Recent advances in EB/X ray -cured composite materials

Arnaud Martin,[1,2] Dorota Pietras-Ozga,[3] Marius Barczak,[3] Michael Krzeminski,[1,2]
Michael Molinari,[4] Brigitte Defoort[2] and Xavier Coqueret[1]

1) Institut de Chimie Moléculaire de Reims - UMR CNRS 7312, Reims, France
2) AIRBUS Defence and Space – Saint Médard en Jalles, France
3) Uniwersytet Marii Curie Skłodowskiej, Lublin, Poland
4) Laboratoire de Recherche en Nanosciences
Université de Reims Champagne Ardenne, Reims, France

Outline

1. Technological background and industrial applications

2. Some basics on mechanisms and kinetics

3. Microheterogenity in networks produced by radiation-initiated chain polymerization

4. Upgrading matrix properties by nano-scale toughening

5. Conclusions and current developments

1. Technological background and industrial applications

Out-of-autoclave curing of high performance composites

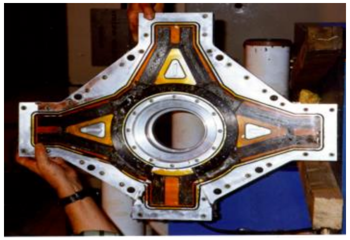
Electron-beam curing pioneered in the late 1980's at Aerospatiale (F) and Acsion (Can)

1st generation

1995-2005

efforts on process control

rocket motor case

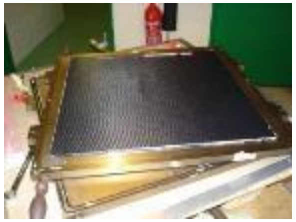


helicopter swash plate

sailboat hull

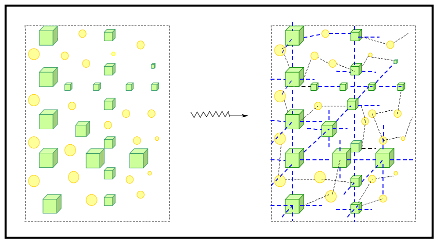
2nd generation since 2006

efforts on material performance

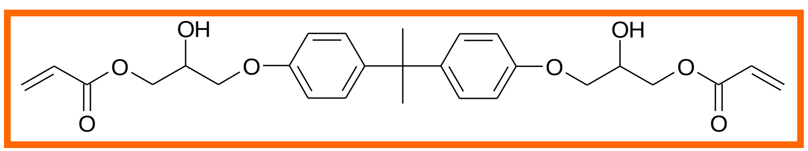


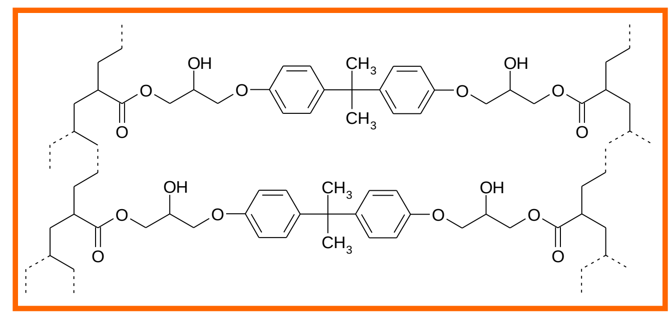
RTM compatible resins : electron beam-cured, vacuum bagged carbon or glass fiber-reinforced composites

Crosslinking polymerization initiated by high energy radiation



- No external heating (RT curing)
- Instant triggering
- Solvent-free mixtures
- Generally fast reactions: instant solidification (compared to thermal polymerization)
- Use of specific chemicals, *e.g. diacrylates*





Control of materials properties achieved by:

1 - Formulation

- Prepolymer, reactive diluents
- initiator if necessary (not for free rad.)
- Additives (surfactants, …)
- Fillers, fibers, pigments

2 - Processing parameters

- Radiation type
- Dose (total, fractioning)
- Dose rate
- Temperature

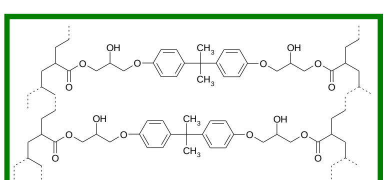
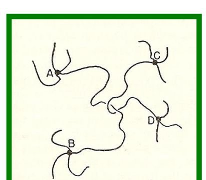
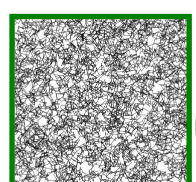
Key points to be mastered

Process parameters
① Dose
Dose rate
Temperature
Electron / mater interaction

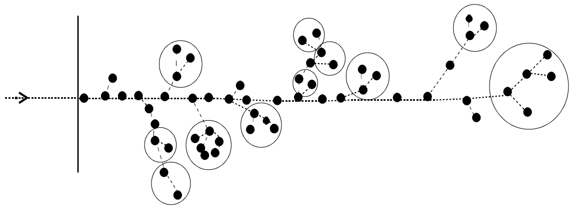
Fiber
Surface
⑥ Roughness
⑦ Chemistry

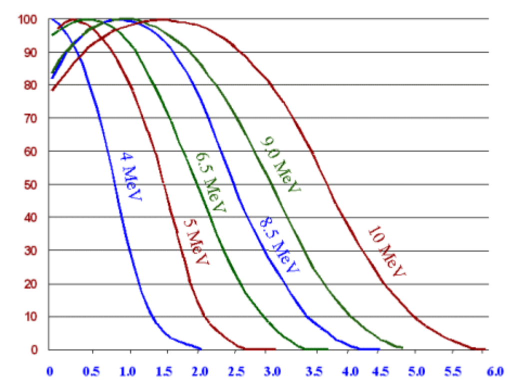
Matrix
③ Thermo-mechanical properties
② Curing kinetics
④ Network formation
⑤ Toughness
⑥ Aging

Fiber / matrix interface
Wetting
⑧ Coupling
⑨ Sizing
Aging

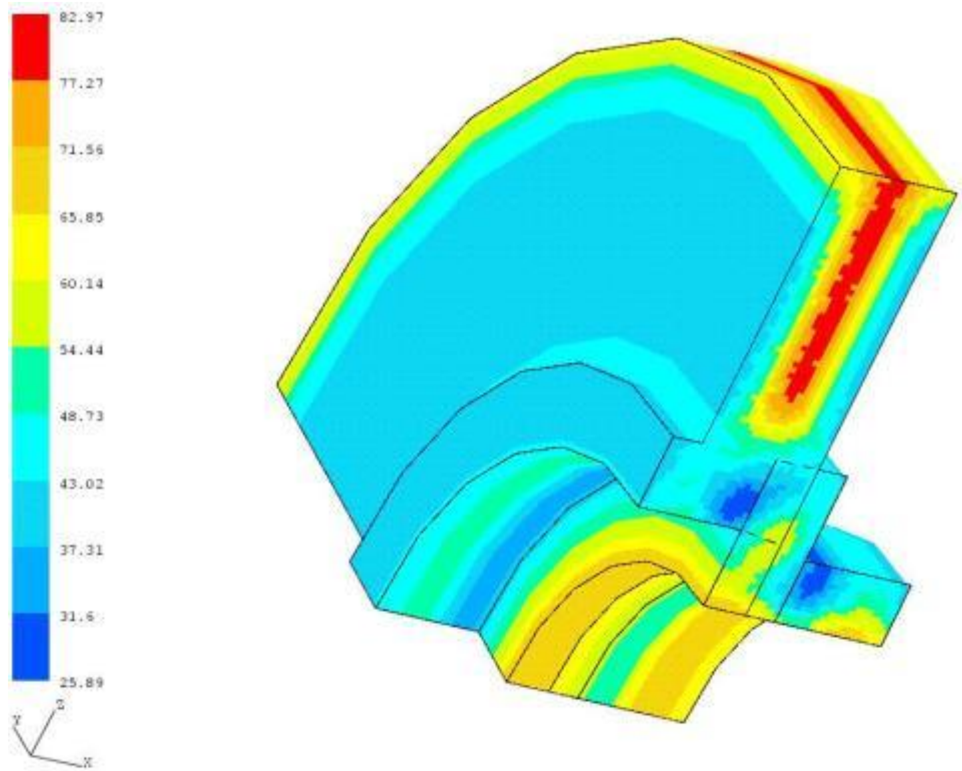
1 - Modeling of dose deposition





Process mastering: Modeling of dose deposition

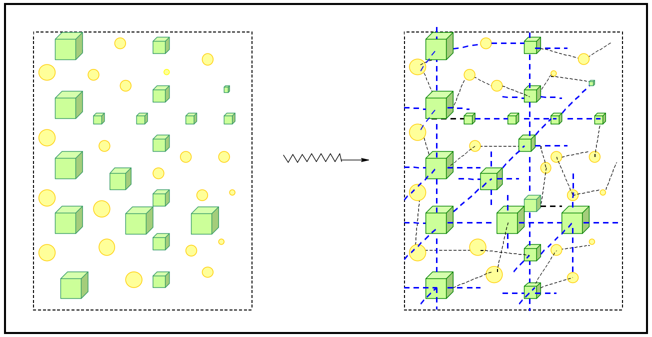
- 3-D EB treatment of complex composite parts

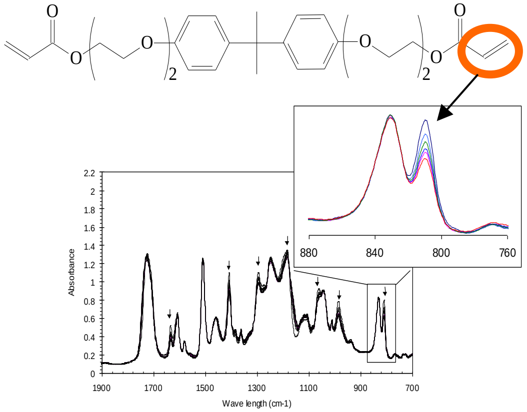


Example: dose distribution in a complex composite part.
Modeling allows for definition / optimisation of the curing cycle.

