Large-scale fabrication of three-dimensional ordered polymer films with strong structure colors and robust mechanical properties

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The self-assembly of colloidal spheres into ordered nanostructures is one of the most common methods of fabricating crystal films, but the resulting films usually have small areas, muted structural colors, and weak mechanical properties. This paper presents a simple method for the large-scale fabrication of polymer crystal films with vivid structural colors and robust mechanical properties. In this approach, when aqueous polymer colloids, colloidal silica particles, and a small quantity of carbon black are blended and then cast on substrates by the casting method to evaporate water, three-dimensional ordered structures are produced, directly forming large-scale polymer crystal films with intense and tunable structural colors and strong mechanical properties.

Introduction

It has been demonstrated that the assembly of colloidal spheres into three-dimensional (3D) ordered nanostructures is a relatively simple, cost-efficient means of fabricating crystal films for certain applications, such as photonic crystals, biosensors, templates, paints, photonic papers, and cosmetics.1–17 The typical procedure for this assembly of colloidal spheres can be described as follows: a substrate (usually silica glass slides or silicon wafers) is placed vertically or tilted into a very dilute suspension of monodisperse spheres. As the solvent evaporates, the surface of the liquid slowly travels down the substrate, coating it with spheres that can assemble into a highly crystalline arrangement with a face centered cubic (fcc) structure, driven by capillary force.18–20 Typical colloidal spheres are so-called “hard” spheres, including colloidal silica, polystyrene, and poly(methyl methacrylate). As a result, the as-obtained crystal films have neither reliable mechanical properties nor desirable sizes.21,22 To solve these problems, some very interesting strategies have been developed.23–30 For example, Wang et al. synthesized polymer latex spheres with hard polystyrene cores and elastomeric poly(methyl methacrylate-acrylic acid) shells, to produce opaline polymer films with notable mechanical strength via vertical deposition.27,28 McGrath et al. synthesized monodisperse colloidal particles composed of poly(styrene-co-N-isopropylacrylamide), which rapidly self-assembled via simple solvent evaporation to form three-dimensional colloidal crystals.30 Very recently, we successfully fabricated three-dimensional polymer crystal films with large-scales and robust mechanical properties through the direct film-formation of a mixture of water-borne “soft” polymer particle latex and colloidal silica,31 and even pure “soft” polymer sphere colloids.32 However, although these strategies can generate photonic crystal films with robust mechanical properties and large-scales, the resulting crystal films are still not suitable for some practical applications because of their lack of enough brilliant structural colors. This is because the conventional self-assembly of colloidal spheres inevitably introduces some random defects, such as missing particles, uncontrolled orientation, mixtures of phases, or dislocations.33–35 These defects decrease the reflectivity of the stop band and scatter the wavelength light outside it. Thus, the light we usually observe not only contains the wavelength corresponding to the expected color but also these unwanted wavelengths. The as-obtained artificial opals tend to have rather muted colors, with flashes of iridescence at specific angles but overall a rather milky and unappealing appearance.36 Until a few years ago, Pursiainen et al. successfully used carbon black to enhance the color saturation of polymer photonic crystals by polymer melting compression.37,38 Recently, Finlayson et al. used a combined process of extrusion (using a twin co-rotating-screw mini-extruder at 150 °C), rolling (linear shear), and edge-induced rotational shearing to produce permanent rolls of opal polymer films.39 The polymer was synthesized by an emulsion polymerization with rigid cross-linked polystyrene spheres as cores, capped by a soft polyethyleneacrylate shell via an interlayer containing allyl-methacrylate as a grafting agent. The photonic crystal film with 0.05 wt% of carbon nanoparticles was found to have a brilliant visual iridescence.

In this article, we present a simple method of fabricating large-scale polymer crystal films with robust properties and intense and tunable structural colors based on our previous results.31,32,40 This process is simply made by casting the aqueous suspension of “soft” polymer colloids, colloidal silica, and a small amount of carbon black on substrates and allowing them to dry at room...
temperature. In comparison to previous techniques, the primary differences and advantages of this approach are as follows: i) the polymer crystal films with vivid colors and robust mechanical properties are easily obtained by directly casting the suspension on substrates and letting it dry at room temperature. Neither multi-step fabrication processes nor special equipment nor high temperature is needed, so this process is truly simple and cost-effective. ii) The structural colors are strong enough that they can be observed easily under natural lighting conditions, and the chroma of the structural colors can be modulated by the carbon black content. iii) Because the polymers are synthesized by batch-rather than seeded-emulsion polymerization and have relatively low glass transition temperatures, polymer colloids are readily obtained and the resulting polymer photonic crystal films are so robust that they can be further processed, e.g., cutting, bending, punching, and so on. iv) This method can be used for mass production of polymer color films of any size from square centimeters to square meters. Thus, this process may have practical applications in coatings, cosmetics, textiles, sensors, photonic papers, and other areas.

