

Heat-Sensitive Polymers Change Color with a Change in Temperature

Thermochromic materials are used to provide a rapid, visual assessment of temperature. Currently available, commercialized thermochromics are based on either liquid-crystal technology or acid-base reactions. Both approaches require the thermochromic material to be microencapsulated to protect the active components from the surrounding environment. Liquid crystals offer a wide variety of color changes but they are not stable to unexpectedly high temperature excursions and they break down after repeated cycling. Acid-base thermochromics, from colored, acid-based dyes, provide sharp transitions and a broad color variety but also break down at high temperature excursions. The organic constituents in the acid-base thermochromics have a tendency to mobilize into the surrounding environment and many of these organic materials are toxic, which limits their use such as in contact with food or beverages. In both technologies, the microencapsulation requirement adds processing cost and typically sets a lower limit on the particle size to 10–20 μm , which prevents use in certain applications such as inks. Researchers at the University of Rhode Island have developed thermochromic pigments that overcome most of these problems.

The scientists use polythiophene derivatives as thermochromic materials. Polythiophenes (shown in Figure 1) have been intensively studied for their ability to become highly conducting when partially oxidized, as electrochromic materials, and also as components in organic light-emitting diodes. These properties are related to the conjugation derived from the alternating double-bond structure present in polythiophene.

As shown in Figure 2, polythiophenes are also thermochromic. They are bright yellow when hot and red when cold. The

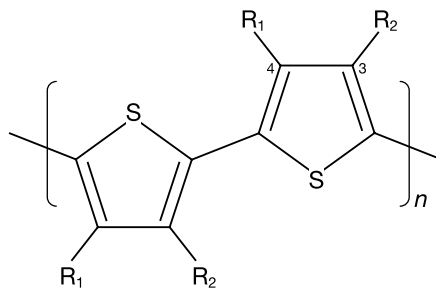


Figure 1. Structure of polythiophene showing the 3- and 4-positions of the thiophene ring; R is either an alkyl or alkoxy substituent.

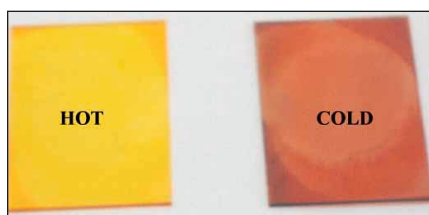


Figure 2. Photograph of a polythiophene above and below the thermochromic transition. In this example, the thermochromic transition is 65°C.

color change is believed to arise from a change in the spatial arrangement of the atoms (conformational change) along the polymer backbone. When the polymer is cold (i.e., below the thermochromic transition temperature, varying from 40°C to 140°C), the polythiophene backbone is nearly planar and the conjugation leads to a small energy bandgap that leads to the low energy absorption. When the temperature is raised above the thermochromic transition temperature, the polymer backbone twists away from planarity, which limits the conjugation length of the electronic system. The shorter conjugation length leads to an increased energy bandgap, higher absorption energy (i.e., from 2.25 eV to 2.58 eV or an increase in the energy of absorption of 0.32 eV), and the observed yellow color.

Not all polythiophene derivatives are thermochromic. Sufficiently bulky substituent groups (R_1 and R_2 , i.e., alkyl or alkoxy groups) are required at specific positions (3 or 4) on the thiophene ring to create a sufficient steric interaction (spatial arrangement of atoms) to cause the polymer chain to undergo conformational twisting. Temperature control is possible because of the delicate balance between the electronic energies, which prefer the planar conjugated structure,

and steric energies, which prefer the twisted conformation to alleviate atom–atom repulsions.

The polythiophene derivatives can be dissolved or blended with a variety of materials, particularly commodity polymers. Since the pigment is polymeric, the diffusion coefficient is small and there is no extraction of the pigment from the host material. The thermochromic pigment has been injection-molded into polyethylene, polypropylene, polystyrene, and polycarbonate and has retained the same thermochromic properties as the pristine polythiophene. Solution casting has been used to create films of polyurethanes and poly(vinylidene fluoride) containing uniform distribution of the thermochromic pigment. Microscopy has demonstrated that the particle size can be as small as 20 nm and still retain the thermochromic properties of the bulk material. Therefore, applications employing plastics, paints, and inks are feasible.

