Cotton Fabric Graft Copolymerization Using Microwave Plasma. II. Physical Properties

Noureddine Abidi, Eric Hequet

International Textile Center, Texas Tech University, P.O Box 45019, Lubbock, Texas 79409-5019

Received 4 July 2004; accepted 28 December 2004
DOI 10.1002/app.22195
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Microwave plasma treatments were applied to lightweight cotton fabric with oxygen, nitrogen, and argon at various microwave power levels and exposure times. The results showed significant effects from the type of plasma, microwave power, and treatment time on the fabric weight loss. Oxygen plasma treatment generates higher weight loss than argon plasma and nitrogen plasma. The breaking strength of the treated fabric was affected mainly by longer exposure time to the plasma. The active centers created within the cellulose macromolecules were used to initiate copolymerization reactions with the vinyl laurate monomer [$CH_3(CH_2)_{10}COOCH{=}CH_2$]. The grafted cotton fabric showed excellent water repellency properties. Repeated home laundering of the treated cotton fabrics revealed no significant effect on the water contact angle or on the quantity of grafted vinyl laurate monomer as determined by universal attenuated total reflectance Fourier transform IR, demonstrating the good durability of the treatment that was applied. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 896–902, 2005

Key words: plasma polymerization; graft copolymers; Fourier transform IR; fabrics/fibers; surface modification

INTRODUCTION

In recent years, plasma technology for surface modifications of textile substrates has attracted more attention.[1–4] The collision of plasma species (radicals, metastable molecules, photons, and charged particles such as ions and electrons) with the textile surface results in a transfer of energy to the molecules of the substrate (cellulose in the case of cotton fabric). This leads to the formation of a variety of new species such as free radicals and ions on the substrate surface. These are chemically active species and could be used as precursors to initiate polymerization reactions when they come in contact with a monomer. The result is the formation of new stable compounds through a copolymerization process.

For many years, the method used to graft monomers on cellulosic fabric was based on the use of initiators (such as ceric ion) for copolymerization between cellulose and the monomer.[5–8] The chief drawback of this method is the generation of highly toxic wastes.

Several studies have been conducted using the radiofrequency plasma process as a tool for textile substrate modification.[9–12] With this technology, active radical centers are created within the cellulose chain and are used as initiators for subsequent copolymerization with other monomers. However, very limited investigations have been reported on the use of 2.45-GHz microwave generator plasma for cotton fabric surface modification. In previous work, we used a universal attenuated total reflectance Fourier transform IR (UATR-FTIR) instrument as a fast and nondestructive technique to monitor the changes resulting from the plasma treatment.[13] We found that Ar plasma at 2.45 GHz generates more active groups on cellulose than either N_2 or O_2 plasma. Furthermore, plasma-induced grafting of vinyl laurate monomer [$CH_3{-}(CH_2)_{10}{-}COO{-}CH{=}CH_2$] to impart hydrophobic properties to the lightweight cotton fabrics was also reported.[13] The results showed that vinyl laurate monomer was successfully grafted onto lightweight cotton fabric, thereby imparting a hydrophobic character to the fabric surface.

This article reports on results obtained from the study of the effect of microwave plasma treatment on fabric weight loss and breaking strength and the durability to repeated home laundering of the plasma-induced grafting of vinyl laurate.

Correspondence to: N. Abidi (n.abidi@ttu.edu).
Contract grant sponsor: Texas Food and Fibers Commission.

Journal of Applied Polymer Science, Vol. 98, 896–902 (2005)

EXPERIMENTAL

Materials

Desized, scoured, and bleached 100% cotton fabric was used in this study. Its construction was 100 ends, 85 picks, and a yarn count of 16.4 × 14.8 tex (36 × 40 English count); its weight was 118.7 g/m^2 (3.5 oz./yd^2). Nitrogen, oxygen, and argon gases were commercial grade. Vinyl laurate monomer [CH_3—$(CH_2)_{10}$—COO—CH═CH_2] was purchased from Sigma–Aldrich and used as received.

