

# Cotton Fabric Graft Copolymerization Using Microwave Plasma. I. Universal Attenuated Total Reflectance–FTIR Study

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Received 8 August 2003; accepted 31 January 2004

DOI 10.1002/app.20442

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The effect of microwave plasma on lightweight cotton fabric was investigated. N<sub>2</sub>-plasma, O<sub>2</sub>-plasma, and Ar-plasma were obtained using a microwave generator at 2.45 GHz under vacuum. The universal attenuated total reflectance–Fourier transform infrared (UATR–FTIR) instrument was used to monitor the changes created after N<sub>2</sub>-, O<sub>2</sub>-, and Ar-plasma treatments. The exposure of cotton fabrics to the plasma for 240 s with a microwave power of 500 W was sufficient to create active carbonyl groups, as shown by the presence of a peak around 1725 cm<sup>-1</sup> in the FTIR spectra of the treated cotton fabrics. Ar-plasma was found to generate more active groups than N<sub>2</sub>-

and O<sub>2</sub>-plasmas. The active centers created within the cellulose chains were used to initiate copolymerization reactions with vinyl monomers to impart hydrophobic character to lightweight cotton fabric. The efficiency of the grafting process and the presence of grafted monomers on fabric surface were confirmed using UATR–FTIR. Testing of treated fabric revealed that excellent water repellency was obtained. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 145–154, 2004

**Key words:** plasma polymerization; graft copolymers; FTIR; fabrics/fibers; surface modification

## INTRODUCTION

Plasma technology is becoming more attractive for surface modifications of textile substrates.<sup>1–4</sup> Plasma is defined as a medium composed of radicals, metastable molecules, photons, and charged particles such as ions and electrons. In general, these particles are generated by exposing a gas (He, Ar, O<sub>2</sub>, N<sub>2</sub>, NH<sub>3</sub>, or a mixture of these gases) to radiofrequency or microwave electrical discharge. Because the gas remains at room temperature, the process is called cold plasma. The highly active species generated gain their energy from an imposed electric field and lose this energy through collisions with neutral molecules such as cellulose. The transfer of energy to the molecules of the substrate leads to the formation of a variety of new species that include atoms, free radicals, and ions. These are chemically active and could be the precursors that initiate a polymerization reaction when they come in contact with a monomer. The result is the formation of new stable compounds through a copolymerization process.

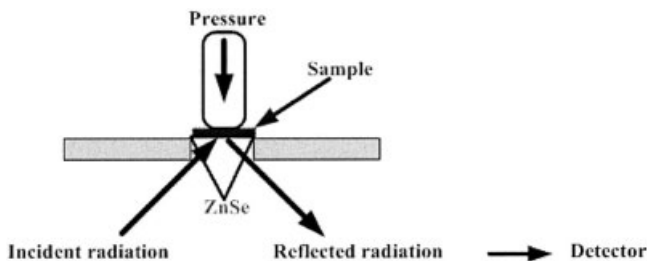
In most plasma applications, the electron discharges are produced by using either radiofrequency (1–100 MHz) or microwave (100–10<sup>4</sup> MHz) sources of power. In general, the increase in the frequency results in

higher electron energy, and thus a higher degree of ionization. The density of the reactive particles (electrons, ions, free radicals) in the plasma is of particular interest. The effect of frequency ( $\nu$ ) on the plasma density ( $n$ ) is given by the formula:  $n = A\nu^2$  ( $A$  is constant). The degree of ionization increases with increasing frequency; thus microwave frequency plasma produces a higher density than that produced by radiofrequency plasma. Thus the advantage of microwave-generated plasma (2450 MHz) compared to conventional radiofrequency-generated plasma (13.56 MHz) lies in a more effective plasma generation, resulting in a faster processing time for surface treatment and/or surface activation.

The plasma technology is constituted of three different processes: (1) Modification of the surface structure of the material itself, under the influence of the glow discharge. This is done primarily with nonpolymerizable precursors such as noble gases, nitrogen, oxygen, hydrogen, ammonia, or water vapor. (2) Deposition of a thin film of polymer on the surface of the material by means of organic, organo-silicone, or organo-metallic vapors. This is referred to as plasma polymerization. (3) Grafting of molecules on the material surface after plasma activation. This is referred to as plasma grafting. The advantage of the plasma treatment over the wet chemistry is that the effects of the plasma do not penetrate more than 100 Å from the surface.<sup>1</sup> Because the bulk of the material is not affected by the treatment, desirable structural characteristics are maintained.

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Contract grant sponsor: Texas Food and Fibers Commission.



**Figure 1** Principle of universal attenuated total reflectance-Fourier transform infrared (UATR-FTIR) instrument.

For many years, the method used to graft monomers on the cellulosic fabric was based on the use of catalysts (such as ceric ion) as initiators of the copolymerization between cellulose and the monomer.<sup>5-8</sup> The chief drawback of these methods is the generation of highly toxic wastes.

Several studies have been conducted using radio-frequency plasma process as a tool for textile substrate modification.<sup>9-12</sup> With this technology, active radical centers are introduced within the cellulose chain and used as initiators for subsequent copolymerization with other monomers. Very limited investigation, however, has been reported on the use of 2.45-GHz microwave generator plasma for cotton fabric surface modification. This article reports on preliminary results obtained from the use of microwave plasma for lightweight cotton fabric activation and grafting.