J. M. Dupillier, Astrium ST

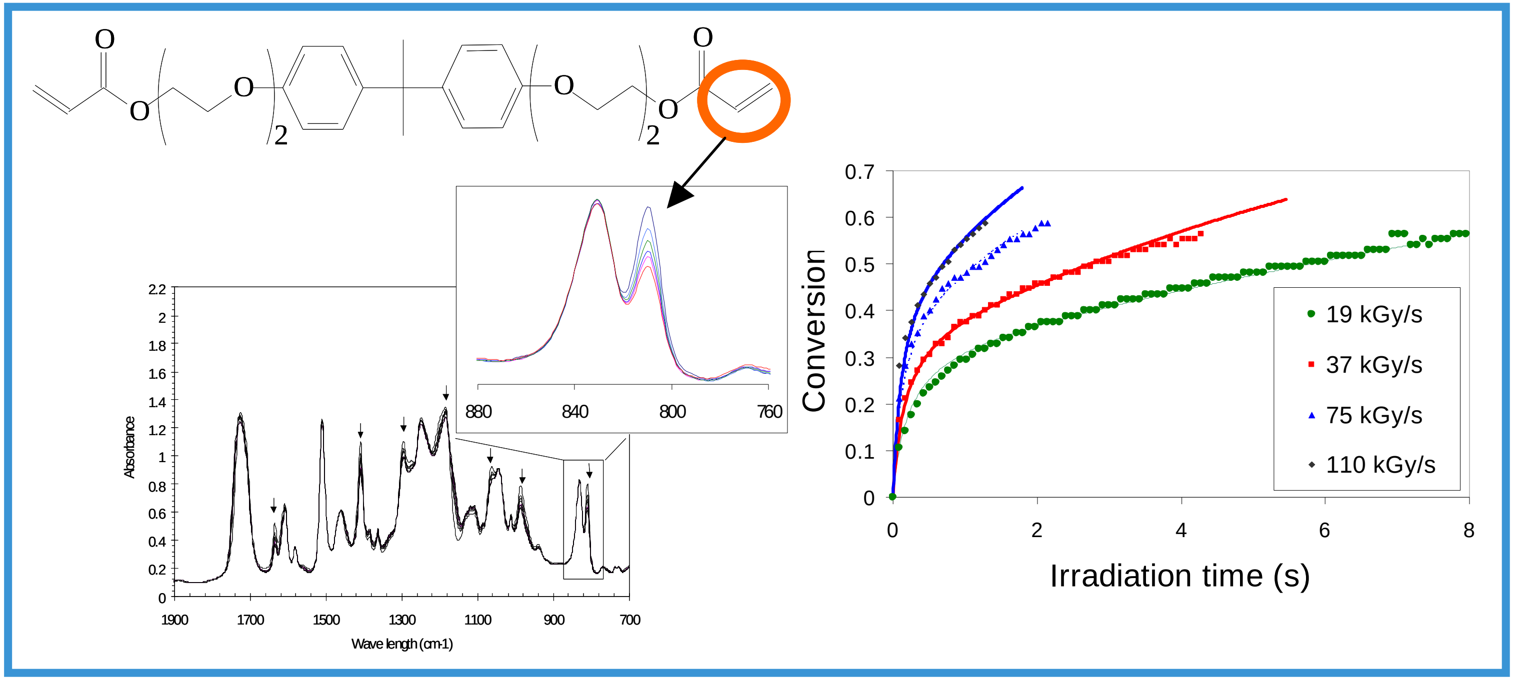
2 – Polymerization process





Process mastering:
Modeling of polymerization kinetics

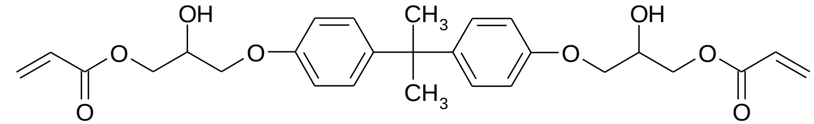
- Monitoring of radiation-induced polymerization



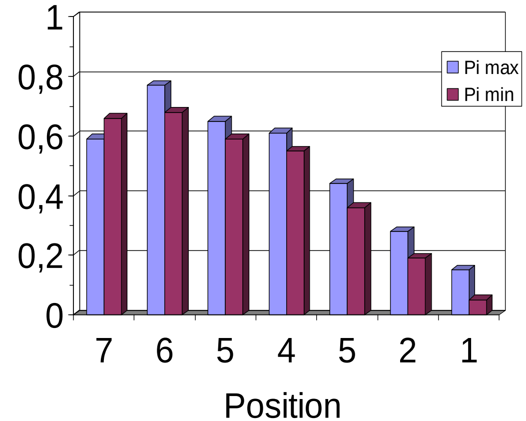
Irradiation of thick samples

10 MeV e^-

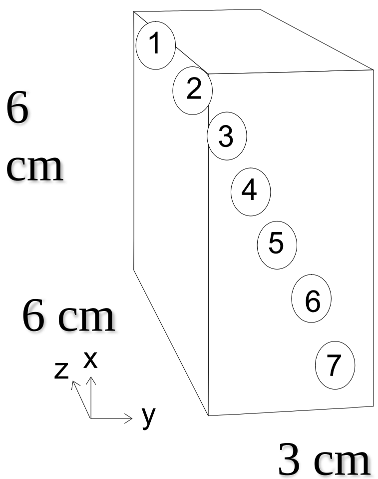
D = 50 kGy



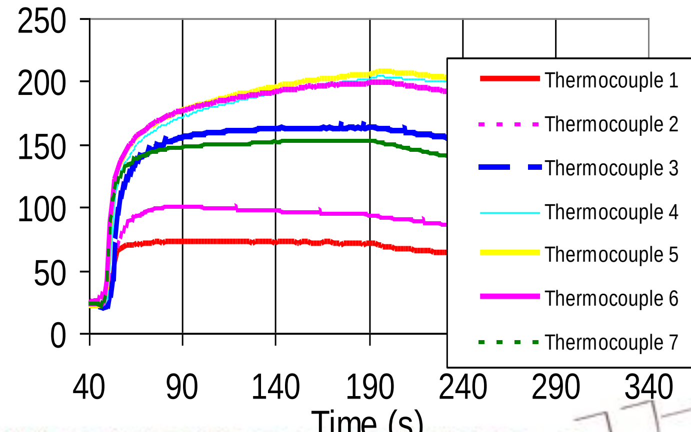
Conversion π



Spatial dependence of conversion and temperature



T(° C)



Bases of the kinetic model (isothermal)

- Mobility restrictions as a consequence of vitrification
  - Determining effect on termination mode (second to first order termination)
  - Gradual decrease of rate constants k_p , k_t
- WLF Relation (Williams Landel Ferry)

$$\frac{\eta_T}{\eta_{T_{Ref}}} = \exp\left[\frac{C_1\left(T - T_{Ref}\right)}{C_2 + \left(T - T_{Ref}\right)}\right]$$

- Linear combination with a weighing function $P(\pi)$ for each regime

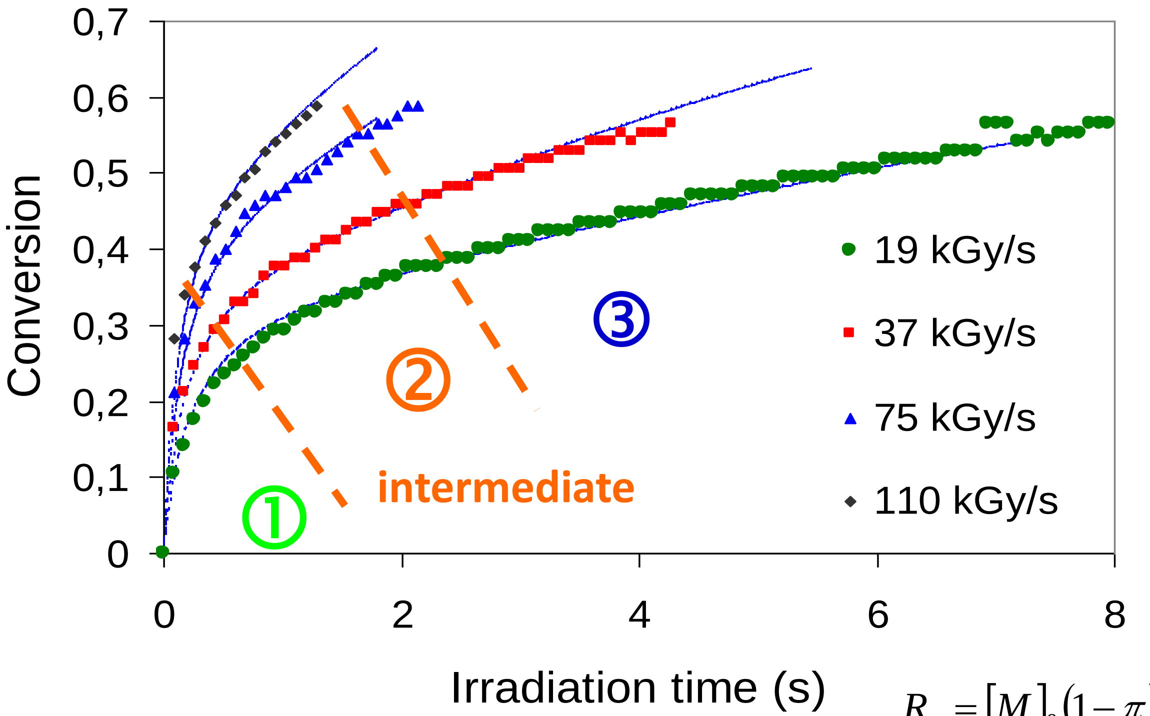
$$P(\pi) = f_N \exp\left[\frac{C_1\left(T - T_g(\pi)\right)}{C_2 + \left(T - T_g(\pi)\right)}\right]$$

$$R_p = [M]_0(1-\pi)\left\{\mathrm{P}(\pi)\left[A\dot{D}^{0.5}\exp\left(-\frac{E_a^1}{RT}\right)\right] + (1-\mathrm{P}(\pi))\left[B\dot{D}\right]\right\}$$

Modeling of polymerization (EB, lab unit)

BPA-epoxydiacrylate under N_2 - T=20° C - variable dose rate

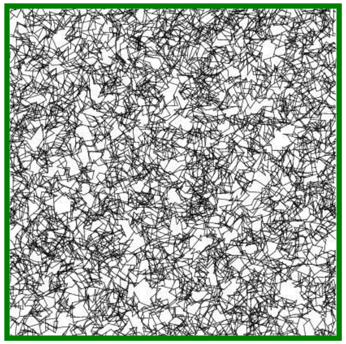
3 kinetic regimes

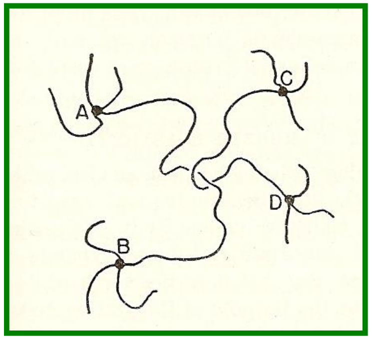


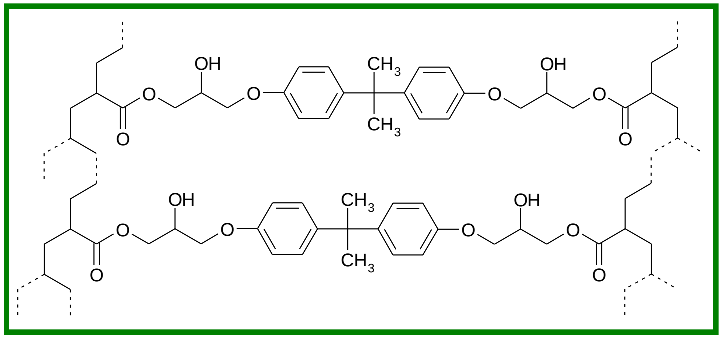
A = 3
B = 0.0032
C_1 = 6.0
C_2 = (0.88 D°) + 96
E_1 = 4.3 kJ.mol^{-1}
E_2= 0 kJ.mol^{-1}

$$R_p = [M]_0(1-\pi)\left\{P(\pi)\left[A\dot{D}^{0.5}\exp\left(-\frac{E_a^1}{RT}\right)\right]+(1-P(\pi))\left[B\dot{D}\right]\right\}$$

