Development of Standard Techniques for the Calculation of Master Curves for Linear-Visco Elastic Materials

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The 1st International Symposium on
Binder Rheology And Pavement Performance

at The University of Calgary

August 13 - 15, 2000

Software Objectives

- Master Curve Production
- Discrete Relaxation and Retardation Spectra Calculation
- Conversions - time to frequency and vice-versa
- Advanced graphing and ease of use to perform complex calculations

Why master curves?

- Powerful tool to understand how asphalt type and chemical makeup affects the visco-elastic behavior of binders
- Enables easy interpolation of properties and avenue for extrapolation

Master Curve Production
Shifting Techniques (Gordon/Shaw)

- Determine an initial estimate of the shift using WLF parameters and standard constants.
- Refine the fit by using a pairwise shifting technique and straight lines representing each data set.
- Further refine the fit using pairwise shifting with a polynomial representing the data being shifted. The order of the polynomial being taken as the minimum value between number of the augment n+1, where n is the number of data points - or - Δf (the number of decades of frequency - or time).

Normalized for density - vertical shift

- To enable all properties to be reported at the density corresponding to the reference temperature (Rouse, 1953)

$$G(T_R, t) = \frac{T_R}{T}\frac{\rho(T_R)}{\rho(T)} G\left(T, \frac{t}{a_T}\right)$$

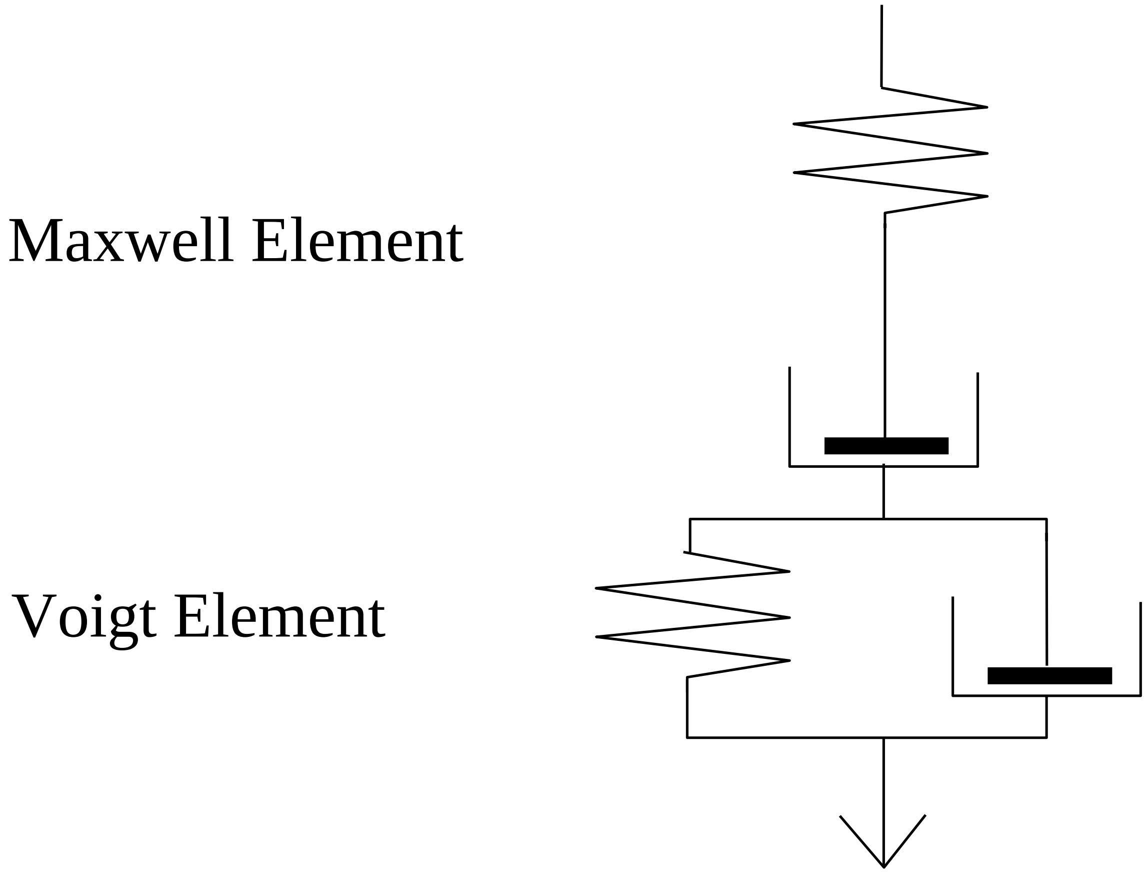
Spectra Calculations
Baumgaertel and Winter (1989)

- Relaxation and Retardation Spectra Calculated
  - for example

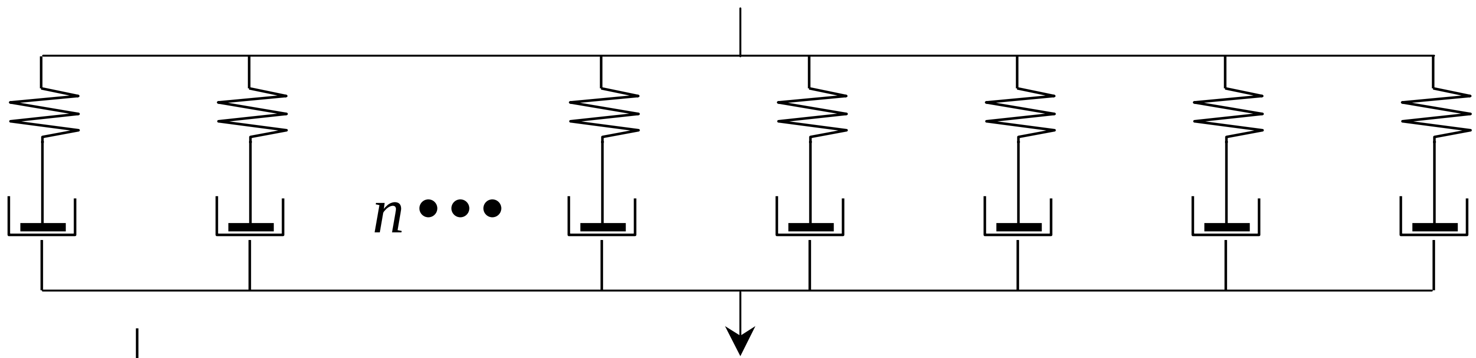
$$G'(\omega) = G_o + \sum_{i=1}^{\infty} \frac{G_i (\omega \tau_i)^2}{1 + (\omega \tau_i)^2}$$

$$G''(\omega) = \sum_{i=1}^{\infty} \frac{G_i \omega \tau_i}{1 + (\omega \tau_i)^2}$$

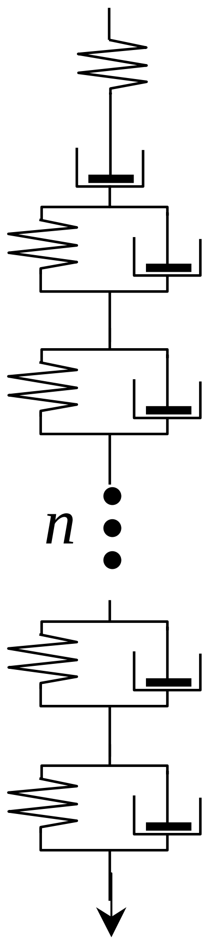
- Enables conversion of time to frequency (and vice-versa) and yields information about molecular structure (Rouse)



