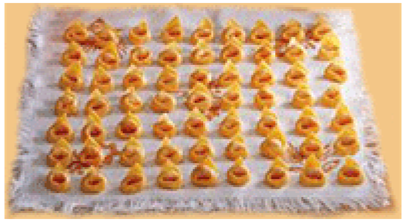
Dipartimento di Ingegneria Chimica Mineraria e Tecnologie Ambientali - DICMA

Alma Mater Studiorum Università di Bologna – Bologna, Italy

Fickian and non-Fickian Diffusion in Solid Polymers

Giulio C. Sarti

From Bologna: **diffusion** of tortellini



diffusion of mortadella

Alma Mater Studiorum - Università di Bologna,

Bologna, ITALY

Diffusion of the university system

UniBO is proud of being the oldest University in western world:

In operation since 1088

In 1988 has celebrated the 9th Centennial of its life

Copernicus, Galilei, Galvani, Malpighi were among

Bologna's Scholars

OUTLINE

- ***Fickian diffusion***
  - *non swelling penetrants ⇒ no relevant deformations and no stresses*
  - *swelling penetrants ⇒ deformations and stresses are induced*
    - *a) how to measure stress effects*
    - *b) how to calculate the stress field*

- ***Non-Fickian Transport***
  - *Effects of swelling and of stresses*
  - *Structural changes and relaxation*
    - *Effects of temperature*
    - *Effects of activity difference*
    - *Effects of pre-history*
    - *Effects of sample dimensions*

⇒

a) Anomalous diffusion
b) Two stage sorption
c) Case II Transport
d) Super-Case II transport

OUTLINE

- ***Modeling Fickian Transport***
  - *non swelling penetrants ⇒ nothing special*
  - *swelling penetrants ⇒ deformations and stresses must be calculated*
    - *Elastic (and viscoelastic) case*

- ***Modeling Non-Fickian Transport***
  - *Lumped models*
    - *Localized swelling (with & without differential swelling stresses)*
    - *Viscoelastic diffusive flux*
  - *General models*
    - *Based on Mixture theory*
    - *Based on a proper expression of the chemical potential in glasses*
      - *Calculate time dependent BC*
      - *Calculate fluxes depending on concentration and deformation/stress gradients*

Acknowledgements

Thanks are due to:

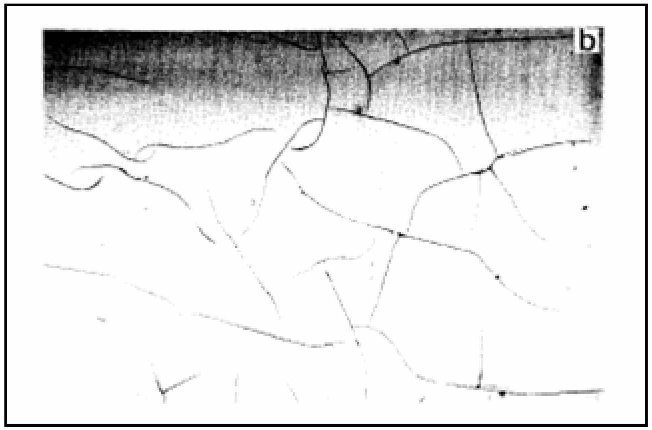
Ruben G. Carbonell-NCSU

Ferruccio Doghieri
Marco Giacinti Baschetti
Maria Grazia De Angelis
Maria-Chiara Ferrari
Jacopo Catalano
and to the group

Penetrants can generate swelling and stresses

In gases and in liquids diffusion does not build up a stress field
In solids in general and in polymeric solids in particular stresses are generated by swelling penetrants

- Crazes and even cracks can be produced
- Morphological changes are induced



Methanol in PMMA

After Tomas & Windle, *Polymer* 1982

Effects of swelling and stresses

Swelling and stress fields may affect diffusion

- through morphological changes
- through solubility changes
    - BC
    - Final solubility
- diffusivity dependence on stress
- through stress dependence of the flux

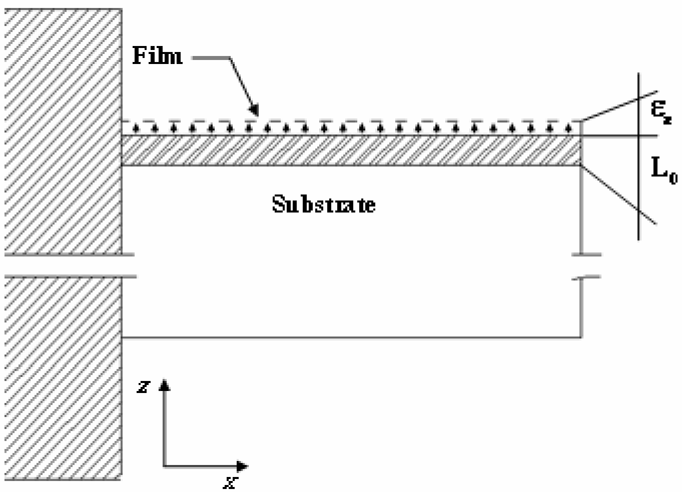
The viscoelastic nature of the polymer introduces relaxation times in the response , which affects the transport process

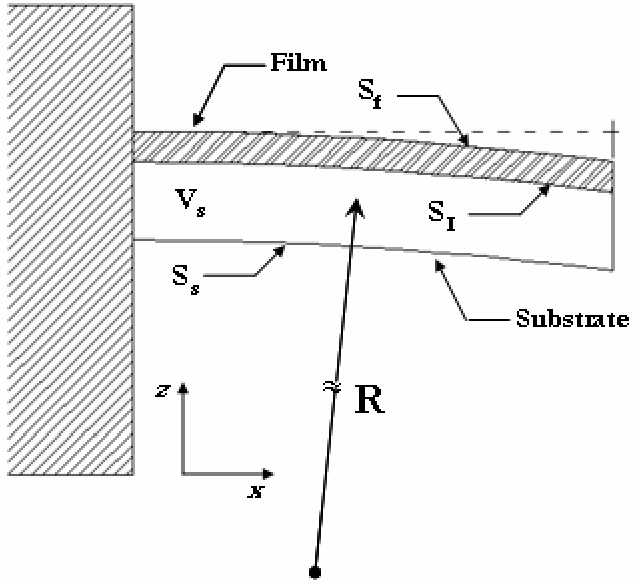
Qualitative interpretation is based on diffusion **Deborah number**, (DEB)D:

$$(\mathrm{DEB})_{\mathrm{D}} = \tau D_{12}/l^2$$

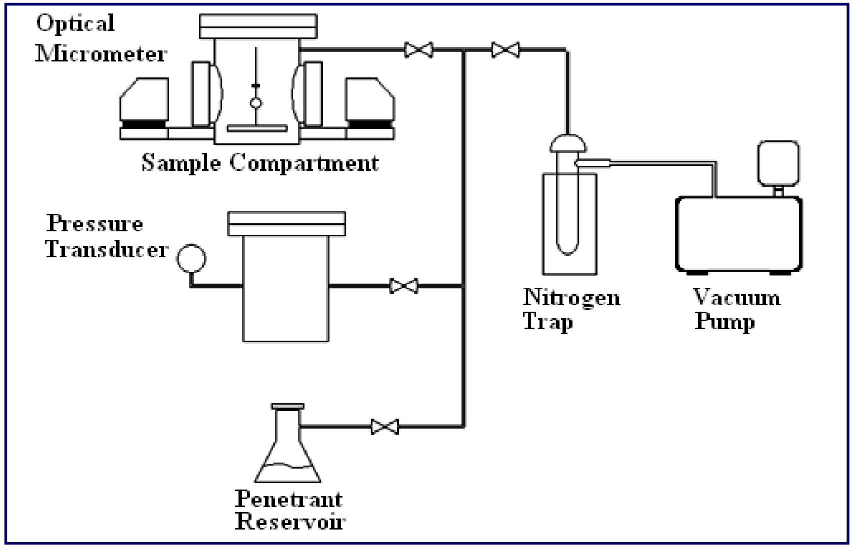
How can stresses be measured

- birefringence
- bending cantilever





How can stresses be measured

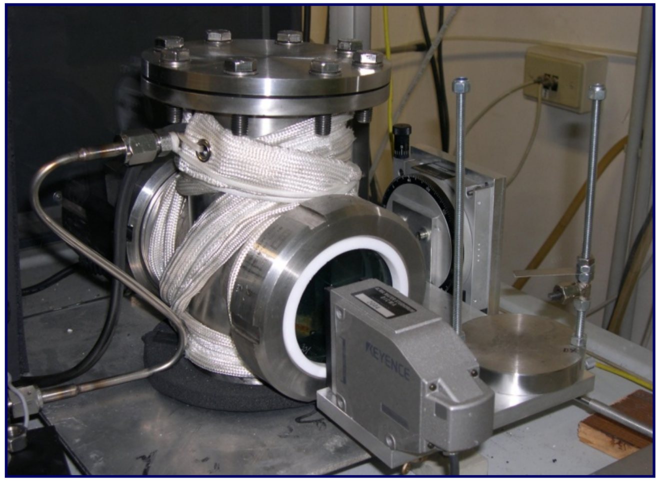


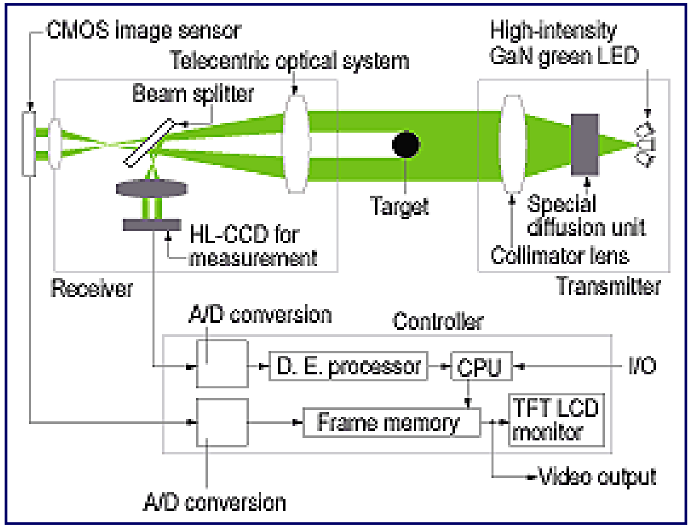
P_{max}= 8 bar
T_{max}= 200°C

Deflection measured through an optical micrometer (Keyence LS7030M)

Precision = ±1µm

Reproducibility=0.15 µm





How can they be described

$$\frac{\partial \mathrm{c}}{\partial \mathrm{t}} = D\frac{\partial^2 c}{\partial z^2}$$

$$c = c_{eq} \qquad \forall P(x,y,z) \in S_f, \quad \forall t$$

$$\nabla c \cdot n = 0 \qquad \forall P(x,y,z) \in S_I, \quad \forall t$$

$$c = 0 \qquad \forall P(x,y,z) \in V_f, \quad t = 0$$

Swelling condition

$$\varepsilon_i^c = \beta(c)c$$

How can they be described

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2}$$

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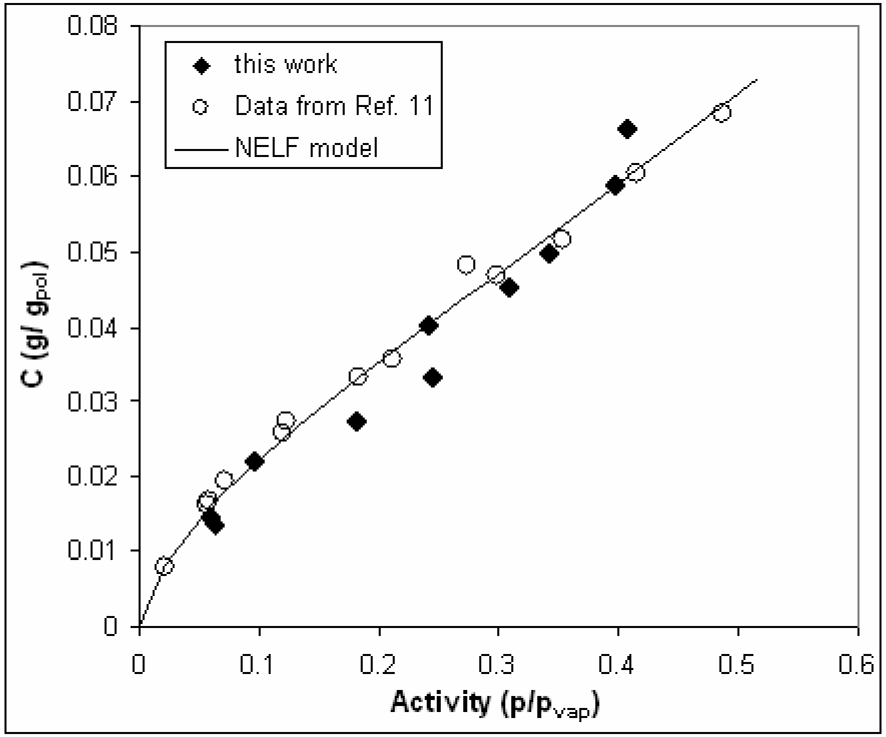
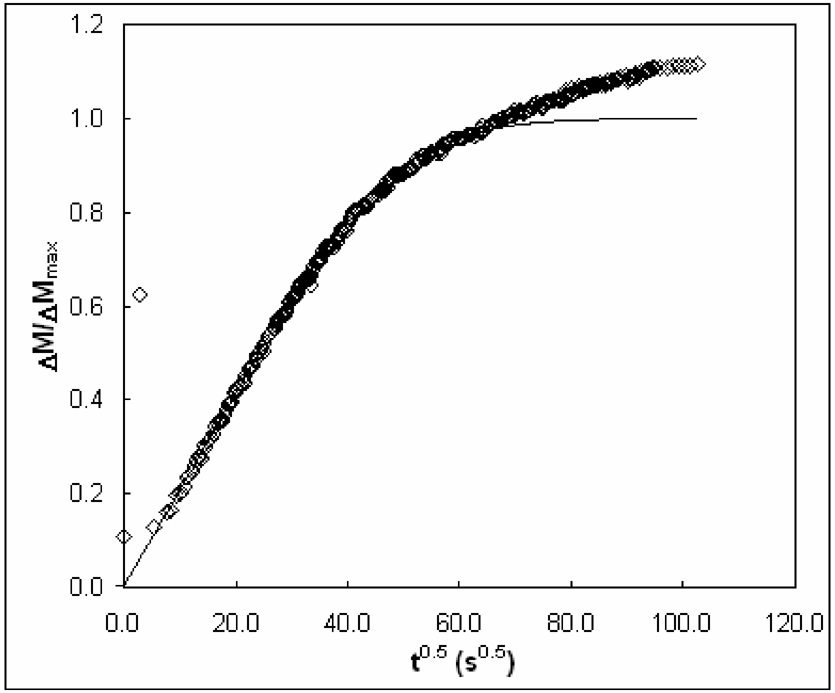
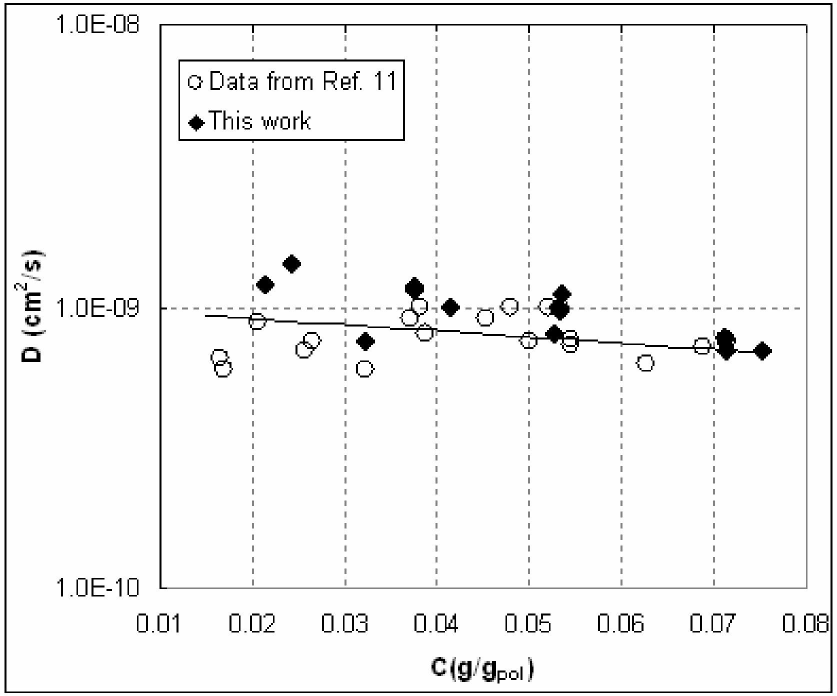