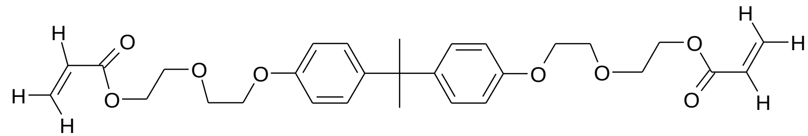
3 - Network structure







Comparison of UV- and EB- cured materials

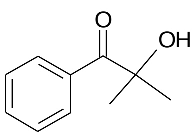


BPA-ethoxydiacrylate

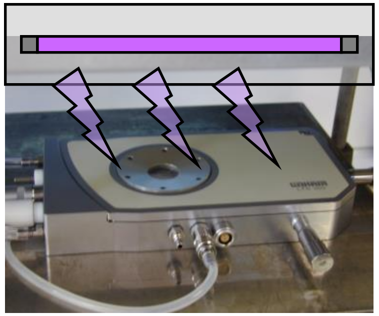
2 mm-thick bar samples

360 nm - 1 mW.cm^{-2}

2-OH, 2-Me propiophenone



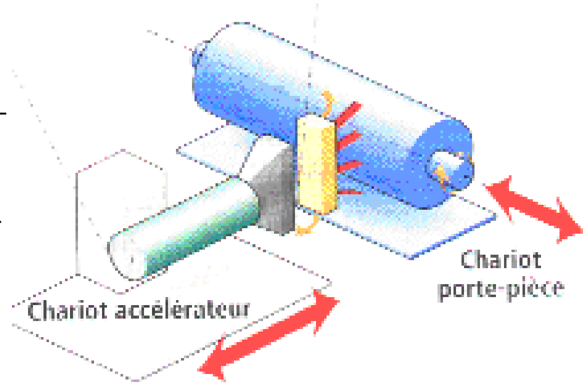
Linkam thermo-regulated stage



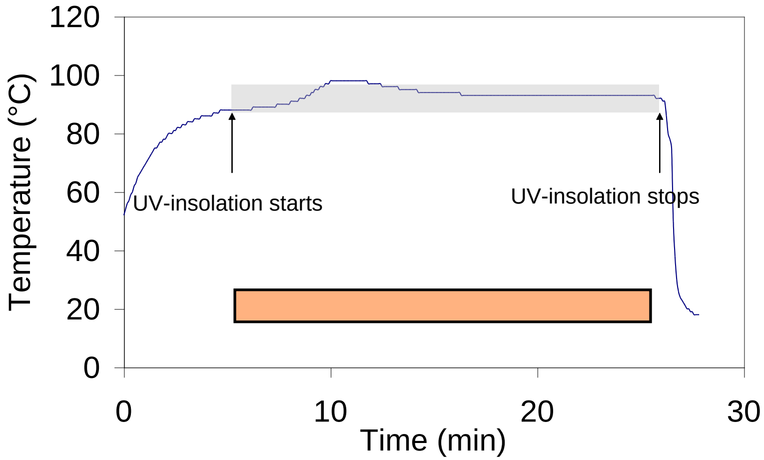
10 MeV e^{-}

20 kW

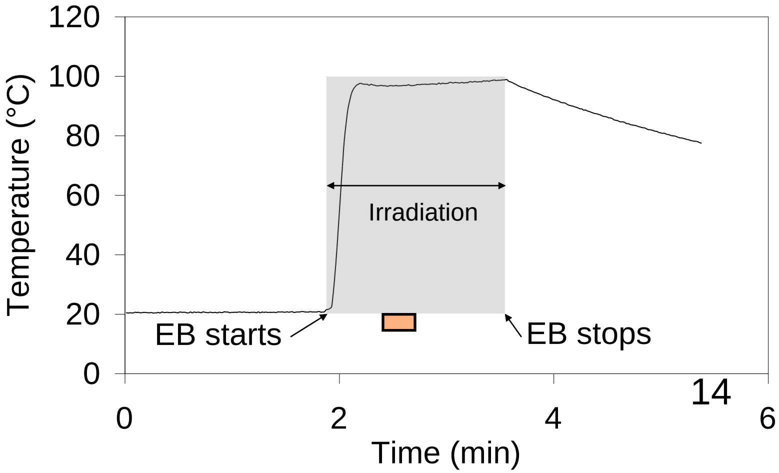
10 kGy.s^{-1}



Slow - isothermal conditions

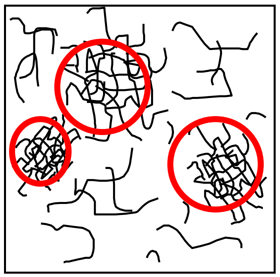


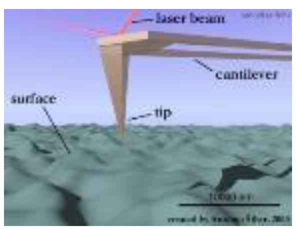
Fast - anisothermal conditions

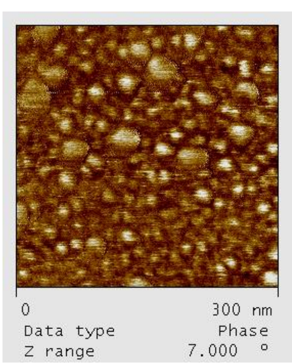


Understanding network formation

Microheterogeneities evidenced by AFM imaging and quantified by modulated-DSC







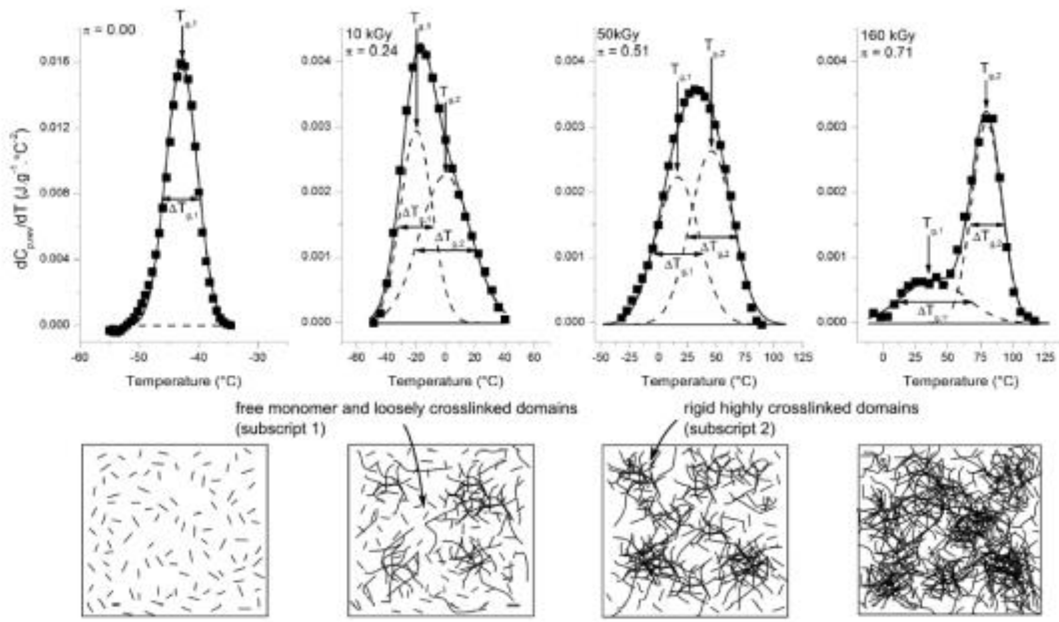
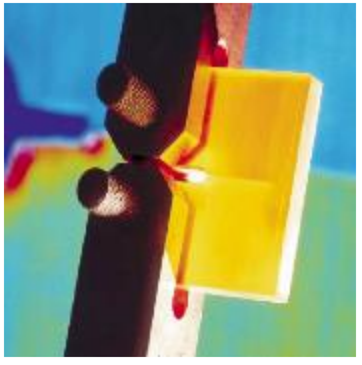


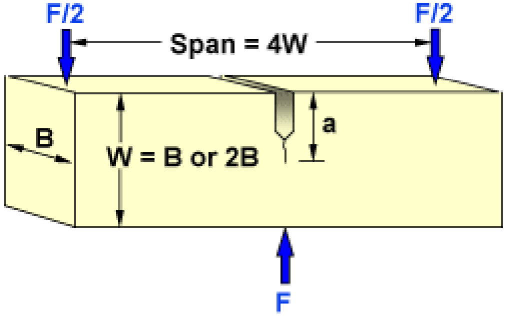
Figure 5. Examples of peak resolutions of the $dC_{p,rev}/dT$ curves for a set of EB-cured ETAC networks (dose and conversion shown on the graphs) and corresponding schematic representation of heterogeneity.