Experimental

Materials

Butyl acrylate (BA), styrene (St), acrylic acid (AA), ammonium persulphate (APS), sulfuric acid, and nitric acid were purchased from Shanghai Chemical Reagent Co. (China). Silica sol (Bindzil 2034DI, 20 nm, pH 3, 34 wt% of solid content) was provided by Eka Chemicals Co. (Sweden). Allyloxyhydroxypropyl sodium sulphonate (HAPS, 40 wt% of solid content in aqueous solution) was donated by Shuangjian Trading Co., Ltd. (China). BP2000 carbon black (20 nm) was donated by Carbot Co. Ltd. Deionized water was used in all the polymerizations. All chemical reagents were used without further purification.

Synthesis of soft colloidal polymer spheres

A surfactant-free emulsion polymerization procedure was carried out as described in the literature. Deionized water (95 g), HAPS (1.0 g), AA (2 g), BA (20 g), St (20 g), and APS (0.25 g) were added into a four-necked flask equipped with an N₂ inlet, a reflux condenser, and a mechanical stirrer. The polymerization was carried out at 75–80 °C for 10 h to produce waterborne polymer latex with a solid content of 34 wt%. The polymer latexes, with various particle sizes, were synthesized by controlling the HAPS content. The glass transition temperature of the polymers was 23 °C, as measured by DSC.

Treatment of carbon black

Carbon black was blended with concentrated sulfuric acid at a stirring speed of 100 rpm for 12 h, and was then centrifuged and washed with deionized water until the pH approached 7. It was then dispersed in deionized water with 0.5 wt% of solid content.

Preparation of polymer crystal films

The polymer latexes were blended with colloidal silica and carbon black at a stirring speed of 200 rpm for 2 min and ultrasonically treated at 300 W power for 2 min at ambient temperature to produce nanocomposite polymer dispersions. The typical weight ratios of silica and carbon black to polymer were 20 and 0.15%, respectively, except where specifically noted. The dispersions were cast on glass or polypropylene substrates in the same area and dried at ambient temperature for 24 h to form polymer photonic crystal films.

Characterization

Raman spectra were obtained with a Dilor LabRam-1B microscopic Raman spectrometer (France), using a He–Ne laser with an excitation wavelength of 632.8 nm. The reflection spectra of the crystal films were taken using a beam spot of 0.04 mm² in area and an integral sphere fiber-optic UV-vis spectrometer (Ocean Optics, ST2000, Dunedel, FL), in which the detection light was collected in a wide range of reflecting angles. The angle dependence of the reflection spectra was recorded using a small numerical aperture lens to collect light reflected at certain angles to improve its angle dependence. Photographs of the crystal films were taken with a Canon Power Shot A95. SEM images of the samples were obtained with a Philips XL 30 field emission microscope. All samples were coated with gold by sputtering prior to observation. The mean size of the polymer spheres was measured by TEM images with a Hitachi H-600 TEM (Japan). The color differences of the crystal films were measured by a spectrophotometer (CM-700d, Konica Minolta Sensing Inc., Japan) according to a Commission International d’Eclairage (CIE) LAB color scale. The LAB system has a lightness scale L and opposing color axes for redness–greenness versus yellowness–blueness, designated A and B, respectively. Each color was represented by a unique point in the three-dimensional coordinate zone used in the LAB system. The L value characterizes the brightness of the color and range between 0 (dark) and 100 (light). The A and B values are the chroma coordinates and characterize the hue and chroma factors. The A axis is red on the positive side and green on the negative side, and the B axis is yellow on the positive side and blue on the negative side. The higher the A and B values, the stronger the colors.

