

# Synthesis, Characterization, and Application of PVP/Chitosan Blended Polymers

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**ABSTRACT:** The purpose of this study was to research the compatibility and application of polyvinylpyrrolidone (PVP)/chitosan blended polymers. The polymers were synthesized at different weight ratios and tested using techniques such as Fourier transform infrared spectroscopy, differential scanning calorimetry, and thermogravimetric analysis to evaluate the compatibility of the blended materials. Incompatibility occurred when the quantity of chitosan exceeded 75%. The addition of PVP was beneficial for the

thermal stability of chitosan, but resulted in inferior strength performance. Furthermore, the blended polymers did not show a color-enhancement effect, but did show elevated water absorption, chlorine resistance, and colorfastness. In addition, the treated fabrics with a higher chitosan ratio in the blended polymer had antimicrobial properties. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 885–891, 2006

**Key words:** blending; fibers; nylon; strength

## INTRODUCTION

Usage of blended polymers is the most effective way to produce new multipurpose materials. During the past few years, researchers have paid considerable attention to the study of polymer blending.<sup>1–5</sup> Nishio et al. conducted a series of studies on cellulose polymer blending and published papers on the rheology, effects, and mechanics. Kubota and coworkers conducted several studies on the electrolyte properties and characteristics of chitosan and derivative polymer materials in membrane applications.<sup>6–9</sup>

Chitosan is the second largest biological polysaccharide (after cellulose) found in nature. It is present in soft-bodied insects and can be synthesized through a deacetylase reaction using chitin as the raw material. Chitin has stable chemical properties, good membrane-forming characteristics and is nontoxic, renewable, and soluble in low-acidity water solutions. It is also an ideal biodegradable material that can be disposed of underground through natural circulation without damaging the environment.<sup>10</sup> The disadvantages of chitin include the lack of processability caused by poor heat tolerance, the ease of degradation by ultraviolet radiation, the lack of water solubility, and

the difficulty of spinning due to poor wet-strength performance.

As a water-soluble polymer, polyvinylpyrrolidone (PVP) has beneficial effects on protection, viscosity, absorbency, solubilization, and condensation, with its most significant features being excellent solubility and biological compatibility. Additionally, PVP has low toxicity and is utilized in a broad range of areas, such as medical, food, cosmetics, and health-related domains. However, issues concerned with the rigid but fragile nature of PVP and its lack of sturdiness have resulted in processing difficulties.<sup>11</sup>

The purpose of the present research was to blend the two materials, chitosan and PVP, at different ratios with the aim of producing a new material possessing the benefits of both. The effects on the properties of nylon dyes, such as water absorption, sweat discharge, chlorine resistance, and colorfastness, were also examined.

## EXPERIMENTAL

### Materials

The following materials were used in this study: PVP (Japan Reagent Industry Corp.), chitosan (OHKA Enterprises Co., Kaohsiung, Taiwan; degree of deacetylation = 85%,  $M_r$  = 400 kDa), reagent grade formic and acetic acid (Wako Pure Chemical Industry Co., Japan), Palatin East Blue RR (BASF Taiwan Ltd.), Acidol Brill Yellow M-5GL (BASF Taiwan Ltd.), Amilan

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Red NW (Yorkshire Chemicals, UK), leveling agent (Jinlev NIA New; Jintex Corp., Taiwan), hydrophilic agent (FC-226; 3M, USA), and chlororesistant fix agent (Intratex CW; Yorkshire Chemicals). Preprocessed nylon fabrics (Chun-Jin Textile Industrial Co., Taiwan) were also used with the following specifications:

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

## Methods

### PVP/chitosan blending

We utilized adequate quantities of chitosan absorbed in formic acid and stirred for 4 h to synthesize chitosan/formic acid solutions of different concentrations (1–4%). Various quantities (4, 8, 12, and 16 g) of PVP were added to the formic acid solutions. The resultant solutions, which were blended with different ratios of PVP/chitosan, were stirred for 2 h. Finally, 100 mL of each blended solution was placed in a glass container and dried in a vacuum oven until a membrane was obtained.

