

PLASMA MODIFICATION OF POLYPROPYLENE SURFACES AND GRAFTING COPOLYMERIZATION OF STYRENE ONTO POLYPROPYLENE*

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Abstract The surface of polypropylene (*i*PP) is modified with glow discharge plasma of Ar, so that the modified surfaces of *i*PP films are obtained. The studies of scanning electron microscopy (SEM) show the surface etching pattern of *i*PP films. The chemical structures of *i*PP films are confirmed by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy. The wetting properties of modified surfaces of *i*PP films are characterized by contact angle, and the free energy of surfaces is calculated. The free radical of modification surfaces of *i*PP is measured by chemical method. The surfaces of *i*PP are achieved with Ar plasma treatment followed by grafting copolymerization with styrene (St) in St. The grafting polymer of St onto *i*PP is characterized by FTIR. The grafting rate is dependent on plasma exposure time and discharge voltage. The studies show that homopolymerization of St is undergone at the same time during the grafting-copolymerization of St onto *i*PP.

Keywords: Plasma treatment of polymer surface; Plasma modification of polypropylene; Grafting copolymerization of polypropylene surface.

INTRODUCTION

Polymers with well-defined functionalized surface properties are widely used in both industrial application and scientific research^[1]. The most attractive approach is to modify the surface of well-established polymer materials without changing their bulk properties. Plasma technology is widely used to treat polymers in order to alter the surface properties^[2]. Plasma treatment is a very important tool in the modification of surface properties. This method was found to have many attractive applications in automobile manufacturing, microelectronics, chemical, biomedical and pharmaceutical industries.

Currently, more attentions are being given to its applications in membrane separation science. One promising result from plasma treatments is that the surface hydrophilicity of membranes can be improved by either plasma treatment or plasma graft copolymerization (PGC) of vinyl monomers^[3, 4].

In general, the surface modification of chemically inert polymer by plasma treatment can introduce chemical reactive groups and achieve functionalization of polymer surfaces. For example, when a non-polymerizable gas, such as argon or helium, is used, the radicals produced would react with the oxygen or the moisture of water in air atmosphere to form peroxides which can further initiate graft polymerization of the monomer, such as acrylic acid, to obtain a hydrophilic surface^[5, 6] or cross linking layer^[7]. If the gas used is polymerizable, these species can collide in the gas phase or impinge on the polymers surface and combine to

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form a graft-copolymer thin-film on the surface^[8–15]. In a word, most of the widely used plasma modifications of polymer surfaces show great advantages as compared with chemical modification. Therefore, surface modification of polymers by plasma treatment is widely used in both scientific research and industrial application^[16–19].

There are many previous researches for graft reaction onto polypropylene (*i*PP) surfaces with plasma modification. For example, Miwa^[20, 21] studied that plasma treated *i*PP surface could initiate styrene (St) polymerization and obtain the grafting polymer of St onto *i*PP (*i*PP-g-St). Huang^[22] completed a similar work. Lu^[23] has studied the reaction of *i*PP which is treated using Ar plasma with styrene under benzoyl peroxide and determined the temperature to obtain the grafting copolymer of *i*PP-g-St. Clearly, the polymer surface which is modified using plasma has a lot of active groups, which could induce grafting copolymerization and polymerization of monomers.

In this paper, the surface modification of *i*PP films is studied by low temperature Ar plasma. The structures and morphology of the modified surface of *i*PP are studied using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). The properties of plasma modification surfaces of *i*PP are characterized by the contact angle, and the free radical on modification surface of *i*PP is measured. The graft reaction of polystyrene (St) monomer onto polypropylene (*i*PP) surface of plasma modification is studied. In the process of plasma induced grafting, plasma generates radical sites on the surface of polymer which can initiate the conventional polymerization of St monomer, as homopolymerization. The factors that influence the molecular weight of the homopolymerization of styrene are also investigated.

