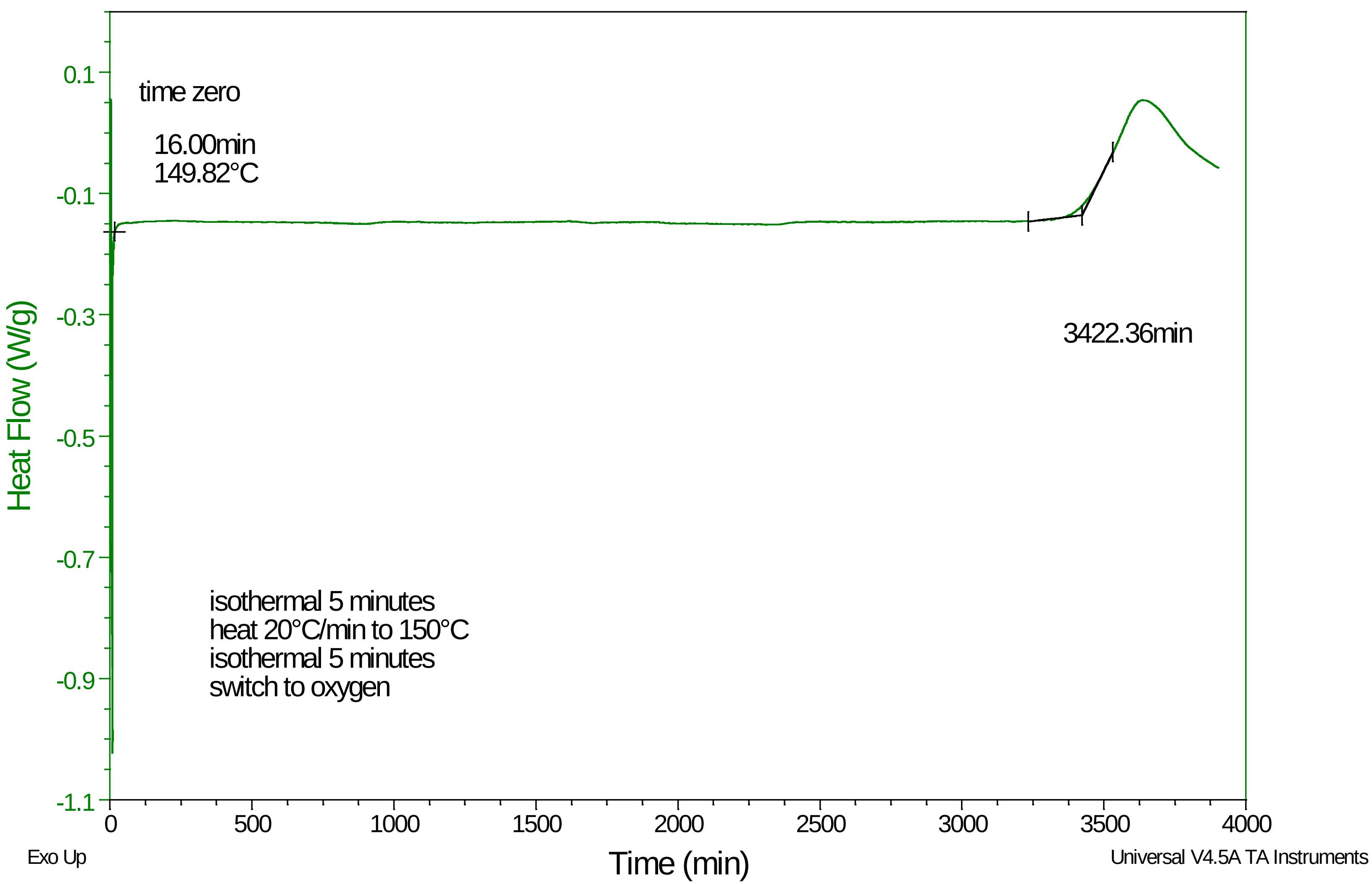
The Problem of Confounded Mechanisms In Accelerated Aging Protocols

Michael P. Sepe
The Material Analyst
Prepared for UL Prospector
November 17, 2015

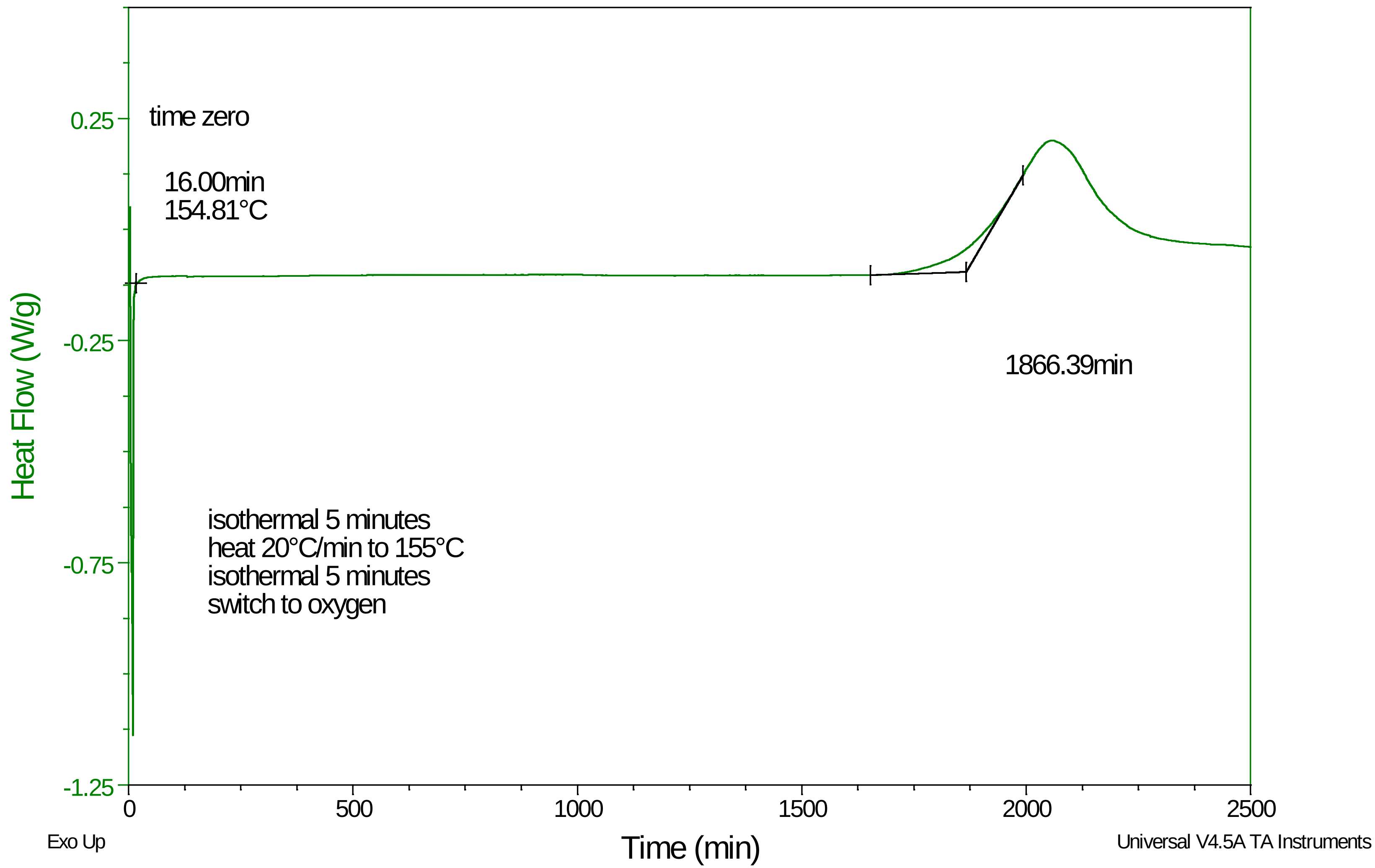
Science is a way to teach how something gets to be known, what is not known, to what extent things are known, how to handle doubt and uncertainty, what the rules of evidence are, how to think about things so that judgments can be made, how to distinguish truth from fraud, and from show.

Richard Feynman

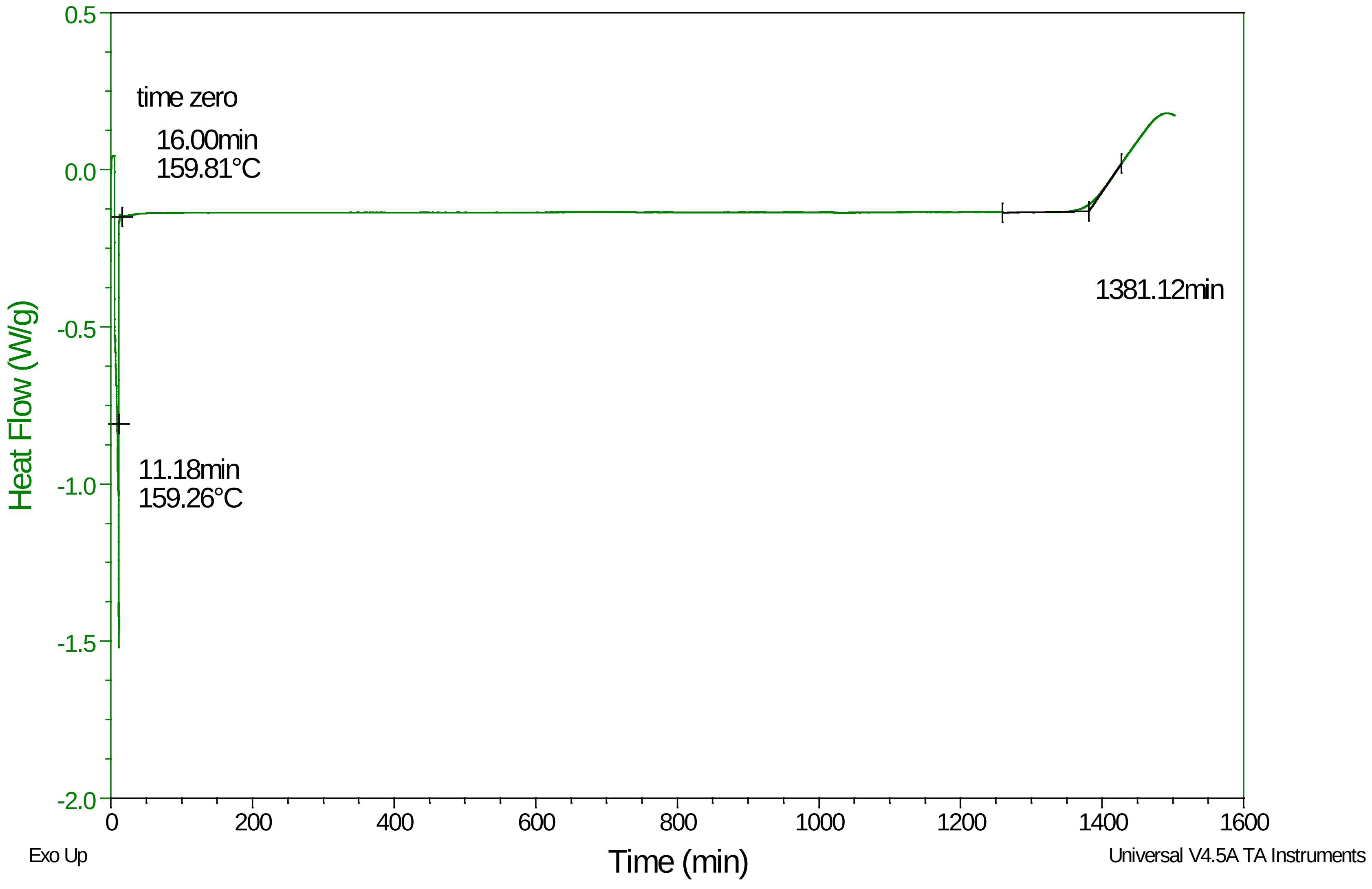
Oxidation Induction Time Test on PP Copolymer at 150 C



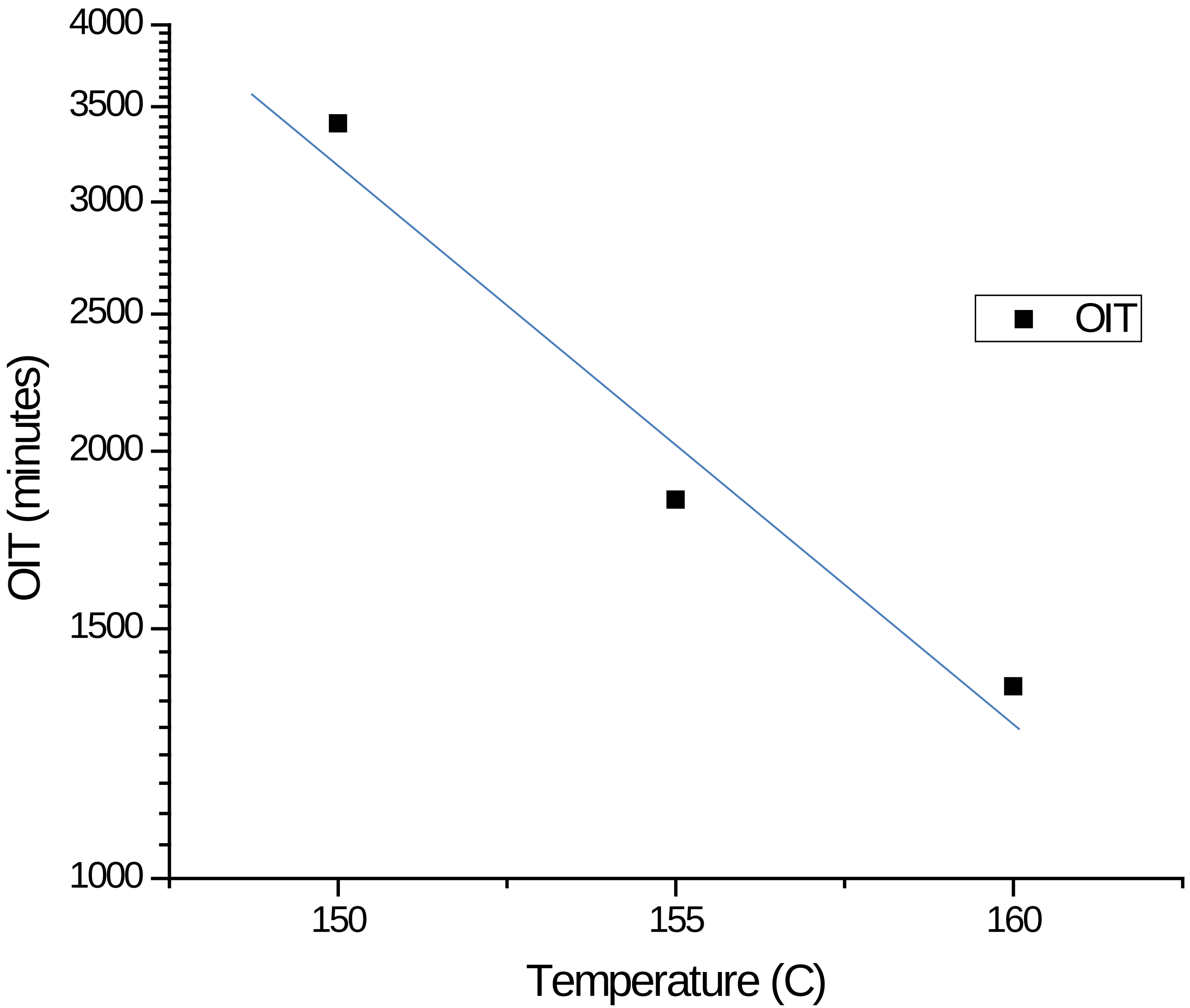
Oxidation Induction Time Test on PP Copolymer at 155 C



