



LignoStarch Tailored modification of starch by radiation-grafting of lignin

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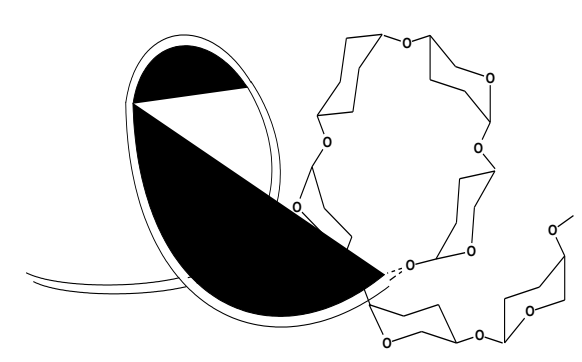
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3) INRA UMR 1318 Institut JPB - AgroParisTech Versailles, 4) DTPCIM - Ecole des Mines de Douai

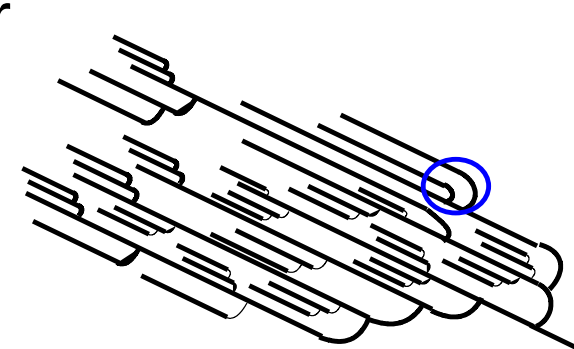
Introduction

Thermoplastic Starch (TPS) represents ca 80% of the biopolymer market, however, unlike petroleum based polymers, TPS is still manufactured by traditional methods of extrusion and injection molding.

Starch is a semi-crystalline renewable biopolymer made of glucose units existing as a mixture of linear polymer chains (amylose) and branched polymer chains (amylopectin). Due to its hydrophilic nature, starch products show retrogradation and varying mechanical properties with time.