Independent measurements

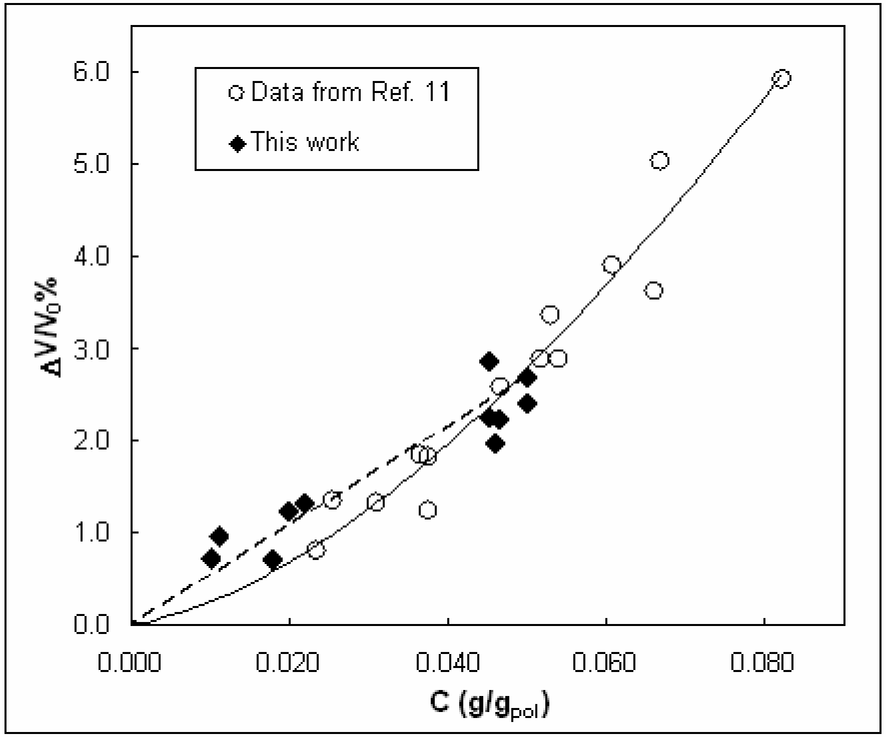




Solubility Isotherms in Glassy Polymers observed behaviors

Swelling condition

$$\varepsilon_i^c = \beta(c)c$$



How it can be described - mechanics

Elastic constitutive equation

$$\varepsilon_x - \varepsilon_x^c = \frac{1}{E}\left[\sigma_x - \nu\left(\sigma_y + \sigma_z\right)\right]$$

$$\varepsilon_y - \varepsilon_y^c = \frac{1}{E}\left[\sigma_y - \nu\left(\sigma_x + \sigma_z\right)\right]$$

$$\varepsilon_z - \varepsilon_z^c = \frac{1}{E}\left[\sigma_z - \nu\left(\sigma_x + \sigma_{zy}\right)\right]$$

Internal consistency (laminate condition)

$$\begin{Bmatrix} \varepsilon_x \\ \varepsilon_y \\ \end{Bmatrix} = \begin{Bmatrix} \varepsilon_x^0 \\ \varepsilon_y^0 \\ \end{Bmatrix} + z \cdot \begin{Bmatrix} k_x \\ k_y \\ \end{Bmatrix}$$

Mechanical equilibrium with external forces and external moments

$$\sigma_z = 0$$

$$\mathbf{N} = \mathbf{0}$$

$$\mathbf{M} = \mathbf{0}$$

Cantilever deflection:

$$\delta = \frac{1}{2} \cdot k_x \cdot L^2$$

Data: from independent source

Acetonitrile in PC over Al cantilevers

Film thickness		0.0155 mm
Young Modulus	- polymer	2400 MPa
	- substrate	64000 Mpa
Poisson Ratio	- polymer	0.47
	- substrate	0.34
Diffusion kinetic		Fickian diffusion $D = 1.9 \cdot 10^{-9}\, e^{-28c}$ (3)
Linear swelling		$\beta(C) = 0.175 \cdot c$ (3)
(3) This work, c in g/g_{pol} , D in cm^2/s		

Substrate: aluminum cantilever (5 x 1 x 0.275 mm)

Cast film from a solution of PC in CH_2Cl_2

Layers model: parameters sensitivity

Once we know

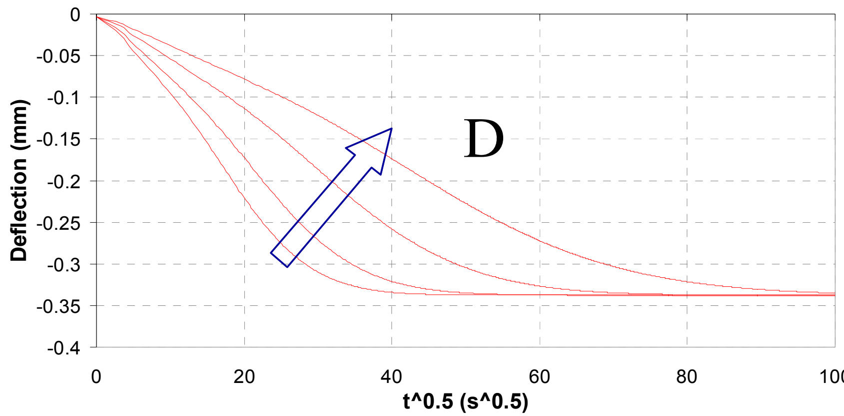
i) the mechanical properties (Young modulus and Poisson ratio),

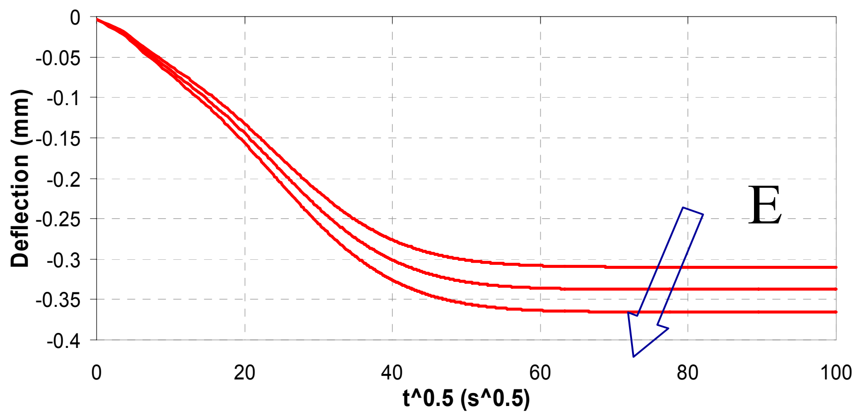
ii) the diffusion coefficient (D),

iii) the concentration profile and the dilation-concentration law

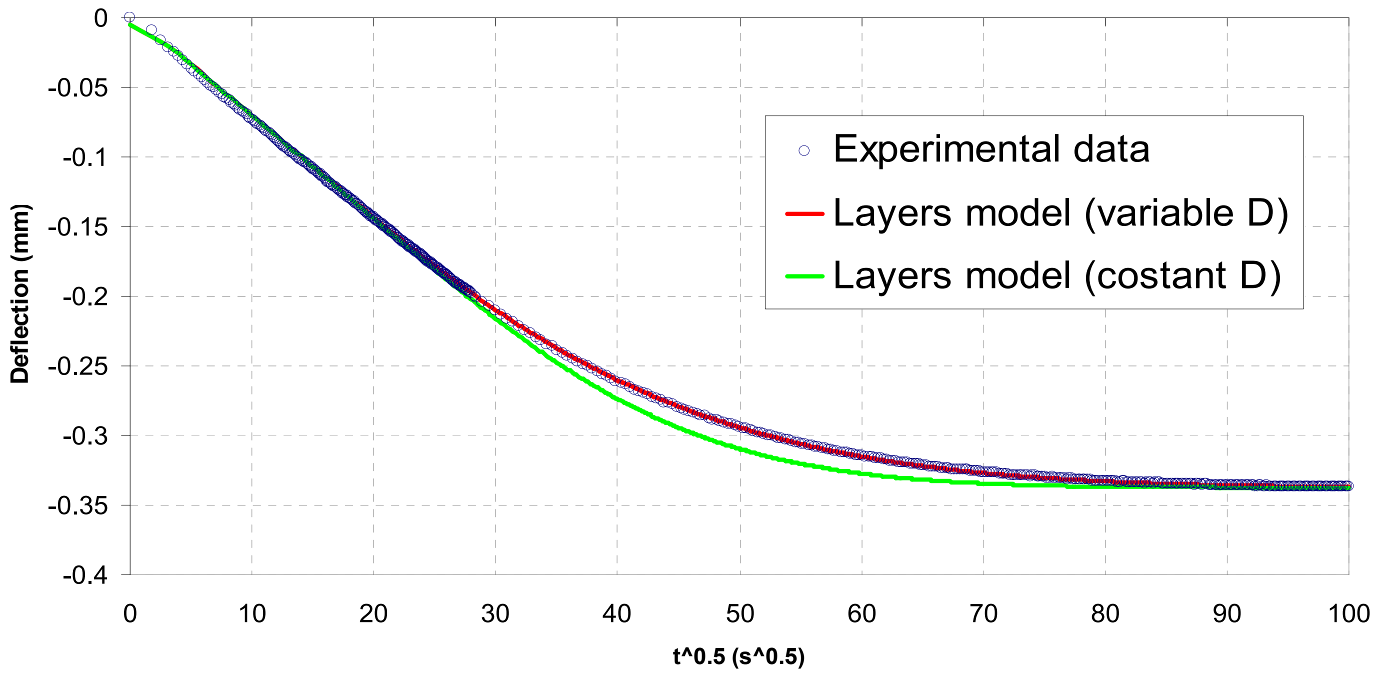
we can calculate:

- **deflection**
- the **stress profile** inside the polymer film.