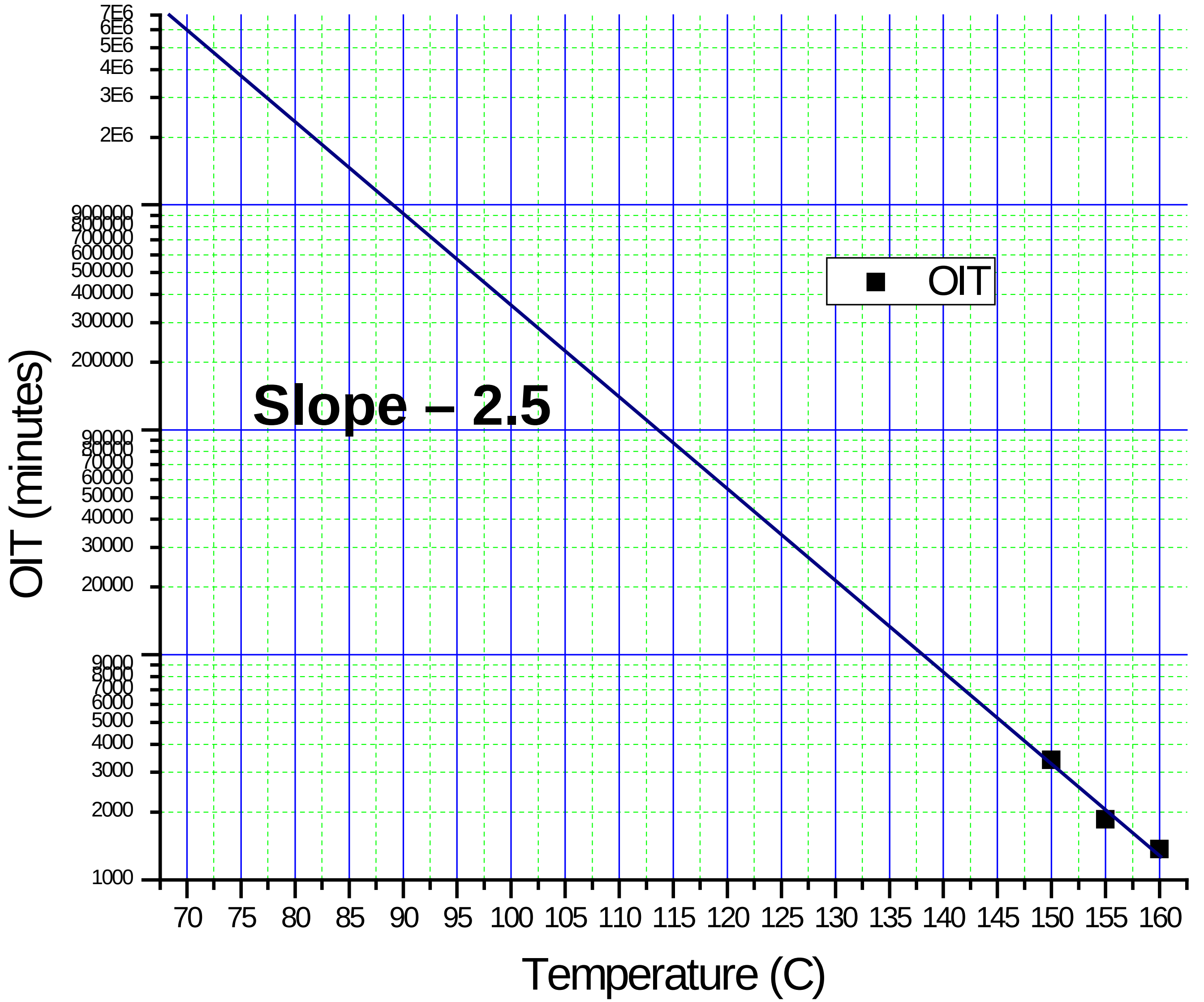
Oxidation Induction Time Test on PP Copolymer at 160 C



Plot of OIT versus Temperature for Three Tests



Plot of OIT versus Temperature - Extrapolated



Arrhenius Equation

$$k = Ae^{-Ea/RT}$$

Where E_a is the activation energy
T is temperature
R is the gas constant

Temperature Coefficient (Q_{10})

$$Q_{10} = (r_2/r_1)^{10/(T2-T1)}$$

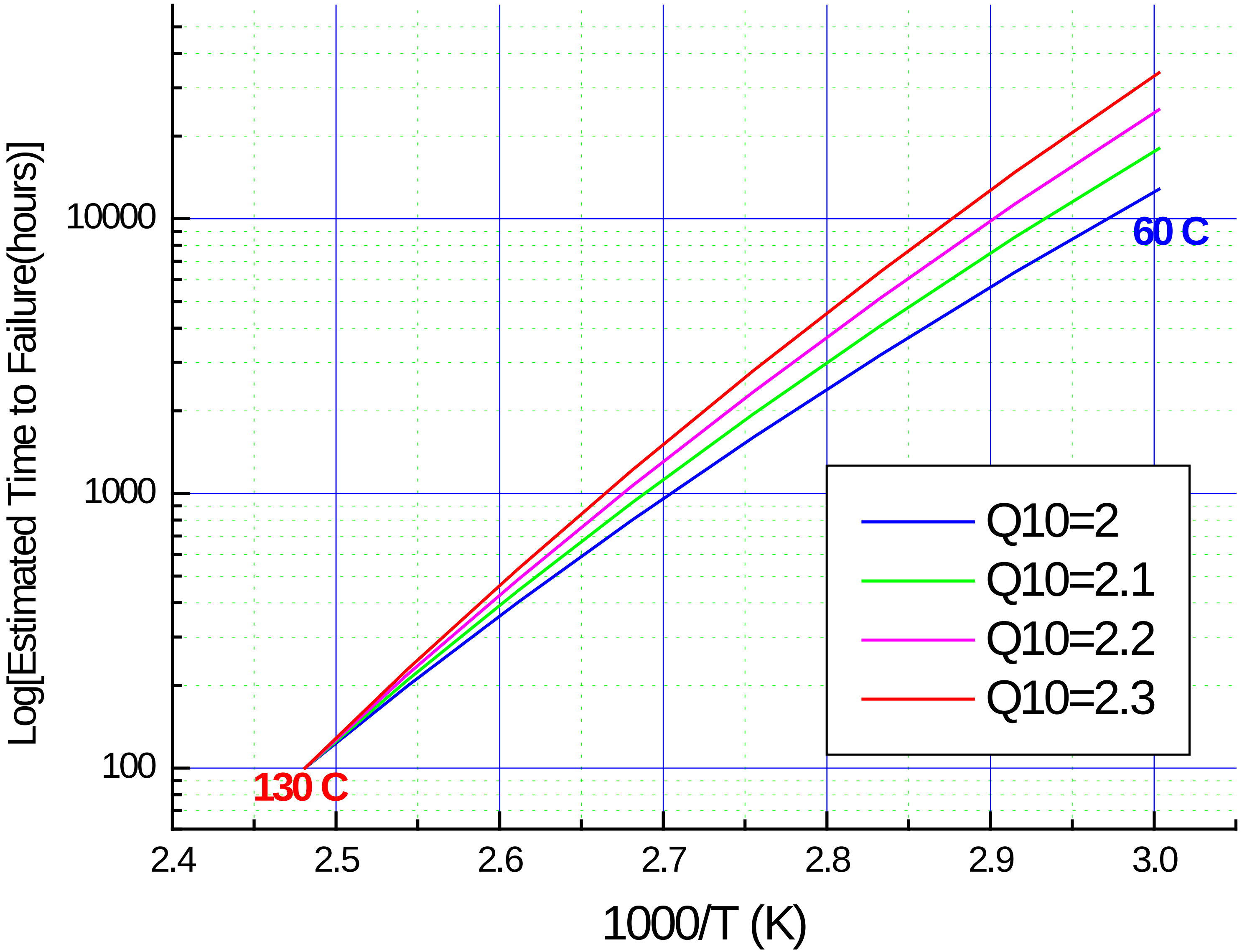
Rearranges to $AF = Q_{10}^{[(T2-T1)/10]}$

Q_{10} Is Typically Considered To Equal 2
Actual Experiments Show A Range of 1.8-2.5

Items To Consider

- Three to Four Experimental Points Should Be Used To Confirm the Aging Factor
- Selected Temperatures Should Not Cross A Key Transition Temperature
- Extrapolations Should Not Extend Across A Key Transition Temperature
- Failure Must Be Carefully Defined (e.g. 50% Reduction In A Key Property Relative to Initial Performance)

Use of Results From One Test Temperature To Predict Time To Failure Using Different Aging Factors



The Problem

Accelerated Testing Models Assume That Oxidation Is the Only Mechanism In Effect and All Observed Property Changes Are Attributed To This Mechanism

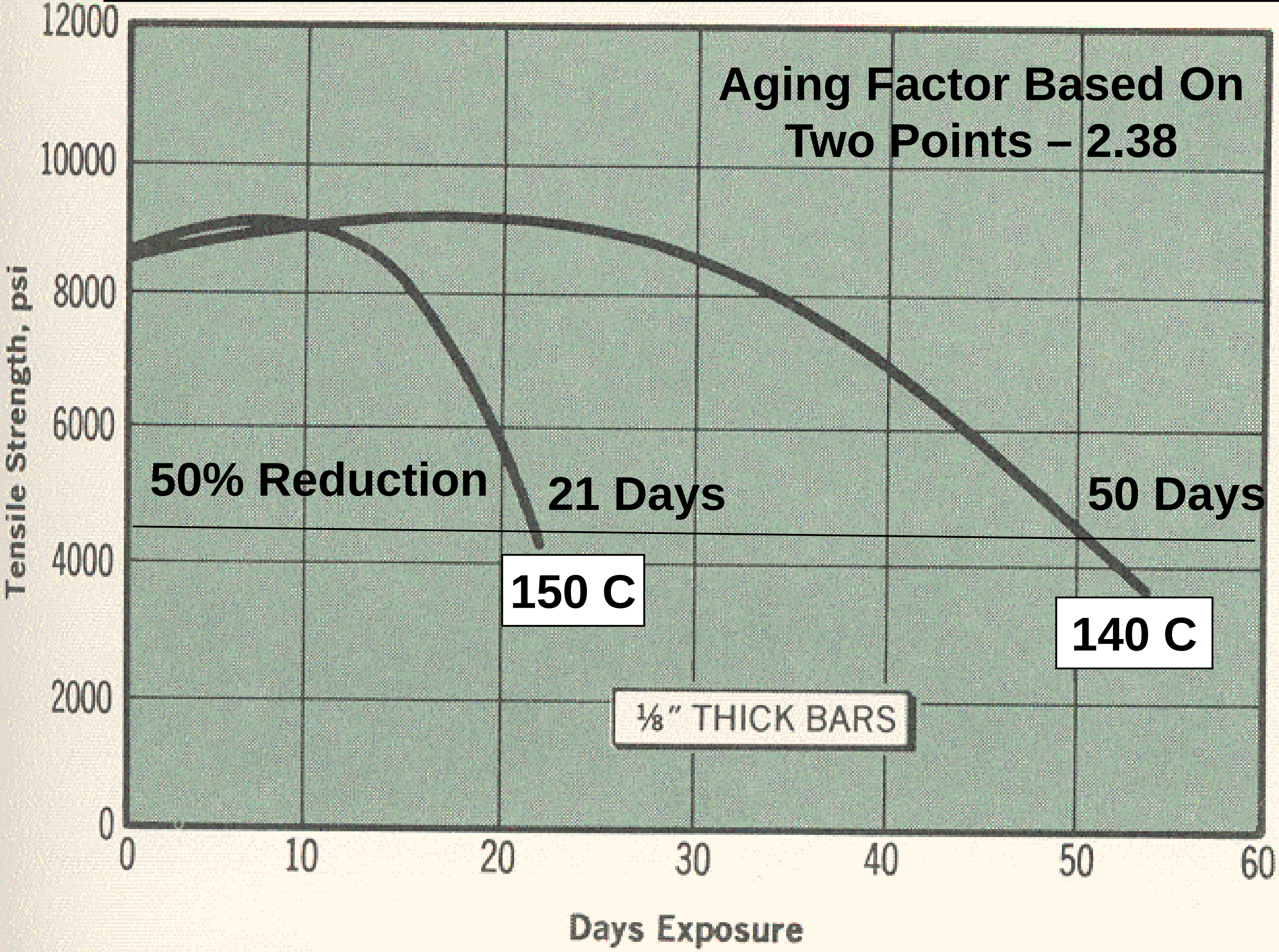
Effects of Elevated Temperature on Polymers

- Chemical Changes
  - Oxidation
  - Chemical Interaction
  - Migration of Mobile Constituents
- Structural Rearrangements
  - Physical Aging
  - Solid State Crystallization
  - Crosslinking
- Relaxation Processes
  - Creep
  - Stress Relaxation
  - ESC

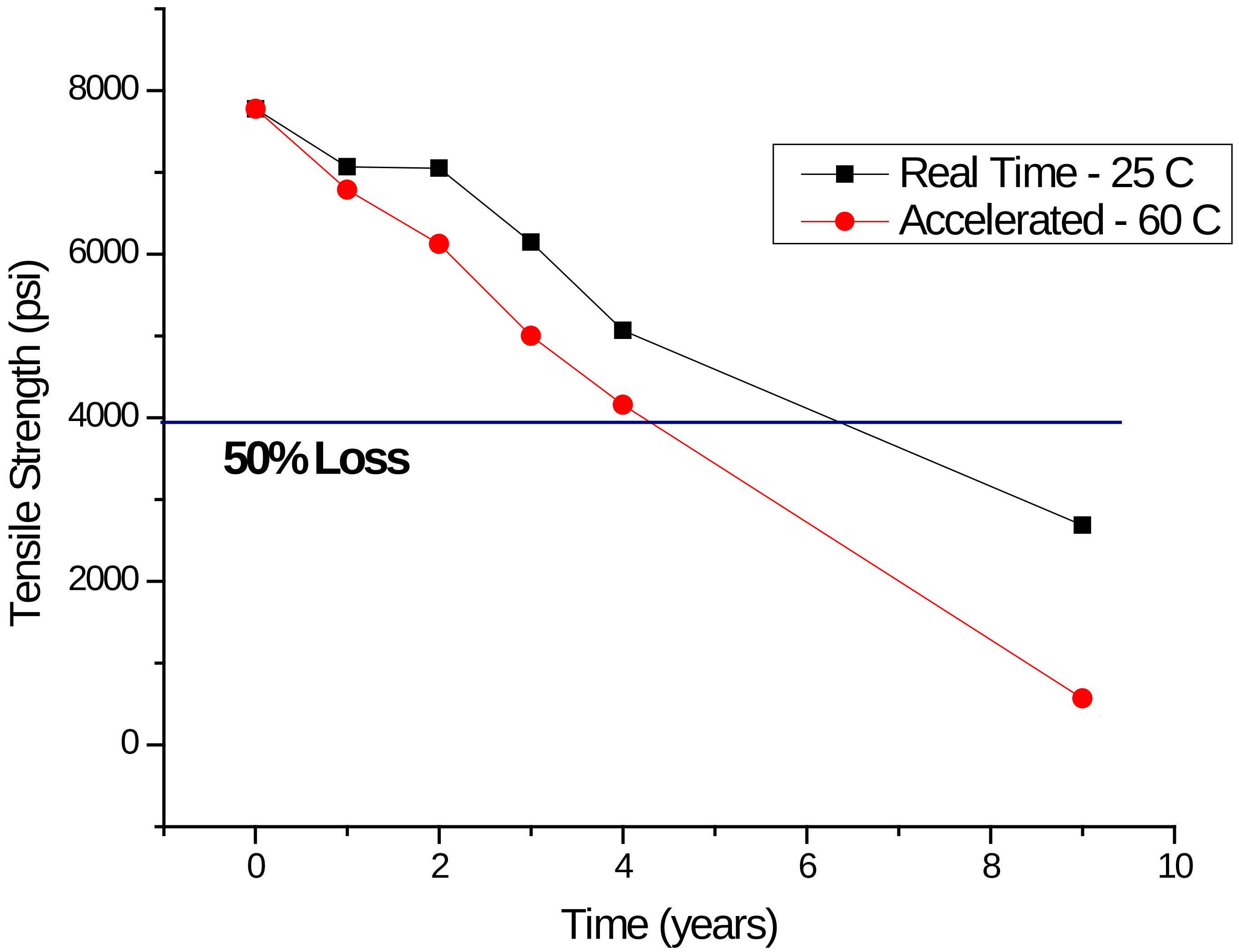
Considerations

- Multiple Processes Frequently Take Place Concurrently
- Some of These Processes Are Thermally Activated (Require a Specific Minimum Temperature To Occur)
- Some Are Relaxation Processes (Will Occur At Some Rate At Any Temperature)
- Approaching or Exceeding Key Transition Temperatures, Such As Tg, May Accelerate These Processes To A Much Greater Degree Than Predicted By Traditional Mathematical Models

Practical Application to Acetal



Comparison of Actual and Modeled Changes In Tensile Strength



Document Guidance

- Aging Temperature Should Be Kept Below 60 C To Prevent Other Effects from Entering the Experiment Such As Changes In Crystallinity
- Solid State Crystallization Occurs Above the T_g of A Polymer
- Several Semi-Crystalline Polymers Have T_g's Below 60 C
  - Polyethylene
  - Polypropylene
  - Acetal
  - Conditioned Aliphatic Polyamides

