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Effect of plasma treatment on crease recovery finish of linen with carboxylic acid

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The effect of helium plasma treatment has been investigated on crease recovery finish of linen fabric using carboxylic acid as crosslinker. After the plasma treatment, 5% increase in wet pickup is observed compared to the control fabric. This plasma treated sample is crosslinked with butyl tetracarboxylic acid (BTCA). The significant increase in crease recovery angle is found as compared to the untreated crosslinked fabric. However, significant reduction in tearing is also observed in both the cases. Tearing strength could be improved to acceptable range by adding silicone softener during cross-linking process. The untreated and plasma-treated fabrics are analyzed by scanning electron microscope and ATR-FTIR spectroscopy to investigate the changes in surface morphology and surface functional groups.

Keywords: Crease recovery finish, Helium plasma treatment, Linen fabric, Plasma treatment

1 Introduction

Fabrics made from natural cellulosic fibres are comfortable to wear in hot climate because of good moisture absorption capacity, air permeability and coolness. But the disadvantage of fabrics made of cellulose is the formation of creases. Linen is also a natural cellulosic fibre produced from the stem of the flax plant. Linen fabrics produced from flax fibres are very strong, absorbent and dries faster than cotton. Garments made of linen provides exceptional coolness and freshness in hot and humid weather. It is a very durable and strong fabric. But linen fabric has a very low elasticity so the fabric breaks if it is folded and ironed at the same place repeatedly over the time. Inherently, linen wrinkles very easily and requires frequent ironing [1].

In industrial practice, people use crosslinker to make the fabric crease free. Formaldehyde base crosslinkers are well accepted by the industries although they are not ecofriendly due to their hazardous effect on human being as well as to the environment.

For this reason carboxylic acid crosslinkers, such as 1, 2, 3, 4-butyl tetracarboxylic acid (BTCA) and dimethyl dihydroxy ethylene urea (DMeDHEU), are alternate options to replace the hazardous formaldehyde based crosslinker for crease recovery finish[2,3]. The carboxylic acid crosslinkers are not gaining interest by the industries due to the need of high concentration of chemicals and high curing temperature during crosslinking. Till now, people are using harmful formaldehyde based crosslinking agents for this type of finish. It has been demonstrated in literature that plasma pretreatment helps to reduce the consumption of chemical during the finishing of natural as well as synthetic fabric.

Plasma at atmospheric pressure is very useful for surface modification of the textiles. Atmospheric pressure plasma, such as corona or dielectric barrier discharge, are suitable for inline continuous treatment of textile materials. Plasma technology does not require large quantity of chemicals, water and energy for the treatment of fabric. It has also been demonstrated by researchers that plasma treatment improves physical properties of linen [4-10].

However, the effect of plasma treatment of linen followed by crosslinking with polycarboxylic acid on crease recovery angle of linen has not been investigated. As BTCA is an effective non-formaldehyde agent for crease resistant finish and plasma helps to reduce the chemical loading on fabric as well as on environment, an attempt has been made in this work to investigate the effect BTCA treatment on crease recovery of linen and how the plasma pretreatment helps to reduce the chemical loading during this treatment.

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2 Materials and Methods

2.1 Materials

100% linen fabric with GSM of 148.5g, ends per inch of 41 and picks per inch of 43, was procured from Ratanmoti Texfab Pvt. Ltd, Kolhapur, Maharashtra, India. 1,2,3,4-Butyl Tetracarboxylic Acid (BTCA) (99%) was procured from Sigma Aldrich, India, Sodium hypophosphite monohydrate (NaH_2PO_2) (99%) was procured from LOBA Chemie Pvt. Ltd., Mumbai, India. Silicone softener was procured from Britacel Silicones Ltd. All chemicals were used as such without any further purification.

2.2 Methods

2.2.1 Bleaching

The linen fabric was scoured and bleached at temperature 85°- 90°C for a duration of 4 h using 8mL/L hydrogen peroxide (H_2O_2) as bleaching agent, 15 %sodium silicate on the weight of H_2O_2, 1mL Tween 80 (non-ionic wetting agent) and sodium hydroxide to maintain the *p*H. After bleaching, fabric was washed and dried.

