Positronium zur Untersuchung weicher Materie

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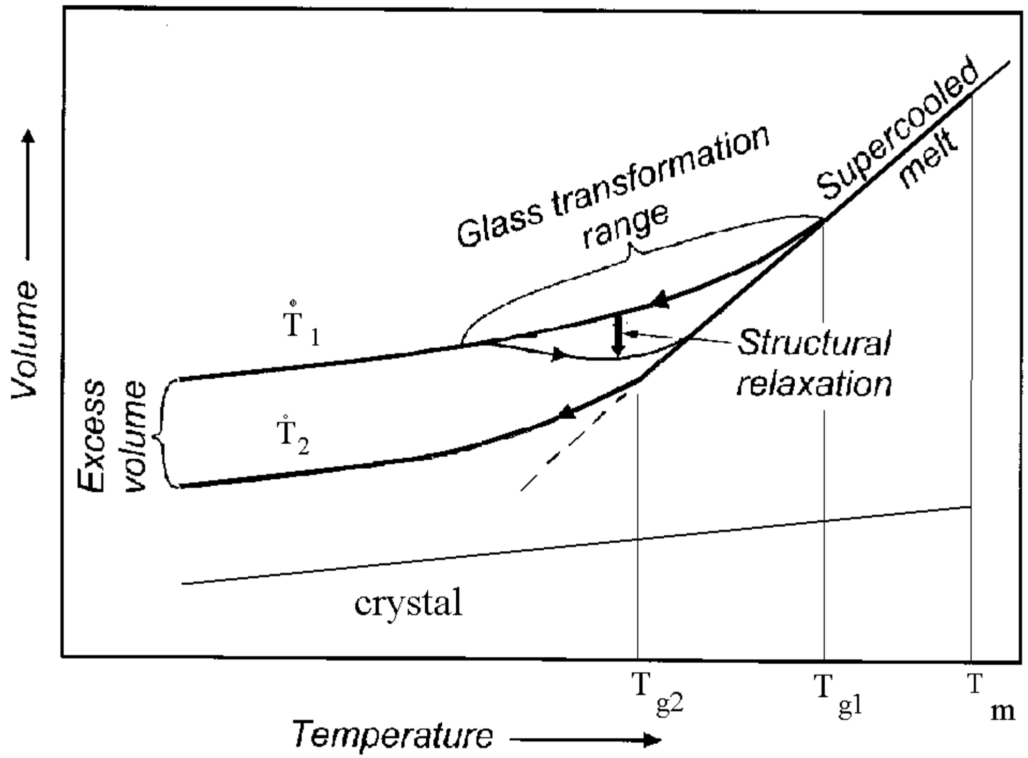
previous work with the help of:
Jan Kruse, Jörn Kanzow (PhD thesis)
W. Egger, G. Kögel, P. Sperr, W. Triftshäuser (beam Munich)



Glass transition:

- change in thermal expansion
- change in molecular dynamics
- T_g time- (heating rate) dependent
- surface vs. volume vs. interface
- bulk transition vs. thin film

Epoxy systems: technological relevant, glue, load bearing, „GFK“

Positron annihilation in polymers

Why polymers?   Which polymers?

What can we learn from intensity and lifetime?

Lifetime $\tau_3 \leftrightarrow$ volume

Surface glass transition in epoxy resins

Glass transition at the surface and in thin films

T_g @surface smaller or larger than T_g @bulk?

Ageing in thin expoxy films

dry thermal and hydrothermal ageing

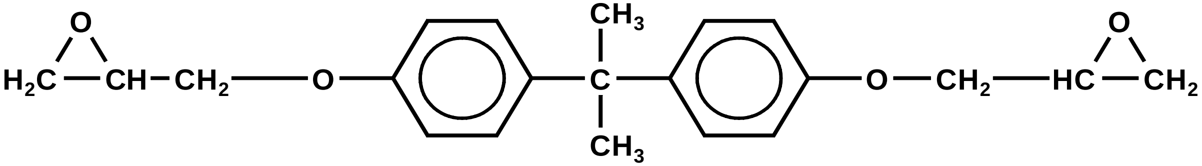
change in free volume? Other changes?

Future experiments with PALS and beam

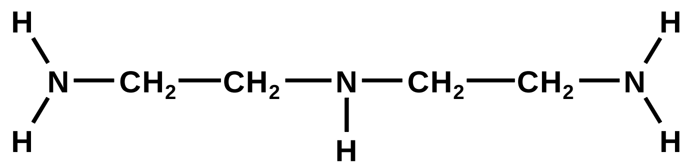
UPSCALEPIM (planned EU Project)

