

Pigment Dyeing of Polyamide-Epichlorohydrin Cationized Cotton Fabrics

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ABSTRACT: A synthesized cationic reagent named polyamide-epichlorohydrin (PAE) was used to cationize cotton fabrics which were dyed with nanoscale pigments after PAE modification. The results showed that when the PAE concentration was below 7% (owf), the K/S value increased nearly linearly with increasing of PAE concentration, and excess that concentration the K/S value did not increase further. With increasing the pH value of cationization bath, the K/S value increased first and then decreased, the maximum K/S value appeared at pH 9–10. Cotton fabrics cationized at 80°C for 20 min exhibited the

best cationizing result. Both the pigment uptake and the color strength reached their own maximum values when the dye bath was neutral. When the pigment concentration was 1% (owf) the addition of 1g/L sodium chloride in the dye bath could decrease the pigment uptake while for 5% (owf) pigment concentration the uptake increased with increasing the amount of sodium chloride. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2736–2742, 2010

Key words: pigment dyeing; cotton fabrics; polyamide-epichlorohydrin (PAE); cationization

INTRODUCTION

In dye bath, cotton fibers are usually negatively charged, so there is some electrostatic repulsion between cotton fibers and anionic dye molecules or pigment particles, which results in low dye uptakes. Cationic modification can make cotton fibers positively charged and improve dyeing properties with anionic dyes and pigments.

The earlier cationic modifiers were fixatives used in after-treatment of textiles dyed with direct dyes.^{1,2} Recent years many researchers used nitrogenous compounds of tertiary amines or quaternary ammonium to modify cotton fibers. Hauser and Kanik examined the acid dye printing properties of cotton cationized with 2,3-epoxypropyltrimethyl ammonium chloride.³ This cationic reagent is also used for increasing reactive dye uptakes and reducing the amount of waste water produced in dyeing and printing process.^{4–7} Cotton cationized can also be dyed with direct dyes.^{8,9} Cotton pretreated with polyepichlorohydrindimethylamine (PECH-amine) exhibited significant higher color yields and good washing fastness, but poorer rubbing fastness.^{10–12} Pretreatment of cotton with reac-

tive cationic reagents containing phenylmonochlorotriazinyl and epoxypropyl groups and, dyeing procedures with acid dyes were investigated in detail by El-Shishtawy et al.¹³

As described above, colorants used for dyeing of cationized cotton were usually anionic dyes such as acid dyes, reactive dyes, and direct dyes. Compared with anion dyes, pigments exhibit very different dyeing effects on cationized cotton fabrics. In our previous work, pigment dyeing properties of cationized cotton were investigated using a polymeric quaternary ammonium salt containing reactive groups, KZ-76.¹⁴ Zheng cationized cotton with N-(3-chloro-2-hydroxyl propyl) trimethyl ammonium chloride and dyed the cotton by exhaust method with pigment.¹⁵

Colorant adsorption on different kinds of fibers is varied according to the colorants used, which can be analyzed by measuring the zeta potentials of fiber/dye interface. In works done by Espinosa-Jimenez et al. surface free energy and zeta potential of the adsorption process of colloidal dye Disperse Blue 3 onto polyester fabric were measured after the fabric was pretreated with *N*-cetylpyridinium chloride.^{16,17} According to Yeung and Shang's research, the action of Ca²⁺ or Mg²⁺ on silk dyeing with reactive dyes was influenced by the electrokinetic properties of silk.¹⁸ In alkaline conditions, the negative zeta potential of silk results in a strong barrier for dye anions. Addition of Ca²⁺ or Mg²⁺ could decrease the zeta

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potential of silk fiber and, accelerated the adsorption of anionic dyes.

On the basis of our previous work, a novel cationic reagent PAE (polyamide-epichlorohydrin) was synthesized. This study explored the modification of cotton fabric with PAE and its exhaust dyeing properties with nanoscale pigment. Effects of pretreatment variables, such as the amount of cationic reagent, pH value, treatment temperature, and time, on color strengths and pigment uptake were investigated. The effect of zeta potentials on color strengths and pigment uptakes was also analyzed.

EXPERIMENTAL

Materials

The fabric used was plain knitted 100% cotton, scoured and bleached (32 tex and 120 g/m²) before use. The binder was an emulsion of polyacrylate, obtained from Daxiang Chemical, Shanghai, China. Other chemicals, such as sodium hydroxide, acetic acid, and sodium chloride were laboratory grade.