The thermochromic transition temperature is sharp (typically occurring over 5°C), independent of the host material, fully reversible, and can be cycled thousands of times. The transition temperature can be varied by changing the substituents on the thiophene ring, and thermochromic transitions can be readily controlled between just above room temperature to well over 100°C. The color of the thermochromic transition can be changed by blending the thermochromic pigment with a heat-stable, nonthermochromic pigment.

Owing to the nonextractability of the pigment, its application to food safety is envisioned in the near term. For example, a coffee cup lid can be one color when the coffee is too hot to drink and another color when it has cooled down sufficiently. Milk cartons can have a strip that changes color when the carton has been sitting out of the refrigerator too long. Other potential applications include paint for fire doors, which can indicate that a fire is on the other side of the door; radiator caps warning of boil-over of the coolant upon opening; and coatings in industrial plants that visually indicate to operators that pipes or engines are overheating.

Opportunities

The University of Rhode Island is seeking to license and commercialize these polymeric thermochromic pigments.

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Low-Temperature Spray Process Creates Adherent and Continuous Coatings of Fine-Grained and Nano-Sized Metal Powders

A low-temperature metal spray coating technology has been developed from observations made by its inventors during particle impact studies conducted at the NASA White Sands Test Facility, Las Cruces, New Mexico. The patented process plus specifically designed spraying apparatus are being further developed and commercialized by the U.S. company, Inovati, in Santa Barbara, Calif. The spray apparatus has been improved over past versions with respect to accelerant gas formulation, powder feeding, spray nozzle design, and the spray parameters for optimal film quality and adhesion.

The process, called kinetic metallization (KM), entails the spraying of metal powders, polycrystalline, usually below 20 μm in particle size, into continuous and well-adhered coatings on various metal and ceramic substrates. The grain size of the coatings is typically less than that of the powder particles, that is, there is no grain growth beyond the particle boundaries.

Coatings produced by KM differ from those generated by flame spraying processes such as high-velocity oxygen flame spray and low-pressure plasma spray because the spraying is performed as much as several hundred degrees below the melting point of the metal powder. As a result, the thermal distortion of the part being coated is minimized. In addition to

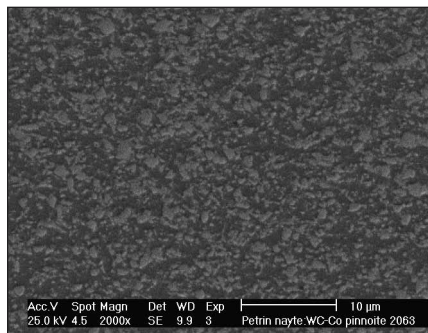


Figure 1. WC-15Co coating applied to 4340 steel (substrate not shown) deposited with the kinetic metallization process.

the fine-grain size of the coatings and the ability to spray nano- and nanostructured powders, further advantages of the KM spray coating process include the ability to co-deposit different materials that would adversely interact if sprayed at high temperatures (e.g., when aluminum is KM-sprayed with any of the transition metals, intermetallics such as aluminides are not formed) and the ability to form diffusion barriers (e.g., Nb on Cu) that would be difficult or impossible to form with a high-temperature spraying process.

No combustible gases are used in the KM process. A two-phase deposition nozzle that directs a gas/particle suspension onto a substrate (metal or ceramic) is used to accelerate micrometer-size powder particles entrained in a carrier gas. The high-

speed collisions (500–1000 m/s) of the micrometer-size powder particles cause very large strains (>100%) and strain rates (>10⁴/s) in the particles, which produce depositions that have cold-worked properties (i.e., plastic deformation resulting from particle impacts produces cold-worked conditions in the coated materials). The formation of true metallurgical bonds occurs when active surfaces of the particles come into contact with the substrate surface or an already deposited material. Metallurgical bonding is achieved exclusively through solid-state reaction (bulk melting does not occur). Postdeposition heat treatment of the depositions can be used to control the microstructure of the deposited material. Pure chromium, nickel, copper, and aluminum have been deposited on both metallic and ceramic substrates. In addition, aluminum alloys and other metal alloys as well as composite mixtures, such as Al-SiC and WC-Co, have been deposited as continuous coatings. Figure 1 shows the submicron matrix (Co) grain size, micron-size reinforcement (WC) particle size, and uniform reinforcement phase distribution obtainable with the KM process. There are no surface area limitations.