Basic Visco-Elastic Model - The Maxwell Model



Relaxation Spectra Model



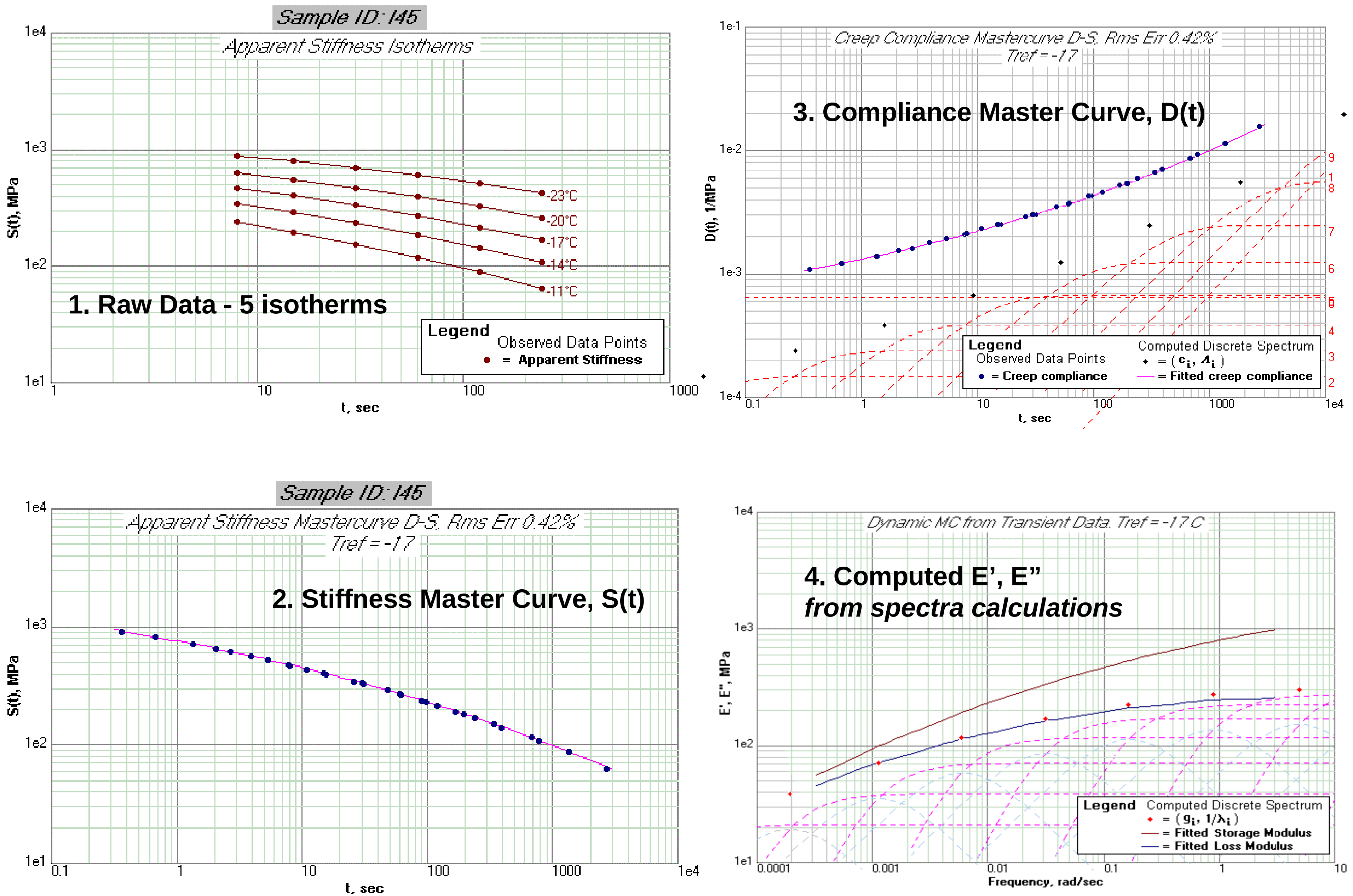
Retardation Spectra Model

Typical Results from Different Equipment

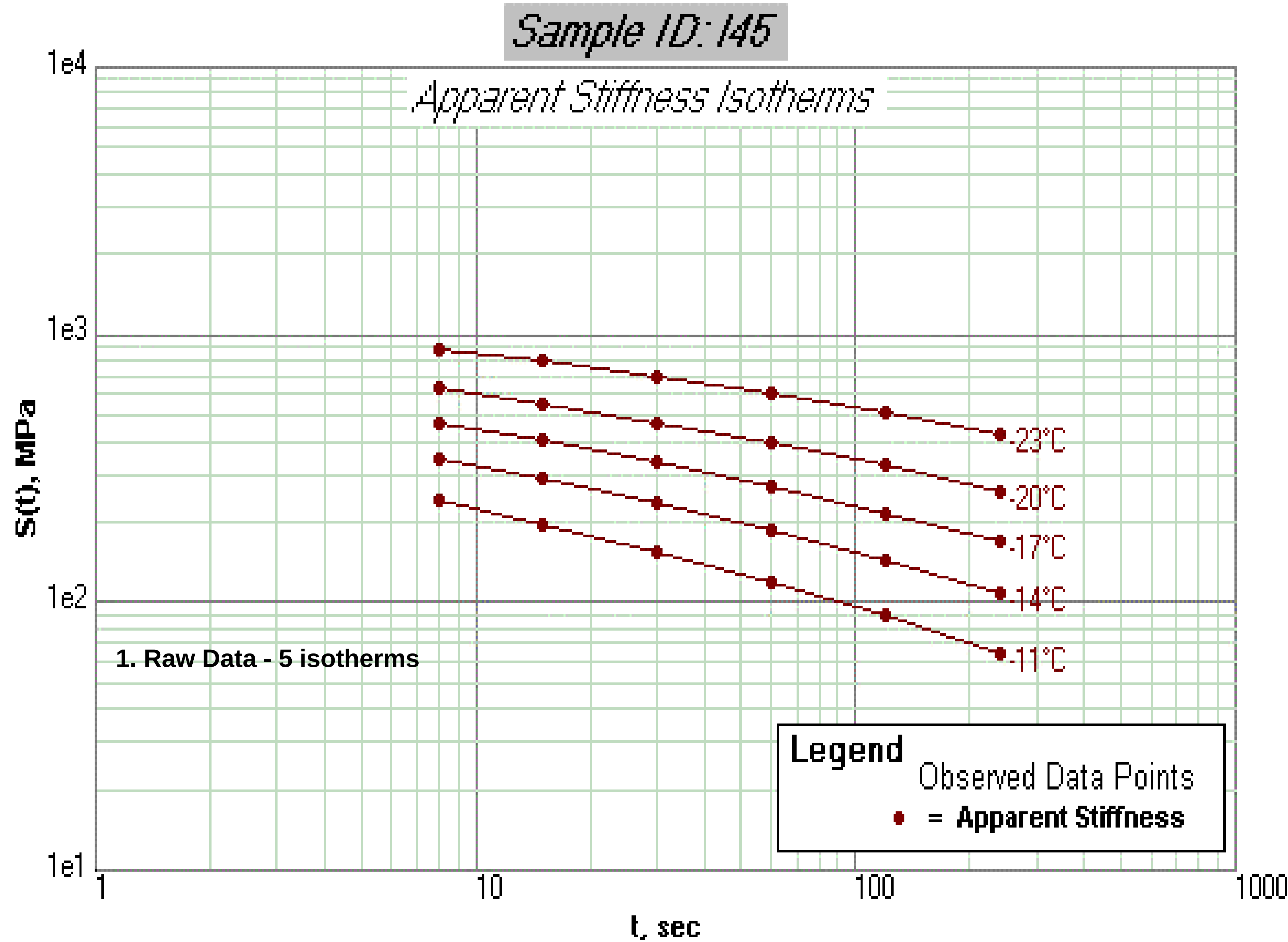
Two example used

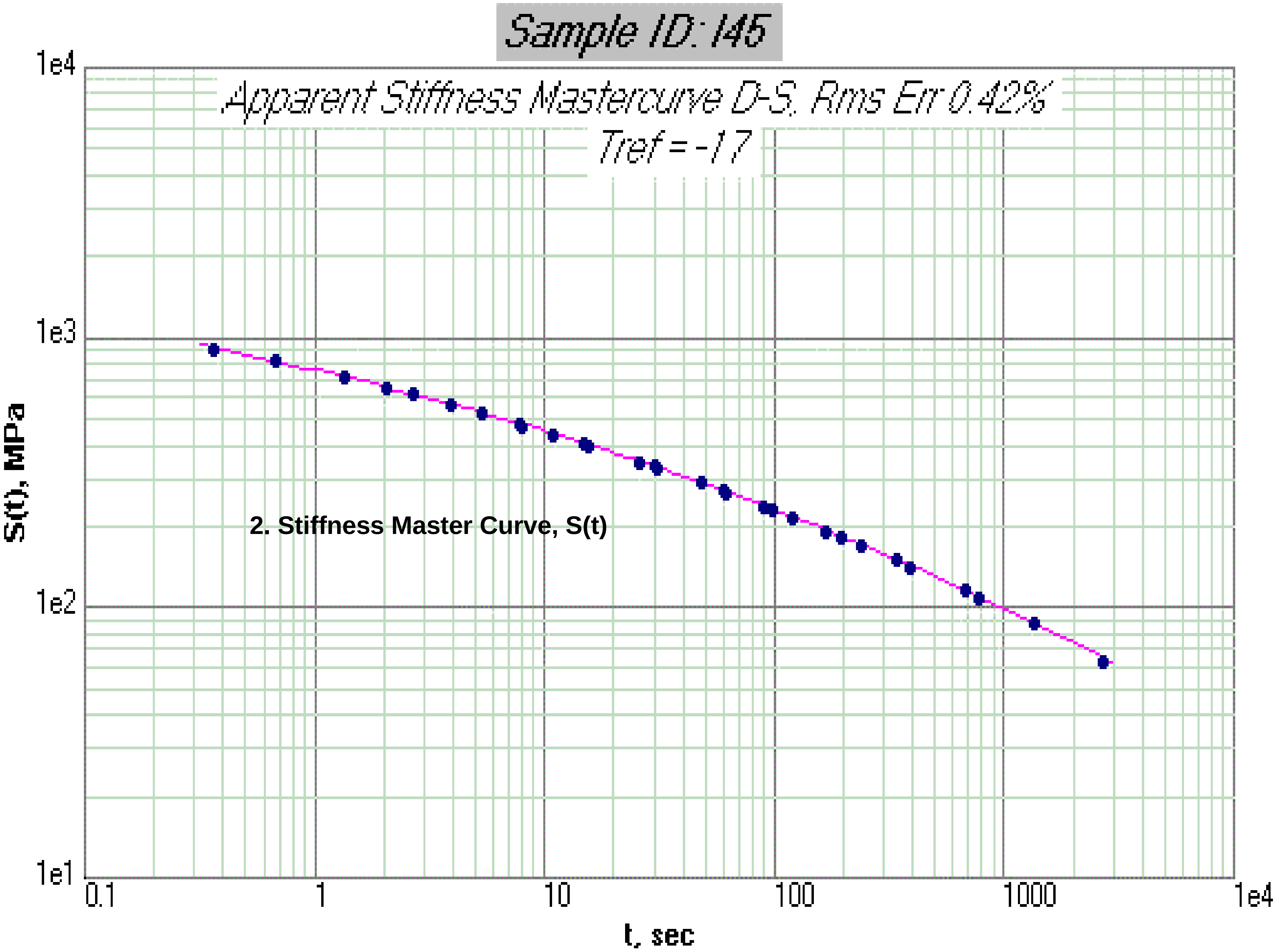
1. BBR
2. DSR

BBR

