

Glass Transition Temperature (T_g) & Mechanical Model of Viscoelastic Materials

Instructor : Prof. Bishakh Bhattacharya
Dept. of Mechanical Engineering
IIT Kanpur
India

E-mail : *bishakh@iitk.ac.in*



Smart Materials Structures and Systems
Laboratory
IIT Kanpur

Contents

- ✓ What is Glass Transition temperature, T_g ?
- ✓ How to develop a Master Curve?
- ✓ Factors affecting T_g
- ✓ Can we develop Mechanical Models?



Glass Transition Temperature (T_g)

- ✓ Definition : The temperature at which the polymer experiences the **transition** from **rubbery to rigid states**.
- ✓ **Below T_g** , it becomes **hard and brittle** like glass, due to **reduction** in the **motion of large segments of molecular chains** with decreasing temperature.
- ✓ Different for each polymer.
- ✓ **Glass transition** happens **only** to polymers in the **amorphous state**.

<i>Material</i>	<i>Glass Transition Temperature [°C (°F)]</i>	<i>Melting Temperature [°C (°F)]</i>
Polyethylene (low density)	-110 (-165)	115 (240)
Polytetrafluoroethylene	-97 (-140)	327 (620)
Polyethylene (high density)	-90 (-130)	137 (279)
Polypropylene	-18 (0)	175 (347)
Nylon 6,6	57 (135)	265 (510)
Polyester (PET)	69 (155)	265 (510)
Poly(vinyl chloride)	87 (190)	212 (415)
Polystyrene	100 (212)	240 (465)
Polycarbonate	150 (300)	265 (510)

$$\int dx = dU - T dS$$

Work done on a material
system = $\int dx = \sigma_{ij} \epsilon_{ij}$

Change of internal energy = dU

Change of entropy = dS

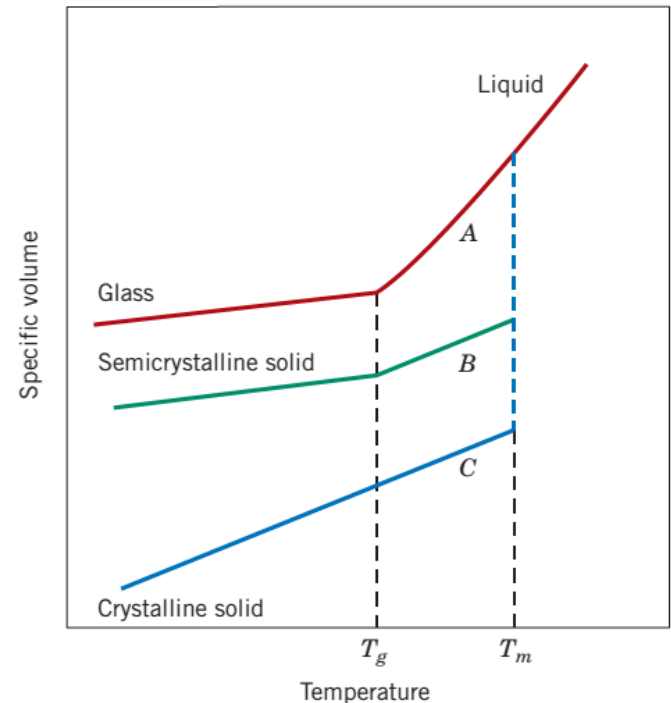


- **Hard plastics** like **polystyrene** and **poly(methyl methacrylate)**, are used **below their glass transition temperatures** (*glassy state*) as their T_g 's are well above room temperature (around 100°C).
- **Rubber elastomers** like **polyisoprene** and **polyisobutylene**, are used **above their T_g 's**, (*rubbery state*), where they are soft and flexible.

Curve A : Amorphous polymer

Curve B : Semi – crystalline solid

Curve C : 100% Crystalline polymers - (hypothetical case)



Five Regions of Viscoelastic behavior

Viscoelasticity = (Viscous + Elastic) behavior

Phase I : Glassy region

- ✓ Relatively high modulus
- ✓ Very hard
- ✓ High resistance to flow

Phase II : Leathery/Glass-transition region

- ✓ Sharp decrease in the elastic modulus
- ✓ Deformation not totally recoverable

Phase III : Rubbery region

- ✓ both elastic and viscous components present
- ✓ Modulus falling rate stabilizes
- ✓ Elastic – high strain rate
- ✓ Viscous – low strain rate

