Shelf Life Prediction Of Medical Gloves

Presented for the ASTM WG Committee for
"Medical Glove Expiration Dating Guidance"

By

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Motivation

- Shelf Life Prediction of rubber Medical Products
- Clients' demand for reliable prediction of part shelf life in the laboratory
- Lack of incorporation of aging effects and chemical degradation
- Assessment is often qualitative - based on quality tests which are very misleading
- Address the nonlinear aging effects (Current FDA/ASTM/ISO Taskgroups)

Importance

- New shelf life prediction criteria
- New material development
- Safety, security and liability
- Material changes due to market trends
- Can reduce the number of product tests
- Cost of unexpected failure is high

Major Issues for Shelf Life

- What is the Mechanism of Aging ?
- How is Aging defined ?
- Can the Activation Energy be defined so that the temperature dependence of the failure can be found ?
- Are the aging mechanisms the same at different temperatures ?
- Can an accelarated test be run in the laboratory ?
- Are the mechanisms the same in the laboratory as in storage ?

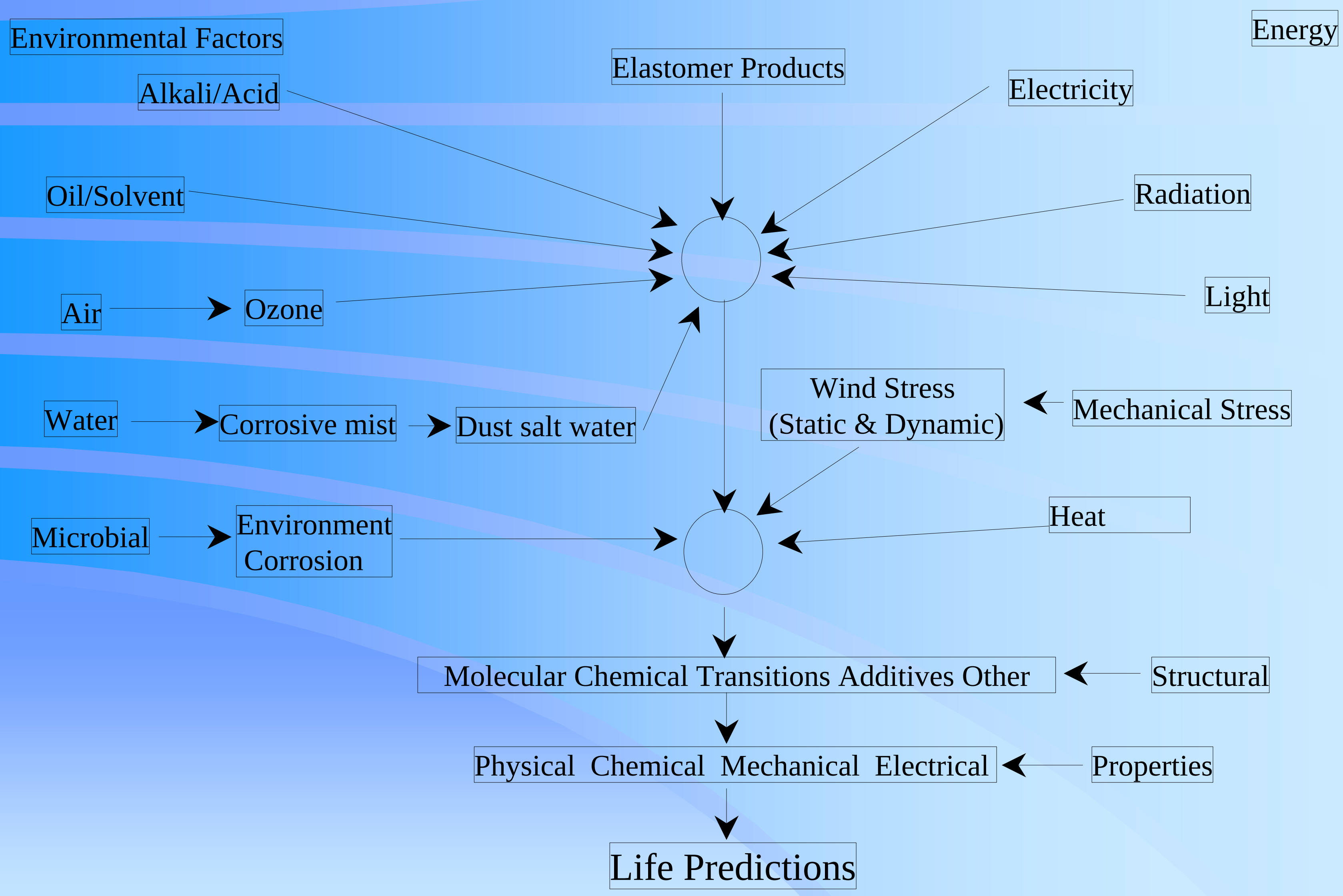
Goals

- Need a scientific methodology for quantitative life prediction of elastomers
- Shelf life prediction
- Establishing the effectiveness of the existing models

Challenges

- Establishing accelerated aging techniques
- Establishing the degradation process/mechanisms
- Developing measurement techniques
- Establishing a basic “practical” model
- Establishing accuracy and reliability
- Establishing a degradation mechanism or aging mode
- Developing a good methodology which covers all thin elastomeric materials

“Natural” Aging



Degradation Process/Mechanism

Thermal	Mechanical
Thermo-Oxidative	Hydrolytic
Photo	Chemical
Photooxidative	High Energy Radiation
Ozone	Side Group Elimination
Random Chain Scission	Substitution
Depolymerization	Plasticizer Loss
Crosslinking	Filler Bonding Change

Accelerated Aging

- The basic requirement for reliable accelerated aging is that the course of degradation is identical at the storage and test conditions
- Measure minimum two structural parameters at a given temperature, physical properties and chemical analysis (extraction, swelling and analysis by mass spectrophotometer)
- Failure mode evaluation by two different techniques
- Incorporating all the aging conditions similar to storage