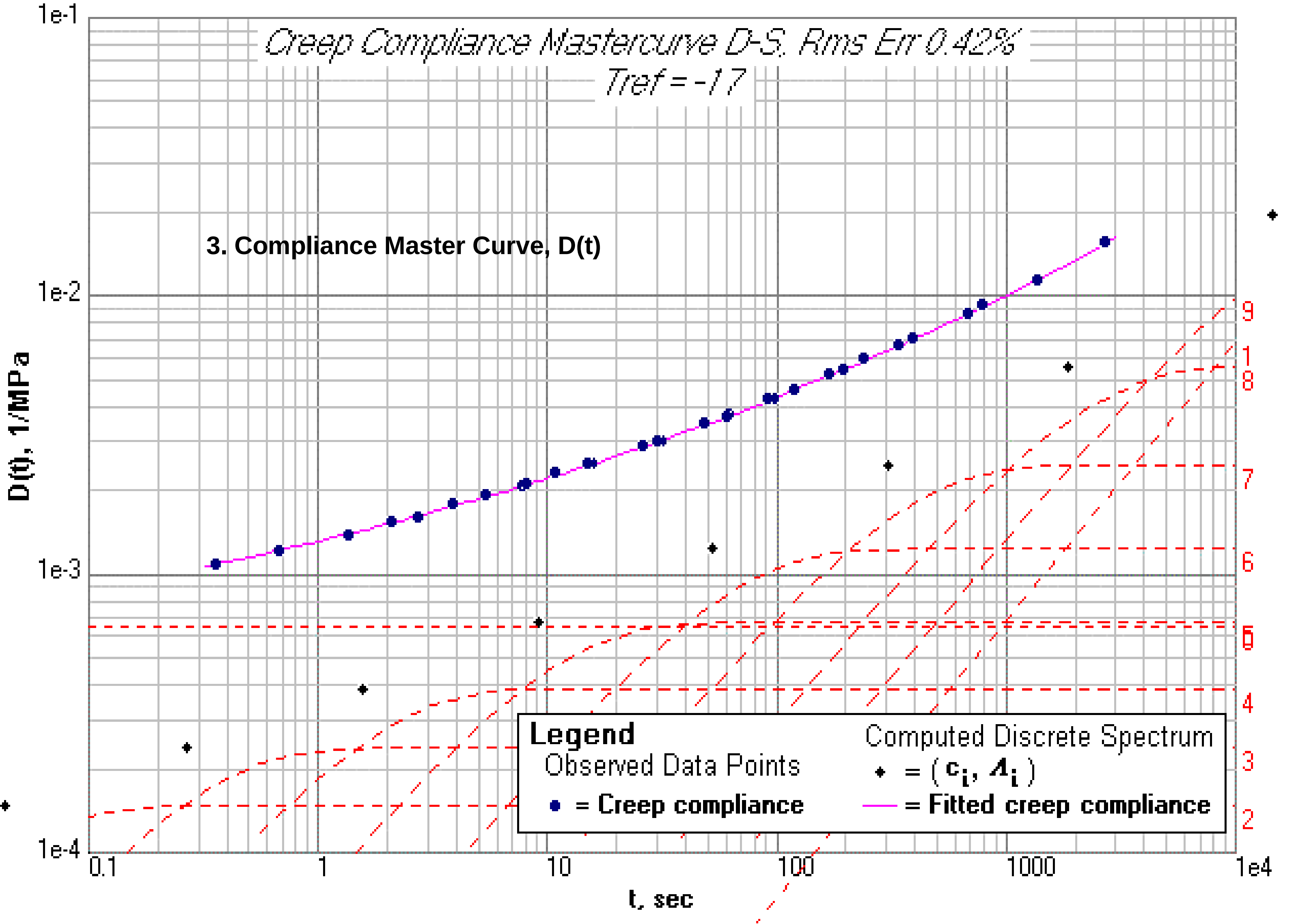


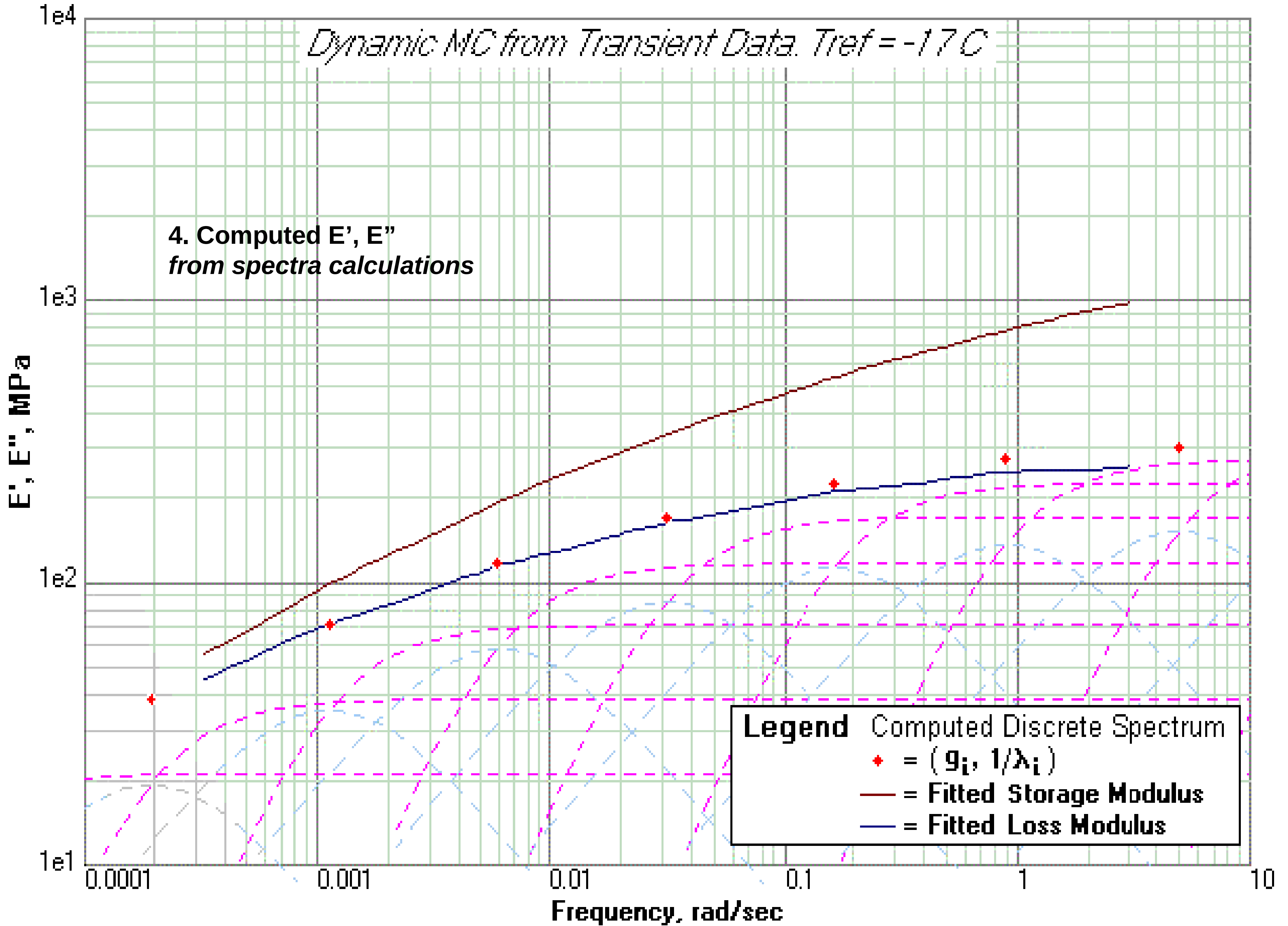
1. Bending Beam Rheometer - Typical Data Set


Sample ID: I45
Apparent Stiffness Isotherms
1e4
1e3
1e2
1e1
S(t), MPa
1
10
100
1000
t, sec
-23°C
-20°C
-17°C
-14°C
-11°C
1. Raw Data - 5 isotherms
Legend
Observed Data Points
= Apparent Stiffness