Phase IV : Rubbery flow region

- ✓ Viscosity starts dominating
- ✓ Modulus starts falling

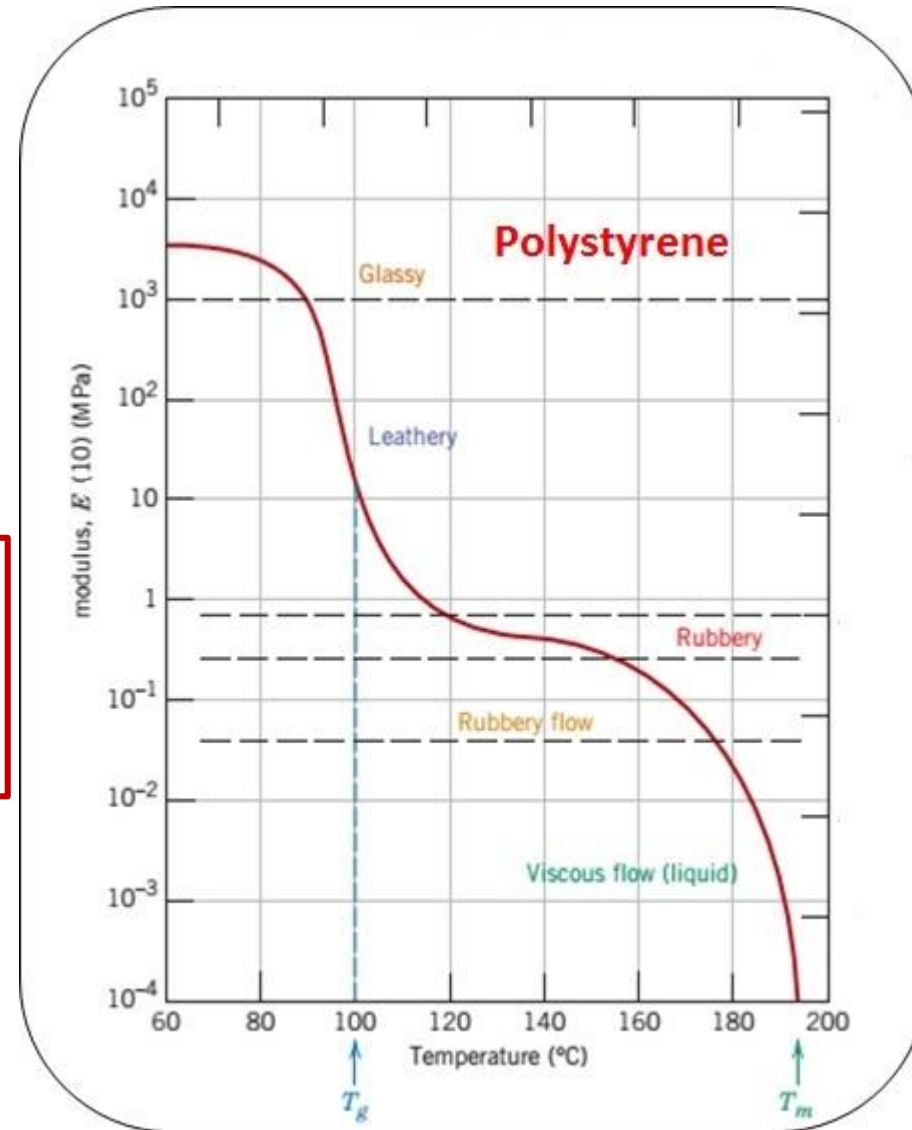
Phase V : Viscous flow region

- ✓ Modulus drops steeply

Finally - decomposition!



Smart Materials Structures and Systems
Laboratory
IIT Kanpur



Time (Frequency)-Temperature shift Factor

- Data available over a limited time scale is generated at several temperatures
- A temperature is selected as reference temperature. The remaining temperature profile is shifted with respect to time (frequency) by an amount necessary to match up the portions of the profile.
- The resulting extended profile for the reference temperature is called a “master curve”.



Shift Factor

- The factor a_T used to bring the curves at various temperatures into congruence is given by: $a_T = \frac{t_T}{t_0}$ where t_T is the time required to reach a particular response at temperature T and t_0 is the time required to reach the same response at temperature T_0 .
- In the frequency domain: $a_{T\omega} = \frac{\omega_{T_0}}{\omega_T}$ since frequency is reciprocal to time.

