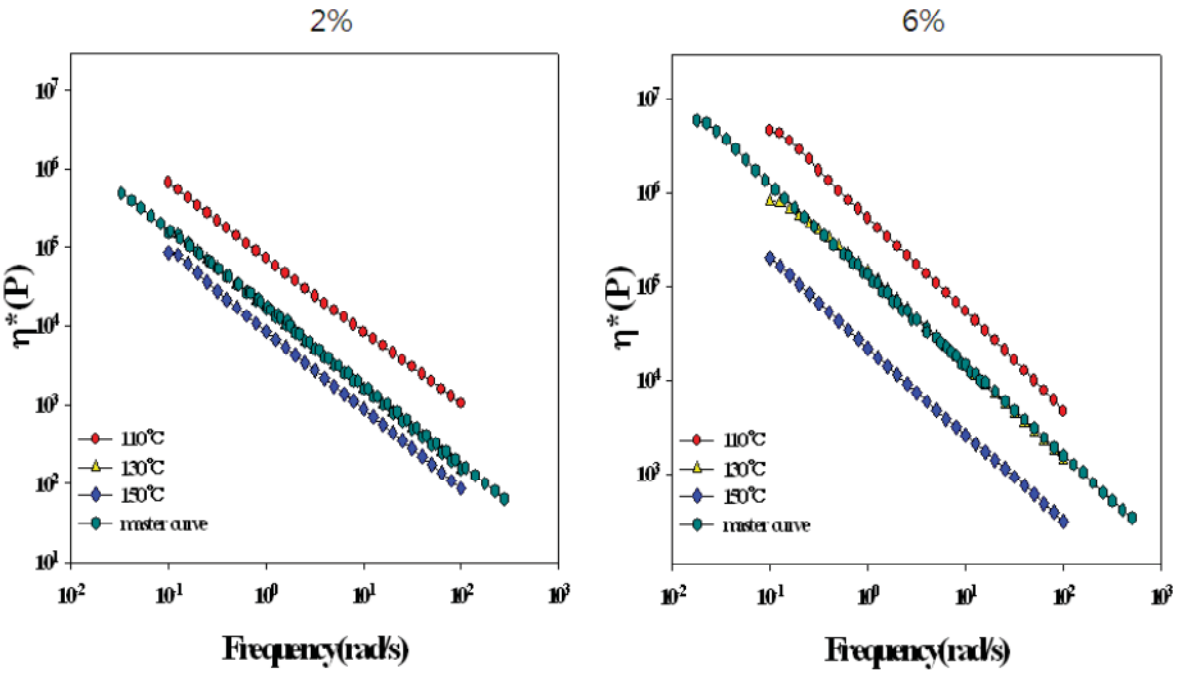
Master Curve



4.4 Polymer selection: stiffness

4.4.1 Temperature dependence

Temperature dependence of modulus, viz G(T), E(T)→Most important clue to engineering application

Figure 4.21 Representative polymers (rubber, amorphous plastics, semicrystalline polymer) G-Temperature curve

Temperature dependence of modulus

i) $T < T_g$ Small decrease of G with T is due to thermal expansion↔Decrease of secondary bond strength→Density decrease→Modulus decrease

ii) Abrupt drop is generated by a viscoelastic relaxation process due to some specific type of molecular movement (Refer to side group (β) and backbone relaxation (α) of PMMA, See 4N7)

NR cis-1,4-polyisoprene

T_g = −70℃ (uncured state)

As cross-linking density ↑ ⇒ increases linearly

$$T_g = T_{g,0} + \frac{\alpha}{M_c} \qquad M_c : \text{mol wt btn cross-links}$$

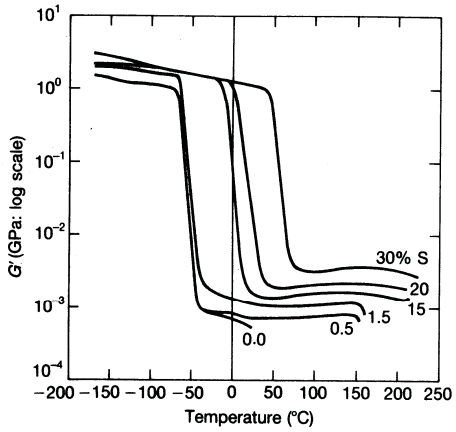
Rubber plateau

As $T \uparrow \Rightarrow G_N^{\circ} \uparrow$, $G = NkT$, $N = \frac{\nu}{V}$, $G_N^{\circ} = \frac{\rho RT}{M_c}$, $\sigma = G(\lambda - \frac{1}{\lambda^2})$

Figure 4.22 Modulus-Temperature of NR depending on crosslink degree

Ex. With 30% cure modulus increases 10^3 times at 0℃!

