

## INTROMISSION OF WATER-REPELLENT AND HYDROSCOPIC PROPERTIES SIMULTANEOUSLY TO PP BY PLASMA DISCHARGE METHOD

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**Abstract** Plasma-induced surface graft copolymerization of acrylic acid on polypropylene non-woven fabric (PP-g-AA) and polypropylene membrane were reported. The extents of grafting were controlled by the plasma and polymerization condition. Hexadecyltrimethyl ammonium bromide was then coupled with the carboxyl group of PP-g-AA to obtain a polyion complex (PIC). At last,  $\text{CF}_4$  plasma was used to give PICs hydrophobic property. The moisture regain and water-repellency of the processed PICs was investigated. The surfaces were characterized using ATR FT-IR and XPS. The result indicates that the products have very high ability to adsorb moisture, even better than cotton fiber. At the same time, the products show excellent hydrophobic property, which can't be wetted by those reagents whose surface tensions were higher than 327 mN/m.

**Keywords:** Polypropylene non-woven fabric; Plasma-induced grafting; Hexadecyltrimethyl ammonium bromide;  $\text{CF}_4$  plasma treatment; Moisture sorption; Hydrophobicity.

### INTRODUCTION

One of the major functions of clothes is to protect the skin from the environment conditions, and the protection of the skin from water such as rain is a fundamental function of clothes. Hitherto, production of water-repellent fibers has been developed by using various fluorine containing polymers, silicones or polyurethanes. On the other hand, comfort with clothes is a subject that should always be kept in mind. So the ability to absorb water vapor, which comes from the body through the skin by perspiration, is another primary functional requirement for garment fibers.

In general, water-repellency is a property in contradiction with hygroscopicity. In order to render water-repellency to fibers, their surfaces must be covered with hydrophobic resins, which are hardly hygroscopic. By far, three methods have been reported to give the fibers water-repellent and hygroscopic property simultaneously by: (1) using different methods for the two faces of the fabric<sup>[1]</sup>, (2) weaving the water repellent and absorptive fibers together<sup>[2]</sup>, and (3) using the hygroscopic resin and water-repellent resin to form a sheath-core structure<sup>[3]</sup>. However, these processes couldn't fully achieve the expected purpose, and the moisture regain of the processed fibers are low comparing with natural fibers.

Radio-frequency glow-discharge plasma treatment is a frequently used method for altering the surface properties of a polymer while maintaining the beneficial physical characteristic of the bulk<sup>[4–8]</sup>. Plasma treatment can change the chemical composition of the surface, and makes the substrates hydrophilic or hydrophobic, depending on the plasma gas used. Treated by fluorocarbon plasma, the surface becomes hydrophobic and water-repellent, because fluorine has been introduced onto the surface<sup>[9, 10]</sup>. On the other hand, an abundance of radical sites can be created on the outer surface upon short exposure to plasma<sup>[6]</sup>, and these active radicals can initiate the graft polymerization of vinyl monomers. By choosing different monomers, the surface property of

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the modified polymer could be pre-devised<sup>[11]</sup>. A good many of investigations have been made to modify various substrates (*e.g.* polyethylene (PE)<sup>[12, 13]</sup>, polypropylene (PP)<sup>[11, 14]</sup>, polyamide<sup>[15]</sup>, silicon rubber<sup>[16]</sup>, poly(ethylene terephthalate) (PET)<sup>[17]</sup>, poly(tetrafluoroethylene) (PTFE)<sup>[18]</sup>, *etc.*).

In this study, a method of combining plasma-induced surface grafting copolymerization with chemical reactions was used to prepare a fabric having water-repellency and hygroscopic property simultaneously. First, polypropylene non-woven fabric was grafted with acrylic acid via argon glow discharge initiation, and then it was processed with hexadecyltrimethyl ammonium bromide (HTMA) to form polyion complex (PIC); thereafter, CF<sub>3</sub> plasma was used to treat the surface of the processed non-woven. Finally, the products were characterized using attenuated total reflection Fourier transform IR (ATR FT-IR) and X-ray photoelectron spectrometry (XPS). Water-repellency and hygroscopic property of the modified sample were measured.