The universal attenuated total reflectance-Fourier transform infrared (UATR-FTIR) instrument was used as a fast and nondestructive technique to monitor the changes resulting from the plasma treatment and grafting with vinyl monomer [ $\text{CH}_3-(\text{CH}_2)_{10}-$

$\text{COO}-\text{CH}=\text{CH}_2$ ]. This monomer was chosen to impart hydrophobic properties to the cotton fabrics.

## EXPERIMENTAL

### Materials

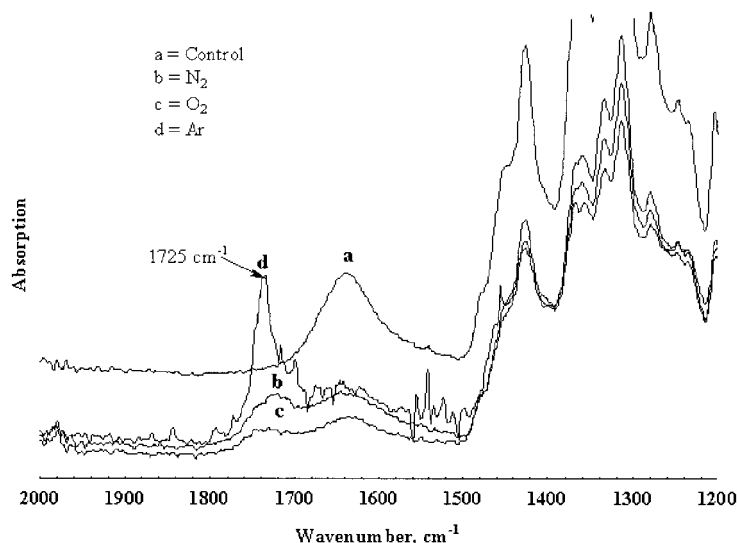
The 100% cotton fabric used in this study was desized, scoured, and bleached. Its construction was 100 ends, 85 picks, yarn count  $16.4 \times 14.8$  tex ( $36 \times 40$  English count), and its weight was  $118.7 \text{ g m}^{-2}$  ( $3.5 \text{ oz. yd}^{-2}$ ). Nitrogen, oxygen, and argon gases were commercial grade. Vinyl laurate [ $\text{CH}_3-(\text{CH}_2)_{10}-\text{COO}-\text{CH}=\text{CH}_2$ ] monomer was purchased from Sigma-Aldrich Co. (St. Louis, MO) and used as received.

### Plasma system

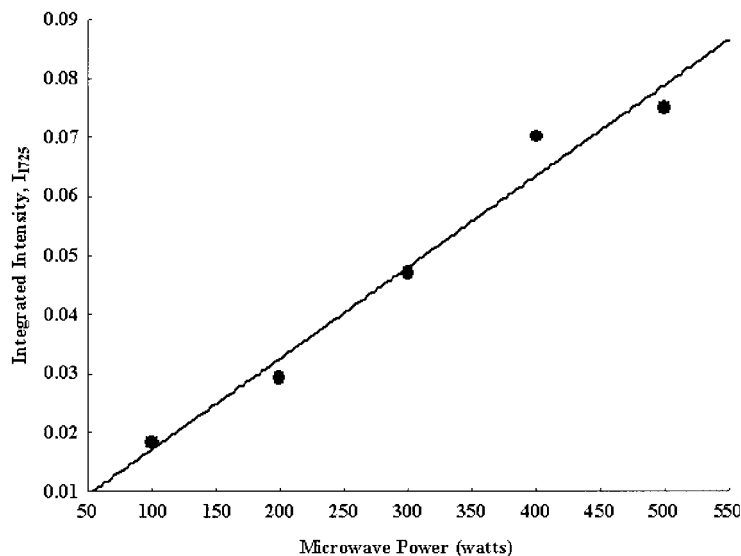
The plasma process chamber measured  $25.4 \times 25.4 \times 25.4$  cm (width  $\times$  depth  $\times$  height). The microwave generator (2.45 GHz) was a regulated magnetron with variable power up to 600 W. This plasma system had a microcontrol processor with LCD display, allowing programming of 10 main processes. The system possessed two gas channels with mass flow controller and magnetic valves for programmed, automatic precise gas flow in the process chamber. Another needle valve allowed injection of corrosive gas in the chamber if needed.

### Cotton fabric treatment

Cotton fabric samples were cut into  $9.8 \times 11$  cm pieces and placed in the plasma chamber in a horizontal position on a perforated screen. The plasma chamber was



**Figure 2** FTIR spectra of (a) control, (b)  $\text{N}_2$ -plasma-treated, (c)  $\text{O}_2$ -plasma-treated, and (d) Ar-plasma-treated samples (2.45 GHz, 240 s, 500 W).



**Figure 3** Integrated intensity of the peak at  $1725\text{ cm}^{-1}$  versus microwave generator power (2.45 GHz, 240 s).  $I_{1725}(\text{Ar}) = 0.002 + 0.0002 \times \text{power}$ ; 0.95 confidence interval (CI),  $R^2 = 0.985$ .