SPP 1369 Interphases and Interfaces

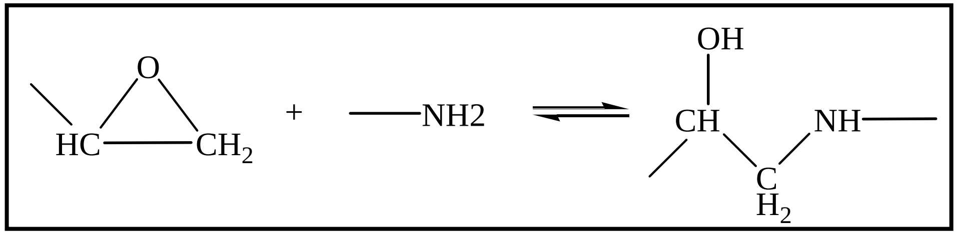
epoxy resin **DGEBA**

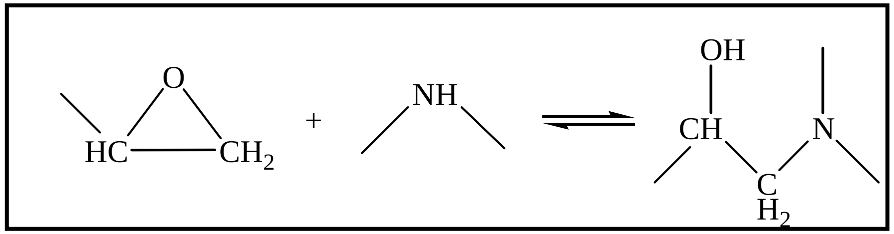


hardener **DETA**



Main cross-linking reactions (oxirane + amine groups):



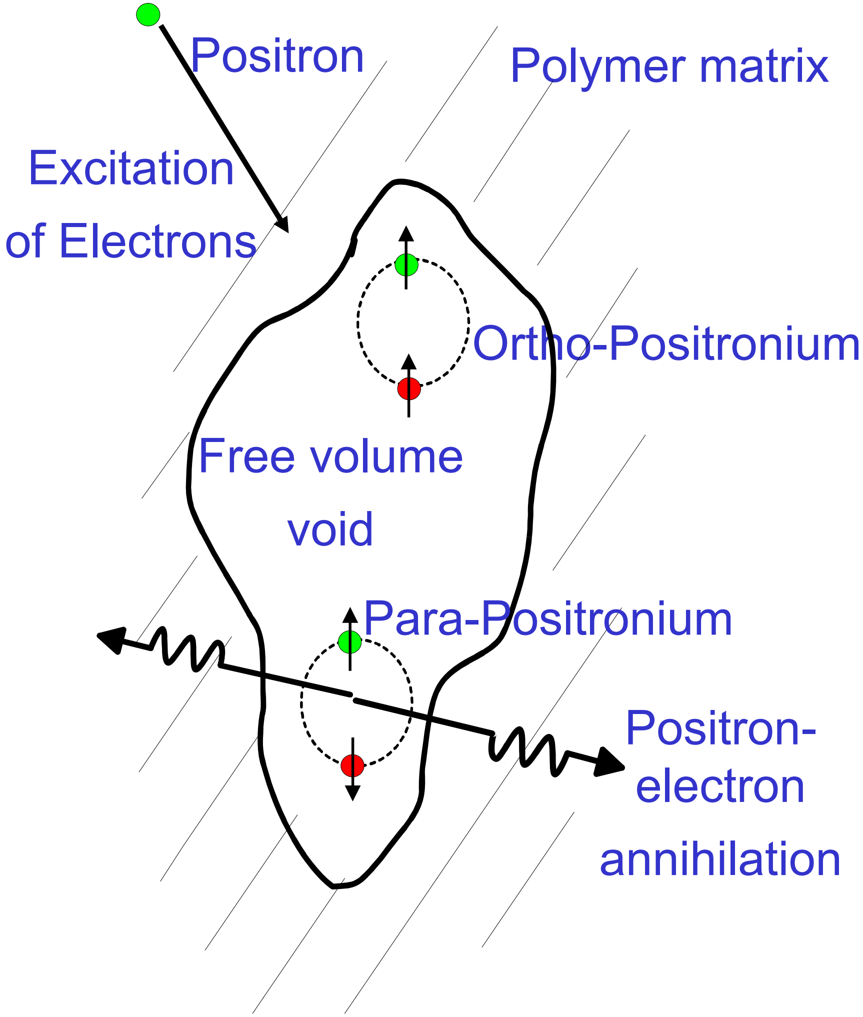


Thin film preparation:

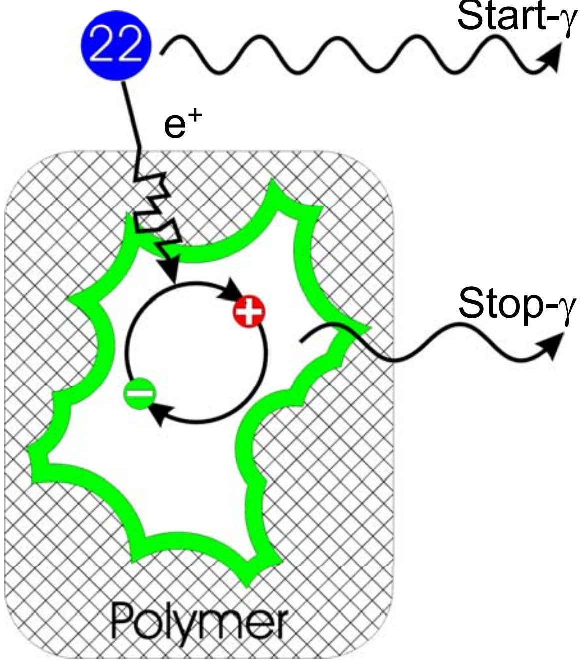
- Mixing, stirring 1 hour => prepolymerisation
- Solvation in methyl ethyl ketone
- Spin coating on metal substrates