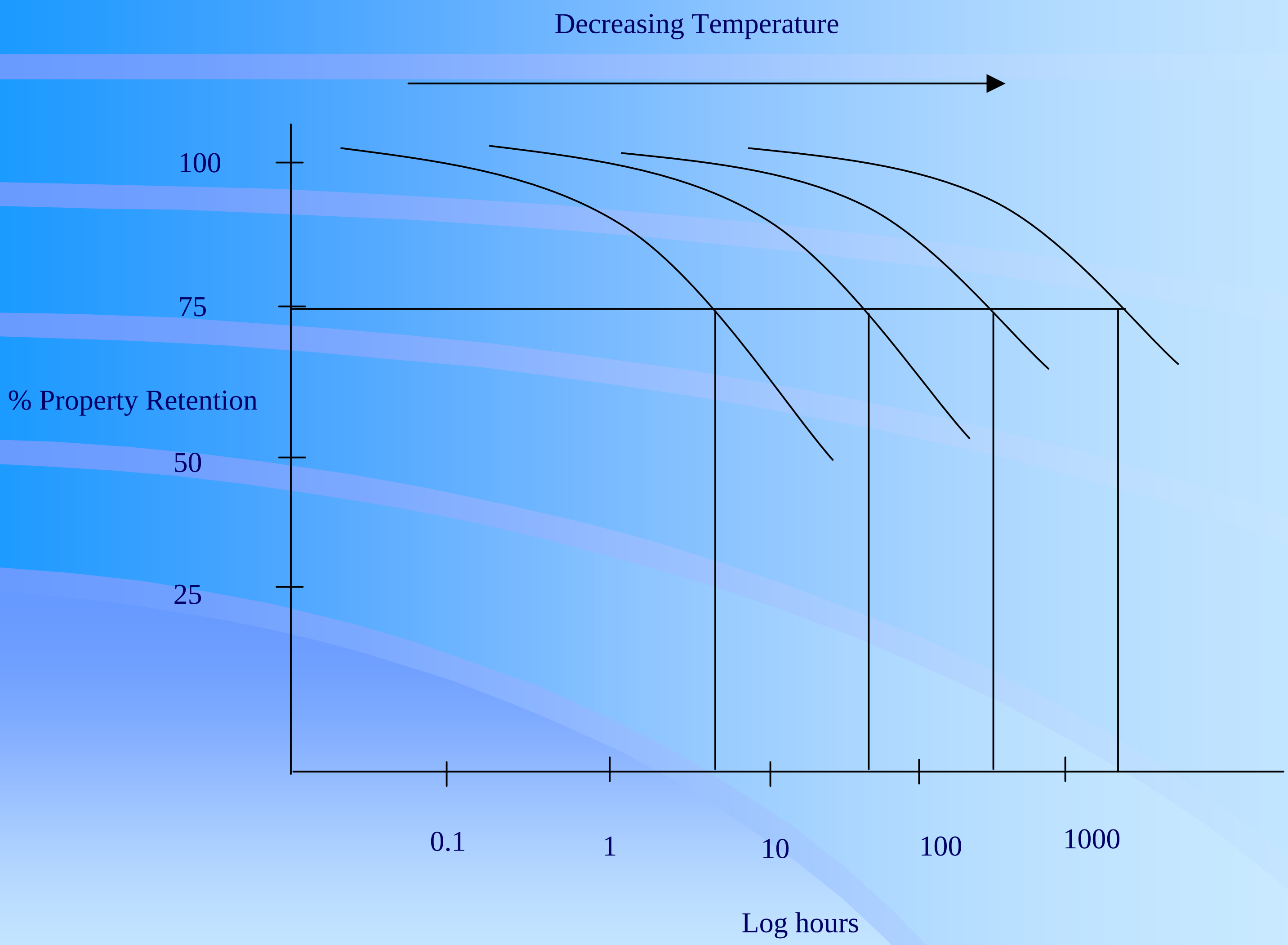
Degradation Monitoring Tests

- Modulus - Tensile Test
- Ultimate Elongation - Tensile Test
- Tensile Strength - Tensile Test
- Tear Strength
- Strain Energy (“Work to Break”) - Tensile Test
- FTIR (Field sample & Lab aged)
- Crosslink Density (Wet Chemistry)
- GC/MS
- Specific Gravity

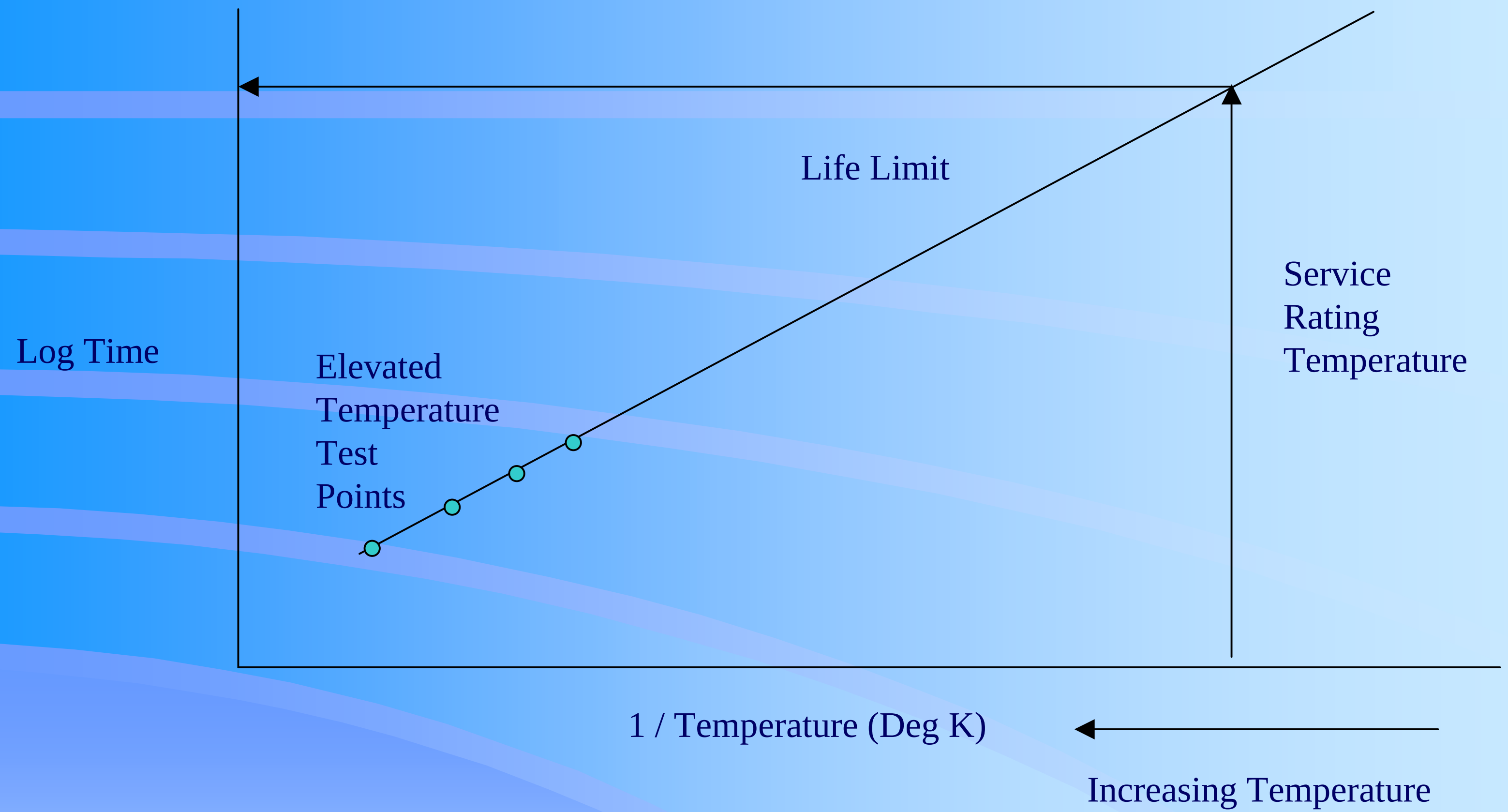
Life Prediction Models

- Arrhenius Life Prediction
- Time Temperature Superposition
- ARDL P & K Method (Activation Energy successive averaging technique)

Time - Temperature Plot



Arrhenius Approach



Typical Arrhenius Shelf Life Prediction Plot for Elastomeric Products

Arrhenius equation

- The Arrhenius Equation has the basic form

$$k = A\, e^{-E / RT}$$

where

- A = proportionality constant
- e = base for natural logarithms
- E = Activation Energy
- R = the gas constant
- T = Absolute Temperature

$$\ln k = - E/ RT + \ln A$$

"In General, for every 10 Deg C that temperature rises, the first order chemical reaction rate doubles"