## EXPERIMENTAL

### Materials and Reagents

Polypropylene non-woven fabric was afforded from Dupont China Holding Co., Ltd. Polypropylene film was the product of 6<sup>th</sup> chemical plant of Beijing. Both samples were purified by Soxhlet extraction with hot acetone for 36 h. Acrylic acid of analytical grade was obtained from Beijing Yili Chemical Factory. It was redistilled under vacuum before used. Hexadecyltrimethyl ammonium bromide of analytical grade (Beijing Chemical Reagents Corporation) and sodium hydroxide were used without further purification.

### Glow-discharge Graft Copolymerization of Acrylic acid

The experimental setup used for plasma-induced graft copolymerization was shown in Fig. 1. Plasma-induced graft copolymerization was performed by two successive processes of the surface activation of the substrates and the followed polymerization of acrylic acid monomer onto the surface.

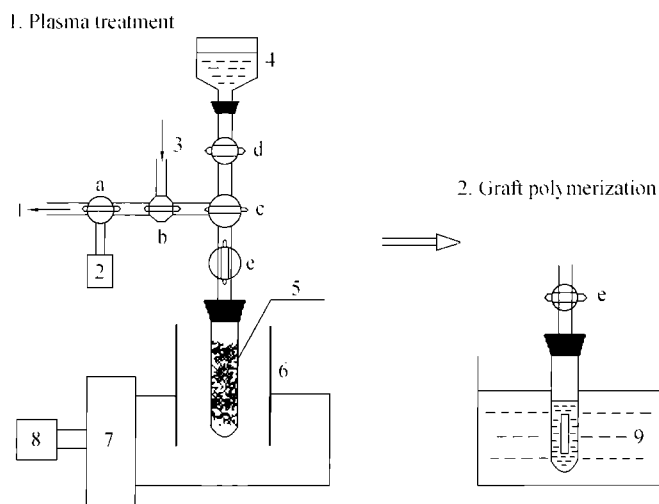


**Fig. 1** Schematic representation of the procedure and the apparatus for plasma graft polymerization

1) Vacuum line; 2) Inert gas inlet; 3) Manometer; 4) Monomer reservoir; 5) Plasma chamber; 6) Copper electrodes; 7) Matching network; 8) Radio-frequency generator; 9) Water bath  
(a), (b) and (c) three way stopcock; (d) and (e) two-way stopcock

The non-woven fabric was placed in the same position each time in the plasma chamber, which was evacuated to 0.02 torr following the introduction of argon three times before glow-discharge. Then argon glow-discharge was generated at a selected power level and for a designated period of time at 0.1 torr. After the completion of glow-discharge, stopcock "a" was closed and stopcock "d" was opened, and then about 40 mL of aqueous acrylic acid solution was admitted to the chamber immediately after the extinction of glow-discharge. Polymerization was carried out at 60°C using a water bath for a period of time. After the polymerization was

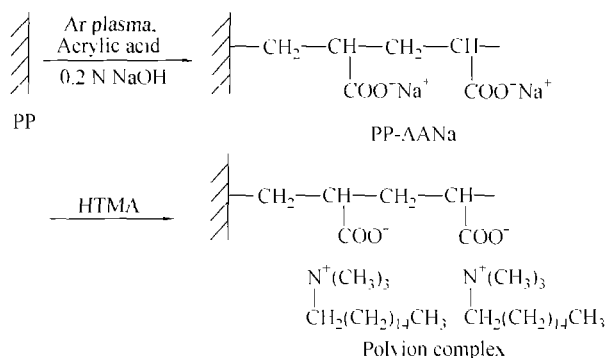
ended, the grafted non-woven fabric was rinsed in boiling deionized water to remove any attached homopolymer and monomer, and then dried at 60°C under vacuum for 24 h and weighed. The grafting yield ( $G$ , %) was calculated as follow:

$$G = (W_2 - W_1)/W_1 \times 100$$

where  $W_1$  and  $W_2$  are the weights of the non-woven fabric before and after grafting, respectively.

#### React with Hexadecyltrimethyl Ammonium Bromide

After plasma graft polymerization, the non-woven fabric was dipped into a 0.2 mol/L aqueous NaOH solution for 30 min at 60°C, to transform the acrylic acid grafted into its sodium salt. Then a polyion complex was formed by immersing these non-woven fabrics into a 0.5 wt% aqueous HTMA solution for 20 min at 75°C. The aliphatic chains were thus grafted onto non-woven fabric surface (See Scheme 1).