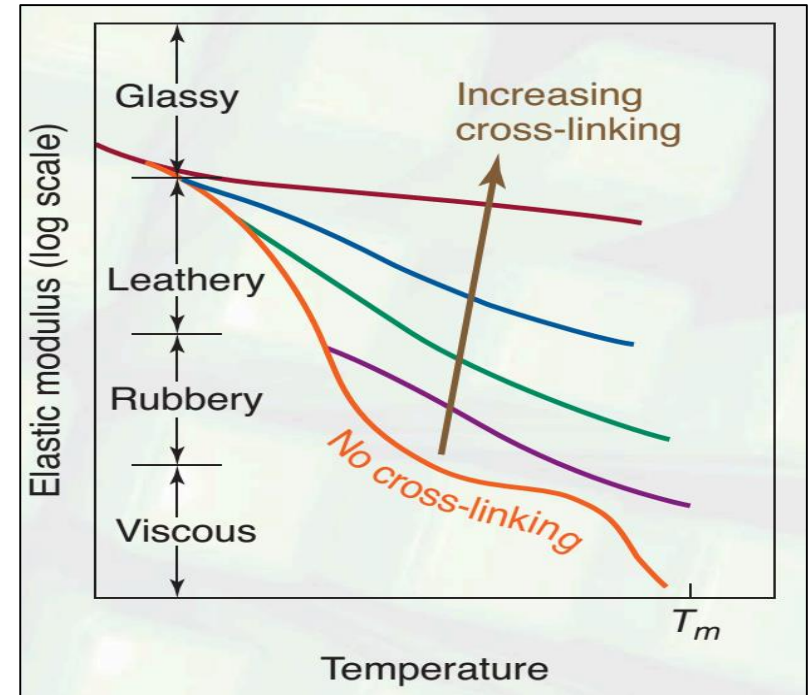
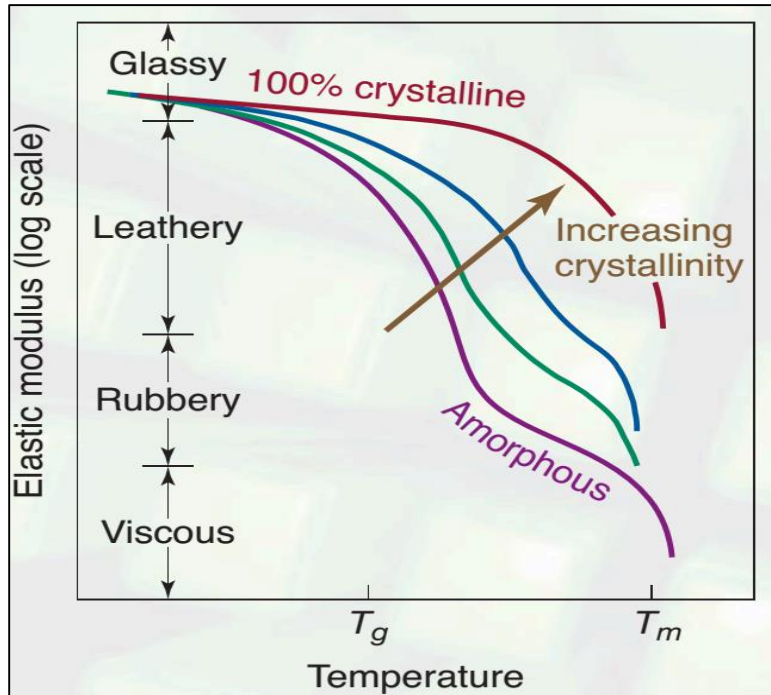


Shift Factor – contd.

- Several attempts are made to predict the temperature dependence of the shift factor
- Ferry proposed the following: $\log(a_T) = \left[\frac{C_1(T-T_0)}{C_2+T-T_0} \right]$
where C_1 and C_2 are material constants.
- Williams-Landel-Ferry proposed for $T_g - 50^\circ < T < T_g + 50^\circ$, and $T_0 = T_g$
- $\text{Log}(a_T) = [-8.86(T - T_g)]/[101.6 + T - T_g]$
(WLF Equation)



Effect of Temperature



Reference: Kalpakjian, Schmid - Manufacturing Processes for Engineering Materials, 5th ed.



Factors affecting T_g

- Chain Length
- Chain stiffness
- Plasticizers
- Crosslinking
- Co-polymers



Effect of Chain Length

- **As molecular weight increases, T_g also increases.**
 - ✓ High density of branches – reduces chain mobility.
 - ✓ Crosslinking - restricts the molecular motion.
- **As molecular weight decreases, T_g also decreases**
 - ✓ Easier movement of molecules.
 - ✓ More inherent free volume in the polymer.

$$T_g = T_{g\infty} - \frac{C}{\overline{M}_n}$$

$T_{g\infty}$: Glass transition temp. at infinite chain length

C : Polymeric constant

Number average molecular weight, $\overline{M}_n = \frac{\sum M_i N_i}{\sum N_i}$

Material	$T_{g\infty}$	C
PVC	351	81000
PMMA	387	210000
PS	373	120000

Where, M_i = molecular weight of i_{th} polymer chain;
 N_i = number of chains of that molecular weight.

