Construction of the Photonic Crystal Structural Colors with High Colorfastness Using the Novel Synthesis Adhesive

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Abstract. Photonic crystal Structural color has received more and more attentions in recent years. However, there are also some drawbacks of these structural colors, such as the cracking and low colorfastness. In this research, the novel adhesive of P(GMA-co-HFBMA)-g-PEGMA which contains the epoxy group and the hydrophobic fluorocarbon chain was synthesized. The chemical structure of the P(GMA-co-HFBMA)-g-PEGMA was characterized by FTIR and EDS spectra. The results of FTIR and EDS spectra revealed that P(GMA-co-HFBMA)-g-PEGMA was successfully synthesized and used as the adhesive for the improvement of the colorfastness. The results revealed that the novel adhesive will be beneficial for the improvement of the rubbing and washing colorfastness of the photonic crystal structural colors. When the usage of 1% P(GMA-co-HFBMA)-g-PEGMA was 0.5 mL, the brightness of the structural color will increase. While the usage was higher than the 1 mL, the brightness of the structural colors will decrease with the increasing of the usage. Therefore, the suitable usage of the 1% P(GMA-co-HFBMA)-g-PEGMA was less than 1 mL. This research will provide the novel method for the development of the photonic crystal structural color with high colorfastness.

1. Introduction

In recent years, natural structure colors have received more and more attentions which are originated from the special physical effect, such as dispersion, scattering, interference and diffraction [1-2]. There are more researches in this field about the fabrication of the structural color photonic crystals on different substrates. Shao et al. reported that various monodisperse microspheres with controllable particle size and excellent monodispersity were prepared by soap free emulsion copolymerization. They were used to form the photonic crystals which were assembled on different kinds of fabrics by gravity deposition, vertical deposition and inkjet printing [3-7].

Nowadays, the beautiful and bright structural colors based on the photonic crystals could be successfully fabricated. However, there are also some drawbacks of these biomimic structural colors, such as the cracking and low colorfastness. The capillary pressures would produce by solvent between colloidal microspheres during the formation of structural color films resulting in the transverse tensile stress, and it will bring about the cracks when the transverse tensile stress exceeds the strength of the critical closed-packed of the film [8-11]. Thus, it is very important to prevent the crack appear during the formation process of structural color films. And due to the weak interaction between the structural color photonic crystals and the substrates, the color fastness of the structural colors is poor. The effective method to reduce the crack is to improve the interaction between the structural color film and the substrate [12-13]. Chen et al. [14] reported that the introducing of the coordination interaction among the microspheres would be beneficial for the assembly of the colloidal particles to form the large-area crack-free quality functional colloidal photonic crystal films. Yi et al.[15] used the
3-aminopropyltriethoxysilane (APTES) to react with PDA of the polydopamine-coated polystyrene core-shell nanoparticles (PS@PDA NPs) forming the crack-free photonic crystal films. In order to reduce the cracking and improve the color fastness of the structural colors on the substrates, the stronger intermolecular force between the structural color photonic crystals and substrates should be introduced, such as the covalent bond.

Therefore, in this research the novel adhesive of P(GMA-co-HFBMA)-g-PEGMA which contains the epoxy groups and the hydrophobic fluorocarbon chain was synthesized. This adhesive was added into the silica photonic crystals anticipating forming the covalent bond to improve the colorfastness. This research will provide the novel method for the development of the photonic crystal structural color with high colorfastness.

2. Experimental Section

2.1. Materials
Polylethylene glycol methyl ether methacrylate (PEGMA, Mr=475) and Glycidyl methacrylate (GMA, 97%), Hexafluorobutyl methacrylate were purchased from Aladdin reagent (Shanghai) Co., Ltd (Shanghai, China). Azo diisobutyronitrile (AIBN) was purchased from Shanghai No.4 Reagent & H.V. Chemical Co., Ltd (Shanghai, China). Dimethylformamide (DMF) and ethyl alcohol were purchased from Shandong Xiya Chemical Industrial Co., Ltd (Shandong, China). Monodisperse silica microspheres (CV <3%, solid content 10%) was purchased from Nanjing Caijing biotechnology co., LTD. (Jiangsu, China).

2.2. Synthesis of P(GMA-co-HFBMA)-g-PEGMA
6 g GMA, 6 g HFBMA and 8g PEGMA were dissolved into the 50 mL DMF and fed into round bottom flask. Then the reaction mixture was heated to 65°C, when HFBMA, PEGMA and GMA were absolutely dissolved, 6 mL AIBN initiator solution (with the concentration of 0.2 g/mL dissolving in DMF) was added under N2 atmosphere. After the reaction system was kept at this temperature for 12 h, the reaction mixture was dried at 50 °C to obtain the crude product. The crude product was washed by anhydrous ethanol for three times to remove the residual solvent and the unreacting HFBMA, PEGMA and GMA, then the product was vacuum freeze dried till the constant weight to obtain the purified P(GMA-co-HFBMA)-g-PEGMA. The chemical structure of P(GMA-co-HFBMA)-g-PEGMA is shown in Figure 1.

![Chemical structure of P(GMA-co-HFBMA)-g-PEGMA](image-url)
2.3. Preparation of Photonic Crystals Structural Coloration

The 1mL monodisperse silica microsphere dispersion aqueous solution with particle size of 210 nm was added into the 4mL deionized water. A certain amount of P(GMA-co-HFBMA)-g-PEGMA copolymer solution (the concentration was 1% which was dissolved in deionized water) was added into the monodisperse silica microsphere dispersion aqueous solution. The atomizing solution is added to a portable atomizer (Air 360 mini+A, Shenzhen banglijian technology co. LTD) to produce aerosol which was spray onto the black paper with the size of 5×5 cm. The colored black paper was dried less than 40 °C for 10 minutes.

