

Synthesis, Characterization, and Applications of Polyvinylpyrrolidone/SiO₂ Hybrid Materials

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ABSTRACT: This research discusses the properties of hybrid materials formed by polyvinylpyrrolidone (PVP) and tetraethoxysilane (TEOS) of different weight ratios, by the sol-gel process, to evaluate the feasibility of its application to process-dyed nylon fabrics. After using equipment including FTIR, ¹³C-NMR, and SEM, it was shown that PVP and SiO₂ are connected by hydrogen bonds, further showing the existence of special functional groups and the porous structure in hybrid materials. The pore size of the hybrid materials, specific volume of pores, and the specific surface area increased with increasing weight ratio of TEOS. In

addition, the TGA testing results showed that the thermoresistance of hybrid materials can be improved. The color of the treated fabrics darkened if dyed nylon fabrics were treated by hybrid materials. When using metal complex acid dye for certain fabrics, when hybrid materials were used in finishing, there was significant improvement to the fabric's hygroscopicity and its colorfastness against chlorine. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1936–1942, 2005

Key words: sol-gel process; hybrid materials; nanocomposites; dyes/pigments; nylon

INTRODUCTION

The science of nanomaterials is an important emerging technology. By making this kind of material, great market potential can be brought to the technology sector, and at the same time, thus having a major impact on the so-called traditional manufacturing industry. Its incalculable influence on the way people live is already emerging. The sol-gel process is one of the primary methods used to make nanomaterials. In the past, various scientists in the field made similar products with this kind of technology, including lenses, ceramics, optometric devices, and catalysts for electronic devices.^{1–8} Moreover, in making nanocomposites, the sol-gel process plays an important role. The process starts by mixing metal organic and metal inorganic compound solutions; after hydrolysis and polymerization, they gradually take the form of gel. Finally, after coagulation, a kind of composite material with high porosity and large surface area will be formed, referred to as a "hybrid material."^{9,10} Because of the strong reaction between H₂O and the macromolecular chains in the gel, the structure and properties of the gel network substantially influence the properties of water contained in it.

The work in this domain has been extensively reported in the literature.^{11–15} While making the gel,

water and catalysts are indispensable. In the past, scientists proposed that the ratio between the applied polymer, metal alcoholate, water, and catalysts in the process is substantially related to the properties of the resulting hybrid material.^{16–19} In addition, when preparing the gel, tetraethoxysilane (TEOS) is the simplest kind of alcoholate; after hydrolysis, it interacts with organic elements, generating polymerization, and through physical or chemical bonding, a hybrid material will be formed. In this hybrid material, the kind of inorganic compound produced is usually SiO₂, which has a latticelike structure, is porous, and has a characteristically rough surface. After being heat-treated at 140°C, the diameter of the dried gel pores would be 30 nm, far greater than that of vaporized water, so it would enhance the hygroscopic property of treated fabrics.²⁰

Polyvinylpyrrolidone (PVP) is a kind of water-soluble macromolecular compound and has properties common with its counterparts, such as colloid protection, viscosity, hygroscopicity, hydrotropicity, coagulation, and strong bonding ability. In synthetic macromolecules, PVP is unusual in that it is soluble in water and most organic solutions and has low toxicity and high physiological compatibility. The excellent qualities of PVP, its usage is becoming more widespread, especially in the fields of medicine, foods, cosmetics, and other areas relevant to human health.

In this experiment, we first prepared PVP and TEOS of different weight ratios, and then produced a gel by mixing them with specified amounts of water and

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catalyst. Subsequently, we oven-dried the gels to eliminate the aqueous part to make PVP/SiO₂ hybrid materials. We discuss what kind of changes would happen to the properties of hybrid materials when the weight ratio between PVP and TEOS changes. Next, we applied hybrid materials to dyed nylon products and evaluated the changes to the color, hygroscopicity, and colorfastness against chlorine in treated fabrics.