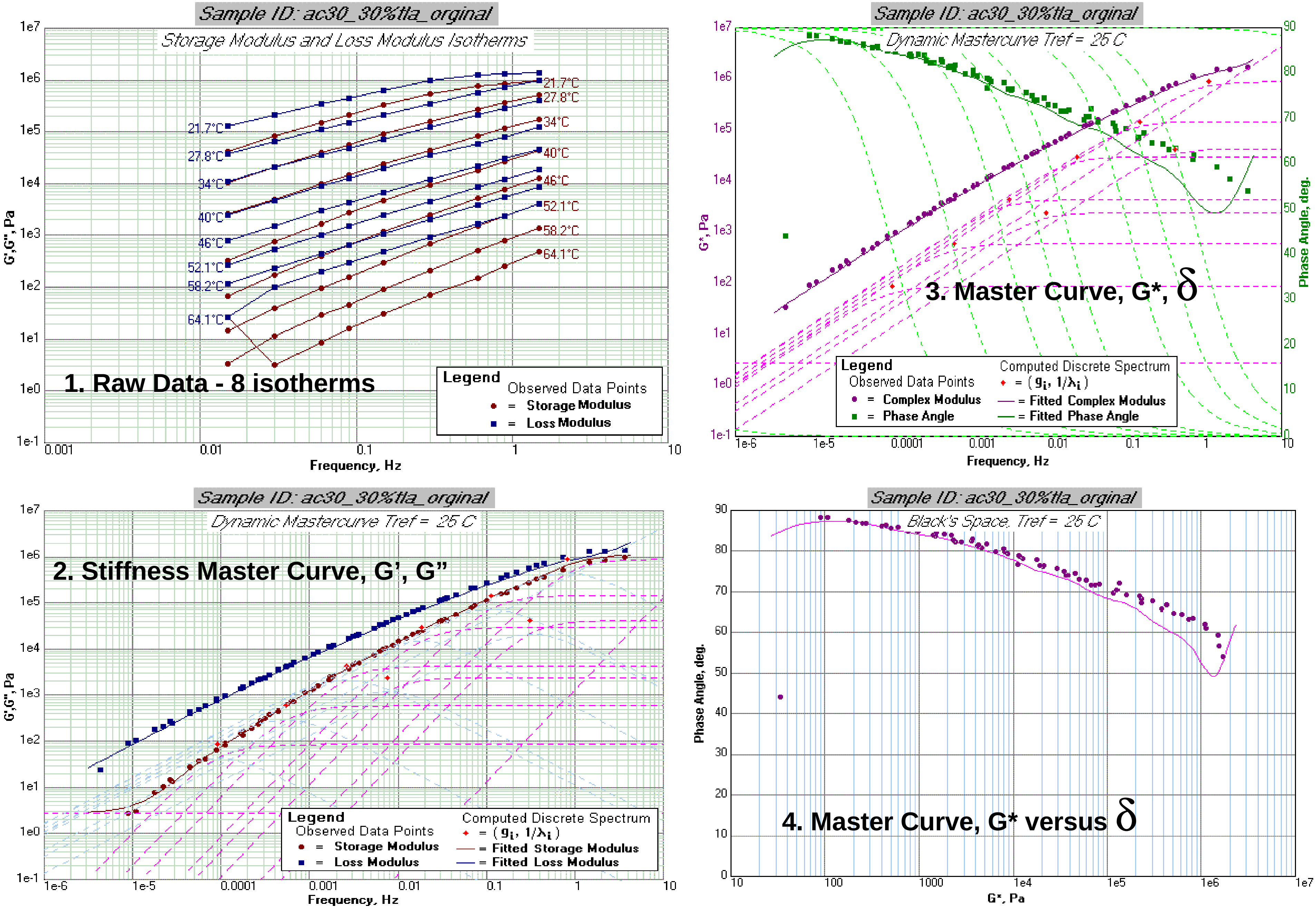
Sample ID: I45
Apparent Stiffness Mastercurve D-S, Rms Err 0.42%
Tref = -17
1e4
1e3
1e2
1e1
S(t), MPa
2. Stiffness Master Curve, S(t)
0.1
1
10
100
1000
1e4
t, sec


Creep Compliance Mastercurve D-S. Rms Err 0.42%
Tref = -17
3. Compliance Master Curve, D(t)
D(t), 1/MPa
1e-1
1e-2
1e-3
1e-4
0.1
1
10
100
1000
1e4
t, sec
9
1
8
7
6
5
4
3
2
Legend
Observed Data Points
= Creep compliance
Computed Discrete Spectrum
= (ci, λi)
= Fitted creep compliance

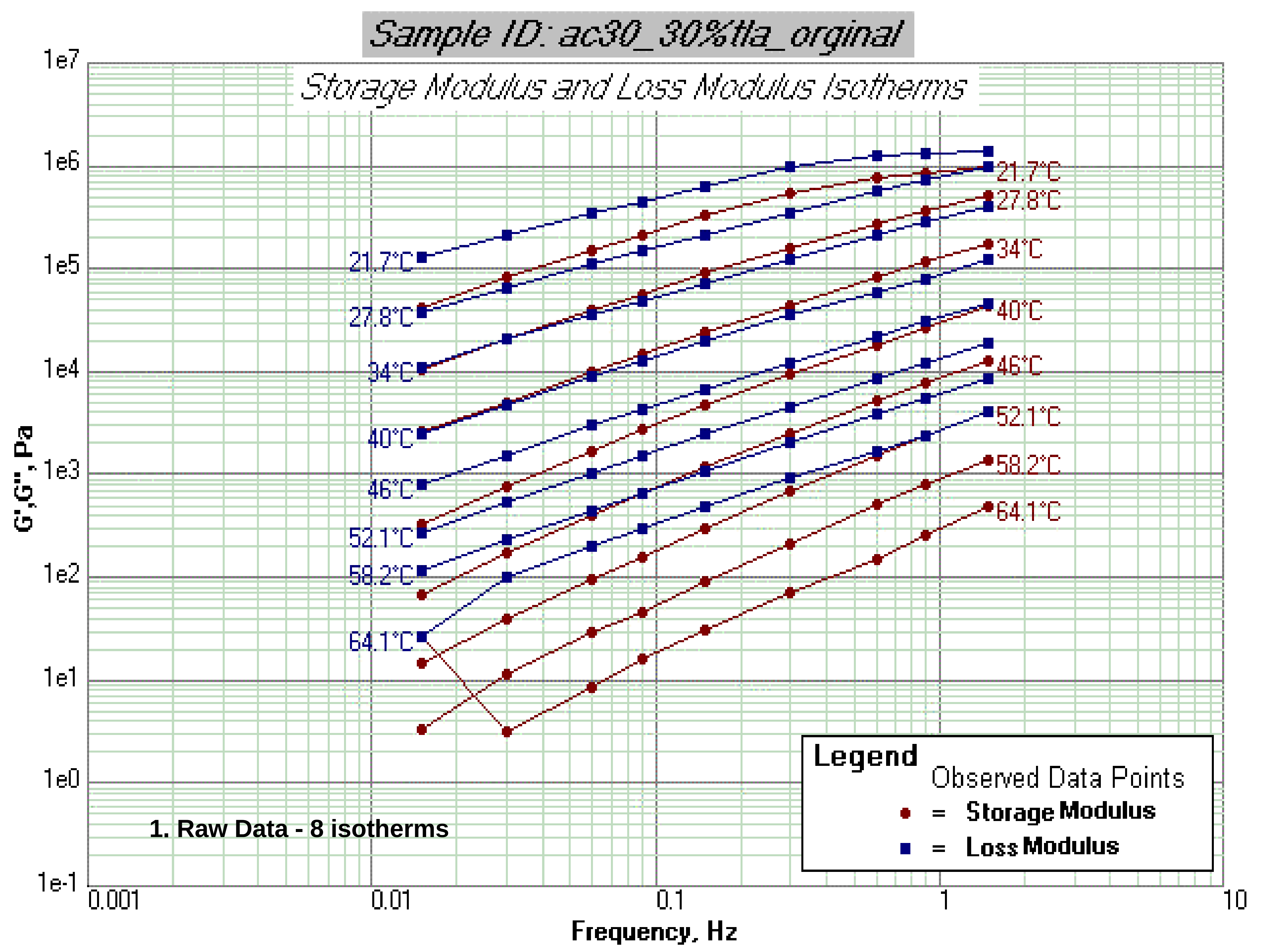


Dynamic MC from Transient Data. Tref = -17 C
4. Computed E', E"
from spectra calculations
1e4
1e3
1e2
1e1
E', E", MPa
0.0001
0.001
0.01
0.1
1
10
Frequency, rad/sec
Legend
Computed Discrete Spectrum
= (gi, 1/λi)
= Fitted Storage Modulus
= Fitted Loss Modulus

