Predicting time-dependent properties of polymers

PJ Gould & IG Cullis

QinetiQ

© Copyright QinetiQ Limited 2010

Acknowledgements

UK MOD

- For funding and support via DTIC

David Porter

- the prime mover behind most of the work

Other members of Hazard consortia

- Cambridge University, FGE, DA Shrivenham, BAE SYSTEMS

QinetiQ

© Copyright QinetiQ Limited 2010

Contents

1 Phenomenology

2 Prediction

3 Mechanical properties

4 Equation of state

5 Integration

6 Summary

QinetiQ

© Copyright QinetiQ Limited 2010

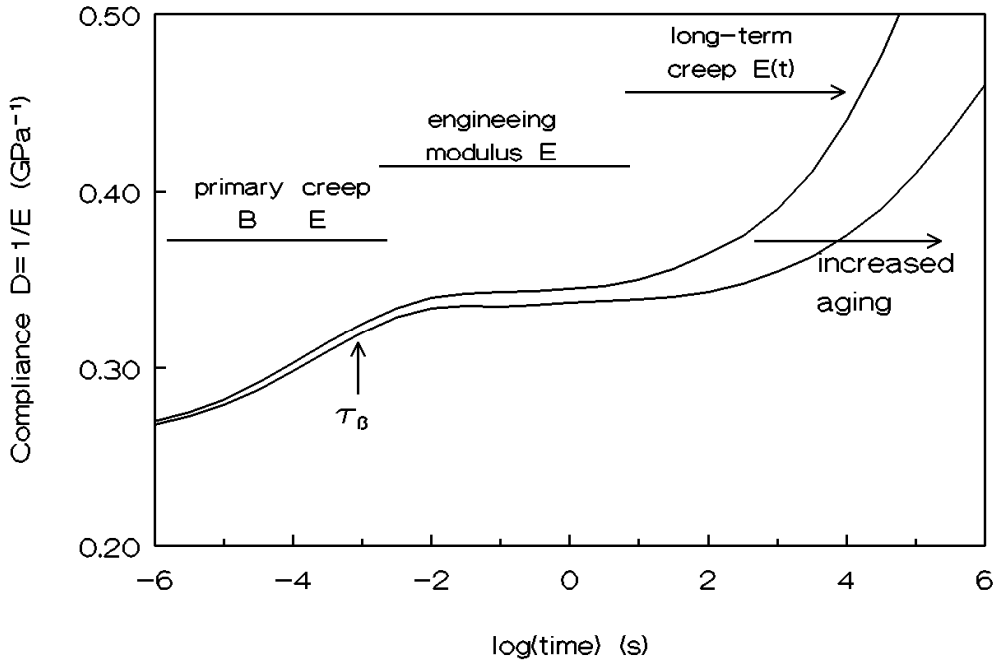
1
Phenomenology

© Copyright QinetiQ Limited 2010

1 Phenomenology

Polymers are visco-elastic materials whose stiffnesses depend upon sampling time.

Investigated using relaxation tests and small-strain cyclic tests

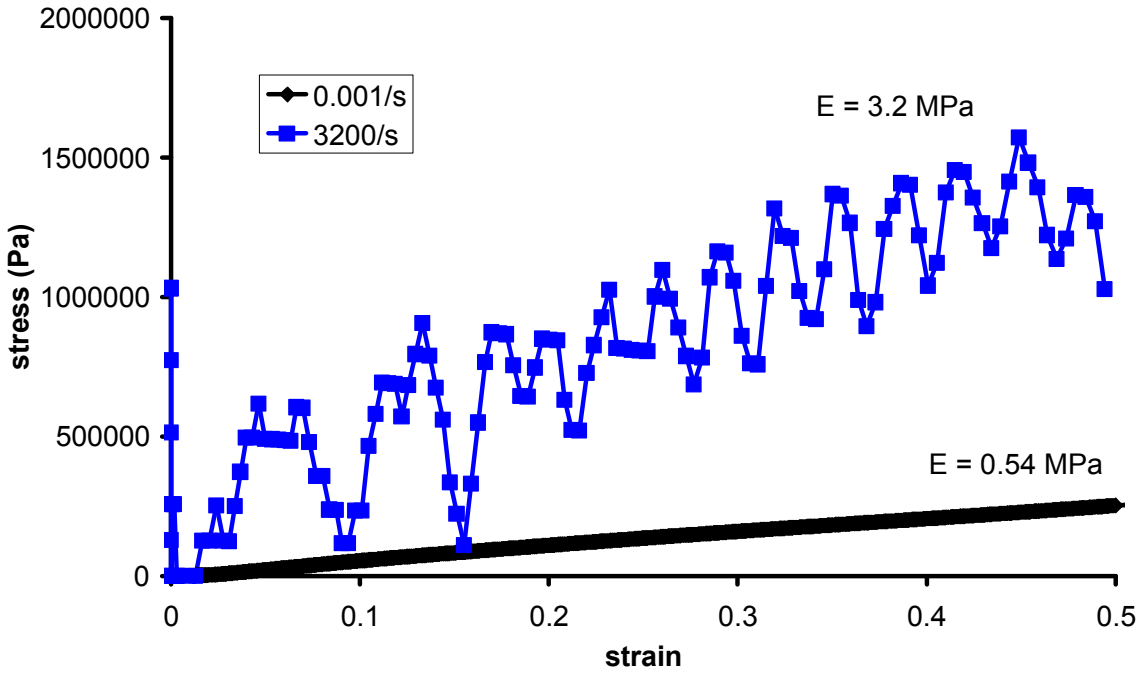


© Copyright QinetiQ Limited 2010

1 Phenomenology

Mechanical tests: low rate vs high rate for a rubber

Six-fold increase in modulus over six decades of rate



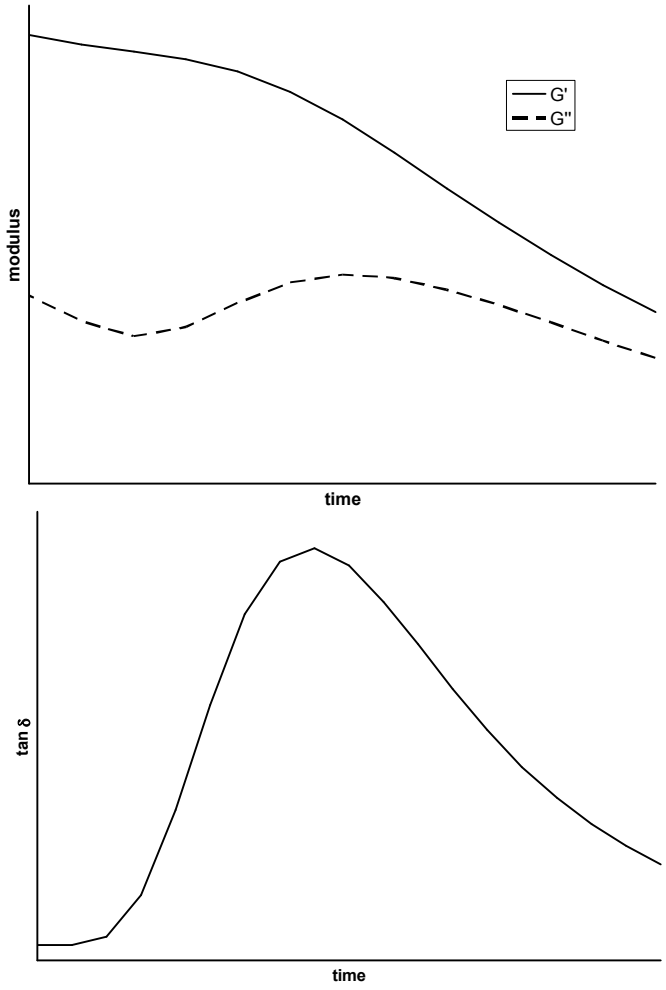
© Copyright QinetiQ Limited 2010

1 Phenomenology

Cyclic loading emphasises viscous behaviour:

- link between time-dependent stiffness and energy absorption
- DMA test (modulus vs frequency)
- Storage modulus G’
- Loss modulus G’’
- Tan δ phase angle lag between input and measured cycles
- Measure of energy dissipated in each cycle

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

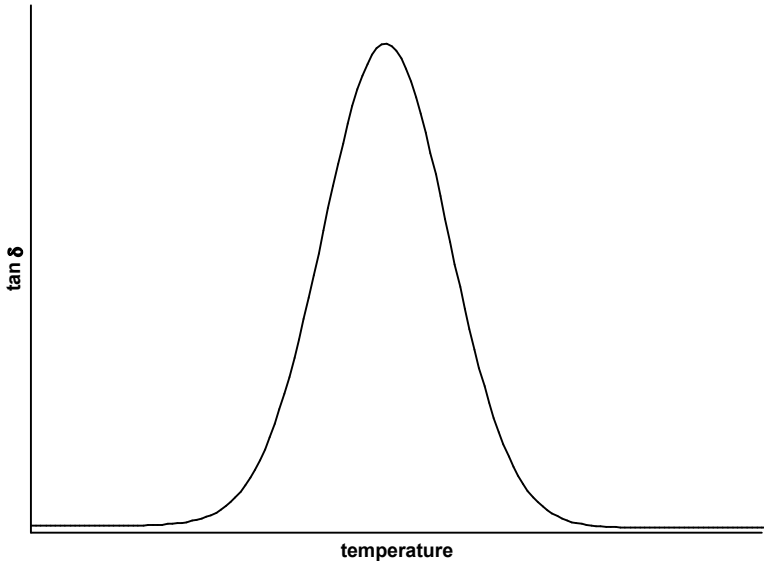


© Copyright QinetiQ Limited 2010

1 Phenomenology

Testing at different temperatures (single frequency) in DMA shows time-temperature superposition