EXPERIMENTAL

Materials

The following substances were used in the experiments: polyvinylpyrrolidone (PVP) and isopropanol, both obtained from Japan Reagent Industry Corp. (Kobe, Japan); tetraethoxysilane (TEOS, Acros Organics, Morris Plains, NJ); FC-226, a hydrophilizing agent (3M Co., St. Paul, MN); Jinlev NL, a leveling agent (Jintex Corp., Ltd., Taipei, Taiwan); Intratex CW, a chlorine-resistant fastener (Yorkshire Chemicals, West Yorkshire, UK); the dyes Palatin Fast Bule RRN and Acidol Brill Yellow M-5 GL, both from BASF AG (Ludwigshafen, Germany), and Amilan Red NW (Yorkshire Chemicals); and pretreated nylon fabrics (Chun-Jin Industrial Co., Ltd., Taipei, Taiwan), whose specifications are $(70 \times 160) \div (24 \times 136) \times 64$ in., indicating that the woven fabric has a warp of 24 and weft of 136 per square inch; the fineness of every warp and weft is 70 and 160 denier, respectively; and the width of the fabric is 64 in.

Methods

Preparation of PVP/SiO₂ hybrid materials

Under proper conditions, we adopted PVP to TEOS weight ratios of 65:35, 55:45, and 25:75. We weighed a specified amount of PVP and dissolved it in 350 mL of isopropyl alcohol (IPA), and designated this as solution a. We added a specified amount of TEOS to 350 mL of IPA solution, added 0.05N HCl to set the pH value as 3, and thoroughly stirred the solution, which was designated as solution b. We adopted the same method as mentioned above, using different weight ratios of PVP and TEOS, to make multiple solutions. Solutions a and b were mixed and stirred for 3 h at 25°C. When the IPA solution evaporated and only half of the original solution remained, we divided the remnant into half and left one half at room temperature to produce a hybrid material of PVP/SiO₂ by drying. The hybrid material was placed in a plastic bag for further tests. The other half of the solution was applied to process fabrics in its liquid form.

Application of PVP/SiO₂ hybrid materials

The nylon fabric was immersed in the dye liquor prepared in advance. The liquor should contain 5% on

weight of fabric (owf) of dye, leveling agent, and 1% acetic acid; in addition there should be 3% owf of hydrophile and 5% owf of colorfastener against chlorine. The liquor ratio was set at 1 : 50. The fabric was dyed for 45 min at 90°C, washed with water, oven-dried, and then placed in a bag. A 40-g sample of PVP/SiO₂ solution, mentioned previously, was added to 400 mL of water, and stirred evenly to produce the steeping liquor. The dyed fabrics were first impregnated for 10 min at room temperature in a PVP/SiO₂ solution. This was followed by squeezing the fabric to a wet pickup of 80% pinning on a frame without tension, after which it was dried at 80°C for 2 min and then cured at 150°C for 1 min. The relevant properties were then measured. For comparison, another piece of test fabric was prepared: it was dyed directly without adding hydrophile and colorfastener against chlorine and immersed in a PVP solution made up with the same concentration, upon which it was soaked and padded for absorption. Then, finally, under the same conditions, the fabric was predried and heat-treated.

Analysis and measurements for the properties of hybrid materials and treated fabrics

The weight loss of hybrid materials was measured by use of a Du Pont 2200 (Boston, MA) weight-loss measuring device; a JEOL 5610 electron microscope (JEOL, Tokyo, Japan) was used to conduct surface observation; a Bio-Rad Digilab FTS-40 Micro-FTIR (Bio-Rad, Hercules, CA) was used to examine special functional groups; and a Bruker (Darmstadt, Germany) Avance 400 NMR device was used to measure the displacement of ¹³C. The properties of the pores of copolymer and hybrid materials were measured by an ASAP 2010 BET surface area analyzer (Micromeritics Instrument Corp., Norcross, GA). The color strength of the treated fabric was measured by a K/S 45/O-L computer color analyzer (HunterLab, Reston, VA) by eq. (1):

$$K/S = (1 - R)^2/2R \quad (1)$$

where K is the absorption coefficient, S is the scattering coefficient, and R is the reflectance of the treated fabrics. When the K/S value is higher, the color of the fabric is deeper.