See rubbery → glass @ 30℃



4.22 Shear modulus *G* of natural rubber for varying degrees of vulcanization at temperatures between −200°C and +250°C (after Wolf).

PVC

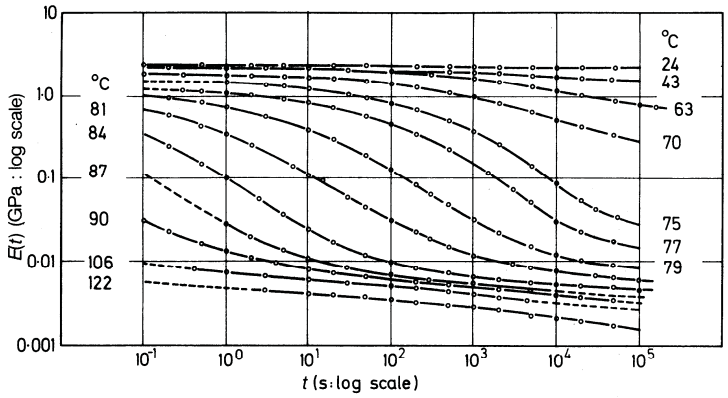
Amorphous plastic

α −relaxation $(T_g) = +70$℃ (unplastized)

with plasticizer (DOP, DBP) : T_g decreases (soft PVC used for flooring)

w/o plasticizer : hard PVC (Pipe, plastic)

Fig. 4.23 Stress relaxation of PVC in 24~122℃



4.23 Stress relaxation modulus $E(t)$ of PVC determined from 24°C to 122°C (after Sommer).

Nylon 6

-Crystallinity ~50%

-Shows two relaxations i.e., $T_g = 50℃$ (Glass → Rubbery transition for amorphous region) and $T_m = 215 - 220℃$.

-Small β rlxn $= -40℃$

-Use temperature $-30℃ \sim 150℃$

Modulus change=0(10) (see Fig. 21)

-Upper use temperature is increased by forming composites with fibers (C/F, G/F, Kevlar) and particles (talc, clay, C/B)

-Conductivity is enhanced w/ the addition of conducting fillers, viz. fullerene (0D), CNT(1D), graphene(2D))

Macroscopic vs nanocomposites

→Chapter 6

Notes

w/ filler reinforcement : modulus ↑

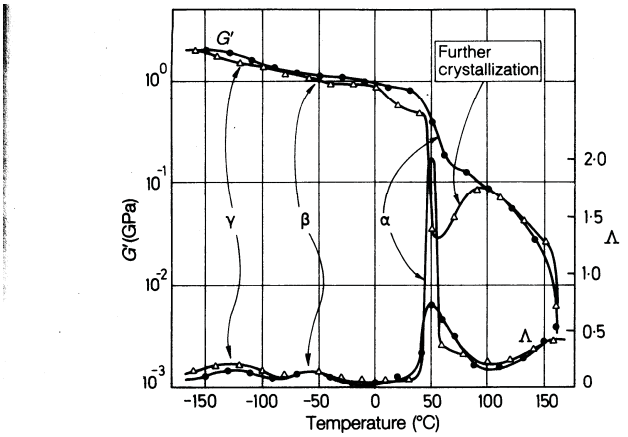
w/ fiber reinforcement (C/F, G/F, Kevlar) : strength ↑, modulus ↑,

Exception: C/B reinforced rubber where strength as well as modulus ↑

Fig. 21 (G-T relationship) is reproduced unless the sample is quenched from melt.

Upon quenching, crystallization is avoided.

Fig. 4. 24 See G′ and Λ for the quenched nylon 66.

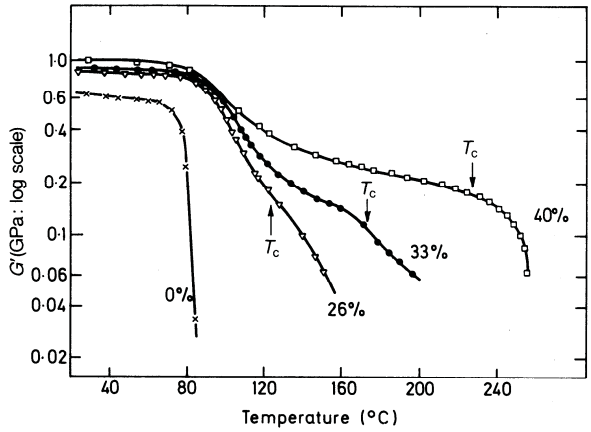


4.24 Temperature scan of G' and Λ for nylon 6.6: one specimen is quenched (△); the other (•) is quenched but heated at 90°C prior to the temperature scan (so as to complete the crystallization). Note that the quenched specimen starts to crystallize when it is heated to 50°C (positive slope of log G–T curve). The dominant relaxation (α) is the glass relaxation of the amorphous fraction which occurs at $T \approx 50$°C (after Wolf and Schmieder).