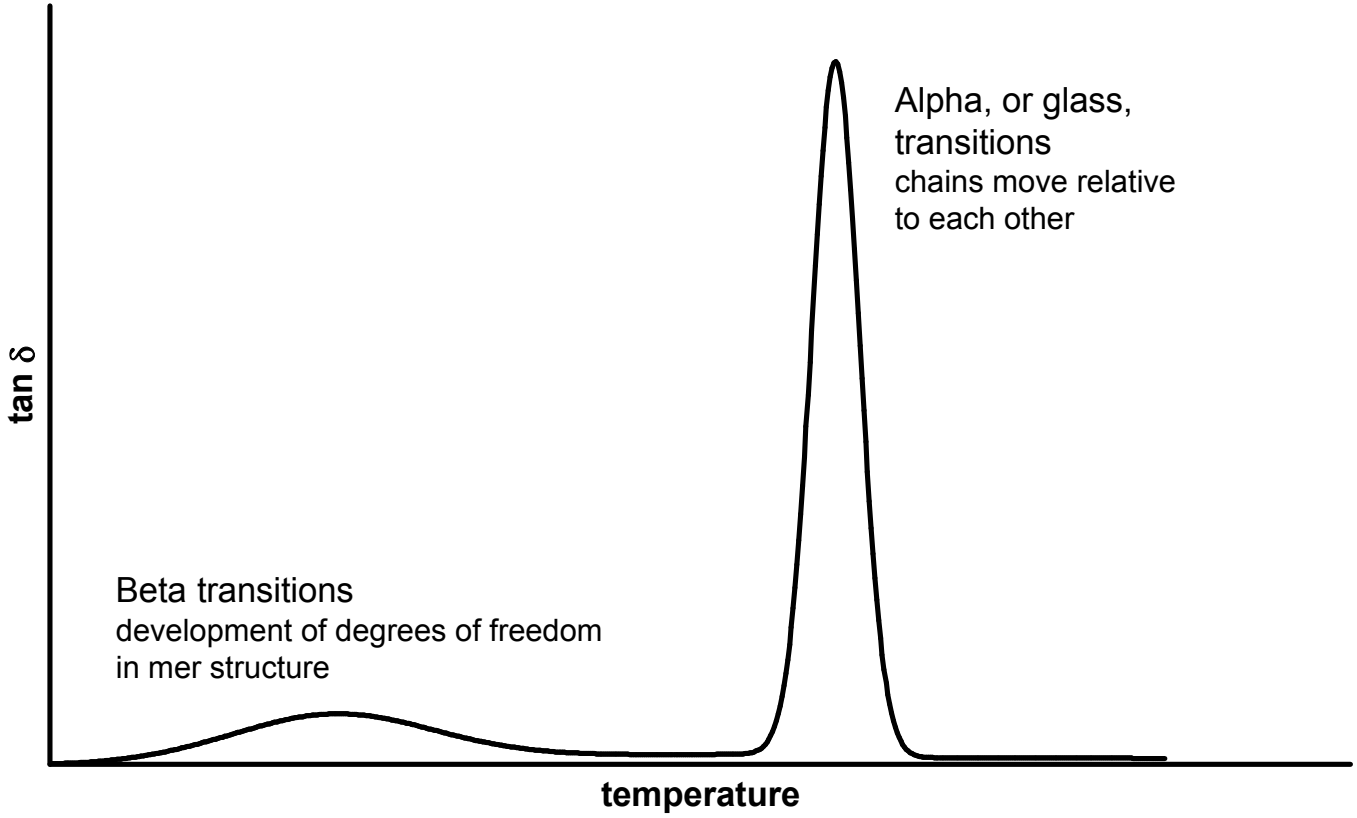
More experimentally practical to generate the necessary wide range of time-dependent data using temperature as proxy



QinetiQ
© Copyright QinetiQ Limited 2010

1 Phenomenology

What does tan δ space look like for a standard polymer?



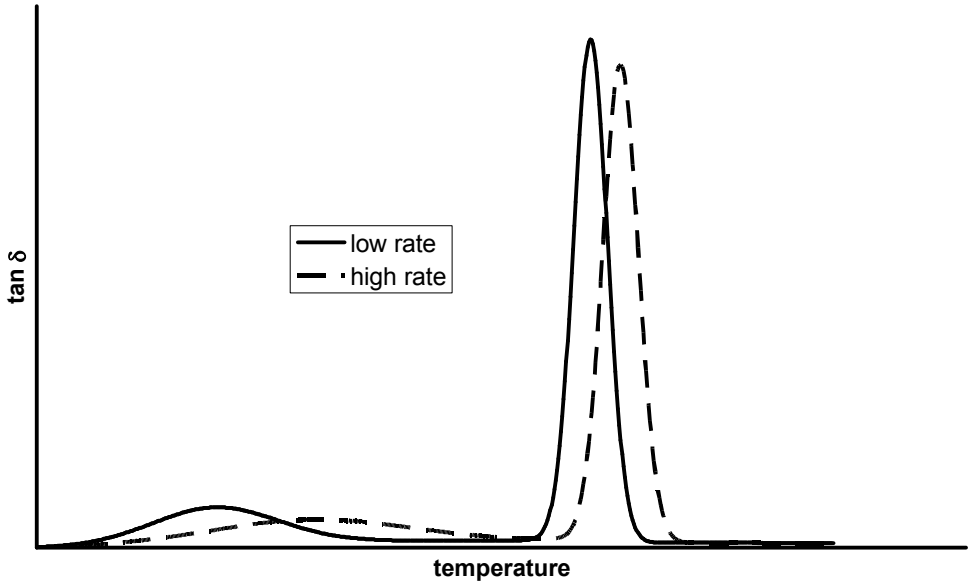
© Copyright QinetiQ Limited 2010

1 Phenomenology

How does tan δ vs T change with rate?

Transition peaks shift, reduce in height and broaden

- Integral underneath spectrum is constant
- Need to specify rate at which the glass transition temperature is measured



