



Finishing of cotton fabrics with poly (N-vinyl-2-pyrrolidone) to improve their performance and antibacterial properties

H.M. Fahmy*, M.H. Abo-Shosha, N.A. Ibrahim

Textile Research Division, National Research Center, Dokki, Cairo, Egypt

ARTICLE INFO

Article history:

Received 18 January 2009

Received in revised form 18 February 2009

Accepted 2 March 2009

Available online 11 March 2009

Keywords:

Poly (N-vinyl-2-pyrrolidone)

Crosslinking

Cotton fabrics

Easy-care finishing

Iodine solution

Antibacterial activity

ABSTRACT

Cotton fabric was thermally crosslinked with poly (N-vinyl-2-pyrrolidone) (PVP) at different conditions including temperature, time, PVP concentrations and molecular weights. Results indicated that treating the cotton fabrics with 4% aqueous solution of PVP of molecular weight 10,000 Dalton followed by drying at 85 °C for 5 min then curing at 160 °C for 3 min results in crosslinking as well as an improvement in some performance properties of that fabrics such as resiliency, tensile strength, and acid dyeability. Post-treating PVP crosslinked fabric with 5% iodine in ethanol solution for 5 h at 50 °C imparts antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*. Moreover, incorporation of PVP in the easy-care finishing of cotton fabrics, as polymer additive, with N,N-dimethylol 4,5-dihydroxyethylene urea as a crosslinker enhances some of the performance properties of finished fabrics such as the nitrogen content, tensile strength and acid dyeability along with decreasing resiliency as well as whiteness index, whereas the ester crosslinking with citric acid, in presence of PVP, enhances resilience, tensile strength and whiteness indices accompanied with a reduction in the %N of the treated fabrics. Infra red spectrum of PVP crosslinked fabric as well as EDX analysis of loaded iodine on PVP crosslinked cotton fabric were investigated.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Easy-care finished cotton fabrics with N-methylol reagents are formaldehyde release which is a possible human carcinogen. Extensive efforts have been made to replace the traditional formaldehyde-based reagents, such as zero formaldehyde-based reactants, the commercial addition product of 1,3-dimethylurea and glyoxal as well as inorganic phosphates (Bajaj, 2002; Frick, 1985). Polycarboxylic acids such as citric acid are believed to crosslink cotton by reaction with cellulose hydroxyl groups through an anhydride intermediate mechanism (Welch & Andrews, 1994). The major disadvantages of using polycarboxylic acids as crosslinking agents for cotton fabrics are the dramatic loss in tensile strength (Fahmy, Samaha, Abo-Shosha, & Ibrahim, 2004) and the yellowing of the cured cotton fabrics (Welch & Peters, 1999). Some attempts were done to overcome these disadvantages such as the addition of tartaric acid, methyl hydrogen silicon and polyethylene glycols to the finishing baths containing citric acid (Welch & Peters, 1999; Ibrahim, Abo-Shosha, El-Nagdy, & Gaffar, 2002).

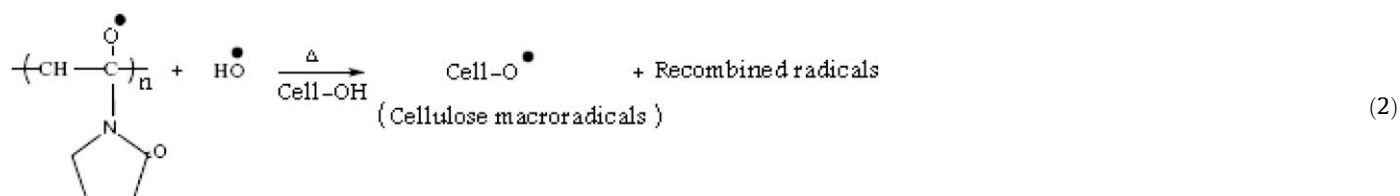
On the other hand, textiles goods, especially those made from natural fibers provide an excellent environment for microorganisms to grow, because of their large surface area and ability to retain moisture (Bajaj, 2002; Ibrahim et al., 2002). There is a large

variety of antimicrobial chemicals, whose functional efficiencies depend on the type of biological attack as well as the method of application to the textile substrate. Those chemicals include inorganic salts, organometallics, iodophors (iodine slowly releasing chemicals), phenols and thiophenols, onium salts, antibiotics, heterocyclics with anionic groups, nitro compounds, ureas and related compounds, formaldehyde derivatives, and amines (Ibrahim et al., 2002). The antimicrobial agents can be applied to textiles by many methods such as insolubilization of such agents in and/or on the fiber, graft polymerization onto the fiber, treatment of the fiber with resins or crosslinking agents, chemical modification of fibers, coating of the fiber surface, and microencapsulation of a chemical agent with the fiber in a matrix (Bajaj, 2002).

