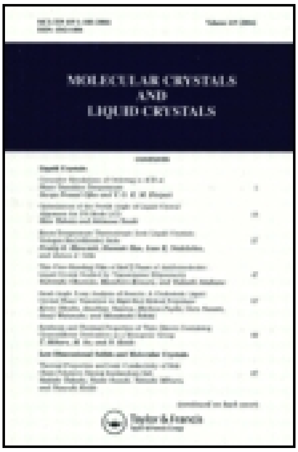

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Optical Properties of Multi-Layer Structures of Nanometric Polymer Photonic Crystals

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Optical Properties of Multi-Layer Structures of Nanometric Polymer Photonic Crystals

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Photonic crystals are attracting a lot of attention due to their ability to manipulate and guide the light. Sandwiching 3-dimensional styrene-based photonic crystals between polymeric multi-layer films such as polystyrene and polymethyl methacrylate is reported in this article. Polystyrene and polymethyl methacrylate solutions and a suspension of polymeric nano particles were cast using a specially designed spin-casting machine to produce a periodic multi-layer structure. In the next step, the optical properties of multi-layer structures were investigated via spectrophotometric techniques. A film of styrene-based nano particles has a blue-green reflection, which being affected by the suspension particles sandwiched between polystyrene and polymethyl methacrylate layers, shifts to red whereas the multi-layer structure demonstrates a green color. Moreover, the effects of the observer's viewing angle on the color shift were studied by means of goniospectrophotometric technique.

Keywords Nano particles; photonics; poly methyl methacrylate; polystyrene; spin-casting

Introduction

Although very old in nature, photonics is a relatively new branch of science that deals with interactions between light and material. Photonic properties were theoretically predicted by Yablonovitch and John in 1987 [1]. Because of continuous advancements in nanotechnologies, material science, optics and physics, photonics has progressed rapidly in recent years. Various applications of photonics include military, industry and medical fields [2].

Photonic crystals (PCs) are the structures which their refractive indices change periodically in space. This repeatability may occur in different dimensions [3–7]. Some wavelengths are strongly reflected and have almost no transmission. This range of wavelengths is known as photonic band gap [8–10].

Polymers play an important role in the development of photonic materials. These materials offer several advantages such as low cost, low processing temperature, safety etc. [11]. The wavelength of light, λ, which is reflected by a three dimensional polymer photonic crystal (PPC), is related to the spacing voids, d, via an approximation of Bragg-Snell's

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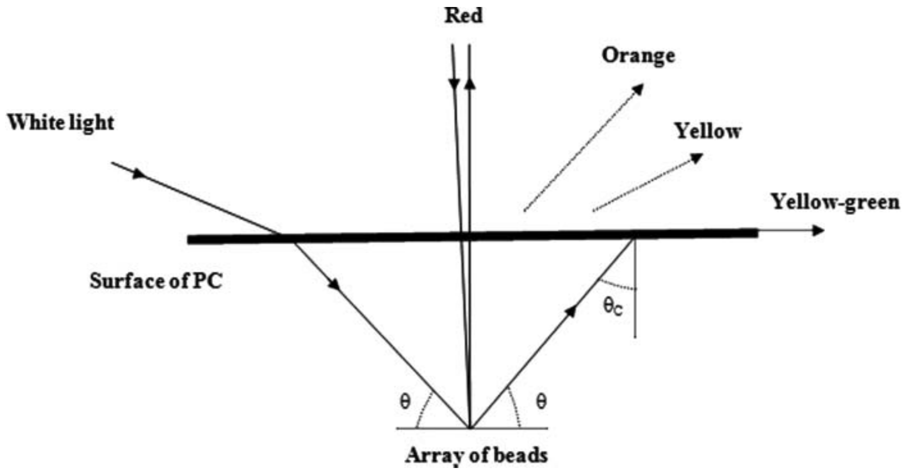

Figure 1. Schematic representation of light-PPC interactions [17].