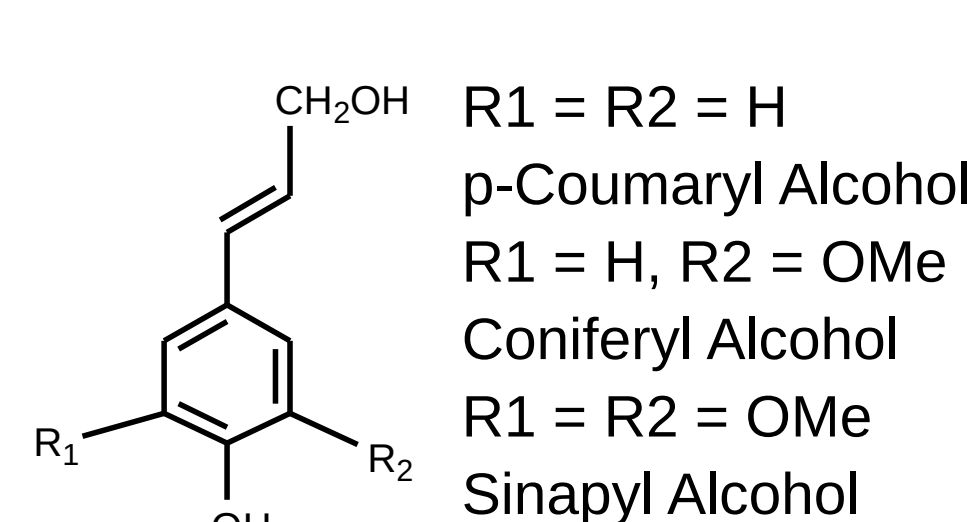
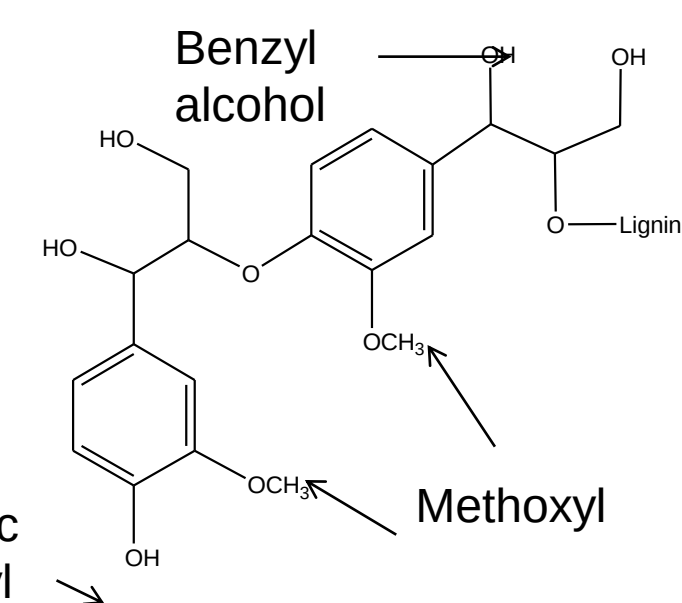
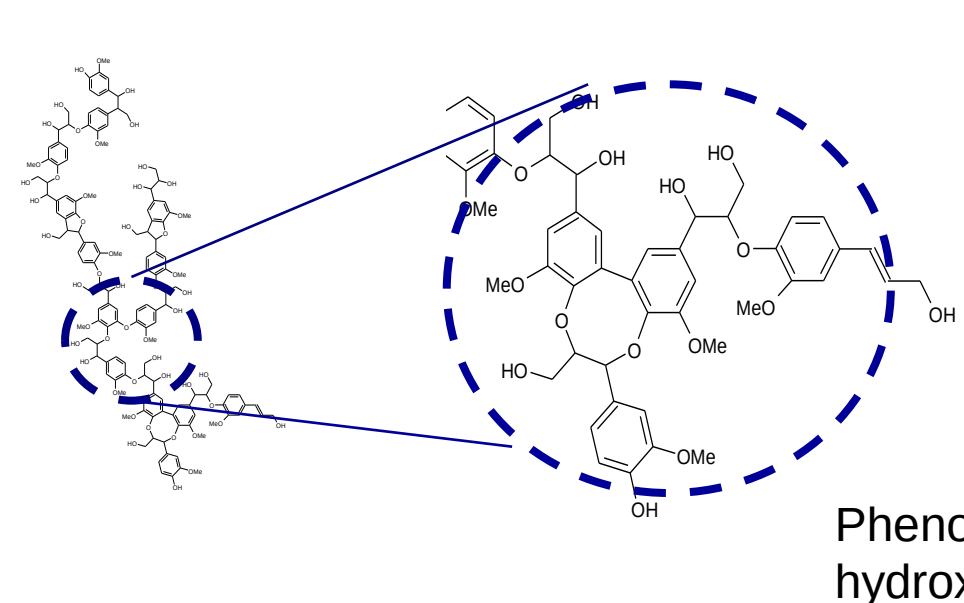


Amylose: Linear polymer chain with α (1,4) branching between glucose monomer units.

