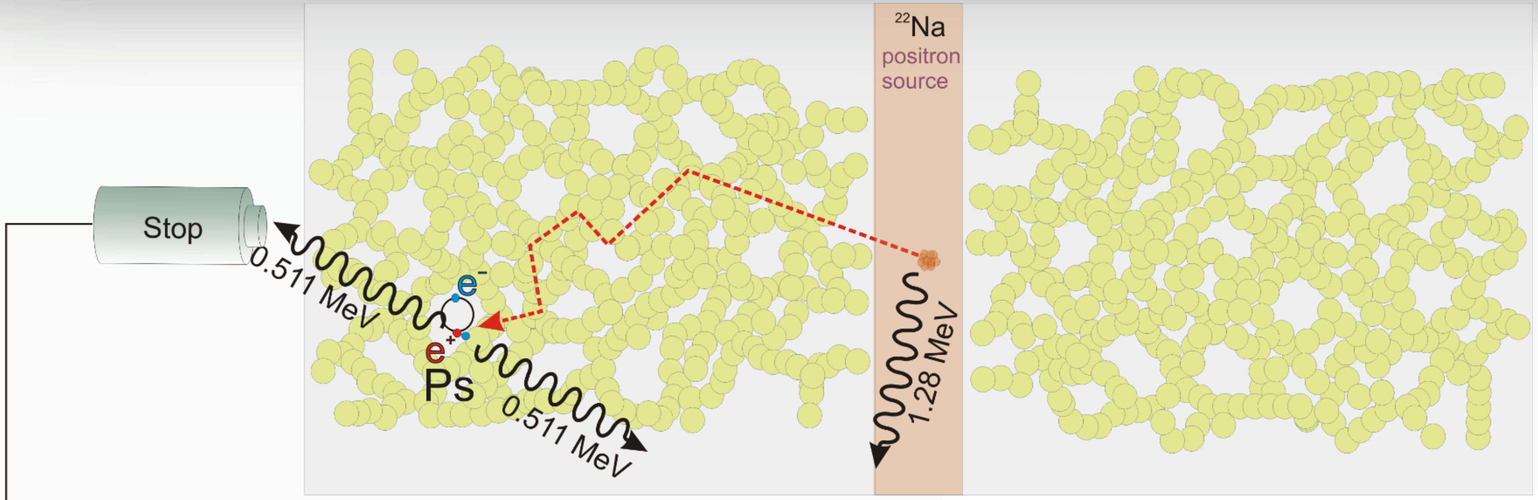
Application of Positron Annihilation Lifetime Spectroscopy in Polymer Composites

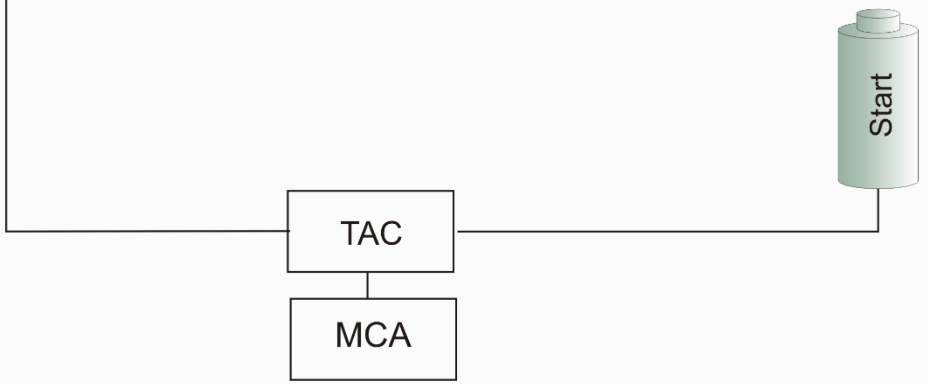
Ewa Dryzek
Institute of Nuclear Physics, Polish Academy of Sciences

Outline

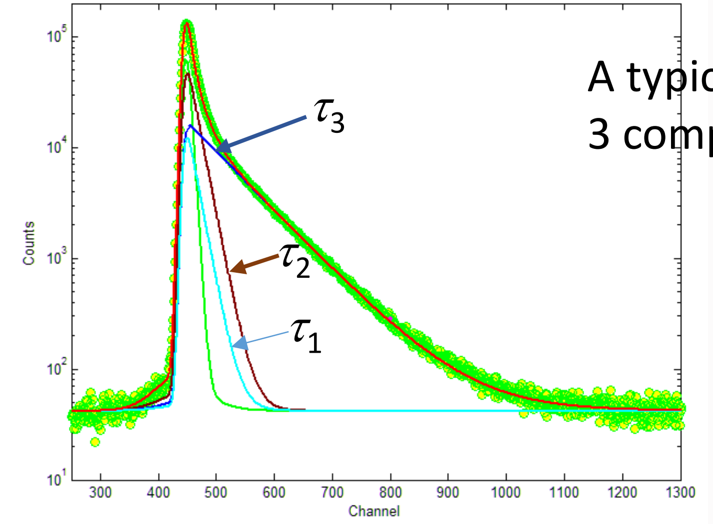
- Positron annihilation in polymers – the free volume
- Polymer blends – miscibility – the interaction parameter
- Composites – definition and classification
- PALS applications to polymer composite studies
  - Interface between the filler and the matrix polymer
  - Free volume changes due to deformation

Positron Lifetime Annihilation Spectroscopy (PALS)





The nanometer-sized free volume holes or cavities are the open spaces or voids that have emerged as a result of the molecular architecture and chain folding in polymers.