law as [3]:

$$k\lambda = 2d\left(n_{eff^2} - \sin^2\theta\right)^{0.5} \quad (1)$$

where k is an integer, n_{eff} is the effective refractive index of the PPC and θ is the angle of incidence of light with respect to the normal vector of the PPC [3]. If spheres are arranged in a hexagonal structure with each sphere touching the other, the relationship between the sphere radius and the spacing of the voids will be [12–17]:

$$d = 1.633\ r \quad (2)$$

Due to total internal reflection and formation of critical angle (θ_c), some wavelengths cannot escape from the PPC. For instance, if red light is observed perpendicularly, yellow-green light will just escape along the surface. All shorter wavelengths will remain within the PPC (Fig. 1) [17].

On the other hand, one-dimensional PPC can be simply produced by polymeric multi-layer films. The wavelength of reflected light, λ_c, is obtained by [5]:

$$\lambda_c = 2(n_A d_A + n_B d_B) \quad (3)$$

where n_A and n_B are the refractive indices of layers, and d_A and d_B are corresponding layer thicknesses, respectively [5]. PPCs are usually fabricated by procedures such as extrusion [18], two photon polymerization [19], layer-by-layer process [2], melt compression [20,21] etc. In these procedures, high processing temperatures, costly equipments and specific conditions are needed.

In this paper, polystyrene (PS) and polymethyl methacrylate (PMMA) were dissolved in their appropriate solvents (i.e. cyclohexane and acetone, respectively). The obtained polymeric solutions along with a suspension of polymeric nano particles were cast on the internal surface of a rotating chamber using a specially designed spin-casting machine. Such process produces a periodic multi-layer structure. At the end, the optical properties of the resulted multi-layer structures were investigated via spectrophotometric and goniospectrophotometric techniques.

Experimental

Material

PS, (1540 grade) was procured from Tabriz Petrochemical Company and PMMA, (Plexiglas HFI-10–101 grade), was provided by Arkema Company. The polymers were used as received. Their refractive indices are 1.59 and 1.49, respectively. The used solvents, i.e. acetone, cyclohexane and carbon tetrachloride, all from Merck Company were used without any further purification. The suspension was prepared as reported in the literatures [22,23]. Such suspension has a core-shell structure, which was prepared by stepwise emulsion polymerization. It consists of polystyrene-based hard core coated with a poly methyl methacrylate-co-butyl acrylate shell. The suspension is monodisperse in the particle size distribution and its average particle size and refractive index are about 160 nm and 1.56, respectively [23].

Preparation of Multi-layer Films

Acetone and cyclohexane were chosen as solvents for PMMA and PS, respectively. A solution of 5 ml carbon tetrachloride in 95ml cyclohexane was used as the inter-layer adhesive [2]. The 100 g/l PMMA and PS solutions were prepared using a magnetic heater-stirrer. To be fully homogenized, the solutions were sonicated during two 15-minute periods. Sonication was employed as a two-step process to avoid solvent boiling and polymer degradation. In addition, a 250 g/l PMMA solution was prepared and cast as the mechanical supporting layer. The resulting solution was treated by the aforementioned procedures. An appropriate amount of 250 g/l PMMA solution was injected into the chamber mounted on the spin-casting machine [24].

The machine ran at 3000 rpm for 2 hours. Afterwards, the chamber was detached from the machine and kept under vacuum in order to remove the solvent residues. Drying process was carried out by two separate 2-hour steps. The temperature was adjusted to 35°C in the first step and 45°C in the second. An appropriate amount of the PS solution was injected into the chamber and put in rotation for the next 2 hours at 2750 rpm. The chamber was detached from the machine and dried under vacuum by the same procedure. This process for PMMA solution was repeated using the same method. If more layers of different polymers are needed to be spin-cast, one may simply repeat the aforementioned steps. This results in a multi-layer cylindrical structure.