Results and discussion

Fabrication and structure of the polymer crystal films

Scheme 1 briefly describes the fabrication procedure. Polymer colloids are blended with colloidal silica and carbon black at room temperature to produce aqueous nanocomposite polymer suspensions, which are then cast on glass or polypropylene substrates and subsequently dried at room temperature for 24 h to directly form polymer crystal films. Fig. 1 demonstrates the
typical cross-sectional SEM images of these films with and without carbon black. It can be seen that these soft polymer spheres can self-assemble into three-dimensional periodic structures with the aid of hard nanosilica particles or nanosilica/carbon black particles. These hard particles fill in the interstices between these soft polymer spheres and can be observed more clearly in the inset magnified images, as shown in Fig. 1a and b. The inset SEM image in Fig. 1b further indicates an fcc structure, showing that the carbon black dopant does not disrupt the three-dimensional periodic structure. After silica particles were etched, the residual carbon black particles remained observable in the interstices between the polymer spheres (Fig. 1c). However, if too much carbon black, e.g., 0.5 wt%, was used, the periodic structure of the opaline film was destroyed (Fig. 1d). This may be because excessive carbon black brings more ions, such as sulphate and carbonylate into the films, destroying the electrostatic forces that drive self-assembly.

Fig. 2 shows the typical Raman spectra of the polymer crystal films with and without carbon black and the pristine acid-treated carbon black. The typical Raman spectrum of pristine carbon black consists of two sharp modes, the G band at 1600 cm\(^{-1}\) and the D band at 1346 cm\(^{-1}\). They were assigned to crystalline graphitized and disordered carbons, respectively.\(^{19}\) When 0.15 wt% of carbon black is doped into the film, the spectrum of the polymer film reveals not only the bands of the crystal film but also the G and D bands of acid-treated carbon black, indicating that carbon black has become embedded in the crystal film. The intensities of the G and D bands of carbon black in the crystal film have been enhanced about eight times relative to those of the pure acid-treated carbon black. The mechanism is not clear at present, and may involve the action of scattered photons in the crystal film on the polar vibration of conjugated carbon bonds.

Fig. 3 Experimental and theoretical reflection spectra of crystal films with different polymer sphere diameters. (a) The upper part corresponds to the polymer/silica crystal films and the bottom to the polymer/silica/carbon black crystal films; (b) theoretical simulated absorption and reflection spectra of polymer/silica/carbon black crystal films; (c) bent polymer/silica/carbon black crystal films.
Effect of polymer sphere size on the crystal films

Fig. 3a reveals the reflection spectra and photographs of the polymer crystal films with and without carbon black, prepared from polymer spheres of 200, 241, and 280 nm in diameter. The films without carbon black have reflectance peaks at 476, 568, and 640 nm, which correspond to purple, green, and light red colors, respectively. After 0.15 wt% of carbon black is doped, the films display sharp reflectance peaks at 456, 565, and 655 nm, which correspond to violet, green, and deep red, respectively.

According to Bragg’s law, the stop band and the color of a three-dimensional periodic structure can be explained using following equation:

$$\lambda = 2nd \sqrt{1 - \frac{1}{n^2} \sin^2 \theta}$$  \hspace{1cm} (1)

Here, $d$ is the distance between the crystalline planes in the (111) direction and is related to the polymer sphere diameter $D$ by $d = \sqrt{2/3} D$ for the fcc structure. The angle $\theta = 0^\circ$ is normal incidence to a sample. The effective refractive index $n$, can be approximated by the following expression:

$$n = \sqrt{f_{\text{polymer}} n_{\text{polymer}}^2 + f_{(\text{SiO}_2 + \text{air} + \text{carbon black})} n_{(\text{SiO}_2 + \text{air} + \text{carbon black})}^2}$$  \hspace{1cm} (2)

Here, $f_{\text{polymer}} = 0.74$ and $f_{(\text{SiO}_2 + \text{air} + \text{carbon black})} = 0.26$ are the filling ratios for the polymer and nano silica particles plus air and carbon black in the fcc structure, respectively. Thus, if the position of the stop band is within the visible range, the films unveil colors. The peak position of the stop band and the color of the crystal film depend on the refractive index contrast between the polymer and the nanosilica/carbon black, the relative filling ratio, and the diameter of polymer spheres. When the crystal film is fabricated from polymer spheres, 20 wt% of colloidal silica and 0.15 wt% of carbon black based on the mass of the polymer, the volume ratio of silica/carbon black/air in the interstices between the polymer is 2.7 : 0.14 : 7.7, so

$$n_{(\text{SiO}_2 + \text{air} + \text{carbon black})} \approx \sqrt{\frac{7.7}{10.5} \times 1^2 + \frac{0.14}{10.5} \times 1.8^2 + \frac{2.7}{10.5} \times 1.452^2}$$

$$= 1.15$$

and $n = 1.44$ with $n_{\text{polymer}} = 1.533$, $n_{\text{SiO}_2} = 1.452$ and $n_{\text{carbon black}} = 1.8$. Thus, the calculated peak positions of the stop bands for the polymer/silica/carbon black crystal films made of polymer spheres of 200, 241, and 280 nm in diameter are 470, 576, and 662 nm, respectively. These values roughly match the experimental peak positions.