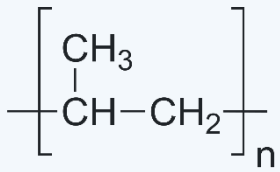


Effect of Chain stiffness

Chain stiffness - Controlled by the **ease of rotation** about the **chemical bonds** along the chain.

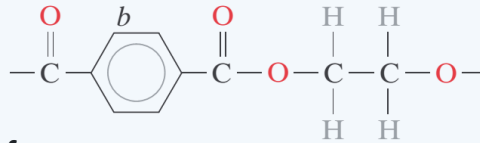
- ✓ Presence of double bonds and aromatic groups lowers chain flexibility and thus increases T_g .
- ✓ Bulky or large side groups restricts chain rotational freedom and flexibility and thus increases T_g .

Example



Polypropylene

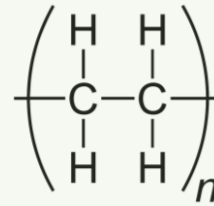
$$\begin{array}{l} T_g = -18^\circ\text{C} \\ T_m = 175^\circ\text{C} \end{array}$$



Polyester

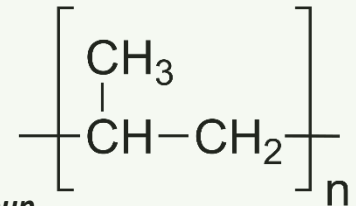
$$\begin{array}{l} T_g = 69^\circ\text{C} \\ T_m = 265^\circ\text{C} \end{array}$$

Presence of
double bond
&
aromatic ring



Polyethylene

$$\begin{array}{l} T_g = -110^\circ\text{C} \\ T_m = 115^\circ\text{C} \end{array}$$



Polypropylene

$$\begin{array}{l} T_g = -18^\circ\text{C} \\ T_m = 175^\circ\text{C} \end{array}$$

Methyl side group
heavier than
H-atom



Effect of Plasticizers

- Plasticizers are the additives that increase the plasticity or fluidity of a material and reduces the hardness and stiffness.
- Example: Phthalate esters in PVC applications imparting improved flexibility and durability.
- Thus, addition of **plasticizers reduces T_g**



Effect of Crosslinking

- Cross-linking **reduces chain mobility**, so T_g will be **increased**.



T_g for Co-polymers

- Made from two different monomers.
- T_g will be some kind of average between the two monomeric materials.
 - ✓ Assuming they were converted into polymer.
 - ✓ Will be based roughly on the weight fraction (%) of each material present in the copolymer.

$$\frac{1}{T_g} = \frac{W_{f1}}{T_{g1}} + \frac{W_{f2}}{T_{g2}}$$

T_g = Glass transition temperature of copolymer (in Kelvin)

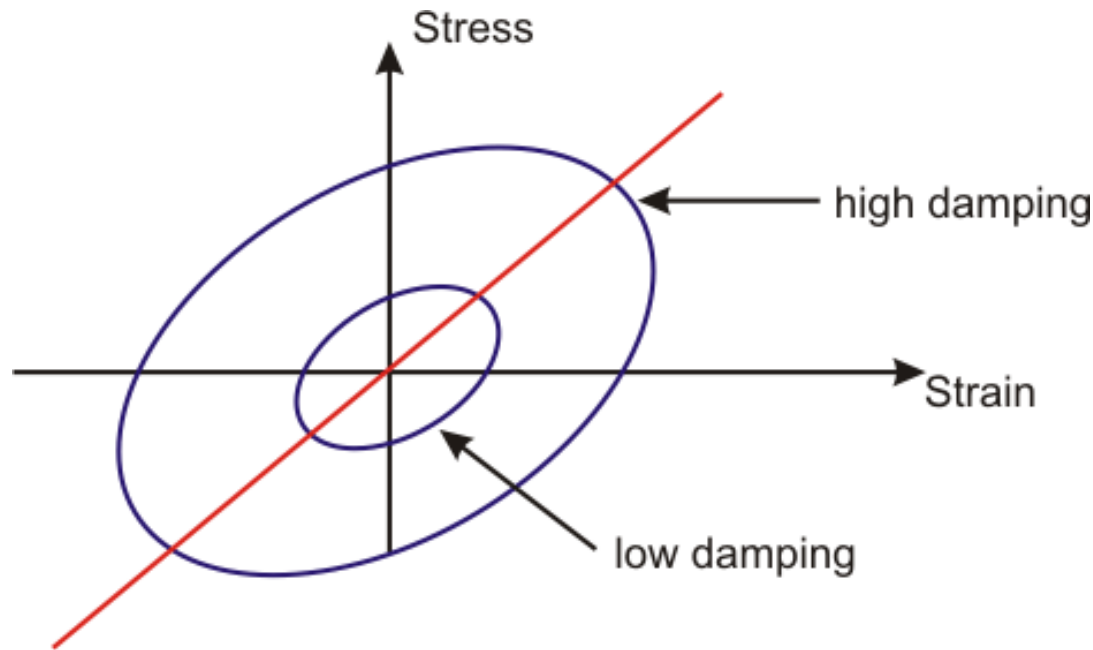
W_{f1} & T_{g1} = Weight fraction & T_g of first monomer (in Kelvin)

