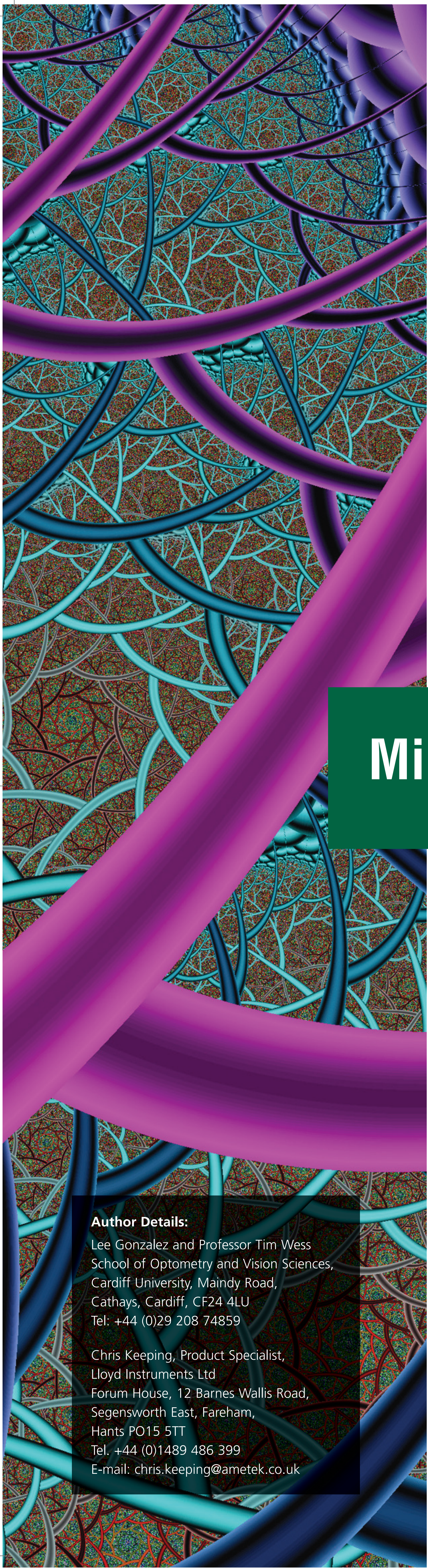

MATERIALS TESTING HELPS WITH THE CONSERVATION OF HISTORIC PARCHMENT DOCUMENTS

Parchment is manufactured from animal hides, composed predominantly of collagen. The most common skins used are from calf, goat and sheep [1]. The manufacturing process removes the hair, lipids and other non-collagenous materials through the use of lime baths, stretching and scraping [2]. Parchments often appear white due to the addition of minerals and finishing techniques. Archeological evidence suggests that parchments were in use as a writing material as far back as 200 BC, it is therefore of no surprise that some of the most valued texts and works of art in history, including the Domesday Book and the Dead Sea Scrolls were recorded on parchment. Even today, parchment is still used to record modern British Acts of Parliament. The preservation of our cultural heritage through the conservation of parchments is therefore of great importance. Understanding collagen interaction and the processes involved in its decay is central to defining the steps necessary to mitigate them. Research sponsored by the National Archives of Scotland and the National Archives of England and Wales is being carried out at the School of Optometry and Vision Sciences, Cardiff University to examine the degradation of historical parchment [3]. Using cutting edge biophysical investigations they are able to examine the changes in structural integrity, mechanical properties and conformational alterations of the collagen structure to identify the stages of degradation and investigate possible causes.

The research projects at Cardiff are investigating the degradation states of parchment and aim to:

- Provide a method of analysis to assess degradation of historical parchment
- Characterise the lipid profile of parchment with particular emphasis on fatty acid content and its role in the degradation process.
- Determine the state of gelatinisation of collagen immediately after manufacture.
- Investigate a suitable cleaning agent that does not induce changes in collagen structure.

Techniques at the disposal of the department for investigation of collagen structure include electron microscopy, synchrotron x-ray diffraction and neutron diffraction, the latter two being carried out at Diamond light source, Harwell UK, SRS, Daresbury, UK, and ESRF, Grenoble, France.

