Elements of Polymer Structure and Viscoelasticity

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Mechanics and Materials II 2.002

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Outline

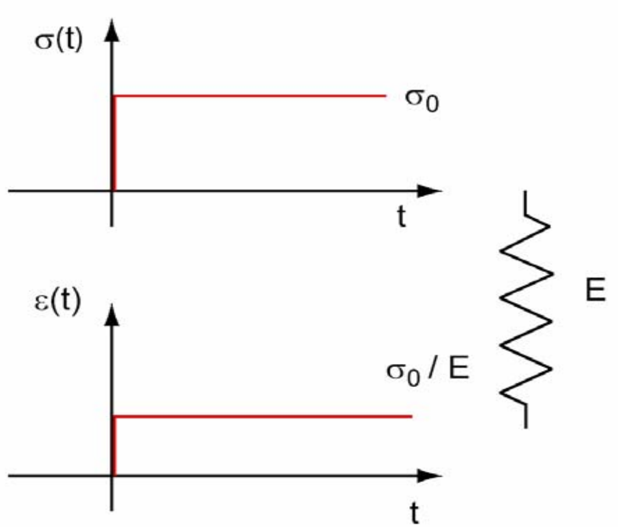
- Elements of polymer structure
    - Linear vs. branched;
    - Vinyl polymers and substitutions
    - Packing of polymer chains
        - Random/amorphous
            - Glass transition temperature, T_G
        - Semi-crystalline
            - Crystalline volume fraction; melting temperature
            - Amorphous T_G
- Elements of linear viscoelasticity
    - Creep and relaxation
    - Analogue models

Idealized Linear Elastic Response

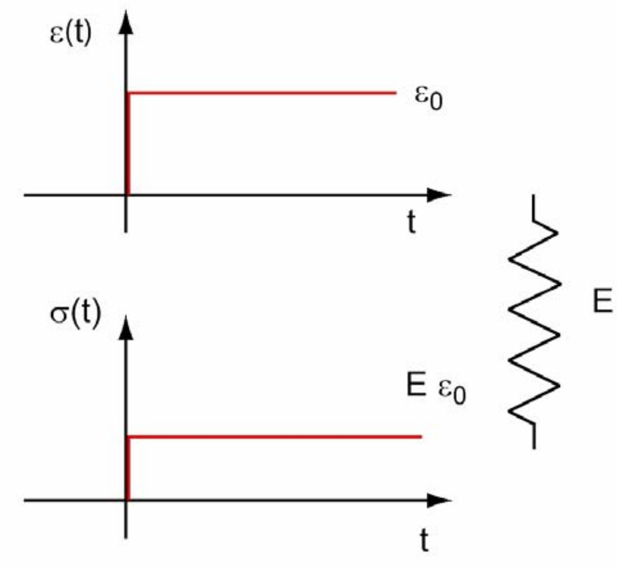
Linear elasticity: $\sigma(t) = E\,\epsilon(t)$

[NO] Creep

INPUT:



