

SURFACE MODIFICATION OF POLYPROPYLENE MICROFIBRE BY PLASMA-INDUCED VAPOR GRAFTING WITH ACRYLIC ACID

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Abstract The hydrophilicity, dyeing and antistatic ability of polypropylene microfibre (PPMF) were improved by plasma-induced vapor grafting with acrylic acid. The effects of plasma discharge time, power, liquid phase acrylic acid temperature and environmental temperature on grafting yield were investigated. The existence of grafted polyacrylic acid (PAA) was verified by ESCA and ATR FT-IR. The morphology of grafted PAA was directly observed by SEM. The wicking test shows that the hydrophilicity of modified PPMF is greatly enhanced. The dyeability test of modified PPMF was carried out using Dispersion Yellow. It was found that the dye uptake ratio is linear to the weight percent of grafting. The antistatic ability was indicated by specific resistance. The specific resistance of modified PPMF was reduced to $10^6 \sim 10^7 \Omega \cdot \text{cm}$, thus the antistatic ability was considerably improved.

Keywords Polypropylene microfibre (PPMF), Plasma-induced grafting, Dyeability, Antistatic ability, Hydrophilicity, Contact angle

INTRODUCTION

As an effective means, plasma technique is widely used to modify polymer surfaces. There are usually three ways to reach this goal. The first one is plasma polymerization^[1-3], in which vaporized small molecules are broken up by plasma and deposited on certain polymer surfaces to form an ultra-thin, pinhole-free functional film. This is an "atomic process"^[1], the controllability and predictability are not good. The second one is plasma surface treatment^[4-6]. This modifies the surface very well at the beginning, but its fatal shortcoming is that the effect of modification will decay with time. In recent years, plasma-induced grafting was introduced as the third way. Taking advantage of active species engendered by plasma on polymer surface, we could graft polymerized alkene monomers to polymer surfaces pretreated by plasma. By choosing different monomers, the surface property of the modified polymer could be pre-devised. It was reported that the obtained surface property was stable when time elapsed^[4, 7-9]. Thus plasma-induced grafting is a prospective method that overcomes the weakness of both plasma polymerization and plasma treatment.

Most of the reported plasma-induced grafting were achieved on the surface of polymeric films (e.g. silicone rubber^[10], polyimide^[11], poly(ethylene terephthalate) (PET)^[4], polyethylene (PE)^[7] or low-density polyethylene (LDPE)^[8] film etc.) using the liquid grafting process. That is to say, the plasma pretreated polymer was immersed into a solution of a certain monomer or pure liquid monomer after exposure to O₂ or air, after which peroxide-initiated grafting occurred. This procedure can easily acquire high grafting yield. As a result, the effect of modification is very distinctive, but the graft quantity is so large that the appearance of the modified polymer could

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alter, and the homopolymers yield during grafting would stick onto the polymer surface, which leads to extensive post-treatment. Recently, Hsieh *et al.*^[4] and Johnsen *et al.*^[8] put forward the vapor grafting method, in which the grafting was initiated directly by the free radicals on the polymer surfaces which were engendered by plasma. However extensive researches were seldom done.

Polypropylene microfibre (PPMF) is speculated to be a widely used synthetic fiber in the textile industry in the near future. Based on its large specific surface area and high inert surface property, PPMF is an ideal object of plasma-induced grafting both for scientific research and practical application. In this paper, vapor acrylic acid was grafted onto PPMF surface, a detailed influence of plasma-induced grafting conditions on grafting yield was investigated. The appearance of PPMF grafted with vapor acrylic acid seemed unchanged, but the wicking test, dyeing test and specific resistance measurement showed that great changes had occurred.