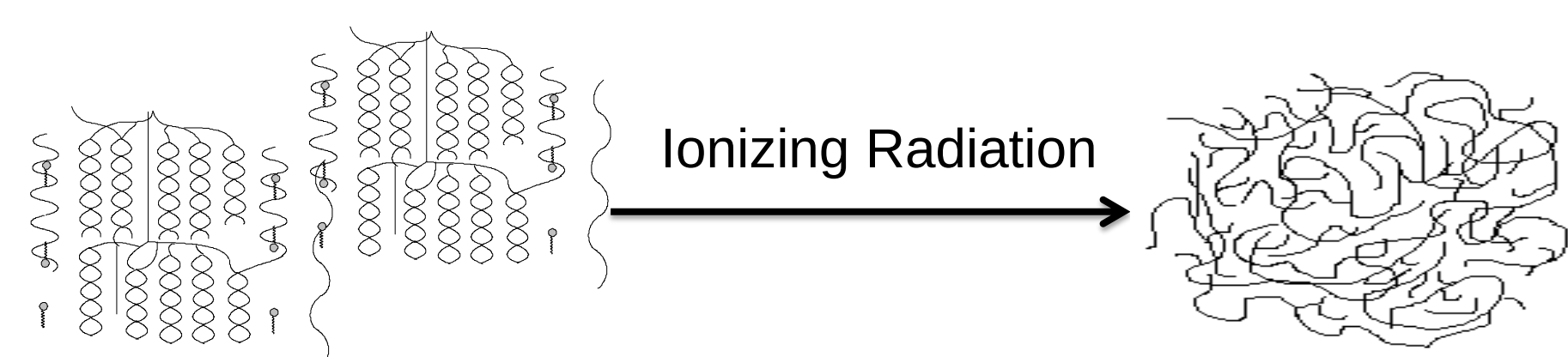


Amylopectin: Polymer chain with α (1,4) and α (1,6) branching between glucose monomer units.

Lignin, another renewable biopolymer and a by-product of the paper industry is hydrophobic and limits water sensitivity of TPS blends. Electron Beam radiation-induced grafting of lignin models onto starch/maltodextrin is shown to result in physical stability of the blends with limited loss of mechanical properties, improved surface hydrophobicity, and to impede long-term retrogradation.

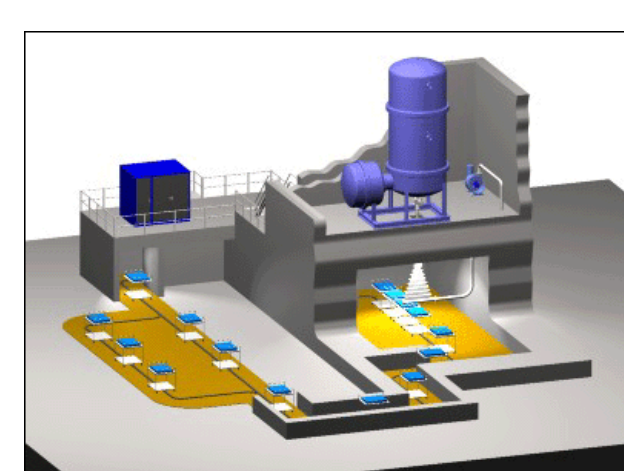
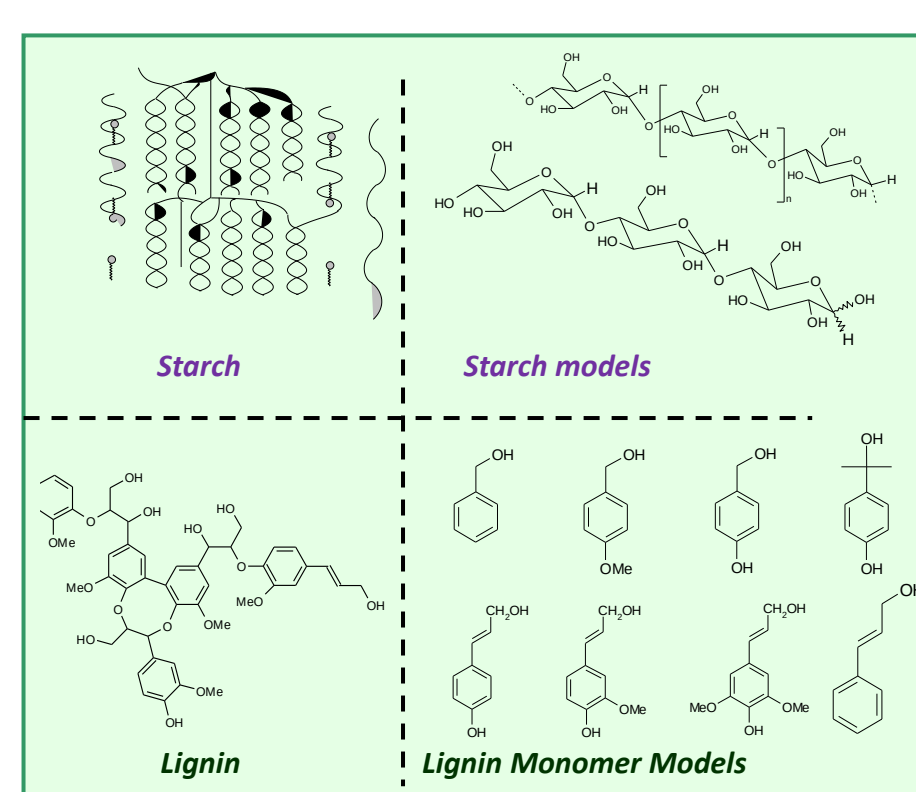
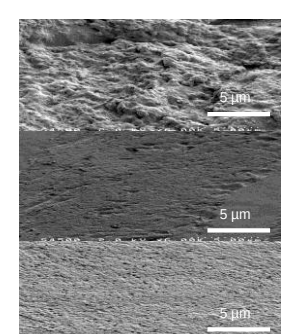
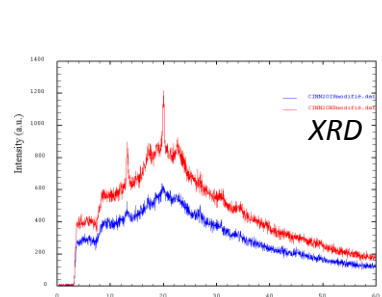