**Scheme 1** Schematic diagram showing the formation of polyion complex

#### CF<sub>4</sub> Plasma Treatment

The CF<sub>4</sub> plasma treatment was performed with a setup as shown schematically in Fig. 2. The frequency of plasma generator was 13.56 MHz. A Pyrex glass tube with an internal diameter of 4.5 cm and a length of 25 cm was used as plasma reaction chamber. The non-woven fabric was put on a sample plate in the chamber. The chamber was evacuated to 0.02 torr, and then CF<sub>4</sub> was passaged into the chamber to an equilibrium pressure of 0.2 torr for several minutes. The samples were then treated at the prerequisite power for a specified period of time.

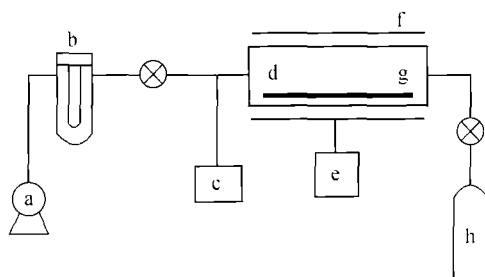


**Fig. 2** Plasma reactor syste

a) Vacuum pump; b) Cold trap; c) Manometer; d) Plasma chamber;  
e) Radio-frequency generator; f) Electrodes; g) Sample plate; h) Gas bomb

#### Surface Charaterizations

ATR FT-IR spectrum of the sample was recorded using a Bruker EQUINOX55 FT-IR spectrometer. Quantitative estimation was made by normalizing the peak intensity of C—H peak at 1456 cm<sup>-1</sup> (methyl group in PP) as an internal reference. The surface-modified PPs were also analyzed with XPS equipment (ESCALAB 220V-XL, V. G. Scientific Co.) equipped with Al K $\alpha$  X-ray source. The X-ray source was applied with 20 kV and 10 mA current intensity. For the samples that formed PIC, the core-level spectra were obtained at different

photoelectron takeoff angles of 15°, 30°, 90° with respect of sample surface; for other samples, those spectra were obtained at the photoelectron takeoff angle of 90°. Throughout the measurements, the pressure in the analysis chamber was maintained at  $9 \times 10^{-9}$  torr or lower. To compensate for the surface-changing effect, all binding energies were referenced to a C<sub>1s</sub> neutral carbon peak at 284.6 eV. The XPS peak deconvolution was performed with XPSPEAK 95 version 3.1 (XPS Peak Fitting Program for Win95 developed by Raymond W. M. Kwok, Chinese University of Hong Kong).

### Moisture Sorption and Water-repellency

Moisture regain was calculated from the weight difference between the dry and conditioned samples. The non-woven fabrics were dried at 90°C for 2 h in vacuum oven. After cooling in a P<sub>2</sub>O<sub>5</sub> desiccator, the samples were conditioned at 20°C for 24 h in a desiccator containing a saturated solution of sodium nitrite to achieve a relative humidity of 65%. The moisture regained was calculated as follows:  $M_s = [(W_b - W_a)/W_a] \times 100$ , where  $W_b$  is the conditioned samples' weight and  $W_a$  is the dry weight.

Water contact angle was the most useful measurement in evaluating the hydrophobic or hydrophilic property of material surface. But it is difficult to measure water contact angles of fabrics because their surfaces are not smooth. In this experiment the hydrophobic property of samples was characterized by checking the wettability of different reagents towards samples' surfaces. In the concrete, 10 µL different organic solvents of known surface tension were dripped onto sample surface, observing if the sample surface can be wetted by these reagents. The solvents used and their surface tensions<sup>[19]</sup> were shown in Table 1.

**Table 1.** The surface tensions of different solvents used

| Solvent                | Ethyl ether | Ethyl acetate | Toluene | Acetic anhydride | N, N-Dimethyl formamide | N-Methyl-2-pyrrolidone | Ethylene glycol | Triethanol-amine | Water |
|------------------------|-------------|---------------|---------|------------------|-------------------------|------------------------|-----------------|------------------|-------|
| Surface tension (mN/m) | 170         | 238           | 285     | 327              | 368                     | 407                    | 465             | 484              | 728   |

All the surface tensions were measured at 20°C

## RESULT AND DISCUSSION

### Relationship Between Grafting Yield and Plasma-Induced Grafting Condition

#### Glow discharge power

The grafting yield was first increased with increasing of discharge power, and reached its maximum at 120 W (Fig. 3a). The result is the same as that observed by Poncin-Epaillard *et al.*<sup>[14]</sup> whose work was concerned with the grafting of N-vinyl-2-pyrrolidone onto plasma treated PP surface. It is assumed that the increase of discharge power will result in the production of more active species on the sample surface, but higher discharge power will make plasma etching more and more prominent, which will result in the deactivation of active species, so the grafting yield will be considerable reduced.