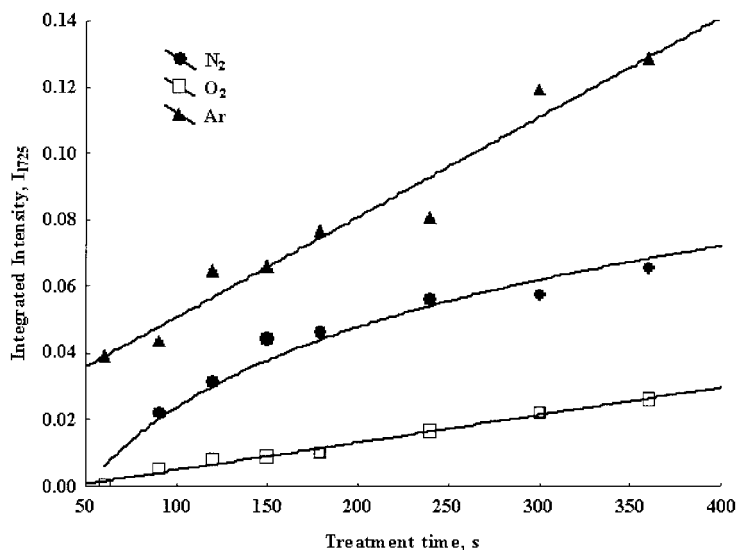
first pumped down to 0.187 Torr (25 Pa) then the gas was injected automatically by opening the gas valves. The mass flow controller allowed accurate control of the gas flow in the chamber, which was kept at 60 mL/min.

To investigate the effect of the nature of the gas, the treatment time, and the microwave generator power, three gases were used ( $\text{N}_2$ ,  $\text{O}_2$ , Ar). The treatment time was varied from 30 to 360 s and the microwave power was varied from 100 to 500 W.

#### Cotton fabric grafted with vinyl monomer

Because of the nonsolubility of the vinyl laurate in water, hexane was used as a solvent to prepare the

monomer solutions with different concentrations. The plasma-pretreated fabrics were immediately immersed in the monomer solution of various concentrations for 1 h and then air-dried. These samples were then placed again in the plasma chamber and treated with microwave plasma. Finally, the treated fabrics were soaked in water several times to remove the ungrafted portion of the original monomer and the homopolymers. The pretreatment allowed cleaning of the fabric surface, increasing hydrophilicity of the surface, and creating active sites for initiation of the copolymerization of cellulose with the monomer. In the second treatment, treatment of both the fabric and the monomer in the chamber resulted in maximum copo-



**Figure 4** Integrated intensity of the peak at  $1725\text{ cm}^{-1}$  versus plasma treatment time,  $t$  (2.45 GHz, 500 W).  $I_{1725}(\text{N}_2) = -0.1366 + 0.0802 \times \log_{10}(t)$ ,  $R^2 = 0.98$ ,  $I_{1725}(\text{O}_2) = -0.0035 + (8.2878 \times 10^{-5})t$ ; 0.95 CI,  $R^2 = 0.991$ ;  $I_{1725}(\text{Ar}) = 0.021 + 0.0003t$ ; 0.95 CI,  $R^2 = 0.979$ .

**TABLE I**  
Variance Analysis: Effect of Type of Plasma Gas and Treatment Time on Intensity of the Carbonyl Band

Parameter	$df^a$	$F^a$	Probability	$I_{1725}^b$
Intercept	1	1123.66	0.000001	
Gas	2	214.18	0.000001	
O <sub>2</sub>				0.012 a
N <sub>2</sub>				0.040 b
Ar				0.077 c
Treatment time	7	30.9	0.000001	
Gas × treatment time	14	4.33	0.000067	
Error	48			

<sup>a</sup>  $df$ , degrees of freedom;  $F$ , variance ratio.

<sup>b</sup> Values not followed by the same letter are significantly different with  $\alpha = 5\%$  (according to the Newman-Keuls test).

**TABLE II**  
Variance Analysis: Effect of Type of Plasma Gas and Postplasma Time on Intensity of the Carbonyl Band

Parameter	$df^a$	$F^a$	Probability	$I_{1725}^b$
Intercept	1	1147.97	0.000001	
Gas	2	229.56	0.000001	
O <sub>2</sub>				0.0069 a
N <sub>2</sub>				0.0414 b
Ar				0.0653 c
Time postplasma	5	4.71	0.00205	
Gas × time postplasma	10	0.88	0.5542	
Error	36			

<sup>a</sup>  $df$ , degrees of freedom;  $F$ , variance ratio.

<sup>b</sup> Value not followed by the same letter are significantly different with  $\alpha = 5\%$  (according to the Newman-Keuls test).

lymerization. Three independent replications were performed and nine FTIR spectra were acquired, totaling 27 spectra for each monomer concentration. All grafted fabrics were conditioned 12 h at  $65 \pm 2\%$  relative humidity and  $21 \pm 1^\circ\text{C}$  before the FTIR measurements.

