TEXAS TECH UNIVERSITY
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Structural Recovery in Glasses: Aging and Rejuvenation

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The Glass Transition is a Kinetic Phenomenon as Measured in the Laboratory

Structural Recovery: The evolution of the non-equilibrium state (or structure) of the glass towards equilibrium.

↓

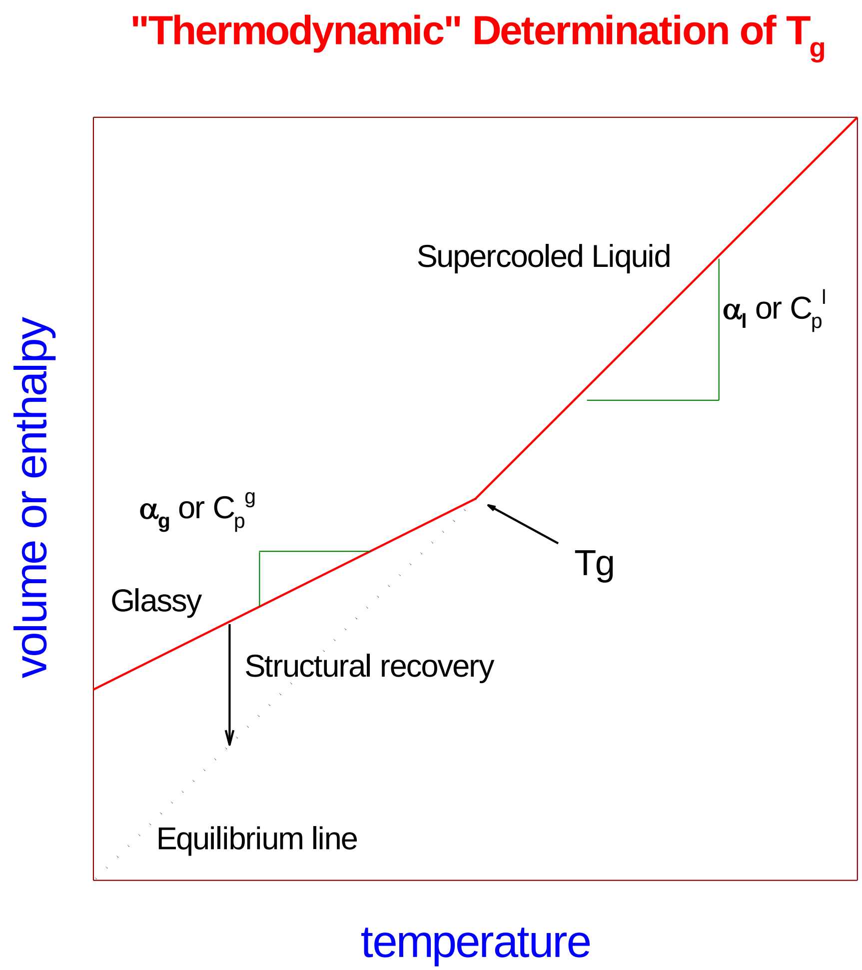
Physical aging is the response of mechanical (or other) property to the changing structure of the glass.

Physical Aging

Physical Aging is the impact of structural recovery on other material properties (other than state-like variables) such as viscoelastic response, yield and failure.

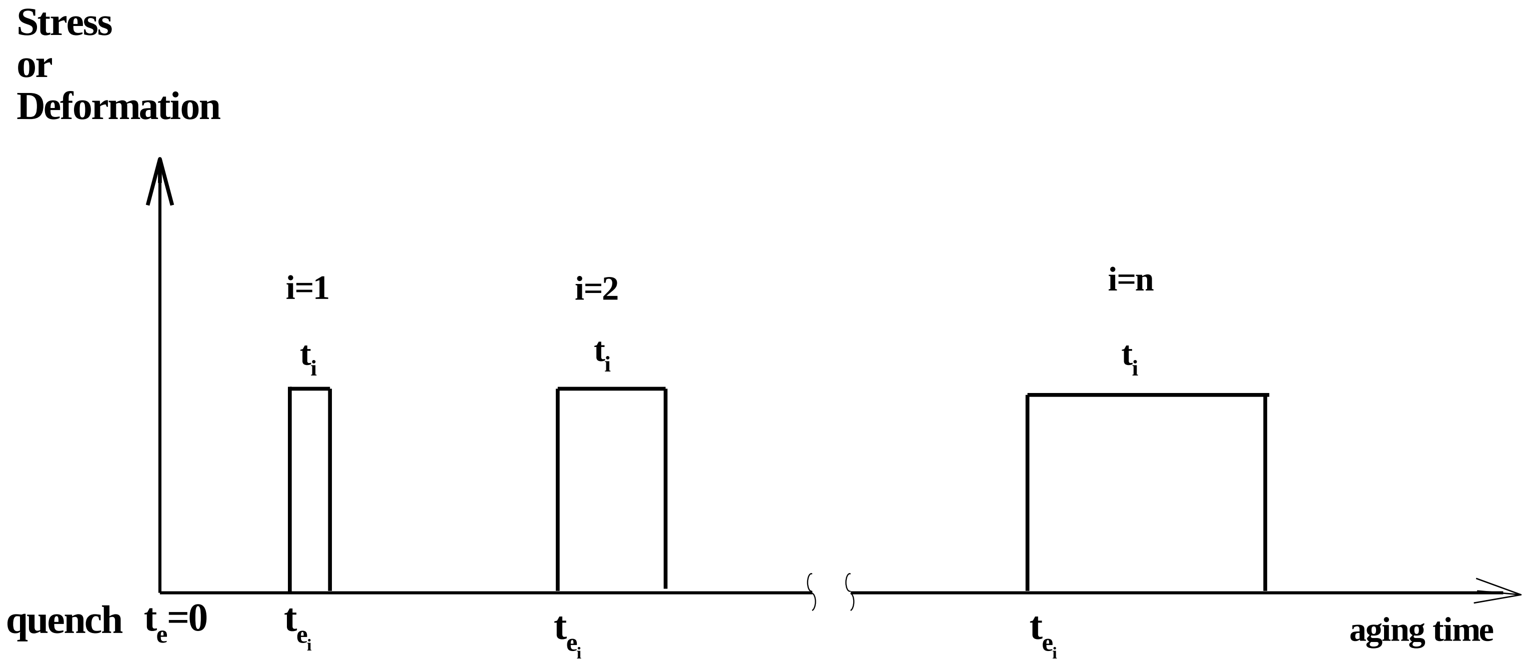
- ***While physical aging was known by the 1960's it was the Seminal book by L.C.E. Struik in 1978 (<u>Physical Aging in Polymers and Other Amorphous Materials,</u> Elsevier) that gave the first successful quantitative look at the problem.***

Physical Aging



Physical Aging

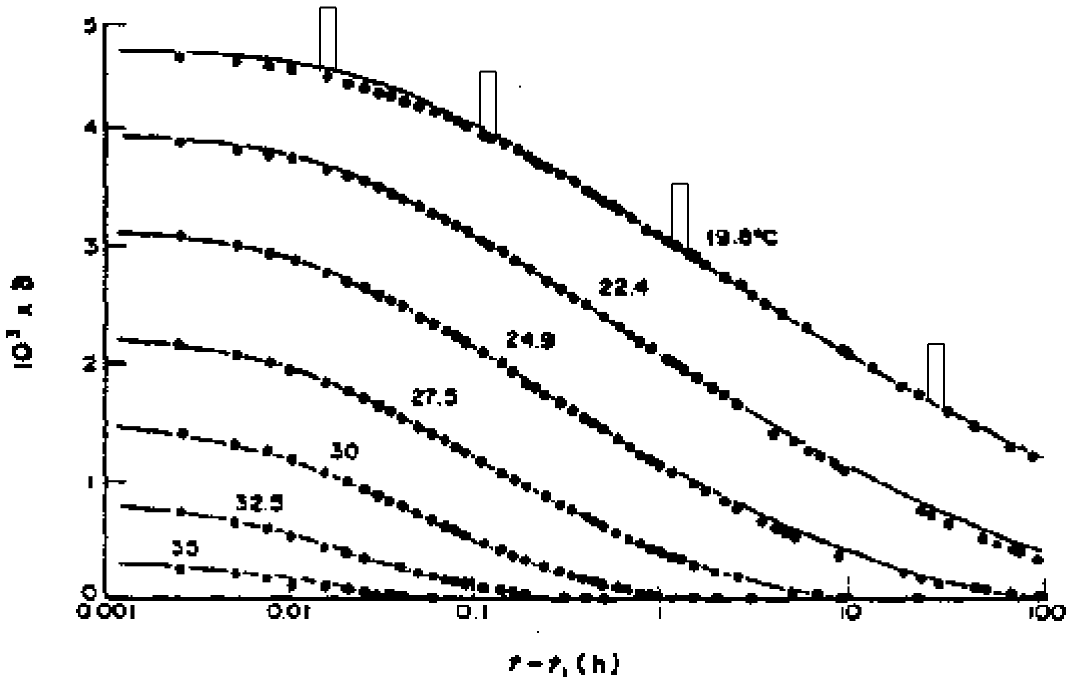
The test protocol proposed by Struik



Physical Aging

Justification for the Struik protocol

$\delta = (v - v_0)/v_0$



After A.J. Kovacs, 1964

Physical Aging: linear viscoelastic regime

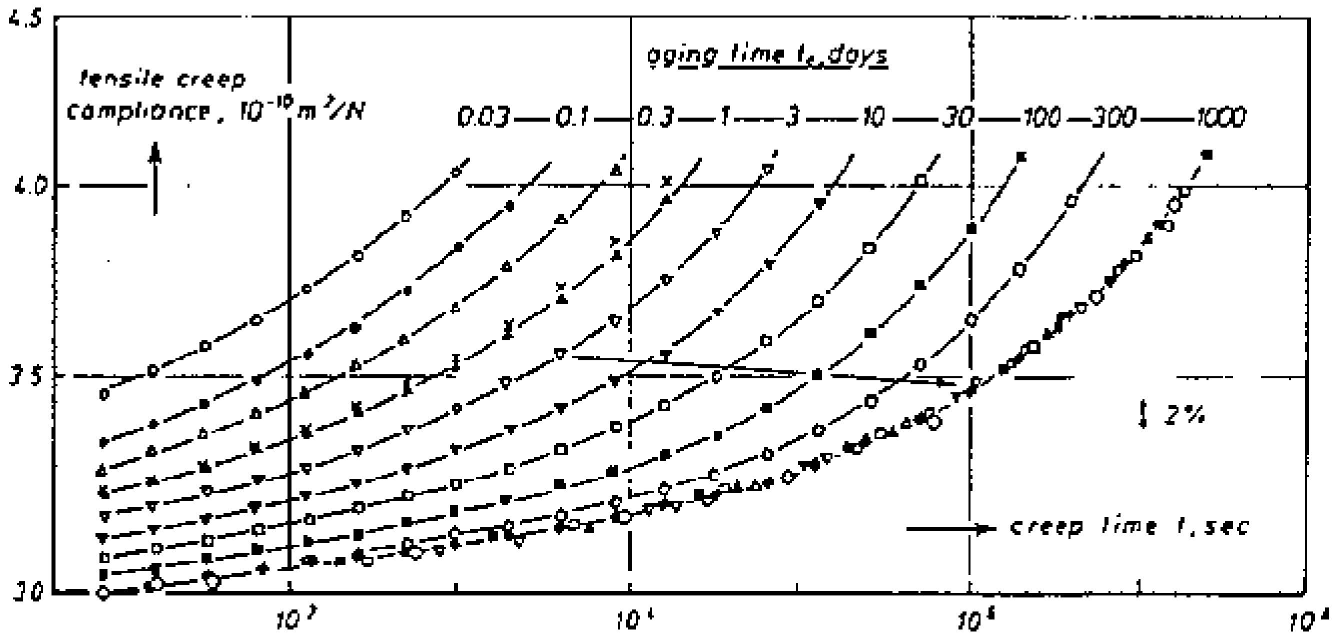


FIG. 3. Tensile creep curves of rigid PVC quenched from 90 °C (i.e., about 10 °C above T_g) to 40 °C during a type I history [after Struik (1978)].

The Aging Time Shift Factor

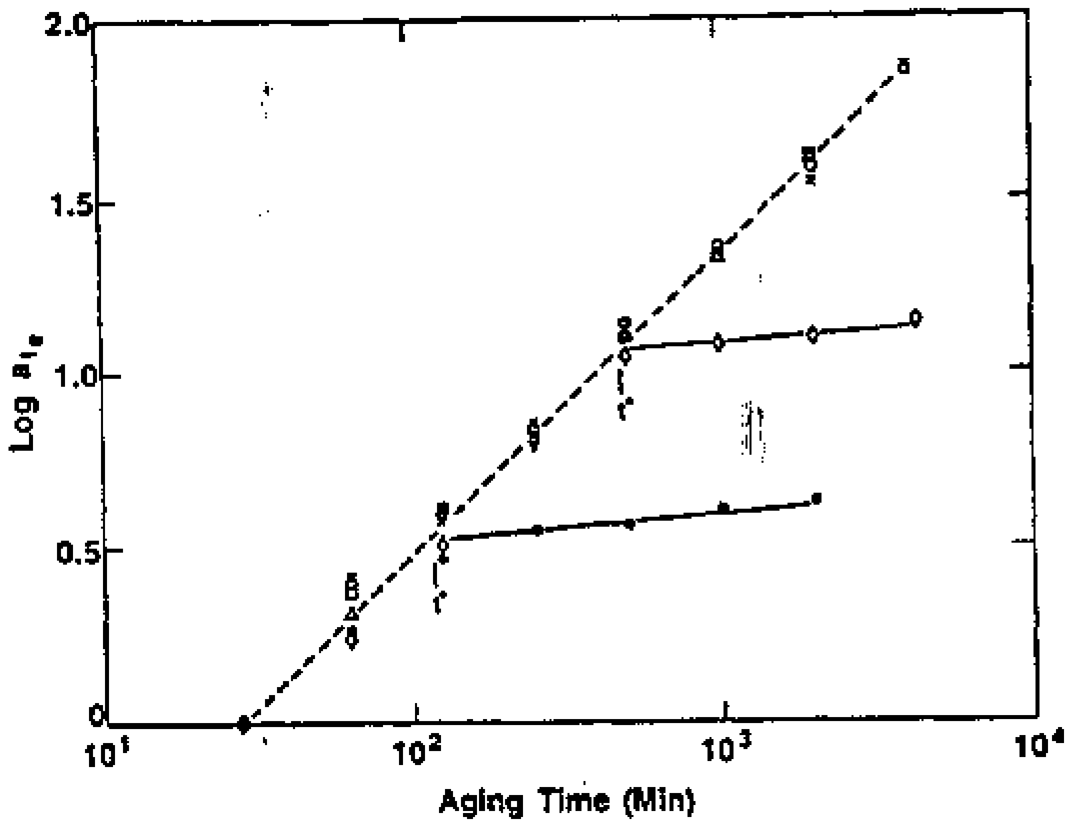


Fig. 10. Double logarithmic representation of aging time shift factor a_{te} vs aging time t_e for an epoxy glass aged at different temperatures below its T_g. $T_g - T$: (•) 30.1 °C; (X) 24 °C; (□) 20.8 °C; (◇) 10.3 °C; (•) 6.3 °C. (After Ref. [14a].)

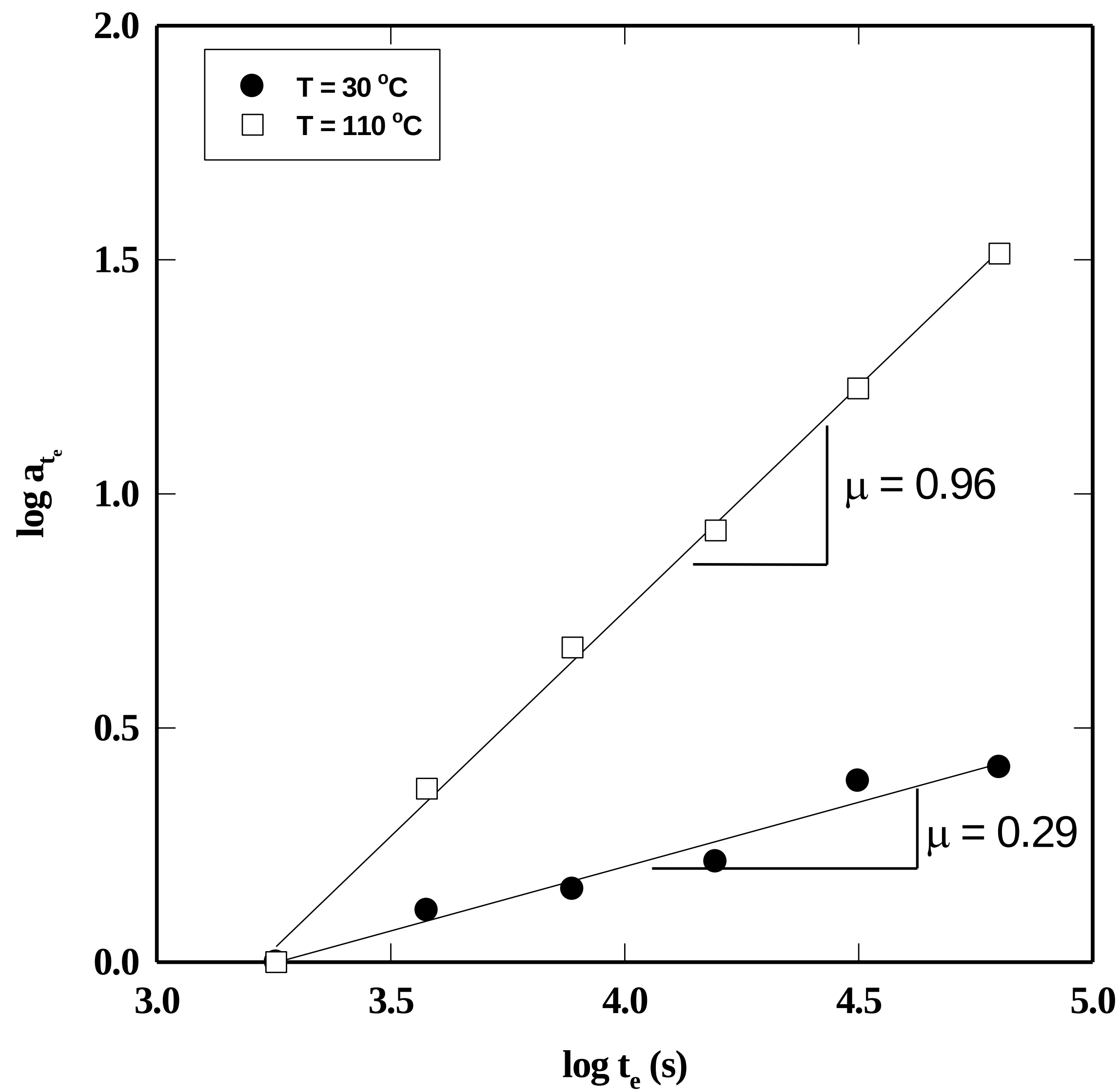


Figure 5. Typical behavior for the aging time shift factor as a function of aging time in the "power-law regime" for a polycarbonate tested at a torsional strain of 3.5% and at two test temperatures, as indicated. Shift rate μ is indicated as the slope of the lines. (After O'Connell and McKenna[24]).