$$\Lambda = \ln \frac{A_n}{A_{n+1}} \qquad \Lambda = \pi \tan\delta \qquad \text{See (32, 33)}$$

Quenched sample is crystallized during heating→Causes modulus rise (Δ)

See also Fig. 4.25 for PET



4.25 Poly(ethylene terephthalate) when quenched from the melt has 0% crystallinity; when it is heated through T_g the modulus drops dramatically as indicated. Specimens of crystallinity 26%, 33%, and 40% have modulus–temperature plots as shown. These three values of crystallinity were produced by heating quenched specimens at the temperatures T_c prior to the temperature scan (after Illers and Breuer).

Water in polymers

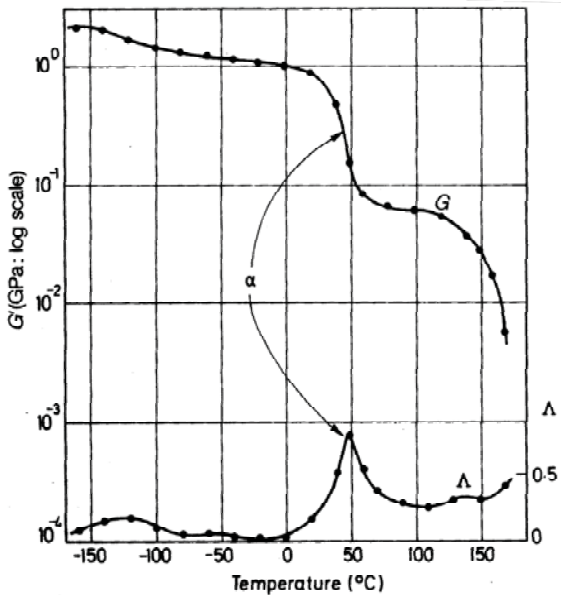
- Water absorption ∝ RH ($=\frac{\text{Partial pressure of water}}{\text{Vapor pressure of water}}$ x 100)
- Hydrogen bonded polymers (nylon, PET…) and polar group containing polymers (POM, PMMA…) absorb water up to several % under 100% RH (*To be treated in Polymer Processing*). (Water is critical to nylon and PET)
- Crystallinity ↑ → water absorption ↓ (∵ Water is mainly absorbed in amorphous domains)

Fig. 4.26 ⇒ Dynamic data for dry PU:

Comparable with nylon →

Two major relaxations above RT, viz. Tg (50°C) and Tm (150°C).

See also two small ones below RT.

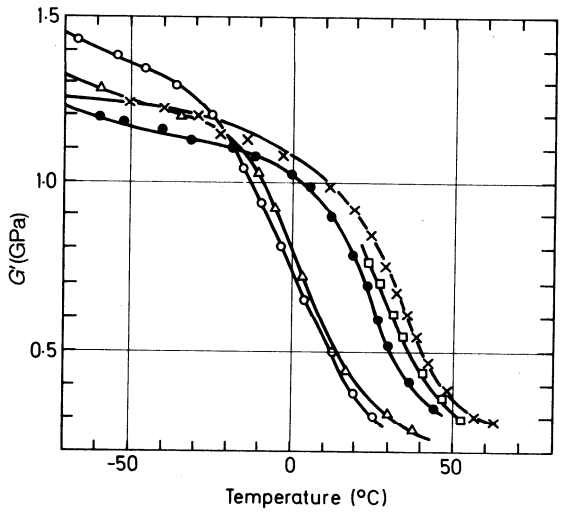


4.26 Temperature scan of G' and Λ for a dry polyurethane with structure

$$-\{(HN)-(CH_2)_u-(NH)-(CO)-O(CH_2)_v-O-(CO)\}_n-$$

with $u=6$ and $v=4$ (after Wolf and Schmieder).