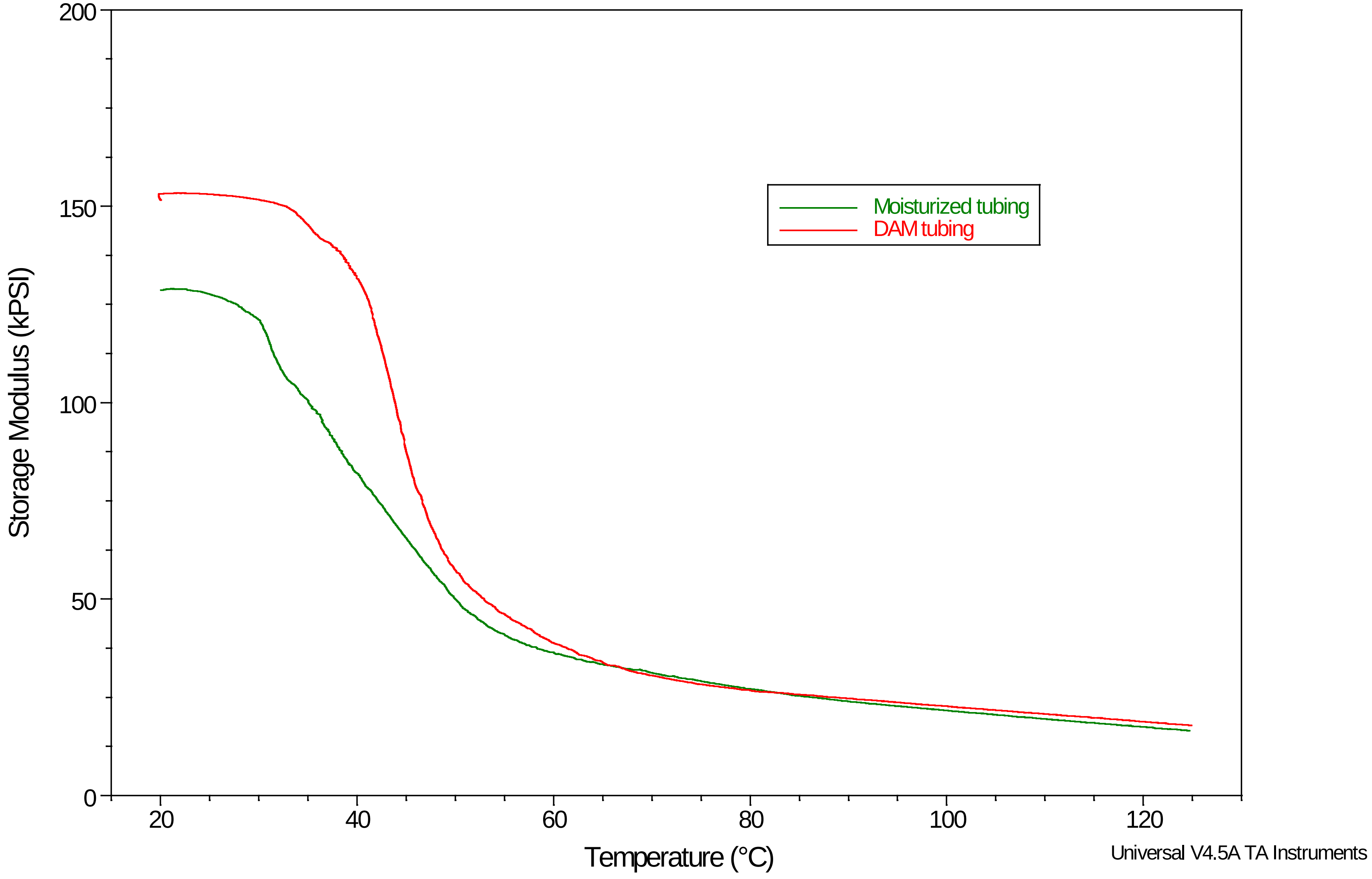
“Aging” Behavior in A Polypropylene

Property	Units	As Molded	Aged 60 Days @ 55^{o}C
Tensile Yield Strength	MPa	26.80	28.81
Tensile Modulus	MPa	1070	1176
Elongation @ Break	%	440	201

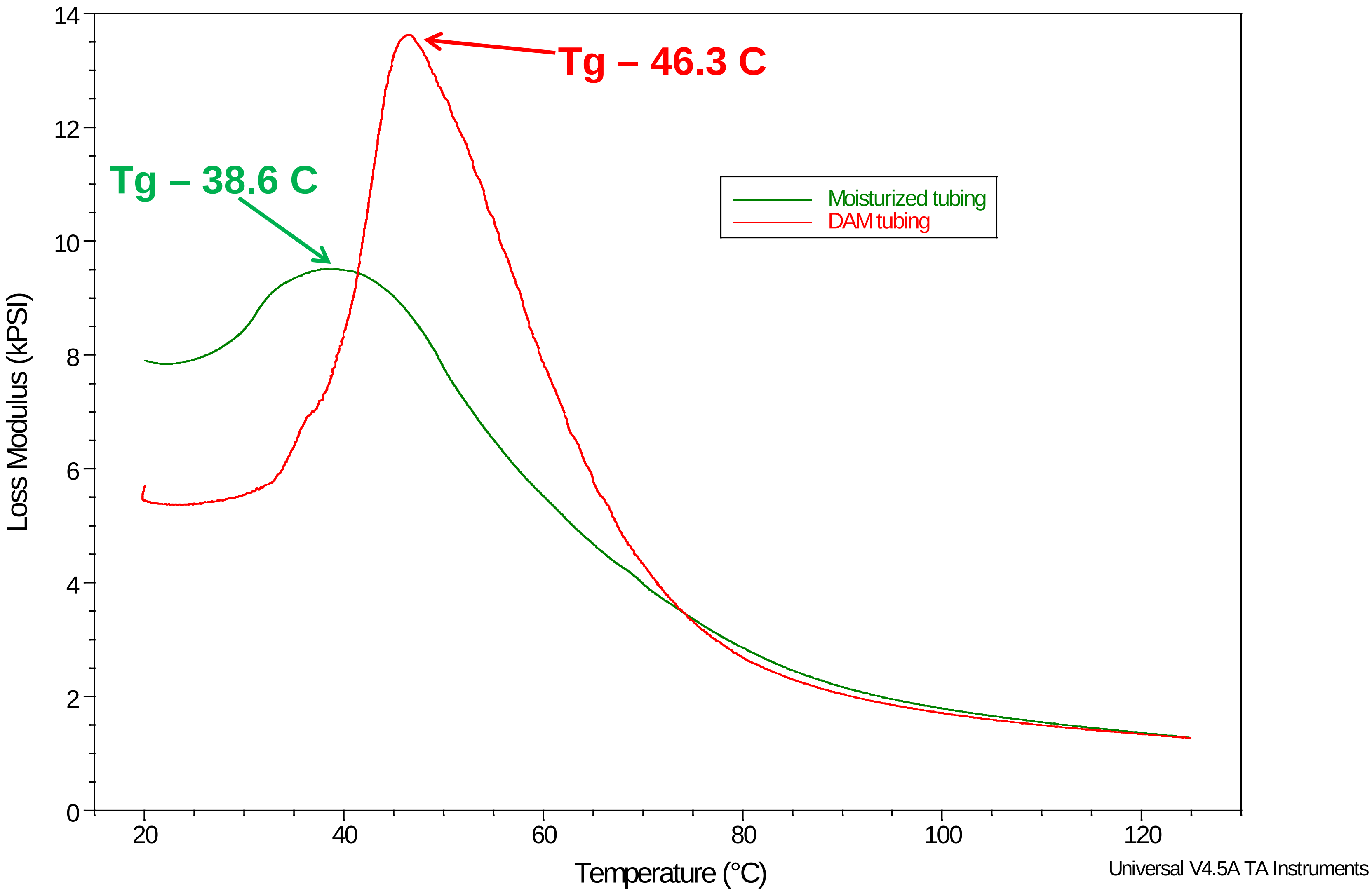
Analysis of Test Results

- Tensile Strength Increases By 8%
- Tensile Modulus Increases By 10%
- Ultimate Elongation Decreases By 55%
- Tests of Molecular Weight and Oxidative Stability Show No Evidence of Oxidative Degradation
- Property Changes Are Consistent With Crystallization

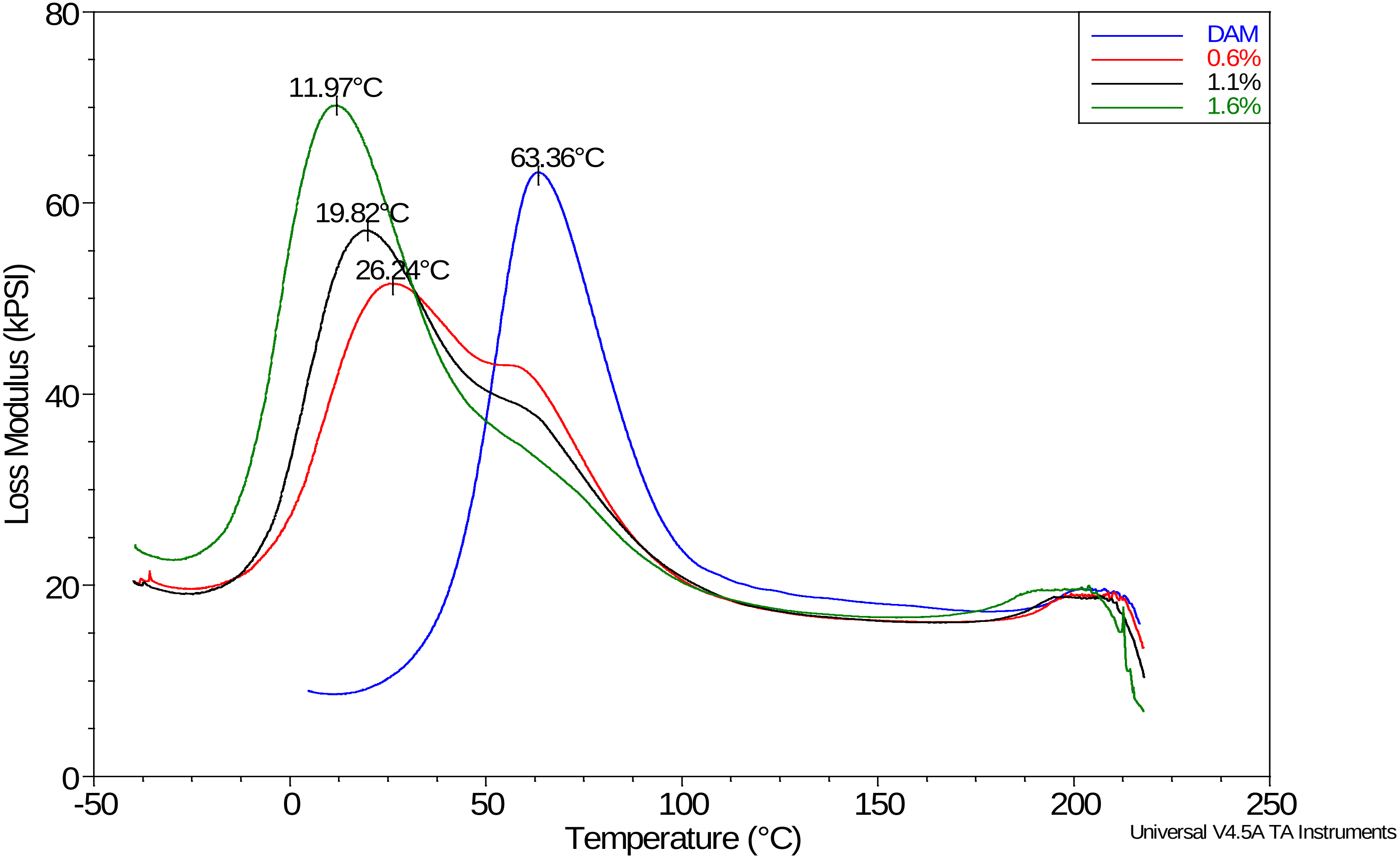
Effect of Moisture Absorption On the Elastic Modulus of Nylon 12



Effect of Moisture Absorption On the Loss Modulus of Nylon 12

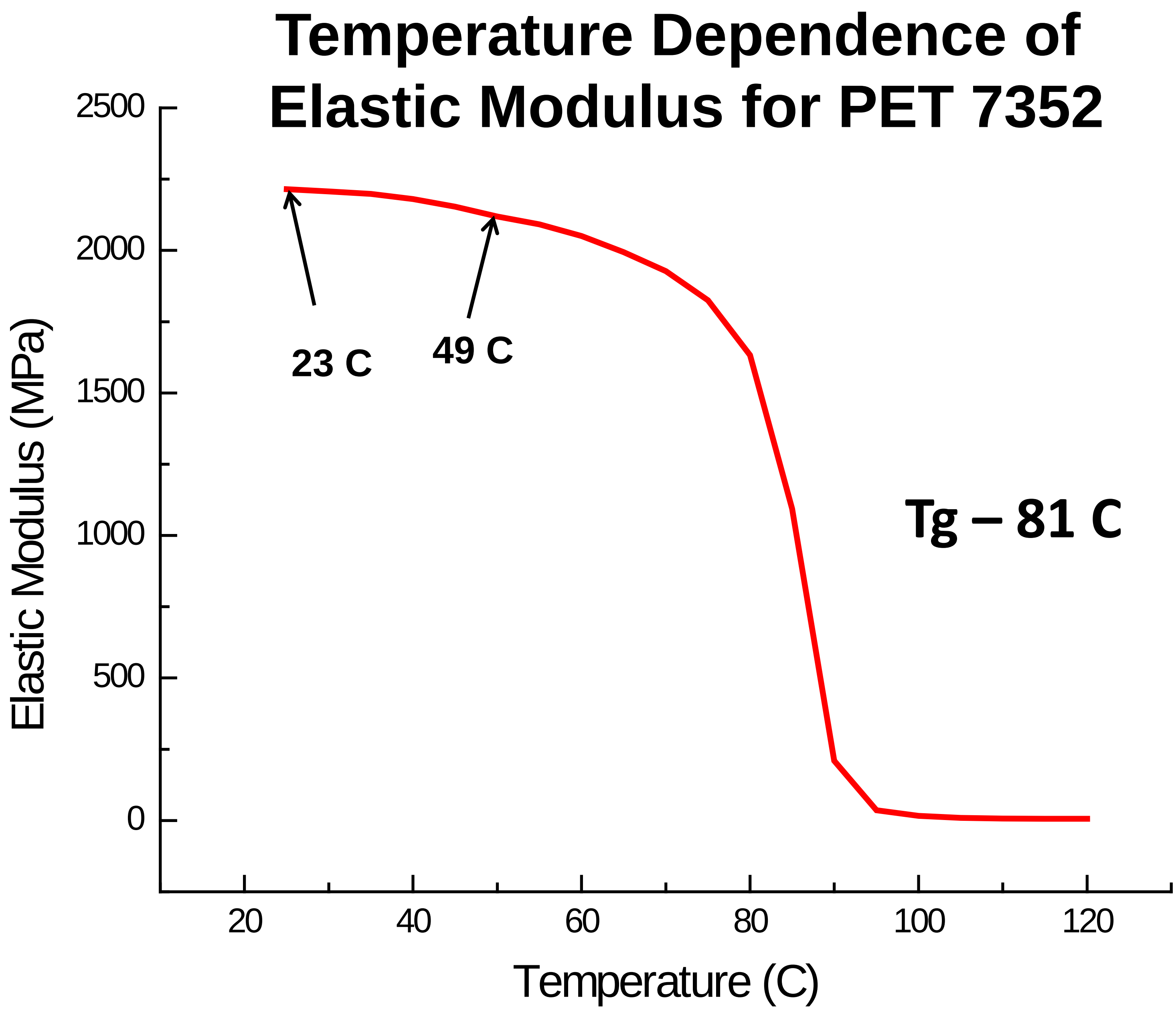


Effect of Moisture Absorption On The Tg Of 35% Long Glass Fiber Nylon 6



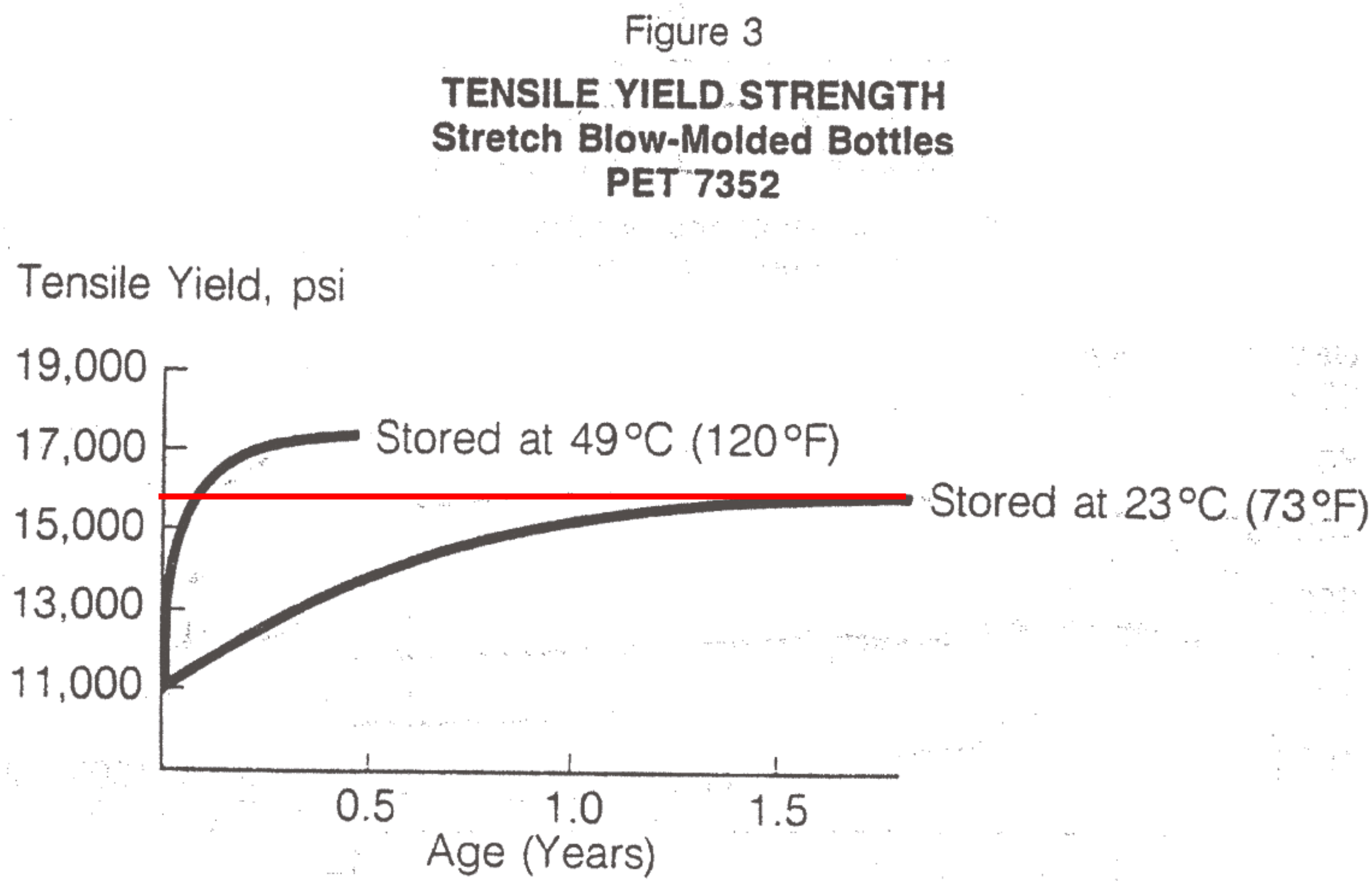
Physical Aging

- Physical Aging Occurs In the Amorphous Regions of A Polymer
- Process Increases Strength and Modulus But Decreases Ductility
- Occurs Above the Beta Transition of the Polymer
- Occurs At A Rate Governed By the Relationship between the Aging Temperature and the Tg
- Occurs More Rapidly In Low Molecular Weight Systems