Plasma treatment of cotton fabric

The plasma process chamber is 25.4 × 25.4 × 25.4 cm (width × depth × height, PLASMAtech Inc., Erlanger, KY). The microwave generator is 2.45 GHz, which is a regulated magnetron with variable power between 100 and 600 W. The system possesses two gas channels with a mass flow controller and magnetic valves for programmed, automatic precise gas flow in the process chamber. The cotton fabric samples were placed in the plasma chamber in a horizontal position on a perforated screen. The plasma chamber was first pumped down to 0.187 torr (25 Pa), then the gas was injected automatically by opening the gas valves. The gas flow rate was kept constant at 60 mL/min.

To investigate the effect of the type of plasma, the treatment time, and the microwave generator power, three gases were used (N_2, O_2, and Ar). The treatment time was varied from 60 to 400 s and the microwave power was varied from 100 to 500 W. Three replications were performed for each treatment.

Percent weight loss after plasma treatment

The percent weight loss (PWL)[13,14] after plasma treatment of the fabric was calculated as follows:

$$\mathrm{PWL} = \frac{(W_p - W_0)}{W_0} \times 100$$

where W_0 is the original weight of the cotton fabric and W_P is the weight of the fabric after the plasma treatment.

Cotton fabric grafted with vinyl laurate monomer

The vinyl laurate monomer was grafted on cotton fabric in hexane solution using the procedure described in our previous work.[13] The treatment time was 240 s, the plasma gas was argon, the microwave power was set at 500 W, and the gas flow rate was 60 mL/min. Three independent replications were performed. All grafted fabrics were conditioned at least 72 h at 65 ± 2% relative humidity and 21 ± 1°C before testing.

Evidence of fabric grafting

FTIR measurements

A Spectrum-One (PerkinElmer, Shelton, CT) equipped with UATR-FTIR was used to acquire the FTIR spectra of the treated fabrics, as described previously.[13] The treated cotton fabric samples were placed on top of a ZnSe-diamond crystal and pressure was applied on it to ensure good contact with the incident IR beam and to prevent loss of the IR incident radiation. The IR spectra were collected using 32 scans with 4 cm^{-1} resolution between 650 and 4000 cm^{-1}. Five FTIR spectra were acquired on each sample from different locations before and after laundering.

Percentage grafting

The percentage grafting (PG) was calculated as follows:

$$\mathrm{PG} = \frac{(W_G - W_0)}{W_0} \times 100$$

where W_0 is the weight of the original fabric before grafting and W_G is the weight of the grafted fabric with the monomer.

Laundering test

Cotton fabric samples were plasma grafted with vinyl laurate monomer. The percentage grafting ranged from 3 to 10% on the weight of the fabric. The samples were weighed, and their UATR-FTIR spectra were acquired. Then, they were subjected to 10 subsequent home laundering and tumble-drying cycles. After each cycle, a sample was taken, conditioned for at least 72 h at 65 ± 2% relative humidity and 21 ± 1°C, and weighed; and the corresponding UATR-FTIR spectra as well as the water contact angle were acquired.

Percent weight loss after subsequent laundering of grafted fabric

The percent weight loss of the grafted fabric (PWLG)[13,14] after subsequent laundering was calculated as follows:

$$\mathrm{PWLG} = \frac{(W_L - W_0)}{W_0} \times 100$$

where W_0 is the original weight of the cotton fabric and W_L is the weight of the grafted fabric after each laundering cycle.

Water repellency test

Evaluations were made on the efficiency of the vinyl laurate grafting to impart a hydrophobic character to the fabric surface and the durability of the grafted fabric to repeated home laundering and tumble drying. To measure the hydrophobicity, the water contact angles of the control and treated fabrics were determined using a Surftens video contact angle goniometer (PLASMAtech Inc).

Breaking strength measurement

The breaking strength of the treated fabric was evaluated according to ASTM D 5035. The fabric strength was measured before and after plasma treatment and grafting. The relative breaking strength was calculated as the ratio of the strength of the treated fabric to the strength of the untreated fabric.

