A flexible and stretchable photonic crystal film with sensitive structural color-changing properties for spoiled milk detection

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A R T I C L E   I N F O

Keywords:
Flexible and stretchable photonic crystals
Nanoprinting
Strain-controllable structural color change
Spoiled milk detection

A B S T R A C T

This study proposes a flexible and stretchable 3D polymer film with photonic crystals for the visible detection of spoiled milk. Thermoplastic polyurethane (TPU) was used as the substrate for the photonic crystal structure. The back barrier layer with a regular array of nanoemispheres of anodic aluminum oxide film was used as a template for electroforming a nickel mold. The nanoemisphere array was then nanoimprinted onto the TPU substrate to form a strain-controllable photonic crystal (SCPC) structure on it. Food spoilage can be easily detected by the structural color change caused by the gas it produces. Experimental results confirmed that the structural color change of the fabricated SCPC TPU film occurred when the elongation (ΔL) of the film reached 0.2 mm (1.2%). Furthermore, spoiled milk detection experiments showed that the proposed SCPC TPU film is a highly intelligent and cost-effective biosensor for detecting spoiled food in a container.

Introduction

Food shelf life is a modern issue where unmarked and unlabeled foods can expire without the knowledge of the user. Milk is the most common food in everyday life, which can spoil easily and is only noticed when opening a container or sometimes even when drinking. A method that visually indicates to the consumer that the milk has gone bad is a new area of research for the food industry and life sciences. In addition to invasive chemical detection methods, recently developed color sensors that react to bacteria and gases generated in the milk container, and can be observed visually, appear to be more practical and cost effective. Ziyaina et al. (2019) proposed a colorimetric sensor based on silica nanoparticles and Schiff’s reagent to detect volatile organic compounds produced by the growth of spoilage bacteria in pasteurized whole milk at different temperatures. Voskoboynikova et al. (2021) fabricated an optical pH sensor membrane based on the change in acidity in milk to adequately visualize the age.

Photonic crystals (PhCs) are nanoscale structures in which the refractive index changes periodically to exhibit structural colors. Structural colors result from light interference phenomena such as Bragg diffraction in nanoscale periodic structures and chromatic polarization in birefringent materials (Hong et al., 2020). PhCs have attracted widespread attention over the past 30 years due to their wide application in optics and photonics (Cai et al., 2021). In particular, they have been used in electro-optic modulators (Li et al., 2020), spectrometers (Chang et al., 2021), quantum emitters (Rong et al., 2020), lasers (Moria et al., 2021), resonators (Yu et al., 2021), nanocavity (Nakadai et al., 2022), sensors (Zhang et al., 2021), and anti-counterfeiting labels (Lai et al., 2022; Wu et al., 2022).

In sensing applications, structural color changes of colloidal crystals can be induced by temperature, force, humidity, wettability, or biodegradation to alter refractive index contrast (change in intensity), structural periodicity (change in bandgap), or both (Schöttle et al., 2021). Techniques used to fabricate structural color materials include lithography (Park et al., 2011), nanoprinting (Espinha et al., 2018), colloidal self-assembly (Hensley et al., 2022), standing wave carving (Ito et al., 2019), and two-photon polymerization-3D printing (Liu et al., 2019).

Traditional electronic and photonic devices are inherently-two-dimensional (2D), and are severely limited by the substrates on which...
they are fabricated (Geiger et al., 2019). Some emerging applications, such as soft robotics, electronic skin, wearable devices, and flexible displays (Peng & Wu, 2019; Gur et al., 2015), prefer soft devices and nonplanar geometries. Therefore, flexible and stretchable optical devices that can mechanically deform without losing their useful optical properties are desired. The basic detection mechanisms of flexible and stretchable optical devices are structural color changes due to diffraction changes in photonic crystals and/or refractive changes in assembled birefringent nanostructures (Li & Yin, 2019).

