NON - LINEAR BEHAVIOUR

LINEAR BEHAVIOUR - asumes small strains and strain rates

SOLIDS - Hooke's law

FLUIDS - Newton's law

VISCOELASTICITY - non linear response as a function of time modeled by assuming a linear relationship between stress and strain. Simple mechanical models were constructed by combining linear elastic and viscous elements

NON - LINEAR BEHAVIOUR - larger strains and strain rates

SOLIDS - will only consider rubber elasticity

FLUIDS AND VISCOELASTIC MATERIALS - some qualitative obsevations

RUBBER ELASTICITY

THERMODYNAMICS REVISTED

$$F = E - TS$$

$$f = \left[\frac{\partial F}{\partial l}\right]_{V,T} = \left[\frac{\partial E}{\partial l}\right]_{V,T} - T\left[\frac{\partial S}{\partial l}\right]_{V,T}$$

Change in internal energy

Change in entropy

For crystalline and glassy solids

$$f \sim \left[\frac{\partial E}{\partial l}\right]_{V,T}$$

For elastomer networks

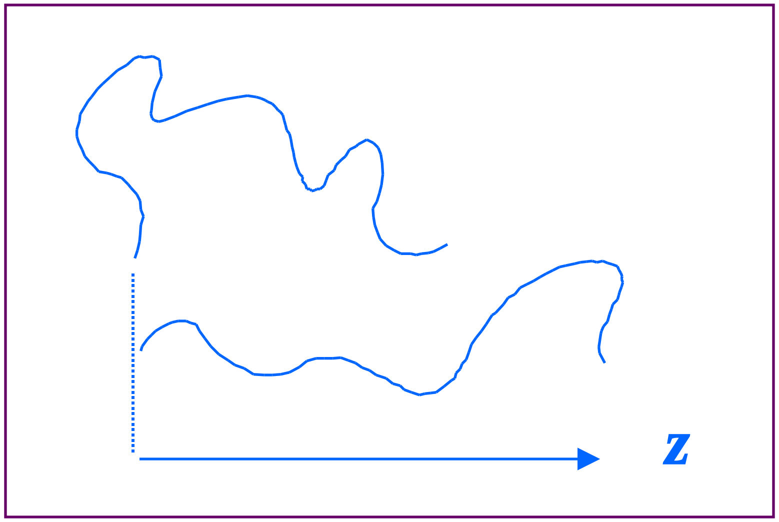
$$f \sim -T\left[\frac{\partial S}{\partial l}\right]_{V,T}$$

STRETCHING OF A SINGLE CHAIN

Stretch along z direction

$$\Omega = P(R) = P(x,y,z) = \left[\frac{\beta^2}{\pi}\right]^{3/2} \exp(-\beta^2 R^2)$$

Probability distribution
Is a Gaussian function
For large N



$$\beta^2 = \frac{3}{2Nl^2} = \frac{3}{2\langle R_0^2 \rangle}$$

$$\Omega = P(R) = P(x,y,z) = \left[\frac{\beta^2}{\pi}\right]^{3/2} \exp(-\beta^2 \{x^2 + y^2 + z^2\})$$