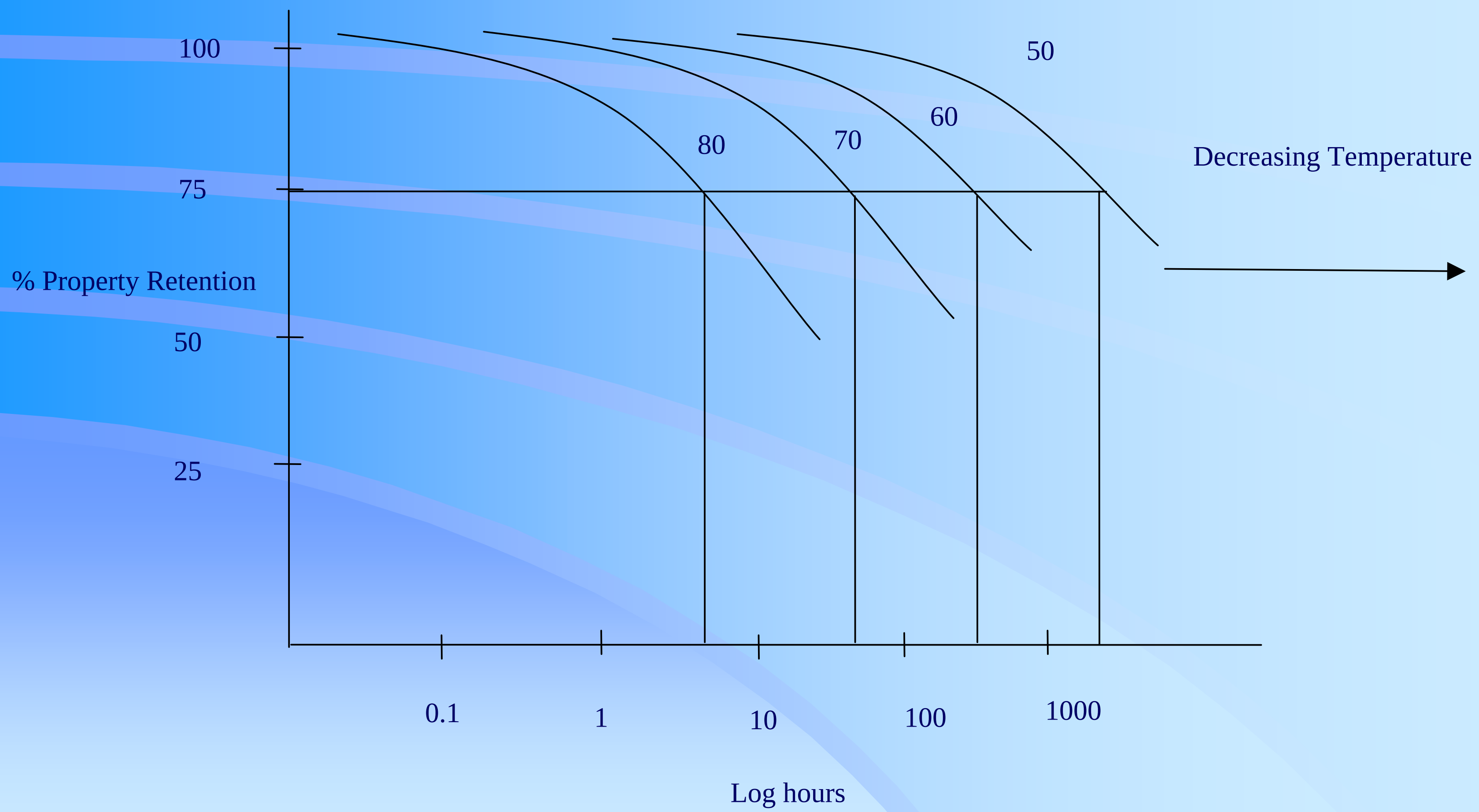
Arrhenius fit : Practical Issues

- An Arrhenius fit provides the worst case estimate of shelf life
- Arrhenius Approach prediction will be better with lower temperature test data
- Lower temperature data need more testing time
- The basic assumption is that the dominant mode of failure is identical at all temperatures and stress levels

Time - Temperature Superposition

$$a_t = \exp \{ E_a (1 / T_{(ref)} - 1/ T_{(age)} \}$$

where Ea is the activation energy, R= gas constant (8.31432 J/K), Tref and Tage are the reference and aging temperatures respectively in Kelvin

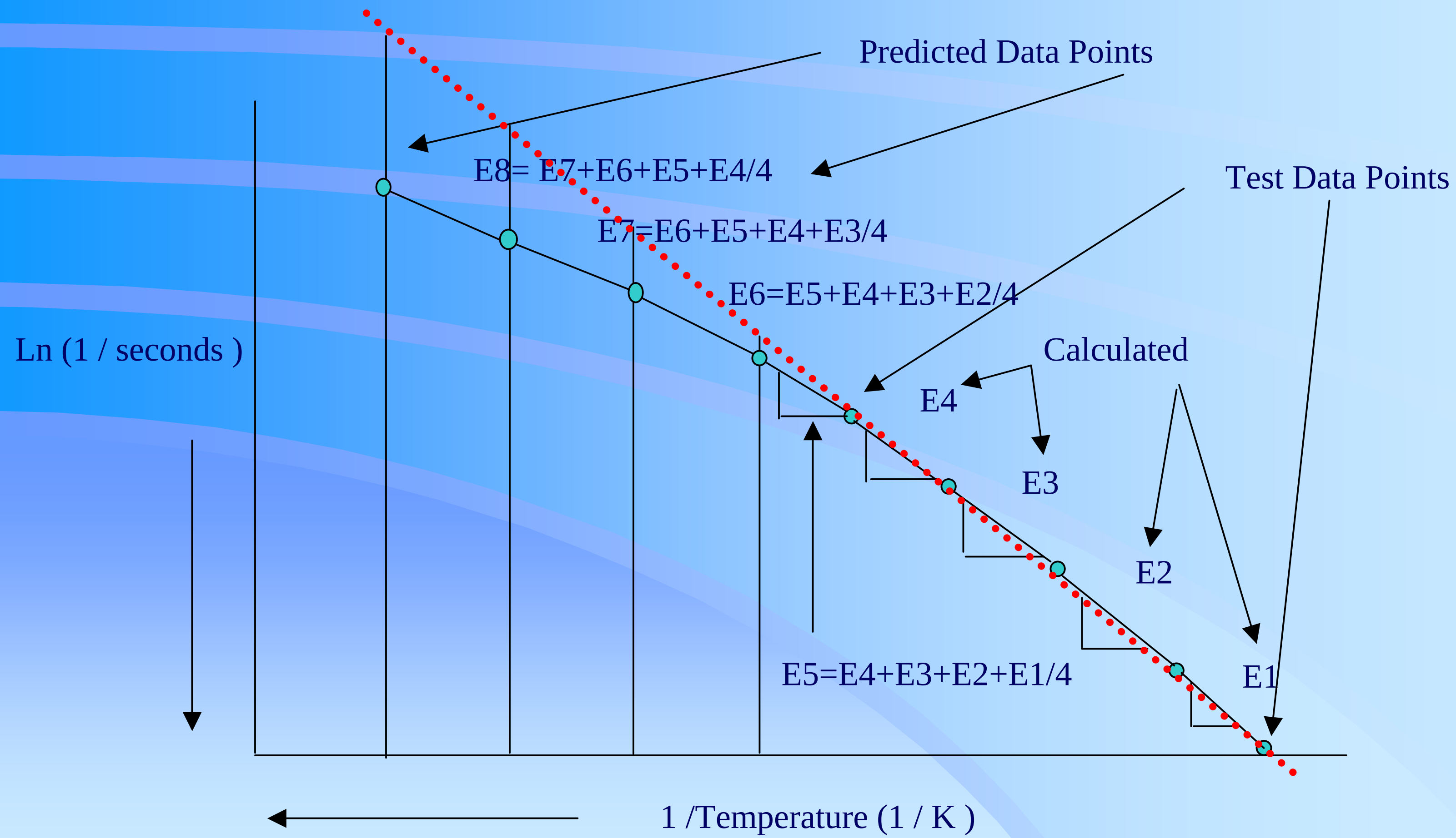


Time - Temperature Superposition : Practical Issues

- Need to calculate Activation Energy
- Assume the activation energy as 84 - 117 KJ/mole
- High sensitivity on “cutoff”