Fig. 3a also shows that the films with carbon black have a lower reflectivity than those without carbon black. For example, the polymer/silica crystal film prepared from the polymer spheres of 241 nm in diameter has about 79.0 and 74.0% reflectivity in the band gap and on the long wavelength side of the stop band, respectively, while the crystal film with 0.15 wt% of carbon black has only 22.0 and 7.0% reflectivity in the stop band and on the long wavelength side of the stop band, decreases of 57 and 67%, respectively. The crystal films from the polymer spheres of 200 and 280 nm in diameter show the same phenomenon. Even so, photographs show that the films without carbon black have low chroma and weak colors that do not match the vivid colors of natural species. The doping of carbon black into the films can enhance the chroma, causing brilliant colors (see the inserted photographs). For ideal, defect-free colloidal crystals, the light must have very strong reflectance in the stop band but very high transmittance in the other wavelengths from the viewpoint of physical foundation to display brilliant structural colors.\(^{41}\)

However, as mentioned above, certain unavoidable defects in the artificial colloidal crystal not only decrease the reflectivity of the stop band but also scatter the long and short wavelength lights outside the stop band. Thus, the light we usually observe not only contains the wavelength corresponding to the stop band but also these unwanted wavelengths outside the stop band. As a result, low chroma and milky white colors appear.\(^{36-37}\) When carbon black is doped, although the overall reflectivity is reduced, unwanted wavelengths, which are usually scattered by defects, can be absorbed by carbon black to give less than 10% reflectivity. Because the color saturation of the polymer films is dependent upon the contrast of the reflectance intensity between the stop band and the wavelengths outside the stop band rather than the absolute intensity of the reflectance, the stronger the reflectance of the stop band relative to that outside the stop band, the sharper the structural colors are. The chroma of the structural colors can be further evaluated quantitatively by the contrast between the reflection of the stop band and the wavelength side of the stop band, namely the height of the reflectance peak. The higher the peak, the greater the chroma of reflected light in the band gap is and the more brilliant the visible colors are. The peak heights of the polymer/silica/carbon black crystal films made of polymers of 200, 241, and 280 nm in diameter are 12, 14, and 18%, much higher than the 1.0, 5.0, and 4.0% of their corresponding polymer/silica crystal films. Therefore, the introduction of carbon black dopant in the crystal films can remarkably increase the chroma, producing very brilliant structural colors that are visible under natural lighting conditions, as shown by the large crystal films in Fig. 3c. These films present good mechanical properties with a maximum impact strength, tensile strength and breaking elongation as high as 50 kg cm, 3.19 mPa and 372%, respectively, and can be processed discretely, e.g., by cutting, puckering and bending. This indicates that “soft” polymer spheres combined with inorganic particles can produce robust crystal films. This is totally different from the traditional crystal films fabricated by the colloidal self-assembly of silica, polystyrene or poly(methyl methacrylate) spheres, which have poor mechanical performances.\(^{41}\)

Another interesting phenomenon is that the strong absorption characteristics of carbon black are modified greatly in the crystal films. The homogeneous carbon black system should cause black films to form due to its strong broad-spectrum absorption. However, when carbon black is doped into the crystal films, its absorption in the stop band becomes very low because the photonic density of states in the stop band is very low.\(^{42-43}\) To verify this, we simulated the three kinds of crystal films with different-sized polymers using a modified layer-KKR method.\(^{44}\) This can simulate the reflection and absorption coefficients of light using a slab of three-dimensional photonic crystals. The photonic crystal consists of a stack of slices parallel to a given surface. These slices may consist of two kinds of components. Each of them can be either a homogeneous plate or a multilayer of spherical particles of given periodicity parallel to the surface.
The refractive index of each component material can be complex. The original code of the layer-KKR method can be downloaded from the website of the computer physics communication program library. In the simulation, the effective refractive indexes of the matrix and polymer spheres are 1.15 and 1.53, according to this experiment. For the simulated absorption of the carbon black particles in the matrix, the imaginary part of the refractive index of the matrix is 0.15. Thus, the theoretical reflection and the absorption spectra are shown in Fig. 3b. The theoretical reflection spectra match the experimental spectra very well, but they also differ from the actual absorption spectra of carbon black. It can be inferred that the carbon black in the crystal films has very little ability to absorb photons in the stop band region but a very strong absorption outside it. It is this characteristic that allows the doped carbon black to restrain the light scattering of unwanted wavelengths and retain low absorption in the stop band. This can ensure that the carbon-black-doped crystal films have a strong reflectance in the stop band, enhancing the chroma of the structural colors. Fig. 4 shows the angle dependence of the spectra as a function of angle. When the angle changes from 10 to 50°, the peak gradually shifts to blue from 538.4 to 458.9 nm. The angle-dependence of the spectra indicates iridescent colors.