[NO] Relaxation

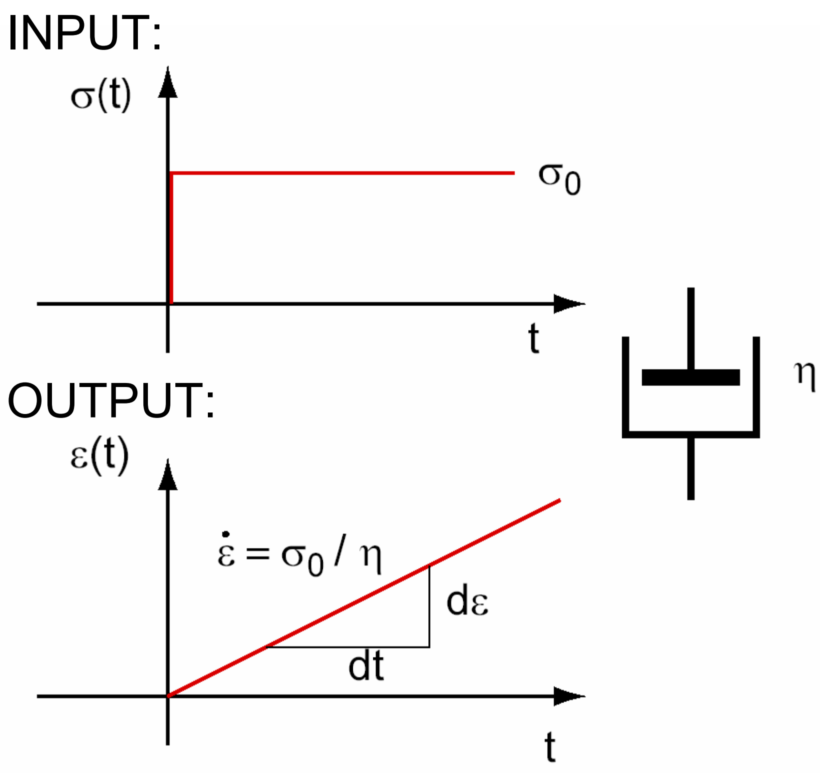


Note: units of E are stress.

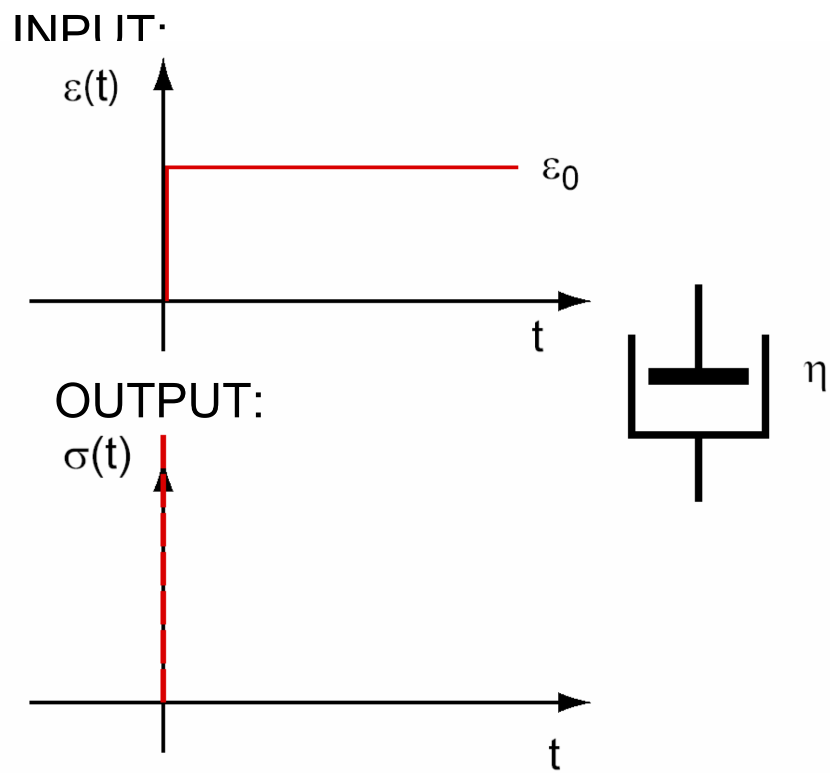
Idealized Linear Viscous Response

Linear viscosity: $\sigma(t) = \eta \frac{d\epsilon(t)}{dt} \equiv \eta\, \dot{\epsilon}(t)$

Creep:



Relaxation:



Note: units of η are stress × time
e.g., sec × MPa

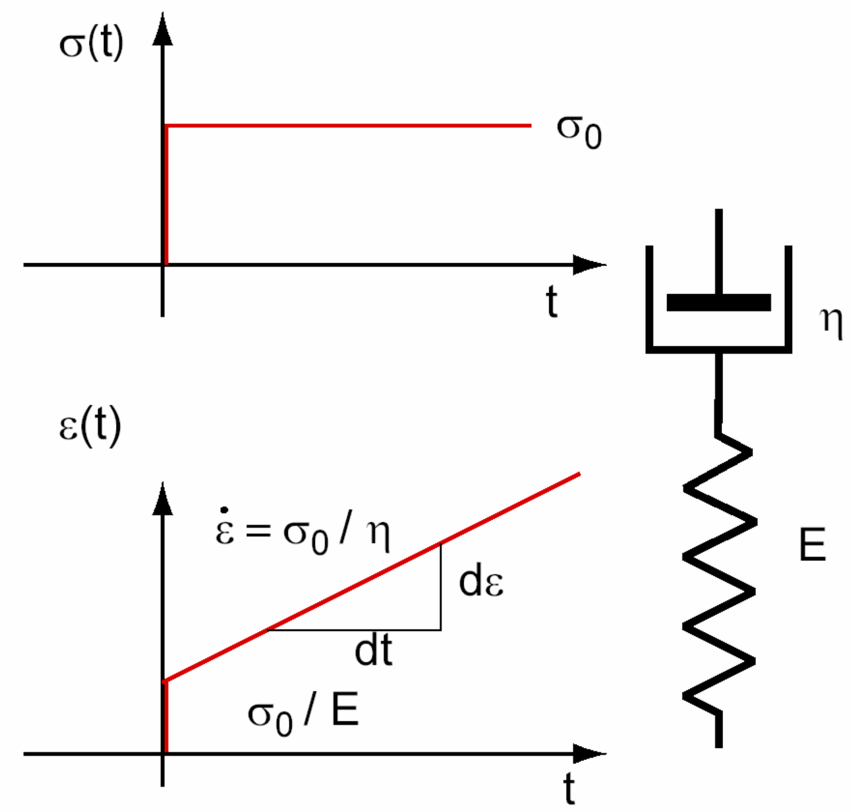
The strain rate (and therefore stress) becomes arbitrarily large during an infinitesimal time interval, and then, like the strain-rate, goes to zero