Temperature Dependence of
Elastic Modulus for PET 7352
2500
2000
1500
1000
500
0
Elastic Modulus (MPa)
23 C
49 C
Tg – 81 C
20
40
60
80
100
120
Temperature (C)

1.8 Years at 23ºC = 30 days at 49ºC When Tensile Yield Strength Is Used



1.6 Years at 23^{o}C = 6 days at 49^{o}C When Free Volume Relaxation Is Used

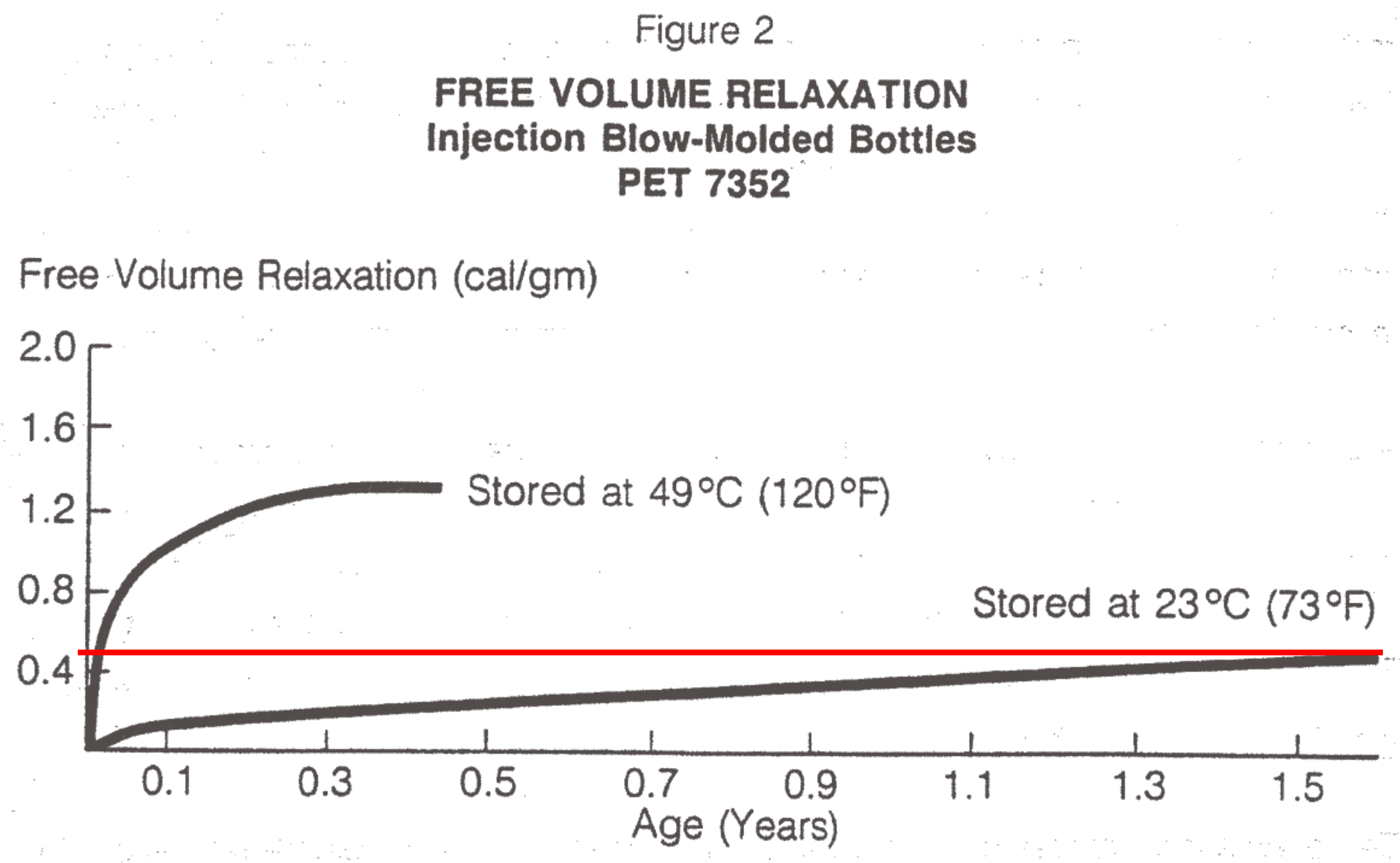
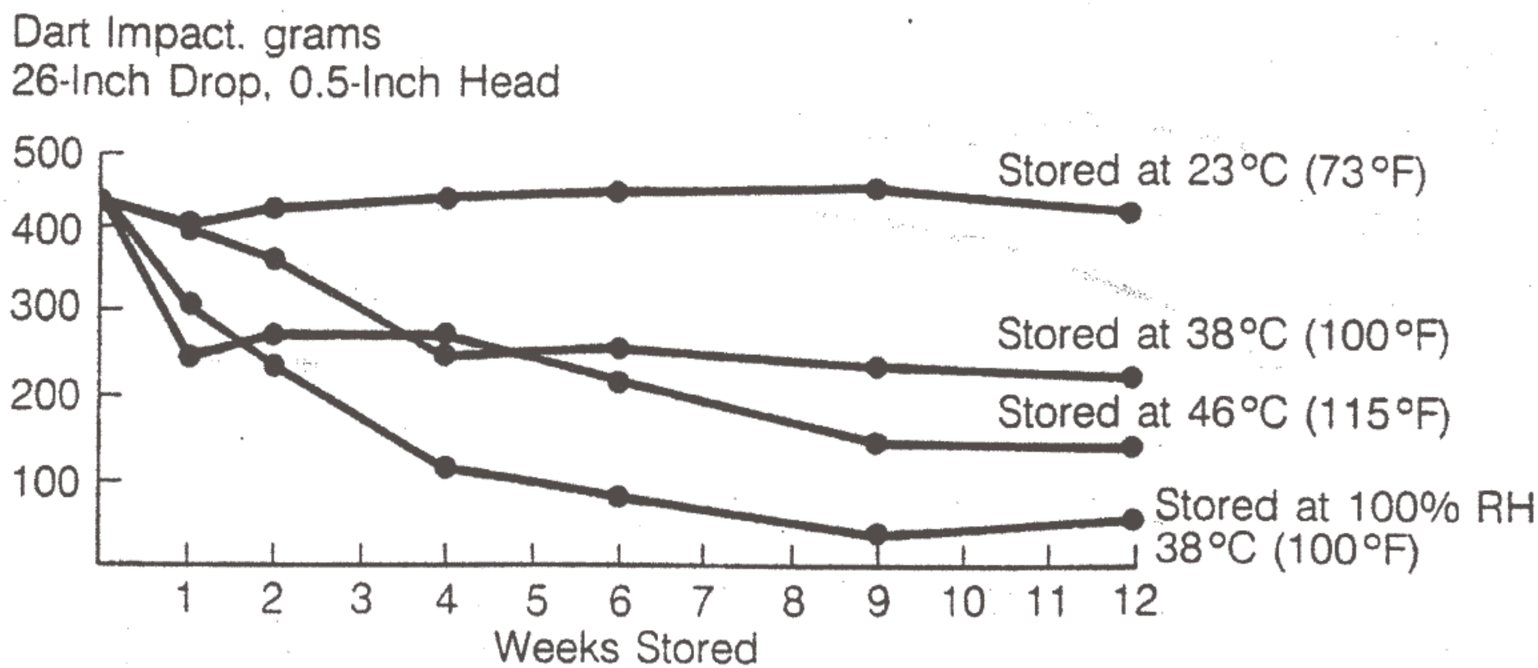


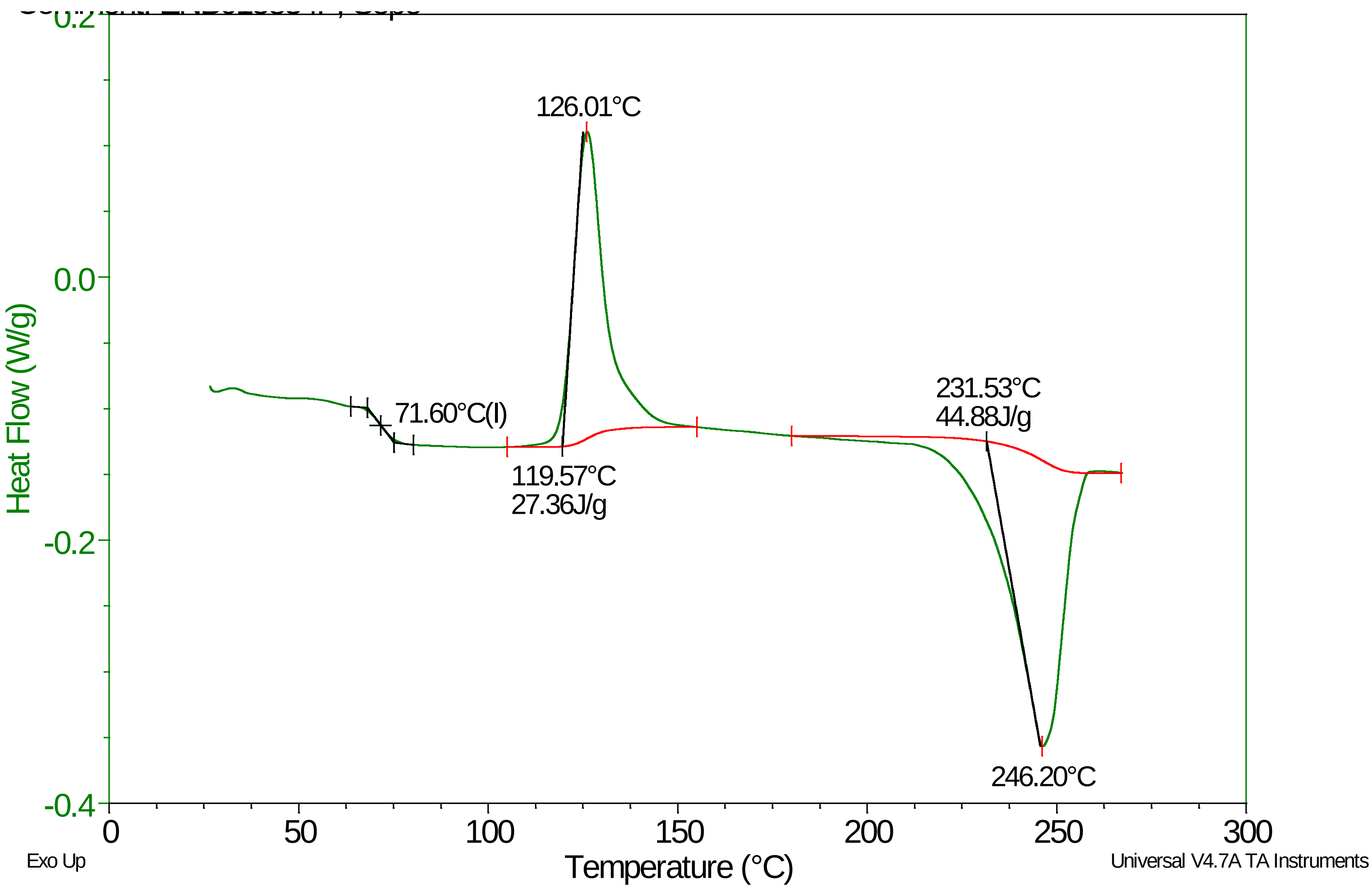
Figure 4

EFFECTS OF TEMPERATURE AND RELATIVE HUMIDITY ON DART IMPACT STRENGTH

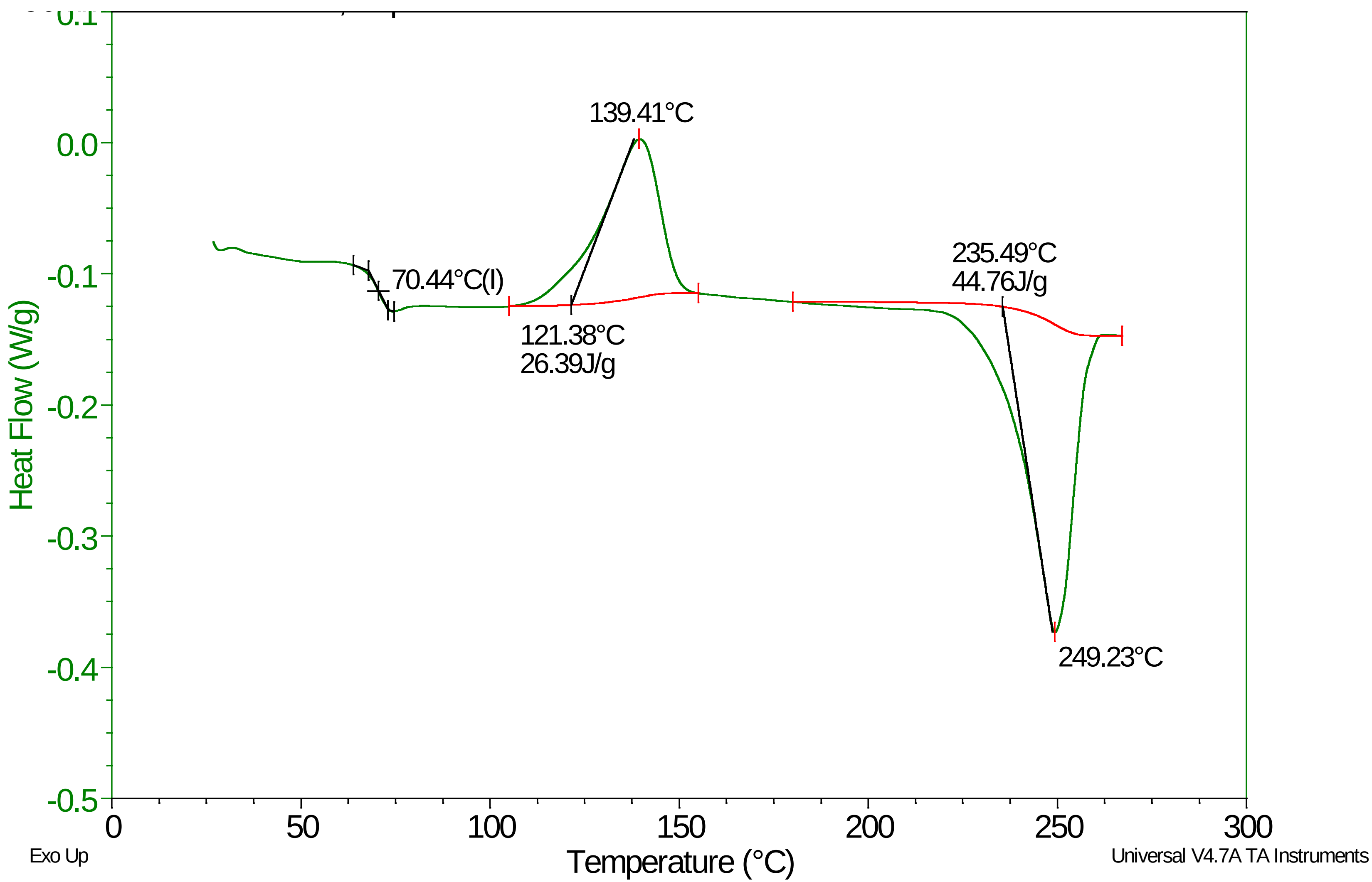
PET 9663 Amorphous Film 0.78 I.V.
0.254 mm (0.010 in.) Thick