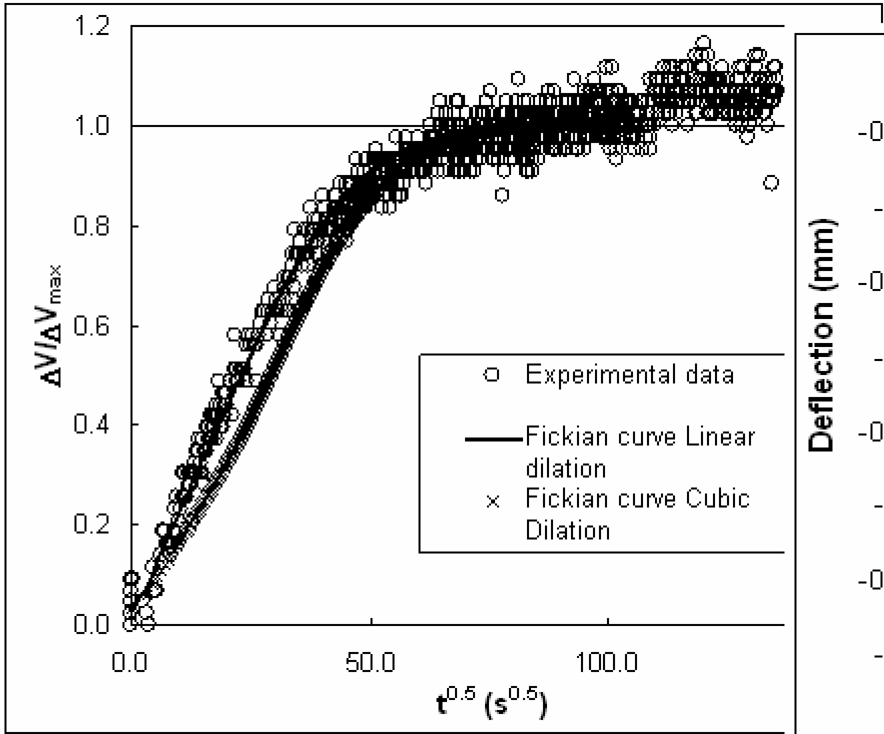
Layers model: variable *D*



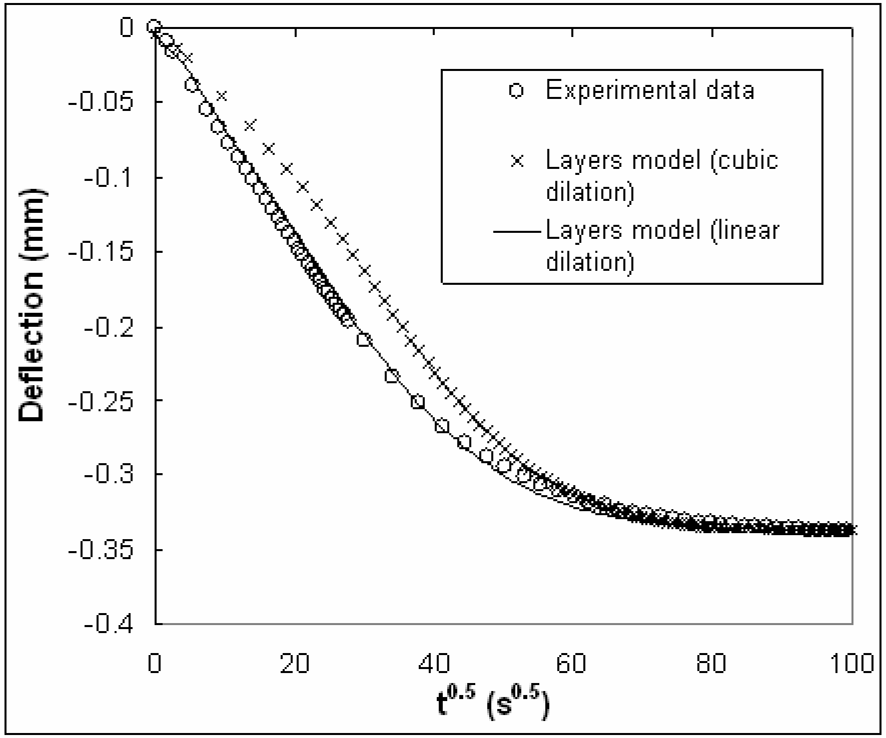
$$D = 0.9e^{-9}\,\frac{cm^2}{s}$$

$$D = 1.9e^{-9} \cdot e^{(-C\cdot 28)}$$

Model predictions vs exp. data

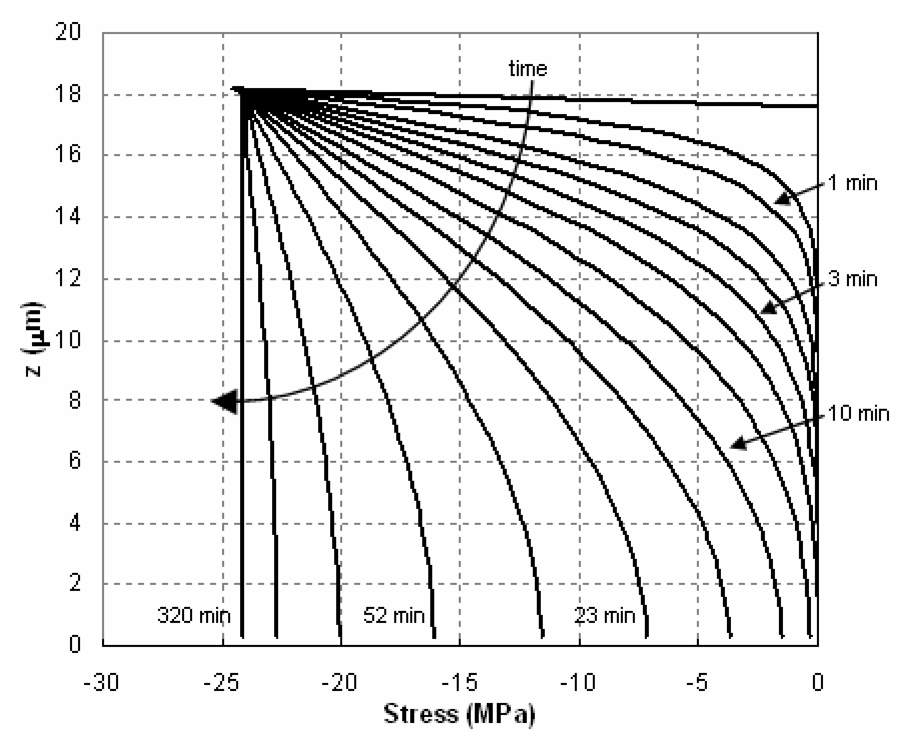


Kinetics of polymer dilation for the system acetonitrile–PC at 40°C experimental data and comparisons with different swelling models



Kinetics of deflection of an aluminum cantilever for an integral sorption run of acetonitrile in PC for an activity jump from 0 to 0.3 at 40°C, sample thickness 16 mm.

Evolution of stress profiles during sorption



Time evolution of the stress profile inside a PC film of d=18 mm, during an integral sorption run of acetonitrile up to an activity of 0.20 at 40°C.

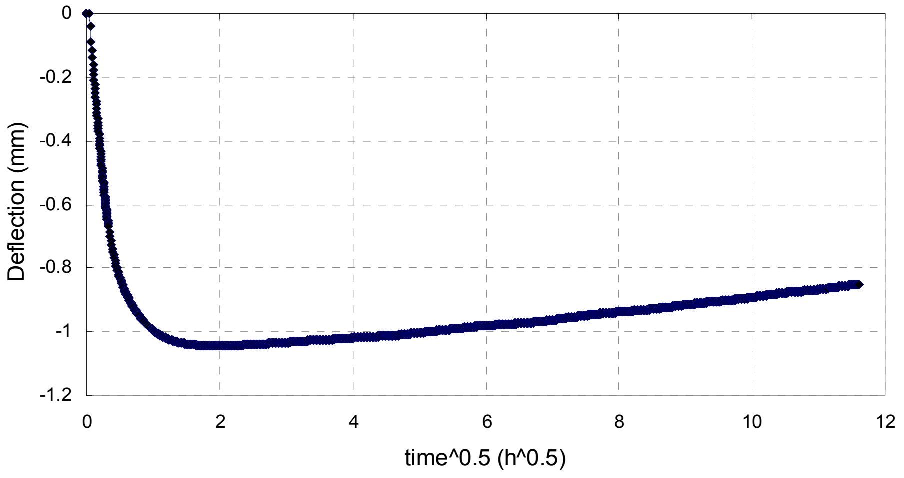
The stress is:

- compressive
- ≅ 20 ÷ 40 MPa

Yield ≅ 62 MPa

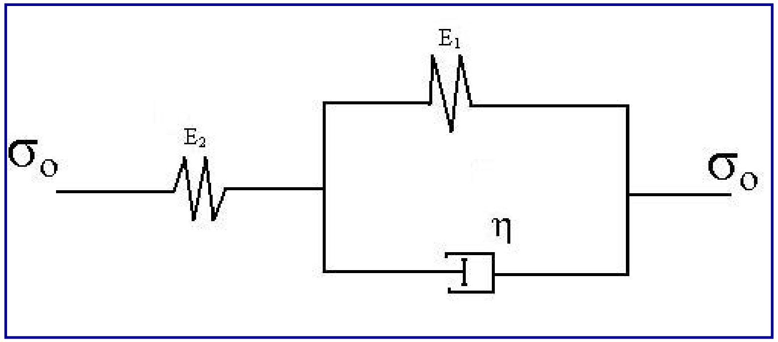
Deflection relaxation dynamics

Long time experiments reveal a decrease of deflection after a maximum is reached

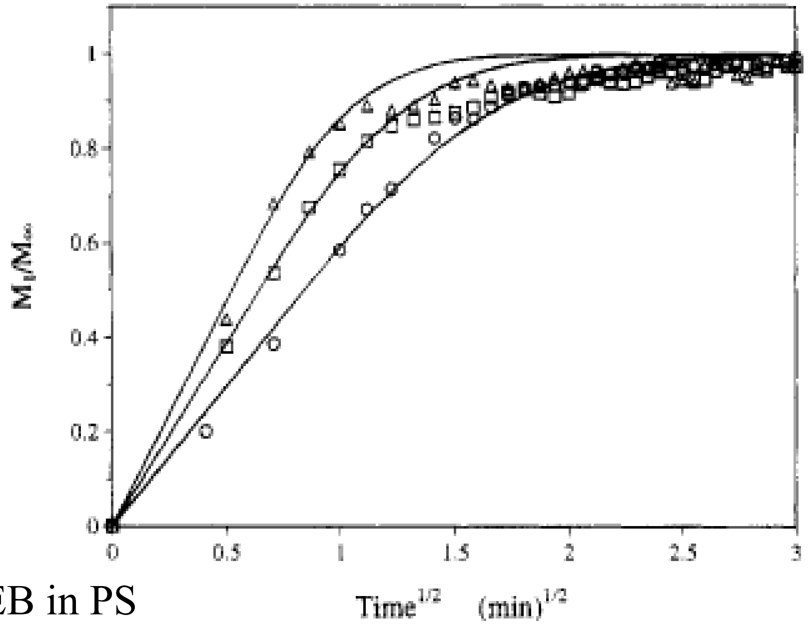


The phenomena is likely related to a stress relaxation due to the viscoelastic behavior of the polymer.

The constitutive equation of viscoelastic materials is being implemented in the mechanical problem



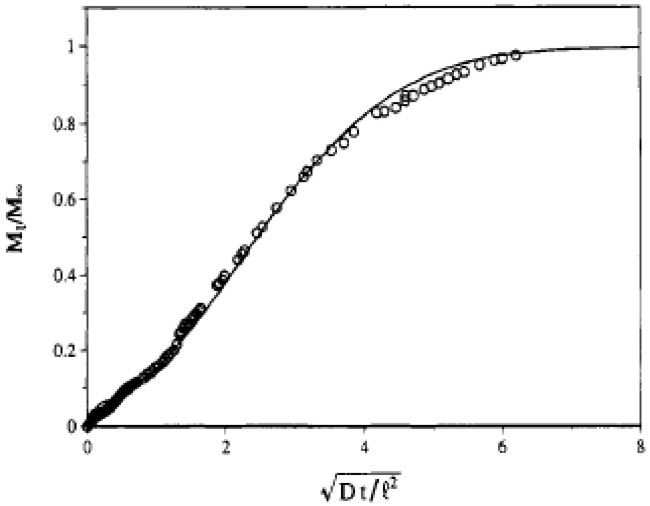
Different behaviors observed

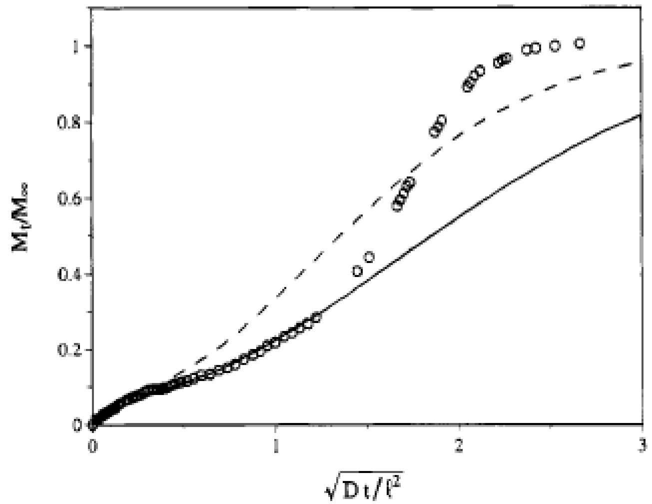


EB in PS

Plot of *M,/M, vs t for* ***(ω1*** **=0.1181), circles,** ***(ω1 = 0.1308 squares), and (ω1 = 0.1425 triangles);*** all three uptake curves show Fickian characteristics (Billovitis et al Macromol 1994)

Different behaviors observed

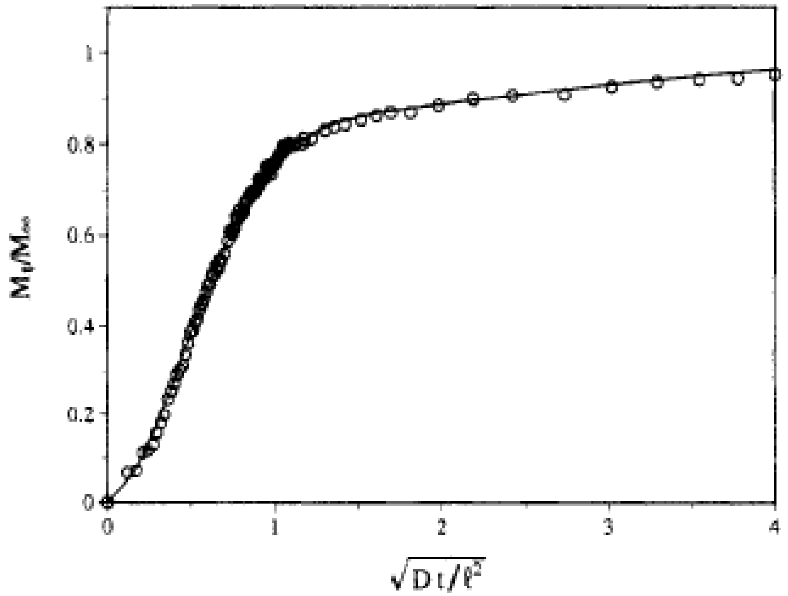


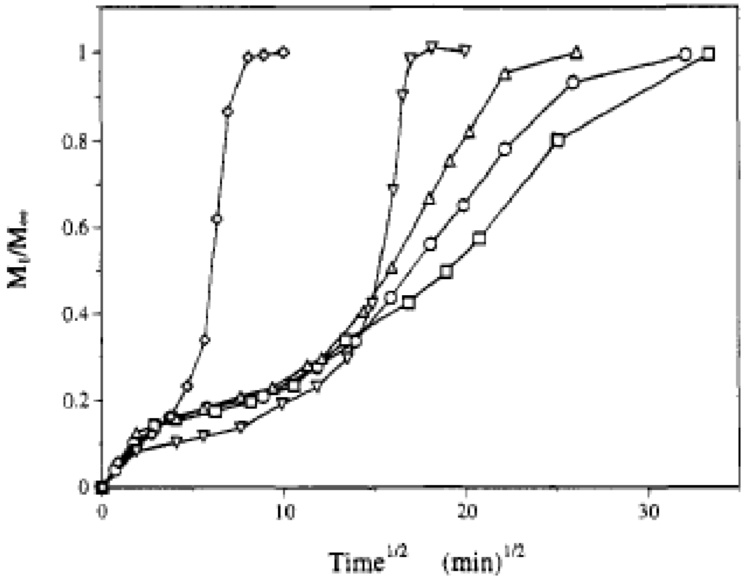


EB in PS
Plot of *M,/M, vs t for* (*ω1* = 0.0276), Fickian characteristics (Billovitis et al Macromol 1994)