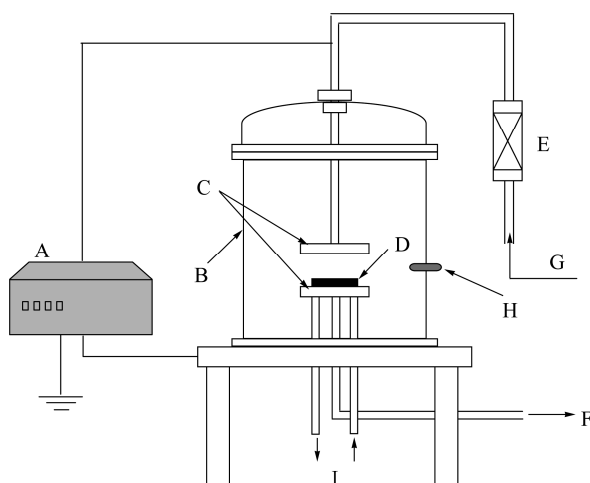
EXPERIMENTAL

Materials and Equipments

Polypropylene (isotactic polypropylene, *i*PP, 1300) is a commercial polymer with weight-average molecular weight $M_w = 4 \times 10^5$, $\rho = 0.91 \text{ g/cm}^3$ and melt flow rate (MFR) = 1.2 g/10min (190°C/2.16 kg). Particle size is about 4 mm. Polystyrene (PS, 666D) has a number-average molecular weight of $M_n = 1.2 \times 10^5$, $\rho = 1.05 \text{ g/cm}^3$.

The styrene monomer was purified by distillation at a reduced pressure before use. Diiodomethane is pure analytically. Ar is purified to 99.995%. The free radical initiator 2,2-diphenyl-1-picrylhydrazyl (DPPH) is pure analytically.

The plasma generator (CTP-2000K) is obtained from Nanjing Suman Electron Co. Ltd., China



Scheme 1 System of plasma surface treatment: (A) plasma mains, (B) vacuum reactor of plasma, (C) electrodes, (D) samples, (E) mass flow meter, (F) vacuum system, (G) gas, (H) vacuum gauge and (I) cooling medium

Plasma Surface Modification

The Scheme 1 shows the system of plasma surface modification. The surface of polymer films is modified by glow discharge Ar plasma of 13.56 MHz. Ar plasma flow is 50 mL/min; discharge voltage is 30, 50, 70 and 90 V, respectively. The pressure of vacuum reactor is 67 Pa and distance of parallel plates is 2 cm. The treatment time of Ar plasma on surface of samples is 5, 10, 30, 60, 120, 300, 600, 900 and 1200 s, respectively. The temperature of samples is at room temperature (°C).

Grafting Copolymerization

In a four-necked round bottom flask, the grafting reaction of St onto *i*PP is carried out under nitrogen atmosphere and the weight ratio of the particle samples of *i*PP to St is 1:125, the reaction temperature is 100°C and 120°C, respectively; the reaction time is 2 h. The product is precipitated in ethyl acetate after the reaction is finished. The part of solids is separated, which is extracted out in a Soxhlet extractor with acetone-methyl acetone mixture for 72 h, and *i*PP-g-St (or *i*PP-g-PS) is obtained after drying. The part of liquid in the product is ethyl-acetate solution of PS. The ethyl-acetate is separated by evaporation and the homopolymer, *i.e.* PS is obtained after drying.

Specimen Preparation

The premixed material was melt and pressure-molded to get slabs of 1 mm as well as about 20 µm thickness at 200°C for 3 min in a heating press at 24.5 MPa, and then the slabs were quickly moved to a cool press at room temperature and 24.5 MPa for 5 min. The 1 mm thick slabs were used to perform XPS, SEM and contact angle tests. The 20 µm films were used in the FT-IR tests.

Characterizations

FTIR measurements

The structure of polymers on *i*PP surfaces was characterized by using a Perkin Elemer spectrum 100 to collect the infrared spectrograph while the XPS spectrograph was collected by a Pekin-Elementer PHI1600ESCA system.

SEM measurements

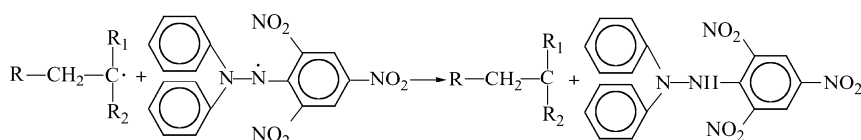
The surface morphology of samples (as *i*PP and modification surface of *i*PP) was observed on a Philips XL 400ST scanning electron microscope.

Contact angle measurements

The contact angle of polymer surface using diiodomethane and water was measured by a DCAT21 dynamic contact angle instrument.