### Application of PVP/chitosan blended polymers

The nylon test fabrics were immersed in a preprocessed dyeing solution (containing 2% of dye, 1 g/L of leveling agent, 1 g/L of acetic acid, 3% of humectant, and 5% of chlorine-resistant color-fixing agent) at a ratio of 1:50 was dyed at 90°C for 45 min, then washed, and heat dried. A 40-g sample of the synthesized blended solution was added to 400 mL of water and uniformly stirred to develop a dipping solution. The dyed fabric was dipped into the blended solution for 10 min using twin alternating pressure processes with 80% pick up. After 2 min of predrying at 80°C and 1 min of heat treatment at 150°C, the fabrics were packaged ready for testing the relevant properties.

### Blended polymer properties: Analysis and measurement

Measurements of the blended polymer functional groups, surface morphology, heat tolerance, and <sup>13</sup>C-absorption status were conducted using a Bio-Rad Digilab FTS-40 Micro Fourier transform infrared (FTIR) spectroscope, a Jeol 5610 scanning electron microscope (SEM), a Du Pont model 2200 thermogravimetric analyzer (TGA), and a Bruker Avance 400 spectrometer. Tensile strength and viscosity were measured using the Alphaten 400 tensile tester based on the ANSI/ASTM D 412–75 and KVF GT-02 specifications.

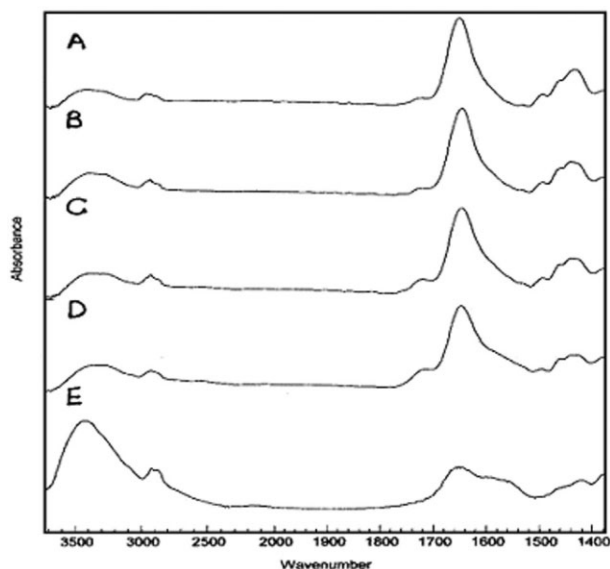
### Test of treated nylon fabrics

Measurements of the fabric water-absorption capability were based on the Adidas method. This method is applied to determine the fabric's ability to transport water from the inside to the outside of the fabric. Drops of water are placed on the fabric inside (back-side of fabric) and the time it takes for the drops to be absorbed and spread to the fabric surface is measured. The chlorine resistance and colorfastness were measured according to the Adidas modified ISO105-E03 standard. The method of determination of the resistance of dyeing and prints to the action of active chlorine on concentration as such is used to disinfect swimming-bath water. The active chlorine concentration of 50 mg/L is intended for swimwear. Color change of tested fabric must be big or at least be equal to 4 just calculate qualified. The K/S values of the treated fabrics were measured by a Nippon ND 300A (Nippon Shiyaku Kogyo K. K. Ltd., Osaka, Japan) color-difference meter, while the softness of the treated fabrics were measured by an INTECO softness tester with a 45° tilted platform. Antimicrobial testing was carried out according to the antimicrobial standards of the Japan Association for the Evaluation of Textiles, and measurements were made according to the quantification methods JIS L1902–1998: bacteriostatic values greater than 2.2 indicated that the test samples were bacteriostatic, and antiseptic values greater than 0 indicated that the test samples were antiseptic.

## RESULTS AND DISCUSSIONS

### FTIR analysis

Figure 1 shows the FTIR results for pure PVP and blended PVP/chitosan. Figure 1 (curve A) depicts clear absorption spectra at 1647 cm<sup>-1</sup> for pure PVP corresponding to amide (I) and also corresponding to the >C=O and C—N groups.<sup>12</sup> The combined PVP/chitosan spectra were smaller than the pure >C=O absorption spectra (1750–1700 cm<sup>-1</sup>). As shown in Figure 1 (curve E), the distinct >C=O and —CONH— group absorption spectra at 1652 and 1570 cm<sup>-1</sup>, respectively, were due to the 85% deacetylase in chitosan; this indicates the existence of residue chitin ingredients. Clear —C—N group absorption spectra were present at 1068 and 1029 cm<sup>-1</sup>, with chitosan possessing —OH and —NH<sub>2</sub> group absorption spectra at 3424 cm<sup>-1</sup>. The three PVP/chitosan blends with different weight ratios (75:25, 50:50, and 25:75) showed distinct >C=O group absorption spectra at 1640, 1638, and 1636 cm<sup>-1</sup>, respectively [Fig. 1 (curves B–D)]. This gradually shifted toward the low-frequency region as the chitosan weight ratio increased. Clear absorption spectra were also demonstrated at 3380, 3378, and 3377 cm<sup>-1</sup>, which corresponded to the