Maxwell Model: an Idealized Linear Viscoelastic Response

Creep:

INPUT:

OUTPUT:



$$
\begin{aligned}
\epsilon(t) &= \epsilon_{\text{elastic}}(t) + \epsilon_{\text{viscous}}(t); \\
\dot{\epsilon}(t) &= \dot{\epsilon}_{\text{elastic}}(t) + \dot{\epsilon}_{\text{viscous}}(t) \\
&= \dot{\sigma}(t)/E + \sigma(t)/\eta
\end{aligned}
$$

- For times near the finite stress jump, all strain occurs in the elastic element;
- During the hold period, all strain occurs in the viscous element

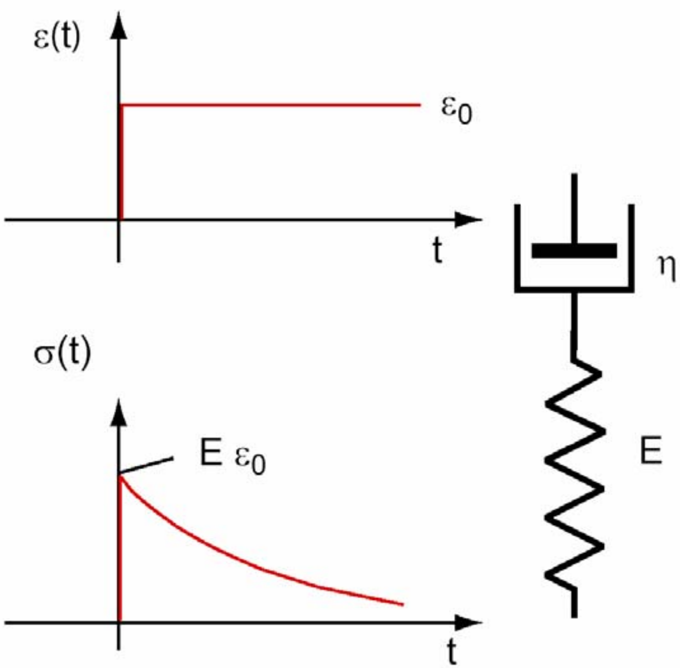
Maxwell Model: an Idealized Linear Viscoelastic Response

$$\begin{aligned}\epsilon(t) &= \epsilon_{\text{elastic}}(t) + \epsilon_{\text{viscous}}(t);\\ \dot{\epsilon}(t) &= \dot{\epsilon}_{\text{elastic}}(t) + \dot{\epsilon}_{\text{viscous}}(t)\\ &= \dot{\sigma}(t)/E + \sigma(t)/\eta\end{aligned}$$

Relaxation:

INPUT:

OUTPUT:



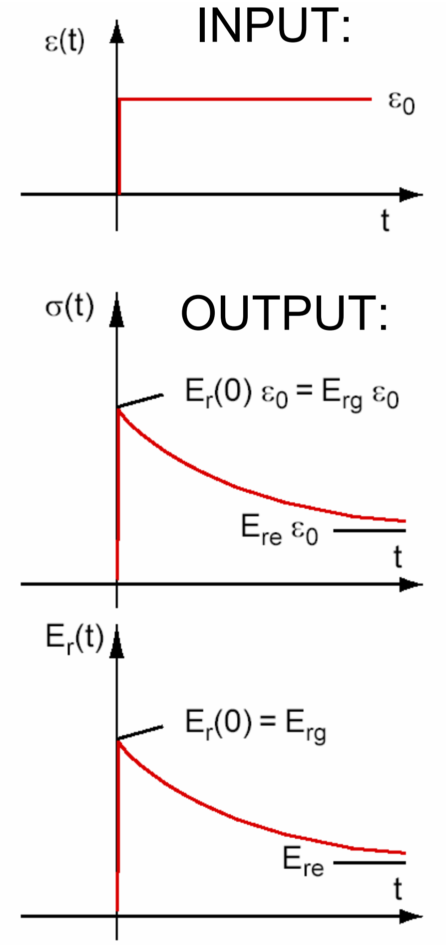
- For times > 0, d $\varepsilon(t)/dt=0$
- During the hold period, elastic strain is traded for viscous strain, and stress drops:

$$\begin{aligned}0 &= \frac{d\sigma(t)}{dt} + \frac{E}{\eta}\sigma(t) \Rightarrow\\ \sigma(t) &= \sigma(t=0)\ \exp -t/(\eta/E)\\ &= \epsilon_0 \times E\ \exp -t/(\eta/E)\end{aligned}$$

Characteristic relaxation time:

$\tau = \eta / E$

“Real” Polymer Relaxation (an Idealization)



Testing of real polymers under relaxation can be used to extract a time-dependent relaxation modulus, $E_r(t)$;
Short-term response: E_{rg};
Long-term response: E_{re}

$$E_r(t) \equiv \sigma(t)/\epsilon_0;$$

$$E_r(t \to 0^+) \equiv E_{rg} \quad \text{(glassy)}$$

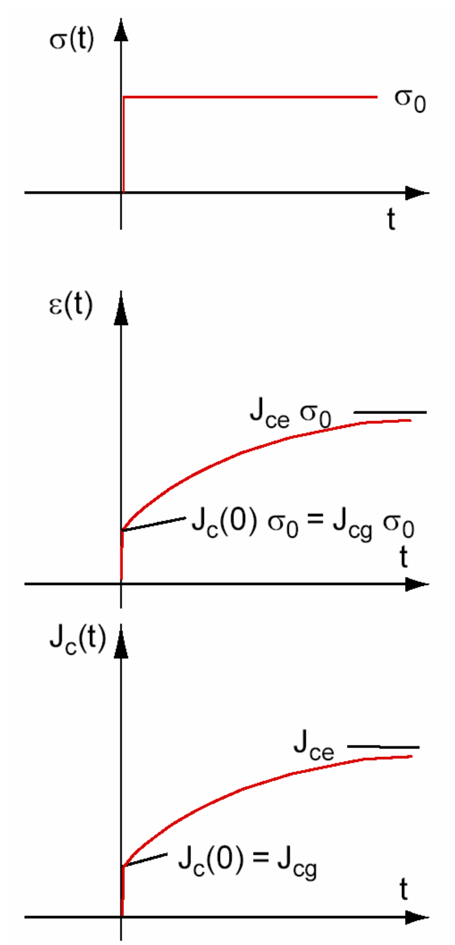
$$E_r(t \to \infty) \equiv E_{re} \quad \text{(equilibrium)}$$

NOTE: provided $|\varepsilon_0|$ is sufficiently small (typically, less than 0.01), the relaxation modulus, $E_r(t)$, is approximately independent of ε_0.

"Real" Polymer Creep: (an Idealization)

INPUT:

OUTPUT:



Testing of real polymers under suddenly-applied constant stress can be used to extract a time-dependent creep function, $J_c(t)$;
Short-term response: J_{cg};
Long-term response: J_{ce}

$$J_c(t) \equiv \epsilon(t)/\sigma_0;$$

$$J_c(t \to 0^+) \equiv J_{cg} \quad \text{(glassy)}$$

$$J_c(t \to \infty) \equiv J_{ce} \quad \text{(equilibrium)}$$

Note: units of $J_c(t)$: 1/ stress

NOTE: provided $|\varepsilon(t)|$ remains sufficiently small (typically, less than 0.01), the creep function, $J_c(t)$, is approximately independent of σ_0.

Relaxation Modulus, $E_r(t)$ and Creep Function, $J_c(t)$: Inverse Functions of Time?