$$S = k \ln \Omega$$

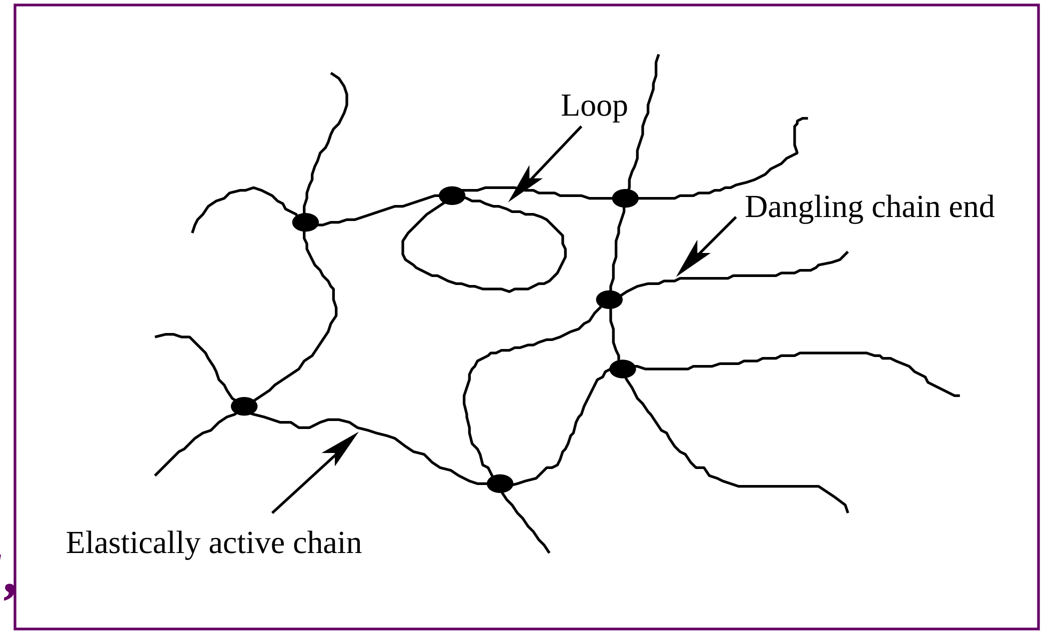
$$\Omega = P(R) = P(x,y,z) = P(0,0,z)$$

$$S = constant - \beta^2 k z^2$$

$$f = 2kT\beta^2 z$$

Hooke's law !
Modulus ~ T!

NETWORKS



We need to consider the stretching of a cross - linked network. real networks have defects.We will consider the stretching of a model network where the functionality of all the cross link points is identical, there are no dangling ends, and the number of segments between all the junction points is the same

