (1/s)
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0.002
0.0022
0.0024
0.0026
0.0028
0.003
0.0032
0.0034
Test Data-Isos
Test Data-Dyns
Model-Kinetic
Model
Tg
x = 0.02

Ln(xdot)-1/T



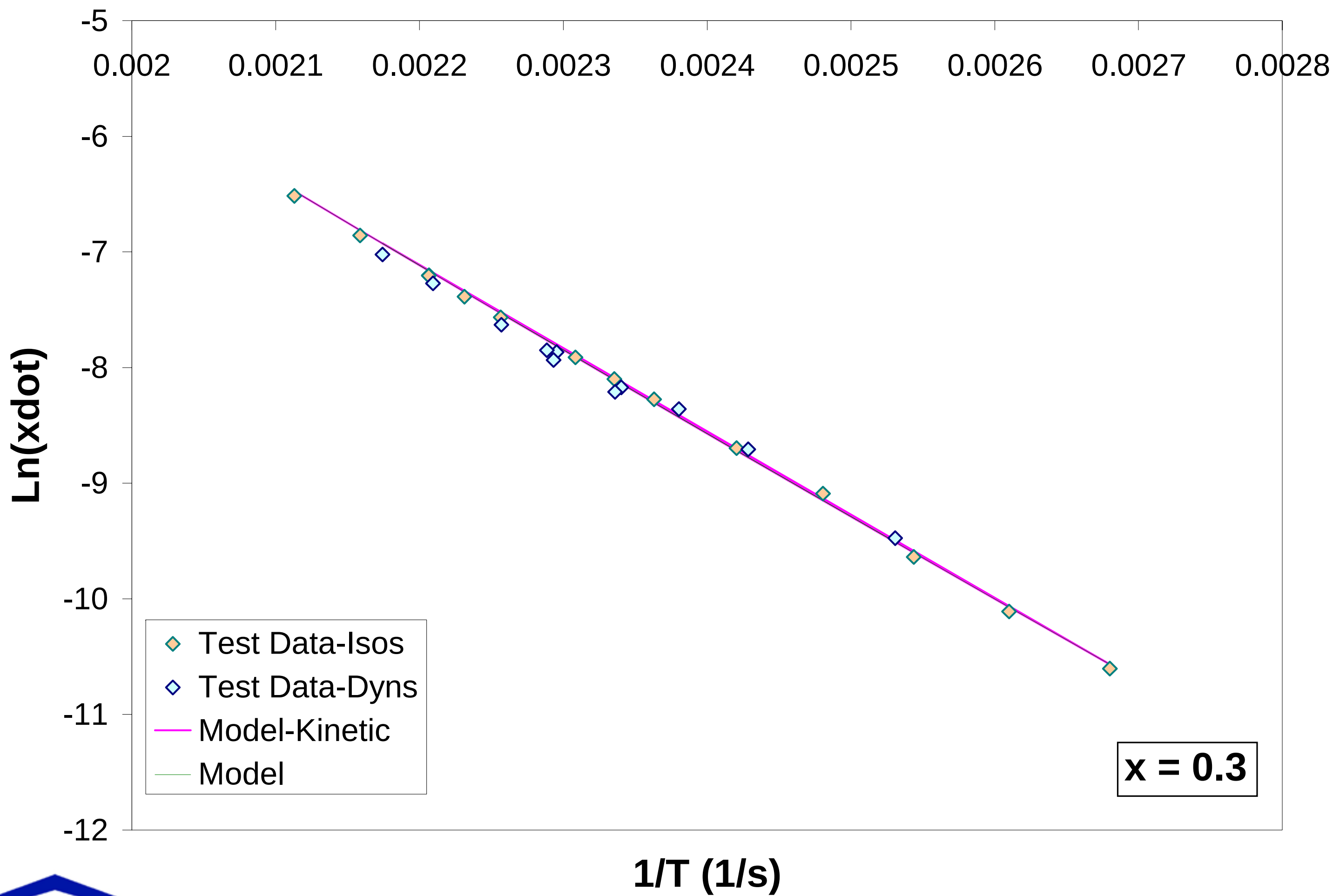
-5
-6
-7
-8
-9
-10
-11
-12
0.002
0.0021
0.0022
0.0023
0.0024
0.0025
0.0026
0.0027
0.0028
Ln(xdot)
x = 0.1
Test Data-Isos
Test Data-Dyns
Model-Kinetic
Model
Tg
1/T (1/s)

Ln(xdot)-1/T

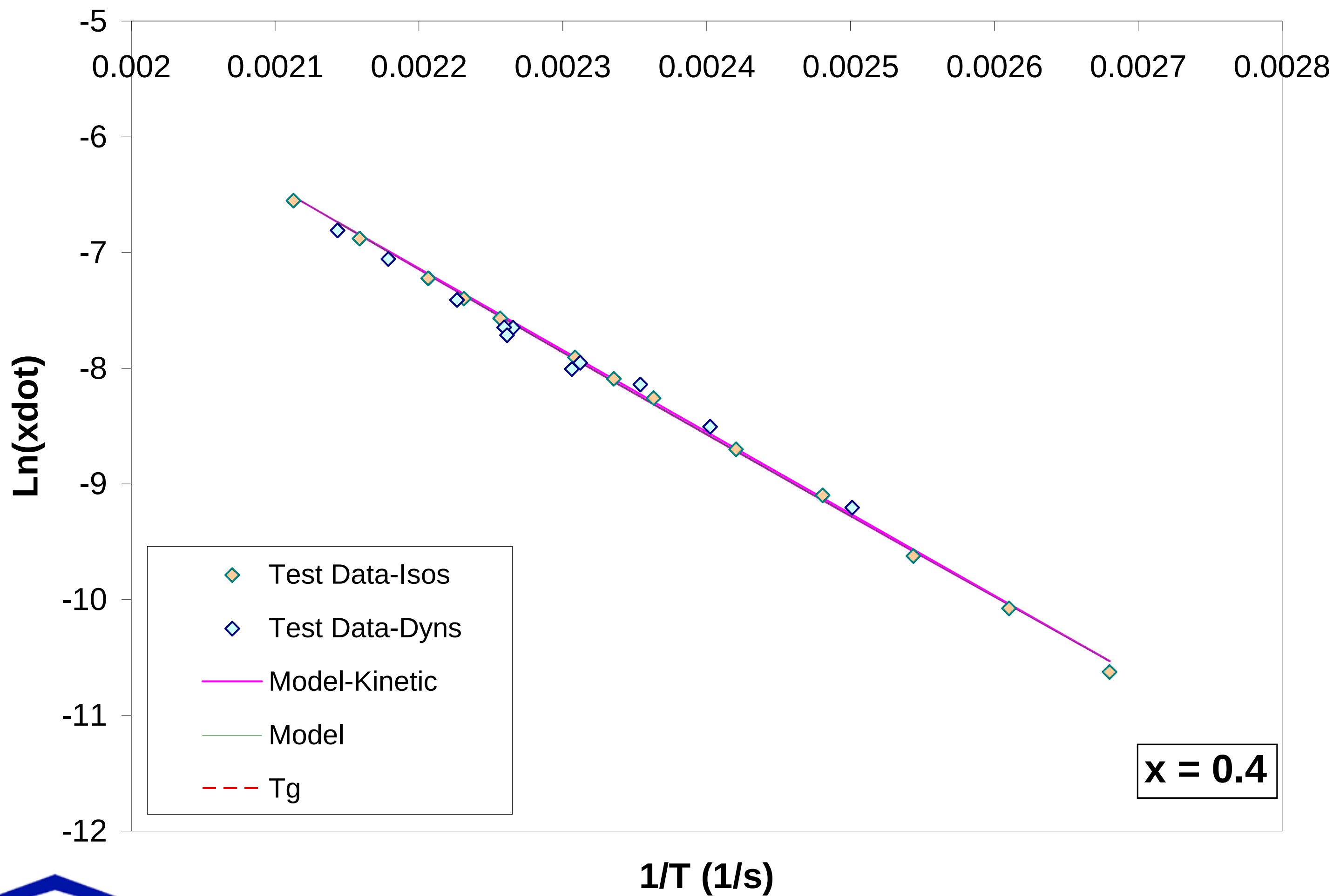


-5
-6
-7
-8
-9
-10
-11
-12
0.002
0.0021
0.0022
0.0023
0.0024
0.0025
0.0026
0.0027
0.0028
Ln(xdot)
1/T (1/s)
Test Data-Isos
Test Data-Dyns
Model-Kinetic
Model
x = 0.2

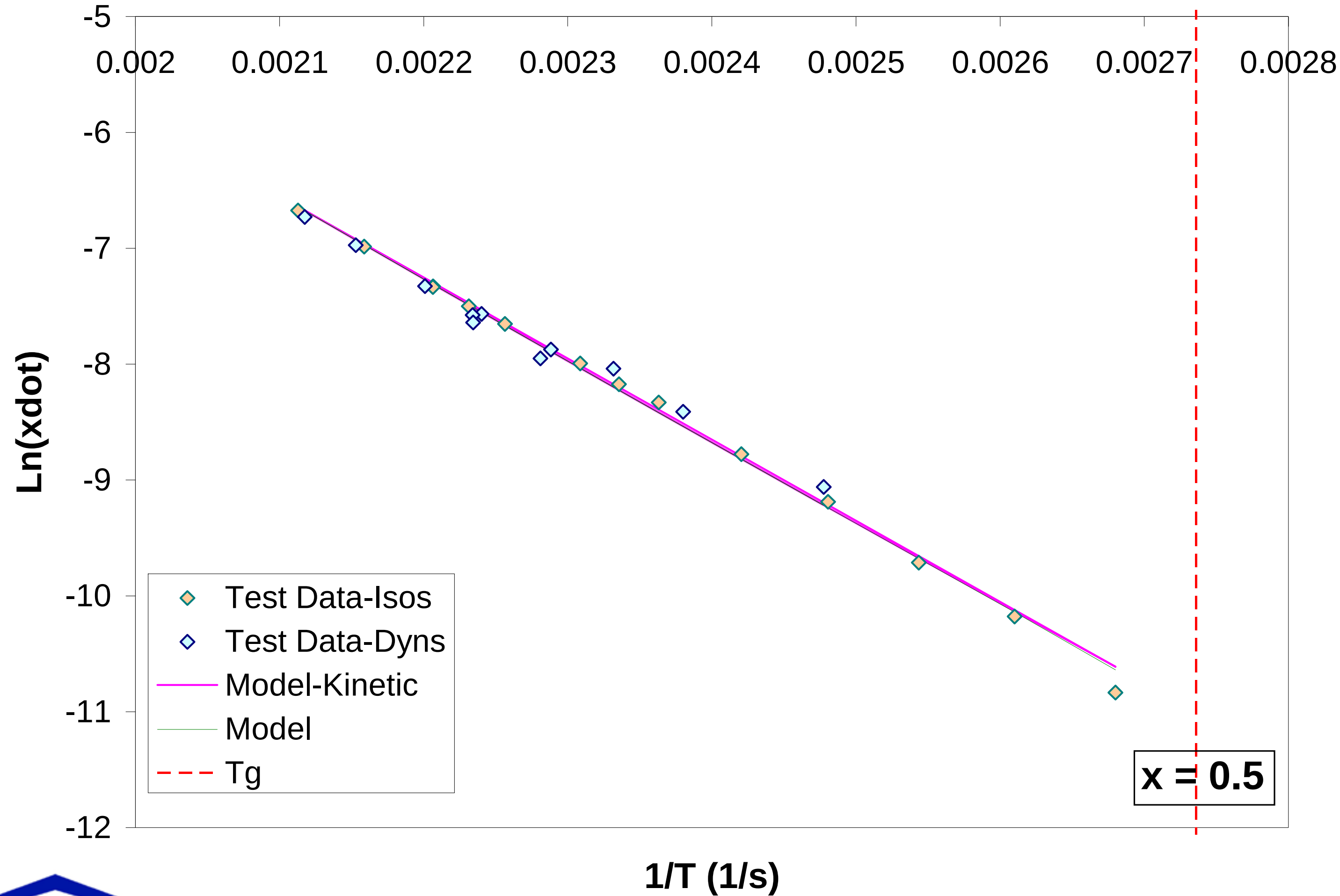
Ln(xdot)-1/T


-5
-6
-7
-8
-9
-10
-11
-12
0.002
0.0021
0.0022
0.0023
0.0024
0.0025
0.0026
0.0027
0.0028
Ln(xdot)
1/T (1/s)
Test Data-Isos
Test Data-Dyns
Model-Kinetic
Model
x = 0.3

Ln(xdot)-1/T

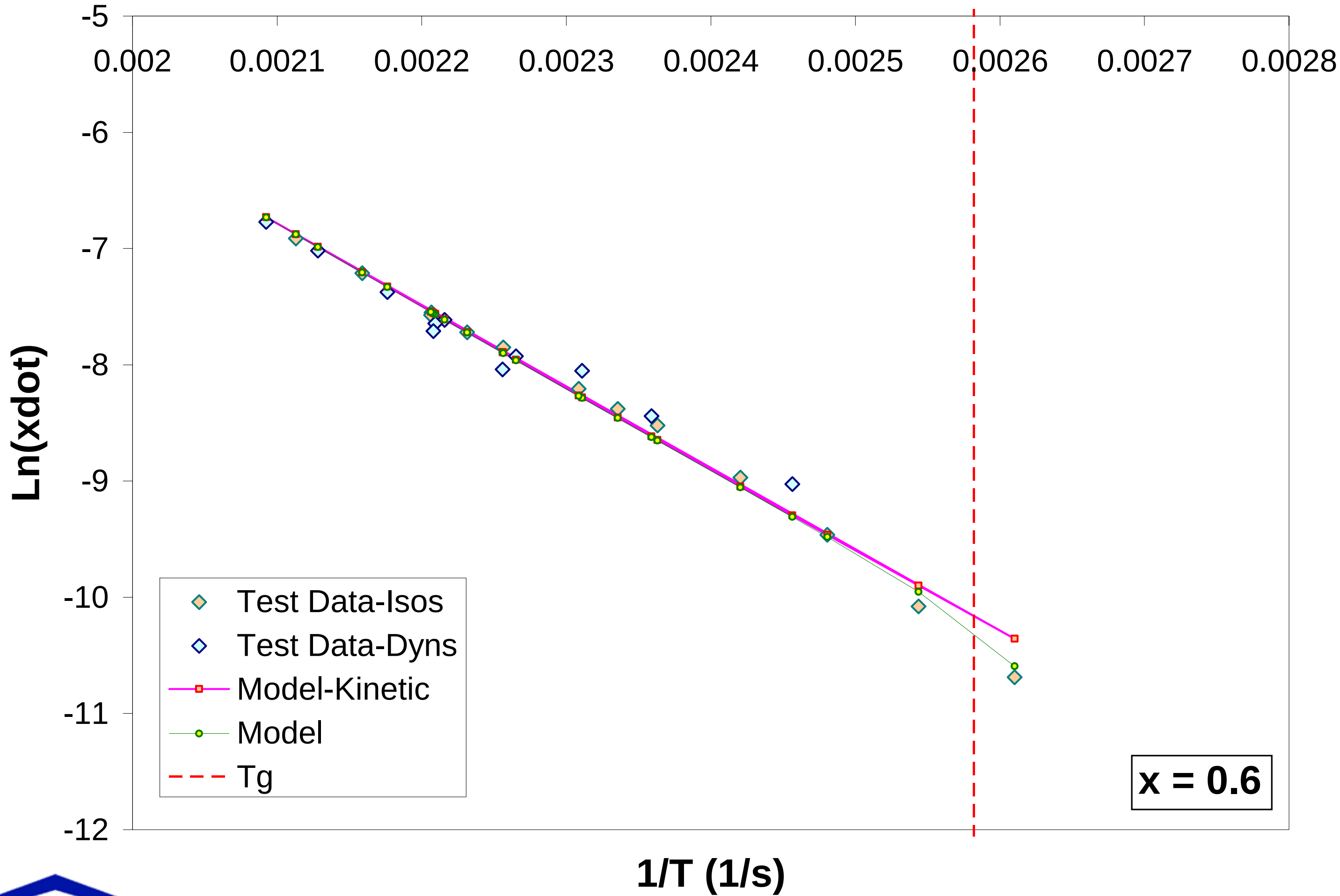

-5
-6
-7
-8
-9
-10
-11
-12
0.002
0.0021
0.0022
0.0023
0.0024
0.0025
0.0026
0.0027
0.0028
Ln(xdot)
Test Data-Isos
Test Data-Dyns
Model-Kinetic
Model
Tg
x = 0.4
1/T (1/s)

Ln(xdot)-1/T

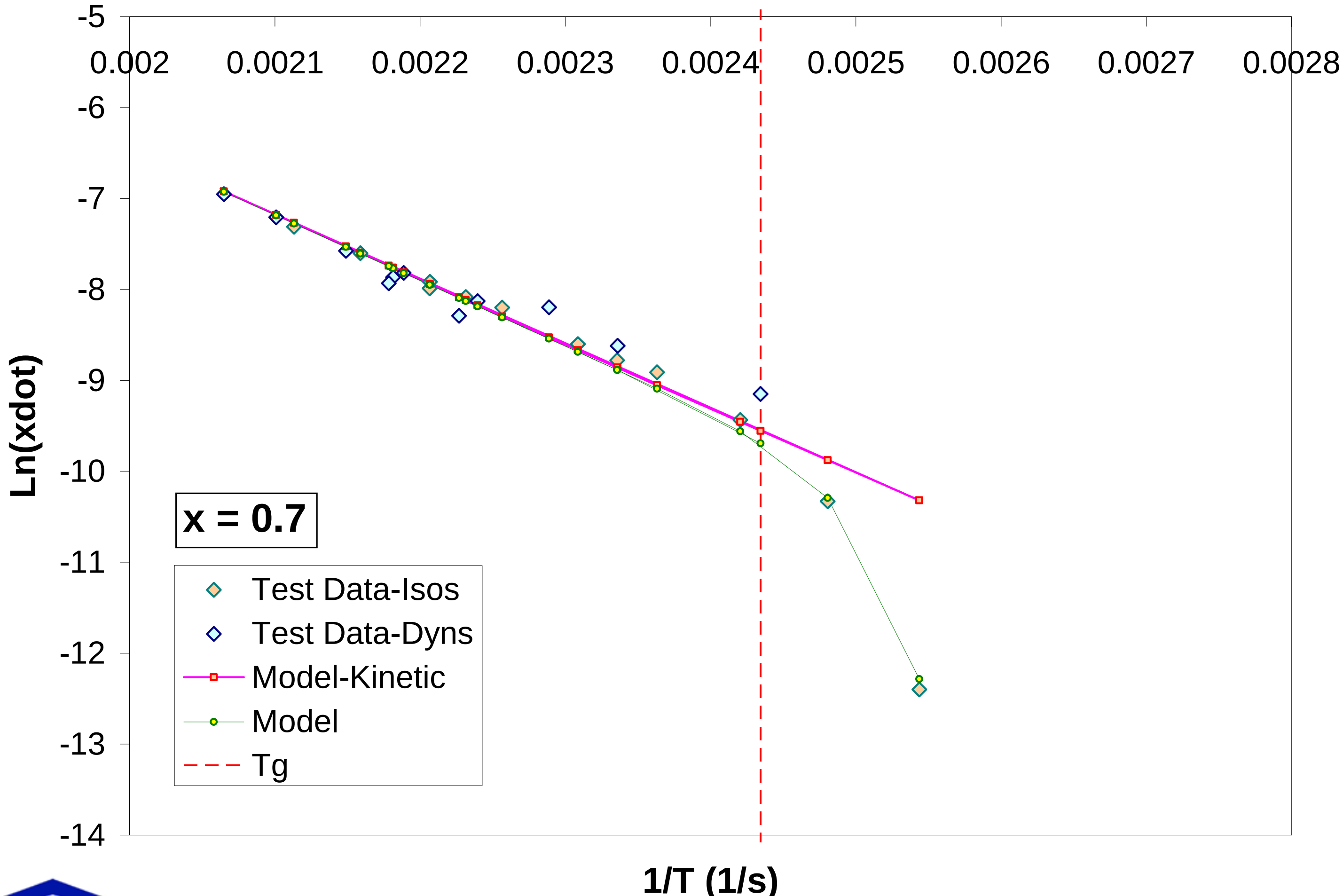


0.002
0.0021
0.0022
0.0023
0.0024
0.0025
0.0026
0.0027
0.0028
-5
-6
-7
-8
-9
-10
-11
-12
Ln(xdot)
Test Data-Isos
Test Data-Dyns
Model-Kinetic
Model
Tg
x = 0.5
1/T (1/s)

Ln(xdot)-1/T

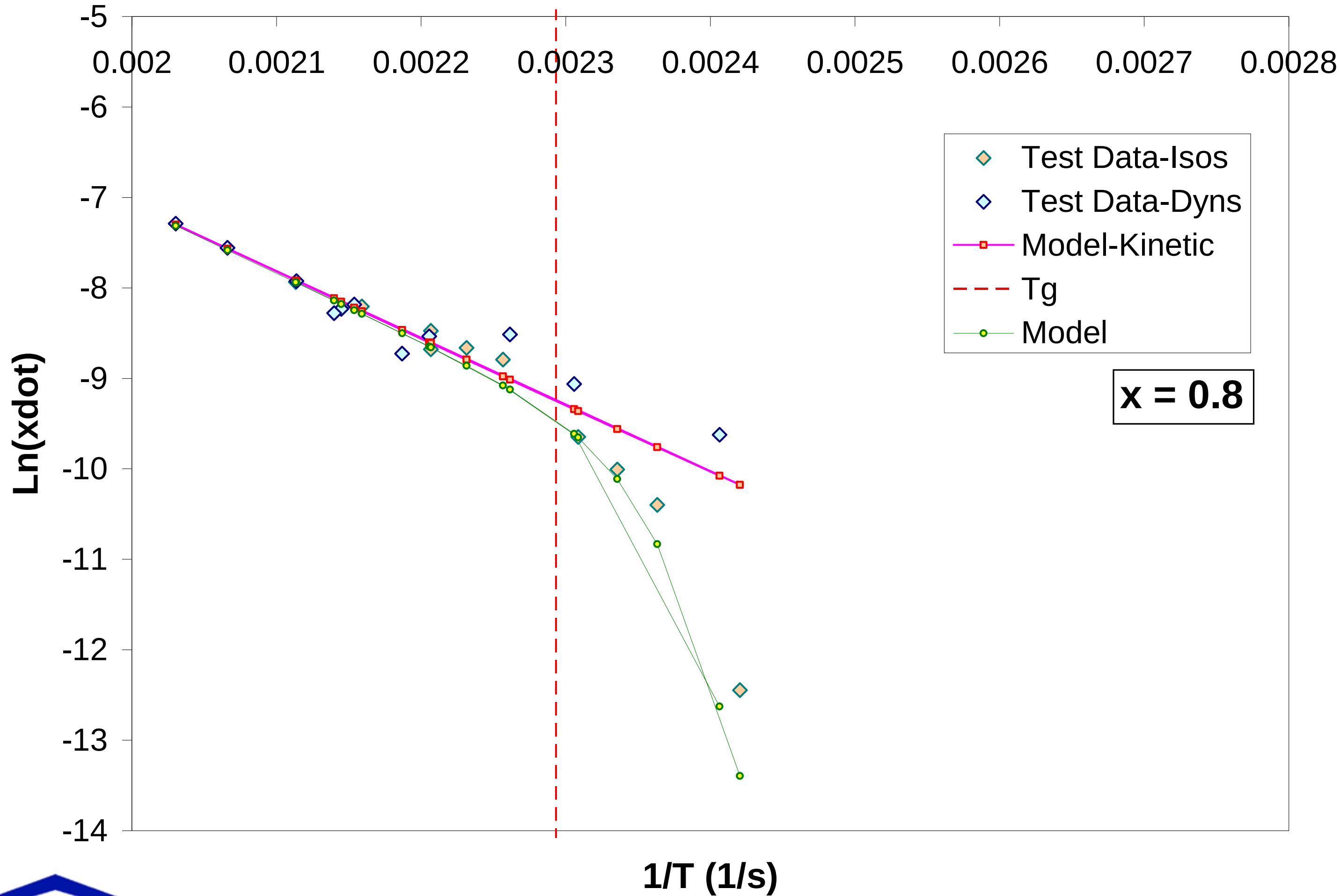

Ln(xdot)
1/T (1/s)
-5
-6
-7
-8
-9
-10
-11
-12
0.002
0.0021
0.0022
0.0023
0.0024
0.0025
0.0026
0.0027
0.0028
Test Data-Isos
Test Data-Dyns
Model-Kinetic
Model
Tg
x = 0.6

Ln(xdot)-1/T



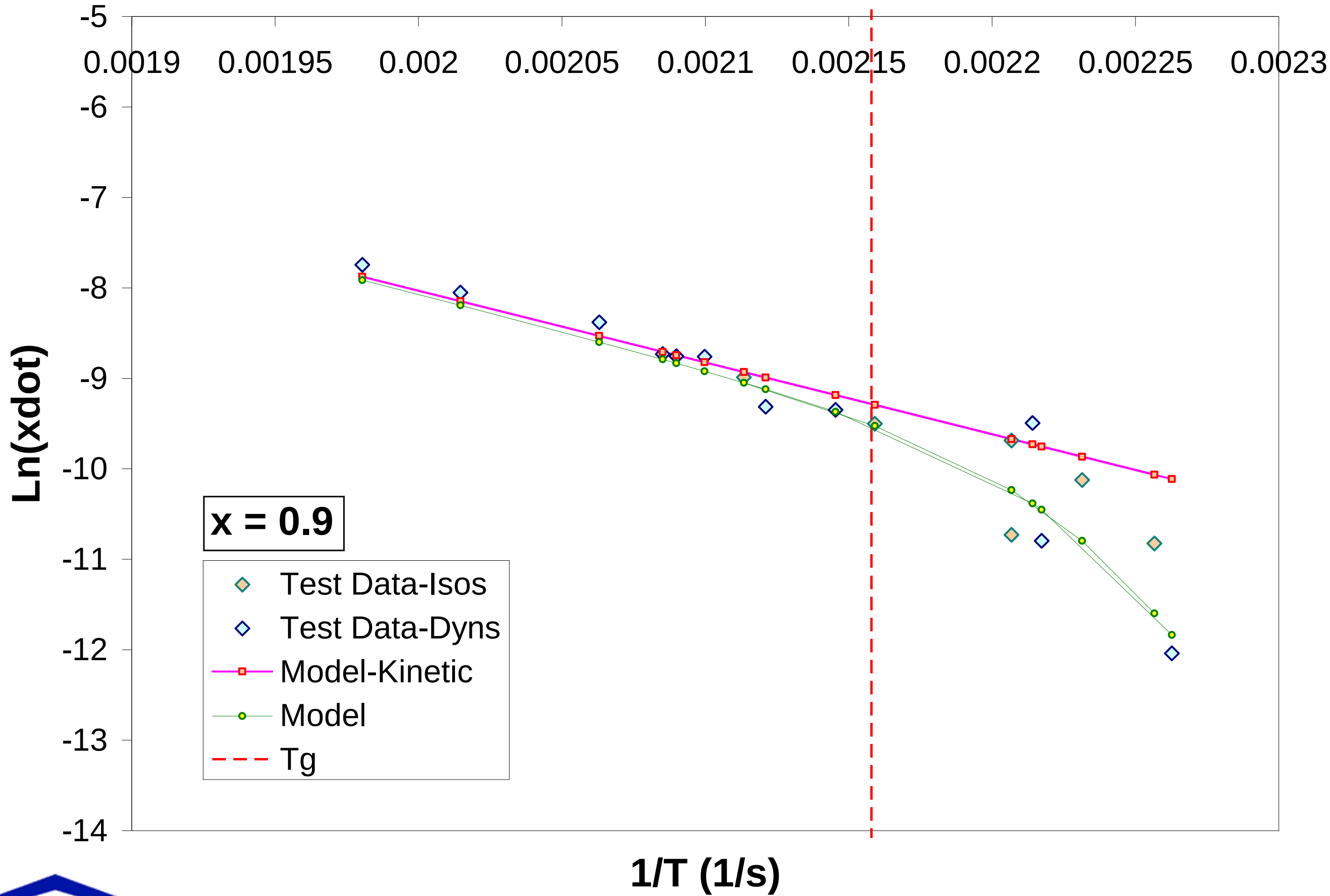
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0.002
0.0021
0.0022
0.0023
0.0024
0.0025
0.0026
0.0027
0.0028
Ln(xdot)
x = 0.7
Test Data-Isos
Test Data-Dyns
Model-Kinetic
Model
Tg
1/T (1/s)

Ln(xdot)-1/T



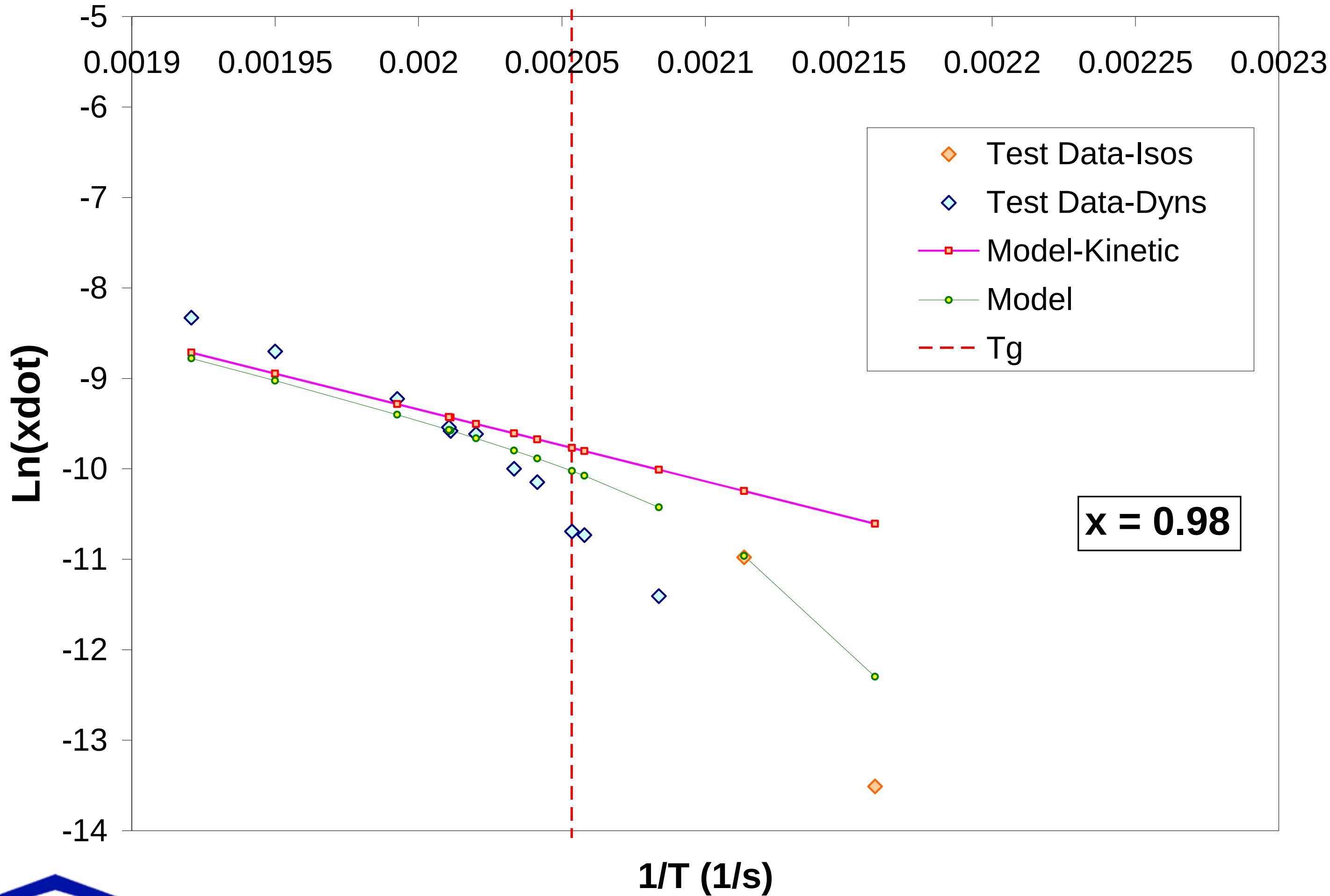
Ln(xdot)
1/T (1/s)
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0.002
0.0021
0.0022
0.0023
0.0024
0.0025
0.0026
0.0027
0.0028
Test Data-Isos
Test Data-Dyns
Model-Kinetic
Tg
Model
x = 0.8

Ln(xdot)-1/T



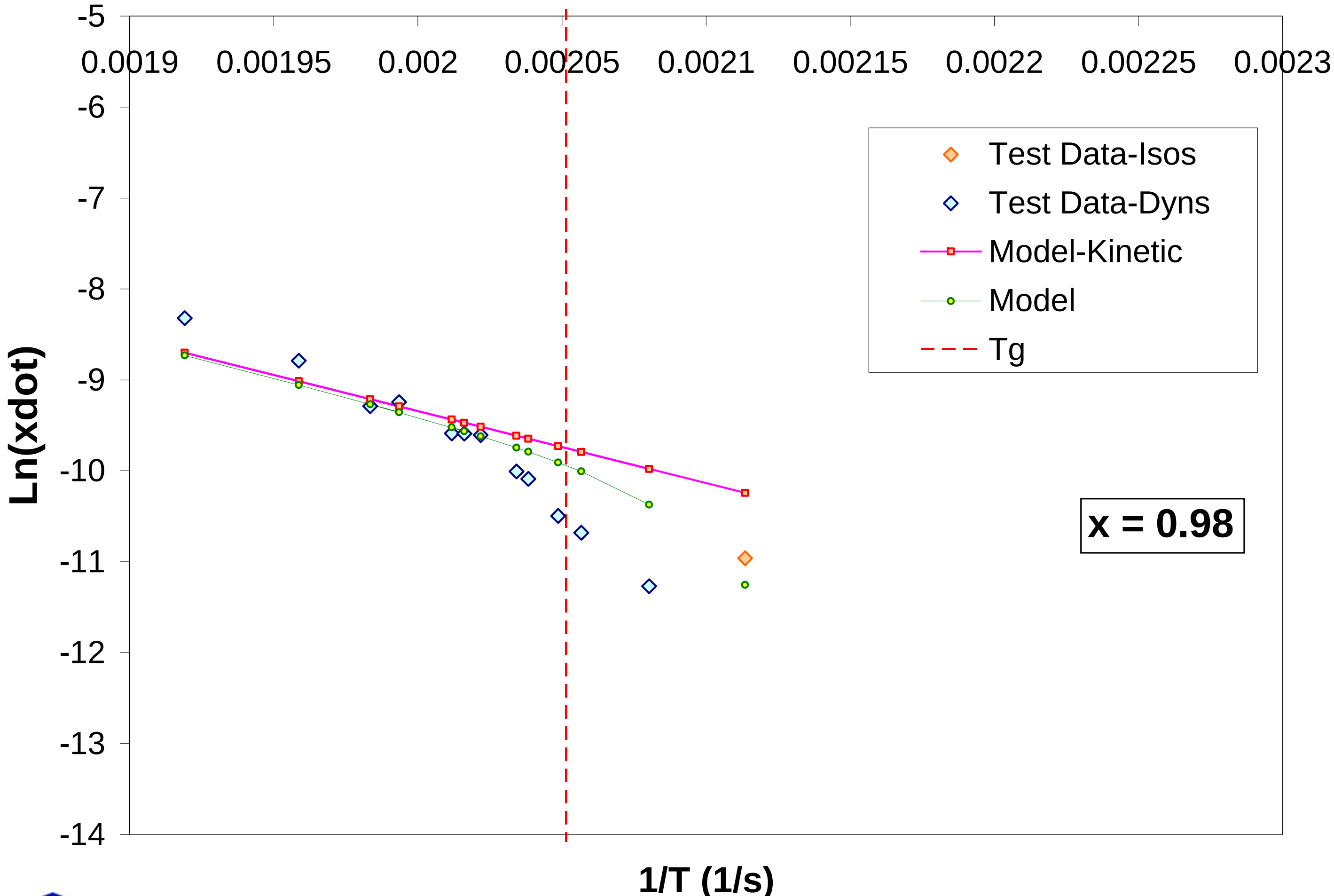
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0.0019
0.00195
0.002
0.00205
0.0021
0.00215
0.0022
0.00225
0.0023
Ln(xdot)
1/T (1/s)
x = 0.9
Test Data-Isos
Test Data-Dyns
Model-Kinetic
Model
Tg

Ln(xdot)-1/T



-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0.0019
0.00195
0.002
0.00205
0.0021
0.00215
0.0022
0.00225
0.0023
Ln(xdot)
Test Data-Isos
Test Data-Dyns
Model-Kinetic
Model
Tg
x = 0.98
1/T (1/s)

Ln(xdot)-1/T



-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0.0019
0.00195
0.002
0.00205
0.0021
0.00215
0.0022
0.00225
0.0023
Ln(xdot)
1/T (1/s)
Test Data-Isos
Test Data-Dyns
Model-Kinetic
Model
Tg
x = 0.98

Model Parameters

Parameter	R1	R2 (unit)
k_0	8506	4.115 (1/s)
E_a	52938	65946 (J/mol)
l	0.000	0.757
r	1.105	0.193
m	1.892	5.627
n_2	1.000	1.000
b	0.000	0.000
n	1.800	0.171

Parameter	Value (unit)
T_{g0}	3 (ºC)
$T_{g\infty}$	220 (ºC)
λ	0.7

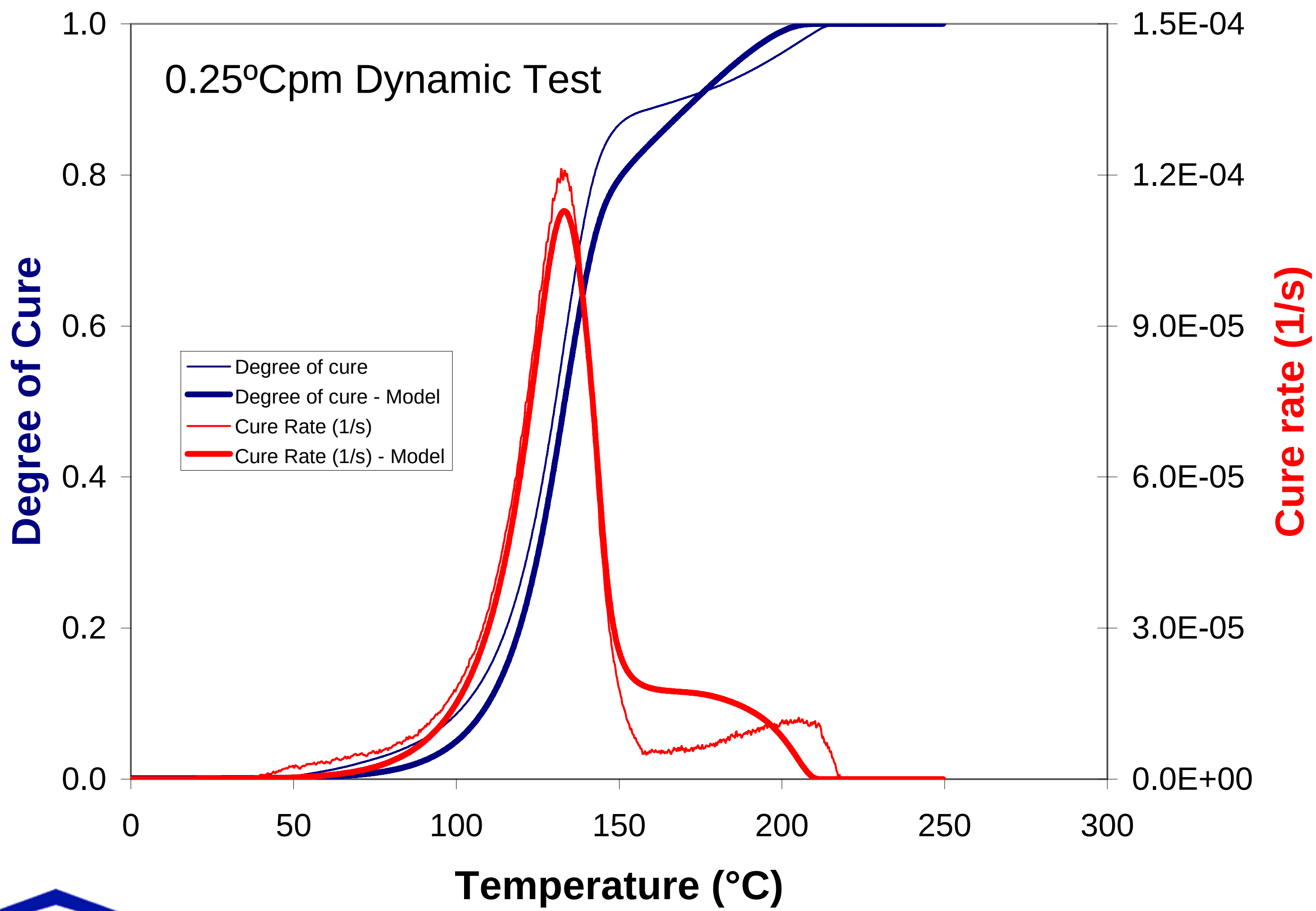
Parameter	R1	R2 (unit)
k_{d0}	2000	7E-3 (1/s)
B	0.35	0.34
a_1	0.00048	4.8E-4 (1/ºC)
a_2	0.00048	4.8E-4 (1/ºC)
T_{ga1}	0	0 (ºC)
T_{ga2}	100	100 (ºC)
b_2	0.025	0.025
b_1	0.030	0.040
T_{gb1}	70	100 (ºC)
T_{gb2}	140	220 (ºC)