However Tg significantly decreases with water contents (Fig. 4.27)



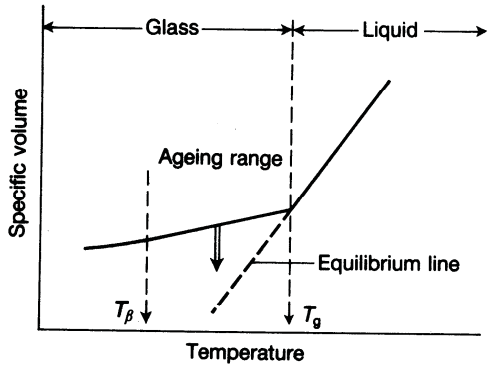
4.27 Temperature scan of G' for the polyurethane of Figure 4.26 containing water as follows: x = 0 mol%; □ = 3.7 mol%; • = 5.6 mol%; △ = 24.5 mol%; and ○ = 28.8 mol%. The α-(glass-to-rubber) relaxation moves to lower temperatures with increasing water content (after Jacobs and Jenckel).

Physical aging (See Fig 28)

When an amorphous polymer is quenched from melt into glass ($T_\beta<T<T_\alpha= T_g$) it is in a metastable condition, and the volume slowly contracts toward the equilibrium line (Isothermal contraction).

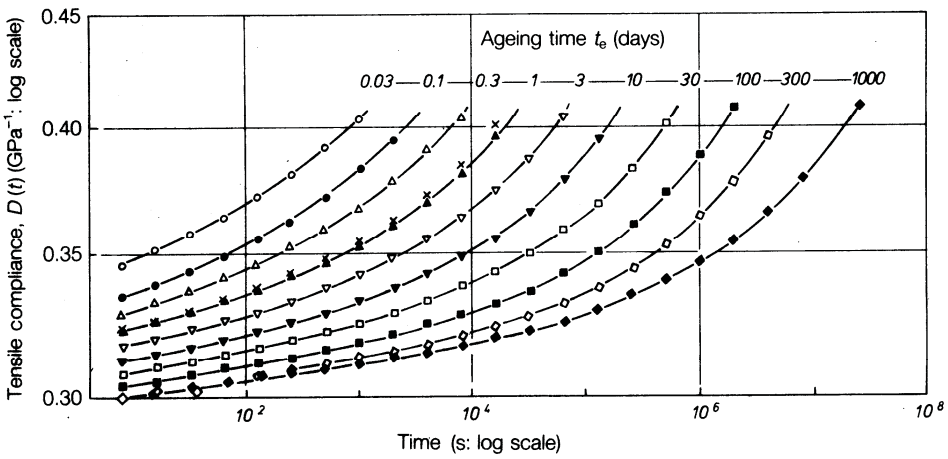
This stiffening process is called **physical aging** which gives slow embrittlement- must be taken into account in design.

(**Chemical aging**=Thermal degradation of main chains at high temperature)



4.28 The origin of physical ageing in an amorphous polymer. After quenching to a temperature below T_g (but above T_β, the temperature of the highest secondary relaxation), the volume slowly contracts: the movement is towards the equilibrium, which is the extrapolated $v - T$ line for the liquid (after Struik).

Figure 29: Physical aging of PVC. Sample was quenched from 90 ($>T_g$) to 20℃($<T_g$), and held at 20℃ for 4 years. As aging time increases, compliance decreases at the same creep time (x-axis), and stiffness increases.



4.29 Tensile compliance of PVC at 20°C. The specimen was quenched from 90°C (20°C above T_g) to 20°C, and kept at 20°C for 4 years. At specific times (t_e) after the quench: 0.03, 0.1, 0.3 days, etc., the compliance was determined. Note the systematic shift of the creep curves. This effect is termed **physical ageing** (see also Figure 4.28) (after Struik).

4.4.2 Stress analysis

Polymer materials are used up to

$T_m - 50℃$ for crystalline polymers, and

$Tg - 40℃$ for glassy polymer

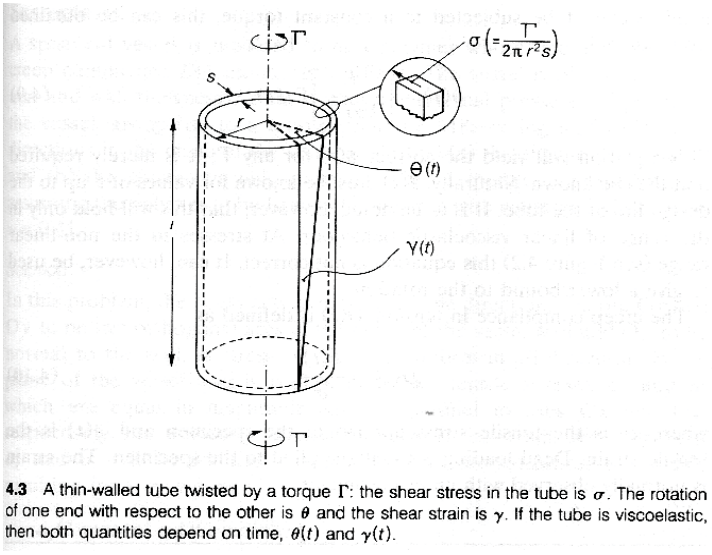
due mainly to the viscoelastic limitations of creep and stress relation.

