Prediction of the life duration of filled elastomers submitted to radiation: how to reach this goal

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安全を科学する

Background

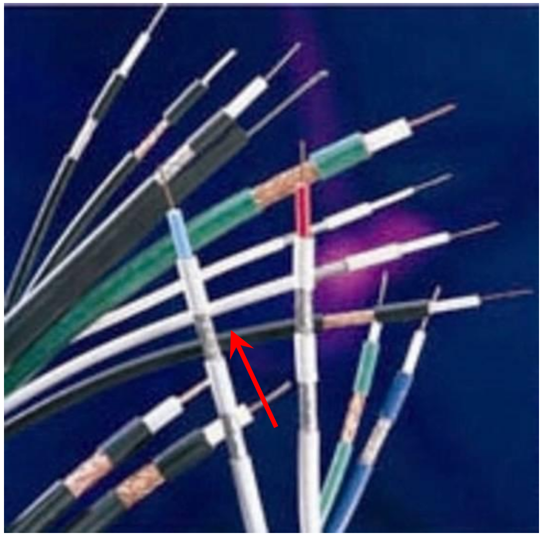
Nuclear plant:

low dose irradiation for long time

=> Sustainability?

serious nuclear accident

=> activation of security systems



Different polymers used in NPP

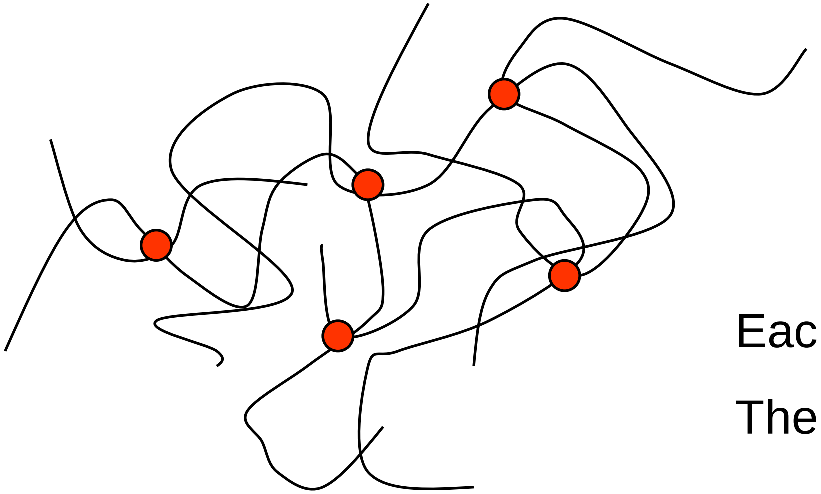
Elastomer: electrical insulation and flexibility

Cables: 50km in reactor building!

2 years to replace them !!

Mandatory to estimate the irradiation resistance of elastomers used in Nuclear Plants

What is an elastomer ?



Each chain is an « entropic spring »

The network is an assembly of spring

Key parameters:

Crosslink density (Mc) → Good description of the modulus

Heterogeneities

Entanglements? Dangling chains?