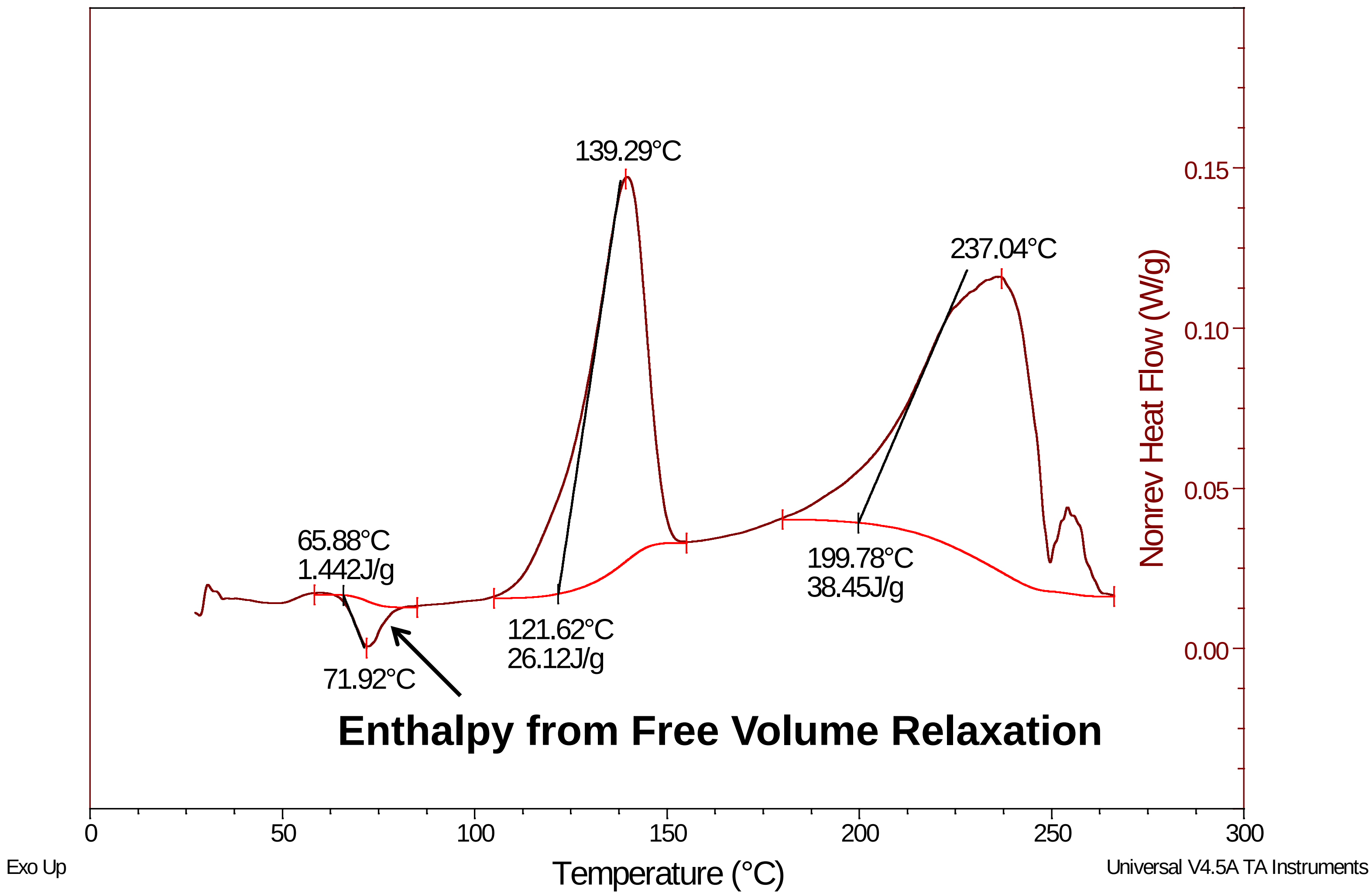
DSC Showing Heat Flow of As-Molded Amorphous PET Polyester



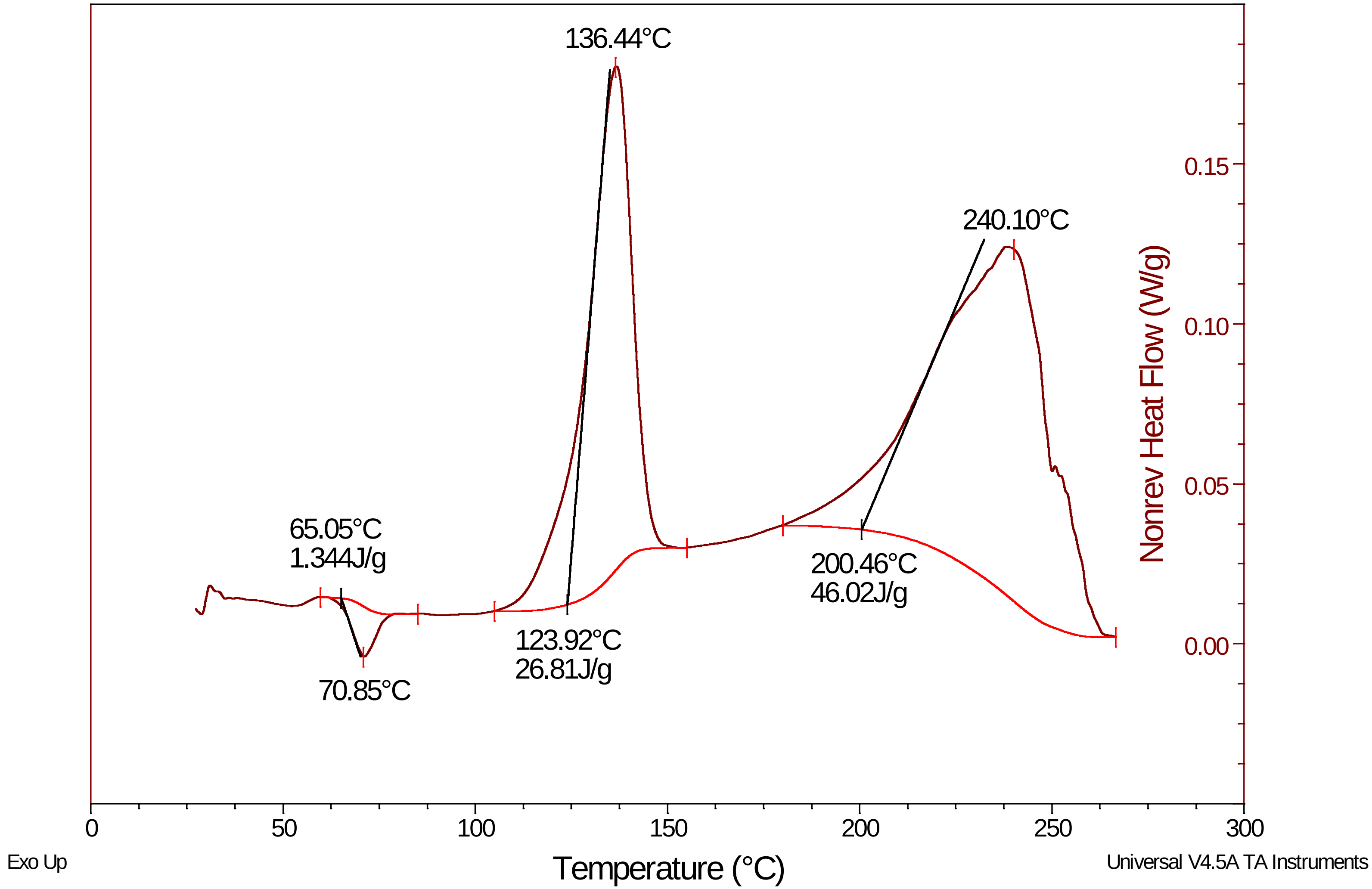
DSC Showing Heat Flow of Amorphous PET Polyester Aged At 50 C for 18.75 Hours



DSC Showing Heat Flow of Amorphous PET Polyester Aged At 50 C for 18.75 Hours



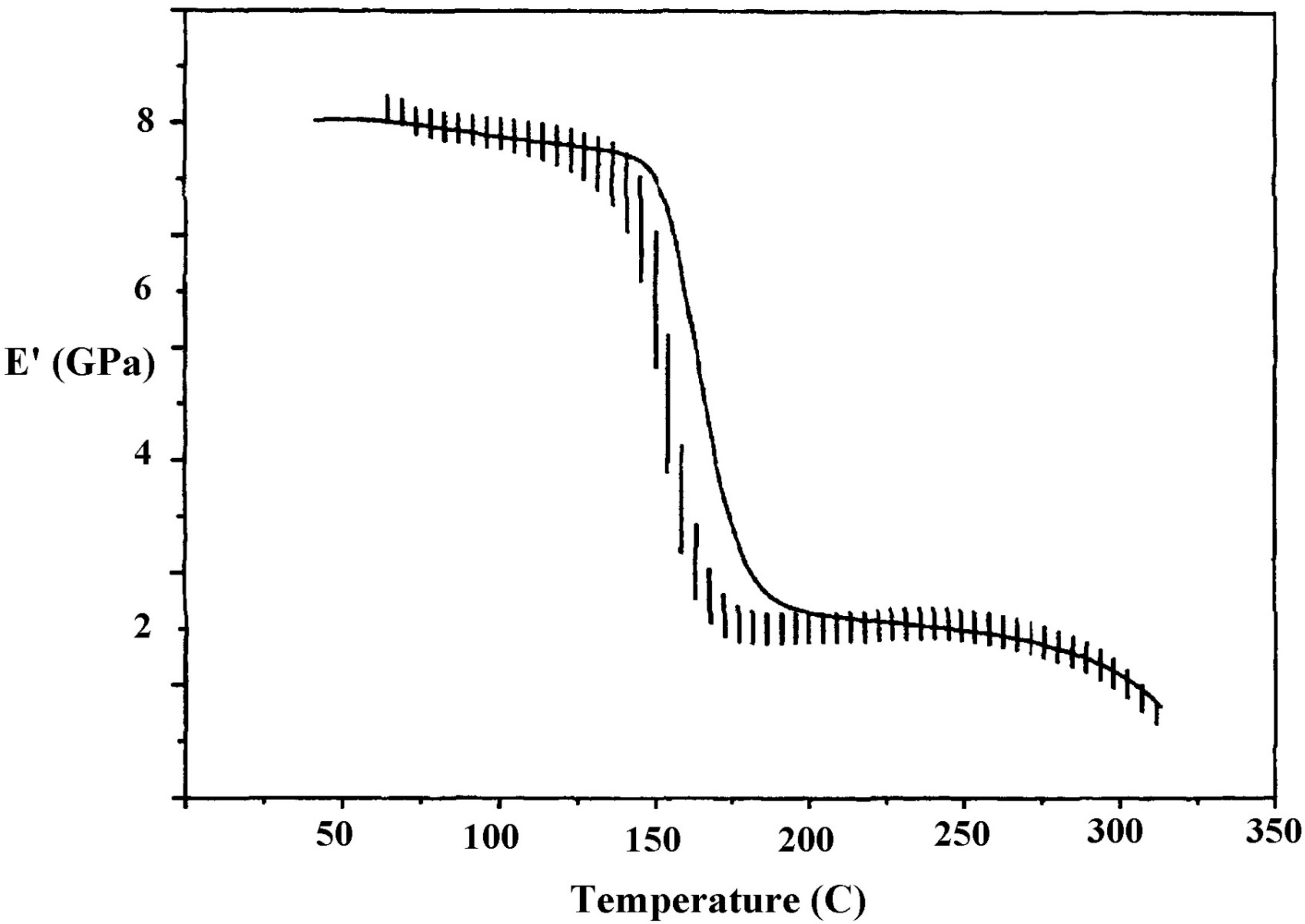
DSC Showing Heat Flow of Amorphous PET Polyester Aged At 20 C for 25 Months



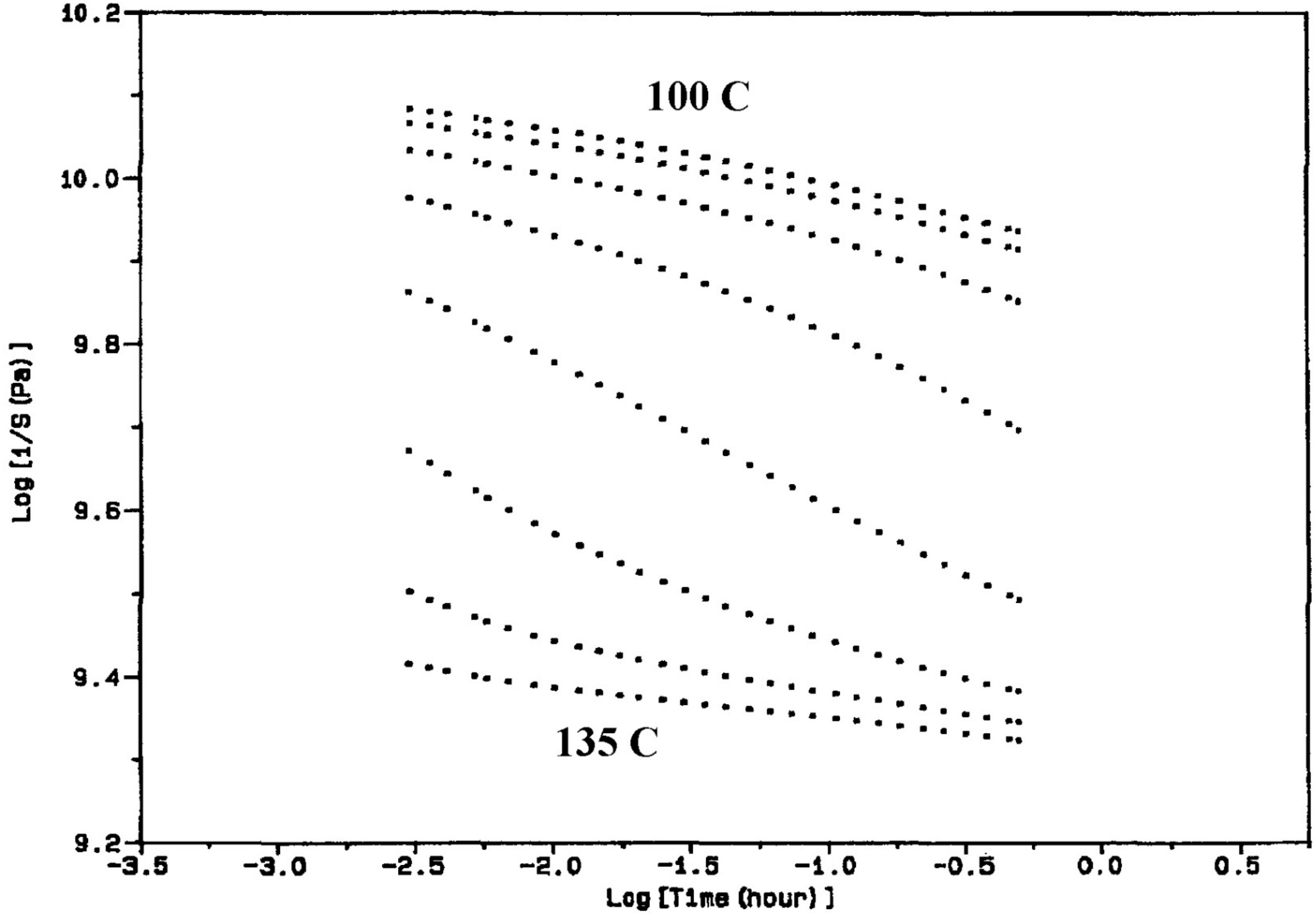
Acceleration Factor for Physical Aging In Amorphous PET

- 18.75 Hours at 50 C Equals 18000 Hours at 20 C
- (18240/18.75) = 972.8
- The Cube Root of 972.8 = 9.91 = Q_{10}
- Studies Conducted At Eastman Obtained A Result of 9.8 Using More Extensive Data
- Physical Aging Is the Dominant Mechanism When Compared To Oxidation