M. Krzeminski *et al.Macromolecules*, **2010**, *43* , 3757

M. Krzeminski *et al.Macromolecules*, **2010**, *43* , 8121

4 - Upgrading matrix properties

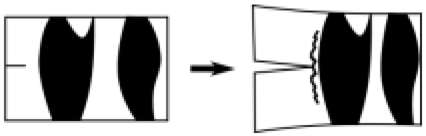




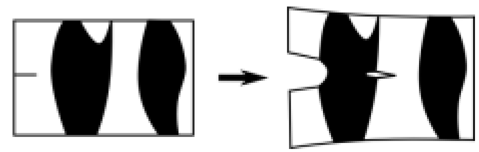
Matrix tougnening with thermoplastic additives

Principles of network toughening:

Polymerization induced phase separation

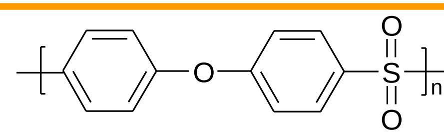


Crack deviation



Crack bridging

aromatic polyethersulfone (PES)



+ epoxy resin + hardener

State-of-the-art in 2005

- «First generation» epoxy or acrylate systems (EB, mid 1990's)

critical stress concentration factor **K_{Ic} = 0.6 to 0.8 MPa.$m^{1/2}$**

- «Second generation» epoxy resins (EB)

K_{Ic} = 0.9 MPa.$m^{1/2}$

- EB-cured epoxy formulations (CRADA EB-cured composites, ORNL, 1999-2002)

K_{Ic} = 1.1 – 1.6 MPa.$m^{1/2}$

- Best commercially available thermally curable expoxy resins

K_{Ic} = 1.6 MPa.$m^{1/2}$

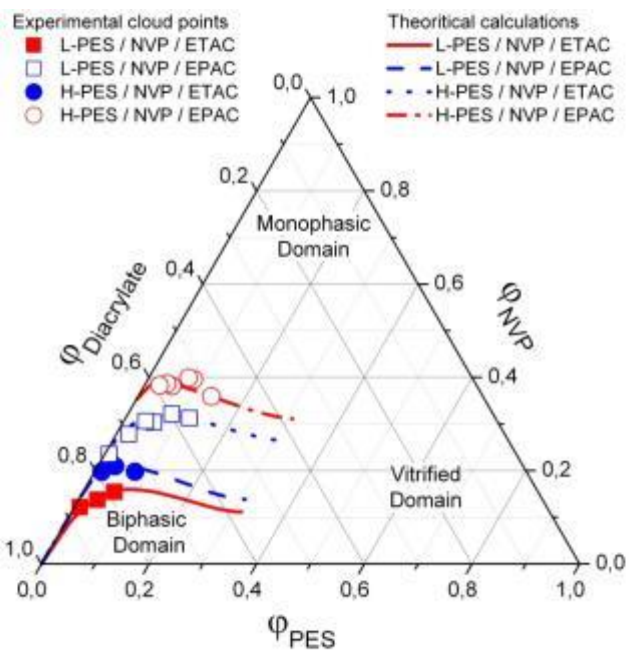
Improvement of matrix toughness

Proposed answer: Radiation-triggered polymerization-induced phase separation

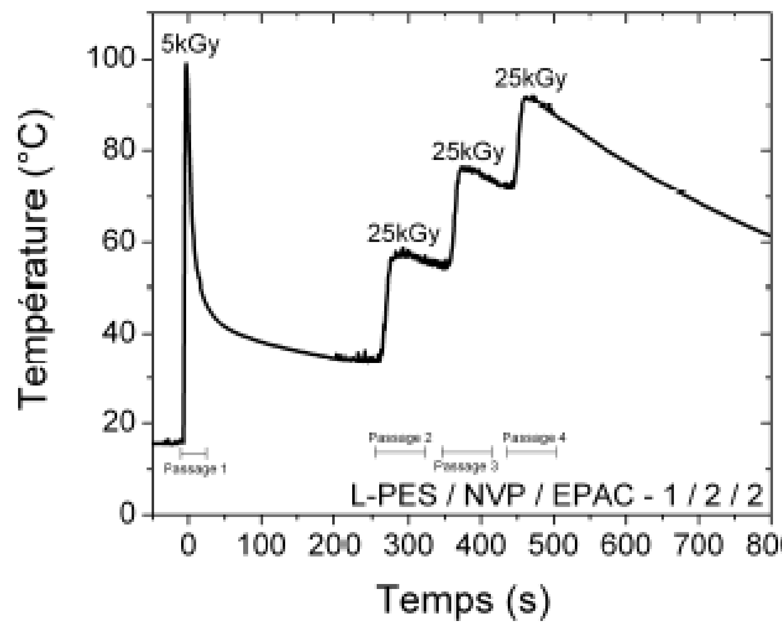
New formulation concept

3 patents pending

- diacrylate, Reactive diluent, Polysulfone
- homogeneous and fluid at RT



- Fast treatment, no need of pre-heating
- Sudden demixtion of PES, nucleation with limited growth



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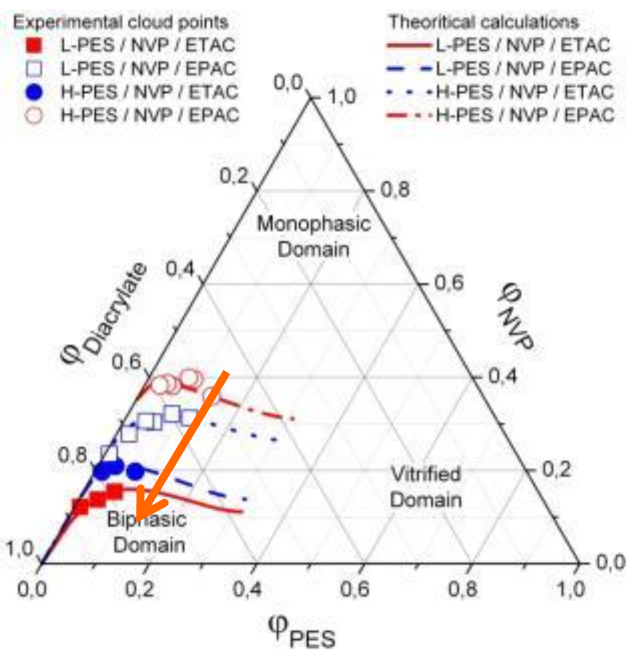
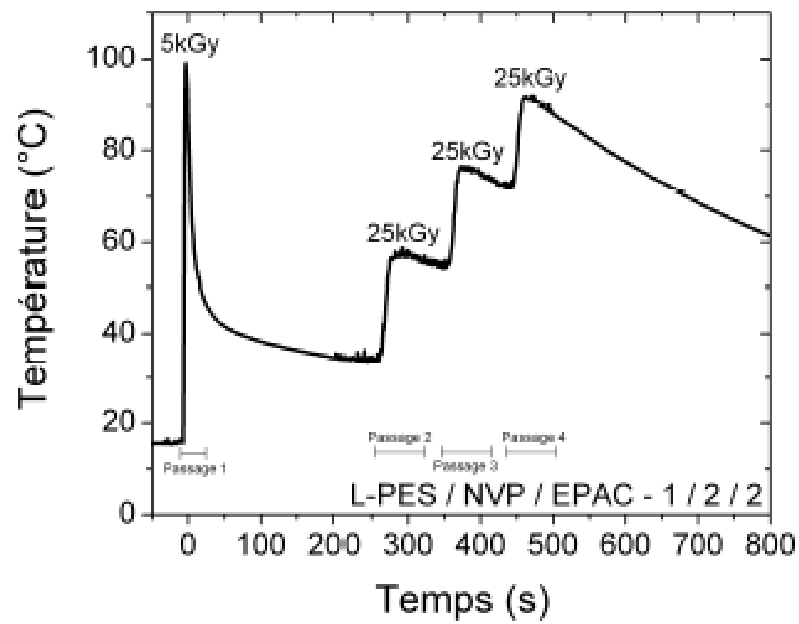
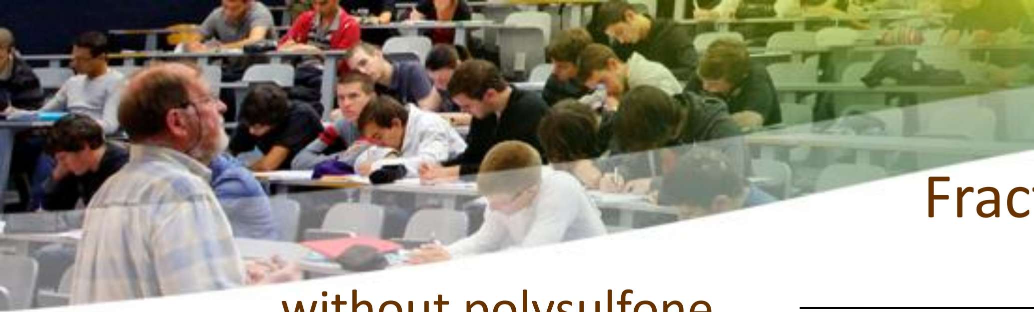
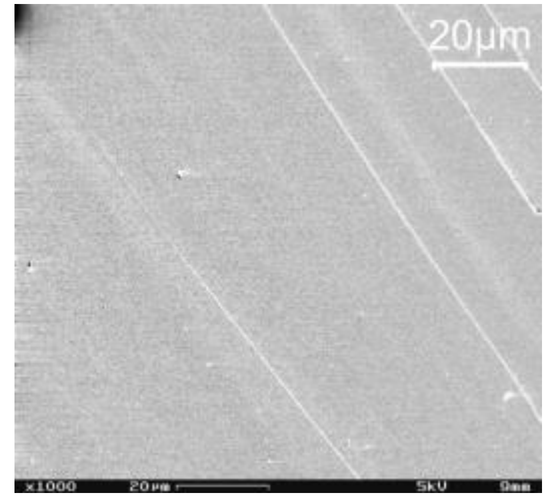






Fracture morphology by SEM analysis

without polysulfone

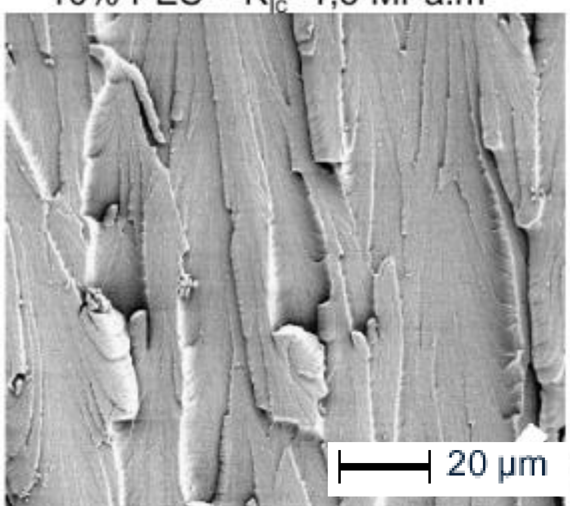


very smooth, featureless surface
typical of a brittle material

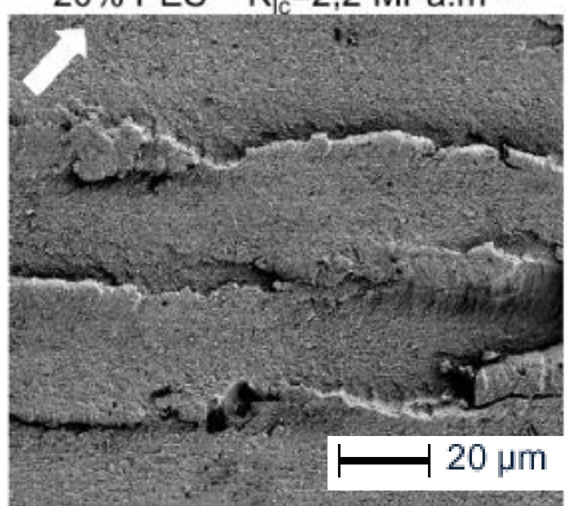
with polysulfone

complex fracture surface with evidence of plastic deformation, typical of a toughened material