Physical Aging: linear viscoelastic regime

Time-aging time superposition:

- *As in the case of the structural recovery, the relaxation time depends on the instantaneous structure of the glass.*
- *Can define an aging time shift factor a_{te}*

$$a_{te} = \tau(t_e)/\tau(t_{e,r})$$

Physical Aging: linear viscoelastic regime

- ***Define the shift rate μ:***

$$\mu = d \log a_{te} / d \log t_e = d \log \tau / d \log t_e$$

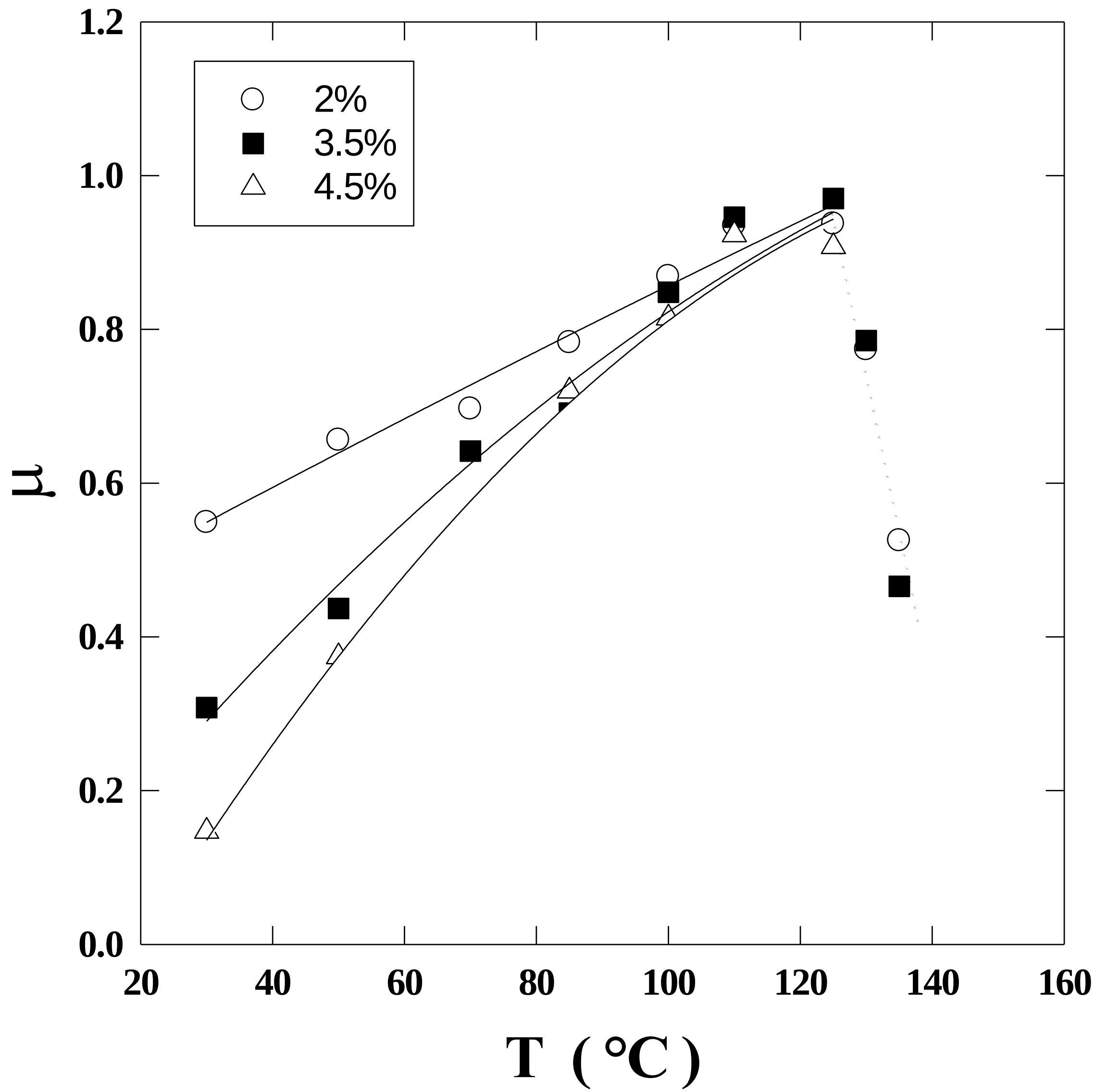
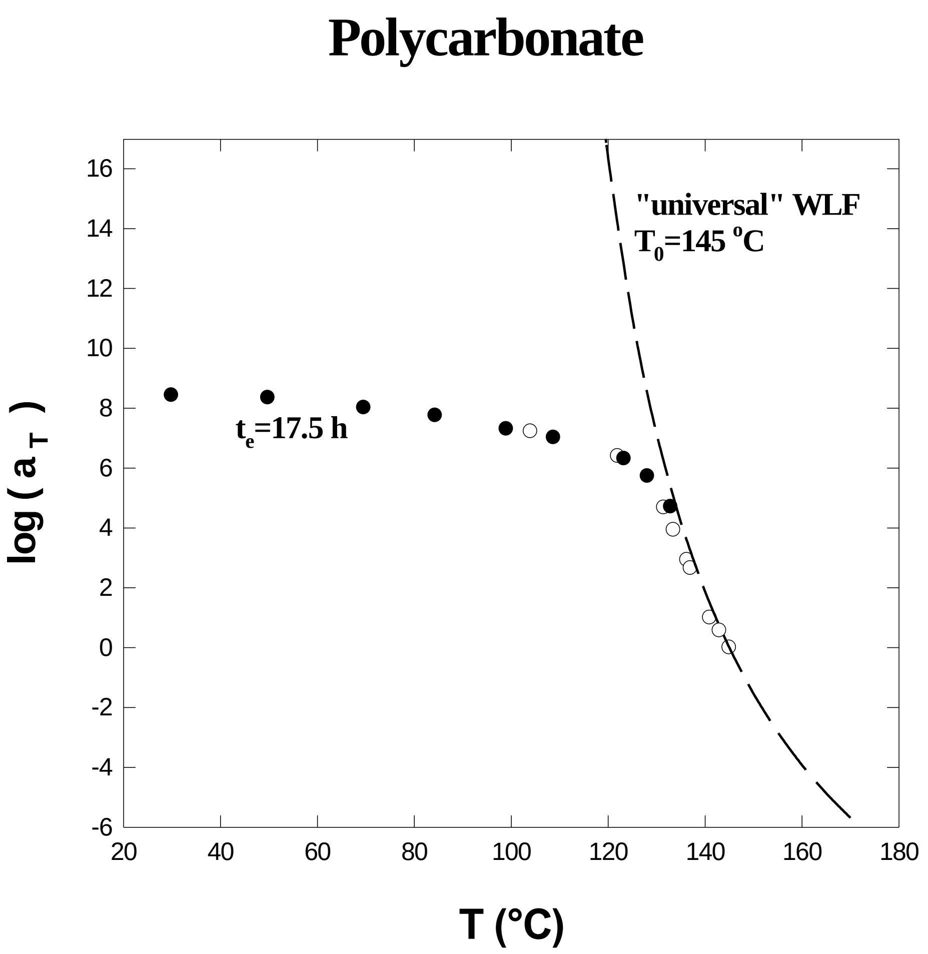


Figure 6. Shift rate in the power-law regime for a polycarbonate glass as a function of temperature and strain magnitude. The glass transition of the material is approximately 142 °C. (After O'Connell and McKenna[24]).

Physical Aging in the linear viscoelastic regime: Aging dependence of temperature shift factors



After Niemiec, et al, 1995

*Elapsed time theory or power law evolution during aging—why?**

$$a_{te} = At_e^{\mu}$$

*This is only valid in the down-jump experiment

Structural recovery/physical aging equations:

$$\delta_H(z) = \Delta C_p \int_0^z R(z-z')\frac{dT}{dz'}dz'$$

Account for:

a) Memory
b) Asymmetry
c) Enthalpy overshoot

$$z = \int_0^t \frac{d\xi}{a_T a_{\delta_H}}$$

$$\delta_H(t) = H(t) - H_\infty$$

$$J(t,t_e) = J(t,\delta(t_e)) = J(t/a_\delta)$$

$$J(t) = J_0 e^{(t/\tau)^\beta}$$

$$a_{t_e} = \frac{\tau(t_e)}{\tau(t_{e,ref})}$$

Elapsed time

$$a_\delta = \frac{\tau(\delta)}{\tau(\delta_{ref})}$$

Structure

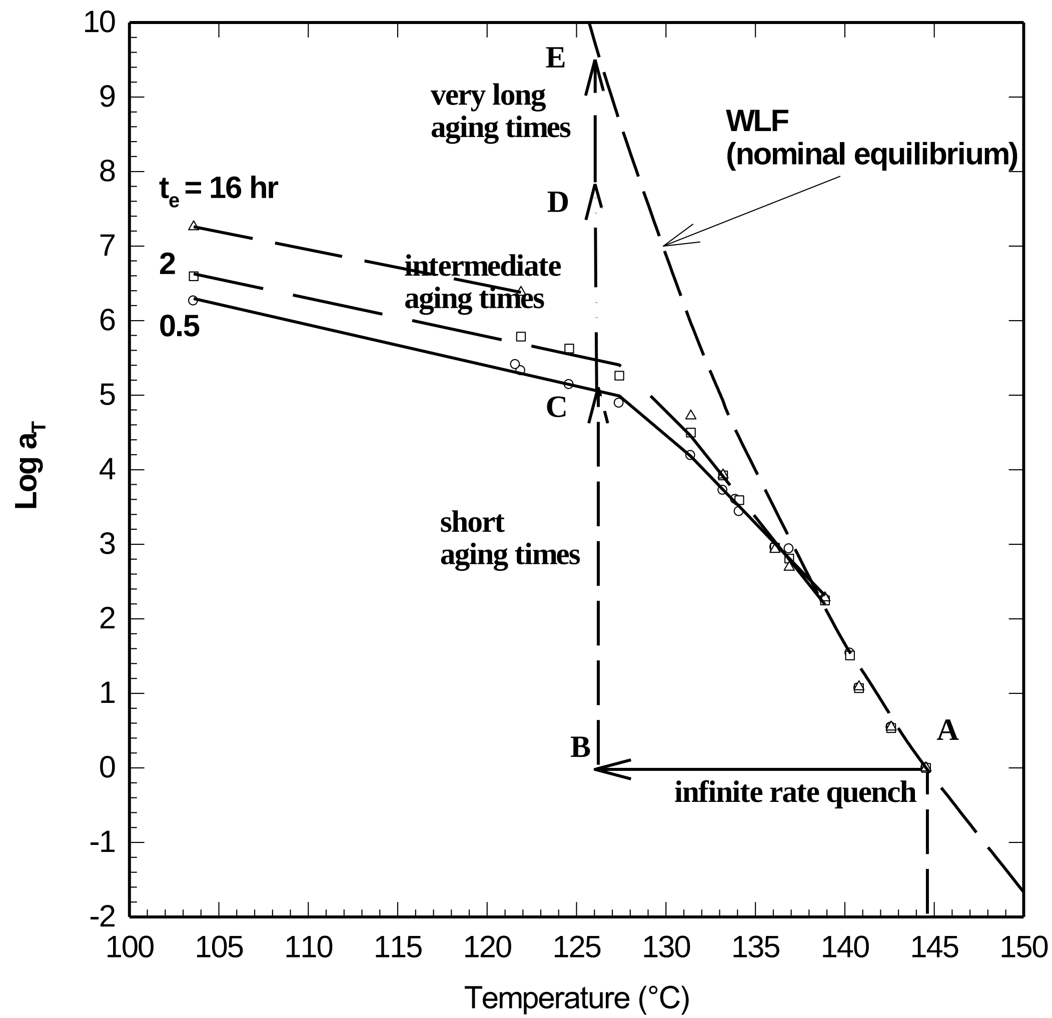


Figure 28. Total shift factor vs. temperature for a polycarbonate glass-former at different aging times. Quench and aging paths and their significance are discussed in text. (Data reported in Cerrada and McKenna[26]).

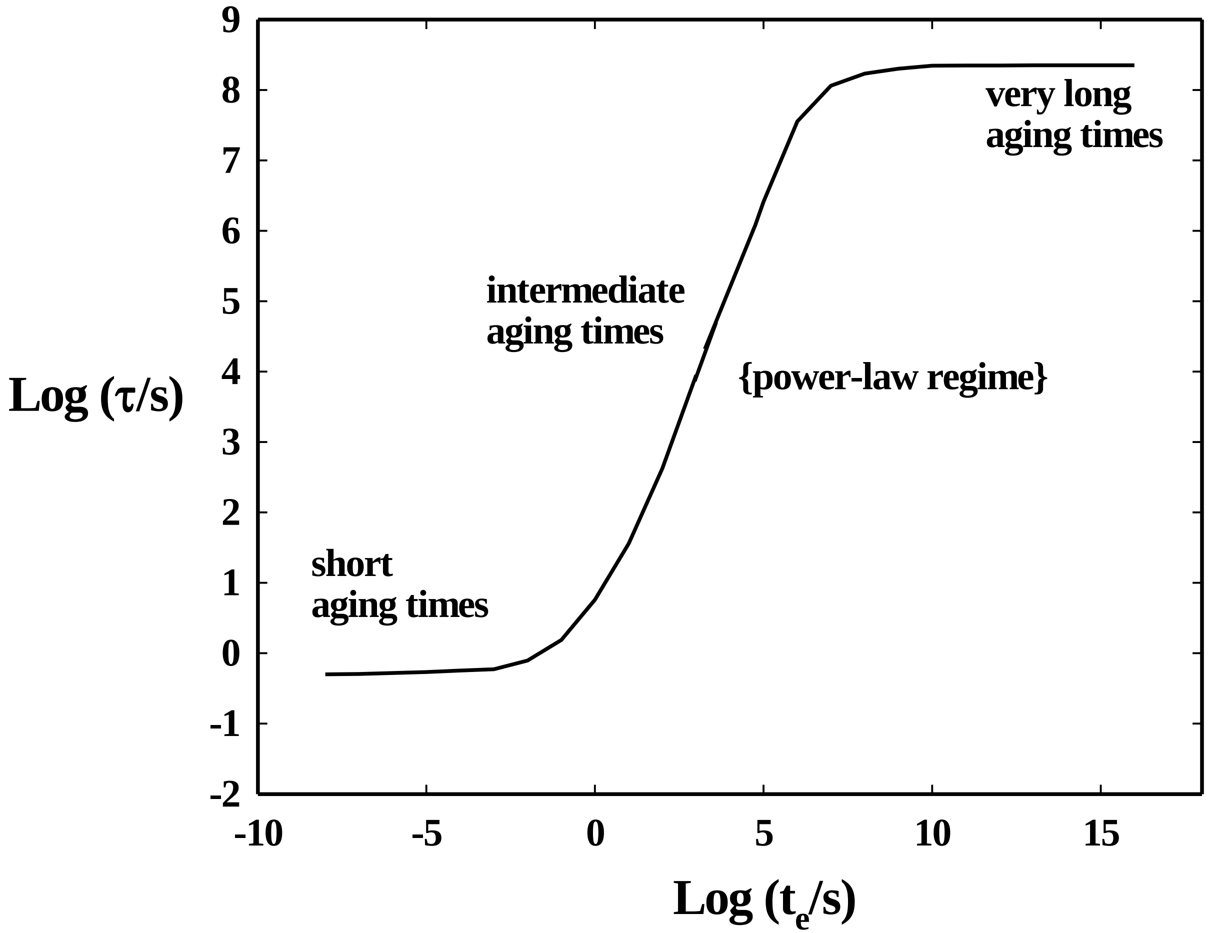


Figure 29. Semi-quantitative schematic of the shift factor vs aging or elapsed time for a material in a down-jump experiment showing the sigmoidal shape that the curve must have due to physical limitations at the short times and the fact that the material reaches equilibrium at long times.

And in other histories?

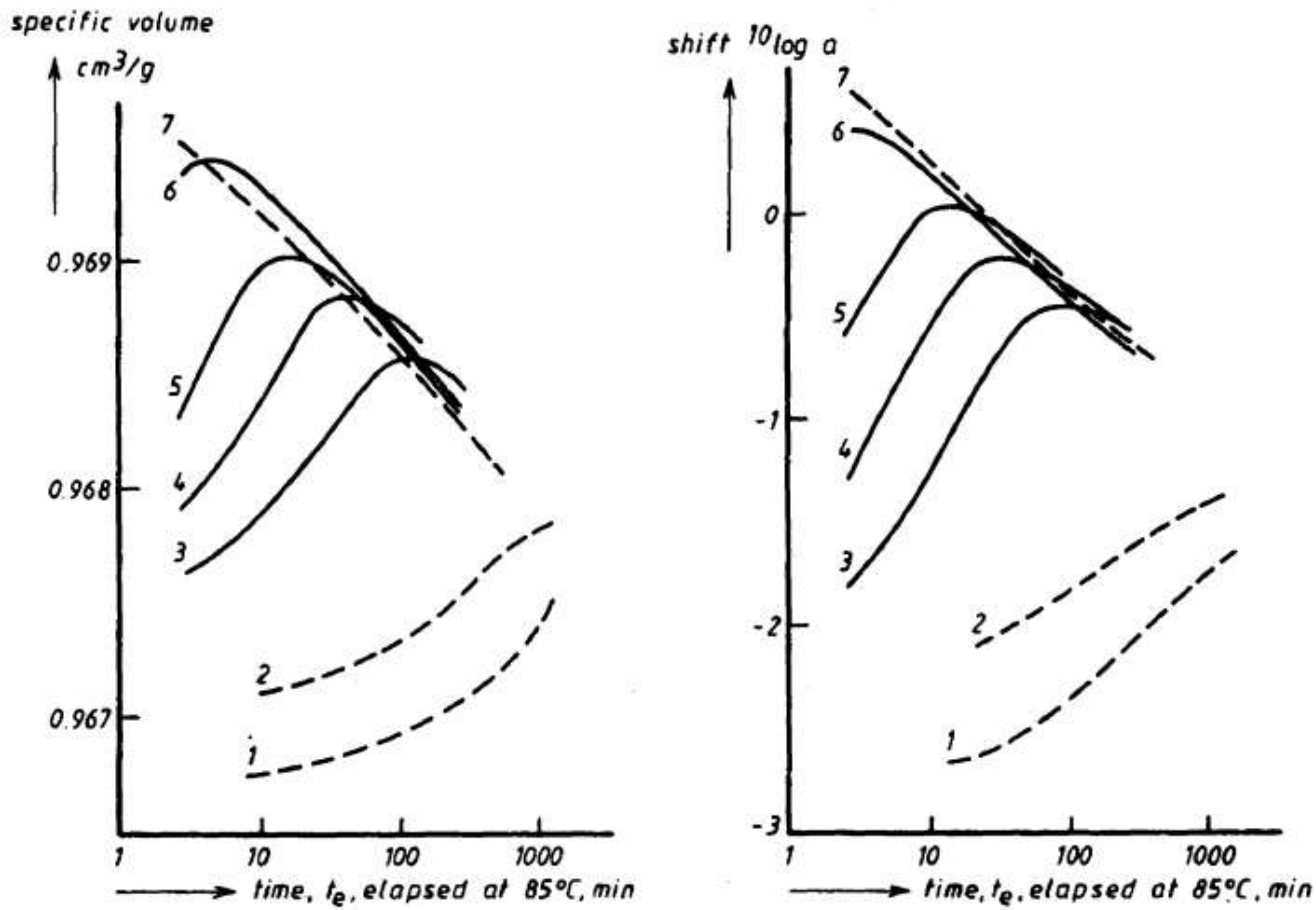
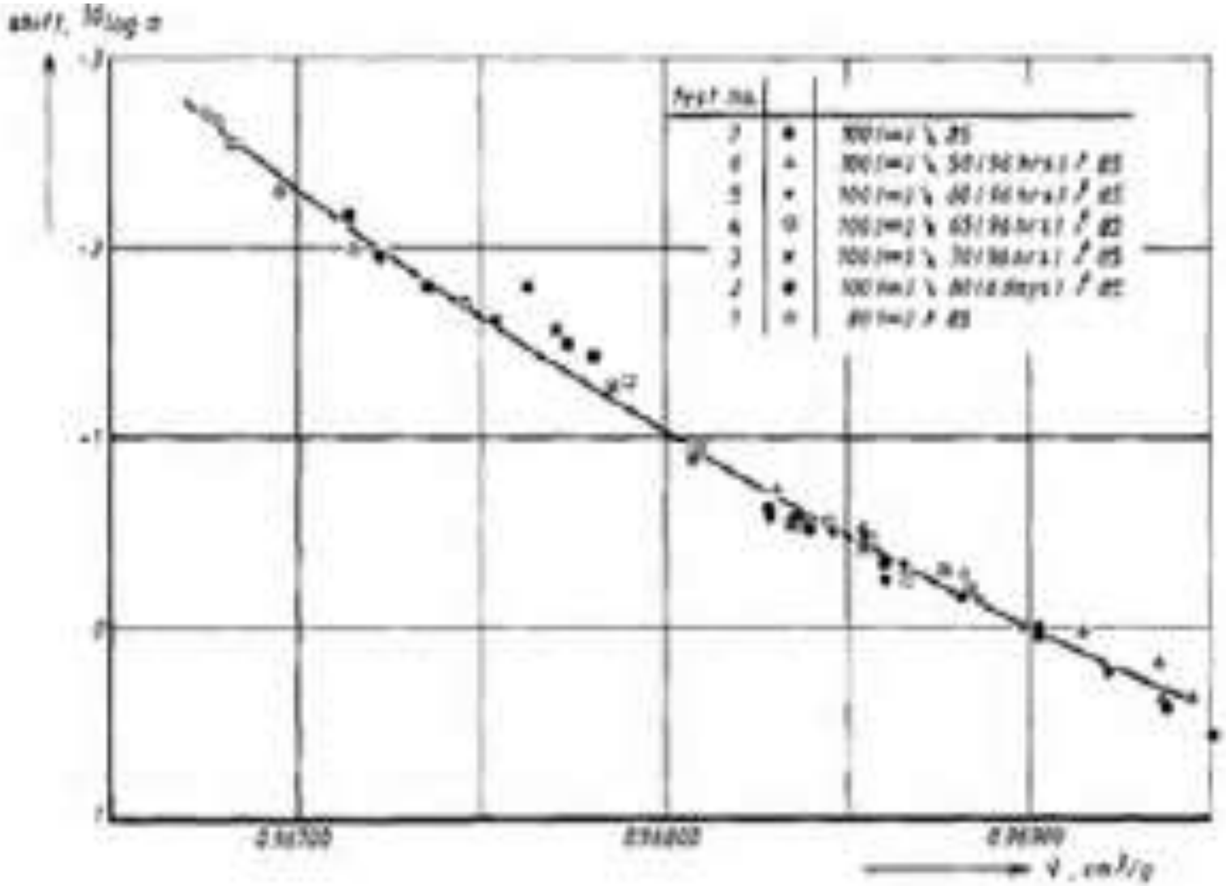