Surface free radical measurements

The free radical of modification surfaces of *i*PP was measured by chemical method. The free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH)^[24] has found many applications due to its high stability and intense purple color that changes, *i.e.* absorption band of DPPH at $\lambda_{\max} = 520$ nm decreases and disappears, whenever it reacts (see Scheme 2).



Scheme 2 Reaction mechanism of DPPH and free radical
R, R₁, R₂ are hydroxide radical or hydrogen.

Therefore, the variation of absorbency could be measured by ultraviolet spectrophotometer when the reaction between DPPH and free radical in carbon tetrachloride solution occurred. The relationship of the

absorbency with the concentration of the free radical is given as $A = abc_1$ or $A = \varepsilon bc_2$, where A is absorbency; a is absorbance index; b is thickness of sample cell; ε is mole absorbance index; c_1 is mass fraction; c_2 is concentration. The relationship of concentrations of free radical, C_{fr} in carbon tetrachloride solution with absorbance is shown in Fig. 1.

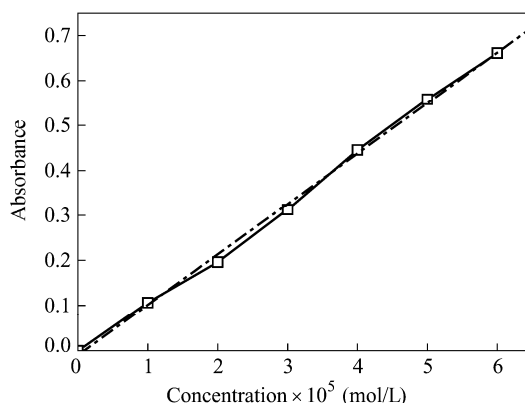


Fig. 1 Relationship between standard solution concentrations of free radical and absorbance

Grafting Yield Calculation

The graft amount of treated polypropylene samples (G_g), *i.e.* the grafting percent, was calculated as follows:

$$G_g = \frac{W_1 - W_0}{W_1} \times 100\% \quad (1)$$

where W_1 , W_0 represent the weight (g) of the sample before and after grafting, respectively.

RESULTS AND DISCUSSION

Ar Plasma Modification of *i*PP Surface

SEM studies

In general, plasma contains several activated species such as electrons, ions, free radicals and some neutral species^[25]. These activated particles in plasma can corrode the surface of polymer under plasma. Thus the surface of *i*PP films is treated using low temperature Ar plasma in the system of plasma surface modification (see Scheme 1) to obtain the modified surface of *i*PP. The surface morphology is investigated using SEM. The differences between the surface morphology of the virgin and plasma treated *i*PP films are shown with SEM patterns in Fig. 2. After 1 min of plasma treatment *i*PP seems to be damaged and small “hole-like” spots on the surfaces appeared, *i.e.* the *i*PP surface is etched. When the surface is treated in Ar plasma for a longer time, the morphology of films surface is severely changed. The pattern formed by “pits” can be seen on the etching surface, it may be the crystalline pattern of the *i*PP film surface.

XPS studies

The structure of modified surface of PP films under different discharge voltages and treatment time of Ar plasma is studied by XPS. The examination of C1s high-resolution peak shows the existence of three components corresponding to different natures of carbon bonds (see Fig. 3).