With respect to the softness, we used a JIS-approved Zhenjiang Inteco (China) horizontal table tipped at a 45° angle. The hygroscopicity and colorfastness against chlorine of the treated fabrics were measured according to AATCC 79 and AATCC 162 methods.

RESULTS AND DISCUSSION

FTIR and ¹³C-NMR analysis of hybrid materials

Figure 1 shows the FTIR of pure PVP material and PVP/SiO₂ hybrid materials. From Figure 1(A), one can

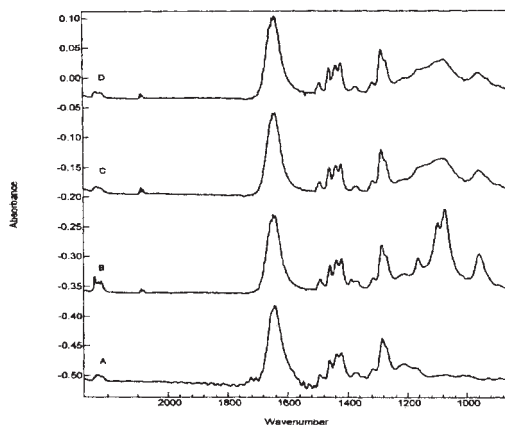


Figure 1 FTIR spectra of hybrid materials: (A) pure PVP; PVP/TEOS ratio: (B) 65 : 35, (C) 55 : 45, and (D) 25 : 75.

see that there is an apparent absorption peak at 1646 cm^{-1} . This is the absorption peak of amide, which is a vibrational absorption band formed by the combination of $>\text{C}=\text{O}$ and $\text{C}-\text{N}$.²¹ Because it is a combination, the peak is lower than that of the absorption peak of pure $>\text{C}=\text{O}$ ($1750\text{--}1700\text{ cm}^{-1}$).

Furthermore, Figure 1(B), (C), and (D) represent the FTIR of PVP/SiO₂ hybrid material with weight ratios of 65:35, 55:45, and 25:75, respectively, where there appears to be $>\text{C}=\text{O}$ group absorption peaks at 1645, 1644, and 1643 cm^{-1} , respectively. Also, with an increasing quantity of TEOS, the absorption peaks gradually move toward lower wavenumbers. Furthermore, there are apparent absorption peaks at 1078, 1086, and 1082 cm^{-1} , which are the absorption peaks of the Si-O-Si group. The above results indicate that the PVP/SiO₂ hybrid material was indeed formed.

Results from the ¹³C-NMR apparatus were used to analyze the chemical shift of ¹³C in the fine structure of macromolecular compounds, such as cubic regularity, comonomer's sequences, and the structure of its defects. Recently, it was also used to prove that macromolecules develop strength of another kind of conformation in their fine structure because of the displacement of local molecular chains.²² Figure 2 represents the ¹³C-NMR of pure PVP and PVP/SiO₂ hybrid materials. It is shown in Figure 2(A) that for pure PVP, there is an absorption peak of $\text{C}=\text{O}$ at 177.6 cm^{-1} , whereas for PVP/SiO₂ hybrid material there are $\text{C}=\text{O}$ absorption peaks at 178.0, 178.2, and 179.4 cm^{-1} , respectively, as shown in Figure 2(B), (C), and (D). Previous reports indicate that if two kinds of materials are bonded by hydrogen bonds in a hybrid material, the absorption peaks of special functional groups on the ¹³C-NMR spectrum will shift toward the upfield.^{23–27} This indicates that in hybrid materials, there would be hydrogen bonds between the $>\text{C}=\text{O}$ group in PVP and the SiO₂ in the inorganic phase. Furthermore, the greater the amount of TEOS contained, the more the