There are extensive facilities for light and electron histochemistry and x-ray diffraction, and there is a well-equipped Biophysics Suite. Materials tensile and compression test facilities are also available.

NOT AN OPEN AND SHUT CASE

In some cases parchments have been discovered in such a bad state of repair that unrolling them and reading the text has proved difficult. Invasive procedures to recover the documents' contents are

Microscopy Focus

discouraged because of their historical and cultural value. A joint project with between Professor Tim Wess and Dr Graham Davies at Queen Mary College, University of London has utilised X-ray tomography to overcome this challenge.

Documents, for one reason or another that cannot be opened are rotated in a beam of X-rays. The transmitted X-rays are then collected on a detector and using computation software the patterns of absorption are reconstructed to produce a computerised replica of the document. Here, the text can be read without unrolling the document.

PARCHMENT STRUCTURE AND DEGRADATION

Parchment primarily consists of a dense matrix of type 1 collagen; the water held within the collagen fibres is critical in maintaining stability, in essence it provides additional sites for hydrogen bonding throughout the collagen matrix. As water is lost, hydrogen bonding is disrupted and the collagen lattice is distorted, making the parchment more brittle *(Figure 1).*

Figure 1. The Declaration of Arbroath, prepared as a formal Declaration of Independence for Scotland in 1320

As the collagen degrades into gelatin, a disordered state, the collagen loses the ability to retain its structure when exposed to rapid changes in temperature, excessive temperatures and humidity. Unfortunately, iron gall ink, which has been in use on parchment from the 12th Century, induces changes in the collagen lattice (at the point of application) [4].

This process is called "iron gall ink corrosion." Over time, chemical processes, in particular the acid hydrolysis and oxidation, catalysed by ferrous ions cause the slow deterioration of the ink; this however is dependent not only on the particular ink composition but the storage conditions of the parchment [5].

MATERIALS TESTING INVESTIGATIONS

Other much simpler measurement techniques, however, have an important part to play in the parchment degradation jigsaw puzzle. It is extremely important to understand the implications of any physical treatment carried out on parchment. Aqueous treatments have always been important in parchment conservation. Although it is acknowledged that treating parchment with water also brings about significant, and often permanent, structural and mechanical changes, less attention has been paid to the characterisation and quantification of these influences, particularly with a view to optimising conservation procedures. For example, the removal of creases and folds in documents being prepared for public viewing is often achieved by treating the material with a mixture of isopropyl alcohol and water at a 90% or 80% alcohol to 10% to 20% water ratio. Unfortunately the isopropyl alcohol displaces water from the collagen and produces a stiff and brittle system.

One alternative is to use glycerol, but although it does not make the parchment brittle, it leaves a greasy residue on the surface, which is not desirable. By using tensile testing methods to measure the Young's Modulus of treated and untreated parchment, the change in stiffness can be quantified.

Author Details:
Lee Gonzalez and Professor Tim Wess
School of Optometry and Vision Sciences,
Cardiff University, Maindy Road,
Cathays, Cardiff, CF24 4LU
Tel: +44 (0)29 208 74859

Chris Keeping, Product Specialist,
Lloyd Instruments Ltd
Forum House, 12 Barnes Wallis Road,
Segensworth East, Fareham,
Hants PO15 5TT
Tel. +44 (0)1489 486 399
E-mail: chris.keeping@ametek.co.uk

