

From additive phosphorylated flame retardants to reactive biobased ones...

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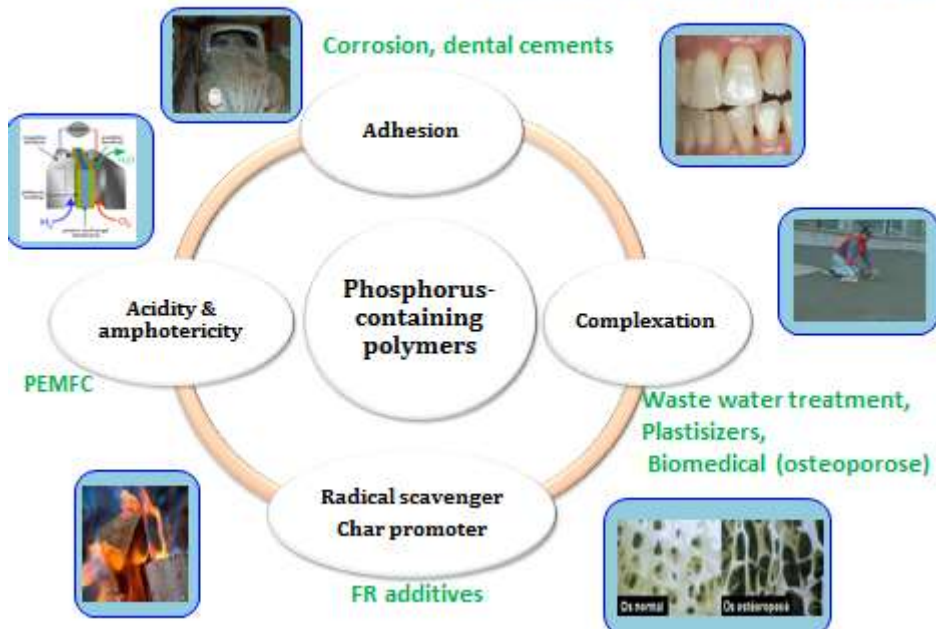
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Equipe IAM (Ingénierie et Architectures Macromoléculaires)

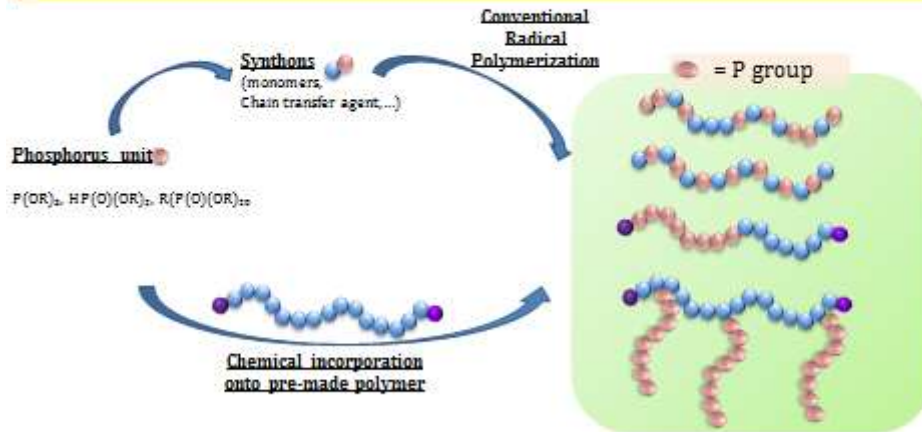
CHEMISTRY: MOLECULES TO MATERIALS



Phosphorus-containing Polymers



Property/ Application → « building » the polymer containing the P group from bottom-up approach



Knowledge on phosphorus organic chemistry required

-Widely used especially for plastic materials (buildings, electronics, transport textile industry)¹

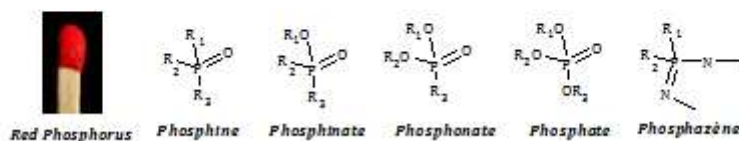
-2016: 2.5 Millions tonnes and 12 billions \$

4 main types of FR:

- Minerals : $Al(OH)_3$, $Mg(OH)_2$, $CaCO_3$, Sb_2O_3 , ...
- Halogenated : chloride and bromide derivatives
- Phosphorus compounds
- Others : nitrogen compounds,...