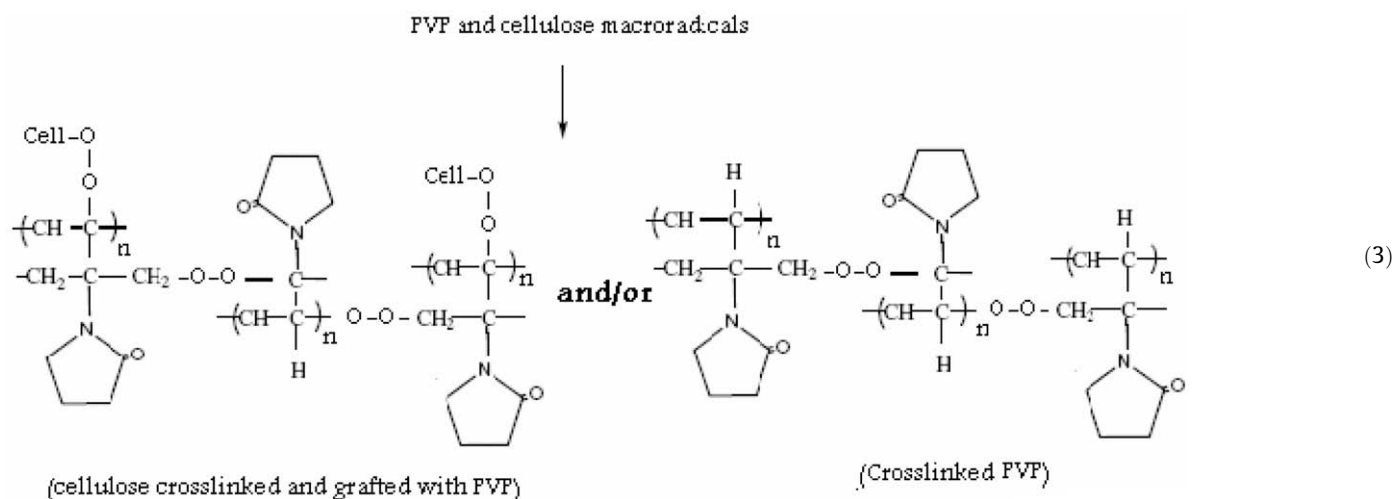
PVP is a synthetic, nontoxic, water-soluble polymer commonly used in a wide range of applications including several pharmaceutical applications. A disadvantage of PVP is the lack of a reactive group which limits its chemical modification. PVP polymers are film formers, protective colloid and suspending agents, dye-receptive agents, binders, stabilizers, detoxicants, and complexing agents (Barabas, 1990). PVP can be crosslinked by heating in air at 150 °C (Blecher, Lorenz, Lowd, Wood, & Wyman, 1980), radiation (Chapiro & Legris, 1986) and potassium persulfate (Can, Kirci, Kavlak, & Uner, 2003). The mechanism of crosslinking of PVP chains by heating has not been definitely explained until now (Can et al., 2003; Diaz, Valenciano, & Katime, 2004). Moreover, PVP form complex with iodine (PVP-I) which is a bactericide with various attractive merits, such

* Corresponding author.

E-mail address: aikal34@yahoo.com (H.M. Fahmy).



(3) Formation of crosslinked grafted cellulose and/or crosslinked PVP:



Factors affecting crosslinking of cotton fabrics with PVP were studied. Results obtained along with appropriate discussion follows.