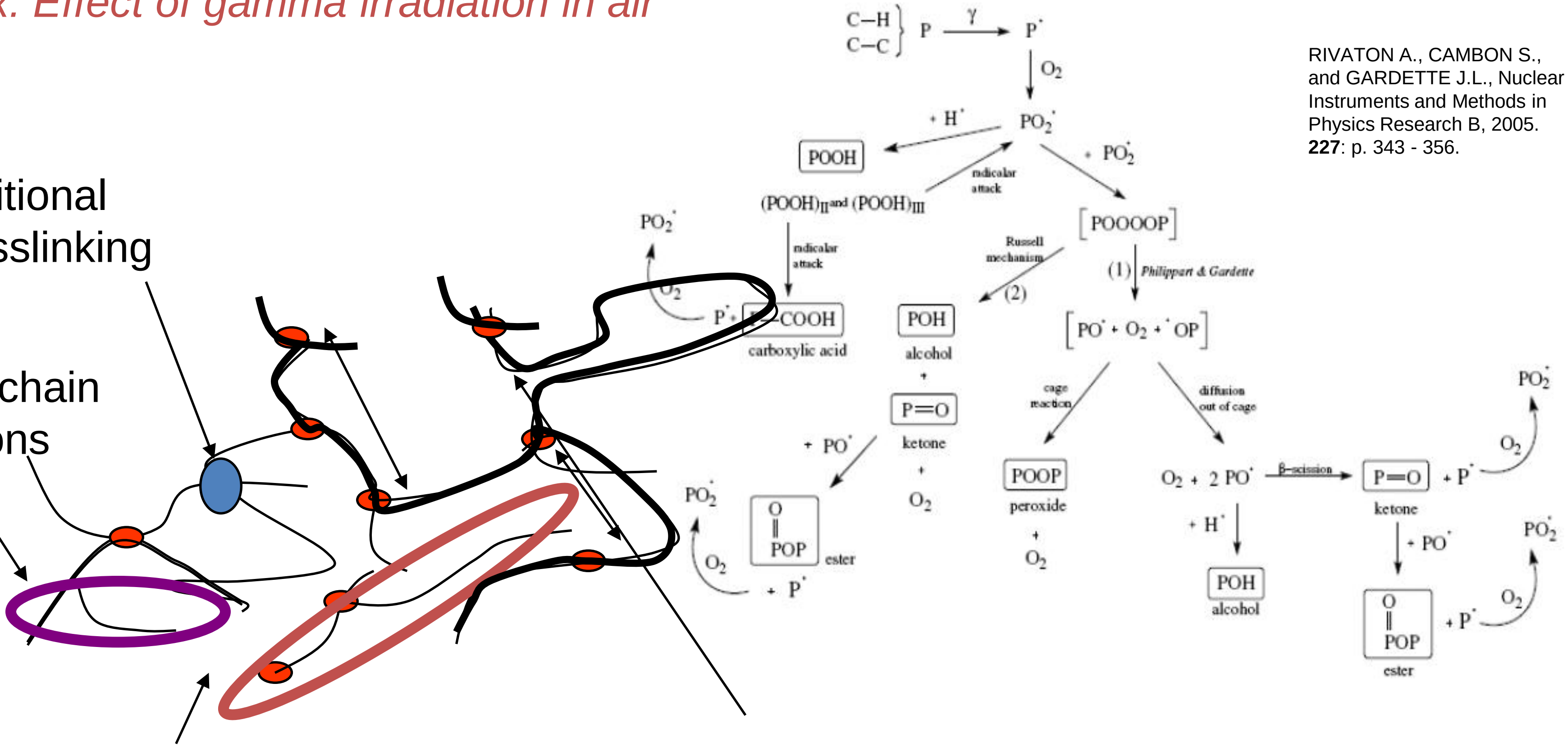
} → Large strain behaviour more difficult to describe

Remark: elastomer formulations are often complex (crosslinking system)

Irradiation of elastomers

Ex: Effect of gamma irradiation in air

RIVATON A., CAMBON S., and GARDETTE J.L., Nuclear Instruments and Methods in Physics Research B, 2005. **227**: p. 343 - 356.



Additional Crosslinking

Free chain portions

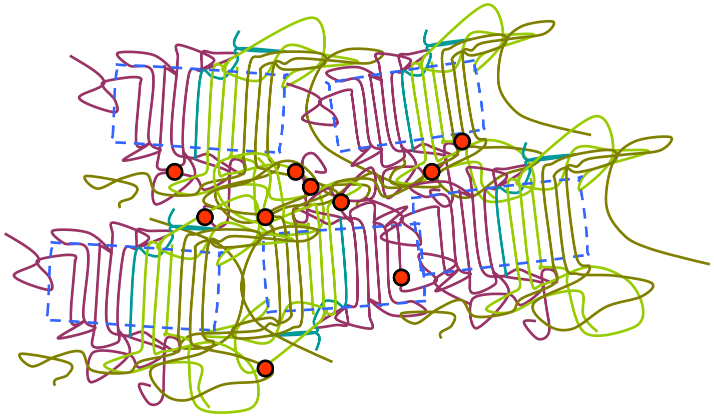
Free chain agglomerates

Increase of the average length of the elastically active chain

Strong dependence on the irradiation condition (temperature, environnement, radiation)