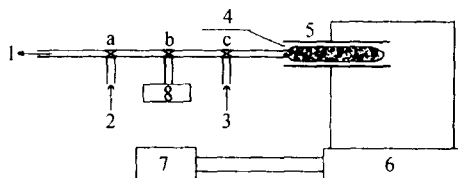
EXPERIMENTAL

Materials

Acrylic acid was obtained from Beijing Qiuxian Chemical Industry Factory. This was redistilled under vacuum (b.p. $\sim 40^\circ\text{C}$) and an inhibitor TMPO was added before use. PPMF was the product of the Chinese Sciences Silpron Corporation, with fiber specification: 75 d/72 f. Before grafting, it was boiled in a bath of 1 : 1000 dodecyl sulphonic acid sodium salt solution for 2 h, then washed with distilled water. Finally it was extracted with acetone for 36 h, and dried in a vacuum desiccator before use.

Grafting Equipment

The plasma-induced grafting system is shown as follows:



- 1) vacuum pump, 2) inert gas inlet, 3) vapor monomer inlet, 4) plasma chamber, 5) copper electrodes, 6) matching network, 7) radio-frequency generator, 8) pressure gauge, a), b) and c) vacuum stopcock

The fiber was placed in the same position each time in the plasma chamber, which was evacuated to 0.02 Torr following the introduction of Ar three times before glow discharge. Glow discharge was carried out at 0.2 Torr. After glow discharge, stopcock "a" was closed and stopcock "c" was opened, and vapor acrylic acid was introduced immediately. The grafting was carried out in a temperature controllable chest.

Measurement

Grafting ratio (abbreviated as G_r)

The weight percent of grafting was used to represent grafting ratio, it was calculated as follows:

$$G_r = (W_1 - W_0) / W_0 \times 100\%$$

where W_1 is the weight of the fiber grafted with acrylic acid, washed by distilled water, and dried to constant weight in a vacuum dessicator and W_0 is the weight of the original fiber.

Hydrophilicity

Wicking property was measured by SB-312 Type Wet Apparatus, which was designed by ICCAS, and produced by Ke-En Instrumental Company, Beijing. A detailed wicking rate test was described

in Chwastiak's report^[12].

Contact angle was calculated by Chwastiak's method^[8] from the result of wicking curve:

$$\cos\theta = [64(1 - \varepsilon)^2 H^2 P \rho_f \eta] / [\gamma K^2 \varepsilon^3 V_T W_f d_f \rho_f^2] \times (m^2 / t) \quad (1)$$

The meaning of each parameter was explained in Chwastiak's work^[12]. In this test, the prerequisite of porosity rate $\varepsilon = 0.5$ was strictly fulfilled.

The relative wicking ratio (abbreviated as W_r) is another measurement of PPMF's hydrophilicity. It is calculated by the following formula:

$$W_r = m_l / m_f \times 100\%$$

where m_l is the mass of wicking liquid and m_f is the weight of fiber's bundle in a measuring tube. To obtain comparable W_r , 500 fibers in 0.33 cm i.d. by ~4 cm long were kept constant.

Dyeing property

Dispersion Yellow was chosen to reveal PPMF's dyeability, water was used as dye solvent, the ratio of dye to solvent was 1:100, and the dyeing solution temperature was 100°C. After the dyeing test, the fiber was washed with distilled water until it was colorless. The dye uptake ratio (abbreviated as D_r) was calculated from the difference of dye concentration before and after dyeing, which is measured using a 721 type spectrophotometer.

$$D_r = (C_0 V_0 - C_1 V_1) / C_0 V_0 \times 100\%$$

where C_0 : the concentration of dye solution before dyeing, C_1 : the concentration of dye solution after dyeing, V_0 : the volume of dye solution before dyeing, V_1 : the volume of dye solution after dyeing.

SEM, ATR FT-IR and ESCA

SEM was measured by HITACHI S-530. A Perkin Elmer 2000 FT-IR System was used to record the ATR FT-IR spectra of the surface. The ESCA was measured by VG Scientific ESCA LAB 220V-XL, CAE = 25 eV.

Specific resistance

The specific resistance was measured by AOVANTEST R8340 Ultrahigh Resistance Measuring Appliance, adopting the two-point method. The charged voltage was 100 V, fiber length 1 cm, charged time 1 min., room temperature 25°C and room humidity 64%.