Concept

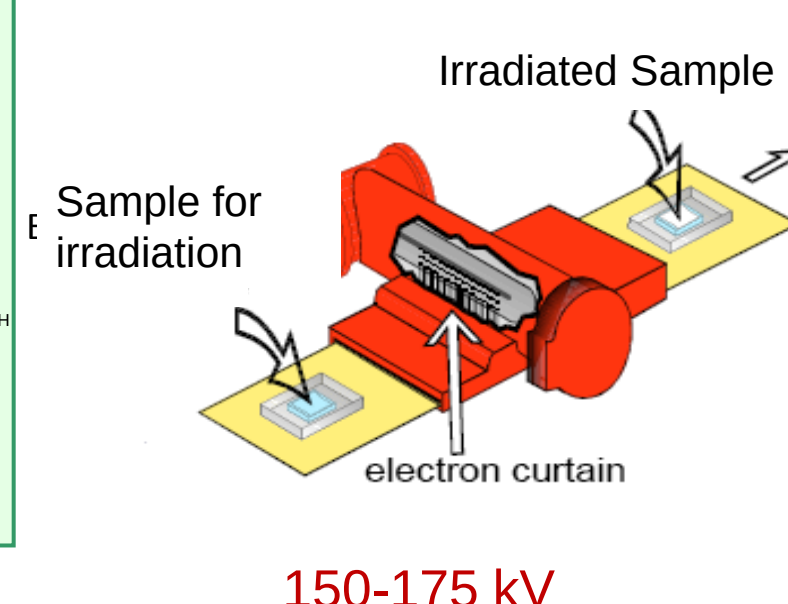


Structural Modifications From :
Scission, Crosslinking, Grafting

The research was carried out in 4 domains:
Method development, Mechanical Properties,
Surface Properties, and Radiation-induced
modifications.