Elastomer can be semi-crystalline

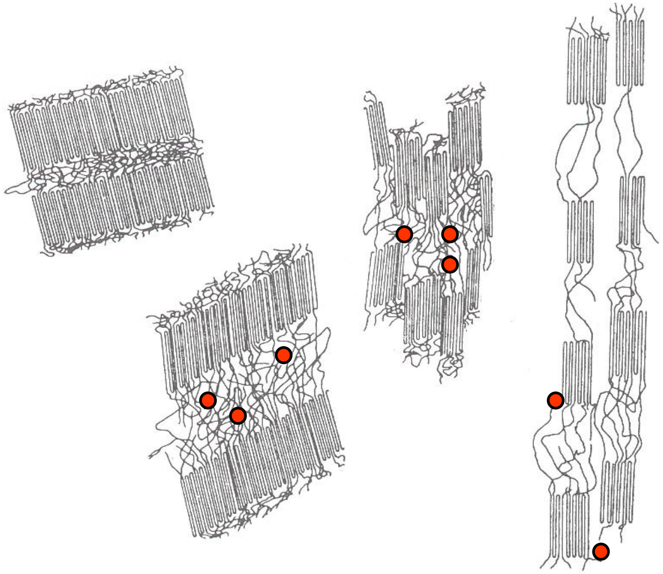
semi-cristalline elastomers:



The cristallites act as:

Fillers

Crosslinks



Key parameters:

Cristallinity ratio (Xc)

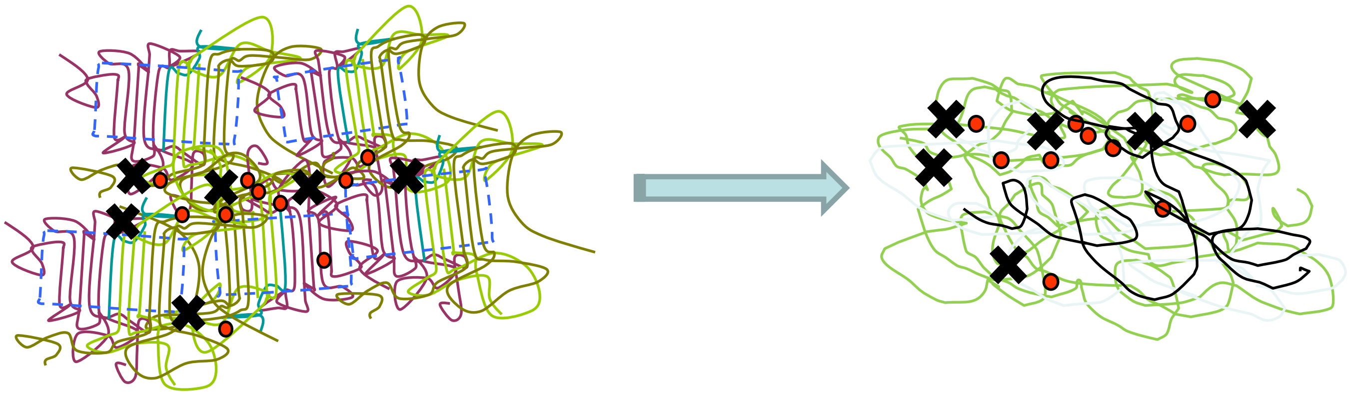
Cristallite organisations

Tie molecules

Above T_m, behavior controlled by crosslinks, below T_m mainly by cristallites (depends on Xc)

Semicrystalline polymers under irradiation

$T_g<T<T_m$ $T>T_m$



Crystals:
→ Low oxygen permeability
→ Higher resistance to irradiation
→ Degradation mechanisms more heterogeneous

Temperature effect:
$T_g<T<T_m$: amorphous phase degraded first
→ chemical effects (oxidation products, etc.)? Effect on crystallization?
$T > T_m$: no more crystal, degradation much faster
At T↘, new semicrystalline microstructure

☞Studies are required below and above Tm
☞Degradation will be different below and above Tm