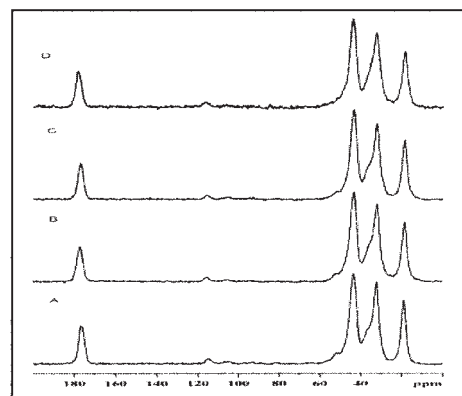


Figure 2 ¹³C-NMR spectra of hybrid materials: (A) pure PVP; PVP/TEOS ratio: (B) 65 : 35, (C) 55 : 45, and (D) 25 : 75.

peak shifts upfield, although it may be not suitable to indicate the hydrogen bond presented between PVP and SiO₂ on the figure of FTIR. However, some reported studies in the literature^{28–31} show that there is hydrogen bonding between the $\text{C}=\text{O}$ in PVP and the OH in SiO₂.

TGA analysis of hybrid materials

Figure 3 shows the TGA thermal property analysis, where Figure 3(A) shows pure PVP: its initiation decomposition temperature is 449°C , and the decomposition rate of macromolecules is $-1.6522\%/^\circ\text{C}$. The content of PVP is lowered to 20% before reaching initiation decomposition temperature, and when the temperature reaches 250°C , the content decreases by 15–16%. This is caused by the strong hygroscopicity of PVP because the content was that of water, which it absorbed while being weighed on the scale. When the temperature reaches 500°C , the remnant is only 7%. From Figure 2(B), (C), and (D), we can see the TGA of PVP/SiO₂ hybrid material with weight ratios of 65:35, 55:45, and 25:75. Compared with that of pure PVP, the

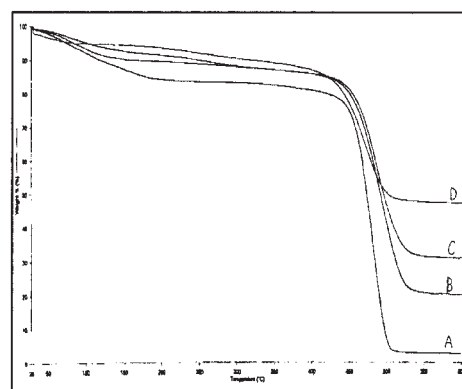


Figure 3 TGA curves of nanohybrid materials: (A) pure PVP; PVP/TEOS ratio: (B) 65 : 35, (C) 55 : 45, and (D) 25 : 75.

TABLE I
PVP/SiO₂ Thermoresistance of Hybrid Materials

PVP/TEOS weight ratio	Property		
	Initiation decompose temperature (°C)	Decompose rate (%/°C)	Remnant ^a (%)
Pure PVP	449.2	-1.6522	7
65:35	488.6	-0.9265	39
55:45	444.4	-0.8208	47
25:75	433.1	-0.5924	50

^a The remnant is the percentage that remains after the temperature reaches 500°C.

initiation decomposition temperatures are, respectively, 488.6, 444.4, and 433.1°C. According to Table I, the decomposition rates are -0.9265, -0.8208, and -0.5924%/°C. We can see that the initiation decomposition temperature decreases as the quantity of TEOS increases; the decomposition rate also decreases. The reason for this phenomenon is that during hydrolysis, Si(OH)₄ was formed by TEOS in hybrid materials. Later, polymerization took place and SiO₂ was formed, but some of the Si(OH)₄ did not totally complete the process, a phenomenon which becomes more apparent with increase amounts of TEOS. However, after Si(OH)₄ decomposes, what remains in the hybrid material is the lattice structure formed by PVP and SiO₂, causing the decomposition rate to decrease. This also means the heat resistance of the hybrid ma-

terial is improved. When the temperature reaches 500°C, the remaining content is 39, 47, and 50%, respectively. From this experiment, we thus show that with increasing TEOS content, there is better heat resistance.