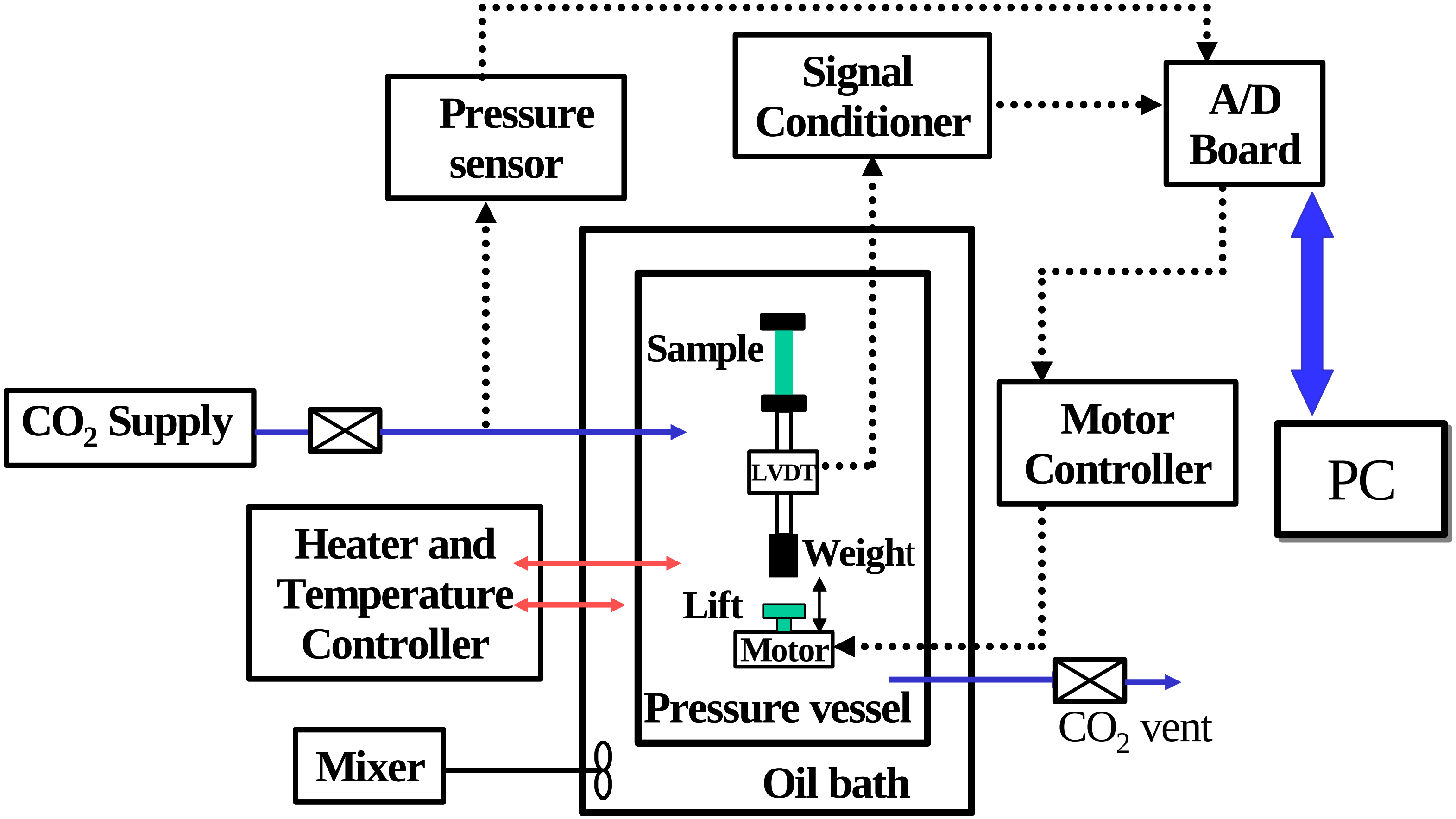
Figure 30. Memory or cross-over experiments in polystyrene showing that both the volume and the shift factor (retardation time) are non-monotonic because the viscoelastic response during aging depends on the specific volume or other state variable and not on the elapsed time per se. (After Struik[6,82]).

Volume dependence of relaxation times for all thermal histories. After Struik (1976)



Physical Aging and Plasticizer Jumps

Experimental system-CO_2 jumps

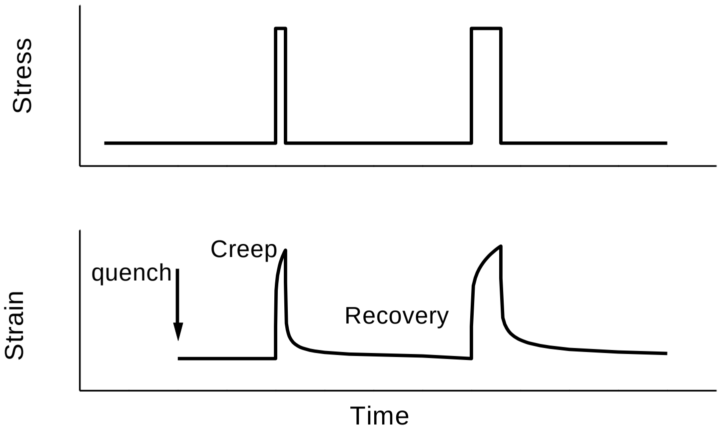


Material

- DGEBA (Dow Chemical) cured with amine terminated PPO (Huntsman) at 100°C for 24 hr
- $T_{g\infty}$=72°C
- Sample thickness: 40-60 μm

Measurements

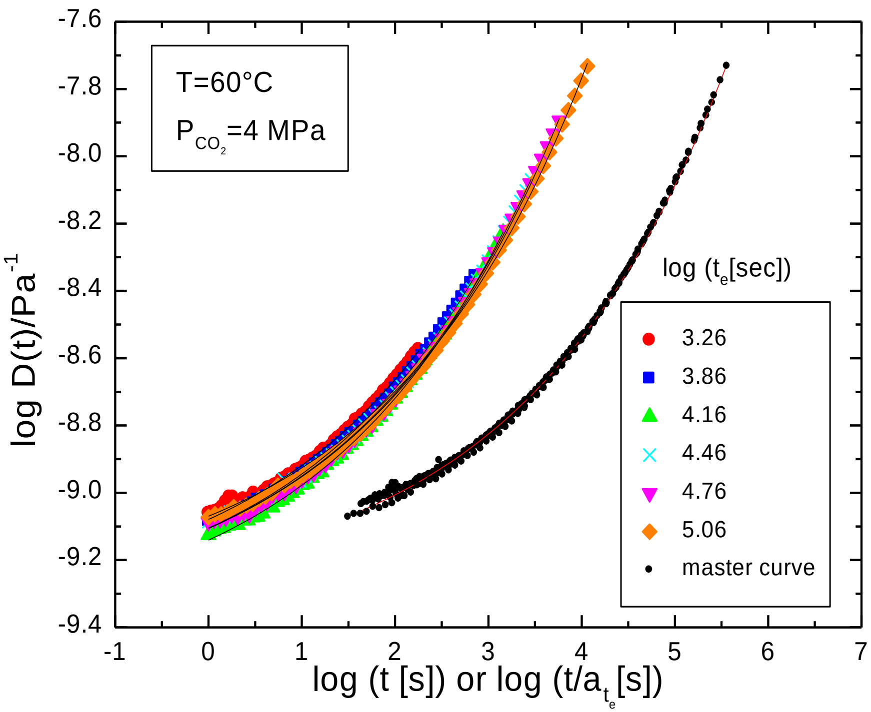
- Sample length change measured using LVDT
- Struik's protocol with σ_0=1.9 MPa.

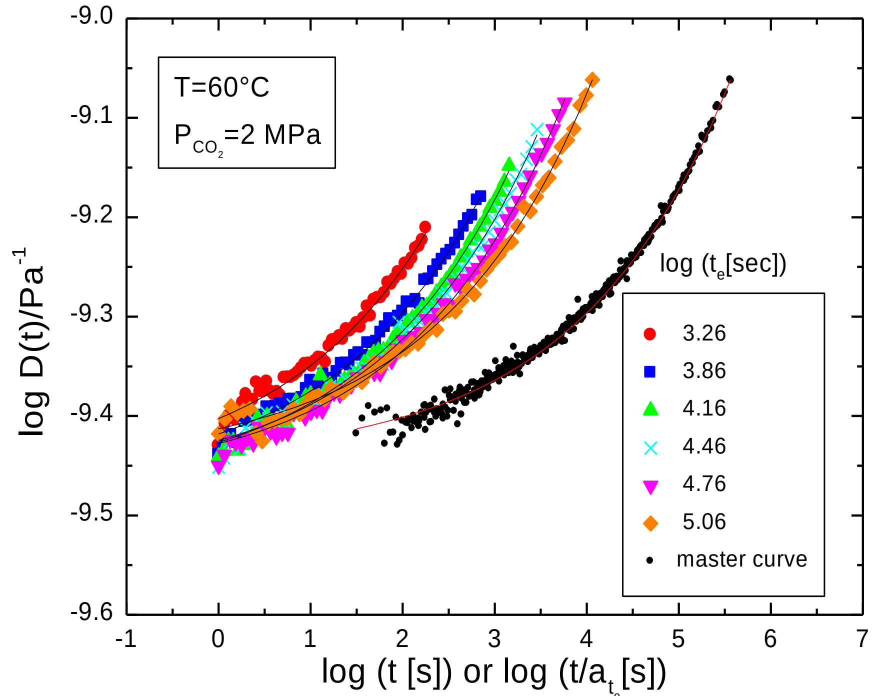


- T_{jumps}: 90°C to 60°C at Pco_2≈0.0 MPa.
- P_{jumps}: Pco_2 =4.3 MPa to various Pco_2 at 60°C.

Physical aging: Jumps to different carbon dioxide pressure under isothermal conditions

Pco_2(initial)=4.3 MPa





Analysis

- The creep data can be represented by the KWW function

$$D(t) = D_0 \left[\exp\left(\frac{t}{\tau}\right)^{\beta} \right]$$

- The physical aging data are further analyzed in terms of a shift rate, μ, as defined by Struik:

$$\mu = \frac{d\log(a_{t_e})}{d\log(t_e)} = \frac{d\log(\tau_{t_e})}{d\log(t_e)}$$

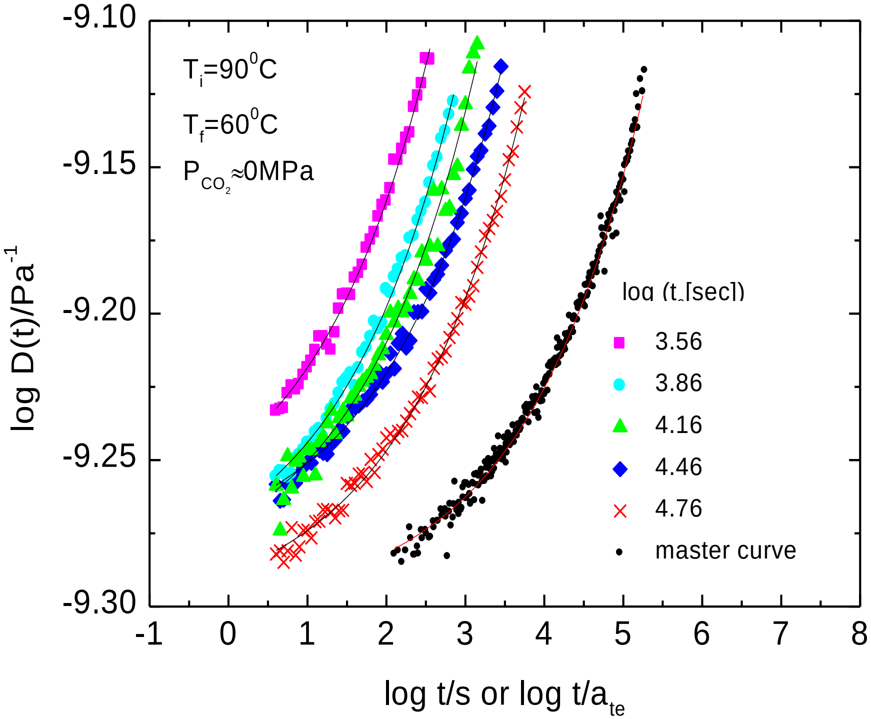
Physical aging: Comparison of temperature and CO_2 pressure jumps

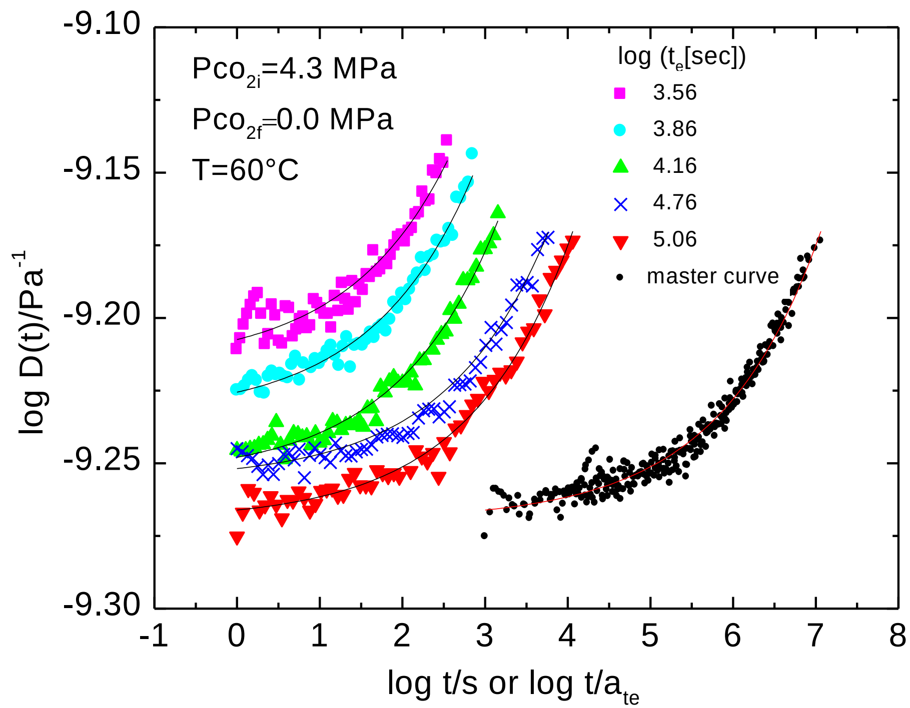
T-jump

β=0.29

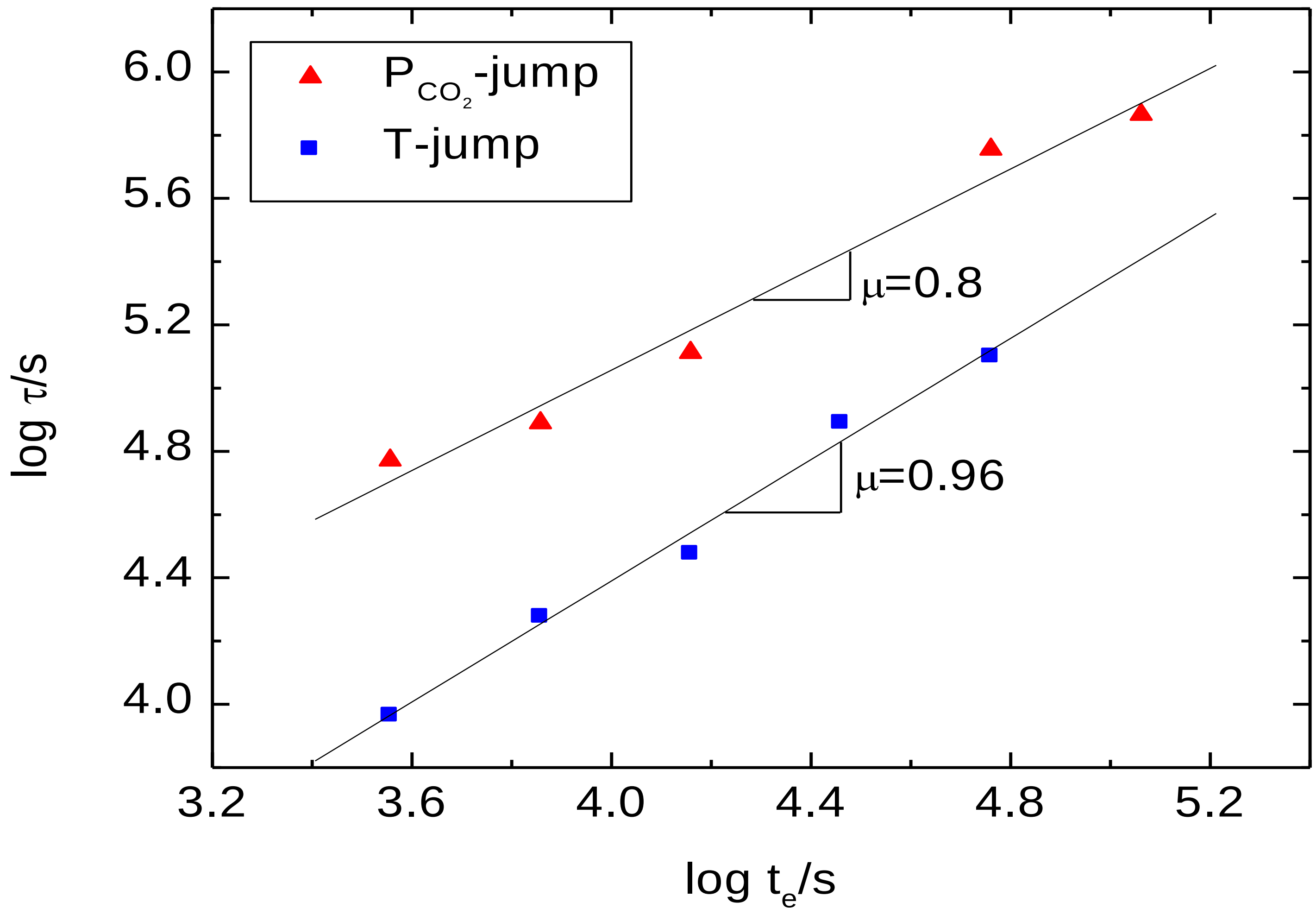
Pco_2-jump

β=0.35





Comparison of KWW relaxation time for T-jump and P_{CO2}-jump



Physical aging after RH jump

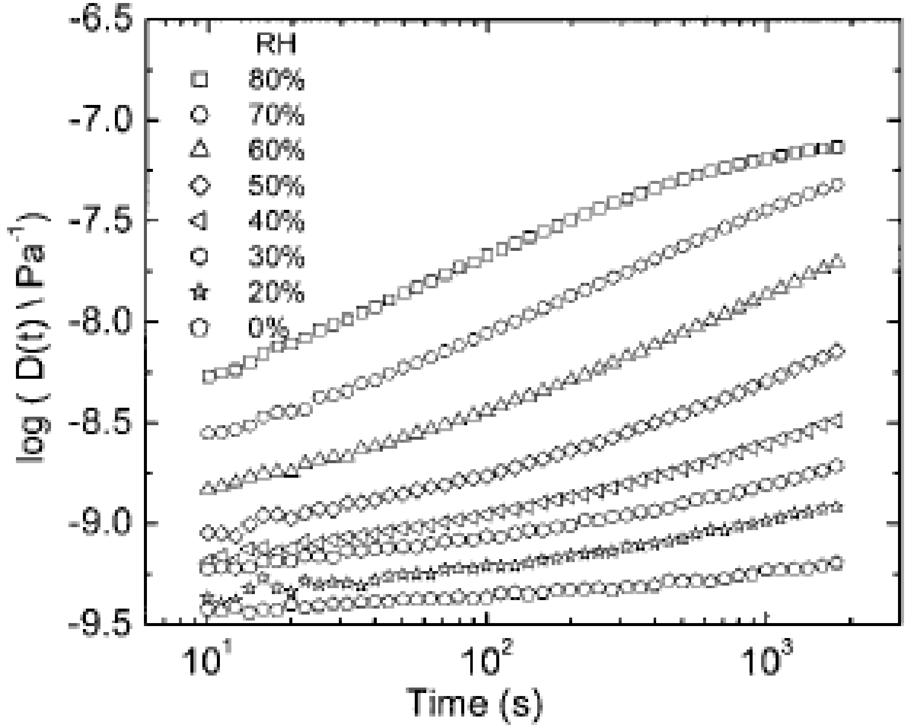


Figure 4. Creep responses after jumps from RH = 90% to different relative humidities. The creep was measured after 10 h aging. All the measurements were performed isothermally at 60 °C.

Physical aging after RH jump-intrinsic isopiestics

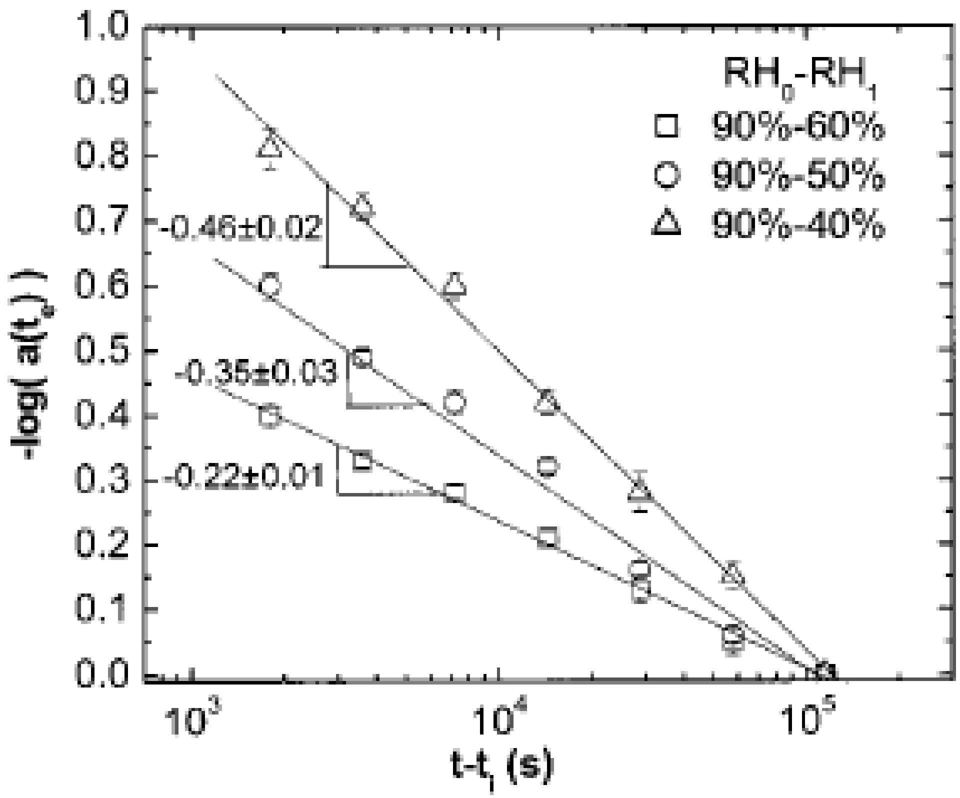


Figure 10. Plot of shift factors $[a(t_e)]$ as a function of aging time for different aging relative humidities as indicated. These are intrinsic isopiestic results at 60 °C.