#### Glow discharge time

The grafting yield was increased with the prolongation of glow discharge time, and then leveled off, and become constant when the glow discharge time was sufficiently long (Fig. 3b). The same phenomenon was observed in the grafting process by Hsiue *et al.*<sup>[13]</sup>. The leveling off of the grafting yield could be attributed to the attainment of equilibrium between the production and deactivation of active species when glow discharge time was long enough.

#### Grafting time

Under a fixed glow discharge condition, the grafting yield was also increased with the length of exposure to acrylic acid monomer (Fig. 3c), and reached a constant value when the time was long than 12 h.

#### Monomer concentration

The dependence of monomer concentration on grafting yield is revealed in Fig. 3(d). The grafting yield was increased with increasing monomer concentration. An autoacceleration behavior, typical of the well-known gel

effect, was observed when the monomer concentration was higher than 10 wt%. As the monomer concentration was over 30 wt%, the system became so viscous that monomer can't diffuse freely, and the change of grafting yield became less significant.

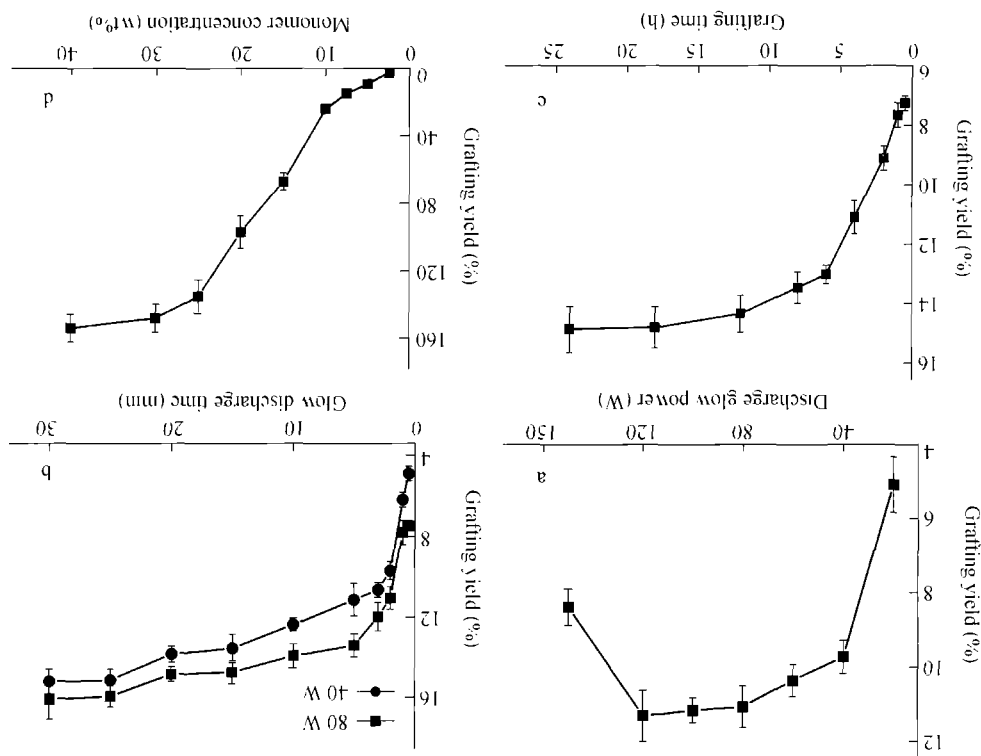


**Fig. 3** Relationship between grafting yield of acrylic acid onto PP non-woven fabric and plasma-induced grafting conditions  
a) Glow discharge power (2 min glow discharge time, 20 wt% monomer concentration and 4 h grafting time); b) Glow discharge time (80 W glow discharge power, 20 wt% monomer concentration and 4 h grafting time); c) Grafting time (80 W glow discharge power, 2 min glow discharge time and 20 wt% monomer concentration); d) Monomer concentration (80 W glow discharge power, 2 min glow discharge time and 4 h grafting time)

