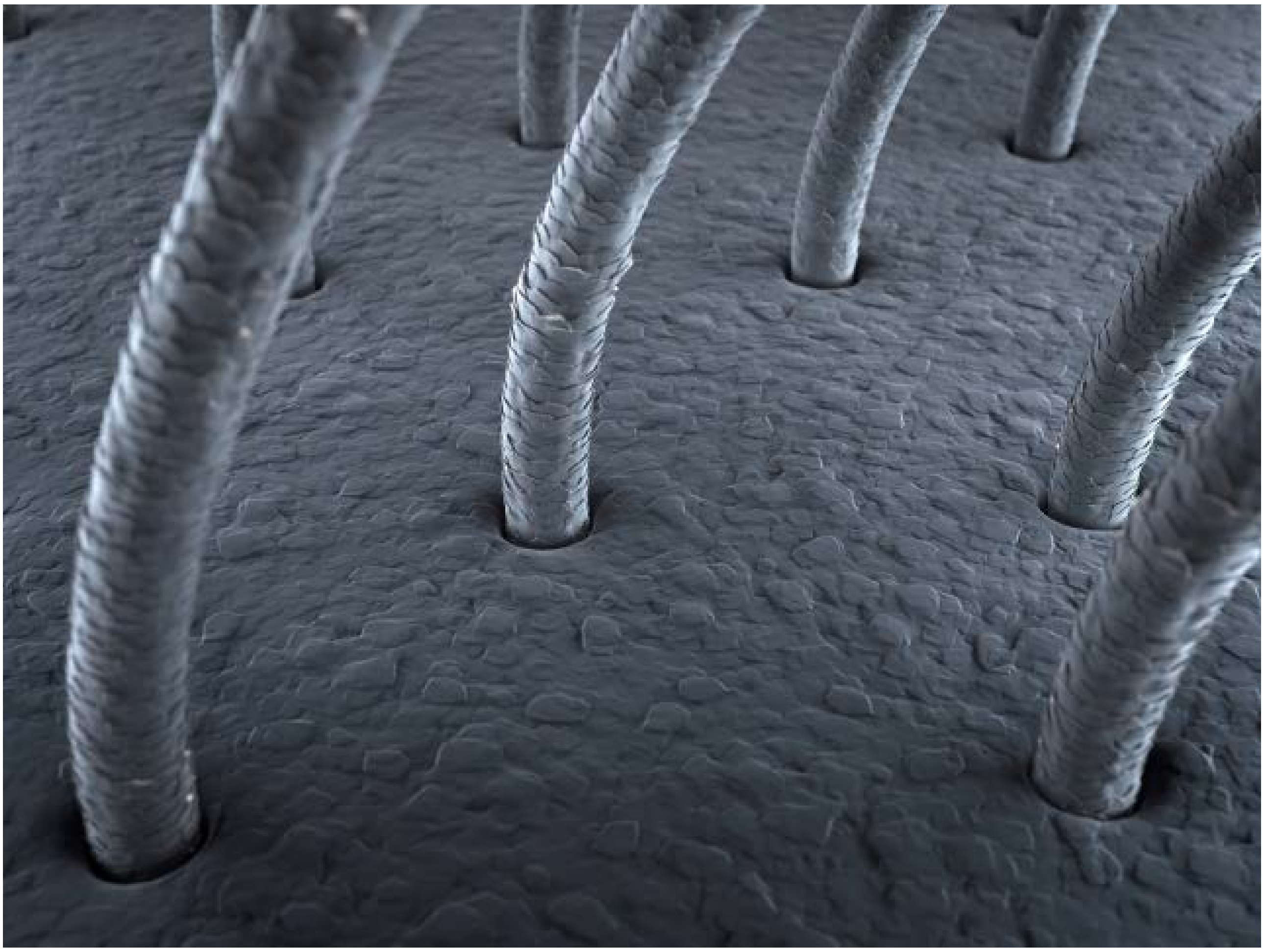
MEASURING THE CHEMICAL & PHYSICAL PROPERTIES OF HUMAN HAIR SURFACES

Dr Chris Pickles



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SUMMARY

The surface characterisation of hair fibres can deliver important insights into the performance of hair care products and in the development of improved product formulations based on an understanding of the connection between product use and the resulting surface properties of the treated hair fibres. This paper reviews the range of relevant hair properties together with the use of topographical and chemical surface characterisation techniques for their determination. Non-contact white light interferometry and 3D scanning electron microscopy are used to investigate topographical consequences such as scale height and hair damage. These techniques provide statistically based metrology of hair surfaces either parametrically or as quantified 3D images. In addition we describe the application of chemical surface analysis techniques including X-ray Photoelectron Spectroscopy (XPS) and Secondary Ion Mass Spectrometry (SIMS) to the determination of chemical residues and natural substrates in terms of material identification, level quantification and spatial distribution. In all cases practical applications are described.

CHEMICAL PROPERTIES OF HAIR

The structure of hair is intimately linked to its chemistry which imparts its particular physical properties. Hair is an outgrowth of the epidermal region of the skin comprising the hair follicle and the hair shaft. New cells are continuously produced in the lower portion of the hair bulb and push the previously formed cells upwards. As cells reach the upper portion of the bulb they begin to change into six cylindrical layers. Melanocytes in the hair bulb produce the melanin pigment which gives hair its colouration. The structure and chemistry of these hair features can be explored through extraction, drying and surface analysis using SEM (Scanning Electron Microscopy) and mass spectrometry - specifically ToFSIMS (Time-of-Flight Secondary Ion Mass Spectrometry).

In the mid-follicle region, the growing cells die, harden and form the hair which is a mixture of hair proteins such as keratin. These proteins and protective fatty acid esters on the hair surface can be characterised analytically to monitor the effects of hair treatments and damage. The most abundant surface lipid on human hair, 18-methyl eicasanoic acid (18-MEA) can be readily detected using ToFSIMS from which its *relative* surface levels can be directly related to the surface treatment(s) applied. 18-MEA is the only covalently bound surface lipid, the level of which is related to the gloss/sheen of hair, and its removal during, say, bleaching processes can be duly measured. Some consumer healthcare companies are looking to protect hair by derivitising lipids *in situ* during hair treatment or by depositing them directly from treatment formulations.