Model's range of validity

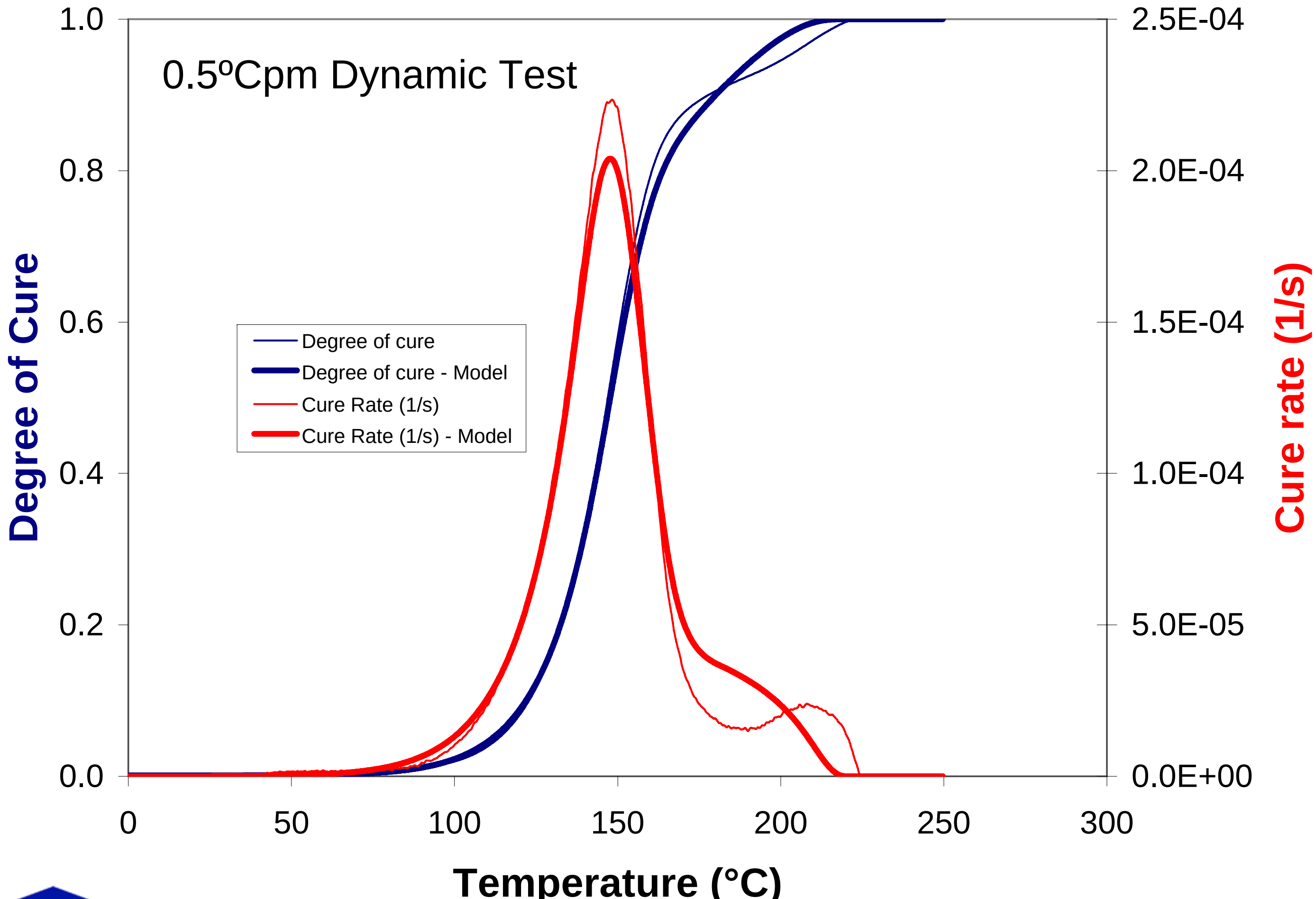
Iso: 100ºC < Temperature < 200ºC

Dyn: ºC < Temperature < ºC

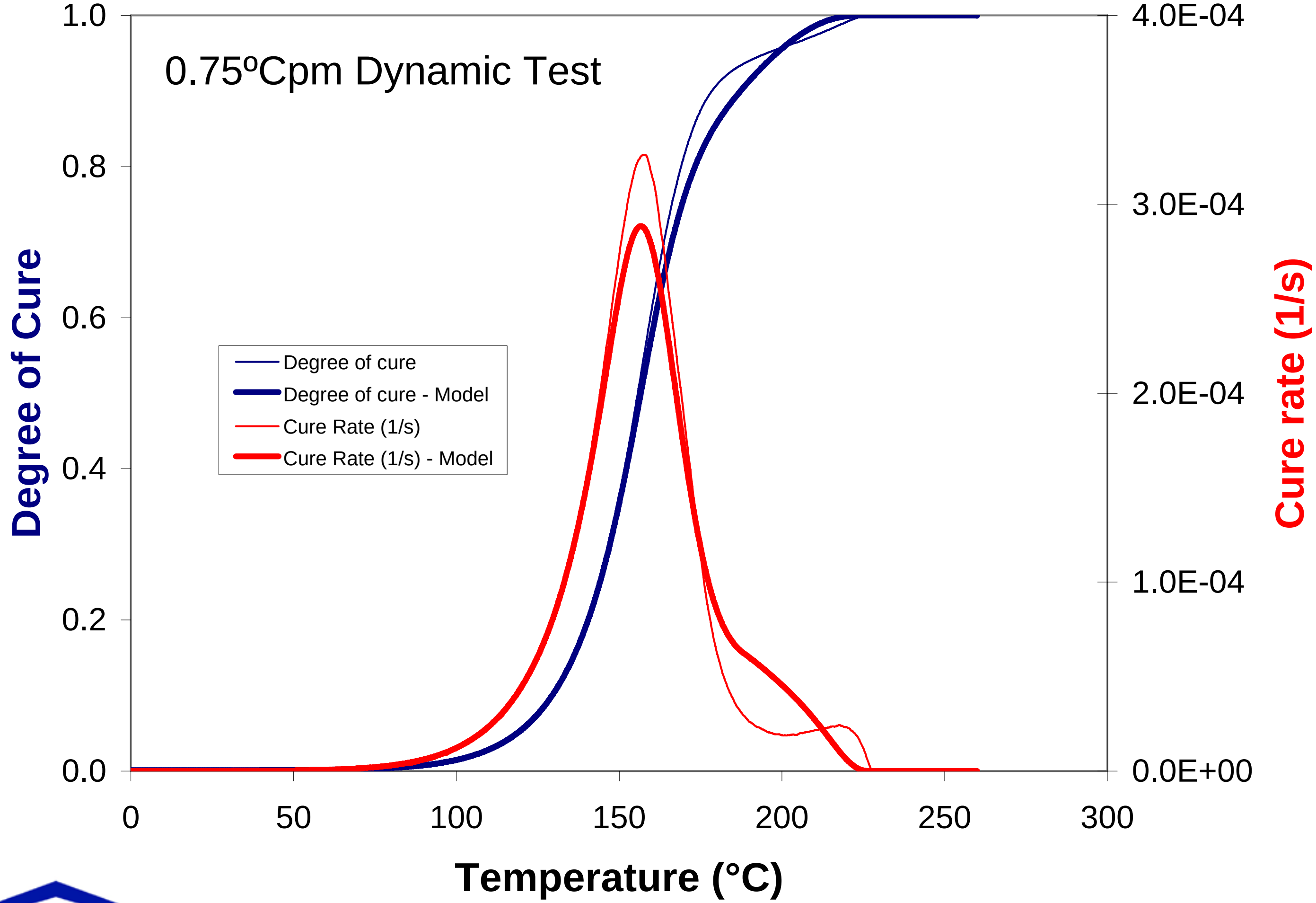
Dynamic Tests – 0.25cpm



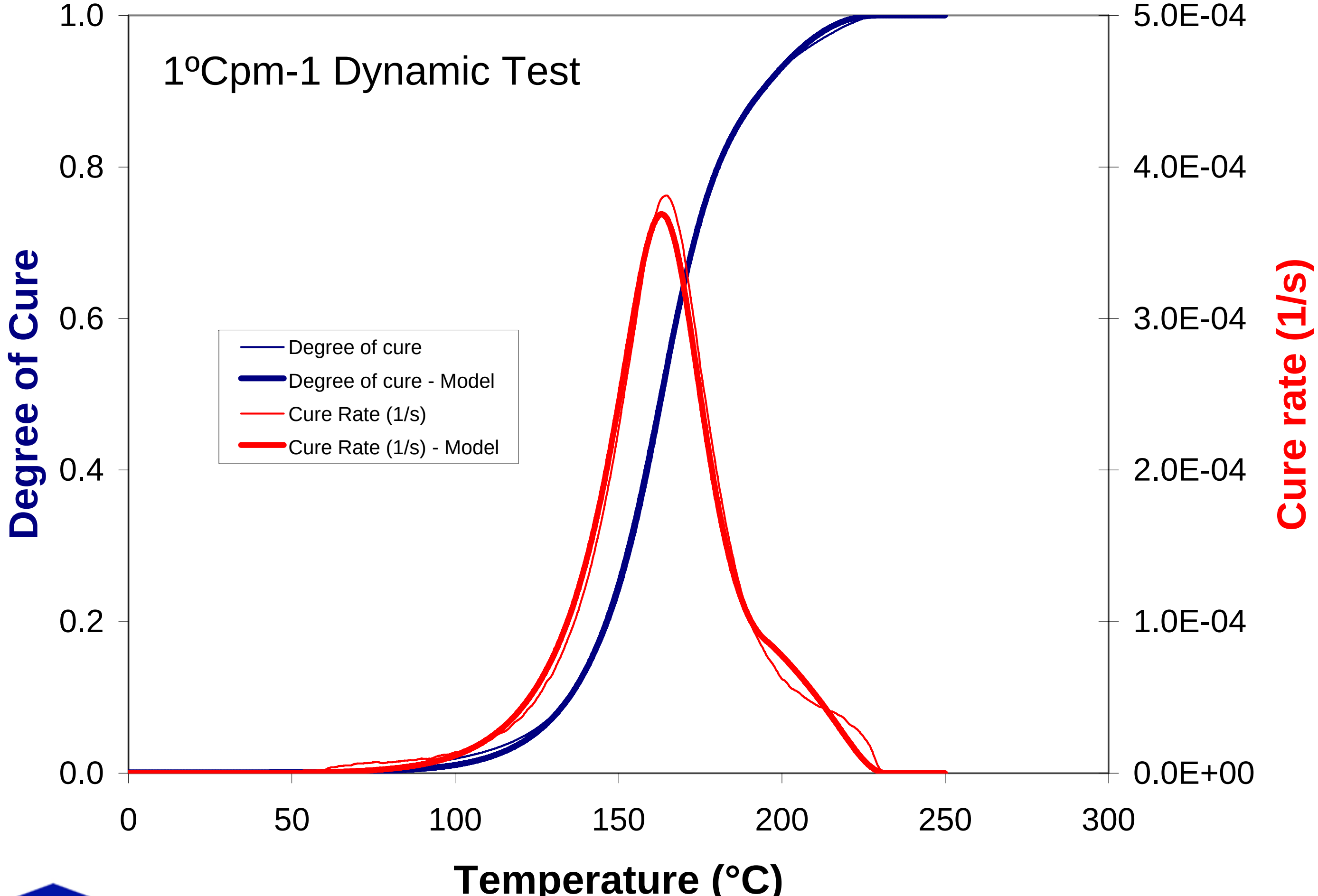
Dynamic Tests – 0.5cpm



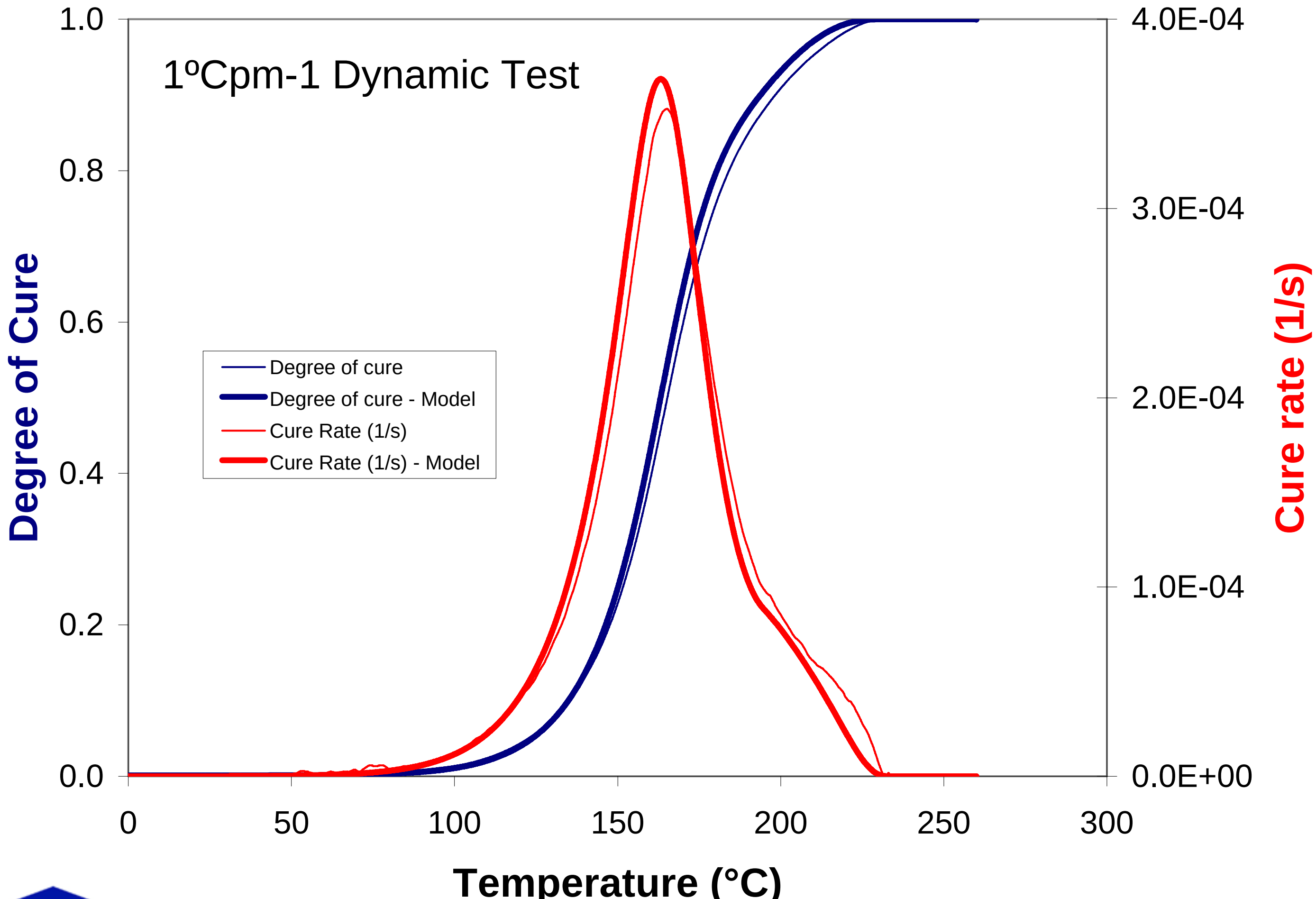
Dynamic Tests – 0.75cpm



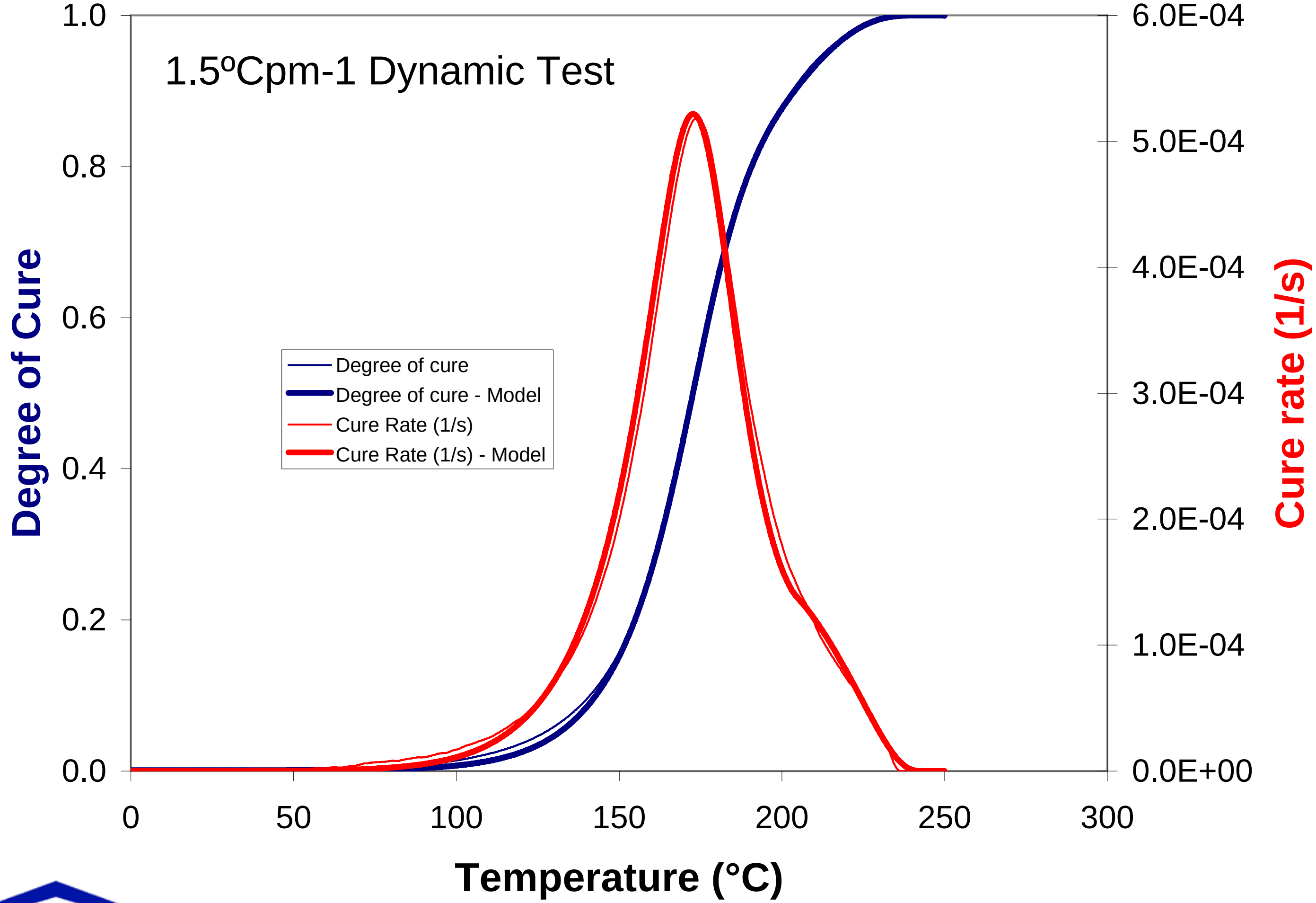
Dynamic Tests – 1cpm-1



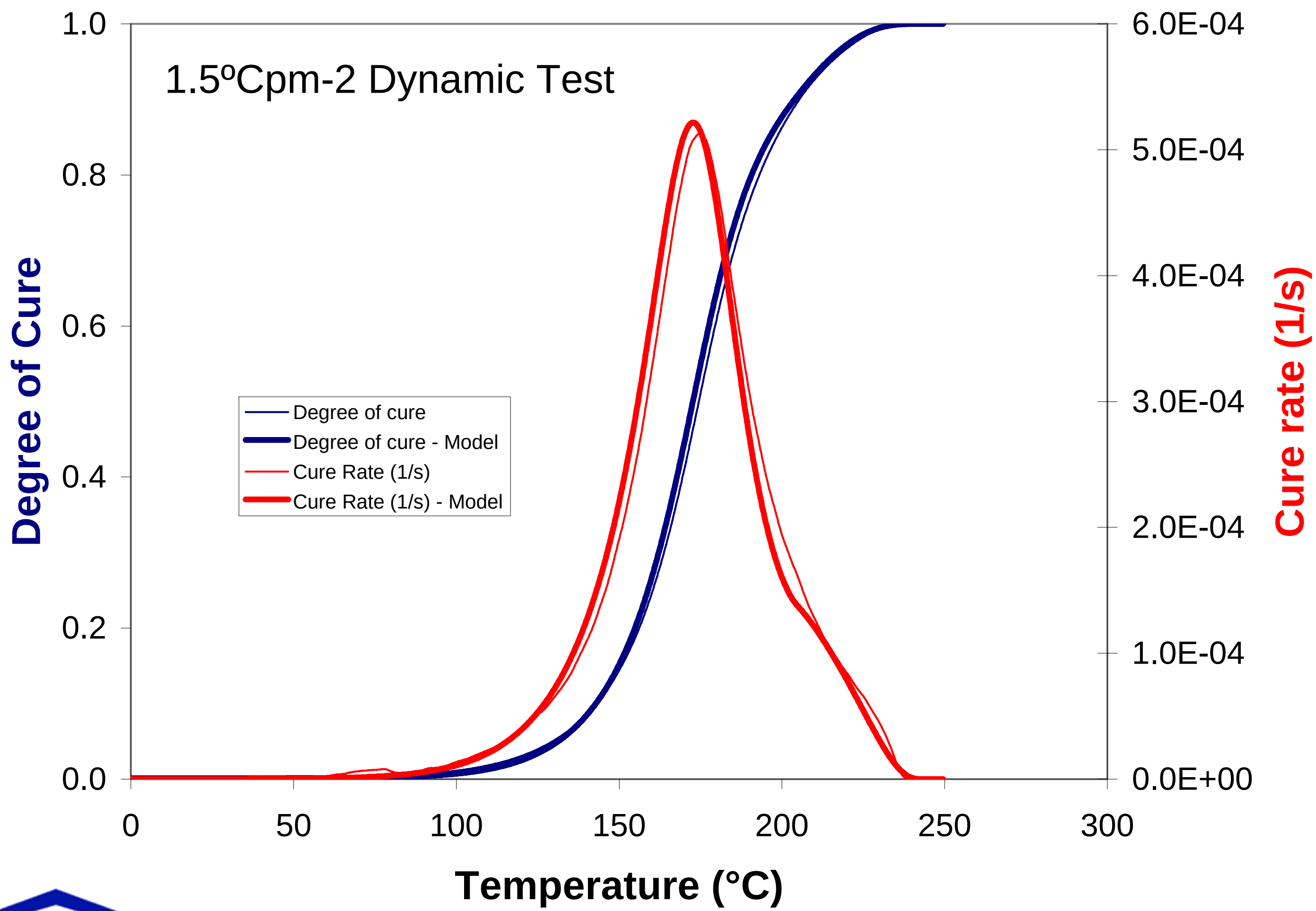
Dynamic Tests – 1cpm-2



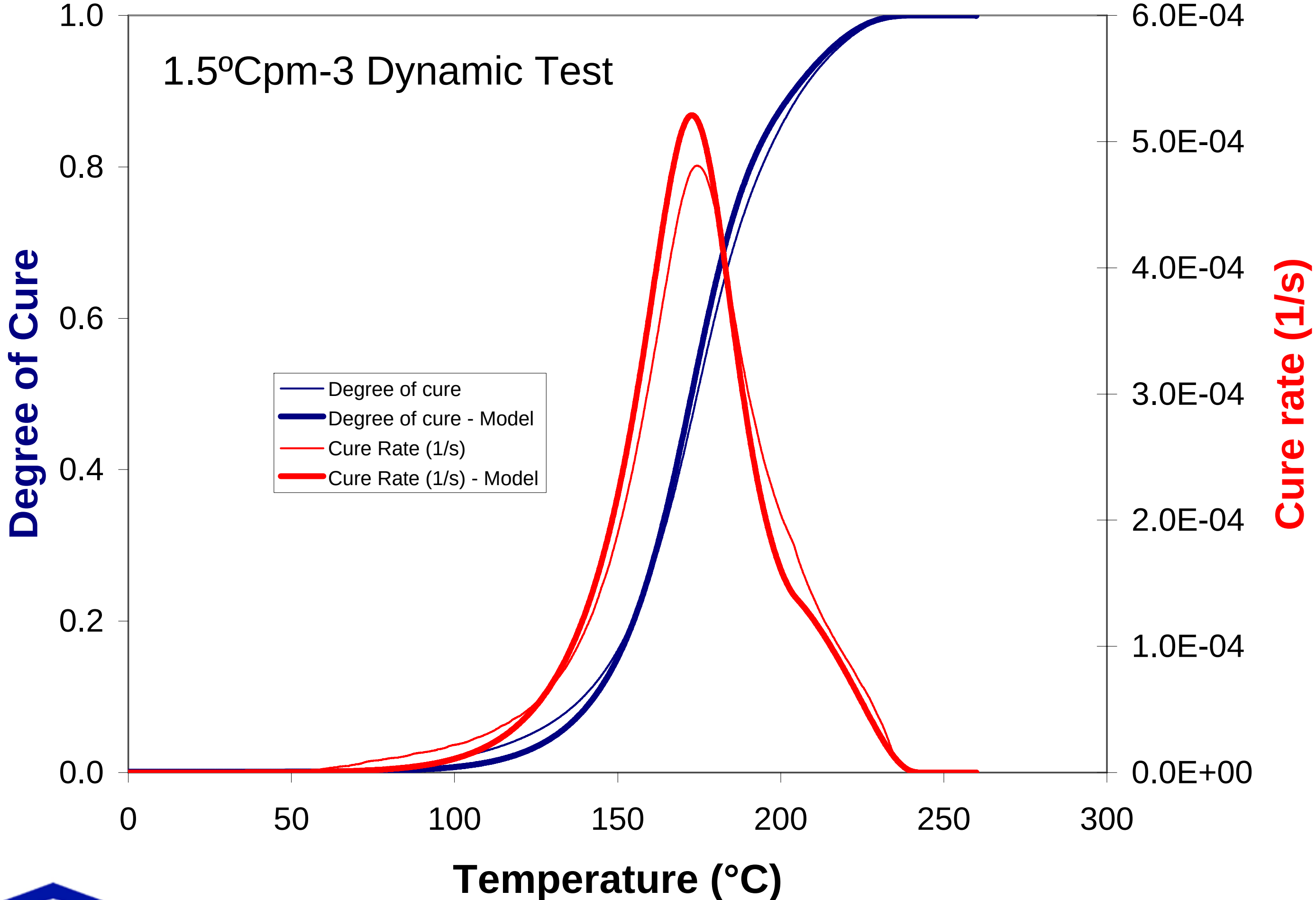
Dynamic Tests – 1.5cpm-1



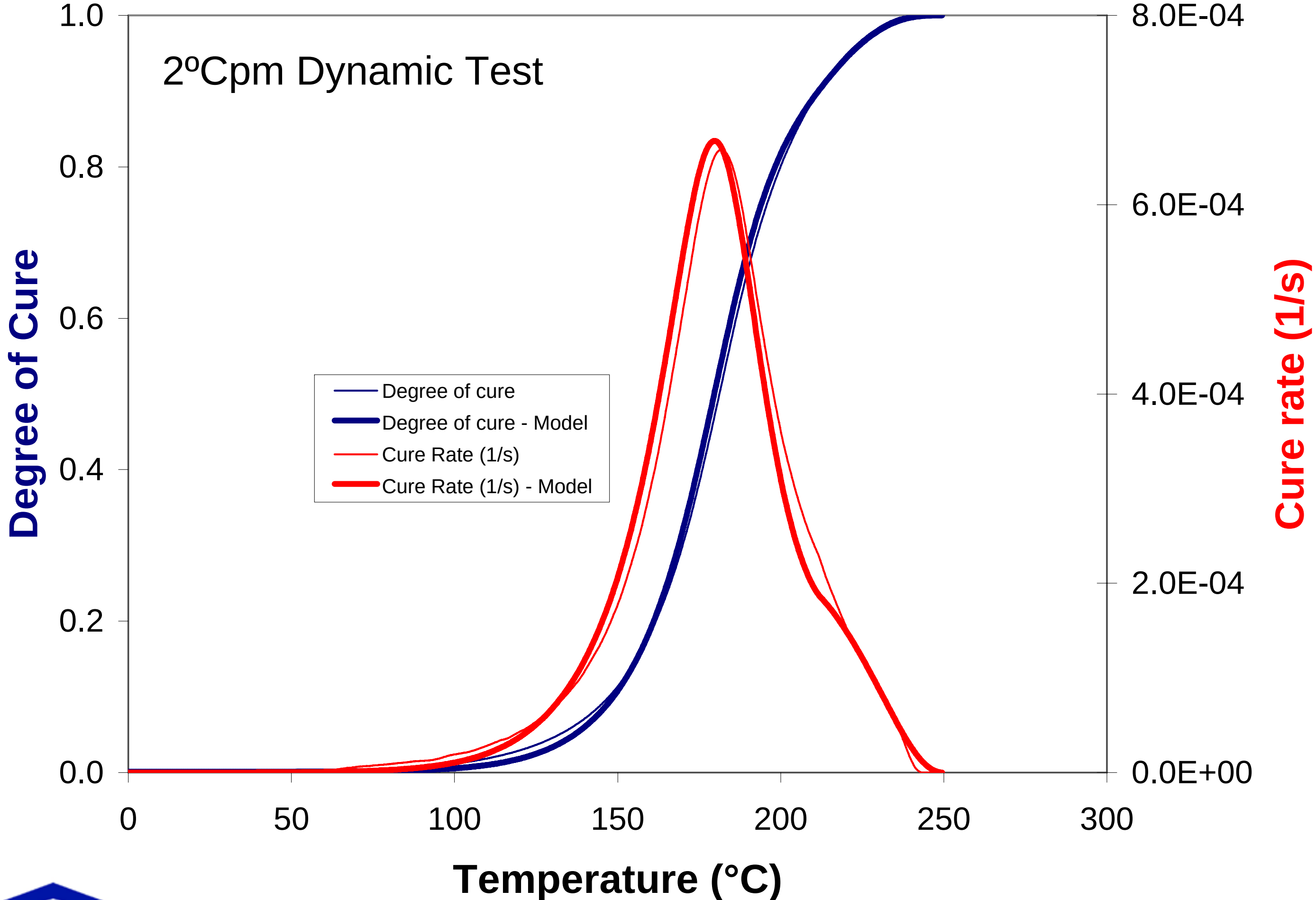
Dynamic Tests – 1.5cpm-2



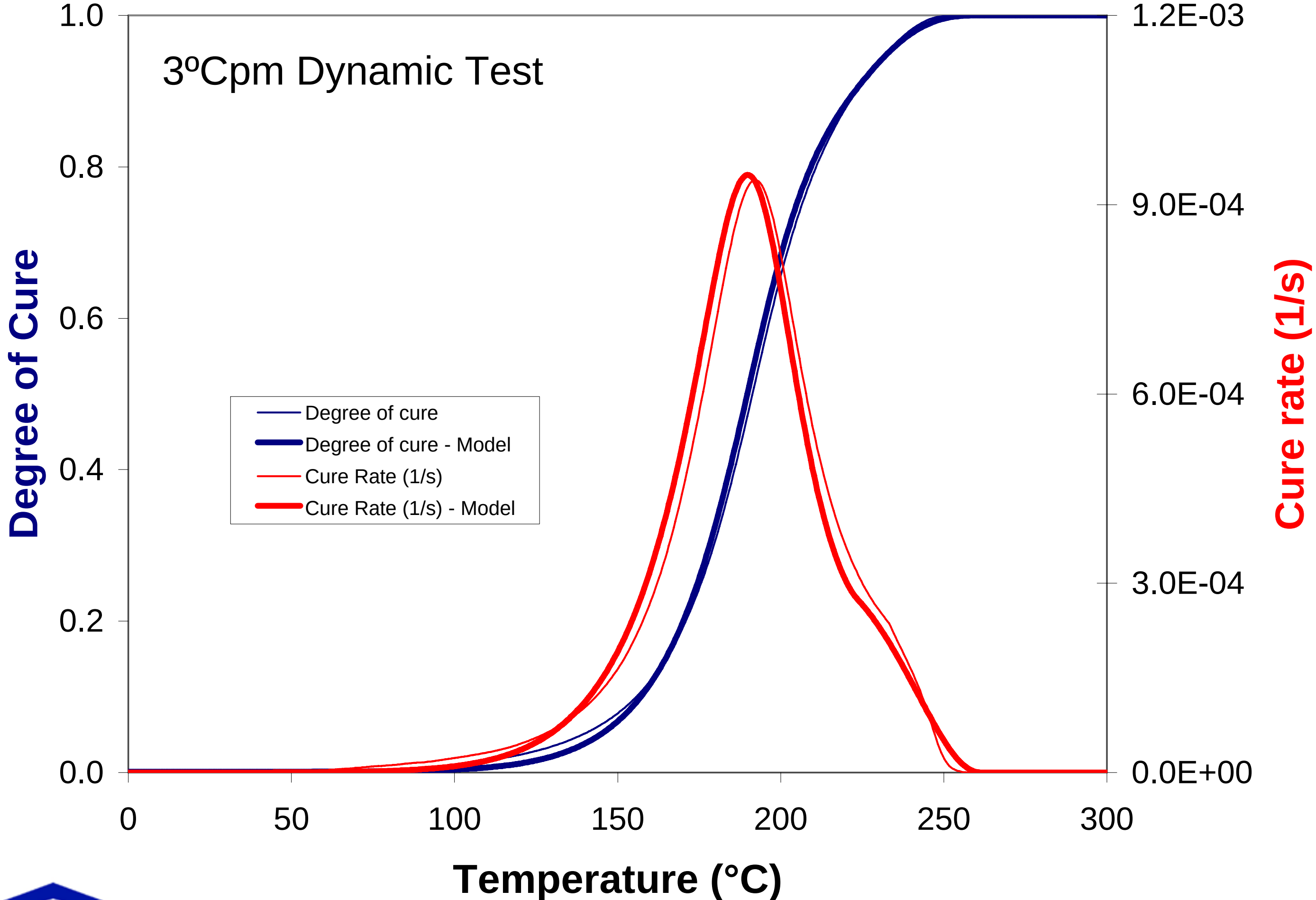
Dynamic Tests – 1.5cpm-3



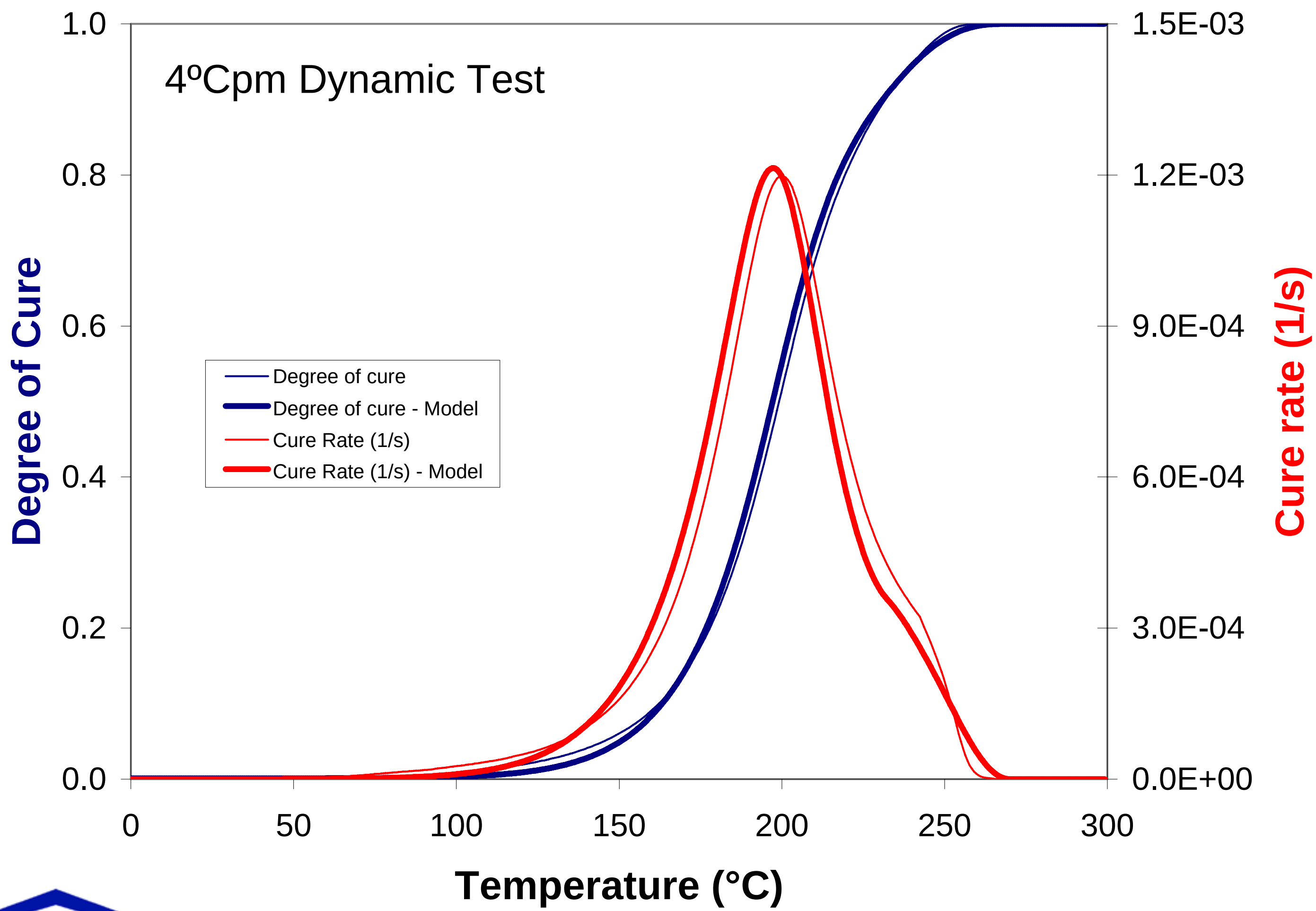
Dynamic Tests – 2cpm-2



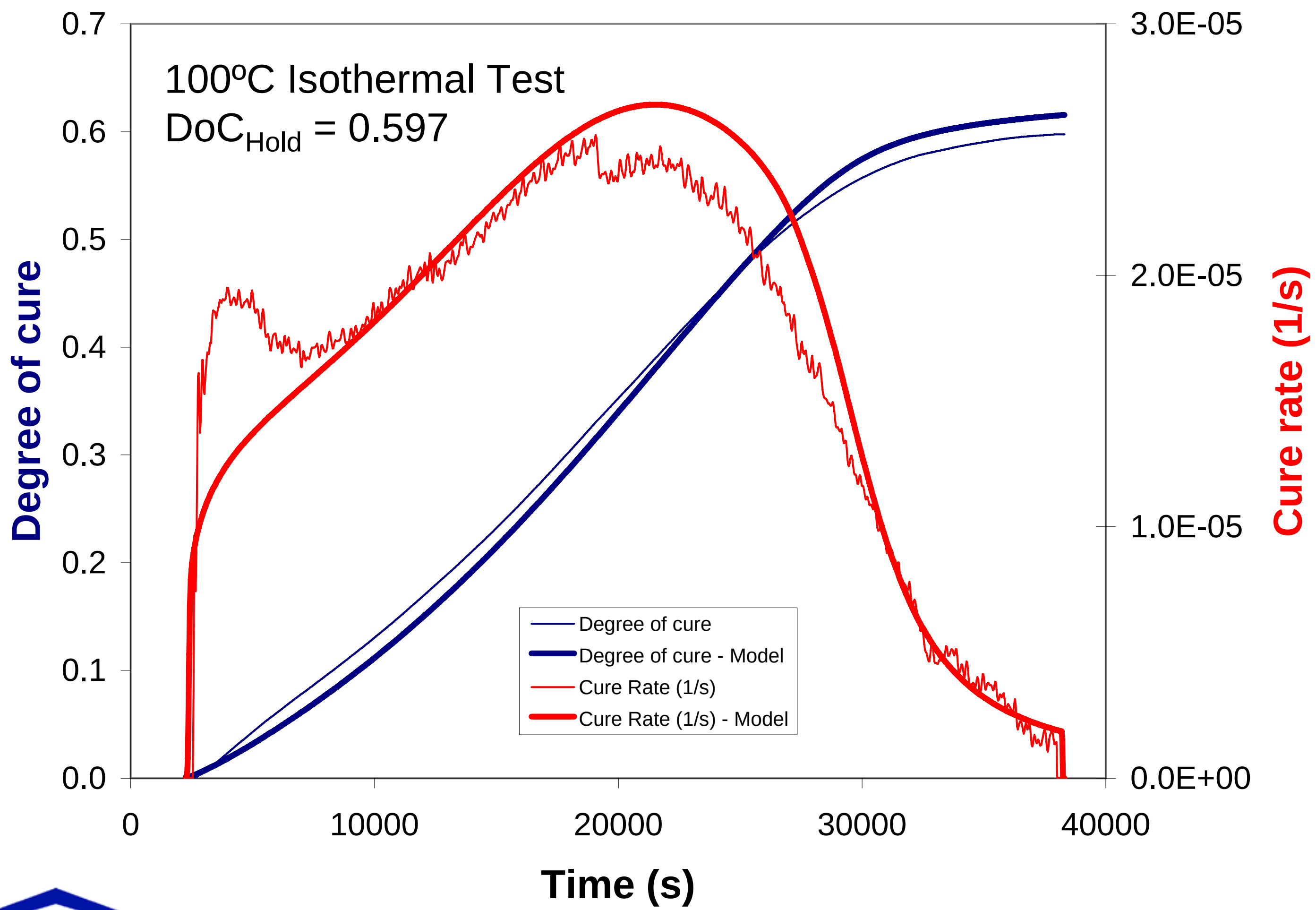
Dynamic Tests – 3cpm



Dynamic Tests – 4cpm



Isothermal Tests - 100ºC



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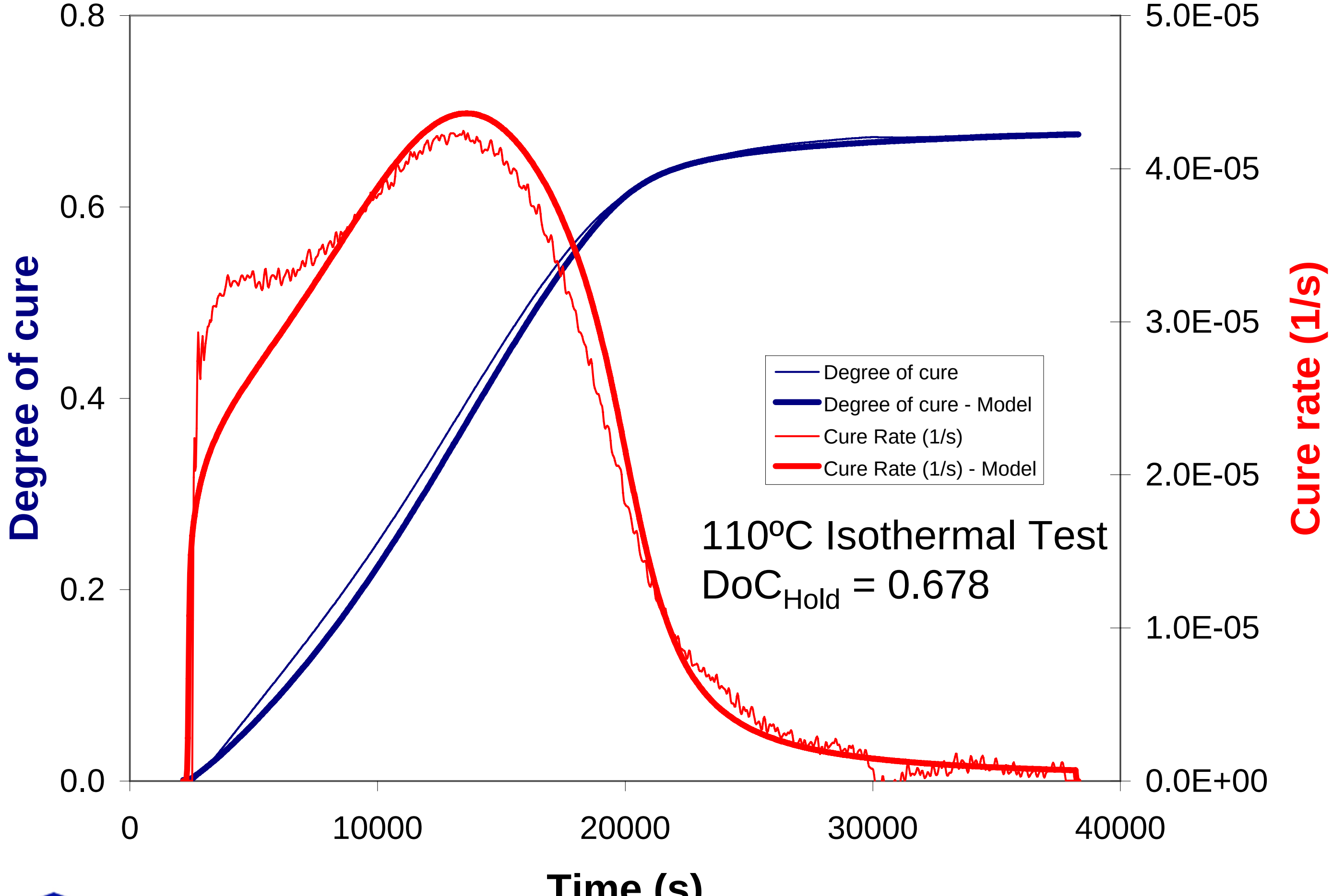
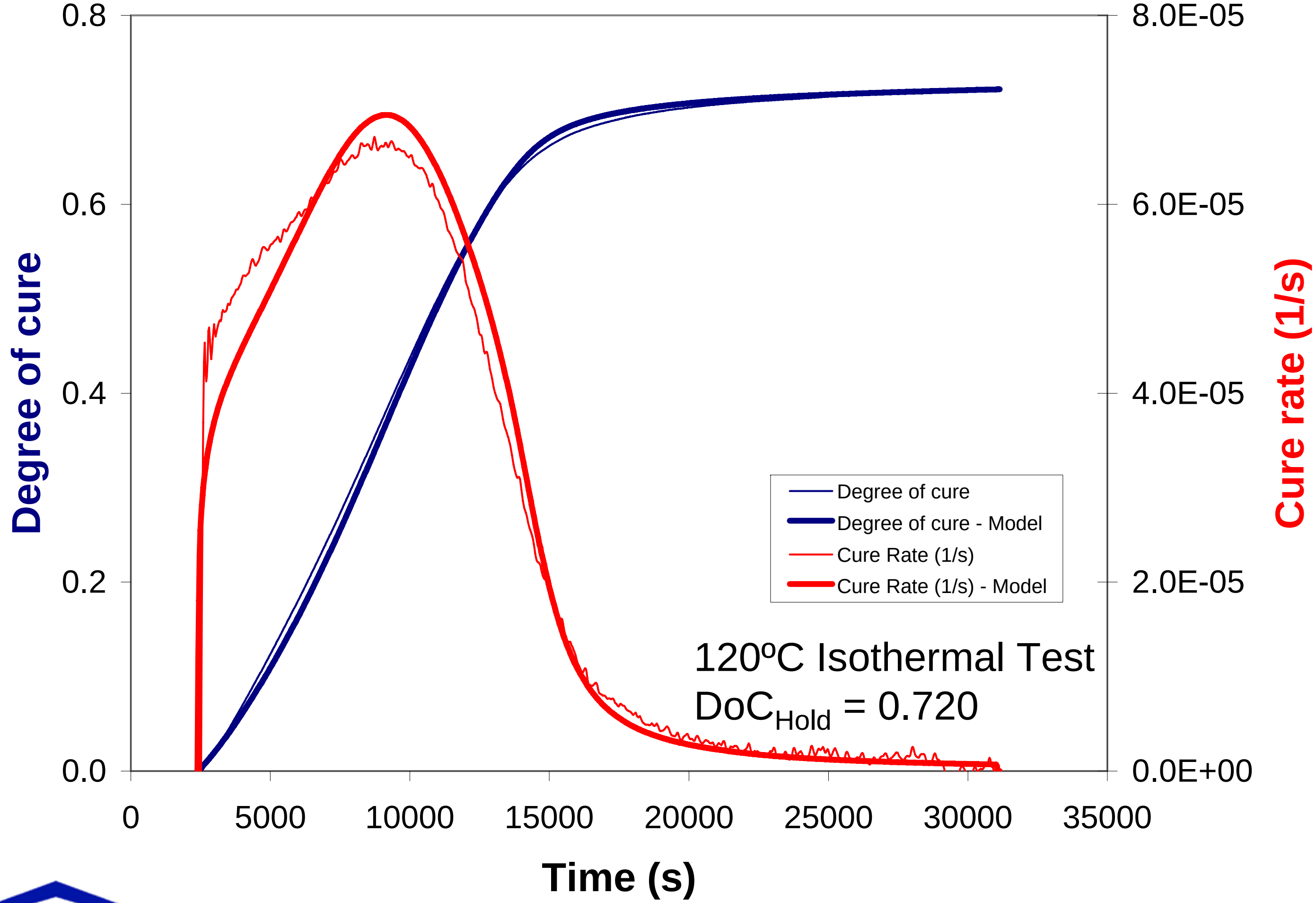
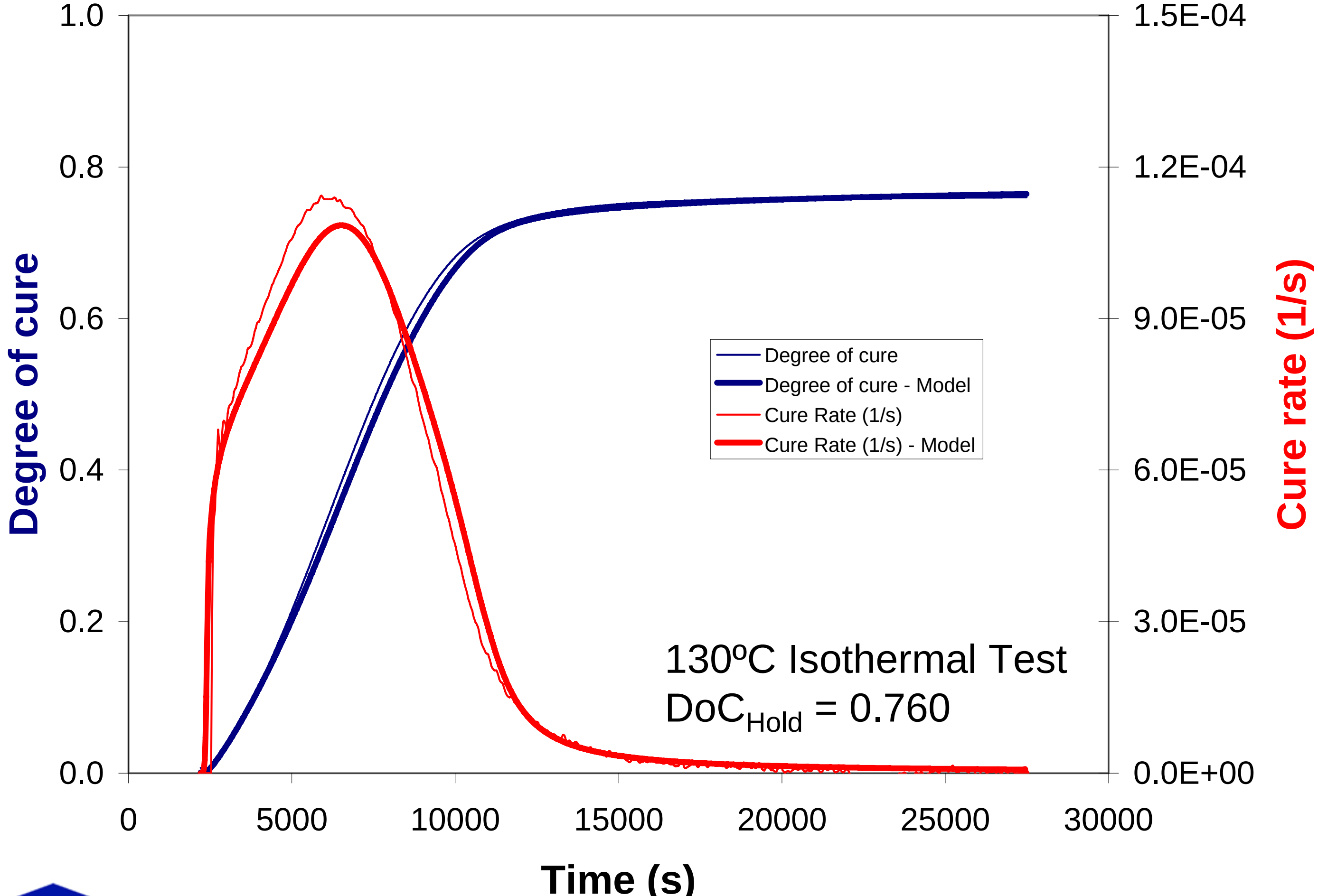
Isothermal Tests - 110ºC