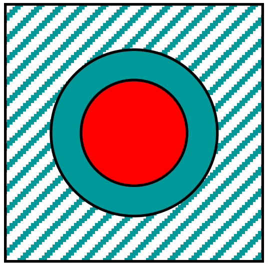
Elastomers are reinforced with fillers

Key parameters of the reinforcement:

-the size

for micron size fillers, modulus well described by models (true whatever the material state)

$$E \sim E_m . F(\phi)$$

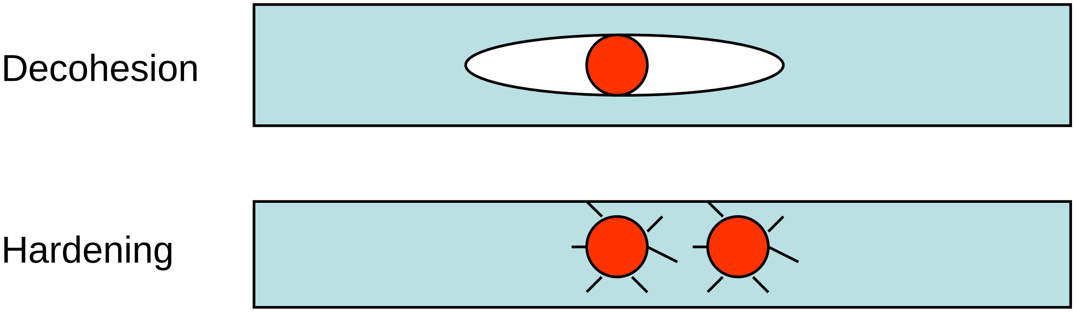


See for instance Christensen and Lo model, Hervé and Zaoui model…

…not for nanoscopic fillers (large interface)

-the surface (i.e. the interface)

important at large strain, where it can control the rupture behaviour (but in general lower strain at break)

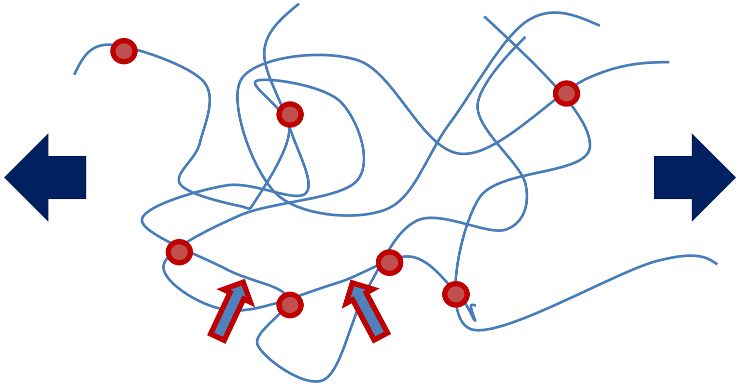


Fillers influence the degradation

1- Fillers *inert* under irradiation

Fillers can:

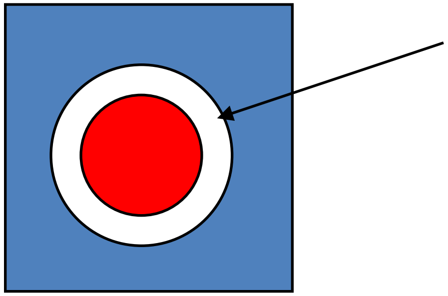
- lower diffusion of molecules involved in the degradation mechanism (longer path)
- adsorb water, oxygen, formulation products...



Spatial heterogeneities expected
Stress concentration

Matrix degradation may induce:

- Reinforcement decrease
- Modifications of filler-matrix interactions
  (*KIM C. et al. 2006, etc.)*
- Heterogeneous degradation can change the reinforcement mechanism (fillers “shielded”)