Surface configuration of hybrid materials

It is observed from the electron microscope photos, shown in Figure 4, that the surface texture of pure PVP material is smooth, even, and small-grained. Moreover, from Figure 4(B), it is shown that small pores exist in the smooth and even surface texture. In Figure 4(C), the pores exist but the surface is rough and displays overlapping features. In Figure 4(D) and (E), not only do the pores exist but the surface is large-grained and continuous. The reason for this is that when the TEOS quantity is small, there is less granular SiO₂ formed by hydrolysis and polymerization, so the pores are easily observable. Nevertheless, as shown in Table II, the diameter of the pore is very small, only about 2.34–3.72 nm. In contrast, when the content of TEOS increases, the SiO₂ grains formed are large and numerous, and most of them form a three-dimensional configuration. Therefore, the distance between each particle is reduced, and the particles seem interconnected, making the photographic image look granular. From Table II we can also see that the pore diameter is rather large, reaching almost 5.10 nm. Nevertheless, the pores in the four hybrid materials created for this experiment are all nanoscaled.

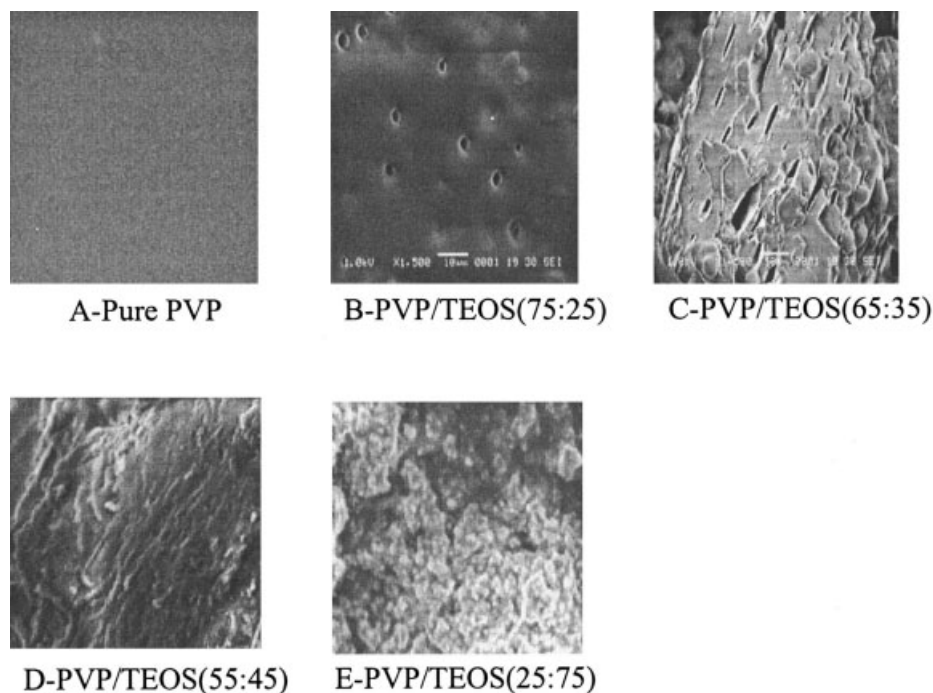


Figure 4 SEM micrographs of hybrid materials of different weight ratios.

TABLE II
Various Properties of Pores of Hybrid Materials
Produced with Different PVP/TEOS Weight Ratios

PVP/TEOS weight ratio	Property		
	BET specific surface area (m ² /g)	Specific pore volume, × 10 ⁻³ (cm ³ /g)	Size of pore (nm)
Silica dry-gel ^a	192.000	1320.00	30.00
75/25	1.9868	1.163	2.34
65/35	2.4850	2.311	3.37
55/45	4.3122	3.635	3.72
25/75	11.1182	14.168	5.10

^a Adapted from Iler³² (under the temperature of 140°C).