Physical aging after RH jump-asymmetry

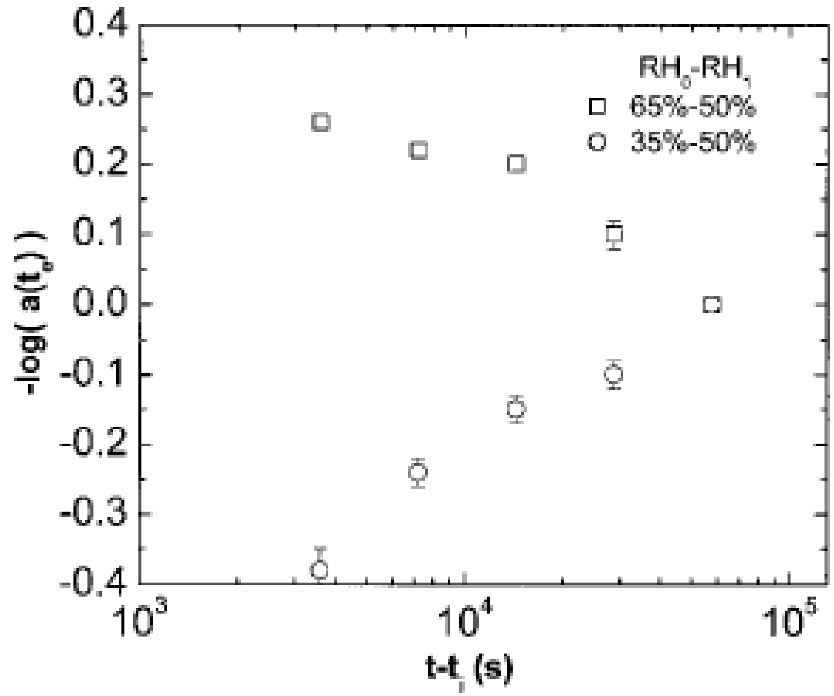


Figure 18. Plot of shift factors $[a(t_e)]$ as a function of aging time for creep responses in Figures 16 and 17, as indicated. These are the asymmetry of approach results at 60 °C.

Physical aging after RH jump-memory

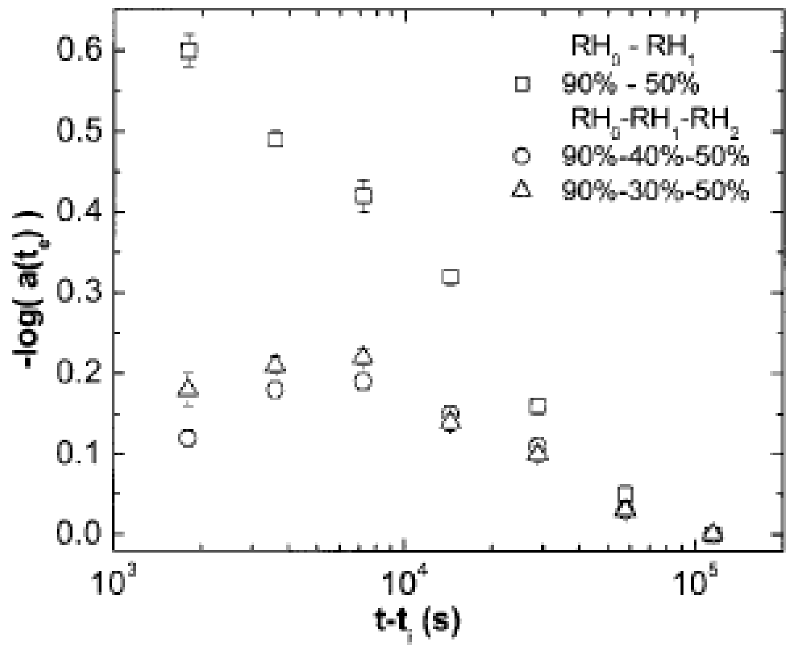
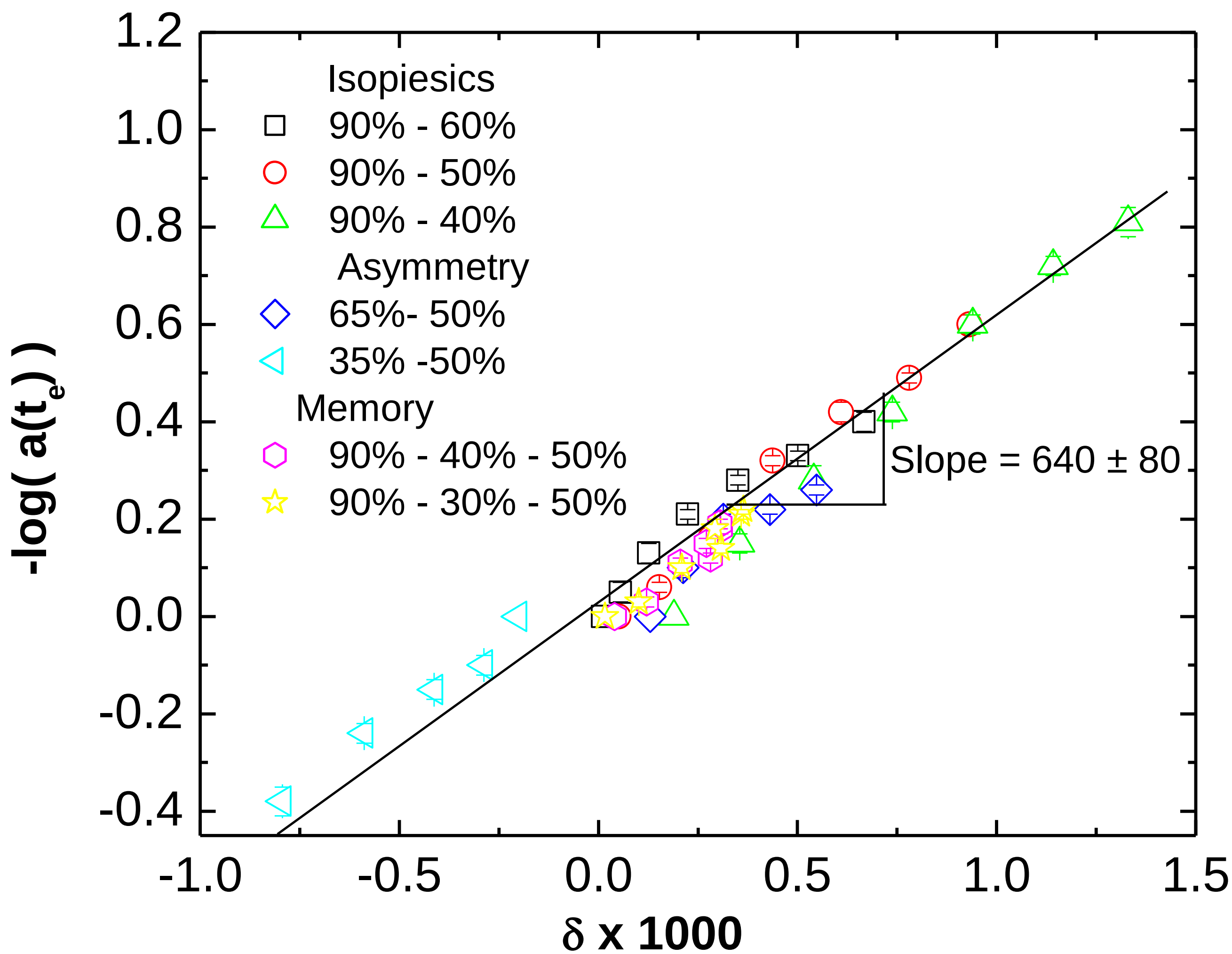
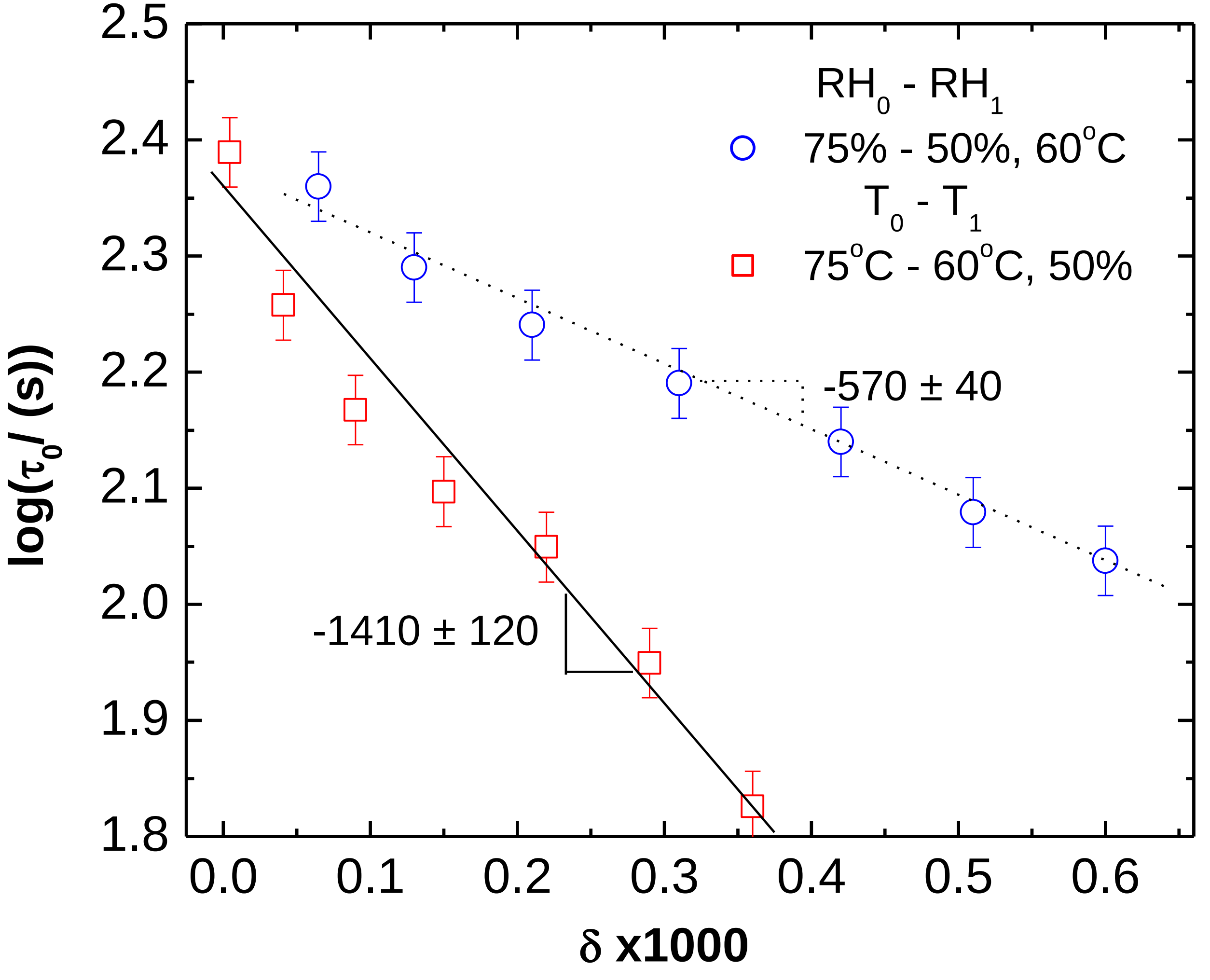


Figure 14. Plot of aging time shift factors [$a(t_e)$] as a function of aging time for creep responses in Figures 8, 12, and 13, as indicated. These are the memory effect results at 60 °C.

Physical Aging: $a(t_e)$ vs. δ



Physical Aging: RH-jump vs. T-jump



Aging occurs in small molecule glasses as well

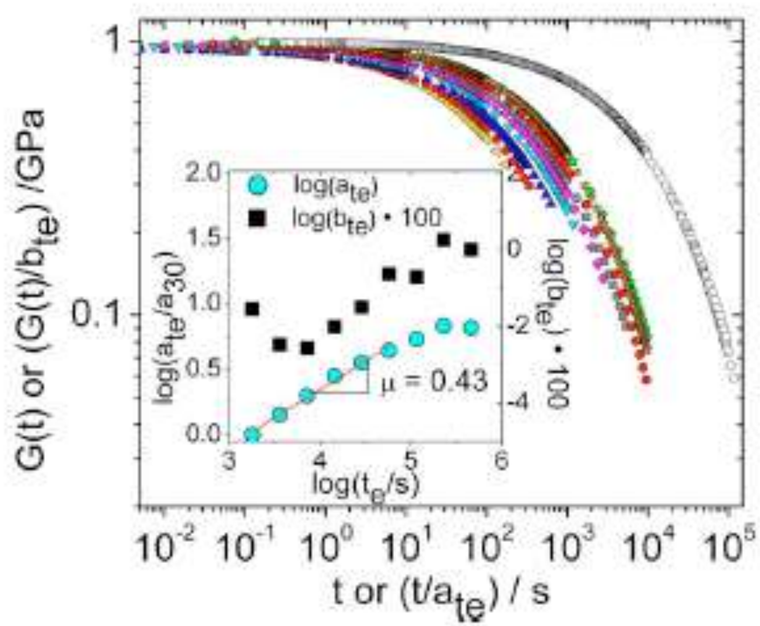


FIG. 6. (Color online) Compliance corrected shear stress relaxation data for different aging times for sucrose benzoate at $T_g - 9$ K (328 K): 30 min (◁, yellow filled), 60 min (○, red filled), 120 min (△, blue filled), 240 min (▽, cyan filled), 480 min (◇, magenta filled), 960 min (□, gray filled), 1920 min (⬠, red filled), 3840 min (○, green filled), 7680 min (☆, orange filled), and the master curve (○, open). The inset shows the aging time shift factors used to construct the master curve. The master curve is offset by one decade for clarity.

Hutcheson and McKenna, JCP, 2008

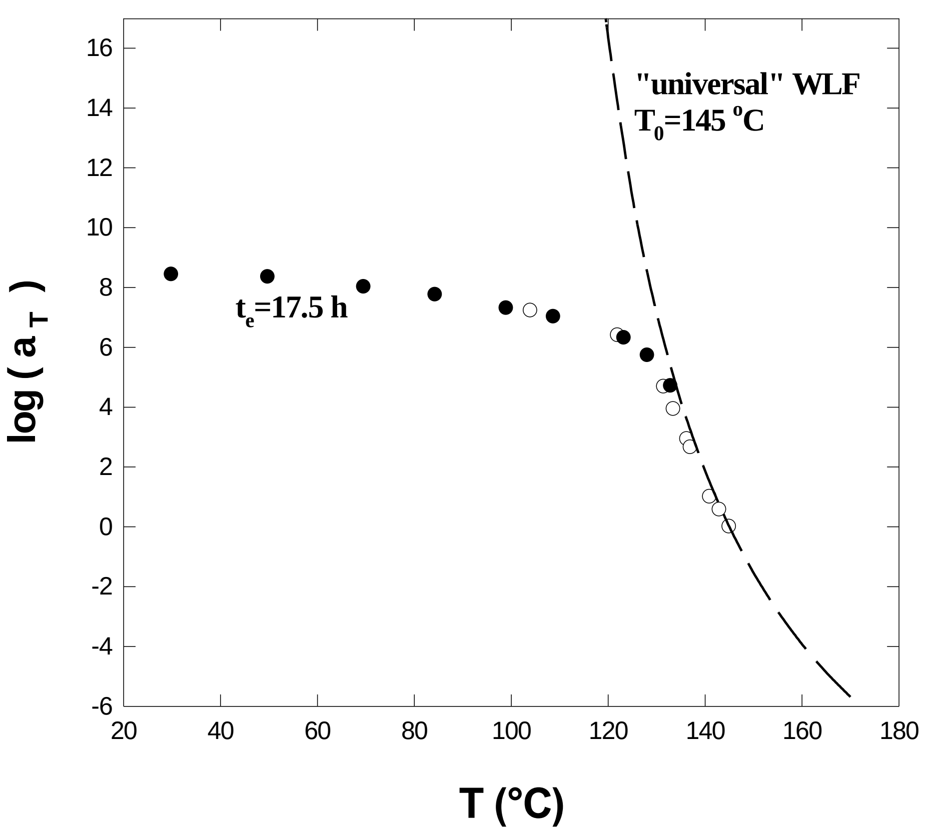
Non-divergent dynamics

- If a material is aged into equilibrium below the “nominal glass transition temperature” do the dynamics reach the extrapolated Vogel-line?

P.A. O’Connell and G.B. McKenna, “Arrhenius-like Temperature Dependence of the Segmental Relaxation below Tg,” Journal of Chemical Physics, 110, 11054-11060 (1999).

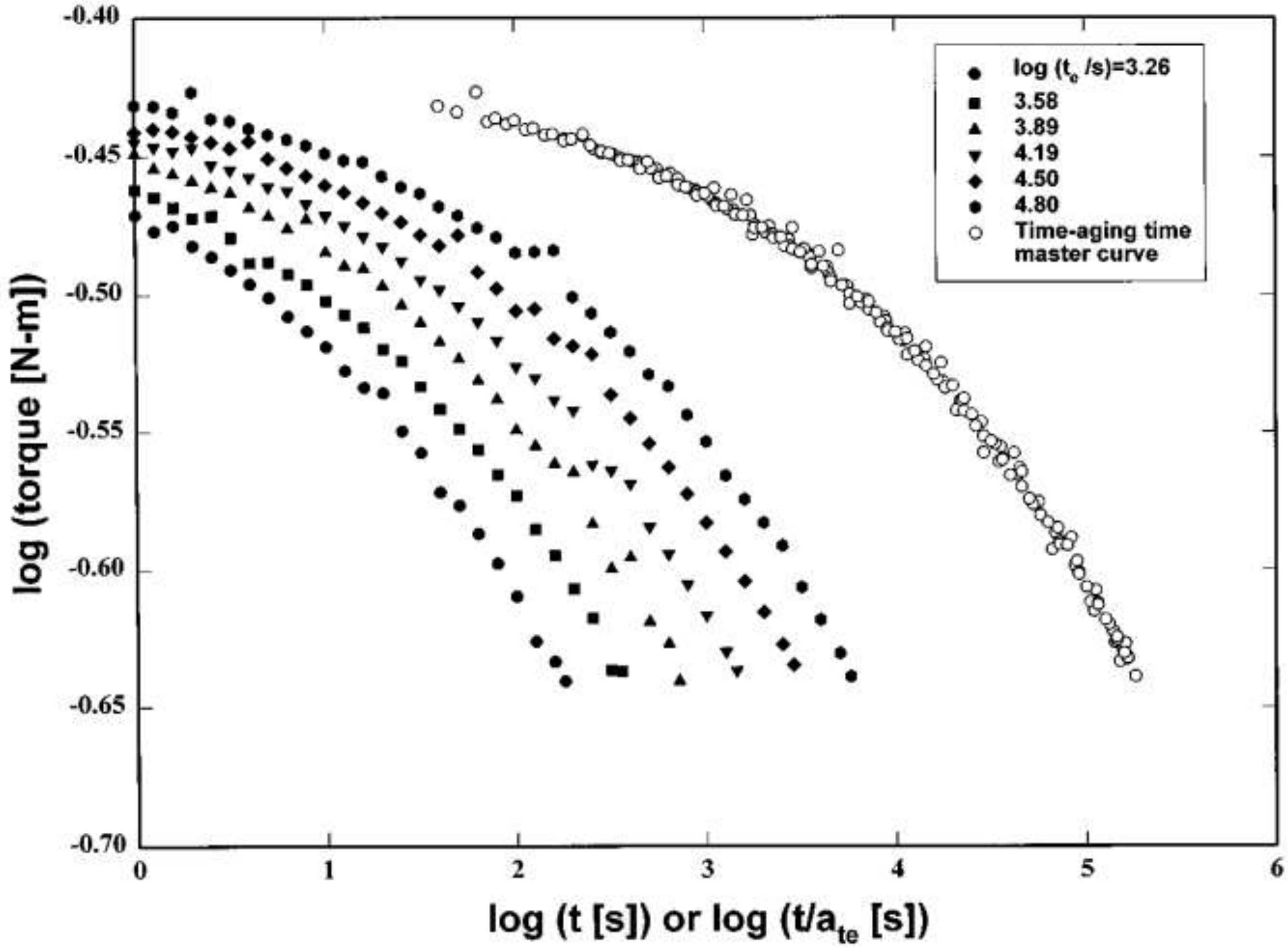
Physical Aging in the linear viscoelastic regime: Aging dependence of temperature shift factors

