NEUTRON TECHNIQUES FOR WOOD CHEMISTRY

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When a new biopolymer is incorporated into an industrial process (e.g. to improve the specificity of an emulsion or a foam or to replace a similar polymer derived from petrochemicals), its interactions with the other components of the solutions have to be well understood to ensure a controlled process. Such knowledge can be obtained through neutron scattering experiments. For instance, neutron scattering experiments allow investigation of the interaction of polysaccharides in solution with surfactants or evolution of films at the surface of a solution. Furthermore, neutron scattering allows us to study how water or a polymer modifies the structure of cellulose fibres, while inelastic and quasi-elastic neutron scattering allows us to follow the dynamics of water adsorption.

Keywords: neutron, characterisation, structure, polymer, wood

INTRODUCTION

Urged by the sudden rise of the price of crude oil, in conjunction with the quest for sustainable and green developments, wood chemistry has broadened its economic and societal impact. A re-examination of the wood chemistry field is suggesting many new applications and therefore many new industrial developments. The validation of these processes needs considerable research and development using all available tools.

Knowledge about materials or chemical reactions is often a key factor when engineering new products or new processes. The deeper and the more exhaustive this knowledge, the more controlled and less risky the manufacturing is. The properties of wood fibres depend to a great extent on their particular structure. This organisation may be characterised on a multiple scale, from the macroscopic level to the molecular one, as shown in Figure 1.

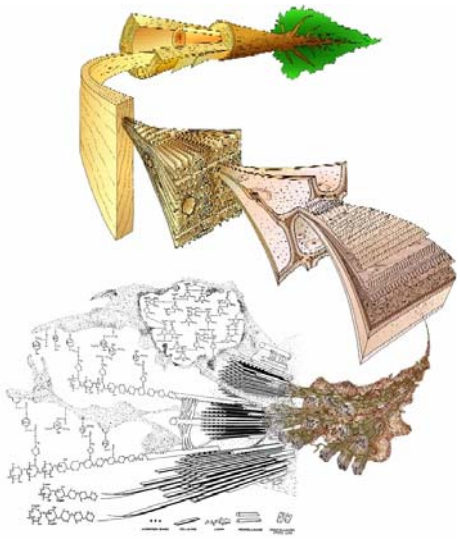

Figure 1: Wood as a multiple-scale material, from the tree to the molecule (illustration adapted from Mark Harrington (1996, ©University of Canterbury) and D. Fengel[1]

To understand and to improve the biochemical conversion underlying wood chemistry, it is crucial to know the conformation of the chains when solubilised. Knowing how polymers, such

as surfactants, graft onto fibres or interact in a polysaccharide/carbohydrate solution greatly helps to build new materials or new chemicals. When dealing with fibres, it is important to know their atomic structure, i.e. the way these chains organise and interact, as for example knowing how polymers, such as surfactants graft on to fibres. This paper gives an overview of the opportunities and of the recent work carried out at the Laue-Langevin Institute (ILL) related to wood chemistry, in order to enhance the potential role of these techniques in the process of innovation in this domain.

Presentation of ILL

The Laue-Langevin Institute is an international research centre at the leading edge of neutron science and technology, where neutrons are used to probe the microscopic structure and dynamics of a broad range of materials at molecular, atomic and nuclear levels. The Institute operates the most intense neutron source in the world, based on a single-element, a 58.3 MW nuclear reactor designed for high brightness. The reactor normally functions round-the-clock during four 50-day cycles per year, feeding neutrons to a suite of 40 high-performance instruments that are constantly upgraded.

The scope of the research carried out at the ILL is very broad, embracing condensed matter physics, chemistry, biology, materials and earth sciences, engineering, and nuclear and particle physics. Much of it impacts on many of the challenges facing society today, from sustainable sources of energy, improved healthcare and a cleaner environment to new materials for information and computer technology. For example, neutron scattering experiments have given us new insights into the structure and behaviour of biological and soft condensed matter, important in designing better drug delivery systems or improving polymer processing. They also provide a unique probe into the phenomena that underpin high-temperature superconductivity or the molecular magnetism that may provide the technology on which the computers of the future are based.

When used as a probe for small samples of materials, neutron beams have the power to reveal what is invisible using other radiations. Neutrons can appear to behave either as particles, as waves or as microscopic magnetic dipoles and it is these specific properties that enable them to uncover information which is often impossible to access using other techniques.

