

XIV<sup>th</sup> International Izmir Textile and Apparel Symposium October 26-28, 2017

# USING PHOTONIC CRYSTALS FOR STRUCTURAL COLORATION OF TEXTILES

## Gonul Yavuz<sup>1</sup>, Andrea Zille<sup>2</sup>, Esen Özdoğan<sup>3</sup>, Necdet Seventekin<sup>3</sup>, António Pedro Souto<sup>2</sup>

<sup>1</sup>Rudolf Duraner / 16140, / Bursa, Turkey

<sup>2</sup>University of Minho / Center of Science and Textile Technology / 4800 – 058 Azurém /
Guimarães, Portuga

<sup>3</sup>EgeUniversity / Department of Textile Engineering / 35100 Bornova / İzmir, Turkey
yavuz.gonul@gmail.com

#### ABSTRACT (10 pt)

In this work, poly (styrene-methyl methacrylate-acrylic acid) P(St-MMA-AA) composite nanospheres were deposited on the woven cotton fabrics. The deposited photonic crystals on the fabrics were evaluated for coating efficiency and resistance, chemical analysis and color variation by optical and SEM microscopy, ATR-FTIR, diffuse reflectance spectroscopy and washing fastness. The photonic nanospheres show an average diameter of 280 nm and display a face centre cubic (FCC) with an average thickness of 10  $\mu$ m.

Key Words: structural coloration, photonic crystals

### 1. INTRODUCTION

Colours are produced from various principles such as optical absorption (e.g. pigment), emission (e.g. light emitting diode (LED)), interference (e.g. bubble soap or rainbow coloration on a compact disc) or scattering (e.g. blue sky or red sunset). The 'structural colour' is a type of coloration originating from microstructure variation at a length scale comparable to the optical wavelength [1]. Structural colour occurs the interaction of light with the nanoscale periodic structures which are called photonic crystals. The structural colour has a variety of potential applications, because of its long-term resistance to discoloration due to chemical change; furthermore, it cannot be reproduced by pigments, and pigment-free coloration is preferable from ecological viewpoint [2-5]. This coloration is generally accompanied with a brilliant metallic luster, and has long attracted scientific interest. Last decade, photonic crystals found a great number of potential applications: inkless printing, reflective flat display, gas sensing, paints, photonic papers and cosmetics. [6-10]



There are also significant challenges for structural colouration on textile industry. In this paper, we report to fabricate structural color on cotton fabric. We applied the three-dimensional face centre cubic (FCC) photonic crystals on the surface of cotton fabrics.

## 2. MATERIALS AND METHODS

#### 2.1. Materials

Commercial black dyed cotton fabric with a warp density of 34 threads cm<sup>-1</sup>, a weft density of 30 threads cm<sup>-1</sup> and weight per unit area of 140 g m<sup>-2</sup> was used in this study. The samples were pre-washed with a 1 g L<sup>-1</sup> of non-ionic detergent solution at 30 °C for 30 min and then rinsed with water for another 15 min in order to minimize contaminations. Styrene (St), methyl methacrylate (MMA), and acrylic acid (AA) were distilled before use. All the other reagents were analytical grade purchased from Sigma–Aldrich, St. Louis, MO, USA and used without further purification.

## 2.2 Preparation of Monodispersed P(St-MMA-AA) Composite Nanospheres

The monodispersed P(St-MMA-AA) colloidal particles were synthesized as follows: 120 mL of aqueous solution (A), containing 0.4 g of  $Na_2S_2O_8$  and 0.8 g of  $NaHCO_3$  in a funnel, and 25 mL of monomer mixture (B), consisting of St/MMA/AA (90:5:5 v/v/v) in another funnel, were added at the same time into a 250 mL three-necked flask. The mixture was stirred at 70 °C in  $N_2$  atmosphere for 5 h to obtain a homogeneous dispersion of particles with uniform size distribution.

## 2.3. Coating of Cotton Fabrics with Photonic Crystals

Cotton sample was dipped in 8% photonic colloid solution for 5 minutes and then dried at 60 °C.

## 2.4. Fourier transform infrared spectroscopy (FTIR)

A Nicolet Shimadzu FTIR spectrophotometer (Madison, USA) with an attenuated total reflectance accessory (ATR) was used to record the FTIR spectra of the fabric samples. Spectra were collected in the region of 4000–400



cm<sup>-1</sup> and at a resolution of 4 cm<sup>-1</sup> with 45 scans at room temperature. A background scan with no samples and no pressure was acquired before the spectra collection.

