

## Synthesis and Characterization of Novel Cellulosics

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The search for alternatives to the fossil-based products has dramatically surged during past few decades primarily due to the problems associated with the scarcity of these sources and global environmental concerns. The steadily growing number of publications, patents and scientific meetings, coupled with the increasing commitments and investments by the public and private sectors to sustain the R&D initiatives are the best indicators of this reality. Among those many alternatives, exploitation of cellulose, as a raw material to develop novel products has been a constant attempt since it has never lost its both economic and industrial impact. Not only is cellulose known for its significant contribution as a raw material to many industries, but it's also as a fascinating sustainable macromolecule, which exhibits wide availability and versatile chemical reactivity to discover novel derivatives for broad range of applications.

Cellulose is found in nature as a condensation polymer of D-anhydroglucopyranose monomers, which are connected through  $\beta$ -1,4 glycosidic linkages. The chemical versatility of cellulose is provided by three units of reactive hydroxyl groups present on each monomer. A wide range of cellulose derivatives has been prepared and studied in the literature in consequence of the chemical functionalization of these three hydroxyl units including esterification, etherification and oxidation. Conversion of cellulose C2/C3 secondary hydroxyl groups to dialdehyde groups in the presence of periodate is an extremely useful method for regioselective oxidation of cellulose and to activate the polymer for further derivatization. Therefore, research is primarily focused on synthesis and characterization of wide range of cellulose derivatives exploiting periodate oxidation methodology.

The first study investigated the use of periodate oxidation as a potential method to synthesize a novel water soluble derivative of cellulose from bleached hardwood Kraft pulp. The work focused on the effect of increase in periodate charge followed by its sulfonation reaction on water solubility, morphology and structure of cellulose fibers. Increased periodate resulted an increase in carbonyl content (0.12-0.28 mmols/g) as well as the sulfonic acid content. Periodate oxidation and sulfonation reaction completely changed the surface morphology of cellulose fibers as observed by SEM and water solubility was significantly increased (2.85 -28.57 g/L) due to the introduction of sulfonic acid groups.

In order to further explore the application of periodate oxidation and sulfonation scheme, this method was employed on bead cellulose to prepare anionic 2,3-disulfonated beads in the second study. The study was carried out at low level of oxidation and sulfonation and it was concluded that slow stirring is required to retain the spherical shape of bead cellulose. Due to the presence of negatively charged sulfonic acid groups the beads were found to be agglomerated in presence of cationic starch, exhibiting their future application in chromatographic separation.

The next study applied the periodate oxidation fragmentation reaction to synthesize novel derivatives from cellulose nanowhiskers considering their increasing demand in various structural and biological applications. First of all, model primary amine compounds such as methyl and butyl amines were grafted to nanowhisker surfaces following periodate oxidation and reductive amination. It was determined that for complete conversion of the carbonyl groups to their corresponding amines an excess of amines (1:20 eq) is required. It was also reported that the nanowhisker surfaces became partially hydrophobic due to the incorporation of non-polar alkyl chains. Furthermore, the introduction of primary amines did not

affect the morphology and crystallinity of the nanowhiskers as examined by AFM and CP MAS NMR spectroscopy respectively.

Based on the previous study a novel drug delivery system was synthesized through chemical modification of cellulose nanowhiskers in the next study. Periodate oxidation and reductive amination reaction was followed to graft gamma aminobutyric acid (GABA) to cellulose nanowhisger as a spacer molecule followed by attachment to syringyl alcohol as a linker molecule. Syringyl alcohol was chosen to control the release of the drug or biomolecule following a classic 1,6-benzyl elimination release mechanism. All the products were identified and well characterized using various techniques such as FT-IR, NMR, XPS and TEM.

The final study employed the periodate oxidized nanowhiskers as cross-linkers to stabilize gelatin gels. Results showed an increase in the degree of chemical cross-linking (0.14-17%) between gelatin and nanowhiskers with the increased amount of aldehyde contents (0.062-0.230 mmols/g). It was concluded that the chemical cross-linking has a significant effect on relative increase in percentage of rigid protons, reduced water uptake ability and reduced pore size of the gels. Not only did chemical cross-linking improve the storage modulus of the gels (150%) and but it also increased the thermal resistance until 50 oC as obtained by rheological measurements.