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Argon Plasma in a New Process for Improving the Physical and Anti-bacterial Properties of Crosslinked Cotton Cellulose with Dimethyloldihydroxyethyleneurea-Maleic Acid

Abstract

This study reports the findings of an argon (Ar) plasma treatment added to the traditional pad-dry-cure process between dry and cure treatments. This new process is called the "pad-dry-plasma-cure process". The crosslinking agent was a mixture of dimethyloldihydroxyethyleneurea (DMDHEU) and maleic acid (MA). Results show that Ar plasma treatment can increase the bonded crosslinking agent (i.e., the nitrogen content). The dry crease recovery angle (DCRA), wet crease recovery angle (WCRA), and tensile strength retention (TSR) of the pad-dry-plasma-cure finished fabrics were higher than those of traditional pad-dry-cure finished fabrics at a given nitrogen content. Additionally it was found that the number of crosslinks per anhydroglucose unit (CL/AGU) and the length of crosslinks of pad-dry-plasma-cure-finished fabrics were higher than that of traditional pad-dry-cure finished fabrics at the same resin concentration in the pad bath. DCRA, WCRA and TSR values of pad-dry-plasma-cure-finished fabrics were higher than those of pad-dry-cure-finished fabrics at the same CL/AGU value. However, activation energies for the pad-dry-plasma-cure process were higher than those for the pad-dry-cure process. The anti-bacterial ability and odour absorption of the pad-dry-plasma-cure and pad-dry-plasma-cure finished fabrics were higher than those for the pad-dry-cure finished fabrics. The surface distribution of crosslinking agents for the pad-dry-plasma-cure process was higher than that of the pad-dry-cure process. Thus the pad-dry-plasma-cure process is excellent for improving the physical properties, bacterial inhibition, and odour absorption of finished cotton fabrics and for decreasing their formaldehyde release.

Key words: *cotton, plasma, antibacterial, crosslinking, crosslink length, crosslinks number per anhydroglucose, surface distribution, odour absorption.*

Introduction

Low-temperature plasma treatment has been widely used to modify the surface of metals, polymer films and fabrics [1, 2]. Previous studies [3 - 9] have shown that this plasma treatment process causes reagents deposited on the surface of materials to change the surface properties of the materials treated. Plasma treatment can increase the reactivity of fibre surfaces, thereby improving the effect of grafting polymerisation. Calvimontes et al. [10] showed that plasma exposure resulted in physical and chemical changes on cellulose surfaces. Ward and Benerito et al. [11] demonstrated that applying plasma treatment before crosslinking agent treatment (i.e., plasma treatment followed by a pad-dry-cure treatment) increases the dry wrinkle recovery angle of finished cotton fabrics [12, 13]. Zubaidi and Hirotsu et al. [14] showed that the breaking strength of finished cotton yarns can be enhanced by pre-treating the cotton yarn with plasma and then grafting the treated yarn with 2-hydroxyethyl methacrylate. Other studies have proven that the surface distribution of crosslinking agents affects the physical properties of fabrics [15, 16]. Additionally some previous studies have shown that the physical properties of finished fabrics are affected by the crosslinking structure of the crosslinking agent in and on the finished fabrics. [17 - 24] demonstrated the effects of ion implantation machine parameters, including the ion energy, dose rate, impulse energy and implantation interval, on the pollen grains of upland cotton implanted with a nitrogen ion beam. The best parameters were thus determined. However, plasma can also be used to generate free radicals on the surface intended to be modified, and can then initiate the graft polymerization of a monomer in a conventional free-radical process. Surface-initiated polymerisation can be conducted by exposing the plasma-activated substrate to monomers conveyed to the surface in either a condensed (bulk monomer or solution) or gas phase [25].