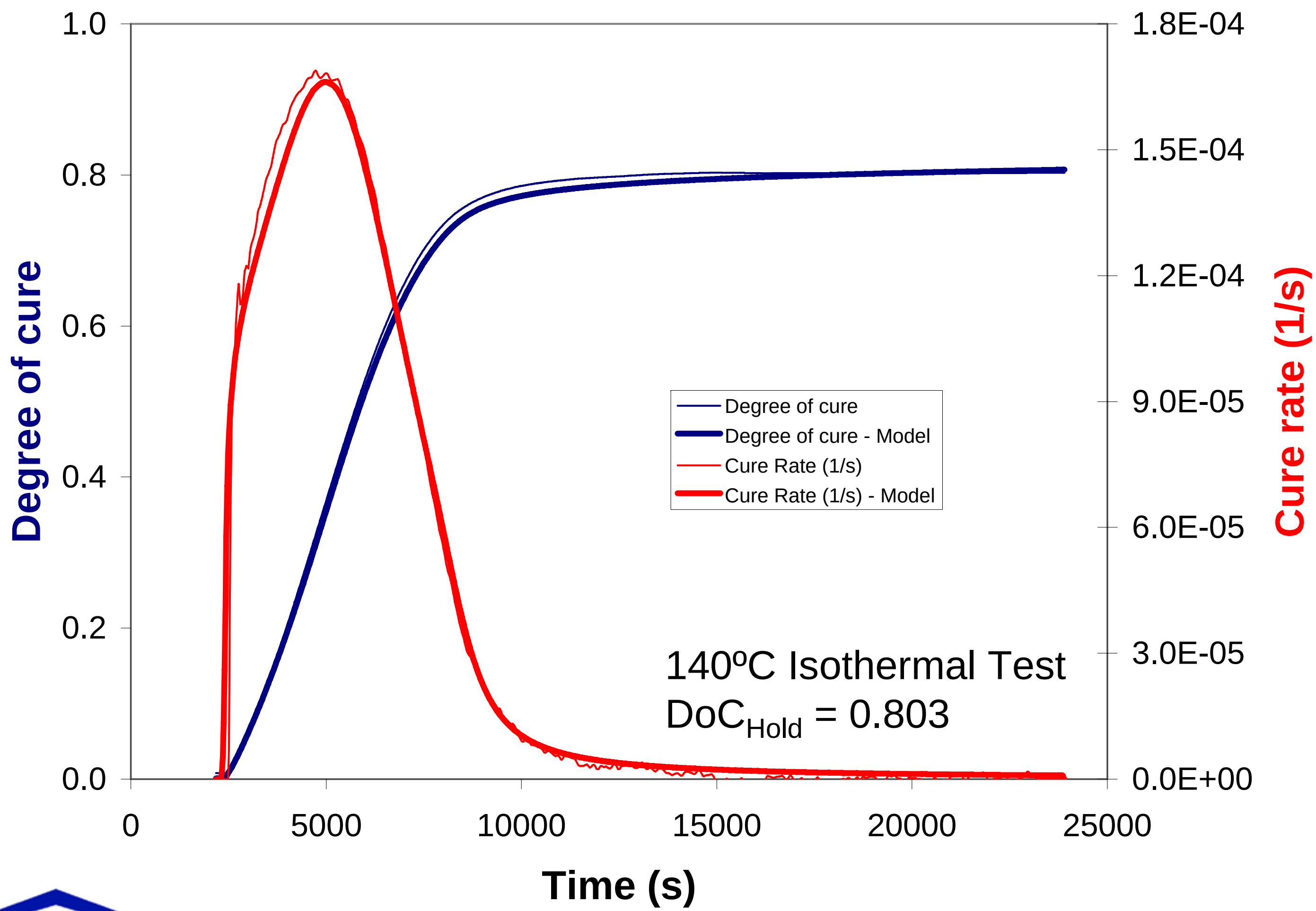
Isothermal Tests - 120ºC



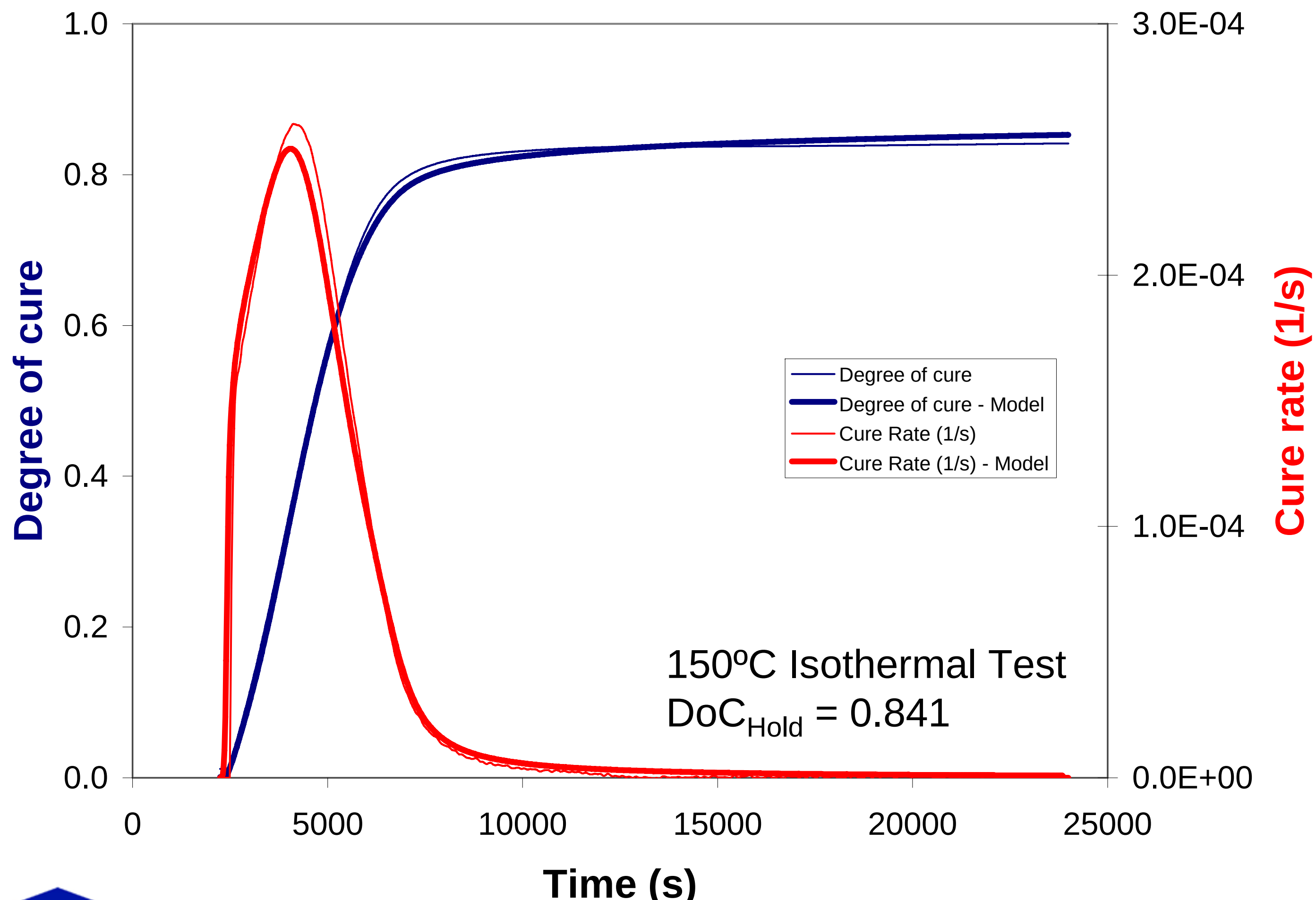
Isothermal Tests - 130ºC



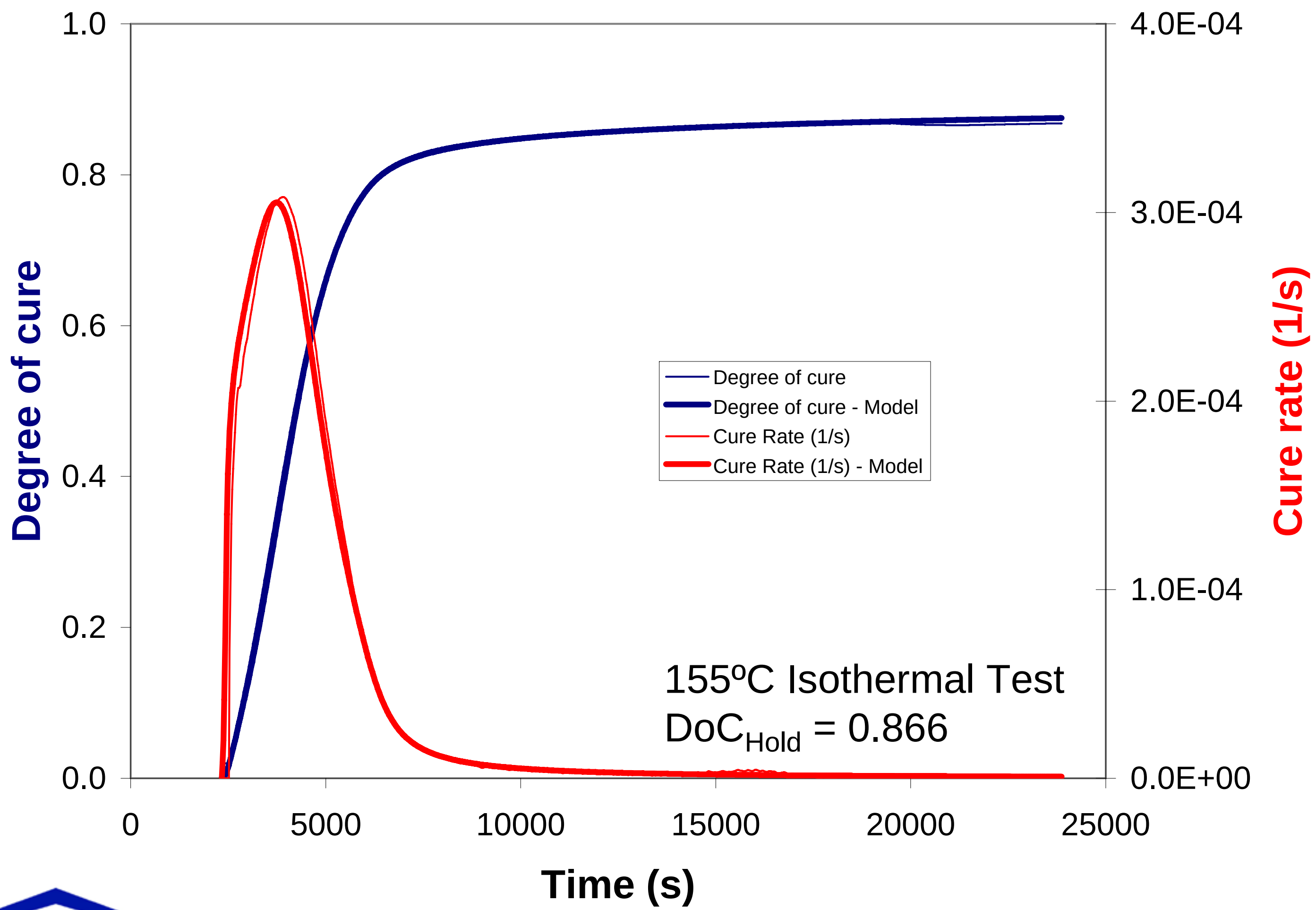
Isothermal Tests - 140ºC



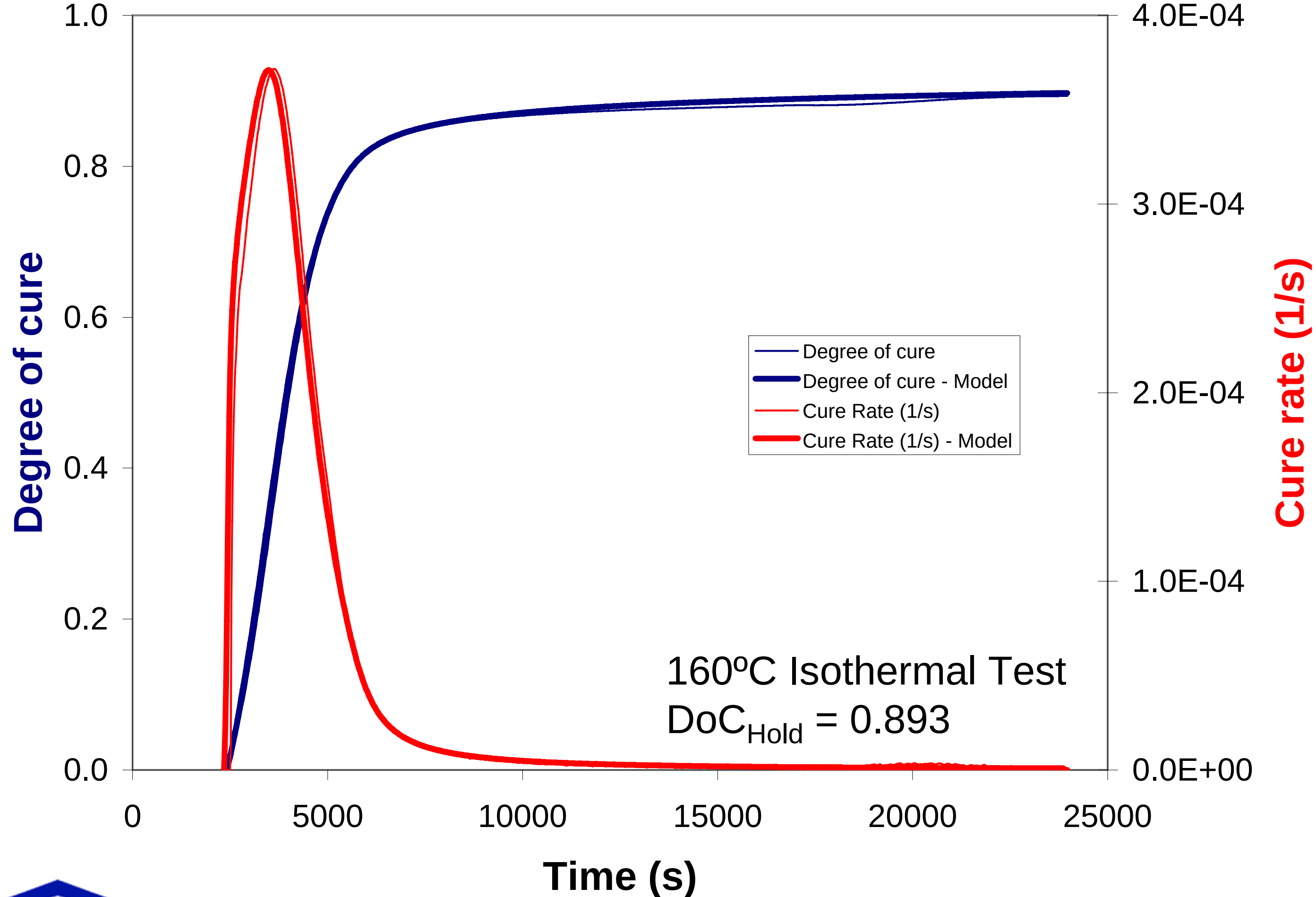
Isothermal Tests - 150ºC



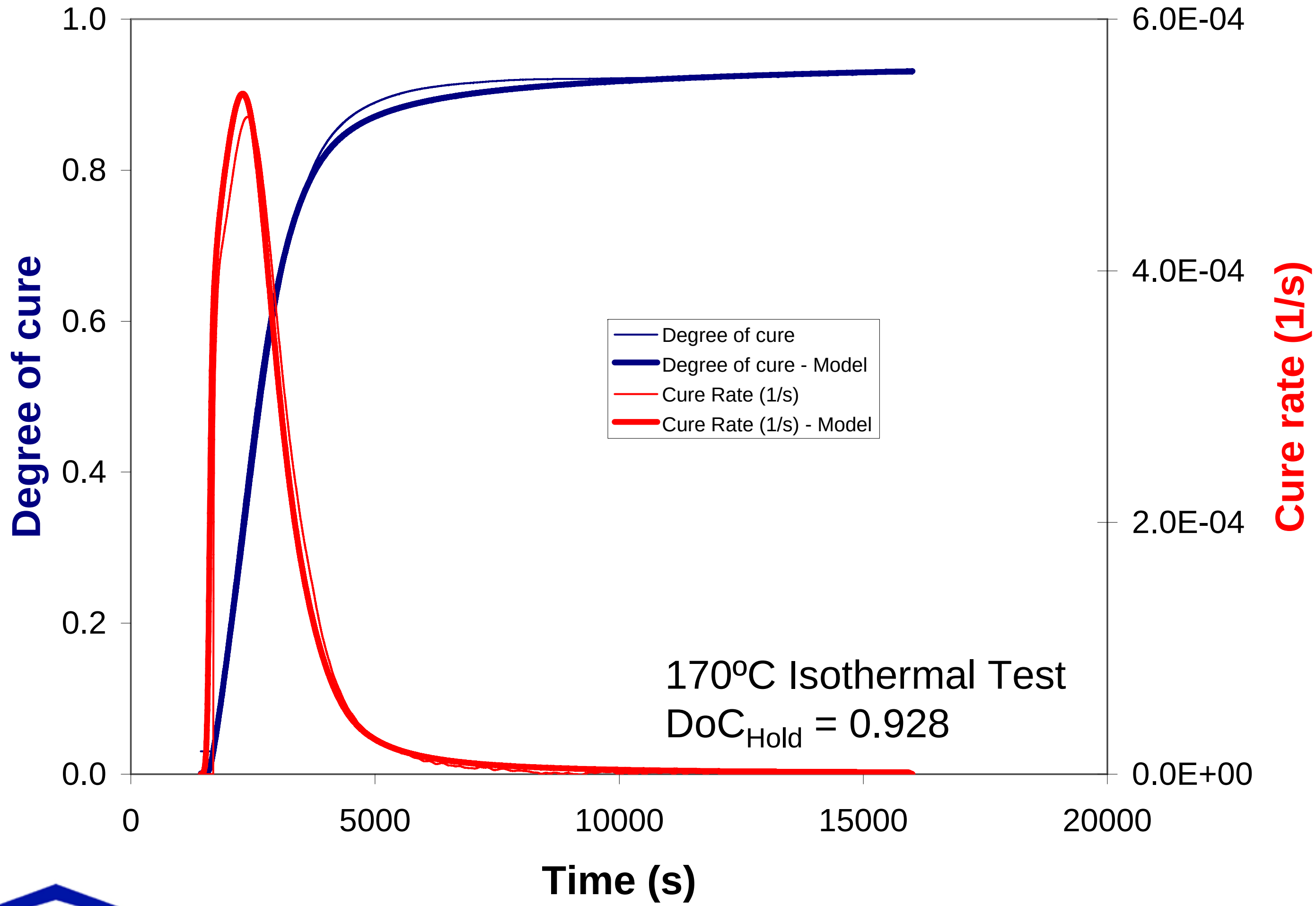
Isothermal Tests - 155ºC



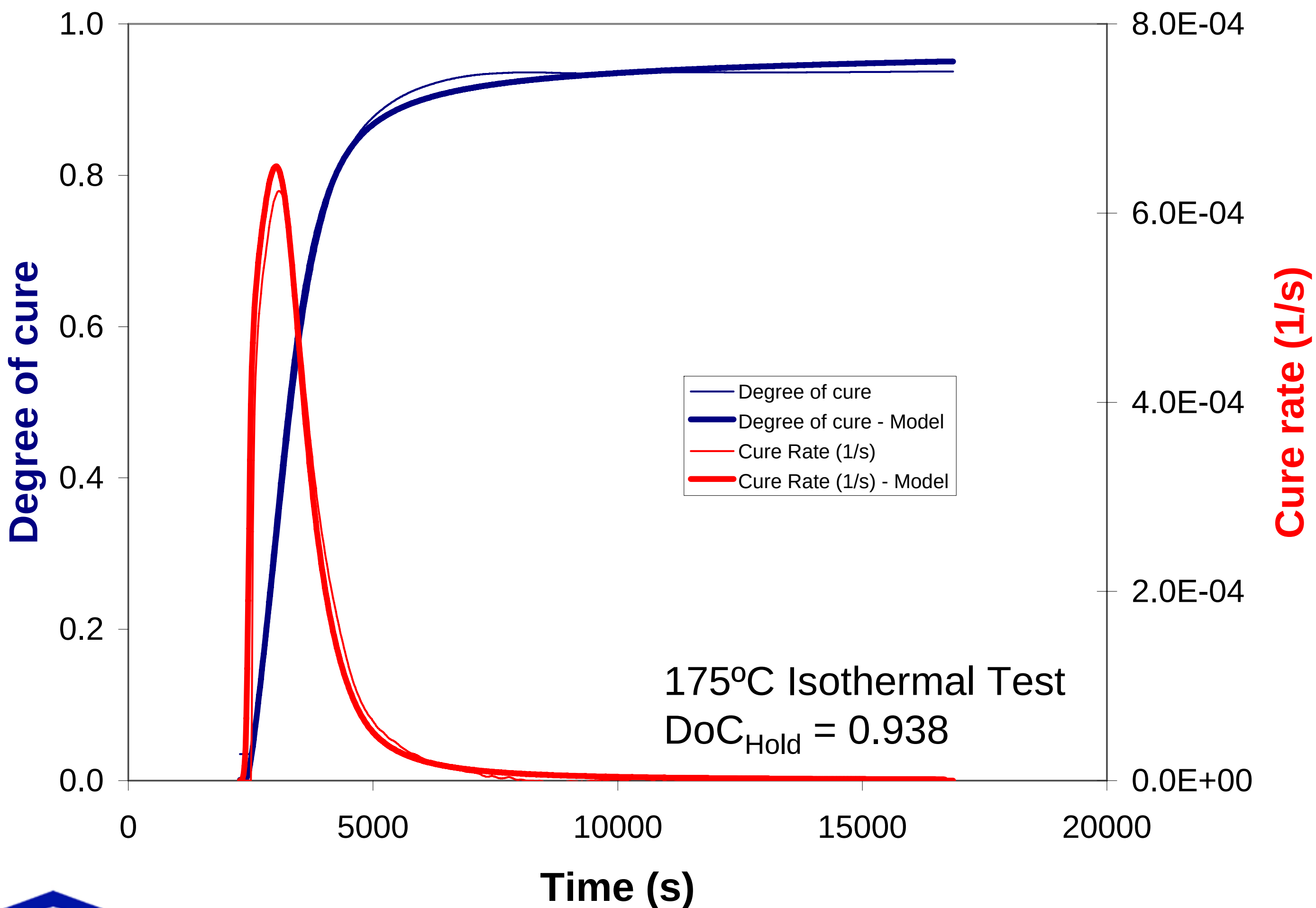
Isothermal Tests - 160ºC



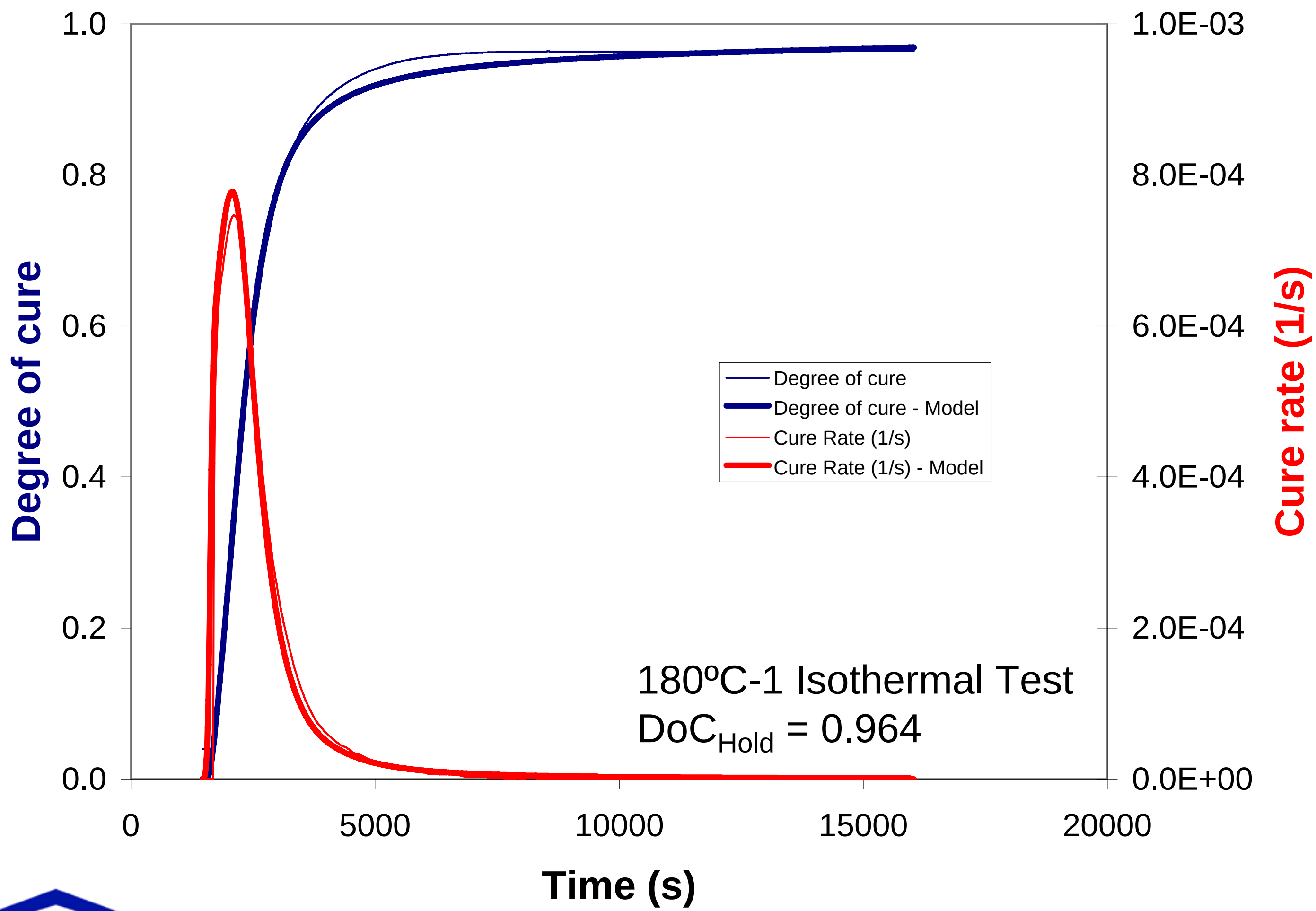
Isothermal Tests - 170ºC



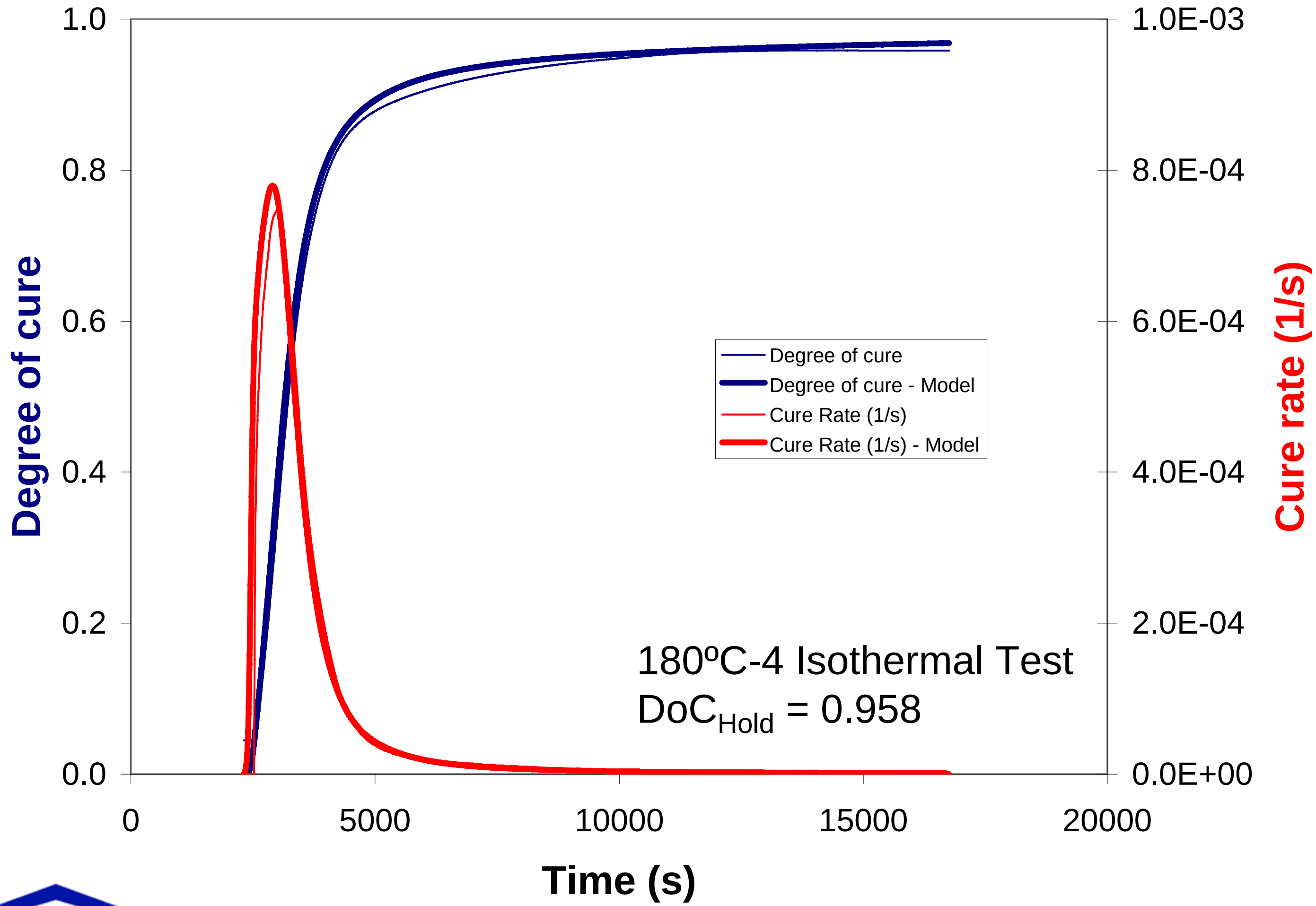
Isothermal Tests - 175ºC



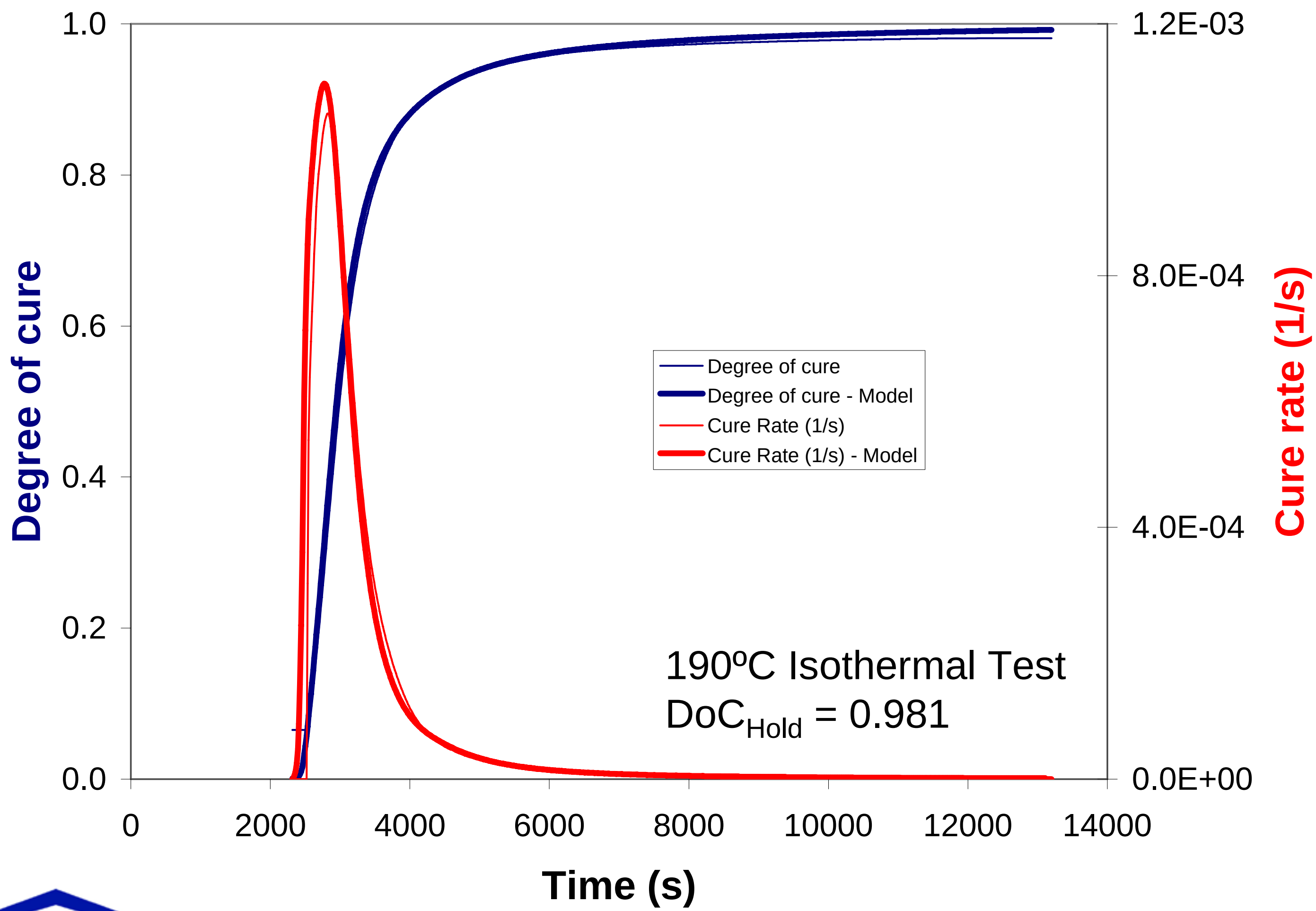
Isothermal Tests - 180ºC-1



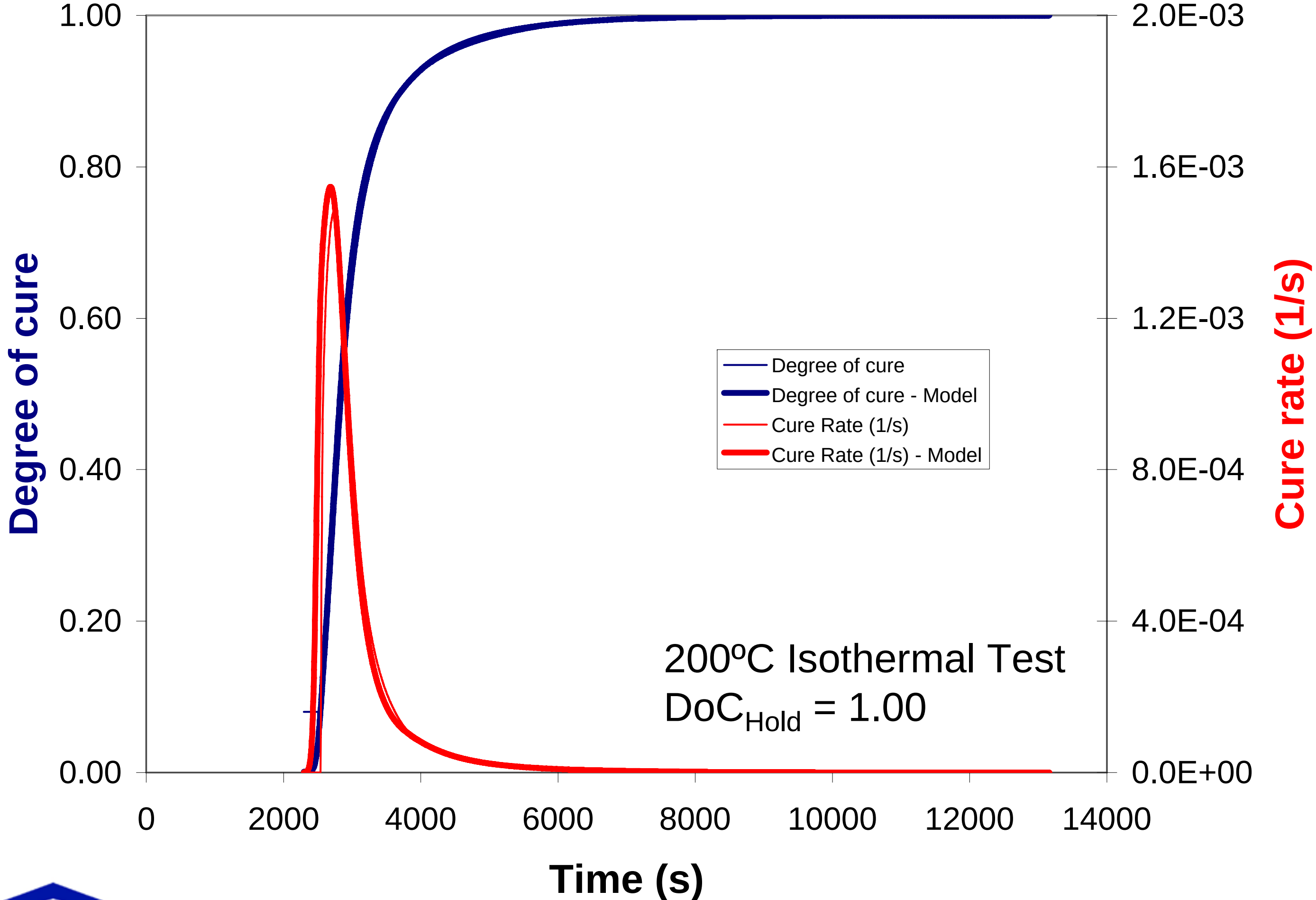
Isothermal Tests - 180ºC-4



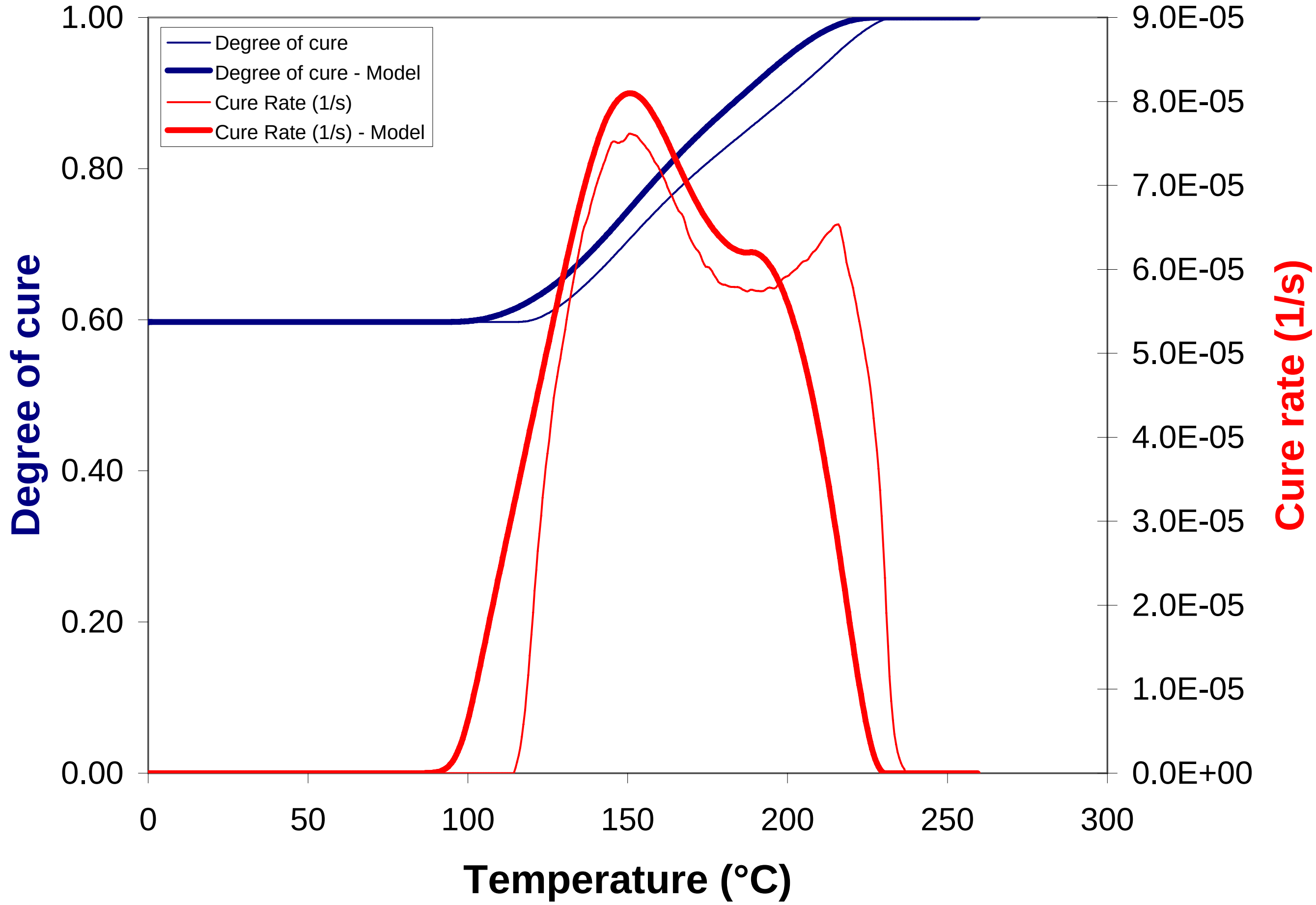
Isothermal Tests – 190ºC



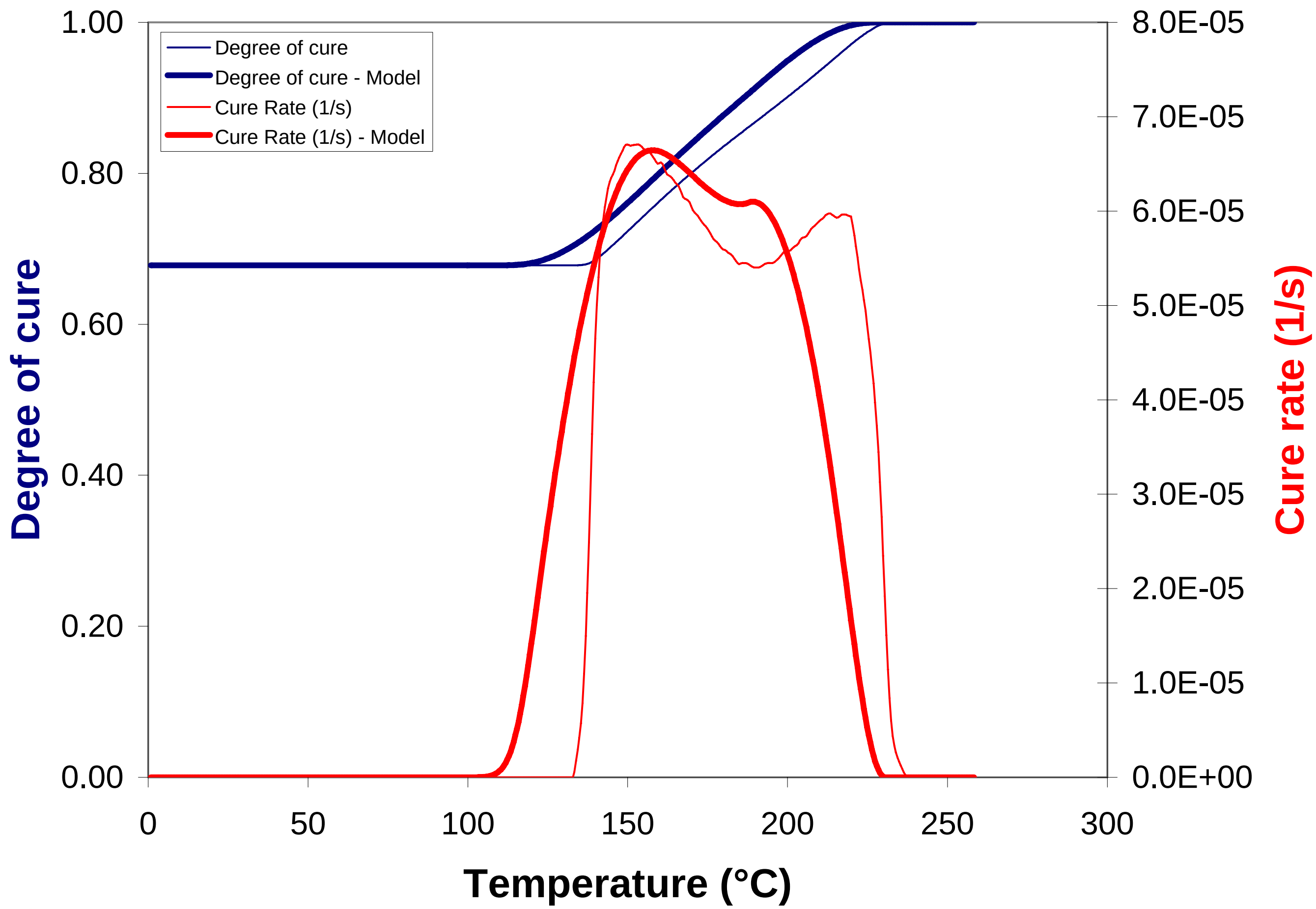
Isothermal Tests - 200ºC



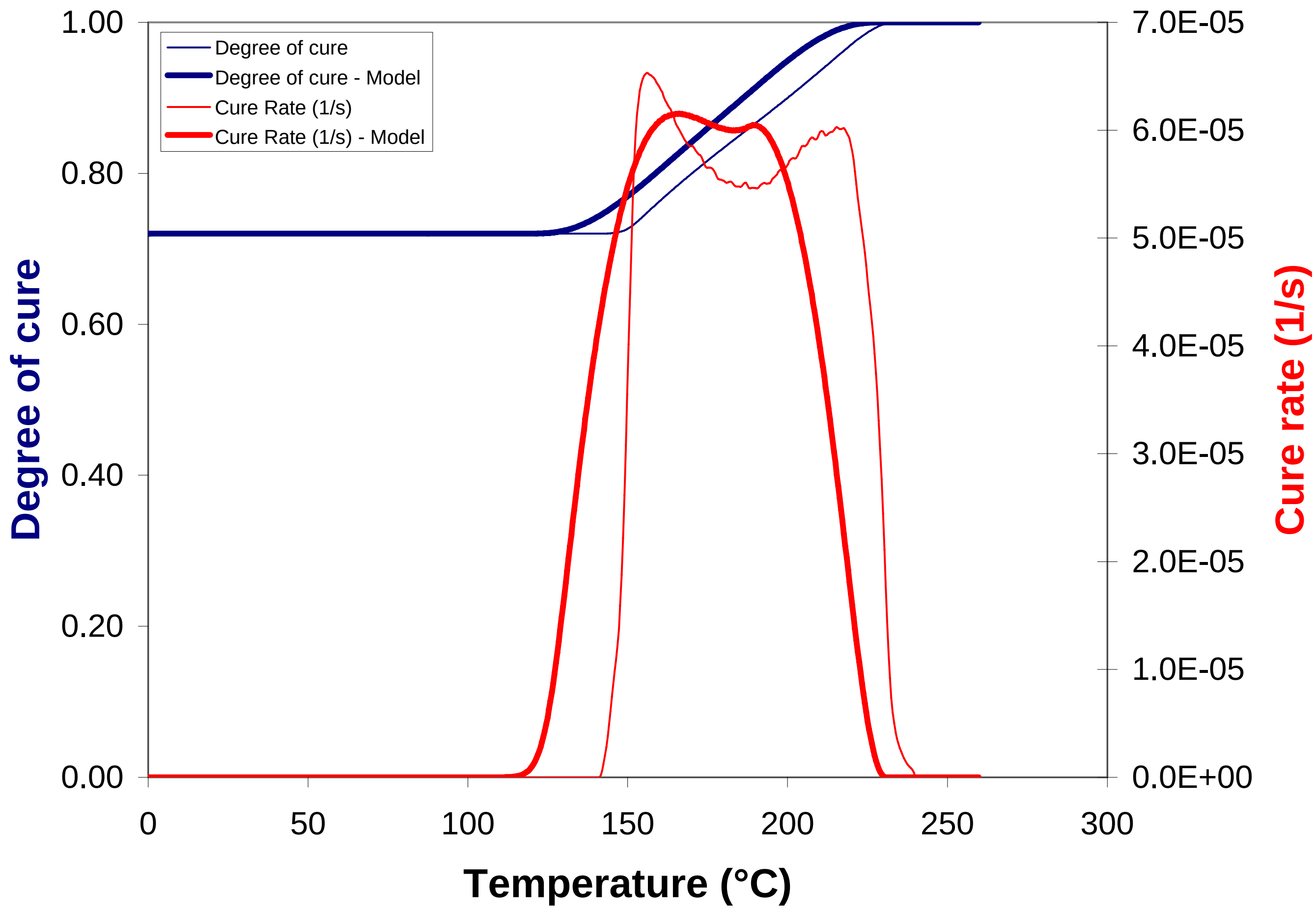
Isothermal Tests - 100ºC-R



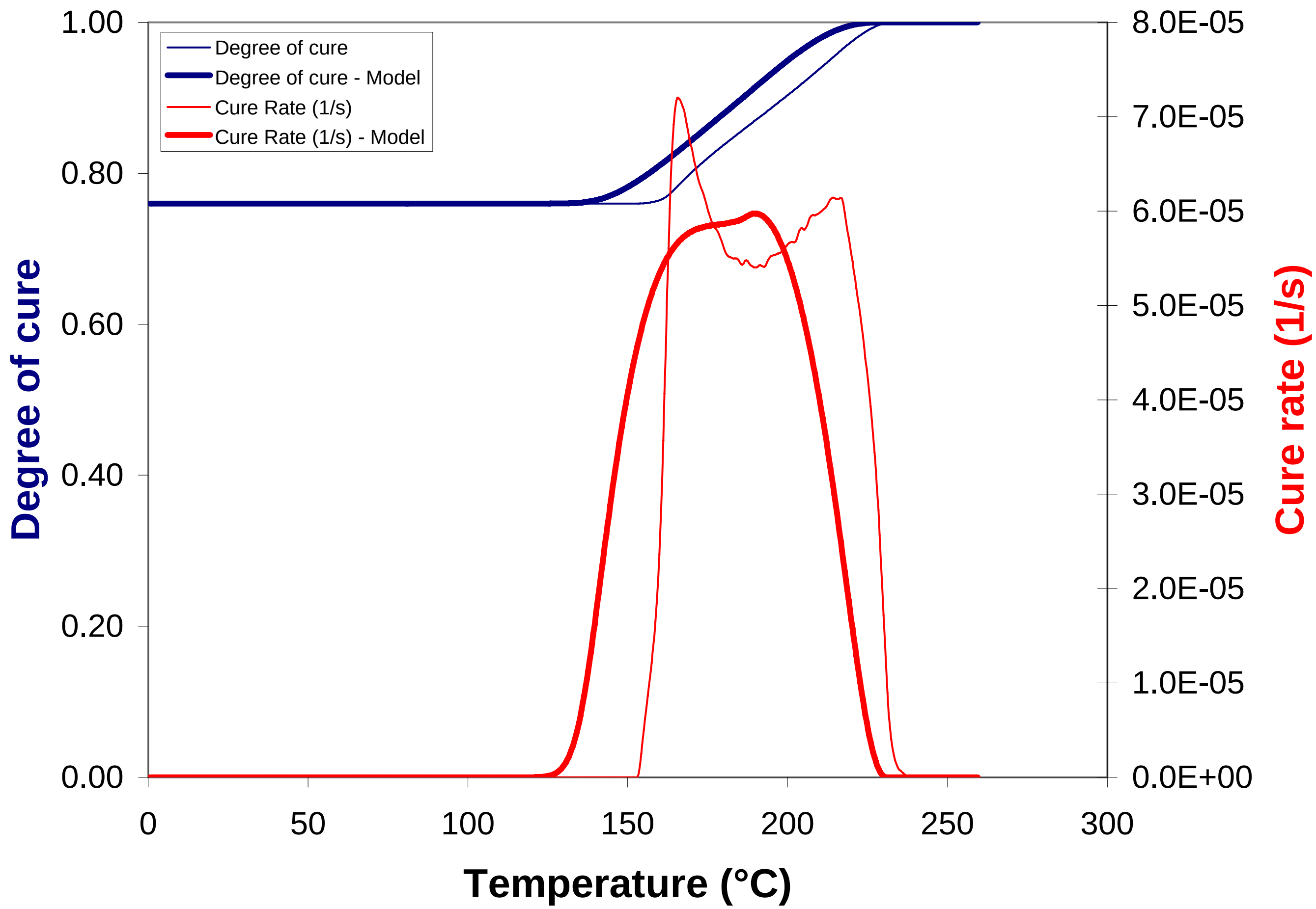
Isothermal Tests - 110ºC-R



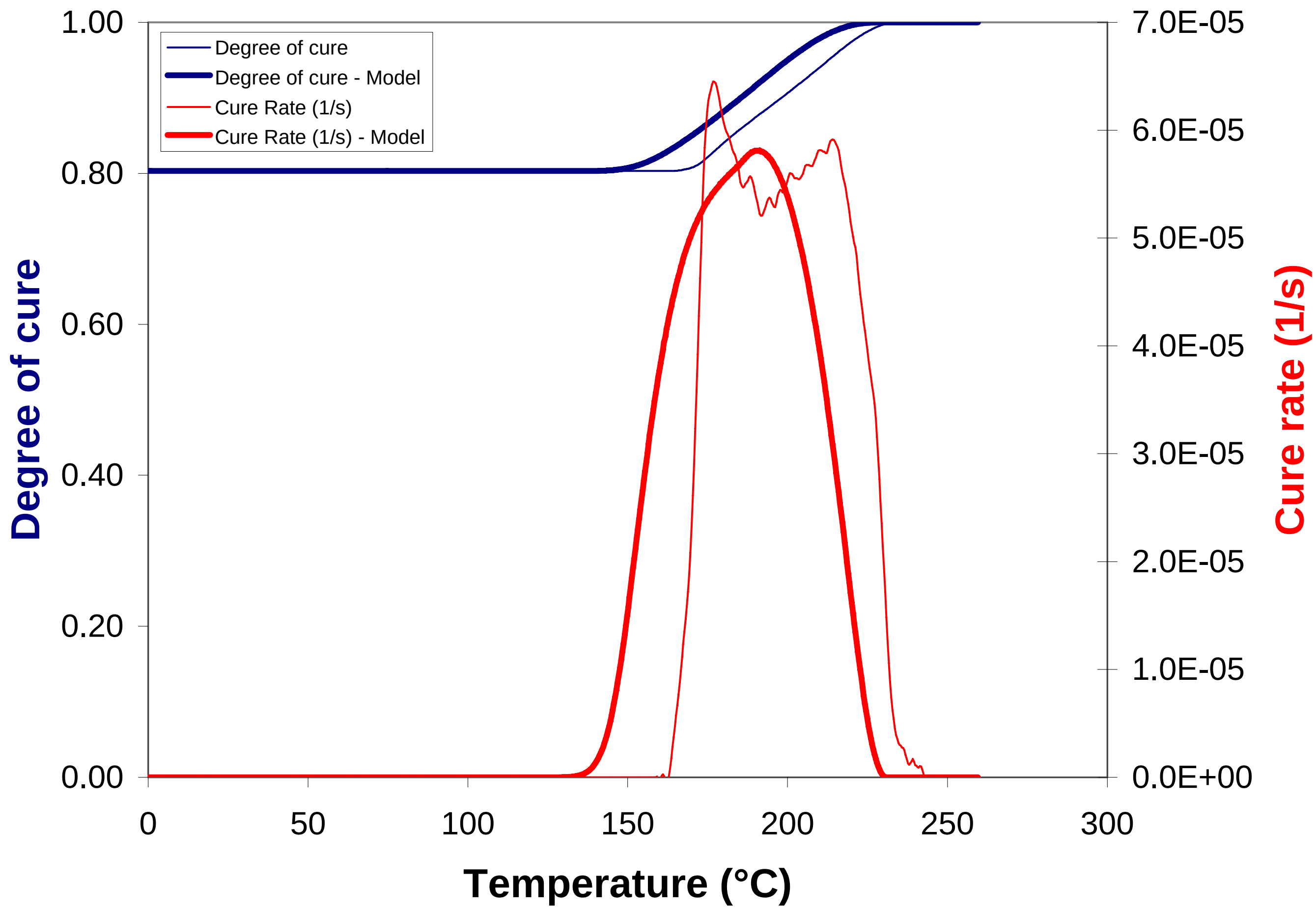
Isothermal Tests - 120ºC-R



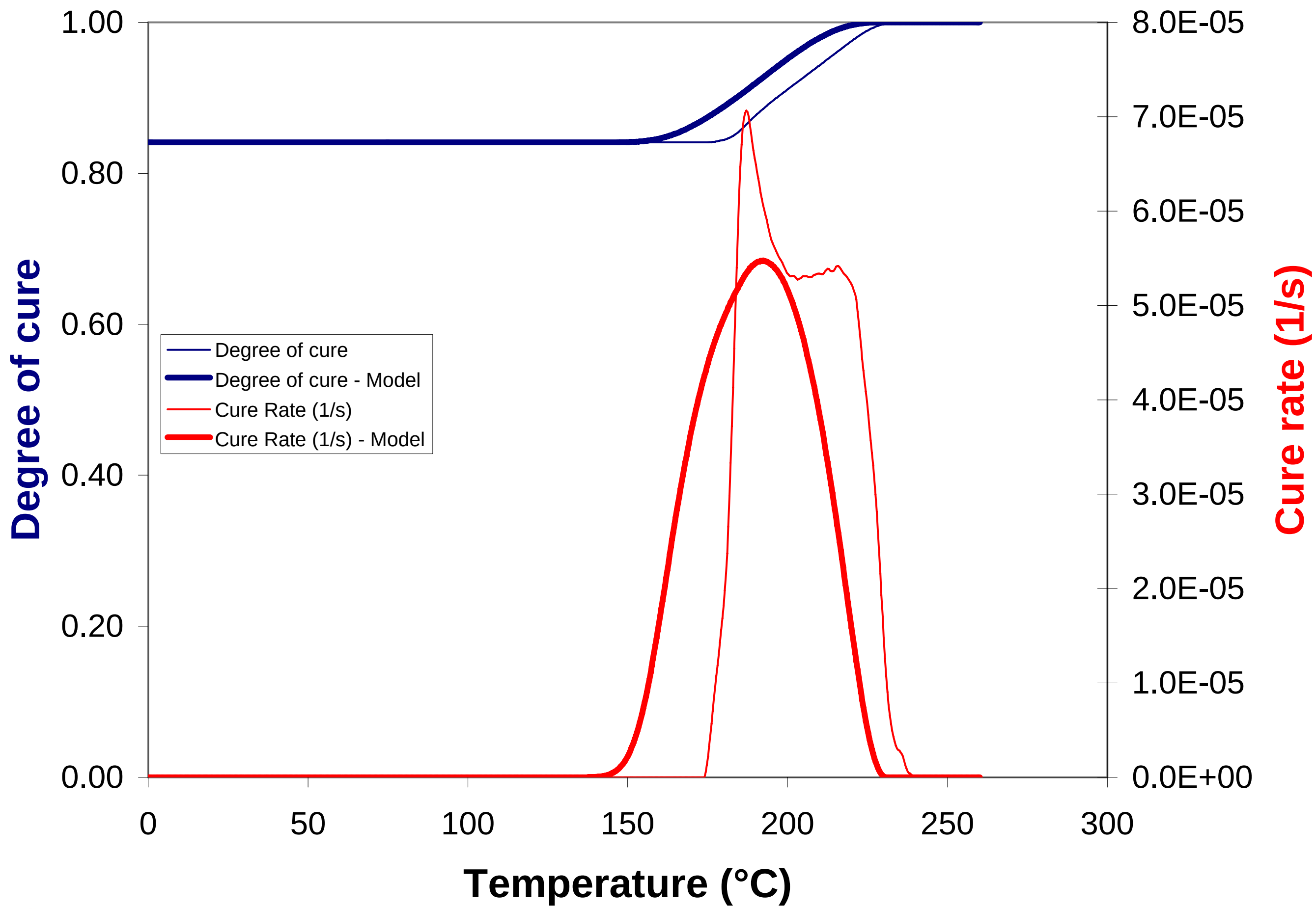
Isothermal Tests - 130ºC-R



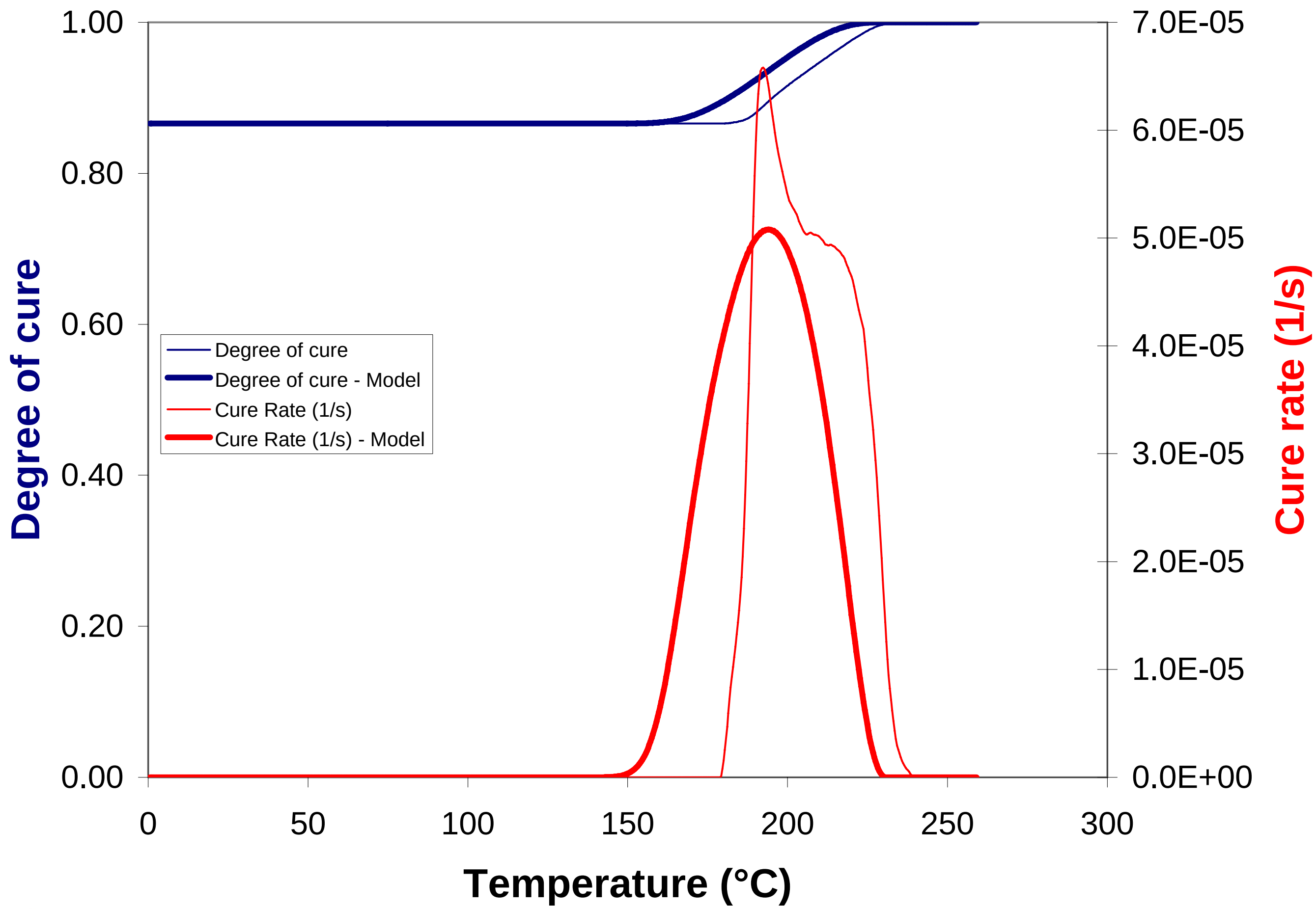
Isothermal Tests - 140ºC-R



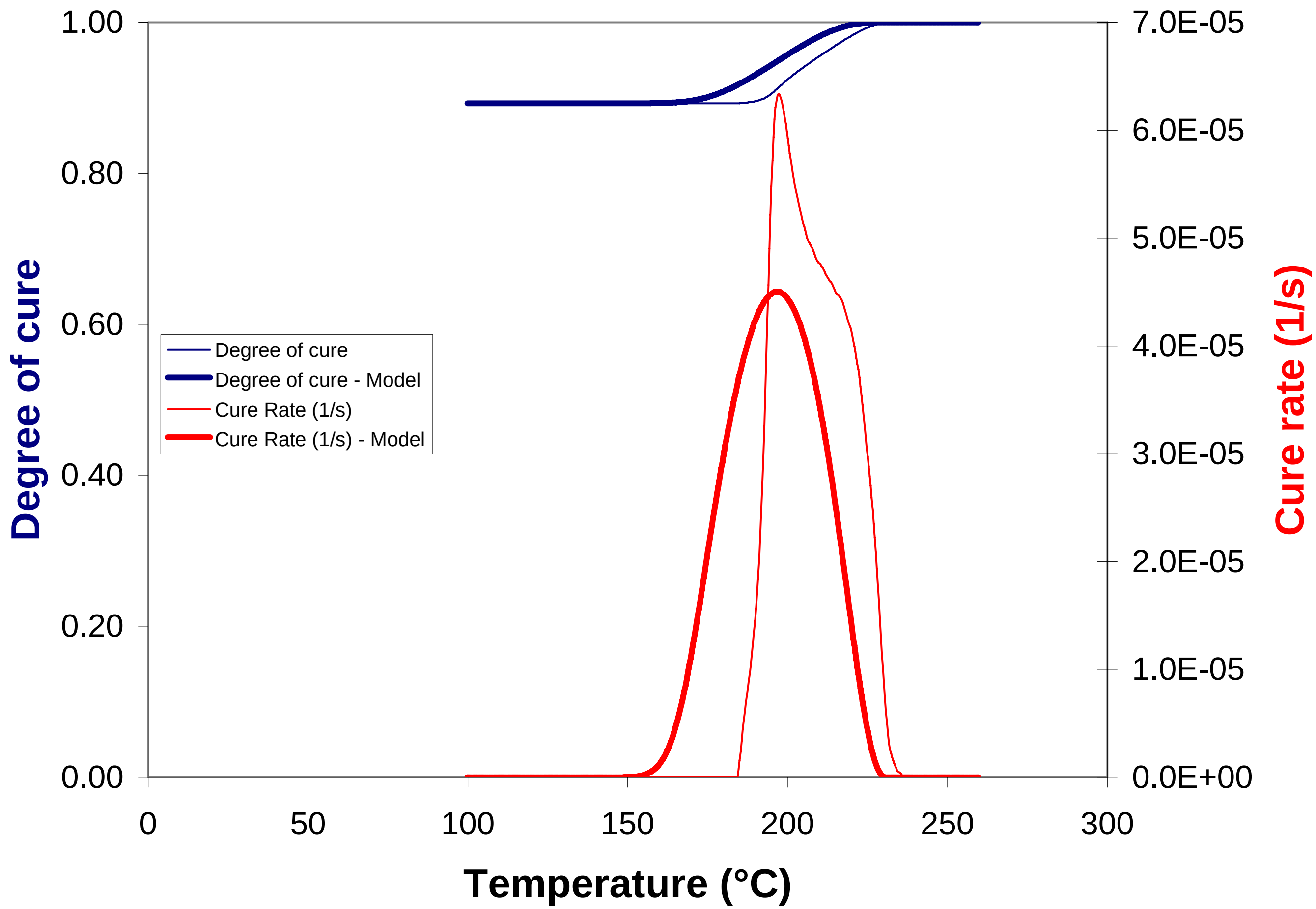
Isothermal Tests - 150ºC-R



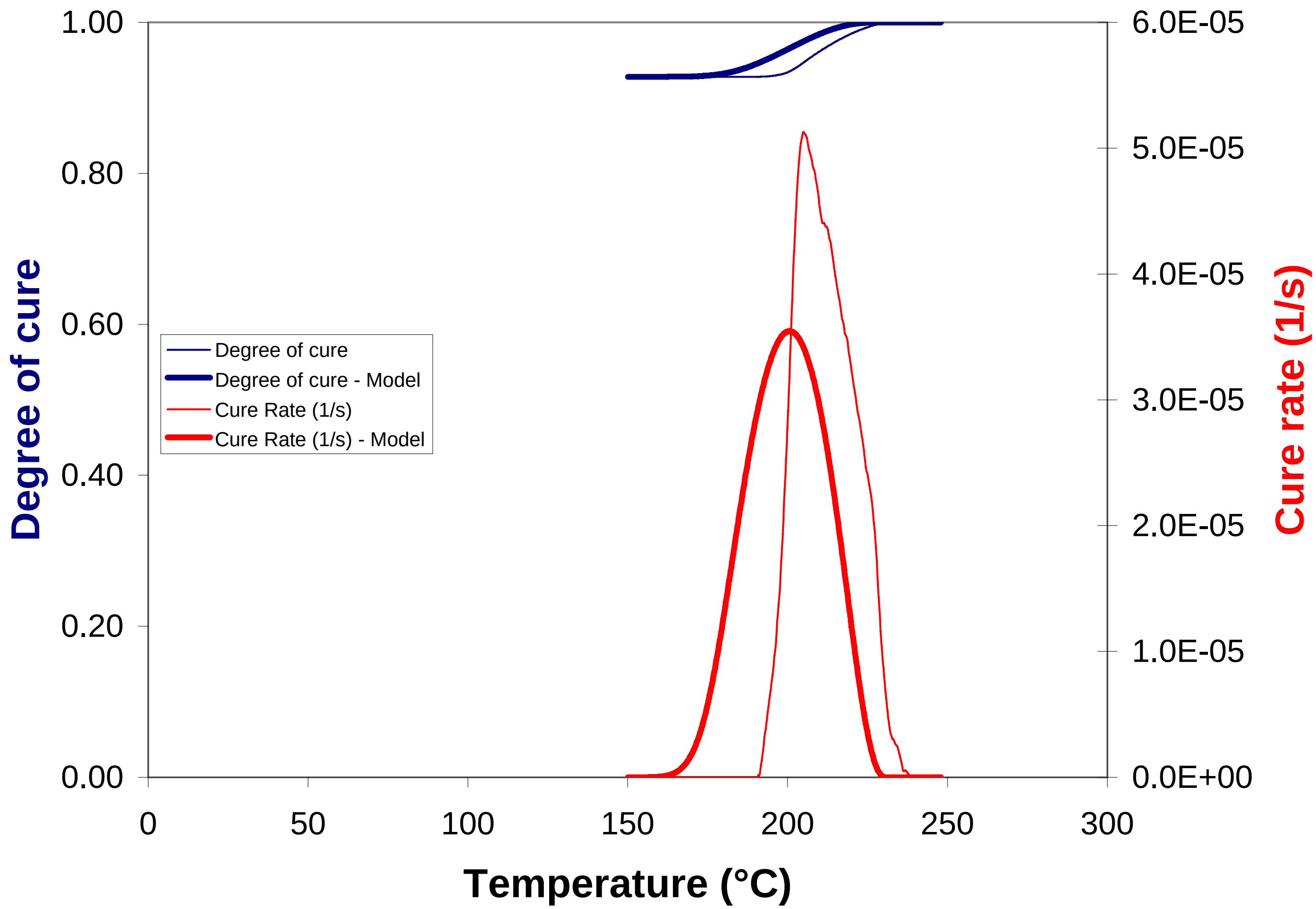
Isothermal Tests - 155ºC-R



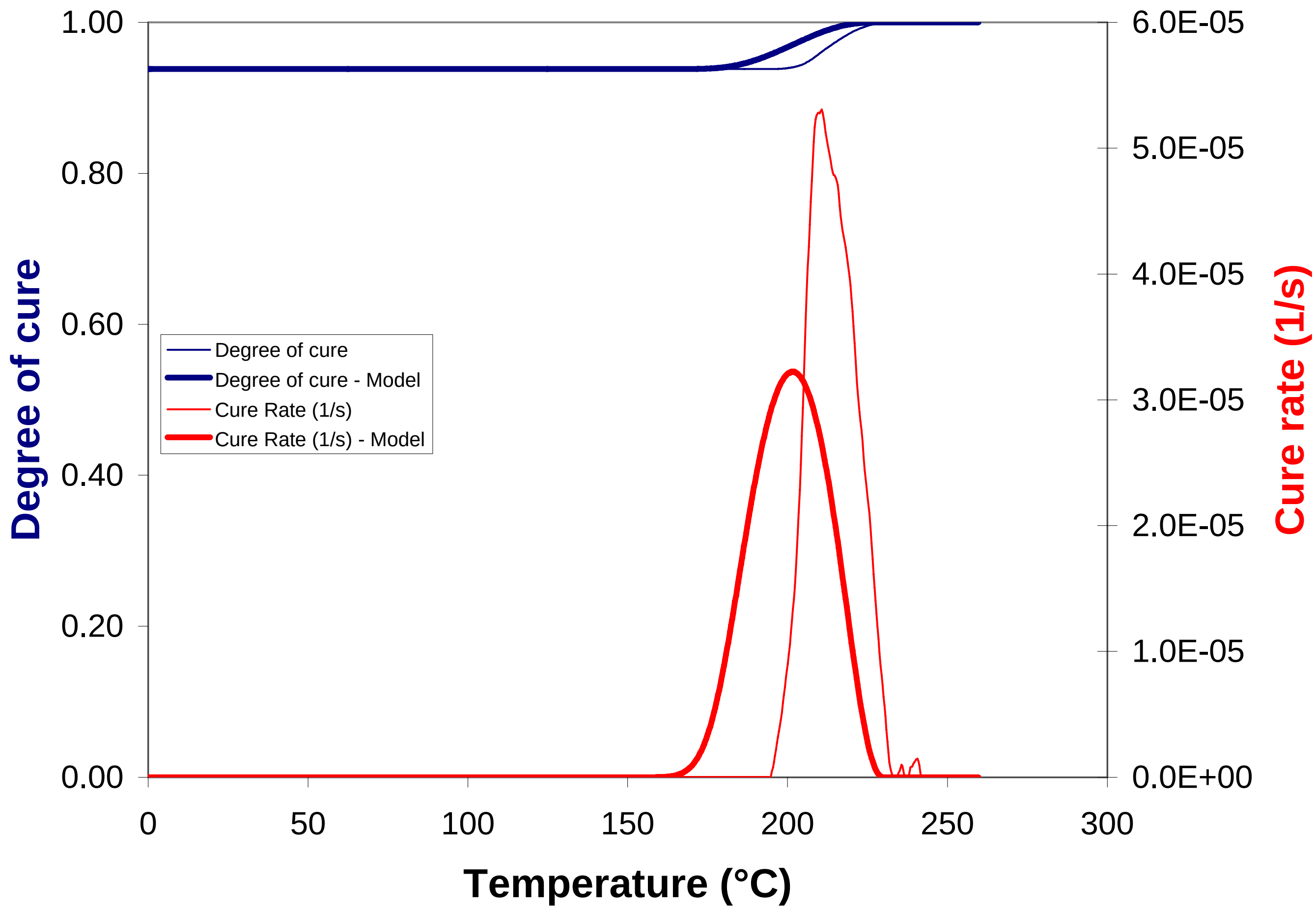
Isothermal Tests - 160ºC-R



Isothermal Tests - 170ºC-R



Isothermal Tests - 175ºC-R



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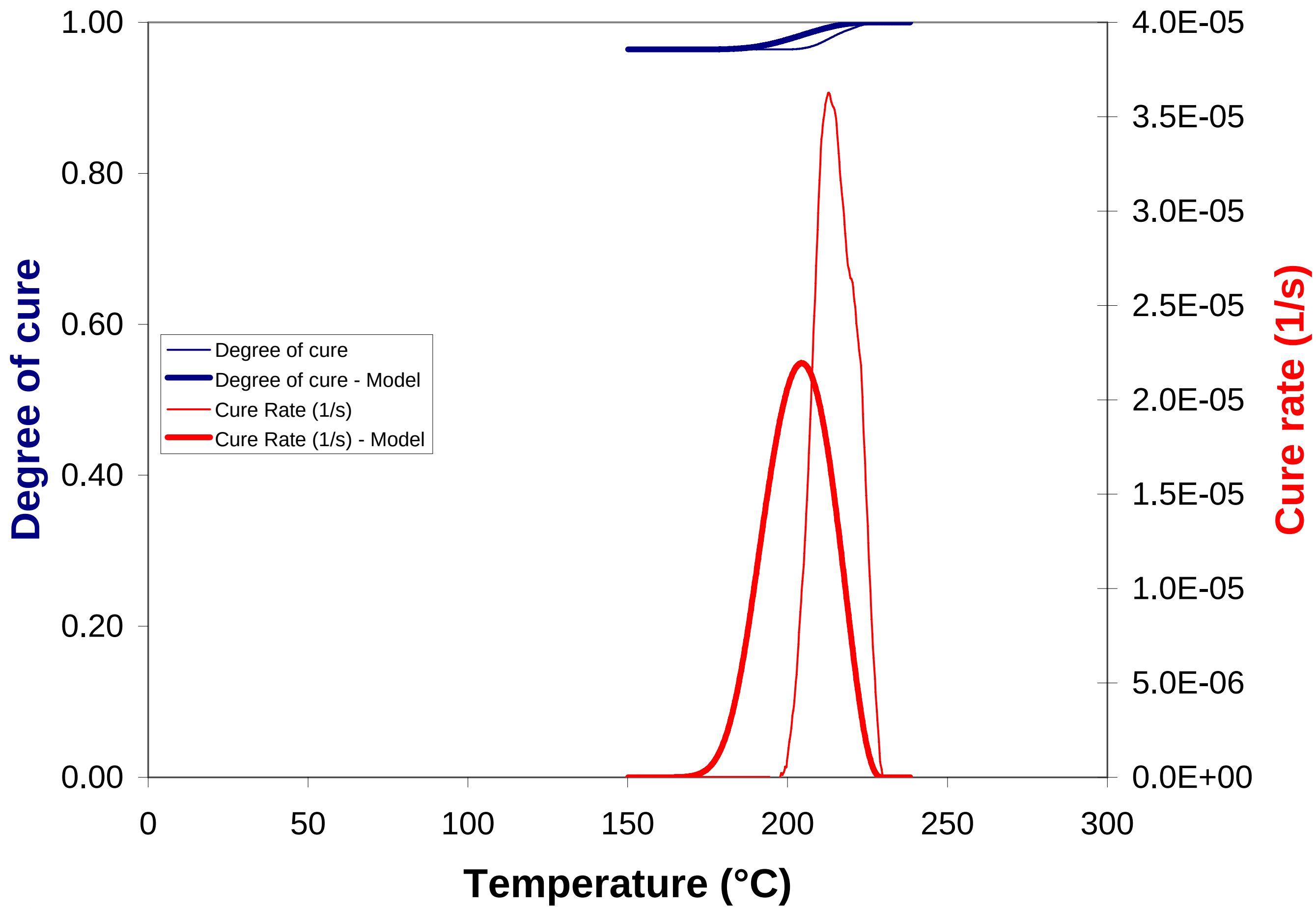
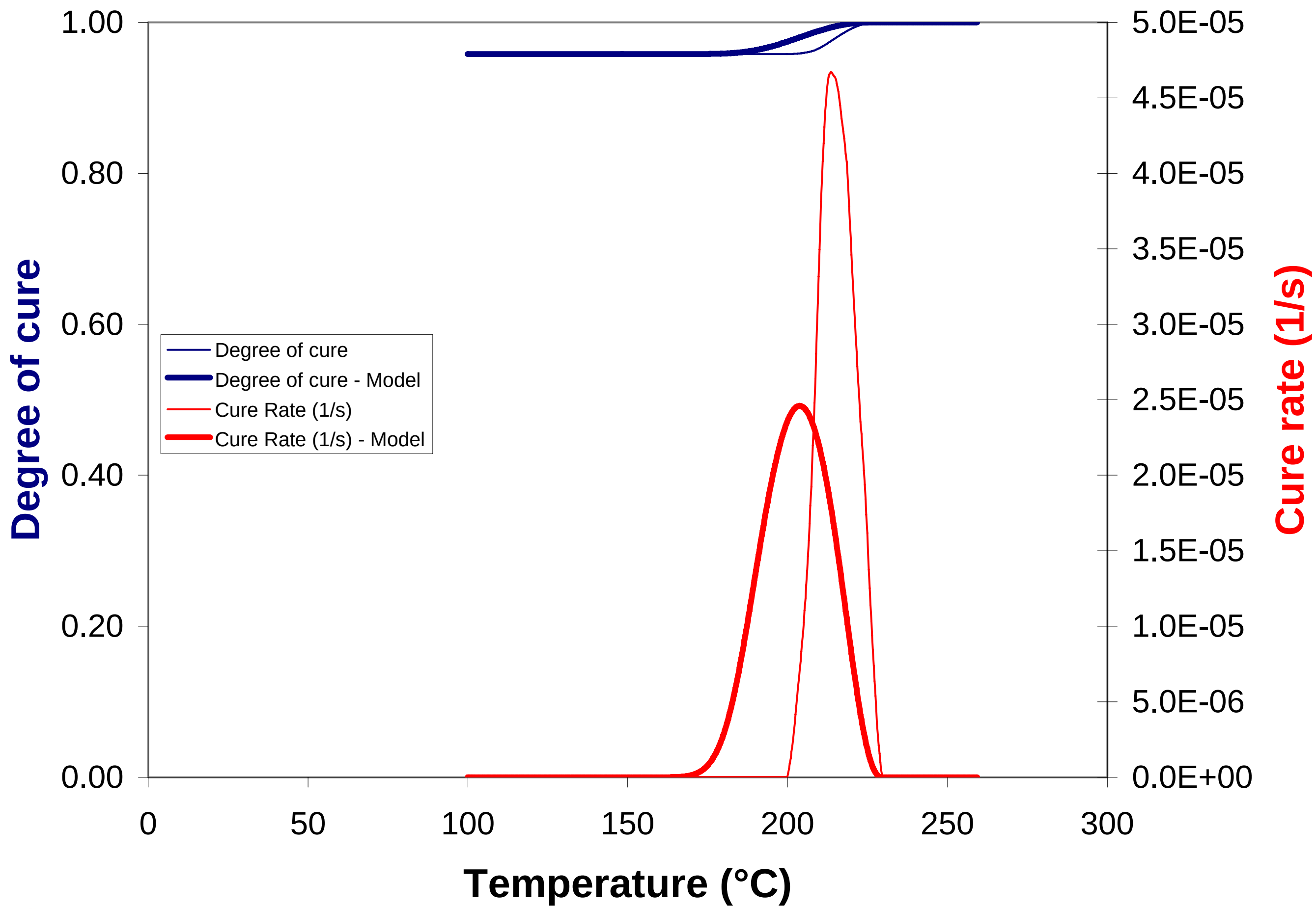
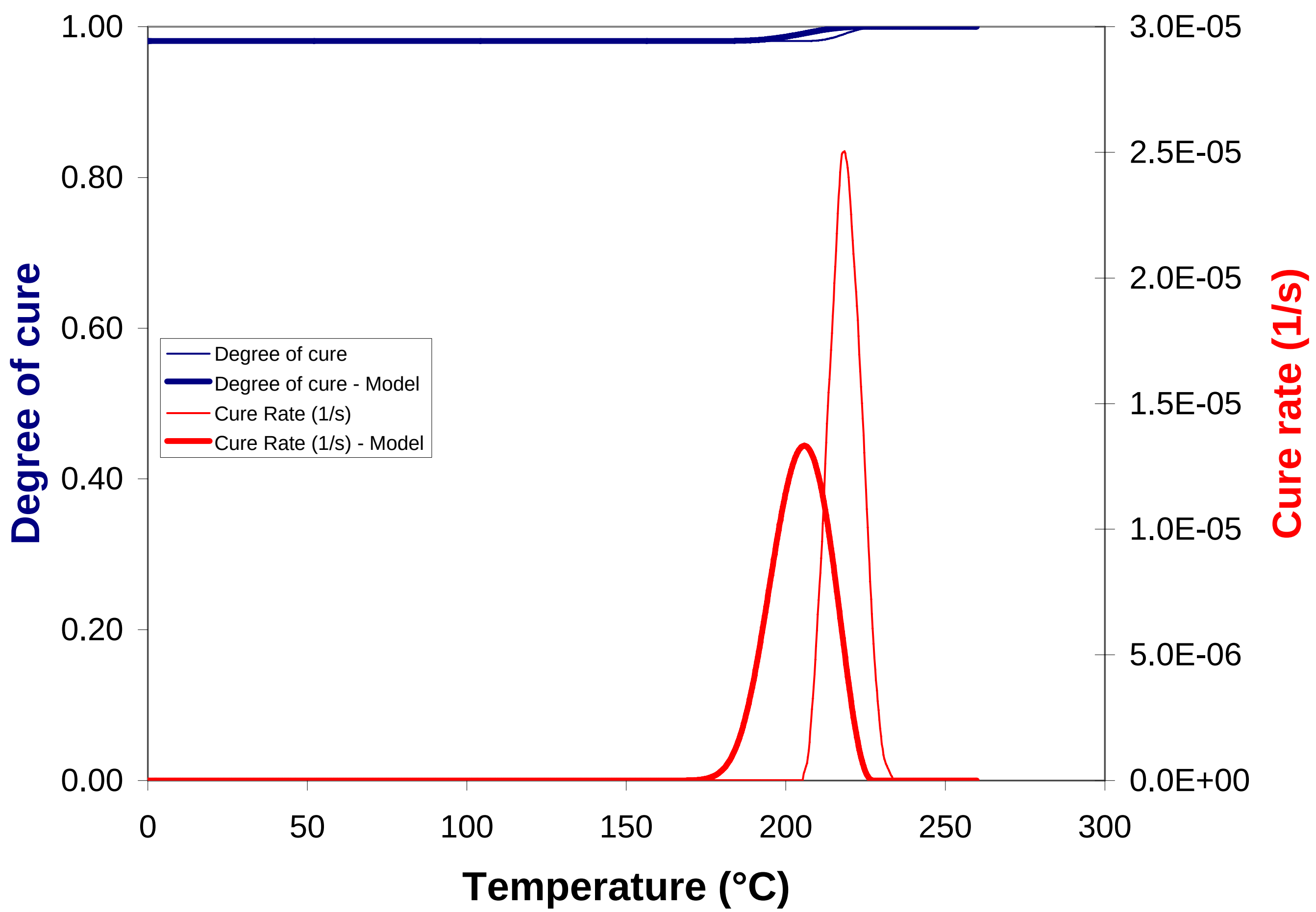
Isothermal Tests - 180ºC-R-1



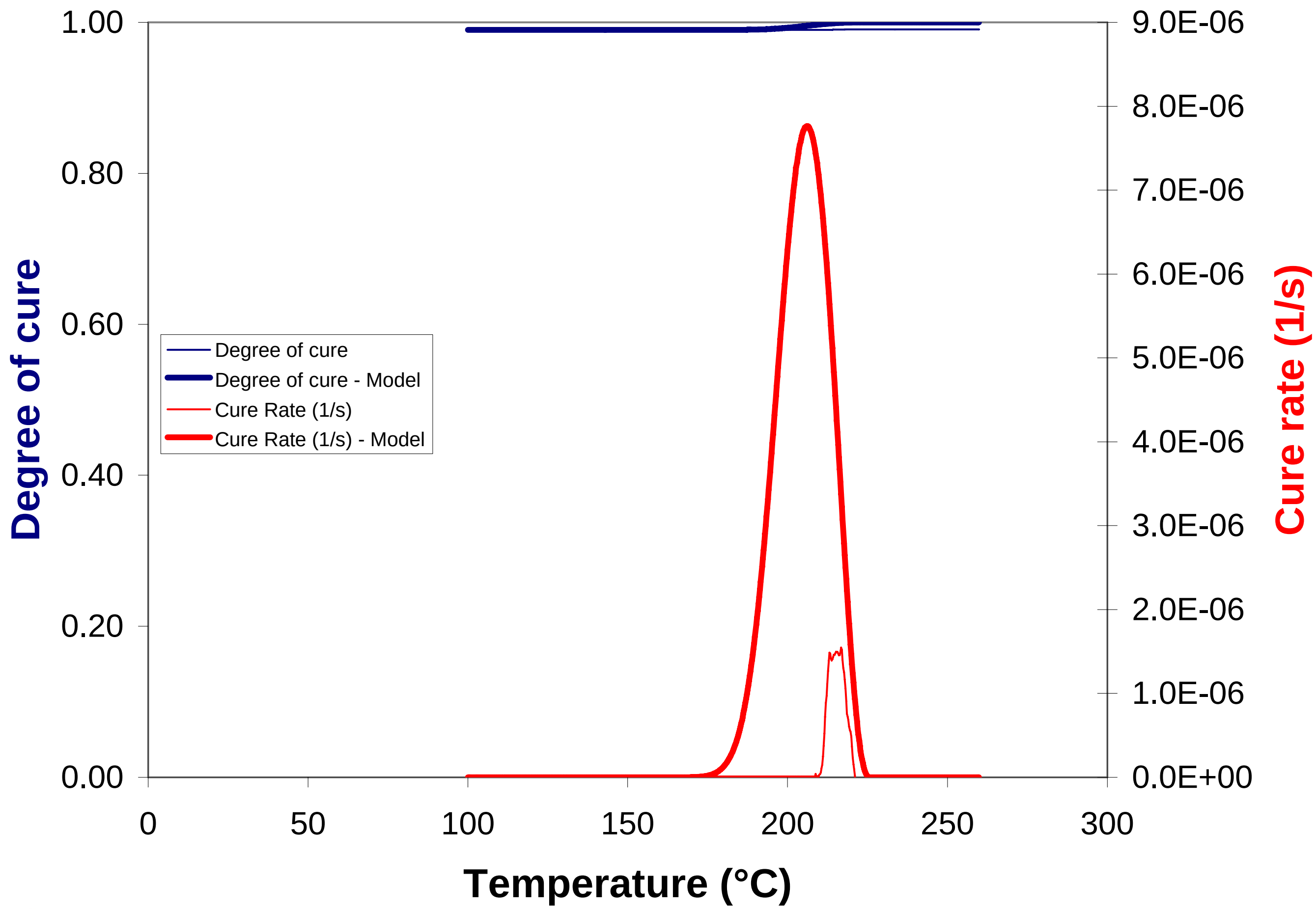
Isothermal Tests - 180ºC-R-4



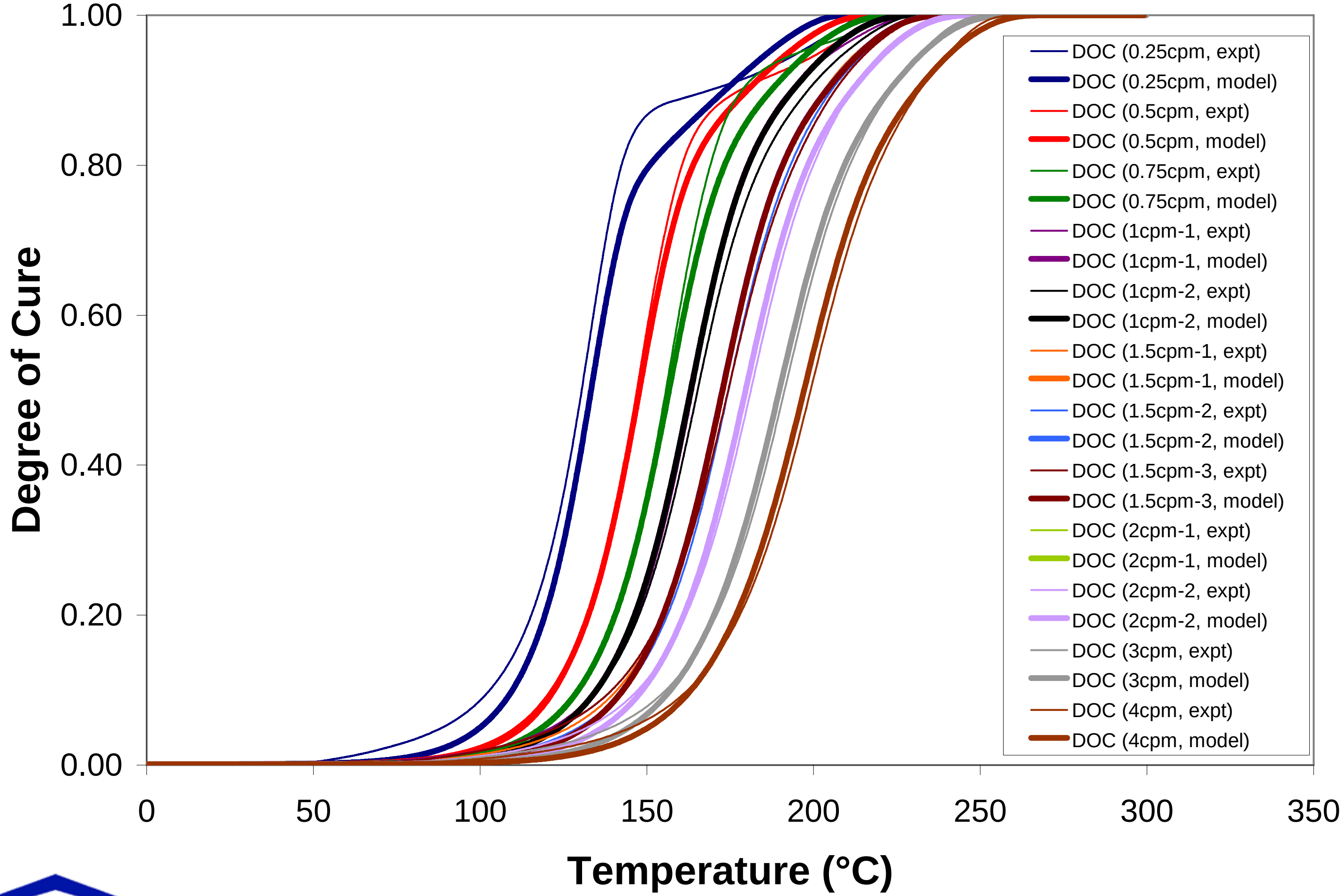
Isothermal Tests - 190ºC-R



Isothermal Tests - 200ºC-R



Dynamic Tests – All



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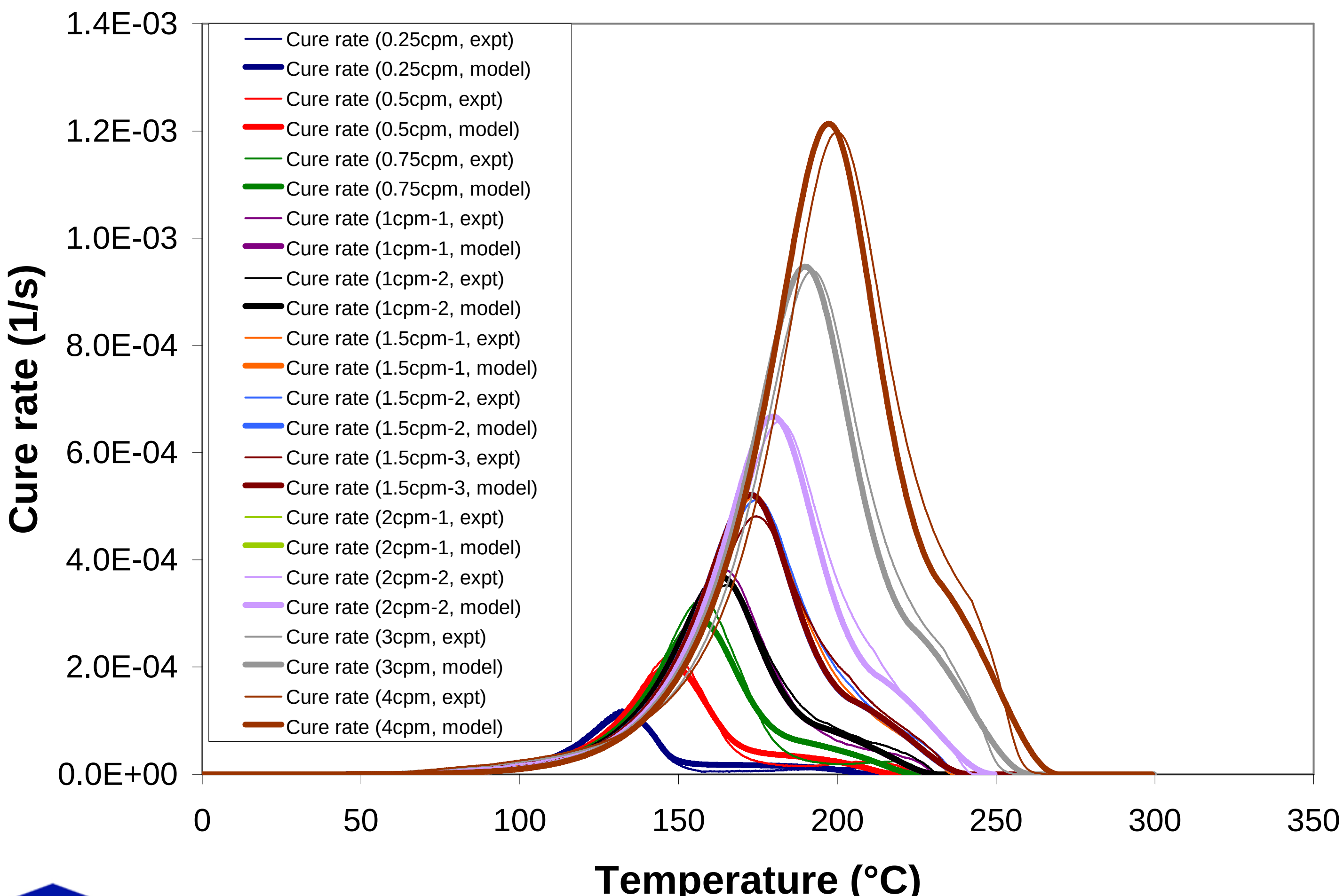
Dynamic Tests – All



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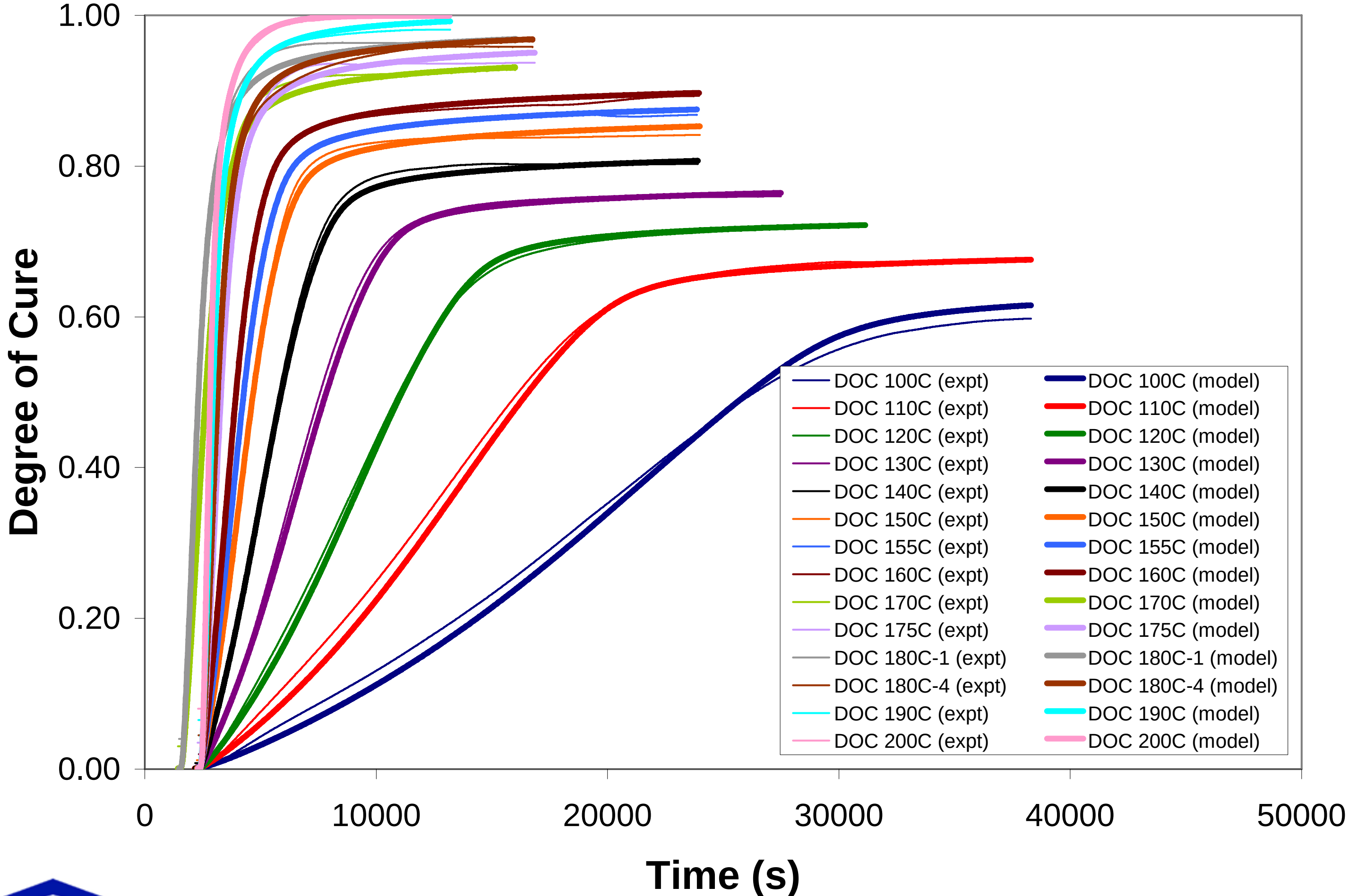
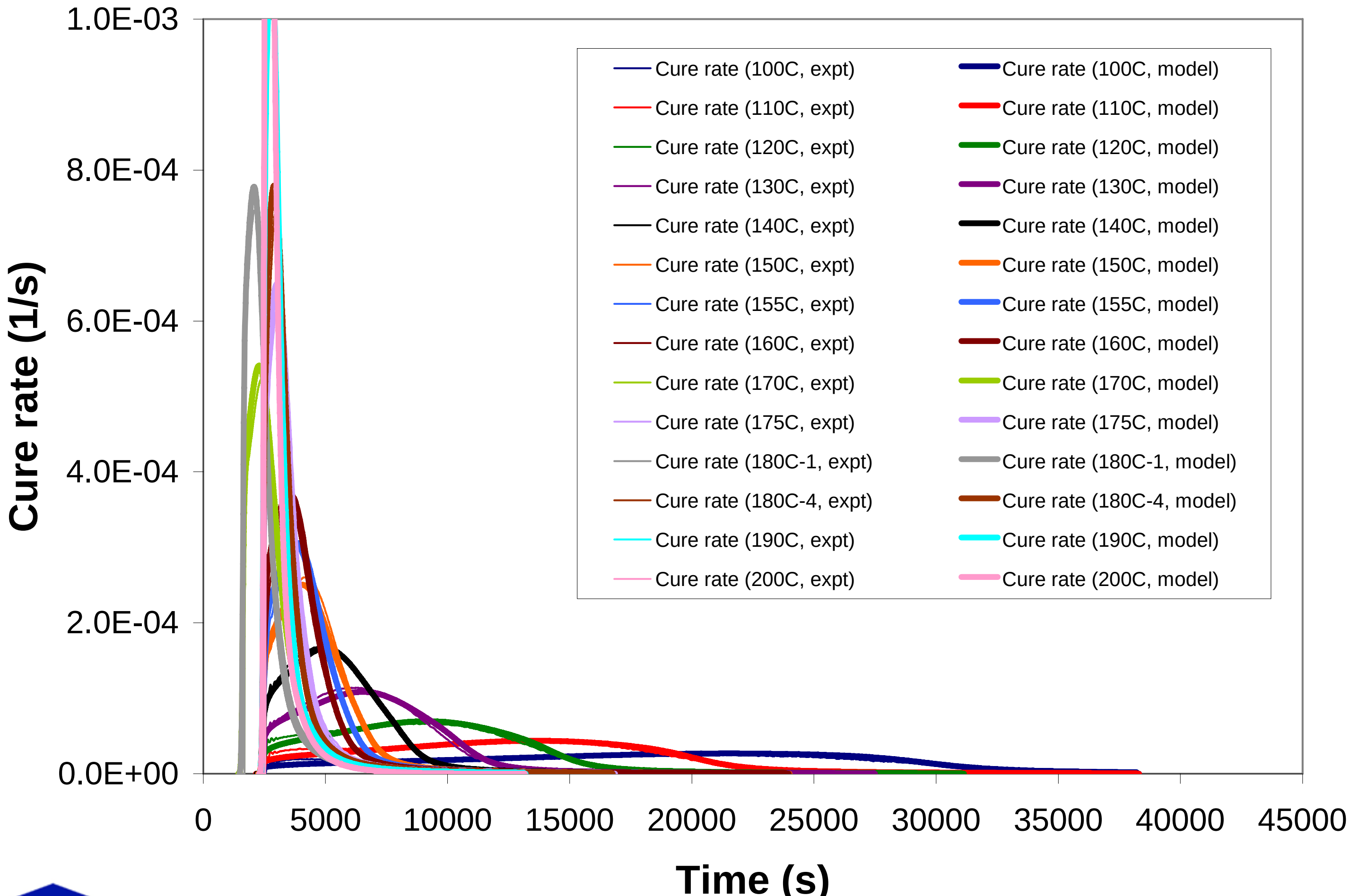
Isothermal Tests – All