Polycarbonate

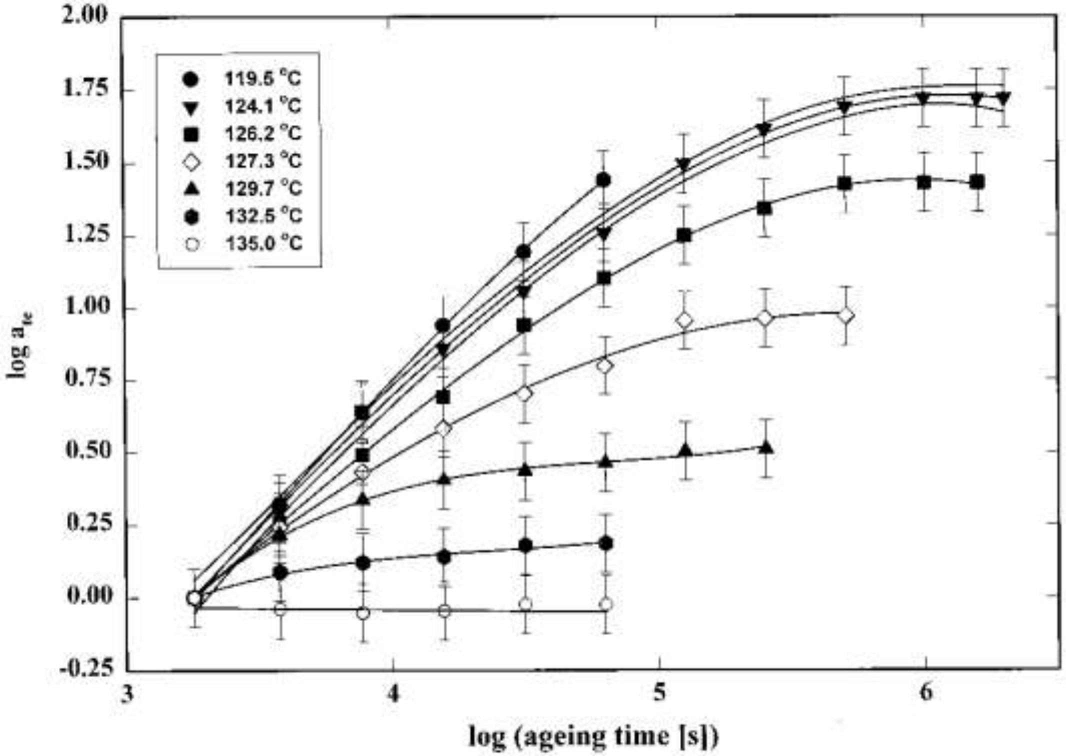


After Niemiec, et al, 1995

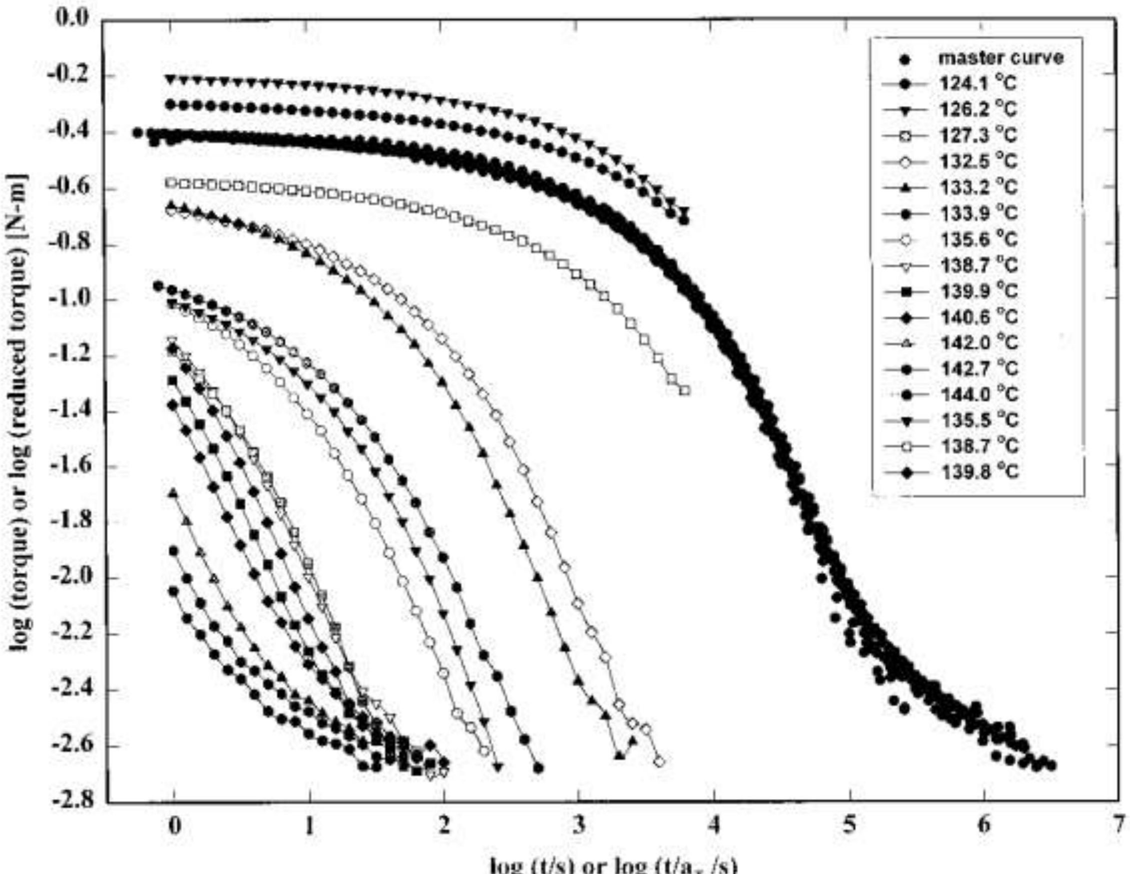
Run an aging experiment: Quench from above T_g to below and "probe" response



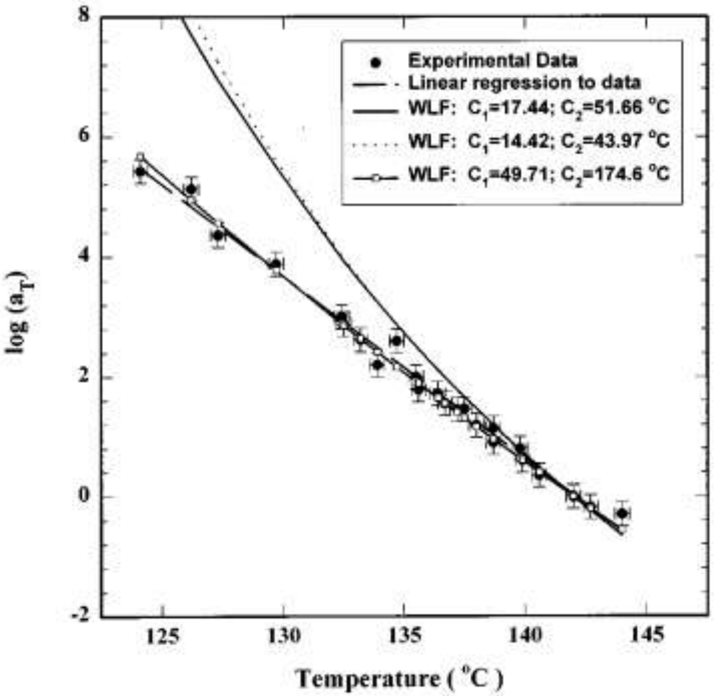
Age into equilibrium

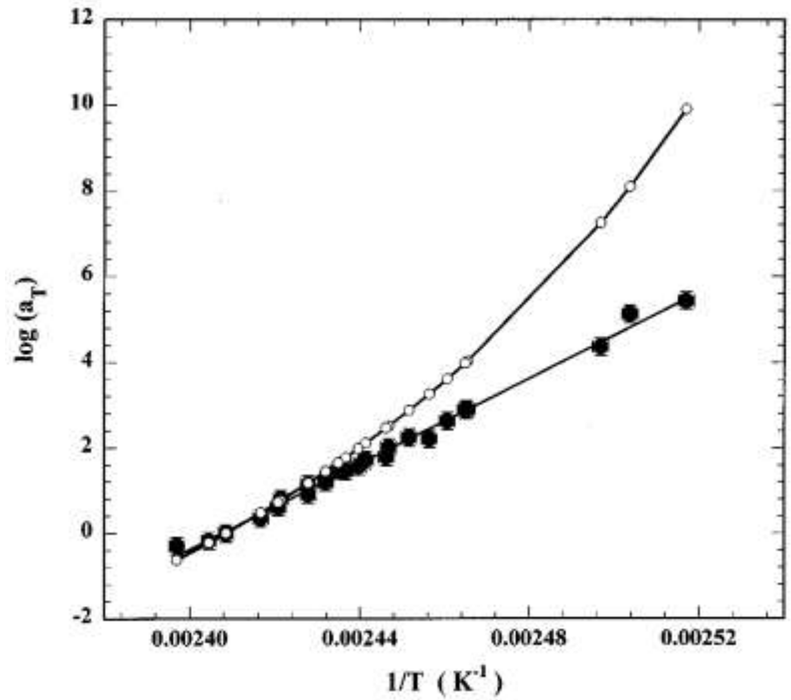


Time-temperature master curves: in equilibrium



Temperature dependence of equilibrium relaxation times (as shift factors)





Vogel-Fulcher divergence is lost

Vogel-Fulcher breakdown

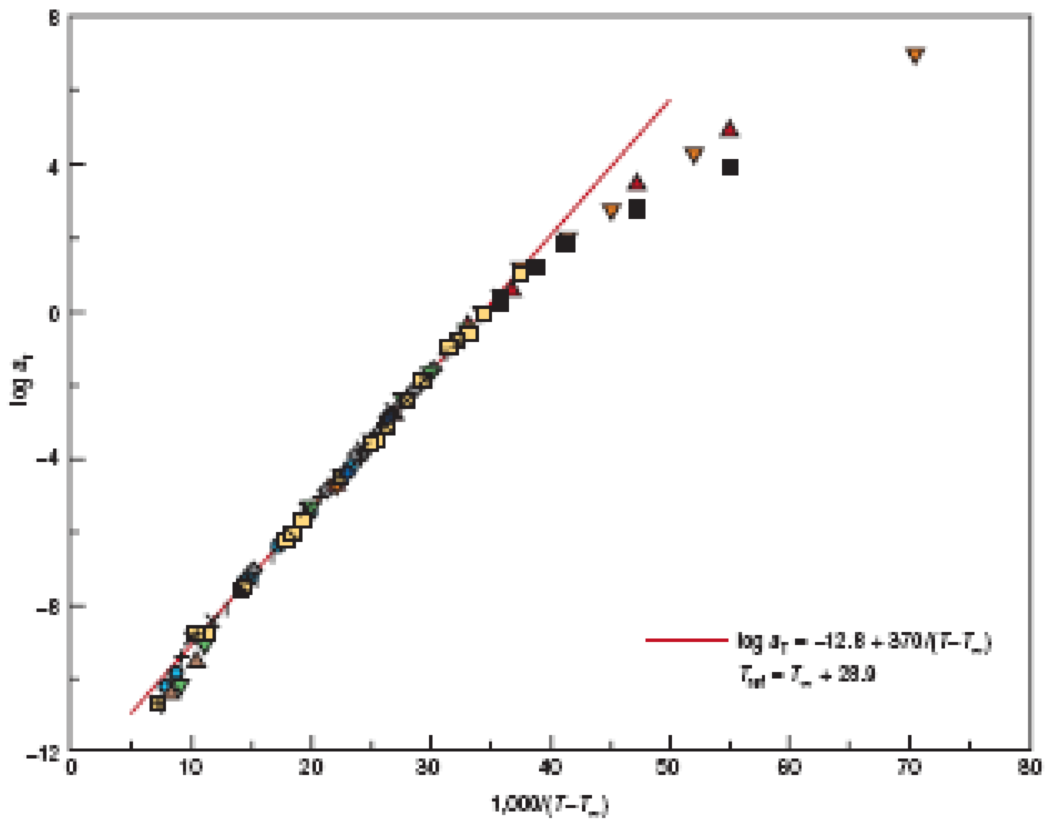


Figure 1 VFT plot of segmental relaxation data (as shift factors a_T) for polystyrene. Experimental and literature compilation from Simon and colleagues[7]. Reprinted with permission from ref. 7. © 2001 Elsevier.

After Simon et al 2001

Aging in the Nonlinear Regime: Outline

- *Effects of large stresses on aging behavior*
  - *Rejuvenation or erasure hypothesis*
  - *Evidence against rejuvenation*
    - *t**
    - *Torsional dilatometry*
- *Superposition of small strains and large strains*
  - *A nonlinear memory effect*
    - *Evidence for and against rejuvenation*
- *Interpretation*
- *Post-yield behavior*
  - *Polyamorphism hypothesis*
- *Implosion*
- *Summary*

Atomistic Simulation of Aging and Rejuvenation in Glasses

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Struik has also investigated the effect of aging beyond the linear-deformation range and reports two additional phenomena: creep at large stresses actually erases (partially or completely) the effect of previous aging (thus rejuvenates the glass by shifting its retardation spectrum towards shorter times), and the rate of aging, μ (*Eq 1*), dramatically decreases as the stress increases. Within a fair ap-

Effects of large stresses on aging:
Into the 'rejuvenation' regime

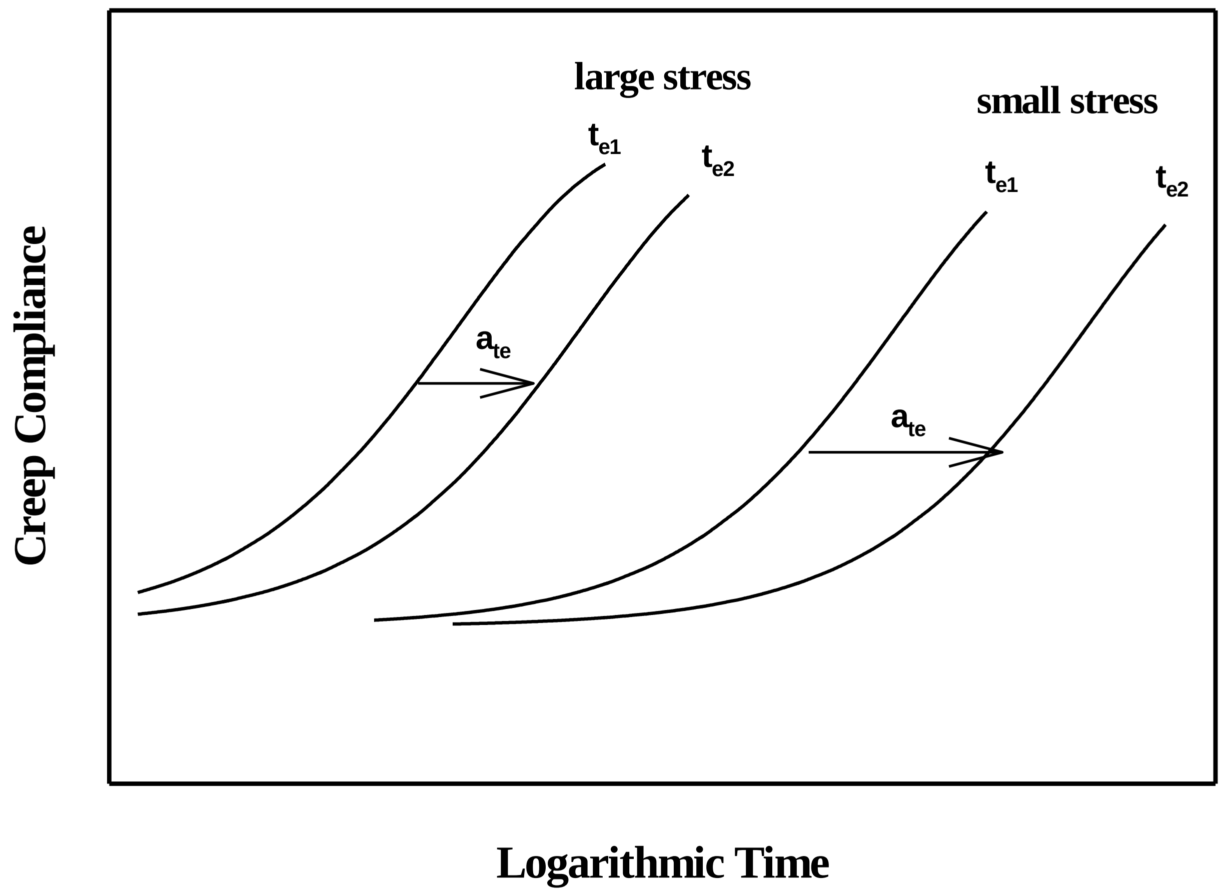


Figure 7. Schematic of the impact of large stresses on the aging time shift factor in a creep experiment. See text for discussion (After McKenna and Simon[10]).

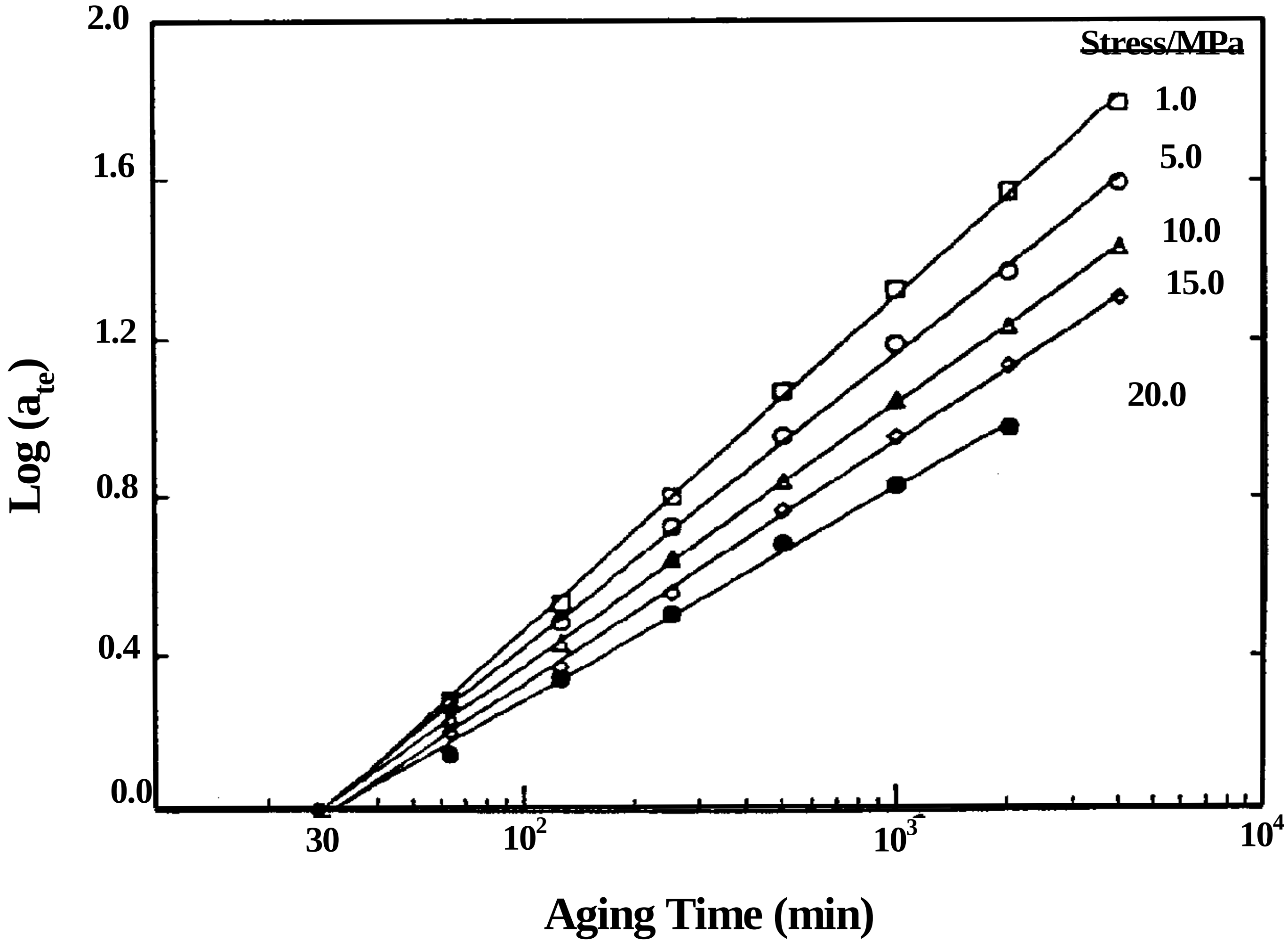


Figure 8. Plot of shift factor vs aging time in the power-law aging regime at different probe stresses, as indicated. The reduction in the slope of the lines, i.e. the shift rate, is illustrative of one “rejuvenation” signature. (After Lee and McKenna[11]).

“Rejuvenation?”