4.4.2.1 Torsion of a circular shaft

Example for quantitative application of viscoelastic data.

At $t = 0$ shaft is twisted to θ..

Calculate torque to maintain the θ (50℃) at $\text{time} = t \rightarrow$Stress rlxn



4.3 A thin-walled tube twisted by a torque Γ: the shear stress in the tube is σ. The rotation of one end with respect to the other is θ and the shear strain is γ. If the tube is viscoelastic, then both quantities depend on time, $\theta(t)$ and $\gamma(t)$.

Shaft length l, radius a

Consider an elemental tube with radius r, and thickness dr.

$$\gamma = \frac{r\theta}{l}$$

Shear stress at time t:

$$\sigma(t) = G(t)\gamma = G(t)\frac{r\theta}{l}$$

Torque $\tau(t)$

$$\tau(t) = \int_0^a \sigma(t)(2\pi r dr)\, r$$
$$= \int_0^a G(t)\frac{r\theta}{l} 2\pi r^2\, dr$$
$$= \frac{2\pi}{l} G(t)\theta \frac{a^4}{4} = \left(\frac{\pi a^4}{2}\right)\frac{G(t)}{l}\theta$$
$$= \frac{N\theta}{l} G(t)$$

With $G(t)$ data $\rightarrow \tau(t)$ predicted

Students practice Ex 4.5.

4.4.2.2 Boltzmann superposition principle (BSP)

Strain at present time, t due to the stress σ_0 imposed at $t = 0$.

$$\gamma_0(t) = \sigma_0 J(t) \qquad (77)$$

Strain at present time, t due to the stress σ_1 imposed at $t = t_1$.

$$\gamma_1(t) = \sigma_1 J(t - t_1) \quad (= \sigma_1 J(s)) \qquad (78) \qquad s: \text{ elapsed time}$$

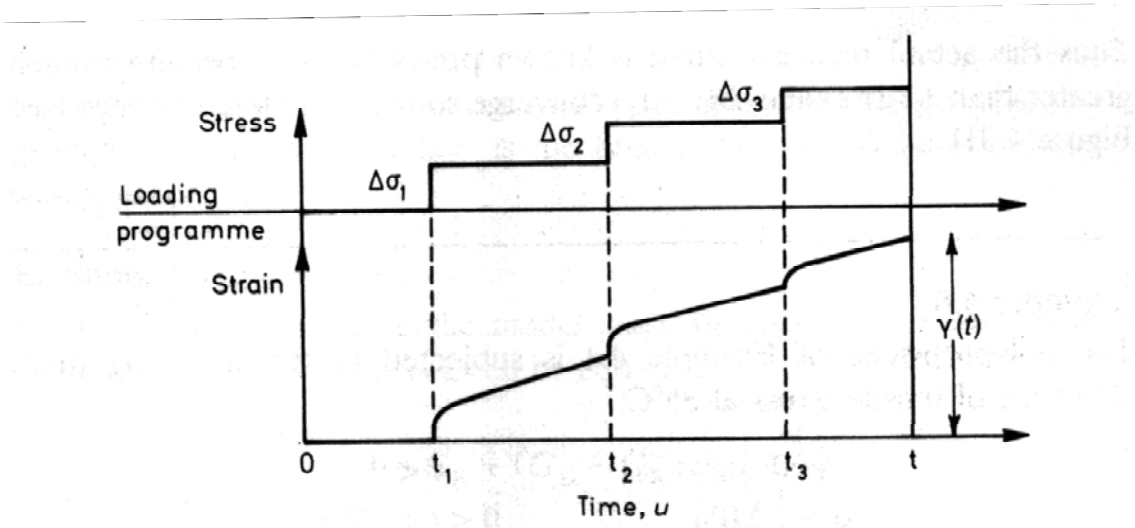
Total strain $\gamma(t)$ at present time due to σ_0 and σ_1(**Boltzmann Superposition**)

$$\gamma(t) = \gamma_0(t) + \gamma_1(t) = \sigma_0 J(t) + \sigma_1 J(t - t_1) \qquad (79)$$

weighting function

Apply a sequence of stress pulse as in Fig. 4.30:

Fig. 4.30 here



4.30 Three stress increments at a sequence of times (t_1, t_2, t_3) leading to a total strain $\gamma(t)$.

Shear strain at present, t is given by

$$\gamma(t) = \Delta\sigma_1 J(t - t_1) + \Delta\sigma_2 J(t - t_2) + \Delta\sigma_3 J(t - t_3) + \cdots \qquad (80)$$

$$= \int_0^t J(t - t') \frac{d\sigma}{dt'} dt' \qquad (81)$$

where $0 < t' < t$ (t': past time)

Tensile strain at present time, t is given by:

$$\epsilon(t) = \int_0^t D(t - t') \frac{d\sigma}{dt'} dt' \qquad (82)$$

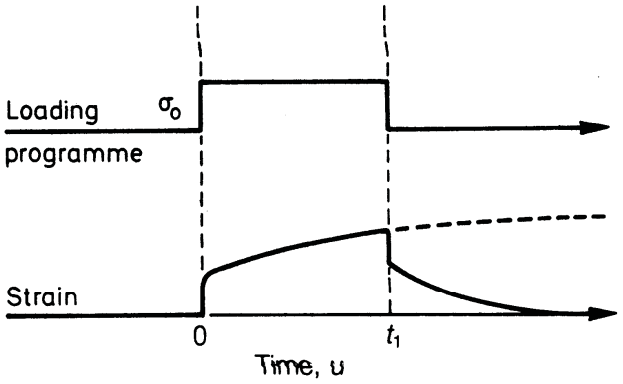
Tensile stress relaxation at present time, t is given by

$$\sigma(t) = \int_0^t E(t - t') \frac{d\epsilon}{dt'} dt' \qquad (83)$$

Two examples for BSP

a)Relationship between creep and recovery

Scan Fig 31 here



4.31 Response of a viscoelastic solid to loading at 0 and unloading at t_1.

$$\left.\begin{aligned} @\ t' = 0,\ \sigma_0 \text{ added} \\ @\ t' = t_1,\ \sigma_0 \text{ removed} \end{aligned}\right]$$

Then

$$\epsilon(t) = \sigma_0 D(t) - \sigma_0 D(t - t_1) \qquad (84)$$

remove!!

Example 4.6

The polypropylene of Example 4.4 is subjected to the following time-sequence of tensile stress at 35°C:

$$\begin{aligned} \sigma &= 0 && t < 0 \\ \sigma &= 1 \text{ MPa} && 0 \le t < 1000 \text{ s} \\ \sigma &= 1.5 \text{ MPa} && 1000 \text{ s} \le t < 2000 \text{ s} \\ \sigma &= 0 && 2000 \text{ s} \le t \end{aligned}$$

Find the tensile strain at the following times t: (a) 1500 s; (b) 2500 s. Assume that under these conditions polyproylene is linearly viscoelastic and therefore obeys the Boltzmann superposition principle.

Solution

Since the time-sequence of stress consists of a series of discrete steps, the discrete form of the Boltzmann superposition principle is the most straightforward to apply. For a series of n steps in tensile stress of magnitude $\Delta\sigma_i$ applied at times t_i, the BSP states (eqn 4.80) that

$$\varepsilon(t) = \sum_{i=1}^{n} \Delta\sigma_i D(t - t_i) \qquad (t_n < t).$$

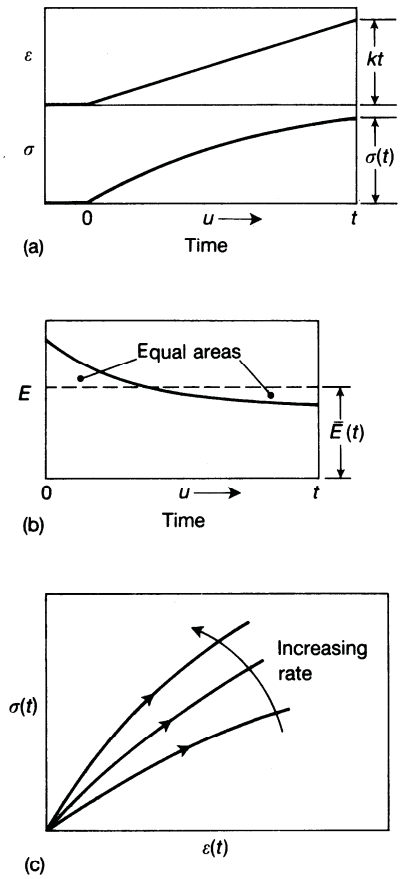
(a) When $t = 1.5 \times 10^3$ s: $n = 2$, $\Delta\sigma_1 = 1$ MPa, $t_1 = 0$, $\Delta\sigma_2 = 0.5$ MPa, and $t_2 = 10^3$ s. Substituting into the BSP yields

$$\begin{aligned} \varepsilon(1.5 \times 10^3 \text{ s}) &= 10^6 \times 1.2 \times 10^{-9} \times (1.5 \times 10^3)^{0.1} \\ &\quad + 0.5 \times 10^6 \times 1.2 \times 10^{-9} (1.5 \times 10^3 - 10^3)^{0.1} \\ &= 3.61 \times 10^{-3}. \end{aligned}$$