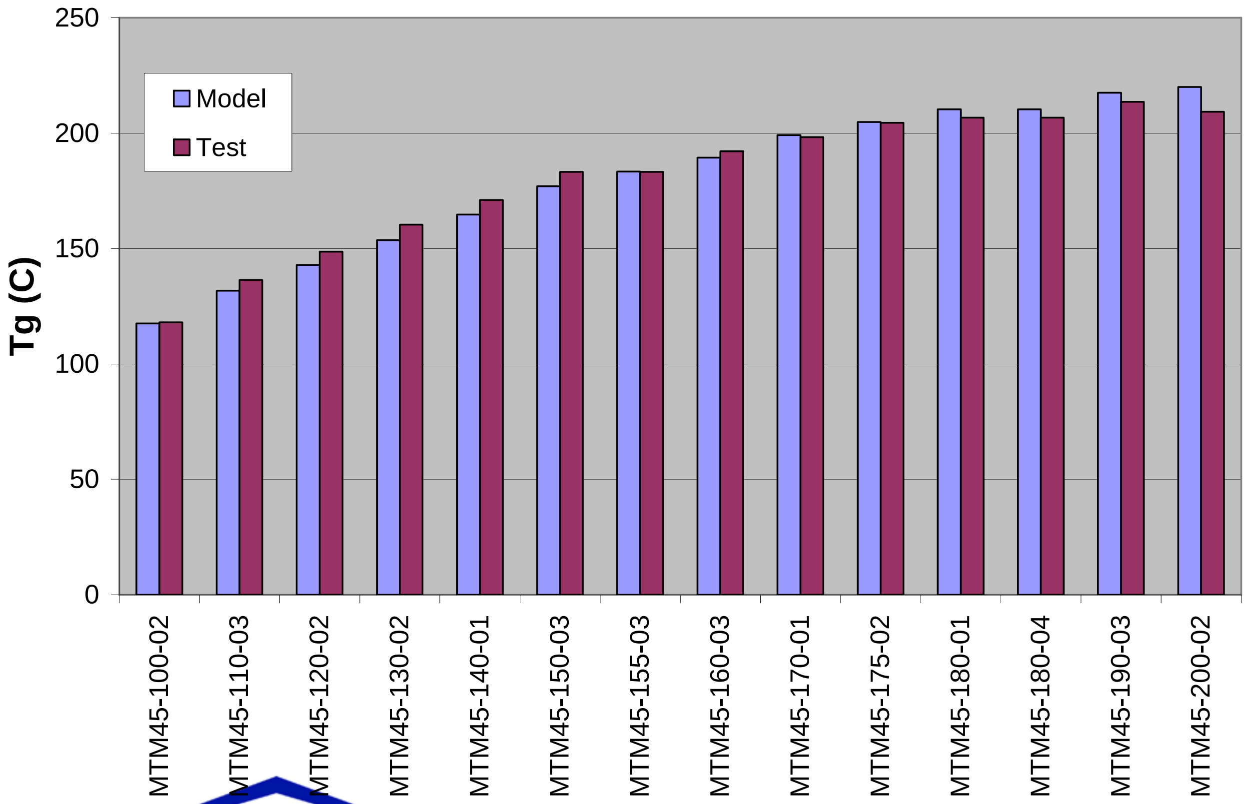


Isothermal Tests – All



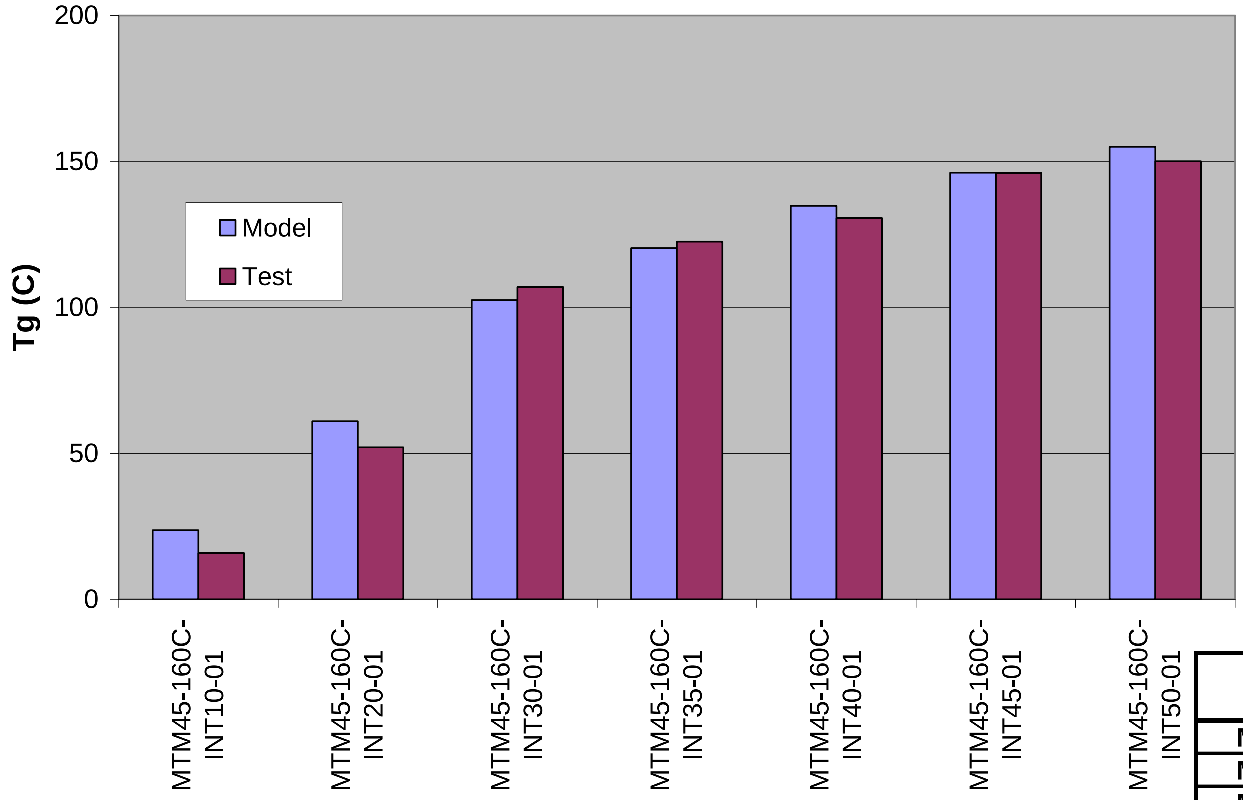
Post-Hold Tg - Isos

Tg values at the end of the hold segment of the isothermal tests were compared to the predictions of the cure kinetics model. Good agreement was observed.



Test	Post-Hold Tg (°C)	
	Test	Model
MTM45-100-02	118.0	117.6
MTM45-110-03	136.4	131.8
MTM45-120-02	148.7	142.9
MTM45-130-02	160.4	153.7
MTM45-140-01	171.1	164.7
MTM45-150-03	183.3	177.0
MTM45-155-03	183.3	183.3
MTM45-160-03	192.2	189.4
MTM45-170-01	198.2	199.2
MTM45-175-02	204.5	204.9
MTM45-180-01	206.7	210.3
MTM45-180-04	206.6	210.3
MTM45-190-03	213.6	217.5
MTM45-200-02	209.3	220.0

Post-Hold Tg - Ints



Test	Post-Hold Tg (ºC)	
	Test	Model
MTM45-160C-INT10-01	15.8	23.7
MTM45-160C-INT20-01	52.1	61.1
MTM45-160C-INT30-01	107.0	102.5
MTM45-160C-INT35-01	122.6	120.3
MTM45-160C-INT40-01	130.6	134.8
MTM45-160C-INT45-01	146.0	146.2
MTM45-160C-INT50-01	150.1	155.0

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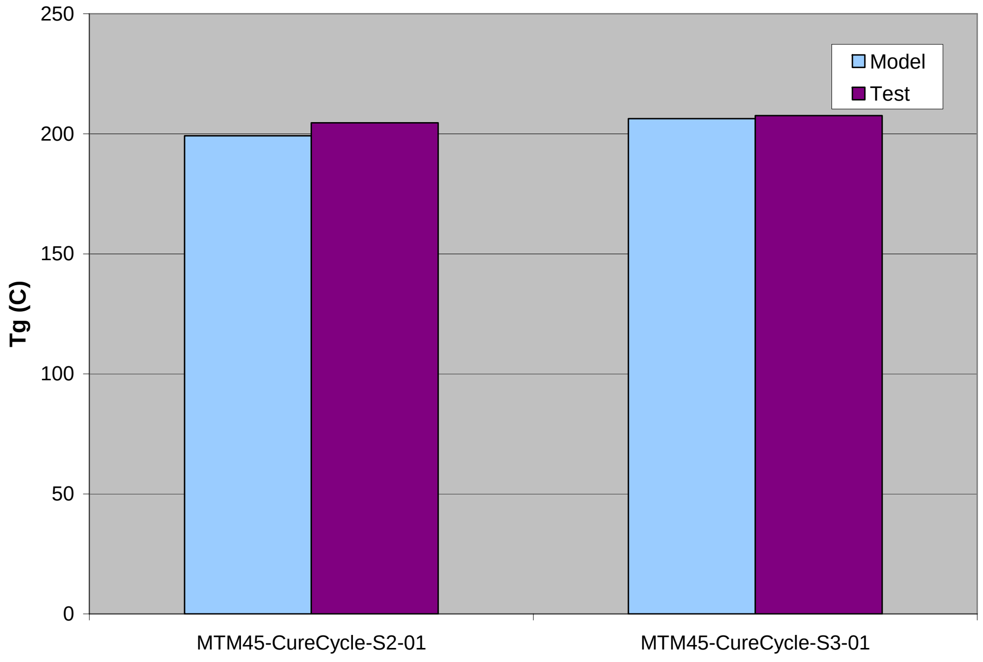
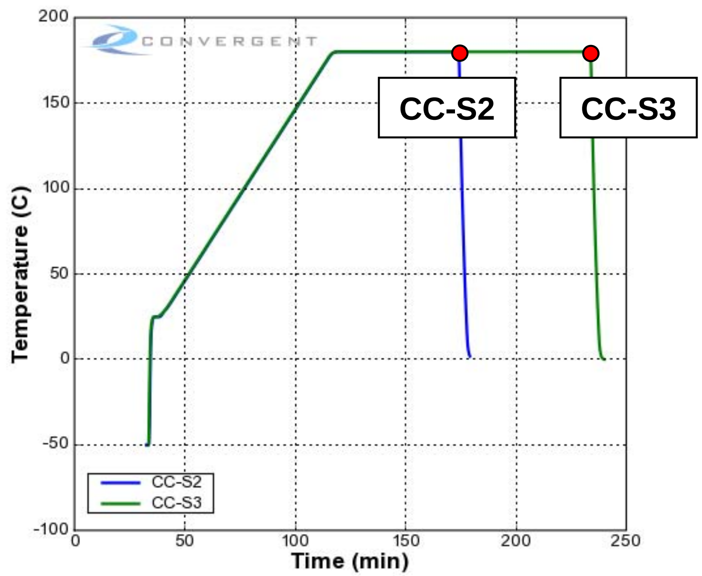
Post-Hold Tg – Cure Cycle



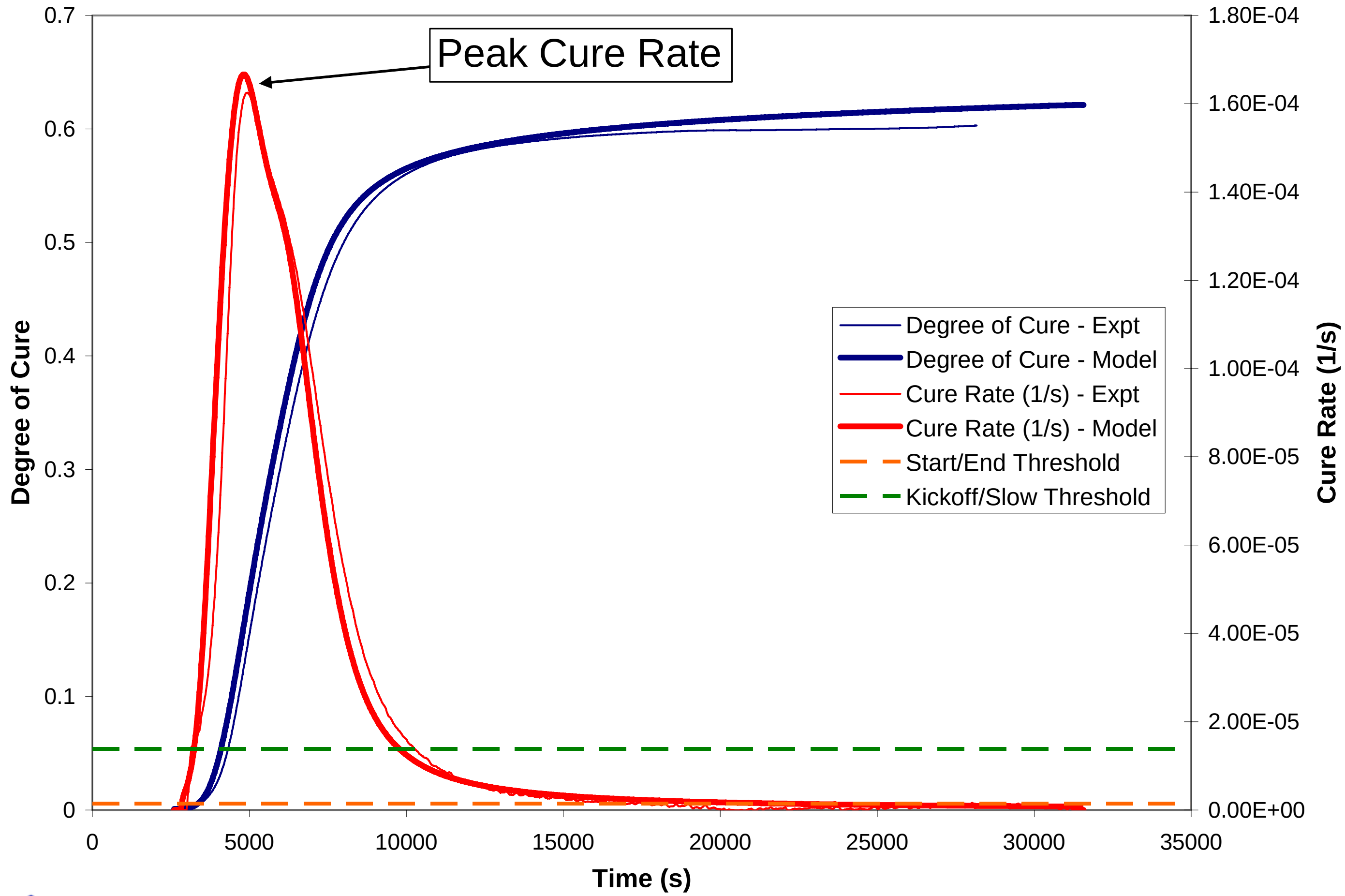


Test	Tg (ºC)	
	Test	Model
MTM45-CureCycle-S2-01	204.6	199.2
MTM45-CureCycle-S3-01	207.6	206.3

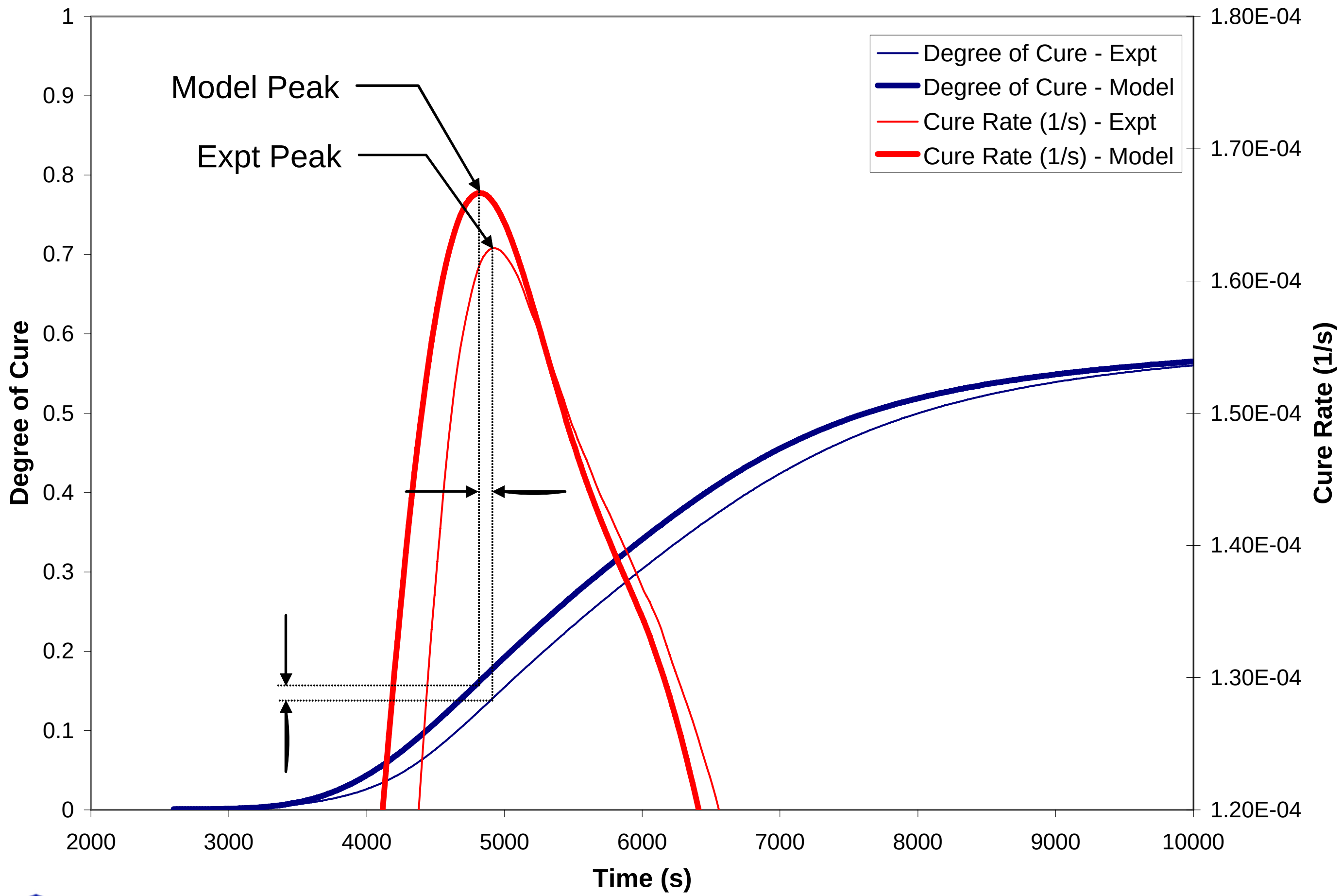
Goodness of Fit - Overview

- Goodness of fit is measured by comparing the test to the model prediction at several key points in the cure history.
- Both timing and DOC error are considered.

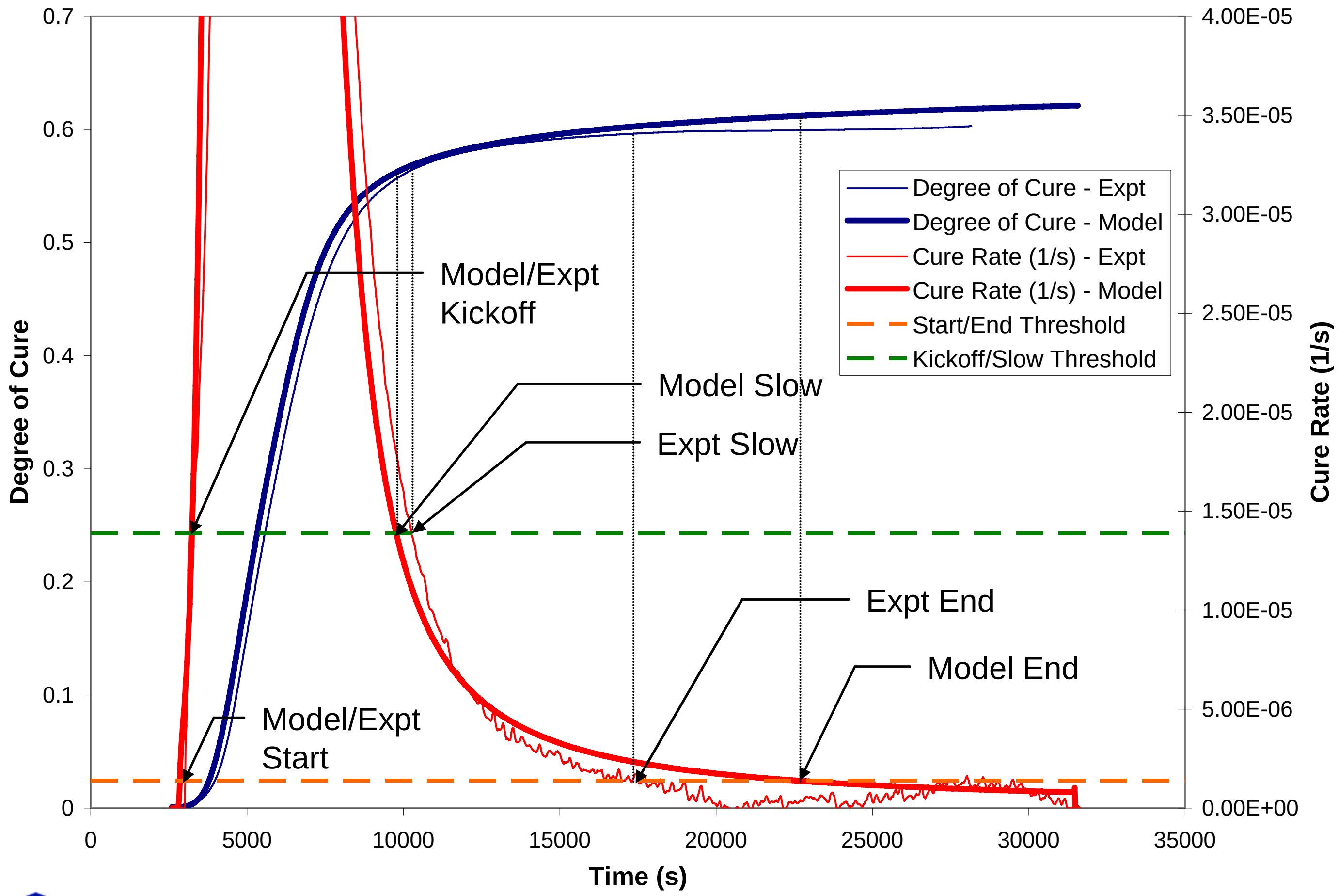
Goodness of Fit – Key Points



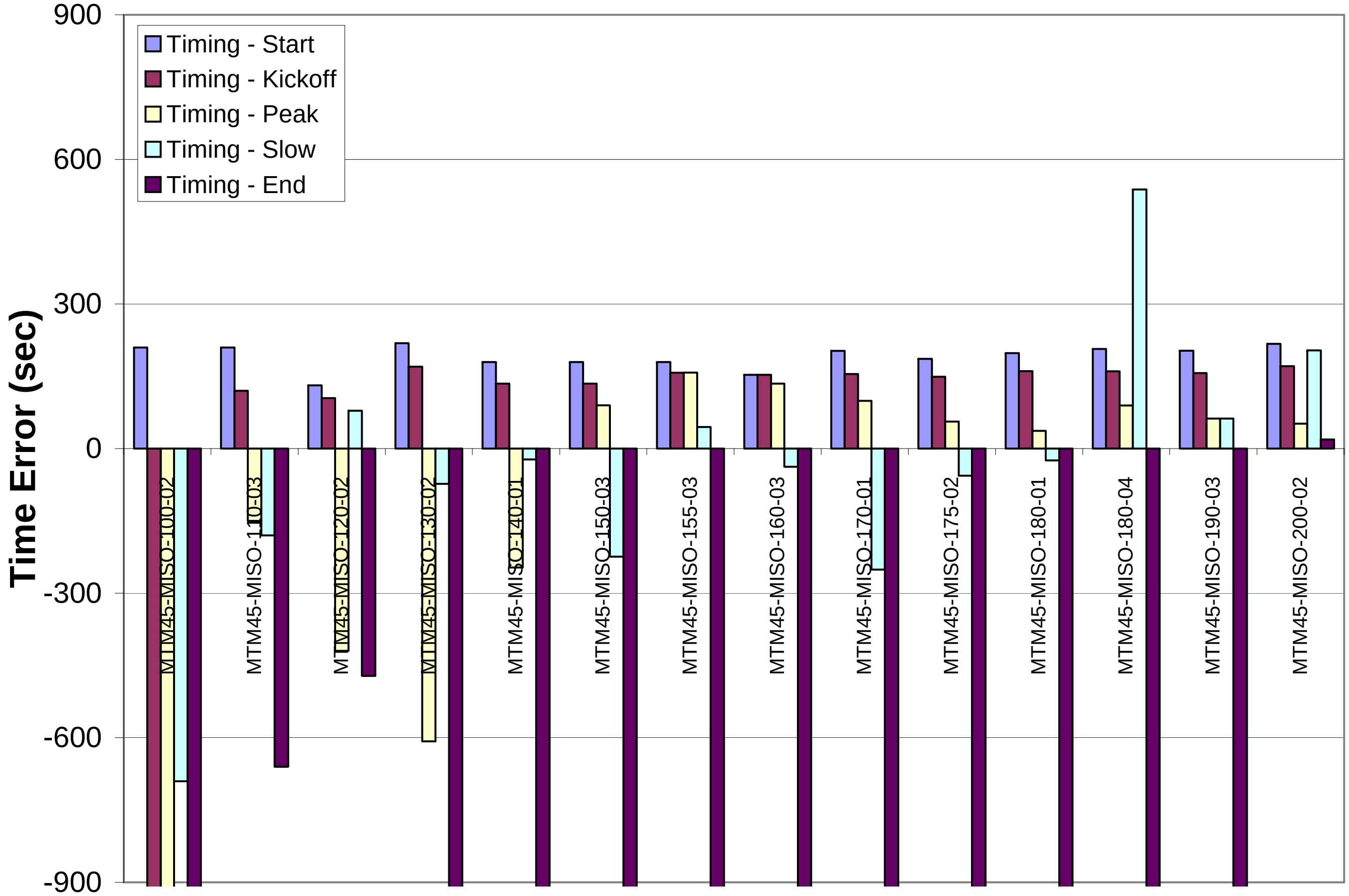
Goodness of Fit – Peak



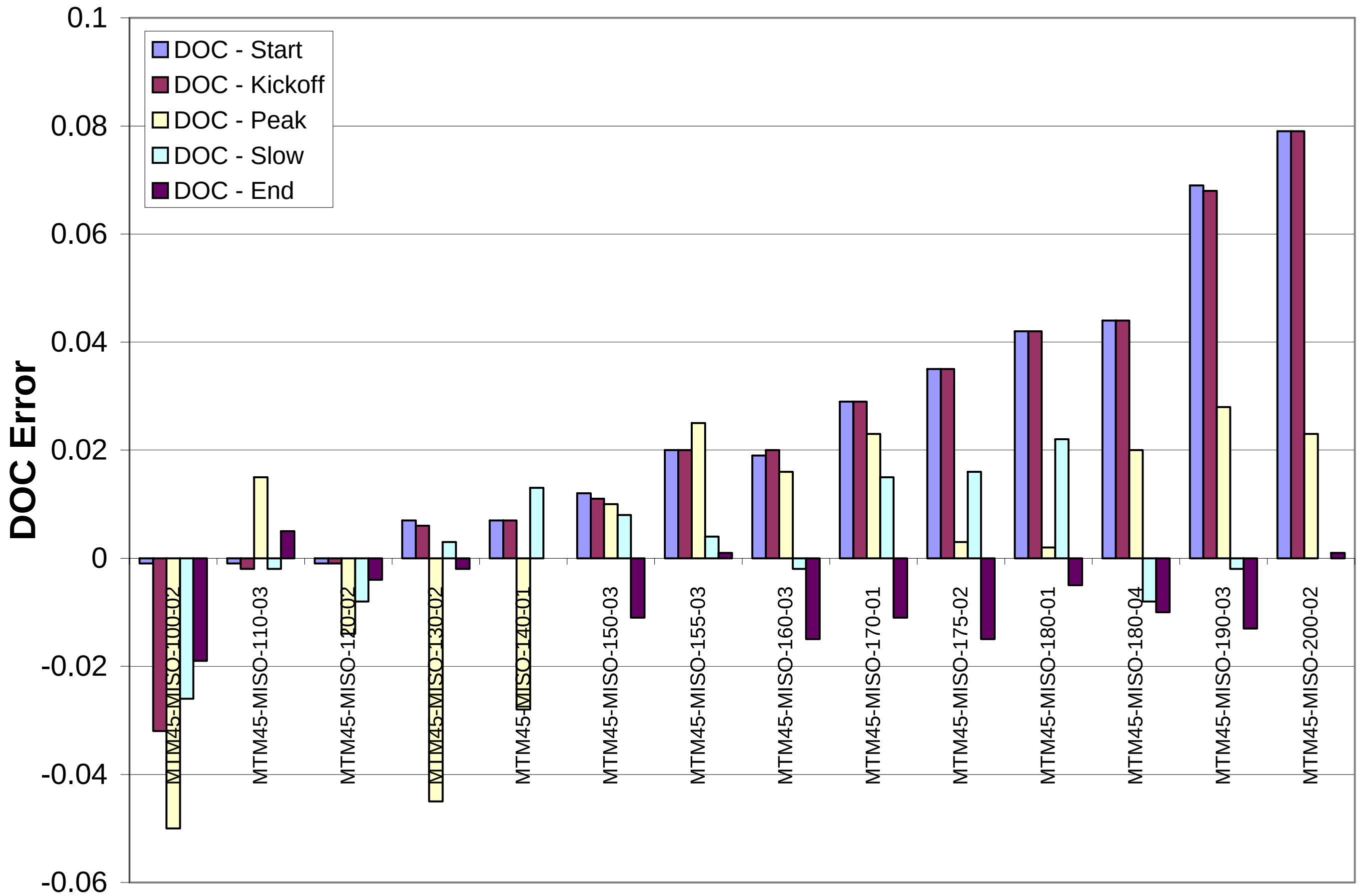
Goodness of Fit – Other



Goodness of Fit – Iso Timing



Goodness of Fit – Iso DOC



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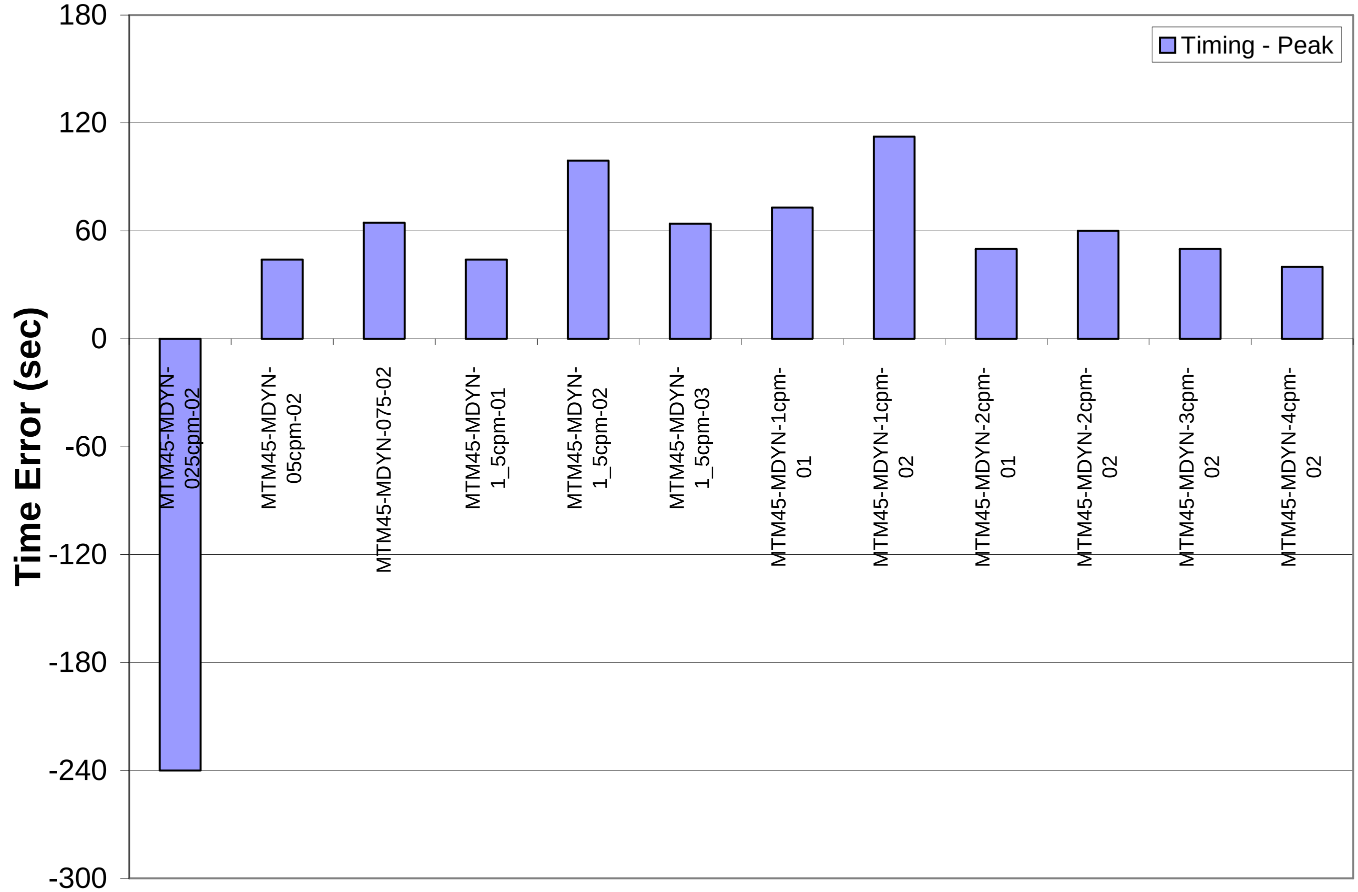
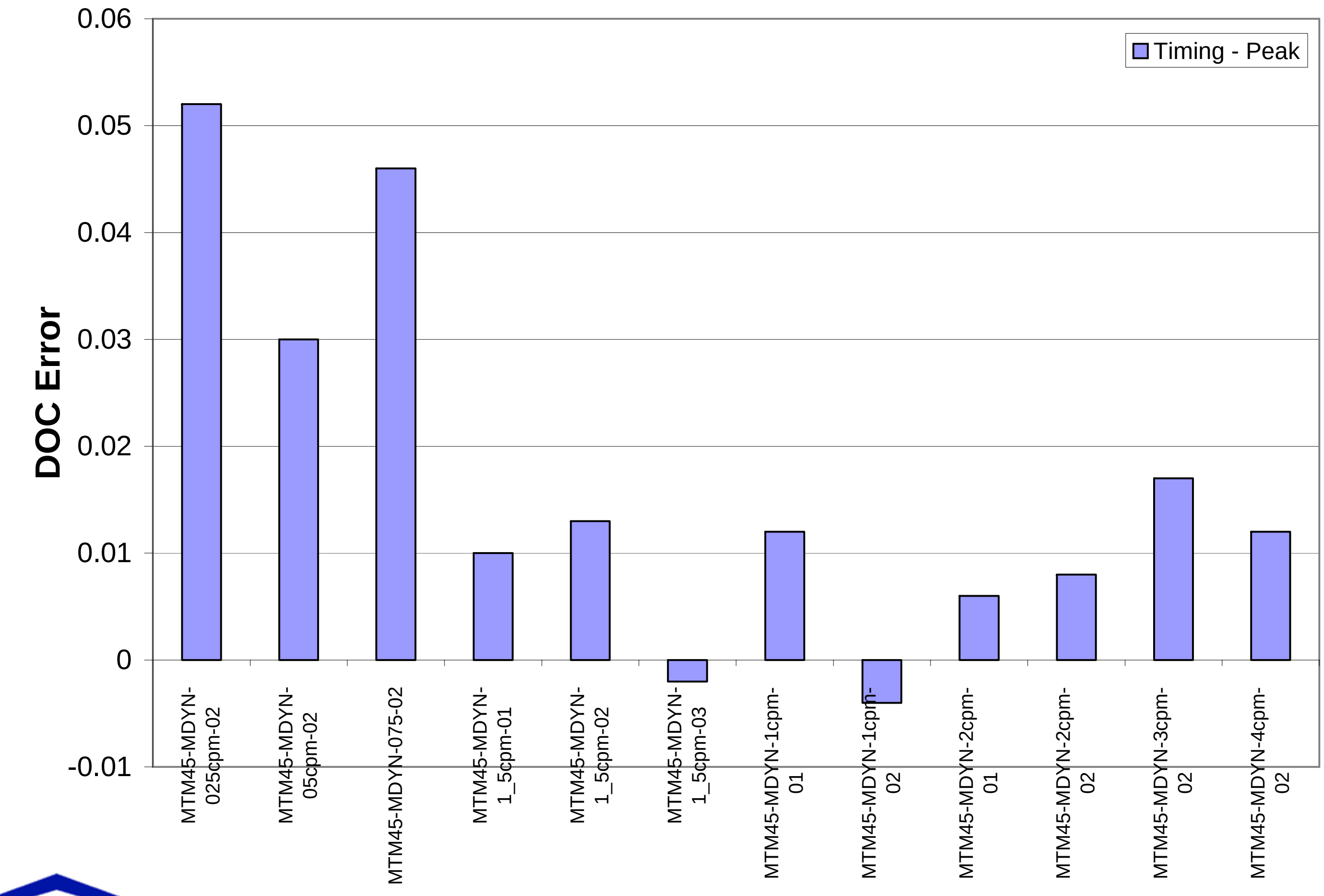
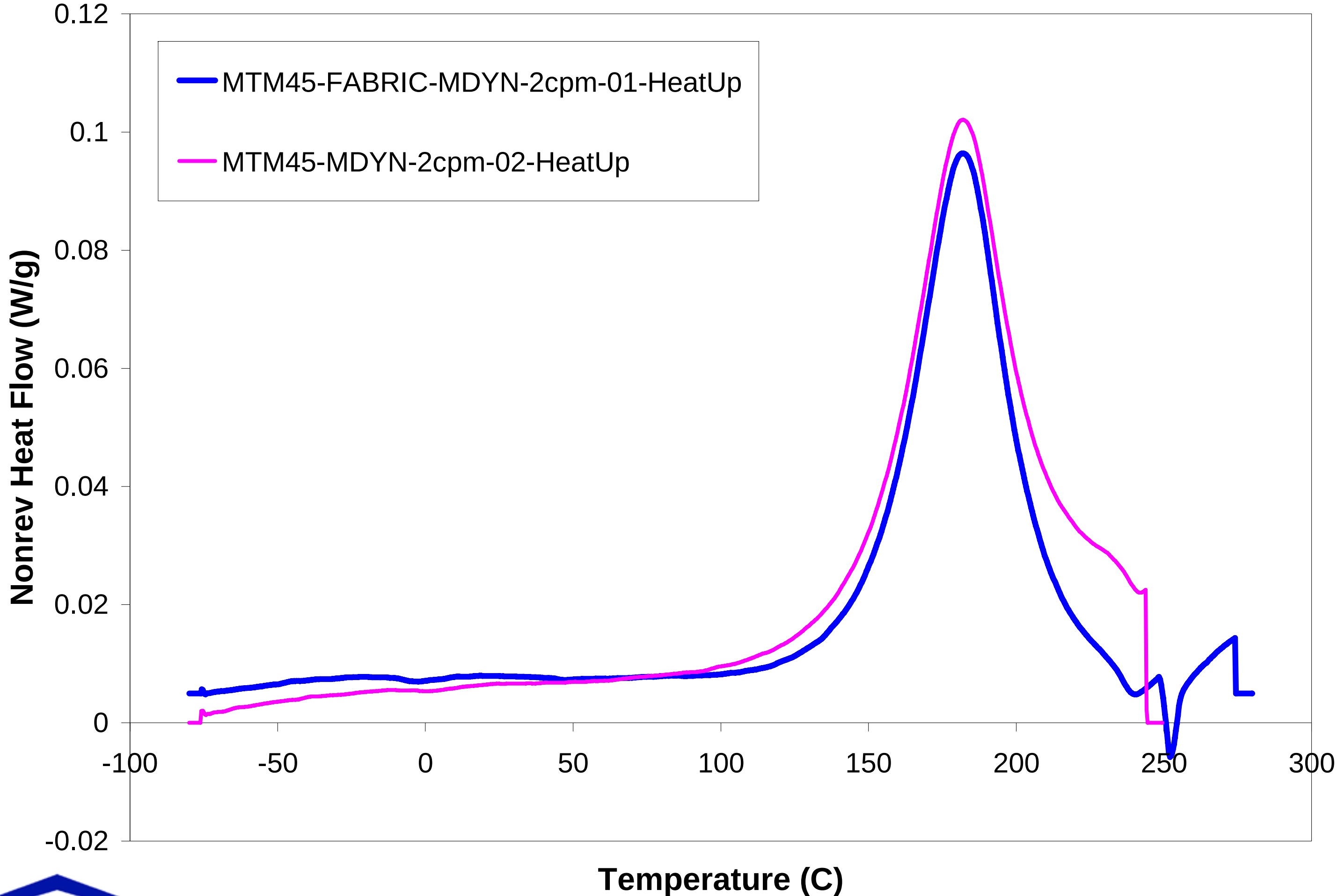
Goodness of Fit – Dyn Timing



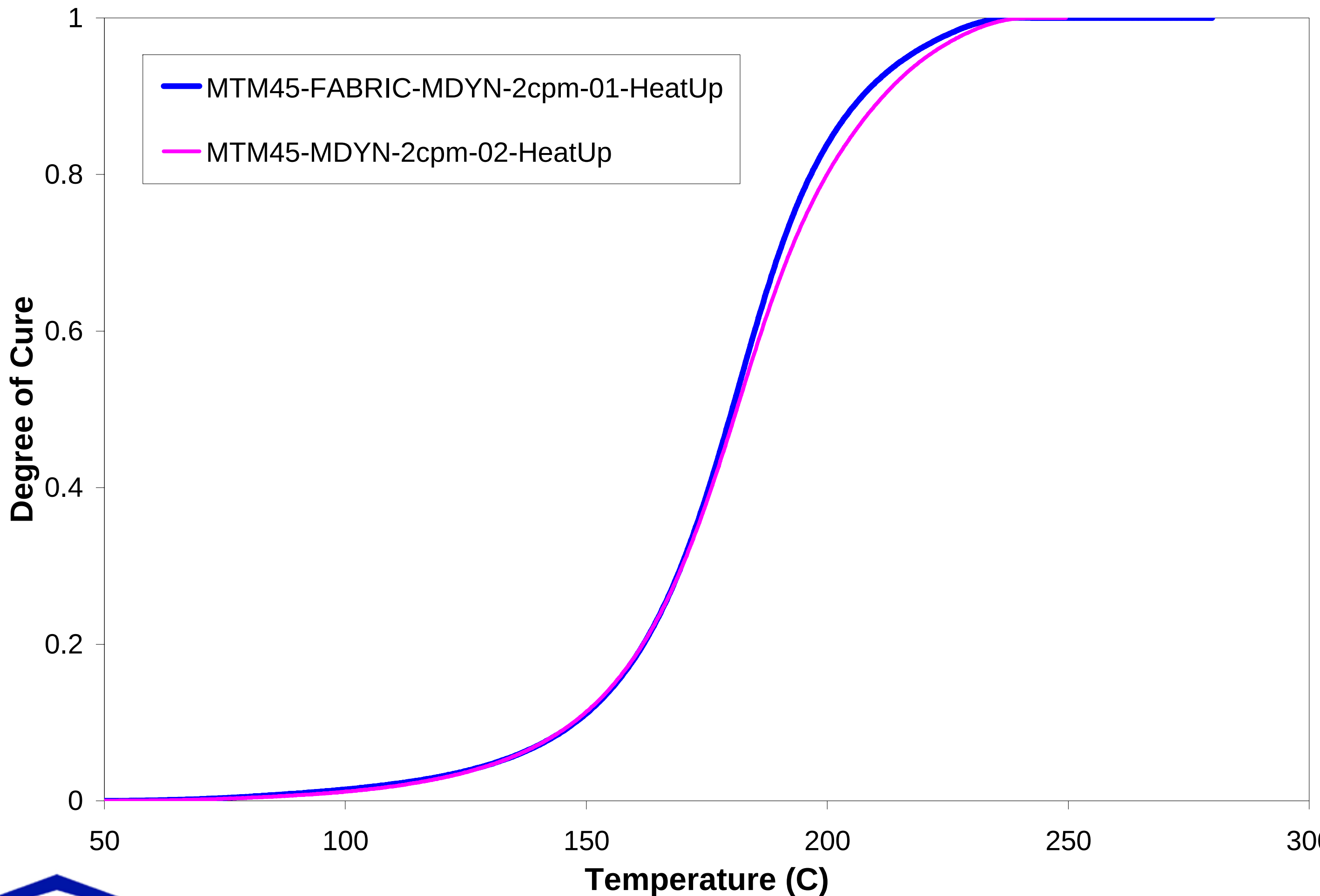
Goodness of Fit – Dyn DOC



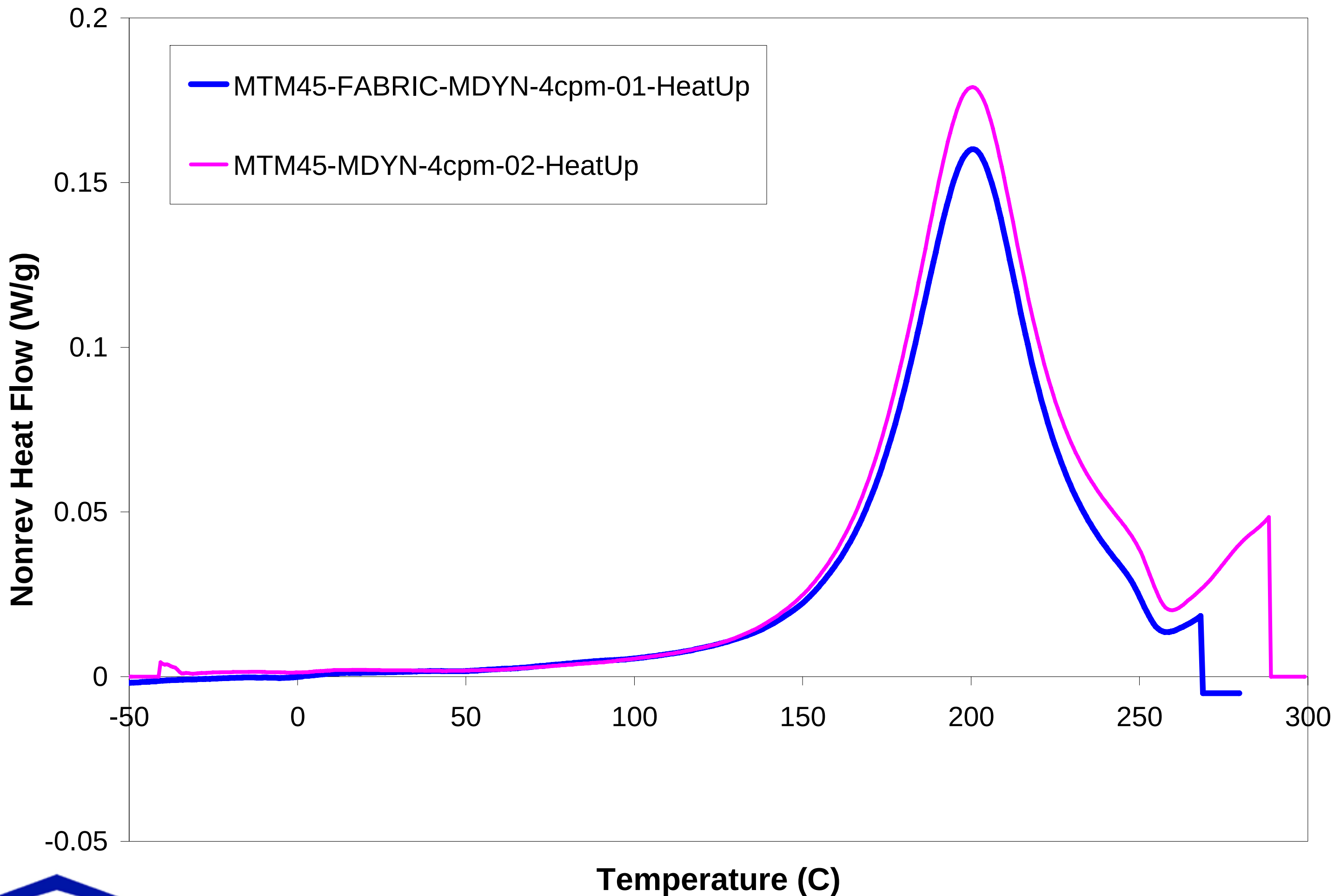
Other Forms – Fabric



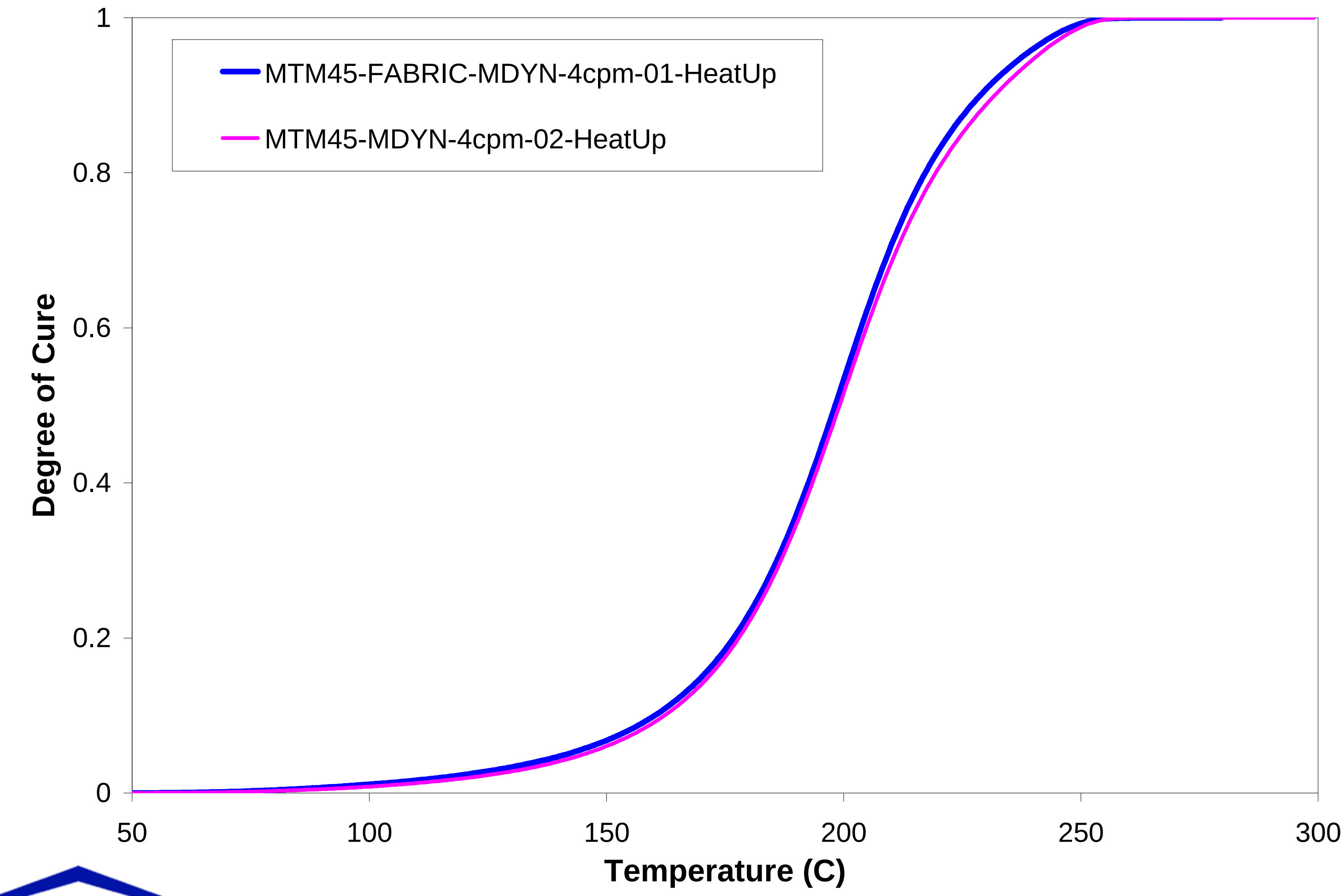
Other Forms – Fabric



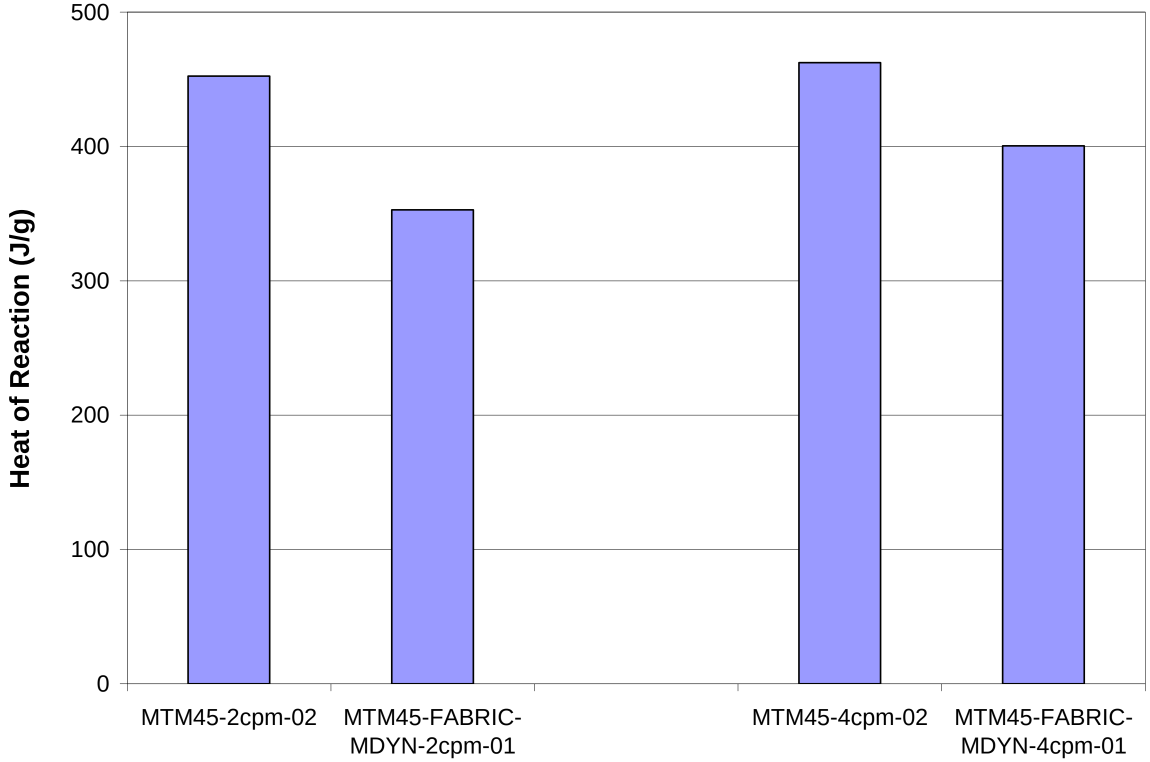
Other Forms – Fabric



Other Forms – Fabric



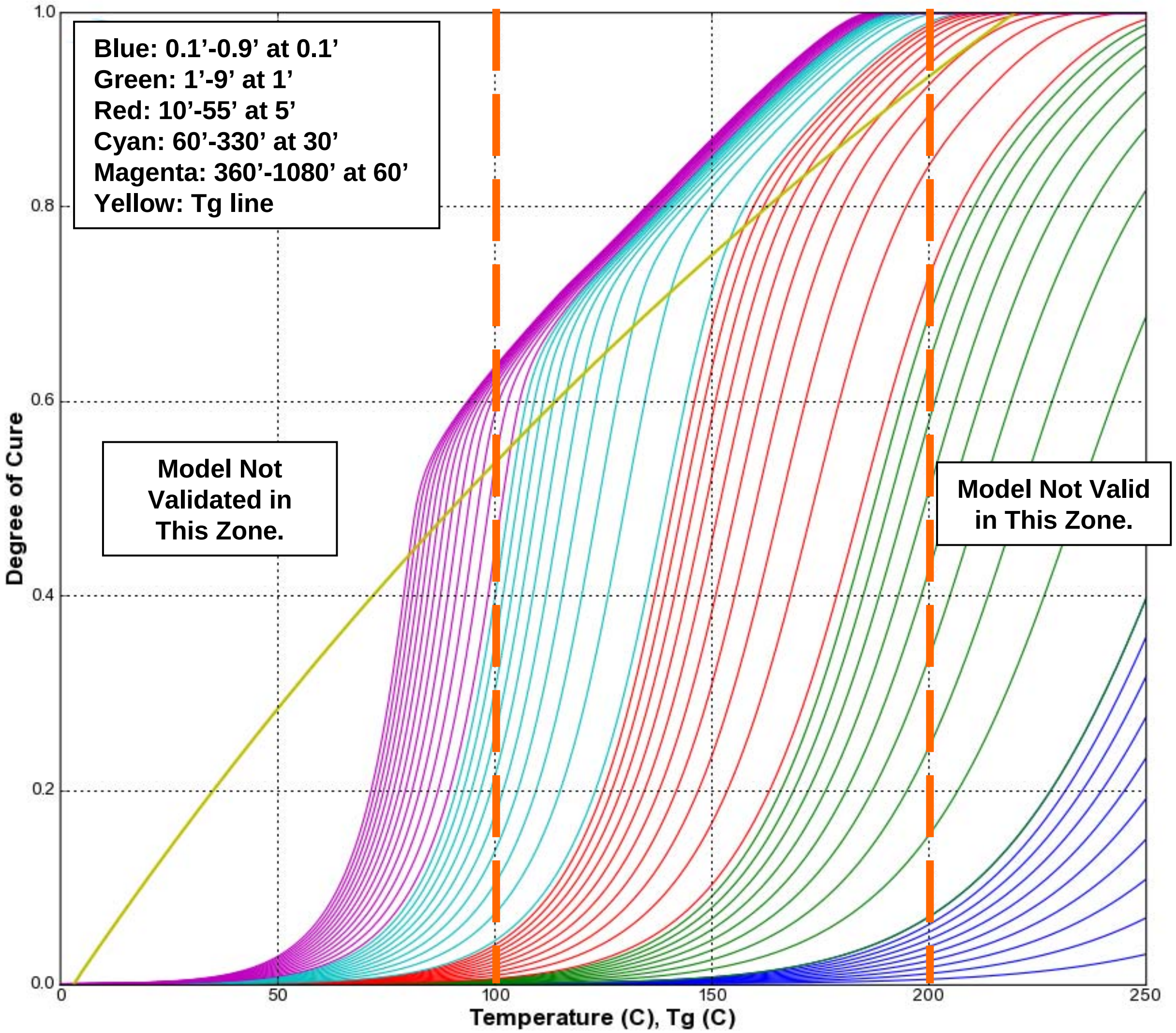
Other Forms – Fabric



Lower total heat of reaction is measured for the fabric compared to the uni prepreg. The curing behaviour of the two forms, however, was found to be very similar. The error in the total HR of the fabric results in conservative estimation of exhothermic events.