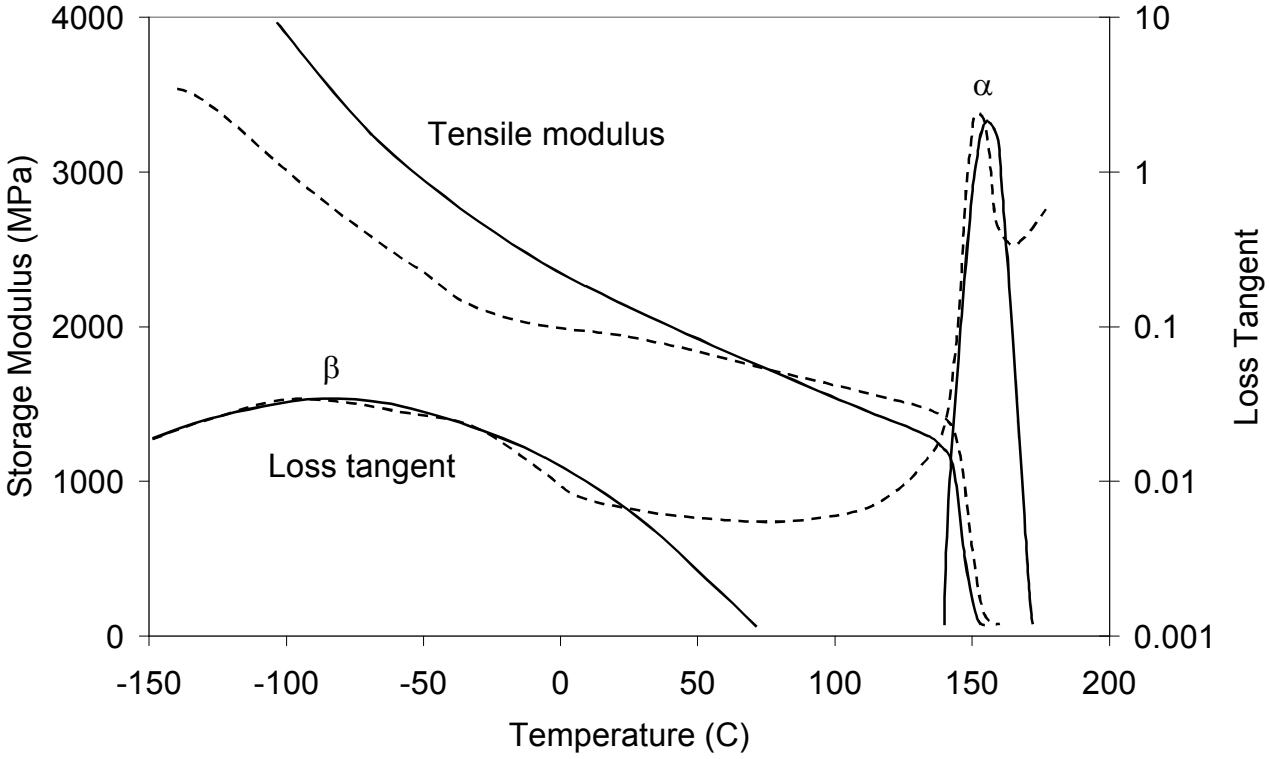
© Copyright QinetiQ Limited 2010

2
Prediction

© Copyright QinetiQ Limited 2010

2 Prediction

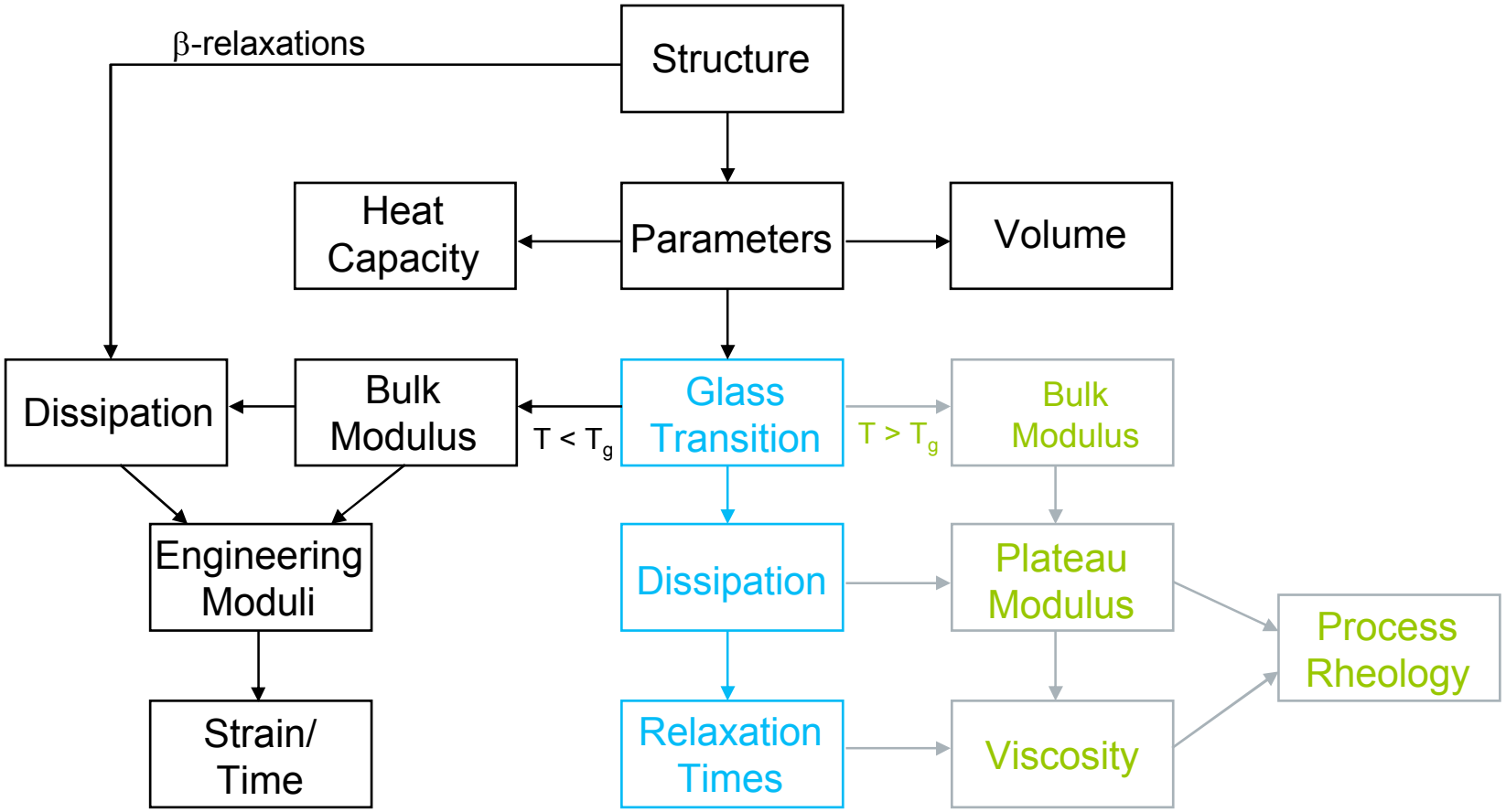
Group Interaction Modelling (GIM) uses chemistry of polymer to predict mechanical and physical properties



D Porter & PJ Gould, International Journal of Solids and Structures, 46 (2009) pp1981-1993

© Copyright QinetiQ Limited 2010

2 GIM schematic



© Copyright QinetiQ Limited 2010

2 Group Interaction Modelling

Parameters used:

- M molecular weight of a group
- V_w (cc/mol) van der Waal's volume of a group
- E_{coh} (J/mol) cohesive energy of intermolecular forces
- θ (K) 1-D Debye reference temperature related to polymer chain stiffness
- N thermal degrees of freedom per group

All of these can be measured, calculated or taken from literature

QinetiQ

© Copyright QinetiQ Limited 2010

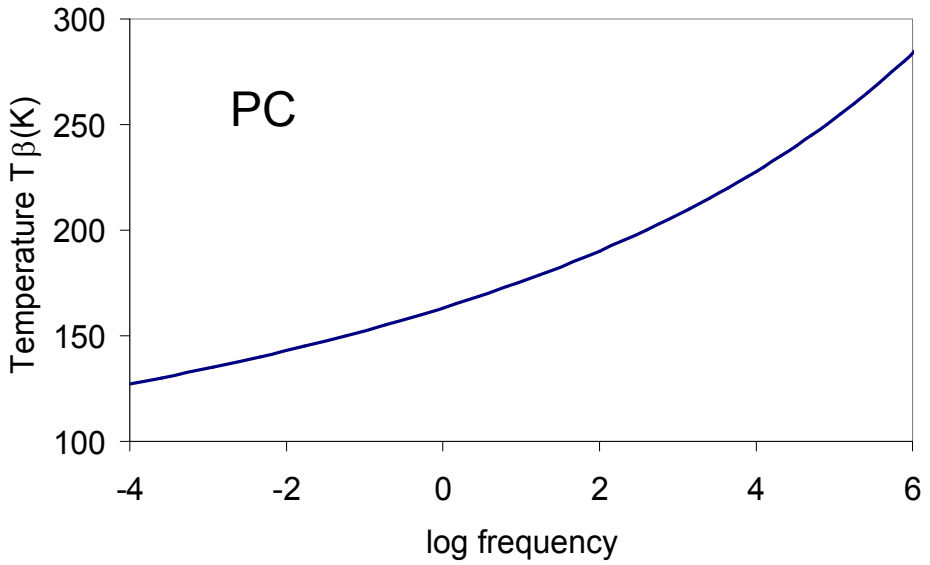
2 Time-dependence in GIM

Loss peaks derive from development of degrees of freedom with time/temperature

For β peaks, N_β develop with Arrhenius activated kinetics

$$T_\beta = \frac{-\Delta H_\beta}{R \ln\left(\frac{f}{f_o}\right)}$$

$$f_o = \frac{k\,\theta_1}{h}$$



Activation energy from quantum mechanics calculation

QinetiQ
© Copyright QinetiQ Limited 2010

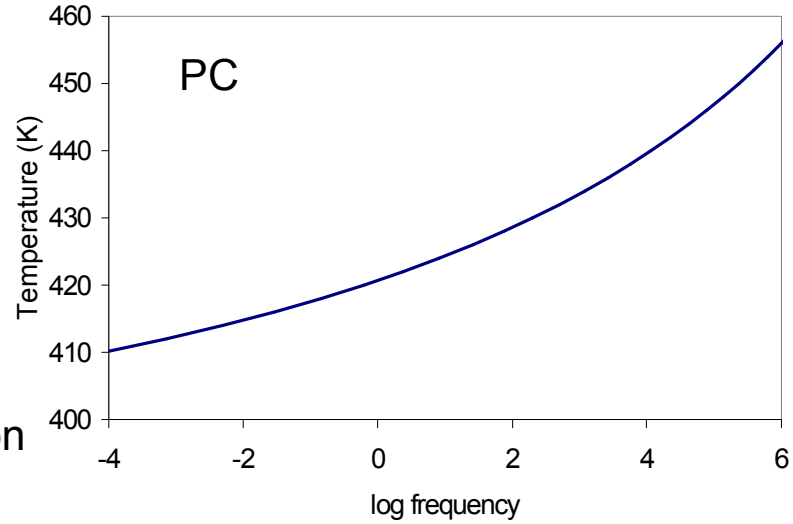
2 Time dependence in GIM

Amenable to direct prediction using physical quantities

Use Vogel-Fulcher method for glass transition

- Relaxation time, f, is a temperature-activated function
- Experimentally observed that glass transition at equilibrium rates (infinitely long time) is 50 K below that at 1 Hz. $T_{gr} = T_g - 50$

$$f = f_o \exp\left(-\frac{1280 + 50\ln\theta_1}{T - T_{gr} + 50}\right)$$



- At infinitely short times predict $T_{gr} = T_g + 70$
- β transitions can "catch up" with glass transition