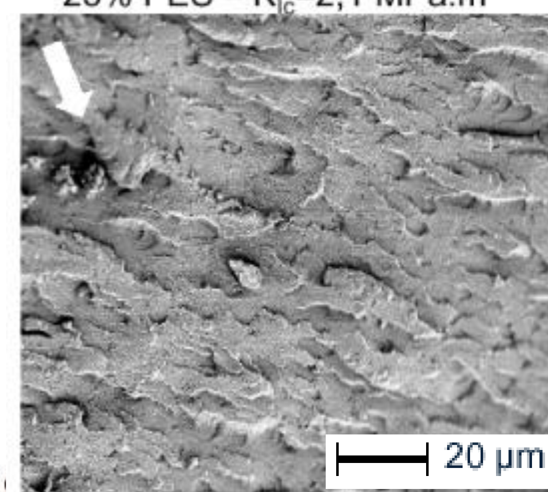
10% PES – K_{Ic}=1,3 MPa.$m^{0.5}$



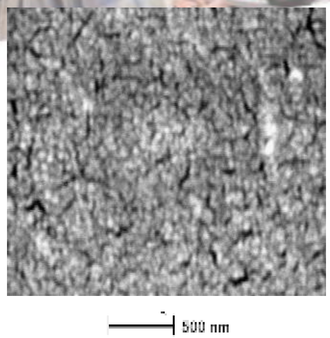
20% PES – K_{Ic}=2,2 MPa.$m^{0.5}$

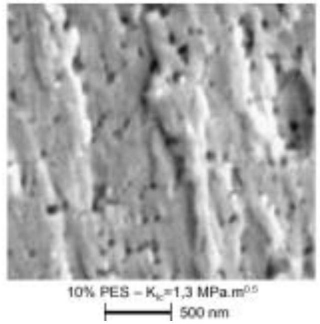


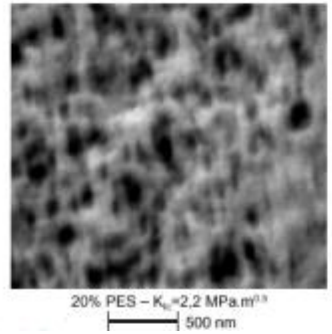
25% PES – K_{Ic}=2,1 MPa.$m^{0.5}$

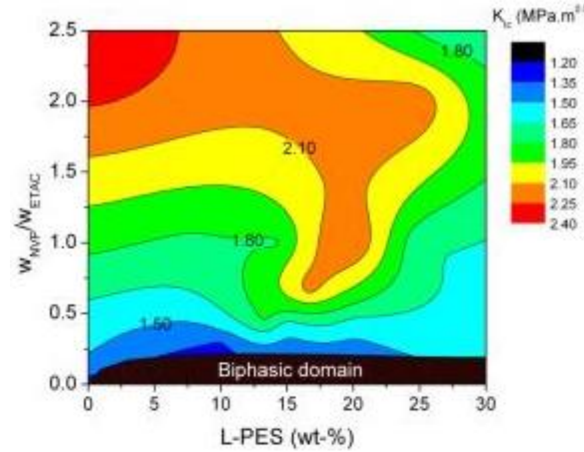


Improvement of matrix toughness

a)


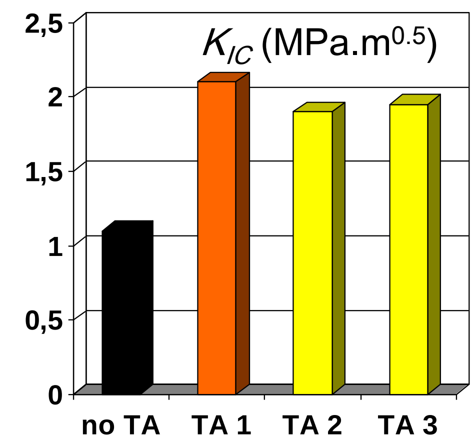
b)


c)


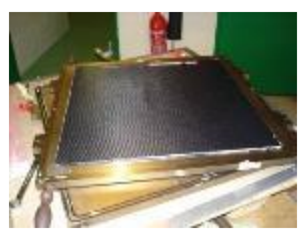


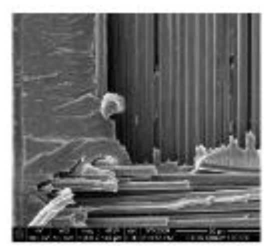
Nanoscaled-morphology of neat (a) and toughened acrylate-based system including commercial high-T_g thermoplastic (b,c) that exhibit

K_{IC} values of ~ 2 MPa.m$^{1/2}$



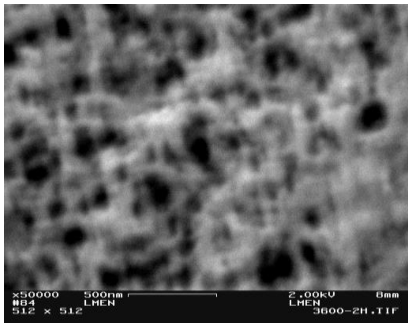
Electron beam-cured, vacuum bagged glass fiber reinforced composites



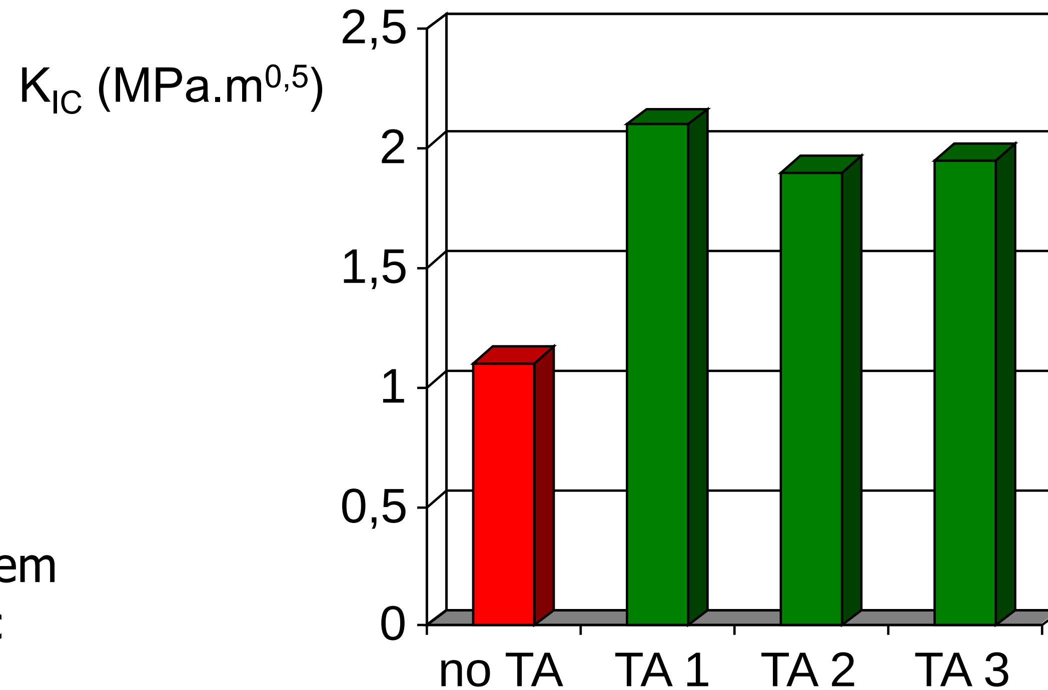


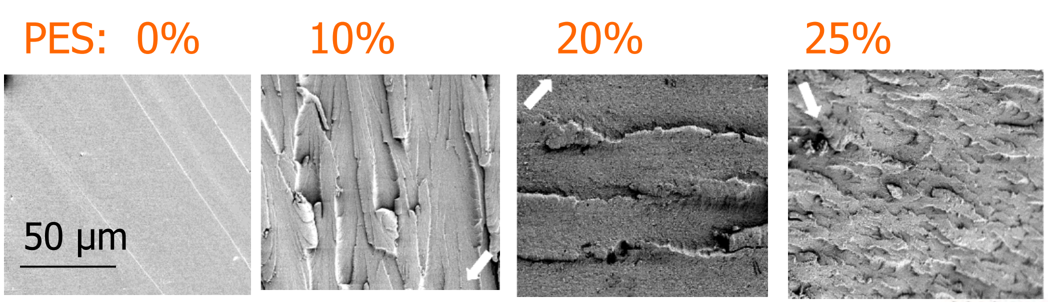
X-ray cured, carbon fiber reinforced composites

Improvement of matrix toughness



Nanoscaled-morphology of toughened acrylate-based system including high-Tg thermoplastic





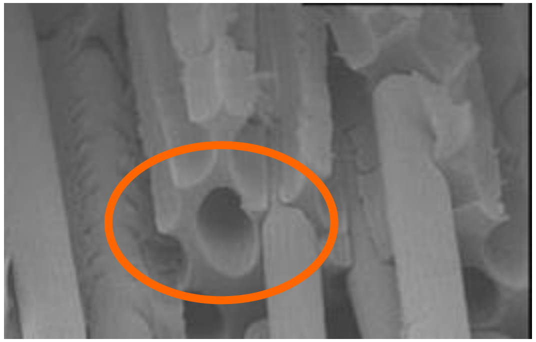
K_{IC} values of ~2 MPa.m$^{1/2}$

2 patents 2009, 2011

Université de Reims Champagne-Ardenne

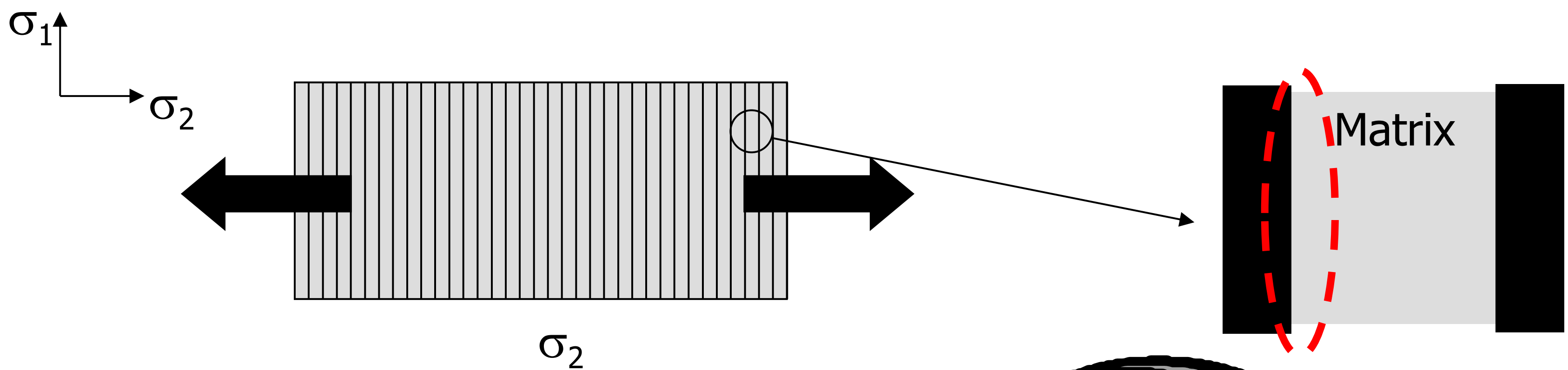
M. Krzeminski *et al. Radiat. Phys. Chem.*, **2011**, *accepted*