Curing conditions:

- 48 h at room temperature+ 1 h post curing at 120 °C

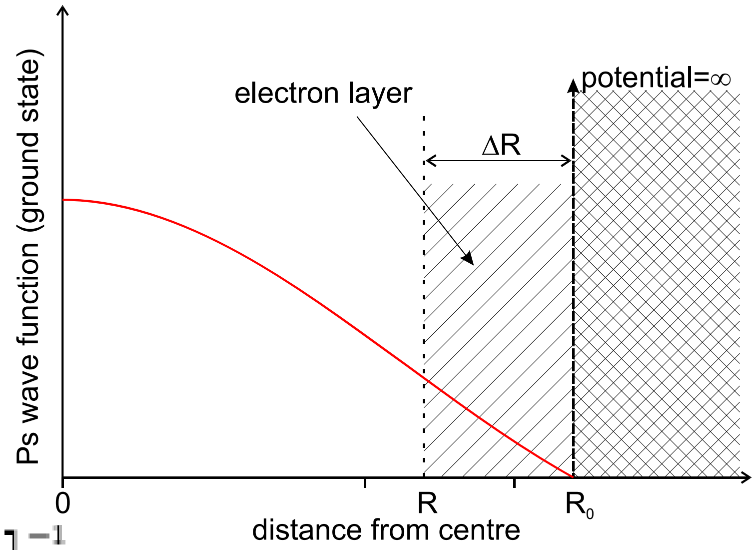


- Average *free volume void sizes* determine average ortho-positronium *lifetime*
- Ortho-positronium *intensity* depends on efficiency of *electron acceptor groups*
- *Surface regions*/ *thin films* accessible by *positron beam technique*
  - Direct depth resolution due to monoenergetic positron beam



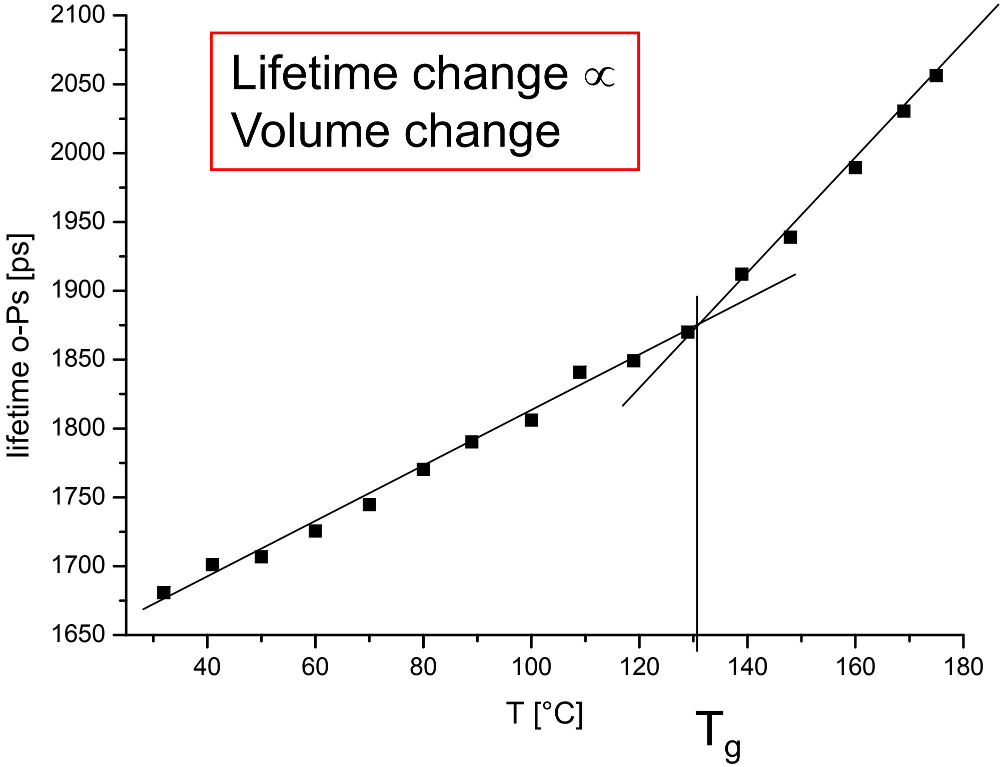
- Radioactive decay → positron
- Positron + electron → ortho-Positronium (o-Ps)
- trapping in voids
- decay by interaction with electrons from wall