The hair shaft comprises dead cells and keratins along with binding material and small amounts of water. Terminal hairs on the scalp are lubricated by sebum from the sebaceous glands of the follicle which can lead to greasy hair. The uptake of product ingredients from greasy hair treatments can be monitored using surface analysis techniques such as ToFSIMS and XPS (X-ray Photoelectron Spectroscopy).

The keratin strands in the hair cortex lie longitudinally through the length of the hair and low sulphur keratin fibres are compressed into bundles held together by a mass of sulphur rich keratins in a fibre-matrix. The fibre-matrix is strong giving hair its particular physical properties. The outermost layer of the hair (the cuticle) is made up of between six and ten overlapping layers of long cells or scales. Each of these scales is around 0.3 µm thick, 100 µm in length, and 10 µm in width. These dimensions vary with age and ethnicity. The scales lie along the surface of the hair like tiles on a roof, with their free edges directed towards the tip. Microscopy techniques such as SEM allow scale height measurements to be made in relation to the use of conditioning treatments, where a glossy appearance may be indicative of scale coverage, or to the use of curling tongs/hair straighteners, which compress the scale heights, again producing a glossy hair finish.

PHYSICAL PROPERTIES OF HAIR

The physical properties of hair depend on its geometry. Physical properties such as elasticity, porosity and texture can vary widely from hair-type to hair-type and the surface physical condition arising from hair care products can vary. These variations allow a range of treatments to be exploited to create different effects and finishes (dye treatments, perms, shampoos, conditioners).

ELASTICITY

Elasticity enables human hair to resist forces that can change shape, length and volume allowing it to recover shape without damage. Wet hair can stretch by up to 30% and return to its original length when dry. Over-stretching hair leads to permanent damage and shaft breakage. Hair elasticity is dependent on the keratin fibres in the cortex. Chemical treatments of hair such as bleaching affect the cortex and such damage changes the hair's elasticity. Hair with poor elasticity stretches less, will not curl, breaks easily on grooming and is difficult to perm. It is useful to determine the elasticity of hair when developing hair treatments.