RESULT AND DISCUSSION

The Relationship between Weight Percent of Grafting and Plasma-Induced Grafting Condition

Glow time
The weight percent of grafting increased with the prolongation of glow time, and reached a maximum at the glow time of 2 min or so. Later, the weight percent of grafting showed a trend of slightly decreasing as glow time was continuously prolonged. But the change became more and more indistinctive; in other words, the weight percent of grafting will be constant when the glow time is long enough (cf. Fig. 1). The same phenomenon was observed in the liquid grafting process by Hirotsu *et al.*^[9] and Lee *et al.*^[10]. The leveling off of the weight percent of grafting could be attributed to the equilibrium of active species engendering and deactivation when glow time was long enough.

In addition, we found that under different discharge power, the optimum glow time corresponding to the greatest grafting ratio was not the same. When discharge power increased, the optimum glow time decreased. It seems that greater discharge power would shorten the leveling off time.

Discharge power

The weight percent of grafting first increased with increasing discharge power, and reached its maximum at discharge power 80 W (cf. Fig. 2). The result was not the same as that observed by Hsiue *et al.*^[7] who grafted liquid acrylic acid to plasma treated PE surfaces. We assume that the increase of discharge power will result in more active species engendered on the PPMF surface, but higher discharge power will lead to higher chamber temperature, and plasma etching becomes more and more prominent, both of which result in surface active species deactivation, so the weight percent of grafting will considerably reduce.

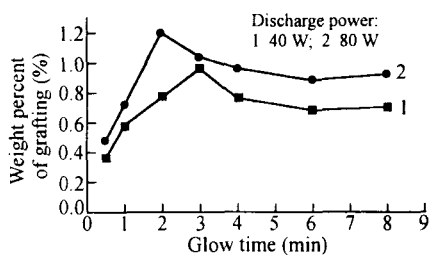


Fig. 1 The relationship between the weight percent of grafting and glow time
Environmental temperature 25 °C, liquid temperature 60 °C
1) Discharge power 40 W, 2) Discharge power 80 W

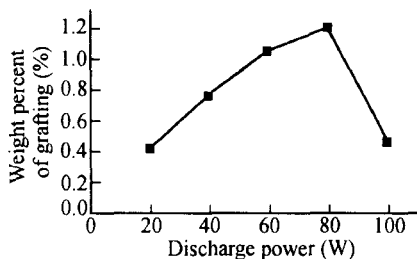


Fig. 2 The relationship between the weight percent of grafting and discharge power
Glow time 2 min, environmental temperature 25 °C, liquid temperature 60 °C

Temperature of the liquid monomer that evaporates acrylic acid into vapor

Vapor grafting differs from liquid grafting due to the fact that the partial pressure of active monomer in the chamber plays an important role in the weight percent of grafting. Higher liquid temperature will introduce more vapor acrylic acid into the chamber, thus the weight percent of grafting increases. This result was concordant with our conjecture (see Fig.3)

Environmental temperature

We found that the weight percent of grafting first increased with an increase in environmental temperature, but too high a temperature would result in its decline. The optimum temperature was around 25 °C. Johnsen *et al.*^[8] has reported a temperature effect on the grafting ratio of plasma-induced vapor grafting acrylic acid to the surface of low-density polyethylene (LDPE) film. From 27 °C to 57 °C, the grafting ratio decreased when temperature rose. We found that from 15 °C to 35 °C, the weight percent of grafting rose at first then dropped when temperature rose (see Fig. 4). We think that increased temperature would first increase monomer activity, thus the weight

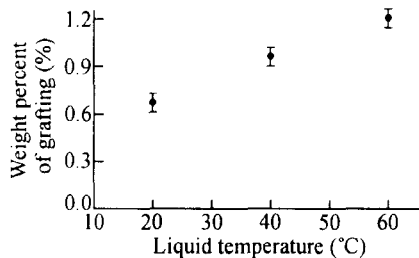


Fig. 3 The relationship of the weight percent of grafting and liquid temperature
Discharge power 80 W, glow time 2 min, environmental temperature 25 °C

