Preparation and Property of TiO$_2$/SiO$_2$ Multilayer Film on the Fabric by Sol-gel Process

Xiaoyan Liu$^{1,2,*}$, Fangfang Huang$^1$, and Weidong Yu$^1$

$^1$College of Textiles, Dong Hua University, Shanghai 201620, China
$^2$Key Laboratory of Textile Science & Technology, Ministry of Education, Donghua University, Shanghai, 201620, China

Abstract: The high light reflection of multilayer TiO$_2$/SiO$_2$ film was prepared on the fabric by the sol-gel process. The size of titania and silica particles in hydrosol was analyzed by Nanosizer, and the morphology of TiO$_2$/SiO$_2$ multilayer film on the fabric was characterized by SEM. The reflection spectra of the samples were tested accordingly, and it showed that the reflection of the fabric coated by multilayer film was higher than that of the monolayer film. Moreover, the reflection increased with the increase of layer number. For sunlight fastness testing, the fabric color changed less with the increase of layer number, which showed the multilayer film on the fabric can improve the light resistance of the fabric. The mechanical property, the bending property and air permeability testing results showed that there was little change for the coated fabric compared with the original fabric.

Keywords: Multilayer film, Sol-gel, Reflection, Coat, Fabric

Introduction

It is always significant to develop the high reflection in textile fields, which not only can protect the inner structure, but also can brighten some important signs for special requirements. It is usual to use film covered on the fabric, where the film can block most of the light energy [1-3].

At present, the highly reflective multilayer film has attracted much interest for material design, such as optical filters, solar control glass/window and so on [4-9]. There are some related research in the theory on the structural design of multilayer thin films for anti-reflection in the field of optics [10-12]. It can exhibit high reflectivity due to constructive interference between light rays reflected from the multilayer. In theory, a group of multilayer film pile composed of the alternating layers having a large refractive index contrast is expected to get very close to 100% reflection [13-18].

In our previous work, the light property of the fabric was investigated by the monolayer using sol-gel process [19,20]. To improve the fabric optical property, the TiO$_2$/SiO$_2$ multilayer film was therefore prepared in this paper. Herein we prepared TiO$_2$ and SiO$_2$ film from the different precursors by sol-gel process, which have refractive index of 1.8-2.2 and 1.2-1.3 respectively. The sol-gel method has been carried out in textiles due to its excellent compositional control, homogeneity at the molecular level, easily mixing of liquid precursor and lower crystallization temperature. Moreover, the microstructure of the thin films deposited by sol-gel process can be tailored by the control of processing parameters [21-23].

The basic kinetics of the sol-gel processes can be well described as the both of hydrolysis and condensation reactions, shown as the equation (1), (2) and (3).

\[
\begin{align*}
M(OR)_{x} + H_2O &\rightarrow M(OR)_{x-1}OH + ROH \quad (1) \\
2M(OR)_{x-1}OH &\rightarrow (OR)_{x-1}M-O-M(OR)_{x-1} + H_2O \quad (2) \\
M(OR)_{x-1}OH + ROH &\rightarrow (OR)_{x-1}M-OR + H_2O \quad (3)
\end{align*}
\]

Where M is a metal species (Ti, Si, Al, Zr, etc.) and R is an alkyl group (methyl, butyl, ethyl, etc.). These reactions generate an oxide skeleton in the solution. Upon exposed to the atmosphere or be heated, the solution gels and becomes rigid.

Experimental

Materials

Tetrabutyl titanate (TBT) and tetraethylorthosilicate (TEOS) were purchased from Sino pharm chemical reagent. Acetic acid was purchased from Shanghai Boer chemical reagent Co., Ltd. Isopropanol was purchased from Changshu Yanggarden chemical reagent Co., Ltd. Hydrochloric acid was purchased from Pinghu chemical reagent Co., Ltd. Plain woven cotton fabric was used as the testing sample.

Preparation of Titanium and Silicon Hydrosol

Tetrabutyl titanate (TBT) was used as the precursor, acetic acid (AcOH) was used to retard the hydrolysis and condensation of TBT, and hydrochloric acid (HCl) was used as the catalyst for TBT hydrolysis. The molar ratio of TBT: AcOH: HCl: H$_2$O was 1:3.5:0.014:100. TBT was dissolved in the acetic acid and the solution was agitated until homogeneous, then the solution was slowly added to the HCl-water mixture and stirred vigorously for 3 hr in a three
necked flask at ambient temperature. A 2.0% concentration of titanium hydrosol was thus obtained with a pH around 2.