ω1 **=** 0.0600 delta P (torr): 4.0-4.9
glass ; two-stage

Different behaviors observed

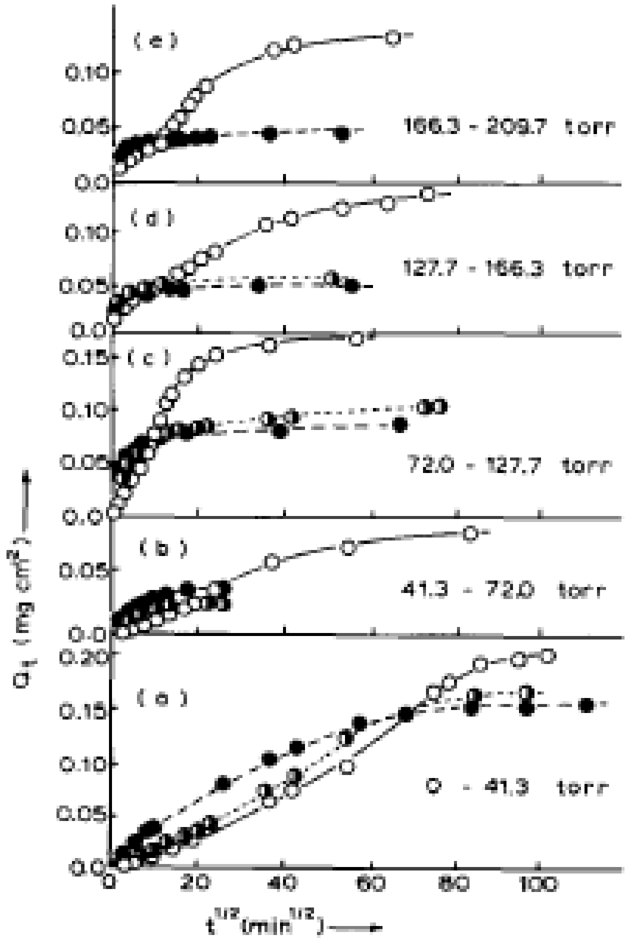




Plot of *Mt/M- vs (t*) for* ***ω1*** =0.1068, P from 7.0- to 7.1 torr *showing the* data and the predictions for two Maxwell elements
After Billovitis et al 1994

Differential sorption data33 for polystyrene/ benzene at 25 "C where the initial pressure is at **47.5 Torr** and the final pressures are
53 (□), **55** (O), **56** (Δ), **59** (V), and **62** Torr (◊).
Effect of activity jump

Different behaviors observed



Series of successive sorption kinetic runs on membrane M-59. Absorption: ○*;* desorption: ●*; resorption:* @. An absorption-desorption-resorption cycle was performed at each step. After Sanopoulou and Petropoulos, J. Plym. Sci. B 1995

Different behaviors observed

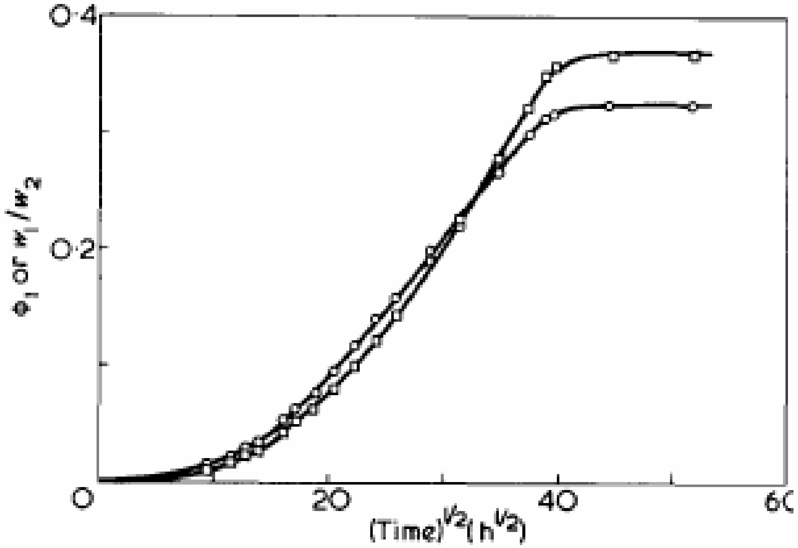


Figure 1 Anomalous Fickian kinetics of n-propyl alcohol absorption in poly(methyl methacrylate) sheets. [Volume fraction or weight ratio, w_1/w_2, as a function of $t^{1/2}$ (T = 318 K)]. Volume fraction ϕ_1, ○; weight ratio w_1/w_2, □

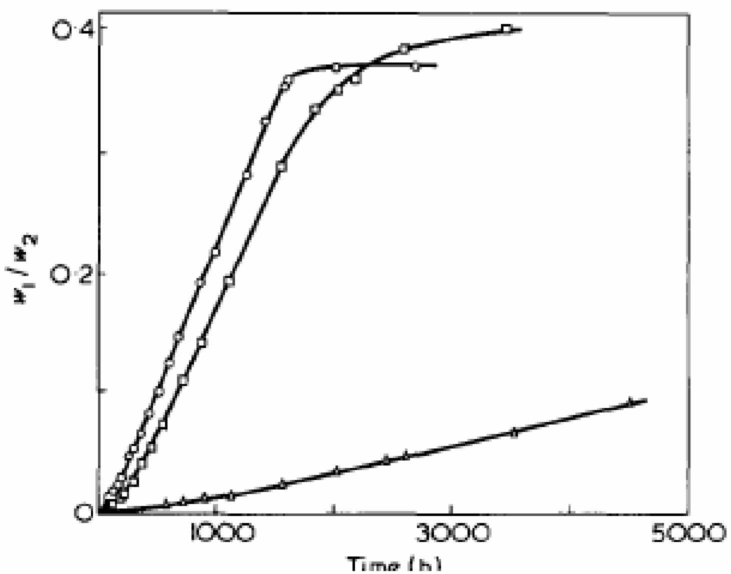
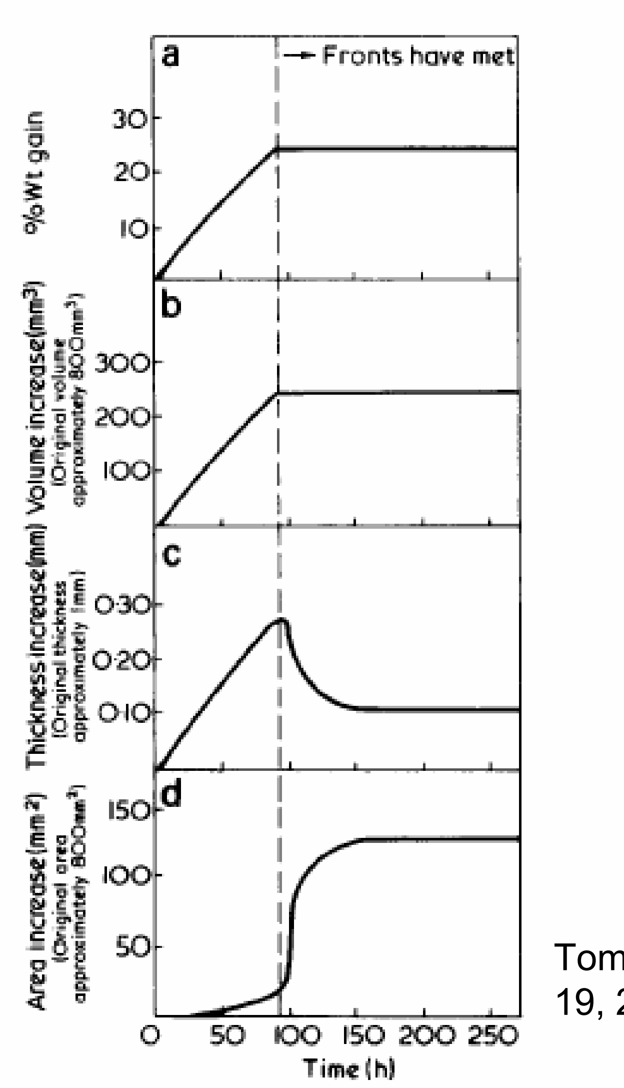
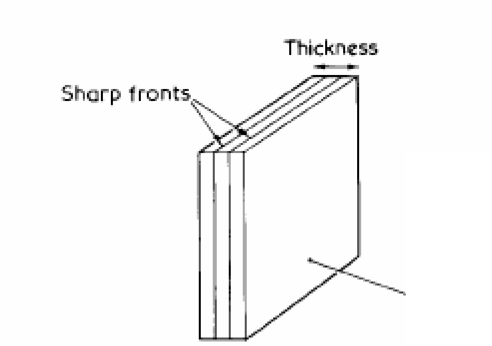
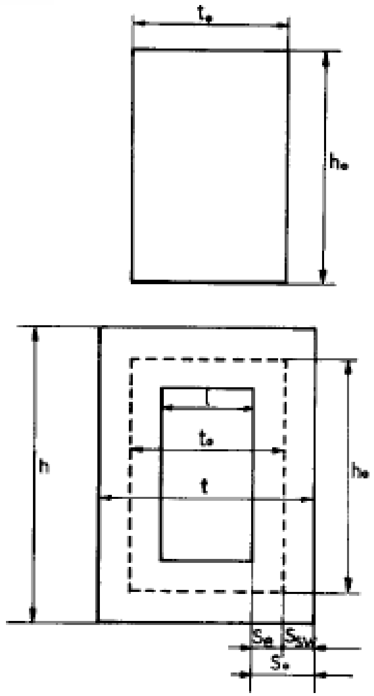


Figure 2 Case II kinetics of n-propyl, i-propyl and n-butyl alcohol absorption in poly(methyl methacrylate) sheets. [Weight of alcohol per original dry sheet weight, w_1/w_2, *versus* t (T = 318 K)] ○, n-propyl alcohol; □, isopropyl alcohol; △, n-butyl alcohol

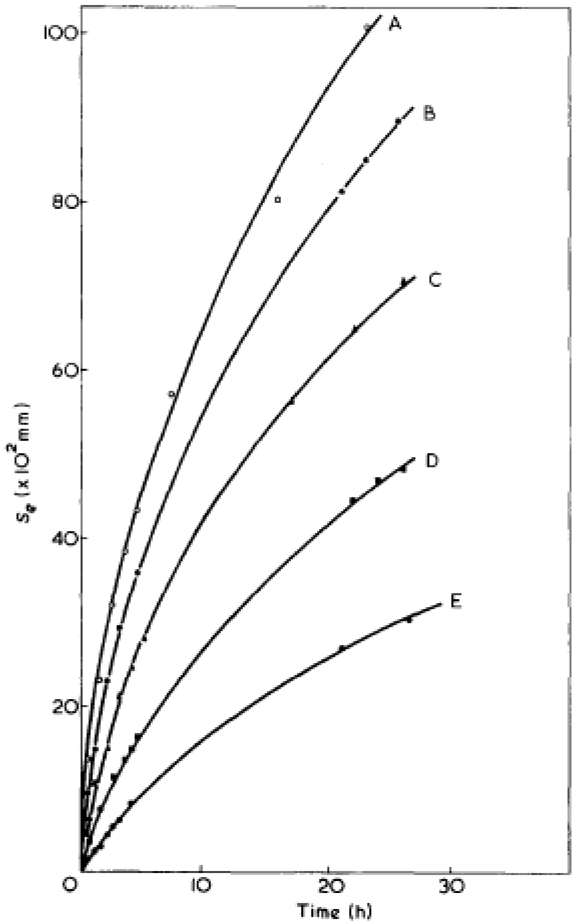


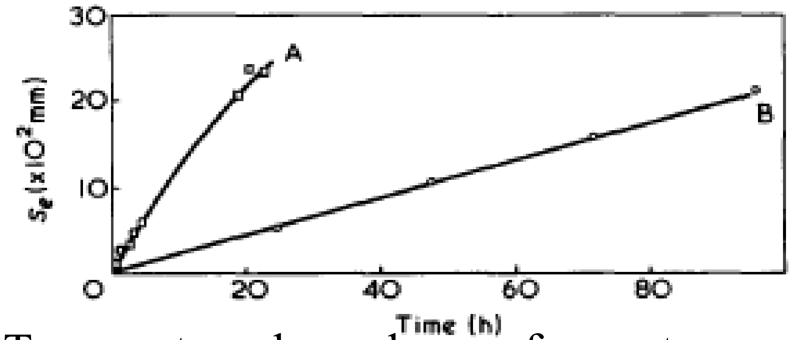




Tomas & Windle Polymer 1978, 19, 255

Effect of temperature

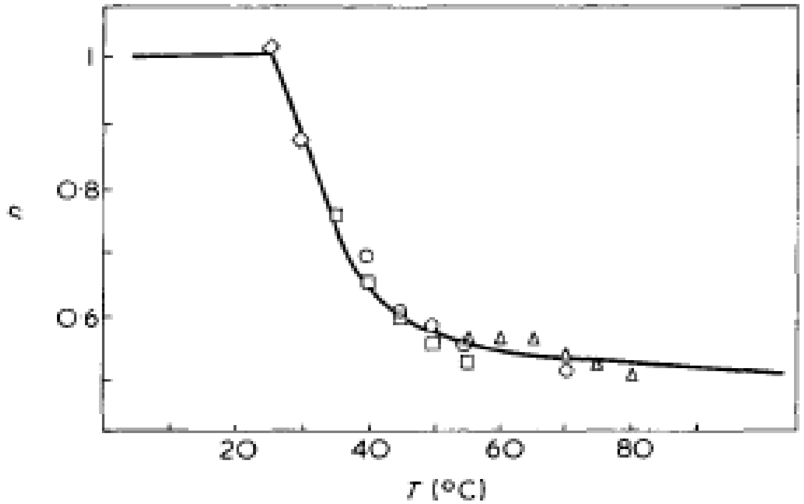




Temperature dependence of n-pentane penetration of polystyrene sheets. A, T = 30°C; B, T = 25°C