2.4. Characterization

The chemical structure of P(GMA-co-HFBMA)-g-PEGMA was characterized by Fourier transform infrared spectroscopy (FTIR) and Energy dispersive spectrometer (EDS). FTIR spectra were recorded on a IRPrestige-21 (Shimadzu, JAPAN) FTIR spectrometer with KBr pellets under air atmosphere. EDS was determined by the Scanning Electron Microscope-Energy Spectrometer (SEM-EDS). The morphology of structural colos on cotton fabric was viewed by a Hitachi S-4800 scanning electron microscopy (SEM) after being sputtered with gold for 20 s. The reflectance curve of structured color fabric was measured by Datacolor 650 spectrophotometer (Datacolor, USA) with a test range of 400-700 nm.

The sandpaper abrasion test was used to determine the rubbing colorfastness of the structural color on the cotton fabric according to the previous research [16]. The sample for testing was placed face-down to the sandpaper weighting 50 g by moving for 5 cm along the ruler, then the sample was moved for 5 cm in the opposite direction along the ruler. This process was defined as one abrasion cycle, the staining area of black particles on the bleached cotton fabric was used to determine the color fastness until it reached the excepted abrasion cycles.

3. Results and Discussion

3.1. Characterization of P(GMA-co-HFBMA)-g-PEGMA

![FTIR spectra of reaction monomer and product](image)

**Figure 2.** FTIR spectra of reaction monomer and product a.P(GMA-co-HFBMA)-g-PEGMA b. HFBMA c. PEGMA

The FTIR spectra of the reaction monomer and product are shown in Figure 2. As can be from Figure 2, in the spectrum of HFBMA and PEGMA the absorption peaks around 2870–2980 cm⁻¹ are attributed to the stretching vibration of -CH₃ and -CH₂, and 1720 cm⁻¹ is assigned to the stretching vibration of
ester C=O, the absorption peak at 1633 cm\(^{-1}\) which belongs to the stretching vibration of C=C bond of HFBMA and PEGMA is disappeared in the spectra of the reaction product. The adsorption peak around 759 cm\(^{-1}\) is assigned to the stretching vibration of C-F in the HFBMA. In the spectrum of the reaction product, some new adsorption peaks are appeared, the peak at 908 cm\(^{-1}\) is assigned to the skeletal vibration of the epoxy group, the peak at 1105 cm\(^{-1}\) is attributed to the stretching vibration of (C-O-C) of PEGMA, and there also exist the peak of C-F at 751 cm\(^{-1}\) belonging to the HFBMA. These results demonstrate P(GMA-co-HFBMA)-g-PEGMA has been successfully synthesized.

![Figure 3. EDS spectra of P(GMA-co-HFBMA)-g-PEGMA](image)

The EDS spectra of P(GMA-co-HFBMA)-g-PEGMA is shown in Figure 3. As can be seen from the Figure 3, the mass percentage of the F element was 7.79 % in the reaction product. This reveal that the HFBMA has been polymerized into the copolymer, thus the P(GMA-co-HFBMA)-g-PEGMA has been successfully synthesized. The results of the FTIR spectra and the EDS spectra revealed that the novel adhesive P(GMA-co-HFBMA)-g-PEGMA has been successfully prepared.

### 3.2. Characterization of the Colors With Different Usage of Adhesive

The colors of the silica photo crystals with different usage of adhesive are shown in Figure 4.

![Figure 4. The colors of the silica photonic crystals with or without different usage of adhesive (a) without adhesive (b) 2 mL 1% P(GMA-co-HFBMA)-g-PEGMA solution](image)

As can be seen from Figure 4, the color of the silica photo crystal on balck paper is blue. And the silica photonic crystal colors with different usage of adhesive was almost the same with the that unused the adhesive.
3.3. Colorfastness of Photonic Crystal Structural Color

The colorfastness of the photonic crystal structural colors was determined by the rubbing fastness and washing fastness. The rubbing and washing fastness of the structural color samples without and with different usage of P(GMA-co-HFBMA)-g-PEGMA is shown in Figure 5.

![Figure 5. The rubbing colorfastness of the structural colors with different usage of adhesive (a) without adhesive (b) 2 mL 1% P(GMA-co-HFBMA)-g-PEGMA solution](image)

As can be seen from Figure 5, the addition of adhesive will significantly improve the rubbing fastness of the structural color samples. When the usage of 1% P(GMA-co-HFBMA)-g-PEGMA solution was 2 mL, the rubbing colorfastness was greatly improved indicating there may be no structural color was removed. This results revealed that the P(GMA-co-HFBMA)-g-PEGMA will be beneficial for the improvement of the rubbing colorfastness.

4. Conclusion

In this research, the novel adhesive of P(GMA-co-HFBMA)-g-PEGMA which contains the epoxy groups and the hydrophobic fluorocarbon chain was synthesized. The chemical structure of the P(GMA-co-HFBMA)-g-PEGMA was characterized by FTIR and EDS spectra. The results of FTIR and EDS spectra revealed that P(GMA-co-HFBMA)-g-PEGMA was successfully synthesized and used as the adhesive for the improvement of the colorfastness. The photonic crystal structural colors with good rubbing colorfastness were obtained. The results revealed that the novel adhesive will be beneficial for the improvement of the rubbing colorfastness of the photonic crystal structural colors.

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