Many optical devices have been developed to achieve stimulus-induced diffraction change in photonic crystals. Arsenault et al. (2006) developed large films of porous elastomeric photonic crystals that could reversibly shift the position of the photonic band structure over a wide wavelength range under a compression–decompression cycle. Schottle et al. (2021) proposed a colloidal crystal-based time–temperature integrator. With latex particles of identical sizes but different glass transition temperatures, the device can provide a homogeneous photonic stopband. The adjustable property to report prolonged medium and short term excessive temperature events makes the device suitable for long term recording and threshold applications. The discoloration of a wet photonic crystal was reported by Yu et al. (2020) while developing a ready-to-use colorimetric indicator of ethanol concentrations, based on their wettability patterns in different segments of silica inverse opal films. This indicator can detect an ethanol concentration as low as 5 %. Yin et al. (2019) experimentally illustrated a stretchable, flexible, and rollable bulk polarization grating film based on a PDMS substrate with tunable periodicity and high diffraction efficiency. The proposed film could be mechanically stretched to shift the central wavelength of the diffraction spectra from 507.5 nm to 474.5 nm. Li et al. (2020) implemented soft lithography to fabricate 2D mechanical-strain-actuated photonic crystals based on a nanohexagon with non-close-packed cylinder holes on a stretchable substrate. The crystals produced as such showed a color change throughout the visible range at 29 % strain. Peng et al. (2021) proposed a flexible and stretchable optical waveguide structure oriented towards tactile perception based on the related properties of optical waveguides and flexible optical materials. This structure showed a strain detection range of 0–12.5 % with an external force detection range of 0–23 × 10⁻³ N. Li et al. (2019) fabricated GaN photonic crystals and microdisks on flexible PDMS films by combining nano/microsphere lithography and laser lift-off techniques. Optical tuning of the photonic band gap of stretchable photonic crystals and whispering-gallery-mode laser emission from bendable microdisks over a remarkably wide range of the proposed GaN–PDMS configurations have been demonstrated experimentally. Mechanically stretchable photonics foresees its emerging applications ranging from artificial skin to soft wearable electronics. Li et al. (2018) monolithically integrated stretchable single-mode photonic devices from chalcogenide glass and epoxy polymer materials on elastomer substrates. Experimental results showed that the fabricated devices can withstand 41 % of the nominal tensile strain and 3000 strain cycles without losing optical performance. Quan et al. (2020) proposed a stretchable, diffractive, color-based wireless strain sensor based on an array of cone-shaped nanostructures on the surface of an elastomeric substrate for the efficient measurement of strain using the entire visible spectrum. The diffractive color can be modulated by changing the grating pitch due to stretching or compression of the substrate.

Recently, many stimuli-responsive optical materials have been developed, enabling the refractive change of composite birefringent nanostructures. Yue et al. (2014) reported a mechano-actuated, soft photonic hydrogel with an ultrafast-response time, a tunable full-color range, and high spatial resolution with low compressive stress. The device can be reversibly switched at high frequency more than 10,000 times without losing its structural color. Hu et al. (2022) proposed a sensitive mechanochomic photonic crystal film with good optical properties by self-assembly of silica particles in di(ethylene glycol) ethyl ether acrylate and fixation of the ordered structures by photopolymerization. Good optical properties include a wide photonic band gap tuning range, high sensitivity, fast responsive speed, durability, wide working temperature range, and excellent reversibility in cycle testing. Poloni et al. (2021) proposed architectural composites exhibiting an orientation-dependent color change resulting from the rotation of reflective coated platelets embedded in a soft polymer matrix and pre-aligned in a well-defined architecture. The initial orientation and spatial distribution of the selected platelets within the soft matrix can be magnetically programmed to create strain-induced architectural color. Howell et al. (2015) developed tunable elastic 1D photonic organic/inorganic composite crystals in the visible spectrum. Experimental results showed that the sensing behavior of the proposed device could produce a visible color shift across the visible spectrum from red to blue by applying over 40 % strain. Chen et al. (2019) proposed stretchable photonic soft materials based on a hydrogel system cross-linked by a crystalline colloidal assembly. The fabricated gel has a full-color tunable range and exhibits photonic shifts of 460 nm that can be reversibly modulated by a small compressive stress.