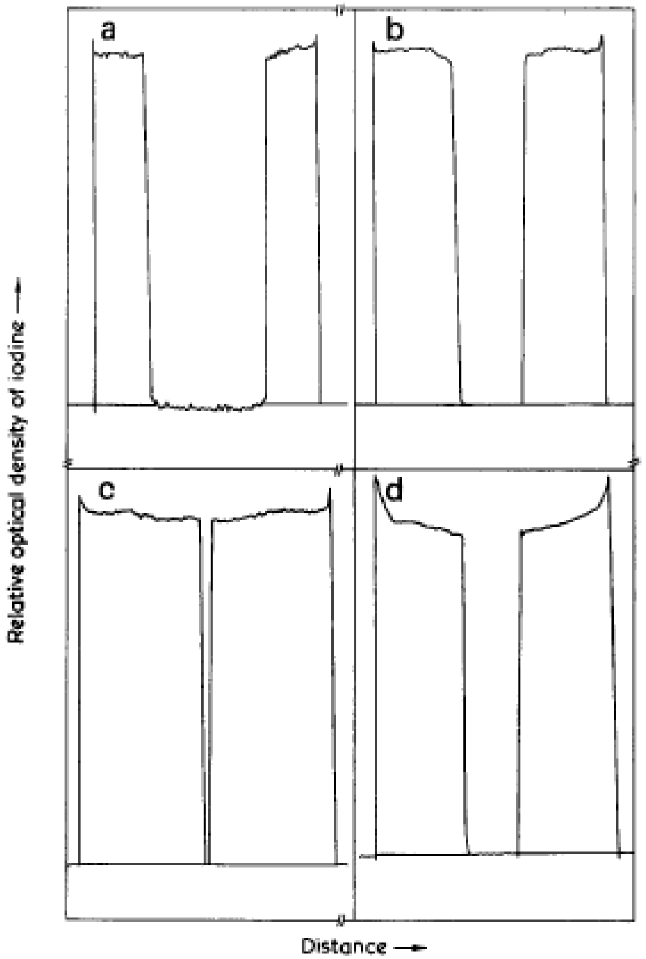
Temperature dependence of n-hexane penetration of polystyrene sheets. A, T = 55°C; B, T = 50°C; C, T = 45°C; D, T =40 °C; E, T= 35 °C, *after Tidone et al., Polymer 1977*

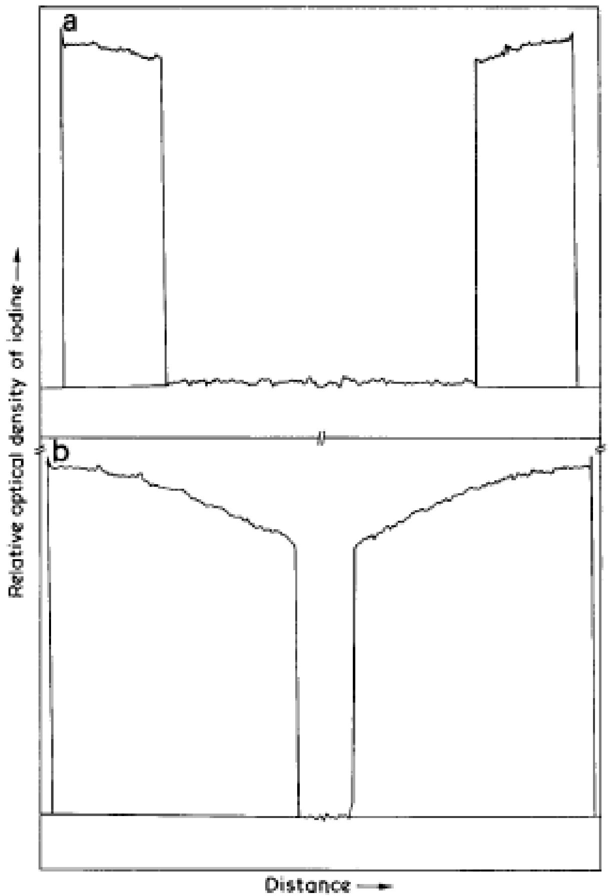
Effect of temperature



Relationship between exponent, *n,* in equation $S_e = at^n$ and temperature, describing penetration of the n-alkane series from pentane through octane in polystyrene sheets. (after Tidone et al. Polymer 1977)

Different behaviors observed

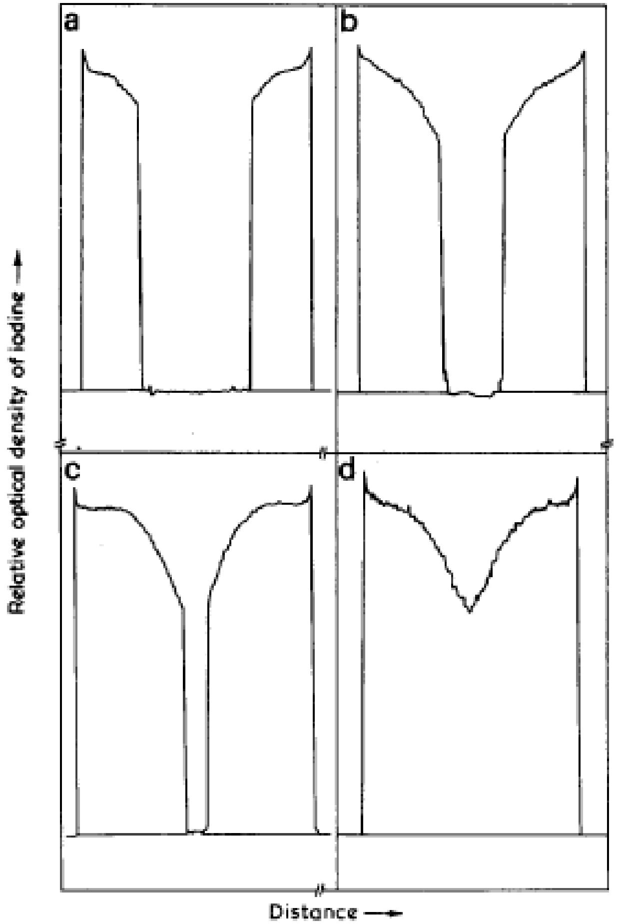


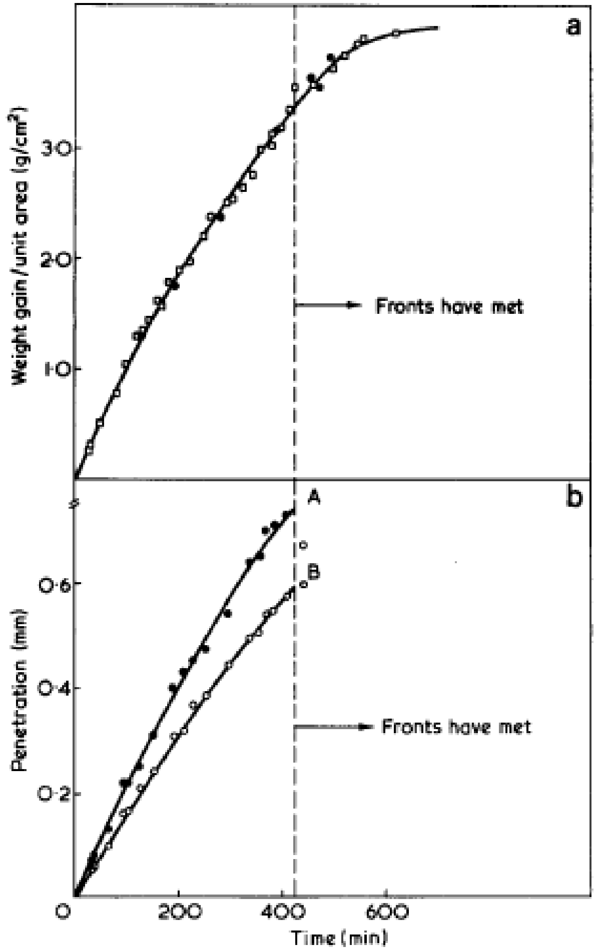


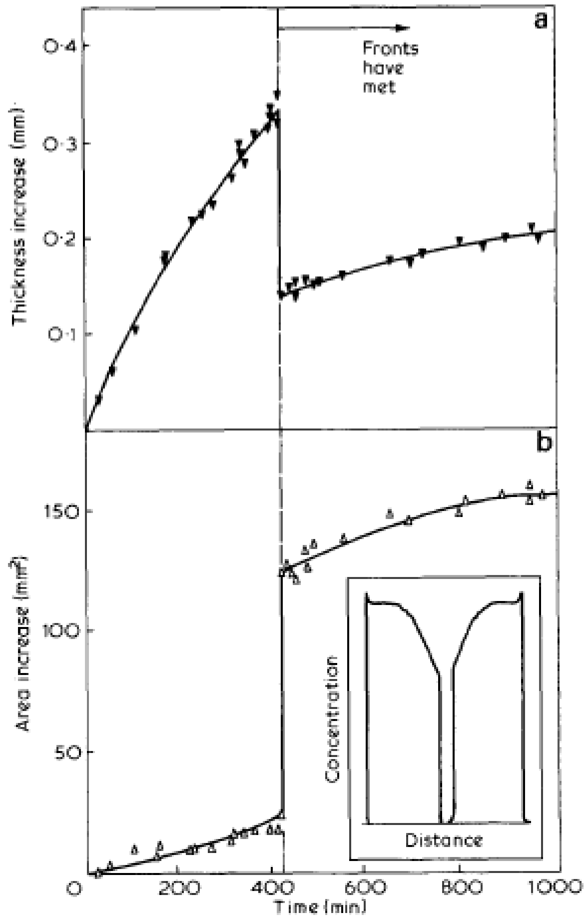
Me-OH in PMMA

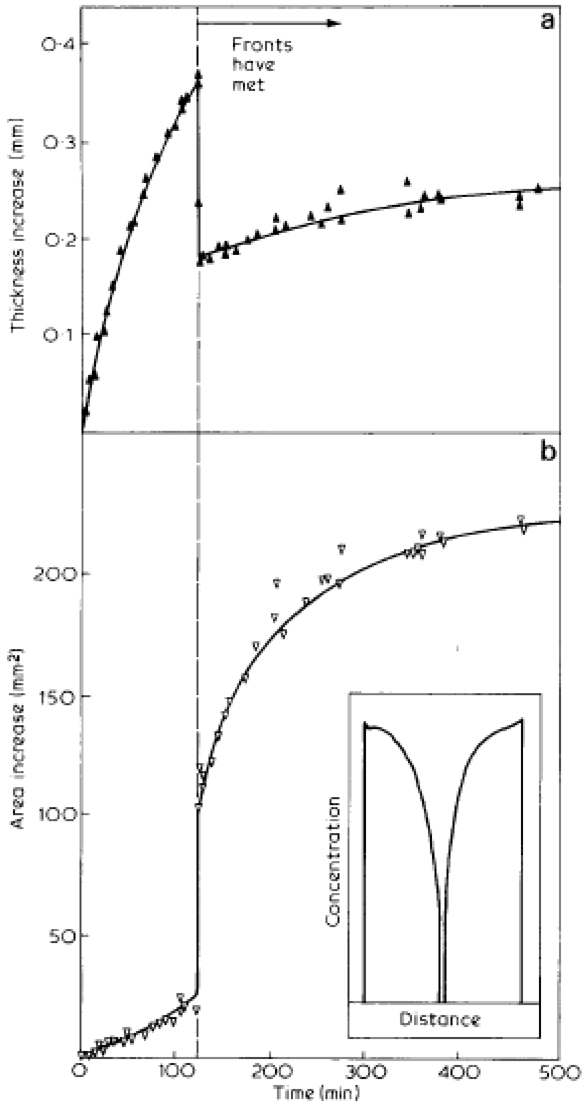
Tomas & Windle Polymer 1980

Different behaviors observed






a
Fronts
have
met
Thickness increase (mm)
O·4
O·3
O·2
O·1
b
Area increase (mm²)
150
100
50
Concentration
Distance
O
200
400
600
800
1000
Time (min)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Distance
O
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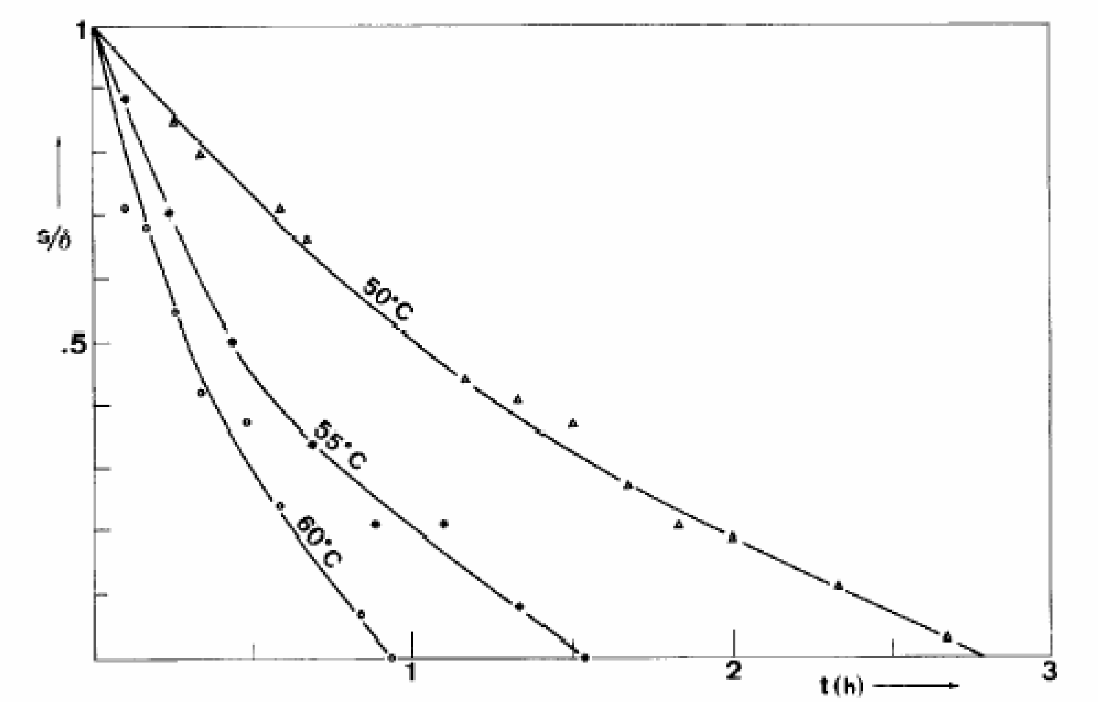
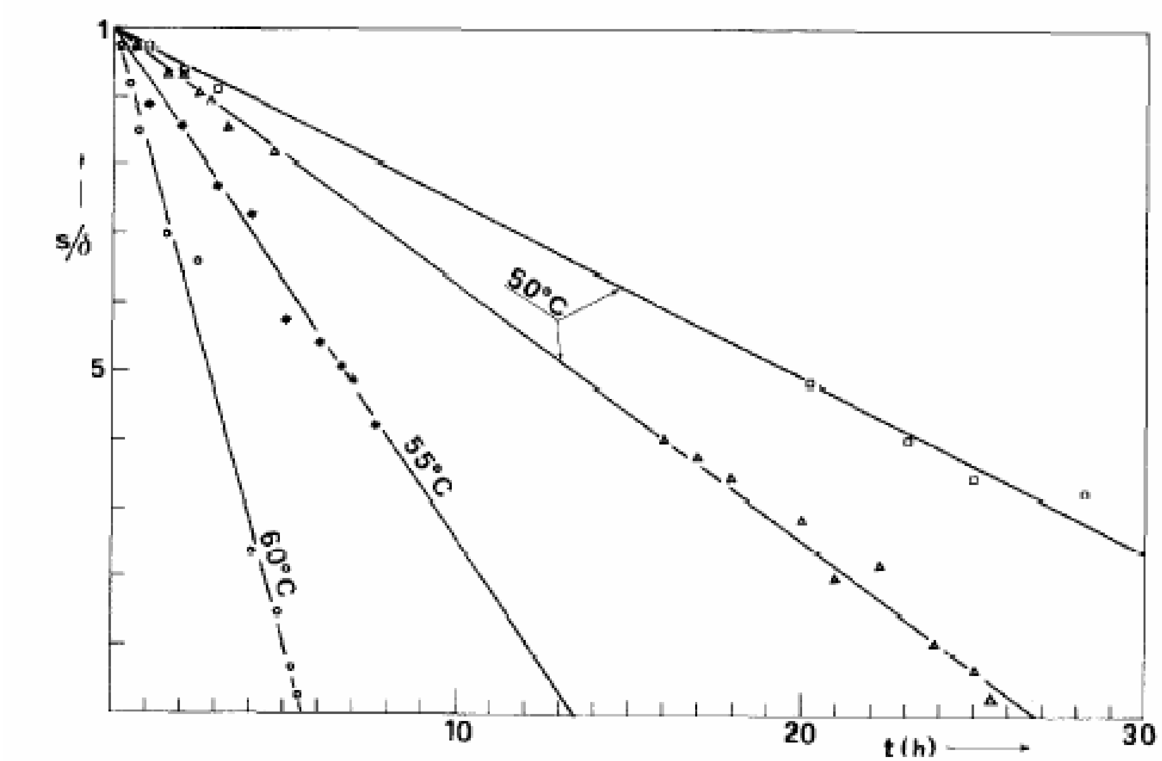
500
Time (min)

