Abstract
A novel composite monofilament fibre containing cholesteric liquid crystalline materials and exhibiting clear thermochromic behaviour has been developed using polymer melt extrusion techniques.

The liquid crystalline material trapped within the fibres changes colour through the full visible spectrum from red to blue as the temperature is increased through a pre-defined temperature range. The behaviour is reversible, readily tunable to a desired temperature range and precise enough that a temperature change of less than 0.5 °C may be observable with the naked eye. These fibres can be knitted or woven into a textile product exhibiting similar thermochromic behaviour.

Applications of textile products exhibiting a reversible temperature dependent colour change are broad. Fibres exhibiting thermochromic behaviour within the body temperature range are predicted to become highly useful in medical applications. For example, incorporation into wound dressings for complete thermal mapping across a wound bed provides a simpler alternative to electronic based temperature monitoring systems. Detrimental developments such as inflammation and infection may be detected in the early stages using this type of system.

Introduction
Thermochromism is a phenomenon in which a material changes colour in response to a change in temperature. Colour in materials is expressed in a number of ways, for example as a result of wavelength absorption, reflection, or scattering. Many different types of materials exhibit thermochromic behaviour through different mechanisms. Examples include but are not limited to melt induced interactions in mixtures, thermally induced tautomerism, and thermally induced changes in crystal fields.[1] Thermochromic materials include leuco dyes, inorganic salts, polymer-gel networks and liquid crystalline materials, among others.[2]

The thermochromic effect may be reversible or irreversible, and may involve a change from coloured to colourless, colourless to coloured, from one colour to another, or through a range of colours as the temperature is increased or decreased.

To be practically useful for precise temperature indication, thermochromic materials need to be readily tunable to a desired temperature range, show clear, accurate and reversible colour changes and exhibit multiple colour changes for a higher resolution. Cholesteric liquid crystalline materials can exhibit thermochromic behaviour satisfying these requirements.

Molecules that form the cholesteric liquid crystalline phase are typically rigid, rod-like in shape and chiral in nature. The term liquid crystal refers to a state intermediate between a crystalline solid and an isotropic liquid, i.e. it flows like a liquid while having some orientational and positional order like a crystalline solid.

Within a certain temperature range, depending on the molecular composition, these materials form the chiral nematic phase, in which the preferred direction of molecular orientation rotates through the sample as shown in Figure 1a. The distance between one full rotation of the molecules is known as the pitch length. The resultant helical arrangement of molecules acts as a diffraction grating and Bragg
reflection occurs where incident light with a wavelength equal to the pitch length is reflected.[3] If the reflected wavelength falls within the visible range, the material will appear coloured. The pitch length is in turn temperature dependent, as shown in Figure 1b. Molecules twist to a greater extent in respect to their adjacent layers at higher temperatures, thus shortening the pitch length and causing the reflected wavelength to shift towards the blue end of the visible spectrum.[4] The opposite occurs when the temperature is decreased.

Figure 1. a) The helical arrangement of molecules in the chiral nematic phase. b) Bragg reflection shifts to shorter wavelengths as the temperature is increased

Within a certain temperature range, called the ‘colour play’ range, these materials appear coloured, where red is seen at the lowest temperature and the wavelength shifts through the visible spectrum to blue as the temperature is increased, as seen in Figure 2. This relationship is not linear, there is some decrease in sensitivity of the reflected wavelength to temperature closer to the blue end of the spectrum. The material is colourless outside the colour play range. The ‘bandwidth’ describes the temperature difference between the appearance of red and blue in the material, while the ‘red-start’ temperature describes the temperature at which red first appears.

Thermochromic liquid crystal (TLC) formulations typically consist of a mixture of multiple components where the compounds chosen as well as their ratios determine the colour play range. Depending on the mixture of commercially available compounds used, the red-start temperature can be fine-tuned anywhere between -30°C to 120°C and the bandwidth between 0.5°C to 30°C.[5,6] This makes these materials appropriate for many applications.

