

Tapping Trees for their Nanotechnology Potential

Assoc. Professor Orlando Rojas and his team in the Colloids and Interfaces Group at the Department of Forest Biomaterials, North Carolina State University are excited by the potential of trees to create a wealth of new products and materials based on nanotechnology.

Assoc. Prof. Orlando Rojas is group director with 15 graduate students and two postdoctoral research associates. He is part of a department that offers a premier teaching and research programme and has adopted an ever-increasing interdisciplinary approach to its research efforts. Linked by biotechnology, nanotechnology, surface science and other disciplines, the department is exploring possibilities of new genetic strains on fibre sourcing, new recycling methods, developing new materials and innovative uses previously thought to be waste. They are also looking at improvements in manufacturing and processing methods.

Current research towards nanomaterials

The dynamics of enzymatic degradation; biosensor development; friction and adhesion in polymeric interfaces; adsorption dynamics and, the separation, derivation and use of natural polymers and surfactants are all areas of interest to Orlando Rojas' group.

"We realize the tremendous potential trees possess as photochemical factories that use air, sunlight and water to produce highly nanostructured materials that are the building blocks for their own construction," says Orlando Rojas. More importantly, he points out, are the opportunities these resources present for the production of sustainable, renewable, recyclable, and environmentally-friendly products to meet the needs of society. Forest products are capable of providing an enormous range of wood-based lignocellulosic materials with a multitude of applications.

Orlando Rojas explains, "Forest biomass is a difficult substrate to analyze at the nanoscale, yet it is a necessity to fully appreciate the unique features of the plant cell walls. A challenge here is that compared with most other organic macromolecules, the polymers in lignocellulosic biomass form highly interconnected structures that are soft, hydrophilic, and non-conducting. The basic interactions of water and biomass and evaluation of nanoscale accessibility and reactivity of the cell wall remain as an important challenge."

His group has made important contributions to a number of key research areas including progress in the topic of lignocellulosics as precursors of high performance biopolymer structures. "We have developed platforms to convert lignocellulosic biomass into value-added materials and (bio)composites," says Orlando Rojas. The use of cellulose nanocrystals in composite nanofibres with hydrophobic polymer matrices is an example of this.

Applications of QCM-D

Some key research developments that have involved QCM-D measurements include initial studies on the adsorption of polyelectrolytes on solid surfaces, where a range of tools was applied to relate the extent and dynamics of adsorption to polyelectrolyte and surface charge densities, the strength of adsorption, etc.

QCM-D has been part of a platform based on quartz microgravimetry to screen pure and multi-component cellulase enzymes and to study the effects of inhibitory components in the hydrolysis of cellulose substrates by studying enzymatic activity. QCM-D is used to test the adsorption of surfactants and polyelectrolytes on cellulose, lignin and other polymeric surfaces. "We have been using QCM-D to screen enzyme activities and test adsorption phenomena on thin films relevant to lignocellulosic and textile materials," notes Orlando Rojas.

Dr. Rojas comes from the Royal Institute of Technology in Stockholm where he worked as a Senior Scientist in the Department of Chemistry, Physical Chemistry after obtaining his Ph.D. in Chemical Engineering from Auburn University. He was also faculty in the Department of Chemical Engineering of Universidad de Los Andes (Venezuela). His research focuses on surface and colloid chemistry and the adsorption behaviours of surfactants and polymers at solid/liquid interfaces.

Dr. Rojas is the 2009 Chair and 2007-2008 Programme Chair of the Division of "Cellulose and Renewable Materials" of the American Chemical Society. He is also Associate Editor of the Journal of Surfactants and Detergents of the American Oil Chemist's Society and was recently appointed Fellow of the Finnish Distinguished Professor Programme.



Dr. Rojas and some of the graduate students in his group who use QCM-D.