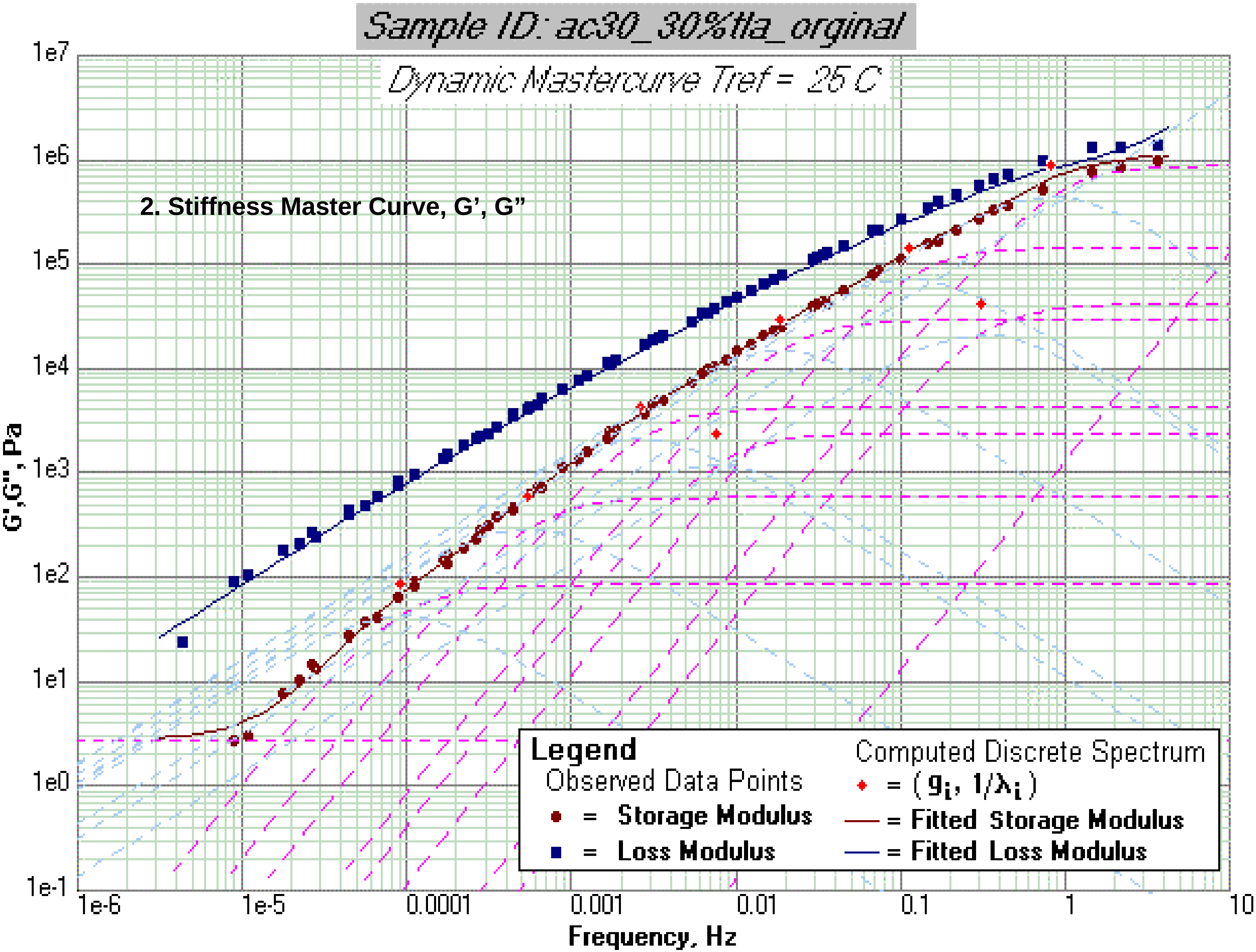
DSR

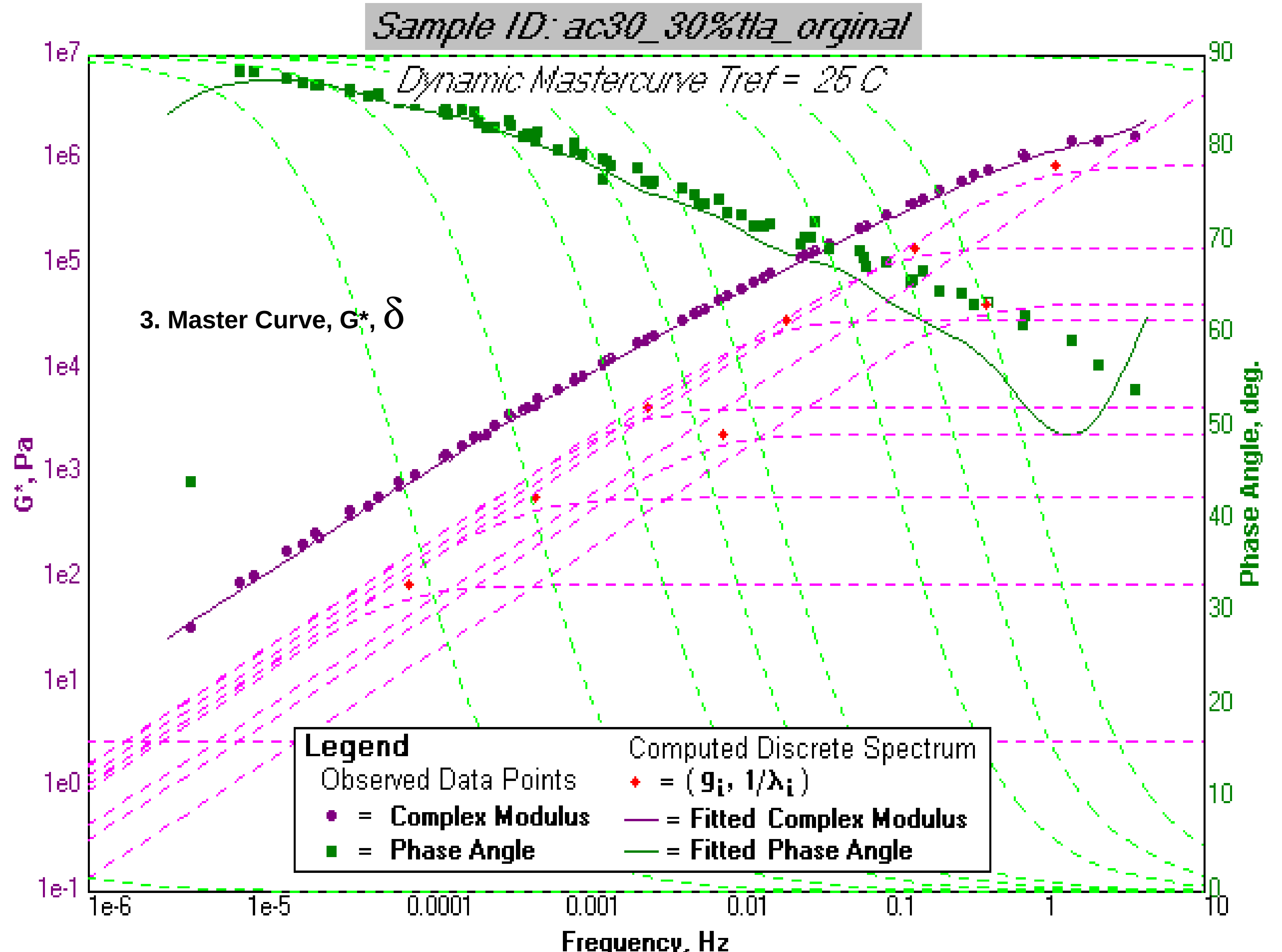


2. Dynamic Shear Rheometer - Typical Data Set

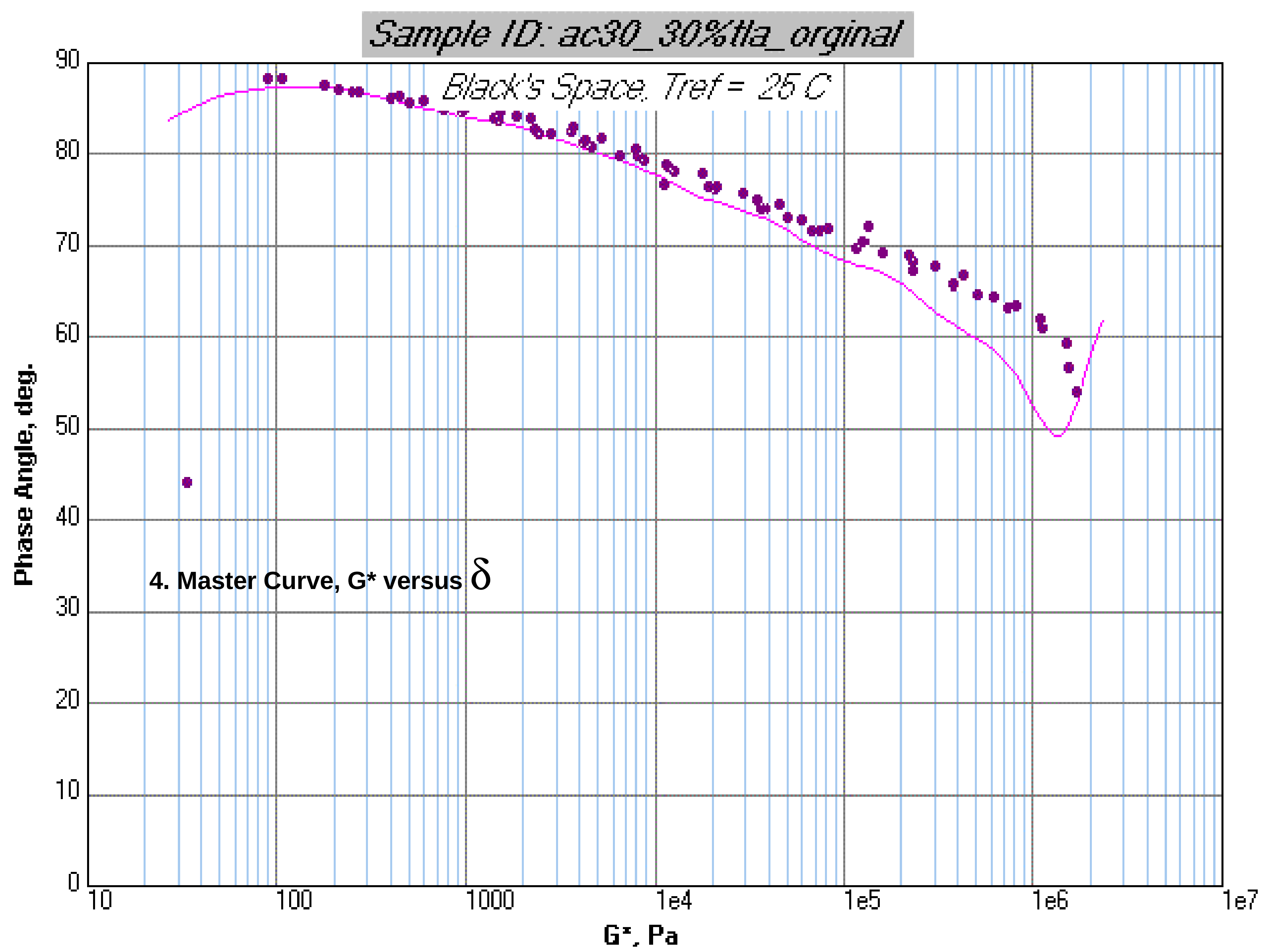


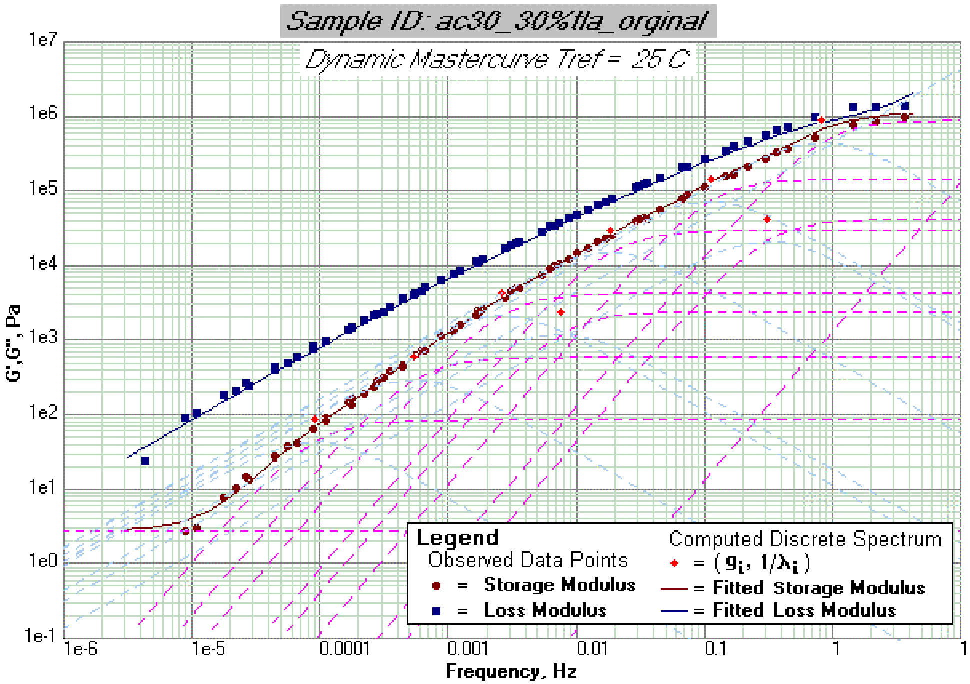
Sample ID: ac30_30%tla_orginal
Storage Modulus and Loss Modulus Isotherms
G',G", Pa
1e7
1e6
1e5
1e4
1e3
1e2
1e1
1e0
1e-1
0.001
0.01
0.1
1
10
Frequency, Hz
21.7°C
27.8°C
34°C
40°C
46°C
52.1°C
58.2°C
64.1°C
1. Raw Data - 8 isotherms
Legend
Observed Data Points
= Storage Modulus
= Loss Modulus

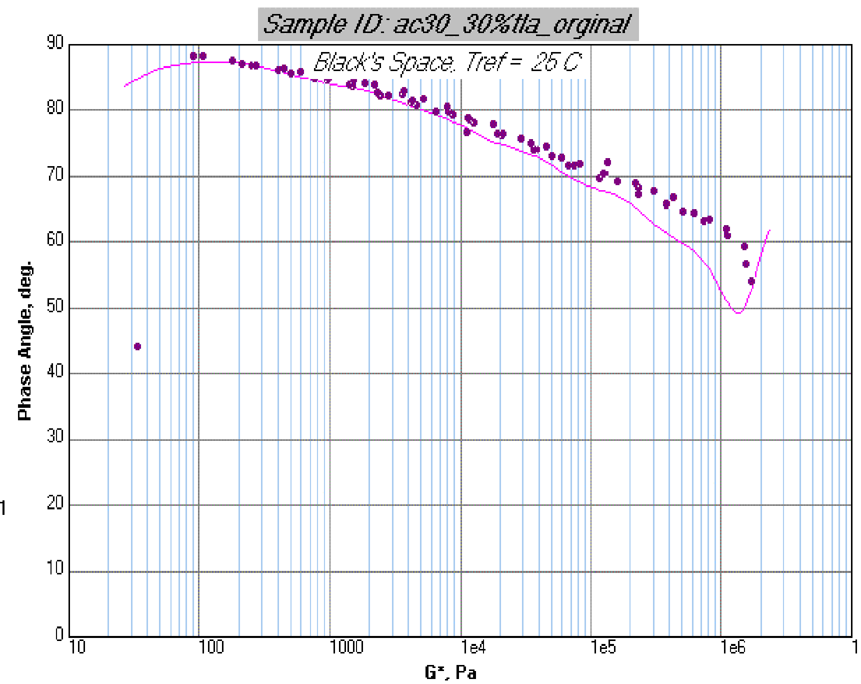

Sample ID: ac30_30%tla_orginal
Dynamic Mastercurve Tref = 25 C
2. Stiffness Master Curve, G', G"
G',G", Pa