2.2.2 Plasma Treatment

The bleached fabric was conditioned for 24 h in a standard atmosphere of 27±2° C temperature and 65% relative humidity. The conditioned fabric was treated with plasma using PLATEX 600 LAB pilot scale machine from GRINP SRL TORINO, Italy. Schematic of the machine is shown in Fig. 1. During the treatment the electrode gap, helium gas flow and power were kept at 1.5 mm, 5 L/min and 5 kW respectively. Treatment time was kept for 2 min and 1 min. In similar set of experiment, oxygen (0.5mL/min) was added to the helium and fabric was treated for 2 min.

2.2.3 Solution Preparation and Padding

Required amount of butyl tetracarboxylic acid and sodium hypophosphite was added to the distilled water and stirred continuously to make a clear solution. Both the fabric plasma treated and untreated was crosslinked by the pad-dry-cure method. Linen fabric was padded in padding mangle (Werner Mathis, made in Switzerland) by 2 dip 2 nip process at a pressure of 2 bar and speed of 1.5 rpm. After padding, the fabric was dried at 80°C for 2 min and cured at 150°C for 2 min using curing machine (Werner Mathis AG from Switzerland). The fabric was given a cold wash then air dried and conditioned before the characterization.

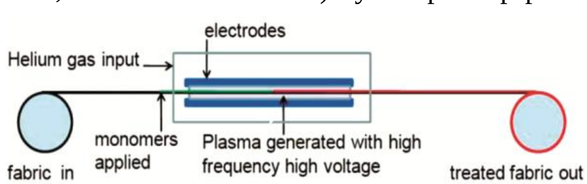

Fig. 1 — Schematic of plasma machine

2.2.4 Crease Recovery Analysis

Crease recovery angle (CRA) of treated and untreated samples were measured by IS (4681-1981 RA 2014) method using Shirley Crease Recovery Tester, England. For every sample, CRA was measured in both warp and weft directions. Average CRA of five individual readings in each direction and their sum is reported. Percentage improvement was calculated, as compared to control linen fabric.

2.2.5 Tearing Strength Analysis

The tearing strength of both the treated and untreated samples was measured using Elmendorf Tearing Tester by ASTM 1424-2009 RA 2013 method. During the test, warp and weft wise tearing strength of untreated, untreated crosslinked and plasma treated crosslinked fabric were measured. In each case, five readings were taken and their average is reported.

2.2.6 Washing

The untreated crosslinked and plasma-treated crosslinked fabric samples were subjected to washing by IS/ISO 105-A01, 2010 method using launderometer. During washing, temperature, rpm and time were kept 40±2°C, 40rpm and 30 min respectively. As per the standard, 1 cycle of standard washing is equivalent to 5 home laundering. After 2 cycles the samples were rinsed and dried. Those dried samples were taken for further evaluation after conditioning.

2.2.7 SEM Analysis

The change in surface topography of the linen fabric after crosslinking was investigated using scanning electron microscope (JSMIT 200) from JEOL Ltd, Japan. During this image acquisition, magnification percentage and applied voltage were kept constant for all samples.

2.2.8 ATR-FTIR Spectroscopic Study

The change in surface chemistry of the linen fabric after plasma treatment was investigated using ATR-FTIR spectroscopy spectrum 2 from Perkinelmer, USA. Overlay spectra of untreated and plasma-treated linen fabric was taken for comparison and analysis.

3 Results and Discussion

3.1 Plasma Treatment of Fabric

3.1.1 Standardization of Treatment Time

100% linen bleached fabric has been used for plasma treatment before crease recovery finish. Plasma treatment was done in atmospheric pressure plasma machine at 5 kW power and helium gas flow at 5 L/min. Duration of the treatment is kept 2 min and 1 min. After 2 min plasma treatment, the wicking height of plasma-treated fabric is found 5 cm as compared to 3.5 cm in untreated fabric and 4 cm in 1 min treated fabric. Those plasma-treated fabric as well as the untreated fabric is then taken for crease recovery finish using BTCA by conventional pad-dry-cure method. After padding, 5% increase in expression is observed in plasma-treated sample as compared to untreated sample at same padding parameter.