A typical lifetime spectrum for polymers with 3 components

τ_1 – p-Ps annihilation – close to 125 ps
τ_2 – free e$^+$ annihilation < 0.5 ns
τ_3 – o-Ps pick-off annihilation – a few ns

$$N(t) = F(t) \otimes \sum_{i=0}^{N} \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right)$$

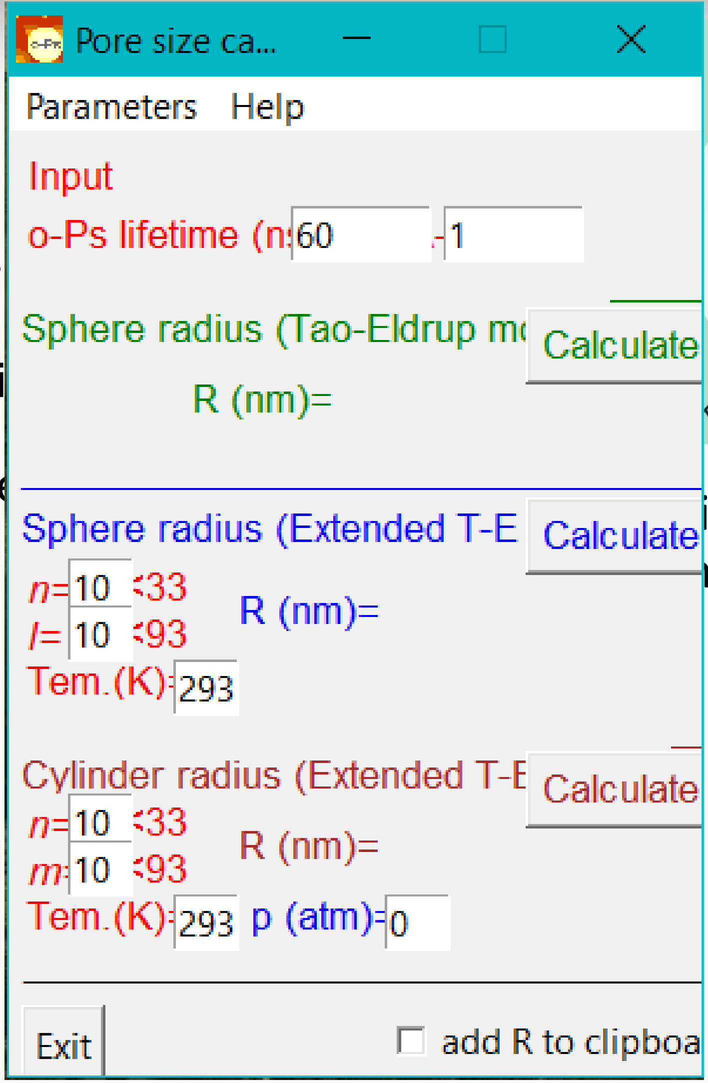
Connection between o-Ps pick off annihilation time and the free volume hole size

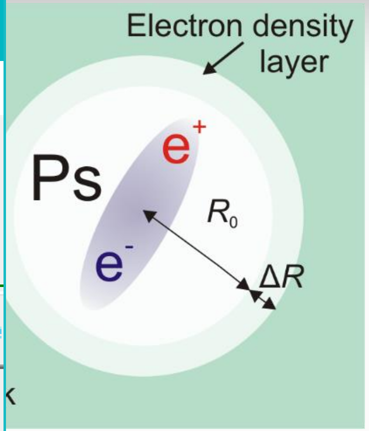
Tao-Eldrup model

$$\tau_{po} = \frac{1}{2}\left[1 - \frac{R_0}{R_0 + \Delta R} + \right.$$

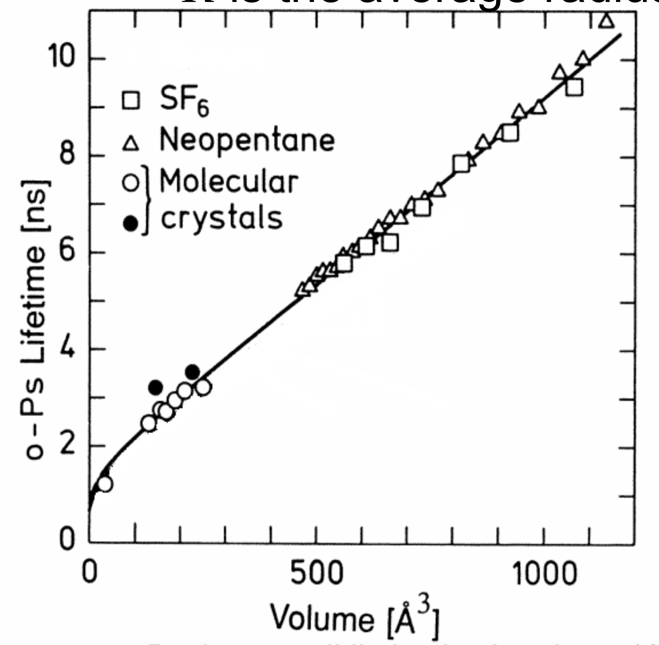
ΔR = 0.166 nm is an empiri

R is the average radius of the





ifetime is determined by the electron nd the physical size of the hole.



https://ifj.edu.pl/private/jdryzek/page_r27.html

E. Mogensen, *Positron annihilation in chemistry*, 1995.

Intensity I_3 of o-Ps

Intuitively, one expects that it reflects the probability of o-Ps formation, then it is a measure of the number density of holes.

