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Tuning of Structural Colors Like a Chameleon Enabled by Shape-Memory Polymers

*Senta Schauer, Jeremy J. Baumberg, Hendrik Hölscher, and Stoyan K. Smoukov**

Nature often uses structuring of materials for coloration rather than incorporating dye molecules, since single-construction materials are capable of producing any vivid visible color in plants and insects. By precisely engineering features that diffract or scatter light, more recently, humans have created similarly intense non-fading colors. Stretchable polymer opals have emerged as a single material which can dynamically shift across the whole visible spectrum using structural colors, by temporary stretching or compression. For energy efficiency and practical considerations, however, it is necessary to fix semi-permanently desired colors without continuous stretching or application of other stimuli or energy. Here, a polymer opal incorporating a shape-memory polymer embedded in its matrix can keep a particular color fixed without the application of external forces, yet can be reprogrammed to a different fixed color on demand. The influence of the material composition on its optical appearance, shape-fixity, and shape recovery abilities in controlled stretch experiments is quantified. High-speed printing-compatible localized compression pattern imprinting is shown to generate stable but easily erasable color patterns. This opens up the potential for durable and energy-efficient yet reusable and reconfigurable displays, wearables, or packaging and security labeling based on such polymeric film materials.

The brilliance and variety of structural colors has fascinated and challenged researchers for many decades.[1–4] A single material with periodic structural features in the same size range as the wavelength of visible light can modulate light in a way that produces striking colors and iridescence. Such colors are, in contrast to pigment based colors, immune to fading caused by UV exposure. Some of the most intense examples of structural colors are found in nature, made of widely available materials including silica, keratin, or cellulose, prominently in butterfly wings, beetle exoskeletons, and bird feathers.[3,5–8] Such colors, however, are static while dynamic color changes as exhibited by squids, chameleons, and other species are dye-based although especially intriguing yet challenging to mimic.[9–11]

One way nature produces intense structural colors are 3D photonic crystals. The closely packed regular arrangement of spheres in a matrix with different refractive index generates a photonic band gap.[12] Biomimetically, while most of the dynamic color changes in dermal chromatophores are due to dispersion and aggregation of pigments, Teyssier et al.[11] recently reported that the panther chameleon *Furcifer pardalis* actively changes its color by tuning the lattice spacing of guanine nanocrystals in its skin.

In photonic crystals, the photonic band gap, hence the color, can be adjusted and tuned by changing sphere diameter, distance, and/or arrangement.[13,14] Recently, various methods to tune the sphere distances in a 3D photonic crystal were accomplished. The vast majority of those studies achieved a change of lattice constant by swelling of the matrix in an appropriate solvent or by implementing the spheres in a soft matrix to attain tunability by stretching.[15–19] Both approaches, however, have some serious drawbacks. While swelling might be fast (i.e., sub-second), reducing the sphere distance by drying of the composite is typically much slower. Furthermore, to keep a constant color, drying has to be prevented by encapsulation or similar measures. Spatially resolved color changes through local application of the solvent are also challenging due to diffusion of the solvent in the composite. Therefore, neither fast color switching nor spatially resolved, static color variations are feasible with photonic crystals tuned by swelling. On the other hand, spheres embedded in a soft, rubbery matrix enable color changes by stretching and compression but they need a

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Dr. S. Schauer, Dr. H. Hölscher
Institute of Microstructure Technology
Karlsruhe Institute of Technology
Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen
Germany

Prof. J. J. Baumberg
Nanophotonics Centre
Cavendish Laboratory
University of Cambridge
Cambridge CB3 0HE, UK

Dr. S. K. Smoukov
School of Engineering and Materials Science
Queen Mary University of London
London E1 4NS, UK
E-mail: s.smoukov@qmul.ac.uk

Dr. S. K. Smoukov
Department of Material Science and Metallurgy
University of Cambridge
Cambridge CB3 0FS, UK

Dr. S. K. Smoukov
Department of Chemical and Pharmaceutical Engineering
Faculty of Chemistry and Pharmacy
Sofia University
1 James Bourchier Ave., 1164 Sofia, Bulgaria

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constant load to keep the color change. These constraints limit their applications to devices where lateral deformation of the color changing material is acceptable and actively controlled. Consequently, the material color cannot be tuned if permanently attached to solid surfaces and load-free color tuning of static colors or complex patterns on flexible substrates is not possible.