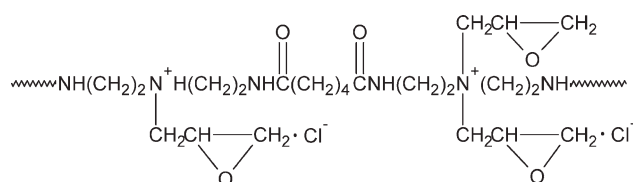
The cationic reagent PAE (polyamide-epichlorohydrin synthesized in our laboratory) was a faint yellow aqueous solution, with viscosity about 18.7 mPa·s. Its structure was shown in scheme 1.

Preparation of nanoscale pigment

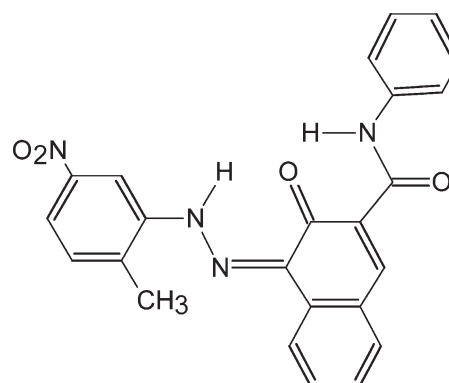
As a conventional pigment, C.I. Pigment Red 22 (illustrated in Scheme 2) used to prepare nanoscale pigment dispersion in this work. Pigment Red 22 powder was mixed with an aqueous solution of anionic polymeric dispersant XG-1(3% on weight of pigment) under stirring in an IKA high-speed mixer (IKA works Guangzhou, China) for 30 min at 10,000 rpm. Then the dispersion was converted to an M-110EHI microfluidiser (Microfluidics Int.) working at a pressure of 22,000 Pa for 2.5 h. The produced pigment dispersion had an average particle size of 128 nm and 20% solid content.

Cotton cationization

Weighted cotton fabric was immersed in an aqueous solution of cationic reagent PAE at a liquor ratio of 30 : 1. The solution pH was adjusted to 11 using 10%



Scheme 1 Schematic structure of the cationic reagent PAE.



Scheme 2 Molecular structure of C.I. Pigment Red 22.

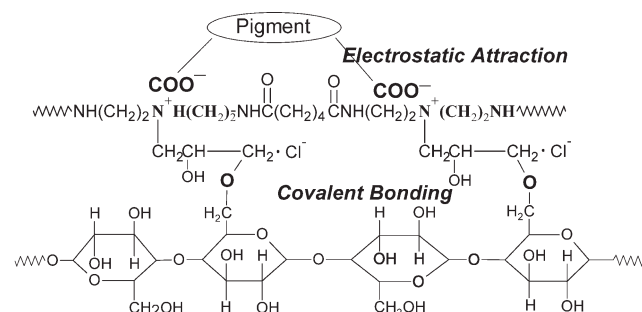
(w/w) aqueous sodium hydroxide. Then bath temperature was raised to 80°C within 10 min and kept at this temperature for 30 min. Finally, the treated fabric was taken out from the bath and rinsed thoroughly with tap water and dried in an oven at 95°C.

Dyeing procedure

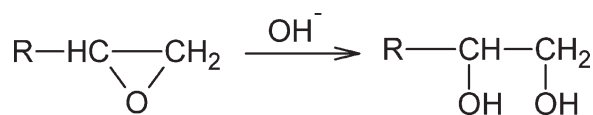
The cationized cotton was dyed with the nanoscale pigment dispersion by exhaust process using a shaker provided with heater and temperature control. The dye bath was consisted of nanoscale pigment dispersion, water, and other auxiliaries at a liquor ratio of 30 : 1. The dyeing process was first carried out at room temperature for 10 min and then heated to 70–80°C within 10 min. After 20 min treatment at this temperature the binder was slowly added into the dye bath and treated for a further 10 min. Finally, the dyed fabric was removed from the bath and washed in a bath containing 2g/L sodium carbonate and 2g/L nonionic detergent for 20 min at 60°C with a liquor ratio of 50 : 1 and then rinsed and dried. The interaction between pigment particles and cationized cotton was shown in Scheme 3.

Testing and measurement

The average particle sizes and Zeta potentials of nanoscale pigment dispersions were measured with a Nano-ZS 90 analyser (Malvern Instruments, England).