Different behaviors observed



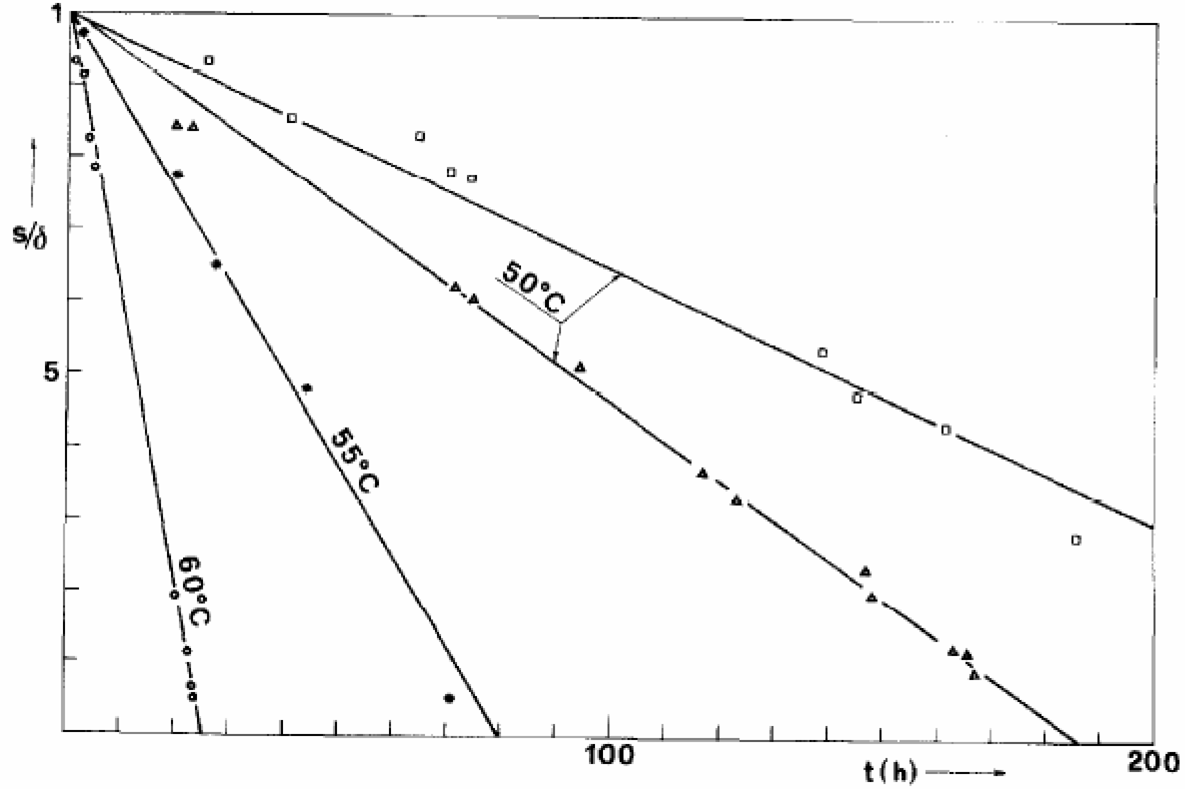
Fractional residual core thickness for methanol sorption in PUMA sheets; 1 mm nominal thickness; as-received samples.
After Masoni Sarti J. Membr Sci 1983

Different behaviors observed



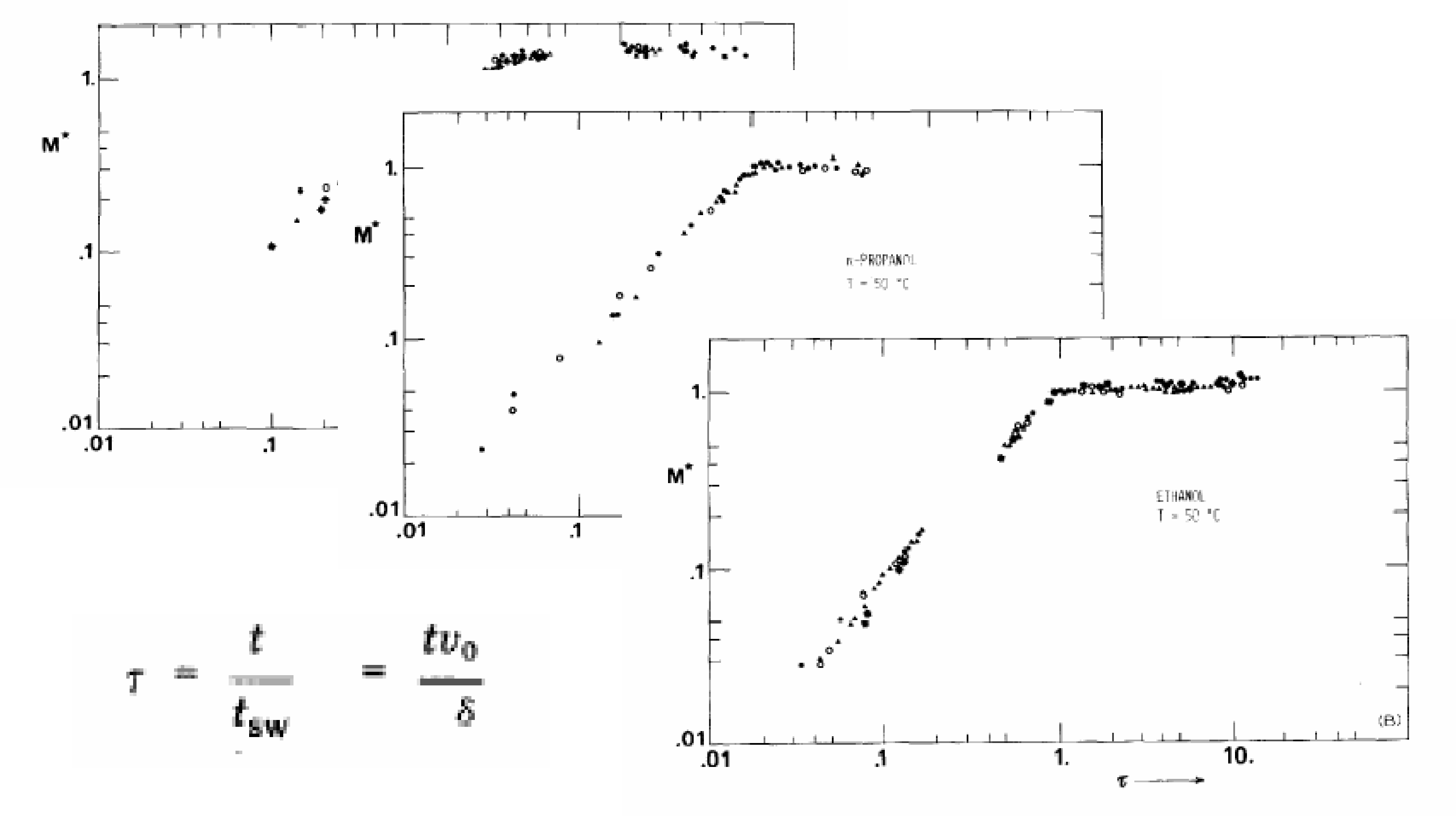
Fractional residual core thickness for ethanol sorption in PMMA sheets; 1 mm nominal thickness; as-received samples: 50, 55, 60 °C; and samples annealed 24 hr at lOO °C, penetrated at 50°C.

Different behaviors observed



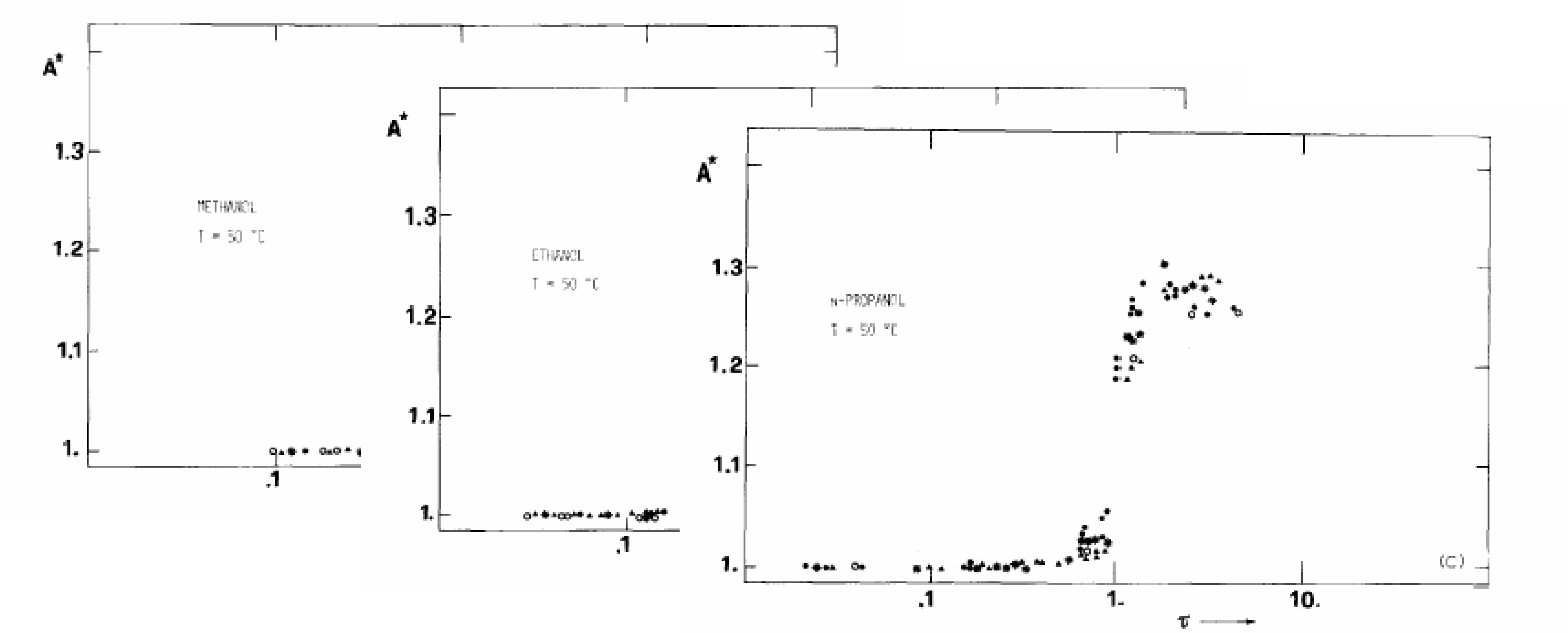
Fractional residual core thickness for n-propanol sorption in Fractional residual core thickness for ethanol sorption in PMMA sheets; 1 mm nominal thickness; as-received samples: 50, 55, 60 °C; and samples annealed 24 hr at lOO °C, penetrated at 50°C.