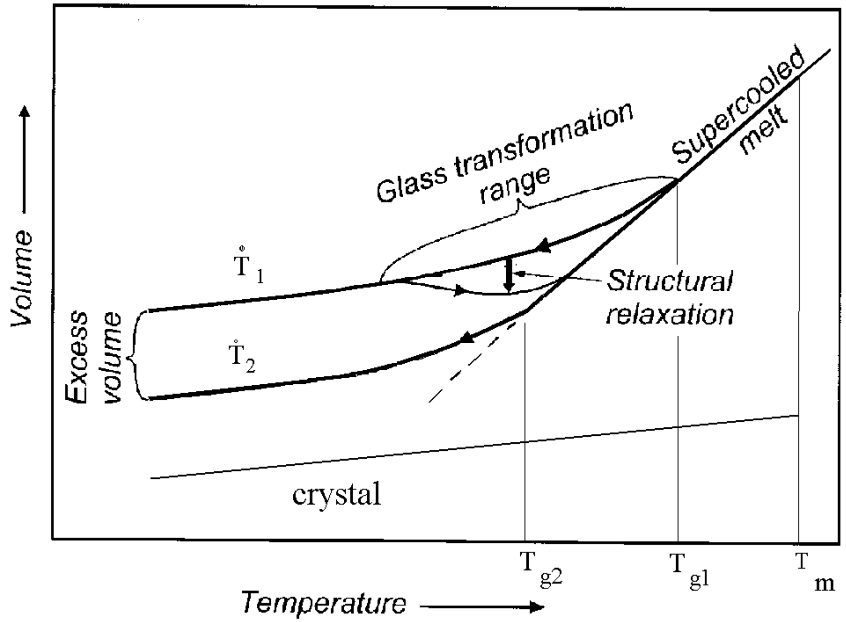
Tao 1972
Eldrup et al. 1981
Jean 1990



$$\tau = \left(\frac{2}{\text{ns}} \cdot P\right)^{-1} = \frac{1}{2}\text{ns} \cdot \left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1}$$

Hole radius r↑⇒ overlap wavefunction, ΔR ↓ ⇒ decay probability ↓ ⇒ lifetime τ_3 ↑

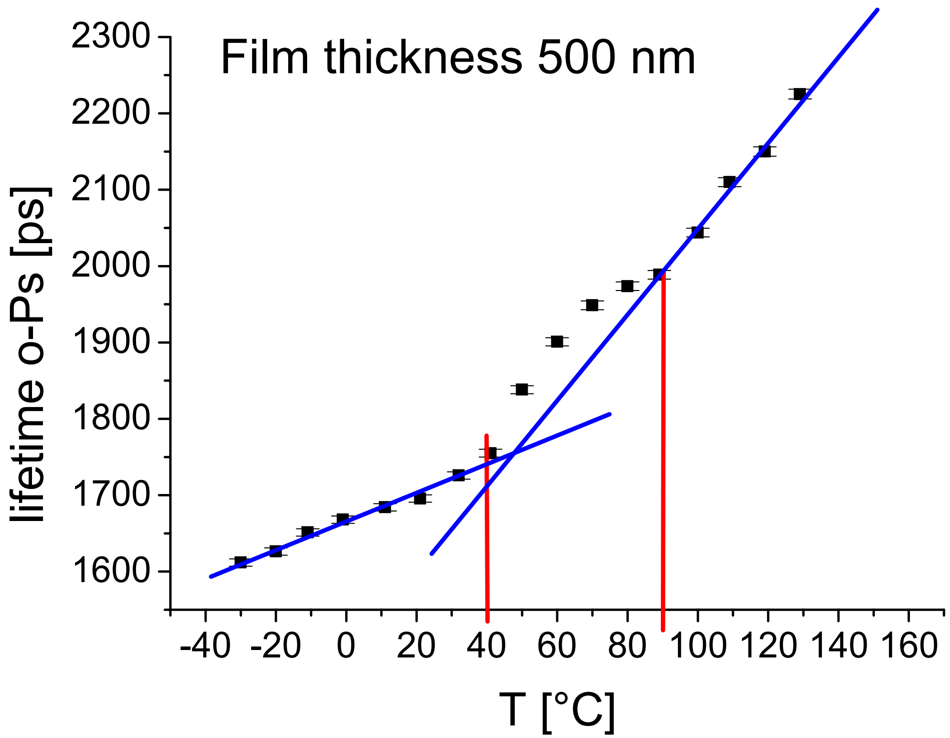




Glass transition T_g detectable via change in hole expansion

(reference measurement, bulk sample, equivalent to conventional technique)

Beam for thin epoxy film (1h post-cured @ 120 °C)



Glass transition between 40 °C and 90 °C
=> T_g much lower than for the bulk

Concave curvature during glass transition competing processes:

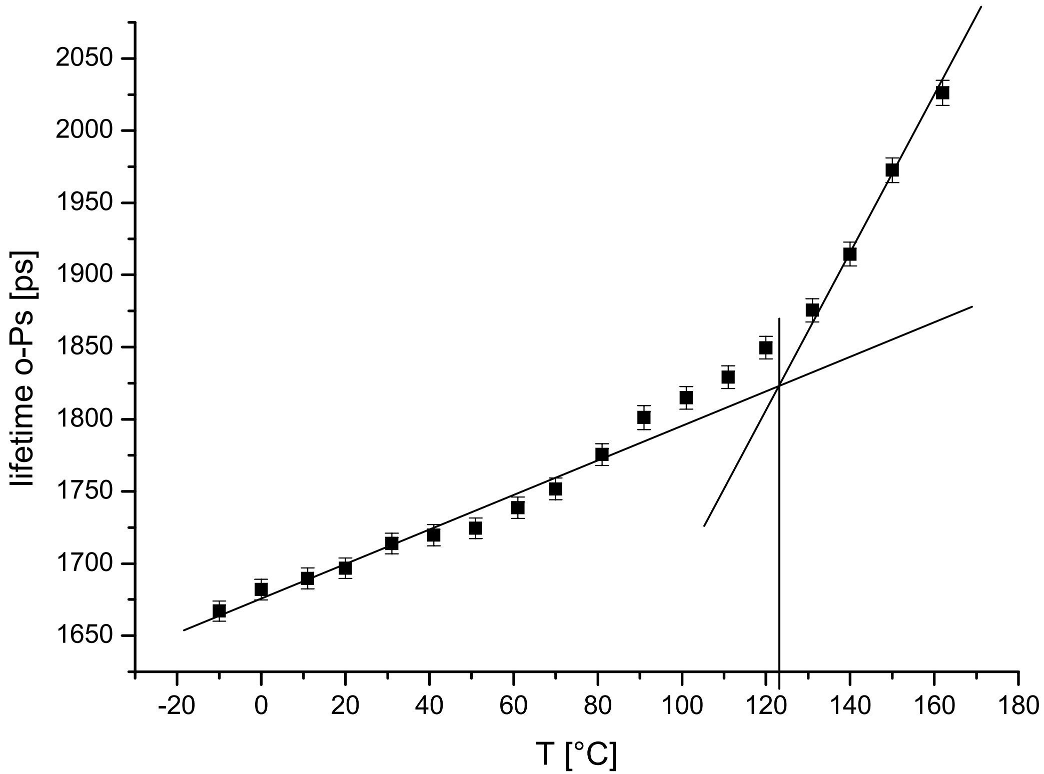
low T_g → increase in lifetime

Post-curing during experiment
(10 K steps, 1 h each step)
→ decrease in lifetime

crosscheck: → cured sample

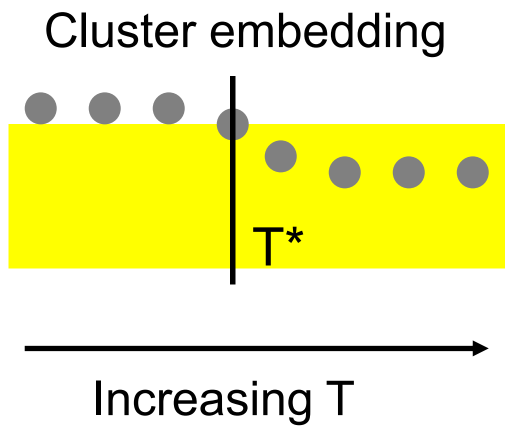
Faupel et al. , (ICPA-13), Mat. Sci. Forum Vol. 445-446, p. 219-223

Beam for thin epoxy film (27h post-cured @ 120 °C)