In order to sandwich the suspension between the layers, an appropriate amount of the suspension was injected into the chamber. This layer has to be deposited between PMMA and PS layers. The machine operated at 2750 rpm for 3 hours. After detaching the chamber, a 2-hour temperature schedule was used; at first 25°C followed by a 35°C overnight. The prepared samples along with their specifications are listed in Table 1. Figure 2 shows a three-layer preform (S3) and the prepared samples. S1 sample was just made of six layers of PMMA/PS. S3, S4 and S5 samples have a PMMA/suspension/PS structure with 1, 2 and 3 periodical repetitions, respectively.

Results and Discussion

In Figs. 3a and 3b, the cross-sections of S1 and S4 samples are shown using optical microscopy (OM) technique. These figures give images in which layers of different polymers are clearly distinguishable. Figure 4 illustrates how suspension layer has been sandwiched

Table 1. The prepared samples and their specification

Sample	Specification
S1	Six-layer PMMA/PS film
S2	One suspension layer on a supportive layer
S3	Three-layer PS/suspension/PMMA film
S4	Six-layer PS/suspension/PMMA film
S5	Nine-layer PS/suspension/PMMA film

between PS and PMMA layers. In this figure, some cracks are observed which may have been emerged during the preparation of the multi-layer films.

All the samples except S1 sample are green-blue in color. This color could be related to existence of nano particles in the suspension layer. Due to their particle sizes, the spacing of the voids, d, is determined to be 130.64 nm (equation 2). Inserting 130.64, 0 and 1.56 for d, θ and n_{eff} in equation 1, respectively, gives a λ_{max} of 410 nm. This value predicts a blue color for the samples. The predicted wavelength is close enough to the

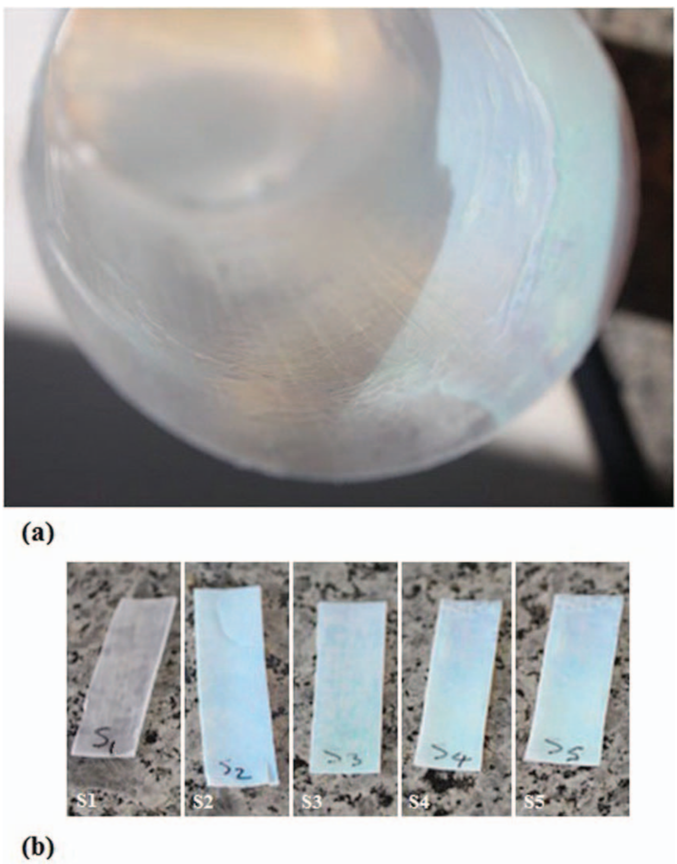

Figure 2. (a) The three-layer preform (S3) and (b) prepared samples.

