

## Modification of Biorelated Macromolecules through Grafting of Short and Long Side Chains

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Macromolecules of natural origin are either characterized by a hydrophobicity and low content of polar reactive groups ( as polyesters ) or by a high number of functional hydrogen bonding side chains . In order to improve the possible use of this materials as bioplastics , the chemical modification of the side chains and/or the combination with other macromolecules are highly necessary. Following our previous and current work in the functionalization [1] and blending [2] of polyolefins we are now attempting similar routes for proteins, polysaccharides and polylactic acid to improve their suitability in the development of innovative multiphase materials combining renewability and biodegradability with advanced thermomechanical and functional properties.

As far a proteins are concerned we combined an experimental approach [3] with a molecular dynamic modelling [4] to study the modification of molecular and supramolecular structure of Collagen and Gelatine. In the experimental approach gelatine was successfully modified according to different routes namely crosslinking with 1,6-diisocyanatohexane (HDI) [5], side chain binding of hydrophobic florescent groups with 1-naphtylisocyanate (NpI) and grafting of isocyanate terminated polypropylenglycole monobutyl ether chains (PPG). The modified gelatine derivatives showed that the modification procedures all based on the reaction of isocyanate with reactive side chains provides materials with a large variety of water swelling and solubility properties.

The controlled modification of cellulose fibres by grafting with a synthetic polymer was also investigated. The first step was the controlled esterification of cellulose fibre surface with  $\alpha$ -bromoisobutyrylbromide (BIBB), an ATRP initiator. Ethyl acrylate (EA) was grafted-polymerised from functionalised cellulose under ATRP conditions with or without the presence of a sacrificial free radical initiator (ethyl  $\alpha$ -bromoisobutyrate). The adopted polymerisation methods allowed to control grafting degree, grafted polymer chain length and, in perspective, grafted polymer structure, namely random and block copolymers.

Finally in case of polylactic acid the number of reactive groups in the original homopolymer was increased by transesterification with citric acid.

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