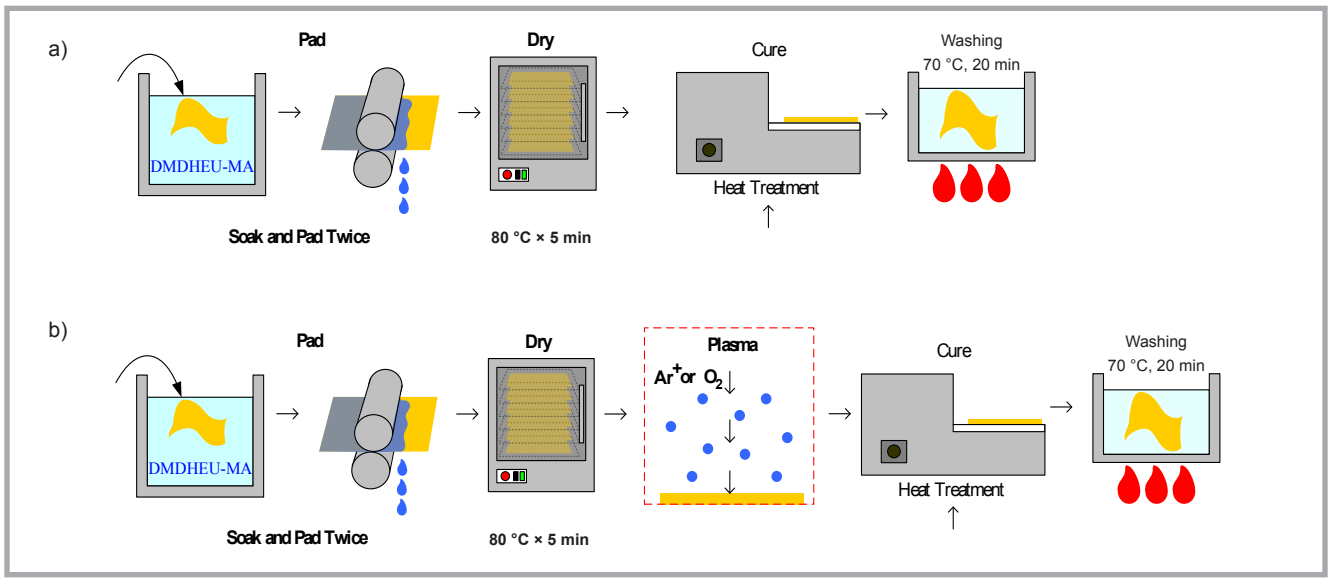

Figure 1. *a) traditional process, and b) the new process (Plasma treatment is added between the dry and cure of the traditional process).*

The influence of the activating gas on the efficiency of grafting a monomer onto a polymer surface (Ar plasma is usually the most efficient) has also been investigated [26]. Surface modification on a polytetrafluoroethylene (PTFE) panel was performed by conducting sequential nitrogen plasma treatments and surface-initiated polymerisation. By introducing COO– groups to the surface of the PTFE panel through grafting polymerisation of acrylic acid (AA), it was shown that the grafting rate is related to the treating time and the power of plasma [27]. Other applications of plasma grafting of polymeric materials have been recently reviewed [28, 29]. Even if plasma is an excellent polymer processing method, most plasma processes require a long time for the grafting and reaction. Therefore conventional plasma treatment is difficult to apply in industrial processes.

DMDHEU have long been used in the textile industry as crosslinking agents for cotton to produce wrinkle-resistant cotton fabrics and garments. It is difficult to substituted by whole other resins because of its low price and efficient improvement of the crease recovery angle (wrinkle-resistant), even though the formaldehyde release from DMDHEU during the traditional process might to induce a skin allergy in the user. In this study, the new plasma process could overcome the shortcomings of the conventional plasma process, namely that it requires a long time for grafting and reaction. The experiments reported in this study involved using dimethyloldihydroxyethyleneurea-maleic acid (DMDHEU-MA) as a crosslinking agent as well as adding argon (Ar) plasma between the dry and cure treatment of the traditional pad-dry-cure process. The new process is called the "pad-dry-plasma-cure process" (see ***Figure 1***), which is similar to our new work [30]. The Ar plasma treatment proposed affects the crosslinking structure and agent distribution, thus improving the physical properties of finished fabrics. There is no grafting time after plasma treatment in this new process, because the conventional plasma treatment process requires a long time to graft or react with materials after plasma treatment (approximately 1 h to 8 h). The plasma-assisted technology in this study could reduce formaldehyde release significantly, which might give rise to a potential process for using DMDHEU as resin to produce wrinkle-resistant fabrics. The DMDHEU-MA-finished cotton fabrics prepared using two different processes (the new pad-dry-plasma-cure process and the old pad-dry-cure process) were compared in terms of the relationship between the physical properties and the degree of crosslinking.

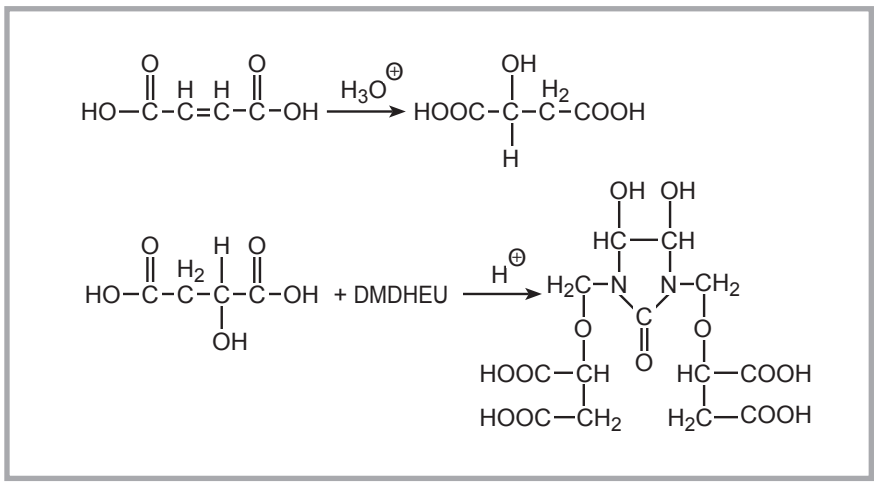

Figure 2. *Formula of DMDHEU-MA.*

Experimental

Materials, synthesis, and preparation

The experiments in this study involved using desized, scoured, and bleached plain woven 100% cotton fabric. The warp yarn was 29 tex and 23.6 yarns/cm, and the weft yarn was also 29 tex and 23.6 yarns/cm. The crosslinking agent that was used was a mixture of DMDHEU (dimethyl dihydroxyl ethylene urea, 30% solid content, Cytec Corp., Taiwan) and MA (maleic acid, ≥99.0%

99.9%, Sigma-Aldrich Chemie GmbH, Germany). DMDHEU–MA products were obtained by using 2, 4, 6, and 8% of DMDHEU to be prereacted with maleic acid (there are two sets of mole ratios of DMDHEU/MA = 1/1) in the presence of an H_2O_2 initiator [0.017, 0.033, 0.050 and 0.067% H_2O_2 (35% v/v), respectively] at 40 °C for 10 min. The maleic acid could be hydrolysed to react with DMDHEU, illustrated as follows (***Figure 2***). DMDHEU-MA has more functional groups (dicarboxylic acid) to crosslink strongly with cotton.