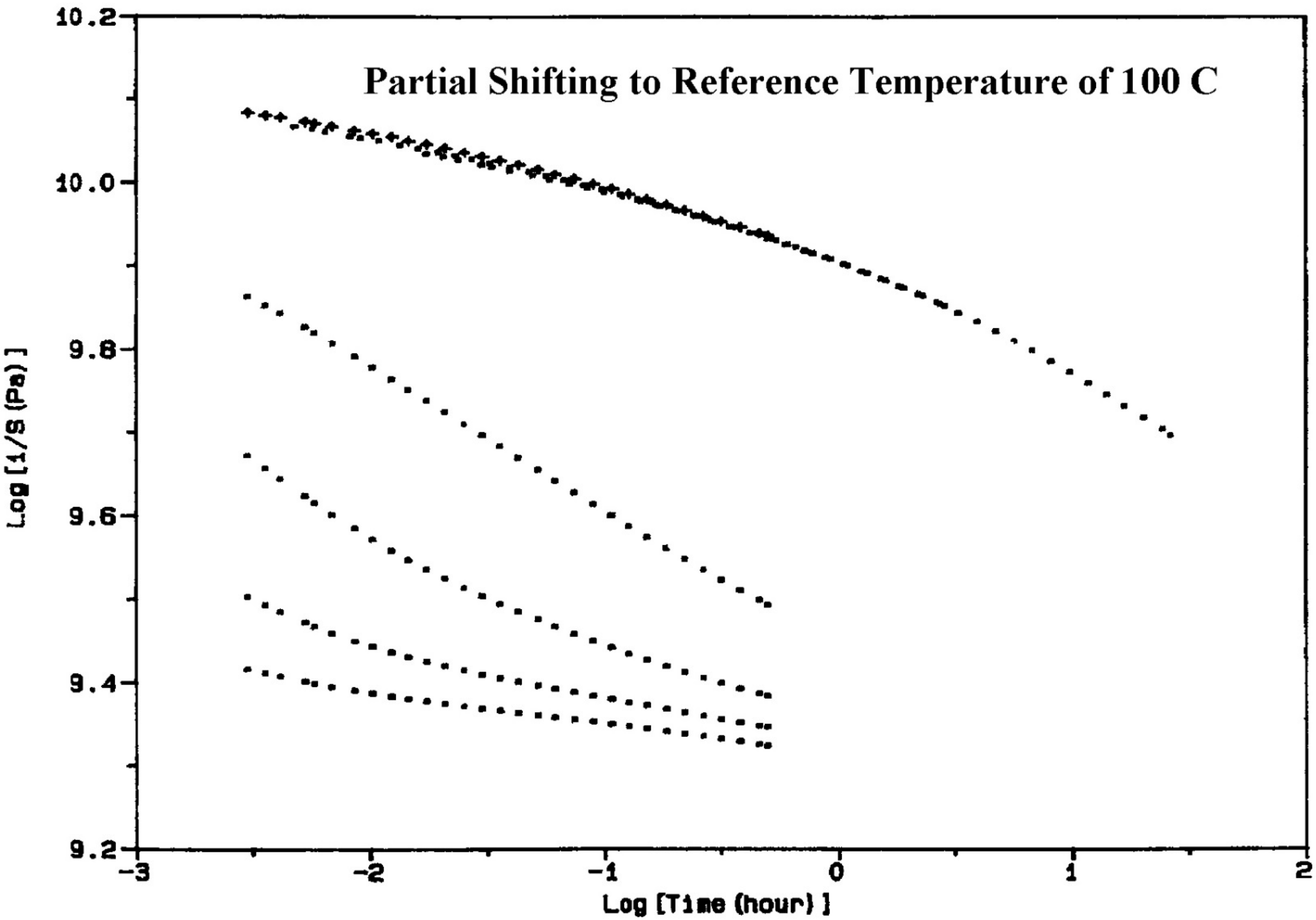
Modulus vs. Temperature Plot Superimposed on Short-term Creep Test Results



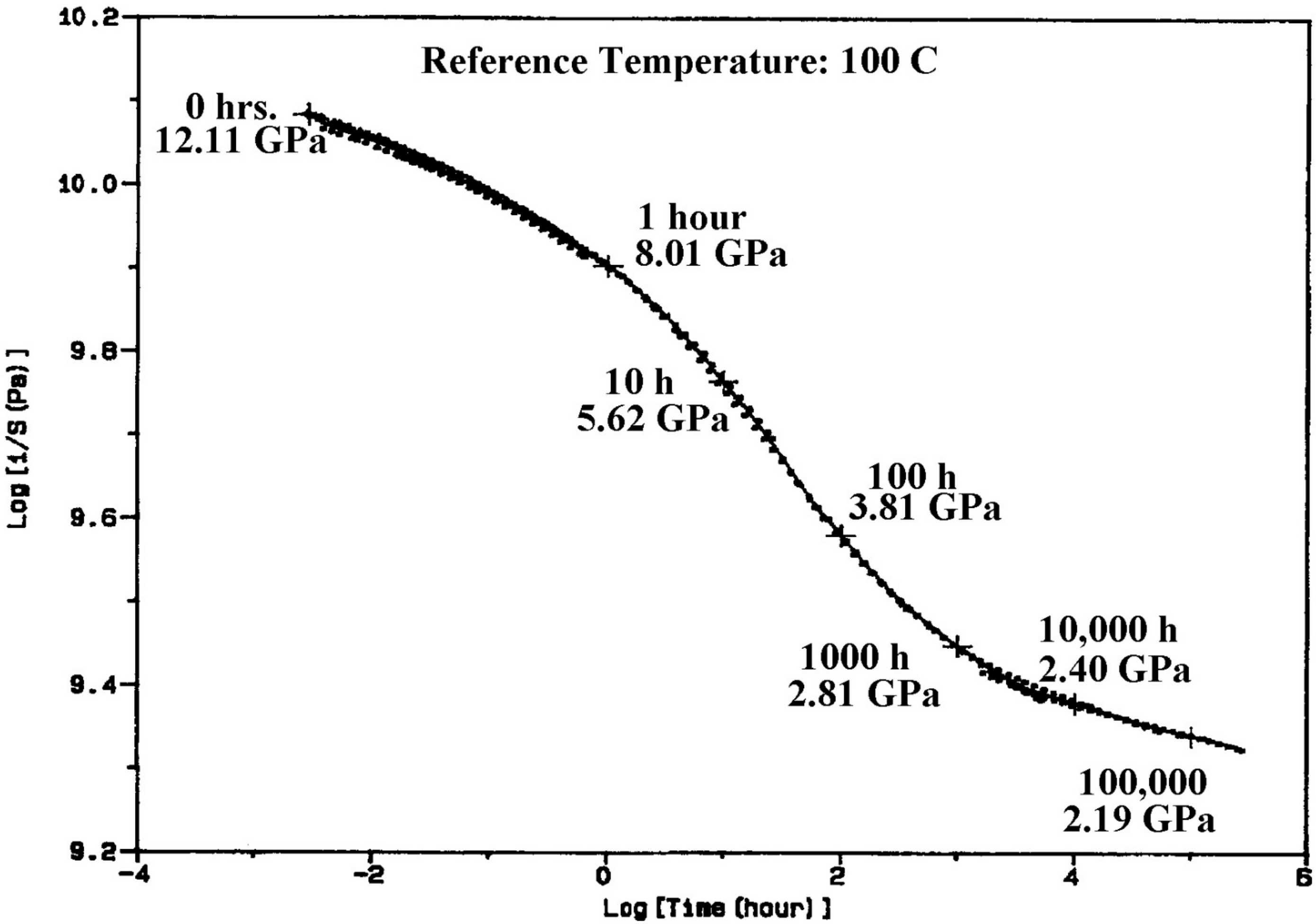
Raw Data for 30-Minute Creep Tests on Vinyl Ester Composite