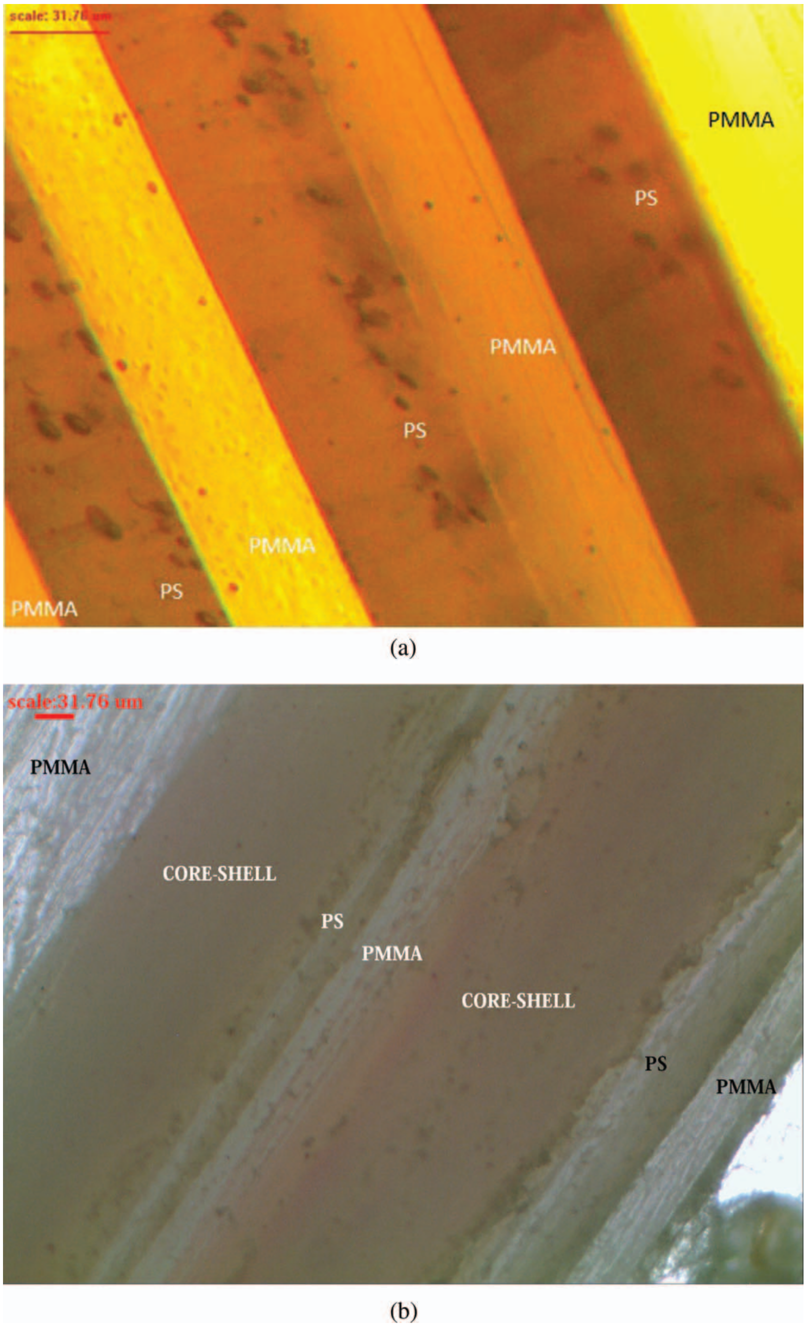

Figure 3. (a) The OM images of cross sections of S1 and (b) S4 samples.

experimentally observed wavelength as will be discussed later. Figure 5 shows scanning electron microscopy (SEM) image of S2 sample cross-section. The square indicated in Fig. 5 reveals a hexagonal arrangement of polymeric beads, which incidentally leads to the emergence of the photonic effect. Some parts of the SEM image do not show an ordered

