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A study on the preparation and application of Ag/TiO_2 complex sol-part 2: Application of Ag/TiO_2 complex sol

Kuo-Shien Huang*, Yih-Sheng Huang, Ruey-Shyang Huang
Dept. of Polymer Material, Kun Shan University, Yung Kang, Tainan - 71003, (TAIWAN)
E-mail : hks45421@ms42.hinet.net
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ABSTRACT

The primary aim of this study is to explore the property of Ag/TiO_2 complex sol and its applications to processing nylon fabrics. Firstly, Ag/TiO_2 complex sols are prepared at different pH values, and then dyed nylon fabric is processed. From results shows, preprocessing of complex sol is very helpful for promoting bacterial-resistance of the fabric, to the exclusion of its dyeability. Moreover, color fixing features excellent fastness of dyeing and bacterial resistance.

KEYWORDS

Sol;
Nylon;
Processing;
Bacterial resistance;
Dyeability.

INTRODUCTION

The gel method is a chemical method in which a metal or semi-metal alkoxysilane is subjected to hydrolysis and polycondensation. In this technology, an inorganic precursor is used with acid-base catalysts to generate reticular compounds. This technology makes it possible for processing at low temperatures, and organic materials can be incorporated into the inorganic phase without decomposition. This method allows the preparation of many products, such as powder, gel, dried gel, fiber and coatings[1,2]. The gel method allows the metal oxide of functional groups to be coated onto various materials, serving the purpose of surface modification[3-10]; for example: glass[11], metal[12] or organic high polymers[13-16]. Similarly, some dyes can be adhered to materials for new applications, such as optical devices or biomedical sensors, etc.[17,18]. In the past, the gel method was used to adhere dyes onto a fabric, but it was thought that the fastness of rinsing of dyed fabric could be improved[19-21]. This study uses the gel method to process nylon fabric with complex sol. In this way, many processing properties, such as resistance to bacteria and UV, are conferred, and color fixing capability is provided to improve the fastness of fabric dyeing.

EXPERIMENTAL

Materials

Titanium *n*-butoxide (99%, TTB) and 3-glycidoxypropyltrimethoxysilane (GYPTMS), tetraethoxysilane (TEOS) were purchased from ACROS ORGANICS, USA; ethyl alcohol, acetic acid, nitric acid, sodium hydroxide, hydrochloric acid, and sodium lauryl sulfate (SLS) were purchased from Shimahisashi Pharmaceutical; ethyl acetoacetate (EAc) was purchased from NIHON SHIYAKU INDUSTRIES; silver nitrate was purchased from Wako Pure Chemical Inc. Ltd.; JINLEV NLA NEW (leveling agent,

TABLE 1 : Various signs of complex sols are defined below

Sign	Definition	Concentration of $AgNO_3$ (g/ml)
4-1	Complex sol prepared with 1ml of $AgNO_3$ at pH4	5.7×10^{-5}
4-3	Complex sol prepared with 3ml of $AgNO_3$ at pH4	1.71×10^{-4}
4-6	Complex sol prepared with 6ml of $AgNO_3$ at pH4	3.42×10^{-4}
4-10	Complex sol prepared with 10ml of $AgNO_3$ at pH4	5.7×10^{-4}
6-10	Complex sol prepared with 10ml of $AgNO_3$ at pH6	5.7×10^{-4}
8-10	Complex sol prepared with 10ml of $AgNO_3$ at pH8	5.7×10^{-4}
10-10	Complex sol prepared with 10ml of $AgNO_3$ at pH10	5.7×10^{-4}

industrial level) was supplied by Jintex Corporation, C.I.; Acid Blue 40 was supplied by Everlight Chemical Industrial Corporation; nylon fabric that had been processed with the following specifications:

$$\frac{70\times 160}{24\times 136}\times 64''$$

was supplied by Promax textile.

Methods

Preparation of complex sol

With vigorous stirring 10ml of butyl titanate (TTB) was added to 30 ml of absolute ethyl alcohol, and then 2ml of acetic acid and 0.2ml of acetylacetone were added. After stirring for 30 minutes, a uniform and transparent solution was obtained (solution A). Distilled water (1ml) was added to 15ml of ethyl alcohol, and 0.1 ml of 1 M nitric acid was added slowly, then the mixture was stirred for 30 minutes to obtain solution B. By adding solution B slowly into solution A, it was possible to obtain a uniform and transparent yellowish sol. After stirring for 1 hour, 40ml of distilled water was added to produce a white sol. At different pH values (2~12), the TiO_2 sol at the concentration specified above was added to a solution of $AgNO_3$, thus forming a reaction system. Stirring was continued for 3 hours to obtain the Ag/TiO_2 complex sol. Next, an Ag/TiO_2 dried complex sol was prepared by drying the sol for 2 hours at 80°C.