## 2.5. Scanning electron microscopy (SEM)

Morphological and chemical analyses of the samples were carried out with an ultra-high resolution Field Emission Gun Scanning Electron Microscope (FEG-SEM), NOVA 2000 Nano, SEM, FEI Company. Secondary electron images were performed with an acceleration voltage between 5 and 10 kV. Backscattering Electron Images were made with an acceleration voltage of 15 kV. Samples were covered with a film of Au–Pd (80-20 wt%) in a high-resolution sputter coater, 208HR Cressington Company, coupled to with a MTM-20 Cressington High Resolution Thickness Controller.

## 2.6. Photographs

Optical photos of the fabrics coated with PCs were taken with a Nikon CoolPix4300 digital camera. The pictures were acquired under natural light, at the same time, environmental conditions, perpendicularly to the fabrics and at the distance of 15 cm.

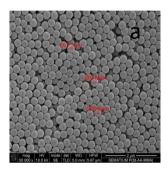
## 2.7. Spectrophotometric measurements

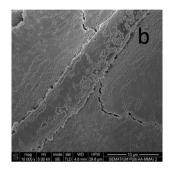
The color of the fabrics was evaluated using a Spectraflash 600 (Datacolor) diffuse reflectance spectrophotometer at standard illuminant D65 (LAV/Spec. Incl., d/8, D65/10°). Five areas on each sample were measured in various positions, and the results represent average values with up to 1% variation. All measurements were performed in triplicate. The responses analyzed were the color characteristics: K/S, L\*, a\*, b\*. K/S is the color strength calculated using Kubelka-Munk's equation (K/S= (1-R)2/2R, where R is the reflectance). L\*, a\*, and b\* are the coordinates of the color in the cylindrical color space, based on the theory that color is perceived by black-white (L\*, lightness), red-green (a\*), and yellow-blue (b\*) sensations. The results were also summarized by the overall color difference ( $\Delta$ E\*) value.

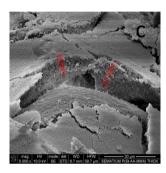
## 3. RESULTS AND DISCUSSION



Monodispersed composite latex spheres of P(St-MMA-AA) were successfully synthesized by soap-free emulsion polymerization. Figure 1-a shows the SEM micrographs of the deposited photonics crystals. P(St-MMA-AA) nanospheres were uniform and particle size was estimated by SEM to be  $280 \pm 20$  nm. Nanospheres coated on the cotton fiber surfaces without large gaps in the cross section. The thickness of P(St-MMA-AA) layer ranging is  $10 \pm 5~\mu m$ .







**Figure 1**. SEM micrographs of the deposited photonics P(St-MMA-AA) composite nanospheres.

Figure 2 displays the photographs of the cotton fabrics coated with the self-assembled colloidal PCs before and after a washing. PCs coated on untreated cotton shows a good structural coloration and iridescent colors. After washing, (Figure 2-b) the fabric did not retain any PCs coating on the black dyed cotton surface and losing iridescence.

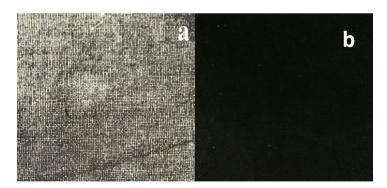


Figure 2. Photographs of sample before and after washing, respectively.

The attenuated total reflectance infrared spectra (ATR-FTIR) of the samples are illustrated in Figure 3. The cotton fabric (CO) display the very intense bands at 1160, 1100 and 1020 cm<sup>-1</sup> assigned to the vibrations of the C-O-C



bond of the glycosidic bridges of the cellulose structure The peaks at 2900 and 2850 cm<sup>-1</sup> may be belong to the C-H asymmetric and symmetric stretching vibrations of aliphatic CH<sub>2</sub>, respectively [12]. The absorption band at 1640 cm<sup>-1</sup>, may be attributed to the amide carbonyl C=O stretching vibrations of the dye of black cotton. The PCs coated fabric displays bands at 3027 cm<sup>-1</sup>, 2922 cm<sup>-1</sup> and 1541 cm<sup>-1</sup>, which are belong to sp<sup>3</sup> and sp<sup>2</sup> CH stretching and to the bending of CH<sub>2</sub> groups of the P(St-MMA-AA) nanosphere, respectively. Moreover, the band observed at 750 cm<sup>-1</sup> can be merely attributed to the out-of-plane C-H deformation of the monosubstituted or 1,2 disubstituted aromatic rings of P(St-MMA-AA) [13].

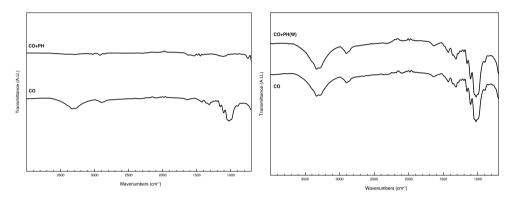


Figure 3. FTIR-ATR spectra of fabrics before (left) and after (right) washing.