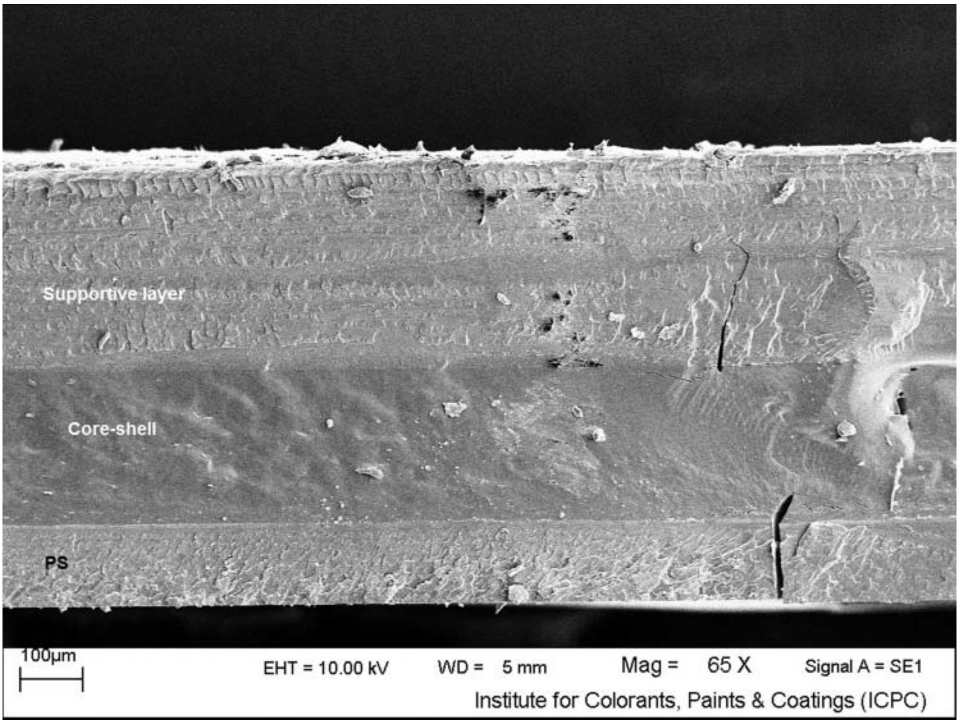

Figure 4. The sandwiched suspension layer between PS and supportive (PMMA) layers.

arrangement which can be resulted during cryogenic breaking of the sample. Furthermore, in this figure a two-dimensional arrangement of the matrix ingredients can be observed, regarding that the sample is formed on a three-dimensional structure, one may imagine some components of the hexagonal arrangements are hidden behind the viewed surface (cross-section). This corresponds to the photonic activity of the prepared samples.

To perform a quantitative comparison, the color of the samples has been quantified by spectrophotometric measurements. Using this method, the reflection curves were obtained by a Color-Eye 7000A spectrophotometer (Fig. 6). In addition, the CIE L*a*b* values, which were calculated under 10^o standard observer and D65 illuminant together with observed colors of samples are listed in Table 2. In CIE L*a*b* color space, colors with $a^* > 0$ possess the attribute of redness, those with $a^* < 0$ greenness, those with $b^* > 0$

Table 2. The CIE L*a*b* values under 10°/D65 standard conditions of the reflectance curves and observed color of the samples

Sample	L*	a*	b*	Observed color
S1	48.0	−0.2	−2.8	Almost clear
S2	72.5	−16.9	−22.3	Greenish blue
S3	73.8	−28.8	−2.5	Green
S4	73.5	−22.4	−5.1	Green
S5	79.0	−22.7	−2.0	Green