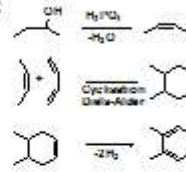
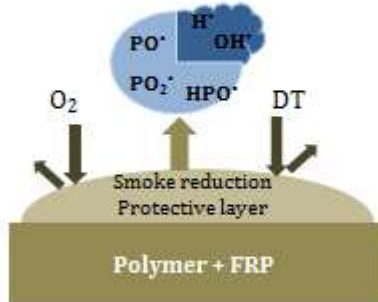
FRP extremely wide family and versatile : depending of oxidation states



3 modes of action for FRP

1- Chemical action in condensed phase :

Formation of a surface layer of protective char



2- Physical action in condensed phase :

Intumescent mechanism

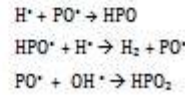
3- Chemical action in gas phase :

Flame inhibition : radical mechanism to interrupt the exothermic processes and to suppress combustion

Efficiency of FRP :

- * chemical structure/polymer matrix
- * interactions with structural environment

Optimisation : synergy with others compounds

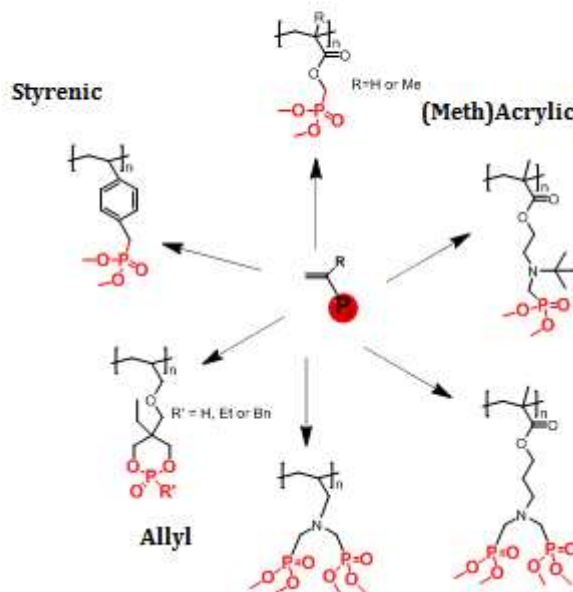


Phosphorus-containing Polymers : First generation of FRP

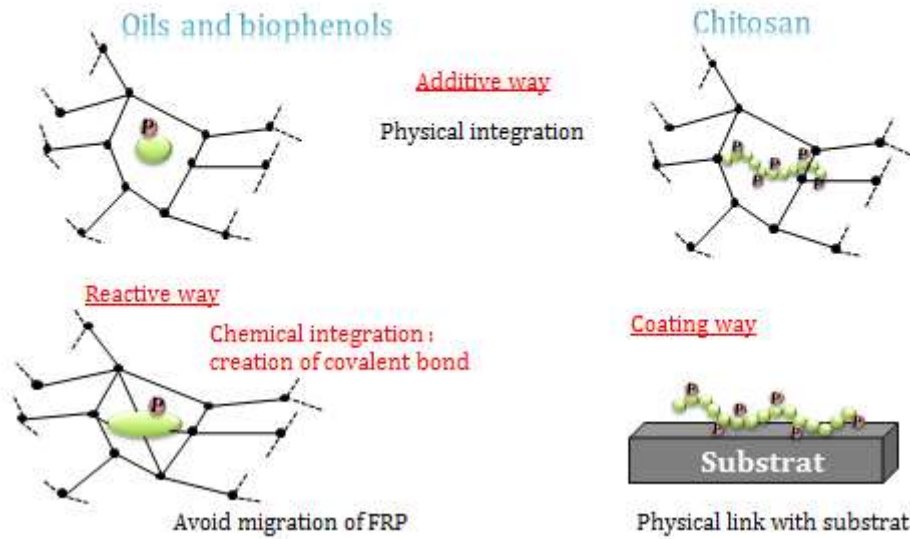
Syntheses of wide range of phosphorylated polymers by radical polymerization