### Evidence of fabric modification and grafting

#### FTIR measurements

The Spectrum-One (from Perkin Elmer Cetus Instruments, Norwalk, CT), equipped with a UATR-FTIR instrument, was used to acquire the FTIR spectra of the treated fabrics. The UATR consists of a ZnSe crystal that allows collecting the FTIR spectra directly from the sample without any special preparation (Fig. 1). The treated cotton fabric sample was placed on the

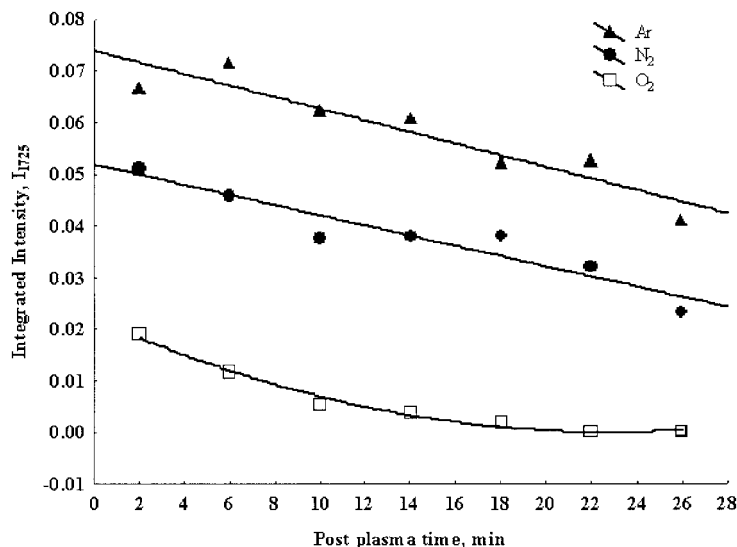
top of the ZnSe crystal, to which pressure was applied, to ensure a good contact with the incident IR beam and to prevent loss of the IR incident radiation. The IR spectra were collected using 32 scans with  $4 \text{ cm}^{-1}$  resolution between 650 and  $4000 \text{ cm}^{-1}$ .

#### Percentage grafting and grafting rate

The percentage grafting (PG) was calculated as follows<sup>13</sup>:

$$\text{PG} = \frac{(W_1 - W_0)}{W_0} \times 100$$

where  $W_0$  is the dry weight of the cotton fabric before grafting and  $W_1$  is the dry weight of the fabric after



**Figure 5** Change of carbonyl band during storage of the plasma-treated cotton fabric in laboratory conditions of  $21^\circ\text{C}$  and 65% relative humidity (2.45 GHz, 240 s, 500 W).  $I_{1725}(\text{Ar}) = 0.0738 - 0.0011t$ ; 0.95 CI,  $R^2 = -0.919$ ;  $I_{1725}(\text{N}_2) = 0.0518 - 0.001t$ ; 0.95 CI,  $R^2 = -0.937$ ;  $I_{1725}(\text{O}_2) = 0.0219 - 0.0019t + (4.246\text{E-}5)t^2$ ; 0.95 CI,  $R^2 = 0.985$ .

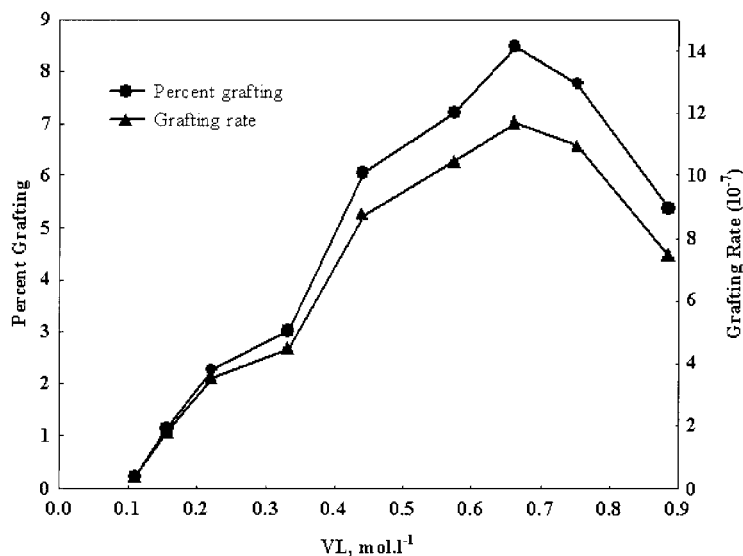


Figure 6 Variation of the percentage of grafting and the rate of grafting with the monomer concentration.

grafting, rinsing, and drying. The grafting rate was calculated using the following formula<sup>13</sup>:

$$GR = \frac{(W_1 - W_0) \times 1000}{(W_m t V)}$$

where  $W_m$  represents the molecular weight of the monomer,  $t$  is the reaction time (in s), and  $V$  is the volume of the grafting solution (in mL). The volume  $V$  is equivalent to 100 mL of hexane + volume of the monomer (varied from 2.8 to 23 mL). The grafted amount (GA) of the monomer on the fabric was also determined using the following formula<sup>14</sup>:

$$GA(\mu g/cm^2) = \frac{W_1 - W_0}{A}$$

where  $A$  is the area of the treated fabric (107.8 cm<sup>2</sup>).

#### Water repellency test

The efficiency of the treatment to impart hydrophobic character to the fabric surface was evaluated by the water repellency test and contact angle measurement. The water repellency, spray test was performed according to the AATCC Test Method 22-2001.<sup>15</sup>

The water contact angles of the control and treated cotton fabrics were evaluated using a SurfTens video