ARDL “P & K” Method

Activation energy (E) is averaged with a successive segment approach



Successive Activation Energy Extrapolation : Practical Issues

- This method is sensitive to changes in activation energy
- Predictions are made depending upon the actual data available
- This method follows the change in Activation Energy

ARDL Aging Procedure

Deg C	30 min	2 hrs	4 hrs	8 hrs	1 week	2 weeks	4 weeks	6 weeks	8 weeks	10 weeks	24 weeks
80	X	X	X	X	X	X					
70	X	X	X	X	X	X	X				
60	X	X	X	X	X	X	X	X	X	X	
50	X	X	X	X			X	X	X	X	X

- Number of test specimens: 13 (Tensile Test)
- Calculate coefficient of variation: CV = s/x (100%)
- Typical requirement: Maximum CV = 15%
- Correlation Coefficient (R^2) of Arrhenius plot

  Case I : $R^2 > 0.97$ use Arrhenius extrapolation

  Case II : $R^2 < 0.97$ use Successive Averaging technique

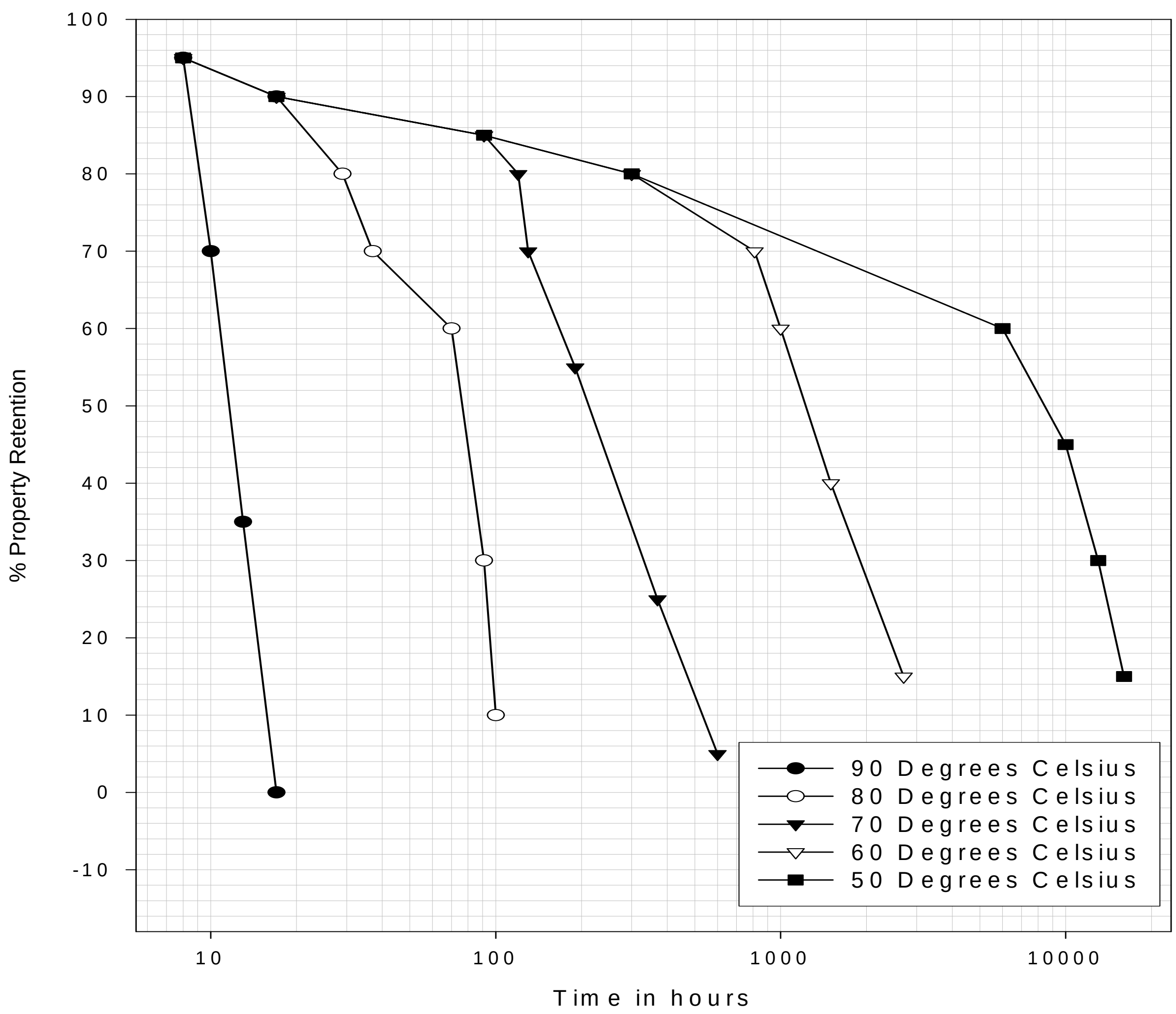
Natural Rubber Compounds

Natural rubber - Gloves

Compound 1

Data at 0.00275 90	1/ T in K Deg Celsius	Data at 0.0028303 80	1/ T in K Deg Celsius	Data at 0.0029127 70	1/ T in K Deg Celsius	Data at 0.00300012 60	1/ T in K Deg Celsius	Data at 0.003093 50	1/ T in K Deg Celsius
Time Hrs	% Property Retention	Time Hrs	% Property Retention	Time Hrs	% Property Retention	Time Hrs	% Property Retention	Time Hrs	% Property Retention
8	95	8	95	8	95	8	95	8	95
10	70	17	90	17	90	17	90	17	90
13	35	29	80	91	85	91	85	91	85
17	0	37	70	120	80	300	80	300	80
		70	60	130	70	810	70	6000	60
		91	30	190	55	1000	60	10000	45
		100	10	370	25	1500	40	13000	30
				600	5	2700	15	16000	15