3.1. Factors affecting crosslinking of cotton fabrics with PVP

3.1.1. Effect of curing temperature

Table 1 shows the effect of curing temperature on some performance properties of cotton fabrics treated with 2% PVP aqueous solution. It is clear, under the conditions studied, that curing the treated sample at 120 °C results in a little increase in both of the %N and TS, reasonable improvement in WRA and K/S as well as a reduction in the WI. This may be ascribed to the favorable effect of the temperature in presence of the air oxygen to form PVP macroradicals (Cen, Neoh, & Kang, 2004) giving rise to the formation of crosslinked and grafted cellulose chains with PVP as well as formation of PVP crosslinked film that deposits on the fabric. Increasing curing temperature to 160 °C is accompanied by a slight increase in %N, a little increase in both of WRA and K/S and a slight decrease in TS as well as WI. Raising the curing temperature beyond 160 °C and up to 180 °C results in marginal reduction in all the aforementioned properties suggesting that higher temperatures may result in termination of radicals and/or the further oxidation of PVP macroradicals giving rise to water-soluble ingredients that can be swept away by washing.

Table 1
Effect of curing temperature on some performance properties of treated cotton fabrics.

Temp. (°C)	%N	WRA (W + F) ^o	TS (Kg)	K/S	WI
Untreated	–	110	57	0.51	81
120	0.14	131	59	1.31	75
140	0.16	140	58	1.33	72
160	0.19	144	56	1.36	70
180	0.15	141	53	1.29	69

PVP molecular weight, 40,000 Dalton; [PVP], 2%; wet pick up, 80%; drying at 85 °C/5 min; curing for 3 min.

3.1.2. Effect of curing time

Table 2 shows the effect of curing time on some performance properties of cotton fabrics treated with 2% PVP aqueous solution. It can be seen, under the conditions employed, that curing the treated fabrics for 3 min is accompanied by increasing the %N, WRA and K/S along with a decrease in TS and WI. This may be associated with increasing of the extent of crosslinking as well as fixation of PVP onto the fabric structure. Further increase in time up to 9 min has marginal effect on the fabric properties.

3.1.3. Effect of PVP concentration

The effect of PVP concentration on performance properties of finished cotton fabrics is shown in Table 3. It is obvious that increasing the PVP concentration up to 6% brings about an enhancement in the extent of %N, WRA, TS, FR as well as K/S accompanied with a reduction in both W and WI. This may be a direct consequence of the further fixation of PVP onto the fabric structure. Beyond 6%, within the range studied, the results indicated a reduction in all the aforementioned properties accompanied with an improvement in the W, WI and FR. This can be attributed to the reduction in the PVP fixed onto the fabric structure as a result of

Table 2
Effect of curing time on some performance properties of treated cotton fabrics.

Time (min)	%N	WRA (W + F) ^o	TS (Kg)	K/S	WI
Untreated	–	110	57	0.51	81
3	0.1878	144	56	1.36	71
5	0.1889	146	55	1.43	71
7	0.1893	148	53	1.51	70
9	0.1894	149	52	1.55	69

PVP molecular weight, 40,000 Dalton; [PVP], 2%; wet pick up, 80%; drying at 85 °C/5 min; curing temperature, 160 °C.

Table 3

Effect of PVP concentration on some performance properties of treated cotton fabrics.

[PVP] (%)	%N	WRA (W + F) ^o	TS (Kg)	K/S	WI	FR (mg cm)	W (s)
Untreated	–	110	57	0.51	81	93	2.5
2	0.1878	144	56	1.36	71	93	2.6
4	0.2131	150	58	1.66	69	94	2.8
6	0.2229	152	59	1.71	68	95	2.9
8	0.2061	143	57	1.44	70	94	2.7

Wet pick up, 80%; PVP molecular weight, 40,000 Dalton; drying at 85 °C/5 min; curing at 160 °C/3 min.

Table 4

Effect of PVP molecular weight on some performance properties of treated cotton fabrics.

PVP <i>M_w</i> (Dalton)	%N	WRA (W + F) ^o	TS (Kg)	K/S	WI	FR (mg cm)	W (s)
Untreated	–	110	57	0.51	81	93	2.5
10,000	0.3745	173	60	1.98	67	98	3.4
20,000	0.2521	161	59	1.84	68	95	3.1
40,000	0.2131	150	57	1.66	72	93	2.8

Wet pick up, 80%; [PVP], 4%; drying at 85 °C/5 min; curing at 160 °C/3 min.

Table 5

The antibacterial activity of cotton fabrics crosslinked with different concentrations of PVP and post-treated with iodine solution.