10 MeV



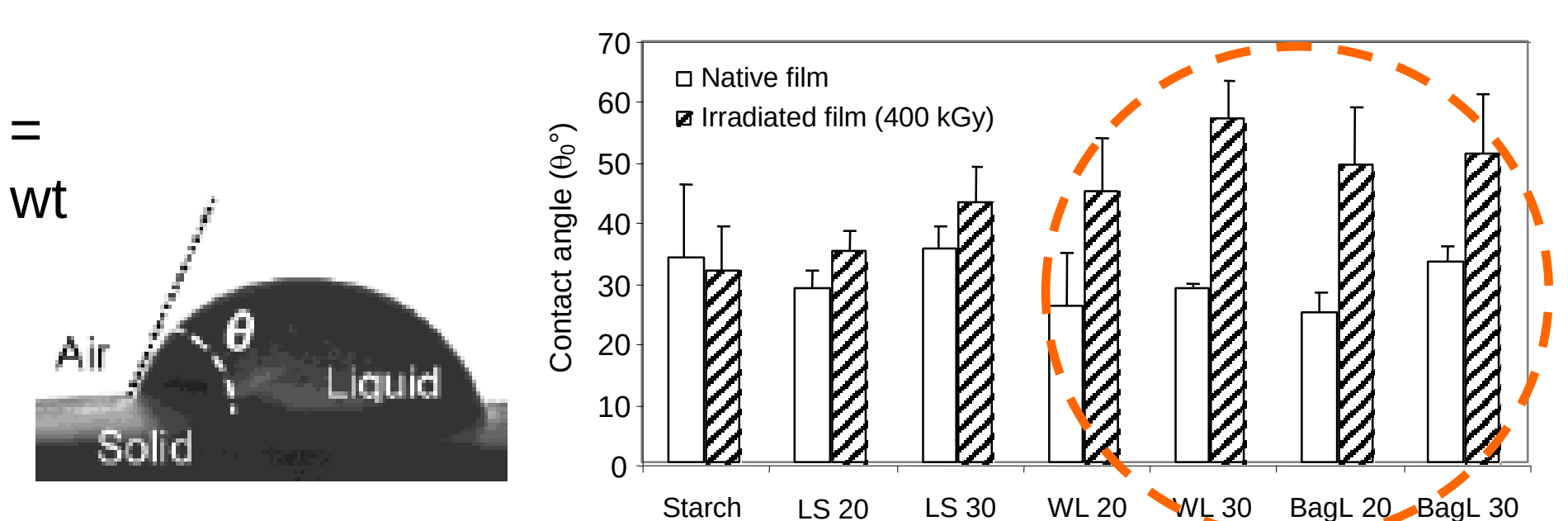
150-175 kV

Surface and Mechanical Properties

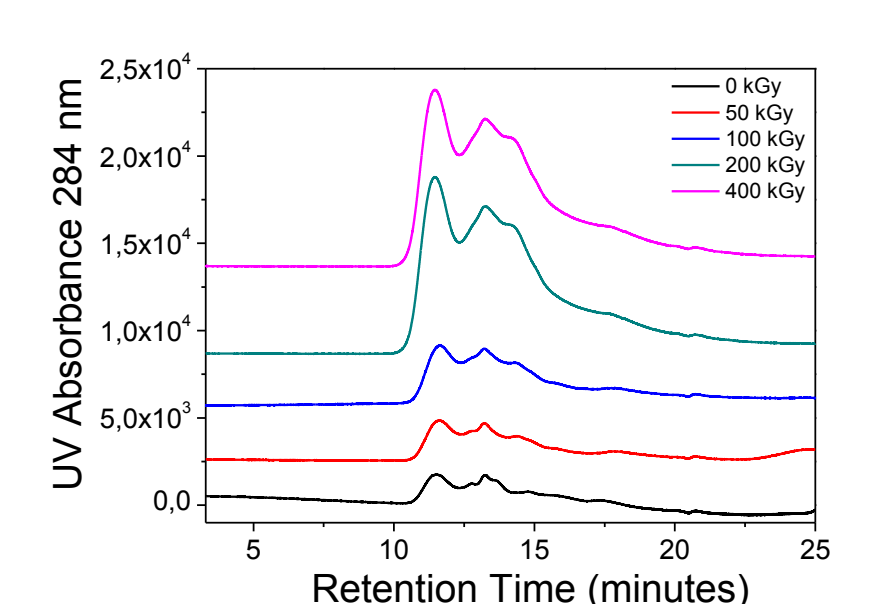
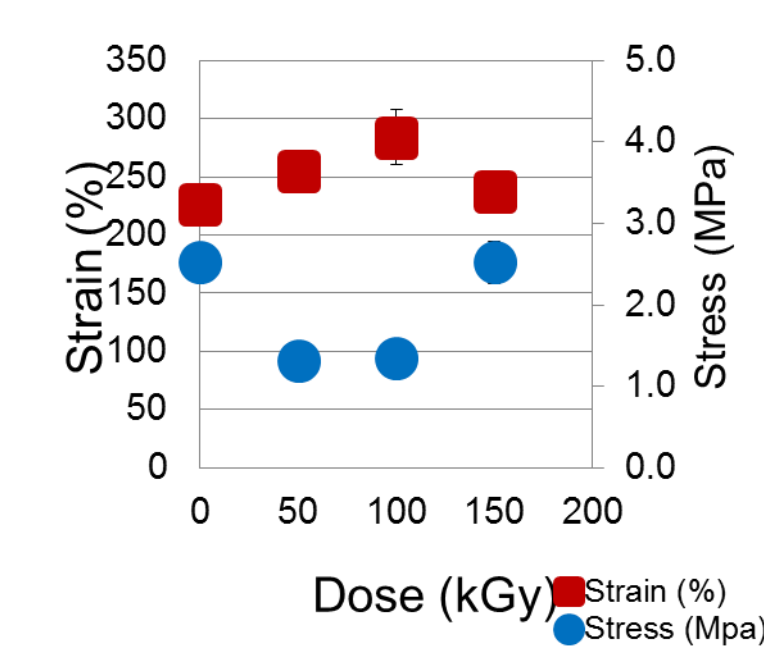
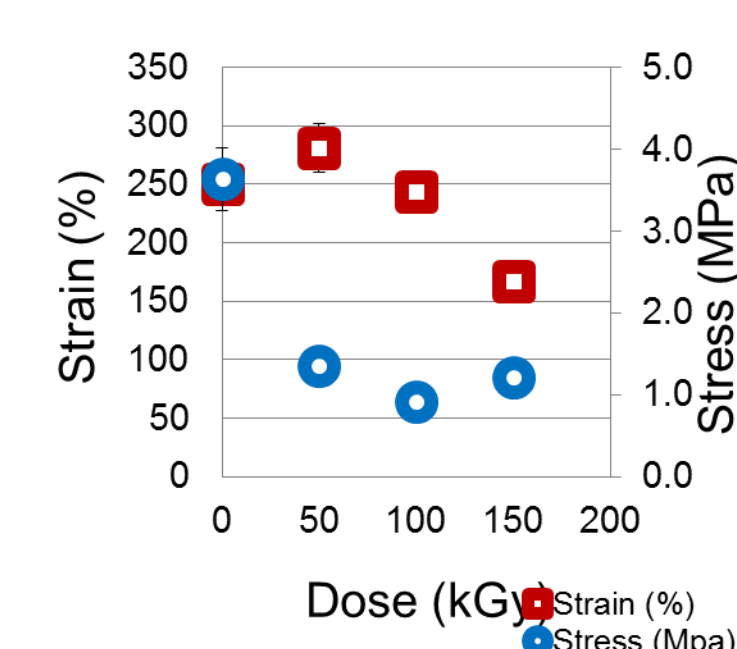
Surface hydrophilicity decreases of the starch lignin blends after irradiation.