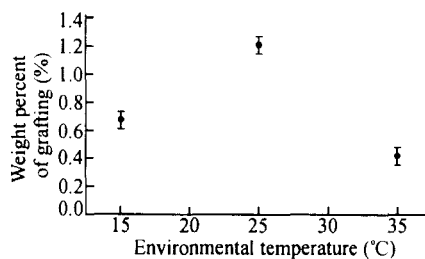


Fig. 4 The relationship of the weight percent of grafting and environmental temperature
Discharge power 80 W, glow time 2 min, liquid temperature 60 °C

percent of grafting would increase. Higher temperatures, as explained by Johnson *et al* [8], would then reduce monomer concentration on the polymer surface or deactivate surface radicals at elevated temperatures, and the weight percent of grafting decreases with increasing temperature.

SEM Photograph

The surface morphology of PPMF experienced different treatment as shown in Fig. 5.

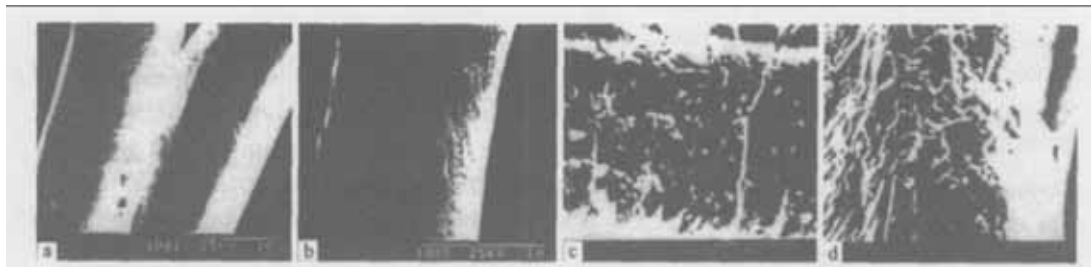


Fig. 5 SEM photographs of PPMF experienced different modification

a) Original, b) Plasma treated PPMF, discharge power 80W, glow time 2 min, c) Plasma-induced vapor grafting acrylic acid, the weight percent of grafting = 0.63%, d) Plasma-induced liquid grafting acrylic acid, the weight percent of grafting = 6.8%

The SEM photographs show that the original PPMF without plasma treatment or further grafting has a clean and smooth surface. After experiencing glowing discharge, the surface was etched, with some craters. The surface of plasma-induced grafting vapor acrylic acid shows lumps of graft PAA particles, most with sizes around 0.2~1 μm . As a comparison, the SEM photograph of a liquid grafting sample is also shown. The grafting yield is so large that the grafted polyacrylic acid almost forms a porous film at the PPMF surface.

ATR FT-IR result

Since the sizes of grafted PAA are in the order of several microns, we can verify the existence of grafted polymers by ATR FT-IR. The ATR FT-IR images of different samples are shown in Fig. 6.

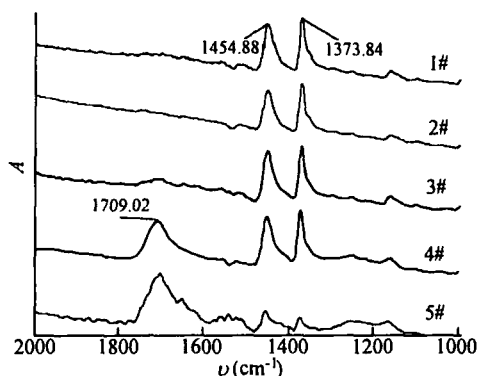


Fig. 6 The ATR FT-IR spectra of different PPMF samples

Spectra 1# Original, 2# Plasma treated PPMF, discharge power 80 W, glow time 2 min, 3# Plasma induced vapor grafting acrylic acid, the weight percent of grafting = 0.32%, 4# Plasma induced vapor grafting acrylic acid, the weight percent of grafting = 1.2% and 5# Plasma induced liquid grafting acrylic acid, grafting ratio 6.8%