PVP (%)	Log reduction of SA and EC at different contact time			
	5 min		15 min	
	EC	SA	EC	SA
2	2	2	5	5
4	4	5	6	6
6	5	5	6	6

Wet pick up, 80%; PVP molecular weight, 10,000; drying at 85 °C/5 min; curing at 160 °C/3 min. The SA or EC concentration is 10⁶ CFU/ml; log reduction of 6 means a complete kill.**Table 6**

Performance properties of cotton fabrics finished with different concentrations of DMDHEU in presence of PVP.

DMDHEU (g/l)	PVP (%)	%N	WRA (W + F) ^o	TS (Kg)	K/S	WI
Blank	–	–	110	57	0.51	81
Control-1	4	0.3745	173	60	1.98	67
50	–	0.2501	201	44.1	1.18	69
50	4	0.6032	192	56	1.96	65
100	–	0.5899	225	39.3	1.40	68
100	4	0.9127	217	53	2.31	64

Wet pick up, 80%; [PVP], 4%; PVP molecular weight, 10,000; [NH₄Cl], 0.1 (based on DMDHEU concentration); pH, 5 (acetic acid); drying at 85 °C/5 min; curing at 160 °C/3 min. Control-1, samples treated only with 4% PVP.

a formation of non-bound crosslinked PVP film on the surface of the fabric which can be easily removed by washing leaving the remaining polymer fixed inside the fabric structure in state of entanglement and crosslinking.

3.1.4. Effect of PVP molecular weight

Table 4 shows the effect of PVP molecular weight on some performance properties of finished cotton fabrics. Table 4 reveals that increasing the PVP molecular weight from 1000 to 40,000 Dalton has a negative impact on the %N, WRA, TS, FR as well as K/S accompanied with a slight improving in WI and W. Increasing the PVP molecular weight consequently increases the finishing bath viscosity which in turn reduces the extent of the PVP penetration into the fabric structure along with formation of PVP crosslinked thin film not tightly bound to the fabrics structures and hence can be easily removed by washing.

3.2. Antibacterial activity of PVP crosslinked cotton fabrics

Table 5 shows the antibacterial activity of cotton fabrics crosslinked with different concentrations of PVP of molecular weight 10,000 Dalton and post-treated with iodine solution. It is clear, irrespective of PVP concentration, that treating with iodine solution imparts the fabrics excellent antibacterial activities against SA and EC as indicated from the reduction in the number of viable cells of both microorganisms within the first 5 min. This can be attributed to the formation of PVP-I complex along the fabrics structures (Xing et al., 2005). Moreover, increasing the concentration of PVP, within the ranges studied, slightly enhances the antibacterial activities as a result of increasing the fixed PVP onto the fabrics structures and formation of more PVP-I complexes.

3.3. Inclusion of PVP in easy-care finishing with DMDHEU

PVP of molecular weight 10,000 was incorporated as a polymer additive in the easy-care finishing formulations. The performance properties of cotton fabrics finished with different concentrations of DMDHEU in presence of 4% PVP are shown in Table 6. It is clear that increasing DMDHEU concentration from 0 to 100 g/l, in absence of PVP, is accompanied by an enhancement in %N, K/S and WRA of the finished fabrics along with a reduction in TS and WI. This could be associated with increasing the extent of crosslinking and the subsequent increasing in the molecular degradation of cellulose structure accompanied with fixation the PVP onto of the finished fabrics matrices

Table 7

Performance properties of cotton finished with different concentrations of CA fabrics in presence of PVP.

CA (%)	PVP (%)	%N	WRA (W + F) ^o	TS (Kg)	WI
Blank	–	–	110	57	81
Control	4	0.3745	173	60	67
4	–	–	141	44	78
4	4	0.2523	162	50	78
6	–	–	152	42	76
6	4	0.1668	178	48	77
8	–	–	167	38	74
8	4	0.1032	206	42	74

Wet pick up, 80%; PVP molecular weight, 10,000; CA/SHP molar ratio, 1; drying at 85 °C/5 min; curing at 180 °C/90 s. Control, samples treated only with 4% PVP.