**Figure 1** FTIR of PVP/chitosan blended polymers (A: PVP, B: 75/25, C: 50/50, D: 25/75, E: chitosan).

—OH and —NH groups. The chitosan —OH and —NH groups absorption spectra at around  $3424\text{ cm}^{-1}$  were found to drift toward the lower frequency zone with the addition of PVP to form blended polymers. Furthermore, the  $\text{C}=\text{O}$  group of PVP showed absorption spectra at  $1646\text{ cm}^{-1}$ , while the blended polymer  $\text{C}=\text{O}$  group shifted toward the lower frequency zone, suggesting the formation of hydrogen bonding between the molecules in the blended polymer and verifying the synthesis of the PVP/chitosan blended material. The shifting of the absorption spectra for the PVP  $\text{C}=\text{O}$  group suggests the existence of hydrogen bonding, as described in previous reports.<sup>13,14</sup>

### <sup>13</sup>C NMR analysis

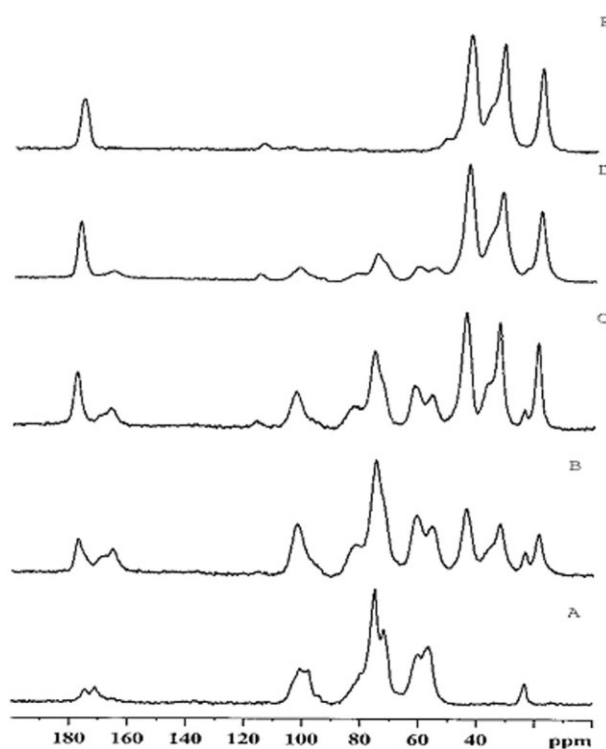
<sup>13</sup>C nuclear magnetic resonance (NMR) analysis can be used as a chemical deviation method for examining the properties of <sup>13</sup>C in a polymer compound microstructure, including stereoregularity, comonomer sequence distribution, and defective structures.<sup>15</sup> Recently, this technique has been utilized to verify the microstructure strength of new structural bodies due to the shifting of the partial molecule chain within the polymer.<sup>16</sup>

Figure 2 shows the <sup>13</sup>C NMR analysis results for pure PVP and PVP/chitosan blends. As indicated in Figure 2 (curve E), pure PVP had clear  $\text{C}=\text{O}$  group absorption spectra at 177.6 ppm, while the PVP/chitosan blends at the different weight ratios possessed distinct  $\text{C}=\text{O}$  group absorption spectra at 178.4, 179.2, and 178.8 ppm [Fig. 2 (curves B–D)]. The shift at 50/50 suggests hydrogen bonding between the PVP and chitosan. The chitosan also showed distinct  $\text{C}=\text{O}$  group