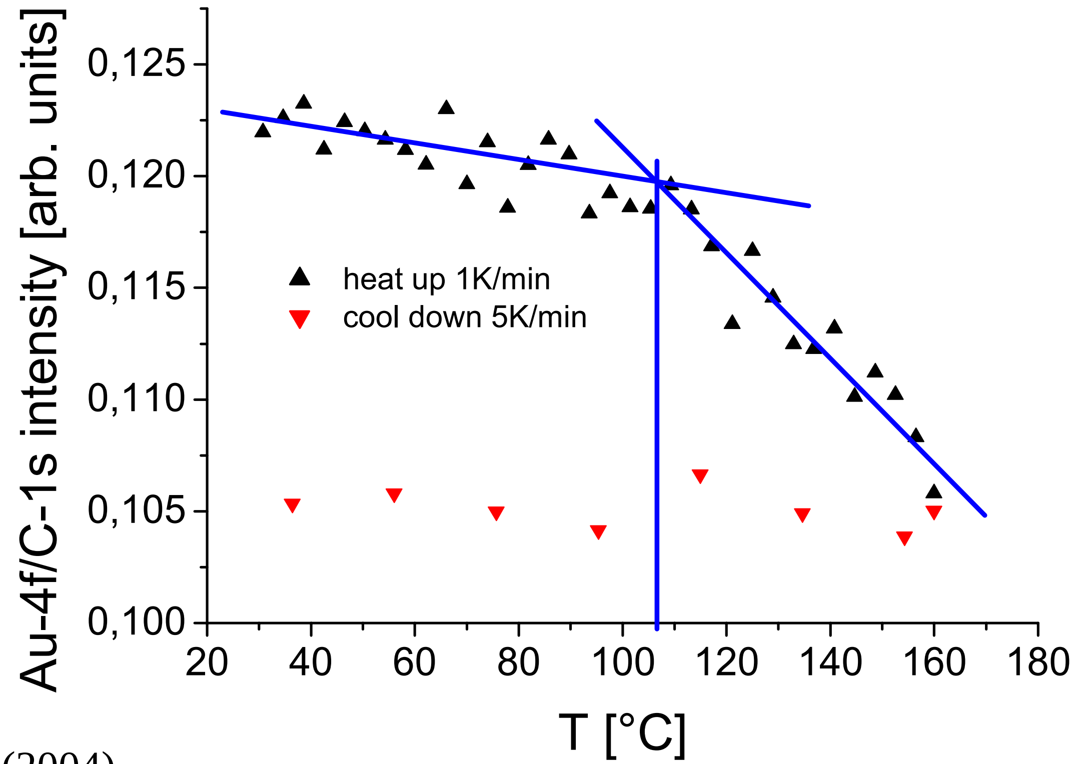


Increase in T_g (~ 120 °C) for intensively post-cured epoxy films

=> thin films behave different from bulk samples



Clusters: Au, *r* ~ 1 nm



Erichsen et al. Macromolecules, 37, 1831 (2004)

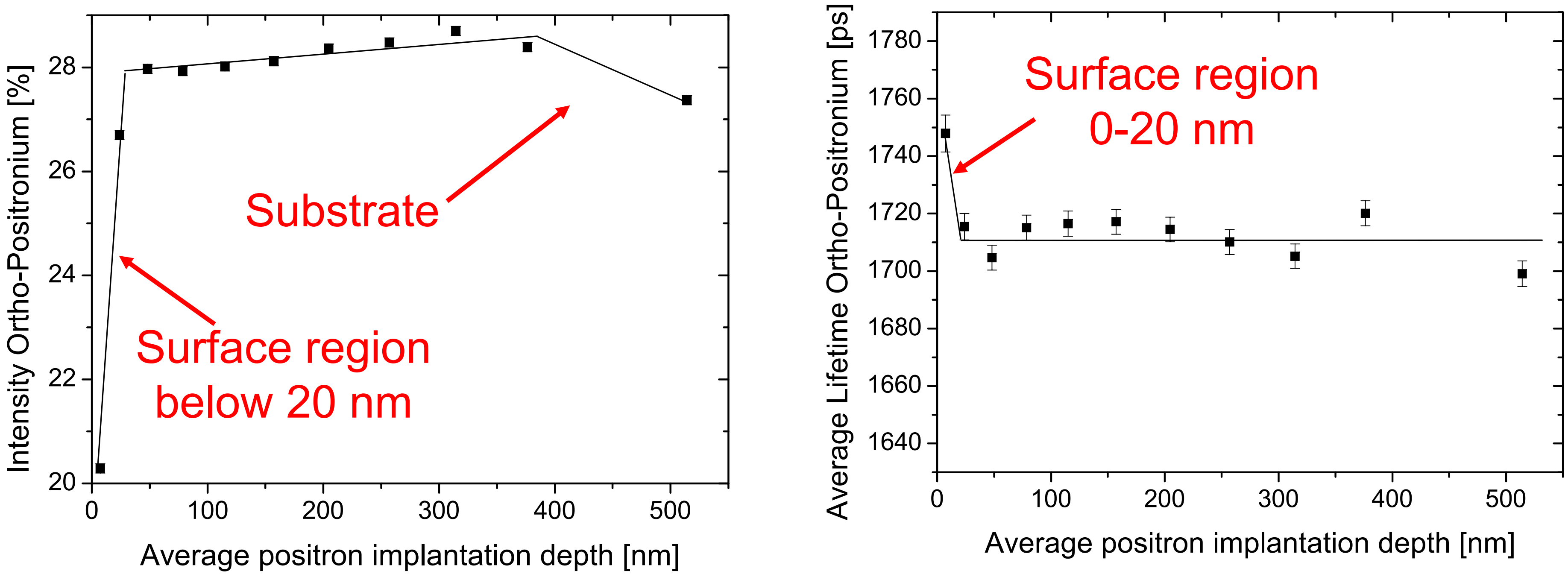
Surface glass transition detectable for thin epoxy films!

Summary: Surface T_g in epoxy resin

Sample	T_g Volume [°C]	T_g Surface [°C]
Bulk, 1h post-cured	130-135	130
5 µm, 1h post-cured	85-115	100-110
500 nm, 1h post-cured	35-90	60-65
500 nm, 27h post-cured	90-130	100-105
	PALS	*XPS*