Test	Tg initial (C)	Tg Final (C)	Raw HR (J/G)	Adjustment Ratio	Adjusted HR (J/G)
MTM45-2cpm-02	2.34	205.65	144.75	0.32	452.33
MTM45-FABRIC-MDYN-2cpm-01	-0.53	171.37	127.039	0.36	352.89
MTM45-4cpm-02	2.23	-	147.99	0.32	462.46
MTM45-FABRIC-MDYN-4cpm-01	0.18	179.94	144.19	0.36	400.53

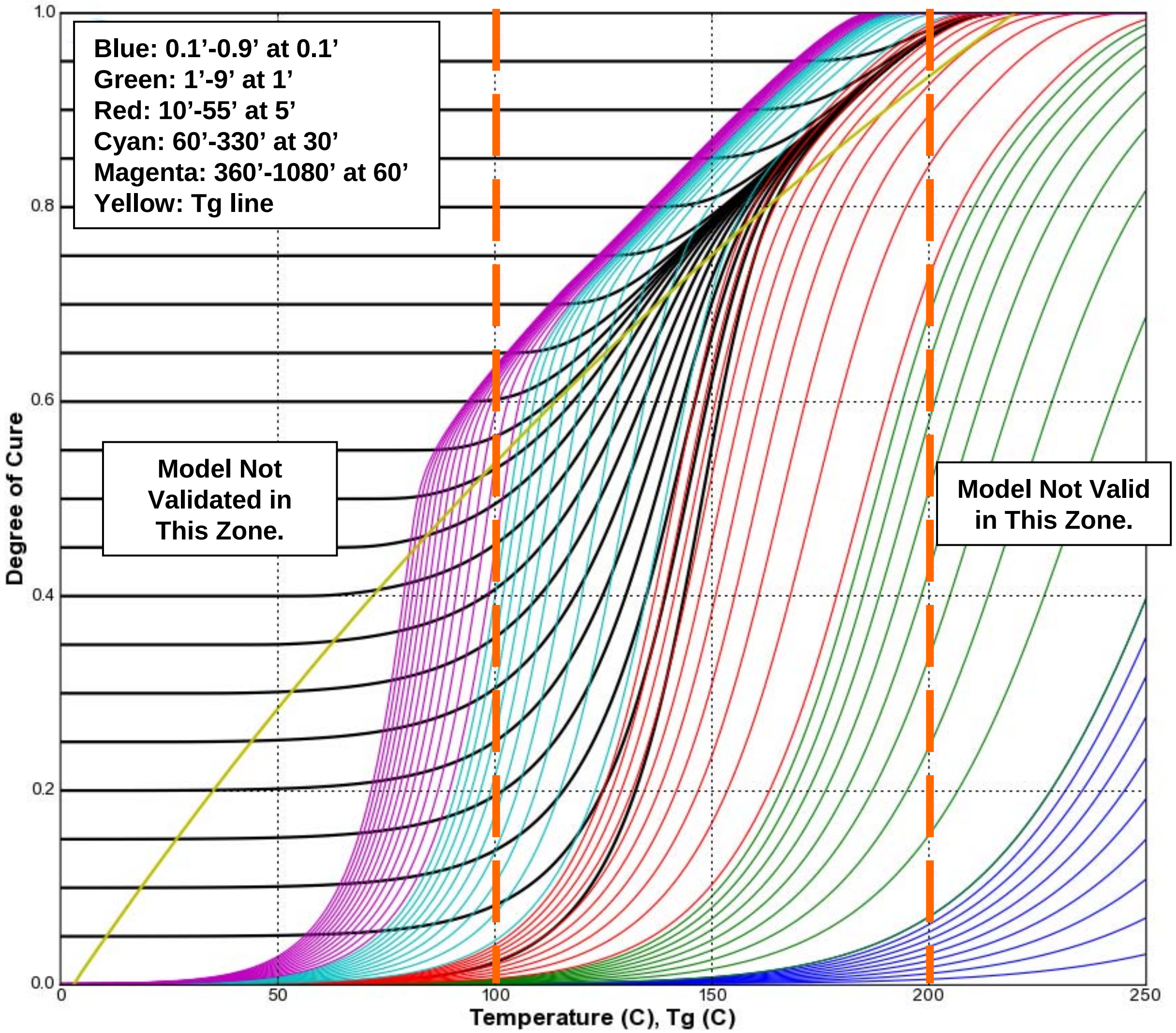
Process Maps - Isothermal



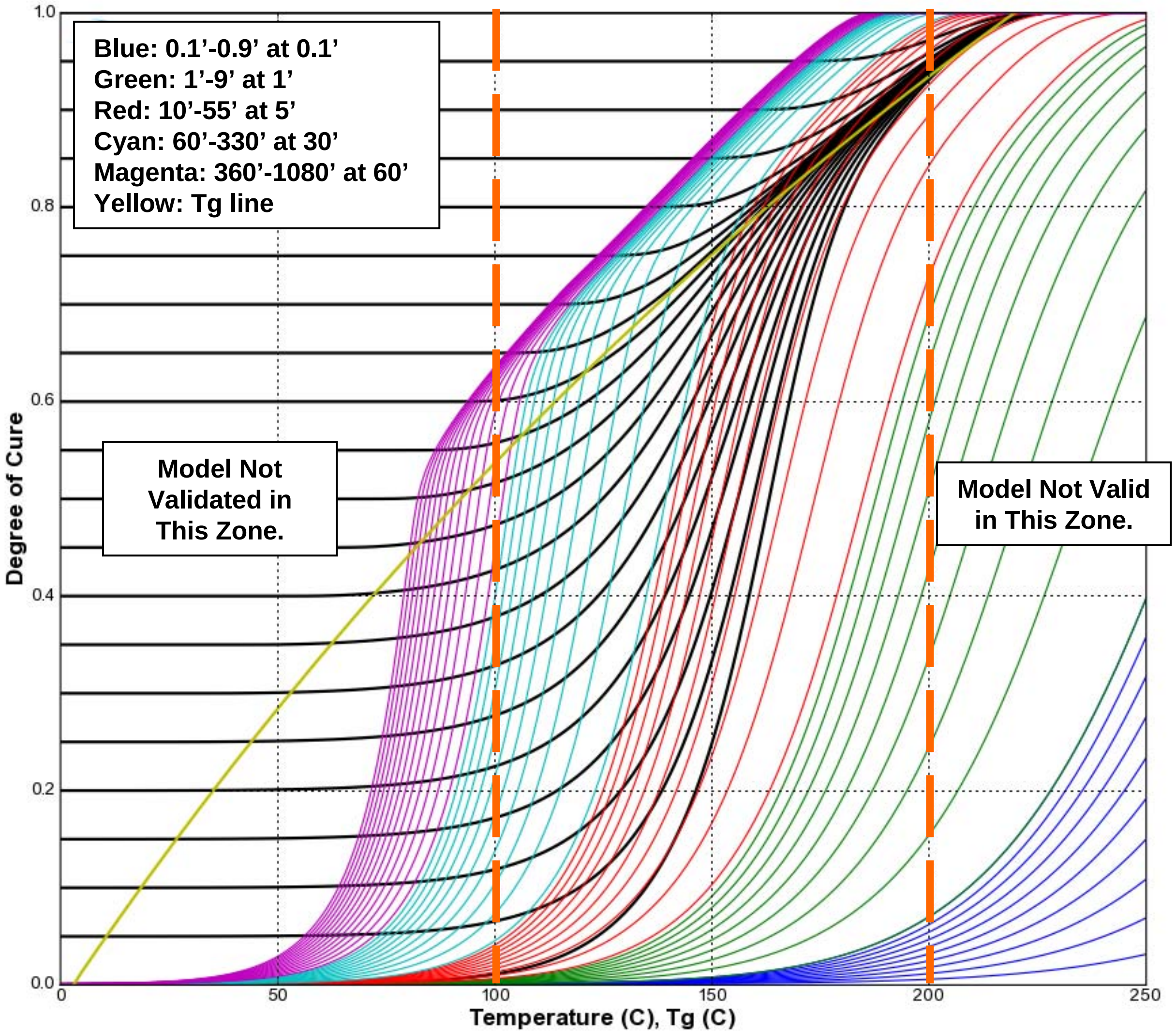
CONVERGENT MANUFACTURING TECHNOLOGIES

GENT TECHNOLOGIES

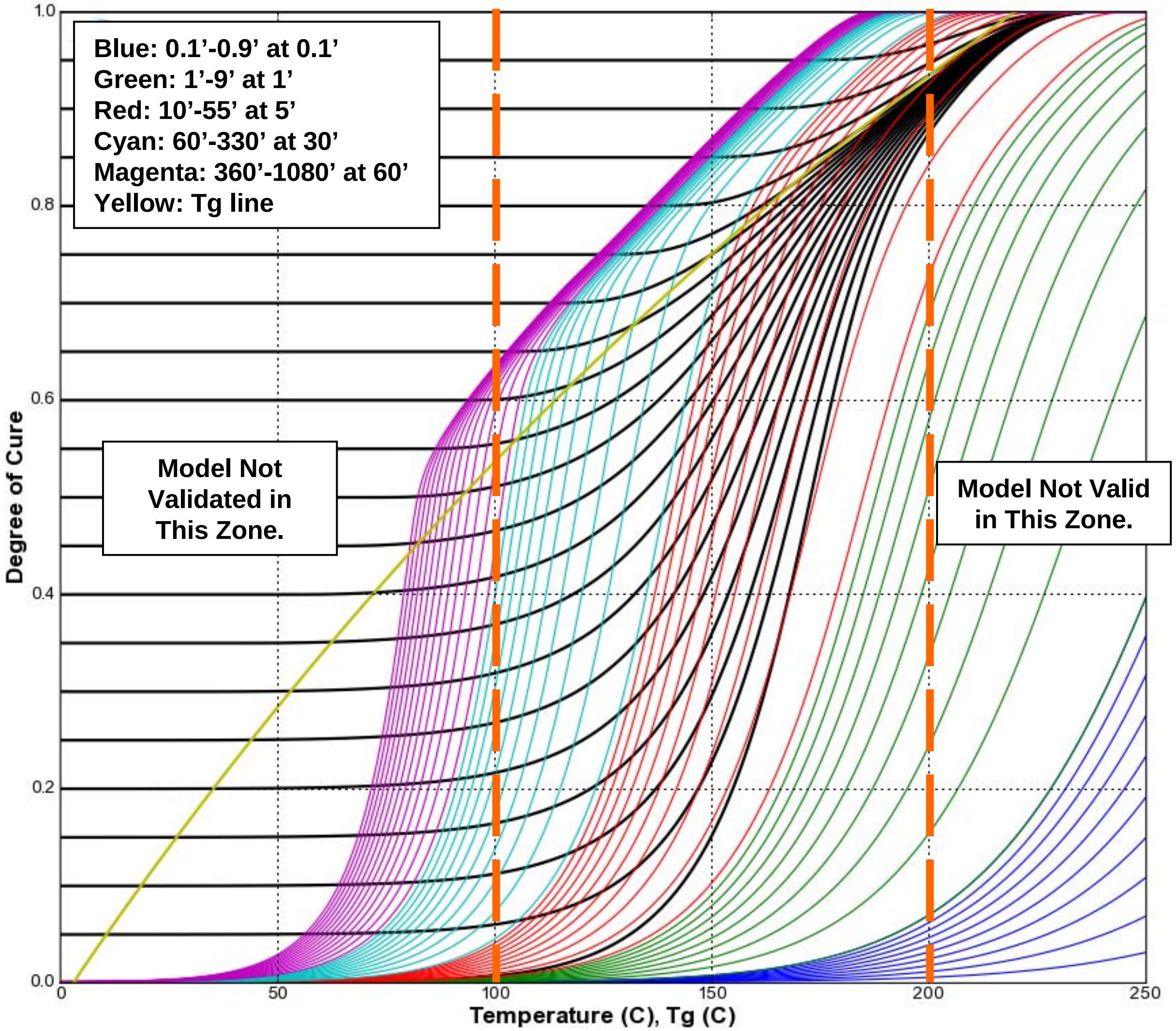
Process Maps – 0.5cpm



Process Maps – 1.0cpm



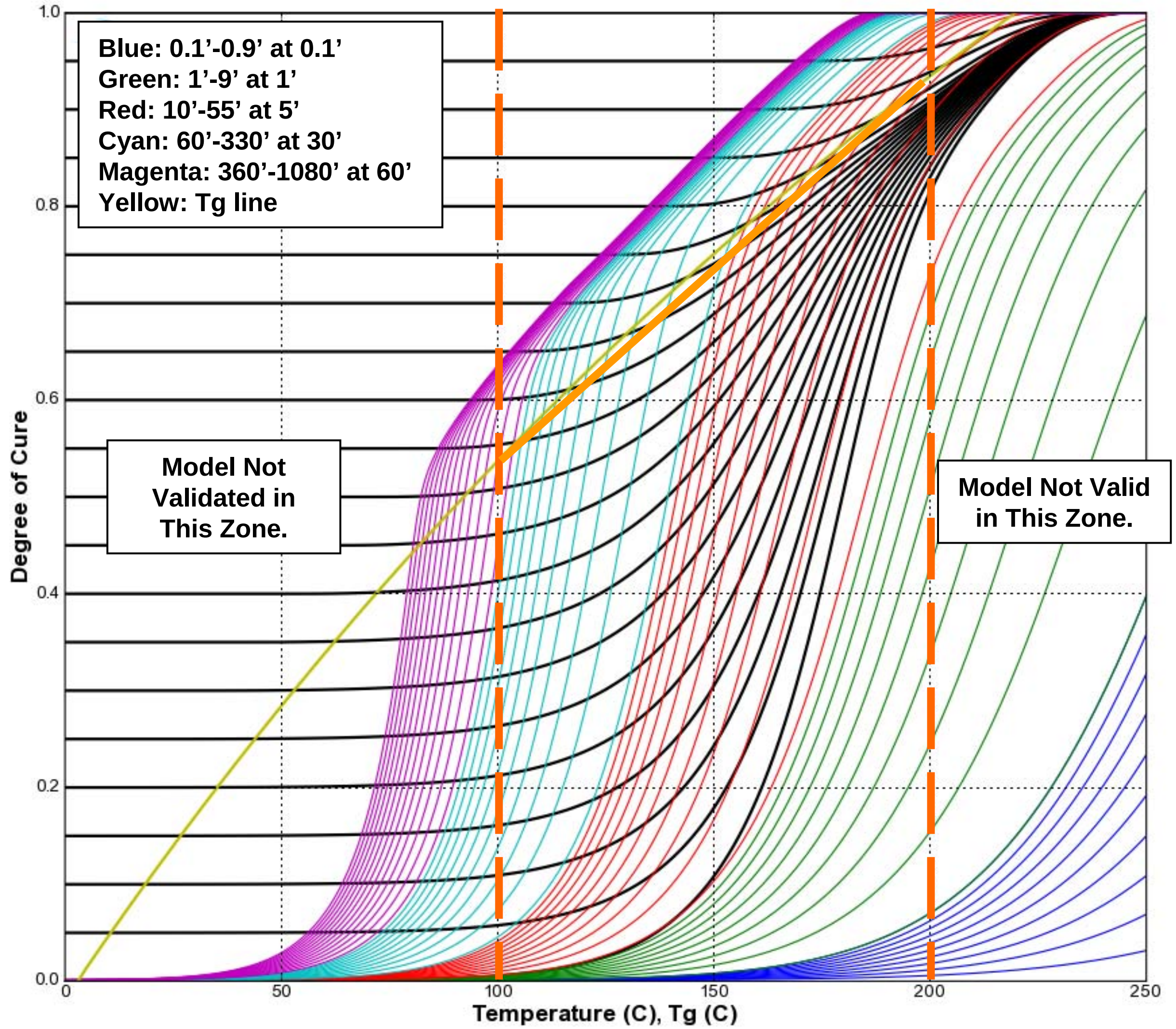
Process Maps – 1.5cpm



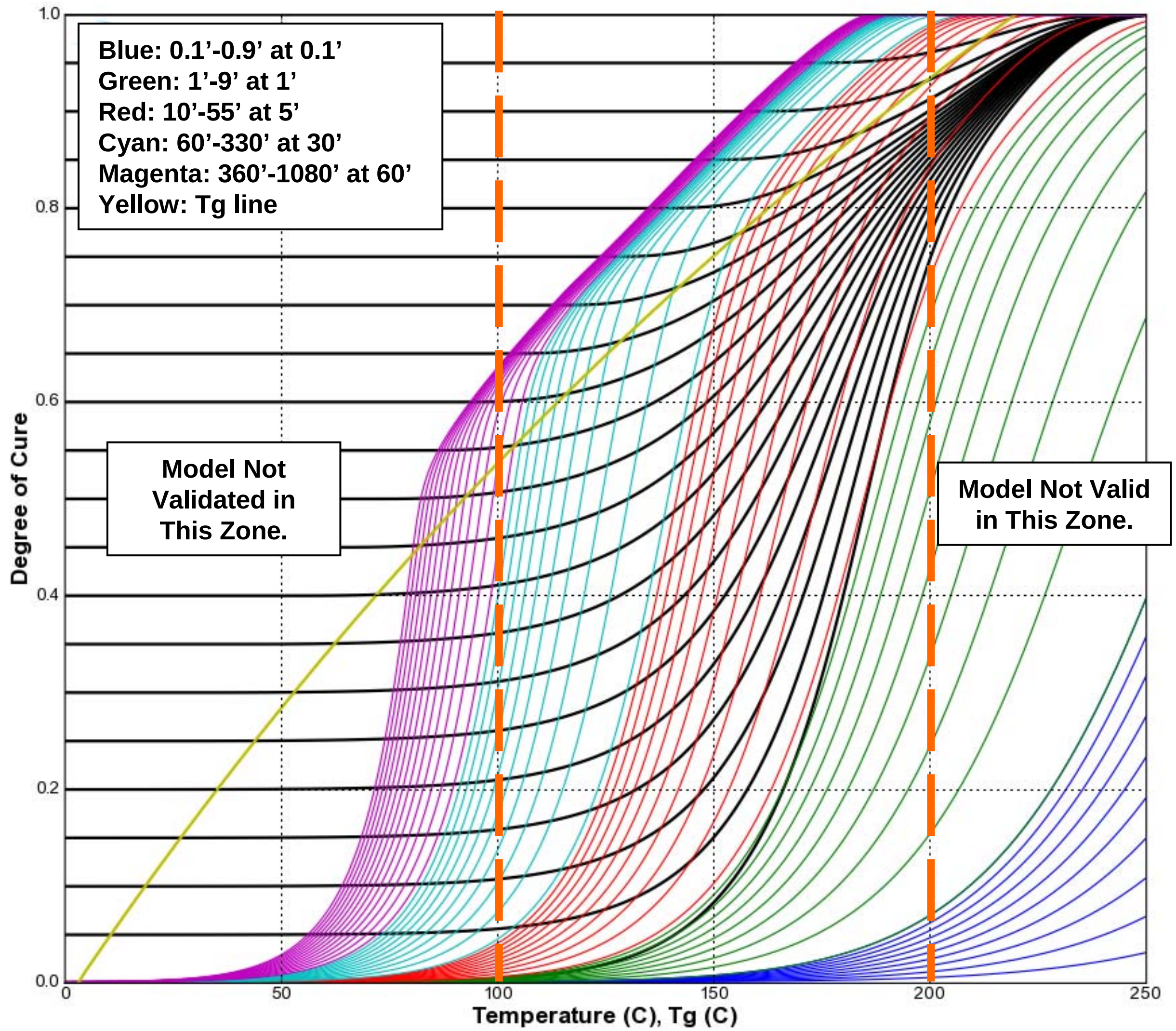
CONVERGENT MANUFACTURING TECHNOLOGIES

GENT TECHNOLOGIES

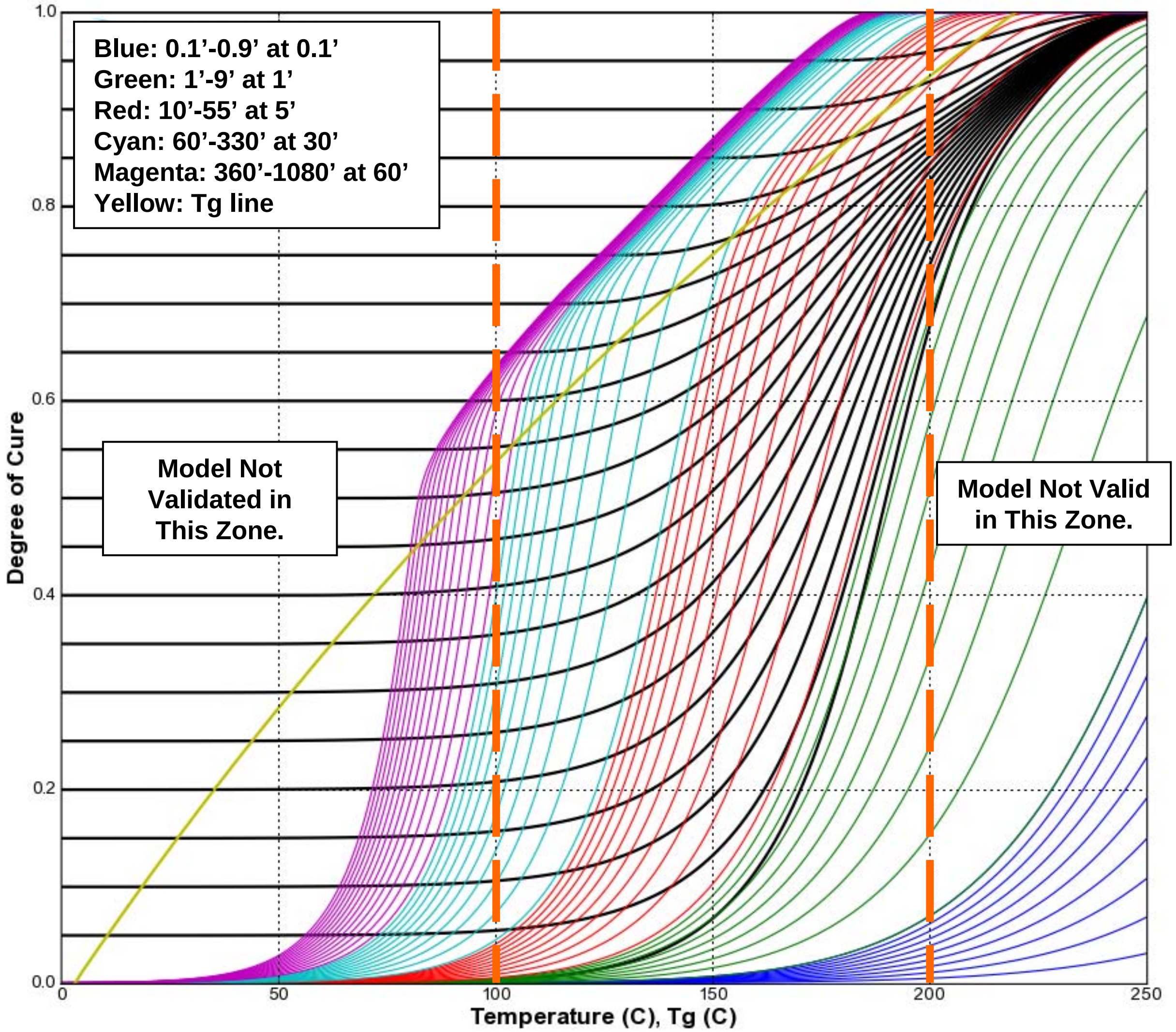
Process Maps – 2.0cpm



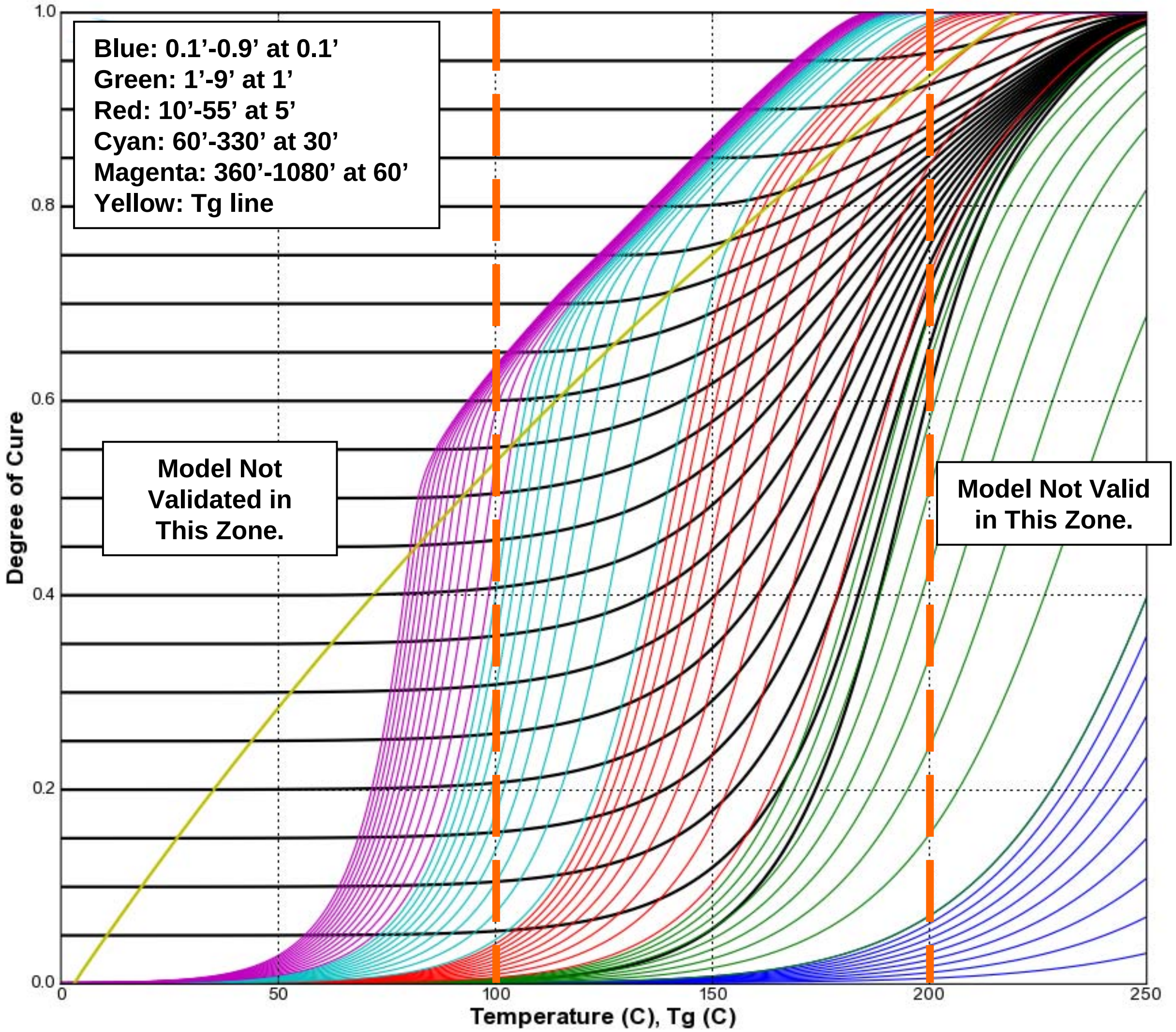
Process Maps – 2.5cpm



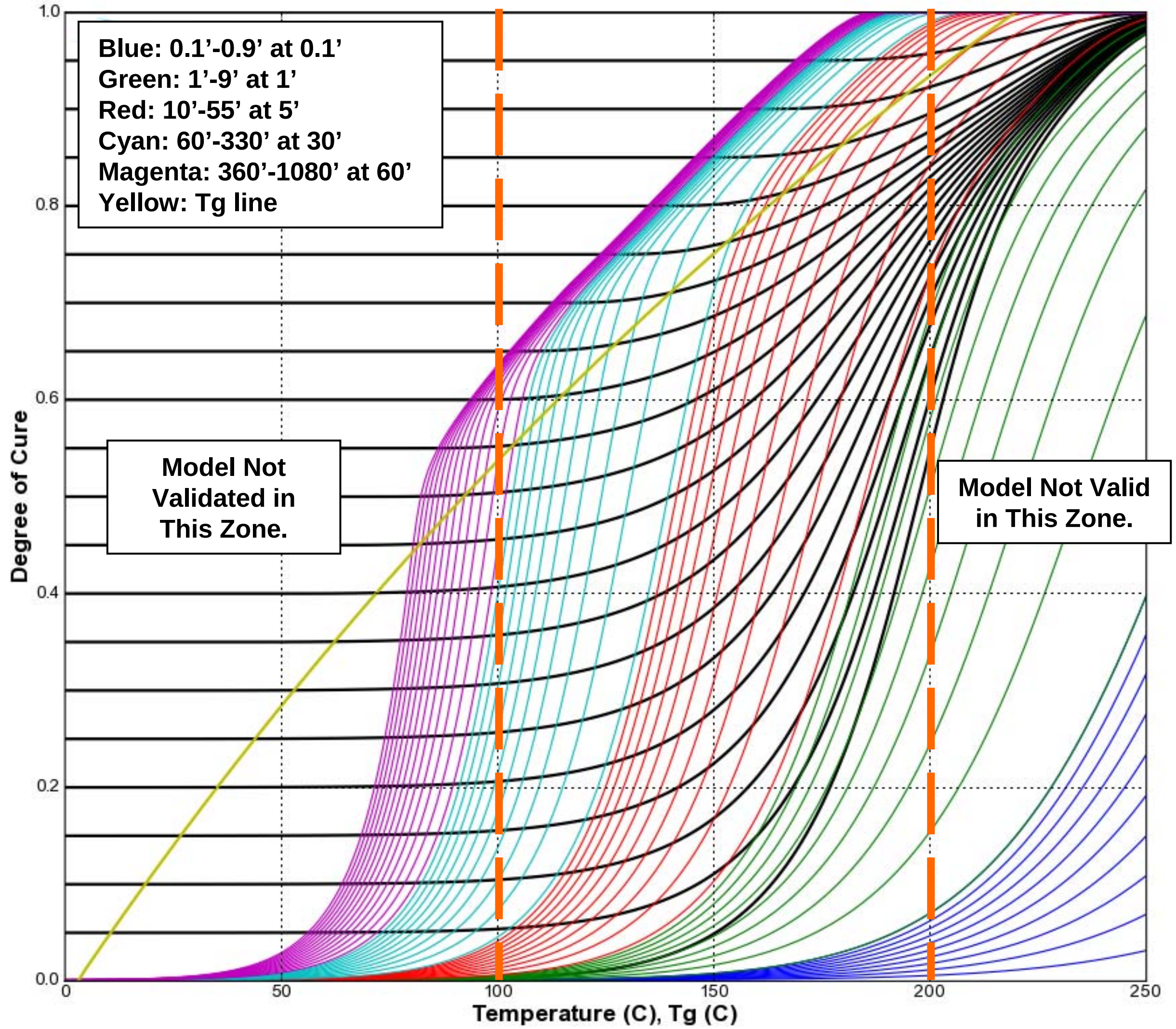
Process Maps – 3.0cpm



Process Maps – 3.5cpm



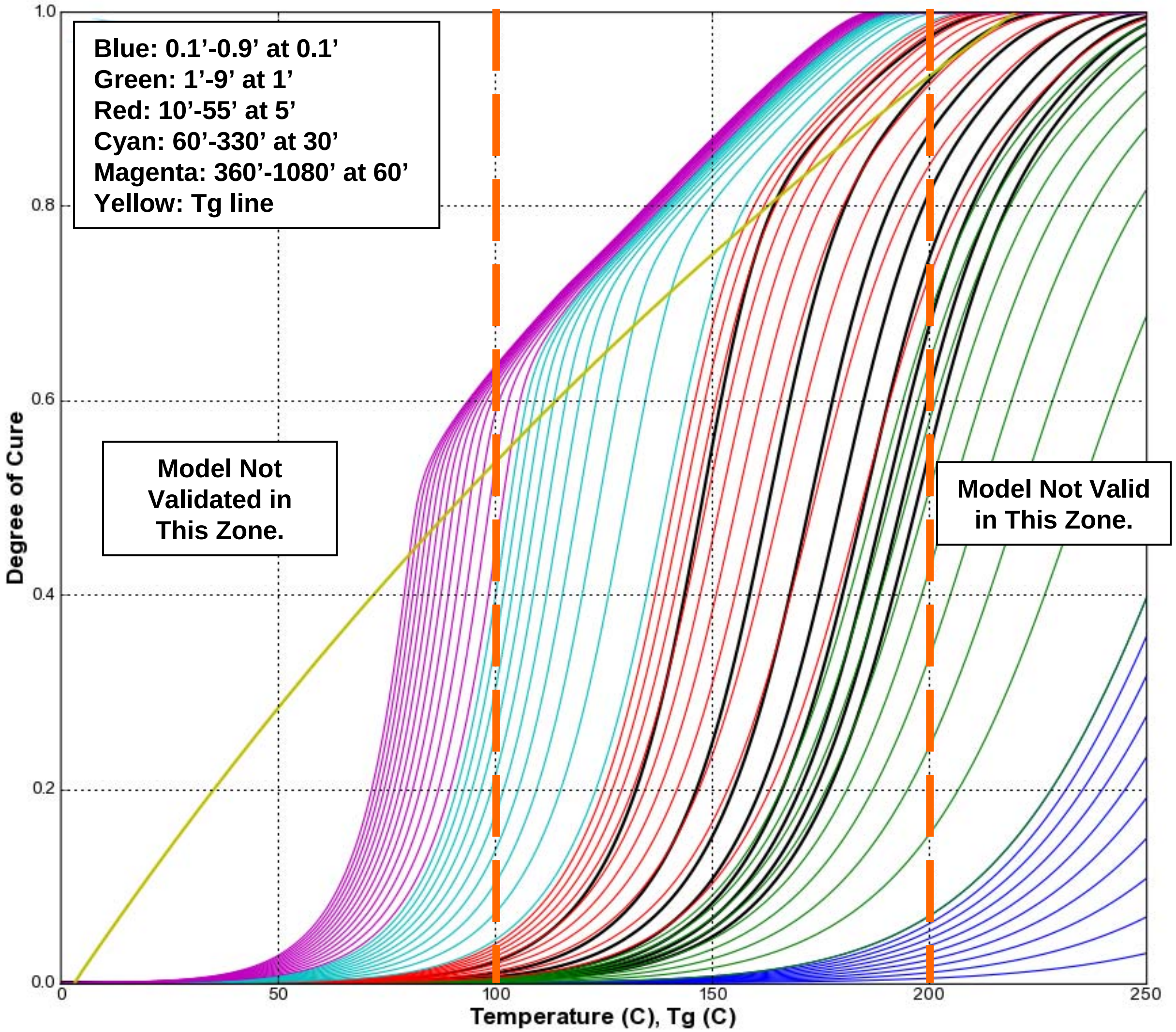
Process Maps – 4.0cpm



CONVERGENT MANUFACTURING TECHNOLOGIES

GENT TECHNOLOGIES

Process Maps – All Dynamic Rates



CONVERGENT MANUFACTURING TECHNOLOGIES

GENT TECHNOLOGIES

Viscosity Model

Nomenclature

η'	Dynamic viscosity or the real part of the complex viscosity
η''	Elastic complex part of the complex viscosity
η^*	Complex viscosity
μ	Material viscosity calculated by the viscosity model

Viscosity Tests

- Material viscosity was measured using a AR2000 Rheometer with parallel plate geometry.
- Dynamic tests at different ramp rates were performed to capture the changes in material viscosity as a function of temperature and degree of cure. A total of 5 tests at 1, 2, 3, 4, and 5 cpm were performed.
- Ramp-Hold tests at 2 cpm were also performed with holds at 125, 130, 135, 140 and 145C.
- Disposable aluminum plates of diameter 25mm were used at a gap of 1mm (sample thickness). Frequency of oscillation was chosen to be 1Hz.

Viscosity Measure

Rheometry tests are performed under sinusoidal oscillatory loads. The classical solution of the viscoelastic behaviour of materials in such circumstances is usually expressed in terms of storage and loss moduli. Considering the following strain function, the resulting stress would be:

Strain applied: $\gamma = \gamma_0 \sin \omega t$

Resulting stress: $\sigma = \sigma_0 \sin(\omega t + \delta)$

where δ is the phase angle between the strain and the stress. Decomposing the stress into in-phase and out-of-phase components, we get:

$$\sigma = \gamma_0 (G' \sin \omega t + G'' \cos \omega t)$$

where *G'* is the in-phase (elastic or storage) modulus and *G"* is the out-of-phase (viscous or loss) modulus.

Viscosity Measure

Alternatively, a complex viscosity η* can be defined with "dynamic viscosity" (η') as its real part and an elastic complex part (η"), defined as:

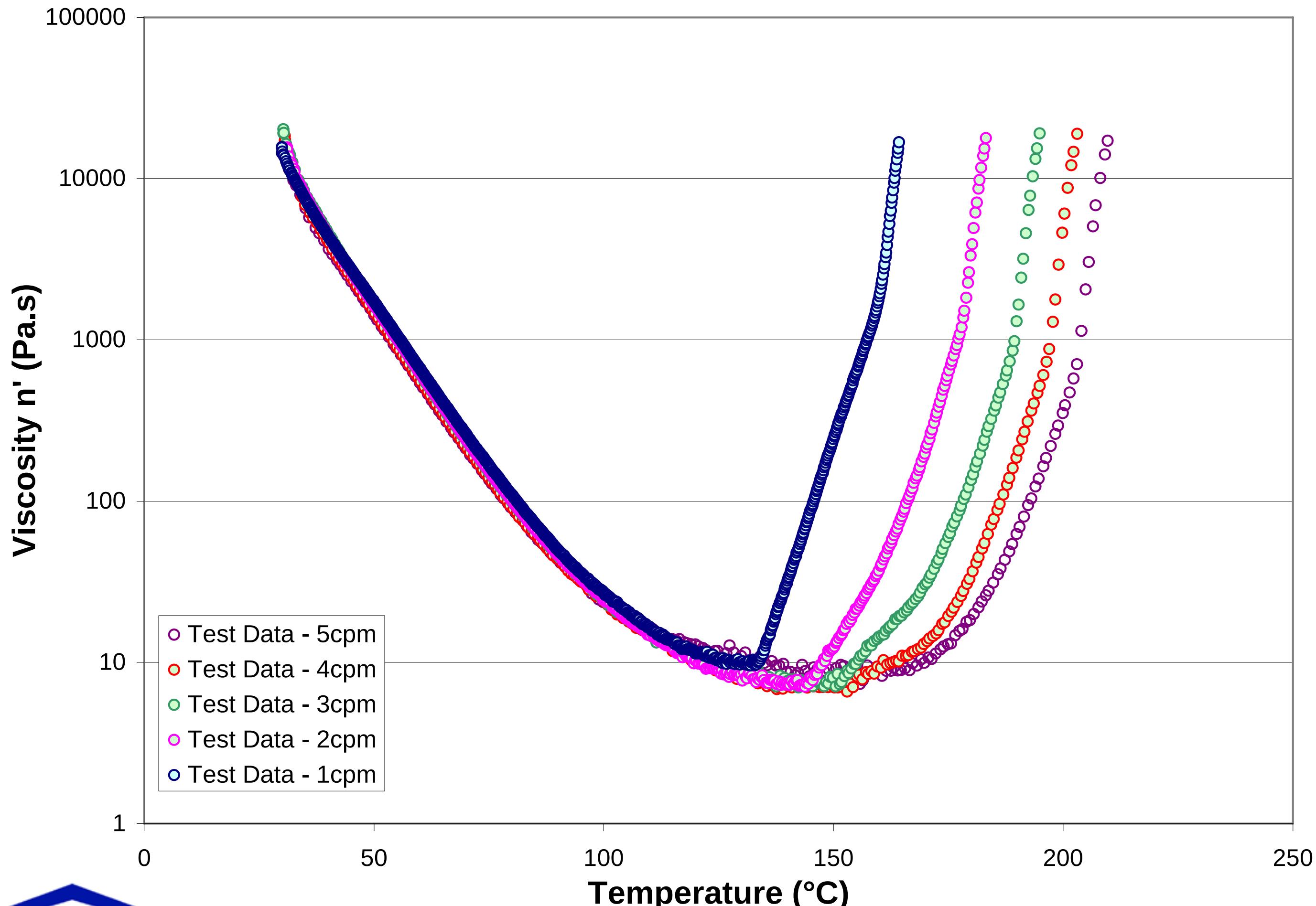
$$\eta^{*} = \eta' + i\eta'' \qquad \text{where} \qquad \eta' = \frac{G''}{\omega} \quad \text{and} \quad \eta'' = \frac{G'}{\omega}$$

For low shear rates, the dynamic viscosity corresponds mainly to the real part of the complex viscosity and can be considered the steady state viscosity of the fluid. In other words:

$$\boxed{\mu = \eta'}$$

The viscosity model developed here is based on the measured η', i.e. the dynamic viscosity response of the material.

Viscosity Tests Summary
Dynamics vs Temperature



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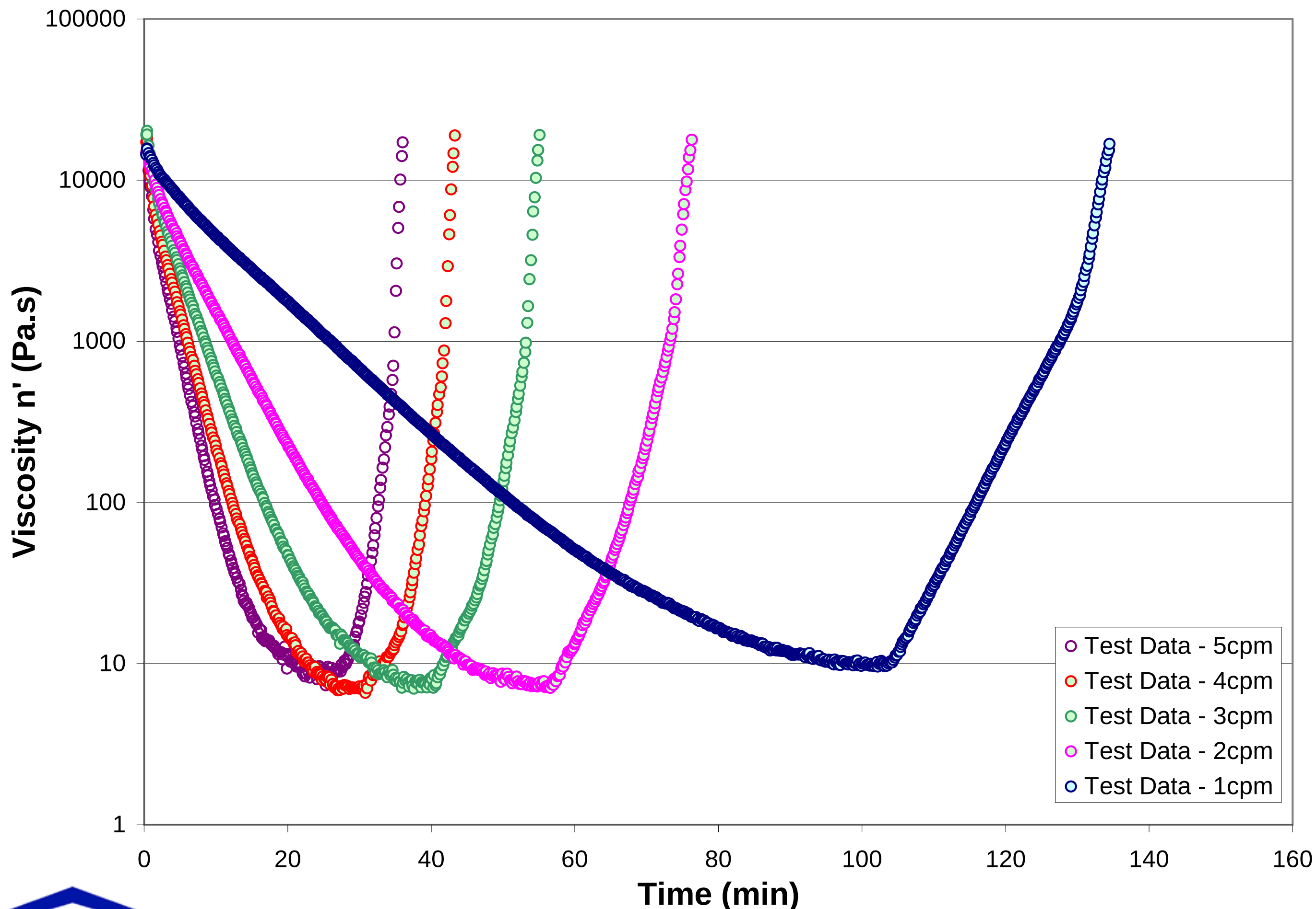
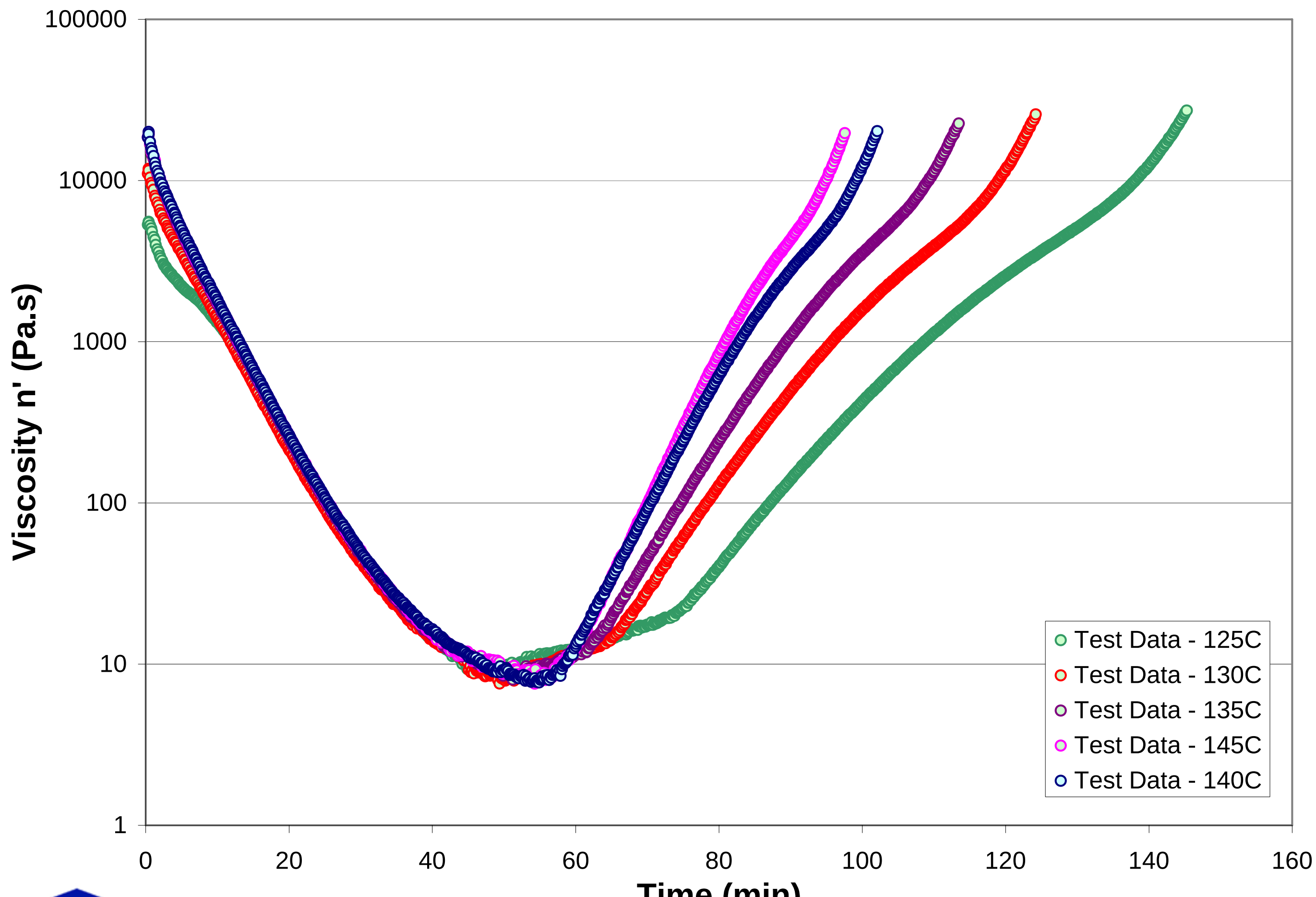
Viscosity Tests Summary
Dynamics vs Time



Viscosity Tests Summary Isothermals vs Time



Mathematical Model

The viscosity model chosen is in the following form[1]:

$$\mu = \mu_1(T) + \mu_2(T)\left(\frac{x_g}{x_g - x}\right)^{\left(A+Bx+Cx^2\right)}$$

where

$$\mu_i(T) = \mu_{0i} e^{\frac{E_i}{RT}} \qquad i = 1 \text{ or } 2$$

x_g is a critical degree of cure

[1]**Khoun and Hubert, Processing Characterization of a RTM Carbon Epoxy System for Aeronautical Applications.**

Mathematical Model

The parameters of the viscosity model are determined by fitting to the experimental results.

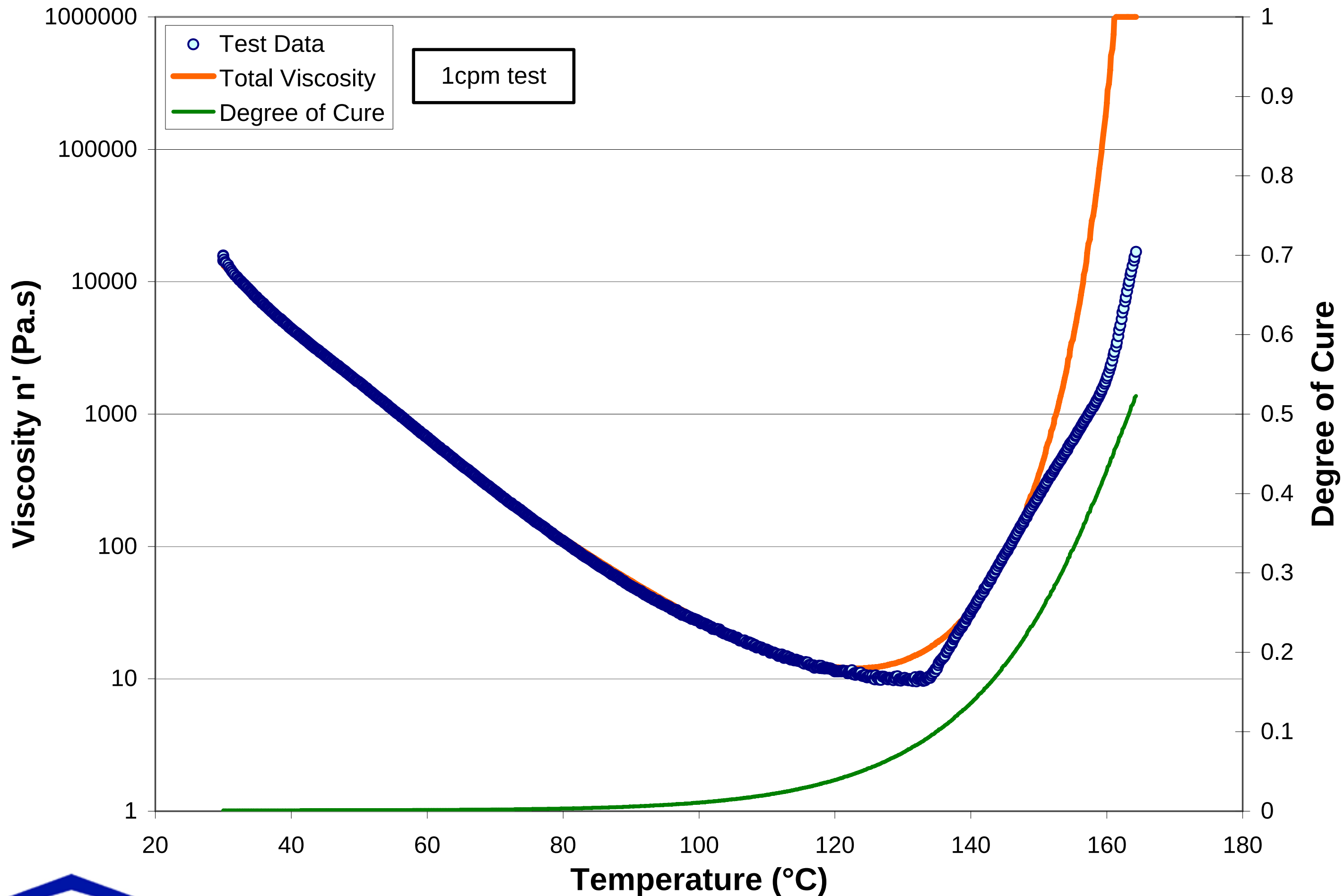
$$\mu = \mu_{01} e^{\frac{E_1}{RT}} + \mu_{02} e^{\frac{E_2}{RT}} \left(\frac{x_g}{x_g - x} \right)^{\left(A + Bx + Cx^2\right)}$$

$$\left\{ \begin{array}{cc} E_1 = 85{,}000 & \mu_{01} = 3.0 \times 10^{-11} \\ E_2 = 8{,}000 & \mu_{01} = 0.3 \\ x_g = 0.6 & A = 9 \\ B = 0 & C = 0 \end{array} \right\}$$

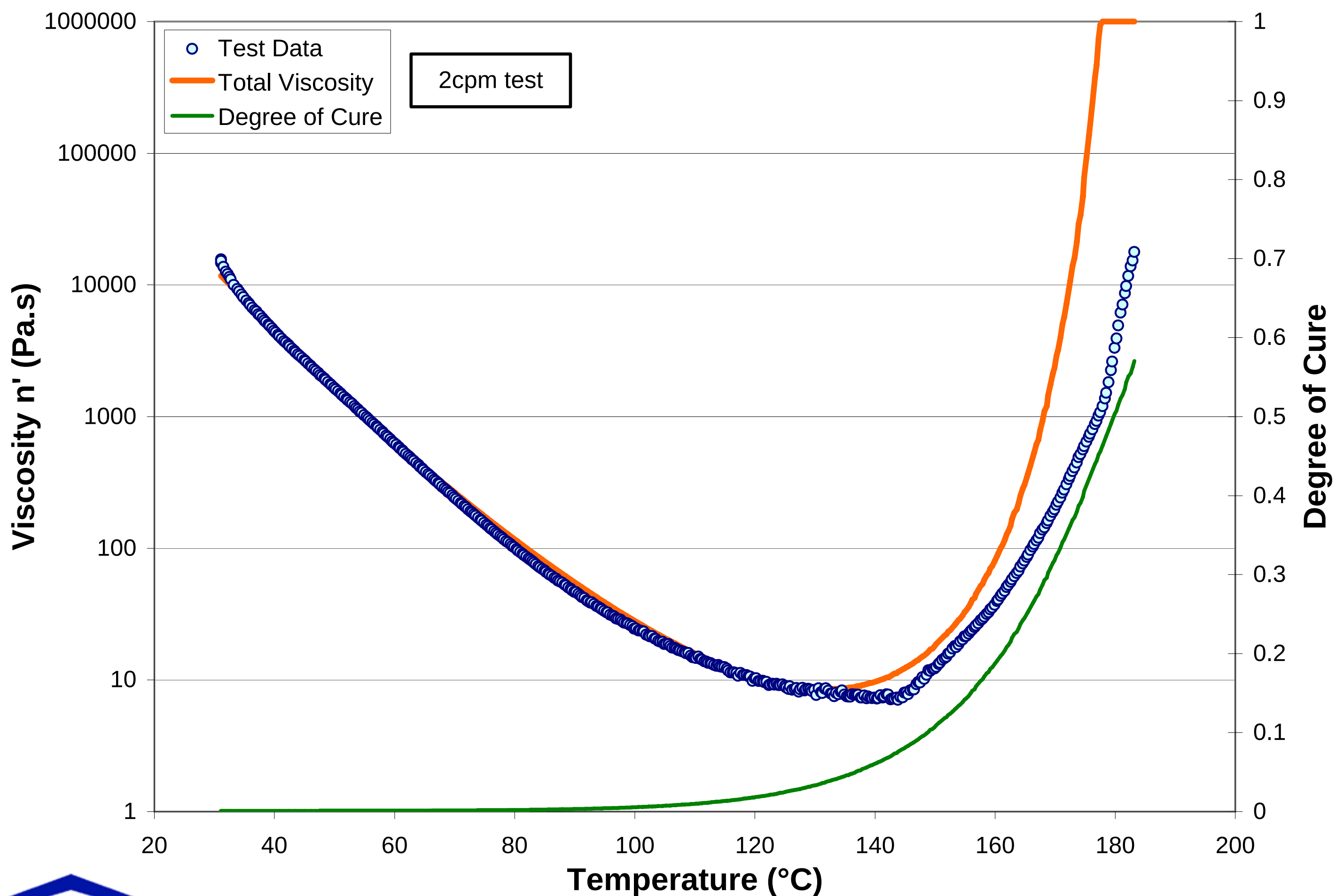
$$\text{if } \mu > \mu_{\max} \text{ then } \mu = \mu_{\max}$$