Scheme 3 Schematic diagram of cotton-PAE-pigment interaction.



Scheme 5 Reaction between free hydroxyl in water and PAE.

were produced and reacted with the hydroxyl groups of cotton fibers and, resulted in more positively charged centers on cotton fibers (see Scheme 4). When the pH value was higher than 9–10 some of the epoxy groups reacted with hydroxyl ions to form hydrolysis products (see Scheme 5), which caused the number of cationic groups grafted onto fibers to be reduced.

Pretreatment temperature and time

To investigate the influence of cationizing temperature and time on color strengths of cotton fabrics, cotton fabrics were pretreated at different temperature and time and dyed with pigments and then measured the color strengths (shown in Fig. 3). From Figure 3 we know that the epoxy groups of PAE molecules could quickly react with the hydroxyl groups of cellulose molecules under alkaline condition. After 20 min's treatment the K/S value nearly reached to the maximum value. It can be seen also that the K/S value was 9.28 at 70°C, 10.12 at 80°C, and 9.62 at 90°C after 20 min's treatment. These data indicated that the treatment temperature can affect the cationic modification and result in different color strengths of dyed fabrics. It might be explained that high temperature increased the reaction speed of PAE epoxy groups with

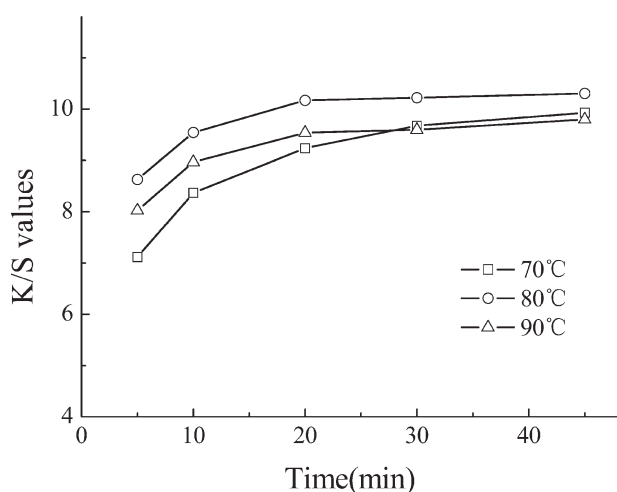


Figure 3 Effects of temperature and time on K/S values. The cotton fabrics were modified with 7% (owf) PAE at pH 9–10 and dyed with 3% (owf) pigment dispersion.

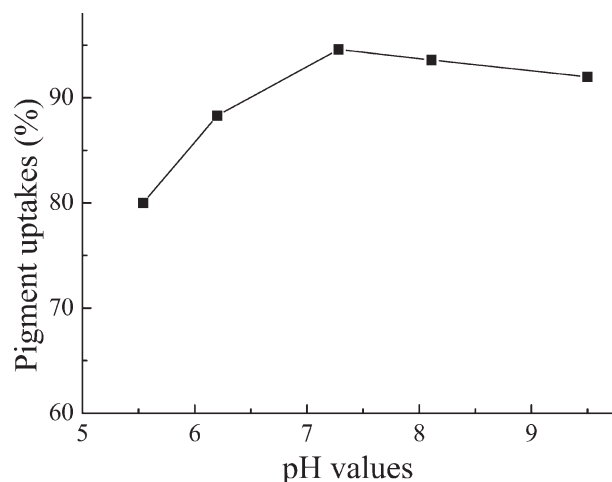


Figure 4 Effect of dye bath pH on pigment uptakes. The cotton fabrics were cationized with 5% PAE (owf) at 80°C for 30 min and dyed with 1% (owf) pigment dispersion at 80°C for 15 min.

hydroxyl groups of cotton fibers. But too high temperature resulted in more epoxy groups to be hydrolyzed and reduced the number of positively charged groups grafted onto cotton fibers.

Dyeing of cationized cotton fabrics

Ph value of dye bath

Zeta potentials of pigment particles and the number of cationic groups of modified cotton fibers are closely related to the dye bath pH value. Figures 4 and 5 showed that both pigment uptakes and K/S values reached their own maximum values when the dye bath was neutral (pH = 7.28). In acidic or alkaline condition pigment uptakes and K/S values were decreased.