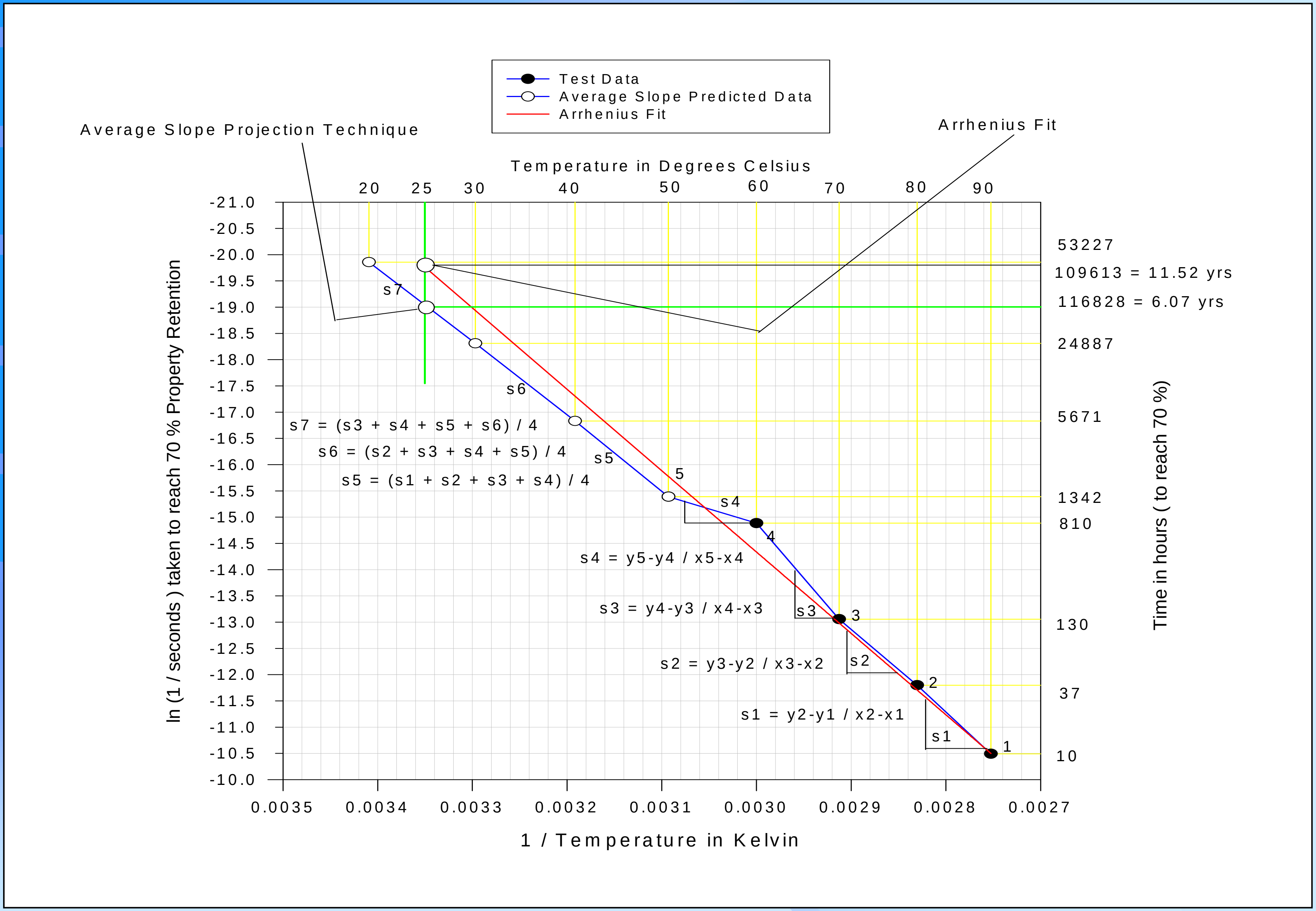
NR Glove Compound 1: Raw Data



Time for aging to 70 % retention of Tensile Strength

Temperature Deg C		50	60	70	80	90
Aging Time (hours)		1342	810	130	37	10

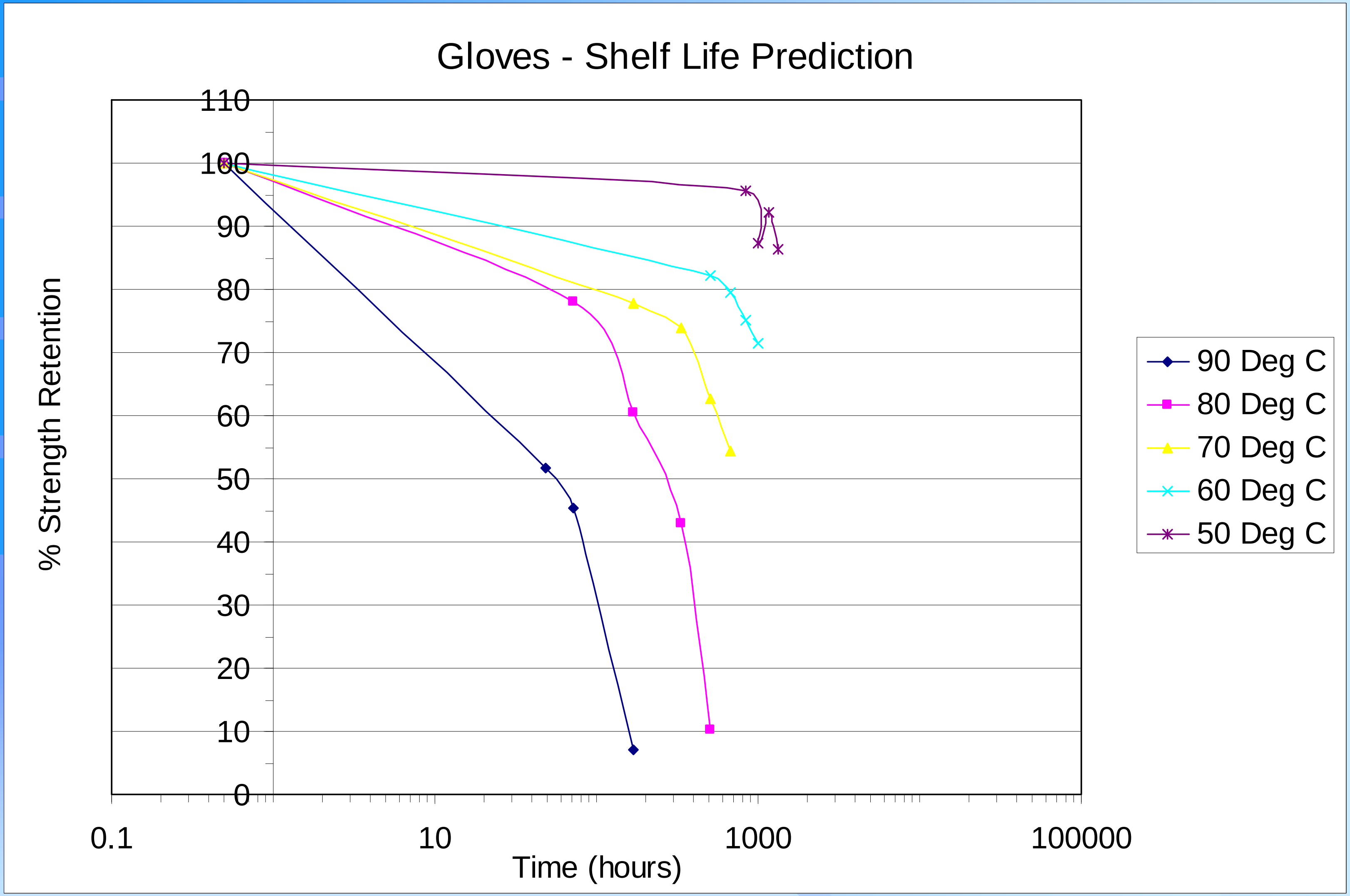
Shelf Life Prediction Curve : NR Compound 1