The aim of this research is to develop a simple and chemical-free method to visualize dairy spoilage, using a stretchable polymer film with a photonic crystal structure, that can change its structural color due to mechanical deformation. In addition, it is also hoped that the proposed fabrication method can eliminate the time-consuming and mass-production disadvantages of fabricating photonic crystals, thereby expanding the application range of photonic crystals. The force generated by the gas from spoiled dairy products pushes and stretches the developed flexible film so that the photonic structure of the flexible film is modified, causing its structural color to change. In our proposed photonic crystal based sensor film, thermoplastic polyurethane (TPU) was used as the substrate for the photonic crystal structure. The backside barrier with a regular nanoarray structure of an anodic aluminum oxide (AAO) film (Rath & Theato 2020) was used as a template to form a nickel mold by electroforming. The nanohemisphere array of the AAO barrier layer was then transferred to the TPU substrate by hot embossing to form a strain-controllable photonic crystal (SCPC) structure on the TPU film.

Materials and methods

Strain-controllable photonic crystal (SCPC) film fabrication

The sequential fabrication processes of the proposed SCPC film (as shown in Scheme 1) are described below.

(A) AAO template fabrication

A uniformly arranged array of nanohemispheres from an AAO barrier layer was used as a template for nanoelectroforming a nickel nanomold with a concave array of nanohemispheres for nanoimprinting. The AAO membrane was fabricated using a specially developed anodizing process. Pure (99.9995 %) aluminum foil (128 µm thick) was cleaned sequentially with acetone, ethanol, and deionized water. Electro-polishing was then performed to polish the foil surfaces using a mixed electrolyte of perchloric acid and anhydrous ethanol with a volume ratio of 1:4 under a constant voltage of 20 V and a current of 0.45 A for 2 min. An AAO membrane with non-penetrated parallel nanochannels and non-oxidized aluminum beneath the barrier layer was obtained by anodizing the aluminum foil in a 3 wt% phosphoric acid solution under an applied voltage of 180 V at 2.5 °C for 3 h. The non-oxidized aluminum was then removed in an aqueous CuCl₂ • HCl solution, prepared by dissolving 13.45 g of CuCl₂ in 100 mL of 35 wt% hydrochloric acid solution. The honeycomb barrier-layer surface of a convex nano-hemisphere array with an average diameter of approximately 465 nm was obtained.

(B) Photolithography

During the photolithography process, the barrier layer was spin coated with 1 µL of AZ 1518 positive photoresist and then soft baked at 100 °C; the piece was then exposed and developed using 2.38 % TMAH developer.

(C) Nanoforming
A gold (Au) thin film of about 10 nm was sputtered (108auto, Cressington Scientific Instruments Ltd., USA) onto the barrier layer surface of the fabricated AAO membrane, under an applied current of 30 mA for 120 s to serve as a conductive layer for electroforming. Annealing was then carried out at 120 °C for 2 h to improve the uniformity of the Au thin film. Electroforming was performed in a sulfamate bath containing nickel sulfamate tetrahydrate [Ni(NH$_2$SO$_3$-4H$_2$O)] and nickel chloride [NiCl$_2$-6H$_2$O] in a boric acid solution [H$_3$BO$_3$], by using a nanoelectroforming system (Model 263A, EGG Ins., Taiwan) with bulk nickel as the anode and the gold thin film-coated AAO barrier-layer surface as the cathode. Prior to electroforming, the electroforming solution was heated to 55 °C. Electroforming was performed at 10 V and 30 mA/cm$^2$ for 4 h, and then the current density was increased to 120 mA/cm$^2$ for 11 h to deposit metallic nickel onto the Au thin film-coated AAO barrier-layer surface. This two-stage electroforming can greatly reduce the electroforming time from 48 h (Peng et al., 2018) to 15 h. Then the electroformed nickel mold was carefully removed from the AAO barrier-layer surface and cleaned with DI water. Thereafter, a 0.2 M NaOH solution was used to remove the AAO remaining on the surface of the nickel mold for at least 1 h. Finally, the fabricated nickel mold was again cleaned with DI water to obtain a complementary concave nanohemisphere array of the original AAO barrier layer. The nickel mold can be repeatedly used to mass produce SCPC polymer films by nanoimprinting.