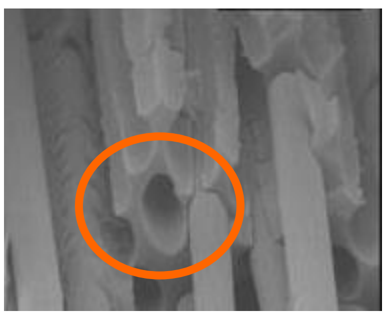
5 – Improving fiber-matrix interface

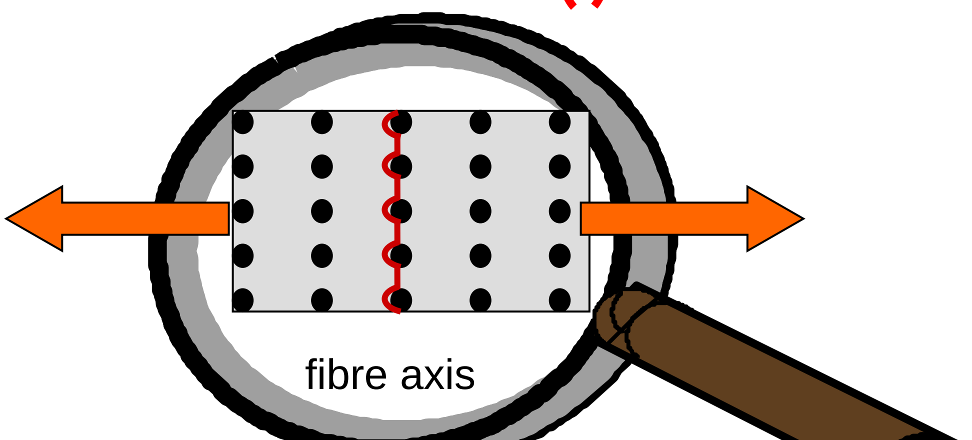


Focus on fibre-matrix interface

Poor transverse properties of radiation-cured composites



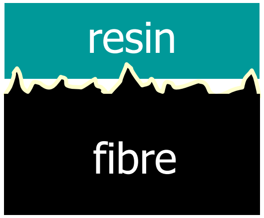


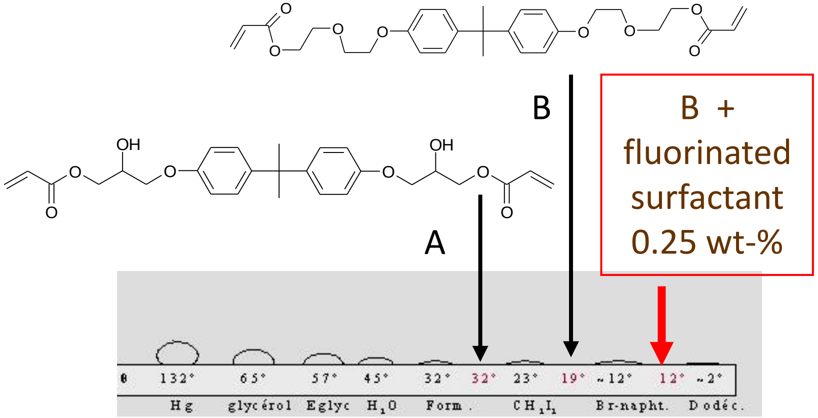


Current value σ_2 = 20-25 MPa → Target σ_2 = 80 MPa

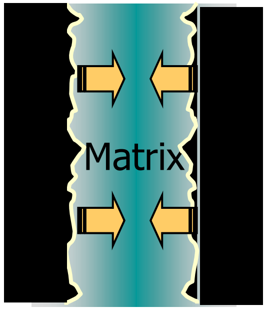
Initial hypotheses for weakness of fiber-matrix interface