Dyeing of nylon fabrics

A 3% solution of acid dye and 1g/L of leveling agent in acetic acid were mixed at a ratio of 1:20 (v/v). The fabric was placed into the dye solution and left for 45 minutes at 105°C, and then the fabric was rinsed and dried.

Application of complex sol

(a) **Preprocessing of complex sol for dyed nylon fabric:** The dyed fabric was placed into the sol solution for 5 minutes with the two-dipping two-nipping method (pick-up = 80%), and dried for 2 minutes at 100°C, then heated for 2 minutes at 170°C. After rinsing and drying, the fabric was divided into two parts; one part was used directly for detection; the other part was used for color fixing.

(b) **Color fixing of dyed nylon fabric:** HCl (15ml of 0.01N) was added to a mixture of 34 ml of TEOS, 6ml of GYPTMS and 50 ml of ethanol, and then stirred at room temperature for 60 minutes to prepare the solution for color fixing. The fabric that was treated with the complex sol was placed into the solution and soaked for 5 minutes with the two-dipping two-nipping method (pick-up = 80%). The fabric was dried for 2 minutes at 100°C,and then heated for 2 minutes at 170°C.

Analysis and measurement

Fourier transform infrared spectroscopy in the attenuated total reflection mode (FT-IR/ATR) spectra of the dried gels was recorded with a Bio-Rad Digilab FTS-200 spectrometer using an MCT detector. A diamond crystal was used as the internal reflectance element. Single-beam spectra were the result of 64 scans. The spectral resolution was $4cm^{-1}$. The K/S of the treated fabrics were measured by a Nippon ND 300A color-difference meter. The antibacterial property of the treated fabrics was measured according to method JIS1902-1998 of the Japanese Association for the Functional Evaluation of Textiles (JAFET), and the following equations were used to calculate bacterial growth, and the bacteriostatic and bactericidal value:

$$\text{Bacterial growth (F)} = \log (M_b/M_a) \quad (1)$$

An F value >1.5 indicates significance in the experiment.

$$\text{Bacteriostatic value (S)} = \log (M_b/M_c) \quad (2)$$

An S value >2.2 suggests that the sample has a bacteriostatic effect.

$$\text{Bactericidal value (L)} = \log (M_a/M_c) \quad (3)$$

An L value >0 suggests that the sample has a bactericidal effect.

M_a = bacterial number in the sample of pure PAA polymer immediately after rinsing. M_b = bacterial number in the sample of pure PAA polymer after culturing for 18–24 h. M_c = bacterial number in the sample of composite hybrid material after culturing for 18–24 h. Investigations of the leaching behavior were performed at 40°C using a Rapid H-type dyeing machine. A 1% (w/v) aqueous solution of sodium lauryl sulfate (SLS) with pH 7 was used as the washing solution. After leaching for 20 minutes, the textile samples were rinsed intensively with water, dried at room temperature and the physical properties were investigated again after 20 washes.

RESULTS AND DISCUSSION

FT-IR

To analyze the property of various sols, Ag/TiO_2 dried complex sol was prepared by drying the sol for 2 hours at 80ºC. Figure 1 depicts FT-IR spectra of Ag/TiO_2 dried complex sols prepared at different pH values. Among dried gels of 1380cm^{-1}and 1625 cm^{-1}, absorption peaks of Ti-O-Ti and >C = O groups are clear, of which >C = O is represented by the >C = O absorption peak of a compound of Ag and ethyl acetylacetone. In Figure 1a-D, there is obviously a C = C absorption peak at 1540cm^{-1}. It can thus be proved that, although $AgNO_3$ is likely to form AgOH under alkaline conditions, it is unlikely to react with Ti $(OH)_4$ to generate Ti-O-Ag after polycondensation. This can be deduced from an obvious O-H absorption peak at 3442cm^{-1}. But, no obvious difference exists in figure 1b-A to 1b-C.