To overcome these impairments, we use state-of-the-art polymer opals and advance their properties by adding a shape-memory polymer (SMP) to the matrix. The enhanced functionality of this composite enables its quasi-static and on-demand reversible color change by stretching or compression due to the matrix' shape-memory ability. The SMP in the matrix keeps the samples' shape (and therefore, the lattice constant of the opals) fixed as long the color change is needed. We quantitatively analyze the influence of the loading ratio between the shape-memory polymer and the polymer opals in terms of shape-recovery and shape-fixity rate. Furthermore, we imprint reversible color changes into sheets of shape-memory polymer opals (SMPOs).

SMPs are polymers, which can remember a first *permanent* shape while they are metastable in a second *temporary* shape. Upon being exposed to a suitable trigger such as heat or light, the polymer loses the temporary shape and recovers the initial permanent shape. This ability arises from the special molecular structure of those polymers in combination with a specific programming cycle.[20–25] Although SMPs have been introduced to the field of optics only recently, their applicability has been already proven.[26–32] The SMP utilized in this study is a thermoplastic, thermally-activated poly(ether urethane) block-copolymer (TecoflexEG-72D, Lubrizol, USA). Since it is completely amorphous it is transparent in the visible range and it is very robust and docile in terms of its shape memory features. Its recovery time can be controlled via the recovery temperature and the recovery process can be even stopped and restarted on purpose.[30–32] We produced the polymer opals presented here by blending different percentages of this SMP with monodisperse core-shell polymer particles and ordering the particles using shear (as developed over the last decade). The particles were produced by emulsion polymerization in the form of core-interlayer-shell spheres which are specifically designed to facilitate photonic crystal formation through shearing. A PS (polystyrene) core crosslinked with butandiole diacrylate is covered by an interlayer of PMMA (poly(methyl methacrylate)) crosslinked with allyl methacrylate to which a soft, rubbery PEA (poly(ethyl acrylate)) shell is grafted. The weight ratio of these materials is 32.5:11.2:56.3 and the respective thicknesses determined by transmission electron microscopy are 206 nm/222 nm/247 nm. More fabrication details of those particles can be found in refs. [33] and [34], and we utilize the most favorable composition for ordered assembly in this study.

For the preparation of the composite material we fed SMP and polymer opals into a twin-screw extruder (HAAKE MiniLab, Thermo Scientific) and mixed them above the SMP's melting temperature at $T = 170$ °C. In order to increase the optical appearance we also added a small amount (less than 0.05%) of carbon black to prevent long-path (broadband) light scattering. This mixing procedure is repeated three times to ensure homogeneous distribution of all three components. The resulting composite exits the extruder as a continuous tape with a cross section of 5×1 mm^2. The embedded PO spheres are poorly ordered at this stage, and the tape uncolored. A subsequent ordering step aligns the PO spheres to a regular lattice.[35–37] This ordering is either performed by shearing the composite over a hot edge after the material is compressed into a film between two polyethylene terephthalate (PET) sheets,[35,36] or by compressing the composite at high temperatures between two smooth plates in a hot embossing machine.[37] The overall fabrication process is schematically illustrated in **Figure 1**.

We investigated the influence of the ratio of SMP to the SMPO matrix on the optical and mechanical behaviors and shape-memory properties by producing six different SMP to PO ratios as well as a pure PO sample as reference. Photos of these extruded tapes are shown in **Figure 2**A. The prepared ratios correspond to 5, 10, 15, 20, 25, and 50 wt% SMP. In the following, we refer to those composites as SMPO5, SMPO10, SMPO15, SMPO20, SMPO25, and SMPO50, respectively. With increasing amount of SMPs, the sample's hue becomes less intense until the bright orange of the PO fades to dull brown which is most obvious for the SMPO50 example. This trend is validated by samples spread between two PET-sheets before and after shearing over a hot edge (photographs in Figure 2B). The intensification of the color brightness by the ordering step from