RESULTS AND DISCUSSION

Effect of microwave plasma

Figure 1(a) shows the percent weight loss of the cotton fabric treated for 240 s at increasing microwave power. In the case of the Ar plasma, the percent weight loss does not exceed 0.4% at 500 W. However, for the O_2 plasma and N_2 plasma, the percent weight loss increases with increasing microwave power. At 500 W, the percent weight loss of the fabric treated with O_2 plasma averaged 1.6%. When the microwave power was kept constant at 500 W and the exposure time of the fabric to the plasma was varied from 60 to 400 s, the O_2 plasma treatment caused a much higher weight loss (3.2%) than Ar plasma and N_2 plasma [Fig. 1(b)]. The statistical analysis showed a significant effect of the treatment time, plasma type, and microwave power on the percent weight loss of the fabric (Tables I, II).

Wong et al. investigated the effect of low temperature radiofrequency plasma (13.56 MHz) treatment of linen.[15] They found that the exposure of linen to O_2 plasma and Ar plasma at 200 W for 60 min resulted in 10.34% weight loss with O_2 plasma and 1.69% weight loss with Ar plasma. The weight loss of the plasma treated fabric is essentially due to the cleaning of the surface contaminants and etching of the fabric.

The breaking strength of the fabric before and after exposure to the plasma was measured. The original breaking strength of the untreated fabric was 52 lbf. Figure 2(a,b) shows the relative breaking strength versus the microwave power and treatment time. The statistical analysis showed no effect of the plasma type or the microwave power on the breaking strength of the fabric (Table III). However, the exposure of the fabric to the plasma for a longer period of time (>300 s) negatively affected its breaking strength (Table IV).

Surface bombardment by plasma species (electrons, ions, excited atoms) can cause breakage of cellulose macromolecule bonds. The resulting polymer fragments can easily crosslink to each other or copolymerize with other monomers. Because the plasma treatment process is limited to surface layers of the material and does not alter the bulk structure of the fabric, the fabric breaking strength is not affected. However, exposing the fabric to the plasma for a longer period of time may result in a depolymerization process; thus, a strength loss could occur.

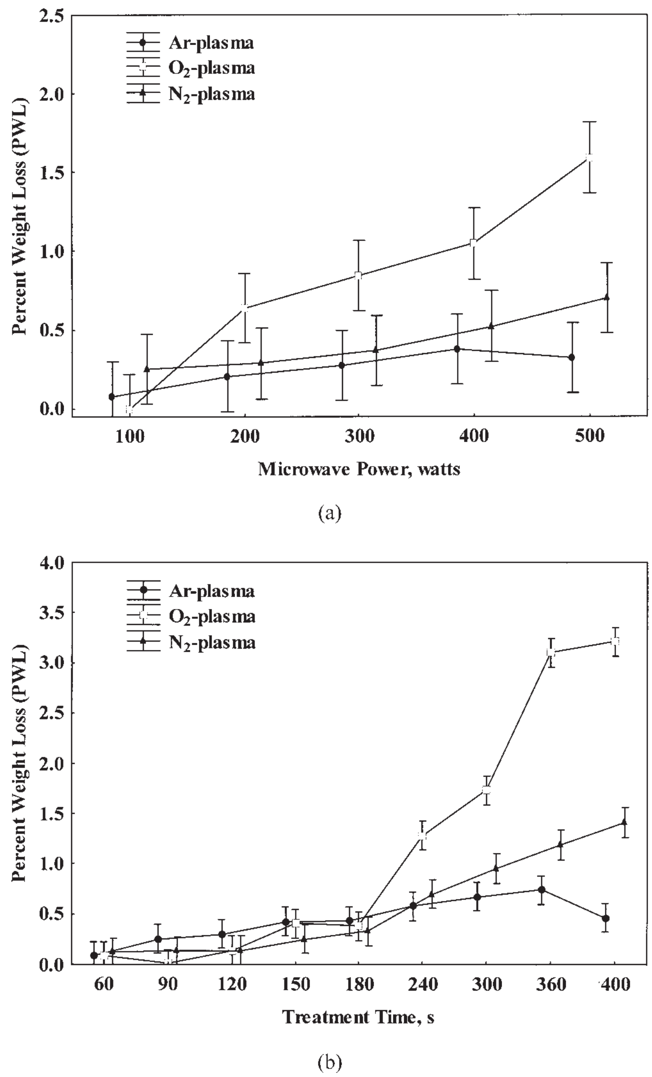

Figure 1 The percent weight loss of the cotton fabric (a) versus microwave power after Ar, O_2, and N_2 plasma treatment (2.45 GHz, 240 s) and (b) versus exposure time to Ar, O_2, and N_2 plasmas (2.45 GHz, 500 W).