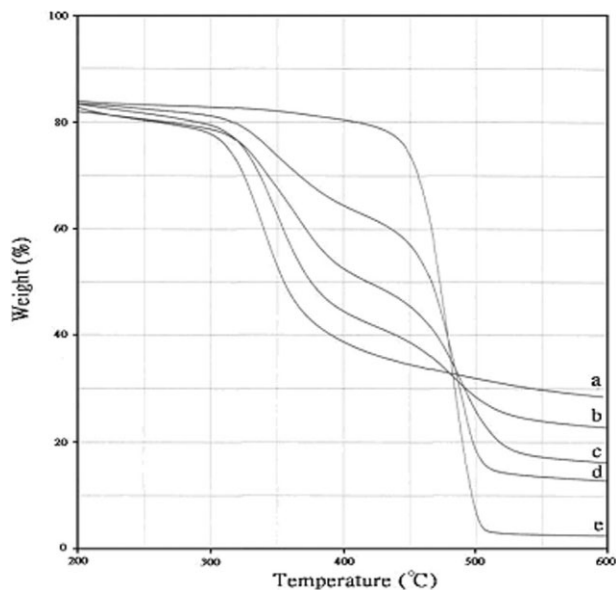
spectra at 174.3, 171, and 165.4 ppm due to the 85% deacetylate, indicating the existence of residual chitin ingredients. The results of the <sup>13</sup>C NMR analysis of the three blended polymers indicate that, in all cases, absorption spectra still exist for chitosan at 165.4 ppm, whereas the spectra at 171 and 174.3 ppm have all shifted toward higher frequency zones (178.4, 179.2, and 178.8 ppm). Based on past research reports,<sup>17–19</sup> we predict that the PVP  $\text{C}=\text{O}$  group within the blend formed hydrogen bonds with the chitosan —OH or —NH<sub>2</sub> group.

### TGA analysis

As seen from Figure 3 and Table I, the 15–16% drop in PVP at the initial 250°C decomposition temperature could have been caused by water absorption during the weighting process, due to the strong water-absorptive nature of PVP. The 20% drop in chitosan at the initial 250°C decomposition temperature differed from the generic 10–12% shown in the figure, which could have been due to the water-absorption capability and the 85% deacetylate in chitosan. A bisectonal decomposition diagram is shown in Figure 3 (curves B–E) (the first section corresponds to chitosan and the second to PVP). Furthermore, the decomposition rate of PVP part in the blended polymer increased as the amount of PVP increased, whereas the decomposition rate of chitosan part in the blended polymer increased



**Figure 2** NMR of PVP/chitosan blended polymers (A: chitosan, B: 25/75, C: 50/50, D: 75/25, E: PVP).



**Figure 3** TGA of PVP/chitosan blended polymers (a: chitosan, b: 25/75, c: 50/50, d: 75/25, e: PVP).

as the amount of chitosan increased. At 500°C, the residue of blended polymers increased as the chitosan quantity increased, because of the faster decomposition of PVP. The residue of pure PVP was 7%, which was clearly different from the 30% shown in Figure 3 (curve B).

### SEM and polarizing analysis

As seen from Figure 4, the SEM images for chitosan and PVP were smooth and even. The SEM images for the blended polymers with PVP/chitosan weight ratios of 75/25 and 50/50 all indicated smooth and even effects [Fig. 4(b,c)]. However, Figure 4(d) shows a clear "island" structure, which could have been the result of an excess of chitosan, indicating the partial compatibility between the two polymers at certain weight ratios. When the quantity of chitosan exceeded 75%, incompatibility occurred.

### Viscosity and tensile strength

As seen from Table II, the viscosity of the blended polymers decreased with the addition of the PVP because of its lack of viscosity. During blending with chitosan, the PVP entering into the chitosan molecule structure destroyed the chitosan molecule chain, resulting in a decrease in viscosity.

Furthermore, the results presented in the table clearly indicate that the strength of the blended polymers was reduced by the addition of PVP. Increasing the quantity of PVP decreased the strength of the blended polymers. This could be due to the rigid and fragile nature of PVP, and the fact that the added PVP

destroyed the continuity of the chitosan molecules, resulting in a decrease in the blended polymer strength. When excessive quantities of PVP were added, the strength of the blended polymers tended toward fragility. Even though the hydrogen-bonding effect between the two could be seen in the FTIR and NMR spectra, the strength of the blended polymers decreased as the PVP quantities increased, for the reasons described earlier.