Function	Dimensions	Trend
$J_c(t)$	1/stress	starts small; grows with time
$E_r(t)$	stress	starts large; decays with time

QUESTION: Are these inverse functions? Is $J_c(t) \times E_r(t) \equiv 1$ for all times?

•**ANSWERS**: In general, they are not precise inverses. However,

•Equilibrium and glassy values are <u>nearly</u> inverse:
•For intermediate times, t. the error in assuming that they are inverse is typically only a few per cent at most…

$$J_c(t \to 0^+) \doteq 1/E_r(t \to 0^+);$$

$$J_c(t \to \infty) \doteq 1/E_r(t \to \infty), \text{ but}$$

$$J_c(t) \times E_r(t) \neq 1.$$

Linearity of Response (an Idealization)

If creep response to stress jump σ_0 is

$$\epsilon(t) = J_c(t) \times \sigma_0,$$

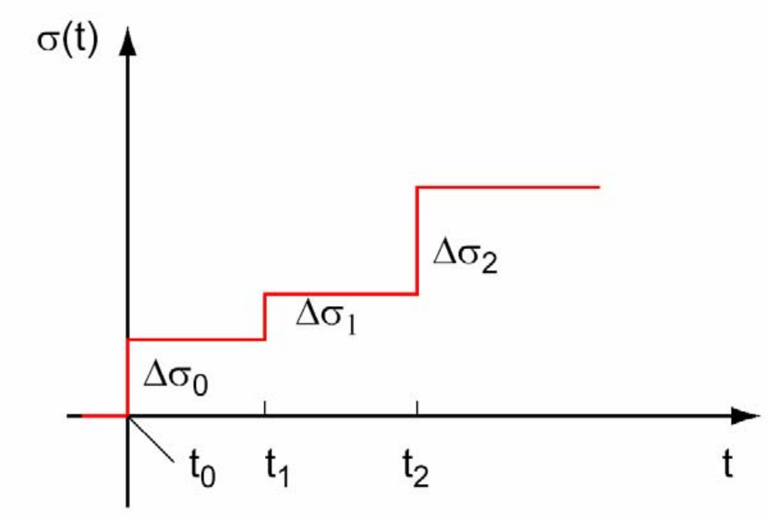
then the creep response to stress jump $\phi \times \sigma_0$ (where ϕ is a proportionality constant) is

$$\epsilon(t) = J_c(t) \times (\phi\sigma_0).$$

NOTE: similar linear scaling of stress relaxation response applies.

Superposition of Loading

Suppose that the stress history input consists of a sequence of stress jumps, $\Delta\sigma_i$, applied at successive times t_i, with t_0=0:

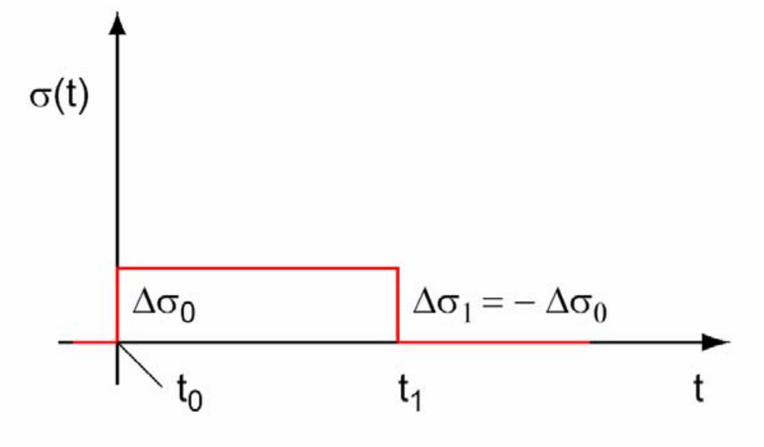


THEN, the resulting strain history is given by

$$\begin{aligned} \epsilon(t) &= \Delta\sigma_0\, J_c(t) + \Delta\sigma_1\, J_c(t-t_1) + \Delta\sigma_2\, J_c(t-t_2) + \ldots \\ &= \sum_{j=0} \Delta\sigma_j J_c(t-t_j) \end{aligned}$$

Special Case: Load/Unload

INPUT:

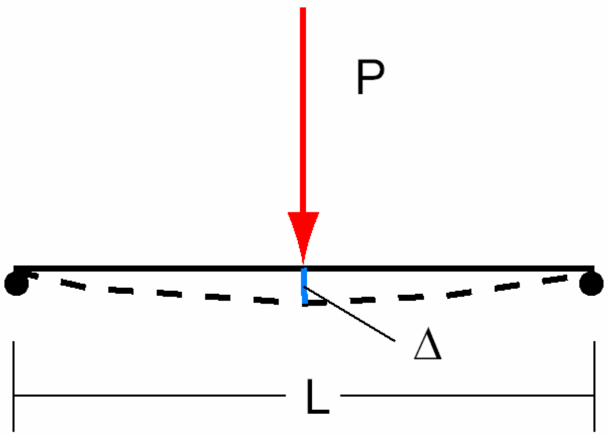


Correspondence Principle

•Suppose that a given load, P, produces displacement vector **u**(**x**) in a linear elastic body having Young's modulus E.
•The displacement vector depends on the position vector
$\mathbf{x} = x\,\mathbf{e}_x + y\,\mathbf{e}_y + z\,\mathbf{e}_z$.
•The magnitudes of the displacement and strain components are proportional to P and inversely proportional to E.

EXAMPLE: Three-point
Mid-span bending:

$$\Delta = -v(x = L/2) = \frac{PL^3}{48IE}$$

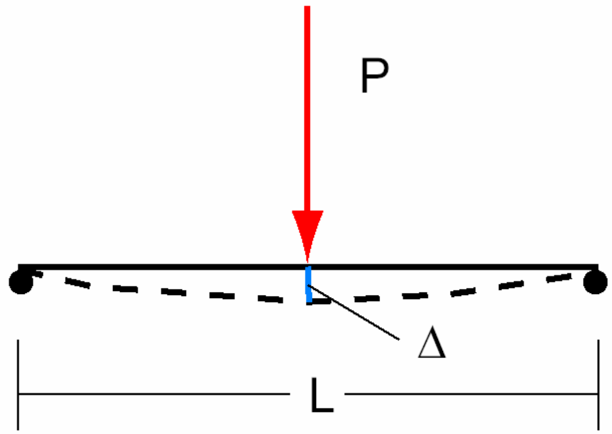


Correspondence Principle

•Now suppose that a given load jump, P(t), is applied to a geometrically identical linear viscoelastic body having creep function $J_c(t)$.
•All stress components in the body are time-independent, and spatially vary precisely as they do in an identical linear elastic body subject to the same load.
•The loading produces time-dependent displacement vector **u**(**x,**t) and corresponding strain components.
•The magnitudes of the displacement and strain components are proportional to both P and $J_c(t)$.

EXAMPLE: Three-point Mid-span bending:

$$\Delta(t) = -v(x = L/2, t) = \frac{PL^3}{48I} \times J_c(t)$$



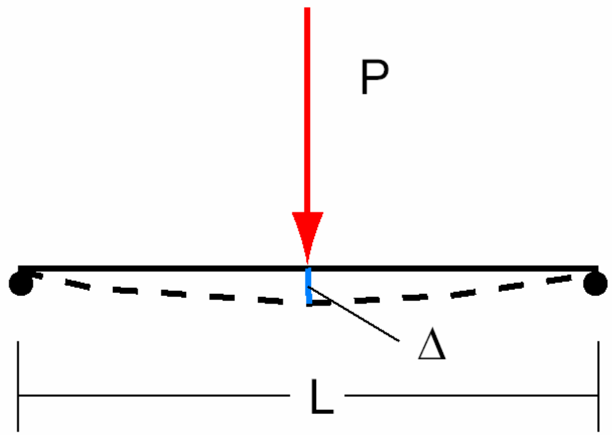
For suddenly-applied load, replace "1/E" with "$J_c(t)$" in an elastic solution.

Correspondence Principle

•Suppose that a given displacement jump, Δ(t), is applied to a geometrically identical linear viscoelastic body having stress relaxation modulus $E_r(t)$.
•All displacement and strain components everywhere in the body are time-independent, and precisely equal those in an identical linear elastic body subject to the same applied displacement.
•These boundary conditions produce time-dependent loads, P(t), and stresses
•The magnitudes of the time-dependent load and of the stress components are proportional to both Δ and to $E_r(t)$.

EXAMPLE: Three-point Mid-span bending:

$$P(t) = \frac{48I}{L^3} \times \Delta \times E_r(t)$$



For suddenly-applied displacement, replace “E” with “$E_r(t)$” in an elastic solution.