Nanoimprinting

Nanoimprinting was performed with a custom machine and TPU (0.2 mm) was used as the substrate for the SCPC films. The nickel mold and two layers of TPU were positioned one after the other on the sample holder plate (below). Two layers of TPU were used instead of one in order to easily remove it from the nickel mold and prevent film deformation. These two layers were melted and combined to increase the desired thickness. A gap of approximately 1 mm was maintained using a thin aluminum foil and placed between the pressing plate and the sample holding plate to control the thickness of the TPU film. If the TPU is too thin, its film may be deformed when peeled off the Ni mold. In contrast, air bubbles could be trapped in the TPU film if it is too thick. The pressing plate was first heated to 145 °C (above the 140 °C transition temperature of TPU), and then the pressing plate was pressed firmly onto the sample holding plate for 8 min with a pressure of 0.15 MPa. The TPU film (0.125 mm) with nanohemispheric array photonic crystals was carefully peeled off the nickel mold after the temperature had cooled to about 40 °C.

**Characterization of the fabricated samples**

The surface morphology and nanostructure topology of the nano hemisphere forming the barrier layer of the fabricated AAO membrane, electroformed nickel mold and SCPC TPU films were characterized by field-emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM), respectively.

**Viewing angle effect experiment**

The device shown in Fig. S1(A) was designed and fabricated to investigate the viewing angle effect of the fabricated SCPC TPU film. The viewing angle effect experiments aimed to analyze the relationship between the angle of the incident light and the camera relative to the structural color of the SCPC TPU film. A camera (Apple, iPhone 7 plus) was placed on the camera holder, an LED was fixed in the light source holder and the sample under investigation was placed on the sample holder. Changes in the structural color of the sample were observed by changing the angular position of either the camera holder or the light source holder. Each stage of the device was designed to be 10° separated. The incident angle $\theta_i$ is the angle between the light source and the normal vector of the specimen, and the angle of diffraction $\theta_d$ is the angle between the camera and the normal vector of the specimen. The angle definitions of the incident and diffracted light are shown in Fig. S1 (B).

In its original form, TPU is a translucent material that allows light to pass through during irradiation. Therefore, the diffraction color has very low visibility. An approximately 10 nm thick Ag film was sputtered onto the surface of the fabricated SCPC TPU film to retain most of the intensity of the structural color, and increase the reflectivity of the irradiating light and the visibility of the fabricated film.

**Stretching experiments**

Fig. S2 shows the schematic of the device designed and fabricated for the structural color stretch deformation experiment. The angular displacement between two adjacent holes on the frame was designed to be 15°. During the stretching experiments, the position of the SCPC TPU film was fixed. The light source and the camera (Apple, iPhone 7 plus) were initially aligned in the same direction perpendicular to the plane of the film. The device has two rollers, a handle, and an axle diameter (d) of 5 mm with a circumference $c = 5\pi$ mm. The film that was firmly attached to the roller axle was elongated by rolling the handle. The rolling angle of the handle was used to determine the length variation of the initial film using Eq. (1).
\[ d_{\text{variation}} = \left( \text{rolling angle} \times 5\pi \right) / 360^\circ \]