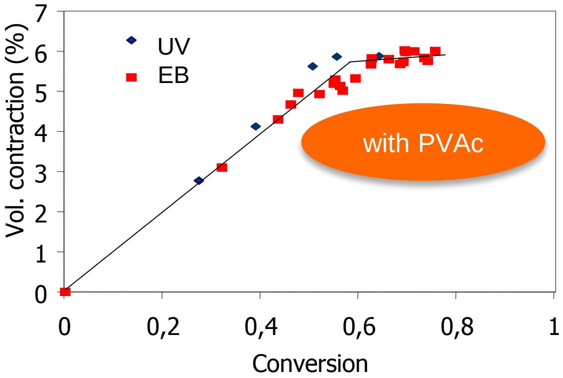
Hyp. 1 - Insufficient wetting



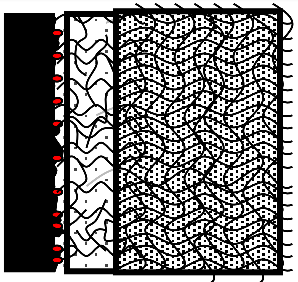


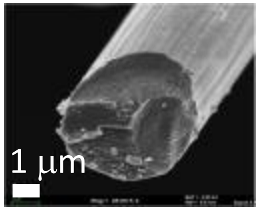
Hyp. 2 - Influence of shrinkage

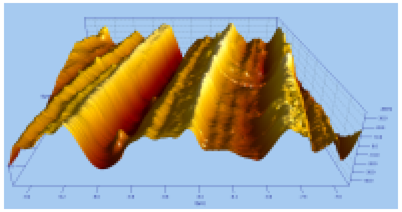




Hyp. 3 - « Chemical mismatch » between fibres and matrix

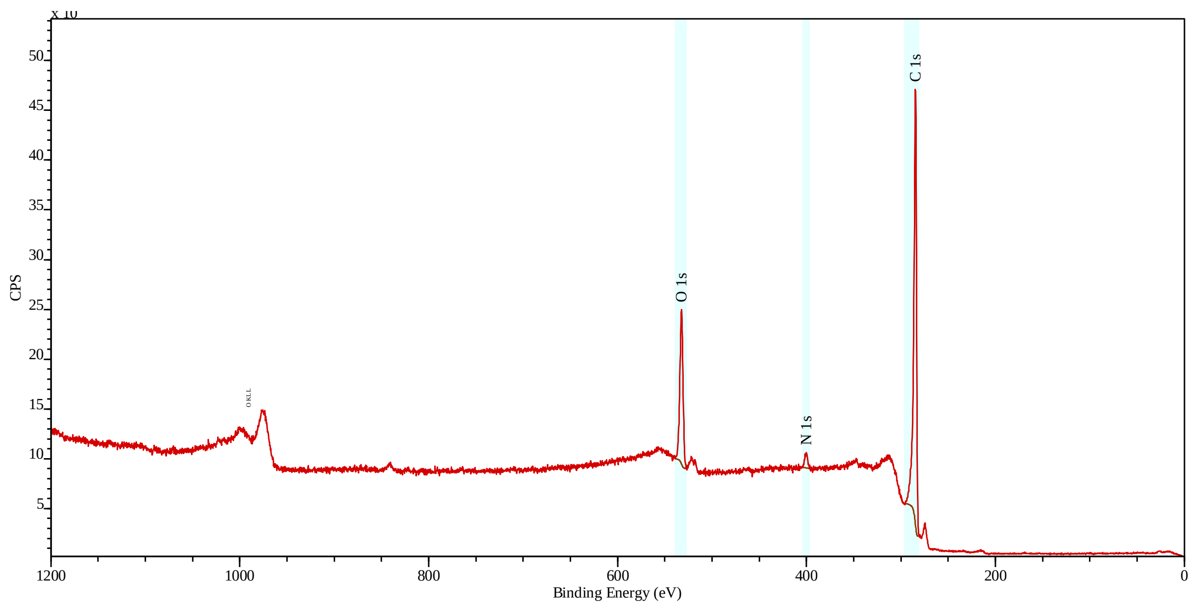






Characterization of carbon fibre surface

X-ray Photoelectron Spectroscopy



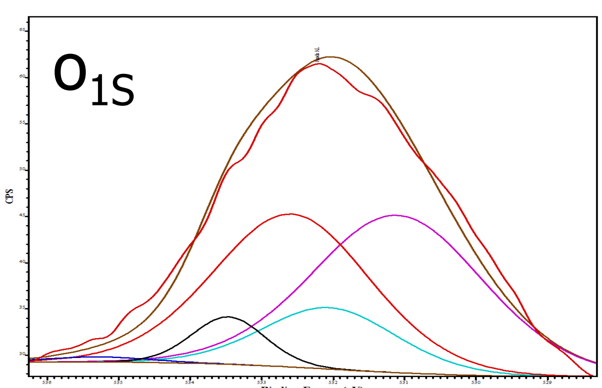
Atomic composition

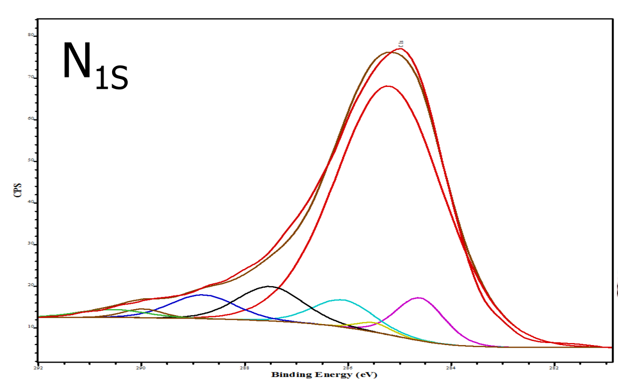
C – 83 %

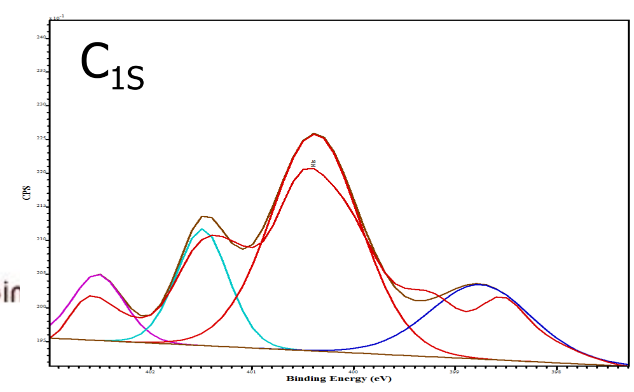
O – 15 %

N – 2 %

High resolution decomposition





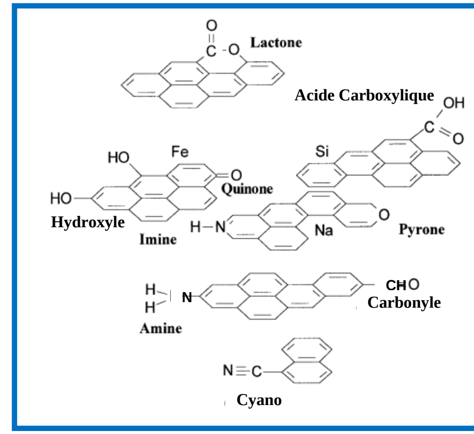


Characterization of carbon fibre surface

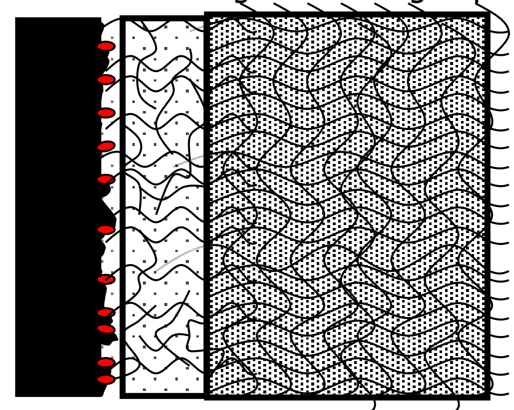
X-ray Photoelectron Spectroscopy

C1s							
C-C	C=C	C-OR C-OH C=N	COOH C-COOR	C=O	C-N	H_2O	CO_2
6	76	5	4	6	1	1	1

O1s					N1s					
Ph=O Ph-C=O	C=O	ROH C-O-C	Ph-OH C-O	H_2O	pyridine	amine amide	pyrrolidone pyridone	pyridinium	nitro	
43	13	38	5	1	20	54	17	-	9	



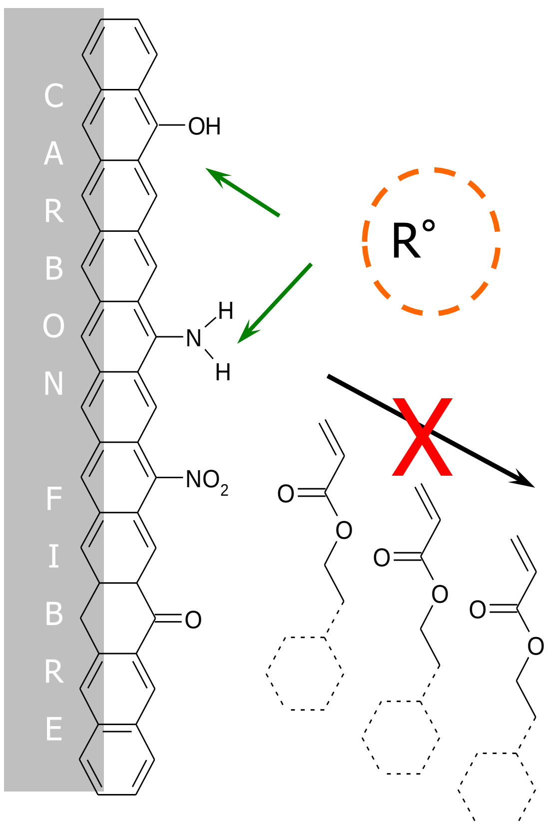
= inhibiting functional groups

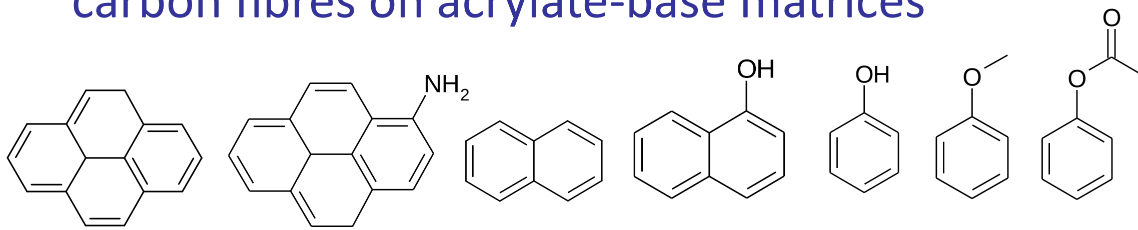


Fibre

Evidencing inhibition effects

- Free radical chemistry: inhibition by mimicking the presence of functional groups present at the surface of carbon fibres on acrylate-base matrices

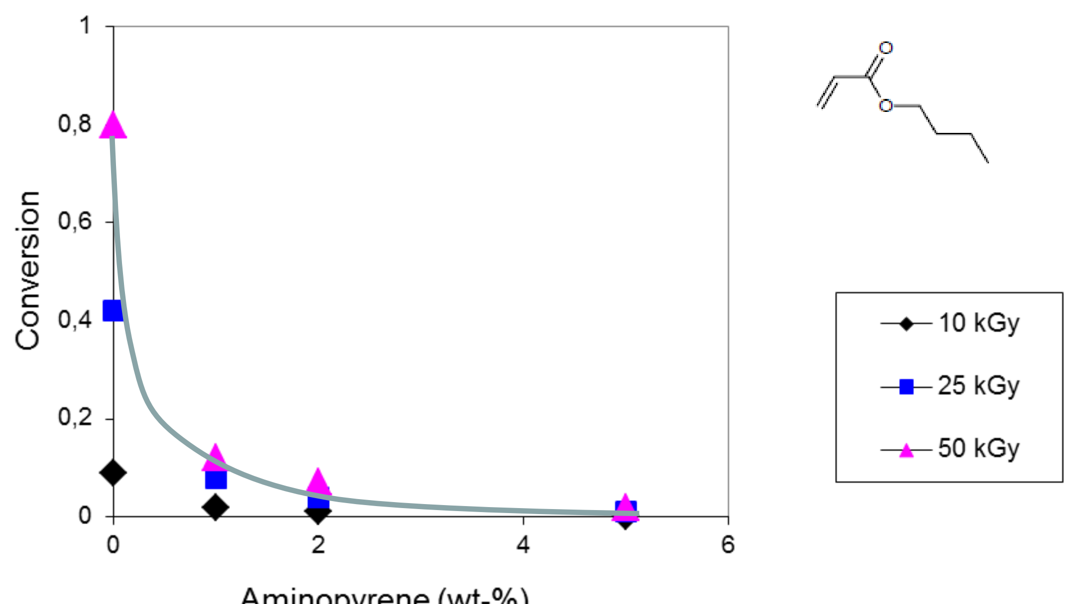




and more ....

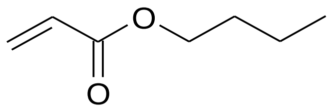
- Reactivity of butyl acrylate monomer under electron beam

10 MeV –Electron beam - doses ranging from 10 to 50 kGy



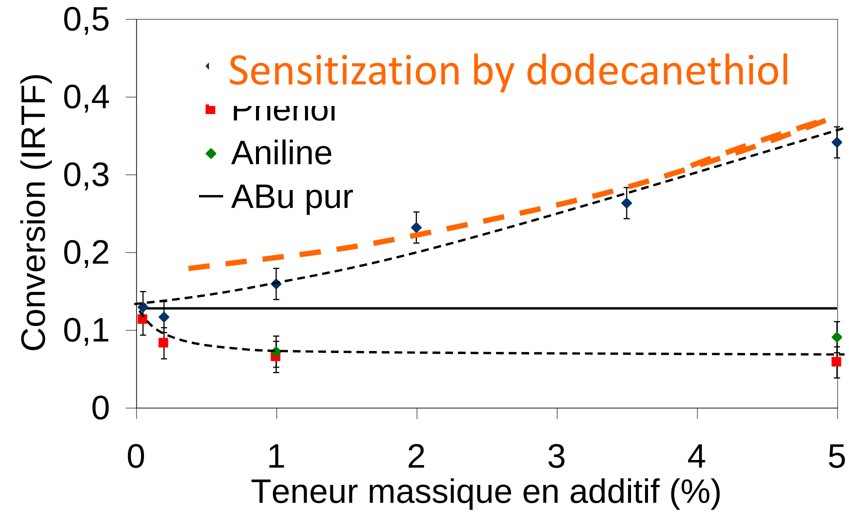
Butyl acrylate polymerization (EB): Sensitization and transfer with thiols

n-BuA



Dodecanethiol $C_{12}H_{25}$-S-H 0, 0.05, 0.2, 1, 5 wt-%

EB irradiation 5 kGy (conversion $\pi < 0.3$)



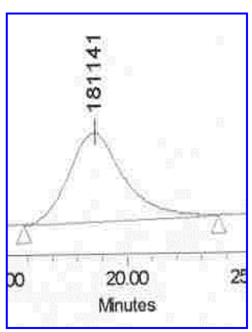
Efficient transfer by dodecanethiol

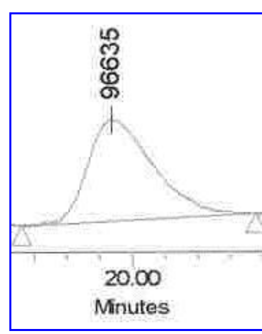
~M-M-M-M° + R-S-H → ~M-M-M-M-H + R-S°

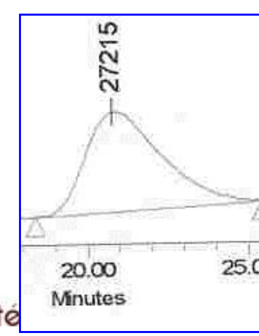
R-S° + n M → RS-M-M-M-M°

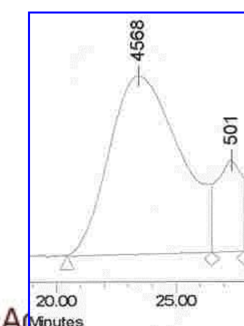
$$\lambda = \frac{R_p}{R_{init} + R_{transfer}}$$

Poly(BuA) MW by SEC





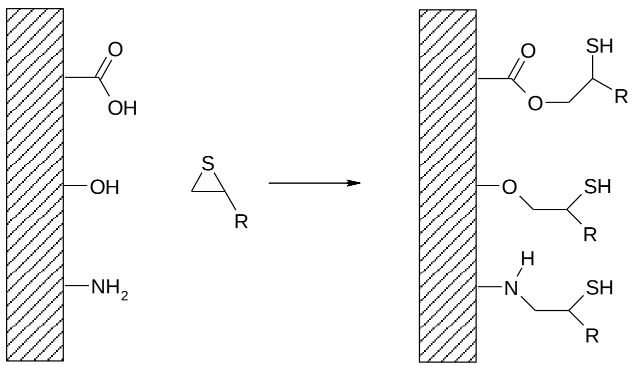




[R-SH] (wt-%) 0.05 0.2 1 5

Enhancement of matrix-to-fibre adhesion

- Optimization of the fibre - matrix interface by new sizing concepts (3 patents since 2006)
- 1 - Direct modification of functional groups