Creep Master Curve in Process for Vinyl Ester Composite



Completed Creep Master Curve for Vinyl Ester Composite



Apparent Modulus As An Expression of Creep Behavior

Expression for Modulus

$$E = \sigma/\varepsilon$$

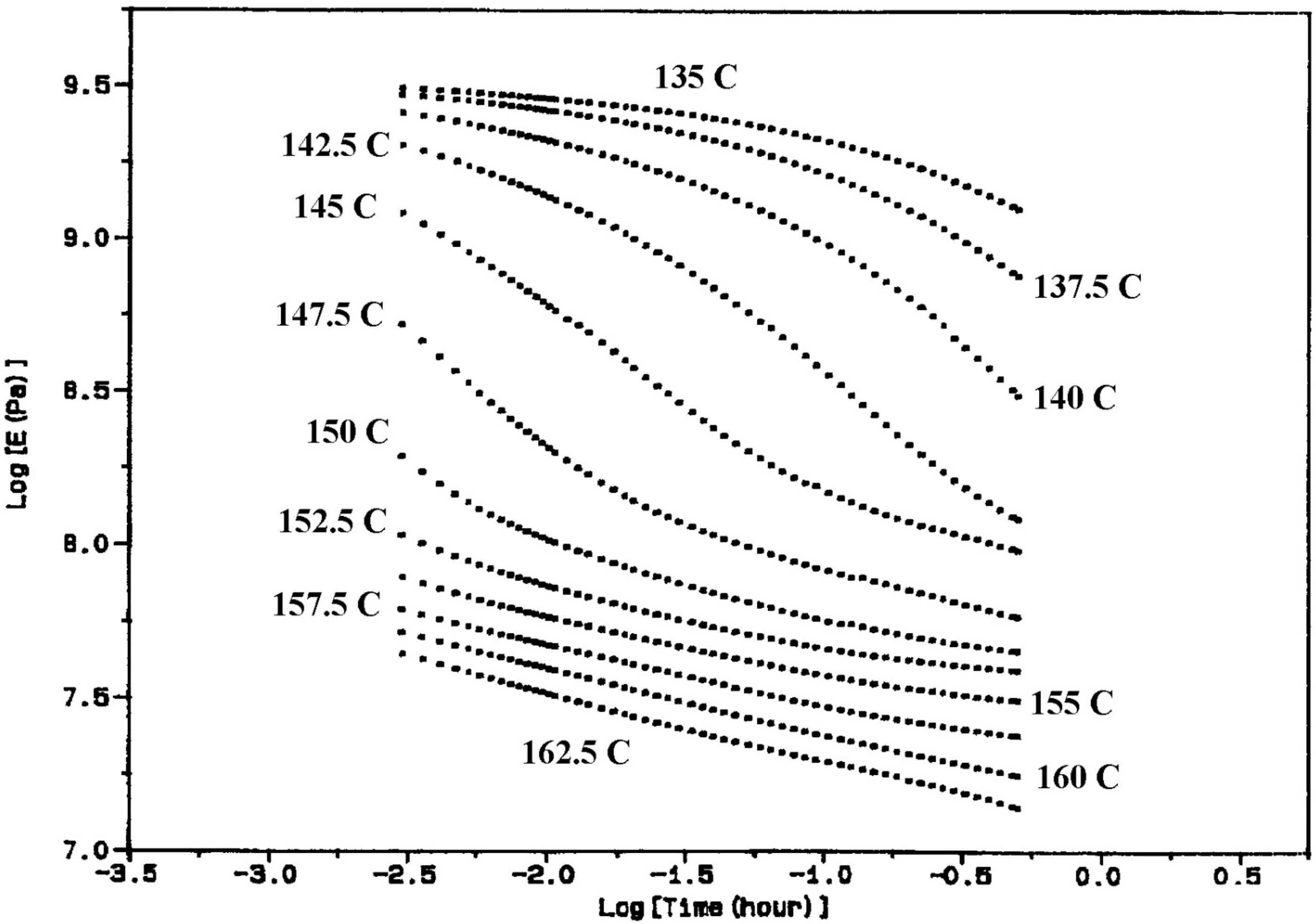
Expression for Apparent Modulus

$$E_a = \sigma_t/(\varepsilon_o + \varepsilon_c)$$

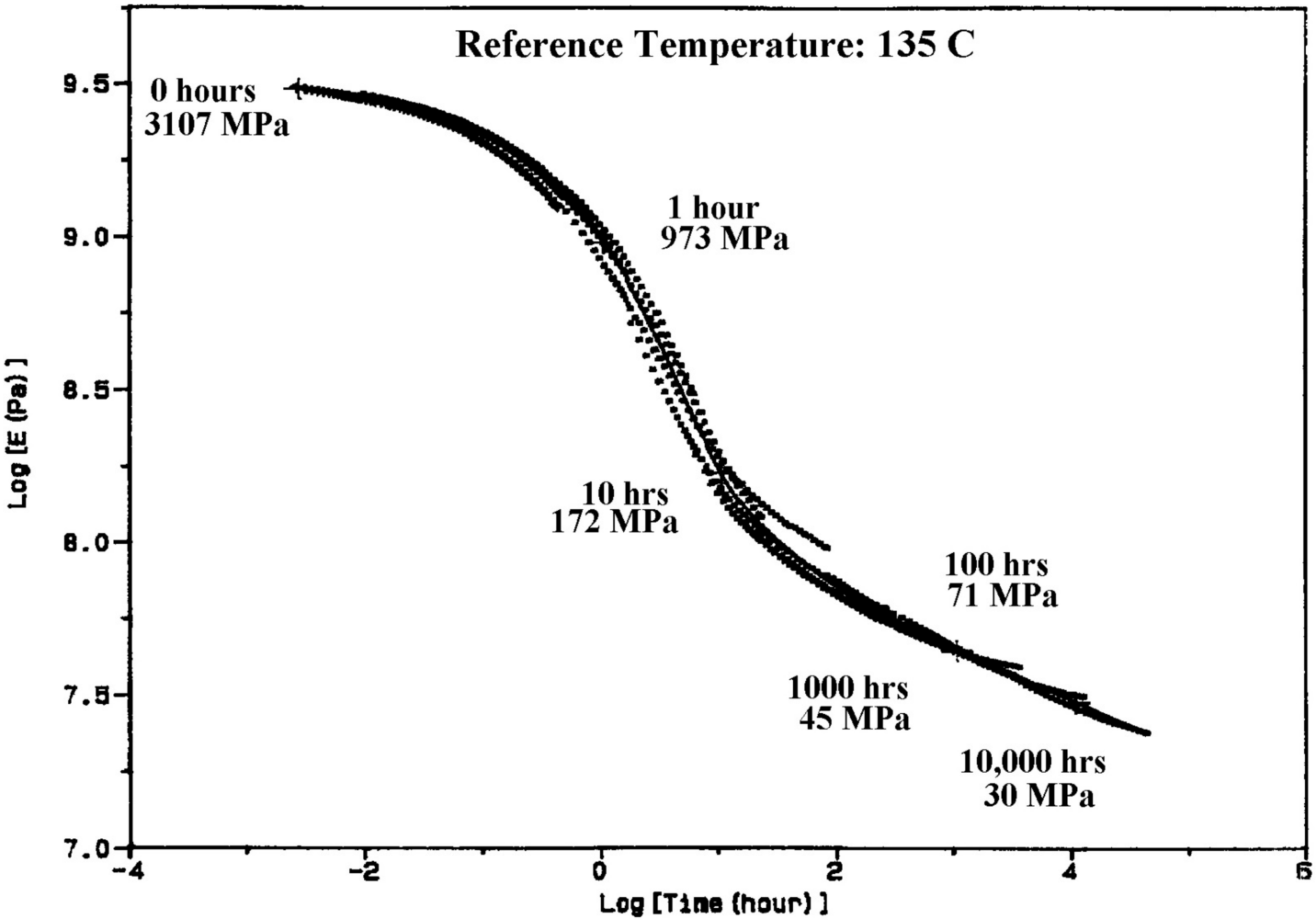
Where ε_o is initial strain

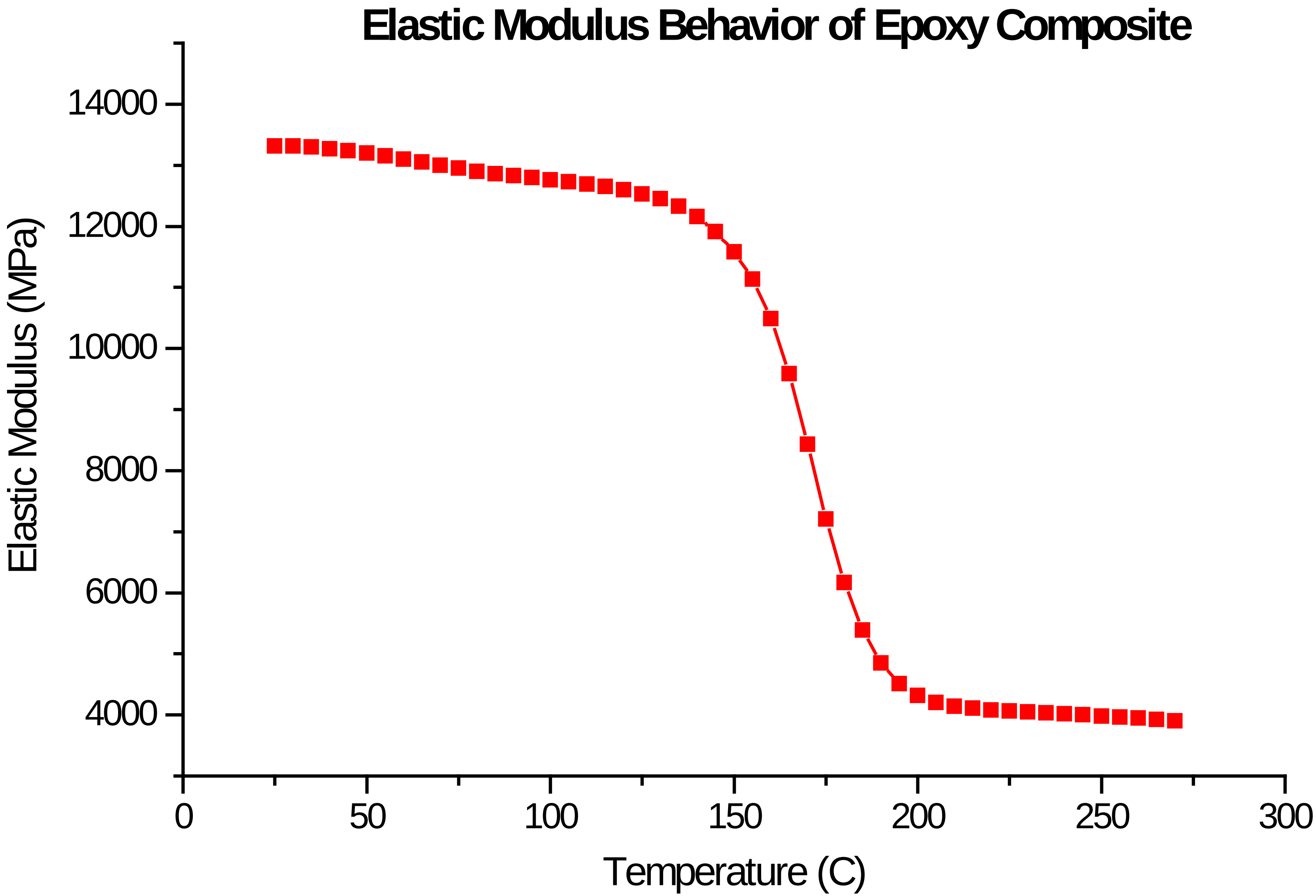
ε_c is creep strain

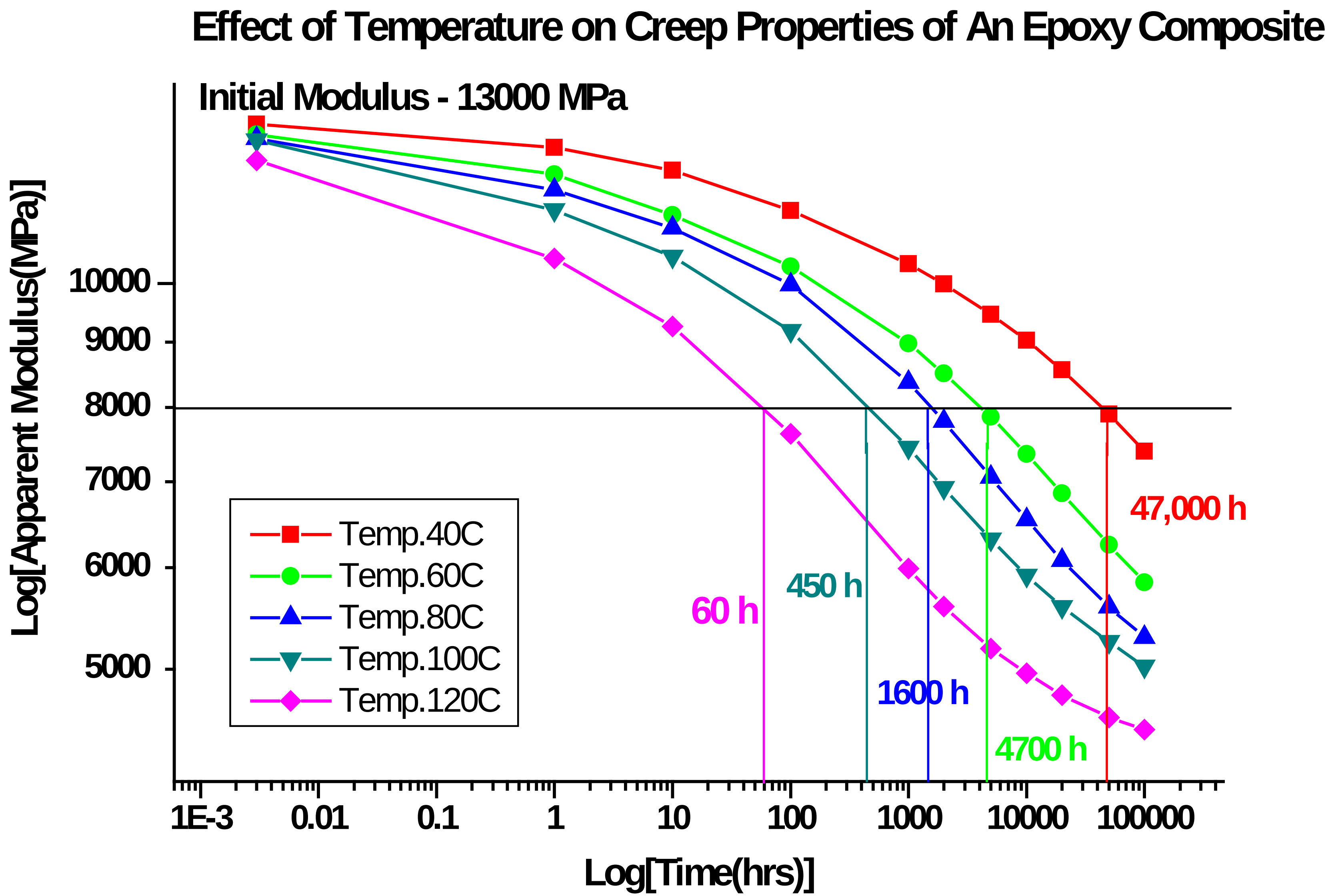
Raw Stress Relaxation Data for A Polycarbonate



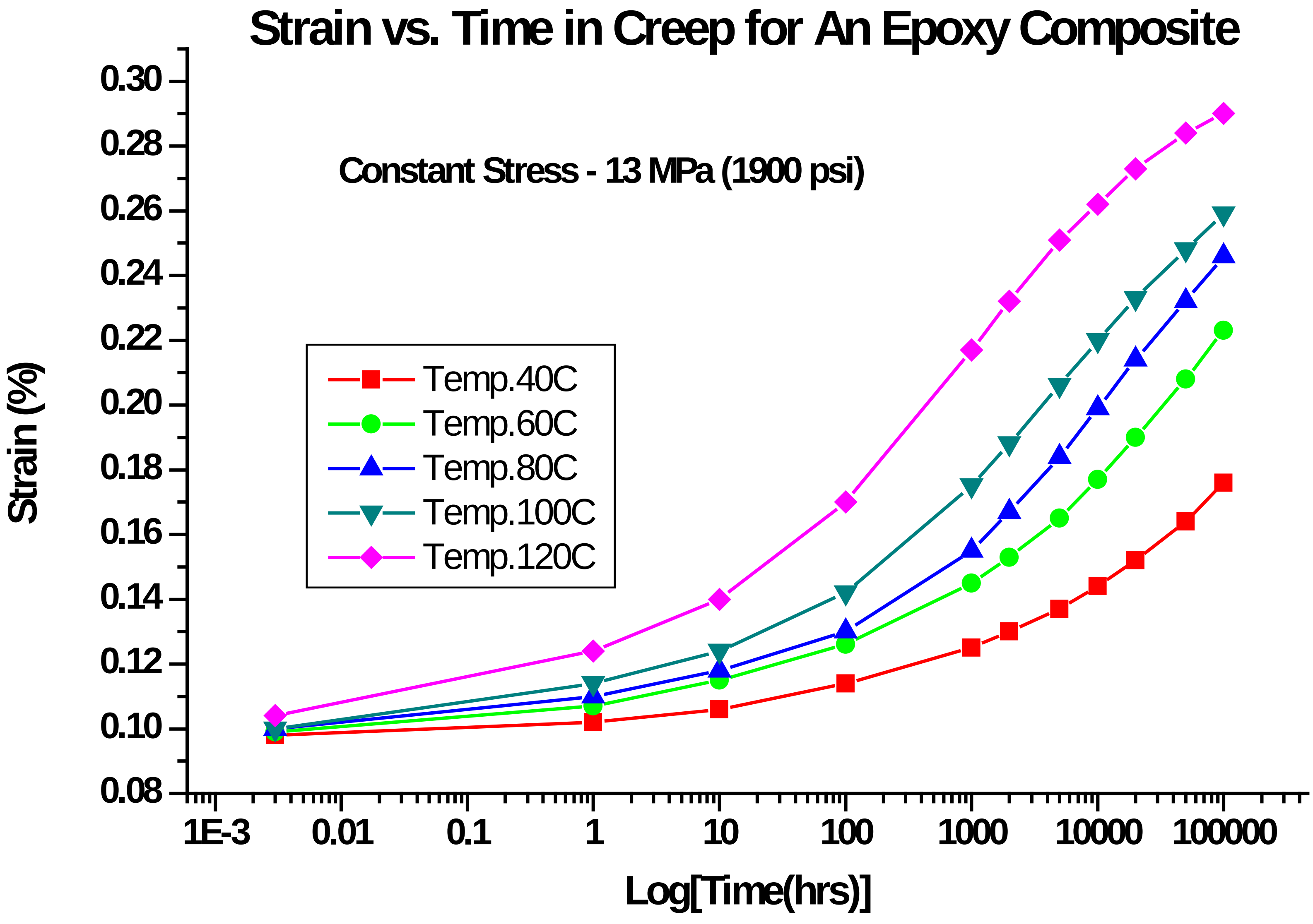
Stress Relaxation Master Curve for Polycarbonate




Elastic Modulus Behavior of Epoxy Composite
14000
12000
10000
8000
6000
4000
Elastic Modulus (MPa)
0
50
100
150
200
250
300
Temperature (C)

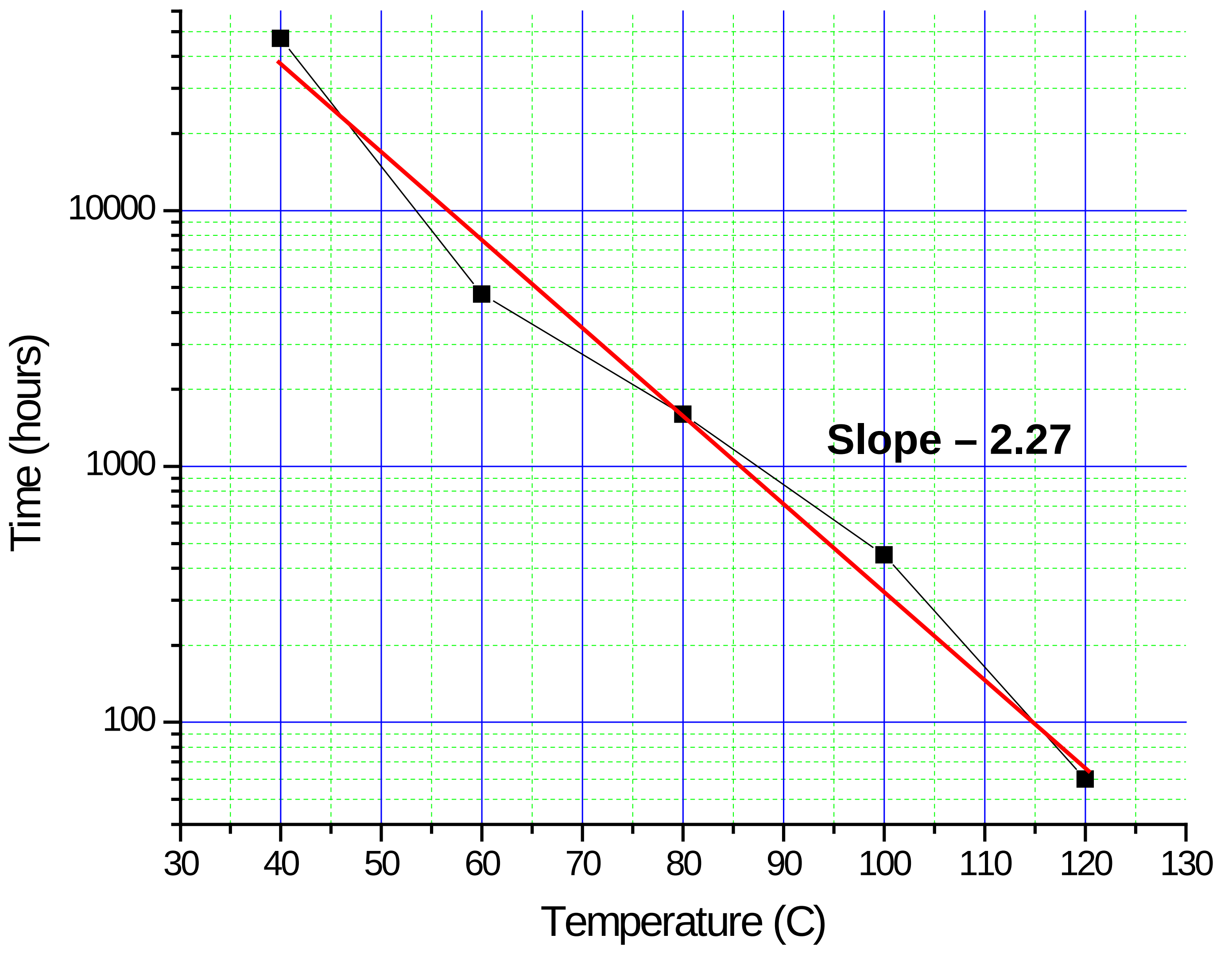


Effect of Temperature on Creep Properties of An Epoxy Composite
Initial Modulus - 13000 MPa
Log[Apparent Modulus(MPa)]
10000
9000
8000
7000
6000
5000
Temp.40C
Temp.60C
Temp.80C
Temp.100C
Temp.120C
60 h
450 h
1600 h
4700 h
47,000 h
1E-3
0.01
0.1
1
10
100
1000
10000
100000
Log[Time(hrs)]

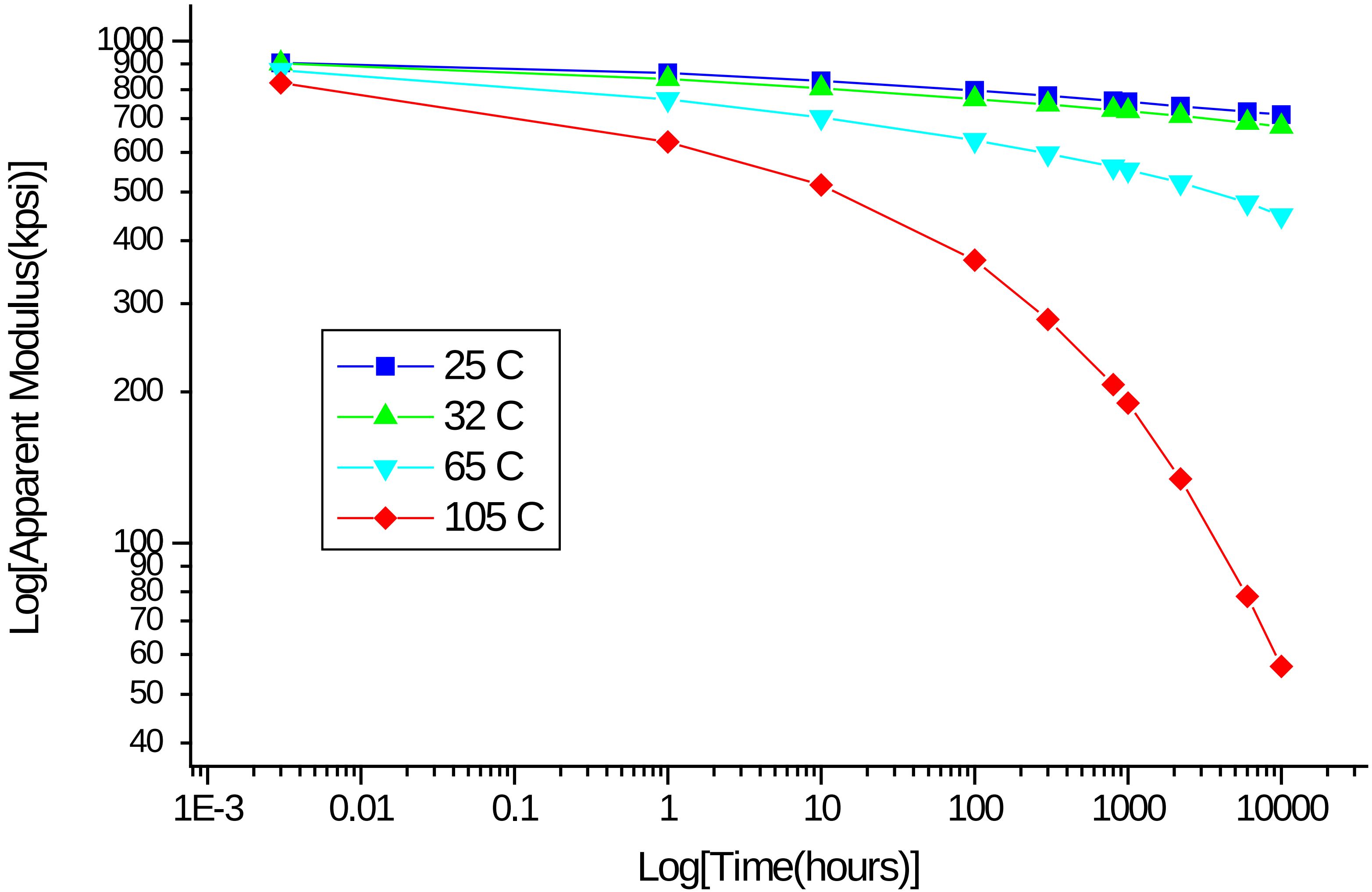


Strain vs. Time in Creep for An Epoxy Composite
Constant Stress - 13 MPa (1900 psi)
Temp.40C
Temp.60C
Temp.80C
Temp.100C
Temp.120C
Strain (%)
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
1E-3
0.01
0.1
1
10
100
1000
10000
100000
Log[Time(hrs)]

