PROBING THE NATURE OF CELLULOSIC FIBRE INTERFACES WITH FLUORESCENCE RESONANCE ENERGY TRANSFER (2007)

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Abstract: Among the most fundamental and practically important properties of paper are the physical and chemical parameters involved in fibre-fibre bonding. Inter-fibre bonding is solely responsible for internal cohesion in paper, because all stresses transferred between fibres operate through fibre-fibre bonds. Although several differing technologies are currently being pursued to improve fibre-fibre bonding the fundamentals of this process are still poorly defined. The future development of cellulosic fibre materials will require an improved understanding on the fibre-fibre interface. Current techniques are unable to provide useful information on the structure of the fibre-fibre interface at relevant length scales or under ambient conditions. A new tool is required that is capable of providing structural information about the formation and behaviour of fibre-fibre interfaces at the nanoscale.

Fluorescence resonance energy transfer (FRET) is identified as a potential new tool for the study of fibre interfaces. In order to develop this tool, it was necessary to successfully label cellulosic fibres with a fluorescent dye pair capable of FRET. A protocol for covalent linkage of fluorophores to natural and regenerated cellulosic fibres was developed and the absorptive and emissive properties of these dyes were characterized. The fluorescent response of these dyed fibres in paper sheets was studied using steady-state fluorescence spectroscopy.

Next, the main objective of the project was pursued, which was to image fibre-fibre interface topography with nanometre resolution. Fluorescence micrographs of fibre crossings were analyzed using the FRETN correction algorithm. The results suggested that energy transfer from coumarin dyed fibers to fluorescein dyed fibres was occurring. The FRETN surface for spruce fibre interfaces was distinctly different from that observed in viscose fibre. The effects of refining, wet pressing and fibre fraction on the spruce fibre interface were investigated with FRET microscopy. It was determined that the method was able to detect statistically significant differences when fibre fraction and wet pressing were varied. Image analysis of fluorescence micrographs of white spruce fibres indicates a FRET signal is being produced at fibre crossings and that it can be manipulated with wet pressing load.

The coalescence of fibre interfaces during drying was observed with the technique and a logarithmic relationship between increasing average FRETN values and drying time was identified. The FRET signal from once-dried fibre crossings increases dramatically after rewetting and wet pressing for a second time. This indicates that the material within the fibre bonds is still compliant after a single drying cycle.

Lastly, a model system of polysaccharides films was employed to investigate the difference between natural and regenerated cellulose fibre interfaces. It was found that cellulose is less capable of reducing the average interfibre distance either through resistance to deformation or the inability to participate in interdiffusion. On the other hand, the xylan films demonstrated a wet pressing response that was similar to that observed for natural wood fibres. The results of the FRETN analysis of the polysaccharide film model systems indicate that lower molecular weight carbohydrates are likely to be significant contributors to fibre interface development.