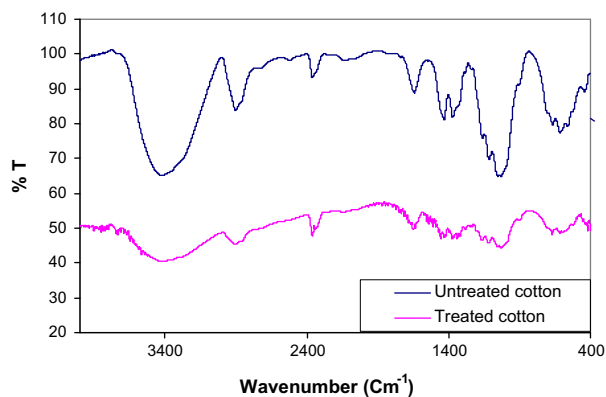


Fig. 1. FTIR spectrum of the untreated and thermally treated cotton fabric with 4% PVP aqueous solution.

(Ibrahim, Bayazeed, Refai, & Hebeish, 1986; Fahmy, 1994). Moreover, incorporation the PVP in the finishing bath enhances the %N, TS and *K/S* along with decreasing the WRA as well as WI of the treated fabrics. This can be associated with the accompanying increase in the finishing bath viscosity, which hinders the diffusion of DMDHEU inside the fabric structure as well as deposition of PVP on the fabric surface (Ibrahim et al., 1986; Fahmy, 1994).

3.4. Inclusion of PVP in easy-care finishing with citric acid

Table 7 shows the performance properties of cotton fabrics finished with different concentrations of CA alone or in presence of PVP. It is clear that: (1) finishing of cotton samples with citric acid (4–8%), in absence of PVP, results in an enhancement in WRA of treated samples along with a reduction in both the TS and WI which can be attributed to esterification of the hydroxyl groups of cotton fabrics with the carboxyl groups of the citric acid via an anhydride intermediate mechanism as well as the formation of unsaturated acids bound to the surface of the finished fabrics (Welch & Peters, 1999; Ibrahim et al., 2002) and (2) inclusion of PVP in the CA finishing bathes brings about an increasing in the WRA, TS and WI accompanied with a reduction in the %N which could be related to the decrease in the extent of ester crosslinking of the cellulosic hydroxyl groups via increasing the viscosity of the finishing bath thereby hindering the diffusion and penetration of finishing agent within the fabric and hence altering the values of the aforementioned properties (Ibrahim et al., 1986; Fahmy, 1994). On the other hand, the WRA of the finished fabrics increases with increasing CA concentration to reach maximum at concentrations of 8% of CA, in presence of 4% of PVP, which can be explained in the light of additional crosslinking due to ionic bonds between the single ended carboxyl groups and the weakly cationic pyridyle groups of PVP (Blecher et al., 1980).

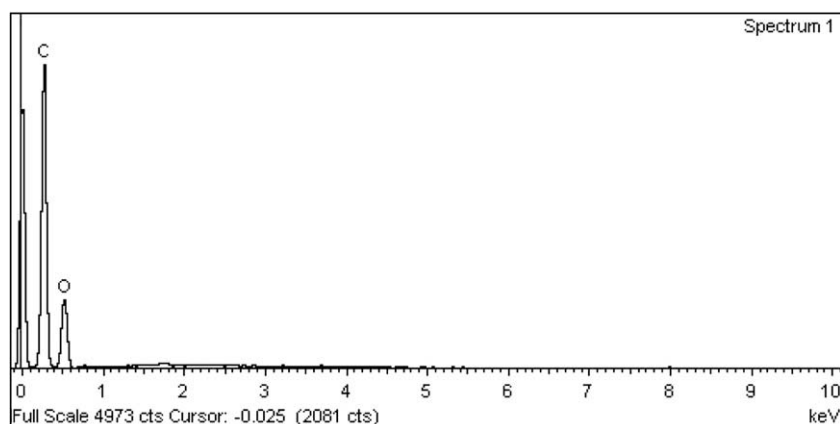


Fig. 2. EDX analysis of untreated cotton fabric.