Silicon hydrosol solution was prepared with tetraethyl-orthosilicate (TEOS) mixed with isopropanol (C\(_3\)H\(_7\)O) as solvent, distilled water (H\(_2\)O) for hydrolysis and hydrochloric acid (HCl) was used as catalyst at 70°C for 80 min. The volume ratio of TEOS:C\(_3\)H\(_7\)O:H\(_2\)O:HCl was 15:40:5:0.07.

**Multilayer Film Preparation on the Fabric**

Before coating films, the cotton fabric was thoroughly cleaned in ethanol with sonication for 30 min and further rinsed with deionized water to remove the surface contaminations, and it was dried. Then it was firstly coated with titanium hydrosol by the adjustable coating device (Baker K003525M006), the coating film thickness was controlled as 1 \(\mu\)m and dried at 100°C for 4-5 min. Silicon hydrosol was next coated on the above fabric. During the multilayer film preparation process, the titanium and silicon hydrosol were alternatively coated on the fabrics, and each film thickness was 1 \(\mu\)m. When each film was formed on the fabric, the fabric was dried at 100°C for 4-5 min.

**Characterization**

In order to find the dispersion situation, the size of titania and silica particles in hydrosol was measured by nanosizer from Malvern Instruments Ltd, UK. The optical property of the samples was tested by Hitachi U-4100 Spectrophotometer. The morphological structure of cotton fabric was measured by JSM-5600LV Scanning Electron Microscopy (SEM), operating at 10 kV. ATLAS 150S+ was used to simulate the sunlight. The mechanical property of original and coated fabrics was tested using YG065 Fabric Electronic Tester with the specimen size 250×50 mm. In YG065 Fabric Tester, the gauge length was 100 mm, and the tensile speed was 100 mm/min. The bending property of the fabric was tested by KES-FB2 fabric style instrument, and the sample was tested as 10×10 cm. Air Permeability Tester (YG461E, China) was used to obtain the air permeability values of the uncoated and coated cotton fabric.

**Structural Design of Multilayer Films**

Multilayer film system was made by different refractive index material, where we used the traditional one-quarter wavelength of reflective film system.

The optical thickness of high refractive index membrane layer (H) and low refractive index membrane layer (L) are equal to one-quarter of the incident ray center wavelength \(\lambda_0\), a film cycle (H+L), its optical thickness is equal to half of the sum of the incident ray center wavelength \(\lambda_0\). There was a diagram of the structure of the composite multilayer film shown as Figure 1.

In Figure 1, the bottom fabric was the substrate, and the high refractive index was the outer layer. The structure can be expressed as the following formula:

\[
G(\mathcal{HL})^N\mathcal{H}A
\]

When only the single layer of high refractive index material \((n_H)\) film was on the substrate \((n_s)\), for the central wavelength of \(\lambda_0\), the combined admittance was \(n_H^2/n_s\), then the reflectivity of perpendicular incident (R) was,

\[
R = \left[\frac{n_o-n_H^2/n_s}{n_o+n_H^2/n_s}\right]^2
\]

With the high and low refractive index alternate, each medium multilayer films of \(\lambda_0/4\) thickness can get high reflectivity, mainly because the reflected light of the interface between the air membrane layer and membrane layer substrate has the same phase.

If \(n_H\) is the high refraction index and \(n_L\) is the lower one, and the outmost layer in the multilayer must be the one which has the high refractive index. The thickness of each layer is \(\lambda_0/4\), the combination admittance for center wavelength \(\lambda_0\) is

\[
Y = \left[\frac{n_H}{n_s}\right]^N \times \frac{n_H^2}{n_s}
\]

is the substrate refractive index, \(N\) is the multilayer layers cycle, \(N+1\) is the layer number. Therefore, when the light is perpendicular incident in air, the reflectivity of center wavelength \(\lambda_0\), the maximum reflection \(R\) is,

\[
R = \left[1 - (n_H/n_s)^N (n_H^2/n_s)^2\right] / \left[1 + (n_H/n_s)^N (n_H^2/n_s)^2\right]
\]

The ratio of \(n_H/n_L\) is bigger, and the layer is more, the reflectivity is higher. Theoretically, if the high and low refractive material were chosen, the reflectivity maybe unlimited to close to be 100% as long as the membrane layer number increased. In fact, because the membrane layer absorption and scattering become less, when the film system is near to a certain layer, the additional two layers do not improve its reflection.