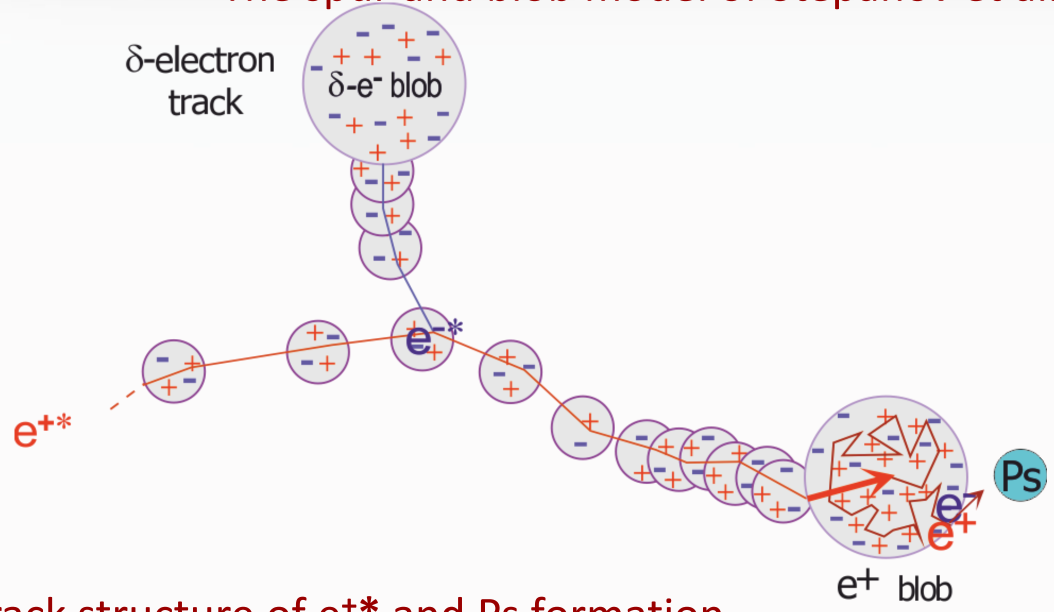
Fractional free volume (FFV):

is the average hole volume obtained from the Tao-Eldrup model.

C is a constant whose value is found to be 0.0018 $Å^{-3}$

The model of Ps formation

The spur and blob model of Stepanov et al.



Track structure of e⁺* and Ps formation

Processes influencing Ps formation and annihilation

- a rise (anti-inhibition) or a reduction (inhibition) of Ps formation probability (positronium creation $e^+ + e^- \rightarrow Ps$ competes with other processes involving free electrons $M^+ + e^- \rightarrow M$)
- chemical quenching and spin conversion
  $Ps + M \rightarrow e^+ + M^-$ o-$Ps + M\downarrow \rightarrow p$-$Ps + M\uparrow$

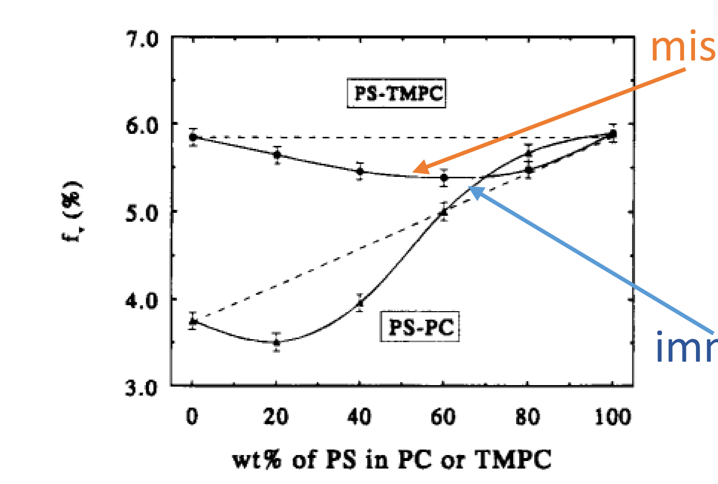
A decrease of I_3 due to inhibition of Ps formation caused by the accumulation of species in the ionization spur during irradiation by the positron source, which competes with Ps formation

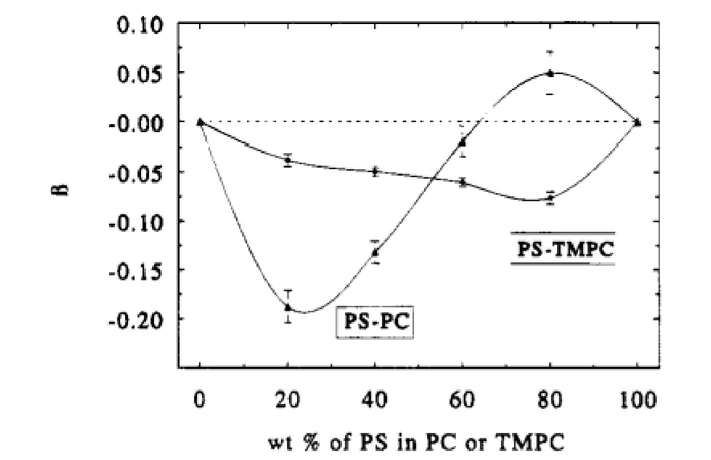
Assumptions regarding the applicability of the FFV:
If no significant change in the PALS spectrum is observed during the time of measurement, I_3 is proportional to the number density of free volume holes.
If $T>T_g$, the lifetime of reactive species becomes too short to influence o-Ps yield.
If $T<T_g$, rejuvenation of the sample is required.