Results and discussion

**Morphological characterization of the fabricated SCPC TPU film**

FE-SEM images (Fig. 1(A) and (B)) were acquired to examine the morphology of the nanohemispheric array that forms the barrier layer of the fabricated AAO membrane and the Au thin film-coated nanohemispheric array. The SEM images show that a uniformly distributed nanohemispheric array was successfully fabricated and the Au thin film was sputtered uniformly and completely covered the surface of the nanohemispheric array. The higher the uniformity of the nanostructure, the more complete the scattering of the incident light; therefore, a luminous structural color can be obtained. The diameter and height of the nanohemisphere forming the barrier layer were measured to be approximately 487.3 ± 14.9 and 135.9 ± 9.3 nm, respectively. The concave nanohemispheres of the electroformed nickel mold and the transparent SCPC TPU films are not easy to unambiguously characterize with SEM. Therefore, AFM images as shown in Fig. 1(C) and 1(D) were acquired to examine the morphology of the electroformed nickel mold and the nanoimprinted SCPC TPU films, respectively. The AFM images illustrate that the nanohemisphere array of the AAO membrane could be transferred to the SCPC TPU film by nanoimprinting using the electroformed nickel mold. The diameter and the height of the concave nanohemisphere were measured to be 491.8 ± 15.9 and 138.9 ± 9.5 nm on the nickel mold, respectively, and 464.2 ± 16.2 and 76.3 ± 9.8 nm, respectively measured on the SCPC TPU film.

The dimensions (diameter and height) of the nanohemisphere on the nickel mold were similar to those on the AAO barrier layer. The height of the nanohemisphere on the SCPC TPU film was half that of the AAO template. The material properties of TPU, such as ductility, viscosity, and malleability, could presumably hinder the TPU molecules from being fully filled into the concave nanohemisphere of the nickel mold during nanoimprinting.

**Structural colors of the SCPC TPU film**

TPU is an easily deformable material. Therefore, the structural colors of the SCPC TPU film subjected to different viewing angles, tensile deformations, and spherical curved deformations were studied by shining a lot of white light onto the TPU surface with different angles of incidence (Fig. S3). The principle of structural coloration can be explained using Bragg’s law (Born & Wolf, 1980):

\[ d (\sin \theta_i + \sin \theta_d) = m \lambda \]

where \( d \) is the distance between the centers of two adjacent nanohemispheres, \( \theta_i \) is the angle of the incident light, \( \theta_d \) is the angle of the diffracted light, \( m \) is the diffraction order, and \( \lambda \) is the diffracted light wavelength.

**Structural colors of different light incidence angles and viewing angles**

The device shown in Fig. S1 was employed to investigate the structural coloring of the SCPC TPU film at different angles of incidence and diffraction.

In its original form, the distance between two adjacent nanohemispheres (\( d \)) of the photonic crystal structure and the diffraction order (\( m \)) are constants. At a fixed angle of diffraction (\( \theta_d \)), the wavelength (\( \lambda \)) of the diffracted light increases with increasing angle of incidence (\( \theta_i \)). Therefore, the observed structure color gradually changed from short-wavelength (blue) to long wavelength (red). In contrast, when the angle of incidence was fixed, the wavelength (\( \lambda \)) of the diffracted light also increased because of the increase in the angle of the diffracted light. Fig. S4 shows the calculated wavelength (\( \lambda \)) of the diffracted light corresponding to different combinations of \( \theta_i \) and \( \theta_d \). The relationships are quite linear.

Fig. 2 shows the observed structure color corresponding to different combinations of \( \theta_i \) and \( \theta_d \). Fig. 2(A) shows the observed structure color with \( \theta_d \) fixed at 30\(^\circ\) and 60\(^\circ\). When \( \theta_d \) was fixed at 30\(^\circ\), the observer structure color remained blue (\( \lambda \approx 450 \) nm) and almost unchanged when \( \theta_i \) was less than 30\(^\circ\); when \( \theta_i \) was 30–50\(^\circ\), the structure color gradually changed from blue to green; when \( \theta_i \) ranged 50–80\(^\circ\), the structure color appeared red. When \( \theta_d \) was set to 60\(^\circ\), a blue structural color was observed when the angle of incidence was less than 20\(^\circ\); green structural color appeared when the angle of incidence was between 20\(^\circ\) and 30\(^\circ\); the structure color gradually changed from green to red when the angle of incidence was between 40\(^\circ\) and 70\(^\circ\); at 80\(^\circ\), the incident light could not fully shine on the SCPC TPU film, resulting in a structural color mixed with red and black. The observed structure colors for different \( \theta_d \) with \( \theta_i \) fixed at 30\(^\circ\) and 60\(^\circ\) are presented in Fig. 2(B). A similar trend to the fixed \( \theta_d \) condition, the displayed structure color showed a red shift as the diffraction angle was increased. Polyethylene and polycarbonate were also adopted as substrates for nano-imprinting the nanohemisphere array PCs on their surface. Structural colors resembling those on TPU were observed (Figs. S5 and S6). Due to their poor