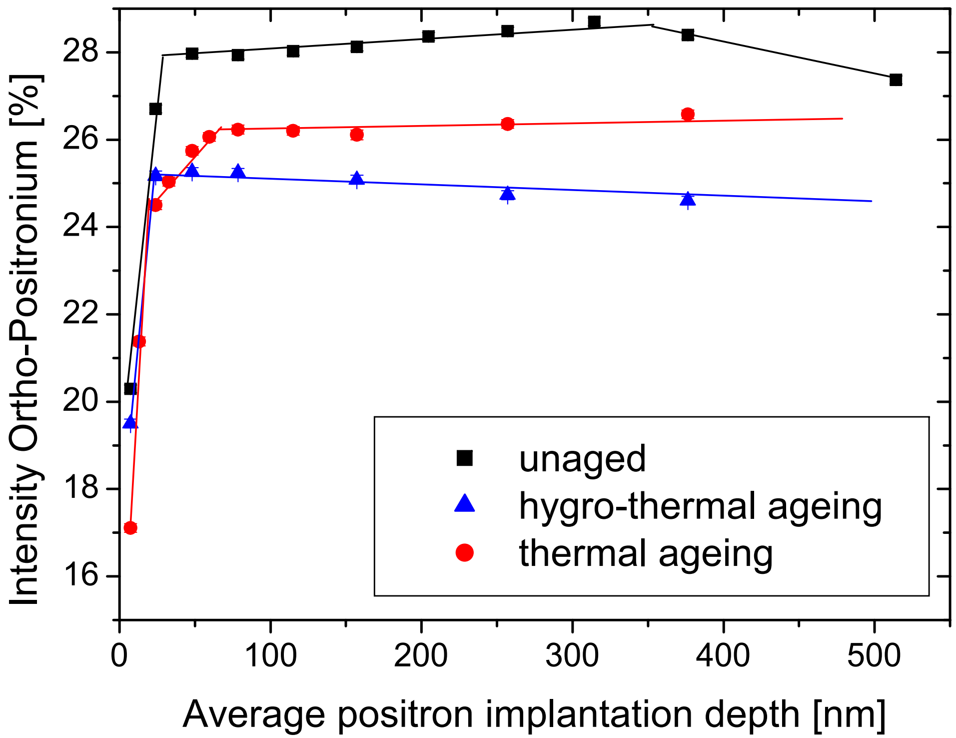
- Surface and volume T_g of epoxy thin films detectable
- Surface $T_g \approx$ volume T_g
- Strong film thickness dependence (for $d < 5$ µm)

PALS of unaged 500 nm thin epoxy film on Au-substrate



- Ortho-Positronium intensity and lifetime almost constant
- Positron implantation into Si-substrate => no positronium formation
- Epoxy surface => Less positronium formation and slight increase of lifetime
  (Intrinsic properties of the PALS beam technique)

PALS analysis of aged thin epoxy films: Intensity



500 nm epoxy film

on Au substrate

- Hygro-thermal
  (wet air with 90 % relative humidity, 40 °C, 100 days)
- Thermal
  (dry Ar atmosphere, 40 °C, 100 days)

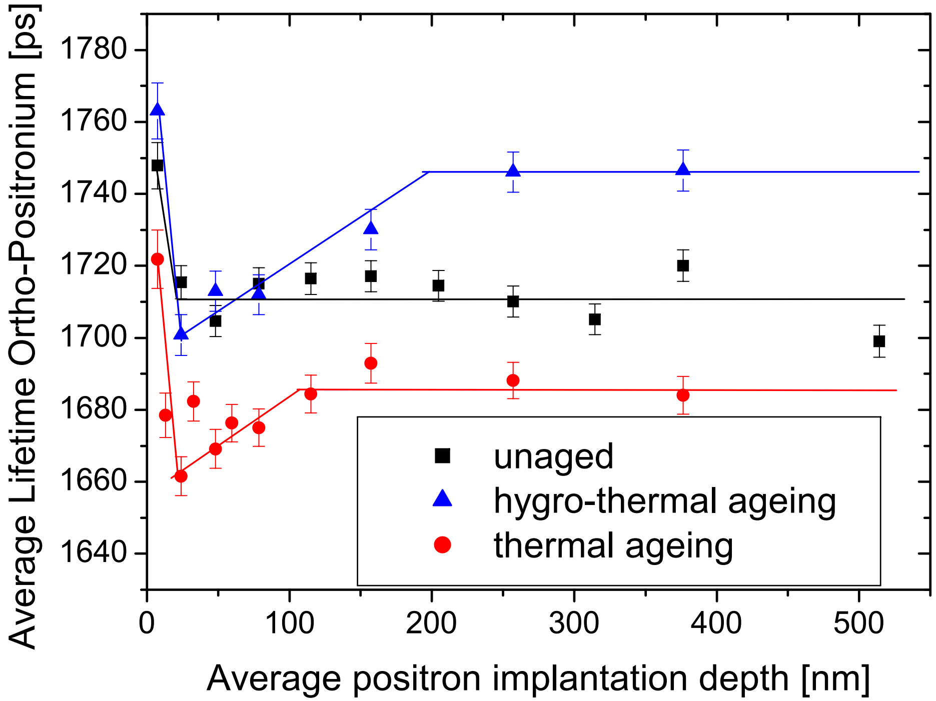
J. Kanzow et al.
Adhesion- Current research and applications,
W. Possart (Ed.), Wiley-VCH, 465 (2005).