Predicted Shelf Life: NR Glove Compound 1

	Years
Arrhenius Approach	11.52
ARDL P & K Method	6.07

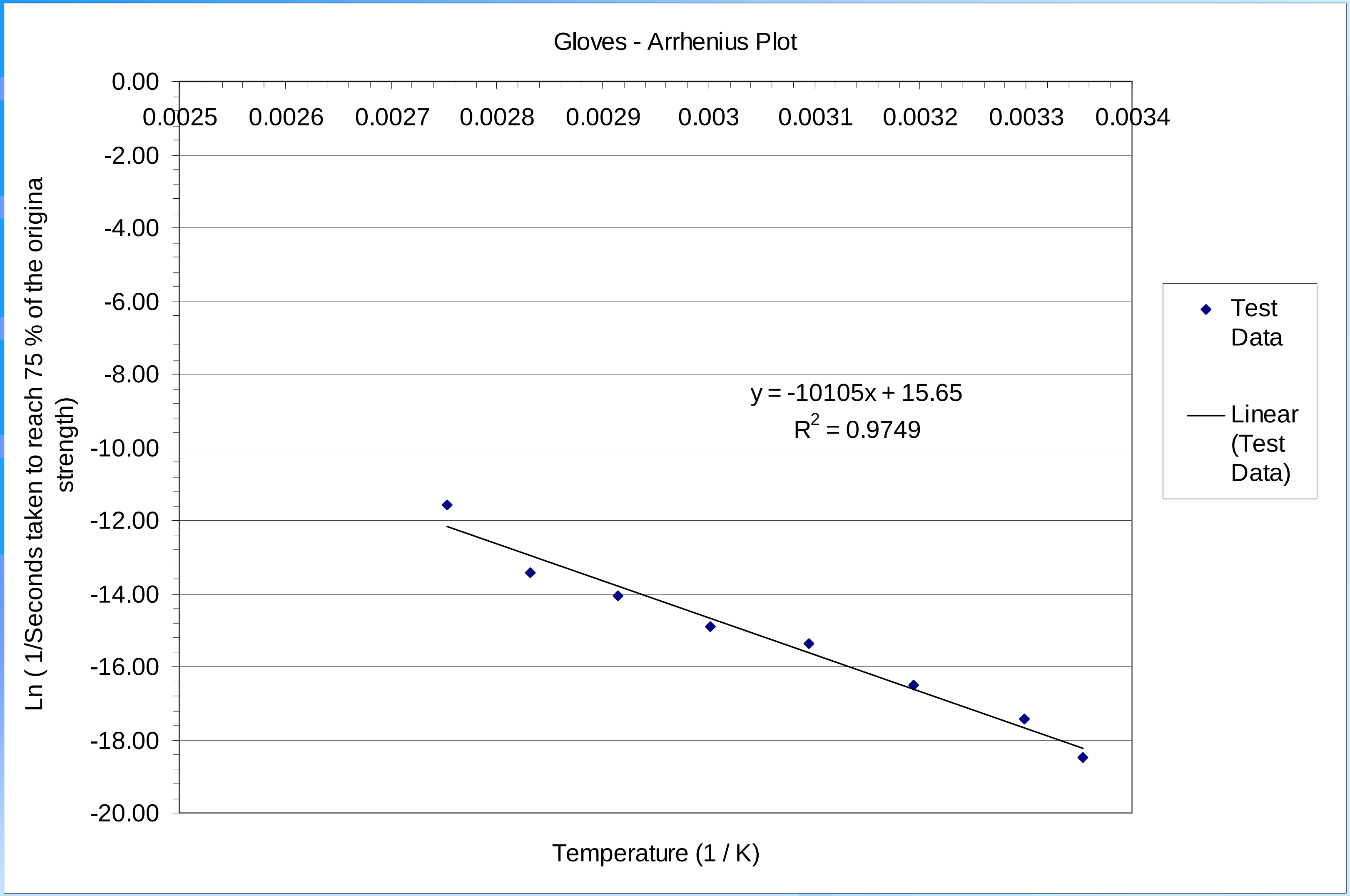
NR: Glove Compound 2: Raw Data



Time for Aging to 75 % Retention of Tensile Strength

Temp DegC	90	80	70	60	50
Aging Time in Hrs	30	30	30	30	30

NR Glove Compound 2 : Arrhenius Plot



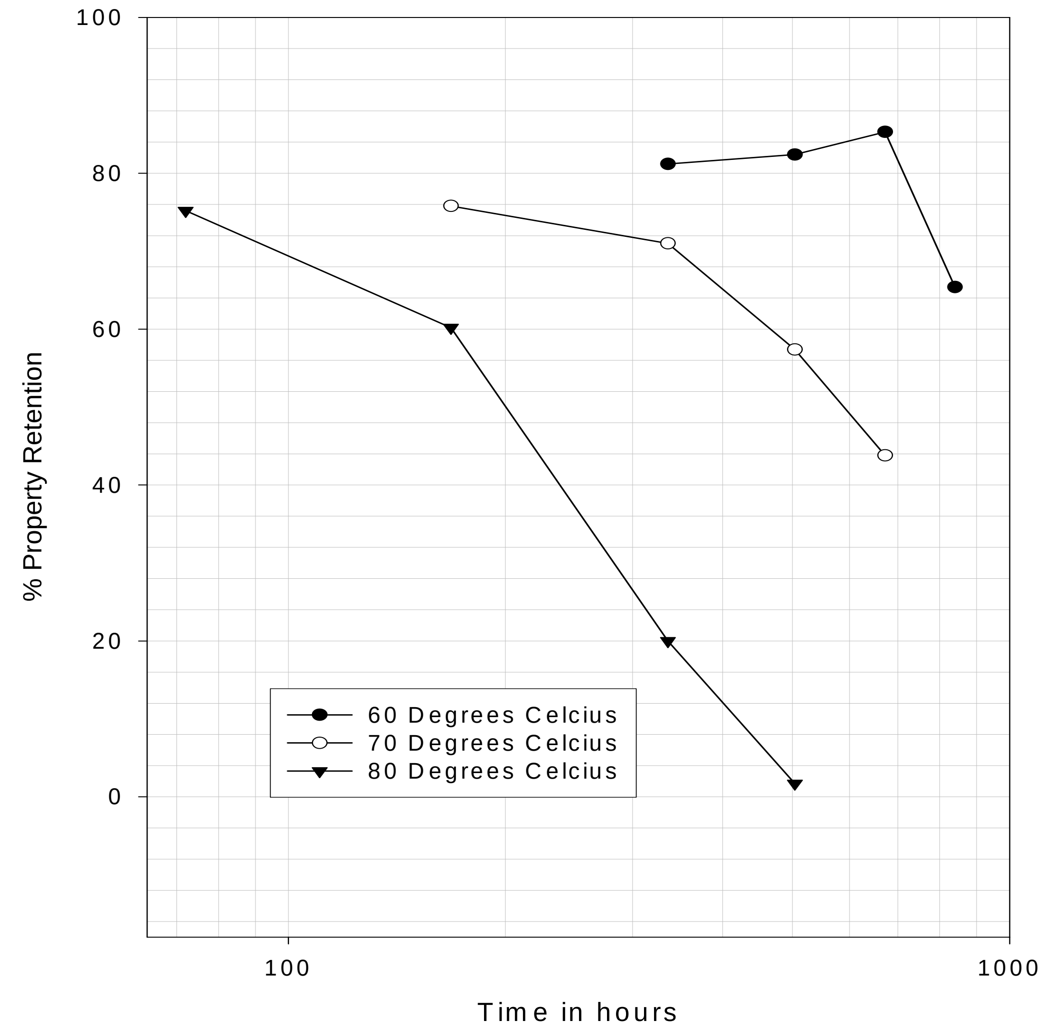
Predicted Shelf Life : NR Glove Compound 2