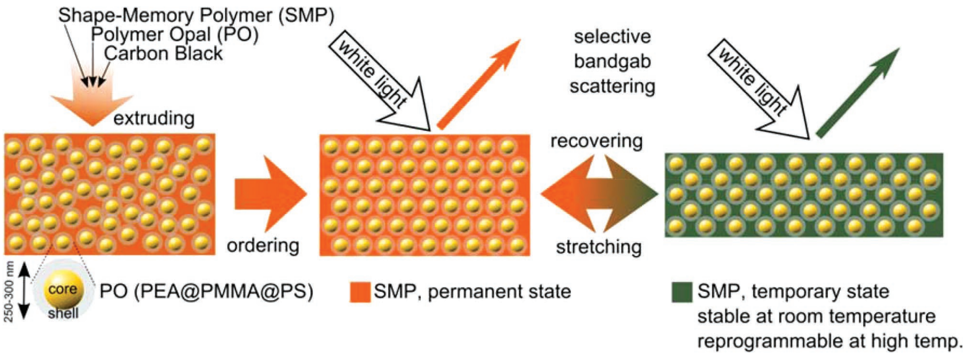

Figure 1. Schematic illustration of the fabrication process and SMPO samples with different contents of SMP. Shape-memory polymer, polymer opals, and <0.05% of carbon black are fed in various ratios to an extruder. After extrusion, the materials are well-mixed and in a subsequent ordering step the opal spheres are aligned. The sample's color can be changed by stretching or compression and recovered via heating through the shape-memory effect.

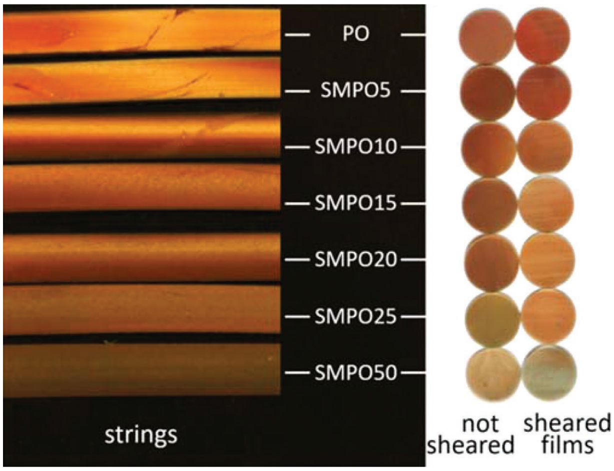

Figure 2. Seven different SMP to PO ratios were extruded into tapes shown by the photograph. With increasing SMP percentage from 0% (top) to 50% (bottom) the brightness of the orange color fades. The photograph on the right shows all SMPO ratios spread between two PET sheets before (left column) and after shearing (right column). Shearing intensifies the color significantly. Larger amounts of SMP dull the color brightness.

the not sheared (left column) to the sheared (right column) films is apparent for all SMPO ratios.

The unique combination of structural color with shape memory enables macroscopic, naked-eye read-outs of programmed stresses and strains in a material by the color displayed. In order to demonstrate the color appearance of the SMPO during a complete programming and recovery cycle we conducted these while capturing the related color changes for SMPO15. Photos of the programming cycle are shown in **Figure 3**A. A 3 × 1 × 40 mm^3 strip of red SMPO15 was gradually stretched by 10% steps to 50%. Thereby, the strip's color changed from red over orange and yellow to green (see Movie S1, Supporting Information). The programming temperature in this case was simply room temperature (21 °C). After releasing the clamps, the sample relaxed to 46%. After putting it on a 60 °C hot plate, the recovery of the initial shape was filmed (see Movie S2, Supporting Information). Sequential photographs from that video taken every 5 s are shown in Figure 2B. The color of the stretched middle part of the strip shifted from green back to red as the sample recovers its original length. This proof of concept experiment demonstrates the continuous color change which can be stopped at any intermediate stage by cooling the sample.[30]

We first characterize the material's mechanical properties and then relate them to its color.

To quantify the shape-memory effect of the produced mixtures, we determined the shape-fixity ratio R_f and the shape-recovery ratio R_r of our six composites. The shape-fixity ratio quantifies how well a material is able to hold the programmed temporary shape. How much the permanent shape is recovered after deformation is specified by the shape-recovery rate. The ratios are commonly defined as[38]