Stepanov, S. V., and Byakov, V. M., *Physical and radiation chemistry of the positron and positronium, in Principles and Application of Positron and Positronium Chemistry*, Jean, Y. C., Mallon, P. E., and Schrader, D. M., Eds., World Scientific, Singapore, 2003, pp. 117–149.

A **polymer blend** - a combination of two or more structurally different polymers or copolymers.

The properties of the blend are not attributable to any of the components.





TMPC-tetramethyl bisphenol-A polycarbobnate

Deviation from the linear additivity of free volume.

f_v – FFV of the blend
f_{v1}, f_{v2} – free volume fraction of the constituents
Φ_1, Φ_2 – volume fractions of the constituents
β – interaction parameter

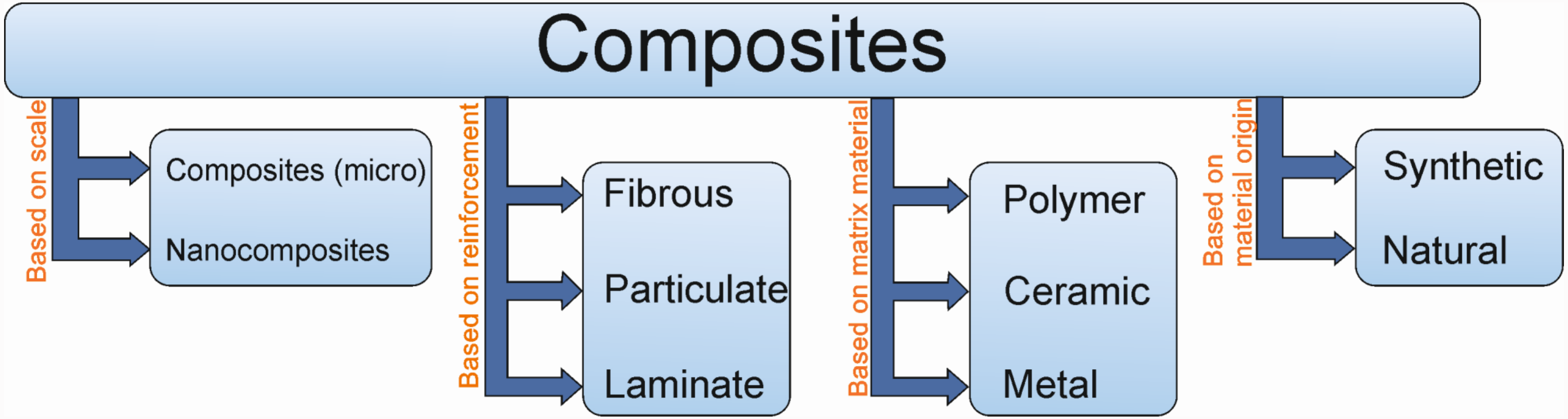
The observed negative deviation of FFV for the miscible blend was interpreted in terms of segmental conformation and packing between dissimilar polymers.

Negative β indicates blend miscibility.
For the PC/PS blend, it exhibited both negative and positive values. The blend could be considered as miscible up to 60% of PS, beyond which it would be immiscible.

Liu et.al. *Macromolecules* 28(1995)5774

Composites

Creating a dispersion of an inorganic or metallic solid in a particulate form within a polymer matrix can be an alternative to the blending of polymers and a way to obtain novel materials with tailored properties.



Biomedical applications

Biomaterials – the most common materials used to repair or replace damaged parts of the human body

Biomedical applications of composites:

- Dental treatments
- Bone tissue engineering
- Drug delivery
- Wound dressing

Fiber-reinforced polymer (FRP) composites are considered as substitutes for metallic/ceramic orthopedic implants for load-bearing applications.
The most commonly used polymers for the orthopedic implants poly(methyl methacrylate), polyetheretherketone, polysulfone, polypropylene, polyethylene, polybutylene terephthalate (PBT), and polyethersulfone (PES)

Nabipour Chakoli, A. *Poly(L-Lactide) Bionanocomposites*. IntechOpen. doi:10.5772/intechopen.85035