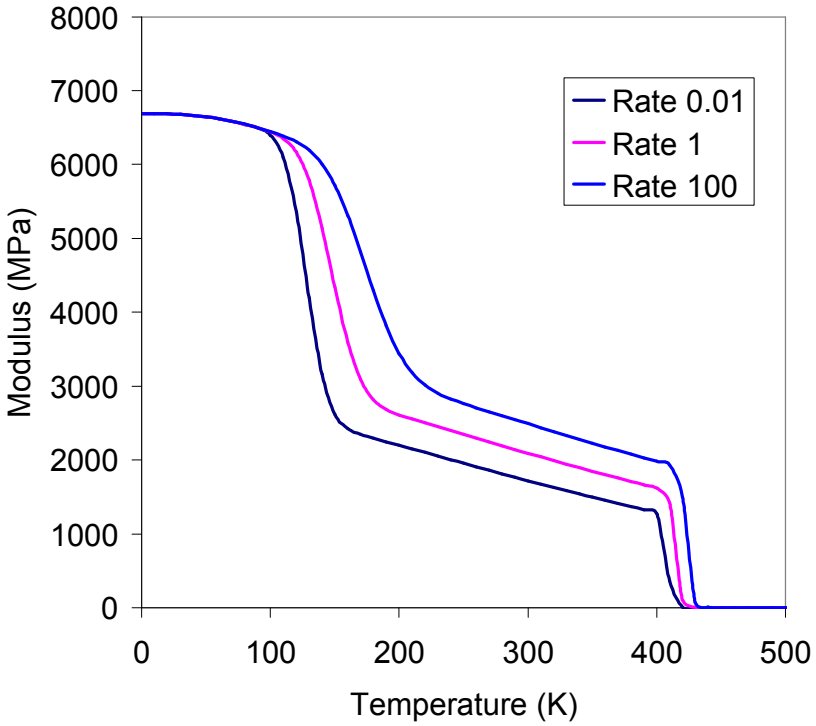
© Copyright QinetiQ Limited 2010

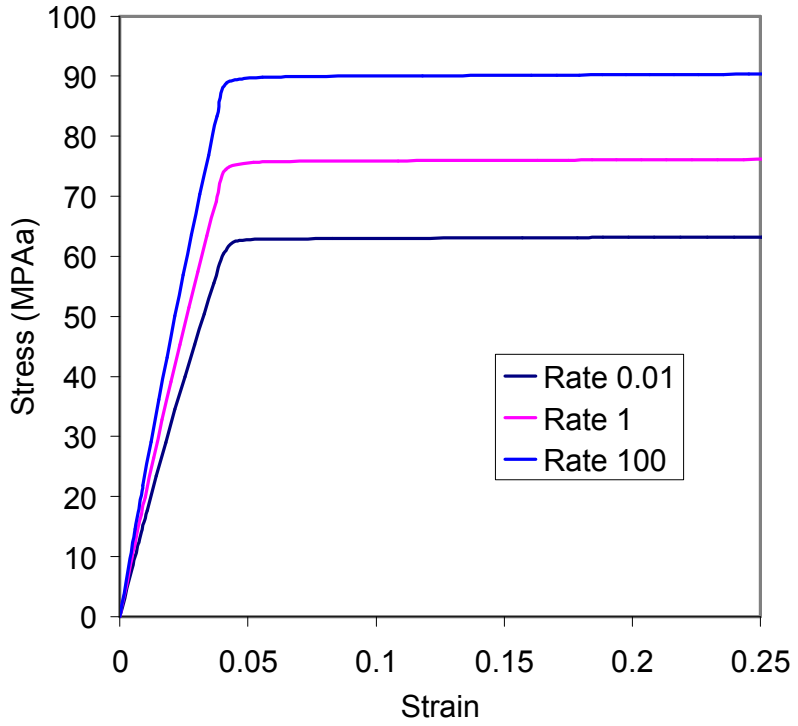
3
Mechanical properties

© Copyright QinetiQ Limited 2010

3 Stress-Strain

Transform DMA modulus to stress vs strain





© Copyright QinetiQ Limited 2010

3 Stress-Strain

We have predictions of expansion and modulus with temperature

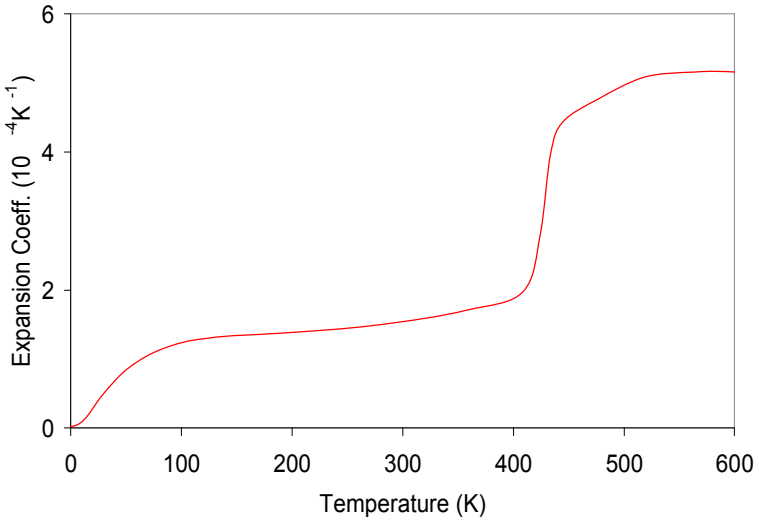
Use temperature as a dummy variable

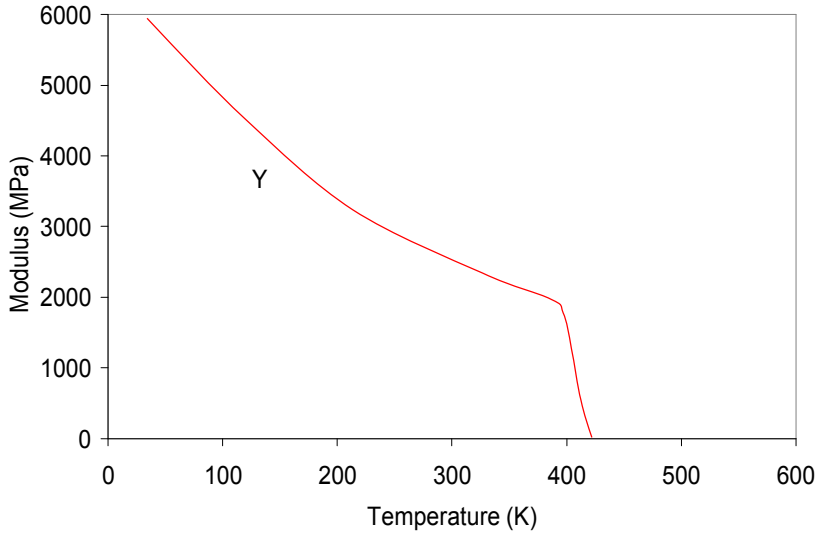
Strain ≡ thermal expansion

Stress ≡ thermal expansion x modulus

$$\varepsilon \equiv \int \alpha \, dT$$

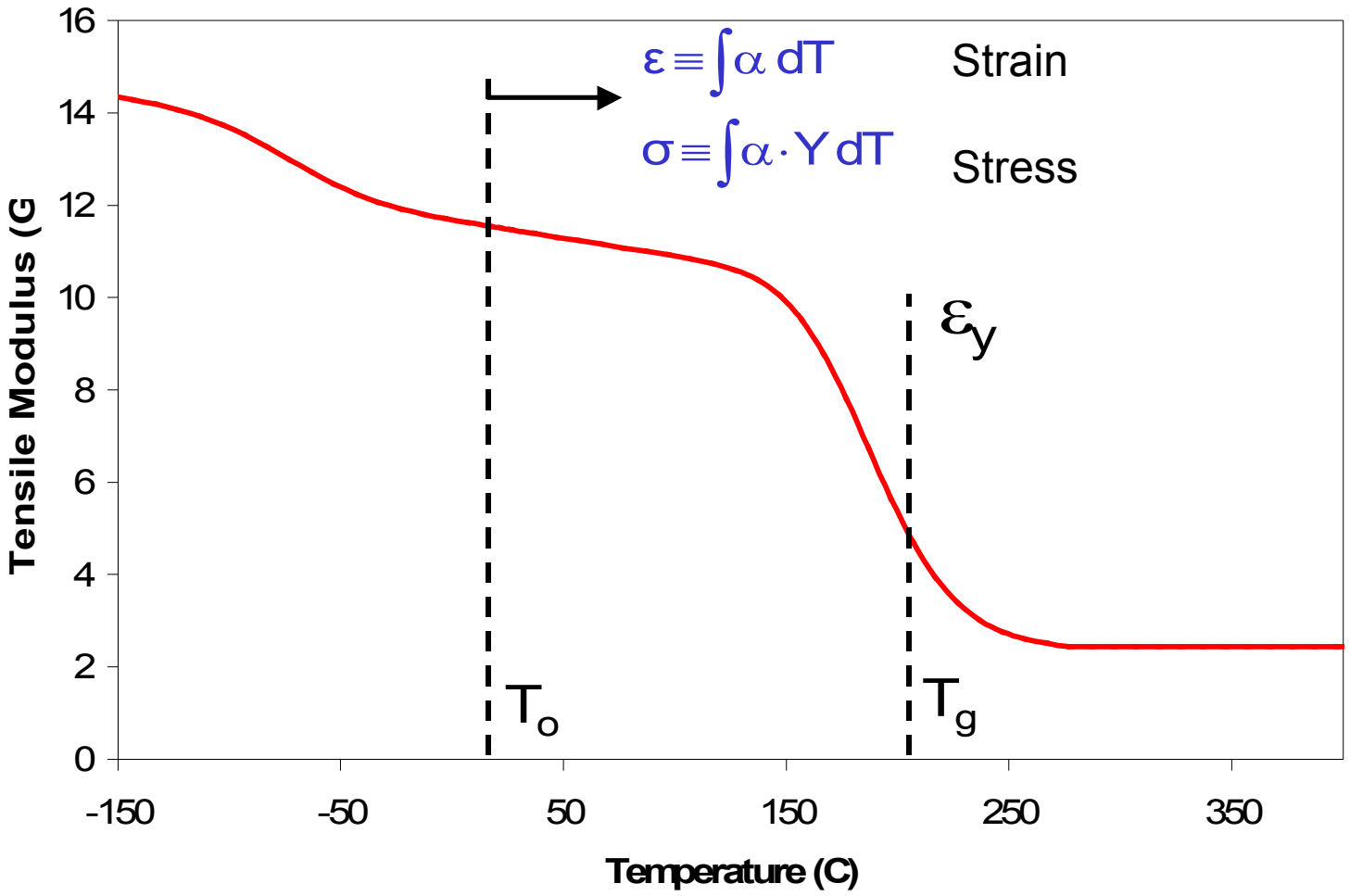
$$\sigma \equiv \int \alpha \cdot Y \, dT$$





