National Textile Center

FY 2003 (Year 12) Project Proposal

Project No. M03-MD14R

Competency: Materials

Nano-Crafted Layered Optical Filaments for Diffractive Colors

Project Team:
Leader Prabir K. Patra/UmassD/Polymer Materials and Engineering
Email: ppatra@umassd.edu Phone: 508-999-8803
Members: Steven B.Warner/UmassD/**swarner@umassd.edeu**/Fiber Science and Materials Engg.
Qinguo Fan/UmassD/**qfan@umassd.edu**/Color Science and Textile Chemistry
Paul D. Calvert/U of Arizona/**calvert@engr.arizona.edu**/Sol-gel Ceramics and Materials
Stephen H. Foulger/Clemson/**foulger@clemson.edu**/Optical Polymers and Photonics

Objective:

The objective of this proposed research is to start from the molecular level to design polymer fibers and filaments with useful and novel optical properties. The chief goal of the project is to gain a fundamental scientific understanding of the optical functionality of mirror fibers that can be used to create fabrics that reflect visible, UV and IR radiation for optimum cooling or transmit selected wavelengths for warming. The second specific aim of our research centers on methods for integrating into fabrics optical filaments with stress or chemical sensing, bar coding or other functions.

Relevance to NTC Mission:

The National Textile Center research emphasizes enhancing the knowledge base that drives the momentum of US industry competitiveness. This proposed research extends well beyond current state-of-the-art traditional fibers. Our research approach to dielectric omnidirectional reflector fibers that contain hidden "bar cods" and sensing materials within the fabric is very unique. The development of such fibers with giant birefringent optics (GBO) and light specific bar codes (LSBC) is an achievable advancement in the textile and telecommunication industries.

State of the Art:

Polymer fibers are ubiquitous in applications such as textile fabrics because of their excellent mechanical properties and the availability of low-cost, high-volume processing techniques; however, control over their optical properties has so far remained relatively limited. Conversely, planar dielectric mirrors are used to precisely control and manipulate light in high-performance optical applications, but the fabrication of these typically fragile mirrors has been mostly restricted to planar geometries and remains costly. We propose to combine and exploit some of the advantages of each of these seemingly dissimilar products in the fabrication of polymeric fiber with an exterior multilayer dielectric mirror. The principle has recently been demonstrated in interesting work at MIT, but the process is impracticable and the materials are too toxic for application to textiles (1). There are two conventional ways to create a mirror: using the surface of a layer of metal, or using a tuned interference stack composed of multiple layers of transparent dielectric materials. Metal mirrors are inexpensive and perform robustly across a broad range of angles, wavelengths and polarization but they exhibit limited reflectivity. Multilayer interference mirrors are routinely used for optical applications requiring high reflectivity and wavelength selectivity. Although they can be designed to achieve a wide range of optical properties each design typically performs across a limited range of incident angles, wavelengths and polarization. A key limitation of multilayered mirror is the decrease of selection of p-polarized light at material interface with increasing incidence angle and below a specific incidence angle the reflectivity of p-polarized light vanishes at a material interface (2). Using series of highly birefringent polymers in place of isotropic dielectrics, multilayer mirrors can be constructed that maintain or increase their reflectivity with increasing incidence angle. Although these mirrors do not possess a complete photonic band gap, it has been shown that they can be designed to efficiently reflect light of all incident angles and polarization across broad, selectable frequency ranges (3, 4). Such polymer mirror fibers or filaments could be incorporated into woven fabrics to produce a wide range of new optical effects.

Colors generated by layered structures are common in nature (Mohan Srinivasarao, Nano-Optics in the Biological World: Beetles, Butterflies, Birds, and Moths, *Chem. Rev.* 1999, *99,* 1935-1961). The iridescence of hummingbird feathers and of beetles, for instance, is due to layers of polymers or polymers and crystals that result in interference effects from the changing refractive index. In butterfly wings the colors arise from pigmentation and from interference between layers of scales or fibers and air gaps. In many cases the animal is also able to tune its appearance during growth or in response to its environment. It is thus clear that there are many environmentally friendly ways of producing interference colors in polymer fibers.