W_{f2} & T_{g2} = Weight fraction & T_g of second monomer (in Kelvin)



Mechanical Model of Viscoelastic Materials

Viscoelastic Materials consist of polymers of variable chain length and filters resulting in the following stress strain diagram



Slope of the major axis of the ellipse is a measure of material stiffness while the ratio of the minor to major axis is a measure of damping



Stress – Strain Relationship

- The force-deformation relationship in a polymer is governed by the loading rate.
- The Stress(σ)–Strain(ε) relationship, in the most general case for the polymers is,

$$[a_0 + a_1 \left(\frac{\partial}{\partial t}\right) + a_2 \left(\frac{\partial^2}{\partial t^2}\right) + \dots + a_n \left(\frac{\partial^n}{\partial t^n}\right)] \sigma = [b_0 + b_1 \left(\frac{\partial}{\partial t}\right) + b_2 \left(\frac{\partial^2}{\partial t^2}\right) + \dots + b_m \left(\frac{\partial^m}{\partial t^m}\right)] \varepsilon$$

Or
$$a_0 \sigma + \sum_{i=1}^n a_i \frac{d^i \sigma}{dt^i} = b_0 \varepsilon + \sum_{j=1}^m b_j \frac{d^j \varepsilon}{dt^j}$$
 Generalized Hooke's Law

- If all the **coefficients** $a_0, a_1 \dots a_n$ and $b_0, b_1 \dots b_m$ are **constant** – **Linear Viscoelastic Material**

For metals, $a_1 \dots a_n = 0$

$b_1 \dots b_m = 0$

Then, $a_0 \sigma = b_0 \varepsilon$

Thus, $\sigma = (b_0/a_0) \varepsilon = E \varepsilon$



Kelvin-Voight (K-V) Mechanical Model

- **Parallel combination** of a linear spring of **stiffness k** and a viscous dashpot of **damping coefficient η**

Linear Spring (elastic) : Stress is proportional to strain

$$\sigma_1 = E \varepsilon_1$$

Linear Viscous dashpot : Stress is proportional to strain rate

$$\sigma_2 = \eta \frac{d\varepsilon_2}{dt}$$

For parallel combination

$$\varepsilon = \varepsilon_1 = \varepsilon_2 \quad \sigma = \sigma_1 + \sigma_2$$

$$\sigma = E\varepsilon + \eta \frac{d\varepsilon}{dt}$$

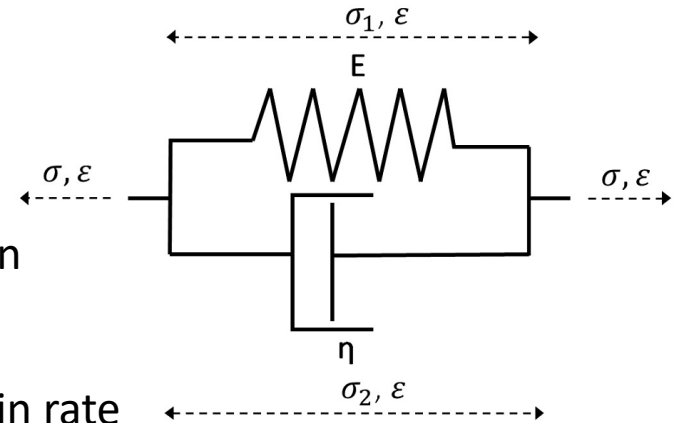
Or

$$a_0\sigma + a_1 \frac{d\sigma}{dt} = b_0\varepsilon + b_1 \frac{d\varepsilon}{dt}$$

$$a_0\sigma + \sum_{i=1}^n a_i \frac{d^i\sigma}{dt^i} = b_0\varepsilon + \sum_{j=1}^m b_j \frac{d^j\varepsilon}{dt^j}$$