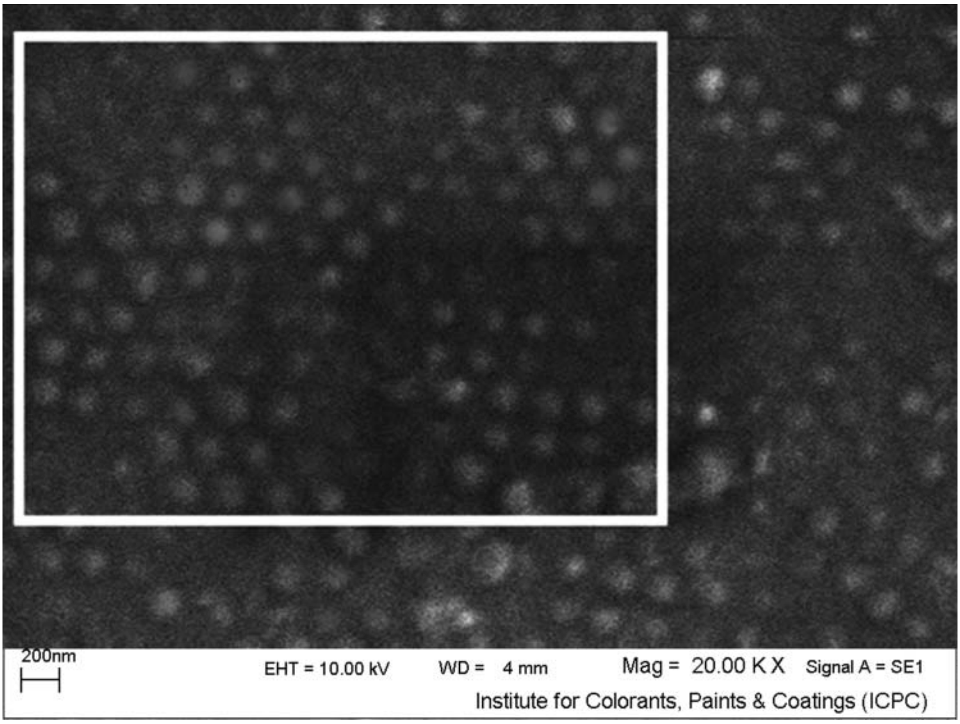

Figure 5. The SEM image of S2 cross-section.

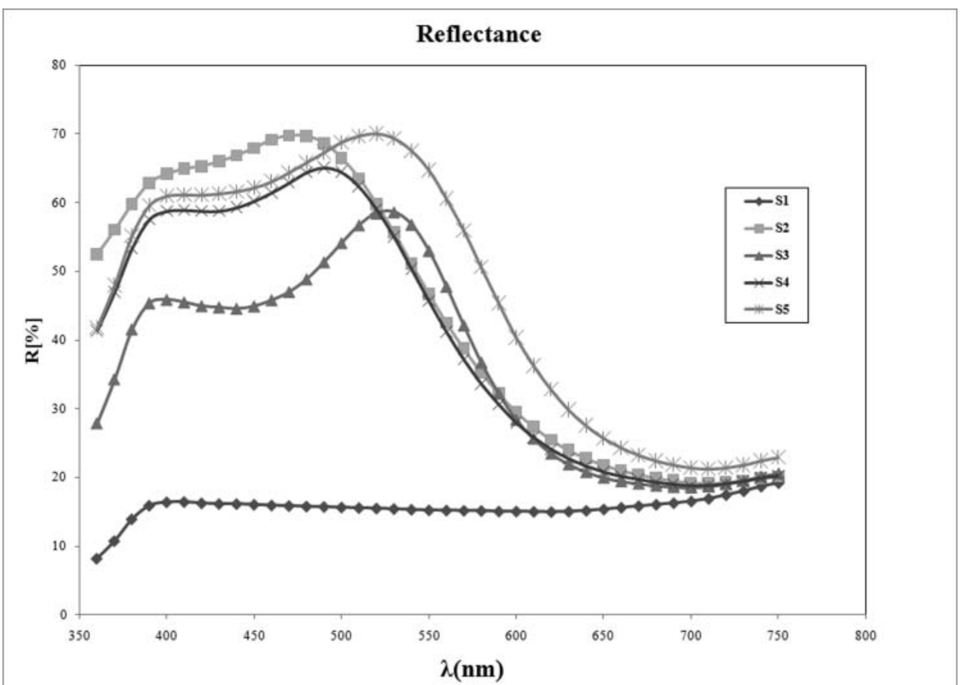

Figure 6. The reflectance curves of the samples.