RUBBER ELASTICITY THEORY

Define extension ratio

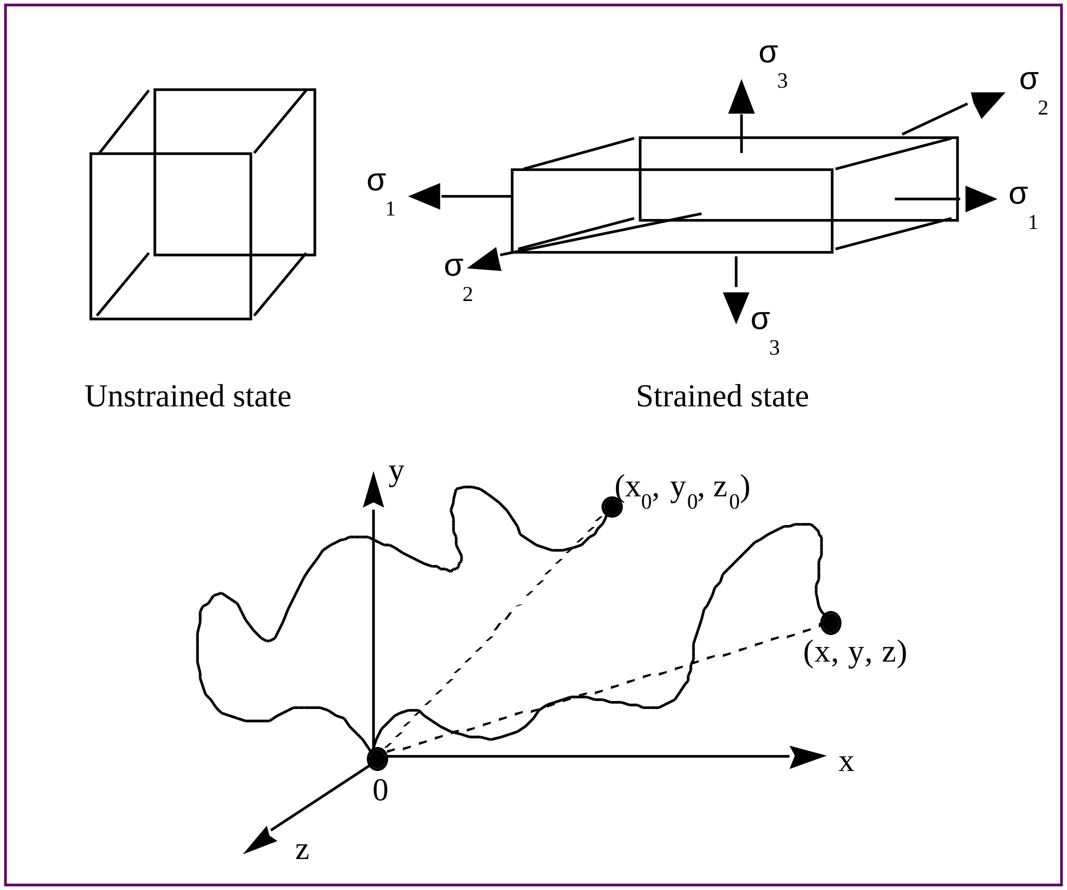
$$\lambda = l/l_0$$

Assume no change in Volume upon stretching

$$\lambda_1 \lambda_2 \lambda_3 = 1$$

In the unstrained state

$$R_0^2 = x_0^2 + y_0^2 + z_0^2$$



Hence $$s_0 = constant - k\beta^2 (x_0^2 + y_0^2 + z_0^2)$$

RUBBER ELASTICITY THEORY

Affine assumption - chaindeforms in exact proportion to Sample as a whole (parent cube on previous overhead)

$$x = \lambda_1 x_0 \quad , y = \lambda_2 y_0 \quad , z = \lambda_3 z_0$$

$$s = constant - \beta^2 k\,(x^2 + y^2 + z^2)$$

$$= constant - \beta^2 k\,(x_0^2 \lambda_1^2 + y_0^2 \lambda_2^2 + z_0^2 \lambda_3^2)$$

$$\Delta s = constant - \beta^2 k\,((\lambda_1^2 - 1)x_0^2 + (\lambda_2^2 - 1)y_0^2 + (\lambda_3^2 - 1)z_0^2)$$