(b) When $t = 2.5 \times 10^3$ s: $n = 3$, $\Delta\sigma_1 = 1$ MPa, $t_1 = 0$, $\Delta\sigma_2 = 0.5$ MPa, $t_2 = 10^3$ s, $\Delta\sigma_3 = -1.5$ MPa, and $t_3 = 2 \times 10^3$ s. Substituting into the BSP now yields

$$\begin{aligned} \varepsilon(2.5 \times 10^3 \text{ s}) &= 10^6 \times 1.2 \times 10^{-9} \times (2.5 \times 10^3)^{0.1} \\ &\quad + 0.5 \times 10^6 \times 1.2 \times 10^{-9} (2.5 \times 10^3 - 10^3)^{0.1} \\ &\quad - 1.5 \times 10^6 \times 1.2 \times 10^{-9} \times (2.5 \times 10^3 - 2 \times 10^3)^{0.1} \\ &= 0.52 \times 10^{-3}. \end{aligned}$$

b)Conventional stress-strain curve



4.32 (a) A constant strain rate leads to a non-linear stress; (b) the definition of $\bar{E}(t)$, the mean modulus; and (c) increasing the strain rate (k) increases the slope of the stress–strain curve.

Specimen is elongated at a constant rate and the stress generated is recorded.

For BSP application, assume at t′=0, strain is imposed such that

$$\epsilon(t') = kt' \qquad \text{(Fig. 4.32a)}$$

So, $\frac{d\epsilon}{dt'} = k$

$$\xrightarrow{(83)} \sigma(t) = \int_0^t E(t-t')\frac{d\epsilon}{dt'}dt'$$

$$= k\int_0^t E(t-t')dt' = -k\int_t^0 E(s)ds$$

$$= k\int_0^t E(s)ds \qquad s \equiv t-t', ds = -dt'$$

$$= \frac{\epsilon(t)\int_0^t E(s)ds}{t}$$

$$= \epsilon(t)\bar{E}(t) \qquad (88)$$

$\bar{E}(t)$: Average of E between $0 \sim t$

Fig. 4.32b: At constant strain rate, $\bar{E}(t)$ decreases as time, t increases → S-S measurement must always **nonlinear** bending downward. ∵At longer time during the test, more of the stress is relaxed to give smaller G (Think G(t) curve).

Fig. 4.32c : As strain rate ↑ (less time and more elastic)→ E ↑

Notes for Chapter 4

4N1 Sag of viscoelastic pipe

Constant stress is most commonly encountered in design.

HDPE pipeline supported on bracket is subjected to a bending stress (σ_o).

The constant stress is the self-weight of the pipeline.

Creep causes sagging between the supports.

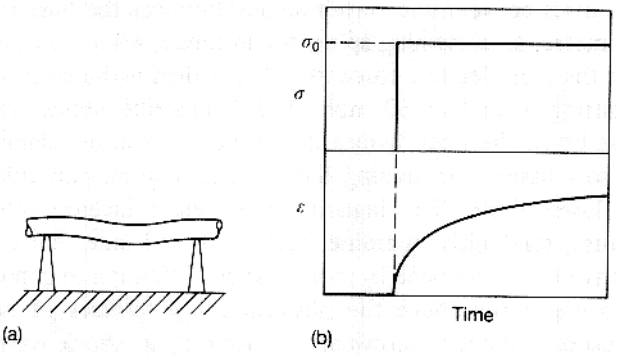
The strain (deflection) is constant for elastic pipe,

but increases with time for viscoelastic materials.

The designer needs to calculate the creep using the creep compliance.

$< \gamma \ \ (t) = \sigma_0 \ J(t) >$ or predict using various models.

Scan Figure 4.33 here



4.33 The increasing sag of a viscoelastic pipe. Essentially constant stress due to the weight of the pipe leads to a time-dependent strain.

4N2 Viscoelastic creep of polymer

Important for olymer gasket, washer, bolt….

Nylon bolt is used to join two rigid plates.

When the bolt is tightened suddenly, it is stretched to a constant value, ε_o.