The double peaks appearing at 1374 cm^{-1} and 1455 cm^{-1} are related to the distortional vibration of methyl in polypropylene. The peak at 1709 cm^{-1} is the characteristic vibrational absorption peak of carbonyl. Sample 1 was the original PPMF, sample 2 was PPMF under plasma

treatment. These had only double peaks of methyl distortional vibration, and no carbonyl peak at 1709 cm^{-1} was observed. After vapor grafting of acrylic acid, the samples of the weight percent of grafting 0.32% showed a small hump at 1709 cm^{-1} as compared with the intensities of the double peaks of methyl. As the weight percentage of grafting is increased, the characteristic peak of carbonyl at about 1709 cm^{-1} becomes prominent. At the weight percent of grafting 1.2%, the intensity of the peak becomes so distinct that it is comparable to that of the distortion vibration peaks of methyl in PPMF. As to liquid grafting, it is interesting to find that the intensity of the double peaks of methyl distortion vibration is far weaker than that of the vibrational peak of carbonyl. This result is concordant with the SEM photograph that liquid grafting yield is large enough to form a porous film at PPMF surface.

Surface Analysis of Samples with Different Grafting Time and Reference Samples

ESCA (Electron Spectroscopy for Chemical Analysis) is an ideal means of measurement to inspect the surface element constitution of a material, with an analysis depth in the order of nm.

According to the ESCA results revealed by Clark *et al.*^[13], Hsiue *et al.*^[7] and Johnsen *et al.*^[8], C_{1s} peak could be deconvoluted into four peaks based on different carbon to oxygen bondings: C_{1s1} (carbon atoms bonded to single carbon or hydrogen), ~285 eV; C_{1s2} (carbon atoms bonded with single oxygen, e.g. alcohol, ether etc.), ~286.2 eV; C_{1s3} (carbon atoms double bonded to oxygen, e.g. carbonyl, aldehydes etc. or peroxide^[7]), ~287.7 eV and C_{1s4} (carbon atoms with three bonds bonded to oxygen, e.g. carboxyl, ester etc.), ~289.1 eV. The original PPMF has a single peak of C_{1s} at the binding energy of ~285 eV. The C_{1s} peak of plasma treated PPMF was deconvoluted into two peaks with binding energy of ~285 eV and ~289 eV, respectively. So the main new functional group introduced to PPMF surface by plasma treatment is the carboxyl group. This result is concordant with that observed by Ogawa *et al.*^[14].

In addition, as we have discussed before, the ATR FT-IR shows no carboxyl group in plasma treated samples. This contrary result of ATR FT-IR and ESCA may be interpreted as follows: ATR FT-IR has an analysis depth of a few μm , while ESCA has an analysis depth in the order of nm; the carboxyl introduced by plasma treatment was limited to the uppermost layer of PPMF — it is too scarce to be discovered by ATR FT-IR.

The C_{1s} peak of PPMF under vapor grafting acrylic acid was deconvoluted into four peaks, which showed a variety of oxidized carbon groups, not merely the carboxyl group of grafted acrylic acid molecules. The results convinced us that there are some other complicated processes of grafting. The sample under 5 min grafting showed a major C_{1s} peak at ~285 eV and three relatively small peaks at other places, revealing various forms of carbon to oxygen bondings. Among the three peaks, the characteristic peak of acrylic acid (~289.1 eV) C_{1s4} is the smallest. The sample experienced 1 h grafting showed considerably increase of C_{1s4} and C_{1s2} , but the cause of the great increase of C_{1s2} during grafting is unknown. Compared to C_{1s4} and C_{1s2} , the increase of C_{1s3} during grafting is indistinctive.