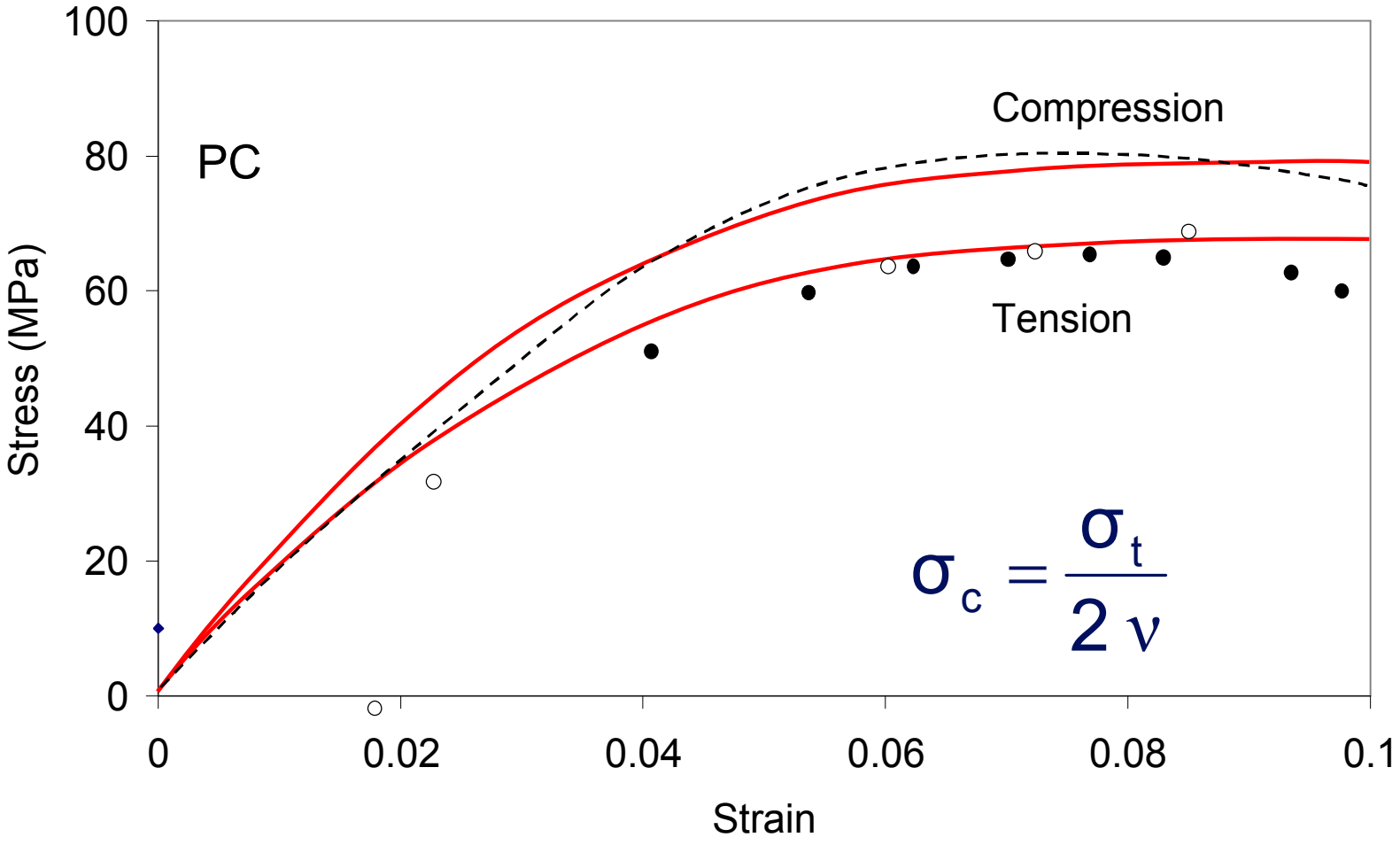
© Copyright QinetiQ Limited 2010

3 Stress-Strain



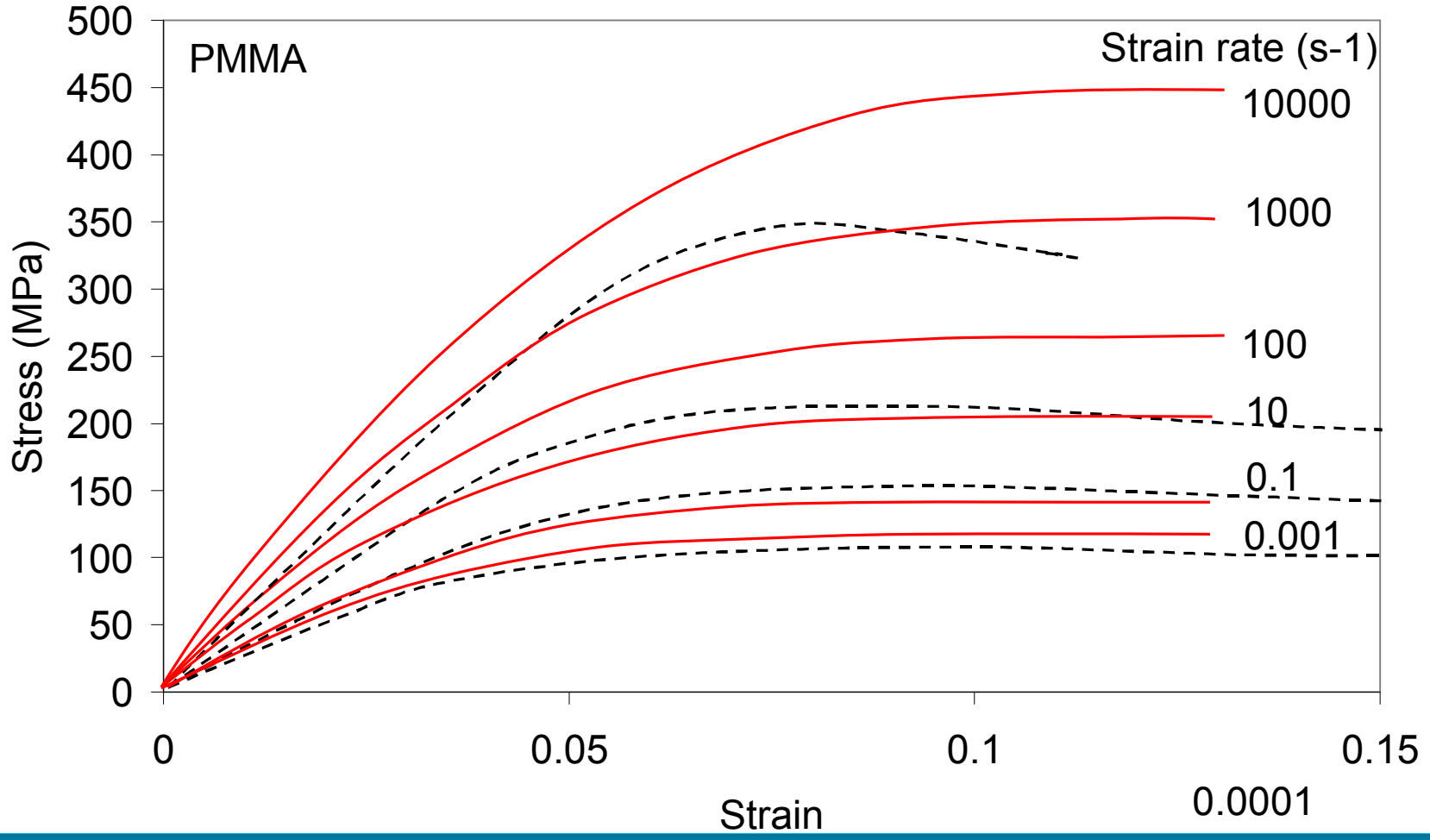
© Copyright QinetiQ Limited 2010

3 Stress-Strain: Validation



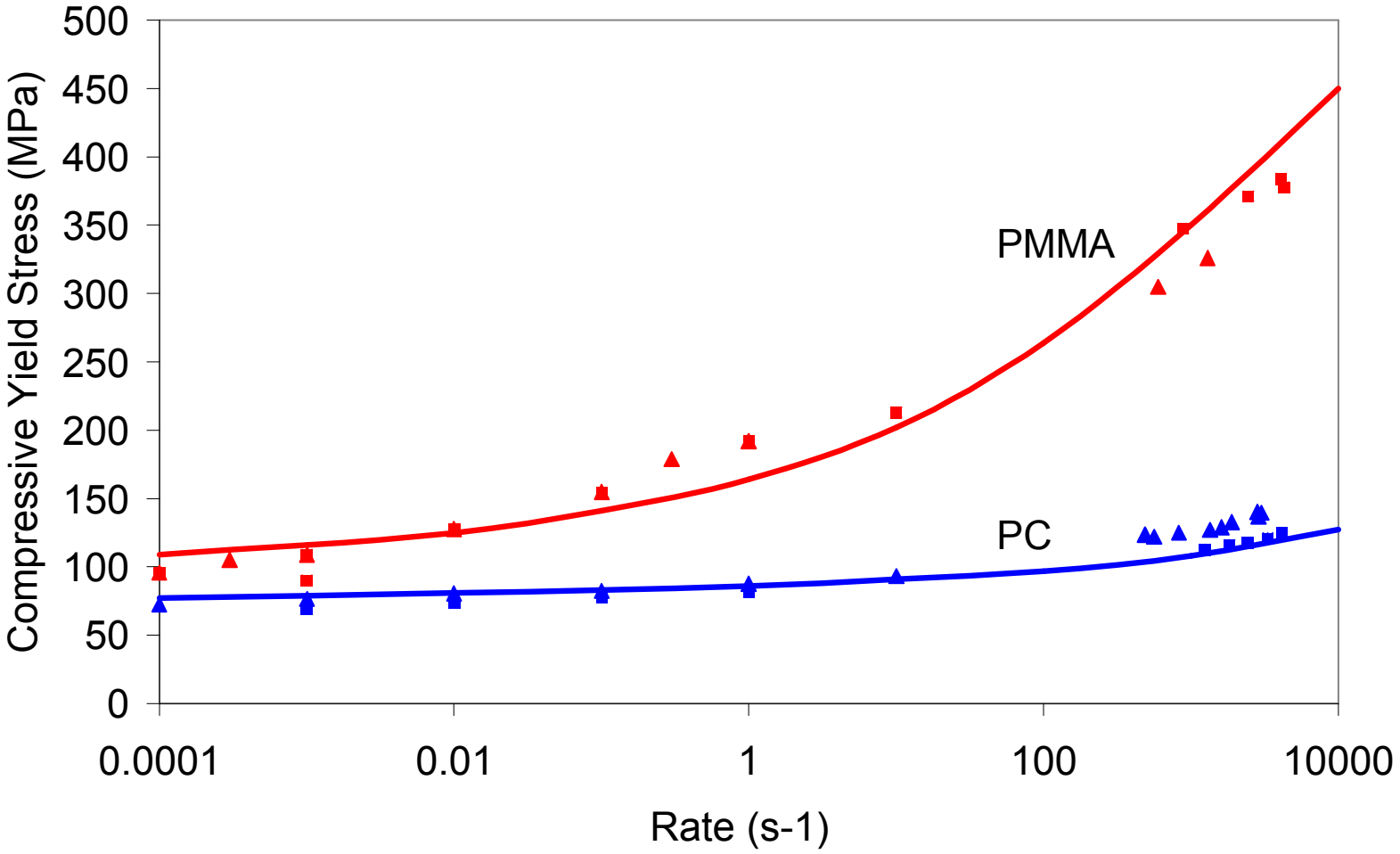
© Copyright QinetiQ Limited 2010

3 Stress-Strain: Rate validation



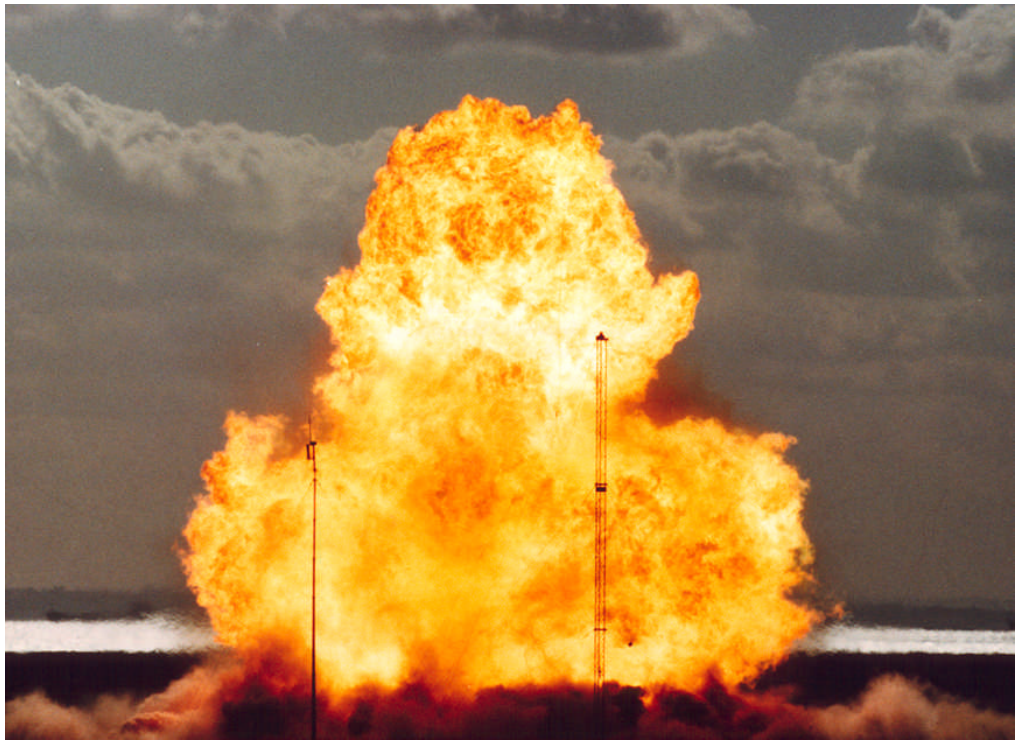
© Copyright QinetiQ Limited 2010

3 Stress-Strain: Yield: Rate validation



QinetiQ
© Copyright QinetiQ Limited 2010