Hence, for this model

$$\begin{aligned} a_0 &= 1, & a_1 &= 0, \\ b_0 &= E, & b_1 &= \eta \end{aligned}$$

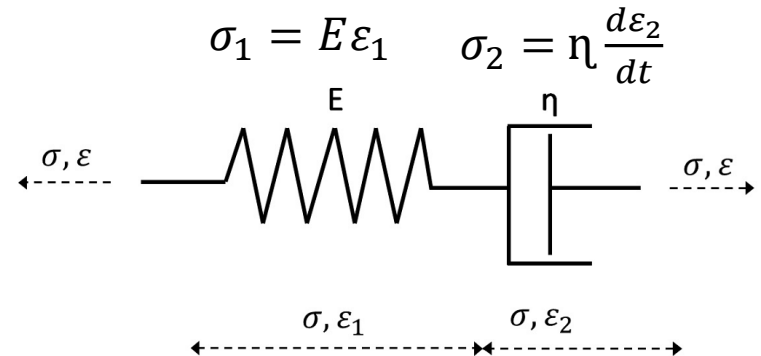


Maxwell Mechanical Model

In this model, the **spring** and **dashpot** are connected in **series**. In this case,

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \quad \dots\dots\dots(1)$$

$$\sigma = \sigma_1 = \sigma_2 \quad \dots\dots\dots(2)$$



Taking derivative of strain w.r.t time (eq.1), we get

$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_1}{dt} + \frac{d\varepsilon_2}{dt} \quad \dots\dots\dots(3)$$

$$\text{Since, } \frac{d\sigma_1}{dt} = E \frac{d\varepsilon_1}{dt}$$

On Substituting the values in right hand side, we get

$$\frac{d\varepsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

$$a_0\sigma + \sum_{i=1}^n a_i \frac{d^i\sigma}{dt^i} = b_0\varepsilon + \sum_{j=1}^m b_j \frac{d^j\varepsilon}{dt^j}$$

Hence, for this model

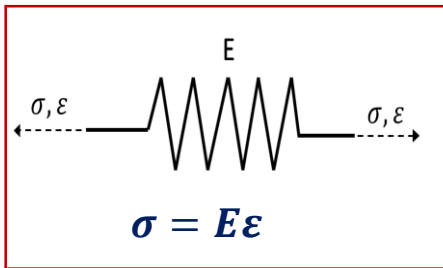
$$a_0 = 1/\eta, a_1 = 1/E, \\ b_0 = 0, b_1 = 1$$



Parameter Models

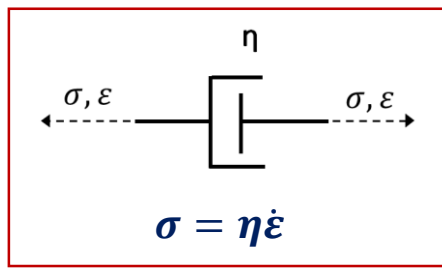
1 PARAMETER

Linear Elastic Spring



- Perfectly elastic behaviour

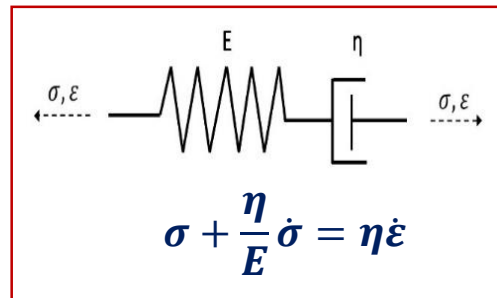
Linear Viscous dashpot



- Perfectly viscous behaviour

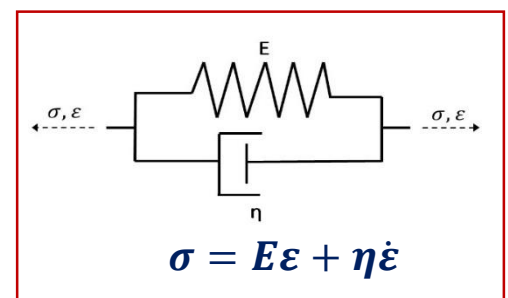
2 PARAMETER

Maxwell model



- Predicts fluid-like behavior.
- Do not describe recovery.

Kelvin – Voigt model



- Predicts solid-like behavior.
- Do not describe stress relaxation.