$$R_f(t,T) = \varepsilon_t(t,T)/\varepsilon_s \tag{1}$$

$$R_r(t,T) = (\varepsilon_s - \varepsilon_r(t,T))/\varepsilon_s \tag{2}$$

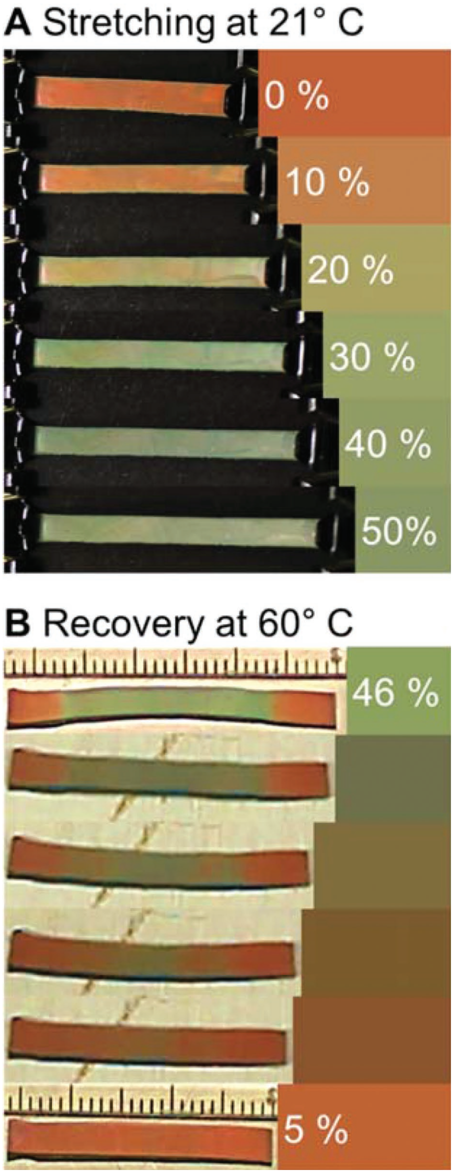

Figure 3. Demonstration of the continuous color change of SMPO15. A) Stretching gradually changes the sample's color from orange through yellow to green. B) After removing the load, the sample relaxes from 50% to 46%. Heating it on a hot plate (T = 60 °C) initiates its shrinkage back to its original length. Coupled with the length change is the color change from green back to orange (see Movies S1 and S2, Supporting Information for more details).

Here, ε_s denotes the programming strain, ε_t is the strain to which the sample relaxes to the temporary shape and ε_r describes the residual strain that remains after full sample recovery. The two ratios are strongly time-(t) and temperature-(T) dependent. The programming temperature has a strong influence on the shape-fixity as it is related to the viscoelasticity of the polymer.[39] For the recovery velocity the temperature plays a crucial role too.[40] Since both programming and recovery correlate to the viscoelastic behavior of the polymer, shape-fixity and recovery rate are a function of time and have to be observed over a reasonable time span.

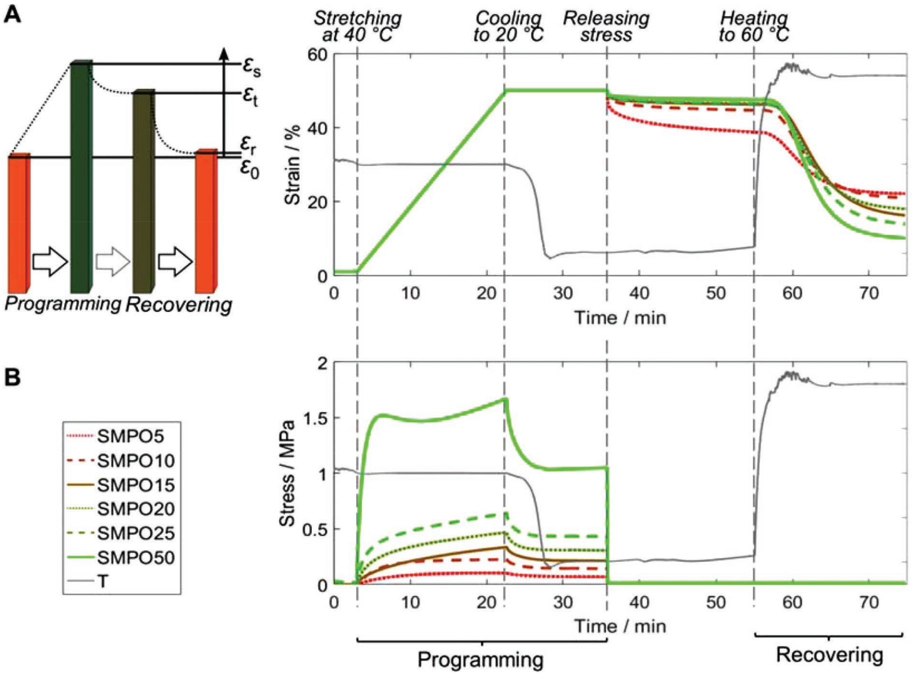

Figure 4. Stretch tuning and mechanical properties of various SMPO ratios. A) The schematic of the programming and recovery process illustrates the time-dependent shape and color change. Strain during the programming and recovery cycles of temperature controlled dynamic mechanical measurements, characterize the mechanical behavior and determine the shape-fixity and shape-recovery rate. B) Stress curves corresponding to the strain cycle in (A).