	Years
Arrhenius Approach	3.31
ARDL P & K Method	1.15

NR Glove Compound 3

Data at 0.0028303 80	1/ T in K Deg Celsius	Data at 0.002912734 70	1/ T in K Deg Celsius	Data at 0.00300012 60	1/ T in K Deg Celsius
Time Hrs	% Property Retention	Time Hrs	% Property Retention	Time Hrs	% Property Retention
72	75.2	168	75.8	336	81.2
168	60.2	336	71	504	82.4
336	20	504	57.4	672	85.3
504	1.7	672	43.8	840	65.4

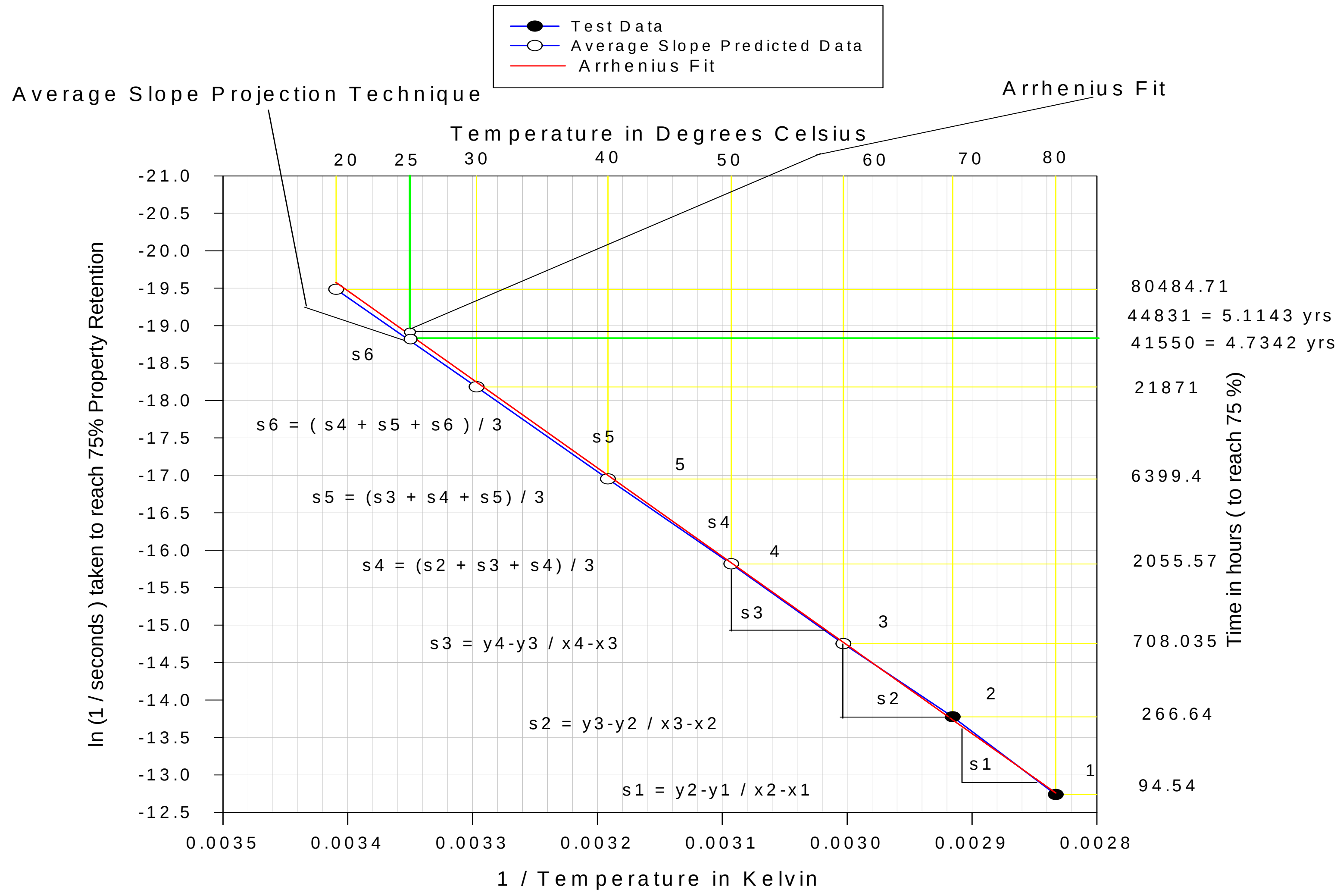
NR: Compound 3: Raw Data



Time for Aging to 75 % Retention of Tensile Strength

Temperture ^{0}C		60	70	80
Aging Time in Hrs		708.035	266.6422	94.53996

Shelf Life Prediction Curve : NR Compound 3

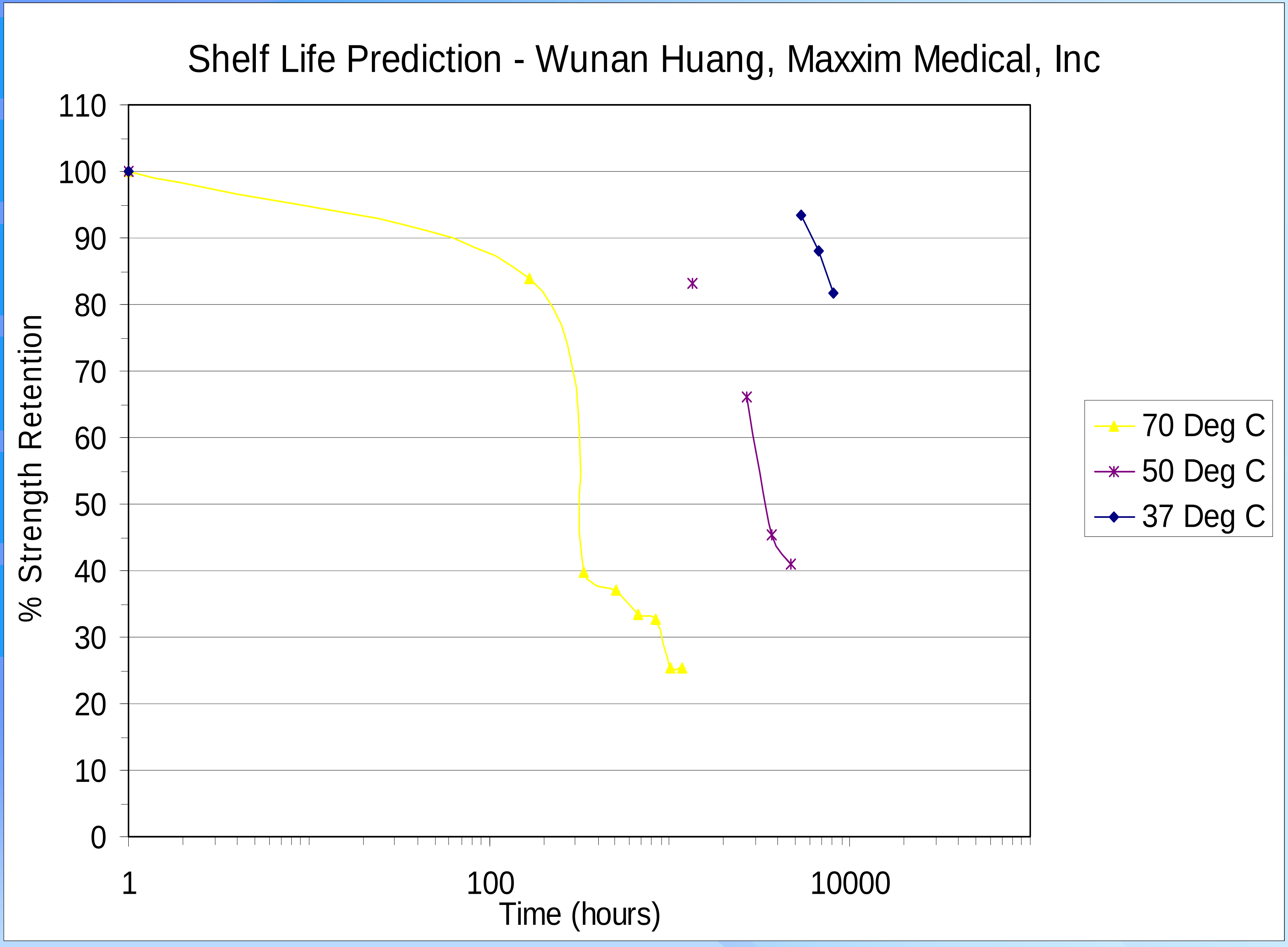


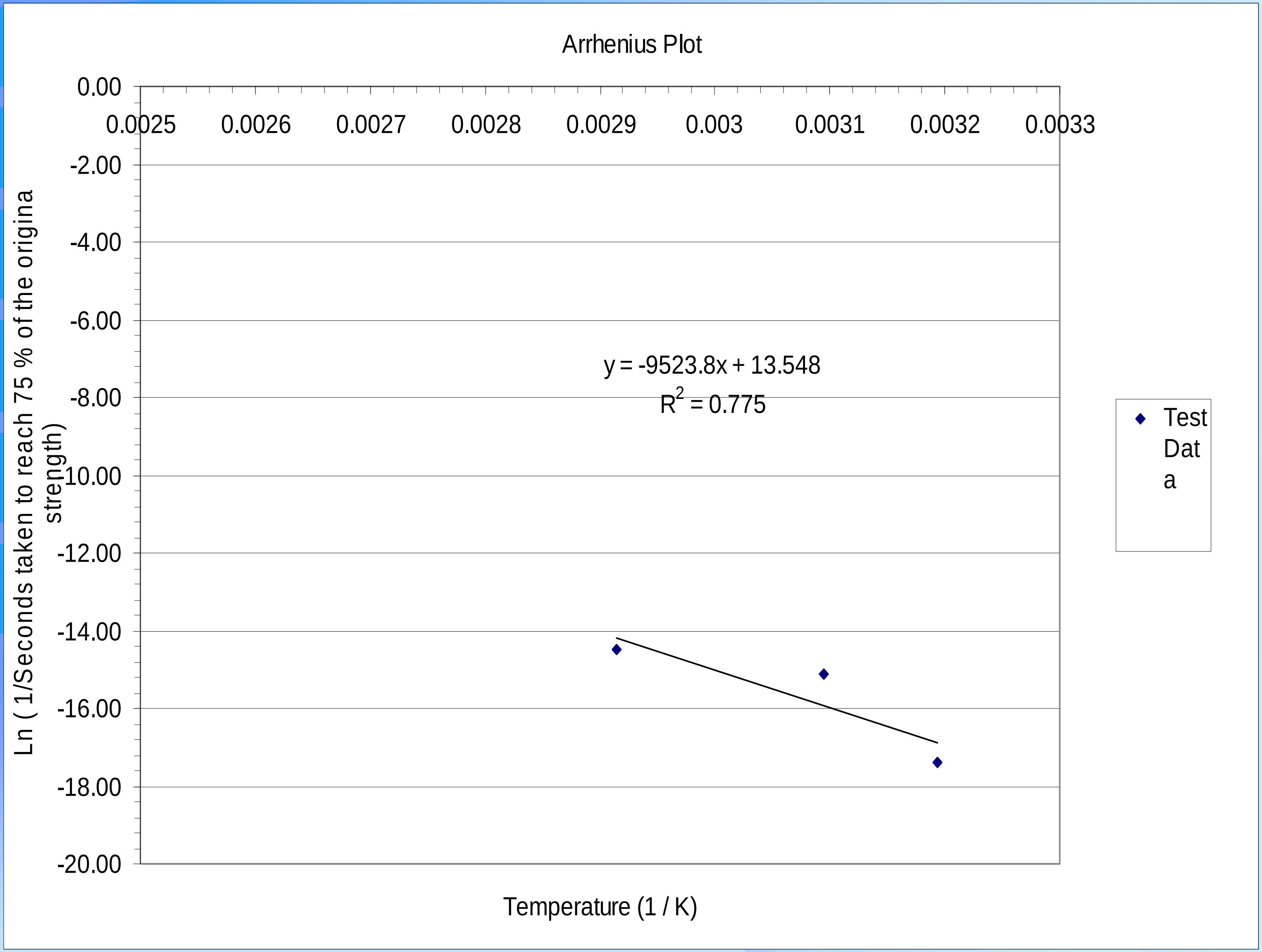
Predicted Shelf Life : NR Compound 3

Shelf Life Technique	Years
Arrhenius Approach	5.11
ARDL P & K Method	4.73

Real time data

- “ Shelf life Estimate Technique for rubber Medical Gloves” Wunan Huang, Maxxim Medical, Inc


Shelf Life Prediction - Wunan Huang, Maxxim Medical, Inc
% Strength Retention
110
100
90
80
70
60
50
40
30
20
10
0
1
100
10000
Time (hours)
70 Deg C
50 Deg C
37 Deg C


Arrhenius Plot
0.00
-2.00
-4.00
-6.00
-8.00
-10.00
-12.00
-14.00
-16.00
-18.00
-20.00
0.0025
0.0026
0.0027
0.0028
0.0029
0.003
0.0031
0.0032
0.0033
y = -9523.8x + 13.548
R2 = 0.775
Test Data
Ln (1/Seconds taken to reach 75 % of the origina strength)
Temperature (1 / K)

Shelf Life Prediction - Maxxim Medical Study

Shelf Life Technique	Years
Arrhenius Approach	6.22
ARDL P & K Method	5.53
Real Time Study	5.6

Shelf Life Prediction - Maxxim Medical Study

Shelf Life Prediction Technique	Segment Activation Energy, KJ/mole					Shelf Life, years