Cotton fabric samples measuring 20 × 20 cm were padded twice to an approximately 80% wet pickup using freshly prepared aqueous solutions of the crosslinking agent consisting of 2, 4, 6, or 8% of the DMDHEU and MA mixture. The ammonium sulfate catalyst concentration was 10%, based on the amounts of the solid content of the crosslinking agent. The pH value of the pad bath was approximately 5.6 - 4.3 at 25 °C (DMDHEU-MA concentration is from 2 - 8%). The drying condition for all of the processes was 80 °C for 5 min, whereas the curing condition was 160 °C for 3 min. The exposure time of the Ar plasma treatment was 5 min. Finally the finished fabric samples were soaped, washed and dried. The RF-O-001 plasma treatment system (Helix Technology Inc. Ltd., Taiwan) with a radio frequency of 13.56 MHz was used. The flow rate of the Ar gas was 50 s/cm^3 at 13.3 mPa. The electrode of the RF plasma source was a 22 × 28.3 cm aluminum plate. The plasma machine was of the cold plasma (low temperature) glow discharge type, and not the corona discharge variety.

Fourier transform infrared spectroscopy

Infrared spectra of the samples were obtained using the KBr disk technique. Samples were prepared to give a dry weight of 1.8 mg after storage in 1-dram vials over P_2O_5 for 3 days. Spectral grade KBr (250 – 300 mg) was ground, transferred to individual sample vials, dried in an oven at approximately 200 °C for several hours, and stored in the oven at 110 °C. Samples were ground and mixed with the KBr and pressed in an evacuated die under suitable pressure. A Fourier transform infrared spectrophotometer (Jasco model FT/IR-3, JASCO Corp., Japan) was used to obtain spectra. Spectra of the samples were obtained by averaging 15 scans with a wavenumber range of 2000 to 750 cm^{-1} and resolution of 2 cm^{-1}.

Nitrogen content

The amount of nitrogen (%) present in the sample was determined using the conventional Kjeldahl analysis [31]. About 0.5 g of the sample was digested with H_2S0_4, together with a catalyst containing 2.8% TiO_2, 3.0% $CuS0_4{\cdot}5H_2O$, and 94.2% K_2SO_4. The residue was treated with NaOH to liberate NH_3, which was subsequently absorbed in boric acid and titrated with HCl. The total bound nitrogen was determined by oxidising and thermally decomposing it into NO_2, which was then detected using an electrochemical detector. NO_2 underwent oxidation at the anode, causing a change in current between the electrodes proportional to the NO_2 concentration. Analyses were done using at least triplicate samples to ensure reproducibility and to exclude statistical errors.

Formaldehyde content [32]

To establish the formaldehyde content, first cut the sample into small pieces. Weigh 2.5 g accurate to 10 mg. For each test specimen, put the weighed pieces into a 250 ml flask with a stopper and add 100 ml of water. Place the stopper tightly and put the flask in an ultrasonic extraction apparatus at 40 °C for 30 min. Then filter the solution into another flask through a filter. Next put 5 ml of the filtered test specimen solution into a tube and 5 ml of standard formaldehyde solutions into further tubes. Add 5 ml of acetyl acetone reagent into each tube and shake it. Keep the test tubes first in a water bath at 40 °C for 30 min and then at ambient temperature for 30 min. Add 5 ml of acetyl acetone reagent solution to 5 ml of water and treat it in the same way as the blank reagent. Afterwards measure the absorbencies in a 10 mm absorption cell at a wavelength of 412 nm against water in a spectrophotometer. For the accuracy and repeatability test, we select the second and fourth standard curve point as the simulated samples after the establishment of the standard curve. Each test is performed in triplicates.

Tensile property

The tensile strengths of the warp yarns were measured using an Instron tensile tester (Instron, United States and Canada). The data of each sample were averaged using 25 measurements, and the value of each measurement was screened to within ± 5%.

Crease recovery

Dry and wet crease recovery values were determined using ASTM standard D 1295-67. The value of crease recovery of each measurement was screened to within ± 3°.

Formaldehyde release

Formaldehyde release was determined using the AATCC Test Method 112-1984 (formaldehyde odour in resin-treated fabrics, determination of the Sealed Jar Method) [33]. Glassaquaria, each with a capacity of 33.5 liters of air, were fitted with Plexiglas covers. Ambient laboratory air drawn through these chambers produced zero HCHO readings. Fabric samples were tested under ambient conditions which averaged 20.6 ± 1.2 °C and 56 ± 4.7% relative humidity. A weighed fabric specimen was hung in the chamber under static conditions for 30 minutes. The tubing was then attached to the HCHO monitor and the air in the chamber was pumped through the instrument for 45 minutes. If the digital readout fluctuated, readings were taken every 10 minutes until the readout stabilised. The final ppm of the HCHO was twice the digital readout. Daily start up and clean up times were lengthy, and hence a maximum of six specimens per day were tested. The samples were suspended over 50 grams water, sealed and heated at 49 °C for 20 hours. Colour development using Nash reagent followed. Results of both tests are expressed as pg formaldehyde per gram of fabric.