### Properties of treated fabrics

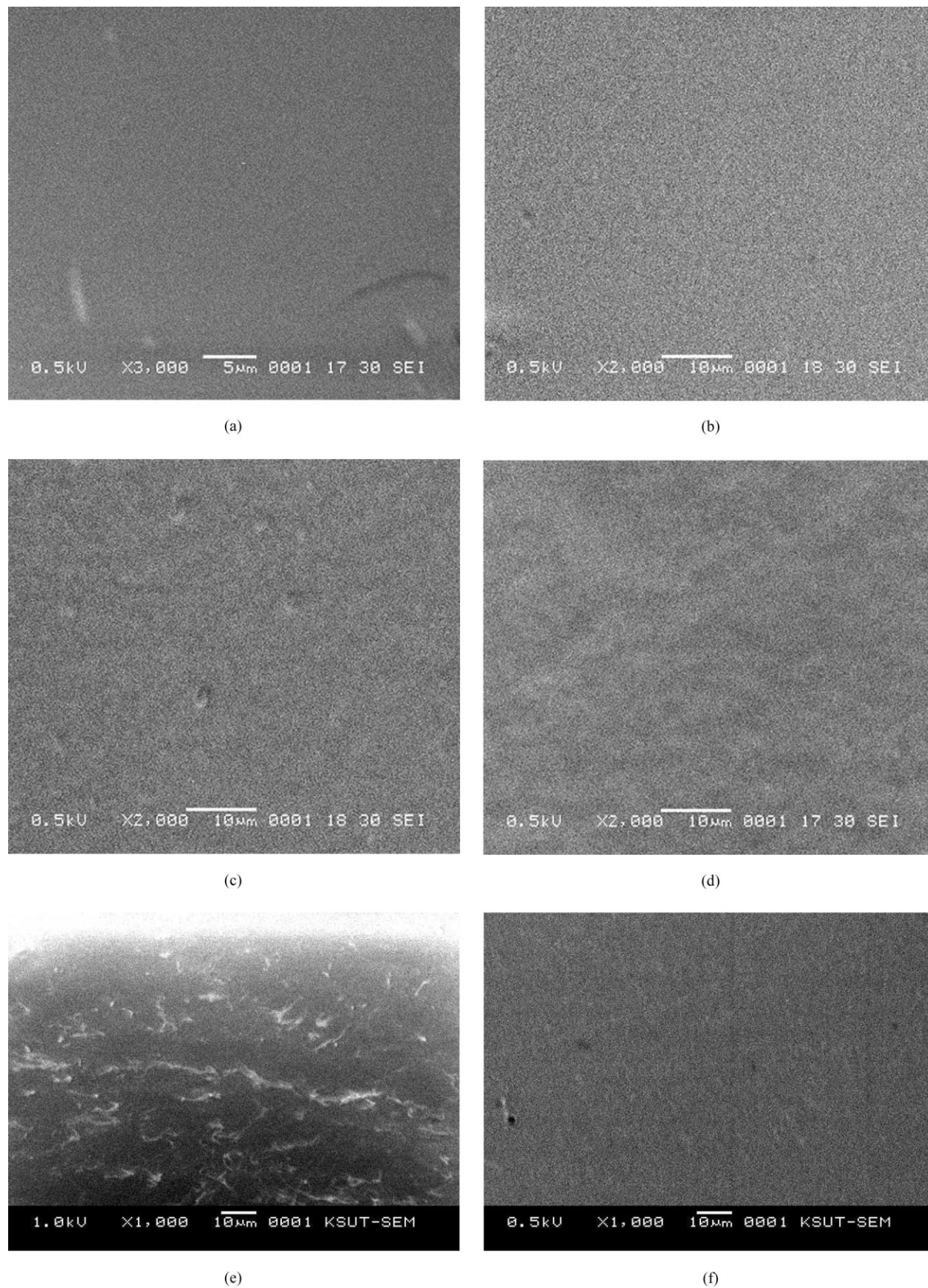
Table III shows the dyeability of the test fabrics following compression and absorption treatment of the blended polymer and dyeing under different conditions. As indicated in the table, the exhaustion properties of raw fibers C and D were not affected when they were simultaneously processed with humectant and chlorine-resistant chemicals. Furthermore, when the test fabric was treated with PVP after dyeing, the color was similar to that of the raw fibers (C and D). However, the red fabric dye showed color enhancement after soaping, because it was an acidic metal-complex dye. The added PVP reacted with the metal complex in the dye, resulting in color enhancement. When treated with blended polymers, the *K/S* value of the fabric was similar to that of the dyed raw fibers (C), although the color-fixation effect of the three dyes was different. This could be related to the chemical structure of the dyes. The color-fixation rate for fabrics dyed blue and yellow was better than in C, indicating that the blended polymers enhanced the bonding effects between the two dyes.