Softer matrix → Lower reinforcement

Fillers influence the degradation

2- Fillers *active* under irradiation

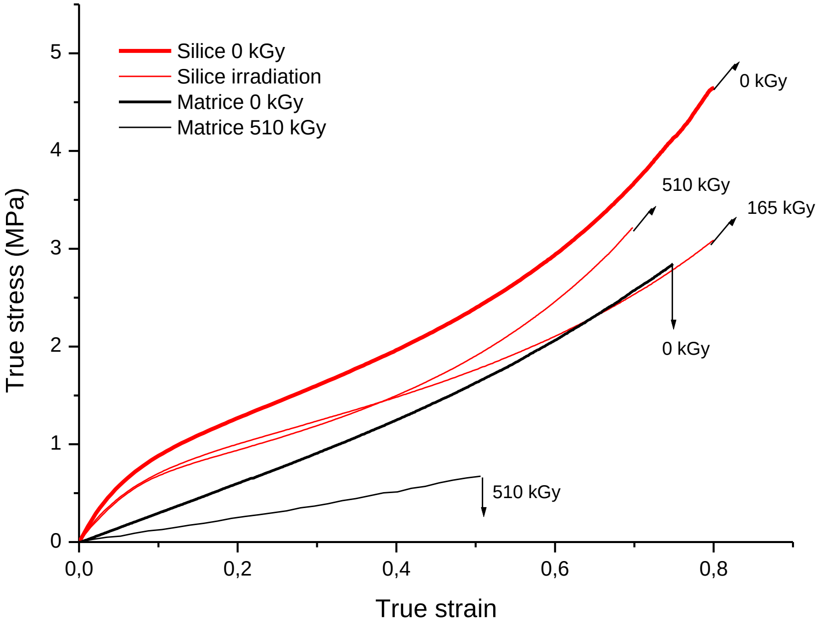
Radicals formation

Formation of *supplementary* by-products (chemical reactions)

Modification of the interface

⇨

Modification of the degradation kinetics
Modification of the filler-matrix interaction



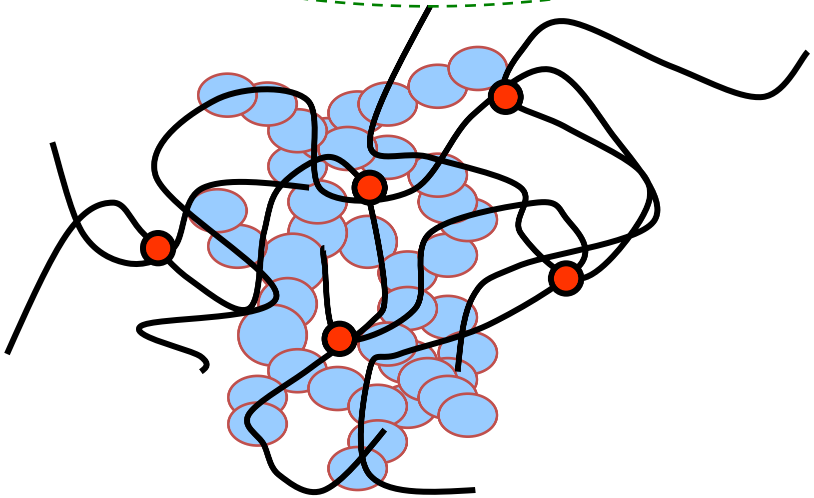
Tensile test, T=80° C (rubbery state), strain rate $0.01s^{-1}$

Stronger hardening at high irradiation dose of silica filled EPDM

Irradiation of elastomers

Elastomer described by:

- crosslinks (elastomer network architecture)
- filler–filler interactions and filler – matrix interactions (when elastomers are filled)
- crystallites presence (when elastomers are semi-crystalline)



Irradiation

How to predict the aging of elastomer materials?

What has been done

A lot of empirical work, first developed :
- Lots of works on ***formulated*** materials: polymer, anti-oxidant, help processing products…and **fillers**.
- Chemical approach of the degradation: quantification of the degradation products to deduce the chemical reactions involved.
- Temperature activation of the degradation reactions: massive use of time temperature equivalence

Problem:
-Tenuous link with properties: prediction by analogy (questionable validity of the analogy and of the time-temperature equivalence)
-Limit of the approach: no real comprehension of the evolution of the mechanical properties

What must be done

3 steps to consider:

Radiochemistry, kinetics

Microstructure changes induced by irradiation

Effects on mechanical behavior

First aspect: radio-chemistry, kinetics

Identification of the different chemical reactions, different kinetics, with different activation energy:

- influence of the chemical nature of the polymer?