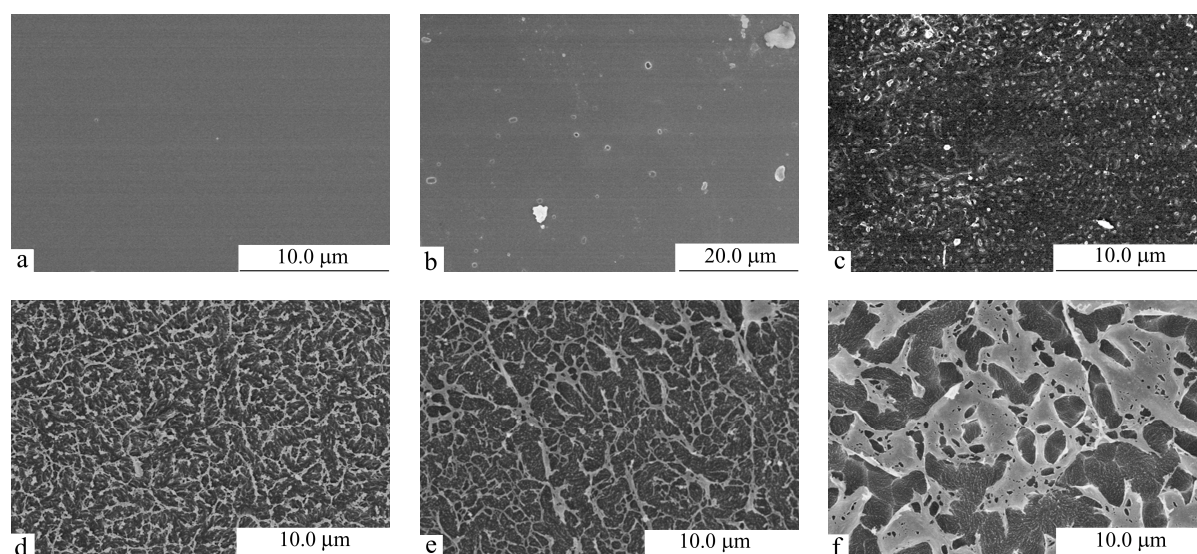


Fig. 2 SEM images on Ar plasma treated surface of *i*PP films under different treatment time of plasma: (a) 0 min, (b) 1 min, (c) 5 min, (d) 10 min, (e) 15 min and (f) 20 min
Discharge voltage: 50 V

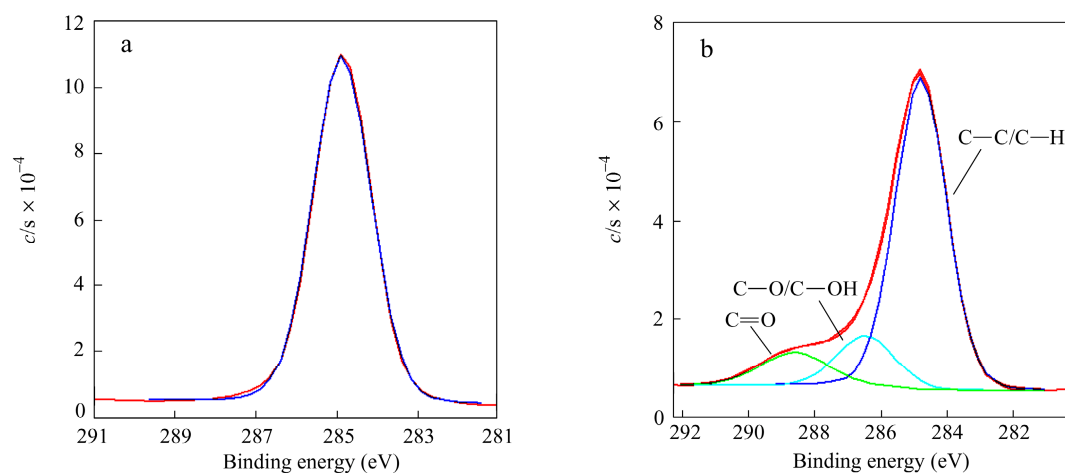


Fig. 3 C1s spectra (XPS) of Ar plasma modified surface of *i*PP films: (a) *i*PP and (b) modified *i*PP
Discharge voltage: 50 V; Treatment time: 15 min

The main contribution fixed at 284.6 eV is hydrocarbon structure of the polymer and represents the C—C and C—H bonds. The second component located at 286.1 eV indicates the presence of species containing C—O bonds such as alcohol, ether and (hydro) peroxide. The component at 288.1 eV reveals the presence of C=O bonds assigned to aldehyde and ketone. The existence C—O bonds and C=O bonds on the *i*PP surfaces shows that there is a spot of air in the system of plasma surface modification.

The theoretical maximum amount of carboxyl and hydrocarbon functionality was calculated using composition of C1s peak area on the surface of modified *i*PP films. These values of functional group composition is shown in Fig. 4, indicated a substantial decrease of C and C—C/C—H contents and increase of O, C—O and C=O contents.