'STATIC'

'Fly away' hair is caused by static electricity. When dry hair is rubbed, static electricity builds up on the hair shafts with like charges repelling each other to give the fly away effect. High levels of conditioning agents in shampoos and/or conditioners reduce this phenomenon. The distribution and location of components from shampoos and conditioners can be monitored using imaging ToFSIMS to produce chemical maps. Strategies to counteract the effect include the use of positively charged polymers to neutralise the negative charges built up through combing.

TEXTURE

Hair texture is related to the diameter of individual hairs (larger hair diameter gives 'rougher' hair) weathering exposure and the use of hair treatments. Hair texture can be monitored using white light interferometry which allows the surface roughness and scale heights to be quantified with nanometre resolution.

POROSITY

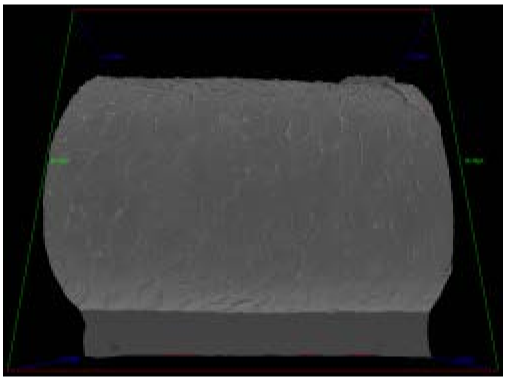
The porous nature of hair shafts is exploited by semi-permanent changes such as dyeing and perming. Treatments open the scales on the cuticle for penetration enabling reaction with the keratin to produce the effect. Over time the scales close up again to protect the hair shaft. Damage to the cuticle and scales makes the fibres prone to split ends. White light interferometry and 3DSEM can be used to monitor surface damage whilst mass spectrometry, and specifically ToFSIMS, can be used to monitor the distribution and location of perming and dyeing ingredients.

An understanding of the physical and chemical properties of human hair has been instrumental in the growth of that part of the consumer healthcare industry. The surface analysis techniques available have allowed the interrogation of hair surfaces and have provided an understanding of the chemical and physical changes associated with treatment products thereby enabling the development of new and more effective hair care treatments.

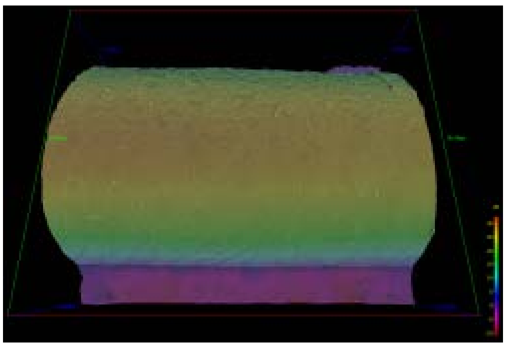
SURFACE CHARACTERISATION METHODS FOR HAIR

3DSEM (3D SCANNING ELECTRON MICROSCOPY)

Available software provides the capability to convert pairs of stereoscopic digital SEM images into a 3D representation of the area sampled. The resultant calibrated image contains z (height) information allowing metrology of macro and micro areas. The main benefit of this is that the metrology of materials which are difficult to determine by other methods (such as rough surfaces, angular metals, cutting tools, fibres) can be easily resolved. Furthermore, compared to white light interferometric methods, the lateral resolution in X and Y is significantly superior.



3DSEM image of a human hair



3DSEM image of a human hair with colour height scale

WHITE LIGHT INTERFEROMETRY (WLI)

White light interferometry (WLI) is an optical metrology technique that provides measurement of the physical characteristics of a material including micro-topography, form and texture surface topography, roughness, dimensional metrology and layer thickness measurement. The resolution of the measurements is <1 µm in the x and y axes and <1 nm in the z-axis. Hence micro-features and topographic variations can be monitored in detail.

Processing of the raw data allows for the generation of a range of data formats including:

Pseudo-colour height maps

The colour scale is calibrated in nanometres, microns or millimetres. This allows 3D graphical representation of surface topography. Derived amplitude parameters allow classification of various aspects of topography - for example, Sa - the arithmetic mean of the deviations from the mean (the statistical average area surface roughness parameter).