Opportunities

Inovati welcomes inquiries about joint application development and custom coating.

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Smart Textiles Created with Embedded Sensors

"Smart" textiles are a special group of electronic and photonic textiles. They are defined as textiles with the capability of monitoring their own physical condition and structural behavior, as well as of sensing external environmental conditions and transmitting the information to other locations. They consist of sensors, signal processing, and communication networks embedded into the textile substrate. Presently available conventional sensors and networking systems are not technologically adequate for such applications. In addition, their integration into textile structures needs to be developed. Fiber-optic technologies are compatible with this type of application and currently present the best choice. A multidisciplinary team at Photonics Laboratories has been developing a new class of smart textiles with embedded fiber-optic sensors

and electro-optic networks. The team's work has focused on the design and development of miniature fiber-optic sensors and on the integration of these sensors, as well as on optical fibers and fine electrical wires, into various textile-based materials as shown in Figure 1. These textiles are made of wool, cotton, polymers, or silk. Some of the envisioned developments include flexible computers and televisions with a large flexible screen that can be folded into pocket size; health-monitoring shirts for special care that will be capable of directly communicating with doctors and providing feedback control for skin drug-delivery systems; a clip-on textile patch that will be usable as a hands-free cell phone with the potential for universal communication; interactive car seats that will communicate with the passenger to provide comfortable conditions; and uniforms for fire fighters, security guards, and special mission personnel

that will provide the information required for their safety and security, as well as transmit information on their health and environmental conditions remotely to a central command facility.

The results achieved to date of integrating lightweight flexible sensors and networks into smart textiles can be divided into three categories:

- development of sensors compatible with textile applications for a number of strain/stress and chemical/environmental conditions;
- integration of these sensors within textile structures; and
- formation of networking connections by integration of optical fibers and electrical wires into the textiles.

At the Photonics Laboratories, two types of strain/stress sensors have been developed and tested for measuring dynamic strain distribution in textiles. They have been applied to parachute

canopy fabric and suspension ropes. The first sensor type is based on using fiber Bragg gratings. These were applied as a short strain gauge for measuring strains in the optical-fiber direction. The second strain sensor type is based on using the modal power distribution within multi-mode optical fibers for strain measurement. This technique can be applied to measure axial and transverse strains. The integration of these two types of sensors has resulted in a sensory system capable of measuring the static and dynamic structural behavior of a parachute during airdrop and inflation, as shown in Figure 2. Several experiments were conducted and the results indicate that these sensors are capable of monitoring the dynamic structural behavior in textiles. In addition, a wireless transmitter/receiver has been developed for remote sensing and transmission of the information to another location.

The second sensor application involves the integration of fiber-optic chemical/environmental sensors into textile structures to detect potentially toxic, gaseous effluents in real-time. Detection of biological or toxic substances is based on the concept of modifying optical fibers (passive conductors) to become chemically sensitive devices. This is achieved by replacing the passive cladding material in a small section of an optical fiber with a chemically sensitive agent. The sensing mechanism is achieved through direct interaction between the light transmitted within the optical fiber and induced perturbations in the modified cladding. A biological simulator, the organophosphate, dimethylmethylphosphonate, (DMMP), has also been used.

In addition to the development and integration of sensors into textiles, the methodology for integration of various types of optical fibers and electrical wires into woven, knitted, and nonwoven textile structures is being developed. These fibers and wires will be used for networking and connections. A large number of different smart textile samples have been fabricated using a full automatic process on regular textile machines. The samples have the ability to detect chemical/environmental conditions and also monitor the structural behavior and their own health. The same technique has been applied for measuring the temperature of the ambient environment. This was achieved by using thermochromic material as the modified cladding on optical fibers.