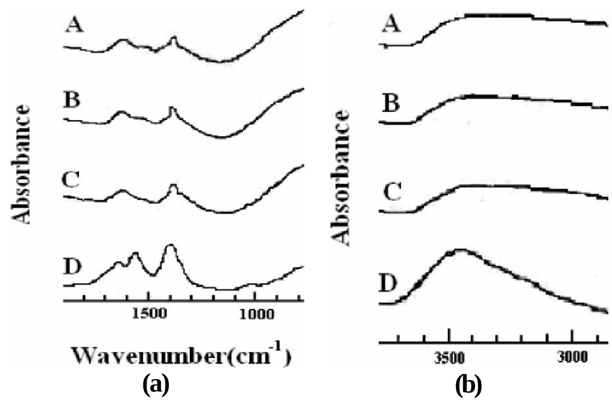

Figure 1 : FT-IR of Ag/TiO_2 dry gel ((A)4-1 (B)4-6 (C)4-10 (D)10-10)

Anti-bacterial effect of fabrics

Figure 2 depicts SEM of dyed fabrics after processing. When the fabric is processed only through the complex sol, the fiber surface contains a little dried complex sol, as shown in Figure 2a. In the case of continued color fixing without rinsing, more fixing agents are observed adhered to fiber surface, as shown in figure 2b. It indicates that the reagent remaining on the fiber surface affords a good fastness for the fabric, as shown in figure 2c. To provide a further insight into their content, EDS detection is required, with the results shown in figure 3 and TABLE 2**.** Si and Ag exist on the surface of fabrics after color fixing. For

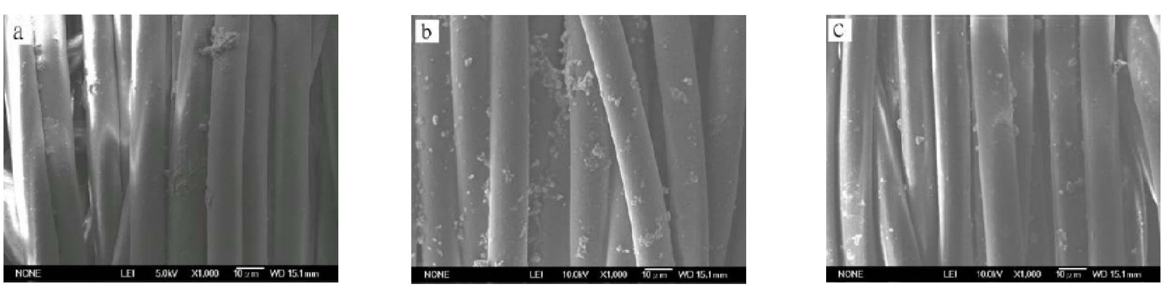

Figure 2 : SEM of treated fabrics, (a) Pretreated fabric with complex sol. (b) After fix treatment (no washing). (c) After fixing treatment and washing 20 times.

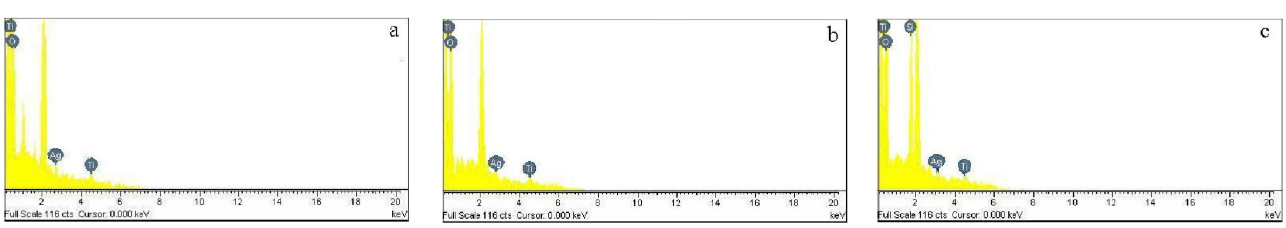

Figure 3 : EDS of treated nylon fabrics. Symbol the same as figure 2. Complex sol is 10-10

TABLE 2 : EDS data of treated nylon fabrics

Elements	Contain					
	Weight (%)[1]			Atomic (%)		
	a[2]	b	c	a	b	c
O	89.56	70.91	76.12	96.87	79.98	84.70
Ti	7.37	4.14	3.87	2.63	2.55	1.44
Si	----	21.97	18.25	----	17.01	13.61
Ag	3.07	2.98	1.96	0.50	0.46	0.25

[1]Relatively weight. [2]a) Pretreated fabric with complex sol, b) After fix treatment (no washing), c) After fixing treatment and washing 20 times

TABLE 4 : Wash fastness of treated fabrics

Samples	Before washing			After washing 20 times		
	K/S	A[3]	B[4]	K/S	A	B
Control[1]	22.78	0	<0	16.07	0	<0
Control[2]	16.59	1.1	<0	16.12	0.6	<0
4-1	17.34	4.1	2.7	16.86	3.2	2.4
4-10	19.08	6.3	3.3	17.98	5.4	2.9
10-10	21.25	6.5	3.3	20.13	5.5	3.0