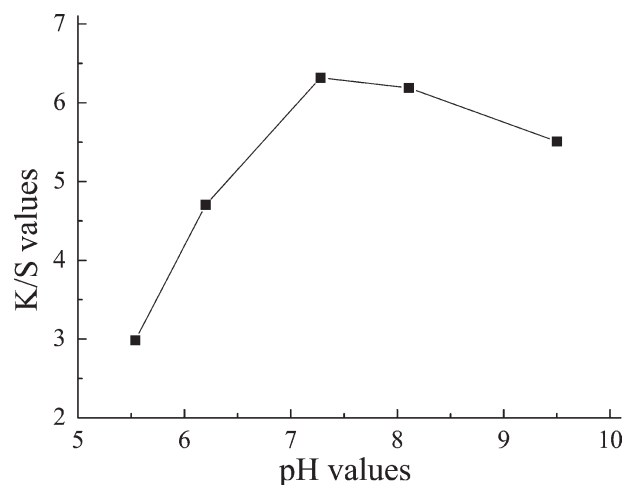


Figure 5 Effect of dye bath pH on K/S values. The cotton fabrics were modified with 7% PAE (owf) at 80°C for 30 min and dyed with 1% (owf) pigment dispersion 80°C for 15 min.

TABLE I
Zeta Potentials of Pigment Particles at Different Dye Bath pH

pH values	4.52	7.28	11.53
Zeta potentials (mV)	-23.6	-46.5	-37.3

The Zeta potentials of pigment particles largely depend on the dye bath pH value as shown in Table I. When the dye bath was acidic, fewer carboxyl groups were ionized, which resulted in a small Zeta potential absolute value. With the increase of pH value much more carboxyl groups were ionized, which caused the increase of Zeta potential absolute value. When the pH value increased to 7.28 the Zeta potential absolute value increased to 46.5 mV. Too much higher pH value (such as 11.53) led to a relatively small Zeta potential absolute value (37.3 mV), which is due to that more polymer dispersants absorbed on the surface of pigment particle were dissolved into the dye bath solution and reduced the number of ionized carboxyl groups on the surface. On the other hand, more Na^+ would compress the electrically charged double layer and also resulted in a lower Zeta potential.¹⁹

Because pigment dyeing of cationized cotton fabrics relies on the static attraction forces between anionic pigment particles and cationic cotton fibers, the pigment uptake and the K/S value exhibited similar trends with the Zeta potential as the dye bath pH value changing. The pigment uptakes and K/S values reached the maximum at pH value about 7.

Effect of NaCl addition

Figure 6 reveals that NaCl addition affects the dyeing rate of cationized cotton fabrics with pigments.

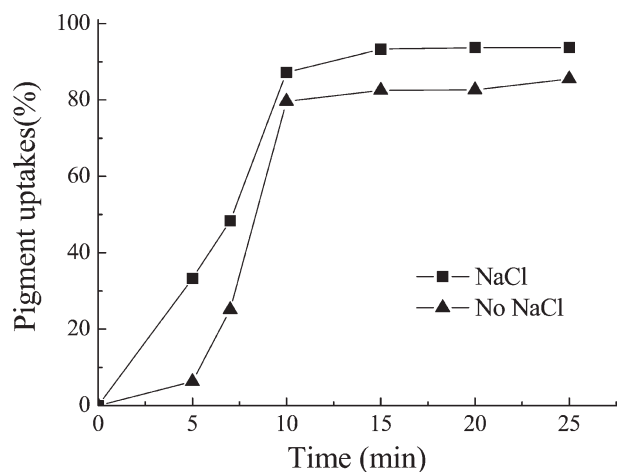


Figure 6 Effect of NaCl (1 g/L) on pigment uptakes. The cotton fabrics were modified with 7% PAE (owf) at 80°C for 30 min and dyed with 1% (owf) pigment dispersion 80°C for 15 min.

When the pigment concentration was 1% (owf) the addition of 1 g/L sodium chloride in the dye bath could decrease the pigment uptakes compared with those no sodium chloride added. It can be seen from Figure 6 that the pigment uptake increased with increasing dyeing time. Especially, within 15 min the pigment uptake increased to 93.3% for the dye bath containing no salt and 82.5% for the dye bath containing salt, respectively. That indicated that the dyeing of pigment onto cationic cotton fabrics was very fast. After 15 min's dyeing the pigment uptake increased very slowly and almost kept unchanged.