The PCs coatings were displayed by the K/S values measurements of the fabrics before and after washing. The K/S value of black cotton is significantly higher than PCs coated fabric. Unwashed photonic crystals coated sample displays to a remarkable difference in the color differences ( $\Delta E^*$ ) and in lightness (L\*). After washing the CO and CO+PH samples display the same lightness and K/S.

**Table 1.** Overall color difference ( $\Delta E^*$ ), color strength (K/S) and color coordinates: lightness ( $L^*$ ), red-green ( $a^*$ ), and yellow-blue ( $b^*$ ) of the fabrics (S.D.<1%).

Sample*	$\Delta \mathbf{E}^*$	K/S	L*	a*	<i>b</i> *
CO	-	590.1	-	-	-
CO+PH	23.6	107.0	23.5	0.5	1.9
CO+PH (W)	0.7	581.8	-0.3	-0.4	-0.6

<sup>\*</sup>CO: Cotton; CH: Chitosan; PH: Photonics; (W): washed

#### 4. CONCLUSION



In this study, PCs fabricated by soap-free emulsion polymerization were applied to a cotton fabric. Overall, considering the fact the structural coloration is successfully produced on the cotton fabric without using any dye or pigment. The structural coloration is potential eco-friendly and low cost coloration technology for textile industry.

#### Acknowledgements

This work is supported by FEDER funding on the COMPETE program and by national funds through FCT-Foundation for Science and Technology within the scope of the project POCI-01-0145-FEDER-007136 and UID/CTM/00264.

## 4. REFERENCES

- [1] SAITO, A. Material design and structural color inspired by biomimetic approach, Science and Technology of Advanced Materials, 2011, vol.12, 6
- [2] SAITO, A. KINOSHITA, S. and YOSHIOKA S. Structural Colors in Biological Systems, 2005, Osaka University Press, p. 287
- [3] KARTHAUS, O., Biomimetics in Photonics, 2013, CRC Press Taylor & Francis Group 6000 Broken Sound Parkway NW, Suite 300
- [4] GE, J., GOEBL, J., HE, L., LU, Z. and YIN, Y., Rewritable Photonic Paper with Hygroscopic Salt Solution as Ink, Adv. Mater., 2009, 21, 4259–4264
- [5] KUILONG, Y., TONGXIANG, F., LOU, S., ZHANG, D., Biomimetic optical materials: Integration of nature's design for manipulation of light, Progress in Materials Science, 2013, 58, 825–873
- [6] BERTHIER, S. Iridescence, 2007, Science+Business Media, Springer New York
- [7] KUMAZAWA, K., TANAKA, S., NEGITA K. and TABATA, H., Fluorescence from Wing of Morpho sulkowskyi Butterfly, Japanese Journal of Applied Physics, 1994, Volume 33, Part 1, Number 4A
- [8] SINGH, M., HAVERINEN, H. M., DHAGAT, P., JABBOUR, G. E., Inkjet printing-process and its applications, Adv. Mater., 2010, 22, 673–685.
- [9] BONIFACÍO, L.D., PUZZO, D.P., BRESLAV, S., WILLEY, B.M., MCGEER, A., OZIN, G.A., Towards the photonic nose: a novel platform for molecule AND bacteria identification, Adv. Mater., 2010, 22, 1351–1354.
- [10] O'BRIEN, P.G., PUZZO, D.P., CHUTINAN, A., BONIFACIO, L.D., OZIN, G.A., KHERANI, N.P., Selectively Transparent and Conducting Photonic Crystals, Adv. Mater., 2010, 22, 611–616.
- [11] ALGAR, I., FERNANDES, S. C. M., MONDRAGON, G., CASTRO, C., GARCIA-ASTRAIN, C., GABILONDO, N., RETEGI, A. and ECEIZA, A.,



Pineapple agroindustrial residues for the production of high value bacterial cellulose with different morphologies, Journal of Applied Polymer Science, 2015, 132, 41237 [12] CHARLES, J., RAMKUMAAR, G. R., AZHAGIRI, S. and GUNASEKARAN, S. FTIR and Thermal Studies on Nylon-66 and 30% Glass Fibre Reinforced Nylon-66 E-J Chem, 2009, 6, 23-3

[13] COSTA L., AVATANEO M., BRACCO, P. and BRUNELLA, V., Char formation in polyvinyl polymers I. polyvinyl acetate, Polymer Degradation and Stability, 2002, 77, 503-10