Reference:

1. Hart, S. D., Maskaly, G. R., Temelkuran, B., Prideaux, P. H., and Fink, Y., *Science* 296, 510 (2002).
2. Weber, M. F., Stover, C. A., Gilbert, L. R., Nevitt, T. J., and Ouderkirk, A. J., *Science* 287, 2451 (2000).
3. Fink, Y., Winn, J. N., Fan, S., Chen, C., Michel, J., Joannopoulos, J.D., and Thomas, E.L., *Science* 282, 1679 (1998).
4. Winn, J. N., Fink, Y., Fan, S., and Joannopoulos, J.D., *Opt. Lett.* 23, 1573 (1998).
5. Kong, J. A., Electromagnetic Wave Theory, EMW Publishing, Cambridge, MA, pp. 370, (2000).

Approach:
We will employ a three pronged approach in multilayer mirror fiber design. This consists of materials identification, fiber preform construction and fiber draw. Materials selection involves the identification of co-processible pairs of transparent materials with differing refractive indices. These would be a polymer and a nanosized inorganic phase, two polymers or a polymer and a crystalline organic filler. The target polymers will be good fiber-formers, including poly (ethersulfone), poly (ethylene terephthalate), poly (methyl methacrylate), polystyrene, liquid crystal polymers and polyetherimide. The inorganic phases will include non-toxic dielectrics such as TiO_2 , SiO_2, ZnO etc.

The combination of materials will depend on the chosen processing route. The MIT approach was to make a multilayered preform and then draw this down to a filament. For their method the two materials should exhibit similar flow properties at the drawing temperature, which requires a low glass transition inorganic material, most of which are toxic. This limitation can be avoided by using a nanoparticle-polymer composite or a second polymer as the high refractive index layer such as birefringent oriented polyester and nano size SiO_2 or the polymer particle systems mentioned above. In the fabrication of the omnidirectional mirror structures, the selected materials should exhibit low optical absorption over a common wavelength band, very similar viscosities at the processing temperature and good adhesion and wetting at the interface between two layers. The selected materials will be used to construct a multilayer preform, which essentially is a macroscopic version of the final fiber. We will coat the polymer film by rolling the polymer onto a glass tube then we will vacuum bag it with polyimide and heat it for consolidation followed by etching out of the glass that leads to the formation of preform. The preform will then be drawn down to filament. It is not essential that the inorganic layer remain intact during processing. If the material breaks up it leaves an air gap or a heavily filled polymer layer; these will also develop colors in the fiber by interference.

We will also develop multilayer coating methods based on sequential self-assembly where ionic polymers or charged particles are deposited as a series of alternately charged layers on a surface. By applying this to fibers, we can build up mutilayers a few microns thick by a series of rapid coating steps. This approach has already been used in the Calvert lab to print multilayers onto polymer sheets. Once co-deposited these self-assembled layers are totally insoluble. The coatings will include sol-gel hybrids with high refractive index and the appropriate rheology for coatings. In situ mineralization (project M00-D08) will also be used to enhance the refractive index difference between the layers, similar to the eye structure seen in figure 1. Mirror fiber reflectivity from both single fibers and arrays will be measured over the range from UV to near IR with an imaging spectrometer. The fiber structure will be analyzed using a Fourier transform infrared spectrometer-microscope combination. We will use gold-coated polymer fiber of matching diameter as a background reference for reflection measurement. Varying the thickness of fiber by varying the fiber draw and layers of materials within will tune the spectral information. We will use the layer thickness distribution developed from an atomic force microscope (AFM) in conjunction with measured refractive index values n_{1x} , n_{1y} , n_{1z} , n_{2x} , n_{2y}, n_{2z} as input for a multilayer optical model. We will measure these refractive indices from thick monolithic polymer films that have undergone same film fabrication process as the multilayer mirror. With the AFM-measured layer profile and dispersive refractive indices values we will match the measured transmission spectra at normal incidence and at 60° with modeled spectra using GBO refractive indices or isotropic refractive indices calculation. We will correlate the precise tuning of reflection spectra from invisible IR to visible radiation with the shifting of the photonic band gap. We will match the measured spectral information with planar-mirror transfer matrix simulation (5). Uniform layer thickness control, interlayer adhesion and inter diffusion through multiple thermal treatment will be assessed by SEM inspection of fiber cross section.