Starch : Glycerol : Lignins =
70 : 30 : 20 or 30 parts by wt

- Lignosulfonates (LS)
- Wheat lignins (WL)
- Bagasse lignins (BagL)



Mechanical Properties can be modified in presence of Lignin-like additives. Radiation-induced grafting of aromatic additives competes chain scission. Final blend properties depend on blend composition and radiation parameters.



Modifications at Molecular Level

- Grafting of aromatic additives overcome chain scission
- Radiochemical yields G(S) and G(X) determined f ([arom])
- H-bonding and supramolecular interactions affect reactivity

Salient Results

- Hydrophobic surfaces can be obtained with $\theta_{\text{water}} > 110^\circ$
- Mechanical properties can be modified in presence of lignin-like monomers despite the ever existing chain scission
- Deformation breaking mechanisms monitored by videotraction
- Composition (plasticizer, aromatic additive) and radiation parameters determine final properties
- Aromatic additives exert strong protective effect against scission
- Starch molecular architecture can be tailored as desired

Conferences and Publications

Award at IRaP 2010 conference, Bethesda MD
Invited conferences at IMRaP 2011, Tihany Radiation Conference 2011,
Gordon Research Conference on Radiation Chemistry 2012

Baumberger et al., *J. Agric Food Chem*, 1998, 46, 2234-2240
Lepifre et al., *Biomacromolecules*, 2004, 5, 1678-1686
Khandal et al., *Radiat. Phys. Chem.* 2012, Vol 81, No. 8 (2012), 986-990
Khandal et al., *Radiat. Phys. Chem.*, in press
3 other publications are in process of review or submission

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