4
Equation of State



© Copyright QinetiQ Limited 2010

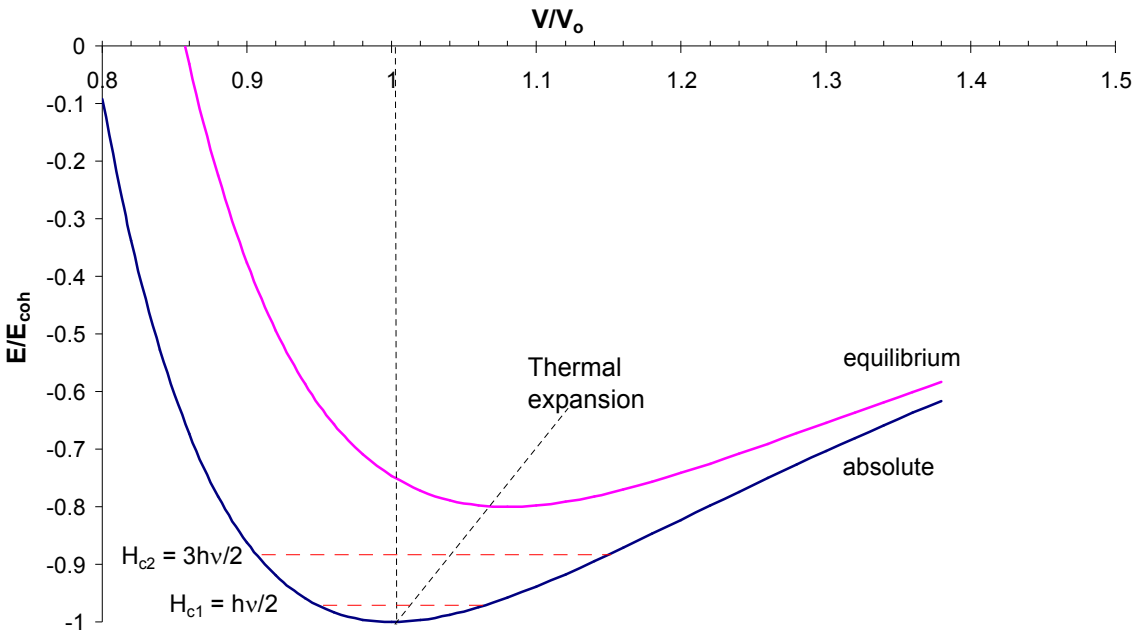
4 Equation of state

Potential function method

- GIM parameters give E(V) at arbitrary temperature via thermodynamics
- Stress and bulk modulus from derivatives of E(V)

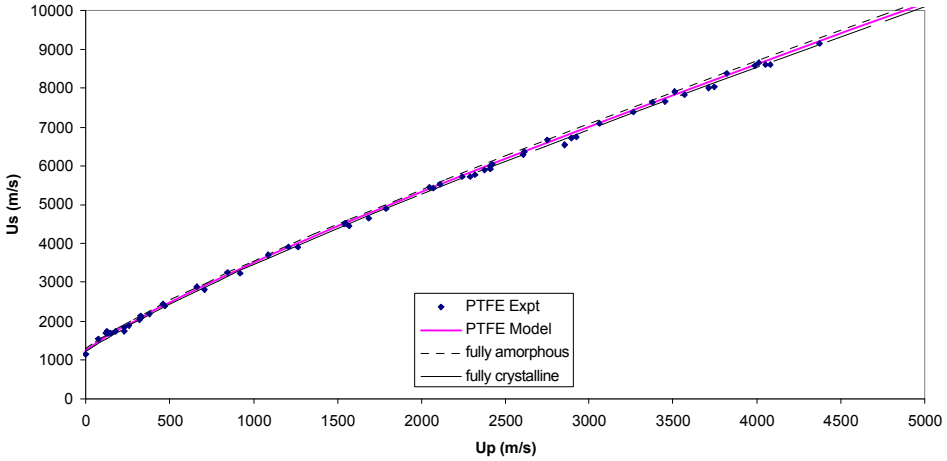
$$P = -\frac{dE}{dV}$$

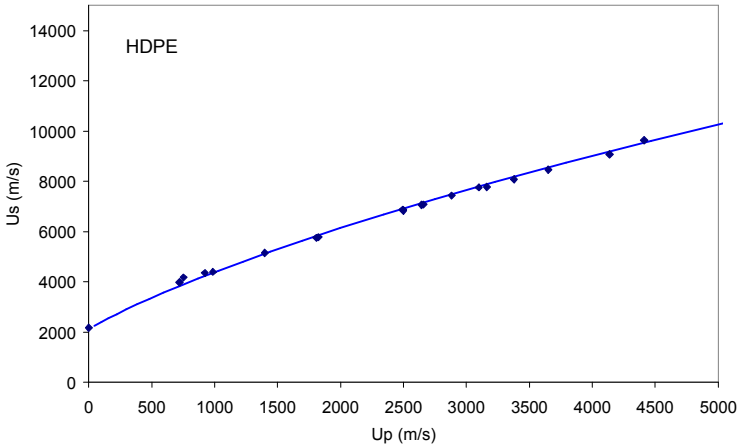
- Correct for strain in chain axis
- Put P vs V into Rankine-Hugoniot equations