$$\boxed{\mu_{\max} = 10^6}$$

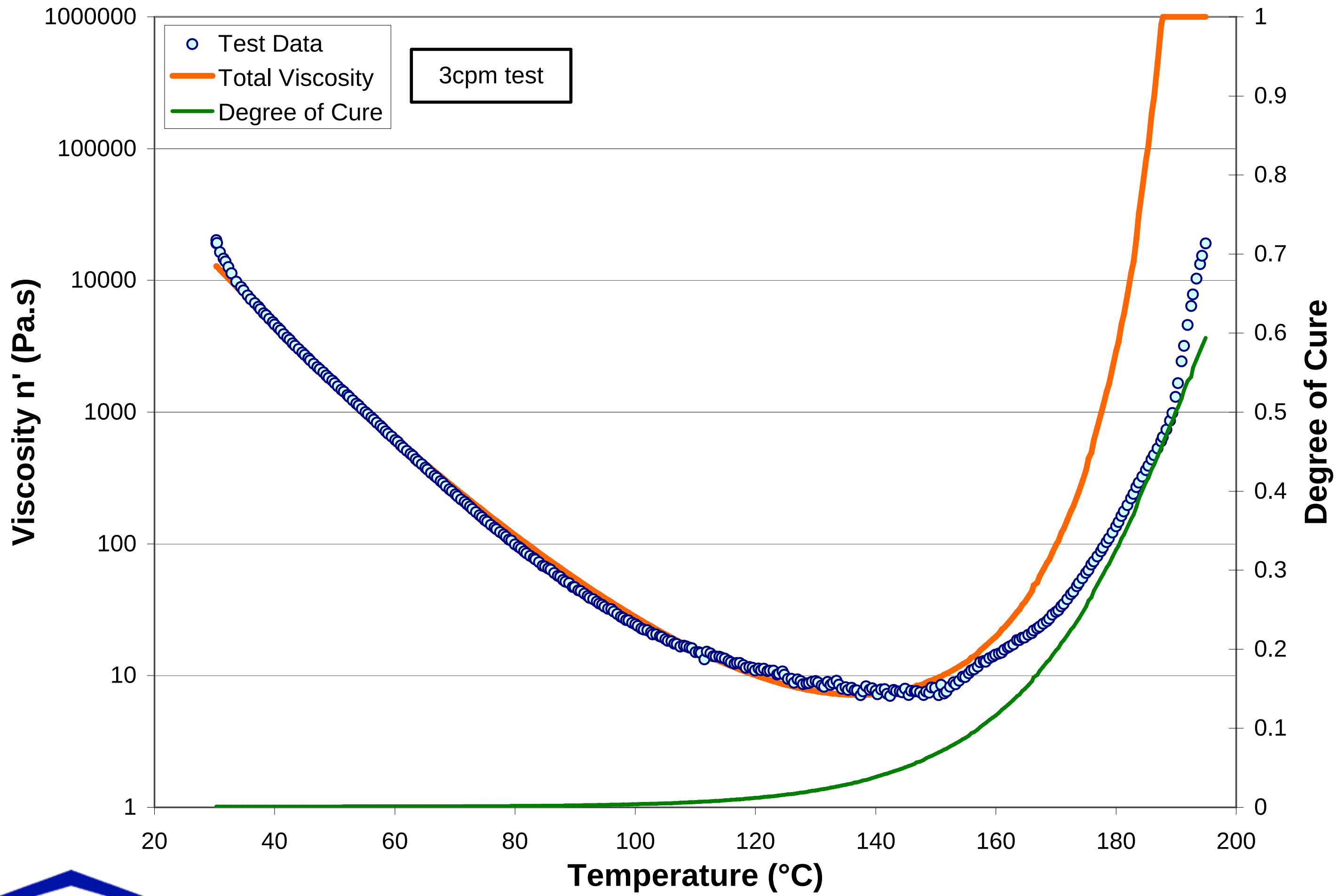
Dynamic Tests – 1cpm



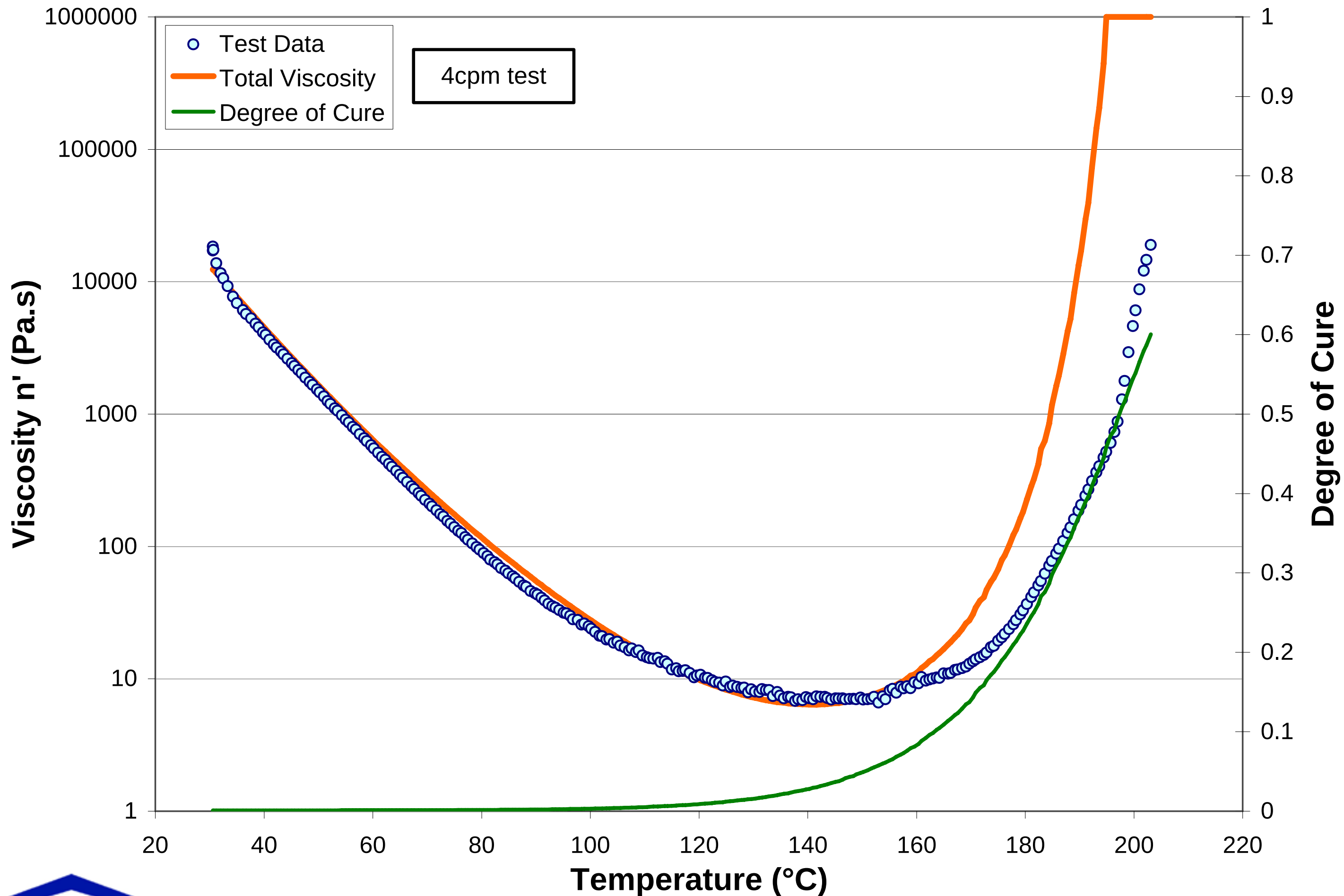
Dynamic Tests – 2cpm



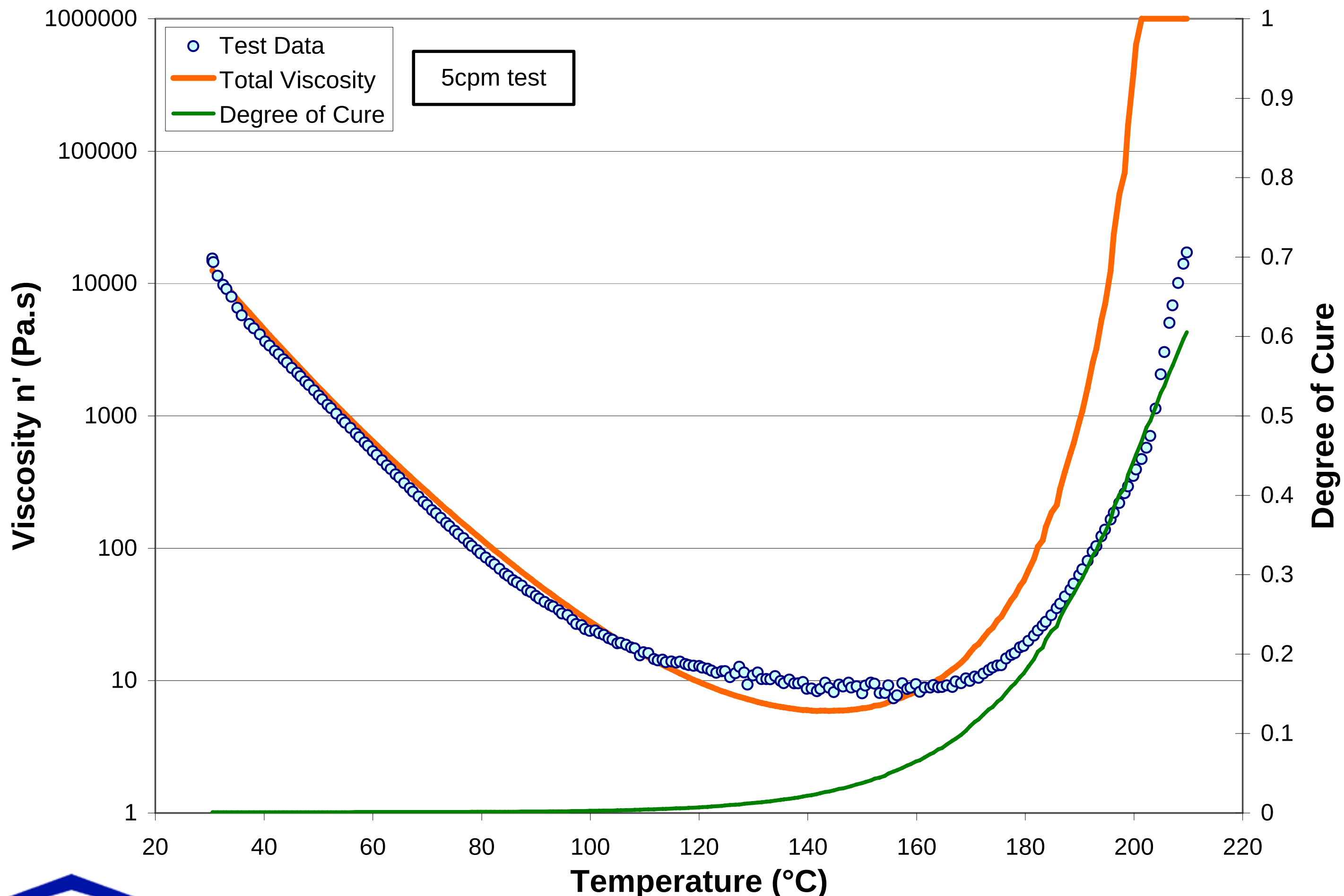
Dynamic Tests – 3cpm



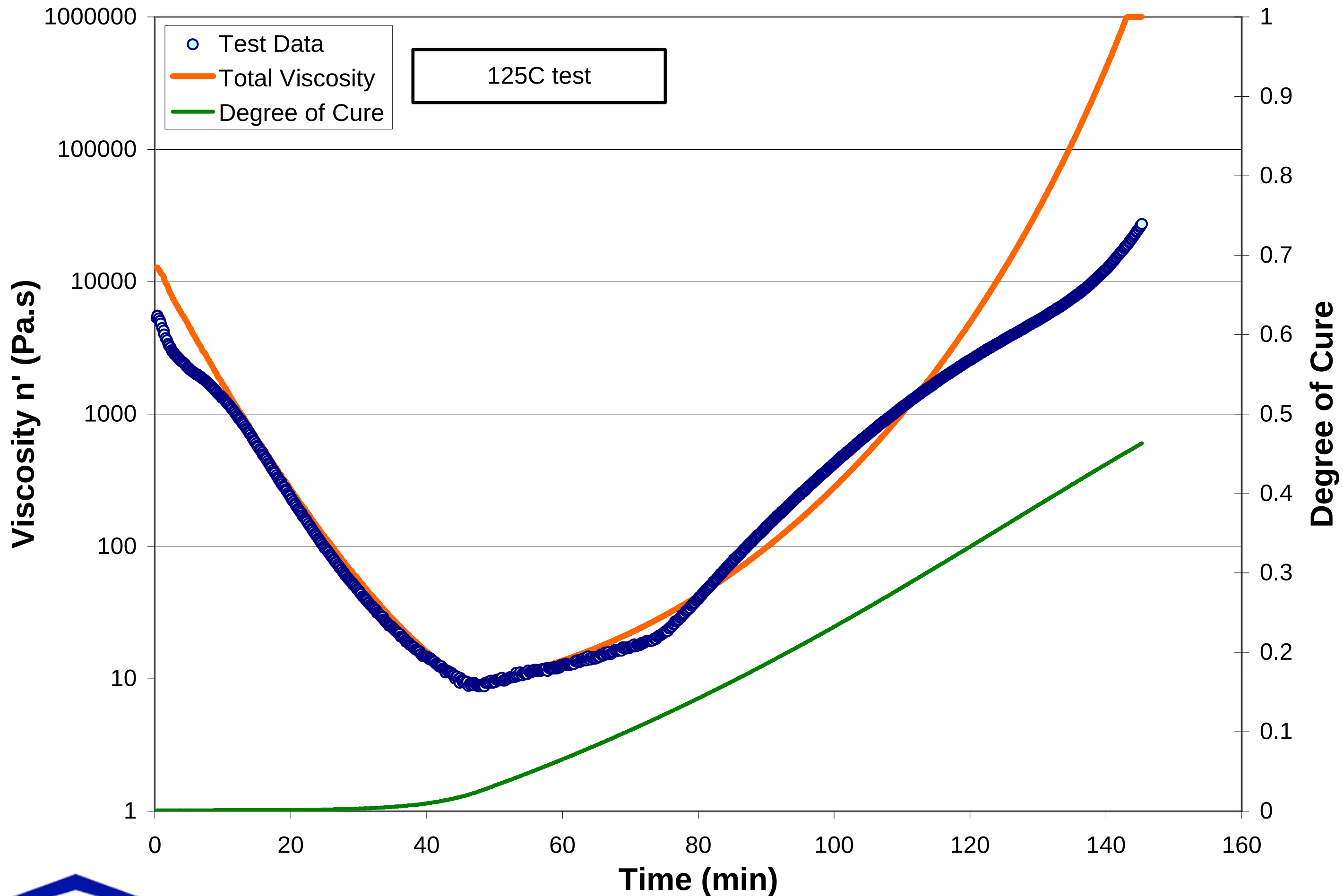
Dynamic Tests – 4cpm



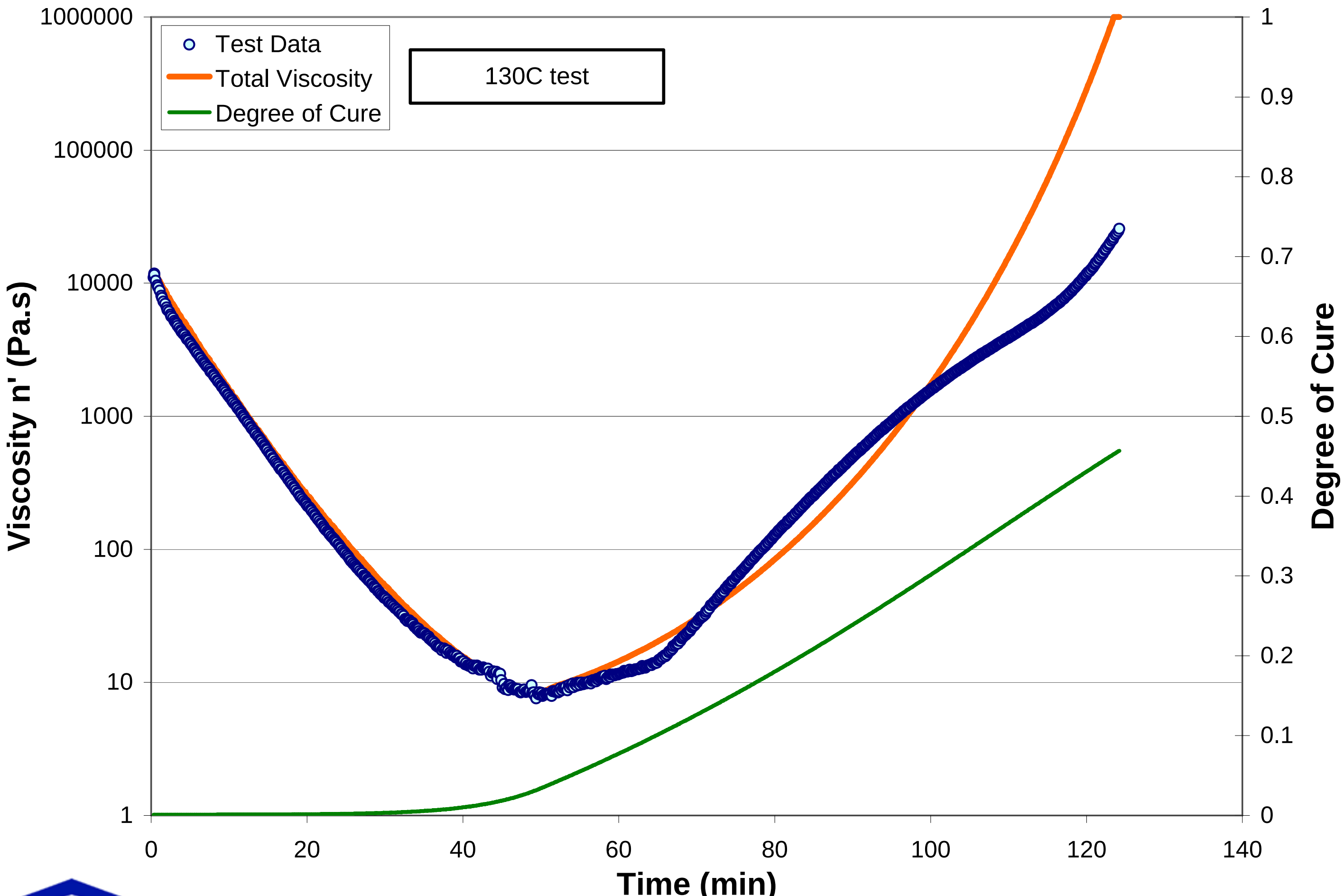
Dynamic Tests – 5cpm



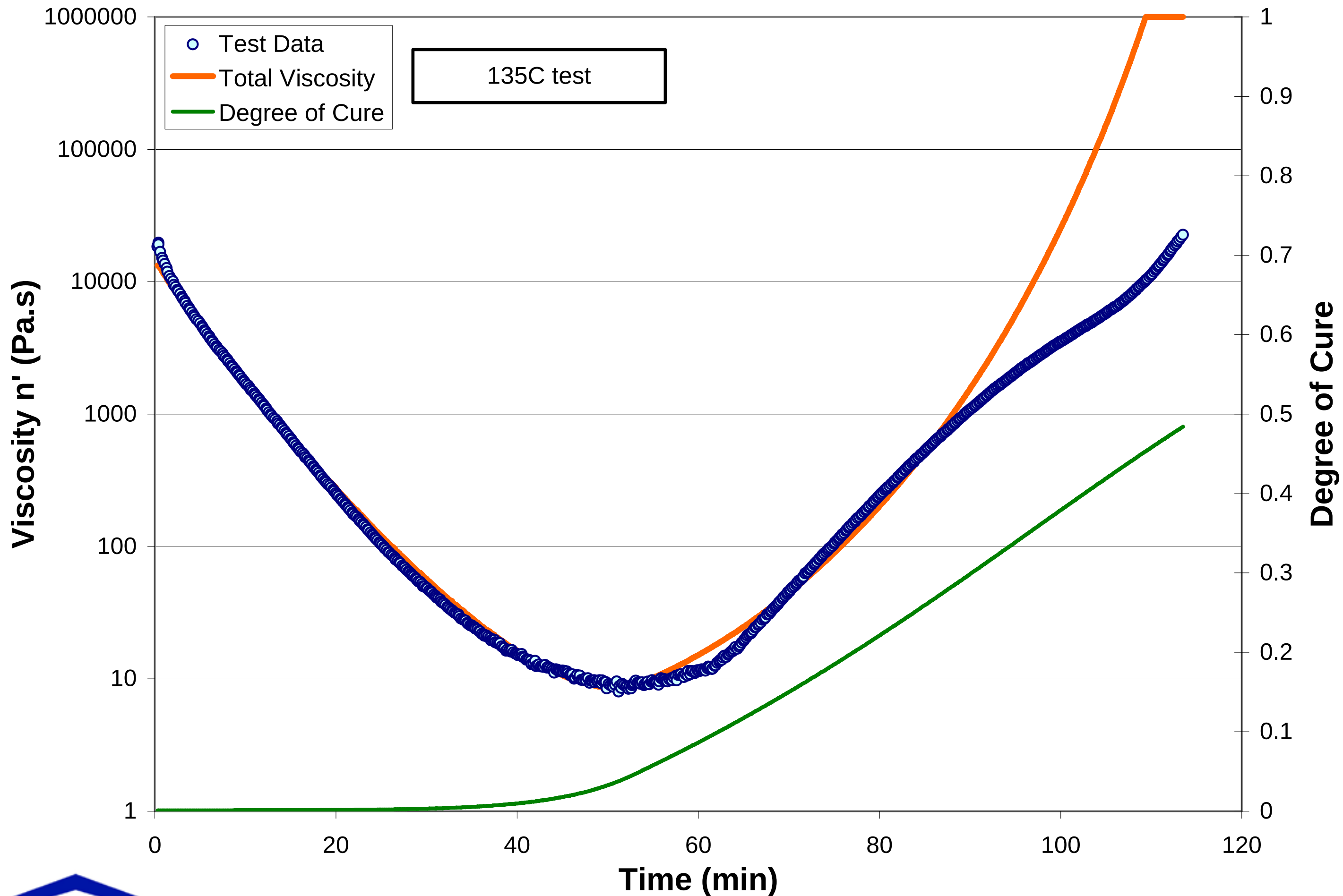
Isothermal Tests – 125C 2cpm



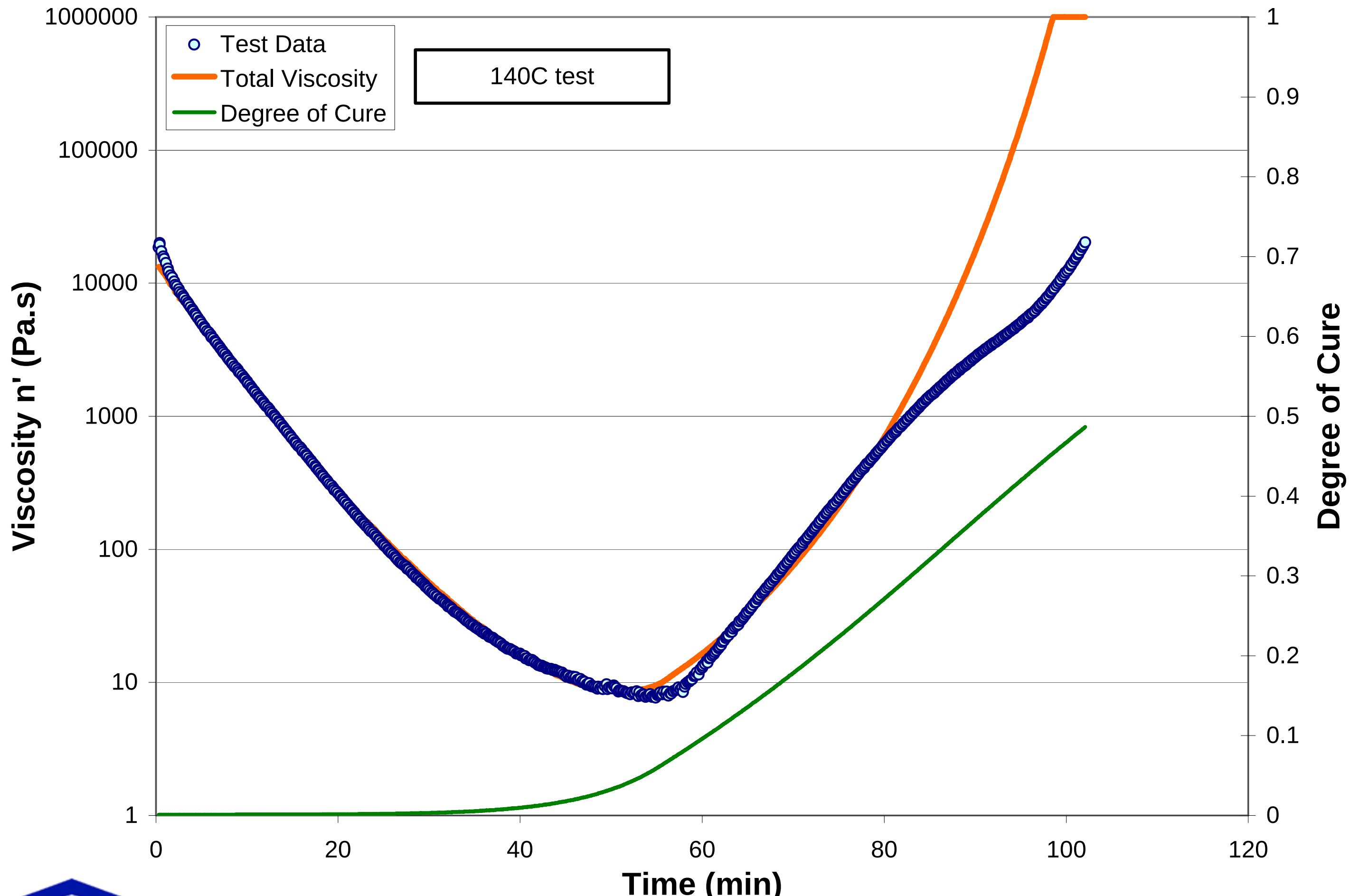
Isothermal Tests – 130C 2cpm



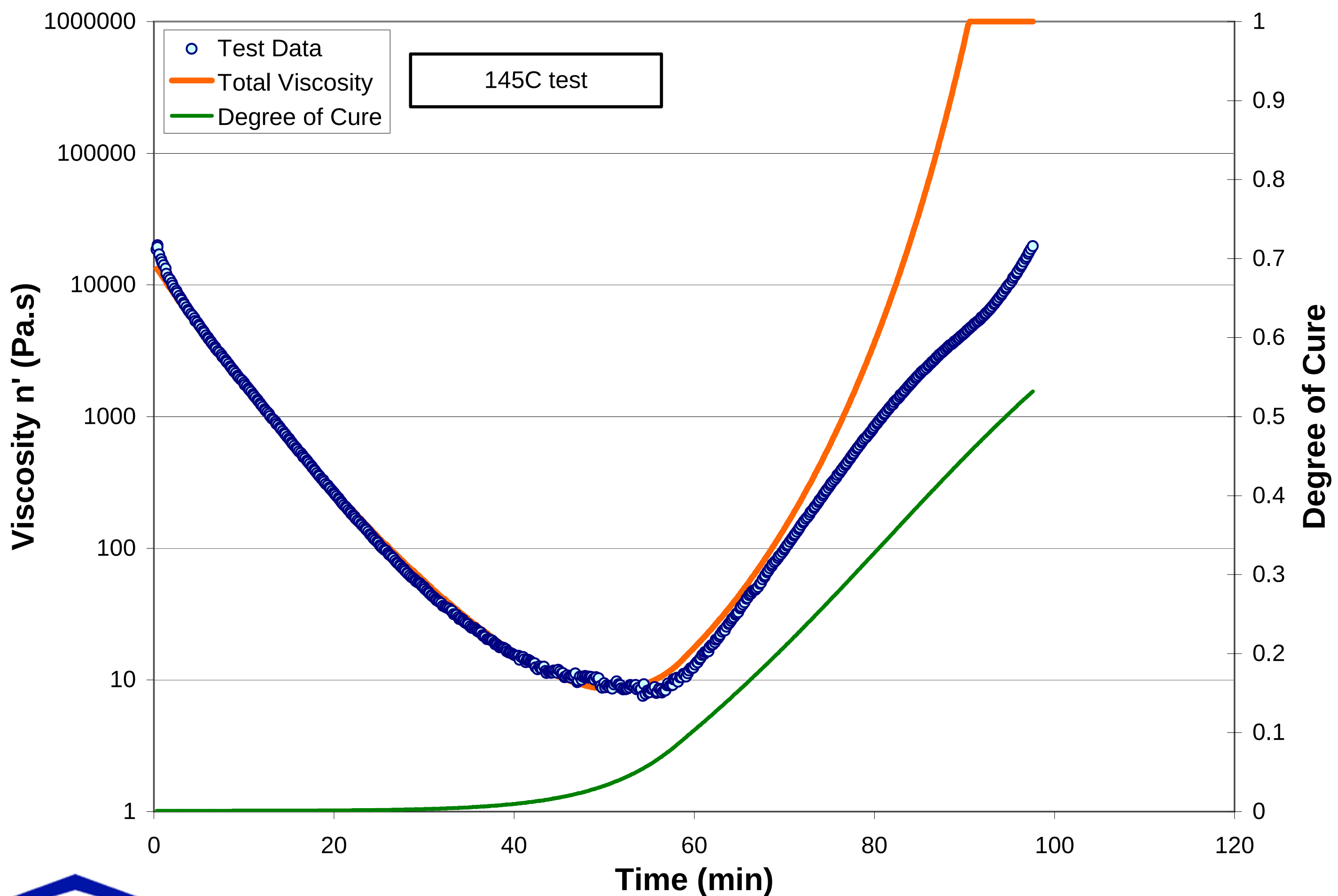
Isothermal Tests – 135C 2cpm



Isothermal Tests – 140C 2cpm



Isothermal Tests – 145C 2cpm



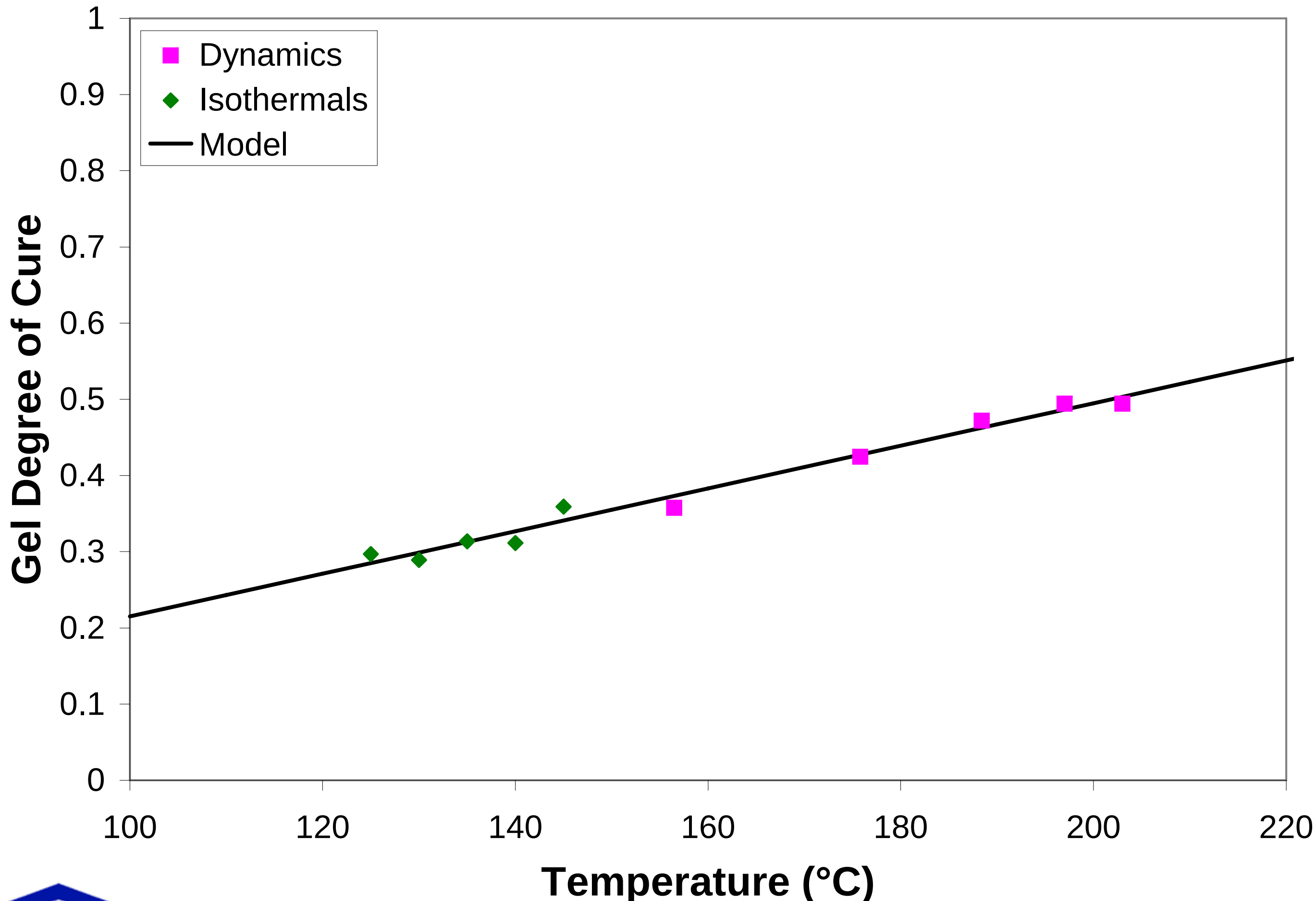
Gel Degree of Cure Model

The gel degree of cure model chosen is in the following form:

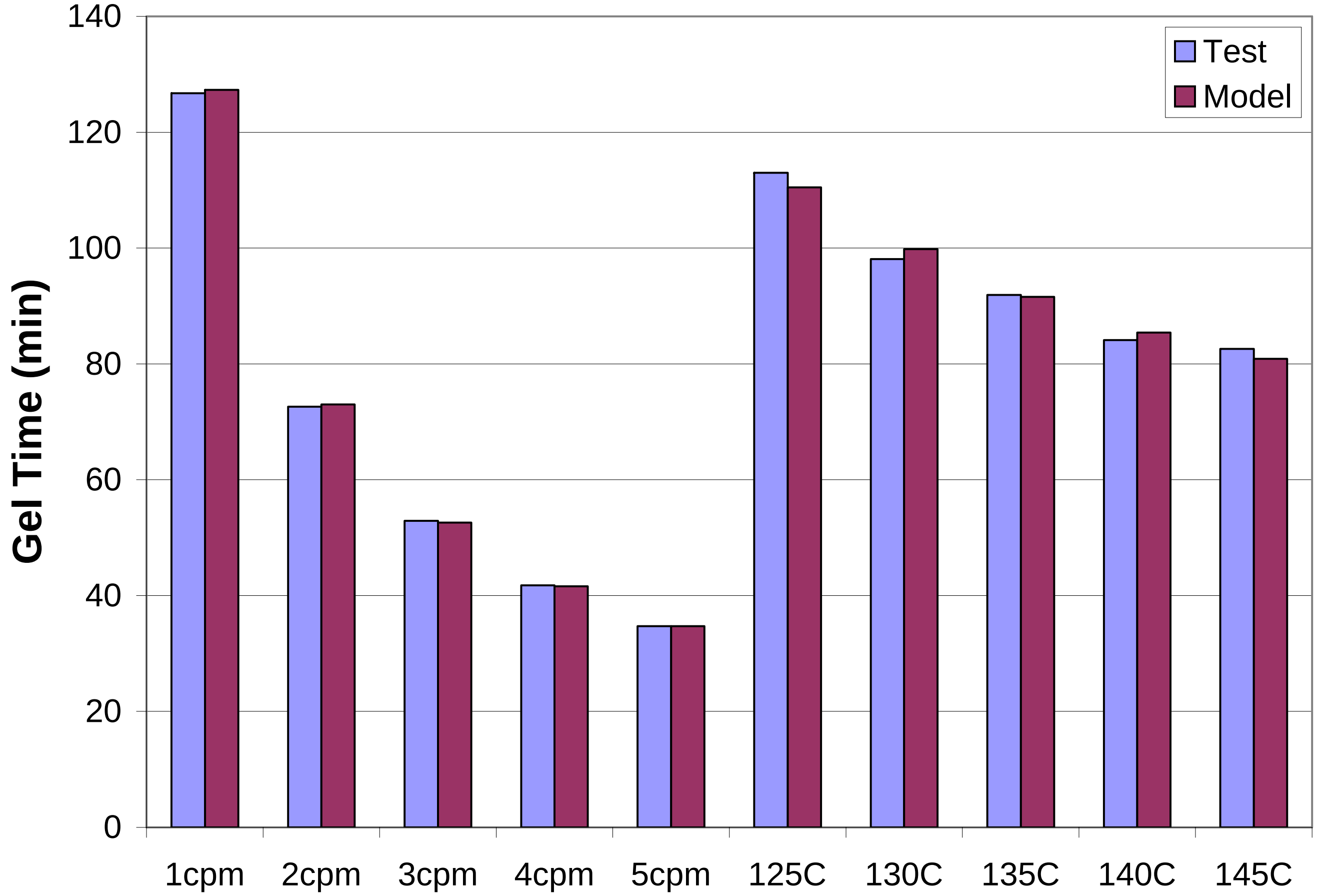
$$x_{gel} = x_{gel_{nom}} + T_f \left(T - T_0\right)$$

Parameter	Value
x_{gel}	0.285
T_f	0.0028
T_0	125
$x_{gel\,\min}$	0.3
$x_{gel\,\max}$	0.5

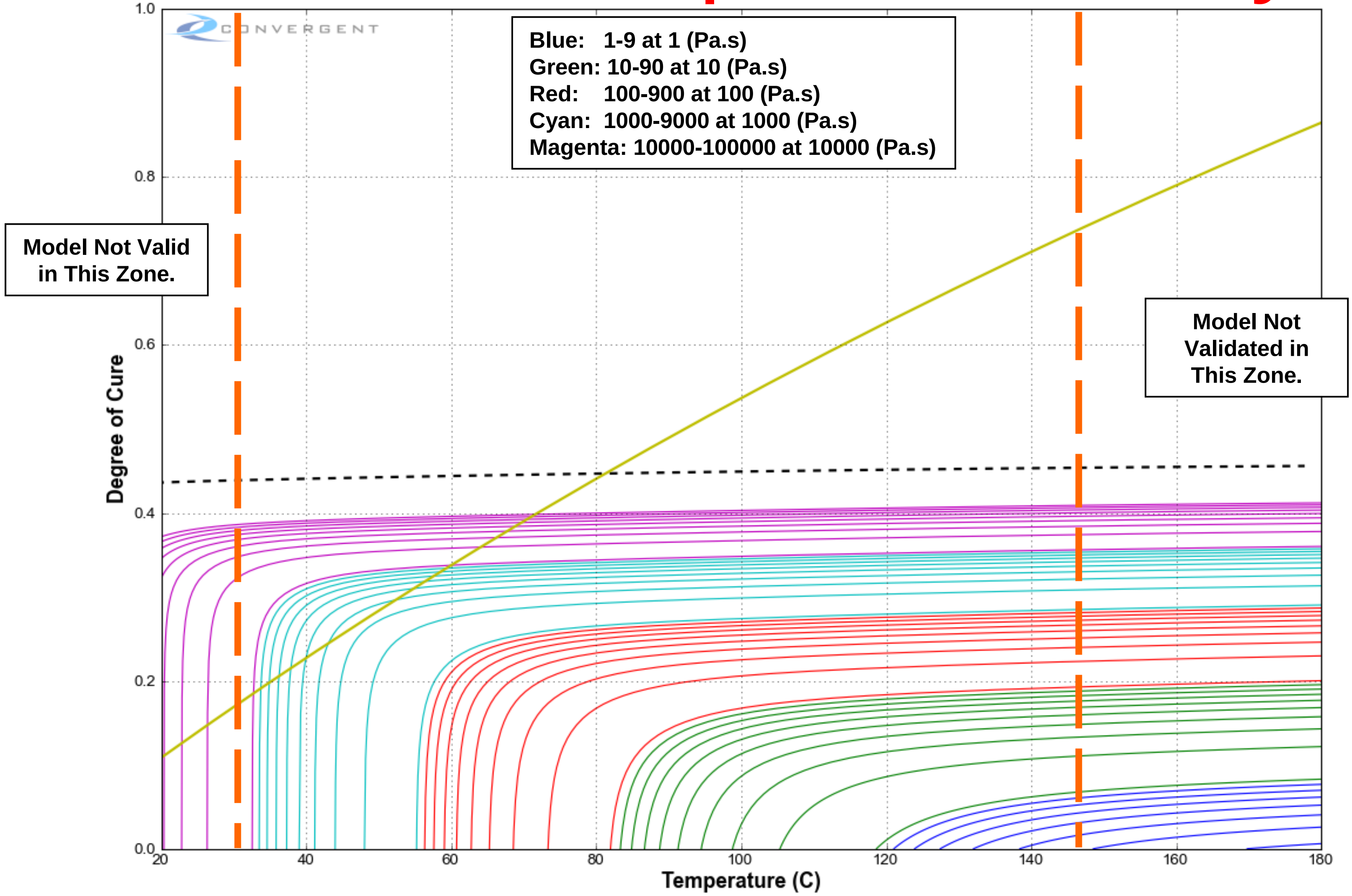
Gel Degree of Cure



Gel Time Predictions



Process Maps – Viscosity



Heat Capacity (Cp) Model

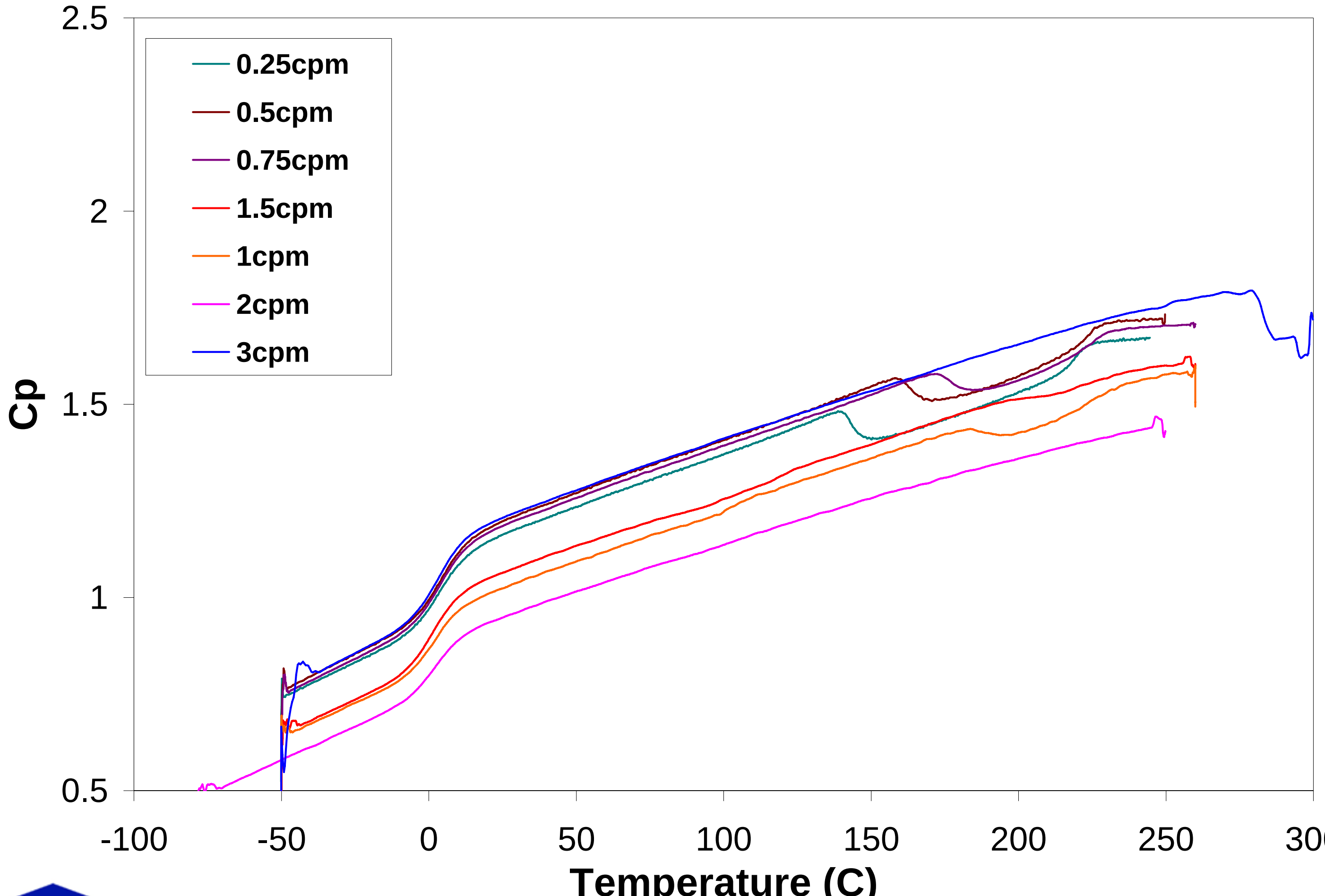
Cp Measurement

- The DSC tests were temperature modulated to obtain a measure of the material's heat capacity, Cp.

- Due to the variability associated with the measured values, some scatter was observed in the Cp response of various tests.

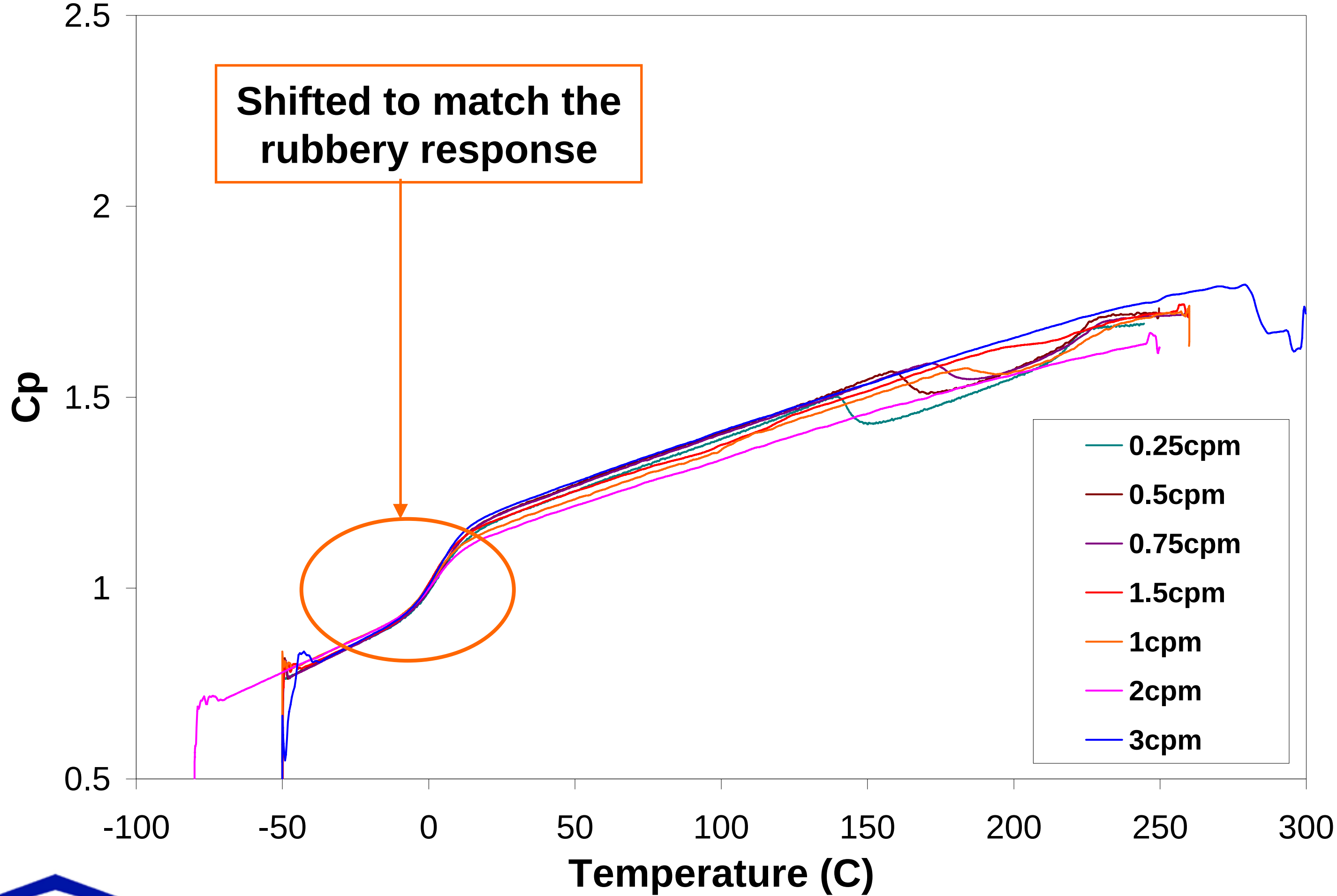
- The Cp responses were modified to match that of a fully cured specimen (identified as reheat tests).

Raw Data



2.5
2
1.5
1
0.5
Cp
0.25cpm
0.5cpm
0.75cpm
1.5cpm
1cpm
2cpm
3cpm
-100
-50
0
50
100
150
200
250
300
Temperature (C)

Raw Data – Anchored to Reheat Test



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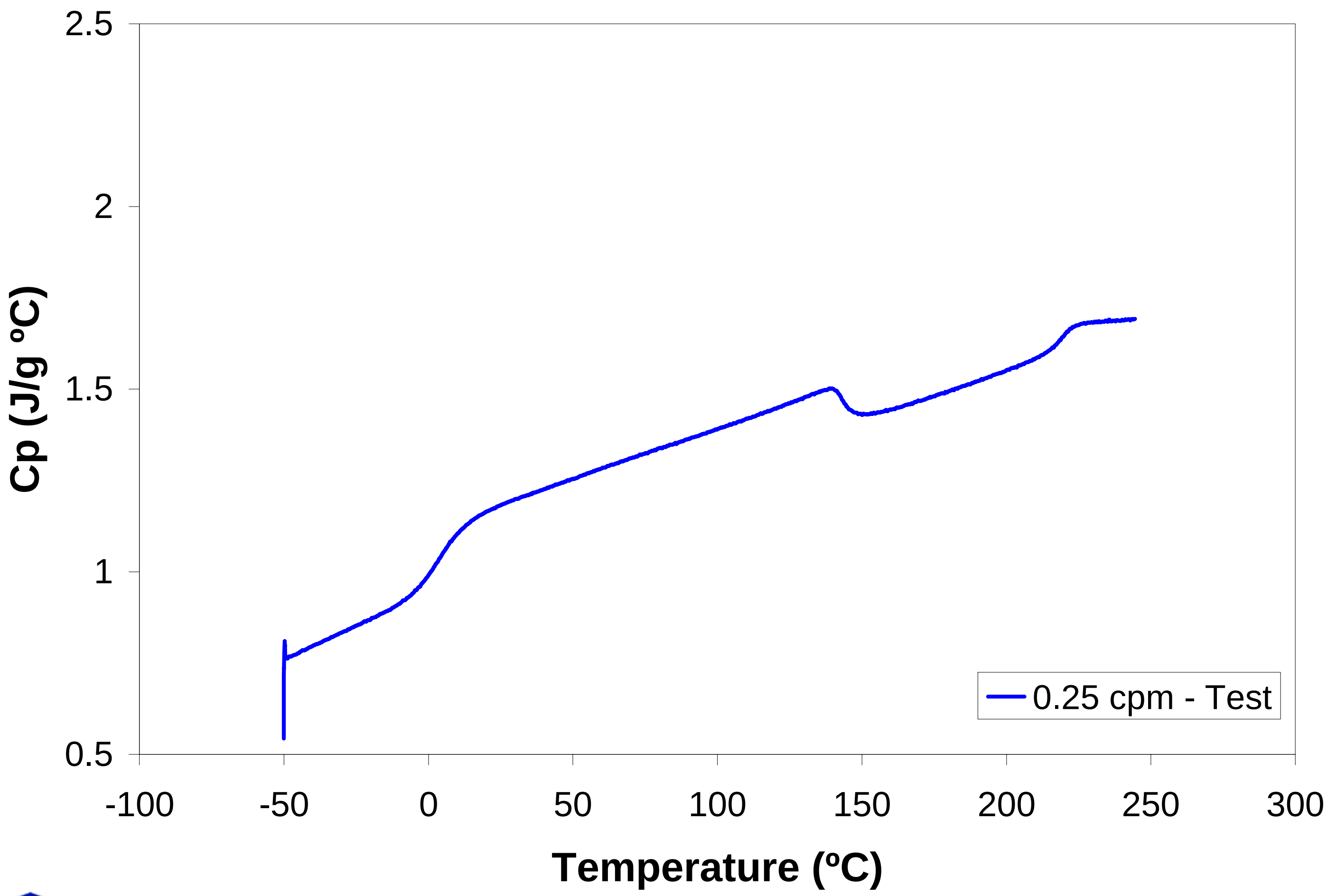
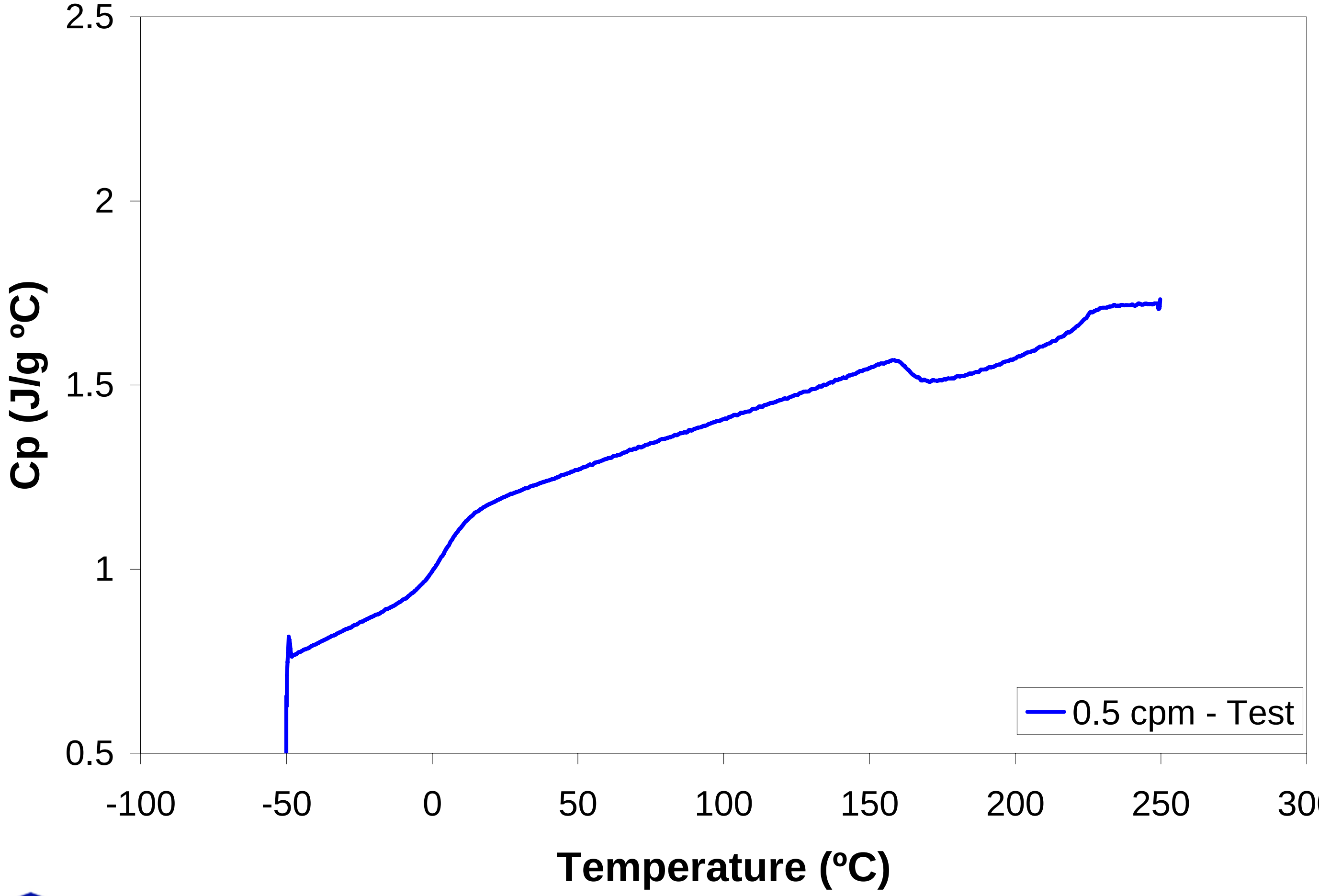
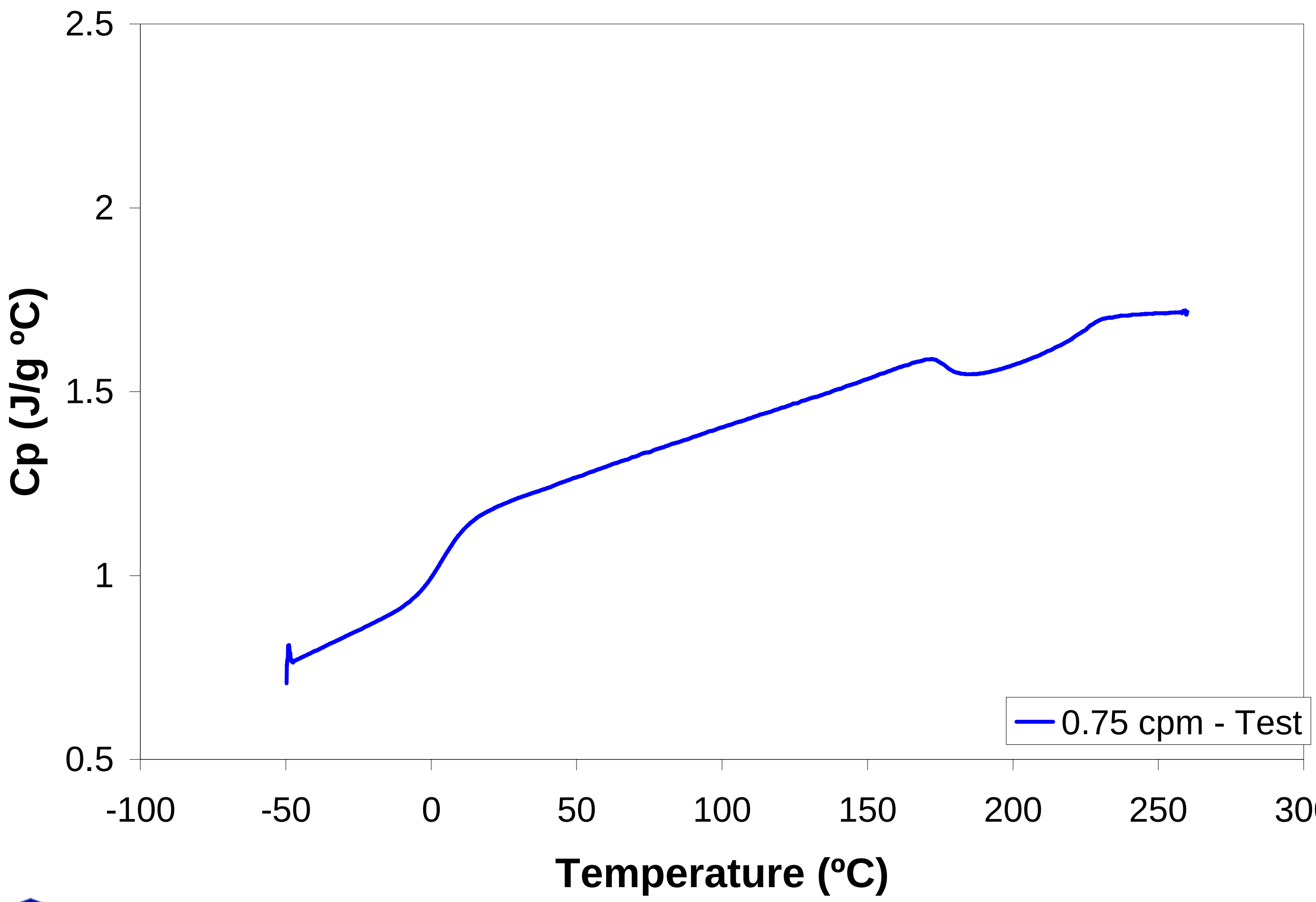
Raw Data – 0.25Cpm



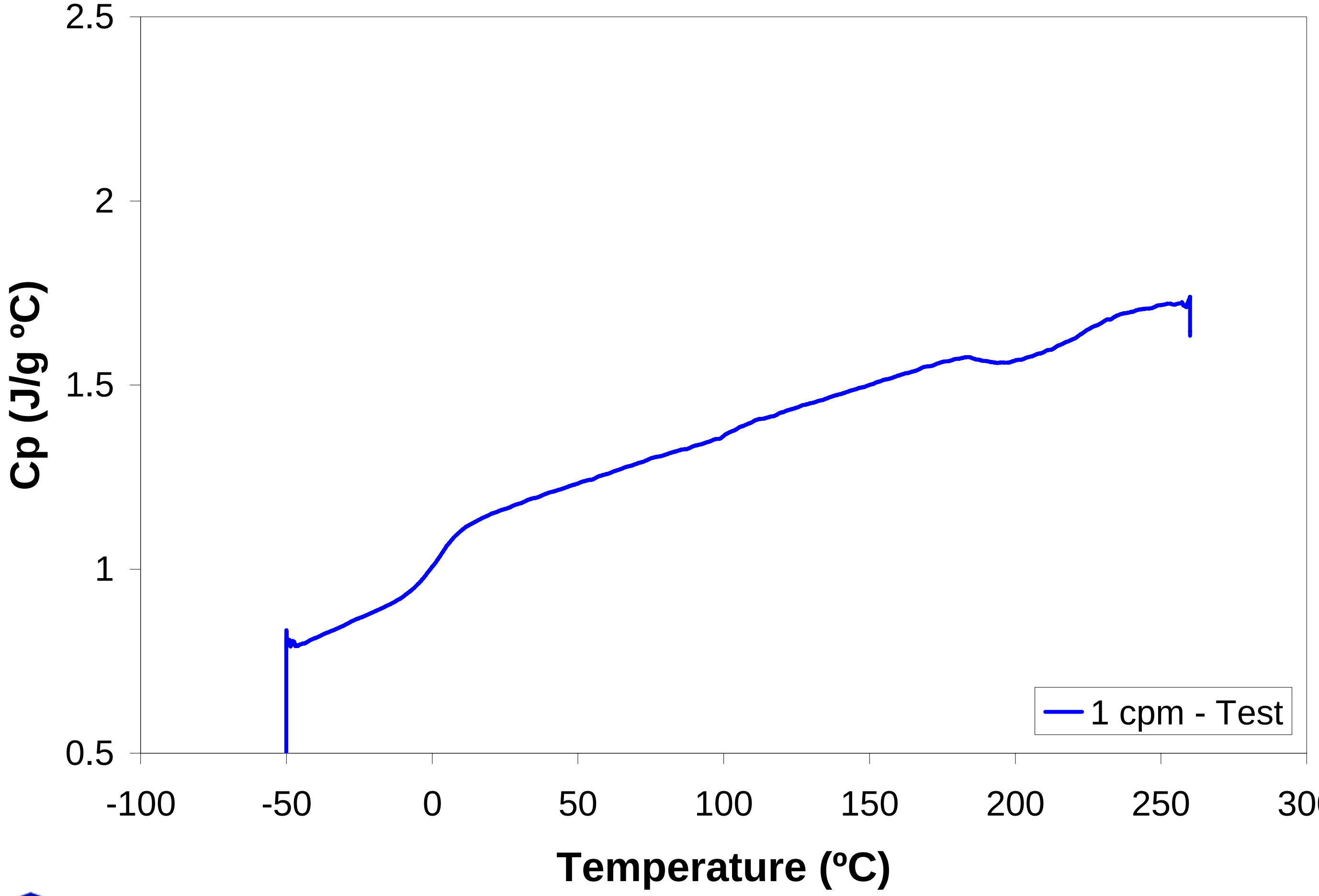
Raw Data – 0.5Cpm



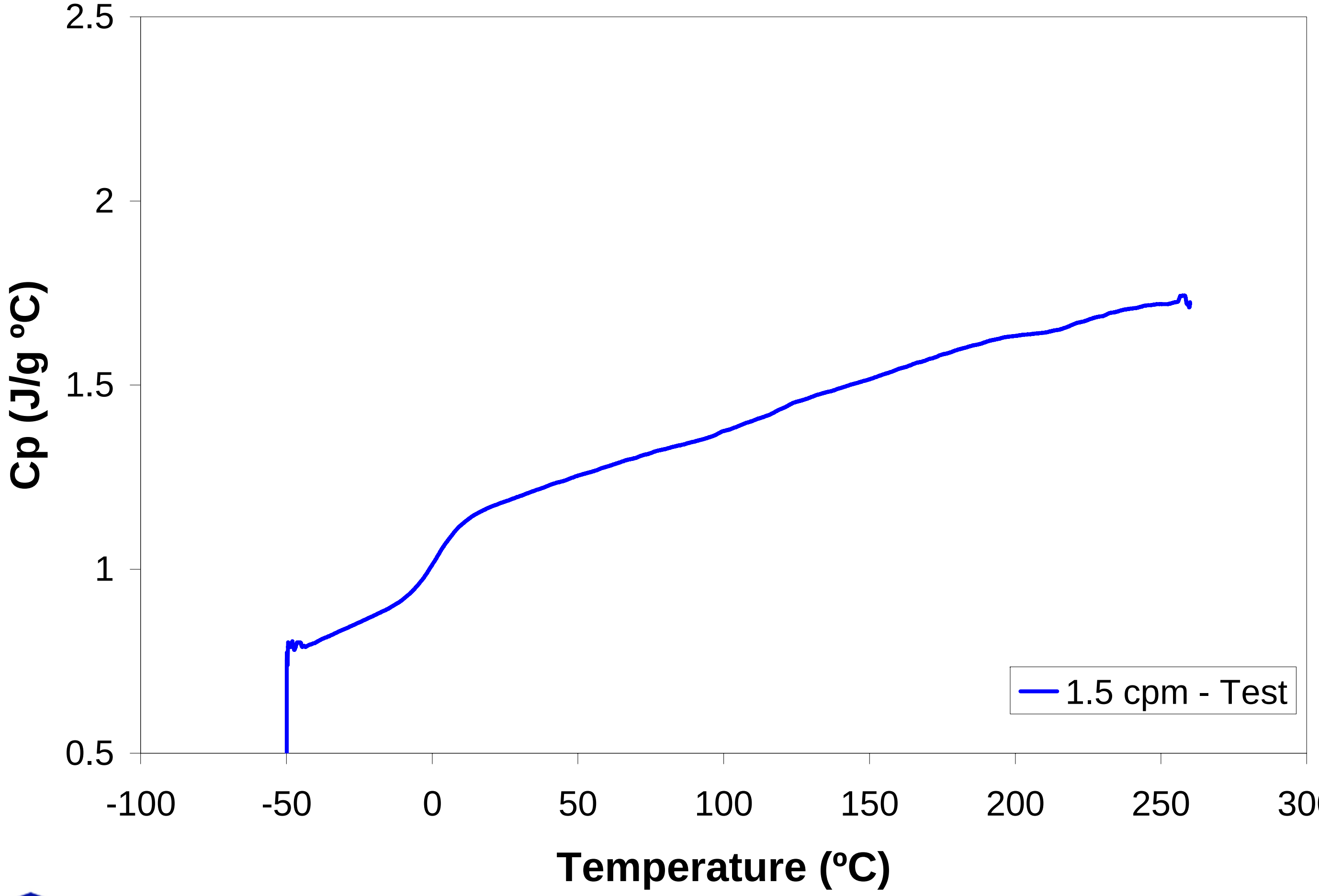
Raw Data – 0.75Cpm



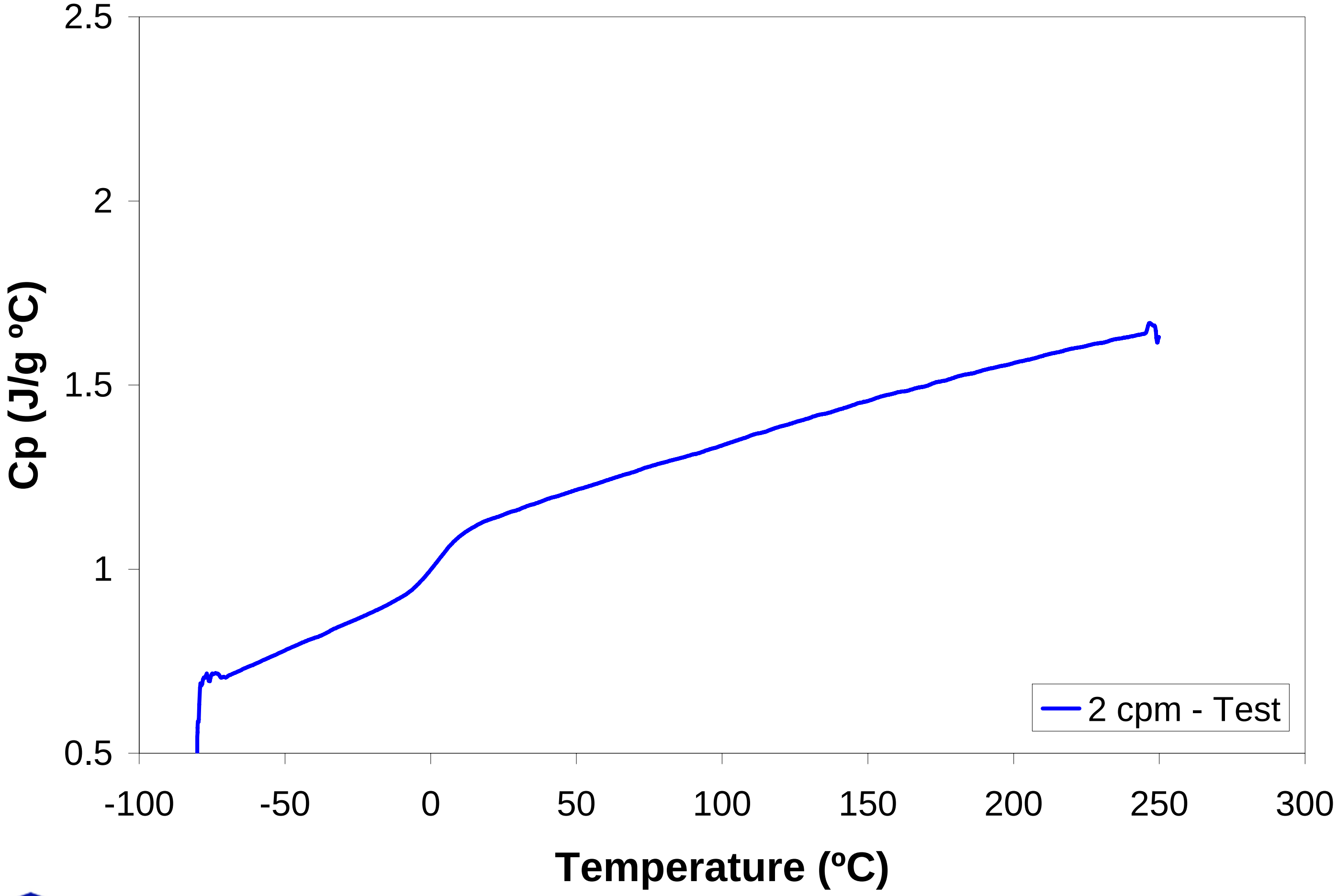
Raw Data – 1Cpm



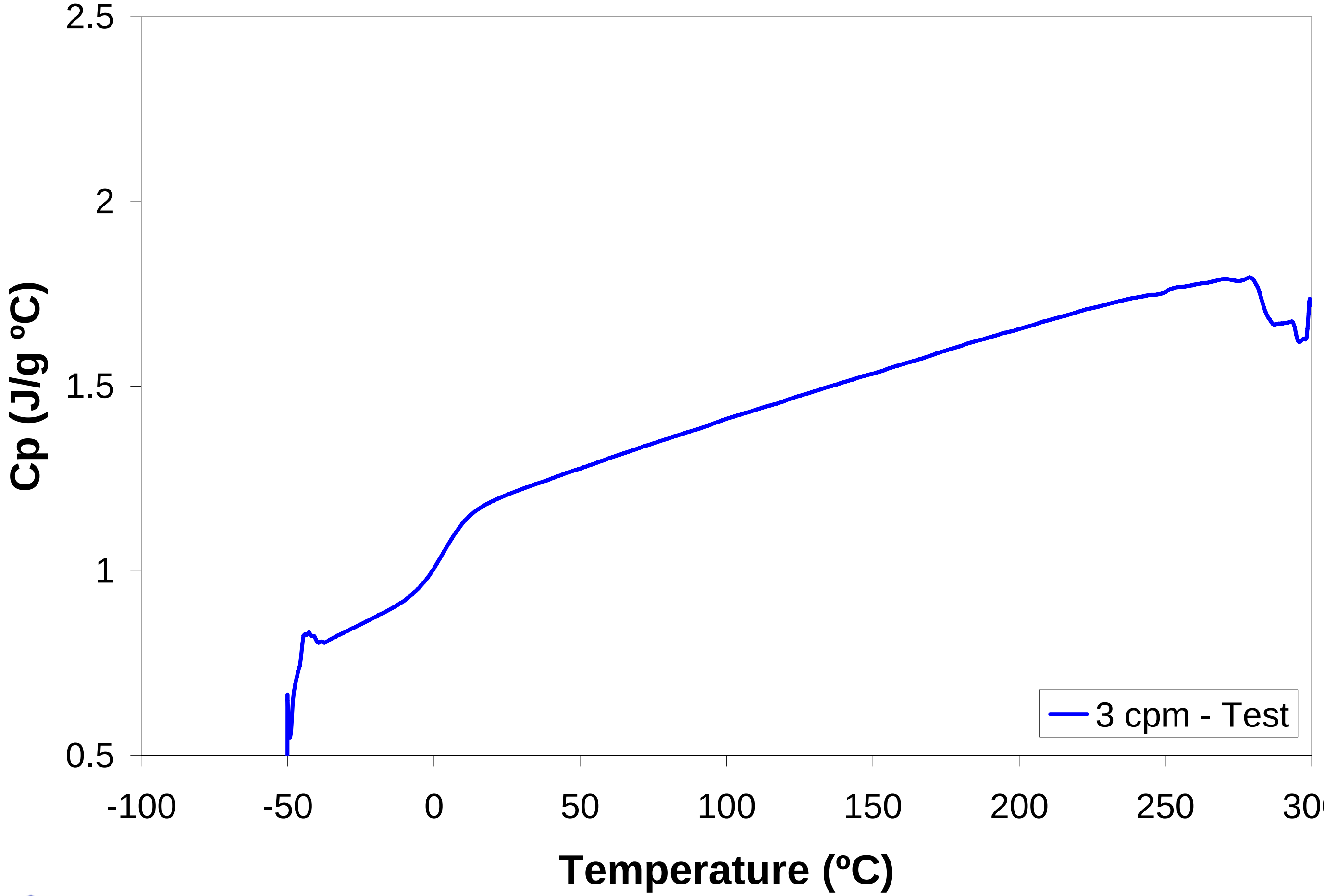
Raw Data – 1.5Cpm



Raw Data – 2Cpm



Raw Data – 3Cpm



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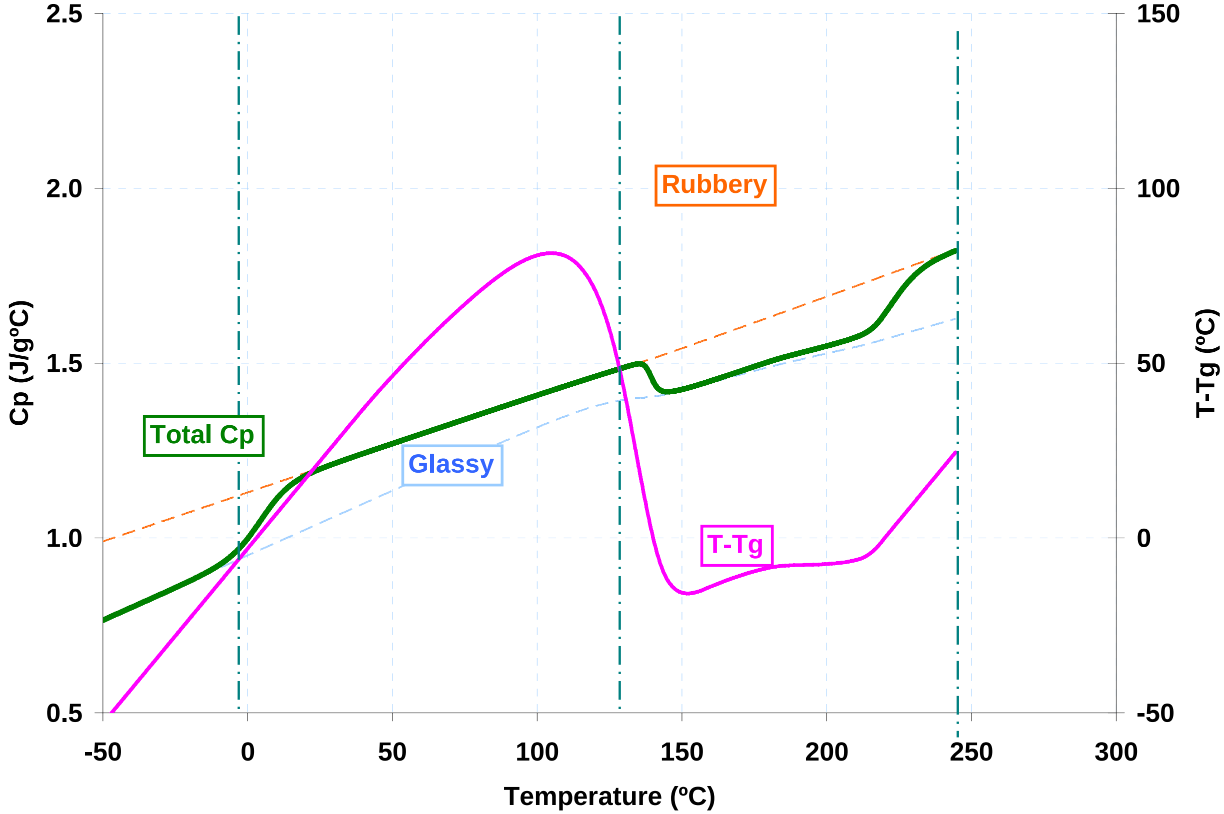
CONVERGENT MANUFACTURING TECHNOLOGIES