To determine the individual strain values of each SMPO mixture we conducted a temperature-controlled dynamic mechanical analysis (Q800 TA Instruments) of one programming/recovery cycle under controlled and automated conditions: the samples were stretched to ε_s = 50% at a temperature of T = 40 °C. Afterward, the samples were cooled down to T = 20 °C and after reaching this temperature they were held under constant strain for additional 5 min. The stress was then released by the machine and the samples were allowed to relax at a constant temperature of 20 °C for 20 min. In the last step, the temperature was increased to 60 °C to initialize the recovery process and the samples could freely shrink for 20 min at that temperature. The recorded strain curve of every SMPO is depicted in **Figure** 4A. Figure 3B shows the corresponding stress profiles together the temperature sequence. For low percentages of SMP in the rubbery PO matrix we observe significant relaxation behaviors. The higher the SMP percentage, the better the sample was able to maintain its programmed shape and above a percentage of 15% no distinct difference between of the relaxation behavior the SMPOs is noticeable. A similar trend becomes apparent for the SMPOs shape-recovery ability: the higher the SMP/PO ratio the better the shape-recovery. For SMP percentages of less than 15% the mixing ratio has a smaller influence than for higher SMP content.

For the calculation of the shape-fixity and recovery ratios we used the values of R_f and R_r at the end of each 20 min time section. The stress curves reflect the increasing stiffness of the SMPOs correlated to the increasing SMP percentage, although it cannot be used to determine the composites Young's modulus since the stretching was not conducted at standard conditions. The resulting values for R_f and R_r are summarized in **Table 1** for each composite. From the mechanical testing of our six different SMPO ratios we conclude that the composite with 15% SMP is the best combination with respect to color intensity, shape-fixity, and recovery ability. Thus, we used this SMPO15 composite for the proof of concept of the presented on-demand color-and shape-tunable imprinted structures. For other applications the most suitable color/shape-memory effect trade-off may be different.

We demonstrated the versatility of our SMPO composites to display a shape-coupled stable color change not only through stretching but also by compression. We fabricated sheets of SMPO by deforming extruded, red SMPO15 tapes into a 25 × 25 × 2 mm^3 substrate by melting and pressing the strings into an appropriate template. **Figure** 5A shows the resulting substrate as a photograph. Details were imaged with an optical microscope (inset), and the topography was recorded with a vertical scanning interferometer (VSI) (right). Initially the sample surface is smooth with a uniform red-orange color. In this substrate, we imprinted the structure of the face of a 1 euro-cent coin at 40 °C (temperature of substrate and coin). This yielded a color change in the areas where the coin's bulges indented the SMPO composite. Figure 5B pictures the depression generated by the coin (for clarity the photograph is mirrored). The microscopy

Table 1. Shape-fixity ratio R_f and shape recovery ratio R_r for the examined SMPO.