[1]K/S of unpretreated fabric is 22.78, [2]dyed fabric was only fixed treatment. [3]bacteriostatic value, [4]bactericidal value

TABLE 3: Dyeing property of treated fabrics

Samples	K/S[2]				Eveness[3]
	Processing methods				
	A	B	C	D	D
Control[1]	----	19.18	16.59	16.12	0.35
			----	16.07	0.21
4-1	19.52	18.63	17.34	16.86	0.64
4-10	20.34	20.19	19.08	17.98	0.48
6-10	21.57	20.23	19.27	18.43	0.51
8-10	21.94	21.71	20.33	18.84	0.37
10-10	27.46	22.28	21.25	20.13	0.98
12-10	29.07	22.59	21.64	20.15	1.12

[1]K/S of unpretreated fabric is 22.78, [2]A: Pretreated with Ag/TiO_2 complex sol., B:(A) through wash and dry, C:(B) again fixating, D:(C)through 20 times washing. [3]Eveness=$(K/S)_{max}$–$(K/S)_{min}$

the fabrics with color fixing before rinsing, the relative weight percentage of Ag, Ti and O will decline, possibly owing to the fact that some of the dried complex sols on the fabric surface are stripped during color fixing. Then, Ag and Si could be removed after rinsing 20 times. TABLE 3 gives the tested dyeability of fabric. The fabric will have a deeper color after preprocessing of the alkali sol. This is primarily because of the larger particle size of Ag/TiO_2 or AgOH. When they are coated onto the fabric surface, there is a greater probability of Ag restoration, leading to a deeper color. However, a portion of the sol is removed after rinsing, and then a light color is restored. In the case of color fixing, the dried fixing agent will yield a little SiO_2 on the fabric surface for color covering. On the other hand, an acid sol will possibly dissolve the dried complex sol coated on the fabric surface, or even dissolve and separate the dye, leading to a light color. After rinsing 20 times, it is found that discoloration of other fabrics, apart from those without color fixing, is improved significantly. This is primarily because the fixing agent forms a reticular structure on the fabric surface, making it difficult for dyes or dried gels to be separated out[20,21]. Although the leveling of all fabrics meets the criteria, the leveling of processing fabric subjected to preprocessing with an acid sol is relatively poor, possibly owing to larger particles of dried gel on the fabric surface. TABLE 4 gives the anti-bacterial properties of various processing fabrics. It is shown that dyed fabrics and processed fabrics have anti-bacterial properties only after color fixing. After preprocessing of Ag/TiO_2 complex sol, the processed fabric has better anti-bacterial properties, due to the silver content. Moreover, a higher concentration of $AgNO_3$ leads to a stronger resistance to bacteria.

Wash fastness of treated fabrics

To explore the effect of color fixing, the dyeing and anti-bacterial properties of processed fabric were determined after rinsing 20 times; the results are given in TABLE 4. After washing 20 times, the dyeing of the fabric with color fixing is reduced only 3–6%, whereas that of the fabric without color fixing reaches 16%. Furthermore, the fabric with color fixing has good anti-bacterial properties.

CONCLUSIONS

This study has prepared Ag/TiO_2 complex sol at different pH values, and then processed dyed nylon fabric *via* traditional soaking, padding, pre-drying and curing. The objective was to explore the property of dried complex sol on one hand; and to study the influence of complex sol upon dyeability and anti-bacterial properties on the other hand. The following conclusions are

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drawn from the test results. (1) Dried complex sols prepared under acid conditions have smaller particles, whereas those prepared under alkaline conditions present a laminated structure. The relative weight percentage of Ag in the dried gel decreases with increase of pH value. (2) The concentration of $AgNO_3$ has an influence upon the weight percentage of dried complex sols but not on the crystal structure. Meanwhile, acid-base conditions have no influence upon the crystal structure of the dried gel. (3) In the case of increasing concentration of $AgNO_3$, specific surface area and the pore volume of the dried gel was increased, but the orifice size becomes smaller. In the case of an excessive amount of $AgNO_3$, there is a reverse effect on particle size. Under alkaline conditions, thre dried gel presents the largest aperture but the smallest specific surface area and orifice volume. (4) Preprocessing of the complex sol contributes to a good anti-bacterial property of treated fabric, and color fixing is also very useful for stable dyeability and anti-bacterial properties.

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