Table 1. C_{1s} binding energy of different oxidized carbon-contain groups and their relative intensity to total carbon content

Sample	Peak									
	C_{1s4}		C_{1s3}		C_{1s2}		C_{1s1}		$\text{C}_{1s}:\text{O}_{1s}$	
	$E_b(\text{eV})$	Cont.	$E_b(\text{eV})$	Cont.	$E_b(\text{eV})$	Cont.	$E_b(\text{eV})$	Cont.		
1 [#]							285	100		10.93
2 [#]	288.97	1.6					284.97	98.4		3.87
3 [#]	289.03	0.78	287.57	2.90	286.10	2.46	284.95	93.86		3.14
4 [#]	289.11	3.65	287.51	3.32	286.11	7.19	285.01	85.84		3.06

The percentage of various oxidized carbon groups to the total carbon content (Cont.), the binding energy of each peak (E_b) and the ratio of carbon to oxygen ($C_{1s}:O_{1s}$) are summarized in Table 1.

We found that the original sample had $C_{1s}:O_{1s}=10.98:1$, with the oxygen content belonging to background oxygen existing in the system. After plasma treatment, the ratio of carbon to oxygen was reduced greatly to 3.87 (sample 2). Plasma-induced grafting further increased the oxygen content (sample 3 and 4). When grafting time was prolonged, the oxygen content increased further.

Wicking Test

The wicking curve of different PPMF is shown in Fig. 7.

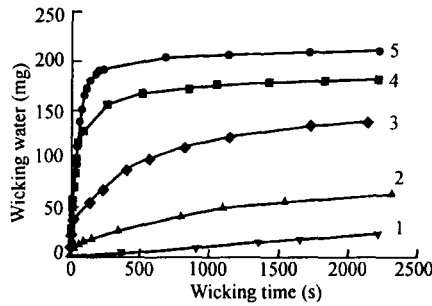


Fig. 7 Wicking curve of different PPMF samples
1), 2) Plasma treated PPMF, discharge power 80 W
glow time: 1) 2 min, 2) 5 min. Wicking test was carried out soon after
plasma treatment, 3), 4) and 5) PPMF of plasma-induced vapor grafting
acrylic acid, Grafting ratio: 3) 0.32%, 4) 0.63% and 5) 1.0%

The original PPMF is hydrophobic, therefore no wicking water was observed. The slope of each curve at the beginning represents the hydrophilicity of each sample. Both plasma treatment and plasma-induced grafting can increase the hydrophilicity of PPMF, but plasma-induced grafting is far more effective. Our researches showed that the hydrophilicity of PPMF increases with prolonged plasma treatment time and also with increased weight percent of grafting. Furthermore, the time (t) needed to reach saturated wicking was shortened when the weight percent of grafting was higher. It is worth noting that the wicking test of plasma treated samples were carried out soon after the treatment, but the samples of plasma-induced grafting were set aside for a month before the wicking test was taken. It shows that the stability of hydrophilicity was produced by plasma-induced grafting to some extent.

The mass of wicking water (m) together with t quantitatively determines hydrophilicity (see Eq. (1)), which is shown by the surface contact angle to water (θ). The relative wicking ratio (W_r) and θ of samples with different weight percent of grafting is shown in Table 2.

Table 2. The relationship between the weight percent of grafting and relative wicking ratio and contact angle

Weight percent of grafting (G_r)	0	0.32%	0.63%	1.0%
Relative wicking ratio (W_r) ¹	0	101%	127%	142%
Contact angle to water (θ) ²	>90°	75.9°	60.5°	58.3°

Measuring tube 0.33 cm i.d. by ~4 cm long, 500 strands of fiber;
Porosity ratio 0.48~0.52, measured by SB-312

Both the relative wicking ratio and θ could be greatly changed even by very small grafting ratio. By further increasing the weight percent of grafting, the contact angle will continuously drop, while the relative wicking ratio continuously increases. Hisiue *et al.*^[7] has reported a stable contact angle around 50° of PE film grafted liquid acrylic acid. Our results show that even though the

grafted polyacrylic acid is much less for plasma induced grafting vapor acrylic acid, the contact angle of the modified PPMF surface could be below 60° too. In addition, because the samples were set aside for 32 ~ 35 days before the wicking test was performed, our θ value supports the viewpoint of Johnsen *et al.*^[8] to some extent and the obtained hydrophilicity by plasma-induced vapor grafting is stable too. Wettability decay of plasma treated polymers has been ascribed to the reorientation of the hydrophilic groups engendered by plasma toward the bulk of the polymers^[4-7]. Considering the large size of the grafted PAA ($\sim 0.1 \mu\text{m}$) observed from SEM, it is reasonable to assume that such reduction could hardly occur in plasma-induced vapor grafting polymers.