Odour absorption

Odor absorption values were measured using the following method, described by Kazuto [30]. The fabric sample treated was suspended in a bottle of poly(tetrafluoroethylene), in which there was 50 ml of ammonia water containing a total ammonia concentration of 200 ppm, kept at a constant temperature of 50 °C in a water bath for 1 min and then cooled at room temperature for 60 min. Finally the residue of ammonia gas in the bottle was measured using a Gastec pump and Gastec detector tube (Gastec Corp., Kanagawa, Japan).

Antibacterial evaluation

The anti-bacterial properties (bacteria inhibition values) of the treated cotton fabrics were tested with *S. aureus* and *E.*

Figure 3. *FT-IR spectra of (a) DMDHEU, (b) DMDHEU–MA, and (c) MA.*

Table 1. *Nitrogen contents of finished cotton fabrics after using various processes. The concentration of crosslinking agents was 4% of the mixture of DMDHEU and MA, the catalyst (ammonium sulfate) concentration -10% based on the amounts of the solid content of the crosslinking agent used, the drying condition - 80 °C for 5 min, and the curing condition was 160 °C for 3 min.*

Process	Plasma conditions			Nitrogen contains, %	Dry crease recovery angle, (W+F)°	Wet crease recovery angle, (W+F)°	Tensile strength retention, %
	Power of plasma, W/cm2	Flow rate of Argon, scm3	Exposure time, min				
Pad-dry-cure	-	-	-	0.58	265	226	54.9
Pad-dry-plasma-cure	0.32	50	1	0.60	268	230	54.8
			3	0.64	273	233	54.6
			5	0.66	276	237	54.4
			7		277	236	54.4
			10		276	236	54.3
		25	5	0.65	274	235	54.5
		100		0.66	276	237	54.4
		200			275	237	54.4
	0.10	50		0.65	273	235	54.7
	0.16				274	236	54.6
	0.64				276	236	54.4
	0.96				275	235	54.6

Table 2. *Physical properties of finished cotton fabrics after using various processes. The power of plasma used was 0.32 W/cm2 and the plasma exposure time - 5 min.*

Process	Resin concentration, %	Formaldehyde, %	Moles/AGU	
			Nitrogen	Formaldehyde
Control	0	0	0	0
Pad-dry-cure	2	0.48	0.0301	0.0259
	4	1.05	0.0671	0.0567
	6	1.31	0.0903	0.0708
	8	1.54	0.1100	0.0832
Pad-dry-plasma-cure	2	0.53	0.0336	0.0286
	4	1.14	0.0764	0.0618
	6	1.41	0.0984	0.0762
	8	1.61	0.1169	0.0870

coli using the technique of AATCC Test Method 100–1998.

Results and discussion

FTIR of DMDHEU-MA

To confirm the crosslinking reaction between DMDHEU and the vinyl group of MA molecules, DMDHEU was used to react with MA in the pad-dry-cure process in the presence of ammonium sulfate as a catalyst. ***Figures 3.a, 3.b,*** and ***3.c***, respectively, show the FTIR spectra of DMDHEU, cured DMDHEU–MA, and MA. The relevant absorbing bands are those of $–CH_2OH$ (1027, 1077 cm^{-1}) for DMDHEU (***Figure 3.a***), and the vinyl group (946 cm^{-1}) of MA (***Figure 3.c***). We determined that the IR spectrum for cured DMDHEU–MA (***Figure 3.b***) almost disappears at 946 cm^{-1} (vinyl group of MA), but generates new absorbing bands of 1156 cm^{-1}. Additionally 1027 and 1077 cm^{-1} shifted to 1015 and 1063 cm^{-1}, respectively. The formation of a new ether group at 1156 cm^{-1} strongly suggests that the reaction between DMDHEU and MA can occur during the pad-dry-cure process. (The absorbing band at 1364 cm^{-1} suggests that it is from the ester group of MA).

Effect of plasma treatment

Table 1 lists values of the dry crease recovery angle (DCRA), wet crease recovery angle (WCRA), and tensile strength retention (TSR) of the different finished fabrics after using the pad-dry-cure and pad-dry-plasma-cure processes. The table shows that the DCRA and WCRA values of the finished fabrics increase when increasing the plasma exposure time and power till optimum treatment conditions, which are 5 min and 0.32 W/cm^2, respectively. These conditions were selected for the following studies. The results indicate that Ar plasma treatment can improve the crosslinking effect after being introduced into the traditional pad-dry-cure process. The increase in DCRA and WCRA of the finished fabrics is caused by the crosslink of the crosslinking agent between cellulose molecules, and the decrease in TRS is caused by the stress concentration after crosslinking of the crosslinking agent between cellulose molecules [34, 35].

Physical properties

Table 2 shows values of the dry crease recovery angle (DCRA), wet crease recovery angle (WCRA), and tensile

strength retention (TSR) of the different finished fabrics after using the pad-dry-plasma and pad-dry-plasma-cure processes. However, the TSR values show an inverse relationship. The crosslinking of the crosslinking agent between cellulose molecules increases the DCRA and WCRA of the finished fabrics, and the stress concentration after crosslinking of the crosslinking agent between cellulose molecules decreases the TSR. Under the same plasma conditions, the DCRA and WCRA values of pad-dry-plasma-cure-finished fabrics are significantly higher than those of pad-dry-plasma-finished fabrics, which indicates that including Ar plasma treatment in the traditional pad-dry-cure process can improve the crosslinking effect.