Study and comparison of polymers structure on fire properties

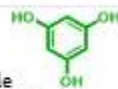


2 strategies in function of biobased building blocks



Phloroglucinol as bioresource:

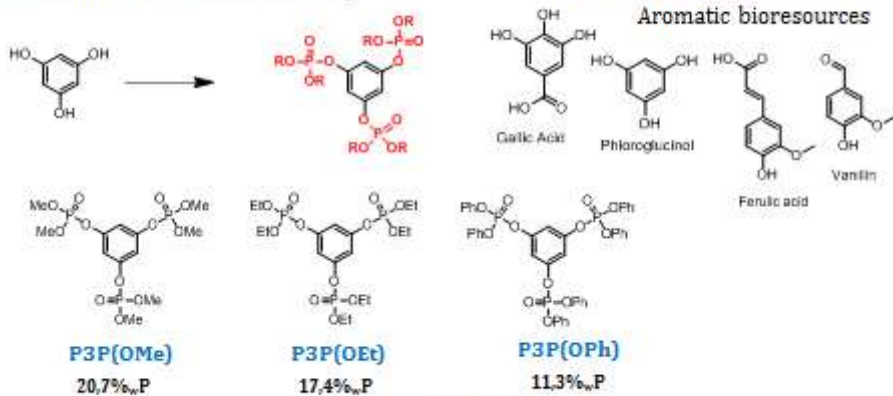
Structure model of the biophenols available
Symmetric structure: similar reactivity of the hydroxy groups



Tanin or lignin derivatives



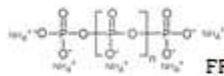
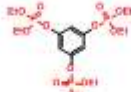
Synthesis of biobased additive FRP



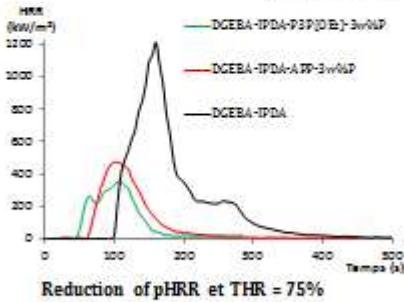
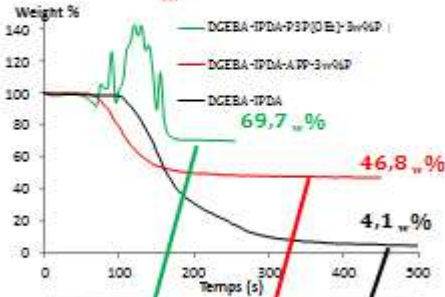
Various P ratios and functional groups

Fire real conditions : Cone calorimeter characterization

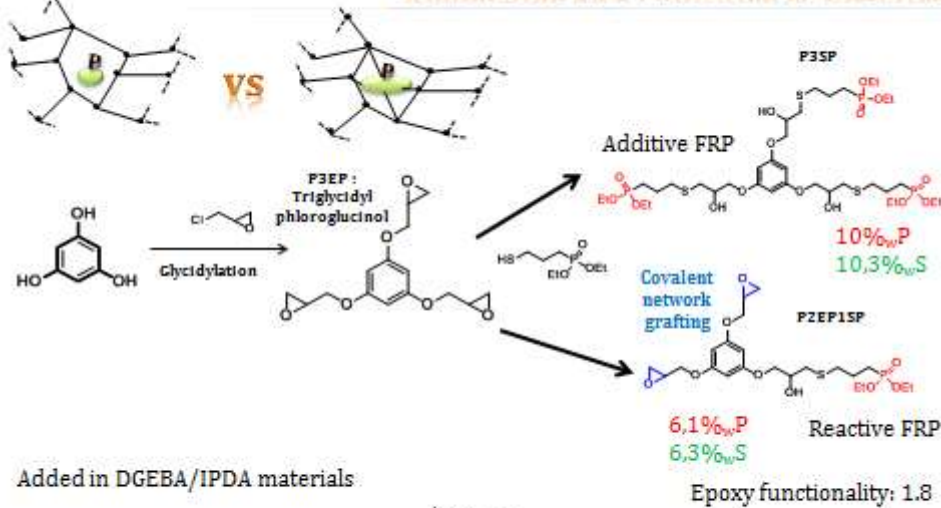
FRP:



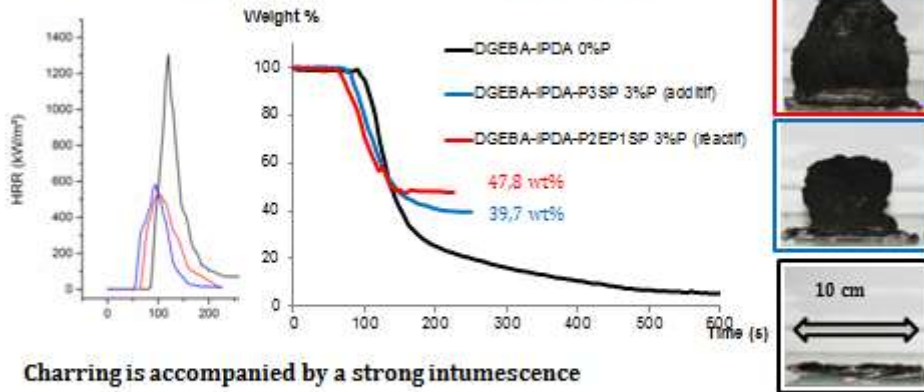
FRP reference



Physical and chemical actions :
intumescence - huge char content -
important decrease of fuel gas release



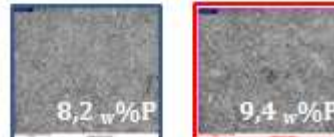
Fire real conditions : Cone calorimeter characterization 35 kW/m²



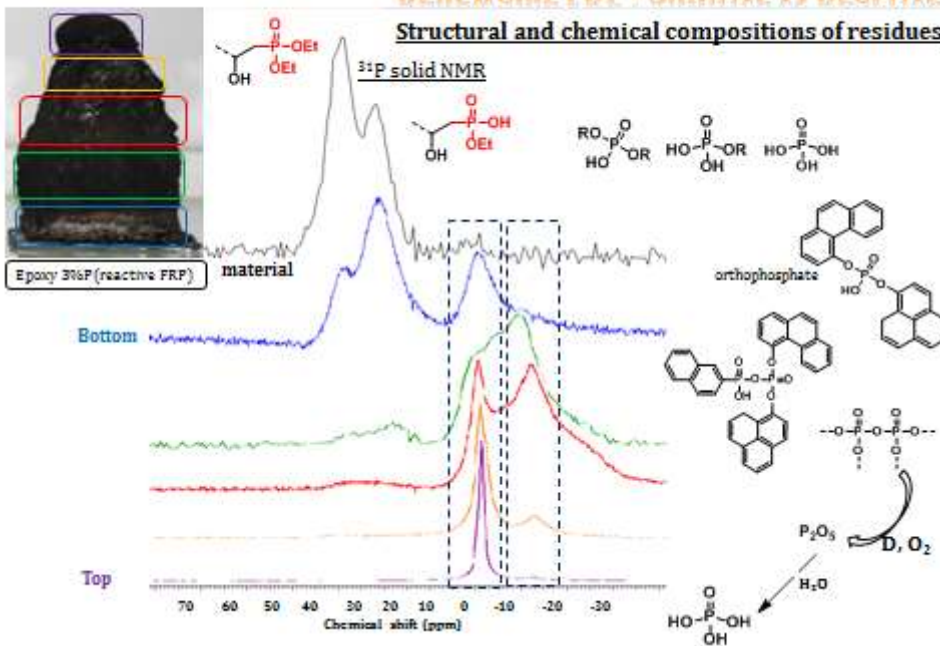
Charring is accompanied by a strong intumescence