Example: EPDM copolymer: different reactions for the three different copolymer units (ethylene, propylene, norbornene) *cf. Colin et al., Polym. Degrad. Stab.*

- new reactions, supplementary radicals promoted by the other ingredients ?:

Example: reactions promoted by the antioxydant *cf. Michaud et al. Polym.Degrad. And Stab.*

Example: silica filled EPDM (formation of crosslinks at the interface) *cf. Planes et al., Comp. Sci. Technol.*

- influence of the local mobility in the diffusion process of the different chemical species and radicals ?

Example: oxygen diffusion and degradation heterogeneties

Example: influence of the cristallinity content on the degradation *cf. Khelidj et al Polym Degrad. Stab., Planes et al. J Polym. Sci.*

Example: influence of the stress

Example : ATH filled EPDM (acceleration of the polymer degradation) *cf. Planes et al. Polym. Degrad. Stab.*

Experimental approach: systematic characterization of the degradation products (FTIR, sol fraction, NMR…) and study of parameters such as cristallinity, temperature, radiation dose, environmental conditions on the kinetics

Theoretical approach: quantum chemistry combined with molecular dynamics

Second aspect: microstructure

What is the resulting microstructure?

- heterogeneities created by the degradation ?:
  - At the scale of the elastomer network?:
    - Example: network heterogeneities
  - At larger scale:
    - Example: sol fraction in degraded EPDM, *cf. Planes et al. Polymer*
    - Example: degradation heterogeneities around the particle, *cf. planes et al. , Polym. Degrad. Stab.*
    - Example: phase separation in plasticised PVC
- modification of the crystalline microstructure: chemi-cristallisation?

Experimental approach: swelling, thermoporosimetry, Xrays (DSC, cristallinity), NMR, microscopy

Modeling approach: quantum chemistry MD

----------------→ Consequences in term of mechanical properties ?

Third aspect: mechanical properties

Consequences on the mechanical properties?

-Modification of the stress strain curve?:

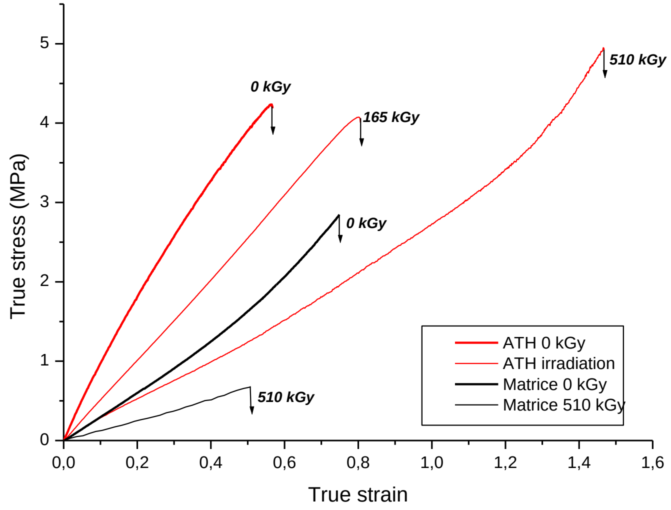
Example: decrease of the stiffness of irradiated EPDM

Example: increase of stress hardening of irradiated silica filled EPDM

-Modification of the rupture properties?

Example: decrease of the rupture properties in EPDM

Example: increase of the strain at break in ATH filled EPDM



Experimental approach: mechanical tests, Dynamic mechanical analysis, fracture properties…

Theroetical approach: Molecular dynamics, discrete modeling, FEM

CONCLUSION

- An approach forgetting the elastomer formulation and how the ingredients are involved in both the reactions and the mechanical properties cannot be satisfactory

- Three aspects to consider in the degradation by irradiation of elastomers: radiochemistry, microstructure, mechanic
- Prediction of life duration of elastomers submitted to radiation: many questions specific to each of these aspects.
- Some are very material dependant (chemistry) others are more general (mechanics)

- Multidisciplinary work : material science and radio-chemistry
- Two approaches to combine:
  - Experimental work : collaboration with Prof. T. Shojji
  - Modelling: collaboration with Prof. M. Kubo