### CF<sub>4</sub> Plasma Treatment Condition

CF<sub>4</sub> plasma treatment was an efficient method to bestow hydrophobic property to a material's surface. When the PP films were processed by CF<sub>4</sub> plasma, an C—F stretching vibration absorption band will appear at 1250 cm<sup>-1</sup>. The relative absorbance of C—F bond at 1250 cm<sup>-1</sup> against C—H bond at 2950 cm<sup>-1</sup> was employed to measure the fluorine concentration in this experiment. The result is shown in Table 2.

**Table 2.** The Relationship between Fluorine concentration and CF<sub>4</sub> plasma condition

| Power (W) | Discharge time (min) | $A_{1250}/A_{2950}$ |
|-----------|----------------------|---------------------|
| 100       | 30                   | 2.37                |
| 100       | 15                   | 2.45                |
| 100       | 5                    | 0.94                |
| 200       | 10                   | 1.91                |
| 150       | 10                   | 1.87                |
| 100       | 10                   | 1.96                |
| 50        | 10                   | 0.64                |
| —         | —                    | 0                   |

$A_{1250}/A_{2950}$  was calculated by the absorbencies at 1250 and 2950 cm<sup>-1</sup> from ATR-FTIR measurement.

Under a fixed glow discharge time of 10 min, the absorbance of C—F bond and  $A_{1250}/A_{2950}$  were all increased with the increasing of discharge power first, and then became constant above 100 W. The absorbance ratio was also increased with the extending of glow discharge time, and then the change became indistinctive over 15 min. So the  $\text{CF}_4$  plasma treatment condition was fixed at 100 W and 15 min discharge time.

### Surface Characterizations

The ATR-FTIR spectra of PP-g-AA non-woven fabrics exhibit three new absorption bands at *ca.* 3000, 1712 and  $1255\text{ cm}^{-1}$  which correspond to the O—H, C=O and C—O of the carboxyl groups, respectively (Fig. 4). The intensities of these peaks increase significantly with increasing of degree of grafting. After the fabric was treated with NaOH solution, the carbonyl band shift from  $1712\text{ cm}^{-1}$  to  $1560\text{ cm}^{-1}$ , indicating that the carboxyl group of AA was transformed into its sodium salt. After the formation of PIC, the absorption band of C—H was increased, because HTMA was coupled with the carboxyl group on PP-g-AA. The samples treated by  $\text{CF}_4$  plasma showed a new absorption band at  $1240\text{ cm}^{-1}$  corresponding to C—F band vibration. This spectroscopic evidence indicates that fluorine has been introduced onto the sample surface (Shown in Fig. 5).

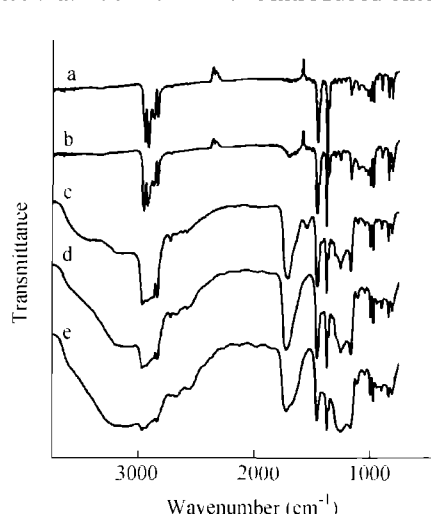


**Fig. 4** ATR FT-IR spectra of PP-g-AA non-woven fabric at vary grafting yield  
a) PP; b) Ar plasma treatment; c) 12.5% grafting yield PP-g-AA; d) 36.15% grafting yield PP-g-AA; e) 68.75% grafting yield PP-g-AA

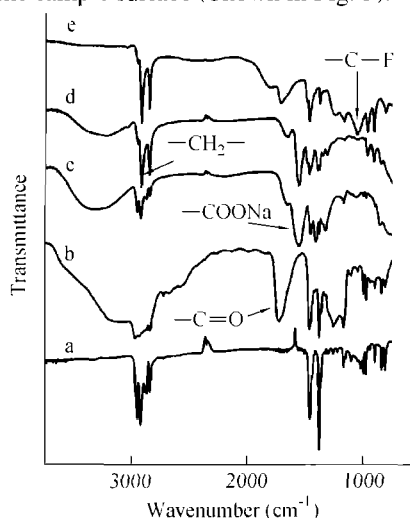


**Fig. 5** ATR FT-IR spectra of the PP non-woven fabric via different process  
a) Original PP; b) AA grafted (36.15% grafting yield); c) NaOH processed; d) HTMA processed; e)  $\text{CF}_4$  plasma treated.