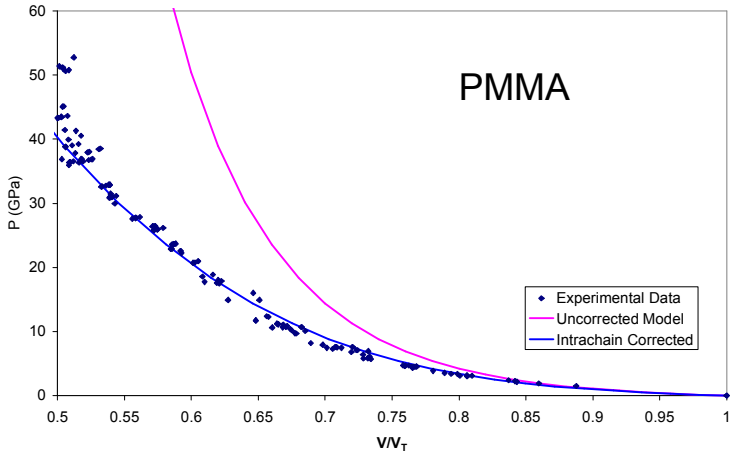


© Copyright QinetiQ Limited 2010

4 EOS Validation



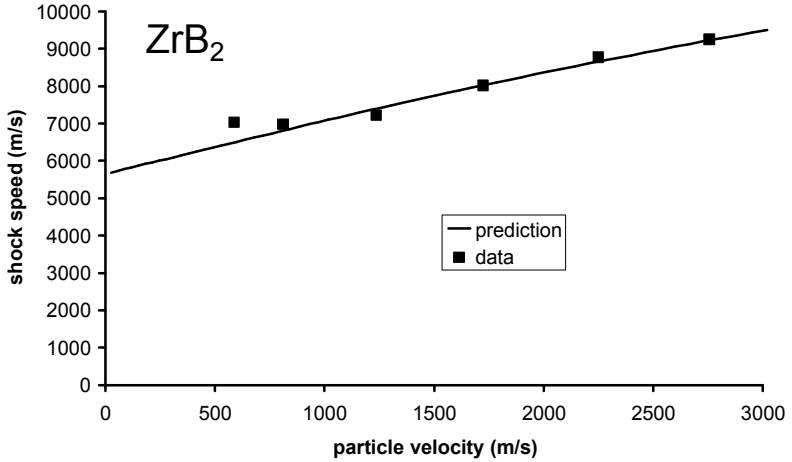


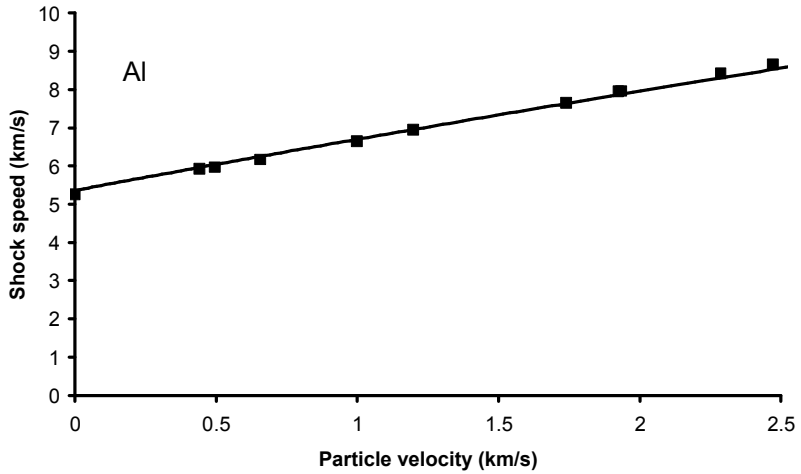


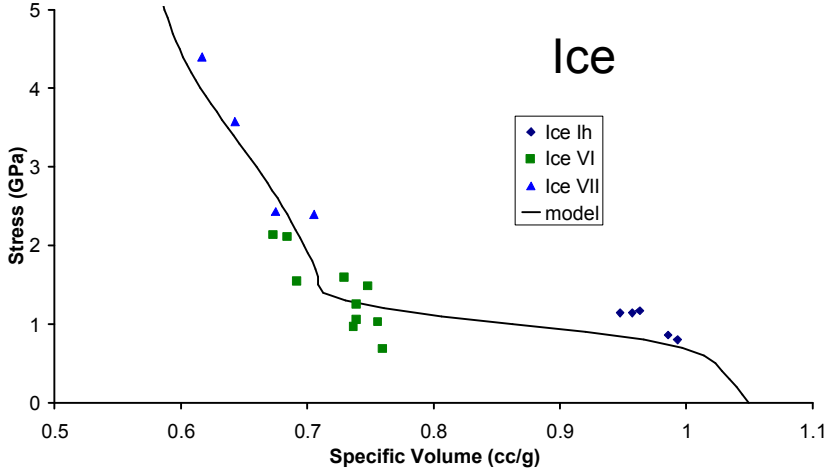
© Copyright QinetiQ Limited 2010

4 Applicability of method

Potential function method is applicable to a wide range of materials with different bonding types

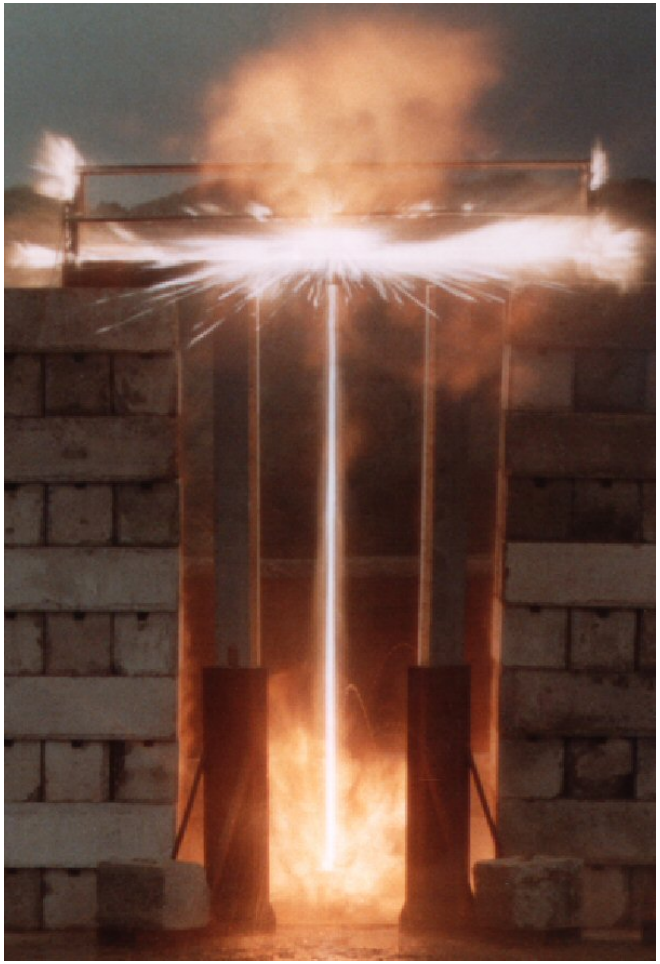






© Copyright QinetiQ Limited 2010

5
Integration



© Copyright QinetiQ Limited 2010

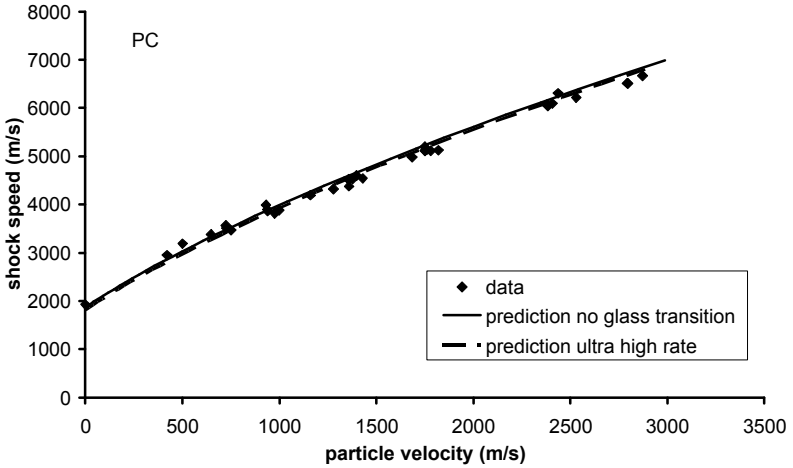
5 Is shock a high rate event?

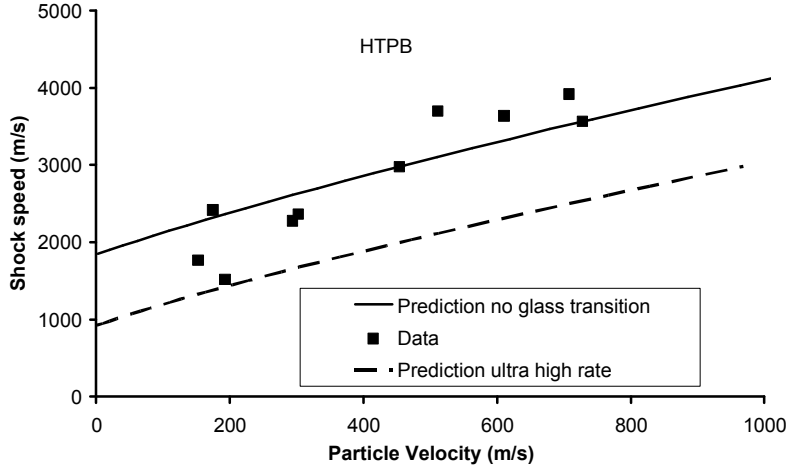
Increased rate shifts transition temperatures for both β and glass transitions

- may reduce degrees of freedom at the temperature of the test
- β transitions are inherent to the molecule
- Glass transitions are cooperative between molecules

At room temperature polycarbonate is below glass transition but HTPB is above.