Profilometry

Enables the generation of line scans across any user-defined XY locus of the sample. This is particularly useful for measuring the magnitude of specific surface features with high accuracy (nm).

Contour map plots (axonometric plots)

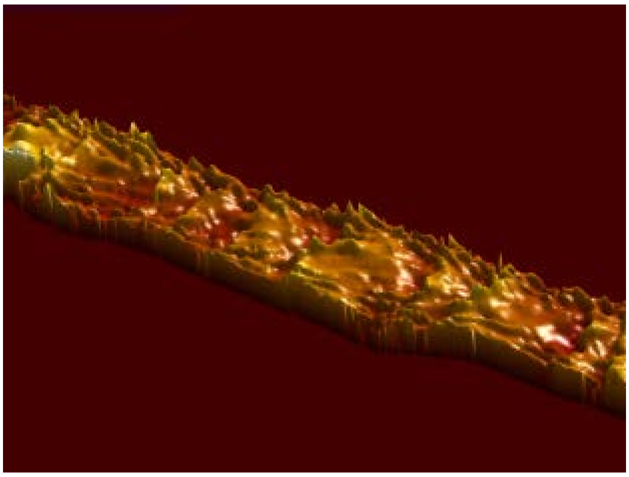
Regions of equivalent height are connected by colour-coded lines.

3D photographs and videos

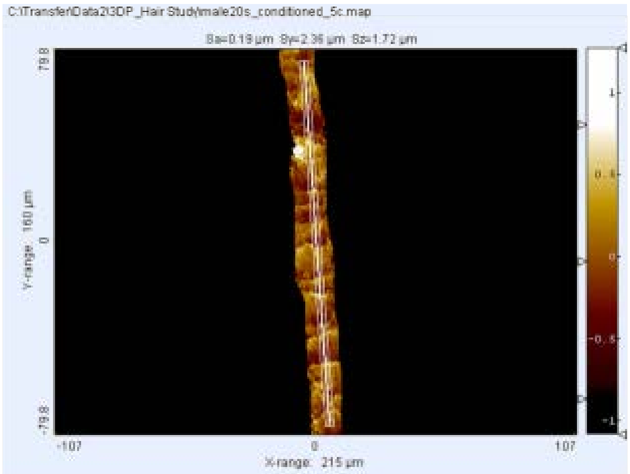
Show the sample in xyz space with variable angle viewing, zoom and variable lighting.

Film thickness (for sufficiently transparent layers)

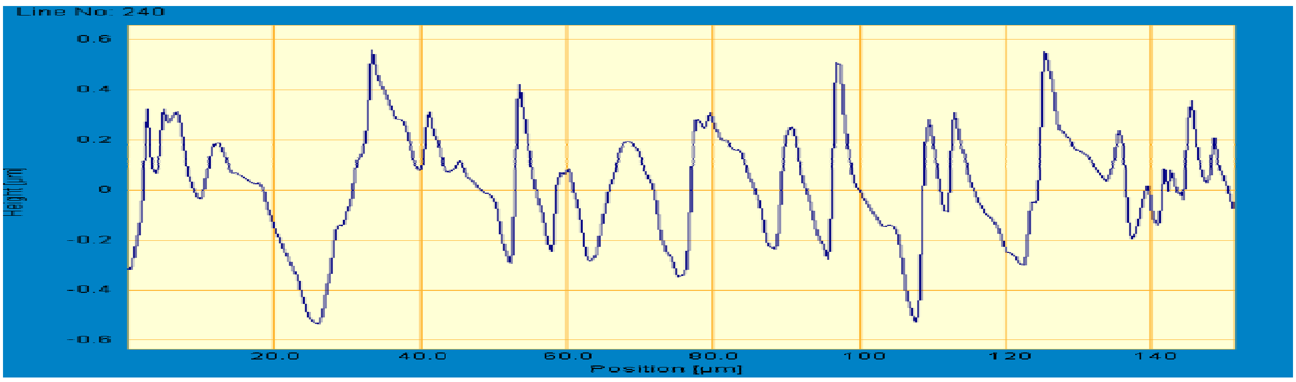
By focusing separately on a coating surface and then on the substrate surface and subtracting the data sets, a film thickness image can be generated and quantified. WLI has limited capability for highly curved surfaces but can be used for scale height determination on individual hair fibres using the line profile feature.