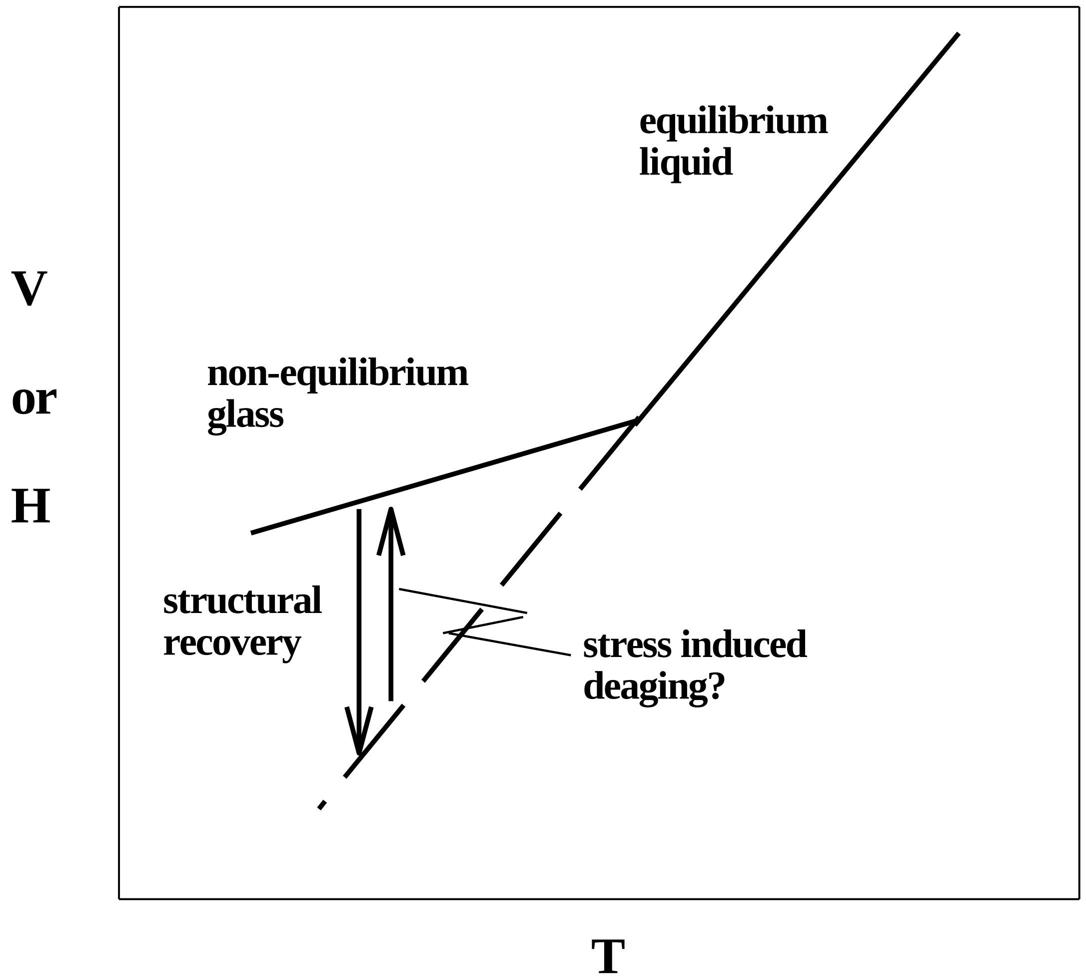
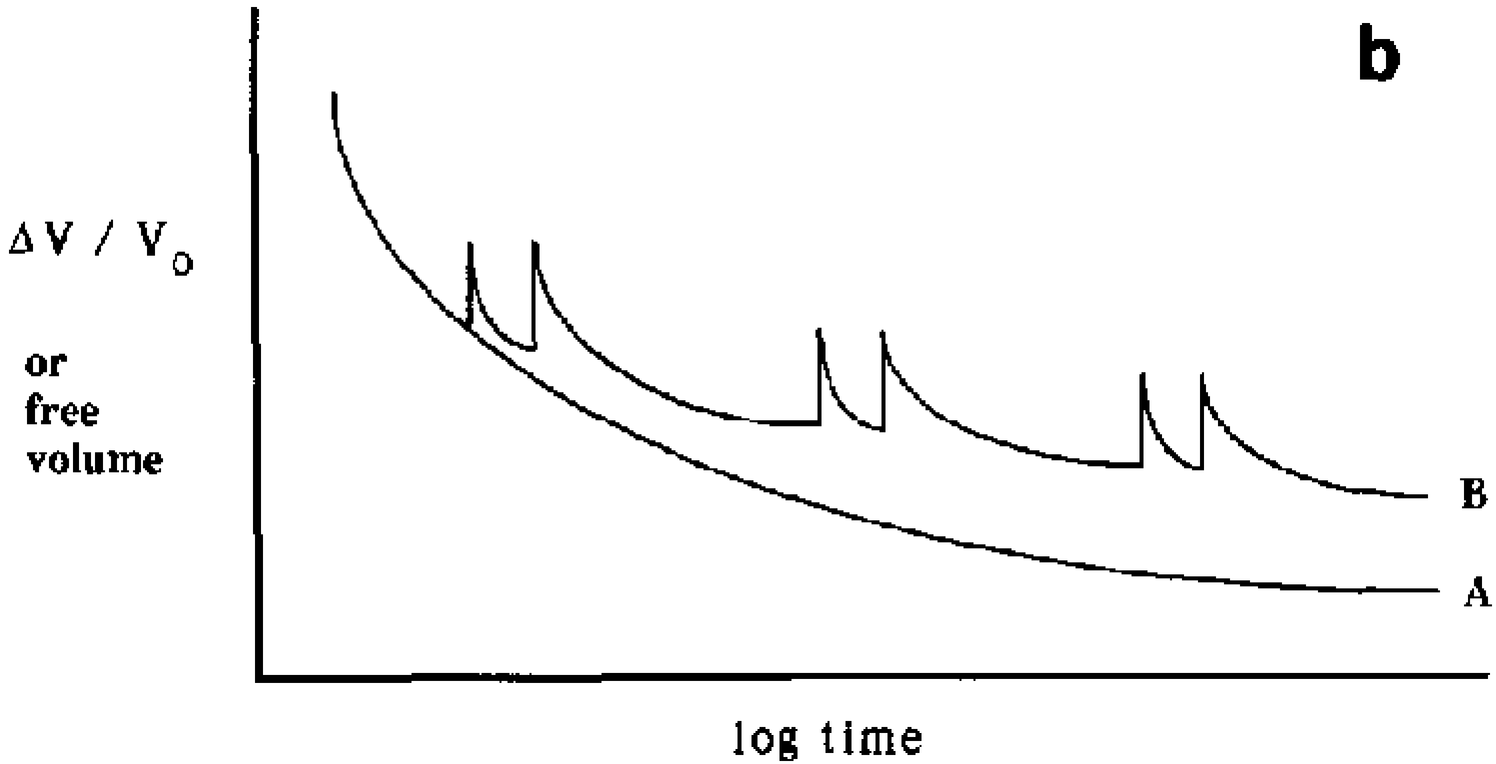


Figure 9. Schematic of the effects of large probe stresses on the thermodynamic state of the glass in the rejuvenation hypothesis. (Adapted from Ricco and Smith[14]).

Schematic of expectations of "rejuvenation" model on the volume evolution in two Cases: A: Physical aging, no mechanical perturbation. B: Mechanically induced Volume enhancement due to "rejuvenation".

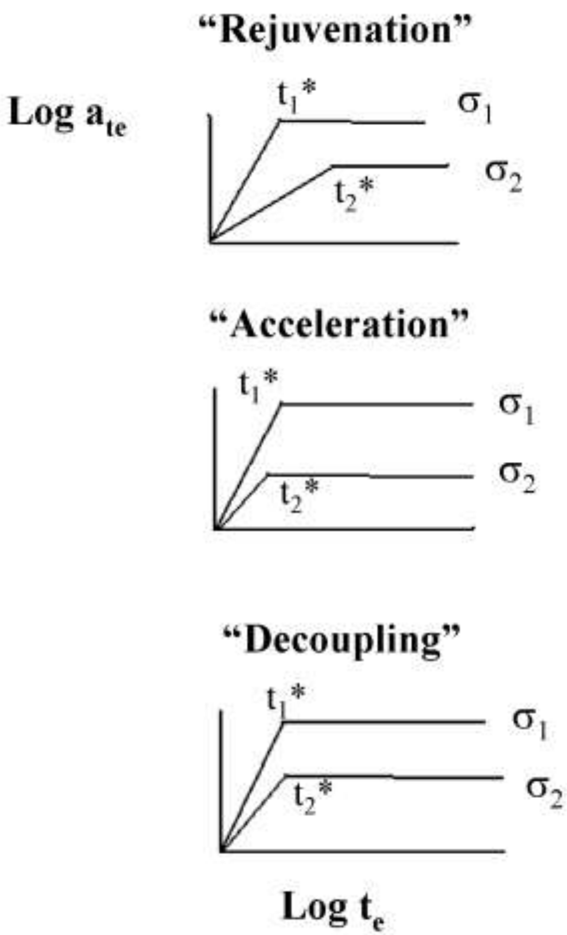


- ***Tests of Rejuvenation***

    >> the equilibration time as a function of stress

    >> torsional dilatometry

The equilibration time as a function of stress



Possible Effects of Stress on Aging Kinetics

$\sigma_1 < \sigma_2$

$t_1^* < t_2^*$

$\sigma_1 < \sigma_2$

$t_2^* < t_1^*$

$\sigma_1 < \sigma_2$

$t_2^* = t_1^*$

The equilibration time as a function of stress

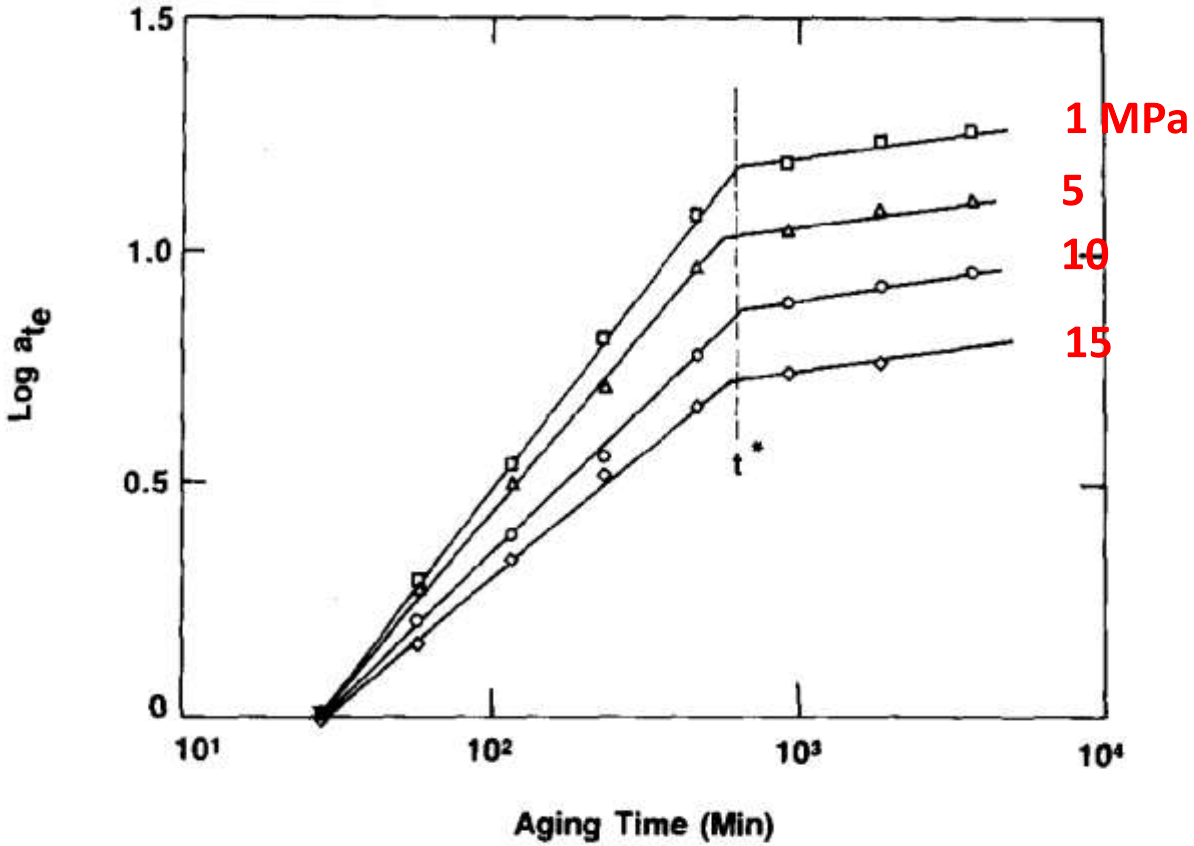


Figure 13. Effect of probe stress magnitude on nominal equilibration time t* for an epoxy glass. Figure shows that there is no effect of stress on t*. Stress Magnitude: (squares) 1 MPa; (triangles) 5 MPa; (circles) 10 MPa; (diamonds) 15 MPa. (After Lee and McKenna[11]).

TORSIONAL DILATOMETER: 0.1 ppm volume sensitivity. 20 ppm long term volume Stability.

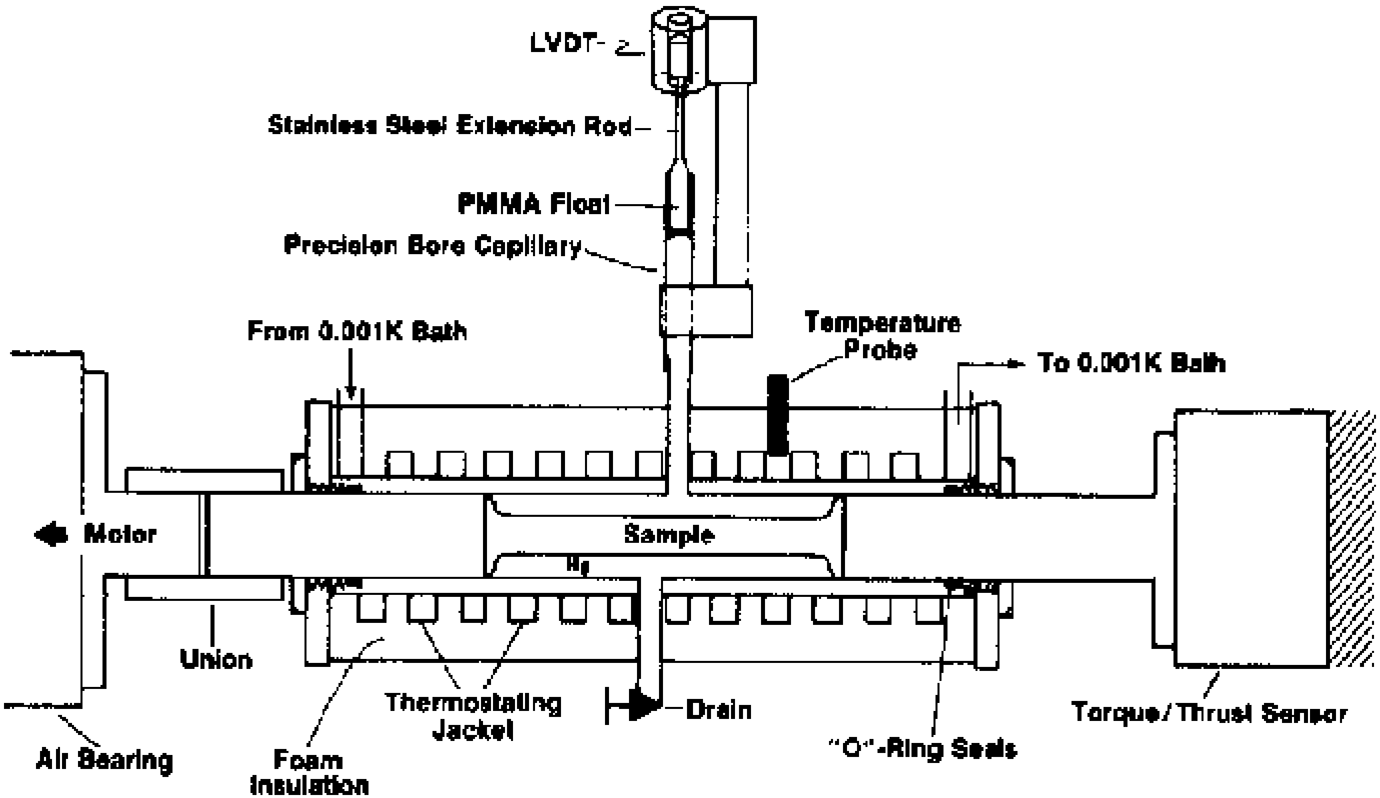
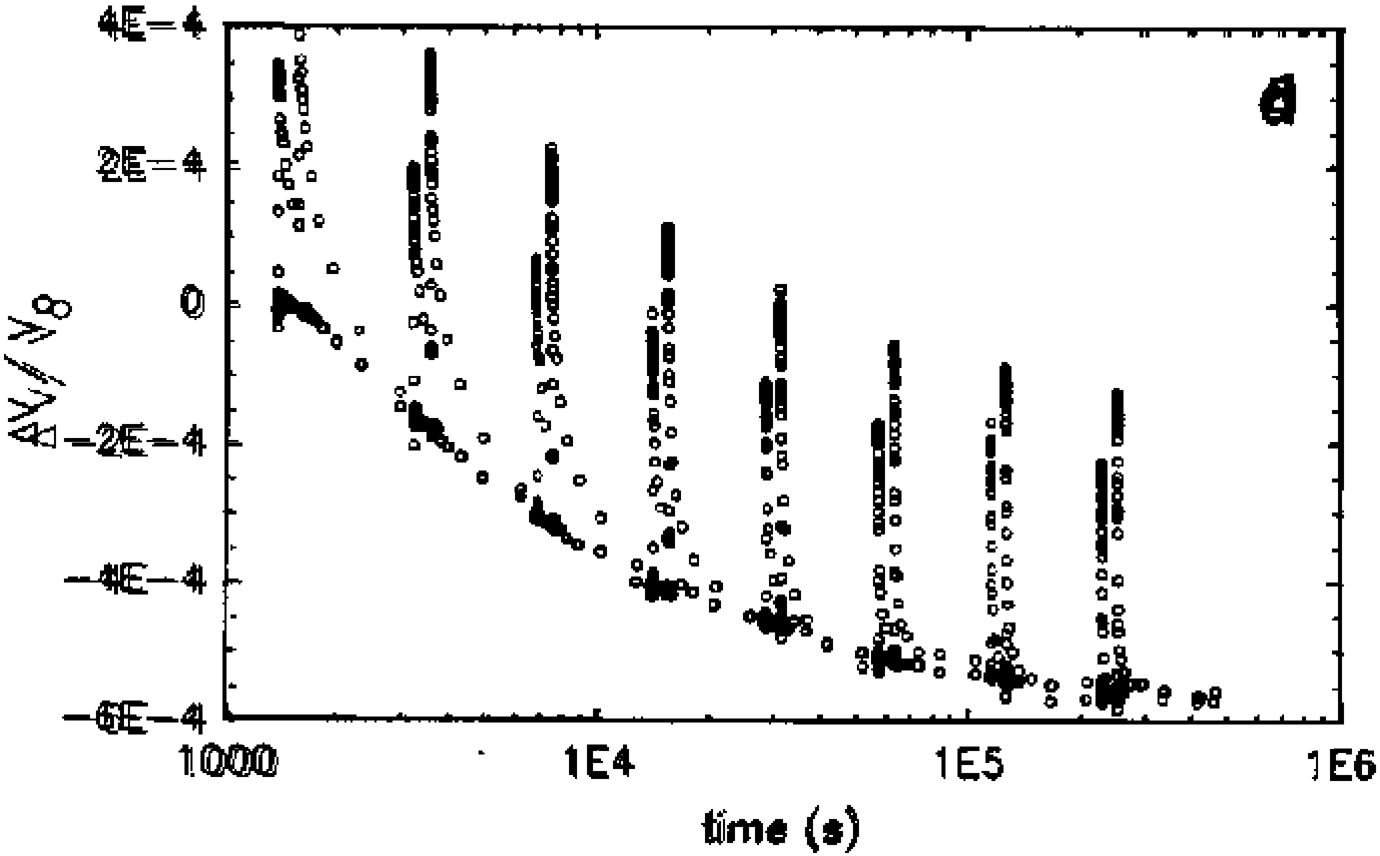


FIG. 2. Detailed schematic of dilatometer chamber. (See text for discussion.)

TORSIONAL DILATOMETRY RESULTS

Comparison of torsional volume changes in sample with zero strain (black) and sample strained to 5 %--well into the “rejuvenation” regime (red). (After Santore, Duran and McKenna.