Cotton fabric graft copolymerization

Plasma-induced graft copolymerization of cotton fabric was performed as detailed in previous work.[13] Because of its ability to generate more active sites to initiate the copolymerization reactions, Ar plasma was selected.[13] The efficiency of the grafting with vinyl laurate monomer was investigated by UATR-FTIR. The presence in the grafted fabric UATR-FTIR spectra of peaks at 1735, 2855, and 2923 cm^{-1} indicates that the vinyl laurate monomer was successfully copoly-

TABLE I
Variance Analysis of Effect of Type of Plasma and Microwave Power on Weight Loss of Fabric

	df	*F*	Probability	PWL
Intercept	1	310.56	0.0000001	
Gas	2	35.53	0.0000001	
O_2				0.82 a
N_2				0.43 b
Ar				0.25 c
Microwave power (W)	4	20.38	0.0000001	
100				0.11 d
200				0.38 c
300				0.50 c
400				0.65 b
500				0.87 a
Gas power	8	5.80	0.000167	
Error	30			

df, degrees of freedom; *F*, variance ratio; PWL, percent weight loss. Values followed by different letters are significantly different with $\alpha = 5\%$ (according to the Newman–Keuls test).

merized with cellulose macromolecules.[13] These peaks were attributed to —C=O stretching and $—CH_2$ symmetrical and asymmetrical stretching vibrations, respectively. Furthermore, the results showed that the vinyl laurate monomer concentration should be kept below 0.664 mol/L for maximum grafting efficiency. Above this concentration, homopolymerization reactions are likely to be dominant.

The water contact angle measurements in the first part of this series showed excellent water repellency.[13] In this second part of the series, we investigated the

TABLE II
Variance Analysis of Effect of Type of Plasma and Treatment Time on Weight Loss of Fabric

	df	*F*	Probability	PWL
Intercept	1	2750.24	0.000001	
Gas	2	247.52	0.000001	
O_2				1.15 a
N_2				0.58 b
Ar				0.44 c
Treatment time (s)	8	240.98	0.000001	
60				0.10 e
90				0.13 e
120				0.19 e
150				0.36 d
180				0.38 d
240				0.85 c
300				1.12 b
360				1.68 a
400				1.70 a
Gas treatment time	16	66.06	0.000001	
Error	54			

df, degrees of freedom; *F*, variance ratio; PWL, percent weight loss. Values followed by different letters are significantly different with $\alpha = 5\%$ (according to the Newman–Keuls test).