Figure 4 shows values of the nitrogen (N) content, DCRA, WCRA, and TSR of the finished fabrics after using various processes. For all of the processes, the N content, DCRA, and WCRA of the finished fabrics gradually increased in conjunction with the resin concentration in the pad bath. However, the TSR values show an inverse tendency. ***Figure 4*** also shows that the N content, DCRA, and WCRA values of the pad-dry-plasma-cure process are higher than those of the traditional pad-dry-cure process at a given resin concentration. This phenomenon shows that Ar plasma treatment may increase the bonded amount of DMDHEU-MA. The higher DCRA and WCRA values of the pad-dry-plasma-cure process may be attributed to crosslinking or grafting of the crosslinking agent with the finished fabrics. The experiments in this study involved using MA as a co-reagent of the crosslinking agent. Therefore the reaction among MA, DMDHEU, and cellulose molecules is strong. The higher bonded nitrogen (crosslinking agent) on the finished fabric is probably caused by greater deposition and grafting of the crosslinking agent. Wong et al. [36] showed that cold plasma treatment could form polar functional groups, such as -COOH, -C=O, or -C-O groups, on the surface of treated linen fibres. These polar functional groups may form hydrogen bonds on finished cotton fibre and may also react with the functional group of the crosslinking agent. A previous study [37] showed that the hydrogen bonds in finished fibres can affect the physical properties of finished fabrics.

Figure 5.a shows the relationships between DCRA and WCRA values of the finished fabrics after using the three processes. WCRA values of the finished fabrics after using the pad-dry-plasma-cure process are higher than those after using and traditional pad-dry-cure processes for a given value of DCRA. ***Figures 5.b*** and ***5.c*** show the plots of TSR against the DCRA and WCRA of the finished fabrics, respectively. These figures indicate that the TSR values of the pad-dry-plasma-cure process are higher than those of the pad-dry-plasma and traditional pad-dry-cure processes at the same value of DCRA and WCRA. The higher TSR values of the pad-dry-plasma-cure process are likely the result of the deposition of DMDHEU-MA on the finished fabrics, which in turn decreases the stress concentration and increases the TRS value. The higher nitrogen content of the finished fabrics after using the pad-dry-plasma-cure process at a given resin concentration in the pad bath (***Table 2***) supports this phenomenon of deposition. These results again confirm

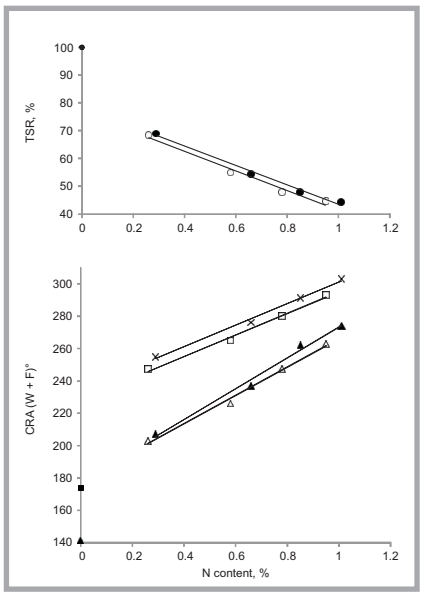

Figure 4. *Values of TSR, DCRA, and WCRA versus the nitrogen contents of the finished fabrics after using (●, ■, ▲) control, (○, □, Δ) the pad-dry-cure process, and the (●, ■, ▲) pad-dry-plasma-cure process, respectively.*