Ortho-Positronium intensity decreases due to *both* ageing conditions

=> Less positronium formation due to an increase of electron acceptor groups

Indication of degradation (confirmed by other techniques)

PALS analysis of aged thin epoxy films: lifetime



500 nm epoxy film
on Au substrate

- Hygro-thermal
  (wet air with 90 % relative humidity, 40 °C, 100 days)
- Thermal
  (dry Ar atmosphere, 40 °C, 100 days)

- Ortho-Positronium lifetime changes <=> free volume changes
- Lifetime reduced by thermal ageing => post curing
- Lifetime increased by hygro-thermal ageing => irreversible ‚swelling‘
- Lifetime decreased in surface-near region => free volume decrease

- Bulk and thin epoxy resins:

    (Surface) glass transition can be clearly detected

    Surface $T_g \approx$ volume T_g

    Strong film thickness dependence (for d < 5 µm)

aged epoxy resins:

    Indication of degradation

    thermal and (stronger) hygro-thermal ageing

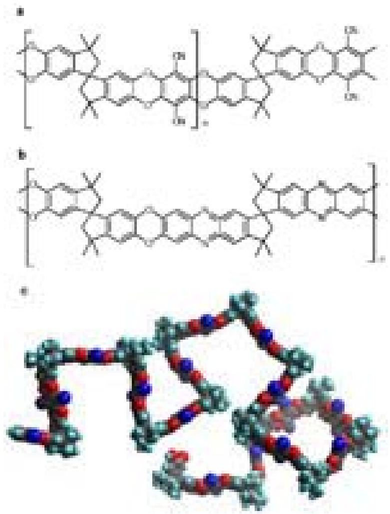
    swelling

- Positron lifetime spectroscopy valuable tool for investigation of polymers

- Beam technique absolutely necessary for thin films / interfaces

PALS and PALS beam for materials science of thin films urgently requested

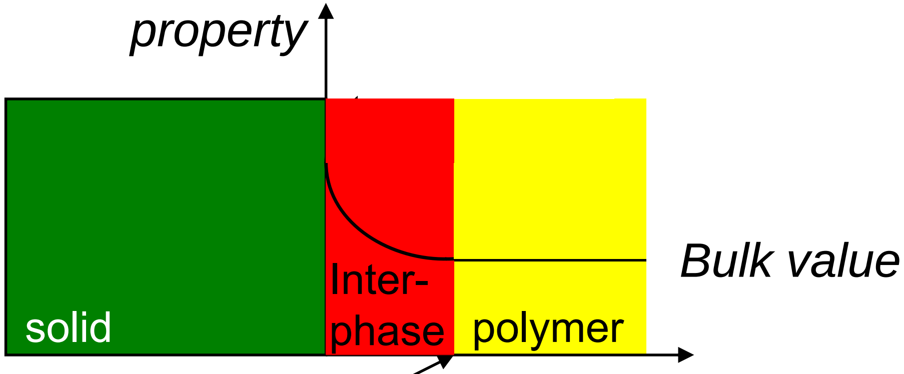
- Membrane polymers
  (PIM's: Polymers with Intrinsic Microporosity)
  EU project underway „UPSCALEPIM“
  our task, Characterisation of thin polymer layers on support



- Bio adhesives
  investigation of microstructure of barnacles adhesives
  porosity, chemical microstructure
  only small amounts availiable

Solid-Polymer Contacts, SPP 1369 Interfaces and Interphases
Ra 796/5 Free volume distribution at polymer-solid interfaces

Scematic of solid-polymer contact



Char. length scale
nm - µm

Increased contribution from interphase

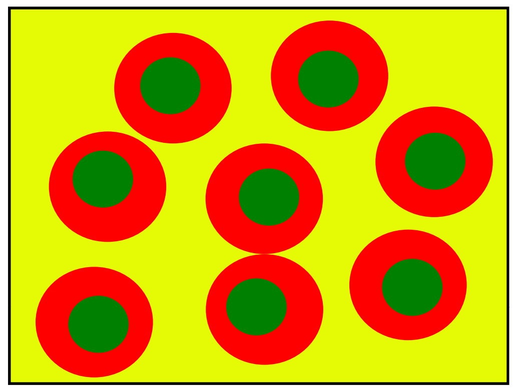
SPP outline:

A) controlled preparation

B) property profiling

C) modelling and simulation

nanocomposite



Our contribution:

Many properties are related to free volume

free volume can be determined by positron annihilation

depth profiling by moderated positron beam

Scientific motivation

- solid-polymer interfaces and interphases are becoming more important (nanocomposites)
- several properties related to free volume
- PALS beam technique valuable experimental tool for investigation of free volume at solid-polymer interfaces
- depth profiling of thin polymer films (comparison surface vs interface effects) and comparison with nanocomposites will give valuable information
- comparison with evaluation of modelling necessary and useful
- project will increase understanding of interphase region and influence on nanocomposites

Our present project

Substrates / polymers:

Cu or Al / epoxy

↔ strong interaction, large interaction zone

↔ influence of interface on curing (cooperation Possart, Schiffels)

Graphite or quartz / polybutatiene

↔ weak interaction, small interaction zone

↔ comparison free volume by PALS with simulations (Binder)

Methods:

- PALS beam: planar interfaces with varying thickness, depth profile
- PALS bulk samples, Kiel: nanocomposites with varying filling factor
- Evaluation of simulations with respect to free volume, comparison

PALS and PALS beam for thin film analysis neccessary