Neutron techniques

Classical techniques

Nowadays, very efficient laboratory techniques are commonly used in order to study the chemical reactions happening in mixtures of chemical compounds, whether they are made of gases, liquids and/or solids. For example, chromatography investigates the presence of chemical compounds. NMR can provide information on the environment of a specific atom, nevertheless the investigation on mixtures involving large molecules remains quite complex. With spectroscopy techniques (such as FTIR or RAMAN), vibrational information specific to the chemical bonds inside molecules are studied. Also, spectroscopy techniques require exhaustive libraries on inorganic compounds; they mainly operate in transparent or reflective modes. One of the key limitations is that the commonly accepted methodology is qualitative rather than quantitative. Moreover, the molecule of interest must be active in the IR region and not reactive to the used wavelength to probe the mixture. Another limitation is that the material under test must have some transparency in the spectral region of interest. Finally, such techniques are not always convenient for studying the mixture in the bulk under varying temperature or shears.

Using modern X-ray sources, most of these limitations are mitigated. The X-ray ultimate tool is the synchrotron source, which is much brighter than the laboratory ones. With X rays, one could use the spectroscopy technique (XPS) to retrieve information on elements or binding.[2] With small angle X-ray scattering (SAXS), structural information could be retrieved (polymer conformation, pores and their interconnections). X-ray fibre diffraction provides insights into the atomic description of the molecules composing the assembly of crystalline cellulose. To illustrate this, Muller *et al.* investigated the morphology of single native cellulose (flax) fibres by means of simultaneous small-angle scattering and fibre diffraction using an X-ray microbeam.[3] Their work shows the presence of disordered cellulose among the cellulose micro-fibrils and of defects inside the crystallites.

Nonetheless, the position of the hydrogen atoms remains invisible to X rays. When crucial, such information could be retrieved using neutron techniques.

The rationale for neutron techniques

The whole purpose of neutron techniques is to understand the intimacy of matter by comparing the properties (such as intensity) of the incident neutron beam with those of the outgoing neutron beam. Unlike X rays, the scattering or the diffraction of neutrons by atoms does not depend on the electron cloud, but on the nucleus. Therefore, only neutron techniques are able to probe in detail certain key structural aspects, such as hydration or hydrogen bonds, which are quite often the key to physical properties of fibres that need to be controlled.

Neutrons interact with the nuclei that compose the matter. They could interact through various mechanisms, from fission of the nuclei to scattering. The scope of our study includes only scattering of neutrons by nuclei and non-magnetic interaction between the beams of neutrons (thermal neutron ~25 meV, i.e. ~1.81 Å). Hence, when a thermal neutron interacts with a nucleus, the neutron is, in most cases, deviated.

When a neutron is scattered by a nucleus, its speed and direction change, while the nucleus remains with the same number of protons and neutrons as before the interaction (see Fig. 2). In an elastic scattering, the kinetic energy of the neutron and the nucleus are not changed by the interaction. In an inelastic scattering, the interaction introduces a modification in the nucleus (an excited state) that could lead to the release of radiation. The contribution to the scattered intensity is different for each isotope; for example, regular hydrogen and deuterium contribute differently. Also, light atoms (low Z) often contribute strongly to the scattered intensity, even in the presence of heavy atoms (large Z). This contribution is called neutron scattering length and represents the interaction of the neutron with the nucleus. The scattering length varies from isotope to isotope in atomic number, rather than linearly. Non-magnetic neutron diffraction is directly sensitive to the positions of the nuclei of the atoms.

Single Crystal and Fibre Diffraction

In the case of periodic arrangement of atoms (i.e. a basic structural unit, a parallelepiped-shaped volume known as the unit cell, which undergoes translational repetition in three dimensions to generate the entire crystal), the incident monochromatic beam is diffracted. The outgoing diffracted beam reveals a pattern. By its symmetry and intensity, this pattern gives information on the crystal organisation and on the composition of the unit cell. In the case of single crystal, the crystallographic technique could be used to describe the structure of the molecules that build the periodic network. In the case of crystal multiplicity, such as that of the fibrils that constitute the fibres, the diffraction still occurs and allows investigation in the sub-structure. Used in studies of crystalline or polycrystalline structures, the diffraction measurements give insights into the molecular structures within the length range from 1 Å to 10 Å. The typical size of a sample is from a few mm^3 to cm^3.

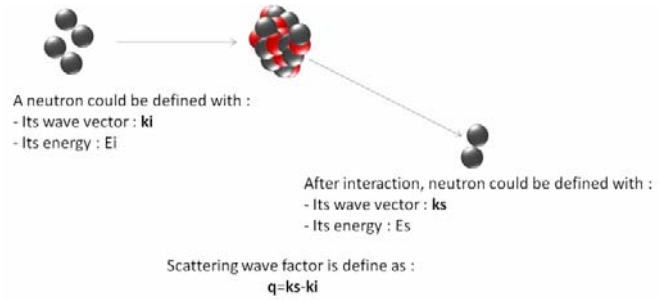

Figure 2: Illustration of neutrons scattering from a nucleus (from Dr. X. Thibault)

Small Angle Neutron Scattering (SANS)

The objective of a SANS experiment is to measure the differential cross-section (probability that a neutron will interact with the sample) with the variation of solid angle (see Fig. 3).