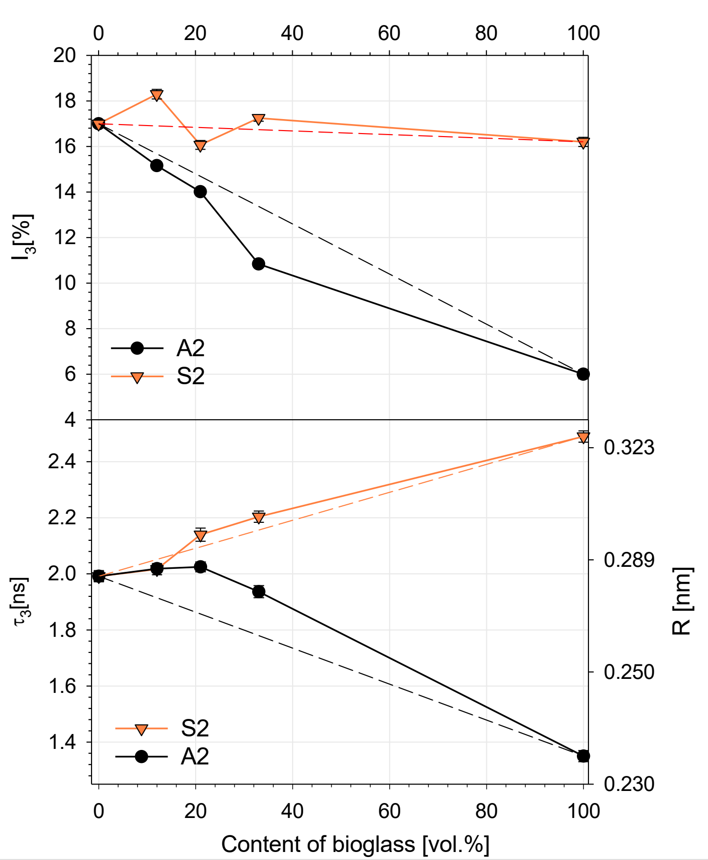
A wide range of synthetic polymers (biocompatibility and biodegradability):

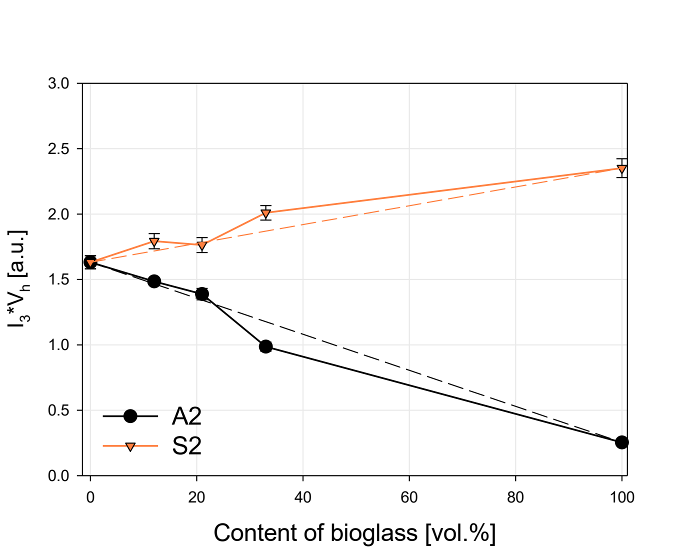
- poly(L-lactic acid) PLLA
- poly(L-lactide-co-glycolide)PLGA
- polycaprolactone (PCL)
- biodegradable polymer/ceramic composites with hydroxyapatite: PLLA/HAP and PCL/HAP

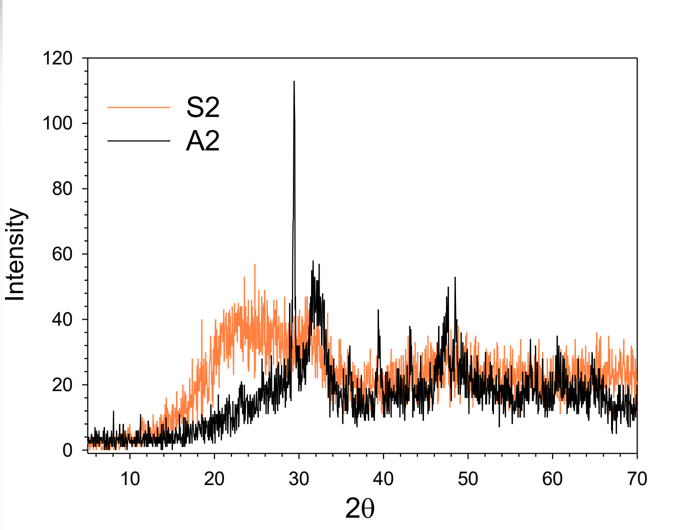
Used, e.g., in orthognathic surgery.

Composites PGLA/bioactive glass

poly(glycolide-co-L-lactide) PGLA
Bioactive glass:
S2 (SiO_2 - 80 mol %, CaO -16 mol %, P_2O_5 - 4 mol %)
A2 (SiO_2 - 40 mol %, CaO - 54 mol %, P_2O_5 - 6 mol %)







XRD patterns

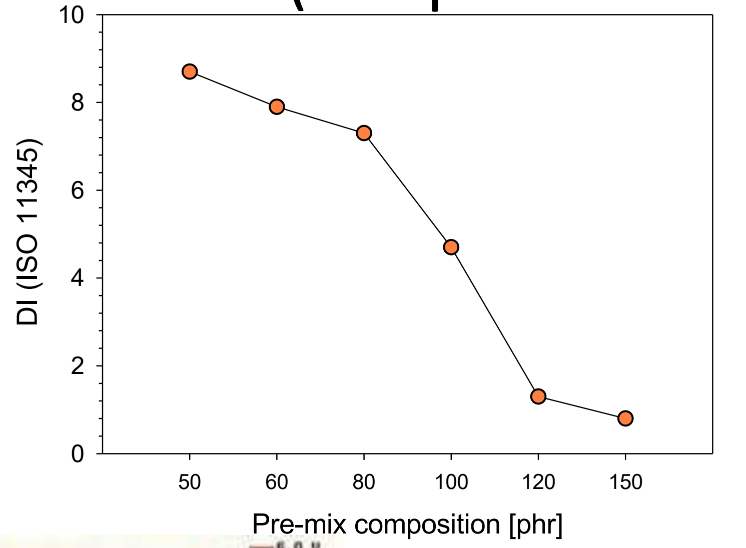
A small deviation of FFV from linear additivity indicates a weak interaction between bioglass particles and PGLA in the microcomposites.