Different behaviors observed

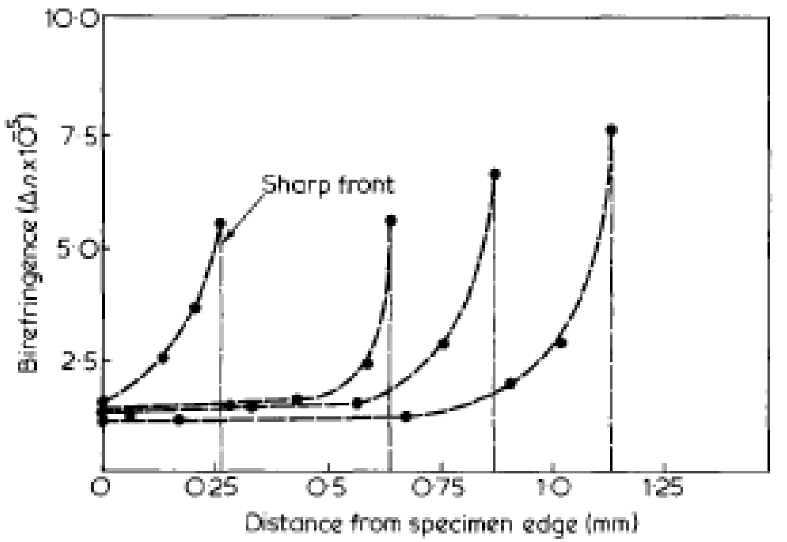


$$\tau = \frac{t}{t_{sw}} = \frac{t v_0}{\delta}$$

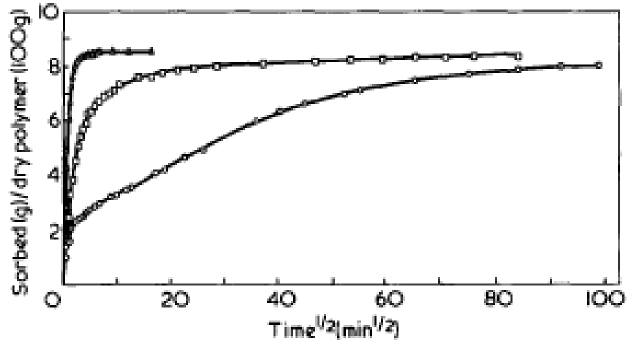
Different behaviors observed



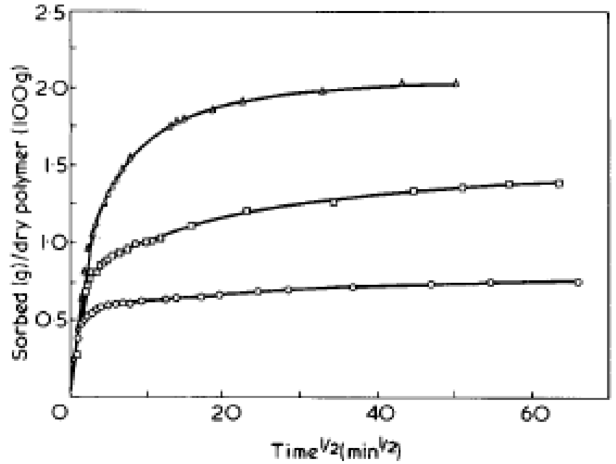
Penetrants can generate swelling and stresses



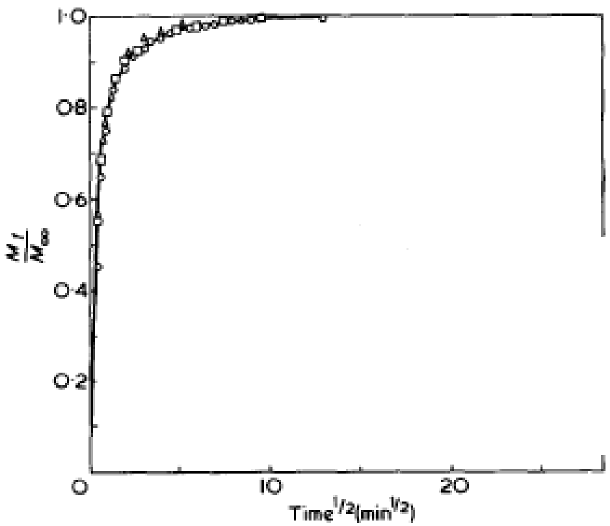
Effects of prehistory



Comparison of n-hexane sorption in preswollen (△), 'as-received' (□), and annealed samples (○) at p/p^0 = 0.75 and 30°C. Sorption-cycle 1, polystyrene, d = 0.534 μm



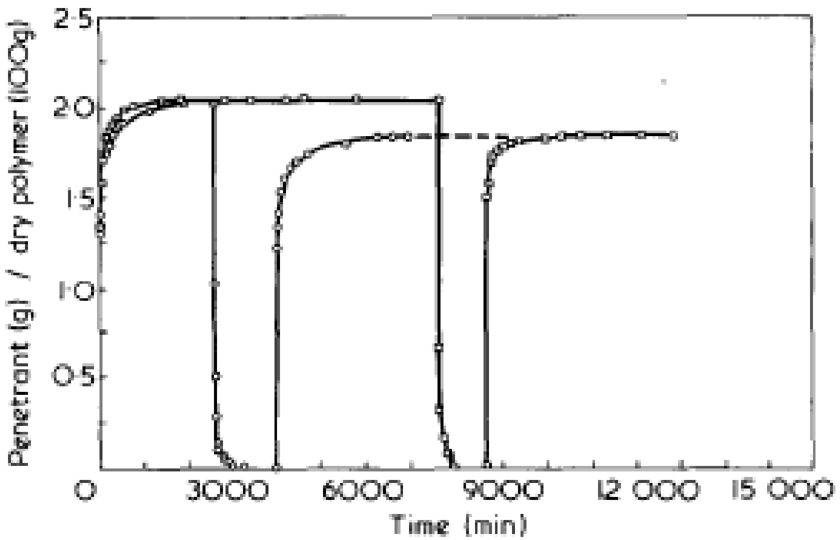
Comparison of n-hexane sorption in preswollen (△), 'as-received' (□), and annealed samples (○) at p/p^0 = 0.10 and 30°C. Sorption-cycle 1, polystyrene, d = 0.534 μm



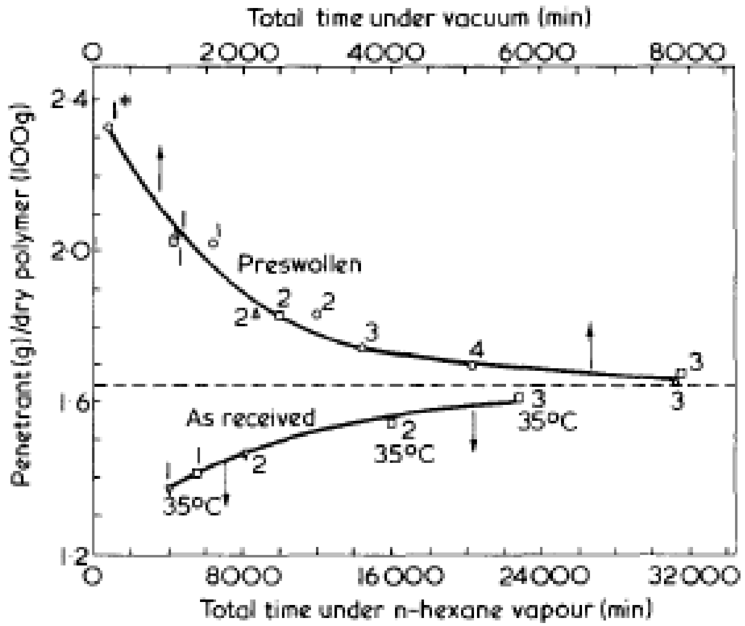
Comparison of n-hexane desorption from preswollen (△), 'as-received' (□), and annealed samples (○) previously equilibrated at p/p^0 = 0.75 and 30°C. Desorption-cycle 1, polystyrene, d = 0.534 μm

After Hopfenberg et al Polymer 1980

Effects of prehistory



Comparison of n-hexane resorption in preswollen samples, contacted with n-hexane for various time intervals during the preceding sorption cycle. Resorption was carried out at p/p^0 = 0.10 and 30°C. ○, sample 1; □, sample 2. Sorption-cycling, polystyrene preswollen d = 0.534 μm



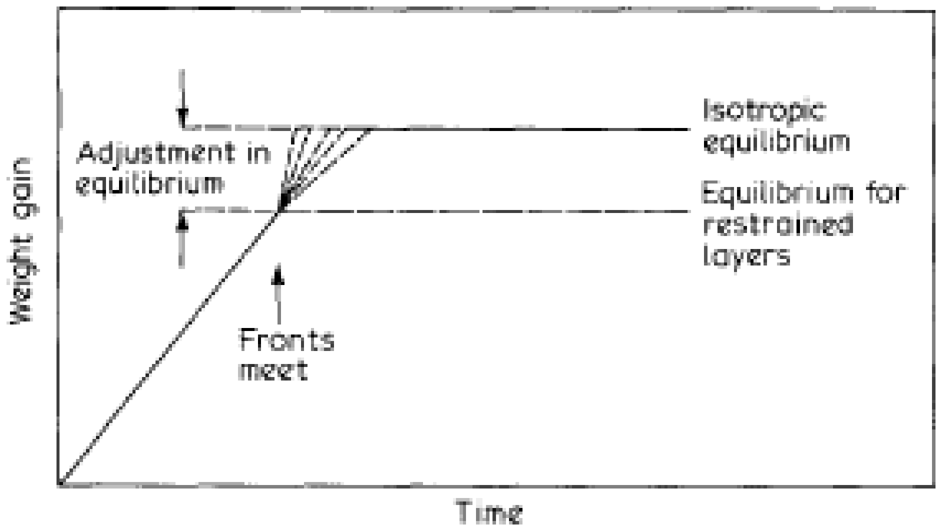
Effect of cycling on the apparent equilibrium sorption of n-hexane at p/p^0 = 0.75 and 30°C in preswollen and 'as-received' samples. Sorption-equilibria, polystyrene, d = 0.534 μm. * Cycle number

Enscore et al Polymer 1980

accelerations

Effects of film thickness !:

Higher δ: no accel
Lower δ: larger acceleration



Modeling

Boundary conditions (solubility and its relaxation)
Localized swelling
Flux dependence on stress and history
- lumped models
- General models

Solubility (BC): from NET-GP

NET GP *General Results*

• ***The Helmholtz and Gibbs free energies under asymptotic pseudo-equilibrium conditions are uniquely related to the equilibrium Helmholtz free energy at the same T, V and composition (T, ρ_1, ρ_2) as :***

$$\hat{A} \equiv \hat{A}_{NEq}\left(T, p, \rho_1, \rho_2\right) = \hat{A}_{Eq}\left(T, \rho_1, \rho_2\right)$$

• ***polymer density ρ_2 is the non equilibrium value measured in the glass***

•***Pressure is not the equilibrium value at the given T, V and composition***

$$\mu_1^{(GP)} = \left(\frac{\partial m\hat{G}}{\partial m_1}\right)_{T,p,m_2,\rho_2} \equiv \left(\frac{\partial \rho \hat{A}_{Eq}}{\partial \rho_1}\right)_{T,\rho_2}$$

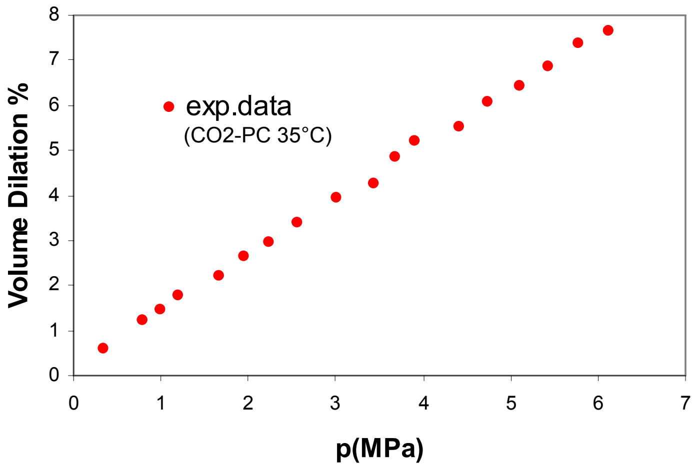
Doghieri & Sarti JMS 1996, Chem. Eng. Sci 1998

Solubility Isotherm from Dilation Data ......

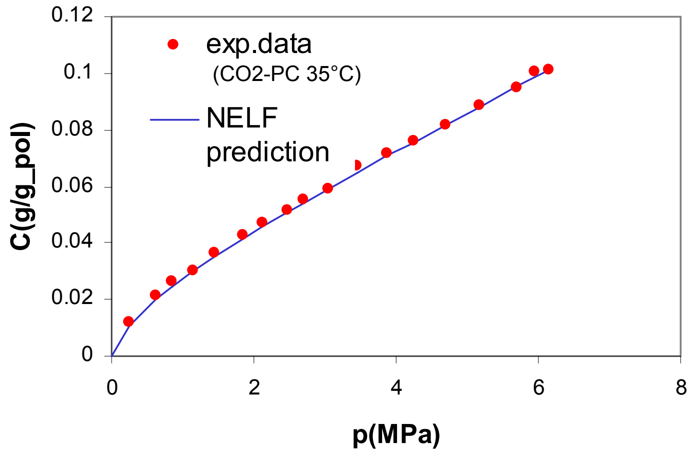
Assume lattice fluid model (SL):

- *The **SL** Parameters (**P*,T*,ρ***) for both penetrant and polymer*
- *The density of the polymer during the Sorption (e.g Dilation data)*

The NELF gives the Sorption Isotherm



(data from Fleming and Koros, 1990)



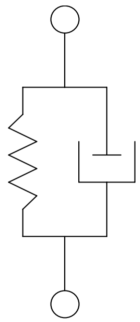
(data from Fleming and Koros, 1990)

Effect of relaxation processes on gas/vapor solubility in glassy polymers: volume swelling model (VS)

Swelling kinetics of polymeric elements induced by sorption processes

Volume dilation modeled through simple Kelvin-Voigt model for bulk rheology:

$$\frac{1}{\rho_{pol}}\frac{\partial \rho_{pol}}{\partial t} = \frac{p^{EXT} - p^{EQ}\left(\Omega, \rho_{pol}\right)}{\eta}$$



solubility data in sorption processes **driven by volume relaxation** phenomena:

n-hexane in PS @ 40°C

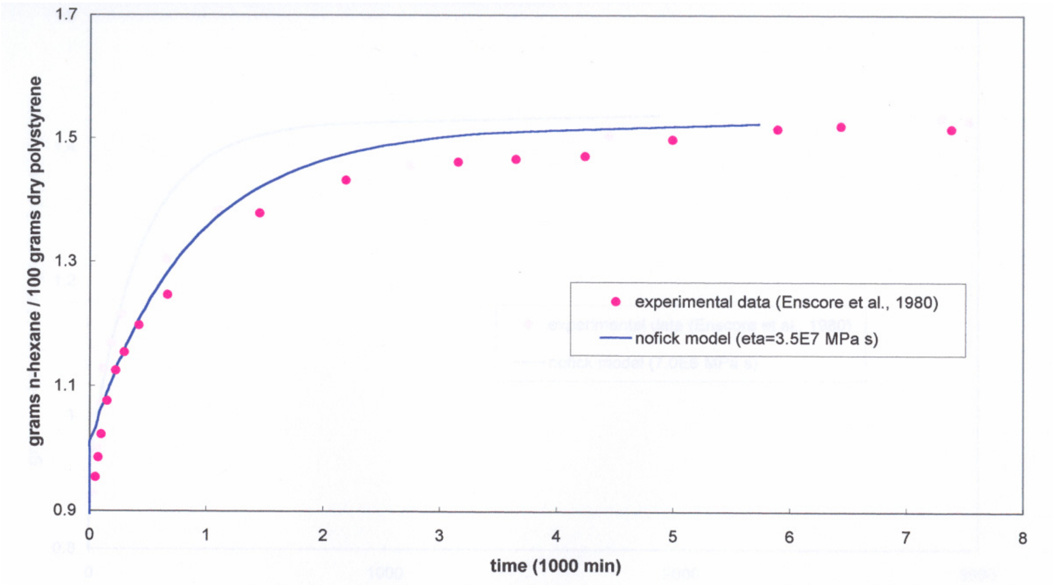
sorption process in microspheres

(d ≈ 0.5 μm)