Superposition of large and small stresses or deformations

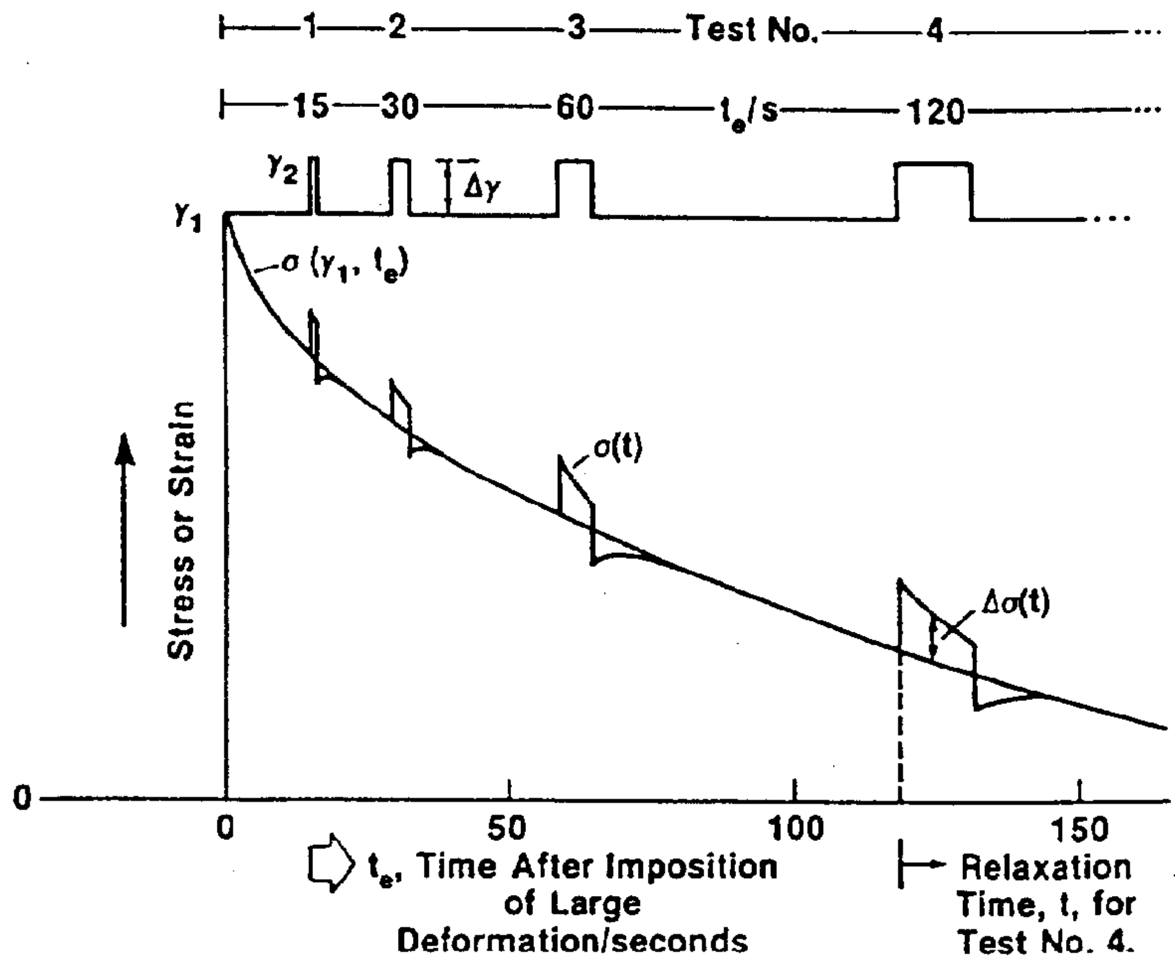
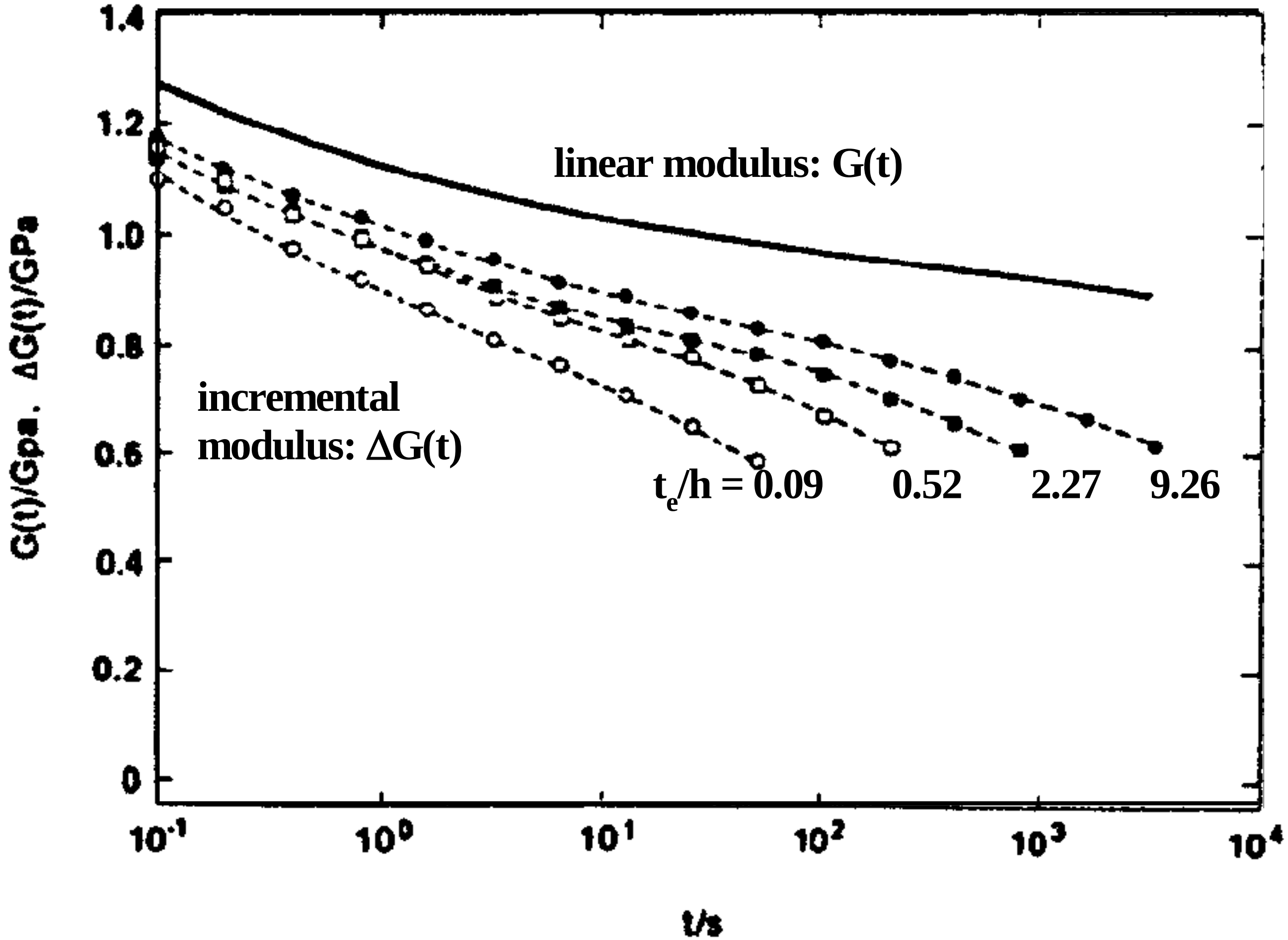


Figure 15. Schematic of strain history for superposition of small deformations on large showing how the incremental modulus $\Delta G(t)$ is determined from $\Delta\sigma(t)/\Delta\gamma$. (After McKenna and Zapas[40]).

Apparent “rejuvenation” for large deformation followed by small deformation. (after McKenna and Zapas).



Viscoelastic Solution to small deformations superimposed on large deformations

$$\Delta G(t,t_e) = \Delta\sigma/\Delta\gamma = \phi'(\gamma_1, t + t_e) + G(t) - G(t + t_e) \quad (6)$$

Non-linear tangent modulus

Linear viscoelastic Moduli

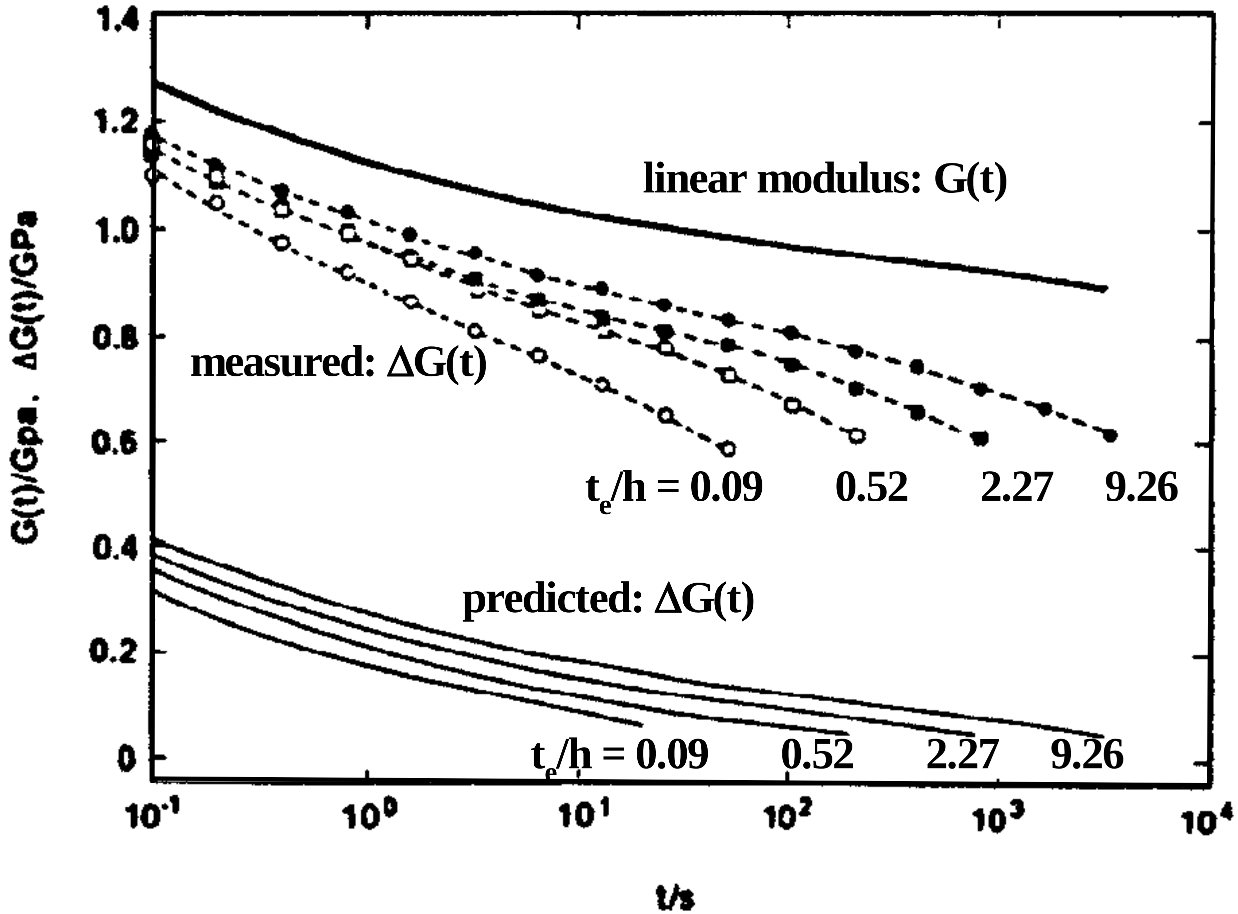


Figure 17. As in Figure 16 but with nonlinear viscoelastic model predictions for incremental response showing much greater softening than the actual measurement. (After McKenna and Zapas[40]).

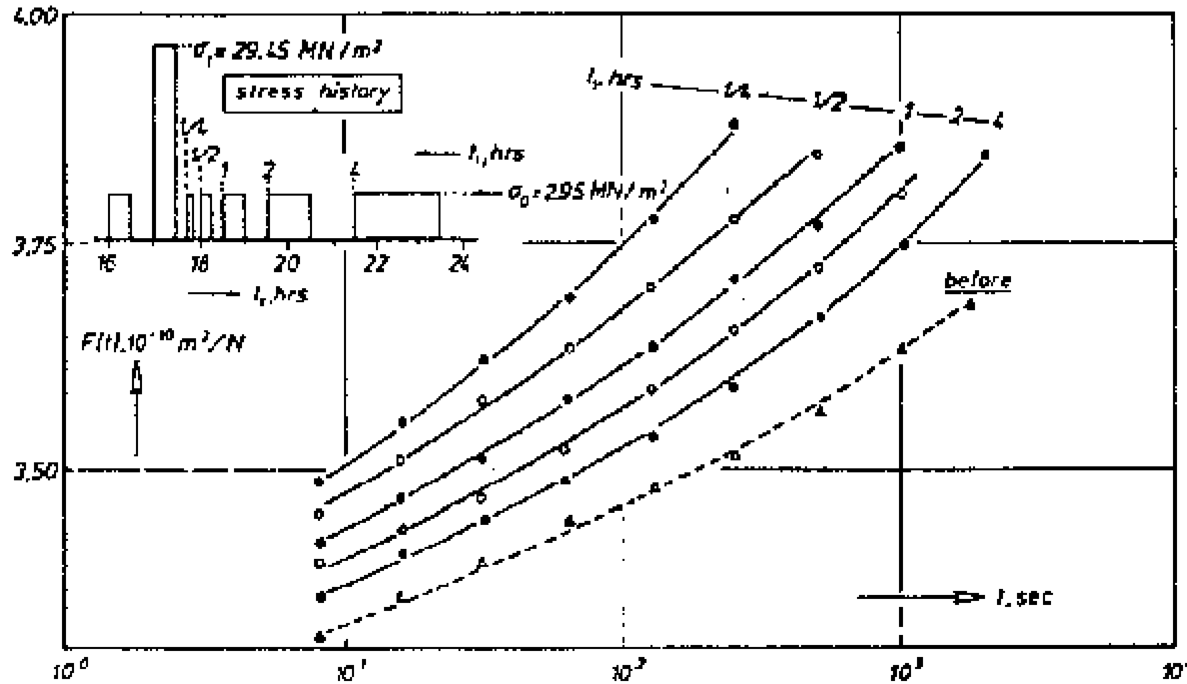


FIG. 7. Tensile creep curves of rigid PVC quenched from 90 °C (i.e., about 10 °C above T_g) to 20 °C during a type III history. Type III creep history is given in insert where a single large probe is followed by small probes of equal magnitude [after Struik (1978)]

Quantitative agreement between "rejuvenation" followed by renewed aging and viscoelastic model

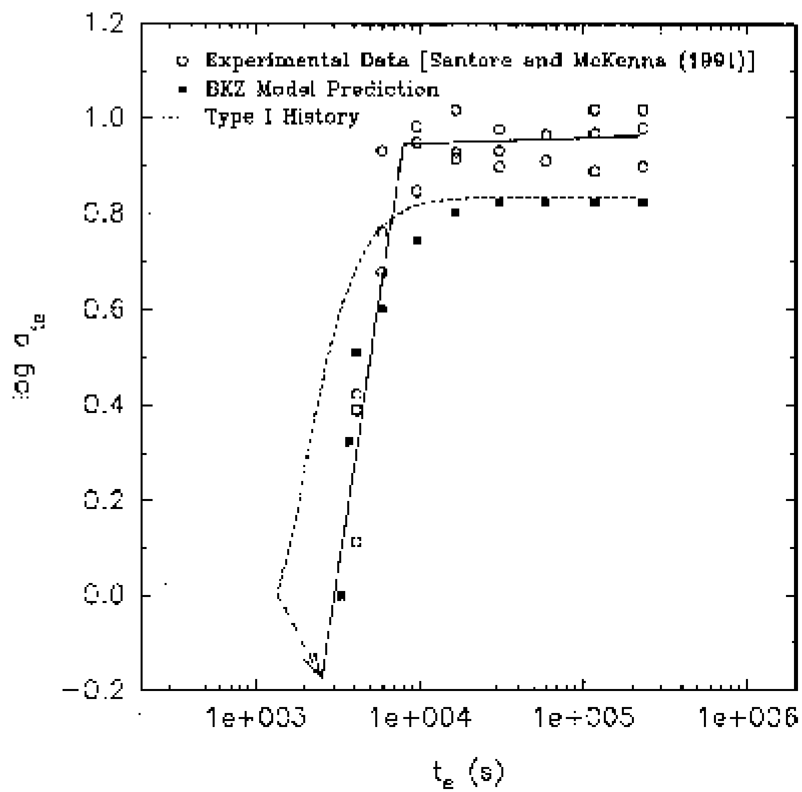


FIG. 18. Logarithm of the aging time shift factor versus aging time for a type III strain history with small $\gamma_s = 0.01$ probes and a large $\gamma_l = 0.04$ probe. Also shown is the exponential fit to experimental data for the type I strain history with $\gamma = 0.01$. Note the reasonable correlation between the values predicted by the modified BKZ theory and those found by Santore and McKenna (1991) from the experimental data.

Interpretation

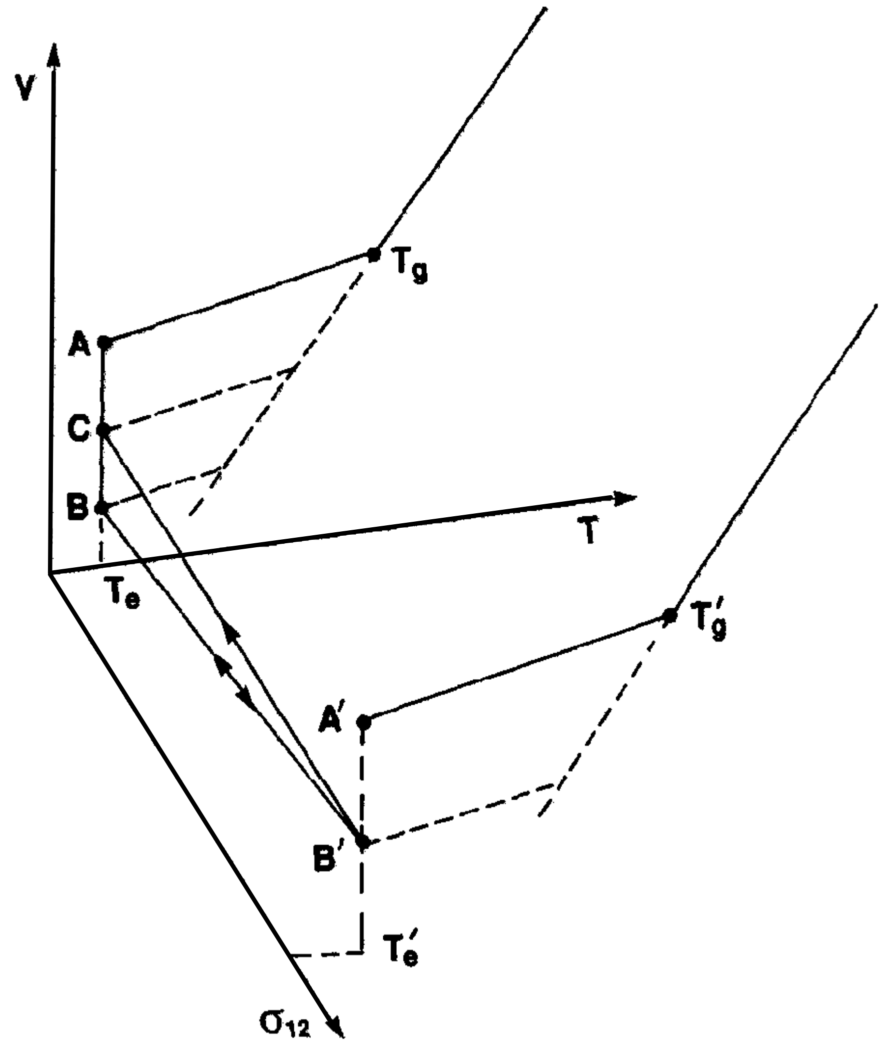


Figure 19. Schematic of a v-T-σ_{12} (volume-temperature-deviatoric stress) surface comparing the stress-induced rejuvenation and non-rejuvenation hypotheses. If rejuvenation occurs, after unloading material should return along line B'-C. If no rejuvenation occurs, upon unloading the material should return along line B'-B. Our results suggest the latter. (Diagram after Lee and McKenna[11]).

Post-yield behavior

>>   evidence for polyamorphism?

Yield stress upon physical aging after a quench from T>Tg to below.

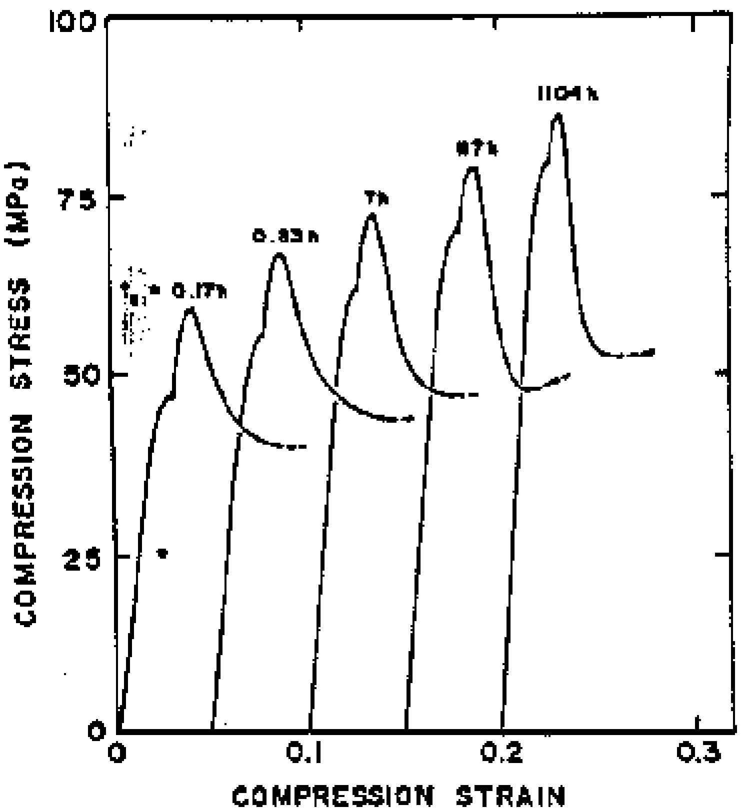


Fig. 16. Typical compression curves obtained at $T_g - 10$ °C for an epoxy glass for different aging times, as indicated. (After Ref. [27].)

“Erasure” or “rejuvenation” due to yield of an epoxy resin. (After Aboulfaraj, G’Sell, Manjelinck and McKenna).