E. Dryzek, E. Pamuła, *Nukleonika* 55(2010)79–83

EPDM/silica mixes

EPDM (ethylene propylene diene monomer) + surface-modified precipitated silica (Coupsil VP 6411)

DI – dispersion index

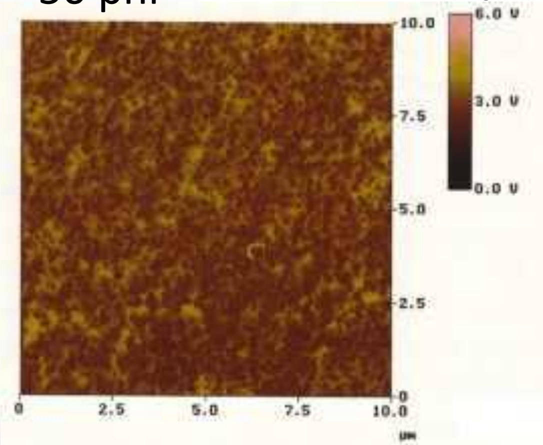


Mixing was carried out under deteriorated conditions. Dilution of previously prepared pre-mixes containing from 60 to 150 phr of silica in the respective amounts of elastomer to obtain the **final filler concentration of 50 phr**.

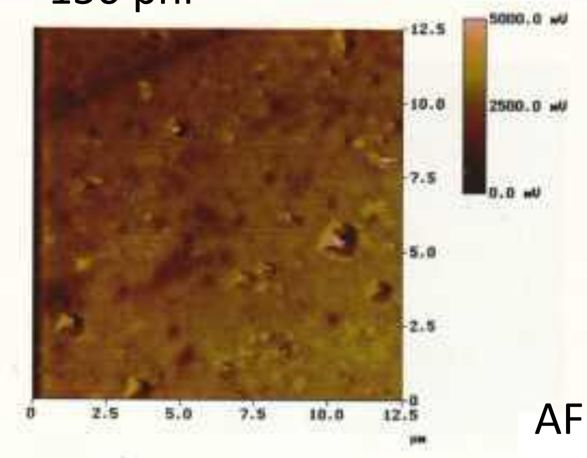
The final composition of the mixes was the same.

A 50 phr sample was prepared in one step.

50 phr



150 phr



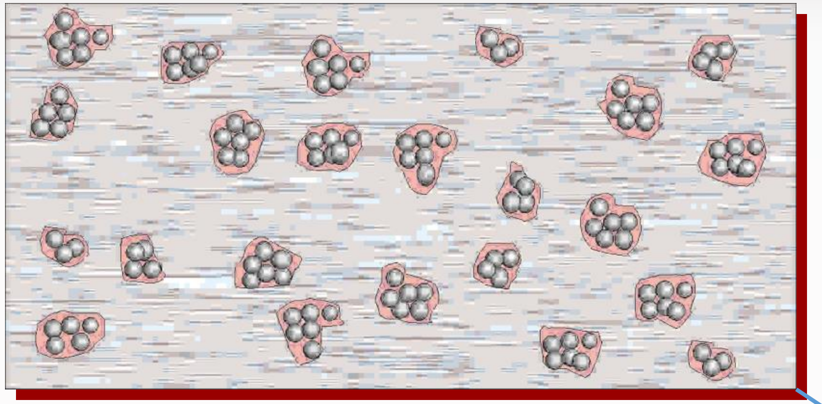
phr –parts per hundred parts of rubber

AFM images

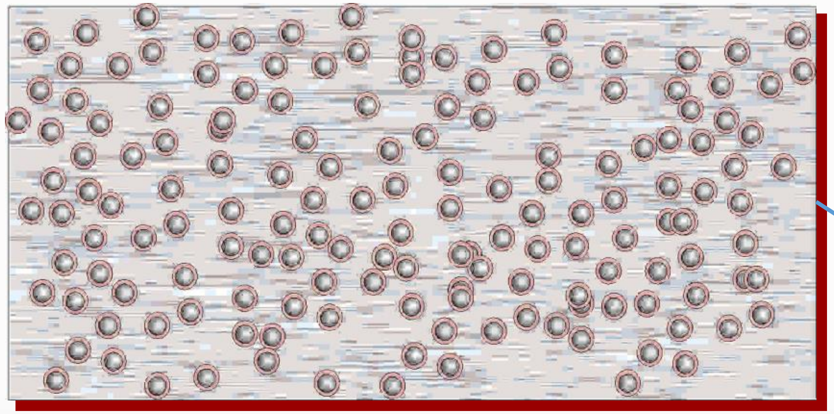
D. Bieliński,(E. Dryzek) et al., *KGK* 57(2004)579