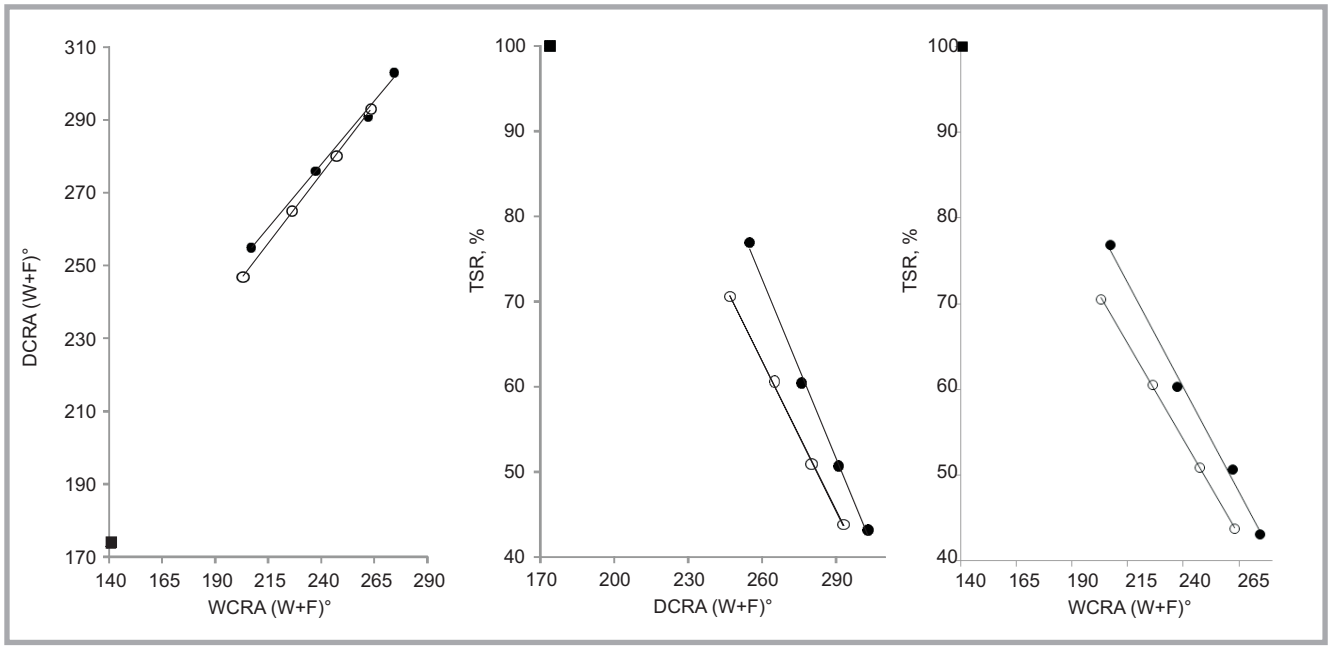

Figure 5. *Relationships among the: a) DCRA & WCRA, b) TSR & DCRA, and c) TSR & WCRA of the finished fabrics after using (■) the control (○), the pad-dry-cure process, and (●) pad-dry-plasma-cure process, respectively.*

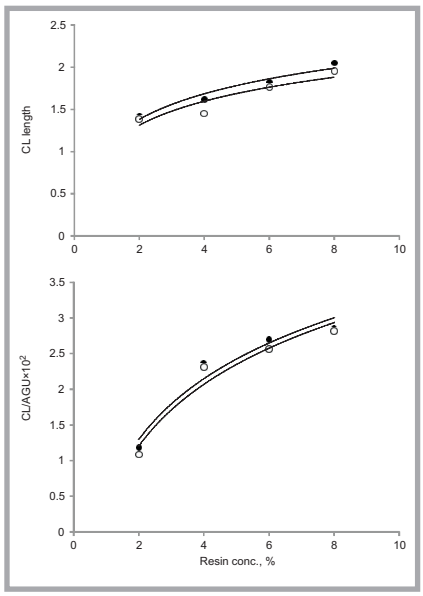

Figure 6. *Plots of (a) CL length and (b) CL/AGU of the finished fabrics versus resin concentration in the pad bath after using (○) the pad-dry-cure process and (●) pad-dry-plasma-cure process, respectively.*

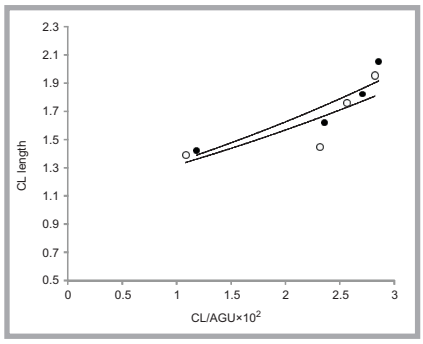

Figure 7. *Plots of CL length versus CL/AGU of the finished fabrics after using (○) the pad-dry-cure process and (●) pad-dry-plasma-cure process, respectively.*

that Ar plasma treatment is capable of improving the physical properties of finished fabrics.

Degree and structure of crosslinking

Research has shown that the physical properties of pad-dry-plasma-cure-finished fabrics are also affected by the crosslinking structure. To confirm changes in the crosslinking structure with the addition of Ar plasma treatment, the nitrogen and formaldehyde contents as well as the number and length of crosslinks for the finished cotton fabrics were investigated, the results of which are presented in ***Table 2***. As expected, in both cases, the nitrogen and formaldehyde contents showed a gradual increase when increasing the resin content in the pad bath. Nitrogen and formaldehyde values of the finished fabrics after using the pad-dry plasma-cure process are higher than those after using the traditional pad-dry-cure process at a given resin concentration in the pad bath. The number of crosslinks per anhydroglucose (CL/AGU) and the length of crosslinks (CL length) of the finished fabrics after using the two processes are shown in ***Table 2*** and ***Figure 6***. In this study, calculation of the CL/AGU and CL lengths followed the methods of Frick and Kottes et al. [38, 39]. The results indicate that both values increase as the concentration of the resin in the pad bath increases. ***Figure 6*** also indicates that values of the CL/AGU and CL length of the finished fabrics after using the pad-dry-plasma-cure process are higher than those after using the pad-dry-cure process at the same resin concentration. As mentioned previously, this phenomenon may be caused by the deposition or crosslinking of DMDHEU-MA in and on the finished fabrics with the addition of Ar plasma treatment. The curvilinear relationships between the length of crosslinks and CL/AGU for the fabric samples finished after using the two processes (***Figure 7***) are similar to those reported previously [18 - 20]. For a given number of CL/AGU, the CL length of the finished fabric after using the pad-dry-plasma-cure process is higher than that after using the traditional pad-dry-cure process. This may be attributed to the higher degree of self-condensation after the addition of Ar plasma treatment. The relationships between the various physical properties and number of CL/AGU of the finished fabrics after using the two processes are plotted for comparison. Based on the relationships between the DCRA and CL/AGU of the finished fabrics (***Figure 8.a***), it was found that the DCRA values of the finished fabrics after using the pad-dry-plasma-cure process are higher than those after using the traditional pad-dry-cure process at the same number of CL/AGU. ***Figure 8.b*** shows the plots of WCRA versus CL/AGU of the finished fabrics. For a given number of CL/AGU, the value of WCRA of the finished fabrics after using the pad-dry-plasma-cure process is higher than that after using the traditional pad-dry-cure process. The plots of TSR versus CL/AGU of the finished fabrics shown in ***Figure 8.c*** reveal that the TSR value after using the pad-dry-plasma-cure process is higher than that after using the traditional pad-dry-cure process at a given number of CL/AGU. It is confirmed that the physical properties