Swelling is more important with the reactive FR

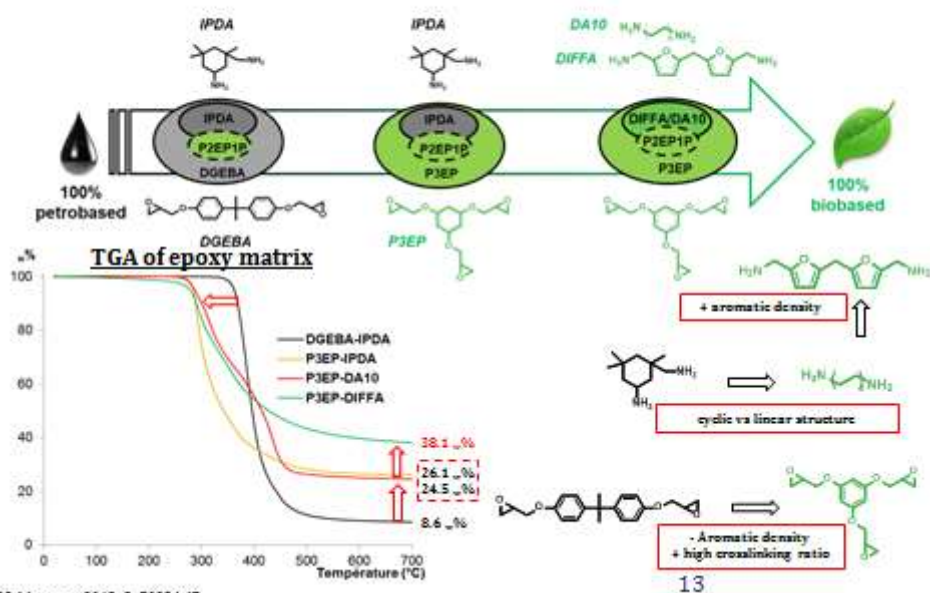
%P reactive approach > %P additive approach



Structural and chemical compositions of residues

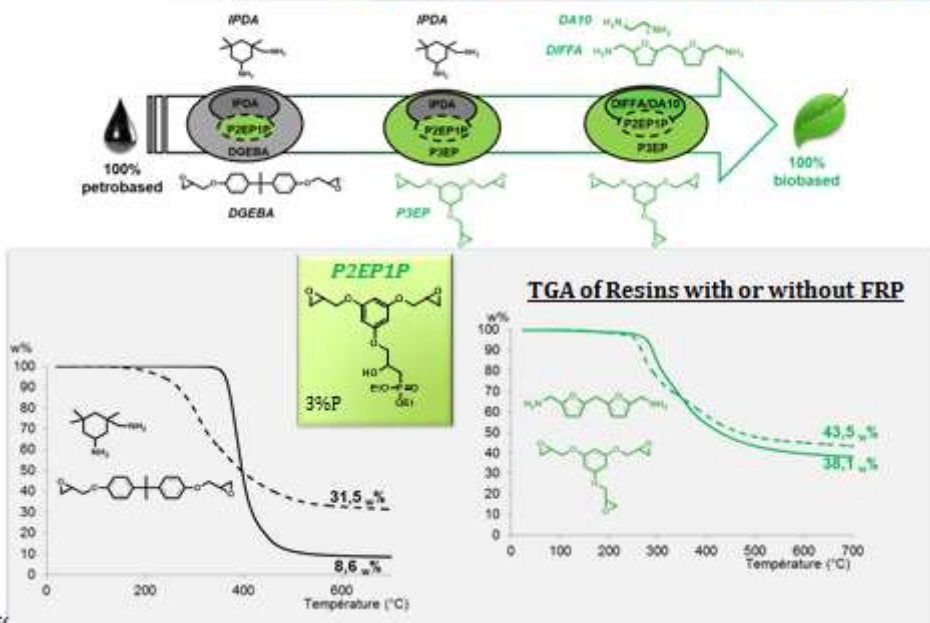


Towards a 100% biobased epoxy resin...