	SMPO5	SMPO10	SMPO15	SMPO20	SMPO25	SMPO50
R_f	0.77	0.89	0.92	0.93	0.93	0.95
R_r	0.56	0.58	0.68	0.64	0.72	0.80

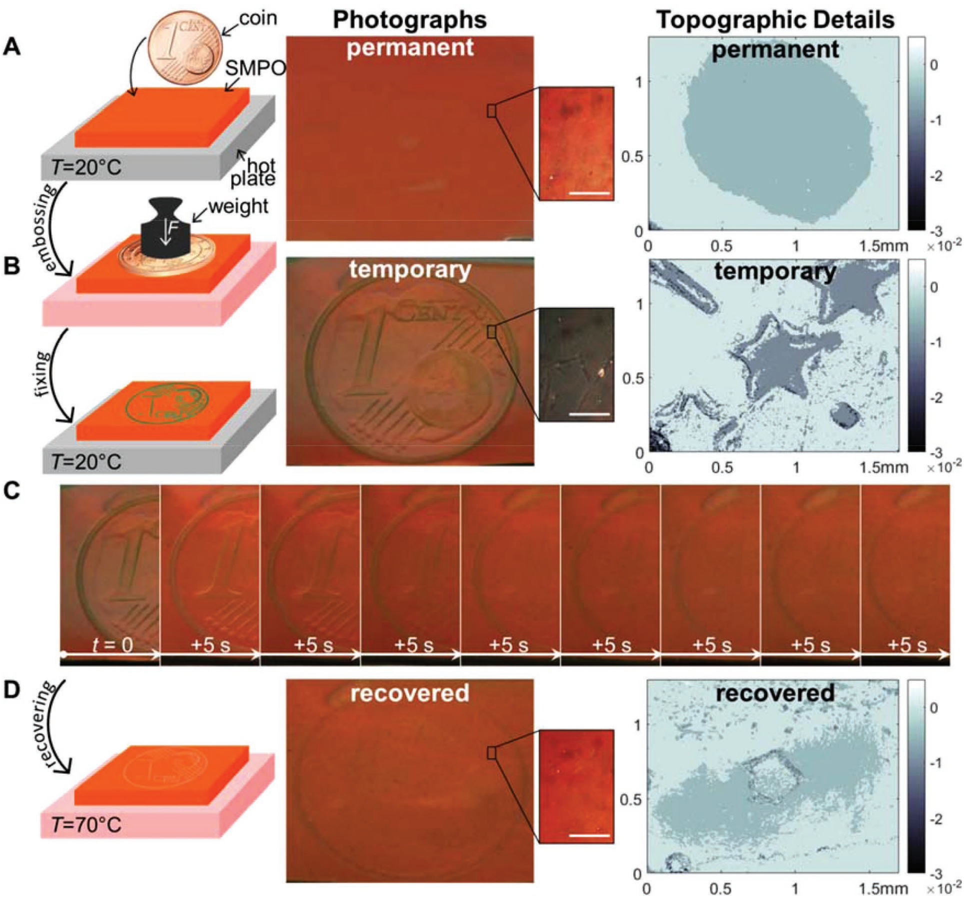

Figure 5. Color change on-demand of temporarily imprinted structures. The left column depicts the procedure schematically, the middle column shows photographs of the respective samples with close ups (scale bars 10 µm), and topographic details of the respective structures are given in the right column. A) The surface of a SMPO15 sample in its permanent shape shows a smooth surface and uniform red/orange color. B) The face of a 1 euro-cent coin is pressed at elevated temperature into the sample's surface. The topography of the coin is well replicated. Compression of the material results in a color change from red to green. C) The sample is heated to the SMP switching temperature whereupon the original shape recovers and the coin indentations fade as revealed by the color change. D) The original shape is almost completely recovered with only slight residual marks of the coin structure.

image in the inset illustrates the distinct color change from red to green in the structure's cavities. The correlated structure depth is revealed by the VSI plot. Indentations of only 10 to 20 µm are capable of inducing significant color change caused by the local compression of the opal lattice. To reset the color and structure back to the initial, smooth, red surface, we increased the sample temperature on a hot plate to 70 °C. The evolution of the recovery is captured by sequential photographs taken every 5 s (see Figure 5C). The gradual disappearance of the coin image is caused by the flattening of the green indentations which gradually go back to red. After 1 min exposure of the sample to the heat source the coin image has nearly vanished both in terms of indentation depth and color (Figure 5D).

The on-demand color tuning of polymer opals introduced in this study promises energy-efficient durable and reusable color patterning in coatings, security, and wearable applications. It is enabled by embedding a shape-memory polymer into a polymer opal matrix. We show that increasing the ratio of SMP to PO in the composite, increases the brightness of the structural color, while increasing the PO improves the programming of shape and color in the material (shape-fixity and shape-recovery ratios). We found the best combination of color intensity and shape-memory properties in the composite to occur at compositions with 15 wt% of SMP. With this material we demonstrated not only excellent tunability of color by stretching but also the ability of the material to remain with a fixed color in defined shapes. This property guarantees a durable color until the recovery process is triggered. We demonstrate that color patterns with high resolution can be produced by imprinting topological features on polymer opal films, locally changing their color. These can be reset to their original color and smooth shape by heating above the transition point of the shape-memory material. Hence, our material paves the way for large-scale labeling or billboard displays, with durable structural color-on-demand PO coatings.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

photonic crystals, polymer opals, shape-memory polymers, tunable structural colors

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