3.2 Crease Recovery Finish

In the first set of experiment, concentrations of crosslinker BTCA and catalyst sodium hypophosphite are kept 60 gpL and 30 gpL respectively. The plasma pretreated as well as the untreated fabrics are padded with the above solution. Those padded fabrics are then dried at 80°C for 2 min and cured at 150°C for 2 min. Fabric samples are finally washed in the cold water to remove untreated chemicals present on the surface of the fabrics after curing and conditioned before the evaluation of crease recovery angle. The crease recovery angle of the linen fabric without crosslinking, crosslinked with BTCA and crosslinked with BTCA after plasma treatment are given in Table 1. Two minute plasma-treated and crosslinked sample shows excellent crease recovery of around 97% as compared to untreated crosslinked samples, so 2 min treatment time is kept fixed for further set of experiments.

3.3 Standardization of Concentration of Crosslinking Agent and Catalyst

To investigate the effect of concentration, plasma treated and the untreated fabrics are finished by varying the concentration of crosslinker and catalyst. During the finish, the concentrations of BTCA and SHP are changed from 60gpL to 20gpL and 30gpL to 10 gpL respectively. The fabric samples are padded with solution containing BTCA and SHP of required amount. These padded fabrics are dried at 80°C for 2 min and then cured at 150°C for 2 min. After curing, fabrics were washed in the cold water to remove unreacted chemicals from the surface, dried and conditioned before the evaluation. The crease recovery angle of all samples is given in Table 2. From the measured values it is found that, the untreated crosslinked and plasma-treated crosslinked fabrics are showing 79% and 97% increase in crease recovery angle respectively as compared to control linen fabric at 60 gpL of BTCA and 30 gpL of SHP. After reducing the concentration of BTCA to 40 gpL and the concentration of SHP to 20 gpL, the untreated crosslinked fabric and the plasma-treated fabrics are showing 50% and 62 % crease recovery respectively as compared to the control fabric. When the concentration is reduced further to 20 gpL and 10 gpL improvement in crease recovery angle is observed only 9% and 11% in untreated and plasma-treated fabrics respectively. As high concentration of BTCA affects strength of the fabric after crosslinking, 40 gpL BTCA and 20 gpL of SHP are kept constant for further set of experiments.

3.4 Effect of Helium and Oxygen Mix Plasma on Linen Fabric

Addition of oxygen generates more functional sites on the surface of the fabric during plasma treatment, so 0.5 L/min oxygen is added with 5 L/min helium during plasma treatment. In this mix plasma, treatment has been done for 2 min at 5 kW. Then plasma-treated and untreated fabrics are taken for crease recovery finish using 40 gpL of BTCA and 20 gpL of SHP. The crease recovery angle of finished fabrics is measured and given in Table 3. From the

Table 1 — CRA of untreated, untreated cross linked & plasma-treated crosslinked samples

Sample	CRA, deg			% increase
	Warp	Weft	Total CRA	
Control	65(7.3)	52(6.2)	117	--
Crosslinked without plasma treatment	103(5.5)	106(7.9)	209	79
Crosslinked with 1 min plasma treatment	108(4.9)	117(9.5)	225	92
Crosslinked with 2 min plasma treatment	107(8.8)	124(7.5)	231	97

Values given in parentheses are standard deviation.

Table 2 — CRA of untreated and plasma-treated crosslinked samples at different concentrations of BTCA and SHP

Sample	BTCA & SHP, gpL	CRA, deg			% Increase
		Warp	Weft	Total CRA	
Untreated crosslinked	60&30	103(6.8)	106(7.9)	209	79
	40& 20	87(9.8)	89(8.1)	176	50
	20&10	66(6.9)	61(7.6)	127	9
Plasma- treated crosslinked	60&30	107(9.8)	124(8.6)	231	97
	40&20	94(8.5)	96(6.9)	190	62
	20&10	66(8.9)	64(9.5)	130	11

Values given in parentheses are standard deviation.