1e7
1e6
1e5
1e4
1e3
1e2
1e1
1e0
1e-1
1e-6
1e-5
0.0001
0.001
0.01
0.1
1
10
Frequency, Hz
Legend
Observed Data Points
= Storage Modulus
= Loss Modulus
Computed Discrete Spectrum
= (gi, 1/λi)
= Fitted Storage Modulus
= Fitted Loss Modulus

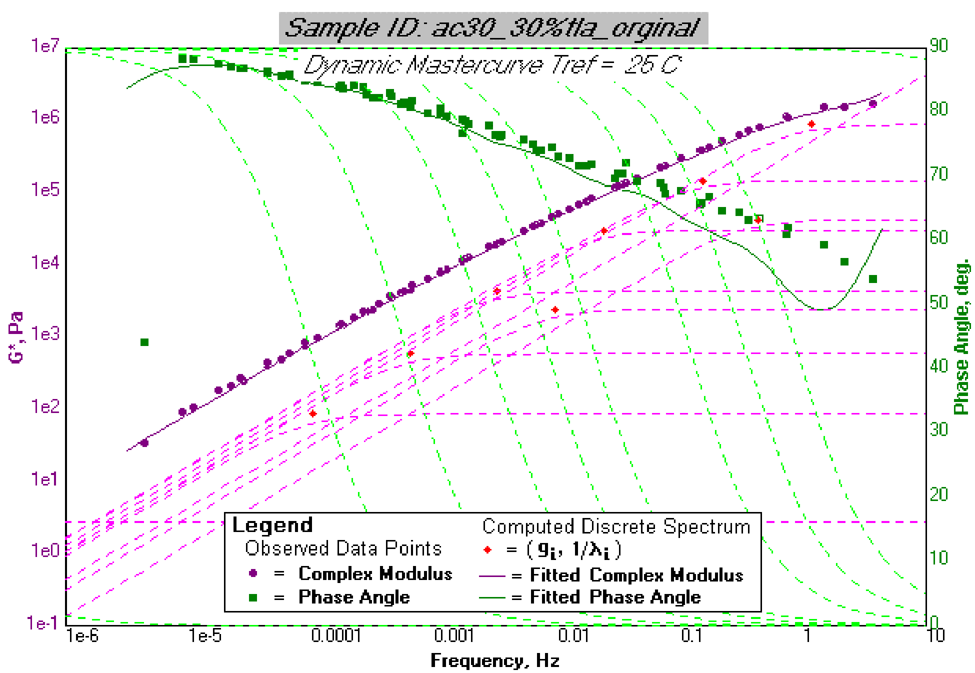


Sample ID: ac30_30%tla_orginal
Dynamic Mastercurve Tref = 25 C
3. Master Curve, G*, δ
1e7
1e6
1e5
1e4
1e3
1e2
1e1
1e0
1e-1
G*, Pa
90
80
70
60
50
40
30
20
10
0
Phase Angle, deg.
1e-6
1e-5
0.0001
0.001
0.01
0.1
1
10
Frequency, Hz
Legend
Observed Data Points
= Complex Modulus
= Phase Angle
Computed Discrete Spectrum
= (gi, 1/λi)
= Fitted Complex Modulus
= Fitted Phase Angle