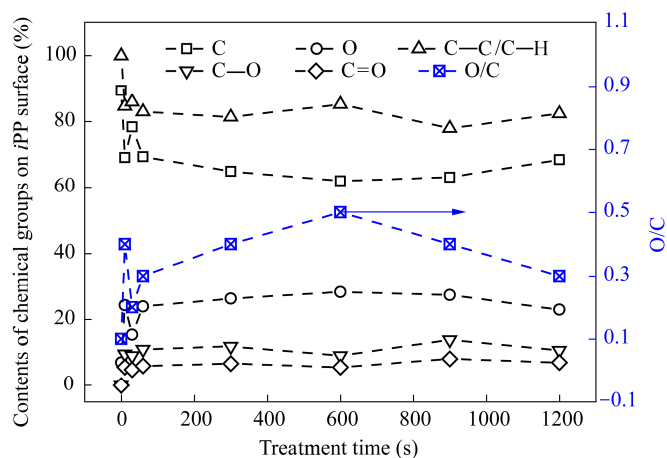


Fig. 4 The relation of content of chemical structure on *i*PP surface with treatment time of Ar plasma
Discharge voltage: 50 V

Also data of O/C of treated *i*PP films increase. Prolonged excitation does not induce further changes. This means that most of the surface reactions occur during the first moment of plasma treatment (Fig. 4).

FTIR studies

In order to obtain more detailed information about the structural changes of *i*PP after plasma treatment, FTIR spectra of the surface were recorded using the ATR technique.

Figure 5 shows FTIR spectra of the untreated and treated *i*PP films. Most of them are found in the range of $1800\text{--}1600\text{ cm}^{-1}$ and indicate a rather large number of different structural features of carbon-oxygen double bonds present in aldehyde and ketone, *i.e.* a couple of peaks at 1640 and 1723 cm^{-1} appear which are attributed to C=O vibration bands. Thus, this result is consistent with that of XPS.

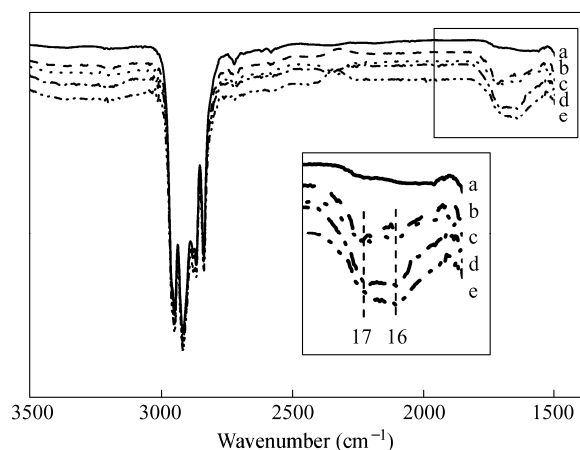


Fig. 5 FTIR spectra of Ar plasma treated surface of *i*PP from 1500 and 3500 cm^{-1} under different treatment time: (a) 0 min (untreatment *i*PP), (b) 1 min, (c) 5 min, (d) 10 min and (e) 15 min
Discharge voltage: 50 V

Contact angle studies

The contact angle and surface tension can be used to characterize surface properties of polymers, such as polarity or non-polarity. The surface tension denotes energy per unit area of solid which can be obtained by contact angle measurements of solid surfaces. There are several methods to obtain surface tension of polymer

films by using contact angle. In this study we select the equation based on force additivity and a “reciprocal” mean, which can be used reliably to calculate the interface tension between polymers or between a polymer and an ordinary liquid^[25]. It is given by

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \quad (2)$$

where γ_{12} is the interfacial tension; γ_i the surface tension; γ_i^d and γ_i^p the dispersion and polar components of γ_i , respectively.

Equation (2) can also be used to calculate γ^d and γ^p of a solid polymer from the contact angles of liquids such as water and methylene iodide. These calculation equations are as follows^[26]

$$\gamma_1(1 + \cos\theta_1) = \frac{4\gamma_1^p \gamma_s^p}{\gamma_1^p + \gamma_s^p} + \frac{4\gamma_1^d \gamma_s^d}{\gamma_1^d + \gamma_s^d} \quad (3)$$

$$\gamma_2(1 + \cos\theta_2) = \frac{4\gamma_2^p \gamma_s^p}{\gamma_2^p + \gamma_s^p} + \frac{4\gamma_2^d \gamma_s^d}{\gamma_2^d + \gamma_s^d} \quad (4)$$

where γ_1 and γ_2 are the surface tension of liquid 1 and 2; θ_1 and θ_2 are contact angle of liquid 1 and 2 on surface of polymer films, respectively. Water and methylene iodide are used in this work, and the surface tensions are listed in Table 1. Therefore, the surface tensions of PP films are calculated by Eqs. (3) and (4) from experimental data of contact angle between *i*PP and water as well as between *i*PP and methylene iodide. Figures 6, 7 and 8 show the experimental results.