Cp Model Basics

• Glassy and rubbery Cp were assumed to be functions of temperature and DoC
• Cp was assumed to transition between the glassy and rubbery responses with changes in T-Tg



Cp Model

The parameters of the Cp model are determined by fitting to the experimental results. The model is formulated as shown below:

Virgin and cured responses: $C_{p_{ij}} = s_{ij}T + c_{ij} \quad \left(i = r, g \quad \text{and} \quad j = 0, \infty\right)$

Glassy or rubbery at ***x***: $C_{p_i} = \left(1 - x\right)C_{p_{i0}} + xC_{p_{i\infty}}$

Total Cp response: $C_p = C_{p_r} + \dfrac{C_{p_g} - C_{p_r}}{1 + e^{k\left[\left(T - T_g\right) - \Delta T_c\right]}}$

Glassy

$s_{g0} = 0.0037 \quad s_{g\infty} = 0.0024$

$c_{g0} = 0.95 \quad c_{g\infty} = 1.04$

Rubbery

$s_{r0} = 0.0028 \quad s_{g\infty} = 0.002$

$c_{r0} = 1.13 \quad c_{g\infty} = 1.2$

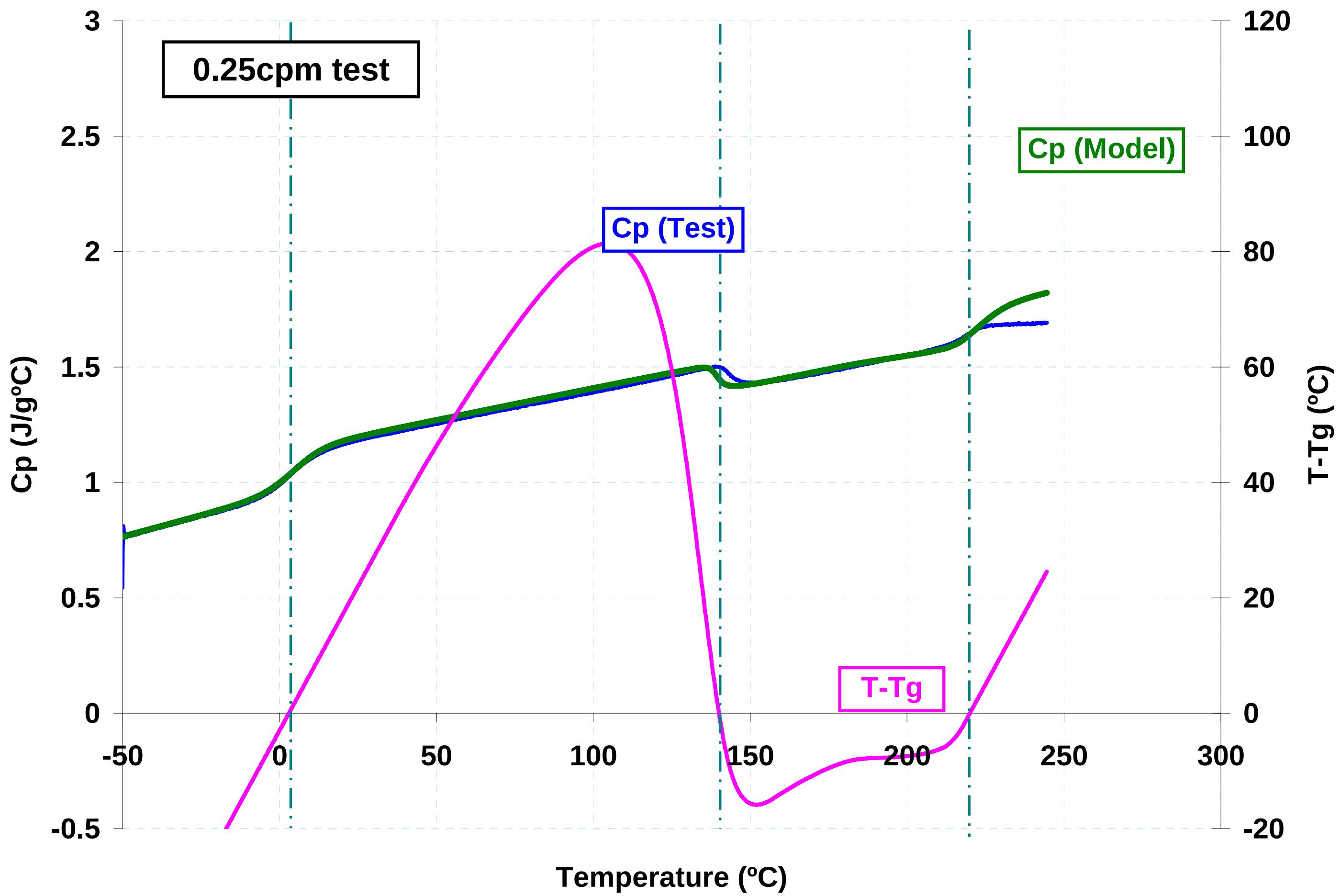
Other parameters

$k = 0.20$

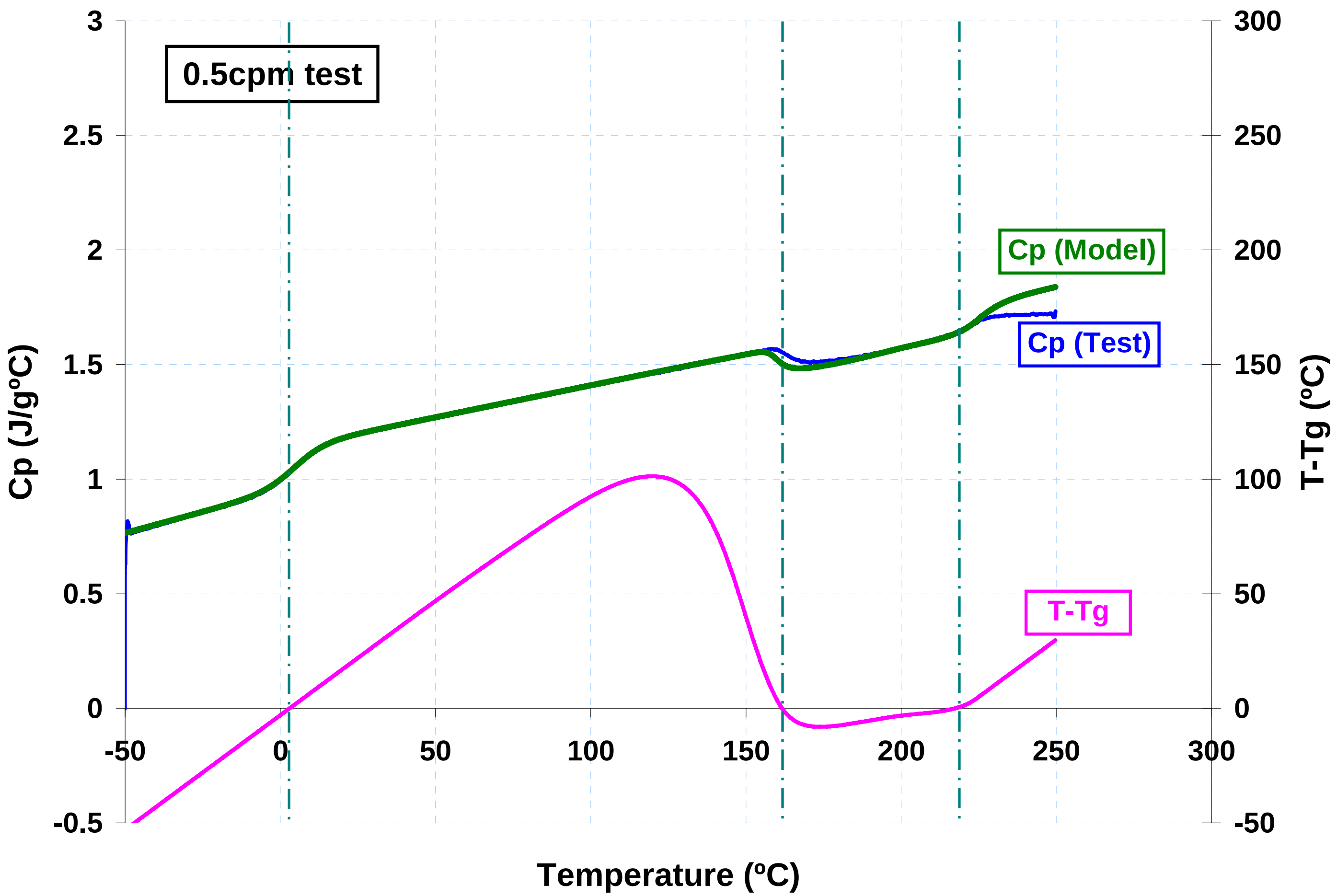
$\Delta T_c = 2$

Valid for temperature values between -20ºC to 200ºC.