Based on the fabric water absorption and sweat discharge capabilities shown in Table IV, fabrics dyed with humectant and chlorine-resistant agents had superior properties compared with the properties of fabrics treated with methods C or D. Fabrics treated with method O showed better results because of the PVP compression and absorption treatment. However, the fastness test for the three fabrics showed inferior results compared with the standard value after five wa-

**TABLE I**  
PVP/Chitosan Thermoresistance of Blended Polymers

PVP/chitosan weight ratio	Initial decomposition temperature (°C)	Decomposition rate at		Remnant <sup>a</sup> (%)
		250°C (%/°C)	500°C (%/°C)	
100/0	449.2	1.01		7
75/25	318.8	0.18	1.01	20
50/50	319.5	0.35	0.49	26
25/75	320.0	0.55	0.17	30
0/100	313.3	0.63		33

<sup>a</sup> The remnant is the percentage that remains after the temperature reaches 500°C.



**Figure 4** SEM of PVP/chitosan blended polymers (a: PVP, b: 75/25, c: 50/50, d: 25/75, e: 15/85, f: chitosan).

**TABLE II**  
Viscosity and Tensile Strength of Blended Polymers

PVP/chitosan weight ratio	Viscosity (CPS)	Tensile strength (kg/mm <sup>2</sup> )	Stretch rate (%)
100/0	15	— <sup>a</sup>	— <sup>a</sup>
75/25	440	12.34	3.66
50/50	2,400	16.17	11.27
25/75	8,500	18.42	12.43
0/100	22,000	32.83	14.88

<sup>a</sup> Lack of measurement due to fragility.

ter rinses. The fabrics treated with methods A or B demonstrated acceptable results, as indicated in the table. After five water rinses, the water-absorption and sweat-discharge capabilities of fabric B were acceptable, and showed similar trends to those of fabrics C

and D. These findings demonstrate that textiles treated with blended polymer after compression and absorption treatment and following dyeing have superior water-absorption and sweat-discharge properties. This could be due to the high complexity of PVP and chitosan resulting in a better reaction with the dye, thereby enhancing the water-absorption and sweat-discharge capabilities of the fabric. Different processing methods did not cause differences in the chlorine resistance. Considering the effects of the different types of dye, it was clear that fabrics dyed with Acidol Brill Yellow M-5 GL were inferior in terms of water absorption, sweat discharge, and chlorine resistance, possibly because of the chemical structure of this dye.

Table V indicates the softness of the fabrics. As shown in the table, the softness of the fabrics deteriorated

**TABLE III**  
Effect of Blended Polymers on Dyed Nylon Fabrics

PVP/chitosan weight ratio	Method <sup>a</sup>	Color strength								
		Amilan Red NW			Palatin Fast Blue RRN			Acidol Brill Yellow M-5 GL		
		(K/S) <sub>0</sub> <sup>b</sup>	(K/S) <sub>1</sub> <sup>c</sup>	F <sup>d</sup>	(K/S) <sub>0</sub>	(K/S) <sub>1</sub>	F	(K/S) <sub>0</sub>	(K/S) <sub>1</sub>	F
75/25	A	28.46	27.84	0.978	22.68	23.37	1.030	11.54	10.72	0.929
50/50		27.97	27.56	0.985	22.74	23.42	1.030	11.23	10.99	0.979
25/75		27.83	27.54	0.990	22.43	23.73	1.058	11.46	11.18	0.976
75/25	B	28.99	28.55	0.985	21.17	21.30	1.006	10.98	10.33	0.941
50/50		28.39	27.62	0.973	20.58	21.44	1.042	10.97	10.78	0.983
25/75		28.52	29.58	0.986	21.68	21.92	1.011	10.81	10.60	0.981
PVP	O	30.10	29.39	0.976	22.70	20.84	0.918	12.70	11.02	0.868
Greige	C	28.87	28.09	0.973	23.30	20.76	0.891	12.76	10.49	0.822
Greige	D	29.53	28.25	0.957	22.73	21.02	0.925	12.09	10.02	0.829

<sup>a</sup> A, after being dyed with dye liquor, pad and soak the fabric with blended polymers; B, apply dye + hydrophile + chlororesistant dye together for dyeing and use the blended polymers for padding, soaking, and curing; 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 + chlororesistant dyeing.