![Fig. 1. Morphological characterization. (A) SEM image of the nanohemispheric array forming the barrier layer of the fabricated AAO membrane; (B) SEM image of the Au thin film-coated nanohemispheric array; (C) AFM image of electroformed nickel mold; (D) AFM image of the nano-imprinted SCPC TPU film.](image-url)
deformation properties of curved surfaces, these two materials are not suitable for a spoiled milk detection application.

The experimental results confirmed that the fabricated SCPC TPU films possess the optical properties of the photonic crystals and that the observed structural colors agree with the theoretically calculated results under different conditions.

**Strain controllable structural color**

Fig. 3(A) is the scheme showing the mechanism of the strain-controllable structural color. Along the stretching direction (x-direction), the distance between two adjacent nanohemispheres was elongated from $d_0$ to $d_x$ and the curvature of the nanohemispheres became flatter. The stretch-induced increase in distance between adjacent nanohemispheres increased the periodicity of the photonic crystals, while the flattened curvature changed the diffraction property of the photonic crystals. In contrast, the distance between two adjacent nanohemispheres was shortened from $d_0$ to $d_y$, and the curvature of the nanohemispheres along the perpendicular stretching (y direction) became steeper. Therefore, the periodicity and the diffraction property of the photonic crystals can also be changed. In particular, the proposed CSPC TPU film can allow changing the periodicity and diffraction by stretching to change the structure colors of the photonic crystals.

The device shown in Fig. S2 was used for the stretching experiments. Fig. 4(A) shows the structural color change of the fabricated SCPC TPU films along the stretch direction. An initial bluing can be observed on the TPU film. When the film was stretched by 0.7 mm to 1.3 mm, the structural color turned dark blue. Then, the structure color gradually turned into patches of green-yellow mixture when the elongation reached 2 mm. The green-yellow mixing range gradually expanded, and more colors ranging from orange to red appeared as the film was further elongated. When the film was stretched to 4.6 mm, a combination of the entire visible spectrum appeared. As the film was stretched further, the photonic crystals lost their structural color and became fully transparent under 9.2 mm stretching. The structural color change of the fabricated SCPC PE films along the stretching direction is shown in Fig. S7(A).

The structural color changed from blue to a combination of the entire visible spectrum and eventually became transparent, since different levels of strain can be attributed to the variation in periodicity and diffraction of the photonic crystals along the stretching (x-direction) direction. The applicable Bragg’s law (Born & Wolf, 1980) can be described as follows:

$$d_0 (\sin \theta_i + \sin \theta_d) = n \lambda$$

where $d_0$ is the original periodicity, $\sin \theta_i$ and $\sin \theta_d$ denote different angles of incidence and their corresponding angles of diffraction on the surface of the nanohemispheres. When $d_0$ was elongated to $d_1$ due to stretching, the curvature of the nanohemisphere also changed accordingly. Therefore, many $\Delta \theta_i$ and $\Delta \theta_d$ appeared on the surface of the nanohemisphere. Therefore, the spectrum appeared rather than a single structural color. When the shape of the nanohemispheres was flat enough, the optical property of the photonic crystals no longer existed. Therefore, the film became transparent.