Dyeability

Dye uptake ratio (D_r) is linear with the weight percent of grafting as shown in Fig. 8.

The dye uptake ratio of original PPMF was around 19%. When the weight percent of grafting increased, the dye uptake ratio increased too, showing that the grafted polar groups on the PPMF surface increased the attractive force of PPMF to Dispersion Yellow. When the weight percent of grafting was around 1.2%, the dye uptake ratio increased to 34% or so. This result shows that plasma-induced grafting is a potential method of resolving the bad dyeability problem of PPMF.

Antistatic Ability

According to our measurement, the specific resistance of the original PPMF was above $10^9 \Omega\cdot\text{cm}$. Plasma induced grafting considerably decreases the specific resistance of PPMF as shown in Fig. 9. The specific resistance was decreased with the increase of the weight percent of grafting. PPMF with a weight percent of grafting 1.2% has a specific resistance of $10^6 \Omega\cdot\text{cm}$ or so, which is lower than the original PPMF by three orders of magnitude. Because plasma-induced grafting acrylic acid greatly increases the hydrophilicity of PPMF, and the ionized functional group's quantity on the PPMF surface, therefore grafted PAA acts as a kind of immobilized surfactant. It is deemed that the fiber's antistatic ability will be excellent if its specific resistance is between 10^6 to $10^8 \Omega\cdot\text{cm}$ ^[15], thus our results show that plasma-induced grafting greatly increases the antistatic ability of PPMF.

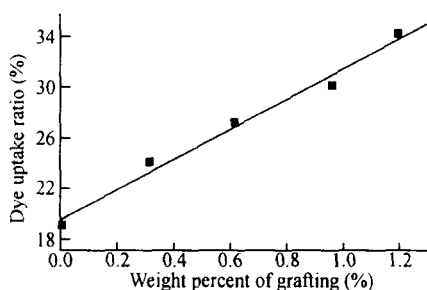


Fig. 8 The relationship between dye uptake ratio and the weight percent of grafting

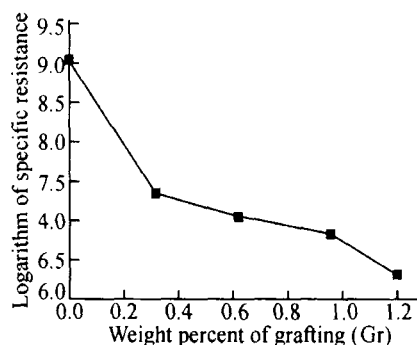


Fig. 9 The influence of the weight percent of grafting on specific resistance

CONCLUSION

Plasma-induced vapor grafting is an effective way to modify polypropylene microfibre (PPMF). The weight percent of grafting is affected by discharge power, glow time, acrylic acid liquid temperature and environmental temperature. The optimum conditions to obtain high grafting ratio are 80 W discharge power, 2 min discharge time, 25°C environmental temperature and higher liquid temperature. The size of grafted PAA is in the order of $\sim 0.1 \mu\text{m}$. Such plasma-induced grafting greatly enhances the hydrophilicity of PPMF without affecting the appearance of PPMF,

thus good hydrophilicity could be fairly distinctive even after a long storage time. The contact angle to water of modified PPMF was around 50°. The dye uptake ratio was linear with the weight percent of grafting, showing that grafted PAA enhances the attractive force of PPMF to Dispersion Yellow. Plasma-induced vapor grafting acrylic acid decreases the specific resistance of PPMF by 2~3 orders, and the lowest specific resistance of modified PPMF was around $10^6 \Omega \cdot \text{cm}$, thus greatly enhancing its antistatic ability.

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