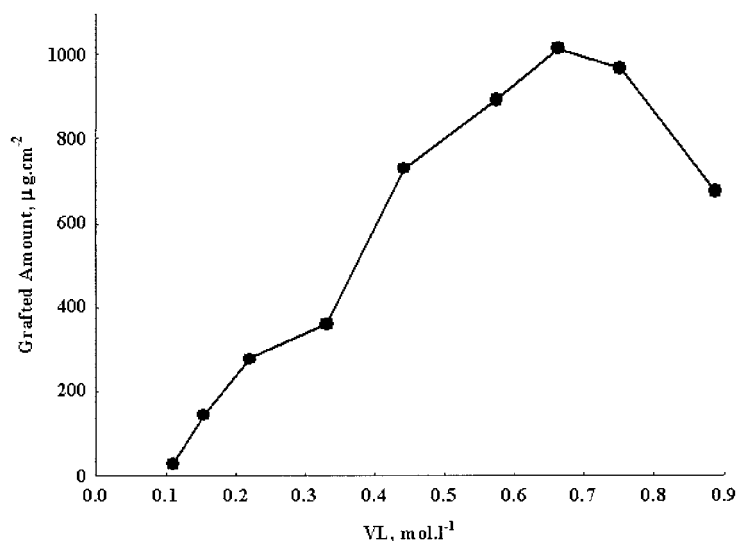
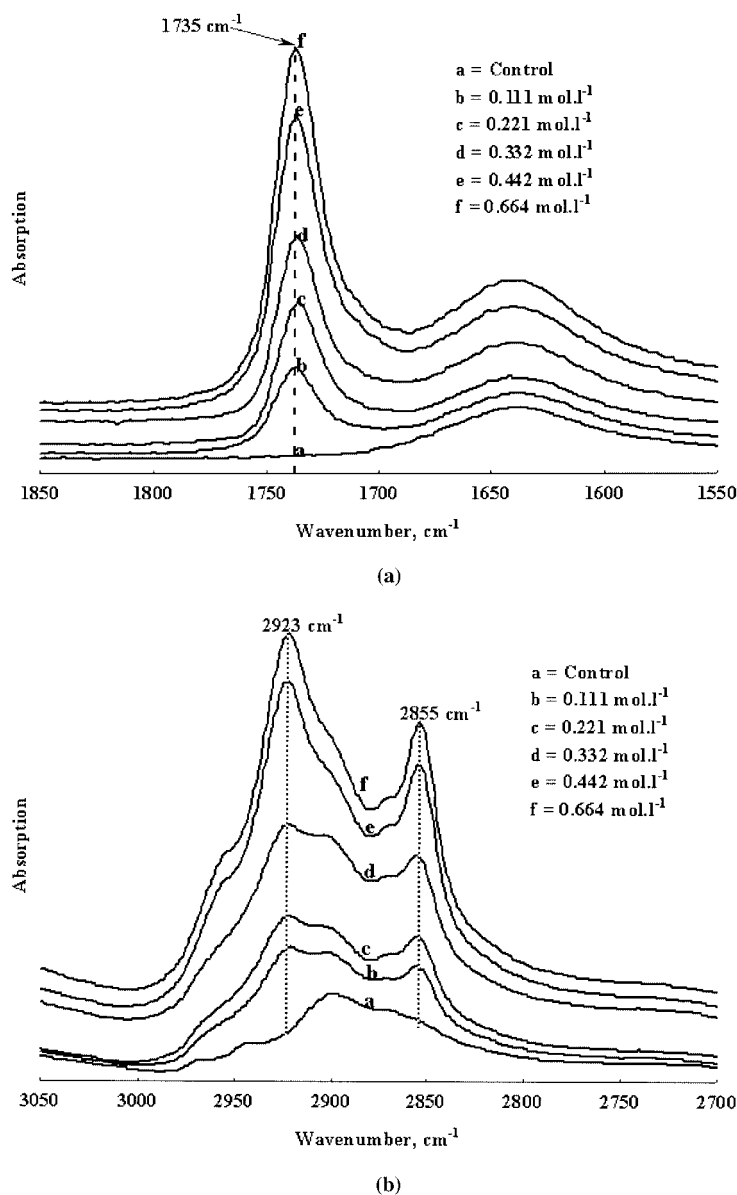


Figure 7 Variation of the amount of grafted monomer (μg cm<sup>-2</sup>) with the monomer concentration.



**Figure 8** (a) FTIR spectra of control fabric and grafted cotton fabric with increasing monomer concentration. (b) FTIR spectra of control fabric and grafted cotton fabric with increasing monomer concentration.

contact angle goniometer (PLASMAtech Inc., Erlanger, KY).

## RESULTS AND DISCUSSION

### Effect of the nature of the plasma gas

Figure 2 shows the FTIR spectra of untreated cotton fabric and treated cotton fabric with plasma of nitrogen ( $\text{N}_2$ ), oxygen ( $\text{O}_2$ ), and argon (Ar) for 240 s at microwave power of 500 W. The spectra were collected immediately after the samples were removed from the plasma chamber. The comparison between the FTIR spectra of treated and untreated cotton fabrics showed the presence of an additional peak around

1725  $\text{cm}^{-1}$ . This peak is attributed to asymmetric stretching vibration of the carbonyl band. This result is in accordance with previous work.<sup>16</sup> The authors reported that the treatment of purified cotton cellulose in radiofrequency plasma of argon, for 30 min with a power of 40 W, resulted in the creation of an additional peak in the FTIR spectra at 1724  $\text{cm}^{-1}$ , which was related to either keto or aldehyde structure. In our work, using microwave plasma of argon for 4 min with microwave power of 500 W was sufficient to activate the cotton fabric surface. This indicates a much faster processing time using microwave plasma. The presence of the additional peak in the FTIR spectra of the plasma-treated cotton fabric is an indication



of the creation of active groups on the surface. Therefore, the effect of plasma treatment on cotton fabric was assessed by observing the evolution of this carbonyl band. To obtain the integrated absorption, this peak was integrated between 1780 and 1685  $\text{cm}^{-1}$ .