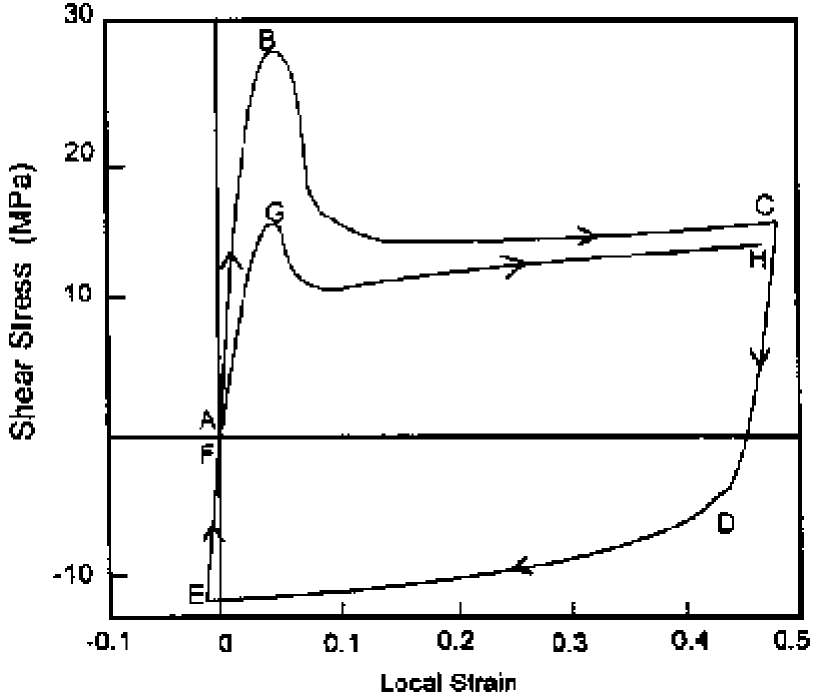
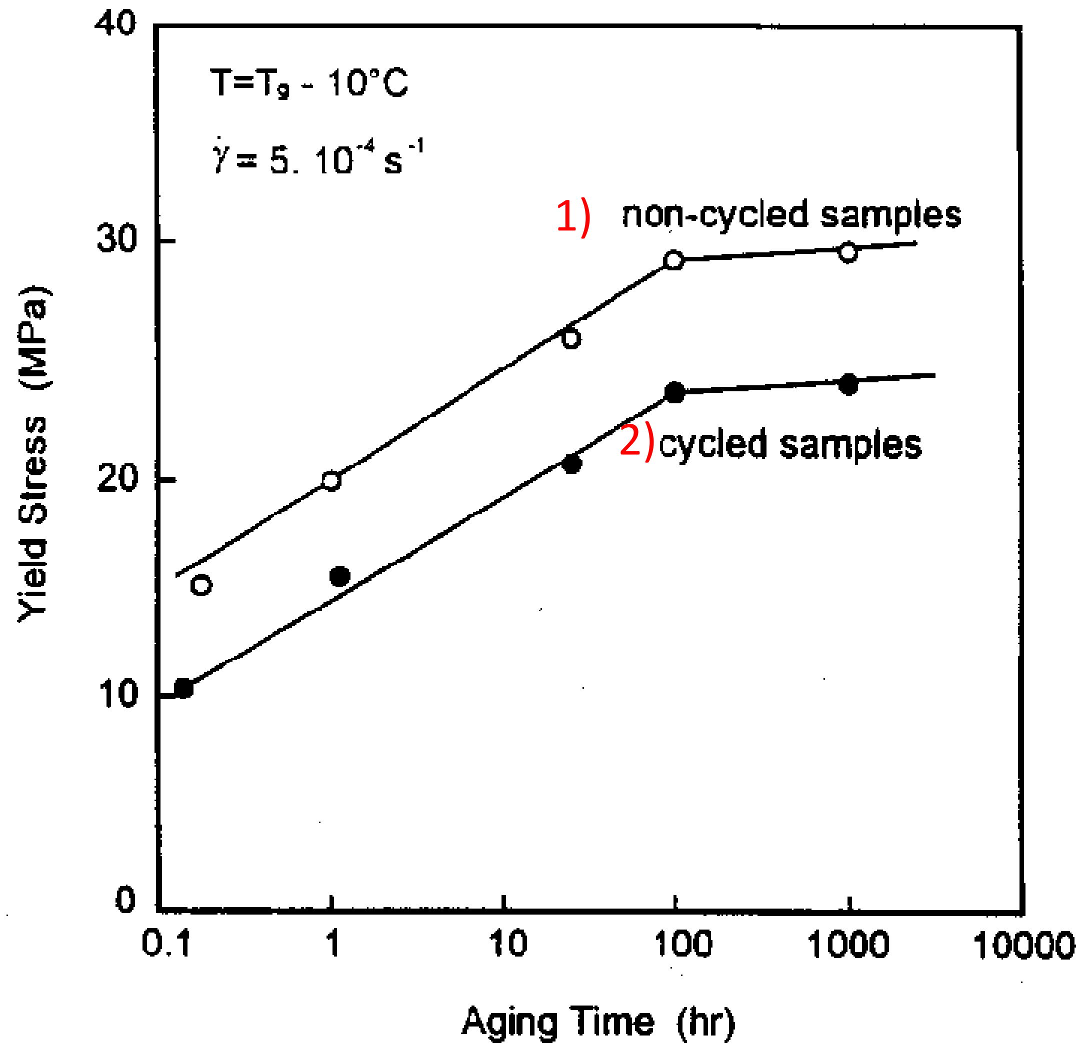


Fig. 8. Plastic cycling of epoxy resin. Sample aged for 10 h at 32.2 °C and deformed at $\dot{\gamma} = 5 \times 10^{-4}$ s^{-1} (ABCDEF). In the present case the aging time was 1 h after plastic cycling (FGH).

Comparison of yield stress evolution after: 1) quench from above Tg to Ta and 2) subsequent to a "mechanical" quench to 50 % strain at Ta. Evidence for two different "states". Is yield a liquid-liquid polyamorphic transition?



Implosion

"IMPLOSION"—Polycarbonate 120 C below Tg.
(After Colucci, O'Connell, McKenna, PES (1997)

Uniaxial Extension Experiments- relaxation modulus

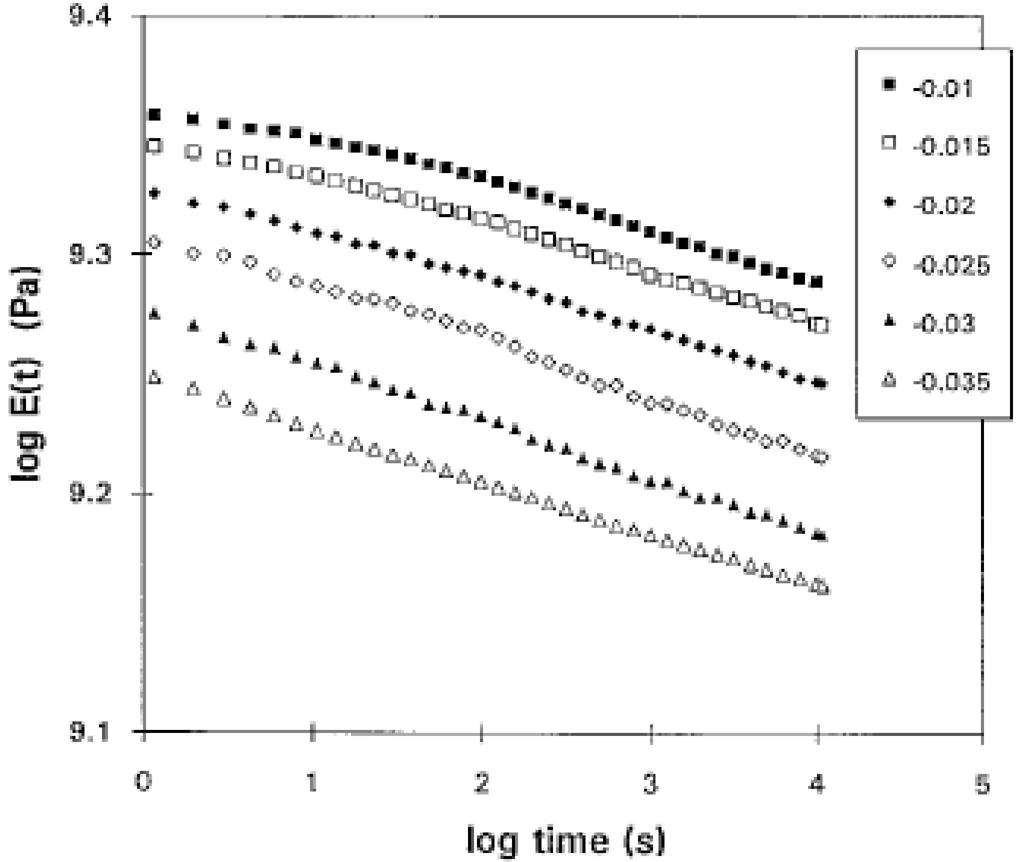


Fig. 2. Stress relaxation modulus as a function of axial strain in compression for GE PC. Numbers in the legend refer to the applied strain level.

Uniaxial Extension Experiments- volume changes

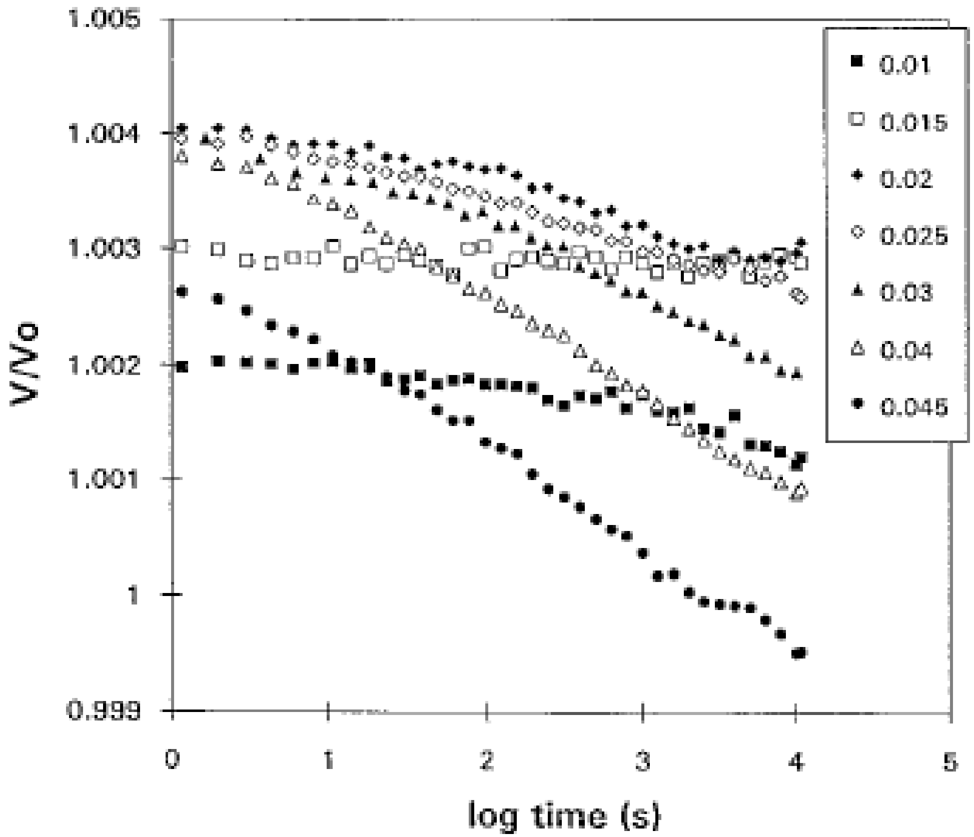


Fig. 7. Time dependent volume changes as a function of axial strain in tension for CP PC. Numbers in the legend refer to the applied strain level.

Uniaxial Compression Experiments-volume changes

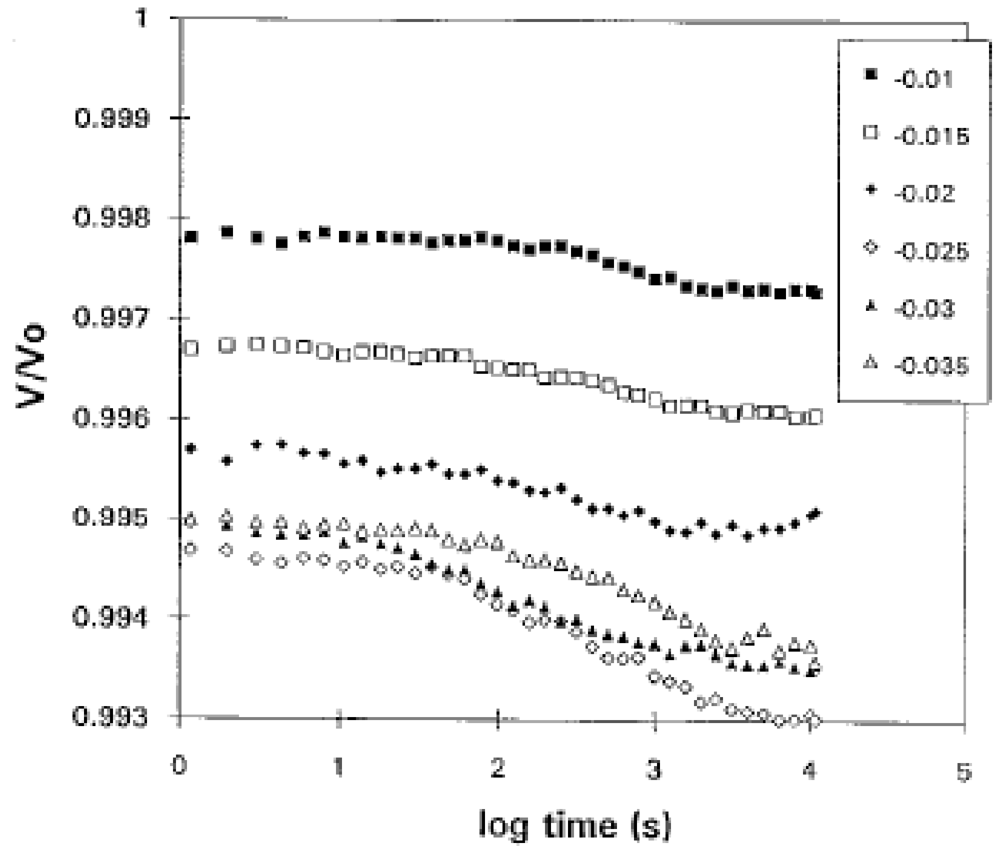


Fig. 9. Time dependent volume changes as a function of axial strain in compression for CP PC. Numbers in the legend refer to the applied strain level.

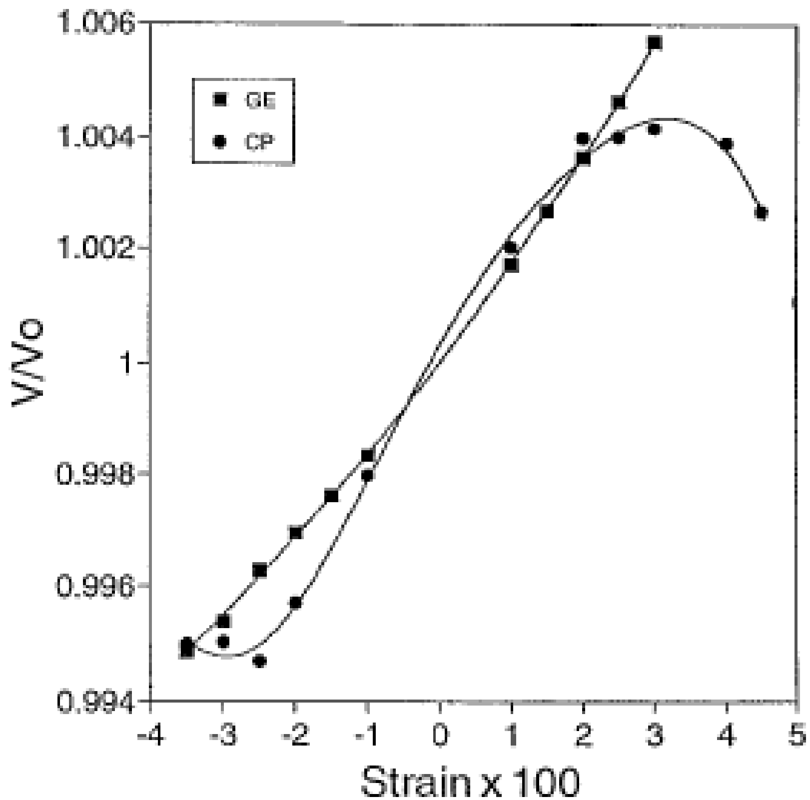


Fig. 10. Comparison of the isochronal V/V_0 responses as a function of applied axial strain for the GE and CP PC samples. The experimental points correspond to V/V_0 values at log time = −0.3 in seconds.

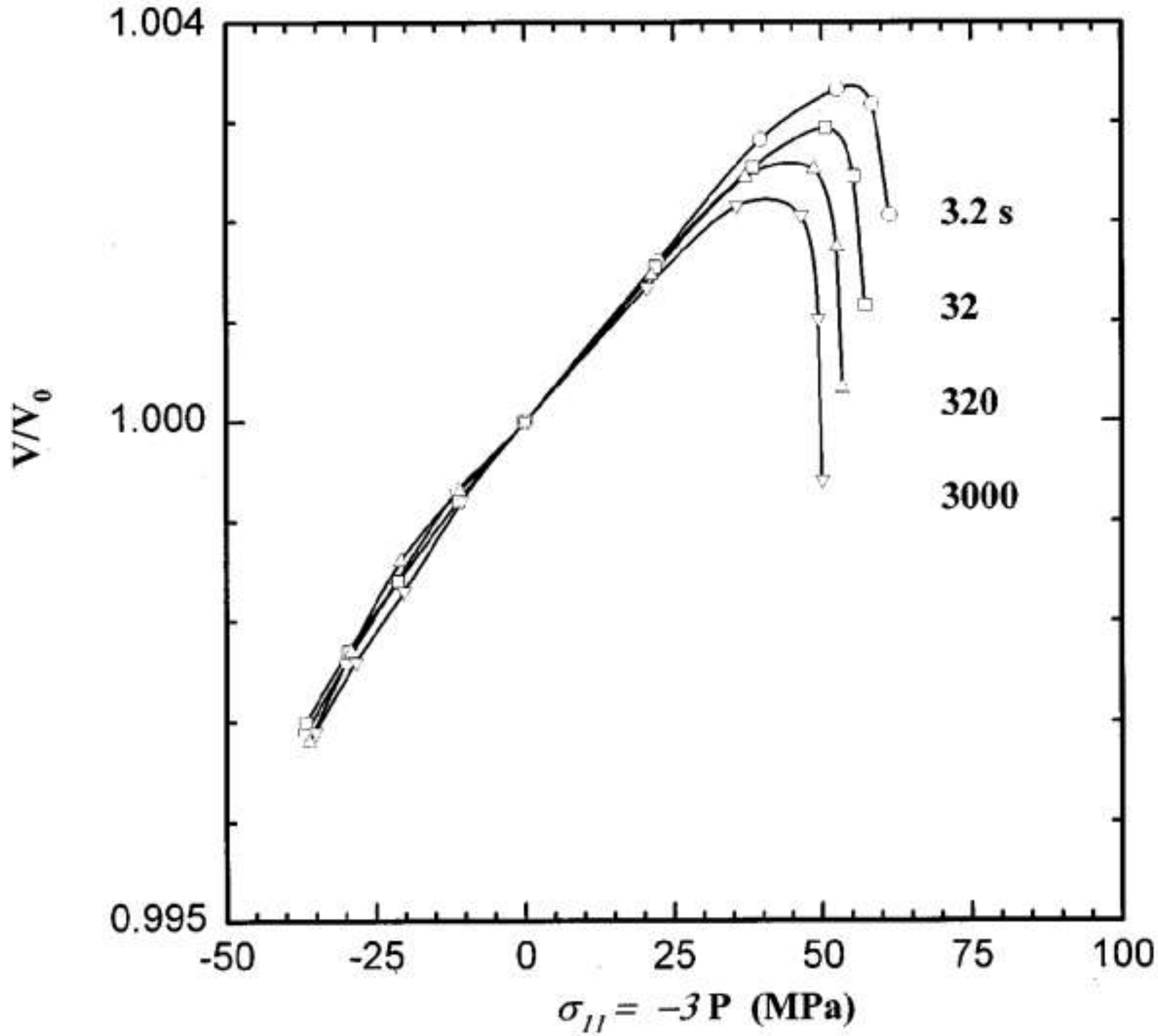


Figure 27. Plot of relative volume vs. applied stress for a polycarbonate glass in single step stress relaxation conditions showing non-monotonic behavior at stresses below the yield point. Times indicate time after loading (isochronal values). Implosion ($V/V_0<1$) occurs for 3,000 s isochrone. (After Pesce and McKenna[75]).

Summary

- *Physical aging is related to the structural recovery of the glass*
  - *Changes in volume/enthalpy, viz., structure, cause changes in the viscoelastic response*
  - *Presented detailed argument against the power law elapsed time theory to describe aging in structural glasses*
  - *Showed in detail how plasticizer jump created glasses (concentration glasses) are different from temperature-glasses*

- *Discussed rejuvenation hypothesis and presented results in sub-yield regime that contradict the rejuvenation hypothesis*
  - *t* or mechanical equilibration time is unaffected by stress magnitude*
  - *Torsional dilatometry shows no change in underlying structural recovery when large deformations applied*
- *In post-yield regime have presented results that suggest that yield causes a polyamorphic transition and does not rejuvenate the glass*
- *Discussed implosion event—"accelerated aging?"*

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The End