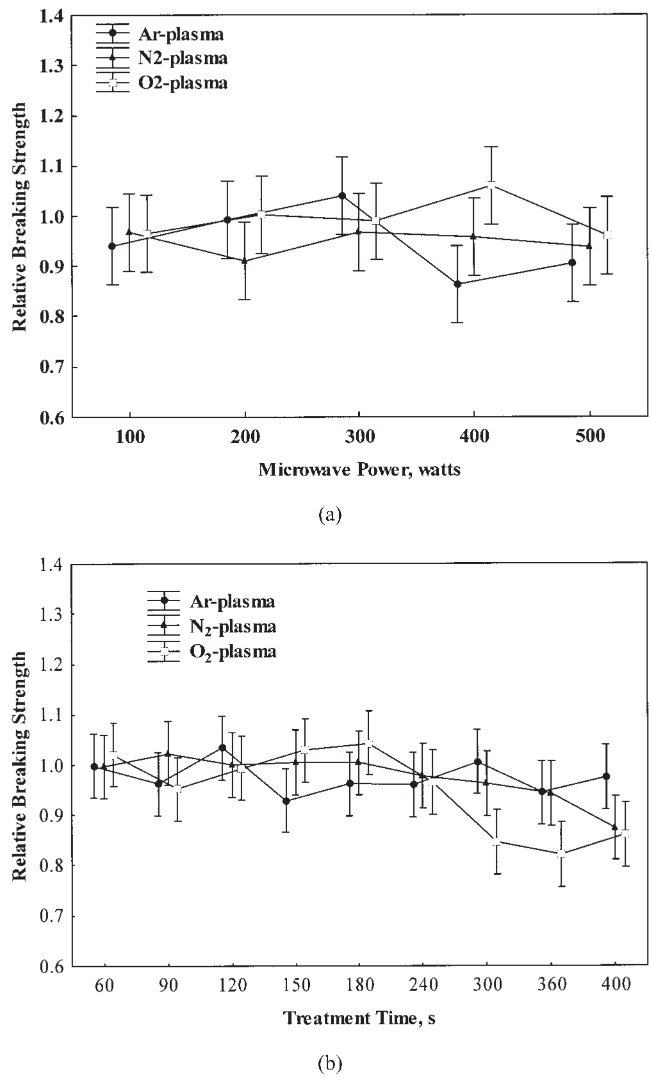

Figure 2 The relative breaking strength of cotton fabric (a) versus microwave power after Ar, O_2, and N_2 plasma treatment (2.45 GHz, 240 s) and (b) versus exposure time to Ar, O_2, and N_2 plasma treatment (2.45 GHz, 500 W).

durability of the copolymerization to repeated home laundering and tumble drying as well as the effect of grafting on the fabric strength.

Desized, scoured, and bleached 100% cotton fabrics are generally hydrophilic. The modification of the fabric surface by grafting with vinyl laurate monomers enables the introduction of aliphatic groups $[—(CH_2)_n—]$. This should impart a hydrophobic character to the fabric surface without altering the bulk properties. Hydrophobic properties of the surface are desirable for water and stain resistance, as well as for reducing the time required for drying the fabric after washing. The grafted cotton fabrics with vinyl laurate monomers were subjected to 10 cycles of home washing and tumble drying. Figure 3 shows the percent weight loss of the cotton fabric that was plasma grafted with vinyl laurate monomer. The graph also

TABLE III
Variance Analysis of Effect of Type of Plasma and Microwave Power on Relative Breaking Strength of Fabric

	df	F	Probability	Relative breaking strength
Intercept	1	9472.59	0.000001	
Gas	2	2.47	0.092980	
O_2				0.99
N_2				0.95
Ar				0.95
Microwave power (W)	4	1.10	0.363775	
100				0.96
200				0.97
300				0.99
400				0.96
500				0.93
Gas power	8	1.83	0.089760	
Error	60			

df, degrees of freedom; *F*, variance ratio.

shows the percentage grafting of each sample before laundering. A rapid weight loss during the first 3 cycles was observed (2%). This is attributed mainly to the removal of unbonded monomer or weakly bonded monomer to cellulose macromolecules. It could be also due to the removal of remaining homopolymers. After 10 washing and tumble-drying cycles, the weight does not exceed 2.5%. If we subtract from this the weight loss due to the 480-s exposure of the fabric (2 × 240 s) to the Ar plasma (2 × 0.6%), the total weight loss after

TABLE IV
Variance Analysis of Effect of Type of Plasma and Treatment Time on Relative Breaking Strength of Fabric

	df	*F*	Probability	Relative breaking strength
Intercept	1	151.29	0.000001	
Gas	2	2.22	0.112077	
O_2				0.95
N_2				0.97
Ar				0.98
Treatment time (s)	8	5.09	0.000015	
60				1.00 a
90				0.98 a
120				1.00 a
150				0.99 a
180				1.00 a
240				0.97 a
300				0.94 ab
360				0.90 b
400				0.90 b
Gas time	16	2.43	0.003026	
Error				

df, degrees of freedom; *F*, variance ratio. Values followed by different letters are significantly different with $\alpha = 5\%$ (according to the Newman–Keuls test).