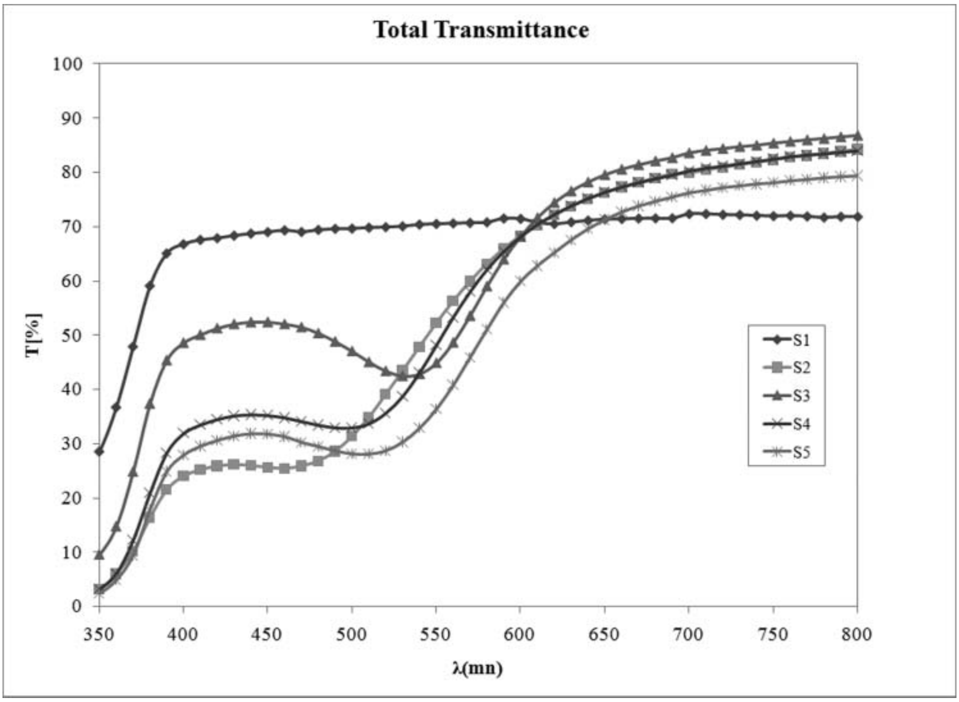

Figure 7. The total transmittance curves of the samples.

yellowness, and those with $b^* < 0$ blueness. The positive L^* axis represents achromatic colors of values between $L^* = 0$ for ideal black and $L^* = 100$ for ideal white. Figure 6 and Table 2 together indicate the color of S2 sample, which is composed of a suspension layer deposited on a supportive layer to be greenish blue. Meanwhile, the color of S3, S4 and S5 samples, which contain a sandwiched structure of suspension layers, is green.

The transmittance curves of samples are shown in Fig. 7. Due to translucency of the samples, d/8^o geometry in total transmittance mode was selected and total transmittance was measured using an integrating sphere. The CIE $L^*a^*b^*$ values of transmittance curves, which were calculated under 10^o standard observer and D65 illuminant together with observed colors of samples are listed in Table 3. Comparing data in Tables 2 and 3 shows transmittance curves are in fact complementary to reflectance curves. When light reaches

Table 3. The CIE $L^*a^*b^*$ values under 10°/D65 standard conditions of the transmittance curves and observed color of the samples

Sample	L^*	a^*	b^*	Obsereved color
S1	87.0	0.1	1.3	Almost clear
S2	77.0	13.2	18.3	Yellowish orange
S3	78.0	17.8	7.1	Reddish orange
S4	76.0	18.3	14.1	Reddish orange
S5	70.0	21.4	14.8	Reddish orange