	80^0C–70^0C	70^0C–60^0C	60^0C–50^0C	50^0C–40^0C	40^0C–30^0C	
Real – time study	-	-	-	-	-	5.6 yrs*
ARDL "P & K" method	110.68	114.43	78.36	101.16**	97.98**	5.53 yrs
Arrhenius Approach***	101.7	101.7	101.7	101.7	101.7	6.22 yrs

Note: * Real - time shelf life, ** Average of previous three segments, *** total slope based on regression analysis of the data from all the temperatures.

Latex Product Stability
Medical Gloves

Aging temperature (^{0}C)	Time (weeks)
80	1
70	3
60	10
50	24

- This time - temperature matrix is established based on ARDL Client Shelf Life Prediction Studies.

Conclusion

- Successive Activation Energy extrapolation along with better obtained property retention data seems to be a good methodology/model for shelf life prediction of elastomers
- It is important to define aging modes/mechanisms
- Correlation between storage and lab data should be established based on a minimum of two testing techniques, preferably one physical test and one chemical test
- Each application should be studied separately for established shelf life prediction methodology

Conclusion (cont..)

- Quantitative shelf life prediction for materials will be a good guide for future specification development
- Sensitivity of the shelf life may be evaluated by modifying the threshold value by ± 10%
- Need more test data for accurate shelf life prediction for thermoplastic elastomers(preferably in 5 degree increments)
- Shelf life prediction as an engineering tool is in the infancy stage of development
- More applications related research is needed to establish the effectiveness of the package on shelf life prediction

ARDL Engineering Group