When the pigment concentration in dye bath was 5% (owf) the pigment uptake increased with increasing the amount of sodium chloride as shown in Figure 7. In contrast, the pigment uptake decreased with increasing the amount of sodium chloride in dye bath when the pigment concentration was 1% (owf).

The reason was that chlorine ions move faster than pigment particles because the former has smaller volumes than the latter. So the chlorine ions first reached the dyeing positions positively charged on cotton fibers and occupied them, which reduced the number of dyeing positions. When the pigment concentration was low, there was not enough concentration gradient to promote dyeing process and, some of the pigment particles remained in the dye bath and could not dye onto the fibers. At high pigment concentrations pigment particles could partly replace the chlorine ions adsorbed onto cationic fibers and dyed on the fibers due to large concentration gradient present at the interface of dye bath and fibers. Besides that, high sodium chloride concentration could compress the negatively charged double layer of pigment particle surface and reduce the Zeta potential and release more positively charged

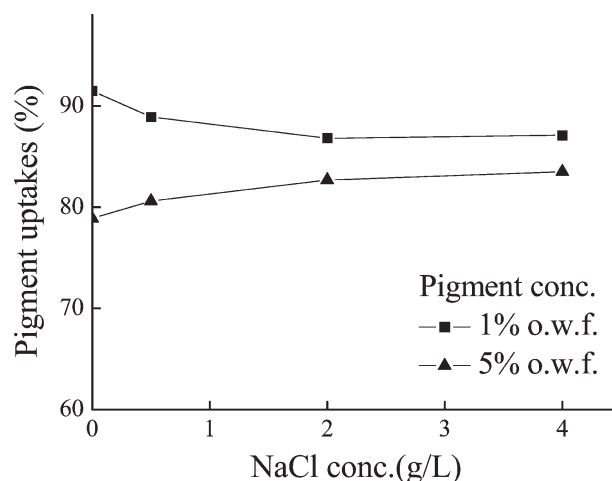


Figure 7 Effect of NaCl concentrations on pigment uptakes. The fabrics were dyed at pH 7 and 80°C for 15 min.

centers for pigments to dye. Therefore, the pigment uptake increased with increasing sodium chloride concentration.

Color fastness

Table II summarized the color fastness of fabrics treated with different cationic reagent concentrations. It shown from Table II that the rubbing and washing fastness of cotton fabrics dyed with pigment dispersion were acceptable for some specialty textiles such as wash-down effect garments. The slightly higher rubbing and washing fastness of fabrics untreated was due to the very low uptakes of pigment. The rubbing and washing fastness properties of fabrics treated with 9% (o. w. f.) PAE were slightly lower than those of fabrics treated with 7% (o. w. f.).

In the later stage of dyeing process, binder was added into dye bath. Color fastness and K/S value were affected by the amount of binder, shown in Table III. With the amount of binder increasing, both rubbing and washing fastness were improved, but K/S values decreased slightly. There was no affinity between fiber and pigment, color fastness of pigment dyed samples depended on binder's properties and its formed film. During drying process, the disperse solids in binder (mainly polymers) coalesce under simultaneous deformation into a film surrounding the pigments. As the formed film was more even with amount of binder increasing, rubbing, and washing fastness were improved. While K/S value decreased slightly, the binder film could affect absorbing and scattering properties of pigment particles. There was some color fastness with no binder addition; this was because there were some interaction force between cationized cotton and negatively charged pigment particles. It was seen from Table III, the washing fastness of pigment dyeing was better; rubbing fastness was worse especially

TABLE II
Color Fastness of Cotton Fabrics Treated with Different Cationic Reagent Concentrations^a

PAE (o.w.f.%)	Pigment uptake (%)	Rubbing fastness		Washing fastness	
		Dry	Wet	Change	Staining ^b
0	8.60	4	3	4	4
1	78.6	3-4	2-3	4	3-4
3	83.7	3-4	2	3-4	4
5	90.3	4	3-4	4	4
7	91.1	4	3	4	4
9	77.9	3-4	2-3	3-4	3-4

^a 0.5% (owf) pigment was used in the dyeing process, and pH was kept at 11 in the pretreatment process.

^b The staining fastness was tested by using a standard cotton fabric as adjacent fabric.