The changes in the chemical structure of the surface-modified PPs were investigated using XPS<sup>[13, 20–22]</sup>. Figure 6 shows the XPS survey scans of PP (Fig. 6, spectrum a), PP-g-AA of grafting yield 46.3% (Fig. 6, spectrum b), PIC (Fig. 6, spectrum c),  $\text{CF}_4$  plasma treated PIC (Fig. 6, spectrum d). As expected, the PP-g-AA surface shows two peaks corresponding to  $\text{C}_{1s}$  (285 eV binding energy) and  $\text{O}_{1s}$  (532 eV binding energy). In the spectrum of PIC an additional peak at 400 eV binding energy based on  $\text{N}_{1s}$  can be found. After  $\text{CF}_4$  plasma treatment, the spectrum shows a new peak at 692 eV binding energy corresponding to  $\text{F}_{1s}$ .

The chemical compositions of the surface-modified PPs calculated from the XPS survey scan spectra are shown in Table 3. An oxygen component (37.27%) was observed on the PP-g-AA surface, due to the carboxyl of the AA grafted on the PP. As a result of reaction with HTMA, a nitrogen component (2.94%) was observed on the surface of PIC, which can be attributed to the ammonium salt attached to the  $\text{COO}^-$  of the grafted AA. After  $\text{CF}_4$  plasma treatment, the fluorine content (40.03%) occupied a considerable portion, which indicates that fluorine has been introduced onto the surface.

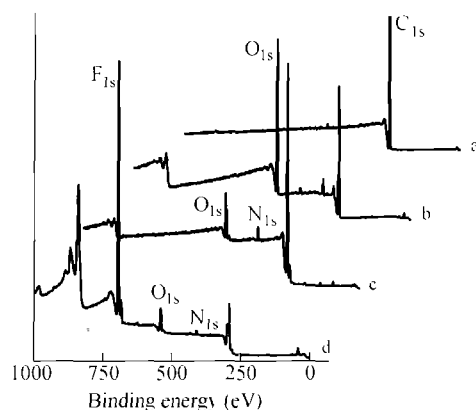


**Fig. 6** XPS survey scan spectra of PP (spectrum a), PP-g-AA of grafting yield 46.3% (spectrum b), PIC (spectrum c) and  $\text{CF}_4$  plasma treated PIC (spectrum d)

**Table 3.** Elemental composition of surface modified PP non-woven fabrics calculated from XPS survey scan spectra

| Substrates                       | Atomic composition (%) |       |      |       |
|----------------------------------|------------------------|-------|------|-------|
|                                  | C                      | O     | N    | F     |
| PP                               | 100                    | —     | —    | —     |
| PP-g-AA                          | 62.73                  | 37.27 | —    | —     |
| PIC                              | 88.44                  | 8.62  | 2.94 | —     |
| $\text{CF}_4$ plasma treated PIC | 50.06                  | 7.92  | 2.00 | 40.03 |

<sup>a</sup> The grafting yield was 46.3%

<sup>b</sup> The  $\text{CF}_4$  plasma treatment condition was 100 W, 0.2 Torr and 15 min.

To identify the composition of PIC processed PP, the XPS measurements were performed with a series of photoelectron take-off angles ( $\theta$ ). The relationship between surface atomic composition and  $\sin\theta$  was shown in Fig. 7. With the increase of  $\sin\theta$ , the concentration of oxygen and nitrogen was increased, but that of carbon was decreased. We can conclude that the PP surface is covered with hexadecyl.