Figure 3 shows the evolution of the integrated intensity of the peak at 1725  $\text{cm}^{-1}$  of treated fabric with Ar-plasma with increasing microwave generator power (100–500 W). The treatment time was kept constant at 4 min. A linear increase of the carbonyl concentration was obtained with increasing microwave generator power. In this study, for maximum plasma efficiency, the microwave generator power was kept at 500 W.

Figure 4 shows the evolution of the integrated intensity corresponding to the carbonyl group after treatment with  $\text{N}_2$ -plasma,  $\text{O}_2$ -plasma, and Ar-plasma. The data shown in this chart are averages of six independent replications. A linear increase of the carbonyl concentration was obtained with Ar-plasma and  $\text{O}_2$ -plasma. However, the treatment with  $\text{N}_2$ -plasma resulted in a logarithmic increase of the carbonyl concentration. The statistical analysis showed significant interaction between gas type and treatment time (Table I). Ar-plasma treatment generates more carbonyl groups than either  $\text{N}_2$ -plasma or  $\text{O}_2$ -plasma for a given treatment time. On average, the concentration of carbonyl groups generated by Ar-plasma is 542% higher than that generated by  $\text{O}_2$ -plasma and 93% higher than by  $\text{N}_2$ -plasma (Table I).

The decrease in the intensity of the peak corresponding to the carbonyl band, when the treated fabrics are stored in laboratory conditions at 21°C and 65% relative humidity, is shown in Figure 5 for  $\text{N}_2$ ,  $\text{O}_2$ , and Ar. The time-related decrease is attributed to the fact that most of the radicals created by plasma irradiation could be converted to peroxides.<sup>17</sup> To avoid decay caused by radicals, after exposure of the fabric to plasma, the plasma-treated fabric was immediately immersed in a monomer solution. In our study, the time between the end of the plasma process and the contact with the monomer solution was estimated to be 30 s, including 20 s for venting the plasma chamber process to the atmosphere. Therefore, the decrease in the concentration of the radicals is minimal and the copolymerization reactions with the monomer could be efficiently initiated. No significant interaction was observed between the nature of the gas and the post-plasma time (Table II).

### Cotton fabric graft copolymerization

Water-repellent lightweight cotton fabrics have the advantage of being breathable, thus allowing water vapor to pass through the fabric but not water droplets. Imparting water repellency to cotton fabric has previously been done by coating with perfluoro ester

**TABLE III**  
Variance Analysis: Effect of Vinyl Laurate Concentration on the Peak Intensity  $I_{1735}$

	$df^a$	$F^a$	Probability	$I_{1735}^b$
Intercept	1	2275.29	0.000001	
VL concentration	8	113.84	0.000001	
0.111				0.0441 e
0.155				0.0424 e
0.221				0.1806 d
0.332				0.2405 d
0.442				0.4107 c
0.575				0.5582 b
0.664				0.6681 a
0.752				0.5834 b
0.885				0.3934 c
Error	234			

<sup>a</sup>  $df$ , degrees of freedom;  $F$ , variance ratio.

<sup>b</sup> Value not followed by the same letter are significantly different with  $\alpha = 5\%$  (according to the Newman-Keuls test).

aziridines,<sup>18,19</sup> zirconium compounds,<sup>20</sup> crosslinking of fluorocarbon resins,<sup>21</sup> and by low-degree substitution of long-chain alkyl groups.<sup>22</sup> All these methods are time consuming, use wet chemistry, and may cause environmental pollution because of the use of additives and catalysts. In addition, treated cotton fabric may lose some important characteristics such as comfort.

In this study we used microwave plasma as a tool to graft vinyl laurate monomer, VL [ $\text{CH}_3-(\text{CH}_2)_{10}-\text{COO}-\text{CH}=\text{CH}_2$ ], onto the fabric surface. The objective was to create a pending hydrocarbon chains on the surface, thereby providing a hydrophobic feature to the lightweight cotton fabric surface. Furthermore, because the plasma effect does not penetrate more than 100 Å, the bulk of the cotton fabric is not affected. Consequently, the natural comfort of the cotton fabric is retained. The vinyl laurate was grafted onto the fabric surface as described in the experimental section using the following plasma conditions: treatment time was 240 s, the gas was argon, the microwave generator power was set at 500 W, and the gas flow was set at 60 mL/min. Figure 6 shows the effect of the monomer concentration in the grafting solution on the percentage grafting and the rate of grafting of the monomer. There is an increase in the percentage of grafted monomer on the fabric surface and the rate of grafting with increased monomer concentration up to 0.664 mol  $\text{L}^{-1}$ , after which a decrease occurred. This diminishing amount of the monomer grafted onto the fabric surface indicates that monomer concentration passed a point that results in homopolymerization reactions. Thus, copolymerization reactions (of the monomers with the cellulose) are crowded out by homopolymerization reactions. When the amount of grafted monomer is expressed in micrograms of monomer per

**TABLE IV**  
**Variance Analysis: Effect of Vinyl Laurate Concentration on the Peak Intensity  $I_{2855+2923}$**

	$df^a$	$F^a$	Probability	$I_{2855+2923}^b$
Intercept	1	4550.14	0.000001	
VL concentration	8	90.11	0.000001	
0.111				0.7182 f
0.155				0.8082 f
0.221				1.2542 d
0.332				1.5332 c
0.442				2.0175 b
0.575				2.5279 a
0.664				2.7370 a
0.752				2.5585 a
0.885				1.9949 b
Error	234			

<sup>a</sup>  $df$ , degrees of freedom;  $F$ , variance ratio.