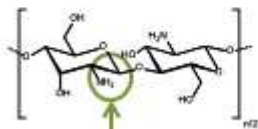
RSC Advances, 2015, 5, 70856-67

Towards a 100% biobased epoxy resin...

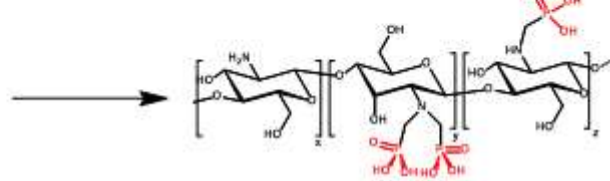


RSC

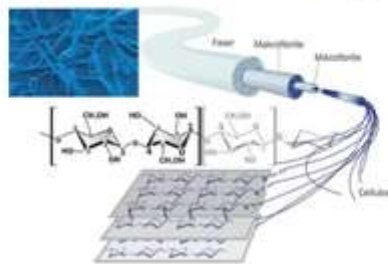
Chitosan



Primary amine function easily alterable

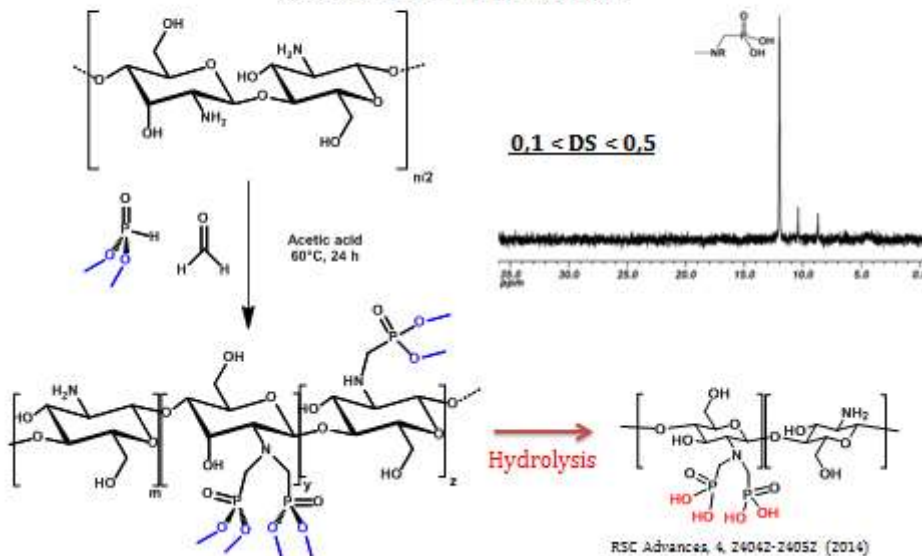


Towards fire protection of fabrics...



Kabachnik-Fields reaction onto chitosan

Reaction between a primary amine, a carbonyl compound and a dialkylphosphonate yielding an α -aminophosphonate