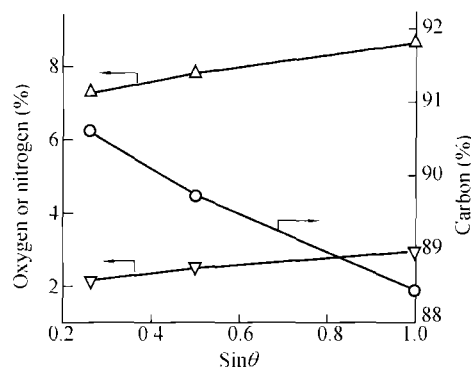


**Fig. 7** The relationship between surface atomic composition and  $\sin\theta$  by XPS measurement

The  $\text{C}_{1s}$  core-level spectra of the surface-modified PPs are shown in Fig. 8. The  $\text{C}_{1s}$  spectrum of the pristine PP surface contains only a single major peak component at 284.5 eV binding energy associated with the  $\text{CH}_2$  species. A new component at 284.5 eV binding energy associated with the  $\text{CH}_2$  species. A new peak at 288.7 eV corresponding to  $-\text{COO}$  of grafted AA was observed on the surface of grafted PP non-woven fabric. After PIC process, the peak at 288.7 eV binding energy was nearly gone, whereas a new peak due to  $\text{C}-\text{N}$  bond appeared at 285.3 eV. It suggests that a majority of carboxylic acid in the grafted AA has reacted with HTMA,

resulting in the generation of ammonium salt. In the  $\text{CF}_4$  plasma treated PIC, several new peaks with binding energy at 293.5 eV for  $\text{CF}_3$ , 291.4 eV for  $\text{CF}_2$  and 289.2 eV for  $\text{C}-\text{CF}_n$  appeared. Another new peak at 286.4 eV may be attributed to  $\text{C}-\text{CF}_2$ <sup>[22]</sup>.

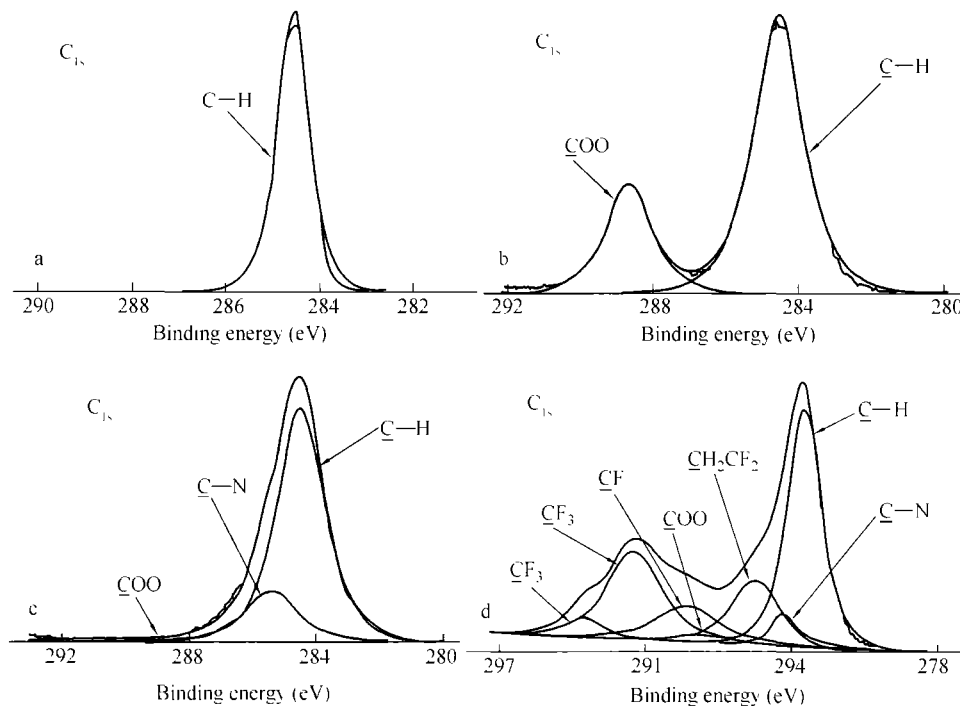


**Fig. 8** XPS  $\text{C}_{1s}$  core-level scan spectra of (a) PP, (b) PP-g-AA (46.2 wt% grafting yield), (c) PIC and (d)  $\text{CF}_4$  plasma treated PIC

### Moisture Sorption and Water-Repellence

The moisture regains of pristine PP non-woven fabric and  $\text{CF}_4$  plasma treated PICs are shown in Table 4. The pristine PP non-woven fabric is unable to absorb moisture.  $\text{CF}_4$  plasma treated PIC non-woven fabrics shows much better moisture absorbability, which increases with increasing levels of grafting. For the modified PP non-woven fabric at 97.4 wt% grafting level, its moisture regain attained 10.27% of the weight of non-woven fabric, which is much higher than that of cotton fabrics (7.32%).