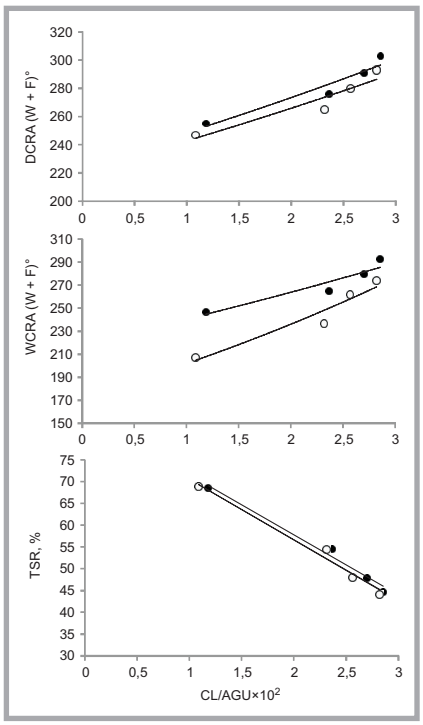

Figure 8. *Plots of: a) DCRA versus CL/AGU, b) WCRA versus CL/AGU and c) TSR versus CL/AGU of the finished fabrics after using pad-dry-cure process (○) and pad-dry-plasma-cure process (●), respectively.*

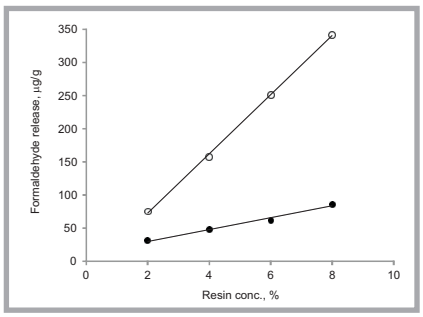

Figure 9. *Formaldehyde release for DMDHEU–MA crosslinked cotton fabrics versus resin concentration in the pad bath after using (○) the pad-dry-cure process and (●) ad-dry-plasma-cure process, respectively.*

of the finished fabrics are affected by the crosslinking structure.

Based on these results and discussions, it is presumed and suggested that crosslinking agent DMDHEU-MA is deposited in and on the finished fabrics with the addition of Ar plasma treatment (the pad-dry-plasma-cure process). These crosslinking agents deposited then crosslink between cellulose molecules during the cure treatment to improve the crease recovery angle. These crosslinking agents deposited also decrease the stress concentration of the finished fabric after using the pad-dry-plasma-cure process, thereby

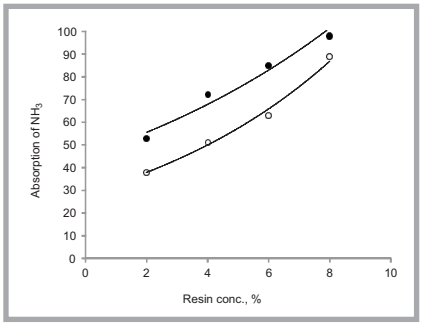

Figure 10. *Odour absorption for DMDHEU–MA crosslinked cotton fabrics versus resin concentration in the pad bath after using (○) the pad-dry-cure process and (●) pad-dry-plasma-cure process, respectively.*

improving tensile strength retention as compared with that after using the pad-dry-cure process. The higher values of WCRA after using the pad-dry-plasma-cure process are mainly caused by the higher value of CL length and the higher degree of fibre expansion of the treated fabrics under wet conditions. Concurrently the higher value of TSR is caused by the higher CL length, which can reduce the degree of stress concentration of the finished fibres. Ar plasma treatment is an excellent addition between traditional dry and cure treatments to improve the physical properties of finished cotton fabrics.

Formaldehyde release

Figure 9 shows the formaldehyde release from the finished fabric, which indicates that it increased with increasing DMDHEU–MA concentration in the padding bath. The higher bonded formaldehyde for pad-dry-plasma-cure finished fabric may cause concerns about an increase in formaldehyde release, which could induce a skin allergy in the user. The value of formaldehyde release for the pad-dry-plasma-cure finished process is significantly lower than that for the pad-dry-cure process. This phenomenon is probably caused by the oxidation of formaldehyde under Ar plasma treatment. It is known that the functional group of aldehyde is easily oxidised to form the functional group of dicarboxylic acid. This result significantly decreases the free formaldehyde and is of benefit for practical use.