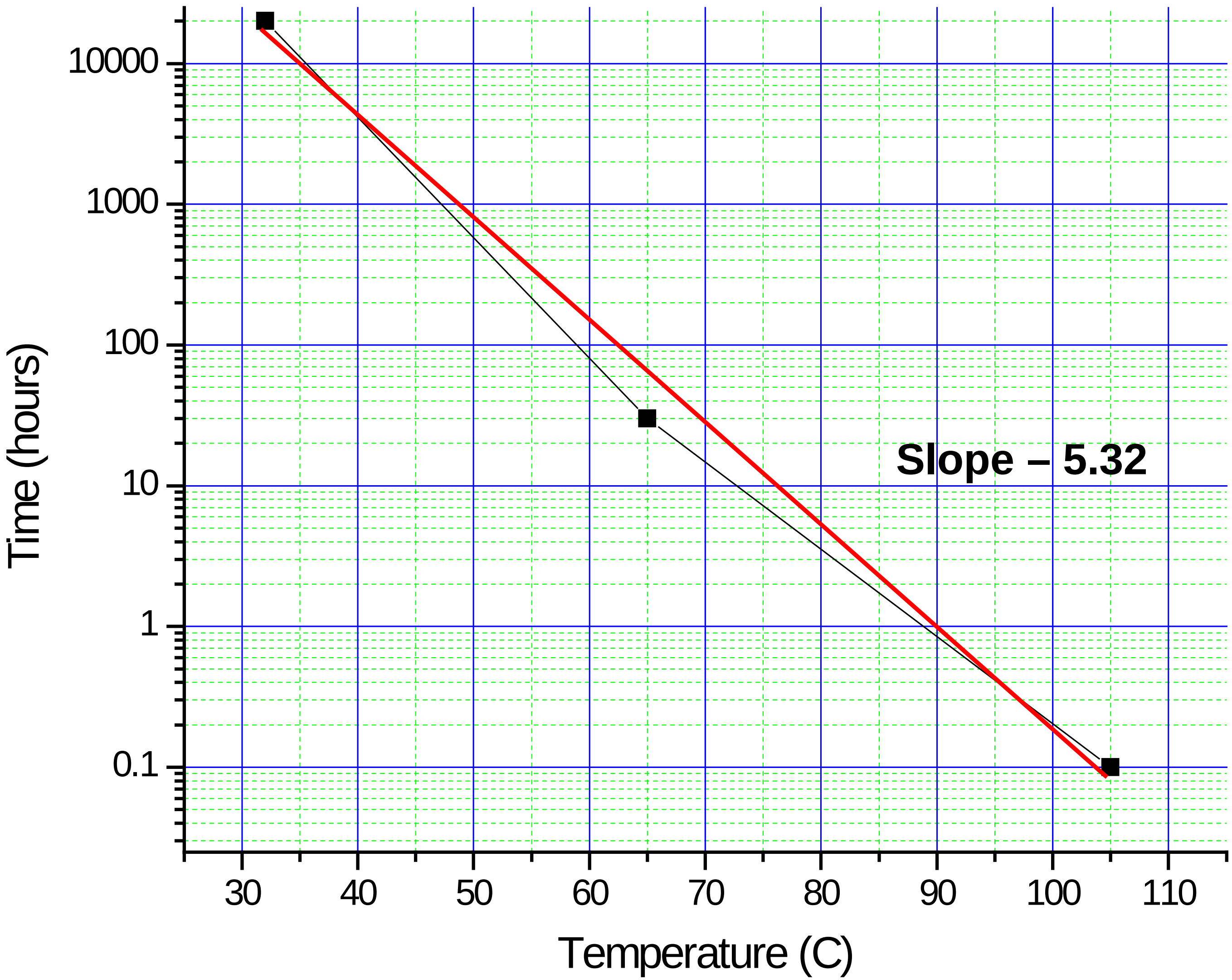
Time – Temperature Relationship To Achieve A Specific Creep Modulus In A Highly Filled Epoxy



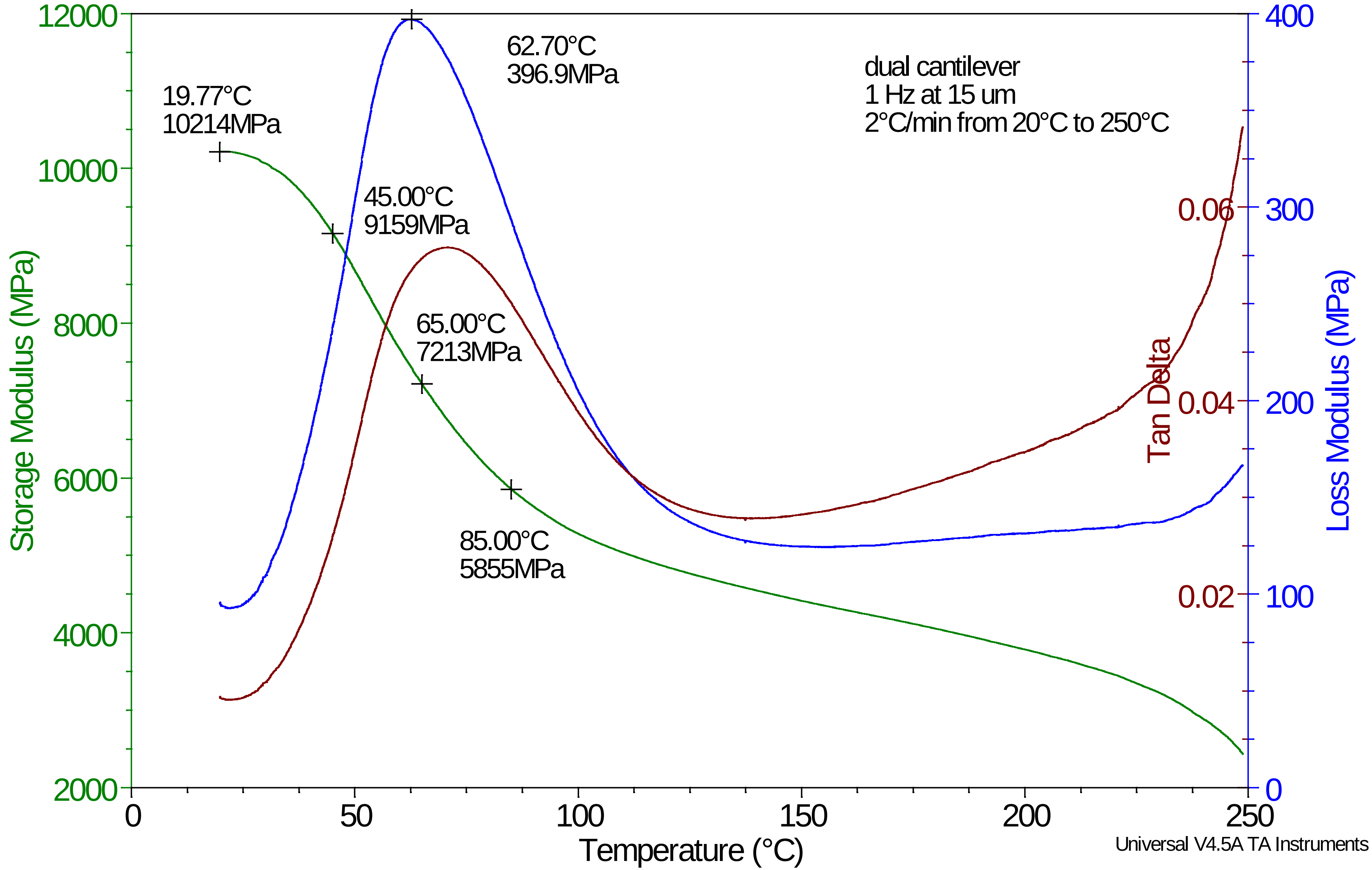
Creep Master Curves for 30% Glass-Filled PPE At Multiple Temperatures

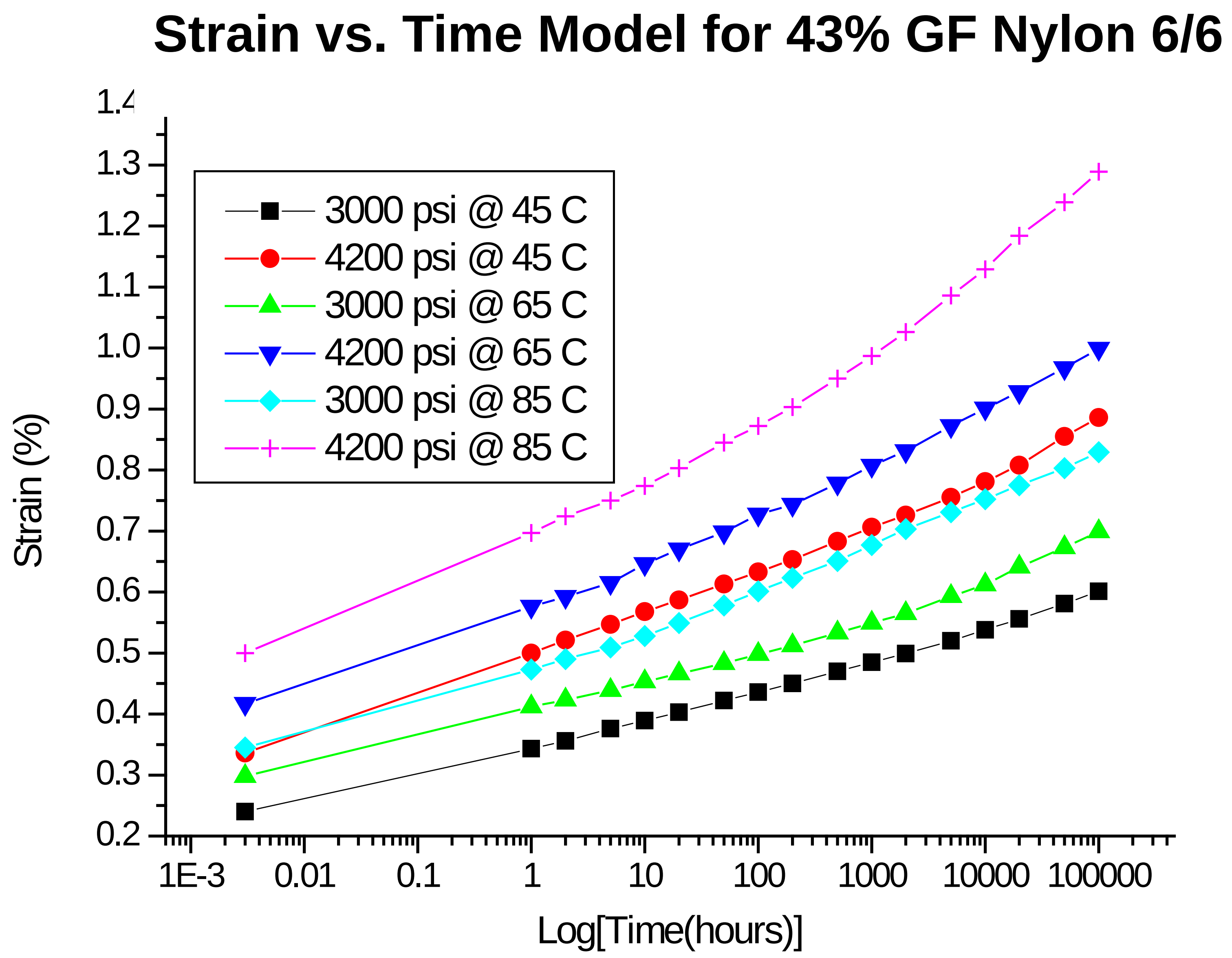


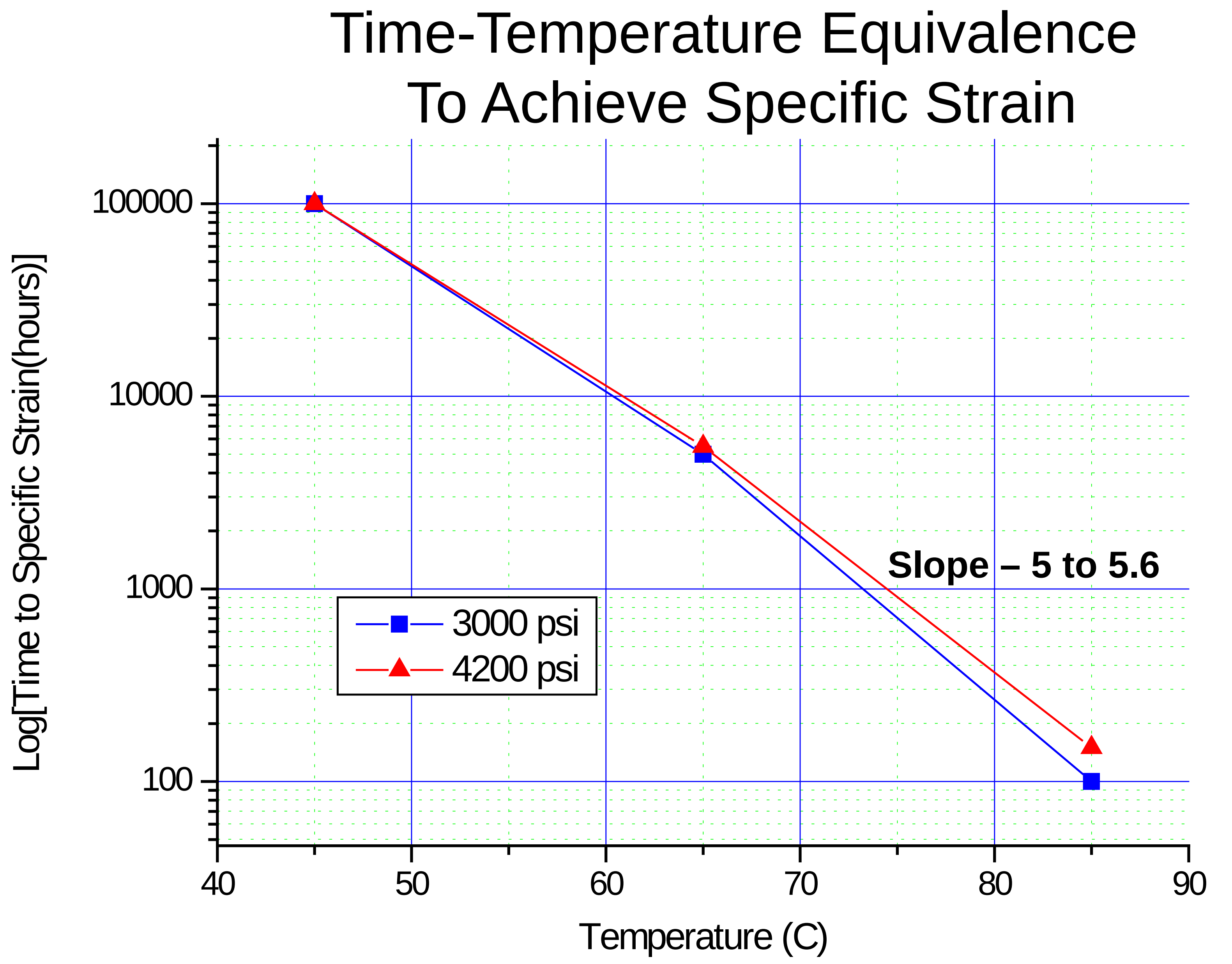
Time – Temperature Relationship To Achieve A Specific Creep Modulus In 30 % GF PPE



Temperature-Dependent Behavior of 43% Glass-Filled Nylon 6/6




Strain vs. Time Model for 43% GF Nylon 6/6
Strain (%)
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
3000 psi @ 45 C
4200 psi @ 45 C
3000 psi @ 65 C
4200 psi @ 65 C
3000 psi @ 85 C
4200 psi @ 85 C
1E-3
0.01
0.1
1
10
100
1000
10000
100000
Log[Time(hours)]


Time-Temperature Equivalence
To Achieve Specific Strain
100000
10000
1000
100
Log[Time to Specific Strain(hours)]
40
50
60
70
80
90
Temperature (C)
Slope – 5 to 5.6
3000 psi
4200 psi

Conclusions

- Elevated Temperatures Used In Accelerated Aging Tests Can Promote Multiple Mechanisms
- These Protocols Tend To Ascribe All the Observed Property Changes To Oxidative Aging
- Frequently Another Mechanism Is Dominant
- Failure To Recognize These Other Mechanisms and Identify the Most Important One Can Result In Flawed Test Plans
- Mechanisms Can Occur In Real Time Testing That Do Not Have Time To Take Place In Accelerated Protocols

Thank you for your time