3 Parameter Model of VEM

We have discussed about two basic models of **VEM Kelvin-Voight (K-V) model** and **Maxwell model**. However, to simulate the complex time dependent behavior of complex VEMs more advanced models are often required. It is easier to establish the constitutive relationship of such systems initially in the frequency domain and then by using inverse Laplace transformation the time- domain relationship could be obtained.

3-Parameter Model of the VEM

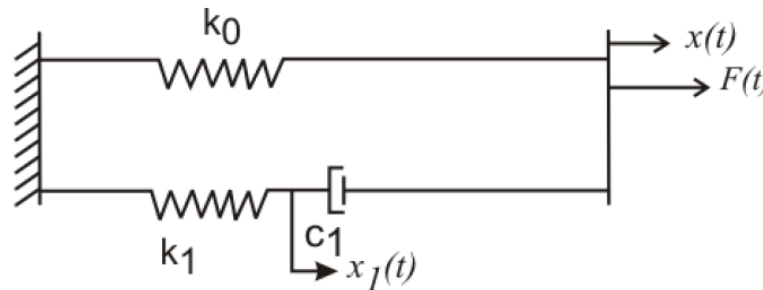


Figure 13.1: 3 parameter model

Consider the 3- parameter model as shown in Fig (13.1). Force applied to the system is $F(t)$ and the displacement at the point of application is $x(t)$, spring k_1 and damper c_1 are in series and the combination is connected in parallel to spring k_0 .

The equivalent stiffness of the system in frequency domain could be written as $k_0 + \frac{sk_1c_1}{k_1 + sc_1}$ where s is the Laplace variable



Transforming $F(t)$ in the frequency domain to $\bar{F}(s)$ and $x(t)$ to $X(s)$, one can express the relationship between them as

$$\left(k_0 + \frac{sk_1c_1}{k_1 + sc_1}\right)X(s) = \bar{F}(s)$$

or $(k_0k_1 + sk_0c_1 + sk_1c_1)X(s) = (k_1 + sc_1)\bar{F}(s)$

Considering the characteristic length of the system to be 'l' and cross sectional area A, we can represent the above relationship in terms of stress $\bar{\sigma}(s)\left(\frac{\bar{F}(s)}{A}\right)$, and strain $\bar{\epsilon}(s)\left(\frac{X(s)}{l}\right)$

as

$$(k_0k_1 + sk_0c_1 + sk_1c_1)\bar{\epsilon}(s) = (k_1 + sc_1)\bar{\sigma}(s) \times \frac{A}{l}$$

After inverse Laplace transformation, the governing equation in time domain: may expressed as

$$[k_1\sigma(t) + c_1\dot{\sigma}(t)] \times \frac{A}{l} = [k_0k_1\epsilon(t) + k_0c_1\dot{\epsilon}(t) + k_1c_1\dot{\epsilon}(t)]$$

or
$$\sigma(t) + \frac{c_1}{k_1}\dot{\sigma}(t) = \frac{l}{A}\left[k_0\epsilon(t) + \left(c_1 + \frac{k_0c_1}{k_1}\right)\dot{\epsilon}(t)\right]$$

$$\sigma(t) + \frac{c_1}{k_1}\dot{\sigma}(t) = \lambda\left[k_0\epsilon(t) + \left(c_1 + \frac{k_0c_1}{k_1}\right)\dot{\epsilon}(t)\right] [\lambda = l/A]$$

