	Experiment title: Development of molecular structure and organisation during the processing of wet cellulose film	**Experiment number**: SC-1036
Beamline: ID02A	**Date of experiment**: from: 25/9/2002 to: 28/9/2002	**Date of report**: 27/8/2003
Shifts: 9	**Local contact(s)**: Dr. Volker Urban	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

A Mahendrasingam*, AK Wright*, DJ Blundell, J Rasburn* and W Fuller

School of Chemistry and Physics, Keele University, Staffs, ST5 5BG, UK

UCB Films, Wigton, Cumbria CA7 9BG, UK

Report:

This report describes the application of time-resolved X-ray diffraction techniques to investigate the development of the molecular structure and organization during the processing of wet cellulose film.

Commercially produced cellulose films (supplied by UCB Films) in the "never-dried" condition were placed into a purpose designed X-ray diffraction camera at a variety of temperatures. These experiments were used to follow changes in molecular conformation (from WAXS) and molecular organization (from SAXS) of cellulose molecules in response to mechanical and thermal stress and during subsequent drying. WAXS and SAXS data was recorded simultaneously with time-resolutions between 0.1 and 1 seconds by ESRF CCD detectors.

Figure 1 displays the typical variation in pore size for a viscose cellulose film compared directly to its relative water content and its relative (110) WAXS reflection (in this case the film is being dried at 50^{o}C over a period of 200 seconds). It can be seen from Figure 1 that the entire drying reaction is essentially completed within approximately 40 seconds; it also gives a

clear indication of the change in molecular organization of the cellulose film during a drying experiment. From Figure 1 also it can be seen that there is a decrease in water content which represents the loss of bulk water within the film (step 1). However there is also a secondary loss of water (corresponding to step 2 on the figure 1), this loss of water corresponds to loss of intermolecular, bound water. The relative water content was calculated by the summation of the X-ray intensities from the water peak on the two-theta scan (approximately 32^{o} on the two theta scan). It is significant that during this secondary loss of water there is a distinct shift in the pore size within the cellulose film. This change in molecular configuration occurs in the vast majority of samples studied.

We have identified that numerous processing and drying factors govern this distinct distribution of pore size within either type of cellulose film. It has been established that the introduction of a doping solution, and its concentration, alter considerably the onset of the acute change in pore size. Further study of samples dried at room temperature showed that both the initial concentration of doping solution and the length of soaking both affected the rate of molecular reconfiguration. The longer the soak times the higher the rate of water loss during step 2, hence higher rates of pore size change. It also has been noted that an increase in temperature also has this effect. Numerous doping solutions were investigated all of which alter the rate of molecular reconfiguration. However it was noted that, when cellulose film infiltrated with a solution of poly (propylene glycol) (PPG), this has a dramatic affect on the rate of molecular reconfiguration. Indeed it was noted that a drying experiment involving PPG could occur up to four times as quick as one without.

Using this collected data it has also been possible to identify distinct physical differences between older viscose technology films and newer (Lyocell type) films. Viscose films are isotropic and have a higher propensity to retain more water than their Lyocell type counterparts. The later, however, are highly anisotropic, with the orientation of the cellulose molecular chain axes arranged along the machine direction.

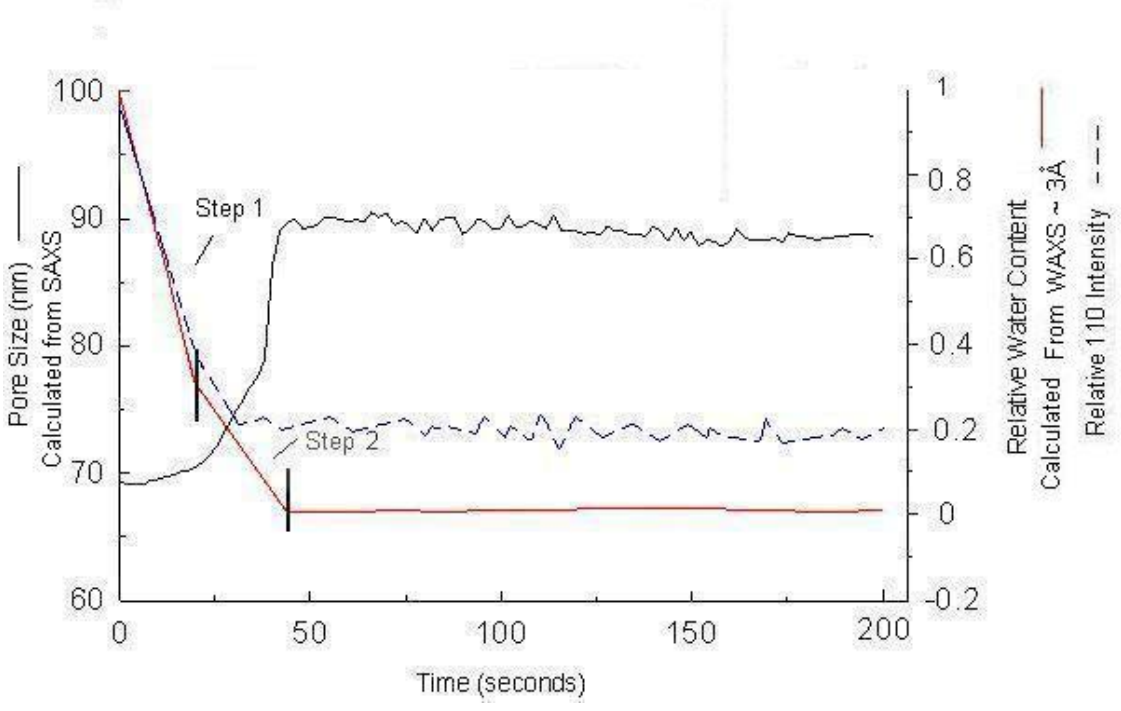

Figure 1: Showing Comparative Change in Pore Size Compared Directly to the Relative Water Content and the Relative 010 Intensity Within a Viscose Film Drying at 50^{o}C