Fig. 5 compares the structural colors of the polymer crystal films with and without carbon black under natural lighting conditions. The crystal films with carbon black have considerably more brilliant colors than those without carbon black.

**Effects of carbon black content on the crystal films**

The effects of the carbon black content on the polymer crystal films are presented in Fig. 6. Without carbon black, the film has around 79 and 74% reflectivity in the stop band region and on the long wavelength side of the stop band, respectively. When 0.05 wt% of carbon black is added, the reflectivity in the stop band and on the long wavelength side of the stop band drops to 28 and 17%, respectively, while the height of the reflectance peak increases from 5 to 11%. Compared to the spectrum of the film without carbon black, the peak causes a blue shift. According to Bragg’s law, the peak position has a relationship with the effective refractive index and the distance between the (111) plane. The addition of carbon black increases the effective refractive index, causing a red shift of the diffraction peak. However, when the polymer spheres self-assemble into ordered structures, some carbon black may cover the surfaces of the polymer spheres by hydrogen-bonding or other molecular forces. This reduces the distance between the (111) plane and causes a blue shift of the diffraction peak. When 0.05 wt% of carbon black is doped, the blue shift resulting from the reduction of the distance between the (111) plane is greater than the red shift from the increasing effective reflective index, so the peak produces a blue shift. When 0.15 wt% of carbon black is doped, the reflectivity in the stop band and on the long wavelength side of the stop band drops to 22.0 and 7% with an increasing peak height of 15%. This increase in peak height is because carbon black absorbs fewer photons in the stop band than in the other wavelength regions when carbon black increases in concentration. When the carbon black content is further increased to 0.25 or even 0.35 wt%, the peak height begins to drop to 9.2 or 4.7%, respectively. For similar crystal films under the same light source, the photonic numbers on both sides of the stop band are limited. Carbon black absorbs more photons on the two sides of the stop band than in the stop band. Saturation numbers can be reached when the carbon black content is increased to 0.15 wt%. When more than 0.15 wt% of carbon black, such as 0.25 or even 0.35 wt%, is used, more photons in the stop band are absorbed and the number of photons absorbed on the two sides of the stop band changes little. The absorption in the stop band increases but little change is seen at other wavelengths. For the crystal films from the polymer spheres of 200 and 280 nm in diameter, the carbon black content has the same influence on the reflection spectra. Compared to the spectrum of the crystal films of 241 nm in diameter with different carbon black contents.
film with 0.15% carbon black, the peak shifts red because of the increasing effective reflection index.

Table 1 summarizes the L, A, and B values of the crystal films from the polymer spheres of 200, 241, and 280 nm in diameter with different levels of carbon black. The L values of the crystal films without carbon black are higher than those with carbon black, and they decrease greatly as the carbon black content increases from 0.05 to 0.35 wt%. This indicates that the crystal film without carbon black is brighter than the films with carbon black, and the brightness of the film decreases with increasing carbon black content. A and B values represent the chroma of the structural colors. The chroma increases when carbon black first increases and reaches a maximum at 0.15 wt% of carbon black. It then decreases when the carbon black content continues to increase to 0.25, and 0.35 wt%. This is consistent with the change in the height of the reflectance peak and indicates that the chroma of the structural colors is tunable by the carbon black content.

Effects of silica content on polymer crystal films

Fig. 7 shows the influence of the silica content on the reflection spectra of the polymer crystal films. Again, the addition of carbon black decreases the reflectivity of the crystal film in the stop band and other wavelength regions. When the silica content increases from 5 to 20 wt%, the reflectivity in the stop band increases from 10 to 22% but only rises from 7 to 8.0% on the long wavelength side of the stop band, with an increasing peak height from 3 to 14%. When the silica content continues to increase from 20 to 35 wt%, the peak height drops from 15 to 8%. That is, the height of the reflectance peak reaches a maximum at 20 wt% silica.