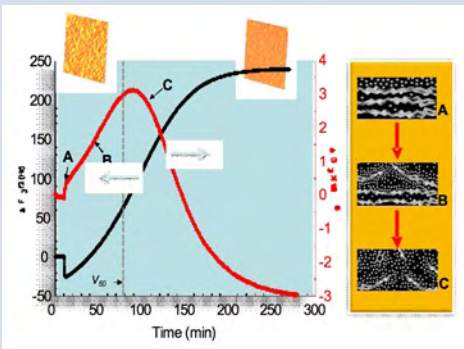


Figure 1 shows the change in frequency (black curve) and energy dissipation (red curve) as a function of time for a cellulose sensor exposed to a dilute solution of cellulase enzyme in acetate buffer (pH 4.5 and 40°C). The cellulase enzyme solution was introduced ca. 10 minutes after injection of the buffer solution. The dip in the frequency curve indicates binding of the enzyme on the cellulose substrate. A fast adsorption is observed after which the frequency increases rapidly with time. This increase in frequency is indicative of the reduction of surface mass due to cellulose hydrolysis by the enzyme. A plateau in frequency is observed after ca. 200 min due to the exhaustion of the film or the inability of the enzymes to degrade the residual cellulose any further. The dissipation curve shows the evolution in viscoelasticity of the film. The panel on the right illustrates proposed morphological changes that result from hydration, enzyme action and film deconstruction upon hydrolytic activity as time proceeds, closely related to changes in the registered energy dissipation (see *Langmuir*, 24(8), 3880-3887(2008)). Illustration adapted from *Langmuir*, 24(8), 3880-3887(2008).

Textile Processing

The group has developed unique platforms to study interfacial phenomena relevant to textile processing. Ultra thin films of PP, PE, PET, nylon and cellulose have been used with QCM-D to elucidate the relationship between bulk and surface composition of lubricant and surfactant films deposited on polyolefin surfaces from surfactant solutions and emulsion systems.

Another research activity has been the study of structure-property relations in polyampholytes with extensive studies of the adsorption of polyampholytes on cellulose and mineral surfaces. The group has proposed their mechanisms of action in inter-fibre bonding. By combining self-assembly and directed assembly technologies with polymer synthesis the group is developing novel high-performance fibres and composite materials based on renewable and recyclable cellulose substrates. "We have demonstrated possible routes to modulate the surface and bulk properties of these materials by using various grafting protocols," says Orlando Rojas.

Another application area for QCM-D is for testing stimuli-responsive properties of functionalized surfaces and in bio-sensing. This is complemented by other tools such as Surface Plasmon Resonance and ellipsometry to measure interfacial phenomena. For Orlando Rojas QCM-D's usefulness comes from its high sensitivity and the fact that the technique is suitable for dynamic, in situ, experiments. "It also provides key information about the effects of solvent coupling that otherwise are difficult to access with other tools," he says, "Data interpretation may be challenging but combined with other experimental approaches, it can be very useful and revealing."

Future Developments

QCM-D will continue to be used in the group's research. They are currently looking at the stimuli-responsiveness of thin films of functionalized cellulose nanocrystals. "We continue our work on cellulose biodegradation via enzymatic hydrolysis. We are also interested in relating tests with QCM with standards in paper and textile industry to measure the durability of surface finishes," says Orlando Rojas.

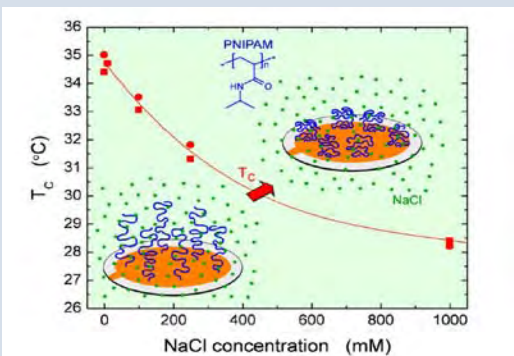


Figure 2 Schematic representation of the effect of salt concentration on the phase transition behaviour of thermoresponsive polymer brushes (collaboration with Jan Genzer's group, NCSU, see *Macromolecular Rapid Communications* 27: 697-701 (2006)).

Figure 3 Quartz crystal microbalance with dissipation monitoring (QCM-D) is employed to determine the effect of salt on the volume phase transition of thermoresponsive polymer brushes. Changes in mass and viscoelasticity of poly (N-isopropylacrylamide) (PNIPAM) layers grafted from a QCM-D crystal were measured as a function of temperature, upon contact with aqueous solutions of varying salt concentrations.

In this illustration the response of PNIPAM brushes grafted on a silicon wafer (dry ellipsometric thickness of the polymer layer of 15 nm) to cyclic changes in salt concentration is shown.