SANS does not attempt to see atoms, but is interested in the organisation averaged in time of particles or aggregates dispersed in continuous media (gaseous, liquid or solid). These measurements are directly linked with the neutron scattering length of the atoms composing the matter of the sample and is related to the shape and the sizes of particles or pores inside a homogeneous medium. As scattering elements are

large (grains, bubbles, micelles, etc.), diffusion occurs at very small angles and brings insights into the structure at a length scale ranging from 10 Å to 1000 Å.

Inelastic Neutron Scattering (INS) & Quasi Elastic Neutron Scattering (QENS)

This technique is similar to SANS, but instead of measuring the differential cross-section, it is used to measure the double differential cross-section (formula), with respect to the variation of solid angle and of flux. This resolves the change in kinetic energy, which occurs when the neutron collides with the sample, i.e. the quantity of energy transferred to the nucleus. Inelastic and quasi-elastic neutron scattering allows following, for example, the dynamics of water adsorption.

Reflectometry

The beam of neutrons shines onto an extremely flat surface where the sample is spread. In neutron reflectometry, the angle of the incident beam is equal to the angle of the reflected beam. The intensity of reflected radiation as a function of angle or neutron wavelength is measured. The exact shape of the reflectivity profile provides detailed information about the structure of the surface, including the thickness, density and roughness of any thin films layered on the substrate (<10 μm in depth, resolution 10 Å to 1 μm).

Examples of studies

Study of cellulose structure using single crystal and fibre diffraction

Neutron diffraction techniques have allowed the complete and thorough description of cellulose in its native forms and the mercerized one.[4-7] Further investigations[8] have revealed the structural pathway for the conversion of cellulose I to cellulose IIII, when cellulose is industrially processed, and have helped understand the bounding rearrangement when cellulose is transformed in ammonia-cellulose and then into cellulose III. Such works show the evolution of hydrogen bonding during the different steps of the industrial process.

Owing to such fundamental studies and to the advent and progress of molecular dynamics, a new kind of models[9,10] allows simulating the behaviour of fibrils in solution with ammonia. In such simulations, all molecules and each atom are simulated objects. The simulation of ammonia molecules penetration into cellulose fibrils could improve the existing chemical treatments and make them more effective, more environment-friendly or economical.

Figure 3: Illustration of a SANS experiment: the incident monochromatic neutron beam is scattered by the sample, the intensity of the deviated beam is measured on the detector. This measurement is then related to the shape, the size and the spatial organisation of the object in the solution (courtesy of I. Grillot, ILL)

INS and QENS

Using QENS,[11] the characterisation of the water adsorbed onto amorphous cellulose is performed in order to increase the knowledge on the mechanism of plant survival under 0 °C. In the transition range -68 °C < T < 0 °C, the water adsorbed onto amorphous cellulose was found to undergo a continuous transition from a high-temperature liquid to a low-temperature amorphous state. In other words, parts of the adsorbed water can be super-cooled by more than 65 °C! Different scenarios are invoked to explain the experimental observations.

Using INS techniques in combination with deuteration of polar group,[12] the dynamic response of certain hydroxyl groups within cellulose is studied. These measurements show that the accessible cellulose is on the surface of the microfibrils and that it corresponds to the disordered domain.

Study of mixtures/fibrous media using SANS techniques

Paper is the main component of a huge quantity of cultural heritage. It is primarily composed of cellulose, which undergoes significant degradation with the passage of time. SANS techniques are used to investigate the supramolecular structure of cellulose[13] and allow accessing to degradation agents, in ancient and modern samples. For the first time, SANS data are interpreted in terms of water-filled pores and show the increasing dimensions of water domains in paper as it undergoes degradation.

SANS techniques may be also used to investigate the structure of microcrystalline cellulose during enzymatic digestion.[14] Two modes of digestion are used for this study: a static and a dynamic one using a stirred suspension recycled through a flow cell. The structure of the nanopores is not modified in the static mode, unless significant agitation is applied.

When a new biopolymer is incorporated into an industrial process (e.g. to replace a similar polymer derived from petrochemicals), its interactions with the other components of the solutions have to be well understood to ensure a controlled process. Such knowledge can be obtained through neutron scattering experiments. An example of this is the preliminary study of cellulose whiskers in order to determine the structure of these surfactant-modified whisker suspensions in an apolar solvent.[15,16] This leads to a model of whisker coated by the surfactant in the solvent.

CONCLUSION

As shown above, neutron techniques are highly valuable in producing knowledge on the structure of cellulosic fibres and in increasing the understanding of biopolymer mixtures or biological processes. As a future prospect for wood chemistry, neutron techniques will have a role to play whether for producing polymers, for replacing the ones issued from petrochemistry, or for pharmaceutical applications, in order to save time in research and development, for example, when information on hydrogen bonding can not be obtained otherwise.

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