

## Functionally Modified Natural Polymers such as Lignin - Synthesis, Characterisation and Photoresponsive Studies

The innovations in the development of materials from biopolymers, the preservation of fossil-based raw materials, complete biological degradability, the reduction in the volume of waste and compostability, reduction of atmospheric carbon dioxide released, as well as increased utilization of agricultural resources for the production of new "green" materials are some of the reasons for the increased public interest. Biodegradable polymers have offered scientists a possible solution to waste disposal problems associated with traditional petroleum-derived plastics. Rising oil prices helped to stimulate early interest in biodegradables in the 1970s, and concerns over the dwindling availability of landfill sites, environmental regulations, and increasing oil prices are reviving interest in biodegradable materials today. Biodegradable polymers may be defined as those which undergo microbially induced chain scission leading to photodegradation, oxidation, and hydrolysis, which can alter the polymer during the degradation process. Another definition states that biodegradable polymers are capable of undergoing decomposition primarily through enzymatic action of microorganisms to carbon dioxide, methane, inorganic compounds, or biomass in a specified period of time. The biopolymers may be obtained from renewable resources and also can be synthesized from petroleum-based chemicals. Blending of two or more biopolymers can produce a new biopolymer designed for specific requirements.

Lignin is a natural composite material in all vascular plants, providing the plant with strength and rigidity. The word lignin is derived from the Latin word *lignum* meaning wood. It is a main component of vascular plants. Indeed, lignin is second only to polysaccharides in natural abundance, contributing 24 - 33% and 19 - 28%, respectively, to dry wood weights of normal softwoods and temperate-zone hardwoods. By decreasing water permeation across the cell wall, lignin renders the plant resistant to biodegradation as well as to environmental stresses. Lignin is an amorphous, aromatic, water insoluble, heterogeneous, three-dimensional, and cross-linked polymer with low viscosity. The molecular mass of lignin is high (600 - 1000 kDa), although not uniform, varying greatly within isolated samples. The molecular mass of lignin is thus difficult to determine, and use of a conventional formula is not possible. Lignin is highly reduced and its carbon content is 50% higher than that of polysaccharides, which makes lignin energy-rich.

Normal softwood lignins are usually referred to as guaiacyl lignins because the structural elements are derived principally from coniferyl alcohol (more than 90%), with the remainder consisting mainly of p-coumaryl alcohol-type units. Normal hardwood lignins, termed guaiacylsyringyl lignins, are composed of coniferyl alcohol and sinapyl alcohol-type units in varying ratios. In

hardwood lignins, the methoxyl content per phenylpropanoid unit is typically in the range of 1.2 - 1.5. Grass lignins are also classified as guaiacyl-syringyl lignins. However, unlike hardwood lignins, grass lignins additionally contain small but significant amounts of structural elements derived from *p*-coumaryl alcohol. Grass lignins also contain *p*-coumaric, hydroxycinnamic, and ferulic acid residues attached to the lignin through ester and ether linkages. The lignin concentration is rather uniform across the secondary wall, but there is a significant increase in lignin concentration at the boundary of the middle lamella and primary wall region.

The present work deals with the development of a series of photoreversible environment-friendly systems based on lignin. The core systems having free hydroxyl groups were functionally modified with selected photochromic molecules such as 1-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)-acetic acid, 2-oxo-2H-1-benzopyran-3-carboxylic acid, 3-((E)-(4-aminophenyl) diazenyl) naphthalen-2-ol carboxylic acid and 4-(1-pyrenyl) butyric acid. The modification was achieved by functional transformation such as esterification. All the chromophoric systems selected for the present study have free carboxyl functions. These carboxylic functional groups were attached to the biopolymeric cores through esterification of the free alcoholic functions of the cores by DCC coupling. The newly developed systems were soluble in polar solvents, "nature friendly" and "Green" in their properties. The esterified products were isolated, purified by column chromatography or membrane dialysis. All the products were characterised by FT IR, UV-Visible, <sup>1</sup>H NMR and fluorescence emission spectroscopic analysis and thermal studies. The systems thus developed are: lignin - 1-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)-acetic acid, lignin - 2-oxo-2H-1-benzopyran-3-carboxylic acid, lignin - 3-((E)-(4-aminophenyl) diazenyl) naphthalen-2-ol carboxylic acid, lignin - 4-(1-pyrenyl)butyric acid. Spectral studies show that all these photochromic systems have successfully introduced into the cores and thermal studies indicate optimum stability for all the products. All the biopolymeric core systems functionalised with photochromic moieties were subjected to UV-Visible absorption studies, light fastening studies, fluorescence emission analysis and thermal analysis. The systems showed excellent light absorption, light stabilisation and fluorescence emission properties.