Table 3 — CRA of fabrics at different stages.

Sample	CRA, deg			% Increase
	Warp	Weft	Total	
Untreated crosslinked and helium & oxygen plasma-treated crosslinked fabric with softener before washing				
Control	65(10.2)	52(11.2)	117	NA
Crosslinked without plasma	82(10)	94(9.2)	176	50
Crosslinked with helium plasma	94(8.8)	96(9.5)	190	62
Crosslinked with helium and oxygen plasma	90(8.3)	102(8.9)	192	64
Untreated crosslinked and plasma treated crosslinked fabric with softener before washing				
Control	65(8.5)	52(9.5)	117	NA
Untreated crosslinked with softener	88(9.9)	85(8.8)	173	48
Plasma-treated crosslinked with softener	97(9.5)	98(10.6)	195	67
Untreated crosslinked and plasma treated crosslinked fabric after washing				
Control fabric	65(10.2)	52(9.6)	117	NA
Untreated crosslinked fabric	87(8.9)	80(8.8)	167	43
Plasma-treated crosslinked fabric	95(9.9)	92(11.2)	187	60

Values given in parentheses are standard deviation.

values it can be concluded that the addition of oxygen gas with helium during plasma treatment is not helping for significant improvement in CRA as compared to the only helium gas plasma treatment, so only helium gas is taken for further set of experiments.

3.5 Analysis of Tearing Strength

Generally, crosslinking of fabric affects its tearing strength due to the restriction in yarn movement. The cotton fabric shows significant reduction in tearing strength after crosslinking and hence the tearing strength of linen fabrics before and after crosslinking has been measured to study its effect. The tearing strength values are given in Table 4. Although there is no significant difference between tearing strength in both the directions and both the cases (with plasma and without plasma), but there is significant reduction in tearing strength (79%) is observed after crosslinking as compared to the uncrosslinked fabric. It shows the restriction in yarn movement after crosslinking is high in linen as compared to other cellulosic fibre. To improve the tearing strength of the fabric further experimentation has been carried out using softener during pad-dry-cure process.

3.6 Effect of Softener on Tearing strength

The crosslinked linen fabric shows significant decrease in tearing strength. To improve it, the fabric is crosslinked in presence of softener. During this experiment, fabric is crosslinked with standardized concentration of BTCA, SHP and 20 gpL of silicon softener. Tearing strength values after crosslinking and softening are given in Table 4. The decrease in tearing strength is observed (57%) in case of untreated fabric, whereas 56% decrease is observed in case of plasma-treated fabric, which is 81% and 82% before softening. The maximum recovery in tearing strength is observed with 20 gpL softener.

Table 4 — Tearing strength of fabric before and after cross linking with and without softener

Sample	Tearing strength, N		% Reduction	
	Warp	Weft	Warp	Weft
Control	53.2(9.2)	52.3(9.5)	NA	NA
Untreated crosslinked fabric without softener	9.51(8.9)	10.95(9.4)	82	79
Treated crosslinked fabric without softener	9.03(8.2)	9.94(6.9)	83	81
Untreated crosslinked fabric with softener	23.09(8.7)	21.75(8.6)	56	58
Treated crosslinked fabric with softener	23.52(10.5)	22.22(9.6)	55	57

Values in parentheses are standard deviation.

3.7 Effect of Softener on CRA

The CRA values of the crosslinked fabric with softener are given in Table 3. There is no increase in CRA in case of untreated fabric after using softener but in case of plasma-treated fabric a mild increase of up to 5% is observed. This might be due to the increase in uptake of softener after plasma treatment.