Effects hybrid materials have on the dyed nylon fabrics

Table III displays the *K/S* values of treated fabric after being dyed and padded by PVP/SiO₂ hybrid materials: after being padded by hybrid materials, the treated fabric grew darker in color. Also, with increasing weight ratio of TEOS, the color darkened even more. The reason for this is that after being padded by PVP/SiO₂ hybrid materials, the fabric carries newly formed SiO₂ particles, which cause light refraction. Also, because PVP exercises strong bonding effects toward the metallic ions in the dye, the color of the fabric is darkened. Moreover, even after washing it with soap, the dyed fabric displays strong colorfastness, especially fabric padded by hybrid material.

Table IV displays the measured hygroscopicity and colorfastness against chlorine of dyed fabric. We can

see from the table that the treated fabric displays good hydrophilic properties, and achieves almost absolute absorbance within 5 s. This is chiefly explained by the existence of PVP. However, treated fabric displays less hydrophilic effect after being water-washed five times, especially the fabric samples dyed without adding hydrophile, some of which cannot even meet the standard of 5 s. This means that the hydrophile has a certain effect in improving the hygroscopicity of treated fabric. When the dyed nylon fabrics were dipped and padded with hybrid materials of higher PVP content, the hydrophilic properties of treated fabric remained satisfactory and reached the standard (<5 s), becoming even better than those of the treated fabric, padded only with PVP polymer. We can see from this that the proper amount of SiO₂ makes the PVP polymer difficult to be washed off; on the contrary, if the PVP polymer does not bond with SiO₂, the PVP polymer will be washed off more easily. Therefore, the proper amount of SiO₂ is important for better durability.

Concerning the colorfastness against chlorine, Table IV shows that, except for those samples dyed by Acidol Brill Yellow M-5 GL, the others all reach the level of 4 in colorfastness and indicate good color retention. This might be caused by the chemical structure of the dye liquor itself. However, although we sought to use the dye liquor that is currently in use by factories, the factories or dealers of dye would not provide relevant information. This is a major drawback to more in-depth investigation because, although it increases its practical application, it also prevents additional research.

TABLE III
Effects of Hybrid Materials on Dyed Nylon

PVP/TEOS weight ratio	Method ^a	Dye								
		Amilan Red NW			Palatin Fast Bule RRN			Acidol Brill Yellow M-5 GL		
		(<i>K/S</i>) ₀ ^b	(<i>K/S</i>) ₁ ^c	<i>F</i> ^d	(<i>K/S</i>) ₀	(<i>K/S</i>) ₁	<i>F</i>	(<i>K/S</i>) ₀	(<i>K/S</i>) ₁	<i>F</i>
65:35	A	27.84	26.57	0.954	24.49	24.12	0.983	10.89	9.31	0.855
55:45		28.21	27.46	0.973	24.16	24.35	0.980	10.34	9.27	0.897
25:75		28.35	27.65	0.975	24.97	24.88	0.973	10.78	9.49	0.880
65:35	B	29.32	28.05	0.957	21.67	21.19	0.975	12.84	10.81	0.842
55:45		29.26	28.19	0.963	21.73	21.32	0.981	13.01	10.95	0.842
25:75		29.47	28.57	0.969	21.86	21.53	0.985	12.69	11.27	0.888
Only PVP	O	30.10	29.39	0.976	22.70	20.84	0.918	12.70	11.02	0.868
Greige C.	C	28.87	28.09	0.973	23.30	20.76	0.891	12.76	10.49	0.822
Greige C.	D	29.53	28.25	0.957	22.73	21.02	0.925	12.09	10.02	0.829

^a A, after being dyed with dye liquor, pad and soak the fabric with hybrid materials; B, apply dye + hydrophile + chlorine-resistant dye together for dyeing and use the hybrid materials for padding, soaking, and heat treatment; O, apply dye liquor for dyeing, then soak and pad it with PVP and heat-treat it; C, dye only with dye liquor; D, apply dye + hydrophile + chlorine-resistant dyeing.

^b *K/S* value of treated fabric before soaping.

^c *K/S* value of treated fabric after soaping.