TABLE III
Effect of Binder on Color Fastness of Dyed Fabrics^a

Binder (g/L)	K/S value	Rubbing fastness		Washing fastness	
		Dry	Wet	Staining	Change
0	6.7575	3	1	3-4	2-3
5	6.6635	3	1-2	4	3
10	6.5880	3-4	2	4-5	3-4
15	5.6154	4	2	4-5	3-4
20	5.5778	4	2-3	5	4

^a The amount of pigment dispersion was 1% (owf).

deep shade samples, and generally wet rubbing fastness was lower than grade 3. However, we can take advantage of the shortcoming of pigment dyeing, lower fastness, to produce wash-down effect garments, colorful jeans.

CONCLUSION

By measuring K/S values we investigated the influence of cationizing conditions, such as PAE concentration, temperature and time, and pH value on the color strengths of the modified cotton fabrics dyed with pigments. The results show that when the PAE concentration was below 7% (owf), the K/S value increased nearly linearly with increasing of PAE concentration and, when the PAE concentration reached 7% (owf) the K/S value did not increase further. With increasing the pH value of cationization bath the K/S value increased first and then decreased, the maximum K/S value appeared at pH 9-10. Cotton fabrics cationized at 80°C for 20 min exhibited the best cationizing result.

Dye bath pH values and NaCl addition could influence the pigment uptakes and color strengths of dyed fabrics also. Both pigment uptakes and color strengths reached their own maximum values when the dye bath was neutral. In acidic or alkaline condition pigment uptakes and color strengths were decreased. When the pigment concentration was 1% (owf) the addition of 1g/L sodium chloride in the dye bath could decrease the pigment uptakes compared with those no sodium chloride added in the dye bath. When the pigment concentration was 5% (owf) the pigment uptake increased with increasing the amount of sodium chloride although it decreased when the pigment concentration was 1% (owf). The rubbing and washing fastness of cotton fabrics dyed with pigment dispersion were lower but acceptable for some specialty textiles such as wash-down effect garments.

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References

1. Burkinshaw, S. M.; Gotsopoulos, A. *Dyes Pigments* 1996, 32, 209.
2. Burkinshaw, S. M.; Gotsopoulos, A. *Dyes Pigments* 1999, 42, 179.
3. Hauser, P. J.; Kanik, M. *AATCC Rev* 2003, 3, 25.
4. Cannon, K. M.; Hauser, P. J. *AATCC Rev* 2003, 3, 21.
5. Kanik, M.; Hauser, P. J.; Parrillo, L.; Donaldson, A. *AATCC Rev* 2004, 4, 22.
6. Hauser, P. J.; Tabb, A. H. *AATCC Rev* 2002, 2, 36.
7. Kanik, M.; Hauser, P. J. *Color Technol* 2003, 119, 230.
8. Kanik, M.; Hauser, P. J. *Text Res J* 2004, 74, 43.
9. Draper, S. L.; Beck, K. R.; Smith, C. B.; Hauser, P. J. *AATCC Rev* 2002, 2, 24.
10. Chen, W. G.; Zhao, S. C.; Wang, X. G. *Text Res J* 2004, 74, 68.
11. Rong, L.; Feng, G. *J Appl Polym Sci* 2006, 100, 3302.
12. Yu, Y.; Chen, S. *J Dong Hua University (Eng Ed)* 2001, 18, 63.
13. El-Shishtawy, R. M.; Youssef, Y. A.; Ahmed, N. S. E.; Mousa, A. A. *Color Technol* 2004, 120, 195.
14. Fang, K. J.; Wang, C. X.; Zhang, X.; Xu, Y. *Color Technol* 2005, 121, 325.
15. Zheng, T. *Text Dye Finish J* 2006, 28, 6.
16. Espinosa-Jimenez, M.; Padilla-Weigand, R.; Ontiveros-Ortega, A.; Ramos-Tejada, M. M.; Perea-Carpio, R. *J Colloid Interface Sci* 2003, 265, 227.
17. Espinosa-Jimenez, M.; Ontiveros-Ortega, A.; Padilla-Weigand, R.; Ramos-Tejada, M. M.; Perea-Carpio, R. *Macromol Mater Eng* 2003, 288, 945.
18. Yeung, K. W.; Shang, S. M. *Proceedings of the 77th World Conference of the Textile Institute, Tampere, Finland, 1997*, p 403.
19. Fu, S. H.; Fang, K. J. *J Dispersion Sci Technol* 2006, 971, 27.