Using $S = \Sigma \Delta s$ *And*

$$\Sigma R_0^2 = \Sigma x_0^2 + \Sigma y_0^2 + \Sigma x_0^2$$

$$(1/3)\Sigma R_0^2 = \Sigma x_0^2 = \Sigma y_0^2 = \Sigma x_0^2$$

$$\Sigma R_0^2 = N \langle R_0^2 \rangle$$

Obtain

$$\Delta S = -(1/2)Nk(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)$$

RUBBER ELASTICITY THEORY

$$\Delta S = -(1/2)Nk(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)$$

Constant volume assumption

$$\lambda_1 \lambda_2 \lambda_3 = 1$$

For simple extension in the x direction the affine Assumption gives

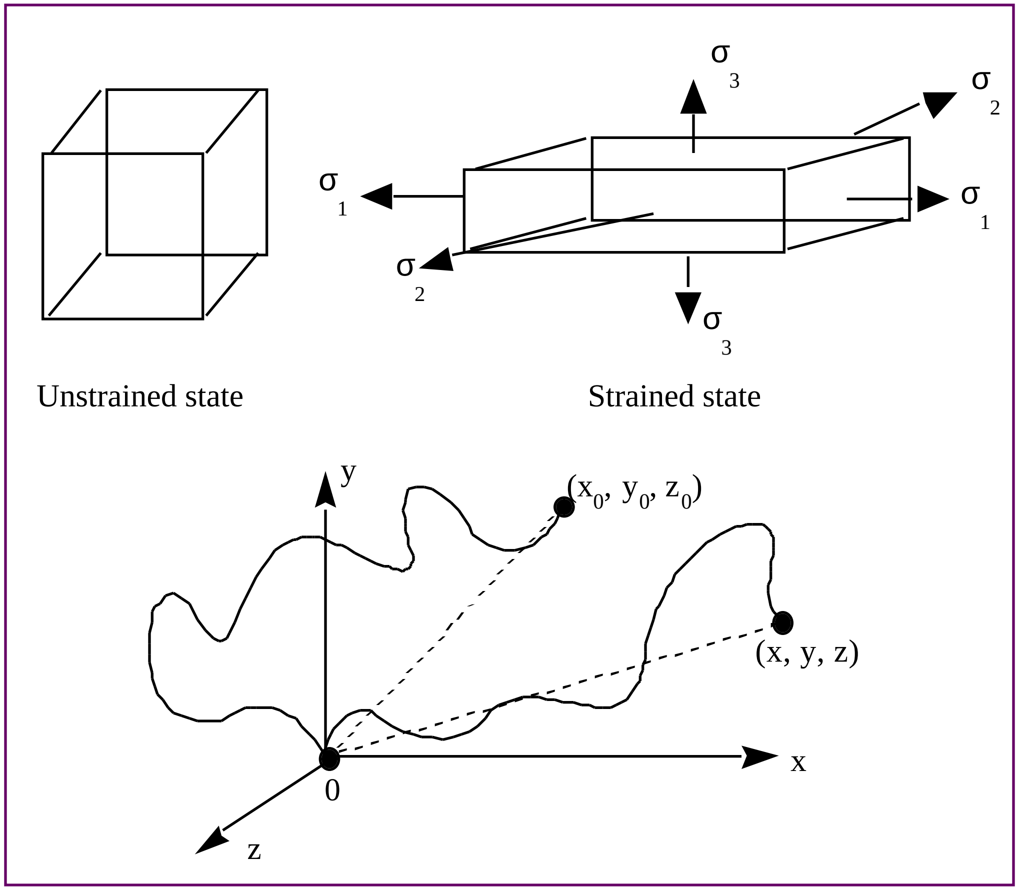
$$\lambda_2 = \lambda_3$$

$$\lambda_1 = \frac{1}{\lambda_3 \lambda_2}$$

Substituting

$$\Delta S = -(1/2)Nk(\lambda_1^2 + 2\lambda_1^2 - 3)$$

Hence

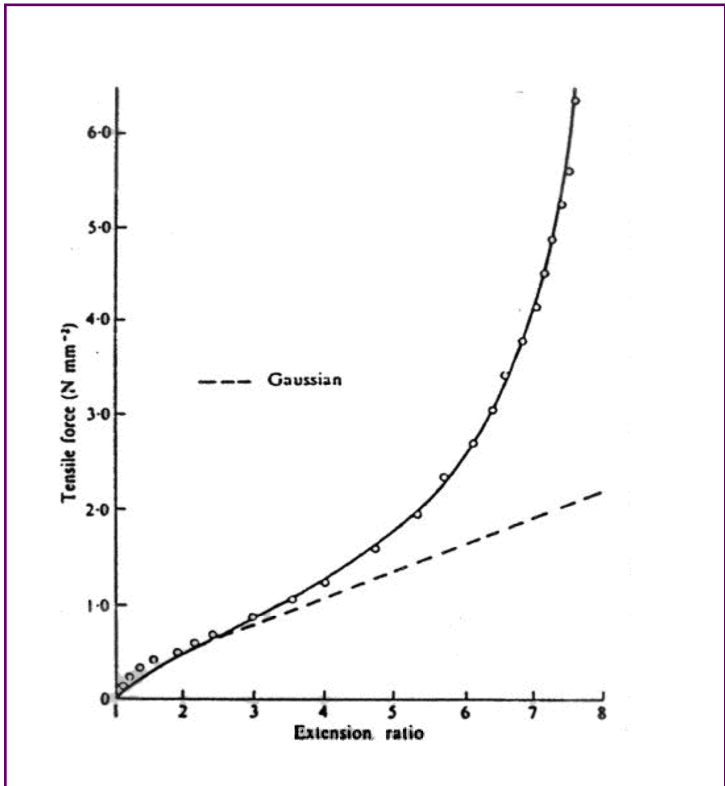


$$f = NkT(\lambda_1^2 - 1\lambda_1^2)$$ *or* $$f = E(\lambda_1^2 - 1\lambda_1^2)$$ *where* $$E = NkT$$

Question - what would happen to a stretched rubber sample upon heating ?