^d $F = (K/S)_1 / (K/S)_0$.

TABLE IV
Effects of Service of Hybrid Materials on Dyed Nylon Fabric's Hygroscopicity and Colorfastness Against Chlorine

PVP/TEOS weight ratio ^b	Method	Property					
		Hygroscopicity (s) ^a			Colorfastness against chlorine (level)		
		Dye					
		Amilan Red NW	Palatin Fast Bule RRN	Acidol Brill Yellow M-5 GL	Amilan Red NW	Palatin Fast Bule RRN	Acidol Brill Yellow M-5 GL
65:35	A	1.84 (2.92)	0.78 (2.45)	2.76 (3.54)	4	4	2.8
55:45		4.05 (5.25)	3.85 (5.12)	4.09 (6.54)	4	4	3.6
25:75		3.44 (4.85)	4.15 (5.72)	3.67 (5.12)	4	4	2.8
65:35	B	0.61 (2.34)	0.71 (2.56)	0.81 (2.78)	4	4	2.5
55:45		1.09 (2.45)	1.38 (2.89)	3.54 (4.59)	4	4	2.5
25:75		1.95 (3.12)	1.13 (2.98)	1.36 (3.01)	4	4	2.5
PVP only	O	2.81 (4.56)	2.43 (5.57)	3.42 (5.27)	4	4	2.9
Greige	C	4.86 (6.78)	4.17 (5.75)	4.18 (6.55)	4	4	3.2
Greige	D	2.69 (7.02)	2.24 (6.05)	3.69 (5.78)	4	4	2.5

^a Values inside parentheses are those measured after being washed five times using the method of water drop loss.

^b As shown in Table III.

Table V displays the measured softness of dyed fabric. From the table, we can see that the factory fabric padded and soaked with PVP/SiO₂ hybrid material has the worst feeling, or hand. The lowest ranked is the one padded and soaked with PVP after dyeing and the one that feels best is the fabric that only went through dyeing. This is because PVP itself is brittle, causing the fabric to feel rough. On the other hand, the SiO₂ particles are also responsible for the roughness. The hand of treated fabric worsens with increasing PVP content, so it also cannot compete with the raw fabric in softness. With less PVP content, the fabric is softer. Samples prepared according to method B in Table V are characterized by an inferior hand because they were dyed with (dye + hydrophile

+ chlorine-resistant) and the PVP itself causes the fabric to feel coarse. Compared against the greige fabric, fabrics containing PVP feel worse to the touch.

CONCLUSIONS

After producing PVP/SiO₂ inorganic/organic hybrid materials by the sol-gel process, the following conclusions may be drawn from the experimental results:

1. Analysis from the results of FTIR and ¹³C-NMR tests show that in PVP/SiO₂ hybrid material there are hydrogen bonds between the organic and inorganic parts.
2. From analysis of the TGA test, we show that the heat resistance of hybrid materials improves with increasing TEOS weight.
3. The surface area, size, and volume of the pores of hybrid materials all increase when the weight of TEOS increases; also, its size is nanoscaled.
4. Hybrid materials have certain effects on improving the hygroscopicity and colorfastness against chlorine of metal complex acid dye factory fabric.
5. All hybrid material-treated factory fabrics have the drawback of diminished softness.

TABLE V
Effects of Hybrid Materials on the Softness of Nylon Fabric^a

PVP/TEOS weight ratio ^b	Method	Softness		
		Dye liquor		
		Amilan Red NW	Palatin Fast Bule RRN	Acidol Brill Yellow M-5 GL
65:35	A	5.8	5.0	6.2
55:45		3.4	3.3	3.7
25:75		2.8	3.0	3.1
65:35	B	5.5	5.4	6.1
55:45		3.5	3.5	5.1
25:75		3.4	3.2	3.9
PVP only	O	3.7	3.9	2.7
Greige	C	2.6	2.9	2.5
Greige	D	2.7	2.6	2.9

^a Original white fabrics 2.4 cm.

^b The label is as indicated in Table III.

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