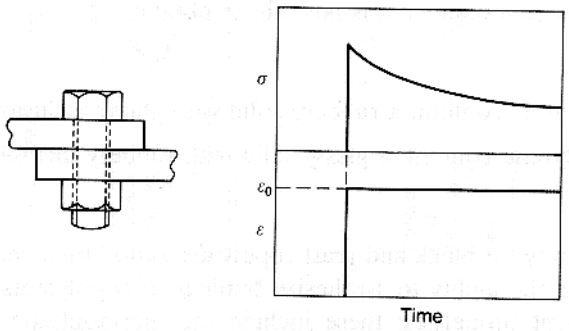
For elastic material, the stress will increases to a constant value, σ_o.

For nylon, stress is relaxed (less tightening force) with time since it is viscoelastic.

The designer should predict stress, tightening force, using G(t) data.

$<\sigma(t) = G(t)\gamma_o>$

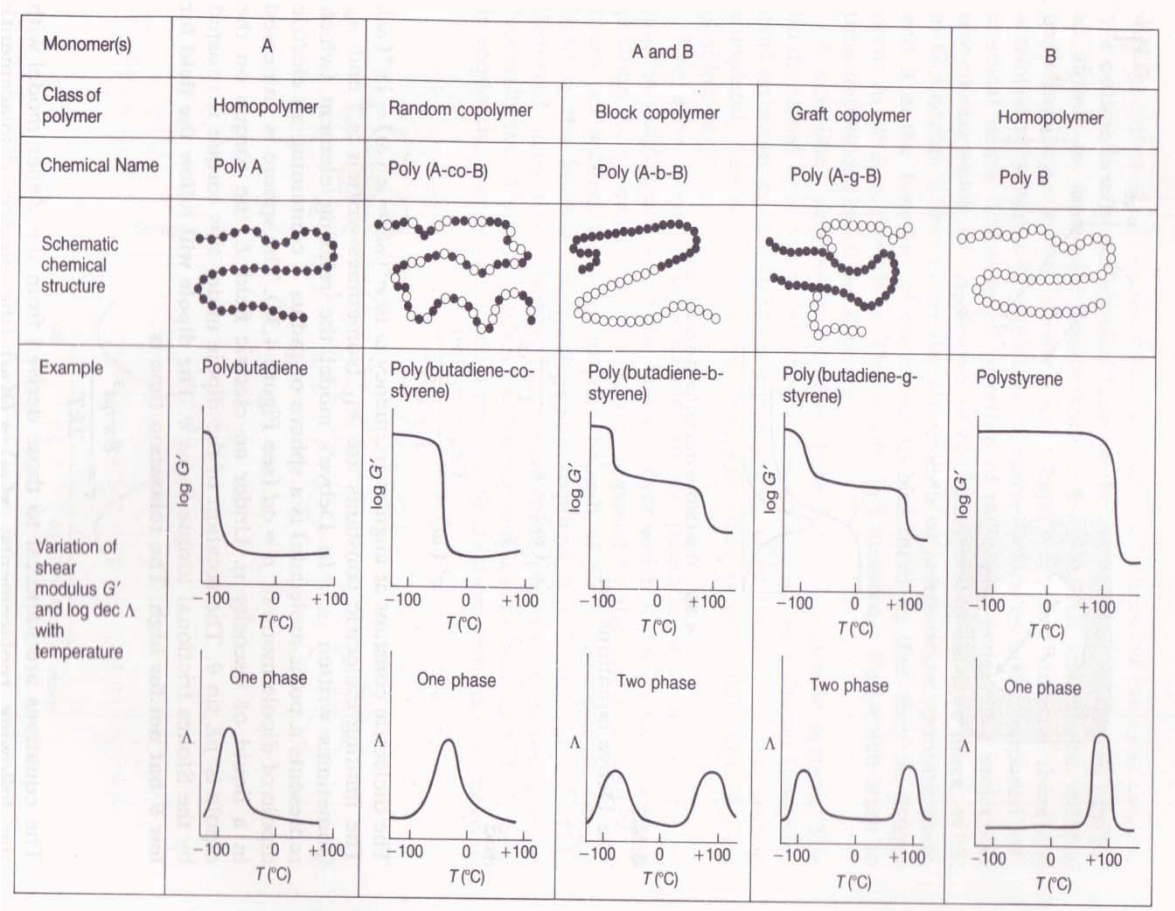
Scan Fig. 4.34 here.



4.34 Stress decay in a bolt as a function of time after tightening: the strain is constant.

4N4 Viscoelastic relaxation for random, block and graft copolymers

Scan Figure 4.35 here



4.35 The mechanical spectra (log G' and Λ at ~1 Hz versus temperature) for copolymers (random, block, and graft).