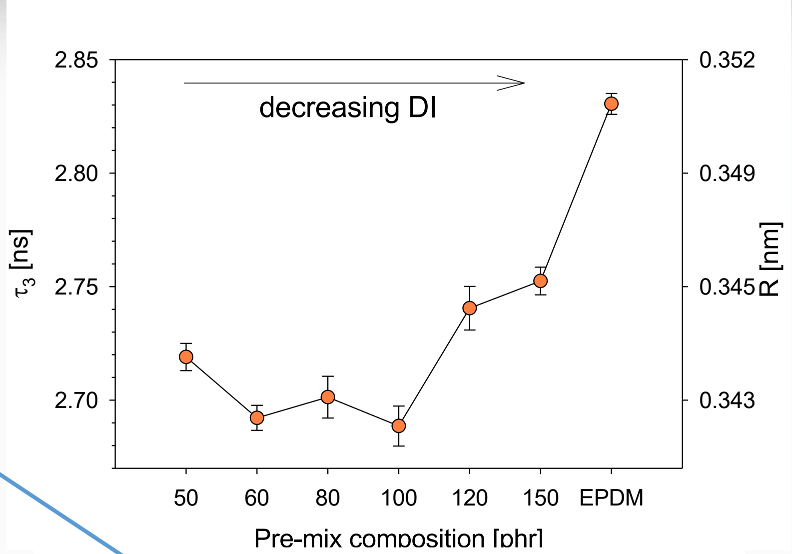
PALS results

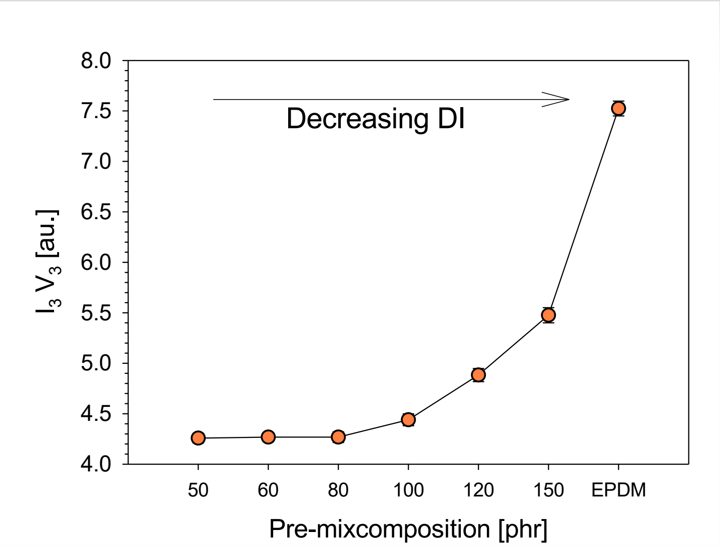
low Dispersion Index (DI)

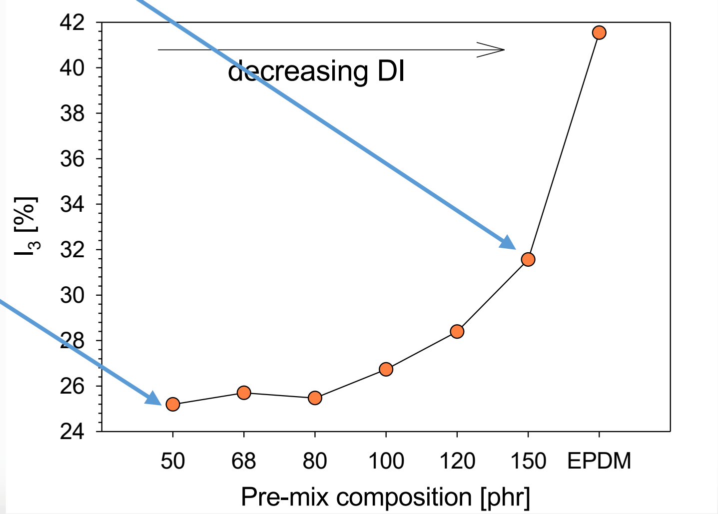


high Dispersion Index (DI)



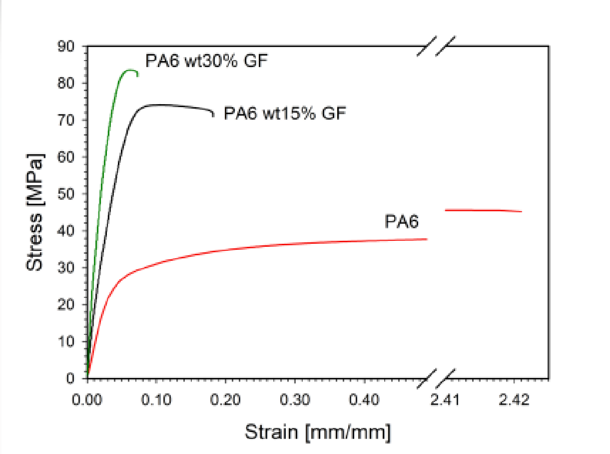




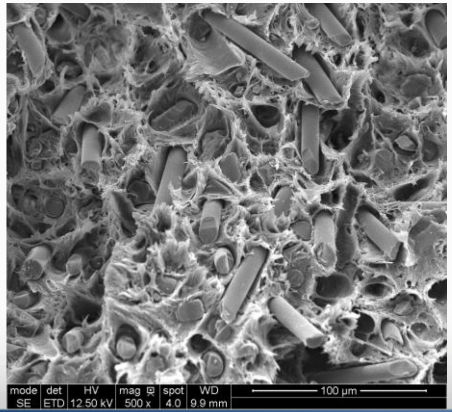


The probability of o-Ps formation in a dense interfacial layer between silica filler particles and the matrix is reduced. This is due to chemical binding between the silica surface and the polymer.