Sample ID: ac30_30%tla_orginal
Black's Space, Tref = 25 C
Phase Angle, deg.
90
80
70
60
50
40
30
20
10
0
10
100
1000
1e4
1e5
1e6
1e7
G*, Pa
4. Master Curve, G* versus δ







3 formats for master curve

- G', G" versus frequency
- G*, δ versus frequency
- G* versus δ (Black space)

Error

Typical Error

Typical error -

BBR - new spec - < 1.25%
Other DSR etc < 5%

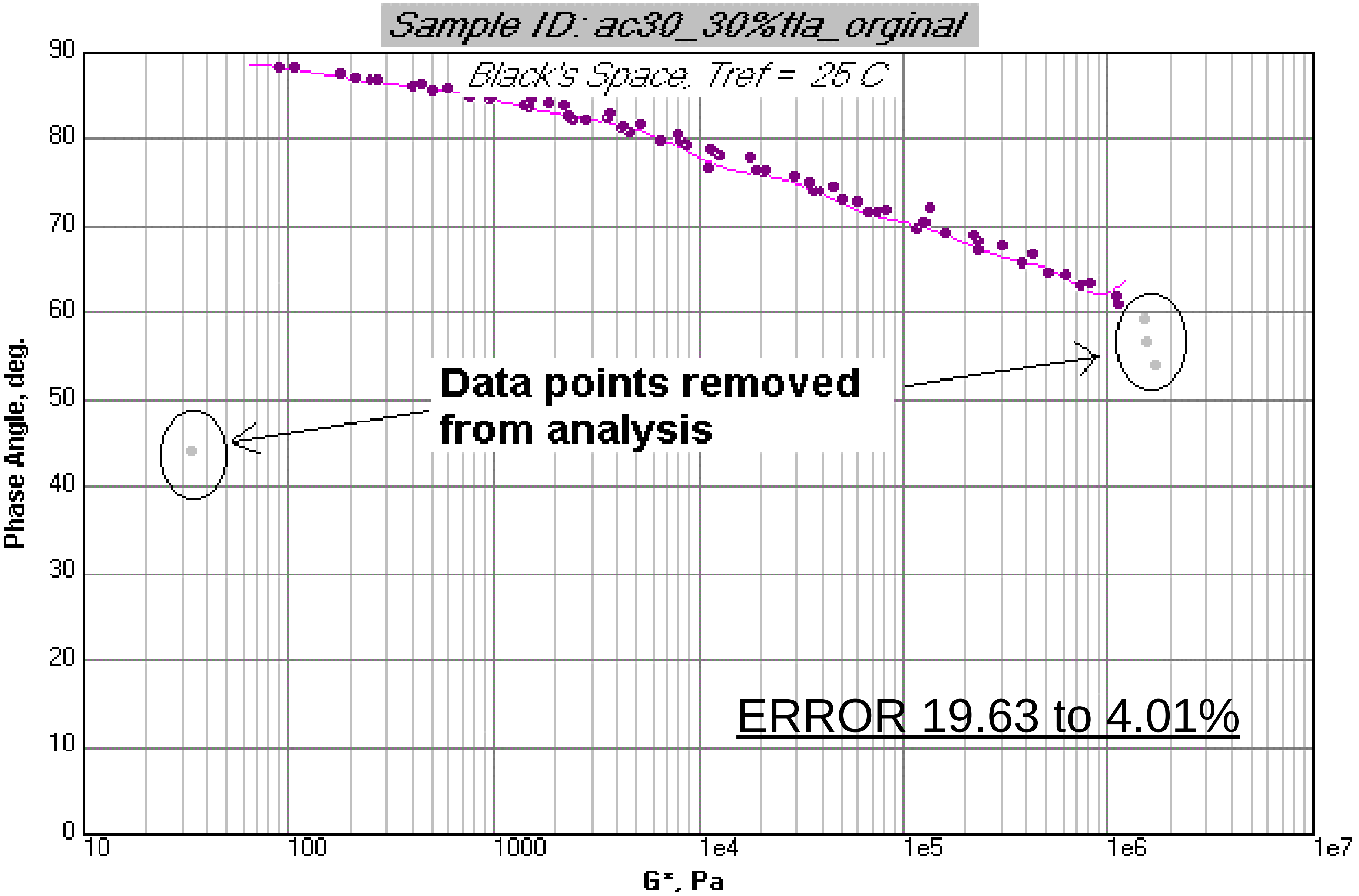
Error need to be determined for various applications. Fit needs to consider “noise” and goodness of fit.

Error Criteria

- Root mean square error

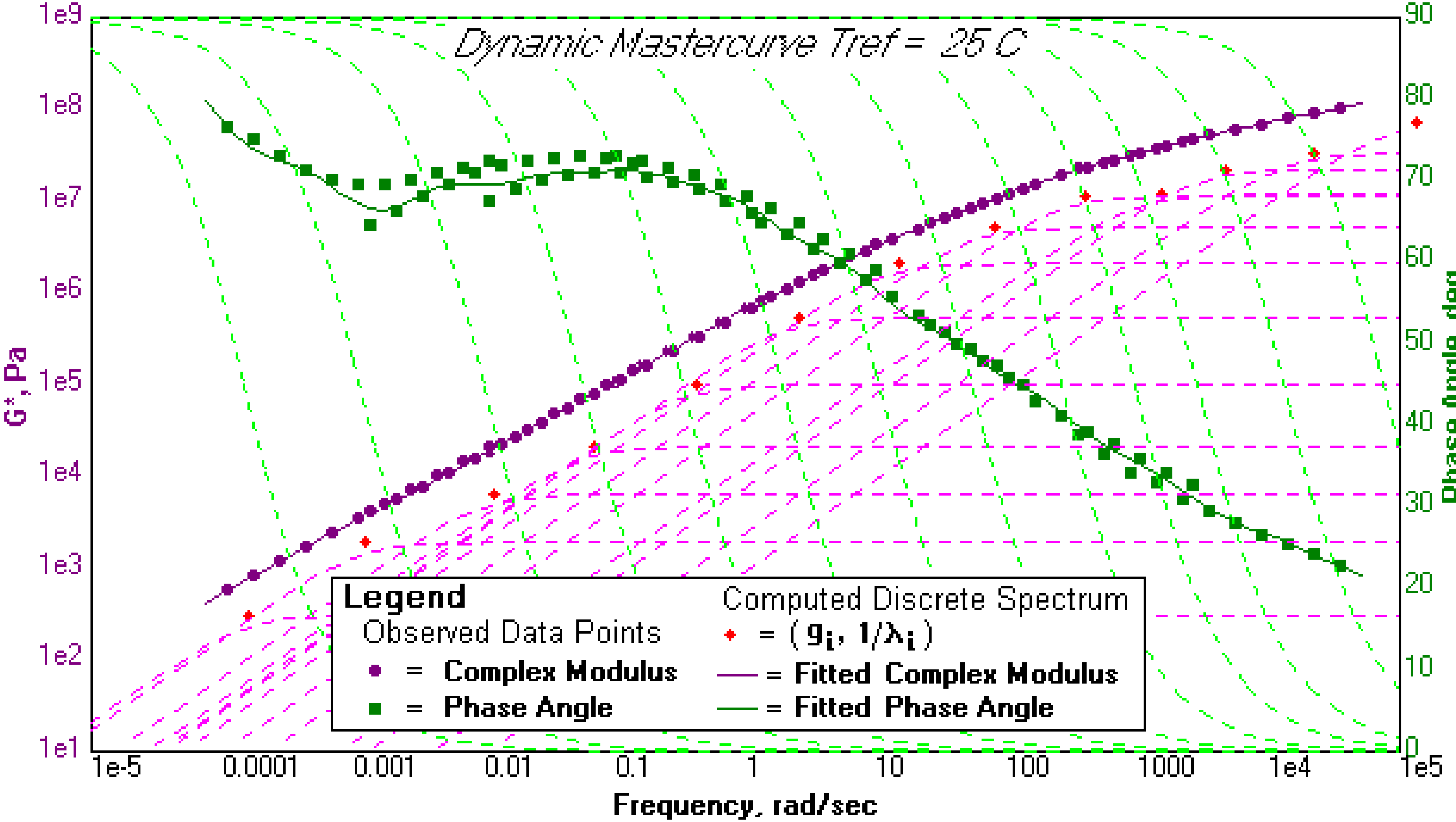
$$Error = \frac{\left(S(t) - S(t)_{fitted}\right)}{S(t)}$$