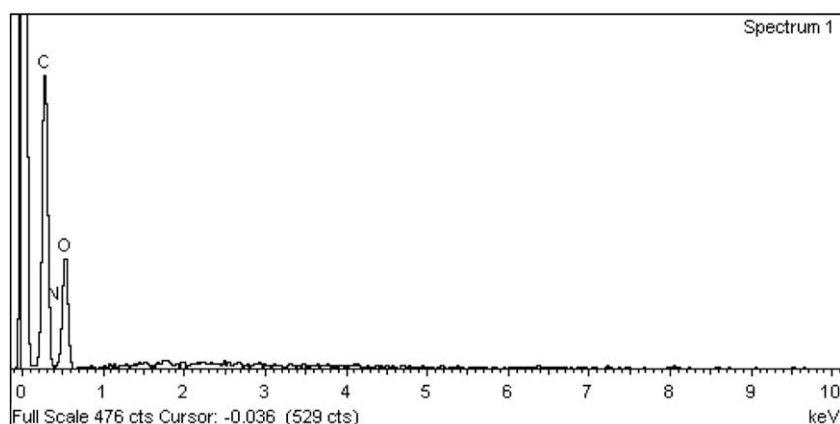


Fig. 3. EDX analysis of PVP crosslinked cotton fabric.

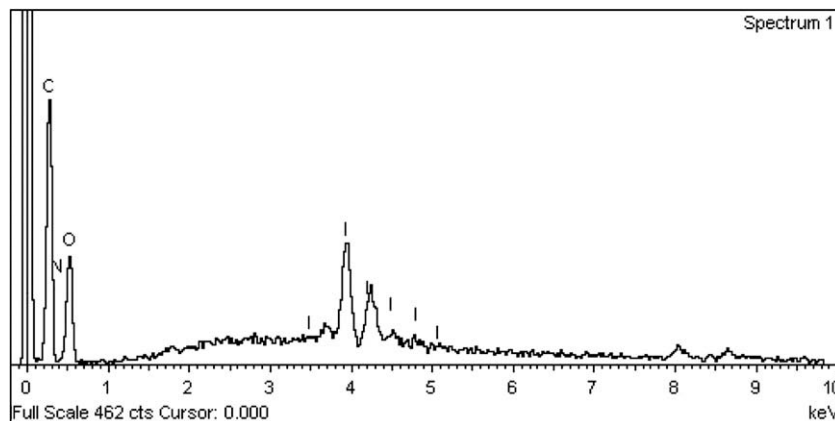


Fig. 4. EDX analysis of iodine post-treated PVP crosslinked cotton fabric.

Indeed, these values were repeated four times and the results were close with an error margin of $\pm 1\%$. The average of which is quoted in this paper.

3.5. Characterization of finished fabrics

The untreated and PVP crosslinked fabric are characterized by investigation their IR spectra. Moreover, the latter fabrics as well as the iodine post-treated PVP crosslinked fabric are characterized using EDX analysis. Given below their discussion.

3.5.1. IR spectra of PVP crosslinked cotton fabric

Fig. 1 shows the FTIR spectra of both the untreated and PVP crosslinked cotton fabrics. It is clear that both spectra have similar peaks such as peak at 3411 cm^{-1} which is corresponding to OH stretching band of cotton cellulose, peak at 1028 cm^{-1} which is corresponding to glycosidic linkage. On the other hand, spectrum of the crosslinked fabric includes a peak at 1286 cm^{-1} which is assigned to the vibration absorption of the C–N, a weak peak at 1644 cm^{-1} corresponding to stretching vibration of C=O group characterized for PVP and weak peaks at 1723 and 1744 cm^{-1} corresponding to C=O of carboxyl and ester groups which may be taken as proofs for opening of the pyrrolidone ring and for the latter mechanism. Moreover, the spectrum of the crosslinked fabric shows stretch bands in the range of $1000\text{--}1300\text{ cm}^{-1}$ corresponding to the C–O of the ester groups indicating the proposed mechanism.

3.5.2. EDX analysis

Figs. 2–4 show the EDX analysis of untreated, PVP crosslinked fabric and PVP crosslinked cotton fabric loaded with iodine, respectively. It is clear that in addition to the elements of carbon and oxygen detected in all samples, the nitrogen is detected in PVP crosslinked sample as a direct consequence of modifying the cellulose structure with PVP (Fig. 3), whereas the nitrogen as well as iodine were detected in the iodine post-treated crosslinked sample (Fig. 4) which may be attributed to the ability of the modified cellulose structure and/or the PVP deposit to pick up and complex iodine.