According to the closed packed fcc structure, the volume fractions of the polymer spheres and the interstices among the polymer spheres are 74 and 26%, respectively. During self-assembly, the outermost water molecules evaporate into the surrounding atmosphere and form a meniscus among the polymer spheres. The distance between the spheres becomes small enough to produce static forces with the evaporation of water. Then the polymer spheres self-organize into periodic structures, driven by static and capillary forces with silica and carbon black filling the interstices. If the interstices are fully filled only with silica particles, the silica content (weight ratio to polymer) should be about 78%. When 5 wt% of silica is used, the volume fraction of the silica is about 1.7%, far below the theoretical maximum volume fraction of 26%. Therefore, when these soft polymer spheres self-assemble into a periodic structure with the aid of 5 wt% silica and 0.15 wt% carbon black used in this experiment, defects are unavoidable. The reason for this is that there are not enough silica and carbon black particles to surround the polymer or fill the interstices to prevent them from forming homogeneous or nonperiodic structures with two dielectric constants within the films. The lower the silica content, the greater the number of non-periodic structures and the fewer the number of periodic structures. These non-periodic structures not only disrupt the shapes of the reflection spectra but also reduce the scattering density of the Bragg diffraction in the stop band region. This means that more photons are absorbed by carbon black in the stop band. If carbon black absorption in the stop band is greater than that of the short and long wavelength sides of the stop band, the height of the reflectance peak drops to a lower value than that of the crystal films without carbon black. With the increase of the silica content, the periodic structure increases. Thus, the scattering density of the Bragg diffraction increases, which causes more photons in the stop band region to escape from the film and decreases absorption by carbon black. The peak height increases gradually with increasing silica content.

The peak height of the film reaches a maximum at 20 wt% of silica content, which occupies about 10.5% of the whole volume. As more silica is used, the viscosity of the system increases. Air and water do not completely evaporate from the suspension, so silica cannot completely fill the interstices during self-assembly. This again disrupts the organization of the periodic structures and decreases the scattering density of the films and the peak heights correspondingly.

### Table 1

| CB: 0.0% | L: 66.8 B: 2.93 | A: 0.15 | L: 72.1 A: 0.46 | L: 68.8 A: 2.10 |
| CB: 0.05% | L: 64.7 B: 5.29 | A: 0.47 | L: 32.9 A: 0.59 |
| CB: 0.15% | L: 62.2 B: 7.33 | A: 0.64 | L: 25.9 A: 0.41 |
| CB: 0.25% | L: 59.4 B: 6.02 | A: 0.60 | L: 10.4 A: 0.62 |
| CB: 0.35% | L: 59.9 B: 2.21 | A: 0.01 | L: 5.9 A: 0.01 |

### Table 2

| CB: 0.0% | L: 10.6 B: 2.93 | A: 0.15 | L: 12.1 A: 0.59 | L: 10.6 A: 1.00 |
| CB: 0.1% | L: 15.1 B: 0.57 | A: 0.15 | L: 12.1 A: 0.15 | L: 12.1 A: 0.07 |
| CB: 0.5% | L: 12.6 B: 13.03 | A: 0.15 | L: 12.5 A: 0.57 |
| CB: 1.0% | L: 13.2 B: 15.90 | A: 0.15 | L: 12.8 A: 1.58 |

Table 2 summarizes the L, A, and B values of the crystal films with various silica contents. The L values of the polymer/silica carbon black crystal films increase with increasing silica content, indicating increasing brightness. This is because silica itself can reflect incident light. The A and B values reach a maximum at 20 wt% of silica, indicating that crystal films with 20 wt% of silica have the highest chroma and the most brilliant colors. This is consistent with the change in peak height.

Conclusions

Based on this study, large-scale, robust, intense, and structurally color-tunable polymer crystal films can be successfully fabricated by a casting method. This method is not only simple and feasible, but the as-obtained polymer crystal films also display brilliant visual iridescence under natural lighting conditions. The chroma of the structural colors is tunable by carbon black content because carbon black in the crystal film absorbs fewer photons in the stop band region than elsewhere. Thus, vivid, controllable structural colors, robust mechanical properties, and large-scales can be produced at levels suitable for practical applications in coatings, cosmetics, textiles, sensors, and photonic papers.

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