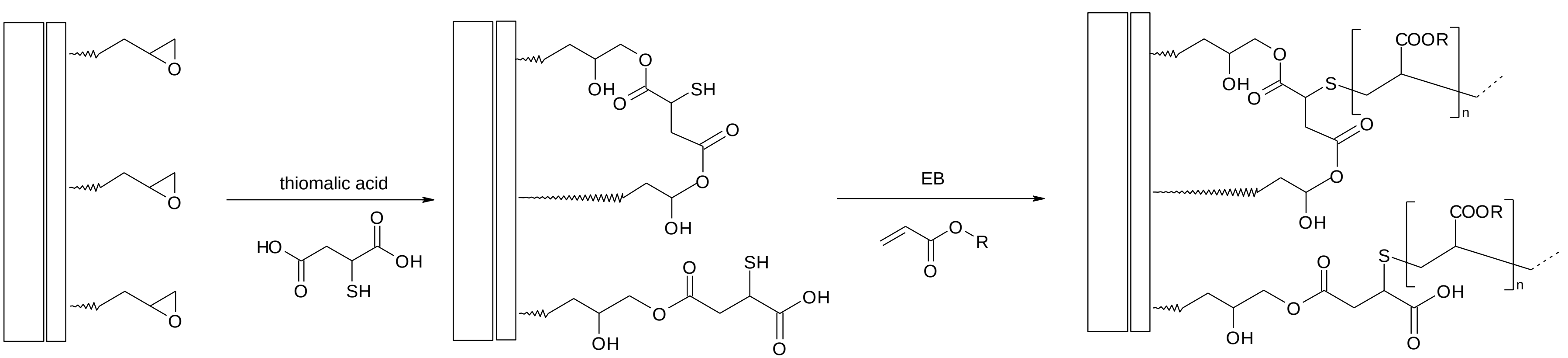
Thiol content

Thickness

Uniformity

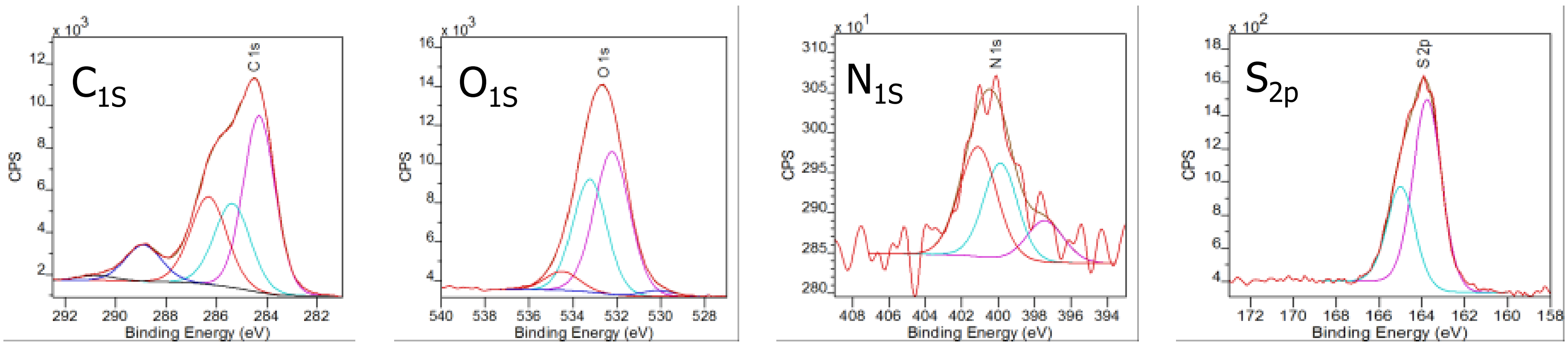
Final efficiency

- 2 - Modification of sizing



Thiomalic acid functionalization (5131)

Surface composition	C at-%	O at-%	N at-%	S at-%	Si at-%
Fibre 5131	76	23	0.5	-	0.5
Fibre 5131 S-modified	69	26	1	3.5	0.5



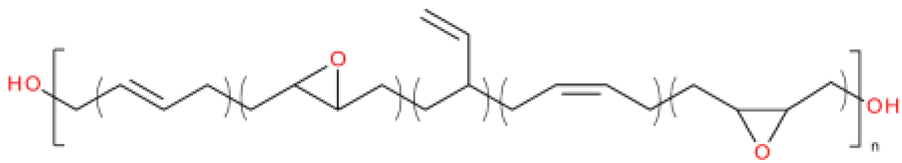
Position (eV)	Concentration (%)	Functional groups
284.3	42.5	C-C
285.4	23.5	C=C
286.3	22.5	C-OR
288.9	10	COOH, C-COOR, C-S
290.8	1.5	CO_2

Position (eV)	Concentration (%)	Functional groups
531.5	9	C=O
532.4	53	C-O-C, R-OH
533.3	31.5	C-O in esters
534.5	6.5	COOH

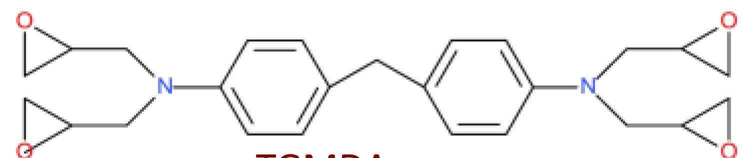
Position (eV)	Concentration (%)	Functional groups
163.8	67	-SH
165	33	

Original fibre sizings including thiol groups

Epoxy prepolymers: EP1 EP2

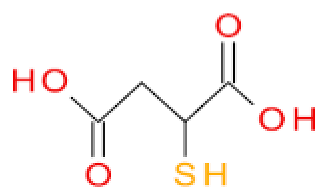


Epoxidized polyBD

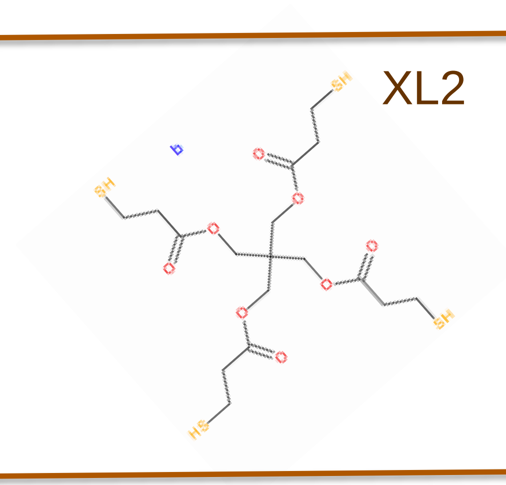


TGMDA

Thiol-based crosslinkers: XL1 XL2



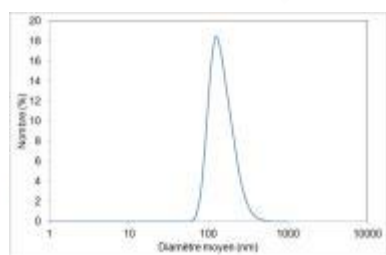
AcSH



PETMP

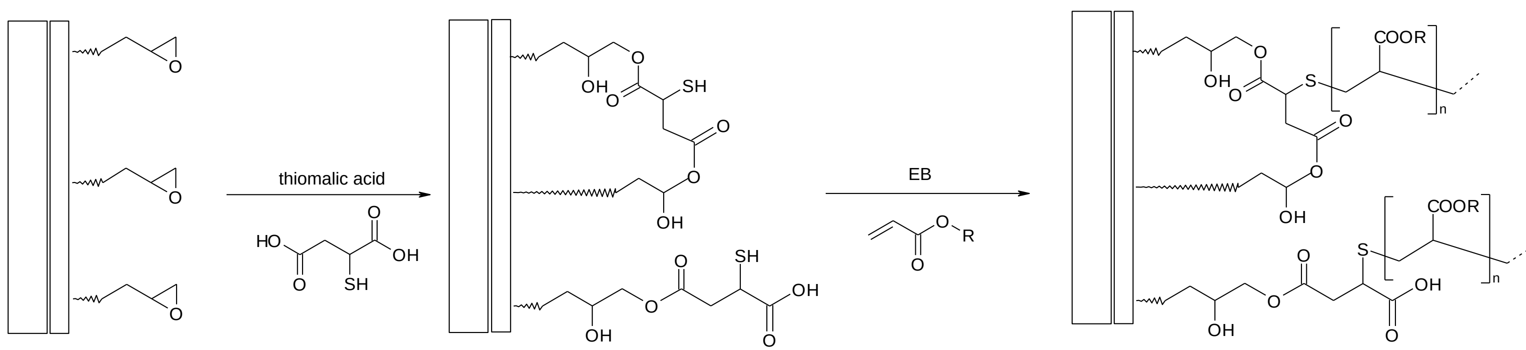
Solvent based and aqueous emulsions

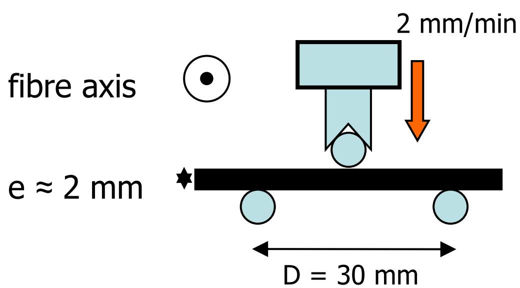
Patent pending (applied 2014)



Enhancement of matrix-to-fibre adhesion

- Optimization of the fibre - matrix interface by new sizing concepts   3 patents 2005-2007

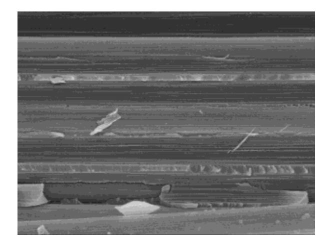




Transverse shear at break

σ_2 = 20-25 MPa

σ_2 > 70 MPa



Summary and perspectives

- Beyond the confirmation of the potential of EB (X-ray) curing
  - out of autoclave, fast and energy saving
  - layer by layer, large or complex structures
- Consolidated knowledge on curing process
  - Experimental methodology
  - Reaction kinetics - Modelling (dose, curing)
  - Reactions occurring at fibre to matrix interface
  - Aging of EB-cured parts
- High level of mechanical properties
  - Transverse properties improved by coupling agents
  - Excellent toughness together with high Tg
- Opportunities for mass fabrication of high performance products

Acknowledgements

- Helène Degrand
- Guy Larnac
- Jean-Christophe Pasquier

Programme PlAneT

Université de Reims Champagne-Ardenne