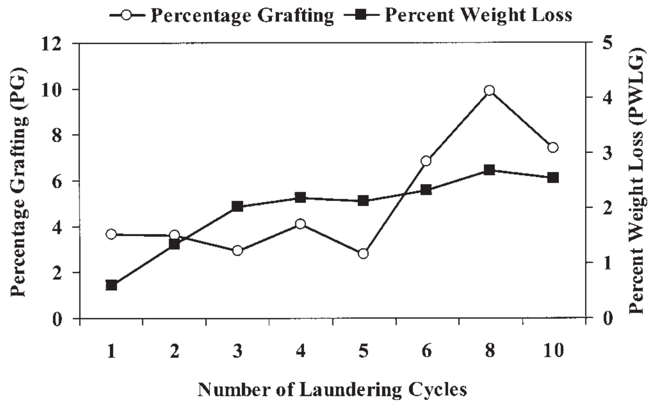

Figure 3 The percentage grafting and percent weight loss versus home laundering cycles for cotton fabric plasma grafted with vinyl laurate monomer.

10 cycles does not exceed 1.3%. In order to determine whether the weight loss observed is related to the amount of vinyl laurate monomer grafted, the UATR-FTIR spectra were recorded before and after laundering on each sample. Figure 4 shows the spectra of the control cotton fabric and the fabric treated with vinyl laurate before and after 10 repeated laundering cycles. The presence of the peaks located at 1735, 2855, and 2923 cm^{-1} indicates that the vinyl monomers are still grafted on the cellulose macromolecules after 10 subsequent laundering and tumble-drying cycles. To obtain the integrated intensity of each peak (I_{1735} and $I_{2855+2923}$), the peak at 1735 cm^{-1} was integrated from 1764 to 1682 cm^{-1} and the peaks at 2855 and 2923 cm^{-1} were integrated together from 3003 to 2746 cm^{-1}. Figure 5 shows the evolution of the relative integrated intensity (RI_{1735} and $RI_{2855+2923}$) during laundering and tumble drying of the grafted samples.

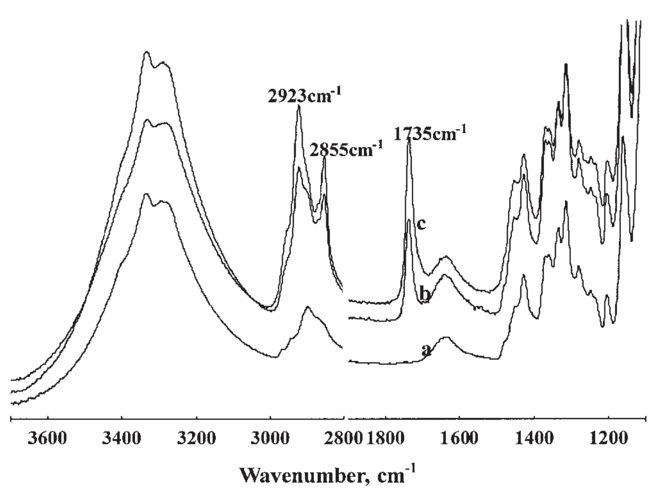

Figure 4 Universal attentuated total reflectance FTIR spectra of (a) control, (b) vinyl laurate grafted fabric before laundering, and (c) vinyl laurate grafted fabric after 10 laundering cycles.

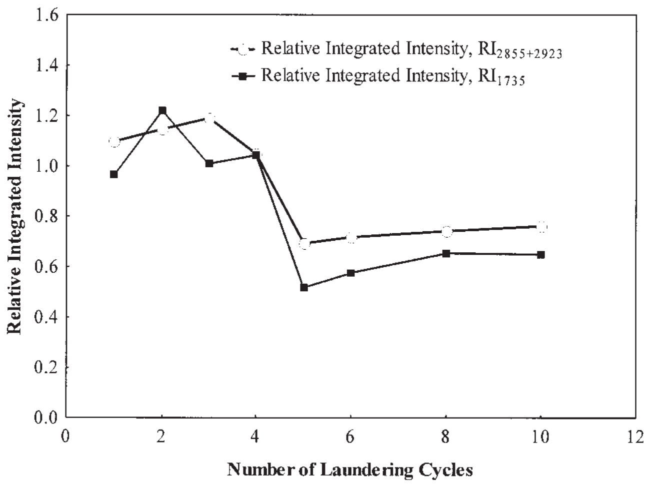

Figure 5 The effect of the number of laundering cycles on the relative integrated intensities (RI_{1735} and $RI_{288+2923}$).