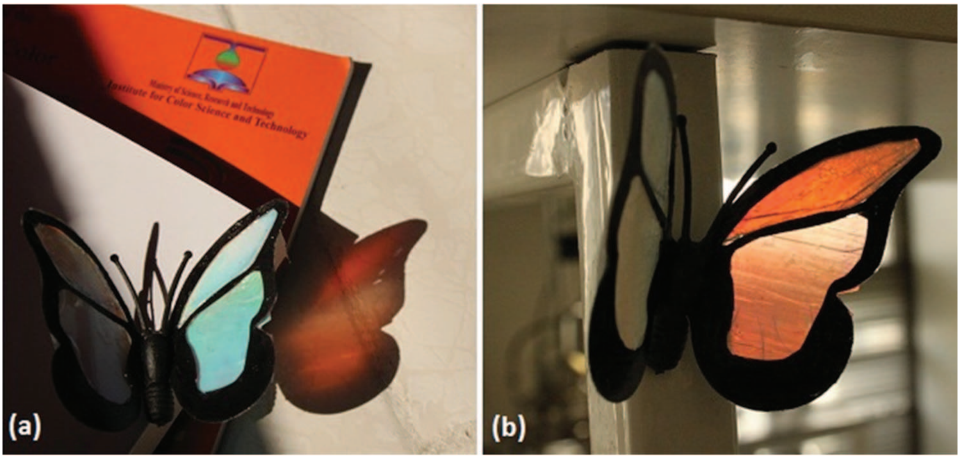

Figure 8. (a) The light source and the observer are in the same side of the sample and (b) on the different sides.

the polymeric beads, is divided into two parts: one part is reflected from the first suspension layer while the other part passes through the bulk.

In structures such as S3, S4 and S5, which suspension has been sandwiched between supportive polymeric layers, the reflected beam travels the other way; it causes the beam to enter the medium with a different angle. Moreover, transmission beam is approximately complementary to the reflective beam. PMMA and PS layers are not thin enough (about 50μm thickness) to have photonic activity in visible range. Putting this thickness and the

Table 4. The goniospectrophotometric data of the samples under 10°/D65 standard conditions

Sample	Angle	L*	a*	b*	Observed color
S2	20°	72.0	−24.0	−8.2	Greenish blue
	45°	67.2	−22.8	−16.6	Greenish blue
	75°	71.0	−13.5	−22.6	Bluish green
	110°	78.9	−3.0	−20.8	Green
S3	20°	79.9	−14.5	−24.9	Bluish green
	45°	77.8	−8.6	−17.6	Bluish green
	75°	78.0	−8.7	−10.5	Bluish green
	110°	81.4	−5.5	−9.1	Bluish green
S4	20°	75.0	−16.2	−20.6	Bluish green
	45°	70.4	−14.7	−19.2	Bluish green
	75°	69.3	−10.2	−15.8	Bluish green
	110°	75.4	−7.8	−12.6	Bluish green
S5	20°	74.2	−15.2	−18.8	Bluish green
	45°	69.1	−16.4	−23.7	Bluish green
	75°	68.4	−15.9	−18.6	Bluish green
	110°	73.4	−12.4	−15.6	Bluish green

values of refractive indices in equation 3, reveals that resulting λ_c does not locate in the visible range. The wings of the artificial butterfly shown in Fig. 8 are made from S3 sample. As illustrated in this Figure, the color of wings depends on the positions of light source and observer. When they are on the same side of the sample, the wing of the butterfly appears green (Fig. 8a). In this situation, the observer is in the position that receives reflective beam; whilst they are in different sides, the wing appears orange (Fig. 8b). In this situation, the observer is in the position that receives transmission beam. Angular changes in viewing conditions affect the observed color of the sample; therefore, it was investigated by a CE 741 GL goniospectrophotometer. The goniospectrophotometric data under 10^o standard observer and D65 illuminant together with observed colors of the samples are listed in Table 4. As seen in Table 4, the color of S2 sample has an angular dependency on viewing conditions more than that of the other samples; but the color of S3, S4 and S5 samples is approximately the same and has a little angular dependency upon viewing. As mentioned before, the observer may receive a spectrum of colors from red to violet wavelengths by changing the viewing angle. The spectrophotometric measurements of S2 prove the mentioned shift from green to blue.

Conclusion

We have described a methodology for sandwiching the suspension of polymeric nano particles between PMMA and PS layers. A non-interpenetrated interface between the polymeric layers was detected in SEM images of the samples' cross-sections, which is an evidence of using appropriate solvents. The spectrophotometric investigations of the samples reveal that the reflectance curves of these samples are approximately complementary to the transmittance curves. In addition, the goniospectrophotometric measurements demonstrated that sandwiching the suspension between polymeric layers restricts its angular dependency on viewing conditions.

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