<sup>b</sup> K/S value of treated fabric before soaping.

<sup>c</sup> K/S value of treated fabric after soaping.

<sup>d</sup>  $F = (K/S)_1 / (K/S)_0$ .

**TABLE IV**  
Effects of Service of Blended Polymers on Dyed Nylon Fabric's Hygroscopicity and Colorfastness Against Chlorine

PVP/chitosan weight ratio	Method	Water absorbency (s) <sup>a</sup>			Colorfastness against chlorine (level)		
		Amilan Red NW	Palatin Fast Blue RRN	Acidol Brill Yellow M-5 GL	Amilan Red NW	Palatin Fast Blue RRN	Acidol Brill Yellow M-5 GL
		75/25	A	1.35 (3.74)	2.45 (4.56)	5.50 (7.85)	4.0
50/50	1.56 (3.47)	3.71 (5.44)		3.77 (5.84)	4.0	4.5	3.0
25/75	1.30 (3.67)	1.52 (3.74)		3.85 (7.02)	4.0	4.0	3.5
75/25	B	1.45 (3.04)	0.89 (2.77)	1.53 (3.12)	4.0	4.0	2.5
50/50		1.50 (3.88)	1.59 (4.01)	3.96 (5.12)	4.0	4.0	2.5
25/75		1.97 (4.02)	0.90 (2.56)	2.47 (4.56)	4.0	4.0	2.5
Only PVP	O	2.81 (4.56)	2.43 (5.75)	3.42 (5.27)	4.0	4.0	3.0
Greige	C	4.86 (6.78)	4.17 (5.75)	4.18 (6.55)	3.5	3.5	2.5
Greige	D	2.69 (7.02)	2.24 (6.05)	3.69 (5.78)	4.0	4.0	3.0

<sup>a</sup> Values inside parentheses are those measured after being washed five times using the method of water drop lose.

<sup>b</sup> As shown in Table III.

**TABLE V**  
**Effects of Service of Blended Polymers on Dyed Nylon Fabric's Softness and Antibacterial Properties**

PVP/chitosan weight ratio	Methods <sup>a</sup>	Softness (cm)			Antibacterial property of Amilan Red NW	Antiseptic property of Amilan Red NW
		Amilan Red NW	Palatin Fast Blue RRN	Acidol Brill Yellow M-5 GL		
75/25	A	3.1	3.2	3.4	1.34	<0
50/50		3.5	2.8	2.7	2.37	0.19
25/75		3.6	3.8	2.7	2.70	0.34
75/25	B	3.5	3.3	3.5	1.06	<0
50/50		3.1	3.3	3.4	2.23	0.20
25/75		3.2	3.1	3.4	2.67	0.31
Only PVP	O	3.7	3.9	2.7	0	<0
Greige	C	2.6	2.9	2.5	0	<0
Greige	D	2.7	2.6	2.9	0	<0

<sup>a</sup> As shown in Table III.

rated with the addition of PVP or compression and absorption treatment of the blended polymers. This was due to the membrane-forming effect on the surface of the lining and the textile caused by the addition of PVP, and the compression and absorption treatment of the blended polymers on the test fabrics resulting in a reduction in the fabric softness. However, there was no direct relationship between the softness of the fabric and the quantity of polymer in the blend. This indicates that the softness of the test fabrics was affected after treatment with the PVP ingredient of the polymer.

In addition, Table V shows that the treated fabrics with a higher chitosan ratio in the blended polymer had antimicrobial properties. This was because the amino groups of the chitosan in the treatment agent easily formed a quaternary amine salt that could trap anionic bacteria and cause their cell walls to stop growing.

## CONCLUSIONS

This research focused on the synthesis of PVP/chitosan blended polymers and their application in the nylon dyeing process. On the basis of the results of these experiments, we drew several conclusions. Examining the blended polymers using FTIR and <sup>13</sup>C NMR analyses proved that hydrogen bonding was present between the PVP and chitosan. Adding PVP to chitosan was beneficial for the thermoresistance of the blended polymer. The viscosity, tensile strength, and stretching rate of the blended polymer appeared to

decrease with increasing quantities of PVP. The blended polymers did not demonstrate a color-enhancement effect on nylon dyes; they were beneficial in terms of water absorption, chlorine resistance, and colorfastness, although the softness decreased. In addition, the treated fabrics with higher chitosan ratios in the blended polymers had antimicrobial properties.

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