Fig. 4(B) shows the structural color change of the fabricated SCPC TPU films with the angles of incidence and diffraction perpendicular to the stretch direction. The SCPC TPU film in this experiment initially

![Fig. 2. Observed structure color corresponding to different combinations of $\theta_i$ and $\theta_d$. (A) fixed $\theta_d$; (B) fixed $\theta_i$.](image1)

![Fig. 3. Schematic representation of the structural color change mechanism. (A) strain-controllable structural color mechanisms; (B) the angle between the deformed photonic crystal and the incident light.](image2)
showed a dark red structural color. Along with the increase in the stretch, the structural color transited to orange and then to blue. Based on the governing Bragg’s law, the wavelength of the diffractive light decreased as the periodicity (d) and angle of incidence (θi) perpendicular to the stretching direction (y-direction) decreased. Therefore, the structure color gradually changed from red to blue. The structural color change of the fabricated SCPC PE films with the incidence and diffraction angles perpendicular to the stretching direction is shown in Fig. S7 (B).

As shown in Fig. 4(A), the structural color change appeared when the elongation (ΔL) of the film reached 0.2 mm (1.2%). The force required to obtain an elongation of 0.2 mm can be estimated by the well-known Hooke’s law (Giuliodori et al., 2009):

\[ F = \frac{\Delta L}{L_0}YA \]

where \( F \) denotes the force required to induce the elongation (ΔL), \( L_0 \) is the original length of the TPU film, Y is the Young’s modulus of TPU, and A is the cross-sectional area perpendicular to the stretch force. The original length (\( L_0 \)) and width of the TPU film was 17 mm with a thickness of 0.1 mm. The Young’s modulus of TPU is 2,580 N/mm². The force required to achieve an elongation of 1.2% can be estimated to be 51.6 N using Equation (3). It is a small force. That is, the structural color change of our CSPC TPU film can be easily achieved by a relatively small stretch force.

**Influence of bending deformation on structure color**

TPU is a flexible, ductile, easy to deform and bend material that makes it easy to form a spherical formation. Glass beads with different diameters were used to adjust the bending deformation of the SCPC TPU film. The SCPC TPU film formed a hemispherical shell on various glass beads of different diameters. As shown in Fig. S8, the structural color of the SCPC TPU film changed due to the curvature variations induced by the glass bead diameter. A clearer edge structure color appeared under a relatively larger curvature of a smaller glass bead. When a larger glass bead (50 mm) was used, the film showed no visible structural coloring. However, because a 30 mm bead was used, small color changes occurred at the edge where blue was the main color and green and red appeared as it got closer to the edge. When 20 and 15 mm beads were used, a much clearer structural coloration can be observed with a broad range of either blue, green, or red. Since the bead size was reduced to 12 mm, a clear coloration is still observed, although the bead was too small to be fully covered by the SCPC TPU film.

Another feature in the incident light was observed and shown in Fig. 3(B), where \( \theta_i < \theta_i' < \theta_i'' \). The greater the curvature, the greater the difference in angle of incidence will be between \( \theta_i, \theta_i', \) and \( \theta_i'' \). According to Bragg’s law, a large angle of incidence leads to a structural color with a long wavelength. The film shows no color change in the center of the sphere, and the entire visible spectrum can be observed at the edge of the film.

The next experiment was performed on a single sphere (diameter 30 mm) covered with the SCPC TPU film. The change in structural color of the SCPC TPU can be observed by moving and rotating the light source and the camera along the roll and the pitch axis, respectively. The film has a curvature change with respect to the incident light because the curved hemispherical shell is symmetrical; hence multicolored bands can be observed. As shown in Fig. S9, the displacement of the ribbon can be observed at different angles. Bending-induced structural color changes in PE, PC, and TPU were investigated (Fig. S10). A band-like distribution of structural colors in the visible light spectrum, caused by different curvatures, could be observed. Because PC is relatively hard and brittle, it can not undergo large bending deformation, while PE and TPU are soft and ductile, so they can be bent greatly.