4. Conclusions

Cotton fabrics can be crosslinked, with better performance properties such as WRA, TS and K/S , by padding in 4% aqueous solution of PVP of molecular weight 10,000 Dalton followed by drying the padded fabrics at 85°C for 5 min then curing at 160°C for 3 min. Post-treating the PVP crosslinked cotton fabrics

with 5% iodine solution for 5 h at 50°C imparts antibacterial activities for such fabrics, irrespective of PVP concentration, against *S. aureus* and *E. coli*. Incorporation of PVP in the easy-care finishing of cotton fabrics with DMDHEU enhances %N, TS and K/S along with decreasing WRA DP rating as well as WI of that fabrics whereas the ester crosslinking with CA, in presence of PVP, enhances WRA, TS and WI accompanied with a reduction in the %N of the treated fabrics.

References

- Bajaj, P. (2002). Finishing of textile material. *Journal of Applied Polymer Science*, 83, 631–659.
- Barabas, E. S. (1990). N-vinyl amide polymers. In *Concise encyclopedia of polymer science and engineering* (pp. 1236–1241). New York: John Wiley.
- Blanchard, E. J., Reinhardt, R. M., & Andrews, B. A. K. (1991). Finishing with modified polycarboxylic acid systems for durable press cottons. *Textile Chemist and Colorist*, 23(5), 25.
- Blecher, L., Lorenz, D. H., Lowd, H. L., Wood, A. S., & Wyman, D. P. (1980). Polyvinylpyrrolidone. In *Handbook of water-soluble gums and resins* (pp. 21–22). New York, NY: McGraw-Hill Book Company.
- Can, H. K., Kirici, B. U., Kavlak, S., & Uner, A. G. (2003). Removal of some textile dyes from aqueous solutions by poly (N-vinyl-2-pyrrolidone) and poly (N-vinyl-2-pyrrolidone)/K2S2O8 hydrogels. *Radiation Physics and Chemistry*, 68, 811–818.
- Cen, L., Neoh, K. G., & Kang, E. T. (2004). Antibacterial activity of cloth functionalized with N-alkylated poly (4-vinylpyridine). *Journal of Biomedical Materials Research*, 71A, 70–80.
- Xing, Chang-Min, Deng, Jian-Ping, & Yang, Wan-Tai (2005). Synthesis of antibacterial polypropylene film with surface immobilized polyvinylpyrrolidone-iodine complex. *Journal of Applied Polymer Science*, 97, 2026–2031.
- Chapiro, A., & Legris, C. (1986). Gel formation in the radiolysis of poly (N-vinyl pyrrolidone). *Radiation Physics and Chemistry*, 28(2), 143–144.
- Díaz, E., Valenciano, R. B., & Katime, I. A. (2004). Study of complexes of poly (vinyl pyrrolidone) with copper and cobalt on solid state. *Journal of Applied Polymer Science*, 93, 1512–1518.
- Fahmy, H. M. (1994). Physico-mechanical characteristics of sizing agents mixtures and their applications in textile processing. MSc Thesis, Cairo: Helwan University.
- Fahmy, H. M., Samaha, S. H., Abo-Shosha, M. H., & Ibrahim, N. A. (2004). Effect of inclusion of cationized starch derivatives in finishing bath on ester-crosslinking of cotton fabric. *Tintoria*, 10, 22–29.
- Frick, J. G. (1985). Bonding in cotton fiber from formaldehyde-free crosslinks. *Journal of Applied Polymer Sciences*, 30, 3467–3477.
- Ibrahim, N. A., Bayazeed, A., Refai, R., & Hebeish, A. (1986). Some basics of easy-care cotton finishing. *American Dyestuff Reporter*, 75(5), 13–21.
- Ibrahim, N. A., Abo-Shosha, M. H., El-Nagdy, E. I., & Gaffar, M. A. (2002). Eco-friendly durable press finishing of cellulose-containing fabrics. *Journal of Applied Polymer Science*, 84, 2243.
- Vogel, A. I. (1975). Elementary practical organic chemistry. In *Quantitative organic analysis* (pp. 652). London: Longman Group LTD.
- Welch, C. M., & Andrews, B. A. K. (1994). Formaldehyde-free DP finishing with polycarboxylic acids. *American Dyestuff Reporter*, 83(9), 19–25.
- Welch, C. M., & Peters, J. G. (1999). DP finishes using citric and tartaric acid with methyl hydrogen silicone. *Textile Chemist and Colorist & American Dyestuff Reporter*, 1, 55–60.