RUBBER ELASTICITY THEORY

- comparison to experiment



$$f = NkT\left(\lambda_1 - 1/\lambda_1^2\right)$$

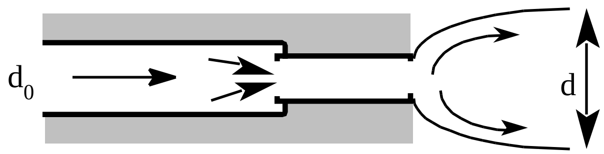
Agreement not bad at strains up to ~ 300%,but the semi - empirical Mooney - Rivlin equation provides a better fit

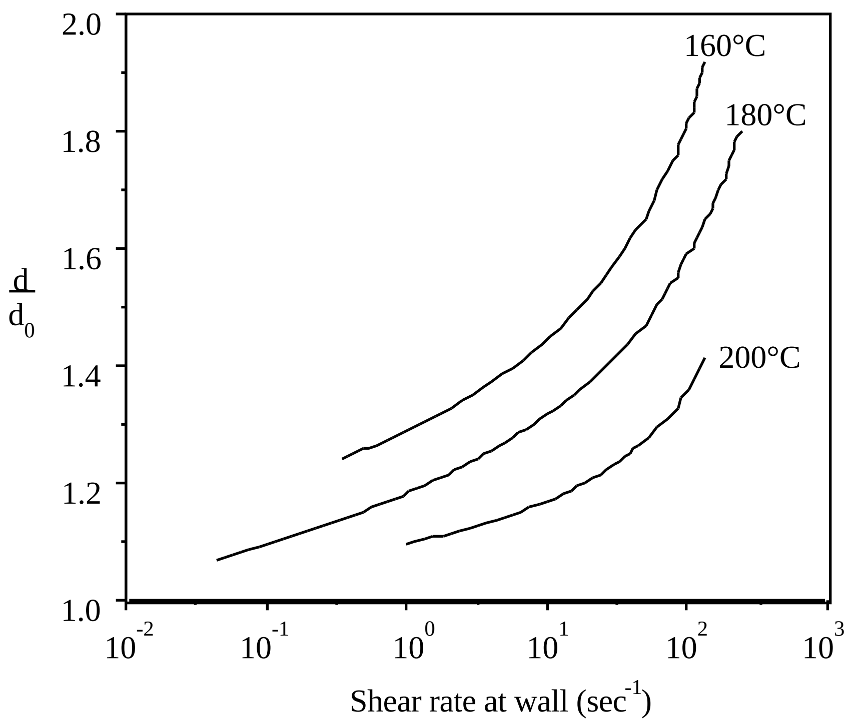
$$\sigma = 2\left(C_1 + C_2/\lambda_1\right)\left(\lambda_1 - 1/\lambda_1^2\right)$$

More advanced theories (eg Flory Constrained Junction Model) does a better job,but this is beyond the scope of this course

Reproduced with permission from L. R. G. Treloar,
The Physics of Rubber Elasticity, Third Ed.,
Clarendon Press, Oxford, 1975.