Hence, the system parameters may be expressed as

$$a_0 = 1, \quad a_1 = \lambda_1 = c_1/k_1$$

$$b_0 = \lambda k_0, \quad b_1 = \lambda \frac{k_0c_1 + k_1c_1}{k_1}$$



Other Variants of the Three Parameter Model

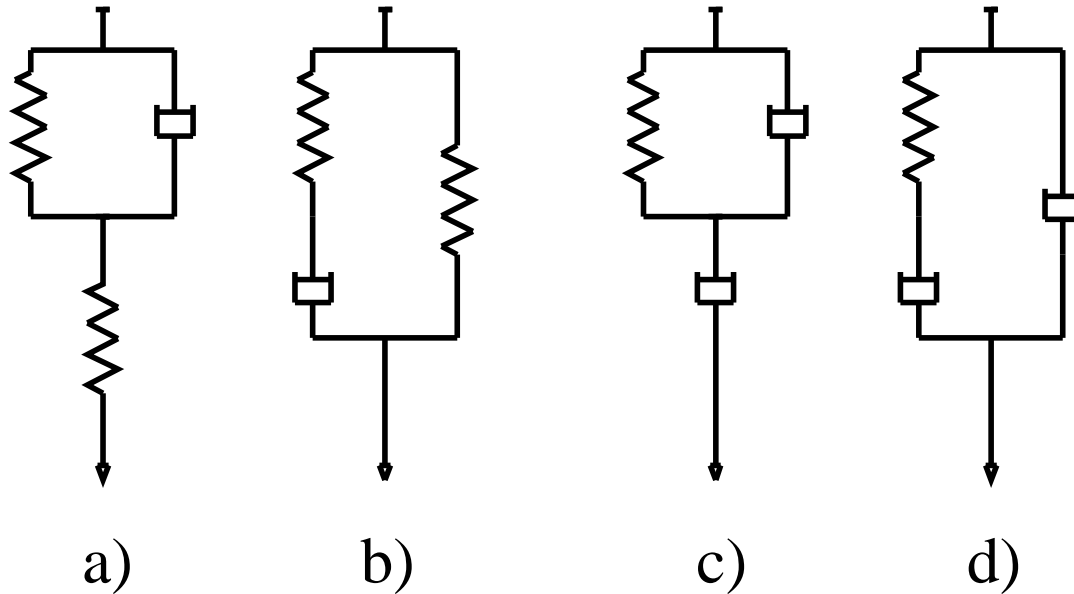


Figure 2: The mechanical representations of the Zener model, see a), b) and of the anti-Zener model, see c), d), where: a) spring in series with Voigt, b) spring in parallel with Maxwell, c) dashpot in series with Voigt, d) dashpot in parallel with Maxwell.



4-Parameter (Burgers) Model

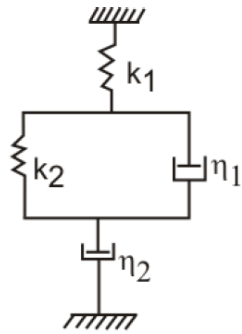


Figure 13.2: Four parameter model

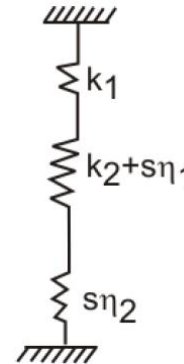


Figure 13.3: Equivalent 4 parameter model

Figure 13.2 shows a four parameter model. In the frequency domain, the equivalent model has been shown in Figure 13.3

The stress-strain relationship may be expressed as

$$\sigma = \frac{k_1(k_2 + s\eta_1)s\eta_2}{k_1(k_2 + s\eta_1) + sk_1\eta_2 + sk_2\eta_2 + s^2\eta_1\eta_2} \varepsilon$$

or

$$\sigma = \frac{sk_1k_2\eta_2 + s^2k_1\eta_1\eta_2}{k_1k_2 + sk_1\eta_1 + sk_1\eta_2 + sk_2\eta_2 + s^2\eta_1\eta_2} \varepsilon$$



After inverse Laplace transformation one may write it as:

$$k_1 k_2 \sigma + (k_1 \eta_1 + k_1 \eta_2 + k_2 \eta_2) \dot{\sigma} + \eta_1 \eta_2 \ddot{\sigma} = k_1 k_2 \eta_2 \dot{\epsilon} + k_1 \eta_1 \eta_2 \ddot{\epsilon}$$

Considering the characteristic length of the system to be 'l' and cross sectional area A, we can represent the above relationship in terms of stress $\bar{\sigma}(s) \left(\frac{F(s)}{A} \right)$ and strain as $\bar{\epsilon}(s) \left(\frac{X(s)}{l} \right)$

$$(k_0 k_1 + s k_0 c_1 + s k_1 c_1) \bar{\epsilon}(s) = (k_1 + s c_1) \bar{\sigma}(s) \times \frac{A}{l}$$

After inverse Laplace transformation, the governing equation in time domain may be expressed as

$$[k_1 \sigma(t) + c_1 \dot{\sigma}(t)] \times \frac{A}{l} = [k_0 k_1 \epsilon(t) + k_0 c_1 \dot{\epsilon}(t) + k_1 c_1 \dot{\epsilon}(t)]$$

Hence, the system parameters are

$$\begin{aligned} a_0 &= \frac{k_1 k_2}{\eta_1 \eta_2} & b_0 &= 0 \\ a_1 &= \frac{k_1}{\eta_2} + \frac{k_1}{\eta_1} + \frac{k_2}{\eta_1} & b_1 &= \frac{k_1 k_2}{\eta_1} \\ a_2 &= 1 & b_2 &= k_1 \end{aligned}$$