Opportunities

Photonics Laboratories, Inc. is seeking to commercialize the patented sensor

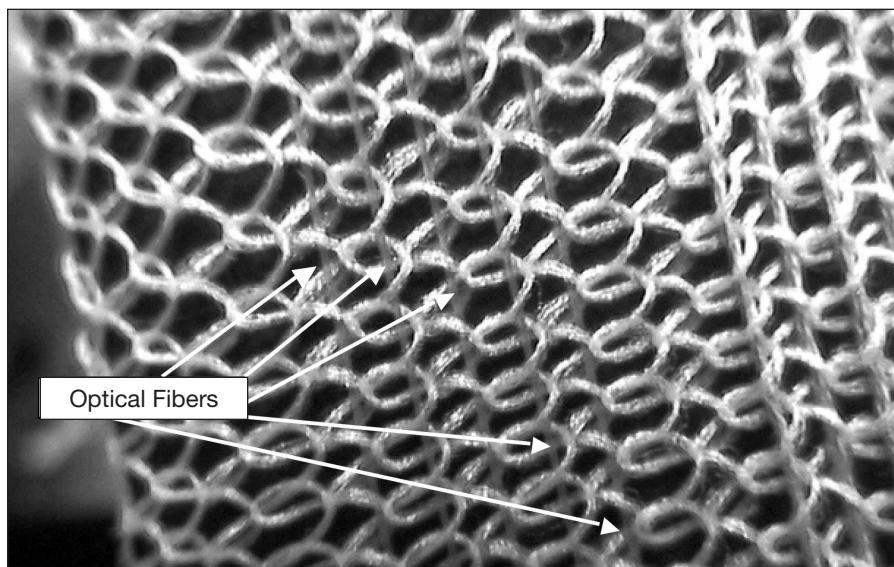


Figure 1. Smart textile with embedded optical fibers.

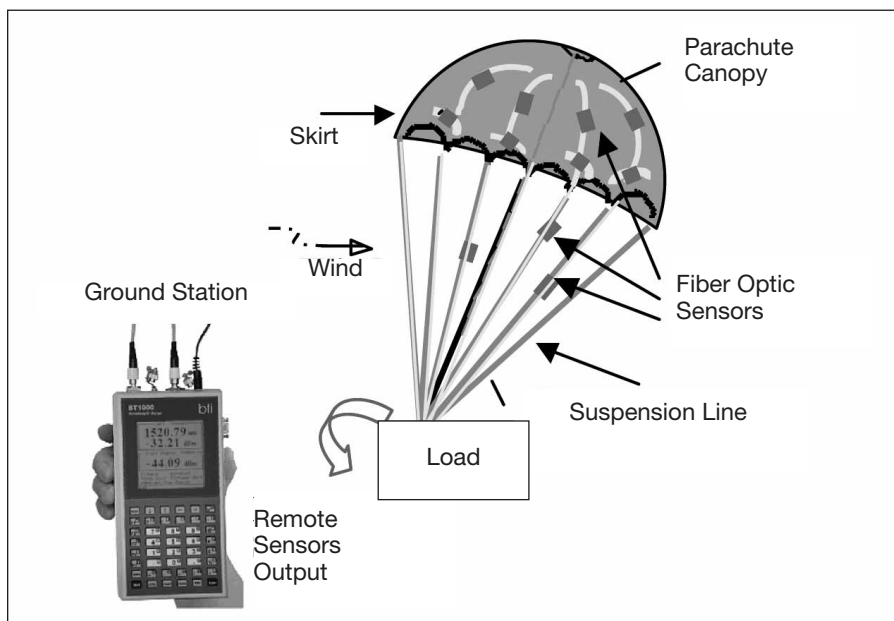


Figure 2. Smart parachute with embedded fiber-optic sensors for measuring dynamic strains during inflation and airdrop tests, as well as for other environmental remote sensor applications.

technologies they have developed for both civil and military applications. They also welcome inquiries about joint applications development.

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