Natural gemstone opals have long been sought after for their bright saturated colours. The study of opals reveals that the colour is produced by their internal structure causing diffraction of visible light. Irridescent fibres that display their tension through colour changes can produce fabrics with an entirely novel look. Researchers at the NanoPhotonics Centre based in the Cavendish Laboratories, (University of Cambridge, UK) in partnership with the DKI (Deutsches Kunststoff-Institut, Darmstadt, Germany) are working on industrially scalable structural colour materials for decorative, security and sensing applications. The Cambridge team led by Prof Jeremy Baumberg and Dr David Snoswell explain the technology behind these striking colour changing materials that are currently being developed for commercial release.

The diffraction causes the enhanced reflection of particular wavelengths of light that gives rise to the very pure and intense colours so characteristic of opals. Colour generated by diffraction is often referred to as 'Structural colour' and is found in a diverse variety of natural and synthetic objects including peacock feathers and the wings of tropical butterflies to dielectric mirrors and photonic crystals created in the laboratory. Commercially, synthetic structural colour materials are interesting because of their:

- Colour intensity: they can look 'metallic' although they usually contain no metal
- Colour play: the colour changes with viewing angle
- Resistance to fade: they contain no UV sensitive dyes

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• Low toxicity: they can be made with benign ingredients like silica and common polymers.

To produce structurally coloured materials it is important to understand the details of the structure required. The key is to produce a material where two translucent materials with different refractive



index are periodically alternated throughout the material in either 1, 2 or 3 dimensions (see Fig 1). The difficulty in making such a structure is the size of the elements which must be close to the wavelength of light, in the region

150- 250nm which is around 500 times smaller than the width of a human hair and beyond the resolution of an optical microscope.

Self-assembling spheres

There are a number of methods to produce ordered structures with such precision. Gemstone opals achieve their structure by the regular stacking of perfectly round glass spheres (*see Fig 2*). Polymer opals also consist of ordered spheres. Using clever chemistry similar to that used in the production of latex paints, a mass of nearly identical spheres for polymer opals are synthesised with a hard central core of cross-linked polystyrene, bonded to a soft outer shell of







polyethylene acrylate that has the consistency of chewing gum (see Fig 3a). When these spheres are subjected to shearing forces at elevated temperatures around 150° C, they self-assemble into an ordered 3D crystal that displays structural colour. The soft shells of adjacent particles deform and blend into a continuous matrix whilst the central cores are ordered in a regular pattern that diffracts light (see Fig 3b). The size of the particles controls the colour of the opals with small, medium and large particles producing blue, green and red opals respectively (see Fig 4). Trace quantities of nanoparticles can also be added to tailor the appearance of the opals. Structural colour is greatly enhanced in polymer opals by the addition of a very small quantity (<0.05 wt%) of carbon black nanoparticles.

Processing potential

Because the cores of the spherical particles are embedded in a matrix of the soft shells the entire crystal is flexible and rubber-like. Nevertheless the shells are not initially chemically bonded together which means that the opals display viscoelastic behaviour and can be made to flow under pressure. This has important commercial implications as the polymer opals can be extruded, rolled, moulded and processed in ways common to the production of plastics. Once the desired shape and ordering of the particles is achieved, the relative position of the spheres can be locked in by chemically bonding the shell



material of adjacent particles through either a thermal or UV initiated cross-linking process. Once a polymer opal has been cross-linked, the polymer opals will no longer flow and they take on the mechanical properties of a durable rubber. Pilot scale production of polymer opals has demonstrated 1 ton batches of particles that have been processed into sheet, films and fibres. Polymer opal fibres in a range of sizes down to 100 microns diameter have then been made in an extrusion process.



Reversible colour change -A new twist

Structural colour materials with rubberlike properties have interesting characteristics. Bending, stretching or twisting polymer opal samples results in a striking colour change. A green sample becomes blue when stretched; a blue sample can turn green when compressed. Bending a green sample can change its colour to red or blue depending on the bending direction (see Fig 5). Deforming the opals changes the spacing between the particle cores and hence affects the structural colour, however these changes are reversible allowing the original colour to be restored.

Thermochromic versions of the polymer

opals have also been produced that add temperature sensing characteristics. Samples have been produced that appear





transparent at room temperature but become gradually coloured as the temperature rises (see Fig 6). The effect relies on tailoring the core and shell materials so that their refractive index is matched at room temperature (sample colourless), but becomes mismatched (sample coloured) on heating due to different rates of thermal expansion between the core and shell. The chemistry of the core and

shell material can be further modified depending on the application. By changing the shell chemistry alone, liquid-like opals, opal putty and hard rubber samples have been produced.

Opals with less flexibility are more suited to making fibres that require tensile strength and a non-sticky surface, and samples have been produced to demonstrate this.

Industrial potential

The colour changing properties, together with the ability to mass produce the opals opens up an exciting range of applications (see Fig 7). Colour changes that occur on bending naturally highlight edges if a sheet of polymer opal is bent around an object. Thin sheet samples can transmit coloured light which is complementary to the reflected colour, producing striking effects. Decorative applications naturally come to mind, however the unique properties are also difficult to reproduce suggesting security applications and brand protection. The colour changes evident on bending and stretching lend themselves to applications where an inexpensive visual indicator of tension or flex is required. But perhaps the most pervasive use of the technology could be for polymer opal fibres woven into colour changing fabric.



100 micron fibre







Closeup photos showing highlights around bends in knitted opal. Polymer opal knitted by Kathryn Phillips

Future challenges

Currently the commercialisation of polymer opals is at the stage of market research and business plan development, with a view to forming a company in 2010. The basic technology is relatively mature, but product development requires investment for particular applications.