In this research Patra, Warner and Calvert will explore various processing techniques to fabricate the fiber preform and subsequent method design for final fiber. Fan, Patra, Warner and Calvert will explore the means of obtaining and investigating spectral information and developing interference colors. Calvert, Warner and Patra will develop sol-gel hybrids and in situ mineralization through nanocomposite development. Foulger will explore the optical functionality of the polymer filament. Patra, Fan and Warner will explore the fiber cross sectional inspection by SEM.

This Year's Goal:

We will begin our work using poly (ethylene terepthalate) and poly (ether sulfone), as the starting polymer. We will examine the thermomechanical and rheological properties of the polymers. We will study inorganic oxides and organic-inorganic hybrids for example polysilsesquioxanes (POSS) as the high refractive index phase. We will construct fiber preform and understand the processes involved. Multilayer self-assembly systems based on titania and zinc oxide nanoparticles and ionic polymers will also be developed and tested. In the subsequent years various other polymers will be studied to design the final fiber by developing nanocomposite via in situ mineralization.

Outreach to Industry:

Both textile fiber and telecommunication industries are potential partners. One of the PIs (SHF) is a former researcher of telecommunication division of Pirelli SpA and therefore we will have active interactions with this company relating to photonic research issues. We will also maintain and expand relationship by sharing our findings in conferences hosted by the Fiber Society, ACS, MRS and others. Textile industries will gain enormously by the development of low loss optical polymeric fibers.

New Resources Required:

A vacuum bag-molding machine will be required. Analytical instruments e.g. FTIR, TGA, DSC and Brabender Extruder and SEM that will be used, for our researches are available at the University of Massachusetts Dartmouth, University of Arizona and Clemson University.

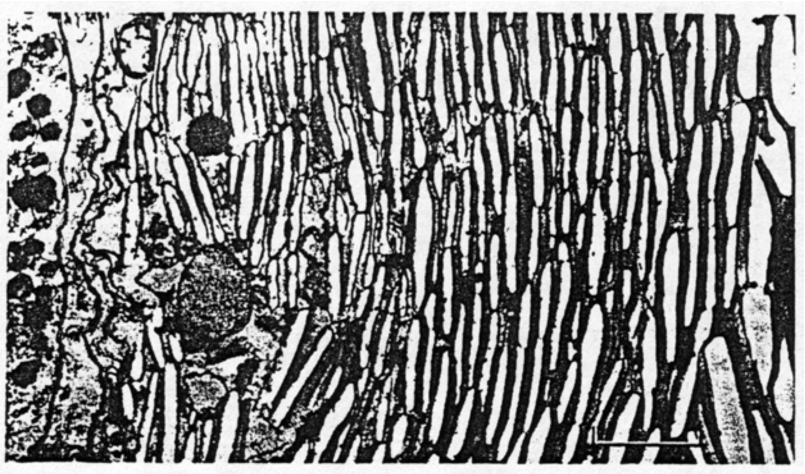

Figure 1. Layered guanine crystals in the reflective back layer of a scallop's eye. Bar = 1micrometer. M. F.Land., "The Optics of Animal Eyes" Contemporary Physics, 29, 435-455, 1988.