NON - LINEAR BEHAVIOUR OF POLYMER MELTS - some qualitative observations

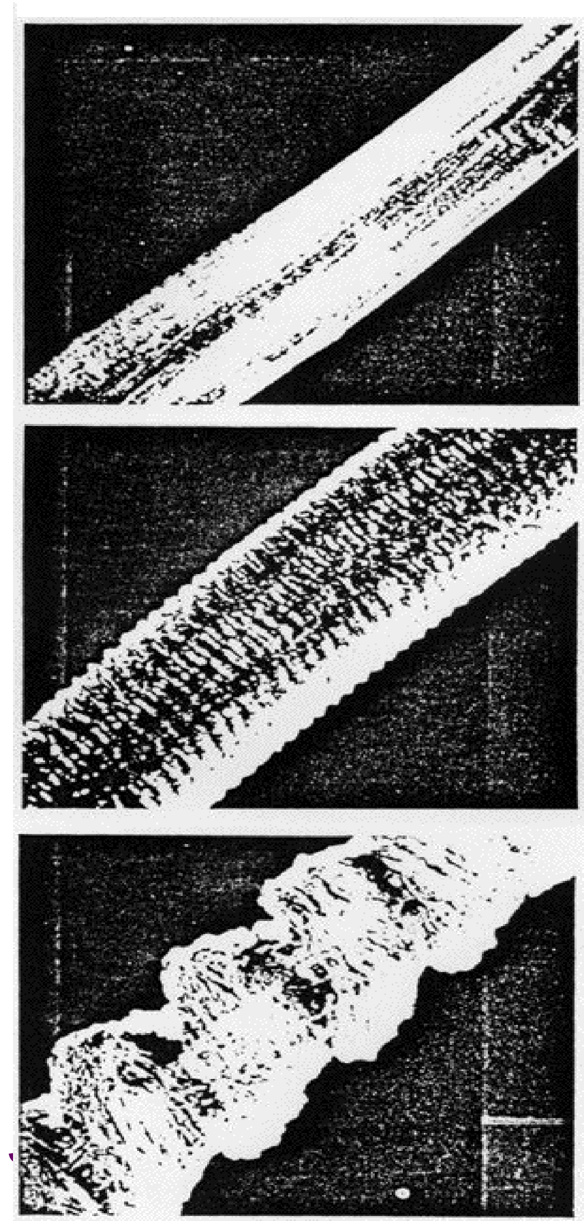




JET SWELLING

Drawn schematically from the data of Burke and Weiss, Characterization of Materials in Research, *Syracuse University Press, 1975.*