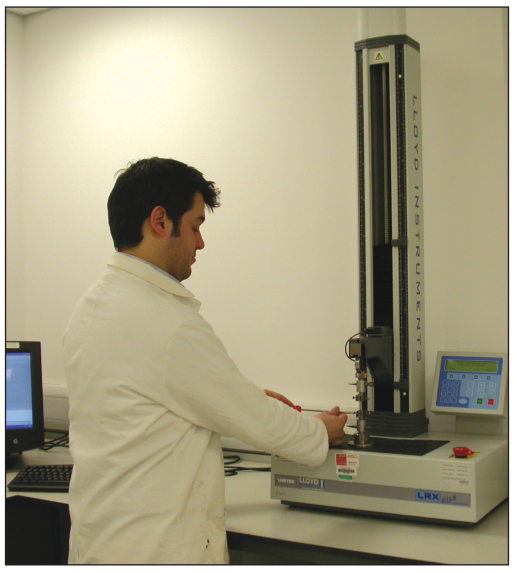

Figure 2. Tensile testing in progress

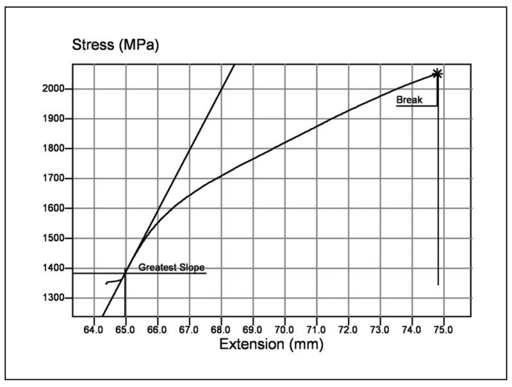

Figure 3. Stress-strain curve for untreated parchment

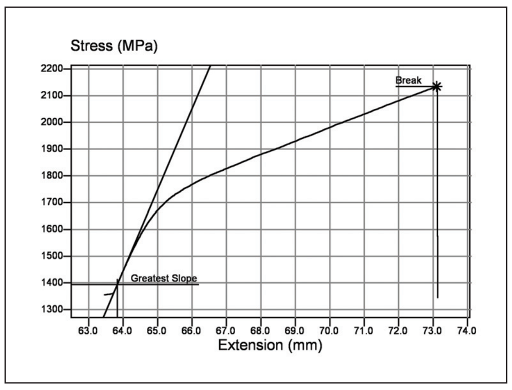

Figure 4. Stress-strain curve for parchment treated with 100% isopropyl alcohol

Young's Modulus, or modulus of elasticity, is a measurement of the rate of change of strain as a function of stress. It represents the slope of the straight-line portion of a stress-strain curve. This method of testing is used to determine a sample's behaviour under an axial stretching load. Small strips approximately 40 mm x 5 mm are cut from treated and untreated parchment samples. Each strip is mounted on an LRXPlus universal single column materials testing machine from Lloyd Instruments, equipped with NEXYGEN™ MT materials test and data analysis software and Ondio™ application builder software and a custom-made sample handling jig *(Figure 2)*.

Tests are carried out on three strips from each sample. *Figures 3 and 4* show the stress-strain curves produced by the software for untreated parchment and parchment treated with 100% isopropyl alcohol respectively. Young's modulus and the final breaking stress are automatically recorded. For the two samples shown here, the measurements are as follows: ≈4MPa and 6MPa respectively. These initial measurements show a measurable correlation between the change in stiffness of the treated material and the treatment method. In principle this technique could be used to evaluate the final stiffness of parchment samples treated with a variety of different solvents and concentrations. By correlating this with the efficacy of each treatment for crease removal, the crease removal treatment could be optimised.

COLLAGEN FIBRE ALIGNMENT

Another interesting phenomenon was observed during the tensile testing experiments. When a parchment is manufactured the animal skin is stretched and pinned at the edges.

This helps to provide a tight surface from which the hair can be scraped. The pinning of the skin is often so tight that the edges of the parchment are seen to change colour. The centre of the animal skin is opaque whereas the edges are translucent. It was unclear to the cause of this feature and it was hypothesised that a thinning of the fat layer that covers the flesh side of the skin may have occurred.

However, during the tensile testing it was discovered that the translucent parchment regains the opaque colour as it is stretched, particularly at the point of breaking where the stress and strain are greatest.

It is now thought that the opaque colour is a consequence of the alignment of collagen molecules in the animal skin.

INTO THE FUTURE

Materials testing has a relevant role to play in the understanding of the properties of ancient parchments and their treatments. Tensile testing allows the ready measurement of other mechanical properties including elastic limit, tensile strength, yield point, yield strength and elongation, so there is potential for this technique to be used further in conservation to evaluate the effects of other treatments on the mechanical properties of the parchment.

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> ***Materials testing has a relevant role to play in the understanding of the properties of ancient parchments and their treatments.***