<sup>b</sup> Value not followed by the same letter are significantly different with  $\alpha = 5\%$  (according to the Newman-Keuls test).

square centimeter of the treated fabric, a maximum of  $1013 \mu\text{g cm}^{-2}$  is reached for  $0.664 \text{ mol L}^{-1}$  of the monomer (Fig. 7).

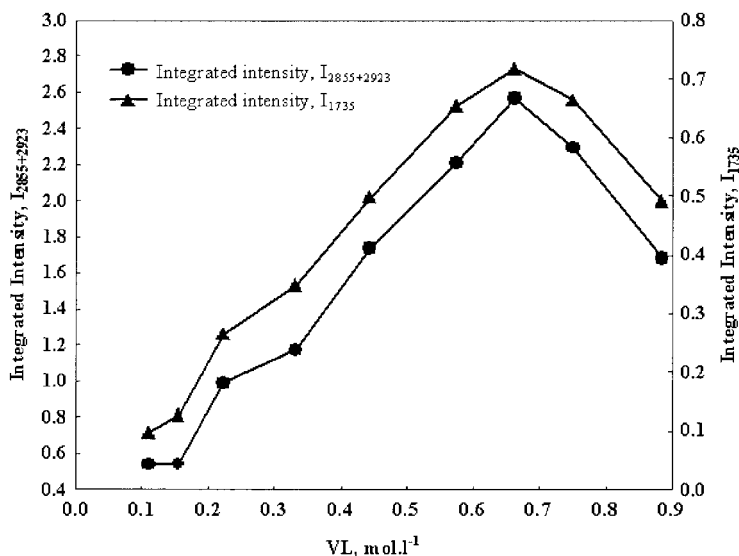
The UATR-FTIR spectra were collected directly on grafted samples without any special preparation. Figure 8(a) and (b) show the FTIR spectra of the untreated fabric and treated with vinyl laurate monomer with increasing concentration. The presence of the peaks located at  $1735$ ,  $2855$ , and  $2923 \text{ cm}^{-1}$  indicates that the vinyl laurate monomer was efficiently grafted onto the cotton fabric surface. These peaks are attributed, respectively, to  $\text{-C=O}$  stretching and  $\text{-CH}_2$  symmetrical and antisymmetrical stretching vibrations. To obtain the integrated intensity of each peak,  $I_{1735}$  and  $I_{2855+2923}$ , the peak at  $1735 \text{ cm}^{-1}$  was integrated from

$1764$  to  $1682 \text{ cm}^{-1}$  and the peaks  $2855$  and  $2923 \text{ cm}^{-1}$  were integrated from  $3003$  to  $2746 \text{ cm}^{-1}$ . The statistical analysis showed a significant effect of the vinyl laurate concentration on the peak intensities of  $1735$  and  $2855 + 2923 \text{ cm}^{-1}$  (Tables III and IV). Figure 9 shows the evolution of the integrated intensity  $I_{1735}$  and  $I_{2855+2923}$  with increasing monomer concentration. The results shown in this chart are the average of 27 measurements (3 independent replications  $\times$  9 FTIR spectra). The intensities of the two peaks increased with increasing monomer concentration up to  $0.664 \text{ mol L}^{-1}$ , then decreased. This behavior is similar to the evolution of the percentage grafting and the rate of grafting. The increase of the vinyl laurate concentration resulted in an increase of the intensities of the peaks  $1735$  and  $2855 + 2923 \text{ cm}^{-1}$ ; the coefficient of correlation ( $I_{1735}$  versus  $I_{2855+2923}$ ) was  $R^2 = 0.997$ .

Figure 10(a) and (b) show excellent correlations between the peak intensity ( $I_{1735}$ ), as determined by FTIR, and the percentage grafting, the rate of grafting, and the grafted amount. The integrated intensity of the peak  $1735 \text{ cm}^{-1}$  can be used to predict the percentage of grafting, the rate of grafting, and the amount of the monomer grafted onto the fabric surface. The following relationships were established:

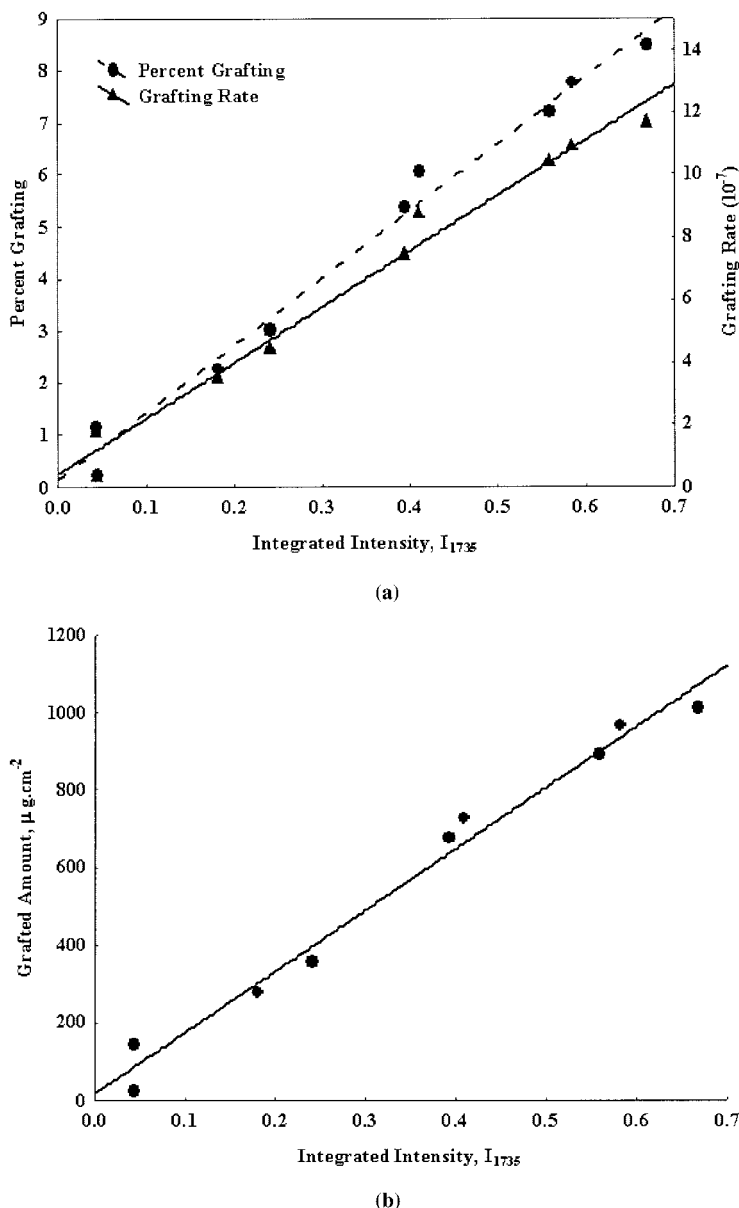
- Percentage of grafting (PG) =  $0.139 + 1292I_{1735}$ , 0.95 confidence interval (CI),  $R^2 = 0.993$ .
- Rate of grafting (RG) =  $(4.12 \times 10^{-8}) + (1.78 \times 10^{-6})I_{1735}$ , 0.95 CI,  $R^2 = 0.990$ .
- Grafted amount (GA) ( $\mu\text{g/cm}^2$ ) =  $17.22 + 1578.4I_{1735}$ , 0.95 CI,  $R^2 = 0.992$ .

The treated cotton fabrics were evaluated for water repellency by measuring the water contact angles and



**Figure 9** Integrated intensities  $I_{1735}$  and  $I_{2855+2923}$  versus monomer concentration.





**Figure 10** (a) Percentage grafting and rate of grafting versus integrated intensity  $I_{1735}$ . (b) Grafted amount versus integrated intensity  $I_{1735}$ .

performing the AATCC spray test (Table V). The untreated cotton fabric had a contact angle  $< 5^\circ$ , which means complete wetting of the fabric. As expected, high contact angles were obtained for treated fabrics. All fabrics treated with vinyl laurate ( $\geq 0.221 \text{ mol L}^{-1}$ ) exhibited contact angles  $> 90^\circ$ , which indicated that the treated fabrics possess a nonwetting surface. The fabric treated with  $0.442 \text{ mol L}^{-1}$  was rated 100 according to the AATCC spray test.

The durability of the treated fabric to repeated laundering and the effect of the treatment on fabric properties (tensile strength and abrasion resistance) are being investigated and will be published in the near future.

## CONCLUSIONS

In this study we investigated the effect of microwave plasma on lightweight cotton fabric.  $\text{N}_2^-$ ,  $\text{O}_2^-$ , and Ar-plasmas were generated using a microwave generator at 2.45 GHz under vacuum. UATR-FTIR was used to monitor the changes created after plasma treatments and showed the presence of an additional peak around  $1725 \text{ cm}^{-1}$ , which indicated the creation of carbonyl groups. Ar-plasma was found to generate more active groups than either  $\text{N}_2^-$  or  $\text{O}_2^-$  plasma. The results of grafting of cotton fabric showed that vinyl laurate could be successfully grafted onto lightweight cotton fabric, thereby producing a hydrophobic sur-

**TABLE V**  
**Contact Angle and Spray Test Rating of Treated**  
**Lightweight Cotton Fabrics with Different Vinyl Laurate**  
**Concentrations**

Monomer concentration (mol/L <sup>-1</sup> )	Contact angle (°)	Water repellency: spray test AATCC TM 22-2001
0	<5	0
0.111	<5	0
0.155	85	50
0.221	115	80
0.332	96	90
0.442	99	100
0.575	95	100
0.664	115	100
0.752	119	100
0.885	115	100

face. Furthermore, the percentage grafting, the rate of grafting, and the integrated intensities of the peak corresponding to the vinyl monomer showed that the monomer concentration should be below 0.664 mol/L for maximum grafting efficiency. Above this concentration, the homopolymerization reactions are likely to be dominant. Testing of the treated fabrics revealed that excellent water repellency was obtained.

In summary, these results indicate that efficient, well-executed copolymerization processes are achieved on lightweight cotton fabrics using microwave plasma technology. The implication is that such processes could be readily engineered to function on a commercial basis.

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

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