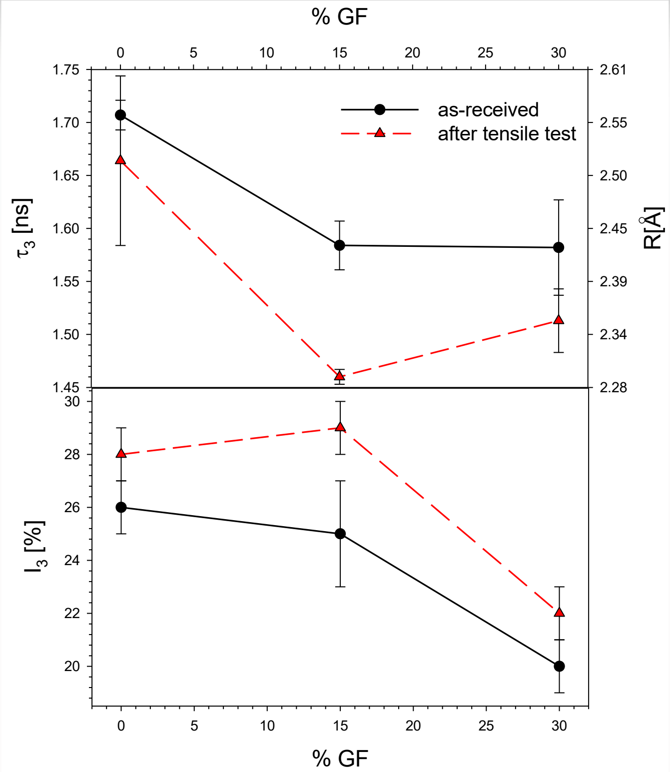
Free-Volume and Tensile Properties of Glass Fibre Reinforced Polyamide 6 Composites

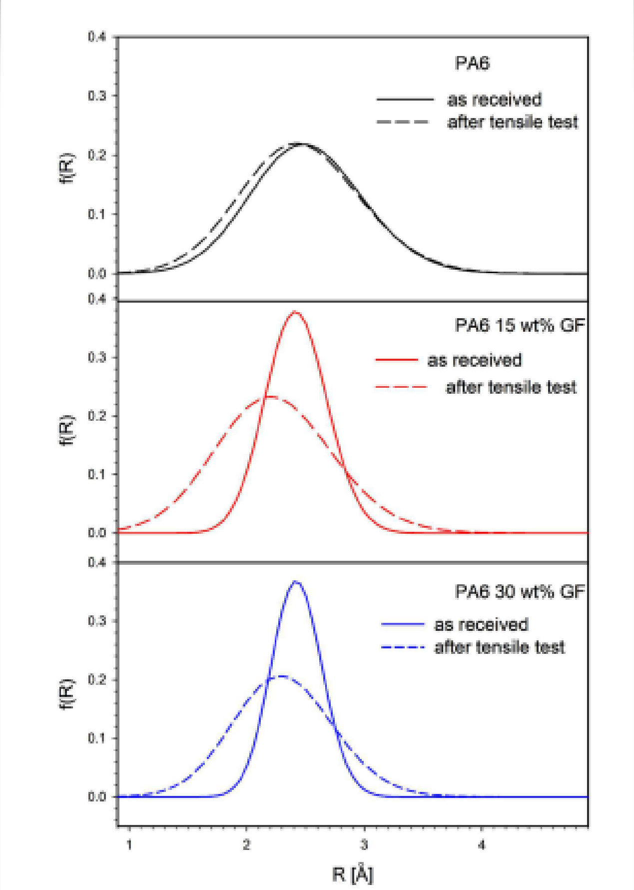


n	Modulus	Yield stress	Tensile strength	Strain at break
[%]	[MPa]			[mm/mm]
PA	760	43	48	2.42
15	1910	74	74	0.15
30	3320	84	83	0.06



The fracture surface of the PAG30 wt% GF SEM image





The initially narrower distributions of the free volume hole radii for the composites became broader as a result of the deformation. Free volume hole sizes became more heterogeneous.

E. Dryzek, et al. *Acta Phys. Polon A* 132 (2017)1501

Conclusions

- PALS is a valuable tool for studies of the interface between the filler (reinforcement) and the polymer composite matrix.
- It can provide information on how deformation affects the free volume in polymer composites.
- The analysis of FFV and the interaction parameter should be treated with caution.

Polymer blends

Most evidence suggests:

miscibility in polymer blends

a strong correlation

negative deviation from linear additivity of the composition dependence of **the o-Ps annihilation lifetime, τ_3.**

less convincing evidence exists

I_3 and **FFV evaluated via $f_v = C\, v_h I_3$**
(sensitivity of I_3 to e^+ source irradiation)

Jamieson, A.M., Olson, B.G., and Nazarenko, S. (2010) *Polymer Physics: From Suspensions to Nanocomposites and Beyond* (eds L.A. Utracki and A.M. Jamieson), John Wiley, Hoboken.