Look at model predictions





QinetiQ

© Copyright QinetiQ Limited 2010

5 Is shock a high rate event?

Model predictions suggest that polymers under shock lose degrees of freedom associated with cooperative motion

- But not those β degrees of freedom that are thermally activated

Need more experiments to determine exactly what happens

- Shock measurements at different temperatures around the glass transition
- Measurements on polymers with different transition temperatures
- Implications for thermodynamics
- Need to take into account effects of pressure
  - Pressure affects transition temperatures via Debye temperature
- Need a better understanding of what a shock actually is

© Copyright QinetiQ Limited 2010

5 Polymers under shock

Why this matters: heat capacity

Polymer heat capacity is a function of number of degrees of freedom

- Sum of skeletal modes and atomic group modes

$$C \approx N\,R\,\frac{\left(\frac{6.7\,T}{\theta_1}\right)^2}{1+\left(\frac{6.7\,T}{\theta_1}\right)^2} \qquad C_E = \frac{R\left(\theta_E/T\right)^2 \exp\left(\theta_E/T\right)}{\left[\exp\left(\theta_E/T\right)-1\right]^2}$$

- At glass transition polymer gains an extra 0.5N from cooperative modes

© Copyright QinetiQ Limited 2010

5 Heat Capacity

Example: HTPB

N = 22, M = 159, θ_1 = 520K

$N_E = 3n - N$

θ_E = 4000K, 1500K

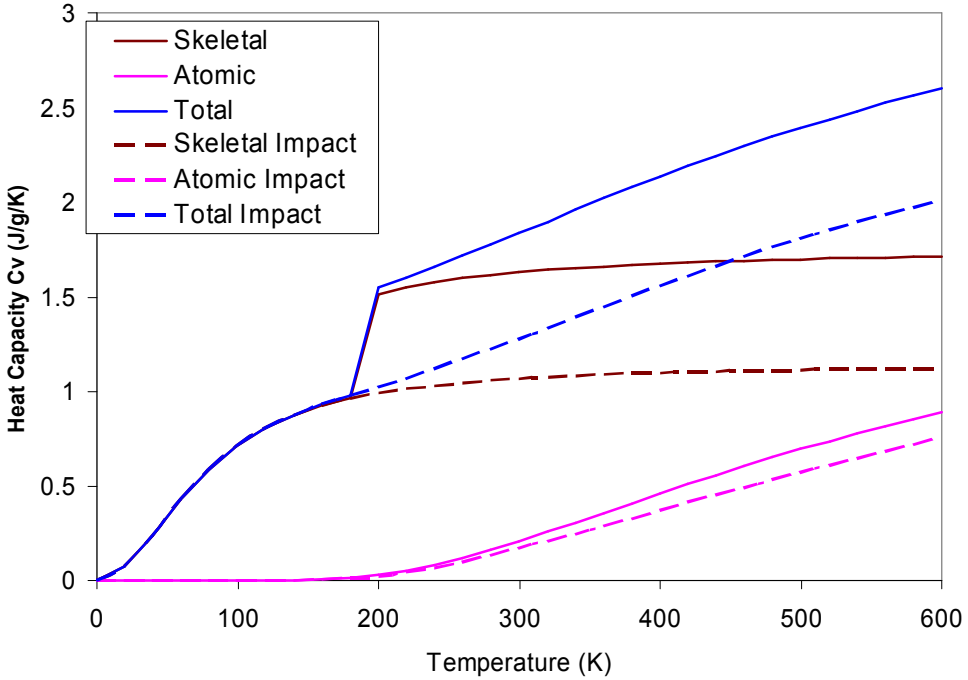
Gains an extra 0.5N at glass transition

- Not under shock

Model predicts C_v = 1.84 J $g^{-1}K^{-1}$

Experimental: C_p = 1.95 J $g^{-1}K^{-1}$ at 300K

Menikoff: C_p and C_v differ by only 5% for these materials



© Copyright QinetiQ Limited 2010

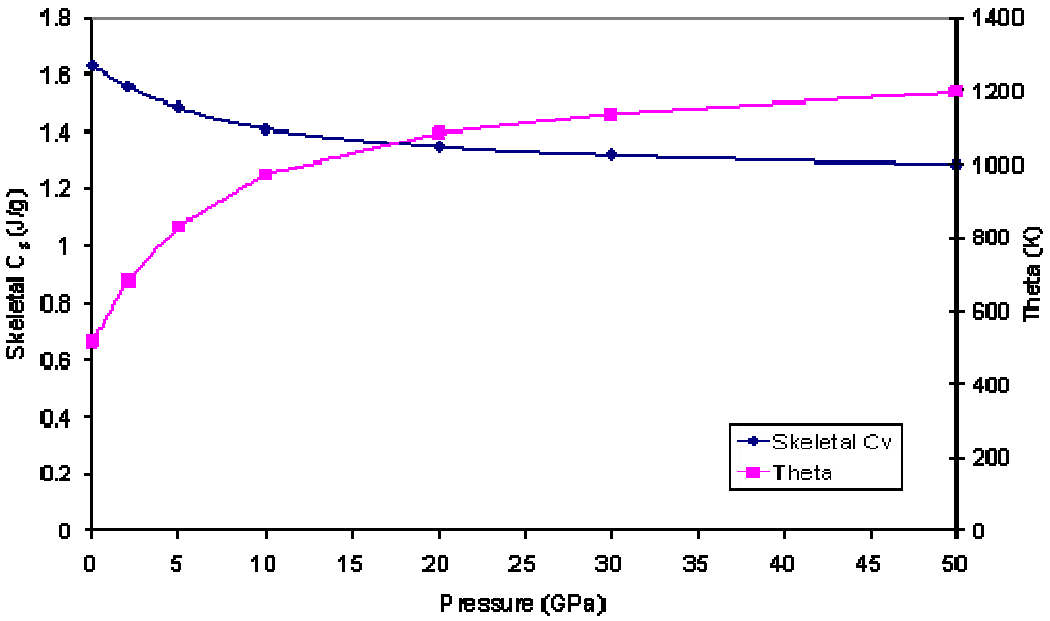
5 Heat Capacity – pressure dependence

Pressure changes the vibrational modes and therefore changes the Debye θ temperatures.

This reduces heat capacity

Use QM to calculate new vibrational modes for different pressures and thus the new θ temperatures

Allows heat capacity to be a function of pressure as well as temperature and rate.



Debye temperatures can be included into model to suggest heat capacities under shock.

At 5 GPa and 300K, HTPB C_v = 1.0 J g^{-1} K^{-1}, RDX C_v = 0.79 J g^{-1} K^{-1}

Can use Dreger & Gupta measurements to give RDX C_v = 0.81 J g^{-1} K^{-1}

ZA Dreger, YM Gupta, J. Phys Chem B 111 (2007) pp 3893 - 3903

QinetiQ

© Copyright QinetiQ Limited 2010

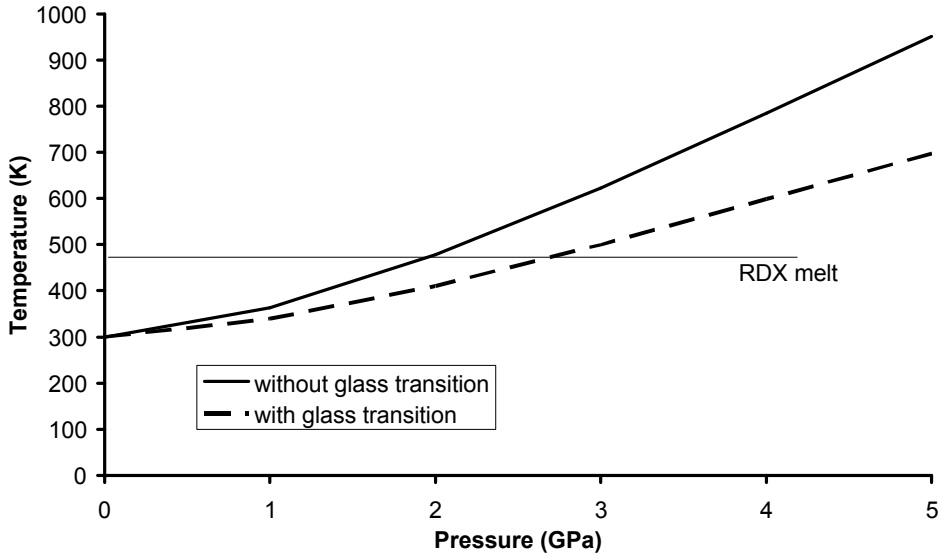
5 HTPB temperature under shock

Pressure- and rate-dependence of heat capacity allows prediction of shock temperature

Has implications for safety of explosives

For example predictions of ignition

- Take RDX melt (478K) as ignition of surface burning
- Pressure required to ignite drops from 2.8 GPa to 2 GPa when compared to standard heat capacity
  - Larger drop if higher temperature is used



© Copyright QinetiQ Limited 2010

6 Summary

Polymers are time-dependent in thermomechanical properties

We can predict their behaviour

Modelling gives insight into behaviour outside the range of experiments

Allows design of new materials and compositions for specific purposes

It is very relevant to safety analysis to get it right

QinetiQ

© Copyright QinetiQ Limited 2010

© Copyright QinetiQ Limited 2010