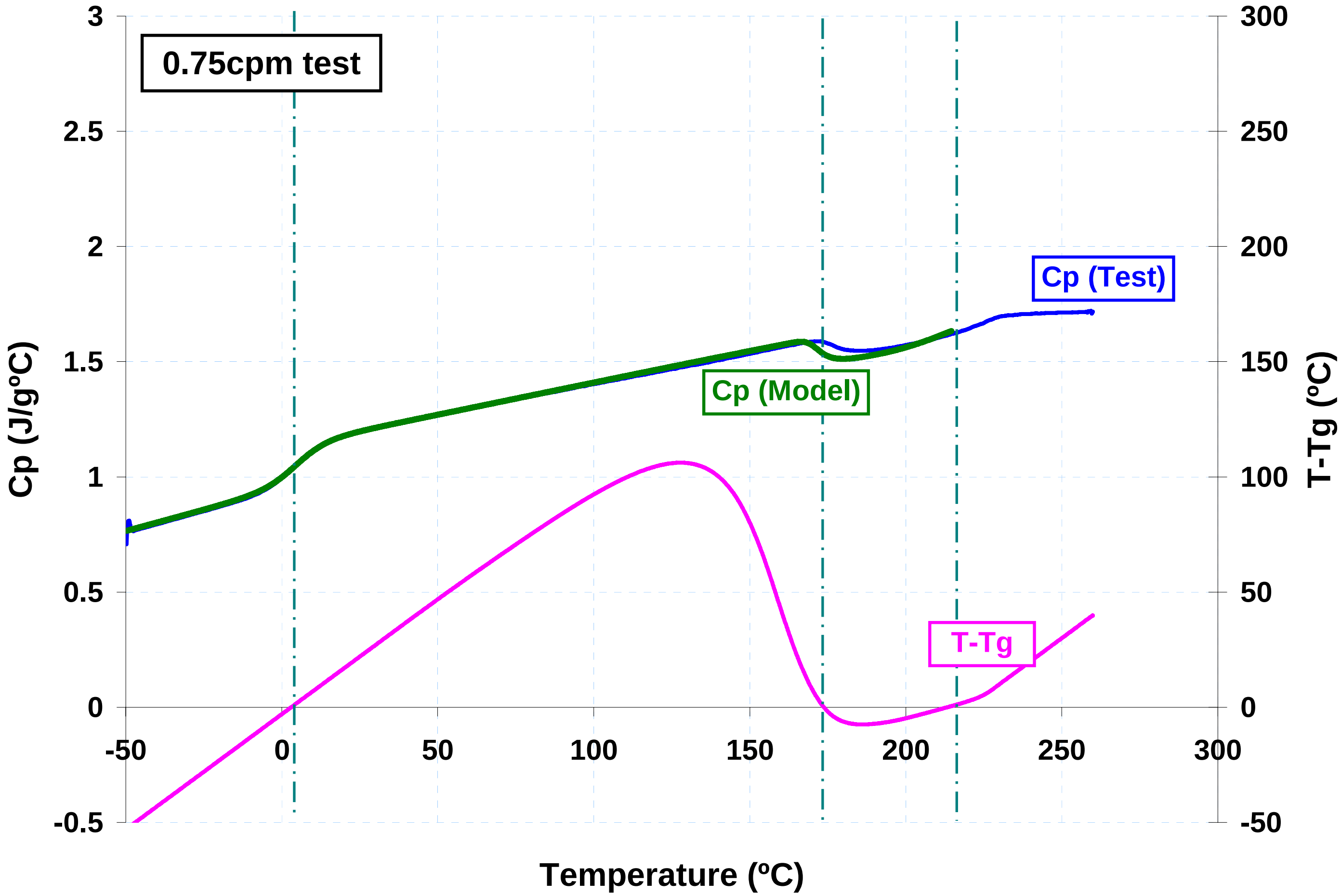
Dynamic Tests – 0.25cpm



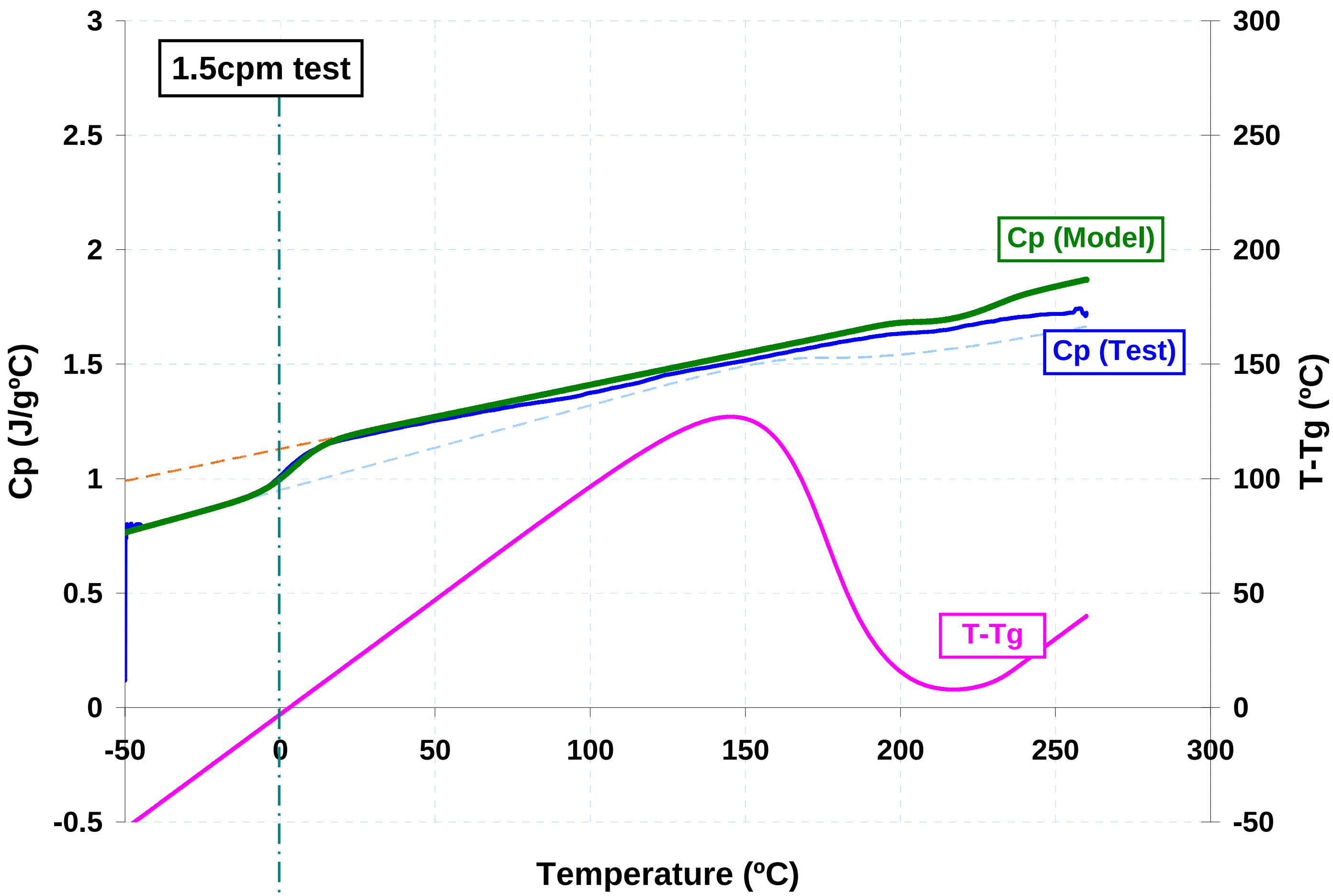
Dynamic Tests – 0.5cpm



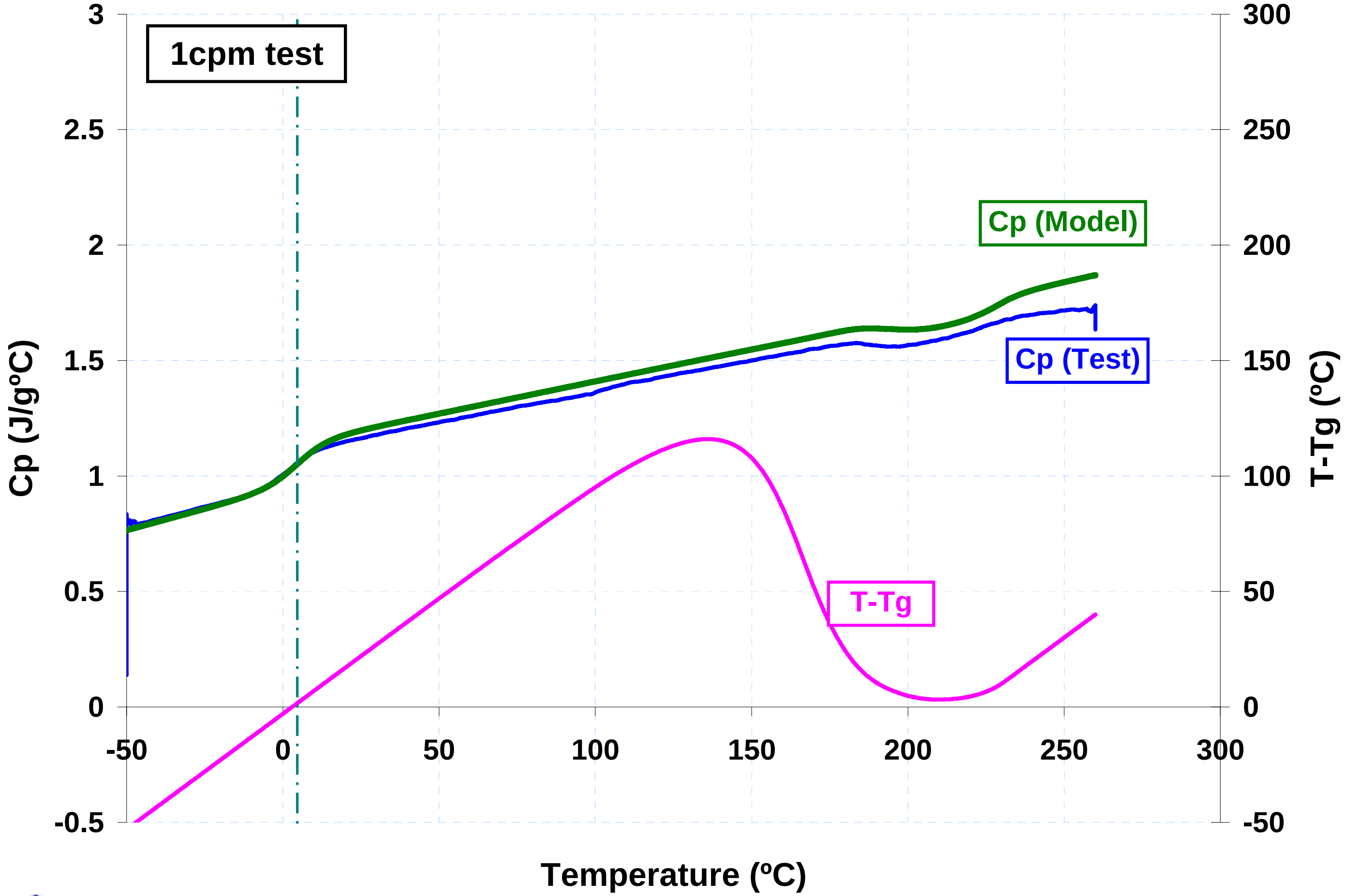
Dynamic Tests – 0.75cpm



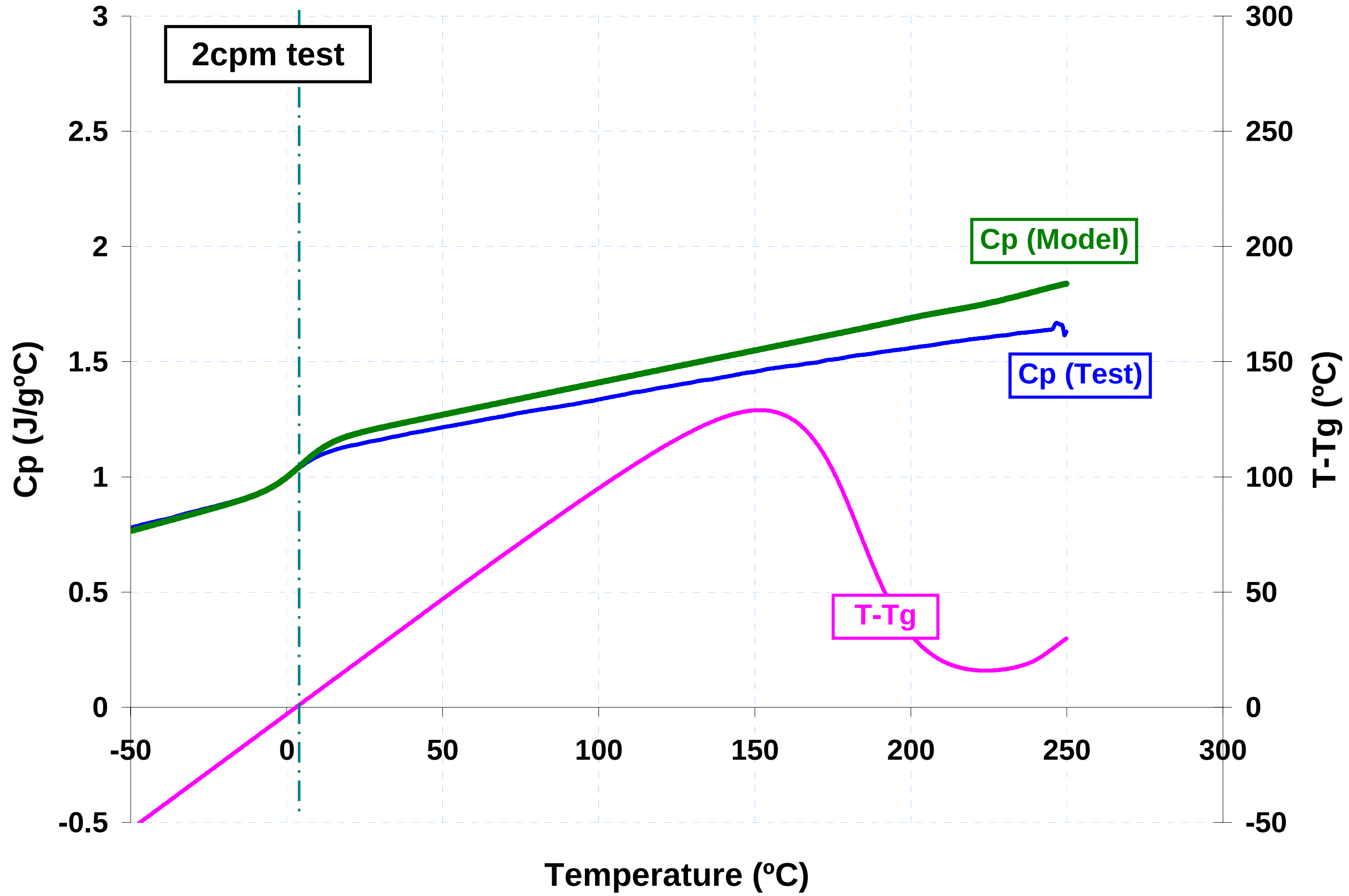
Dynamic Tests – 1.5cpm



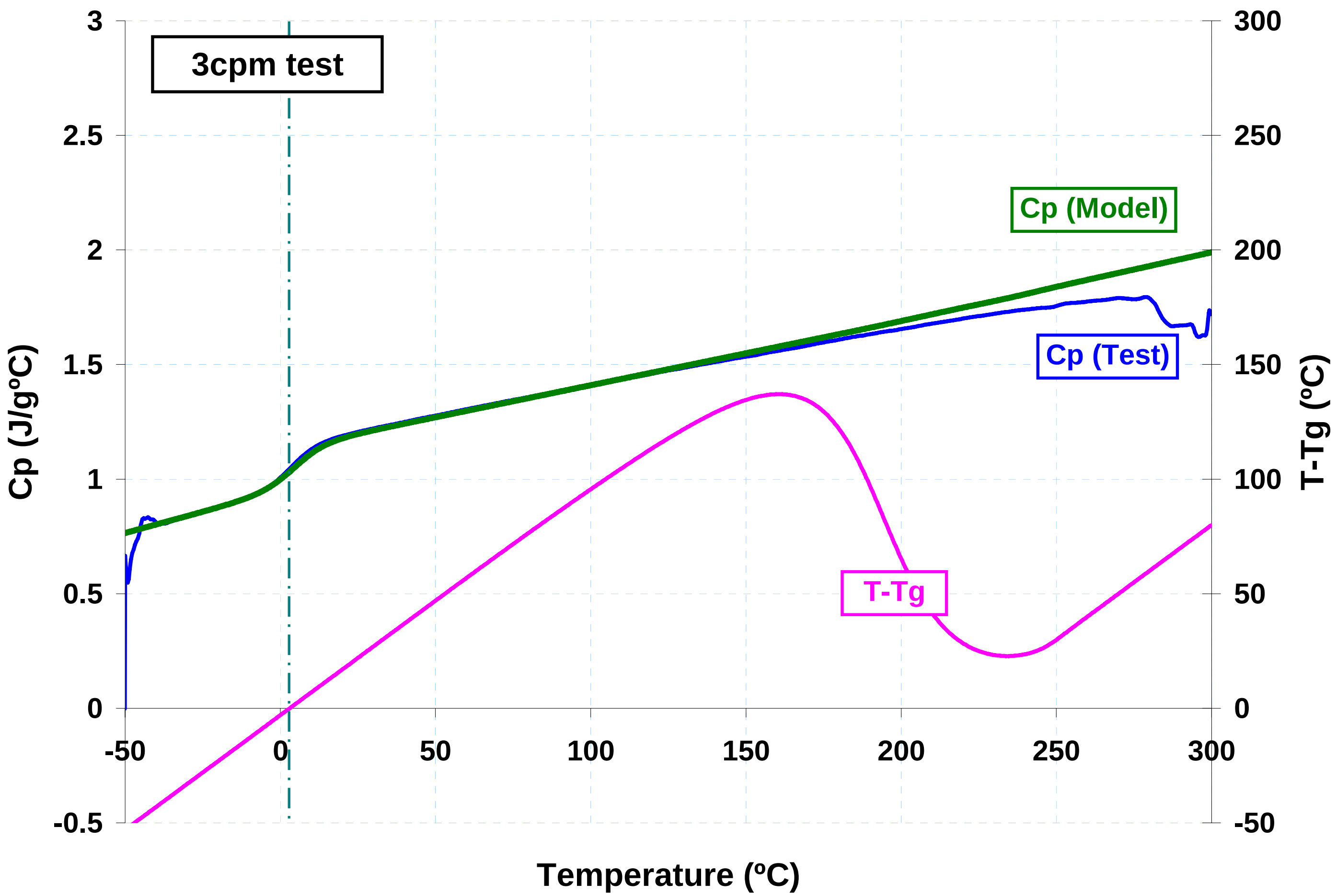
Dynamic Tests – 1cpm



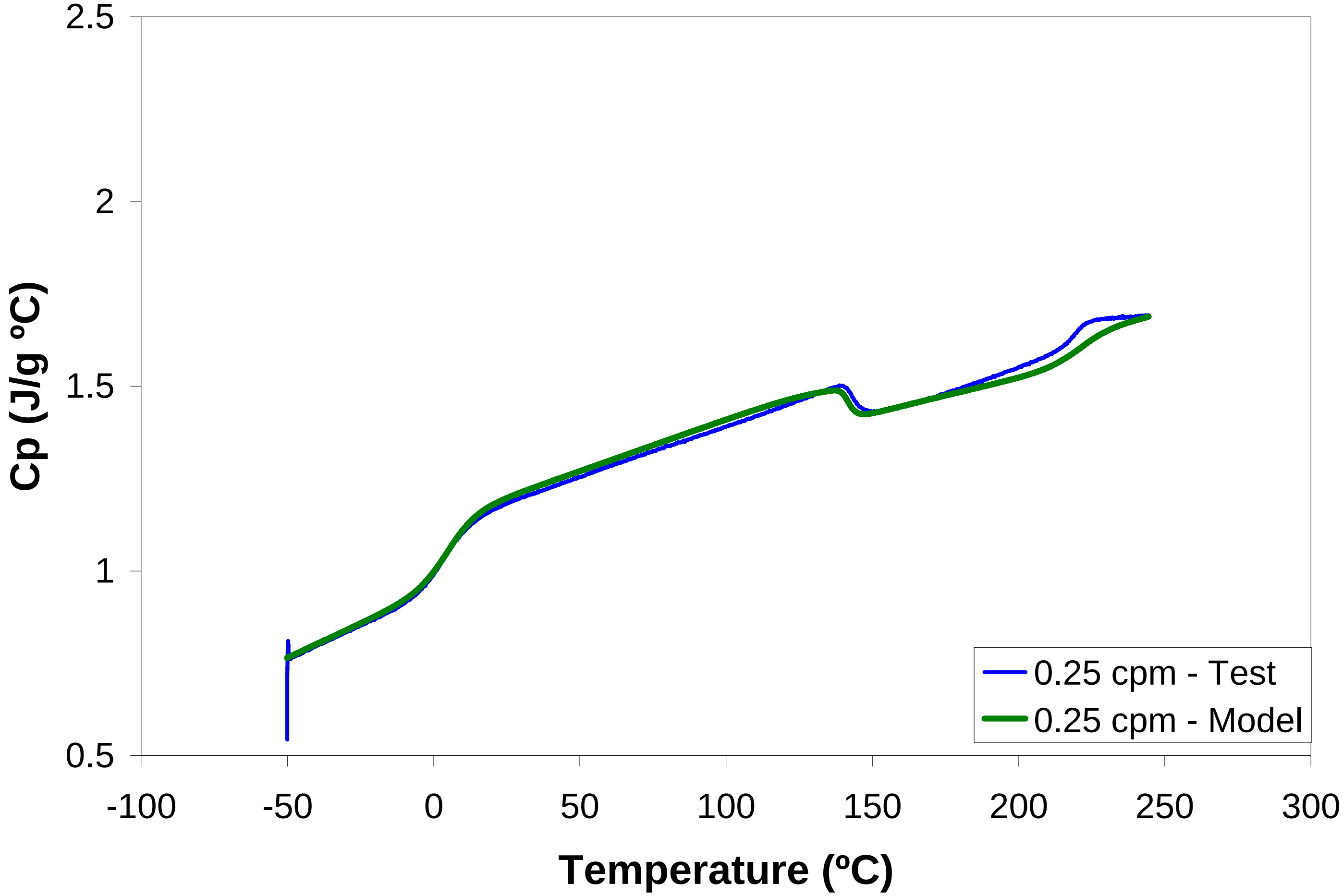
Dynamic Tests – 2cpm



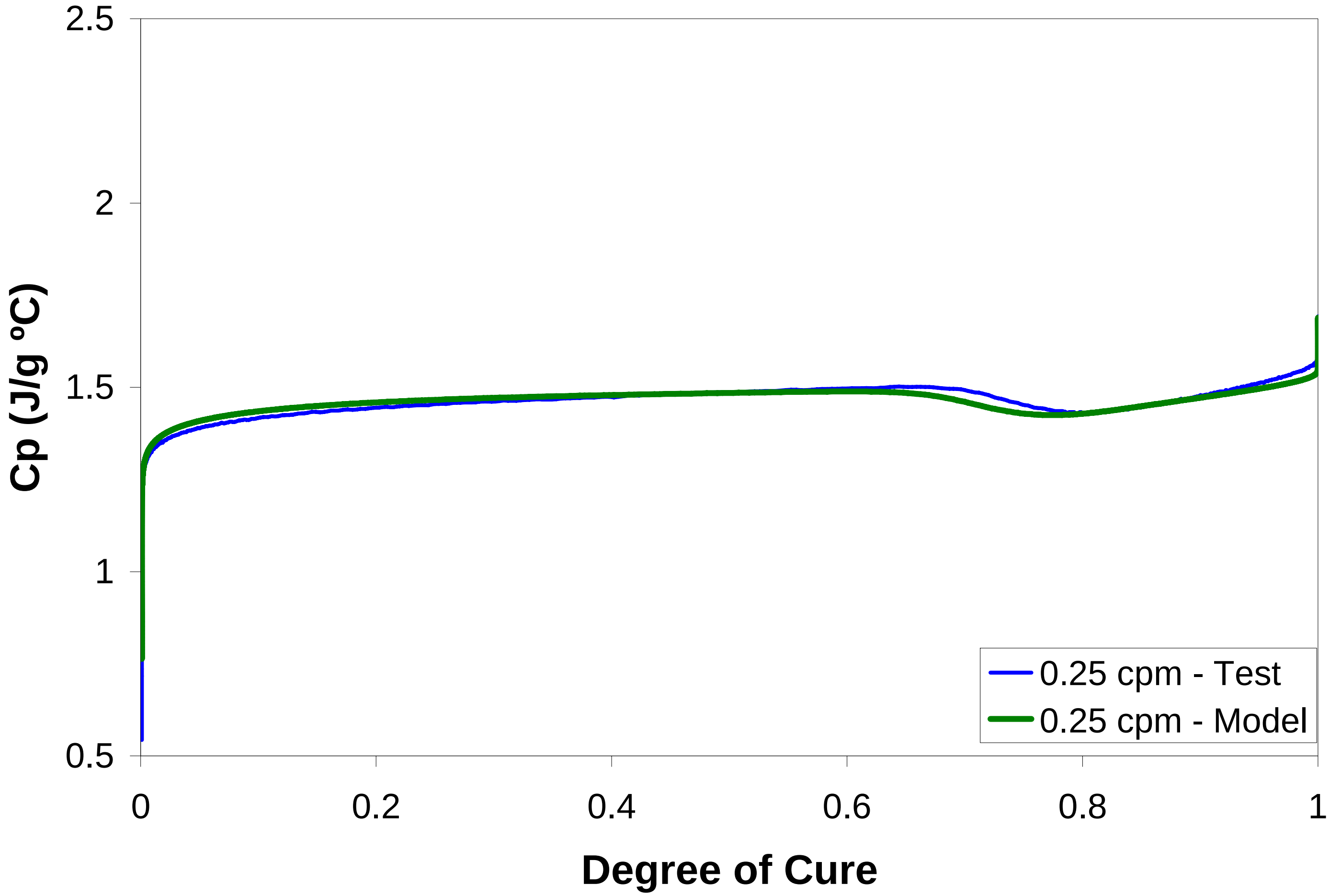
Dynamic Tests – 3cpm



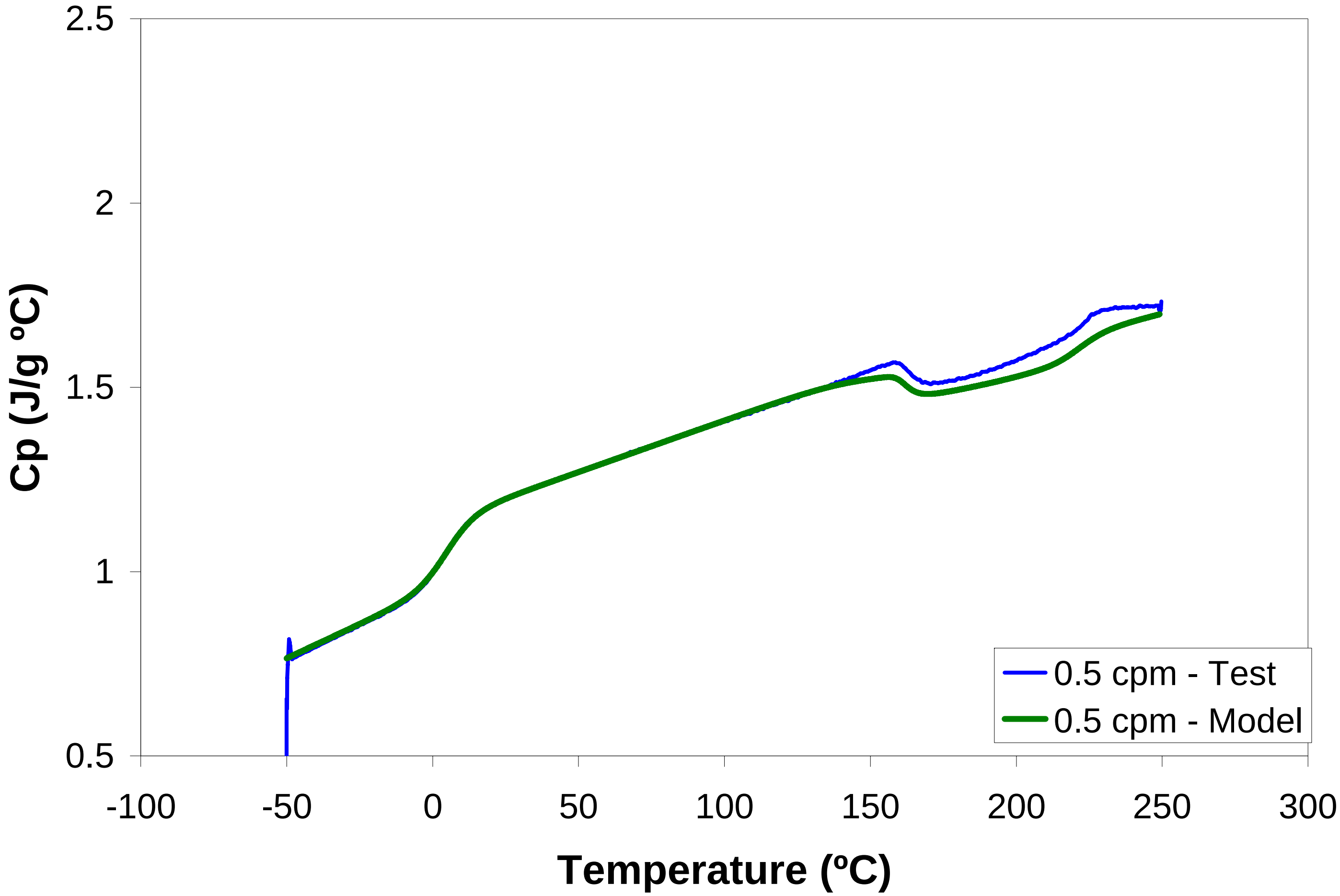
Dynamic Tests – 0.25cpm



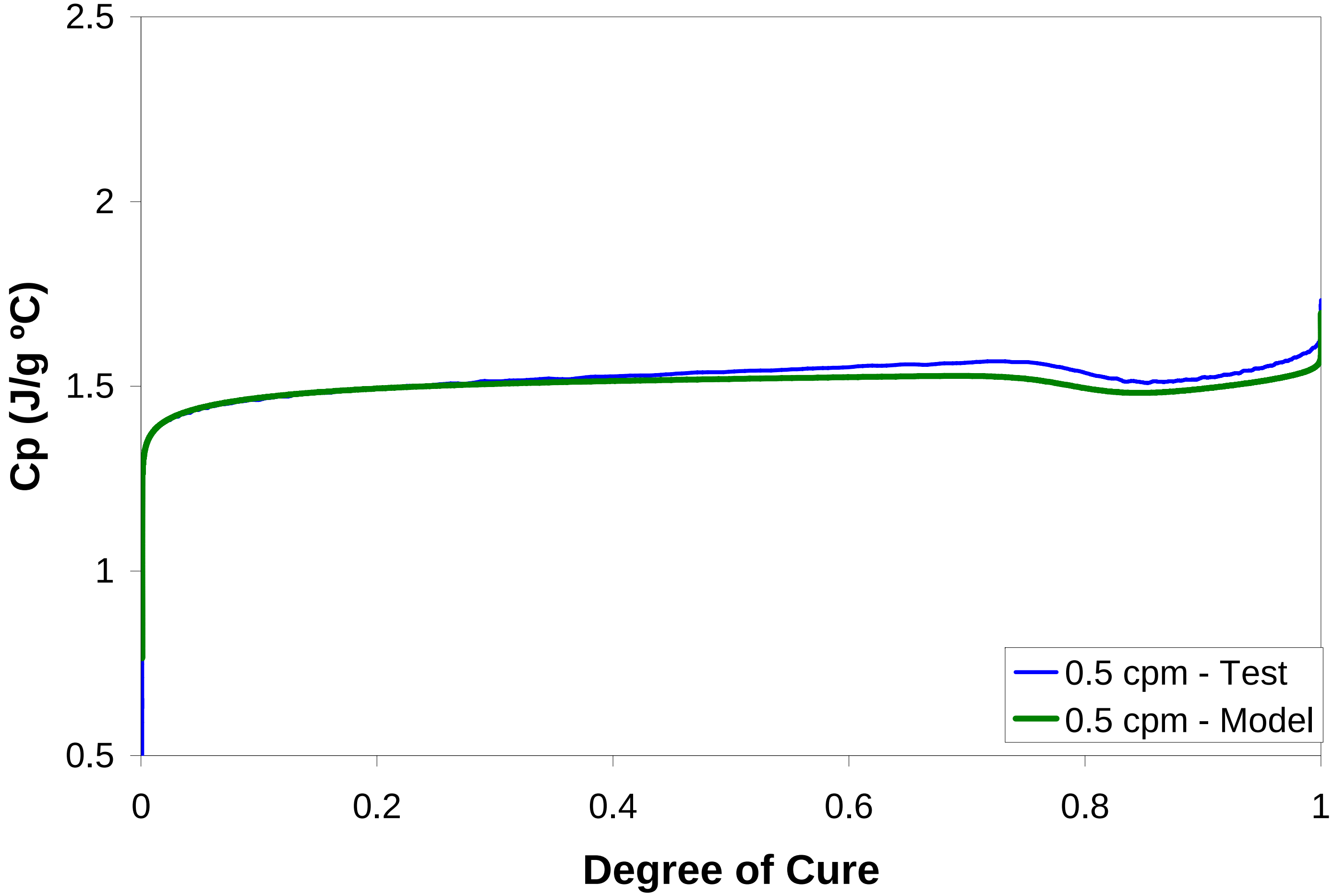
Dynamic Tests – 0.25cpm



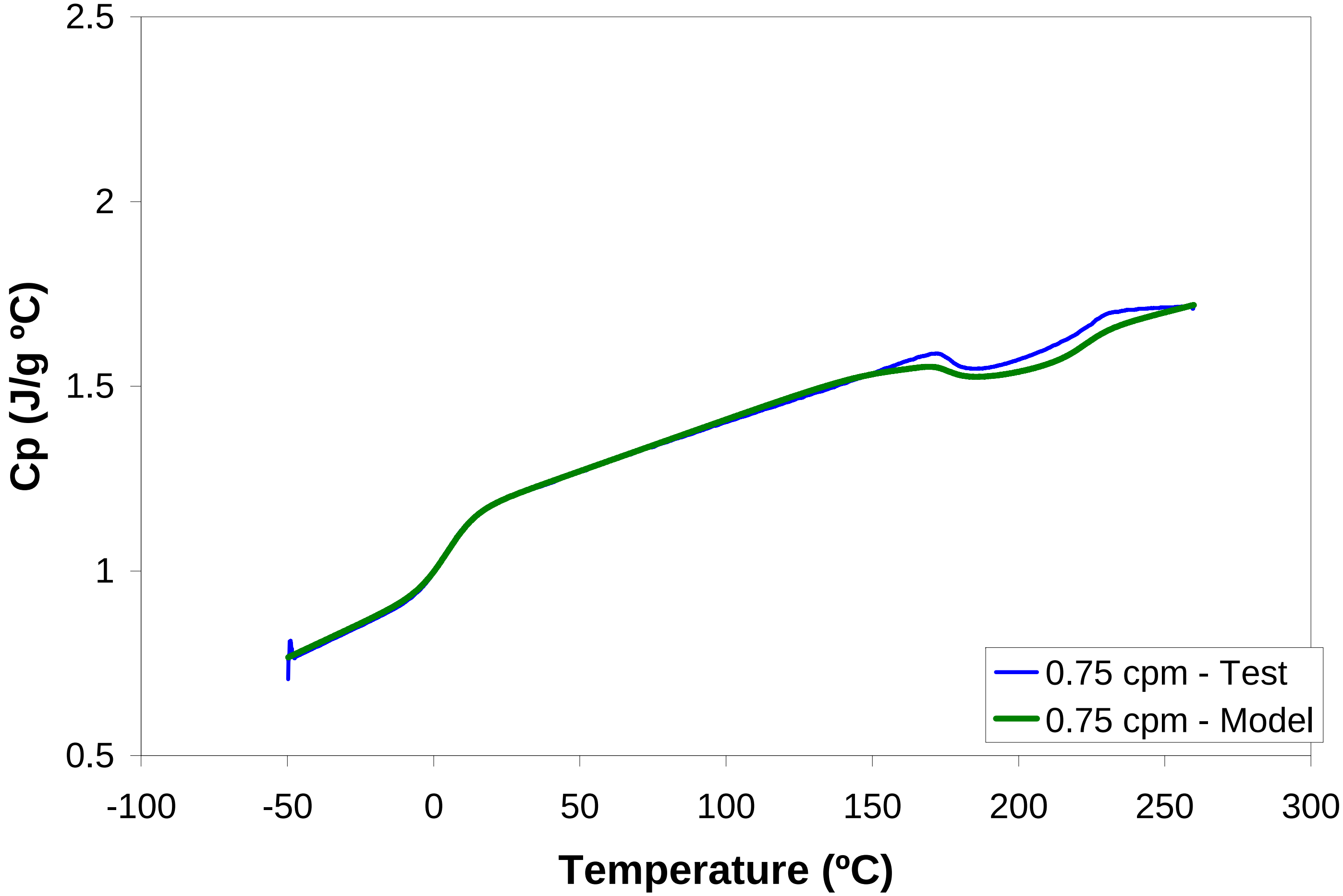
Dynamic Tests – 0.5cpm



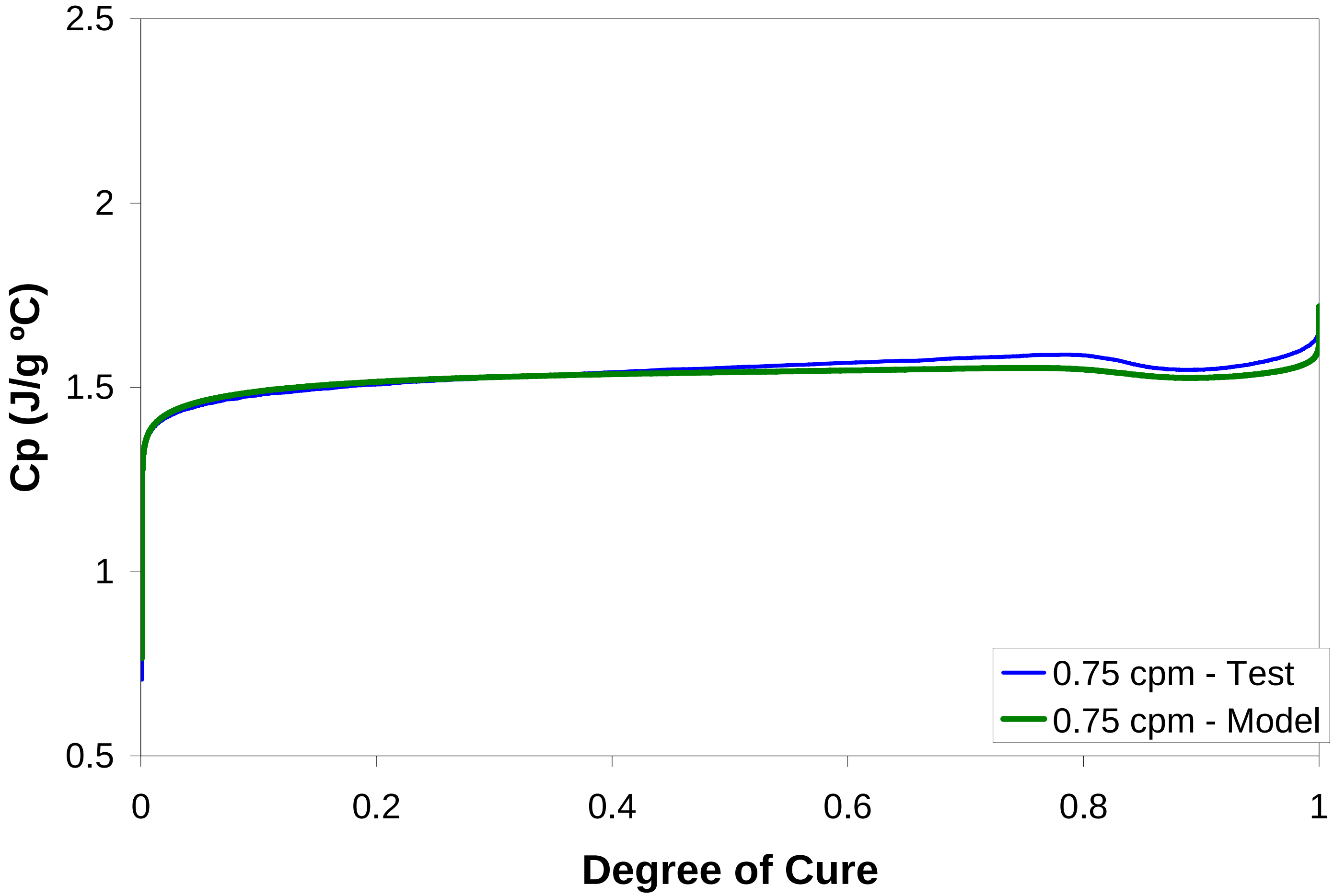
Dynamic Tests – 0.5cpm



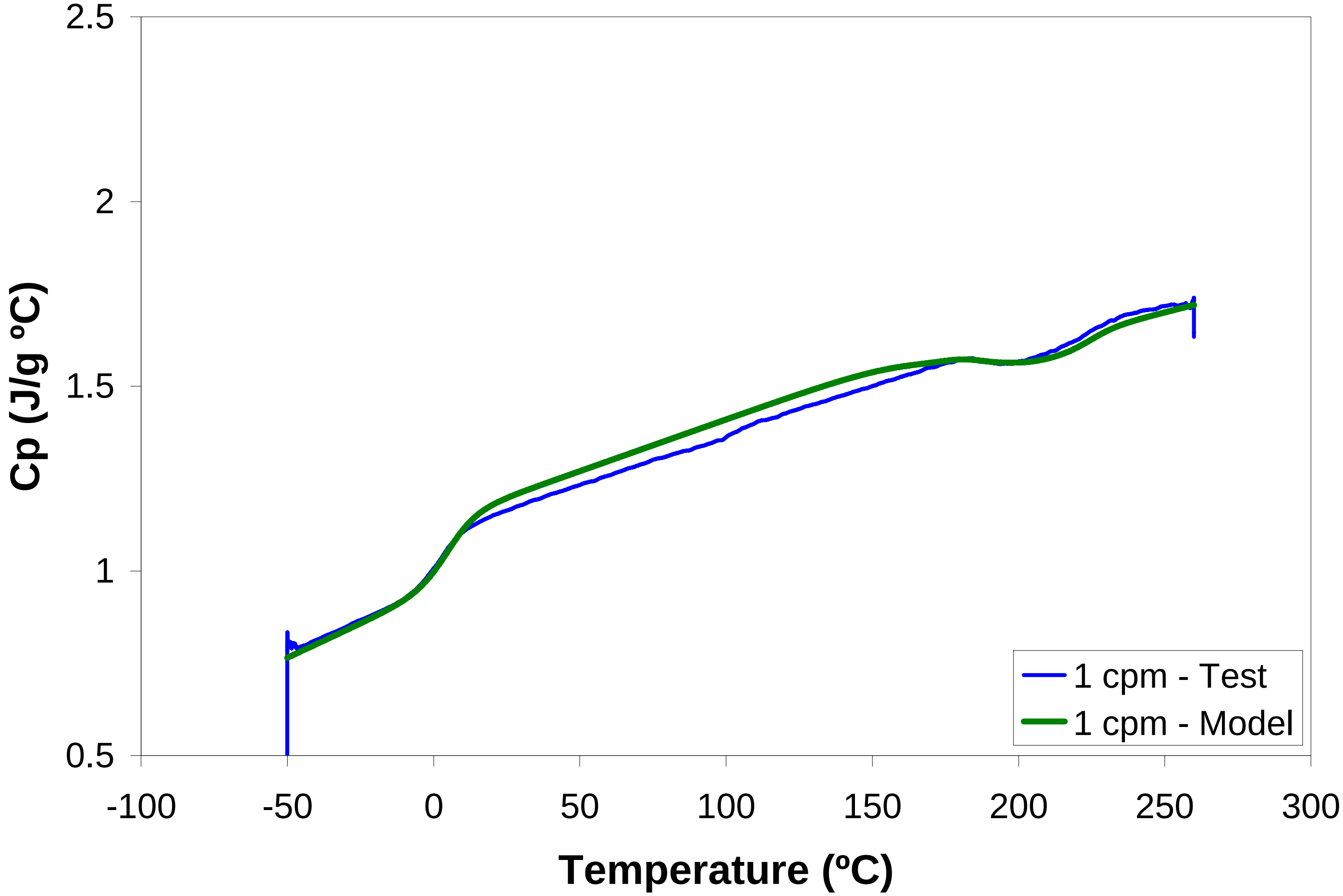
Dynamic Tests – 0.75cpm



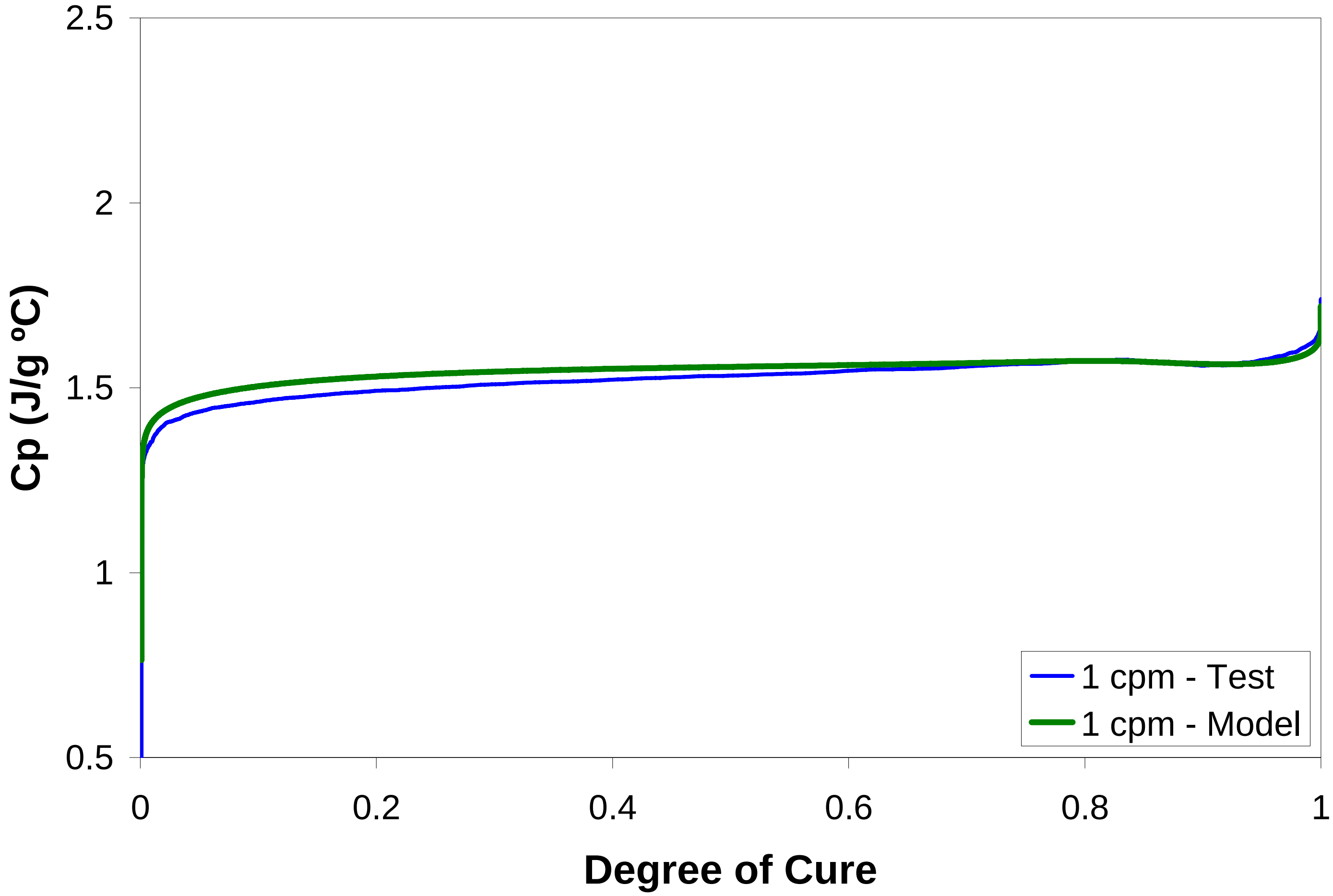
Dynamic Tests – 0.75cpm



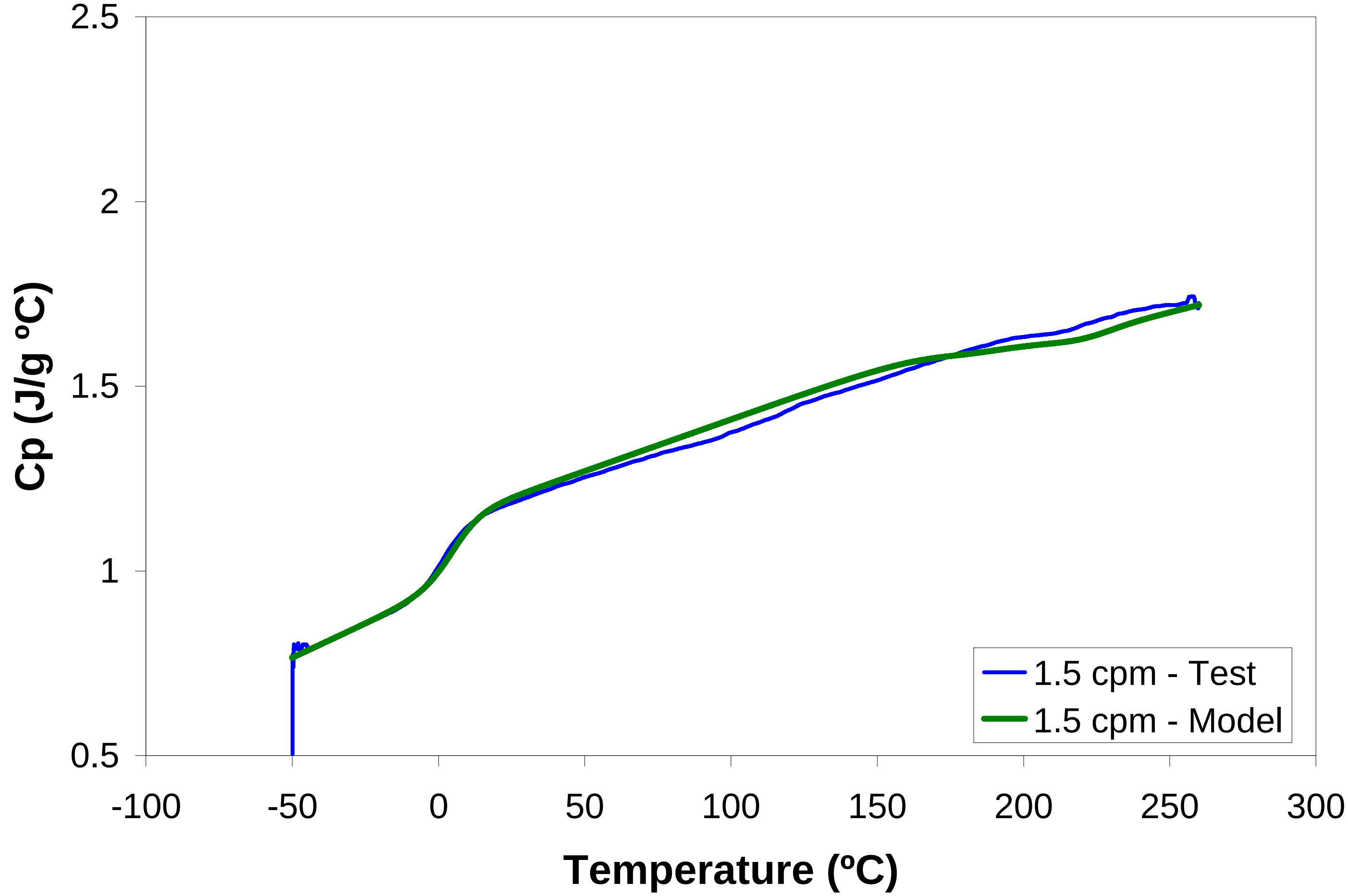
Dynamic Tests – 1cpm



Dynamic Tests – 1cpm



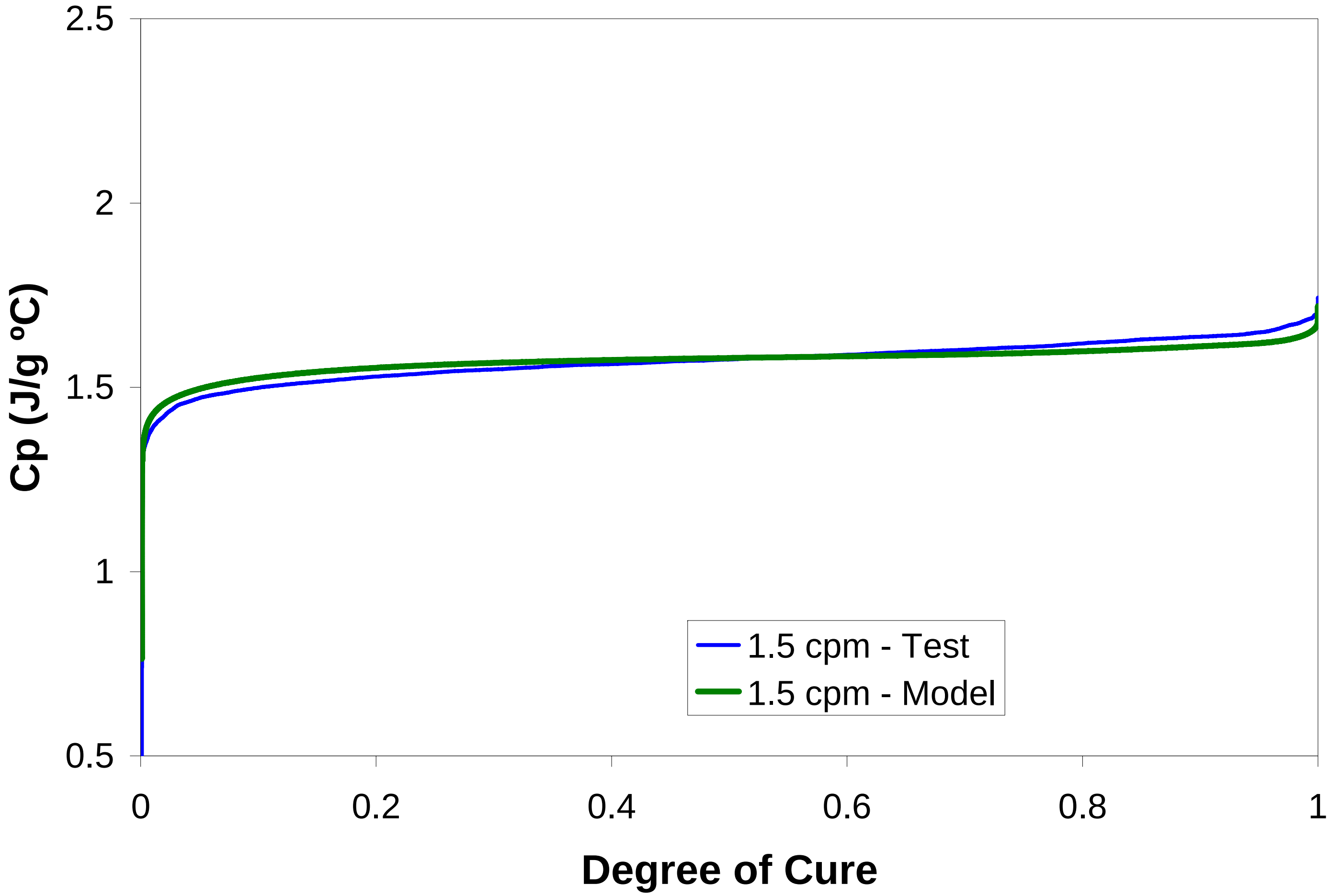
Dynamic Tests – 1.5cpm



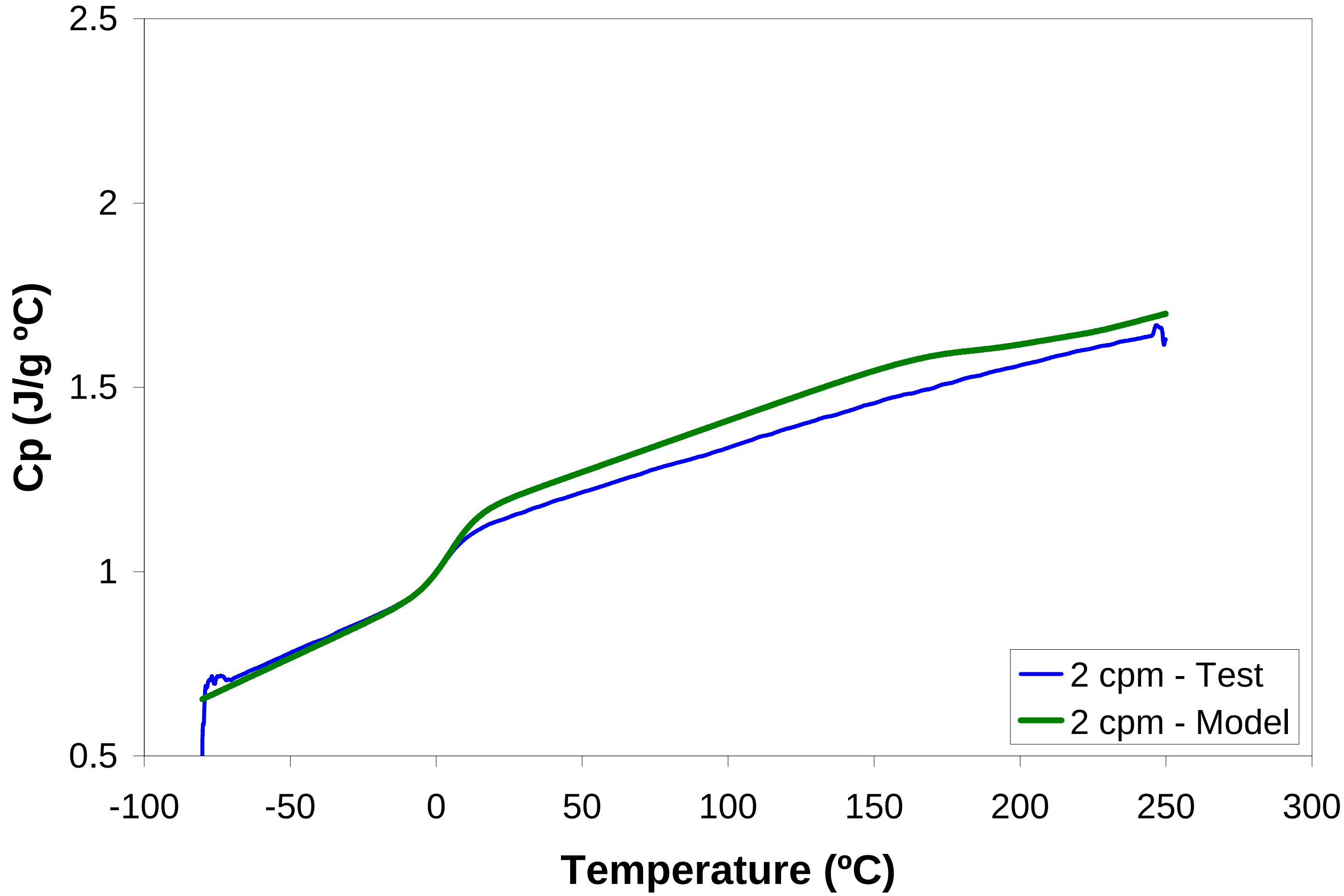
NCAMP

CONVERGENT MANUFACTURING TECHNOLOGIES

Dynamic Tests – 1.5cpm



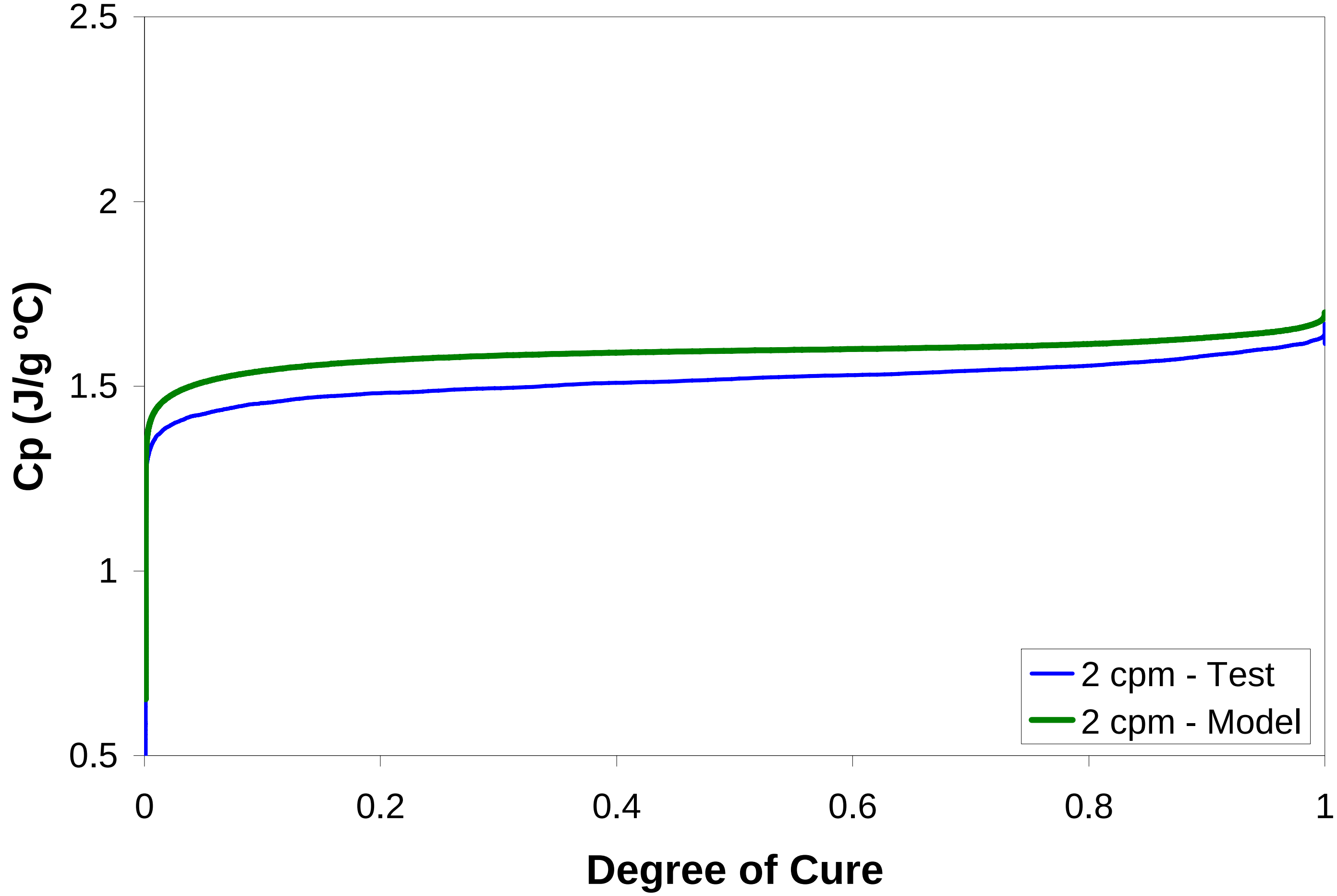
Dynamic Tests – 2cpm



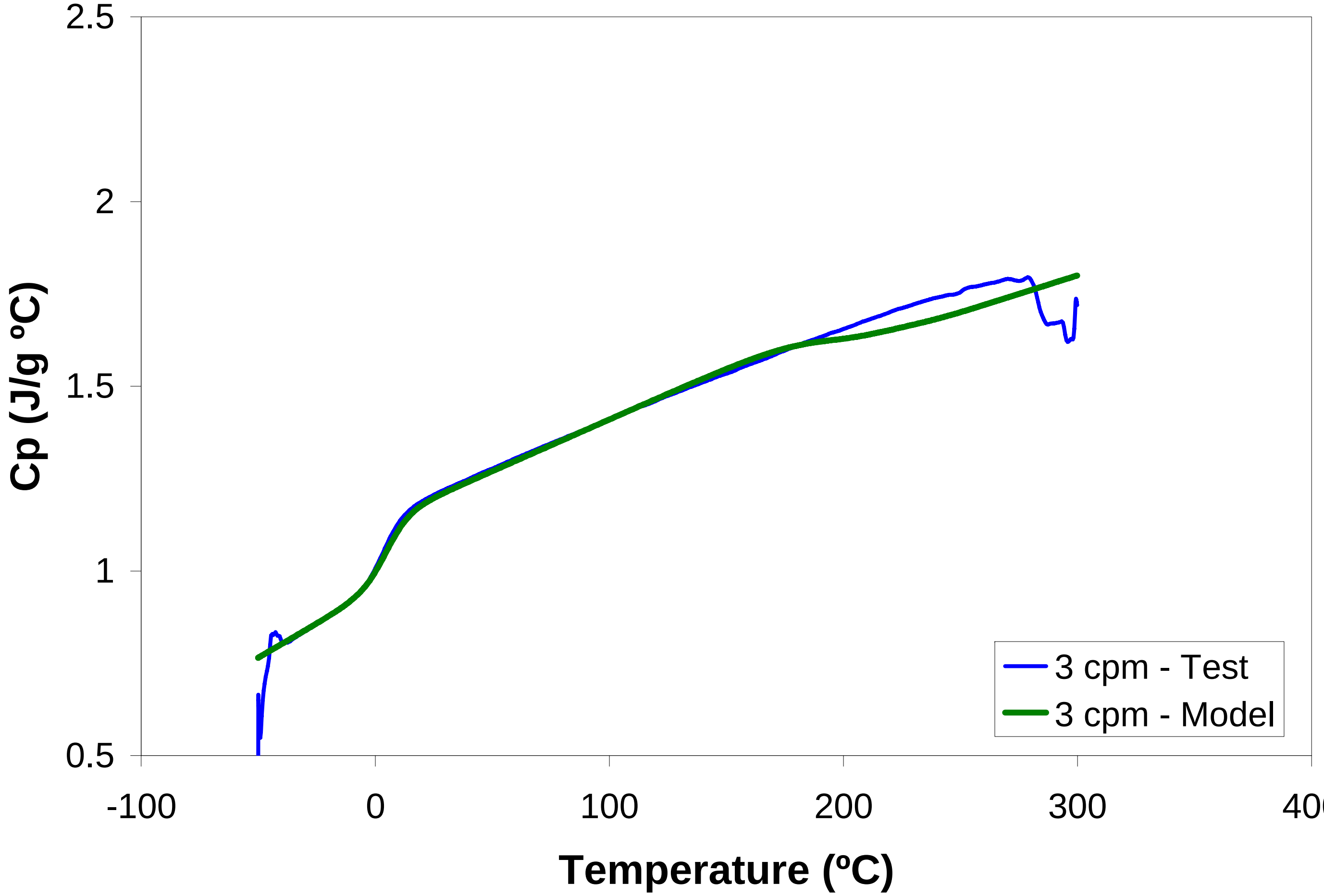
NCAMP

CONVERGENT MANUFACTURING TECHNOLOGIES

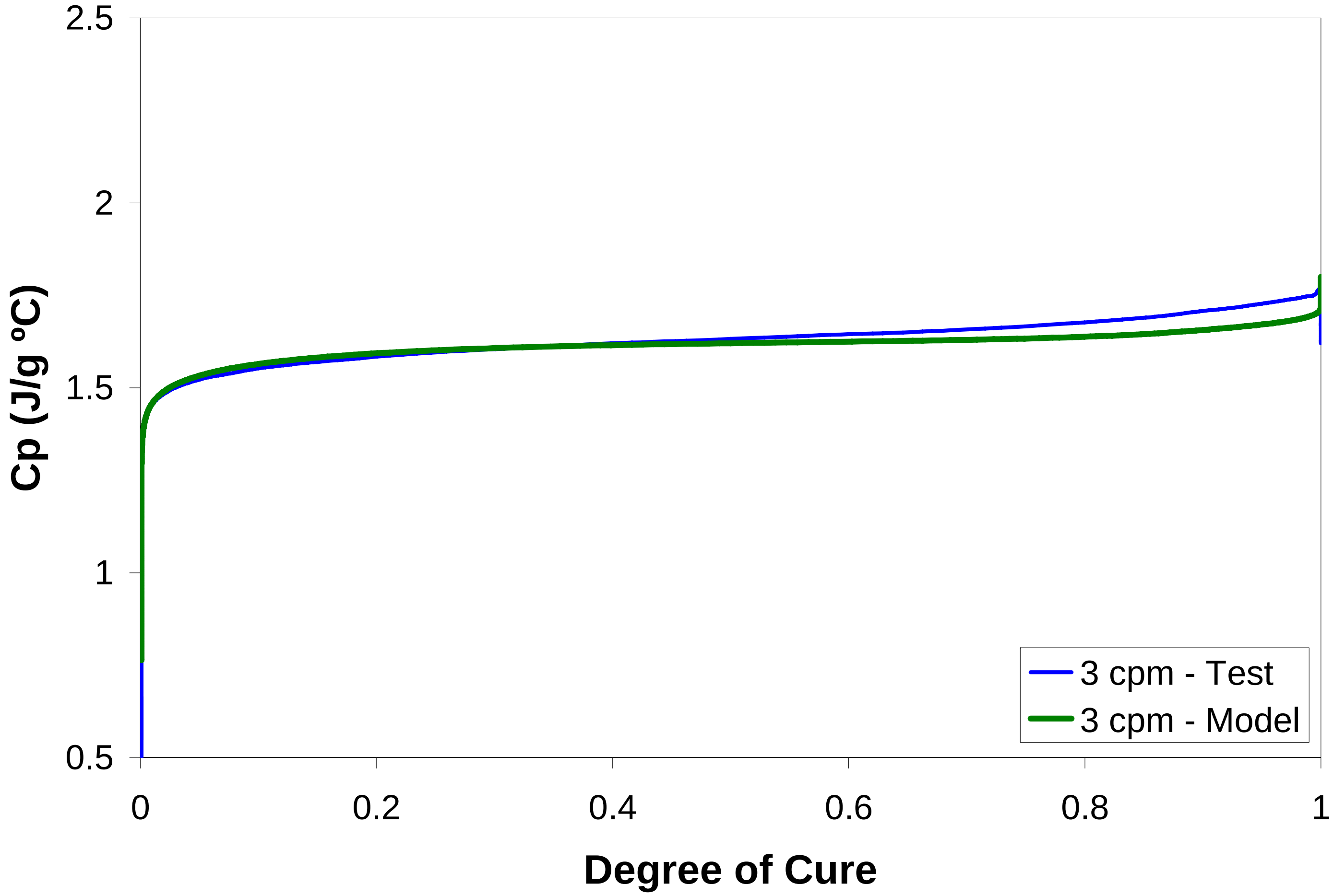
Dynamic Tests – 2cpm



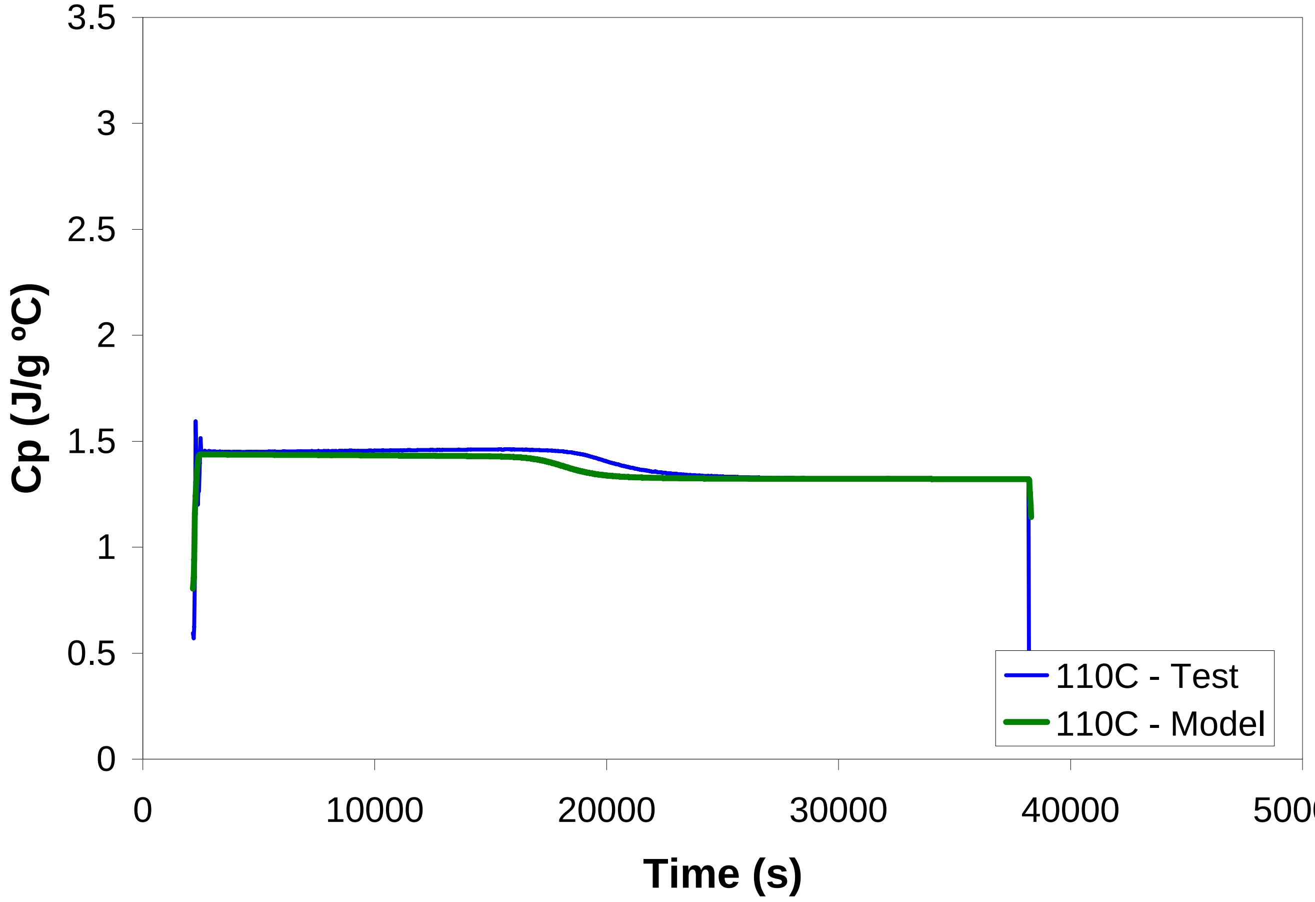
Dynamic Tests – 3cpm



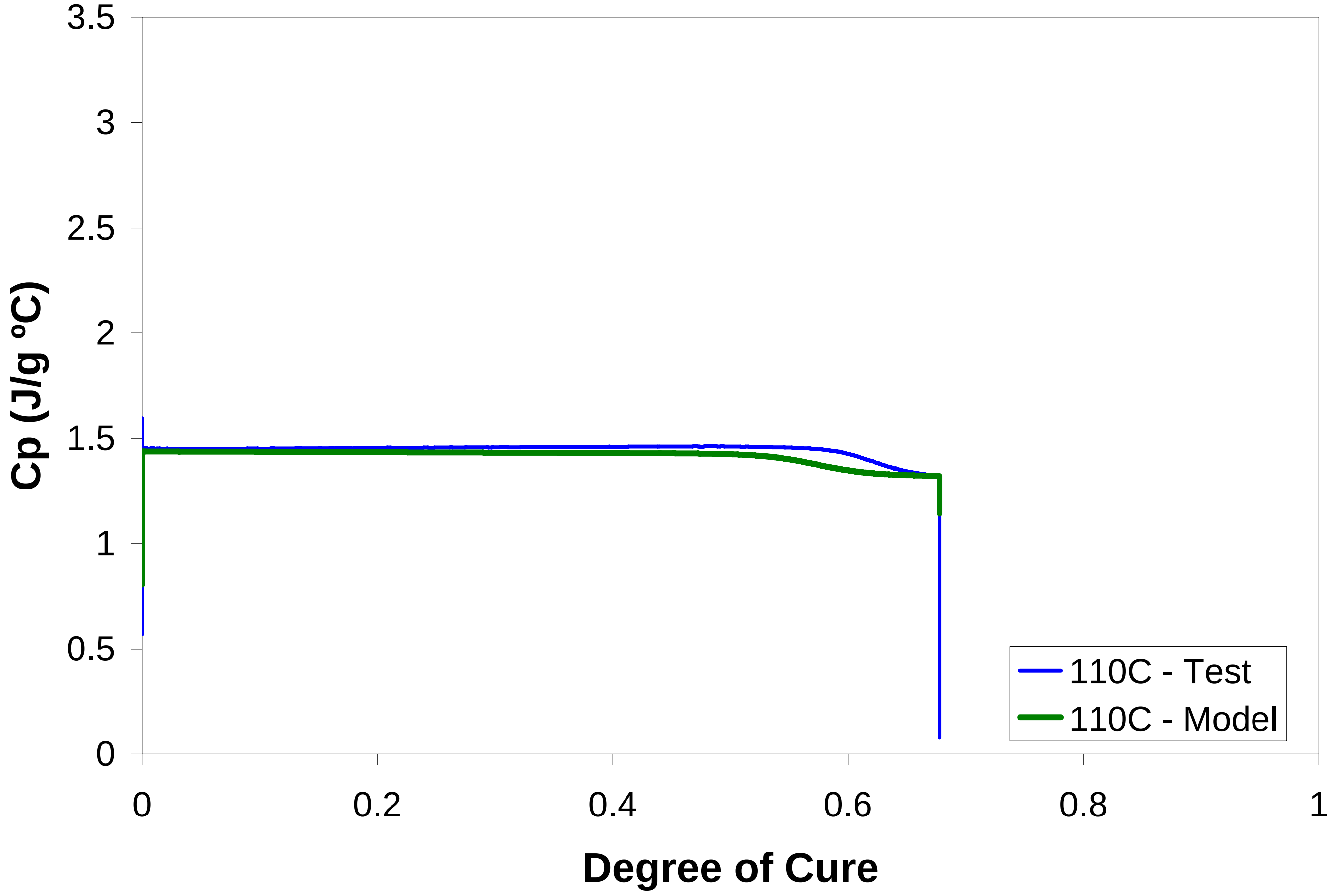
Dynamic Tests – 3cpm



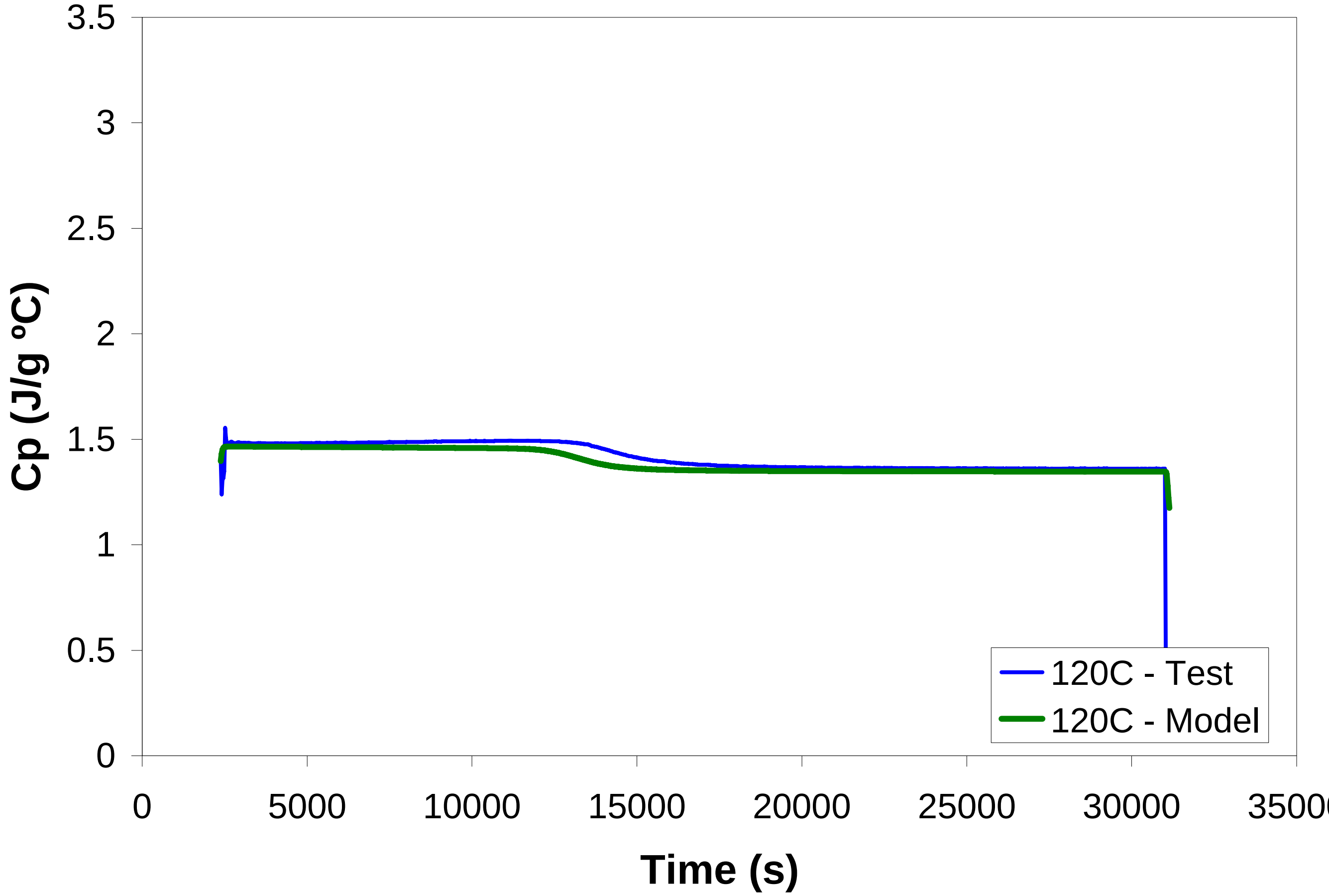
Isothermal Tests – 110C



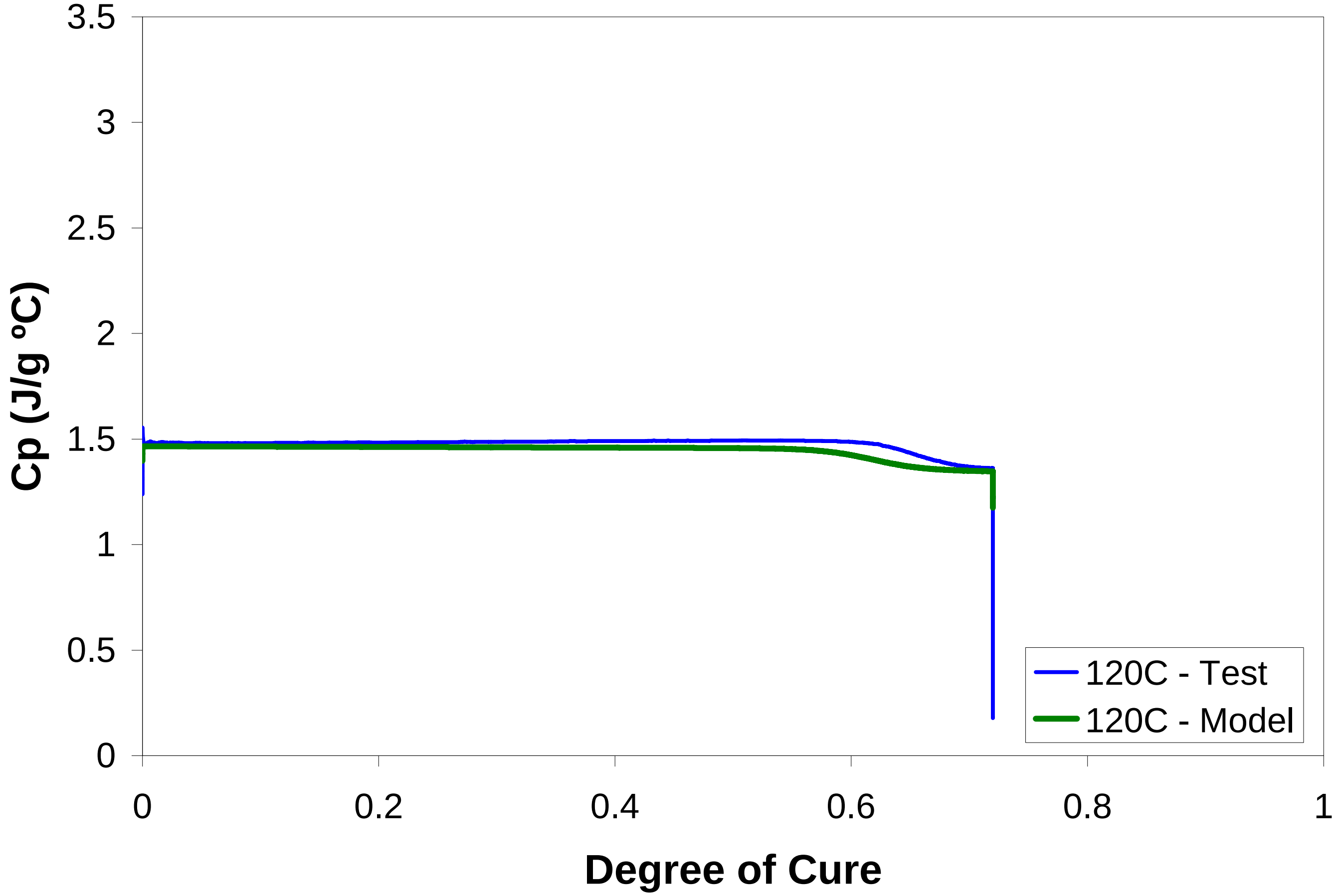
Isothermal Tests – 110C



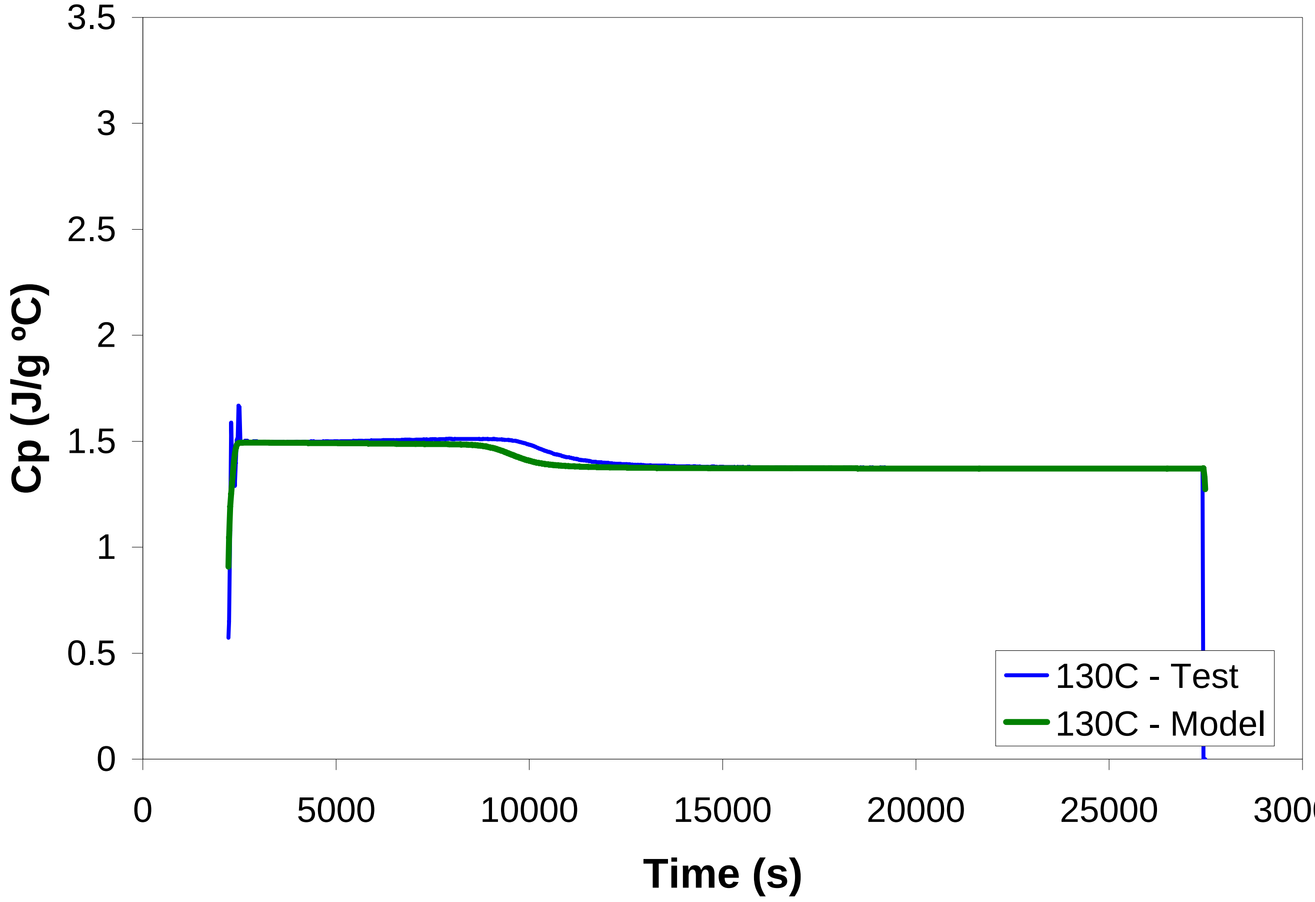
Isothermal Tests – 120C



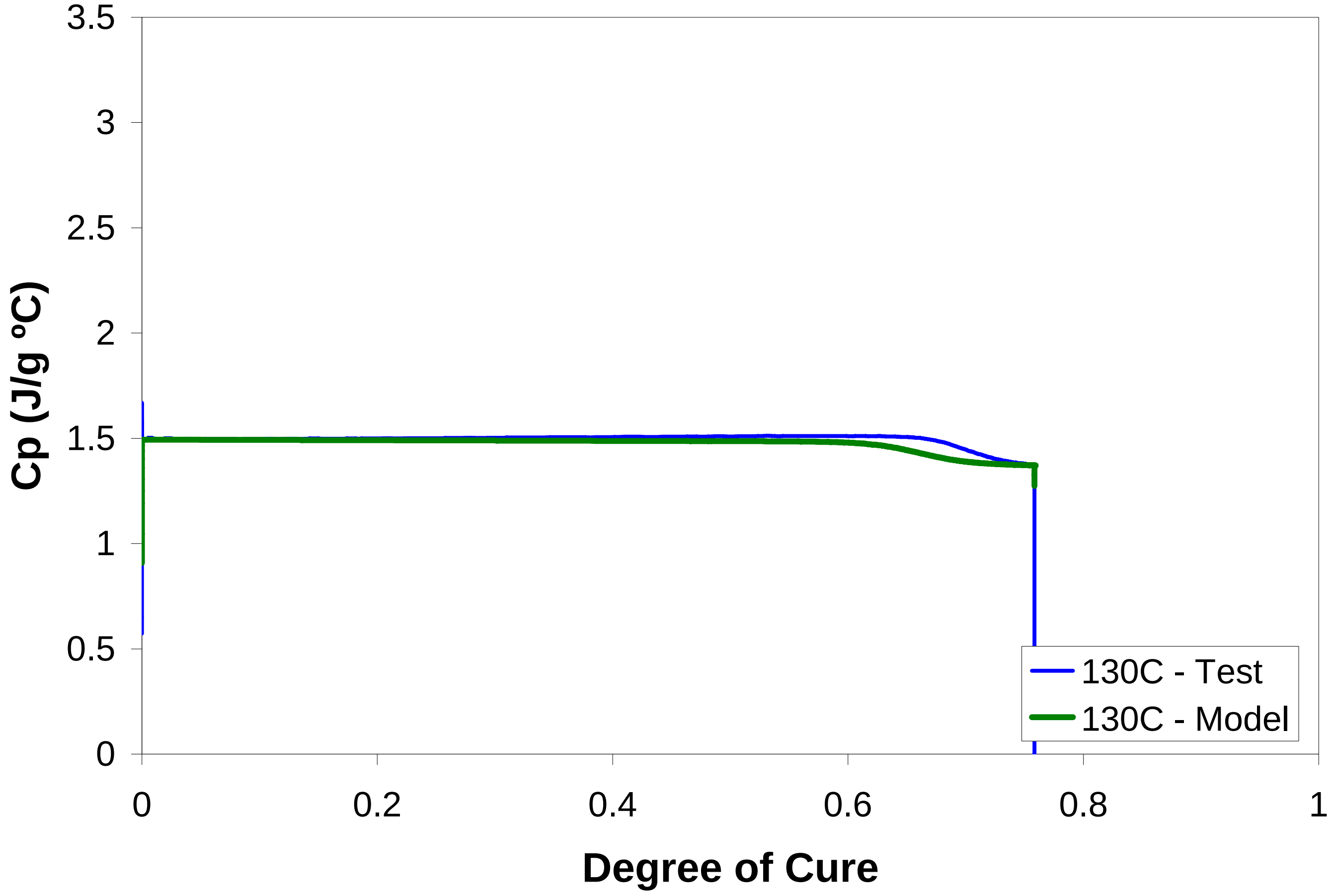
Isothermal Tests – 120C



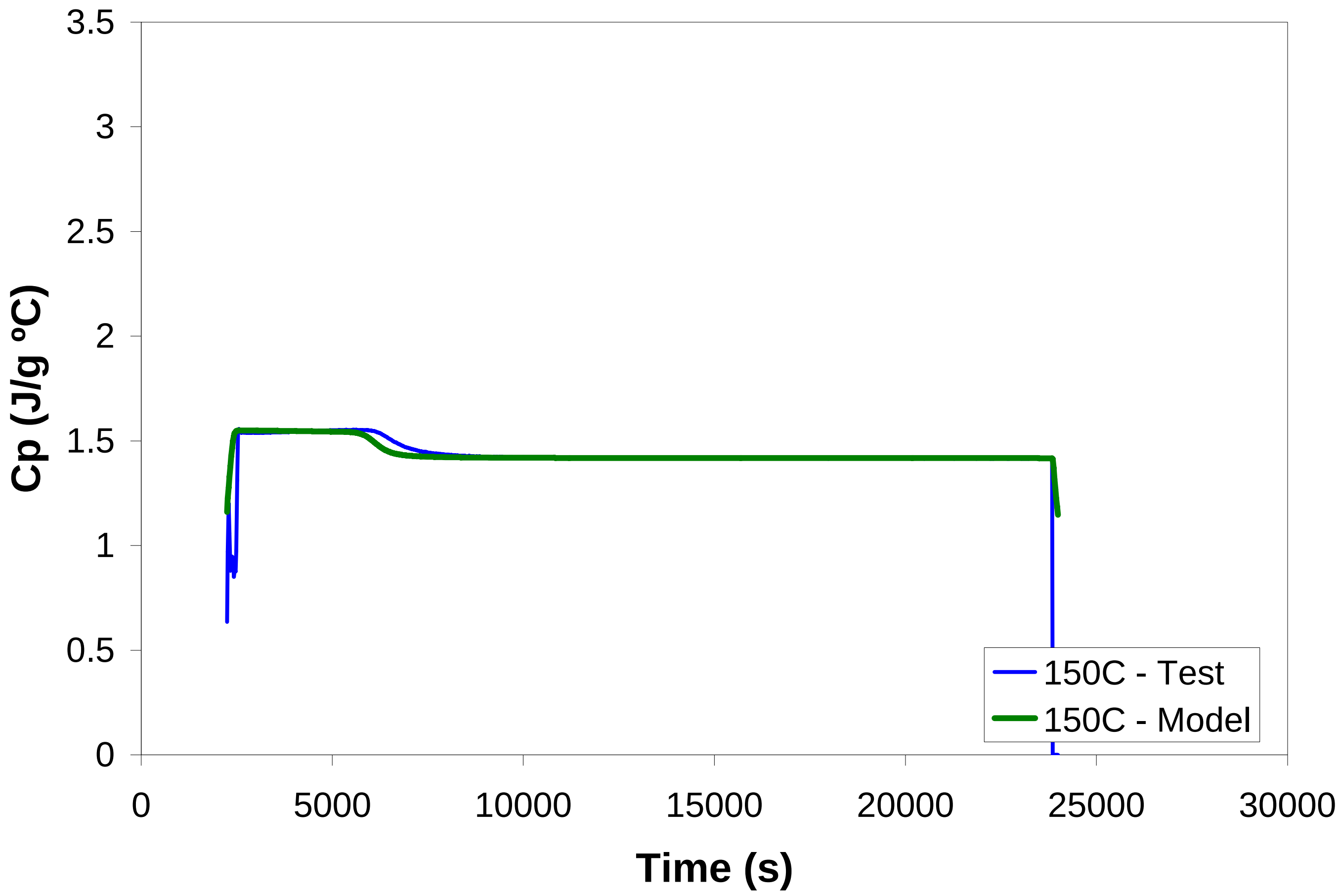
Isothermal Tests – 130C



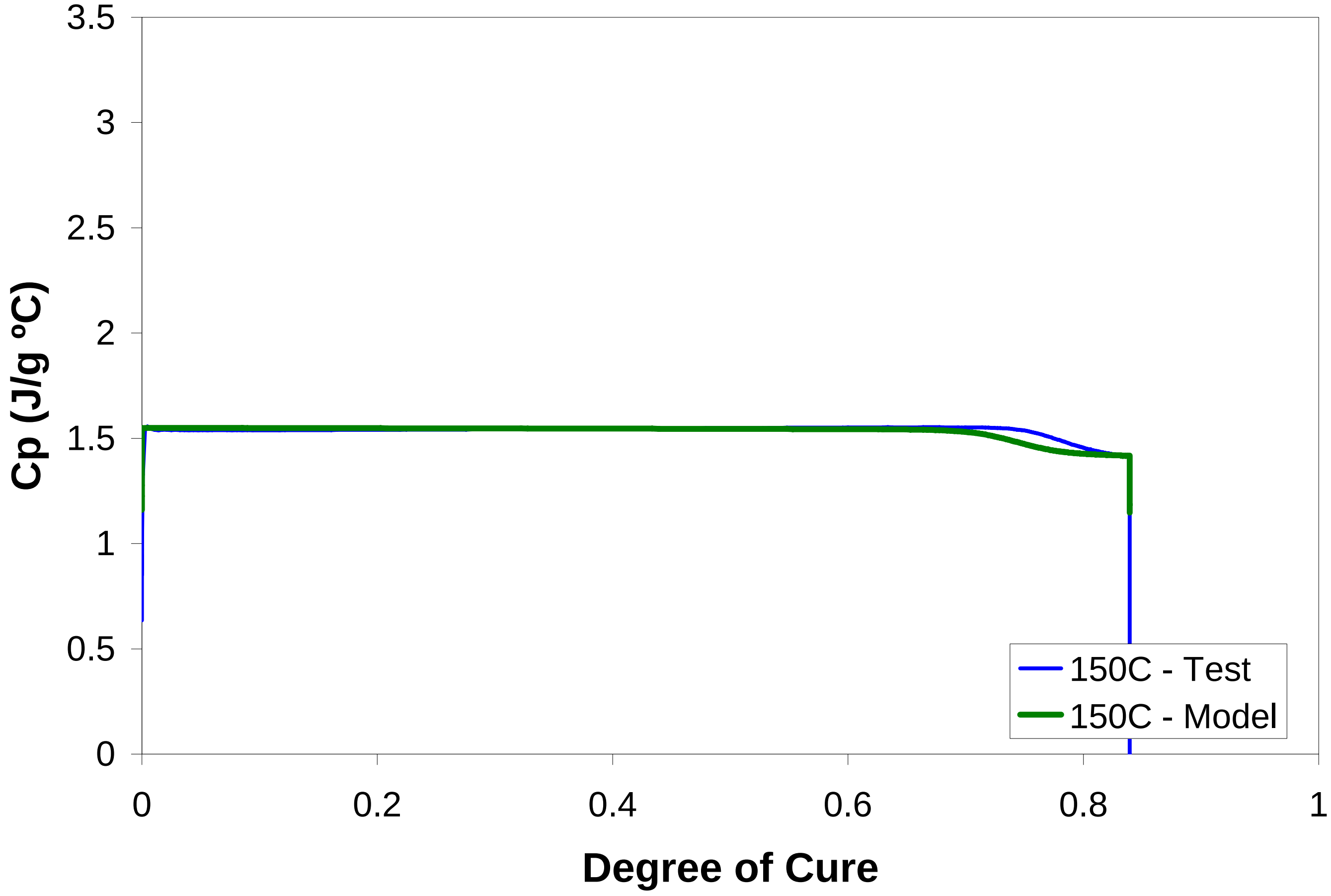
Isothermal Tests – 130C



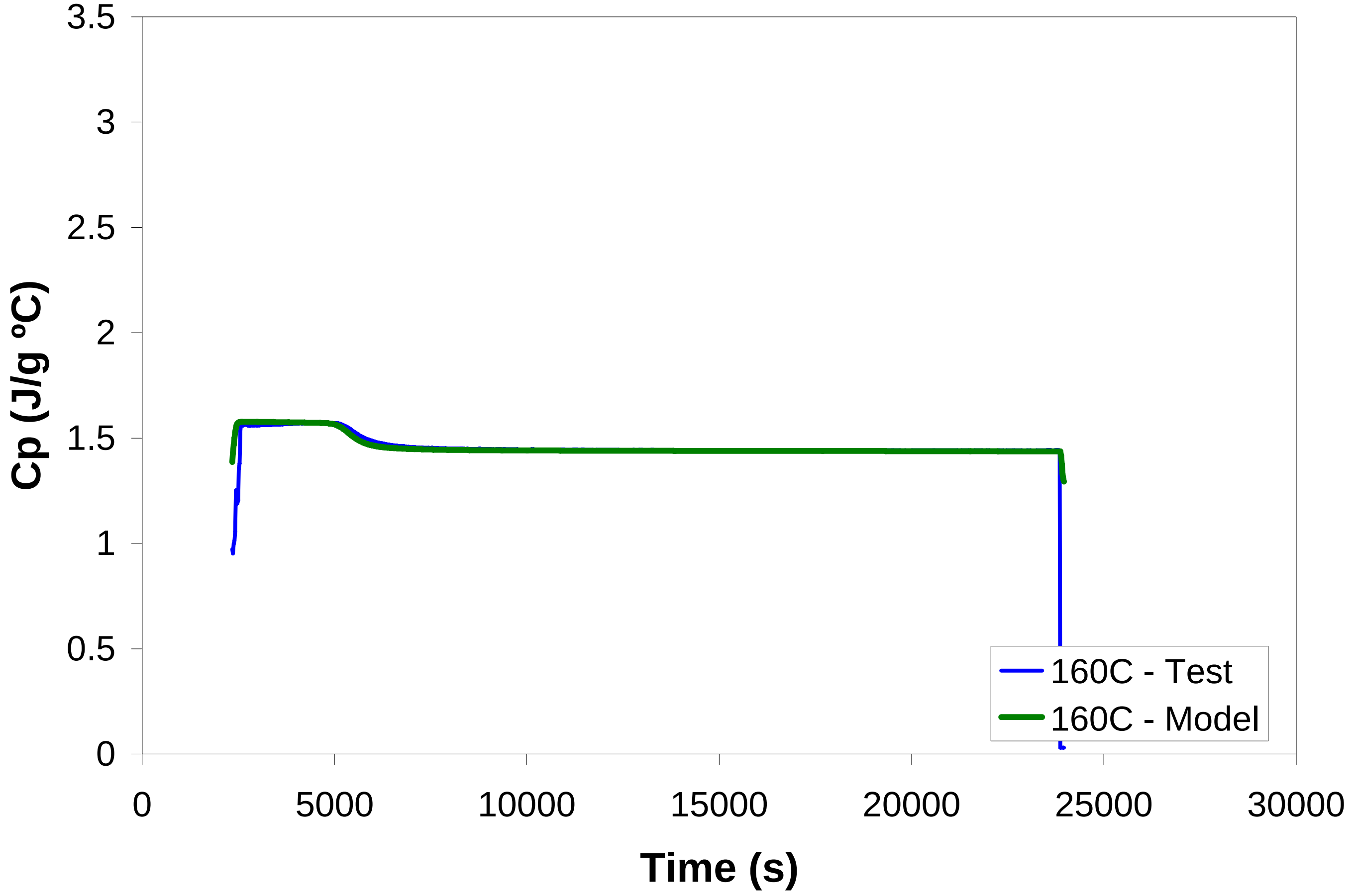
Isothermal Tests – 150C



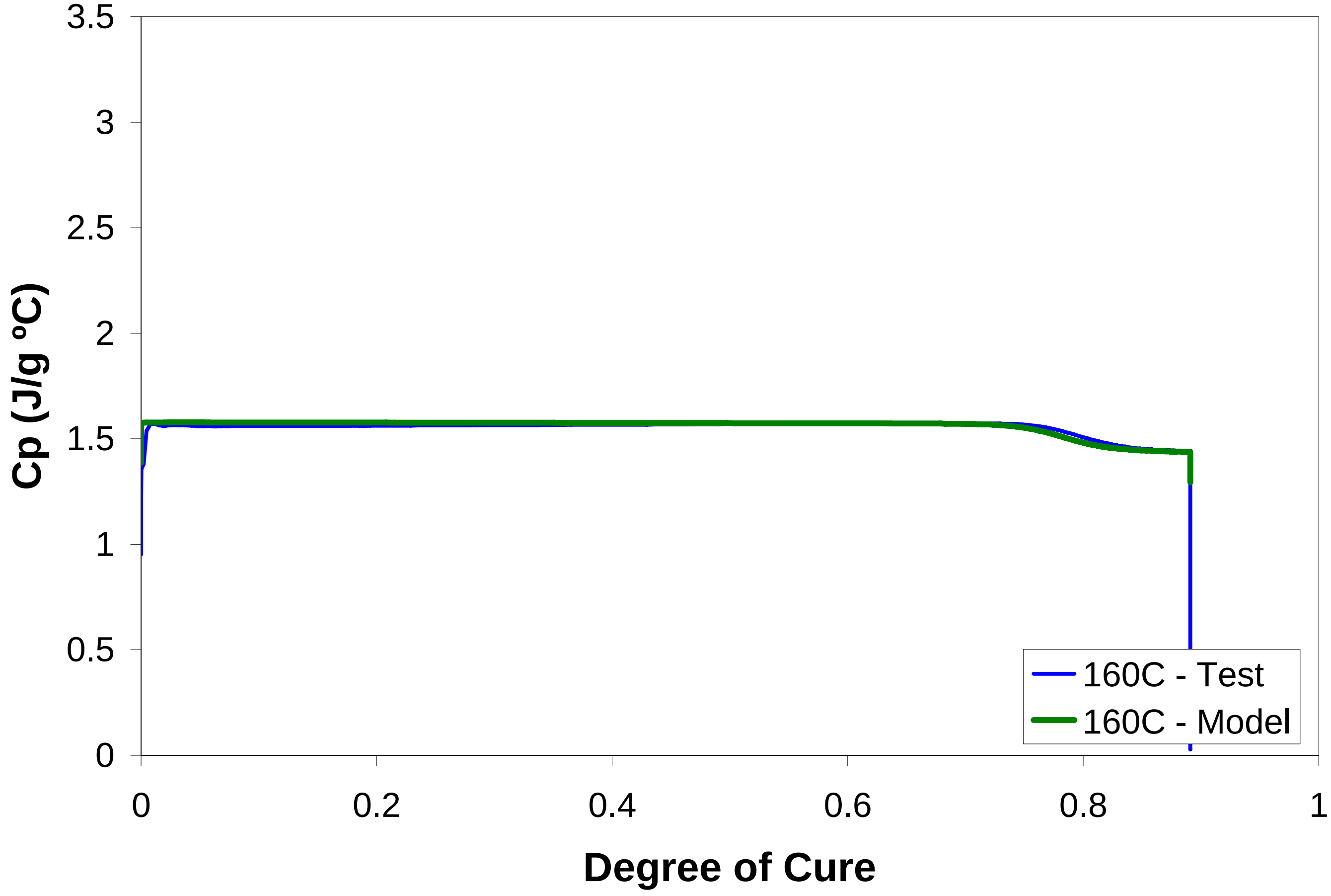
Isothermal Tests – 150C



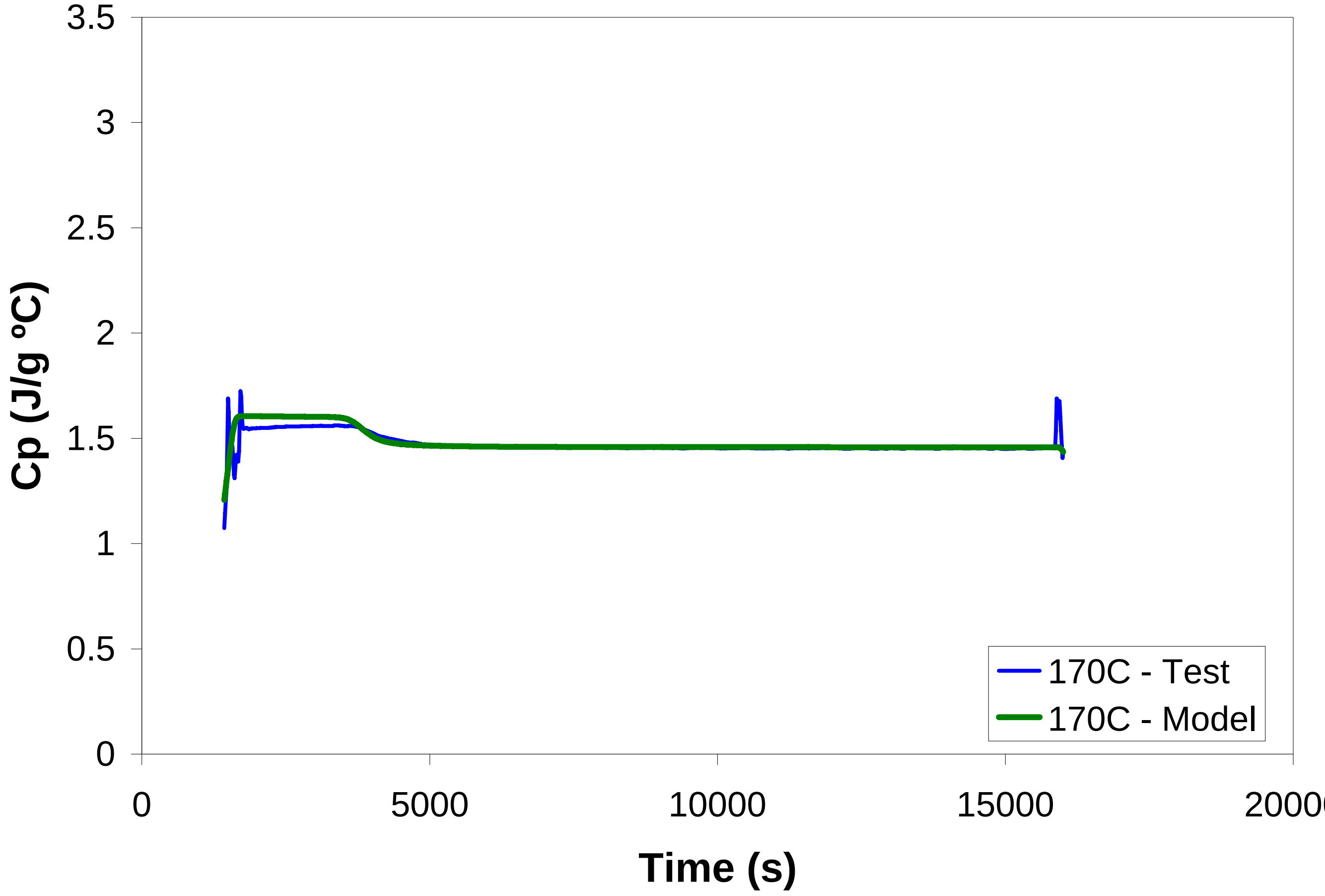
Isothermal Tests – 160C



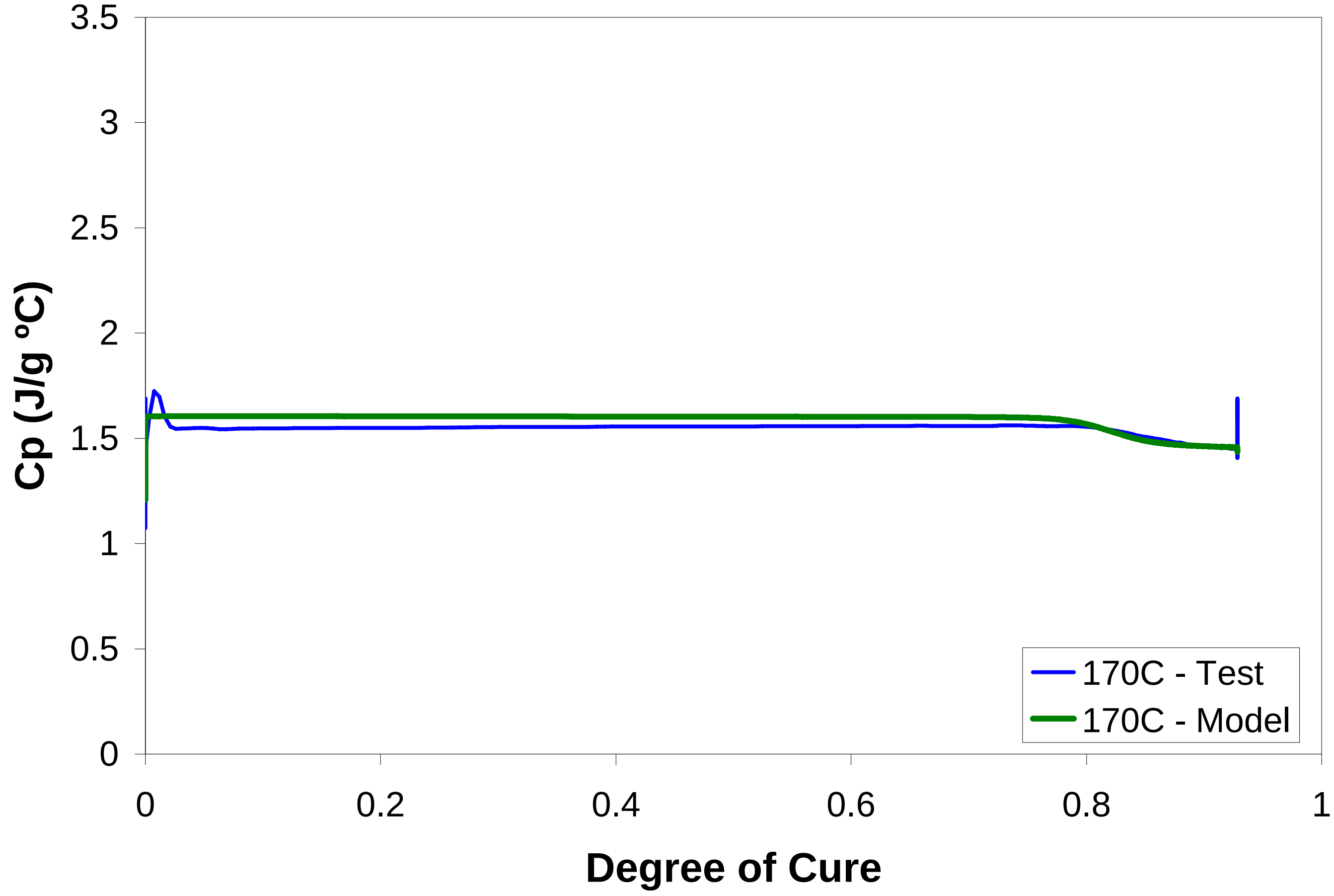
Isothermal Tests – 160C



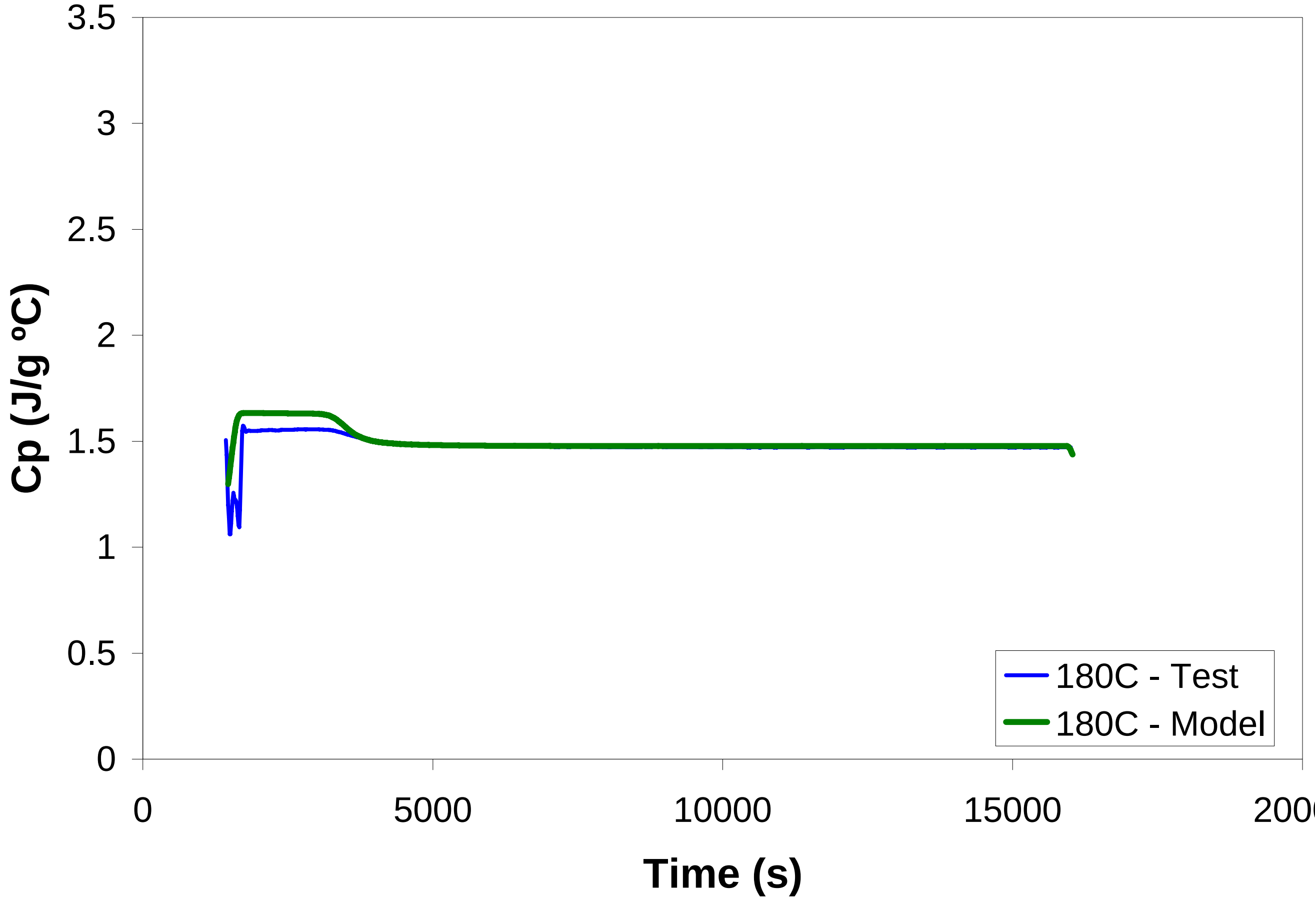
Isothermal Tests – 170C



Isothermal Tests – 170C



Isothermal Tests – 180C



Isothermal Tests – 180C