**Detection of spoiled milk with the SCPC TPU film**

The Food and Agriculture Organization of the United Nations estimates that about a third of all food produced, manufactured, and/or sold worldwide is wasted or lost. Dairy products account for almost 17% of this waste. Milk loss is a problem that drastically affects the economy and the environment. Using a chemical-free and inexpensive method to detect spoiled milk would be a great benefit. The sensitive structural color change property of the proposed SCPC TPU films was further used to detect spoiled milk.
The experiments were conducted by attaching the SCPC TPU film to the orifice of a milk container (Kirkland’s 1 Liter whole milk) and placing the camera and light source over the container. For fresh milk, with no gas pushing out of the container (no curvature change), the SCPC TPU film showed a blue structural color as shown in Fig. 5(A). When the milk was spoiled, the SCPC TPU film was pushed onto a curved surface by the generated spoilage gas inside the container and showed multiple structural colors on the opposite edge (Fig. 5(B)). Experiments with plastic bottles had similar results (Fig. S11).

The structural color change of the SCPC TPU film resulting from the bending of the film increased from flat to some degree. This increased the periodicity and the angle of incidence; therefore a long-wavelength such as green or red was observed. Compared to the results of the bending deformation experiments shown in Fig. S10, the structural color pattern shown in Fig. 7(B) has the same appearance. These images, marked by the red frame, indicate that the film in Fig. 7(B) and the film marked by the red frame in Fig. S10 have a similar curvature. In addition, the results of spoiled milk detection show that the proposed SCPC TPU film is a highly intelligent and cost-effective biosensor for detecting spoiled food in a container.

The nano hemisphere array of the AAO barrier can be further replaced by a similar structure fabricated by photolithographic process integrated with thermal melting of the photoresist (Chu et al., 2020). In doing so, the photolithographic process can facilitate patterning of the nanohemisphere array and tuning of the size of the nanohemispheres to obtain desired structure colors. In addition to the demonstrated TPU, PE, and PC, other thermoplastic polymers that can be stretched or bent due to small stretching or bending, strain can also be used as the substrate. In addition to the demonstrated detection of spoiled food, the SCPC films developed in this study can also be used as an intelligent sensor to detect structural cracks and material deformation.

Conclusion

In this study, we successfully designed and fabricated novel flexible and stretchable polymer films with photonic crystals of uniformly distributed nanohemispheres, which allow the simultaneous change of photonic crystal periodicity and angles of incidence on the nanohemisphere surface with small stretch and pressure strain. Experimental results confirmed that the fabricated SCPC TPU films possess the optical property of photonic crystals, and that the structural color change of our SCPC TPU film can be easily achieved due to the relatively small stretching force. Experimental results confirmed that the structural color change of the fabricated SCPC TPU film occurred when the elongation (ΔL) of the film reached 0.2 mm (1.2 %). The sensitive structural color change characteristic of the proposed SCPC TPU films was further used to detect spoiled milk by attaching the SCPC TPU film onto the orifice of a milk container (Kirkland’s 1 Liter whole milk). Spoiled milk could be easily detected by the structural color change caused by the gas it produced. The results of spoiled milk detection showed that the proposed SCPC TPU film is a highly feasible smart biosensor for detecting spoiled food in a container. In addition, the proposed structural color change detection method did not cause any chemical contamination of the target food. The developed SCPC TPU film can be used to replace the currently used aluminum foil seal.

CRediT authorship contribution statement

Do Thi Vien Thao: Methodology, Data curation. Wei-Tzu Weng: Data curation. Nguyen Van Hieu: Formal analysis, Writing – review & editing. Cheng-Chung Chang: Conceptualization, Methodology, Validation, Formal analysis, Funding acquisition. Gou-Jen Wang: Conceptualization, Methodology, Validation, Formal analysis, Writing – original draft, Writing – review & editing, Supervision, Funding acquisition.

Fig. 5. Textured color variation of the SCPC TPU film cover on a milk container opening. (A) fresh milk; (B) spoiled milk.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The authors would like to thank to the Ministry of Science and Technology of Taiwan under grant number MOST-104-2221-E-005-028-MY3 and MOST 110-2634-F-005-006 for their financial support of this research.

Data Availability Statement

The data supporting the results of this study are available in the supporting material of this article.

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