3.8 Wash Durability of Functionality

To investigate the durability of the crease recovery functionality to the number of washing cycle, fabric sample is washed using AATCC standard method as mentioned in earlier section. After 10 numbers of home washings, fabric samples are rinsed, dried, conditioned and evaluated. The values of crease

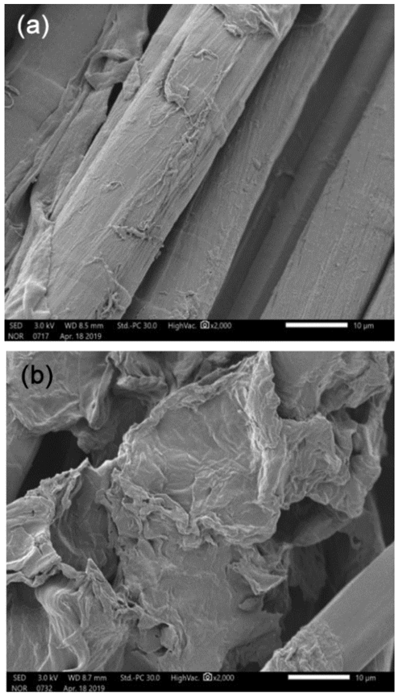

Fig. 2 — SEM images of (a) untreated crosslinked and (b) plasma-treated crosslinked linen fabrics

recovery angle are given in Table 3. There is no significant decrease in CRA in both the crosslinked fabric (untreated and plasma-treated). It shows that crosslinking is durable to washing.

3.9 SEM Analysis

Linen untreated crosslinked and plasma-treated crosslinked fabrics are observed under scanning electron microscope to investigate the alteration in their surface topography. Scanning electron micrographs of both the sample are shown in Fig. 2. Fibre surface is looking smooth due to the thin layer deposition of applied crosslinker. This deposition is observed more in case of plasma-treated sample as compared to untreated sample.

3.10 ATR-FTIR Analysis

Helium gas plasma treatment in presence of air helps to create hydroxyl groups on the surface of the fibre. Untreated and plasma-treated linen fabrics are analyzed using the ATR-FTIR analysis to investigate the changes in surface chemistry of the linen after plasma treatment. Overlay of the spectra is shown in Fig. 3. In this overlay spectra, pick at 3336.84 cm^{-1} can be assigned to the OH stretching. Ratio of the intensity of this peak to the intensity of unchanged C-O-C peak is 0.4 in case of untreated and 0.5 in case of plasma treated fabric. This increase in intensity of OH groups is due to the plasma treatment which helps in increasing the wicking and wet pickup.

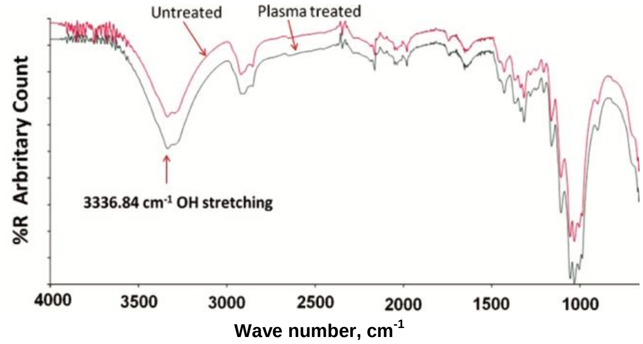

Fig. 3 — ATR-FTIR spectra of untreated crosslinked and plasma-treated crosslinked linen fabrics

4 Conclusion

An attempt has been made to impart crease-free finish on linen using BTCA assisted with plasma treatment. Stable glow plasma could be generated with helium. Plasma treatment could increase 5% wet pickup compared to the untreated linen. Improvement in crease recovery angle up to 18% is observed after plasma treatment for 2 min before crosslinking with BTCA as compared to untreated linen. Plasma treatment could assist to get 12% improvement in CRA as compared to untreated linen even at low concentration, 40 gpL of BTCA and 20 gpL of SHP. However, reduction in tearing strength of up to 79% is observed in both the cases. Tearing strength could also be improved successfully to acceptable range by adding silicone softener during crosslinking process. Addition of oxygen does not help much to improve absorbency. The effect of crosslinking is found durable to 10 home laundering. From SEM images, more chemical deposition is found on the surface of plasma-treated linen fibre after crosslinking. Increase in intensity of OH functional groups after plasma treatment is confirmed from the ATR FTIR analysis.

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