WLI 3D image of a human hair



2D topographical image with ‘thermal’ height scale and statistical surface roughness parameters



Line-scan analysis along the length of the hair giving scale height values

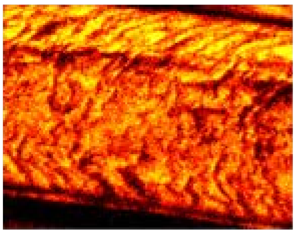
The technique is ideal for addressing the effects of hair applications, such as conditioners, on the surface structure modifications achieved from their use.

TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY (TOFSIMS)

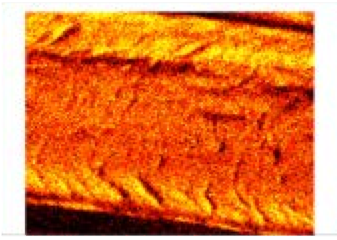
In ToFSIMS the sample surface is bombarded with a pulsed beam of primary ions. Secondary ions are sputtered from the sample surface and these are mass analysed to provide detailed surface chemical information on elements, chemical groups, molecules and polymer fragments. ToFSIMS is analytically highly sensitive (<ppm detection levels) and although it is not directly quantitative it can provide some semi-quantitative information.

ToFSIMS analysis provides mass spectra and chemical species spatial distribution images. The retrospective data processing capability of the instrument is particularly useful when a selected area of the sample is scanned in *spectrum-per-point* mode. In this mode a mass spectrum is acquired at each (μm scale) pixel point for the field of view and the resulting two-dimensional array of spectra is used to construct area specific species maps.

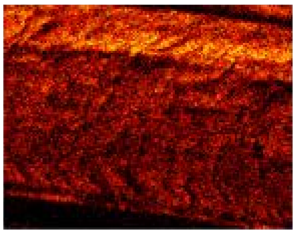
The versatile chemical mapping of molecular species available from the ToFSIMS technique has been applied to the study of residual substances on the surface of human hair. These include both natural (e.g. sebum) and synthetic (e.g. hair products) materials. Human hair has a diameter of around 60 - 70 μm. The sub-micron capability of the SIMS technique generates spectacular high resolution images showing the spatial distribution of residues with ppm sensitivity (brightness indicates abundance).