Odour absorption

Figure 10 shows that odour absorption (NH_3 absorption) increased with an increase in DMDHEU–MA concentration in the padding bath; and the pad-dry-plasma-cure is higher than pad-dry-cure at the same DMDHEU–MA concentration. The higher odour absorption could be attributed to more COOH functional groups after conducting the plasma treatment. We can reasonably suggest that NH_3 gas can also be absorbed by the crosslinking agent when DMDHEU-MA is deposited on the finished fabrics with the addition of Ar plasma treatment (the pad-dry-plasma-cure process). These DMDHEU–MA crosslinks or grafts are deposited between cellulose molecules during cure treatment to improve odour absorption.

Antibacterial evaluation

The bacterial inhibition values were defined as $[(M_b–M_a)/M_b]\times100\%$. The M_b and M_a values are the numbers of bacteria for the finished fabrics for a nourishment time period of 0 h and specific hours, respectively, according to the method described by Hu and Jou et al. [40]. ***Figure 11*** shows that values of the antibacterial ratio of the various treated fabrics for both *S .aureus* and *E. coli* all increased with increasing exposure time in testing. As shown in ***Figures 11.a*** and ***11.b***, the values of bacterial inhibition of the various treated fabrics were ranked pad-dry-plasma-cure > pad-dry-cure at a given exposure time. The higher bacterial inhibition values for pad-dry-plasma-cure-treated fabric may be caused by the higher surface distribution.

Conclusions

This study reports the inclusion of Ar plasma treatment in the traditional pad-dry-cure process before cure treatment and after dry treatment. This new process is called the pad-dry-plasma-cure process. This study also investigates the effects of Ar plasma treatment on finished cotton fabrics. Experimental results show that the addition of Ar plasma treatment can increase the crosslinking effect between the crosslinking agent and cellulose molecules to improve the physical properties of the finished fabrics. DCRA, WCRA, and TSR values of pad-dry-plasma-cure-finished fabrics are higher than those of pad-dry-cure-finished fabrics with the same nitrogen content and CL/AGU. The butyl group of maleic acid is likely excited during Ar plasma treatment, and then becomes grafted with the functional group of the cellulose fibre and DMDHEU during cure treatment. DMDHEU-MA was then deposited and grafted on the surface of the finished cotton fabric to improve its

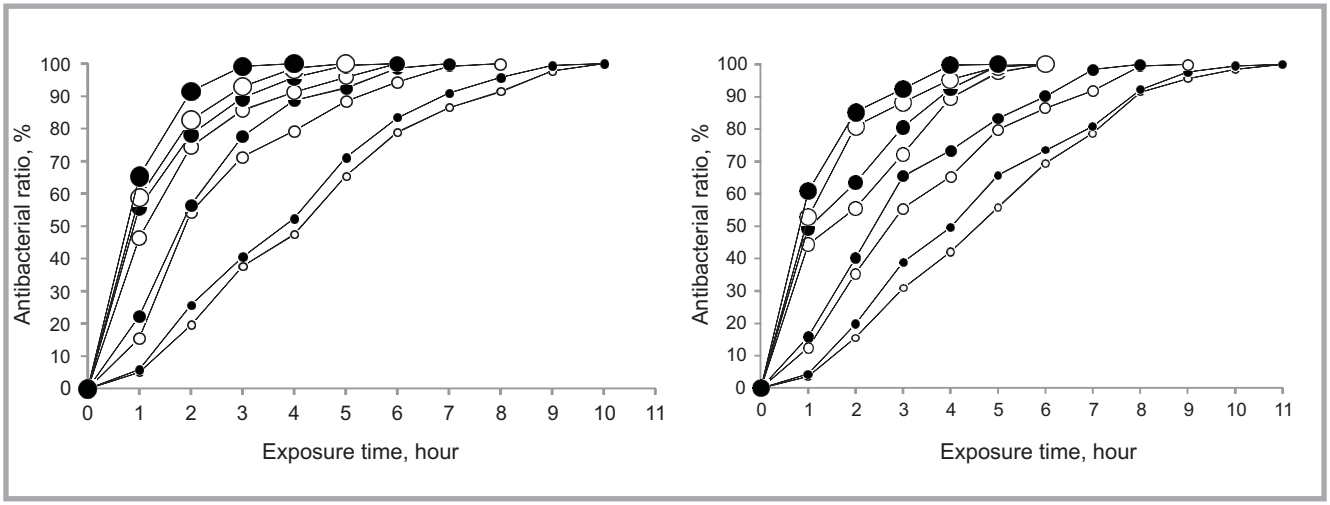

Figure 11. *Bacteria ratio for (◦) 2%, (○) 4%, (○) 6%, and (○) 8% of resin concentration for the pad-dry-cure process and (•) 2%, (•) 4%, (●) 6%, (●) 8% of resin concentration for the pad-dry-plasma-cure process for (a) S. aureus and (b) E. coli.*

CRA values. This phenomenon may also decrease the stress concentration of finished cotton fabrics to improve their TSR values. Otherwise the anti-bacterial ability and odour absorption of the pad-dry-plasma-cure finished fabrics were higher than those of the pad-dry-cure finished fabrics. Thus the pad-dry-plasma-cure process is excellent for improving the physical properties, bacterial inhibition, and odour absorption of finished cotton fabrics and for decreasing their formaldehyde release without a long grafting time. The new process may be useful for practical applications in the field of durable press finishing

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