Figure 2. a) The defining features of a TLC formulation and b) the non-linear relationship between reflected wavelength and temperature.

TLC materials in the bulk form are viscous oily fluids and are highly sensitive to external contamination. Thus for many applications, liquid crystals must be isolated from the external environment. There are a number of ways in which liquid crystals can be incorporated into a host medium, examples of which are shown below in Figure 3.

Figure 3. Three different ways in which TLCs can be incorporated into a host polymer: a) as a thin film sandwiched between two polymer sheets; b) microencapsulated, and incorporated into a paint or dispersed through a transparent polymer matrix; c) directly dispersed as droplets within a transparent polymer matrix by means of phase separation.
It is important to ensure that when incorporated into another medium the liquid crystalline material can still form the chiral nematic phase. Any disruption in the ability for the chiral molecules to form this phase will destroy the material's thermochromic behaviour.

This work is focused on the development of a composite fibre containing the TLC material where the thermochromic behaviour is preserved in fibre form. The fibre is intended to be knitted or woven into a textile product for thermal mapping applications, especially within body temperature ranges.

**Materials and Method**

The TLC used in this work consists of mixtures of three or more different cholesterol derivatives tuned to change colour through various colour play ranges near the body temperature range (between 25-40°C). The liquid crystals were incorporated into a composite monofilament fibre approximately 100µm in diameter by means of a polymer melt extrusion technique. The resultant thermochromic behaviour of these fibres has been studied.

**Results and Discussion**

Composite fibres exhibiting thermochromic behaviour through a number of different colour play ranges have been successfully developed using polymer melt extrusion techniques.

Figure 4 shows the thermochromic behaviour of a composite fibre tuned to change colour between 32 and 36°C. Figure 4a illustrates the change in appearance of the fibres as the surrounding temperature is decreased through the working temperature range, while Figure 4b shows the relationship between temperature and the maximum reflected wavelength of incident light onto the fibres.

The thermochromic behaviour is completely reversible, very rapid (<1 sec), and has not been observed to change over time (≤2 months) providing the fibre does not remain exposed to UV light, to which liquid crystals are sensitive.

A colour gradient from the red end of the spectrum to the blue is clearly observed within these fibres when an appropriate temperature gradient is applied. Figure 5a shows fibre onto which a sharp temperature gradient has been applied, while 5b shows the thermochromic behaviour of fibre on a bobbin as a result of the bobbin being held by a warm hand. It can be seen that there is a clear outline of the hand print left on the fibres.
The fibre also shows promising retention of its thermochromic behaviour when knitted into a thin tube and twisted into a tight bundle, as shown in Figures 6a and b respectively.

Fibres exhibiting the thermochromic properties of TLCs are expected to find use in many applications, especially in the medical field as an alternative to electronic based temperature monitoring systems due to their high temperature accuracy and tunability. These fibres could be woven into a textile and incorporated into a wound dressing, for example, for complete thermal mapping of the wound bed and surrounding tissue by clinicians and patients over the time the dressing is worn. This may enable early detection of harmful changes in the wound bed such as inflammation and infection which would otherwise slow or prevent wound healing, allowing for more effective treatments and faster wound healing.
closure. Alternately, thermochromic fibres could be incorporated into stockings, socks or gloves for the monitoring of skin temperature at the extremities of limbs to ensure there is no detrimental loss in blood supply to these areas for patients who have had surgery or who suffer from severe venous insufficiencies.

**Conclusion**
This work has led to the formation of a novel composite fibre which exhibits clear thermochromic behaviour due to the incorporation of thermochromic liquid crystalline materials. These fibres have the potential to form various textile products which may be used to accurately and rapidly map temperature in various applications, especially in the medical field. The thermochromic behaviour is completely reversible, readily tunable and temperature differences of less than 0.5°C are observable with the naked eye.

**References**