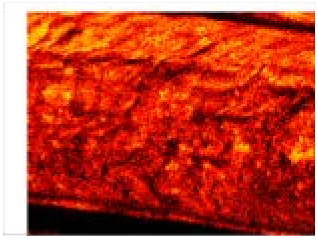
Keratin



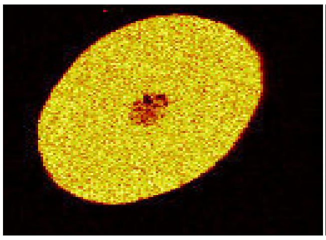
Silicone



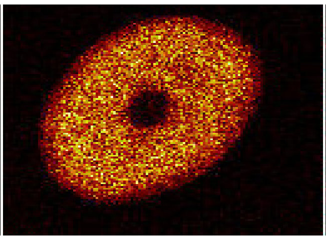
Fatty Acid



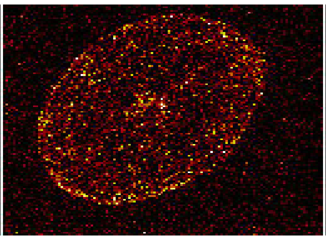
Alkyl Sulphate



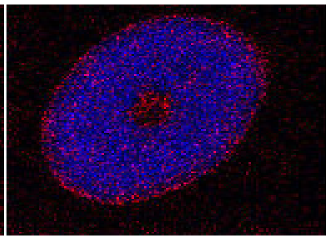
Protein



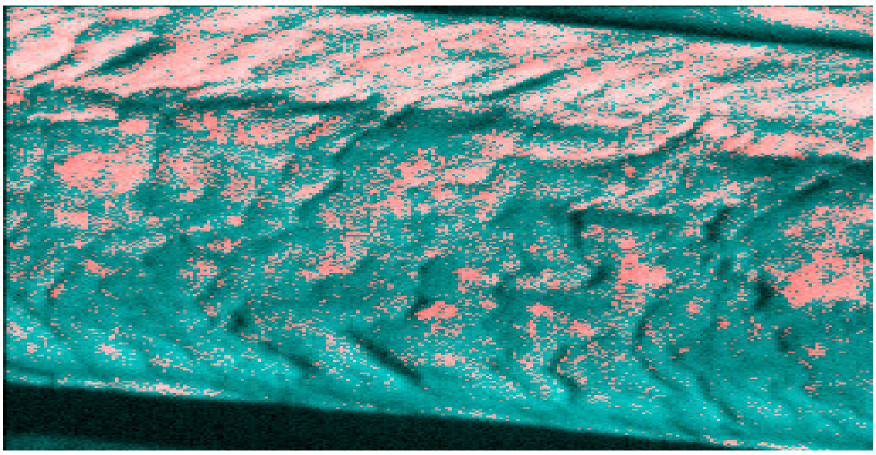
Alkyl Sulphate



Oleate



Total Ion Map



False colour overlay of alkyl sulphate (red) on keratin (green)

Product residues can be readily identified and their spatial distribution followed using this technique. This is important in hair product development not only from an efficacy standpoint but also in terms of ensuring potential adverse effects are addressed effectively.

CONCLUSION AND FUTURE PERSPECTIVES

Surface chemical mapping and topographical profiling has been used to support several areas of hair research, development, failure investigation, manufacturing issues and product claim studies over the last 20-25 years and particularly over the last 10 years. Lucideon has been at the forefront of these developments and is the only provider in Europe with the capability to deliver qualitative and quantitative chemical composition imaging by four separate techniques in addition to quantitative physical form imaging in 2D, 3D and video formats. Together with the other surface characterisation techniques it can be expected that the application of chemical and physical surface imaging technologies will spread more widely in the hair sector as their power to inform product and process performance phenomena becomes increasingly recognised.

ABOUT LUCIDEON

Lucideon is a leading international provider of materials development, testing and assurance.

The company aims to improve the competitive advantage and profitability of its clients by providing them with the expertise, accurate results and objective, innovative thinking that they need to optimise their materials, products, processes, systems and businesses.

Through its offices and laboratories in the UK, US and the Far East, Lucideon provides materials and assurance expertise to clients in a wide range of sectors, including healthcare, construction, ceramics and power generation.

ABOUT THE AUTHOR

DR CHRIS PICKLES - CONSULTANT TO LUCIDEON

EXPERTISE IN: AUTOMOTIVE; POLYMERS; SURFACES & COATINGS

Chris holds a Degree in Chemistry, a PhD in Polymer Science, and a Postdoctoral Fellowship.

AEROSPACE

Chris has been supplying surface analysis capabilities to the aerospace industry for over three years with particular emphasis on carbon reduction programmes involving composite developments, coating analysis and lubricant developments in relation to the introduction of biofuels.

AUTOMOTIVE

Chris has worked in both the aftercare sector as a Company Technical Manager and in tier one supply chain manufacturing as Managing Director.

Chris has been responsible for the plastic injection moulding and blow moulding manufacture of automotive component systems including highly technical mouldings such as fuel tanks and 3D spoilers. In addition Chris has also managed an integral supply chain utilising Toyota production system protocols.

POLYMERS

During his career, Chris has spent four years researching copolymer design for bulk property manipulation and the statistical mechanics of PVC to determine conformational sequencing. Chris's knowledge also encompasses plastics manufacturing, including injection moulding of glass-filled nylon and co-extrusion blow moulding of complex 3D components.

SURFACES AND COATINGS

In the field of surface science, Chris has conducted research projects on alternative material sources for surfactants and detergent product re-formulation. These include the re-launch of a branded fabric washing product in Brazil and the design of a surfactant system utilising renewable resources. As Technical Manager in the automotive aftercare industry he has managed the development and quality control of spray paints for high speed aerosol filling.