TABLE VI
Variance Analysis of Effect of Number of Washing Cycles on Relative Integrated Intensity ($RI_{2855+2923}$)

	df	*F*	Probability	$RI_{2855+2923}$
Intercept	1	513.04	0.000001	
Washing cycles	7	3.42	0.007656	
1				1.10 ab
2				1.14 a
3				1.19 a
4				1.04 abc
5				0.69 c
6				0.72 c
8				0.74 bc
10				0.76 bc
Error	32			

df, degrees of freedom; *F*, variance ratio; $RI_{2855+2923}$, relative integrated intensity. Values followed by different letters are significantly different with $\alpha = 5\%$ (according to the Duncan test).

Here, the relative integrated intensity is the ratio of the integrated intensity after laundering to the integrated intensity before laundering. The graph shows that, during the first four washing cycles, the amount of grafted vinyl laurate is not affected. However, there is a significant decrease of the peak intensities I_{1735} (with $\alpha = 5.6\%$) and $I_{2855+2923}$ between the first cycle and 5 washing cycles (Tables V, VI). No further changes are observed after 5 washing cycles. Although there is a significant decrease in the amount of vinyl laurate grafted during laundering, these results suggest that the efficiency of the treated fabric to impart hydrophobic properties may not be affected.

The relationship between the water contact angles and the number of home laundering cycles is shown in Figure 6. Clearly, the water contact angles are not affected by repeated home laundering, which means that the ability of the fabric to repel water is not affected. Indeed, a statistical analysis of variance did not show any significant effect of the number of home laundering cycles on the water contact angles (Table VII). This indicates that the grafting of vinyl laurate monomer on the cotton fabric surface using Ar plasma activation is durable to washing throughout 10 washing cycles.

The average relative breaking strength of the fabric treated with Ar plasma is 0.93 and that of the fabric grafted with vinyl laurate monomer is 0.88. It should be pointed out that the plasma-induced grafting of vinyl laurate involved[13] an initial pretreatment of the fabric with Ar plasma at 500 W for 240 s, impregnating the fabric in the monomer solution, drying the impregnated fabric, and a second treatment with Ar plasma at 500 W for 240 s. Consequently, the fabric is exposed to the Ar plasma for 480 s, which results in

TABLE V
Variance Analysis of Effect of Number of Washing Cycles on Relative Integrated Intensity (RI_{1735})

	df	*F*	Probability	RI_{1735}
Intercept	1	182.41	0.000001	
Washing cycles	7	2.24	0.056497	
1				0.96
2				1.22
3				1.00
4				1.04
5				0.52
6				0.58
8				0.65
10				0.65
Error	32			

df, degrees of freedom; *F*, variance ratio; RI_{1735}, relative integrated intensity. Values followed by different letters are significantly different with $\alpha = 5\%$ (according to the Duncan test).

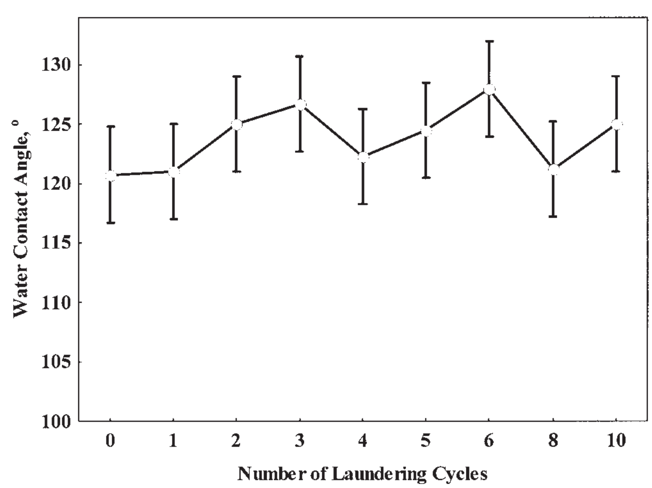

Figure 6 The effect of the number of laundering cycles on the water contact angle of cotton grafted with vinyl laurate monomer.