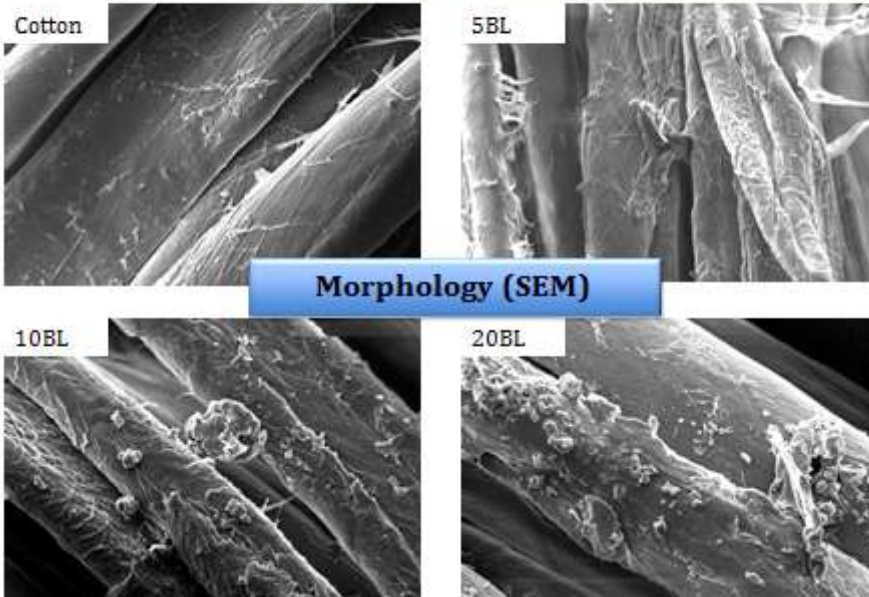
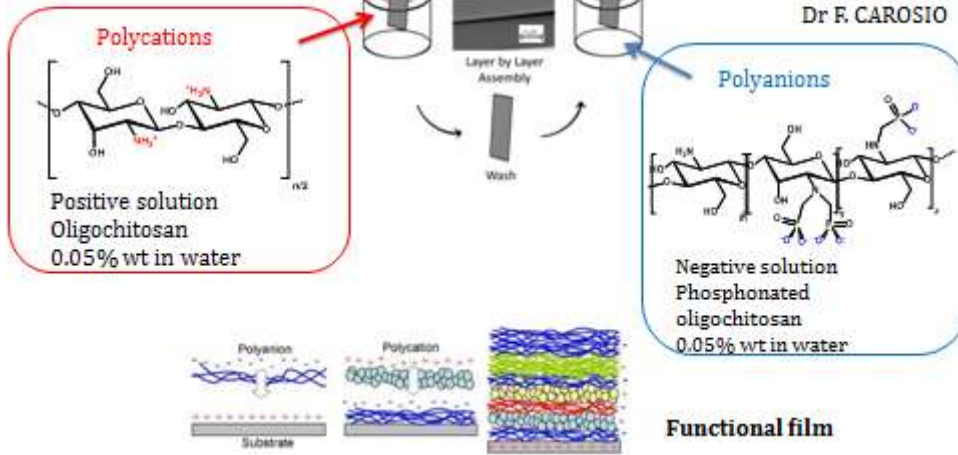


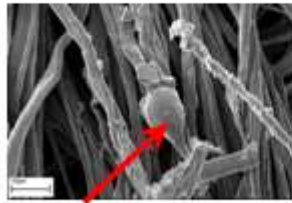
Process used to create polyelectrolyte multilayer films by LbL assembly

Cotton FABRIC as substrate



Pr. G. CAMINO
Dr F. CAROSIO





Formation of few randomly dispersed bubbles



Intumescent behavior!

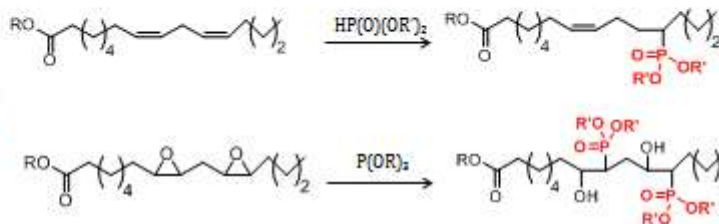
Vertical flame test



	Cotton	5BL Chit-PChit	10BL Chit-PChit	20BL Chit-PChit
Burning time [s]	11	11	11	14
Afterglow [s]	43	0	0	0

Afterglow suppressed

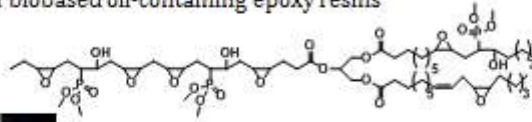
Oils



Towards fire protection of aliphatic polymers...

Flame retardant properties : First results

Added in biobased oil-containing epoxy resins



Phosphonated Algal Oil as reactive flame retardant



Flame vertical test

Material without phosphorus



1w% P material



High level of residue and afterglow suppressed

Achievement of phosphorus-containing FR



New FRP powerful and compatible on various polymer matrices

Thank you for your attention.

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CHEMISTRY: MOLECULES TO MATERIALS