$$rms(\%) = 100\sqrt{\frac{SSRE}{12}}$$

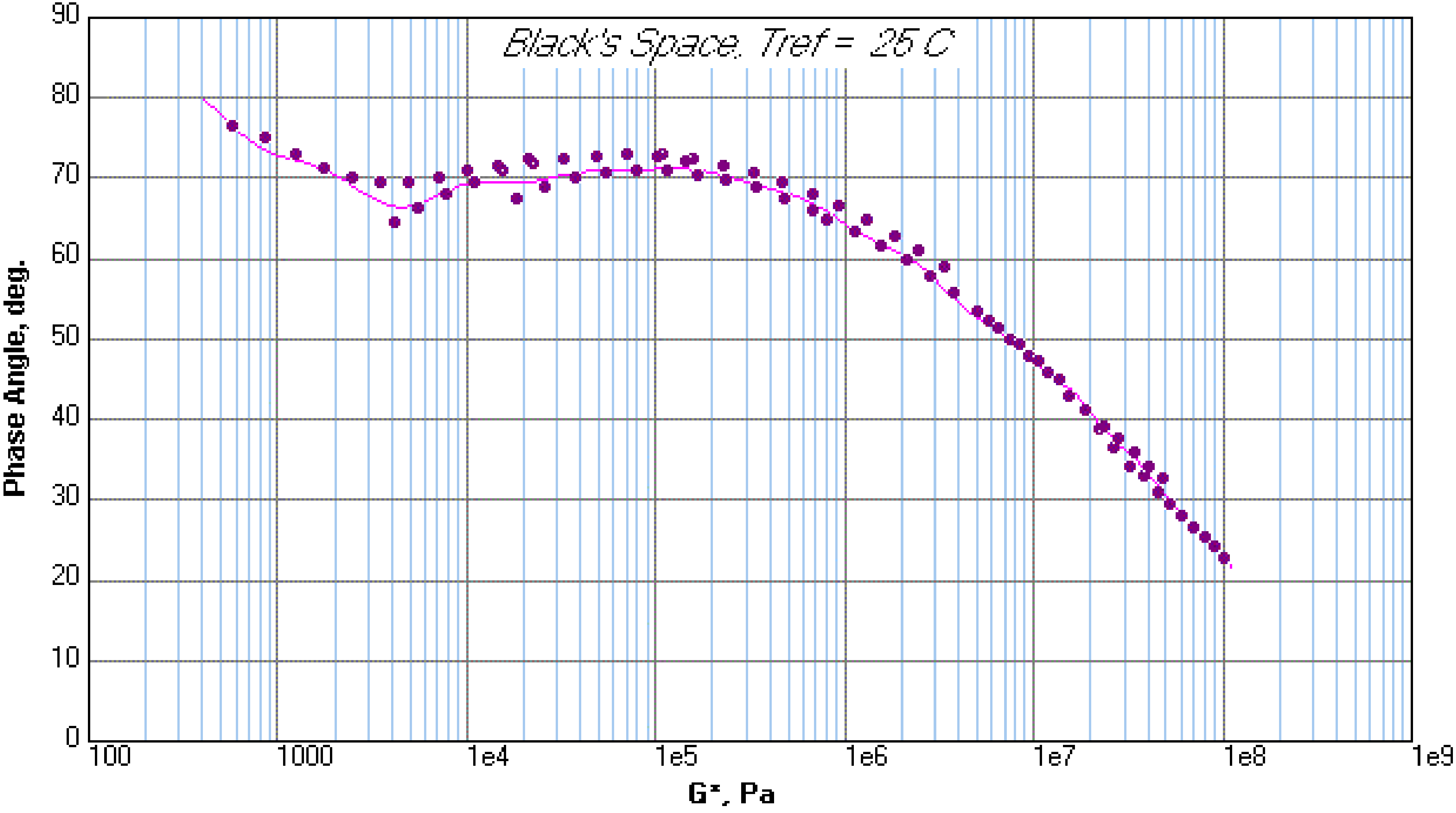


Sample ID: ac30_30%tla_orginal
Black's Space, Tref = 25 C
Data points removed from analysis
ERROR 19.63 to 4.01%
Phase Angle, deg.
G*, Pa
90
80
70
60
50
40
30
20
10
0
10
100
1000
1e4
1e5
1e6
1e7

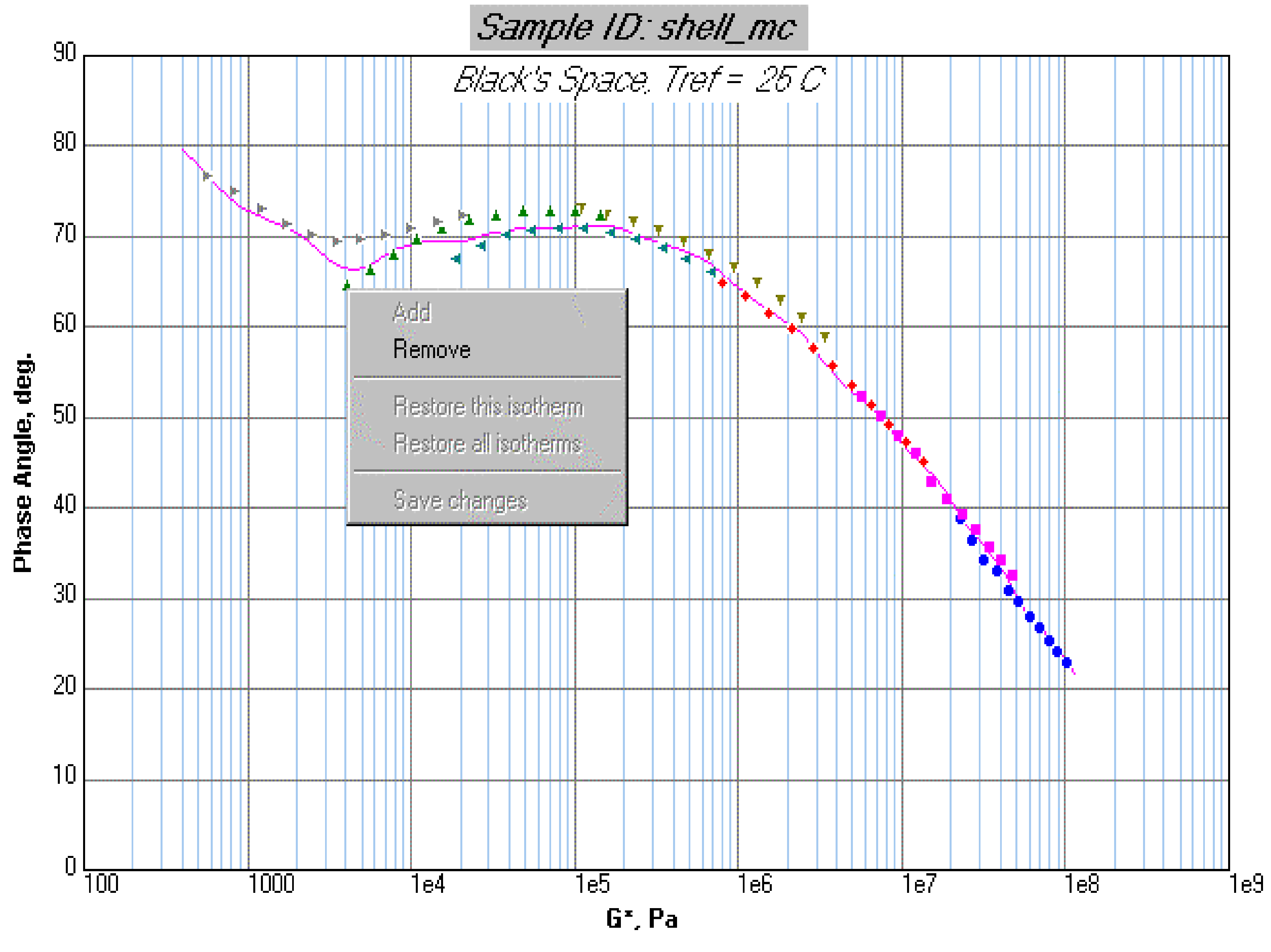
Polymer modified binders



Black space



Black's Space, Tref = 25 C
Phase Angle, deg.
90
80
70
60
50
40
30
20
10
0
100
1000
1e4
1e5
1e6
1e7
1e8
1e9
G*, Pa



Sample ID: shell_mc
Black's Space, Tref = 25 C
Phase Angle, deg.
G*, Pa
0
10
20
30
40
50
60
70
80
90
100
1000
1e4
1e5
1e6
1e7
1e8
1e9
Add
Remove
Restore this isotherm
Restore all isotherms
Save changes

Conclusions

- Software developed for rapid production of master curves
  - Shifting based on Gordon and Shaw
  - Inter-conversions enabled
  - Interpolation rapid and easy to perform
  - Graphs in different formats allows understanding of data
  - RMS error criteria - a measure of goodness of fit
  - Works well with modified binders and mixtures