MELT FRACTURE



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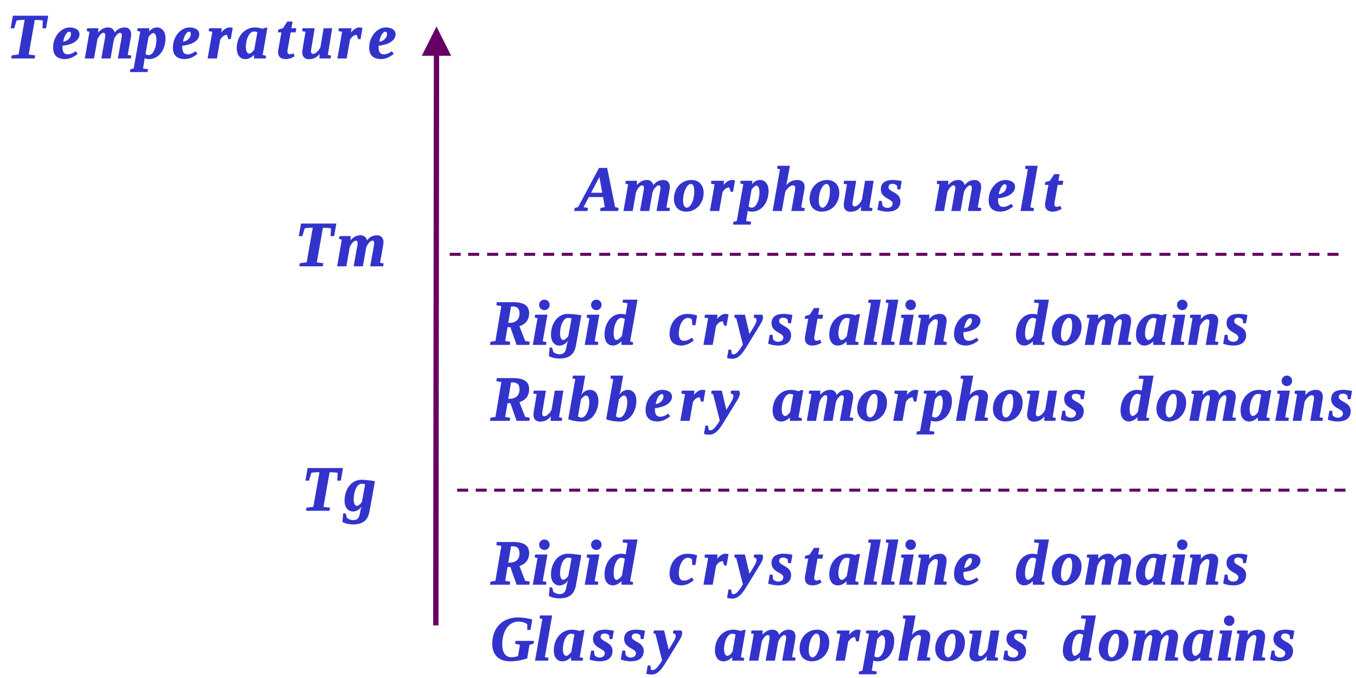
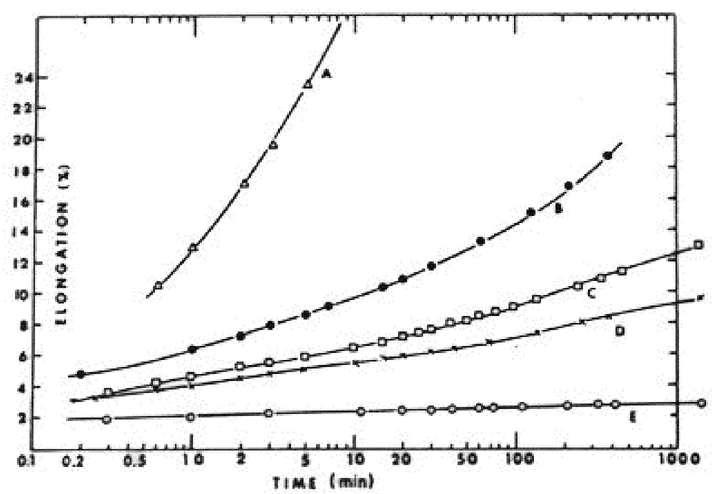
SEMI - CRYSTALLINE POLYMERS

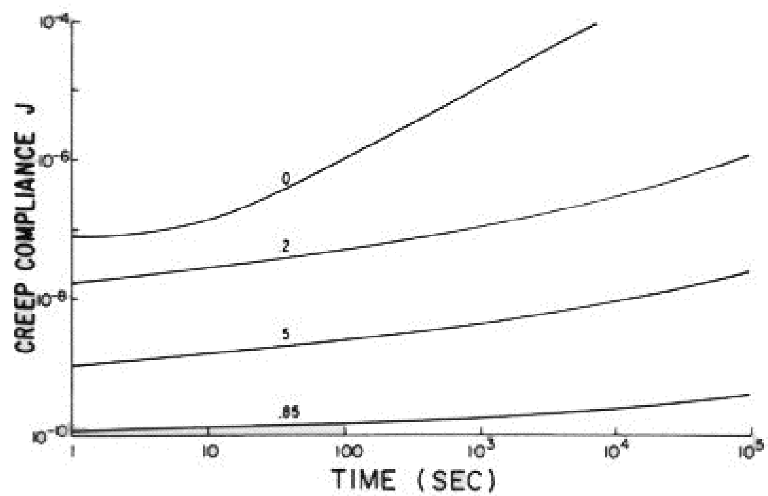
NON - LINEAR RESPONSE TO STRESS.SIMPLE MODELS AND THE TIME - TEMPERATURE SUPERPOSITION PRINCIPLE DO NOT APPLY



EFFECT OF CROSS - LINKING AND CRYSTALLINITY ON CREEP



INCREASING CROSS-LINKING



INCREASING CRYSTALLINITY