Activity jump 0 → 0.1

Exp. data from Enscore et al., Polymer 1980

Fitting parameter = bulk viscosity



Mass transport model for gas sorption in glassy polymeric systems with both diffusion and volume relaxation

$$\frac{\partial \rho_{sol}}{\partial t} = -\underline{\nabla} \bullet \underline{J}$$

$$\underline{J} = -\mathcal{D}\, \rho_{sol}\, \underline{\nabla}\mu$$

$$\frac{1}{\rho_{pol}} \frac{\partial \rho_{pol}}{\partial t} = \frac{p^{EXT} - p^{EQ}\left(\Omega, \rho_{pol}\right)}{\eta}$$

Example of simulation results for n-hexane sorption in PS films

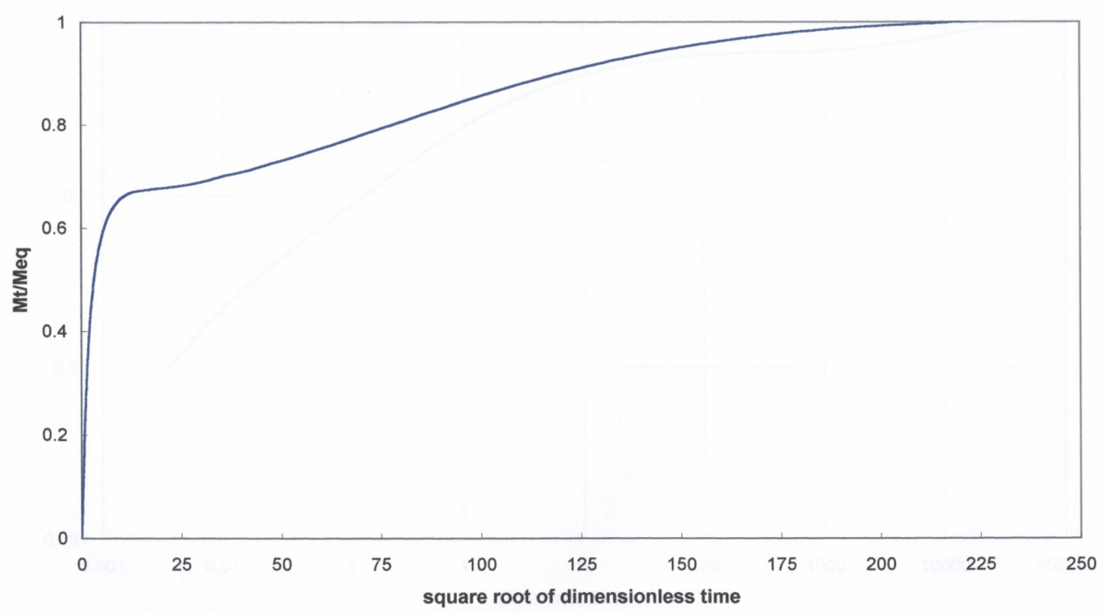
T= 40°C

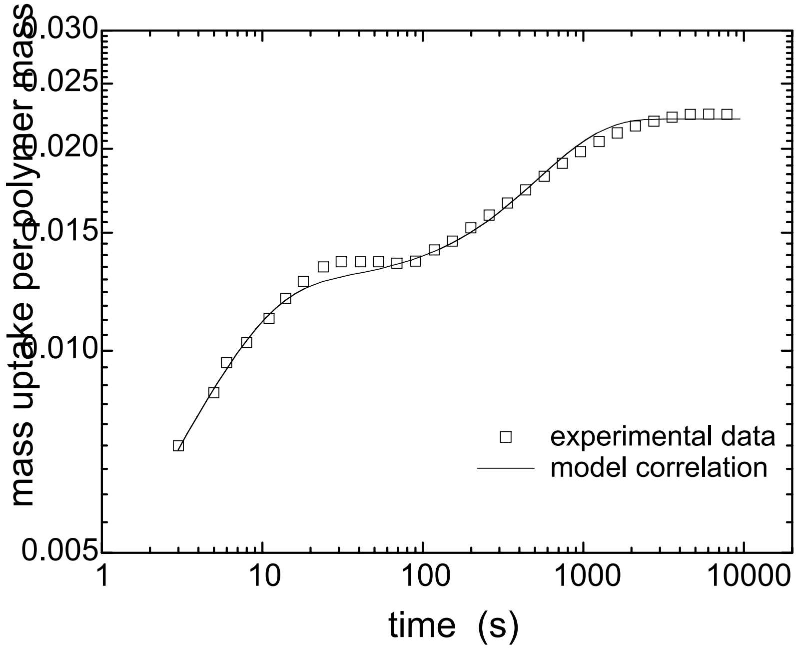
Film thickness = 1 μm

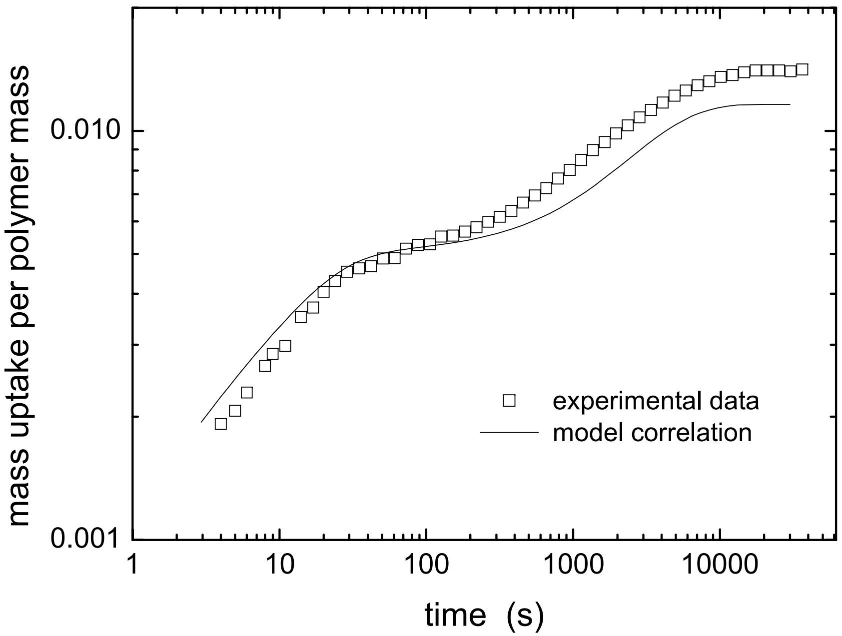
activity jump 0 → 0.1

Diffusion coefficient from Vrentas and Duda Free Volume Theory

Bulk viscosity from analysis of relaxation data







Kinetics of CO_2 sorption in PMMA film for sorption step from 12.4 *bar* to 23.4 *bar*. Comparison of experimental values with model results.

Kinetics of CO_2 sorption in PMMA film for sorption step from 25.4 *bar* to 33.1 *bar*. Comparison of experimental values with model results.

Rate-Type (RT) lumped models for viscoelatic diffusion

$$\frac{\partial \rho_{sol}}{\partial t} = -\underline{\nabla} \bullet \underline{J}$$

$$\tau \frac{\partial \underline{J}}{\partial t} + \underline{J} + \mathcal{D} \rho_{sol} \underline{\nabla} \mu = 0$$

$$\frac{1}{\rho_{pol}} \frac{\partial \rho_{pol}}{\partial t} = \frac{p^{EXT} - p^{EQ}\left(\Omega, \rho_{pol}\right)}{\eta}$$

Hyperbolic problem accounting for

•a relaxation time τ in the flux

•relaxation phenomena in volume swelling and in relax in BC

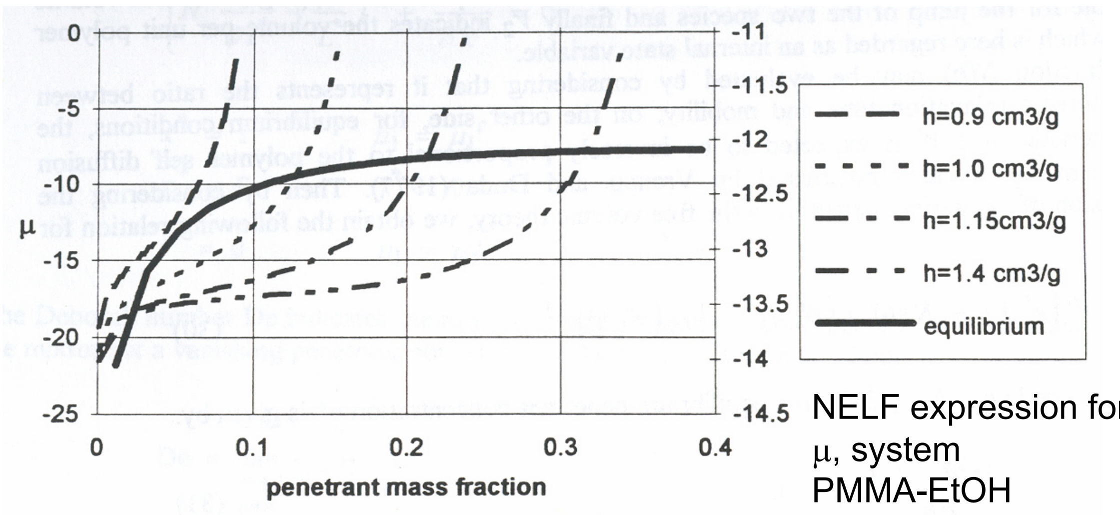
Thermodynamic Analysis for the development of shock concentration waves in the system

Results from the application of 2nd law:

Necessary condition for the formation of shock concentration waves is that:

$$\left(\frac{\partial^2 \mu}{\partial \rho_{sol}^{\ 2}}\right)_{\rho_{pol}} > 0$$

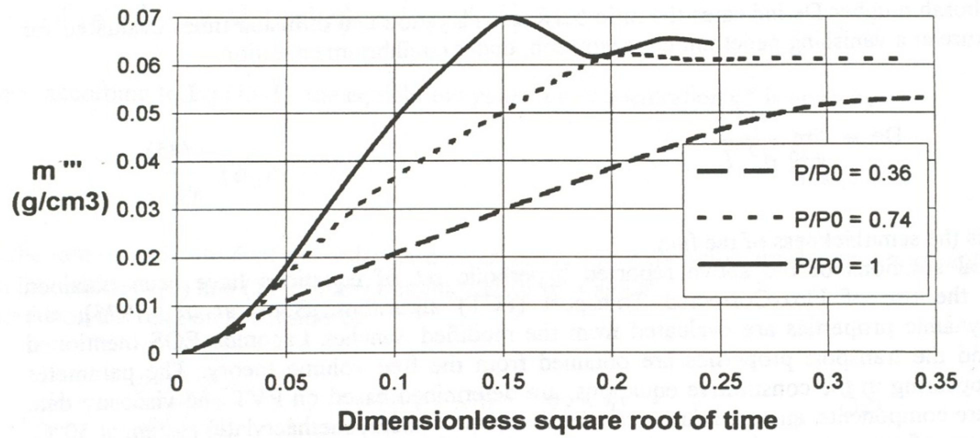
at least in a concentration range

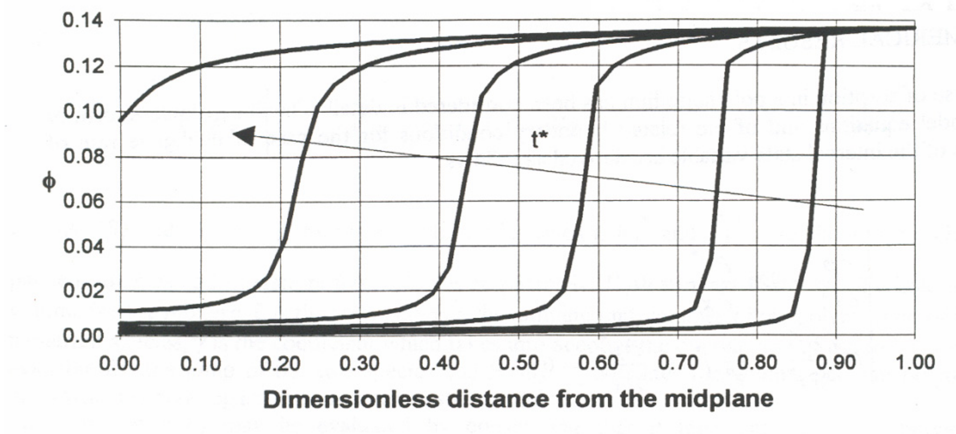


NELF expression for μ, system PMMA-EtOH

Example of simulation results for RT sorption model: case of negligible volume swelling

Sorption kinetics for the case of ethanol-PMMA system at 30°C ρ_{pol} =1.10 g/cm^3 e diffusivity exponentially increasing function of concentration:
Effect of external solute fugacity





Examples of concentration profiles from simulation of sorption process for ethanol in PMMA (De = 30)

More general models

$$\mathbf{j}_2^1 \equiv \varrho_1(\mathbf{v}_1 - \mathbf{v}_2) = \frac{\varrho_1\varrho_2}{\varrho m_{12}}\left(\frac{1}{\varrho_1}\nabla\cdot\mathbf{T}_1 - \frac{1}{\varrho_2}\nabla\cdot\mathbf{T}_2\right);$$

Mass balance

+

Mechanical problem
with viscoelastic response

e.g. Billovitis, Macromol. 1994

Caruthers & Peppas Chem Eng Sci 1992, 1996

Petropolulos et al Macromol 2002

Doghieri et al. 2004, 2005


THANK YOU FOR YOUR KIND ATTENTION