**Table 4.** The difference of moisture regain between moisture sorption and desorption of the  $\text{CF}_4$  plasma treated PIC

| Sample                             | Grafting yield (%) | Moisture regain (%) |
|------------------------------------|--------------------|---------------------|
| $\text{CF}_4$ plasma treated PIC 1 | 12.5               | 1.20                |
| $\text{CF}_4$ plasma treated PIC 2 | 36.15              | 4.82                |
| $\text{CF}_4$ plasma treated PIC 3 | 68.75              | 7.43                |
| $\text{CF}_4$ plasma treated PIC 4 | 97.4               | 10.27               |
| Pristine PP                        | —                  | 0.0                 |
| Cotton                             | —                  | 7.32                |

Table 5 shows the wettability of eight solvents on the samples' surfaces. The pristine PP non-woven fabric (sample A) shows lyophobic property for the solvents whose surface tensions exceed 407 mN/m. After grafting with AA and reacting with NaOH (sample B), the non-woven fabric can be wetted by water (surface tension is 728 mN/m), and their surfaces become hydrophilic. PIC process (sample C) makes the surface hydrophobic toward solvents whose surface tensions are higher than 465 mN/m, because the surfaces are covered with hydrophobic hexadecyl. After  $\text{CF}_4$  plasma treatment (sample D-1, D-2 and D-3), the PP non-woven fabrics become very hydrophobic, but the hydrophobic property decreases with the increase of AA grafting yield. In

addition, the NaOH processed PP-g-AA non-woven fabric was treated by CF<sub>4</sub> plasma also (sample E). But this method cannot produce a satisfying hydrophobic property, and the resulting sample can still be wetted by all these solvents except water.

**Table 5.** The wettability of several solvent on the surface-modified PP non-woven fabrics

|     | Sample                                    | Grafting yield (%) | Surface tension of solvents (mN/m) |     |     |     |     |     |     |     |     |
|-----|-------------------------------------------|--------------------|------------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
|     |                                           |                    | 170                                | 238 | 285 | 327 | 368 | 407 | 465 | 484 | 728 |
| A   | Pristine PP non-woven fabric              | —                  | ×                                  | ×   | ×   | ×   | ×   | ○   | ○   | ○   | ○   |
| B   | Grafted and NaOH processed sample (A)     | 46.3               | ×                                  | ×   | ×   | ×   | ×   | ×   | ×   | ×   | ×   |
| C   | PIC processed sample (B)                  | 46.3               | ×                                  | ×   | ×   | ×   | ×   | ×   | ○   | ○   | ○   |
| D-1 | CF <sub>4</sub> plasma treated PIC 1      | 12.5               | ×                                  | ×   | ○   | ○   | ○   | ○   | ○   | ○   | ○   |
| D-2 | CF <sub>4</sub> plasma treated PIC 2      | 46.3               | ×                                  | ×   | ×   | ○   | ○   | ○   | ○   | ○   | ○   |
| D-3 | CF <sub>4</sub> plasma treated PIC 3      | 127.4              | ×                                  | ×   | ×   | ○   | ○   | ○   | ○   | ○   | ○   |
| E   | CF <sub>4</sub> plasma treated sample (B) | 46.3               | ×                                  | ×   | ×   | ×   | ×   | ×   | ×   | ×   | ○   |

× Wetttable; ○ Non-wetttable

## CONCLUSION

Treatment of PP non-woven fabric with argon plasma glow discharge followed by graft copolymerization of AA on its surface was used to prepare PP-g-AA. The graft copolymerization is affected by the glow discharge power and time, polymerization time as well as monomer concentration. HTMA was ionically immobilized on the surface of the fabric, and then CF<sub>4</sub> plasma treatment was performed. All these processes give the PP non-woven fabric with hygroscopic and hydrophobic properties simultaneously. After these treatments, their surfaces were characterized using ATR FT-IR and XPS. The modified non-woven fabric shows a high moisture regain, even higher than cotton fabrics. CF<sub>4</sub> plasma treatment makes the non-woven fabric so hydrophobic that it can't be wetted by those reagents whose surface tensions are higher than 327 mN/m.

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