TABLE VII
Variance Analysis of Effect of Number of Washing Cycles on Water Contact Angle of Treated Cotton Fabrics with Vinyl Monomer

	df	*F*	Probability	Water contact angle (°)
Intercept	1	35830.10	0.000001	
Washing cycles	8	1.81	0.119109	
0				121
1				121
2				125
3				127
4				122
5				125
6				128
8				121
10				125
Error	27			

df, degrees of freedom; *F*, variance ratio.

higher strength loss. Therefore, the strength loss may be due to higher exposure time to the plasma rather than to grafting with vinyl monomer.

It is remarkable, though, that the strength loss documented in this study is very low when compared to the strength loss obtained by treating the fabric with traditional textile finishing resin. In that case, the strength loss can exceed 50%.[16] Further investigations will involve the optimization of plasma treatment conditions to maximize grafting efficiency while retaining the original physical properties of the cotton fabric.

CONCLUSIONS

The effects of plasma treatment on the physical properties of lightweight cotton fabric were investigated. Oxygen, nitrogen, and argon plasmas were generated under a vacuum by means of a microwave generator at 2.45 GHz. The results showed that O_2 plasma generated higher weight loss than N_2 and Ar plasmas. The fabric breaking strength was not affected by the microwave power or by the type of plasma. However, longer exposure time to the plasma may result in significant strength loss that is due to excessive etching and depolymerization. Plasma-induced grafting of vinyl laurate monomer on the fabric surface resulted in stable cellulose–vinyl laurate copolymers. Water contact angle measurements after repeated home laundering did not show any significant effect on the water repellency of the grafted cotton fabric. The fabric strength losses with plasma treatment were only a fraction of the losses experienced with traditional textile finishing resin.

The authors thank the Texas Food and Fibers Commission for providing the financial support for this project.

References

1. Bhat, M. V.; Benjamin, Y. N. Textile Res J 1999, 69, 38.
2. Yasuda, T.; Gazicki, M.; Yasuda, H. J Appl Polym Sci Appl Polym Symp 1984, 38, 201.
3. Wong, K. K.; Tao, X. M.; Yuen, C. W. M.; Yeung, K. W. Textile Res J 1999, 69, 846.
4. Radetic, M.; Jocic, D.; Jovancic, P.; Trajkovic, R. AATCC Rev 2000, 32, 55.
5. Vitta, S. B.; Stahel, E. P.; Stannett, V. T. J Macromol Sci-Chem 1985, A22, 579.
6. Sharma, V. N.; Daruwalla, E. H. Textile Res J 1976, 46, 398.
7. Arthur, Jr., J. C. J Macromol Sci-Chem 1970, A4, 1057.
8. Lepoutre, P.; Hui, S. H.; Robertson, A. A. J Appl Polym Sci 1973, 17, 3143.
9. Ward, T. L.; Jung, H. Z.; Hinojosa, O.; Benerito, R. R. Surface Sci 1978, 76, 257.
10. Pavlath, A. E. In Techniques and Applications of Plasma Chemistry; Hollahan, J. R.; Bell, A. T., Eds.; Wiley: New York, 1974.
11. Jung, H. Z.; Ward, T. L.; Benerito, R. R. Textile Res J 1977, 43, 217.
12. Benerito, R. R.; Ward, T. L.; Soignet, D. M.; Hinojosa, O. Textile Res J 1981, 51, 224.
13. Abidi, N.; Hequet, E. J Appl Polym Sci 2004, 93, 145.
14. Louati, M.; Elachari, A.; Ghenaim, A.; Caze, C. Textile Res J 1999, 69, 381.
15. Wong, K. K.; Tao, X. M.; Yuen, C. W. M.; Yeung, K. W. Text Res J 1999, 69, 846.
16. Abidi, N.; Hequet, E.; Turner, C.; Sari-Sarraf, H. J Appl Polym Sci, submitted.