Table 1. The data of experimental reagents

Experimental liquids	$\gamma \times 10^3$ (N/m)	$\gamma^d \times 10^3$ (N/m)	$\gamma^p \times 10^3$ (N/m)
Water	72.8	50.7	21.8
Methylene iodide	50.8	6.7	44.1

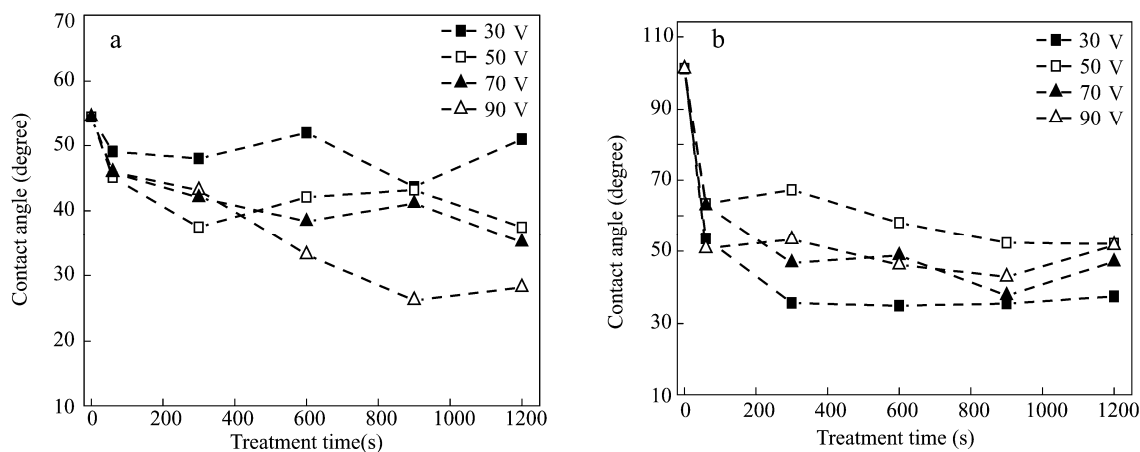


Fig. 6 The relation of contact angle of *i*pp surface with treatment time of plasma: (a) water and (b) diiodomethane

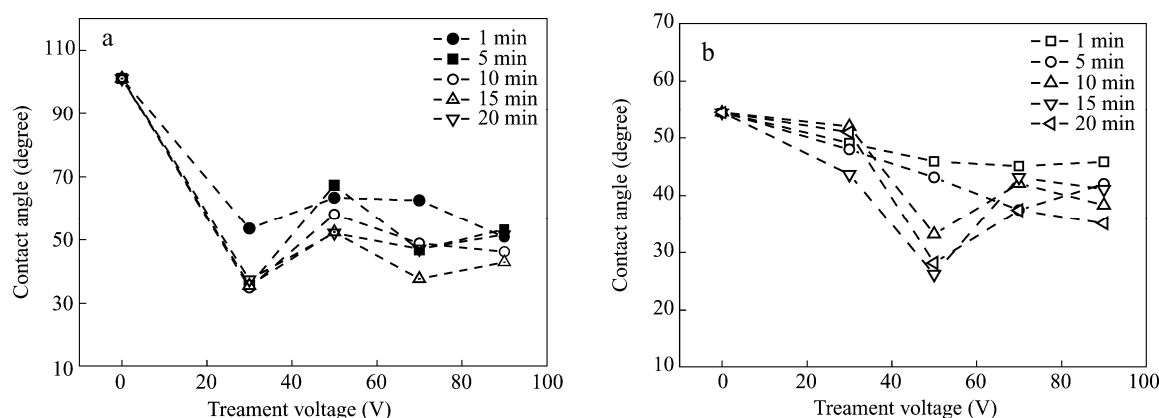


Fig. 7 The relation of contact angle of *i*PP surface with treatment voltage of plasma: (a) water and (b) diiodomethane

In Fig. 8, data for treated *i*PP films show a substantial increase of surface tensions, γ . Also the polar component, γ^p , indicates a substantial increase. The dispersion component, γ^d , is nearly unchangeable. We observe a decrease in contact angles for water and diiodomethane at the first minute of plasma treatment. It means that the modification is very effective by introducing polar groups to the surface (see Fig. 6).

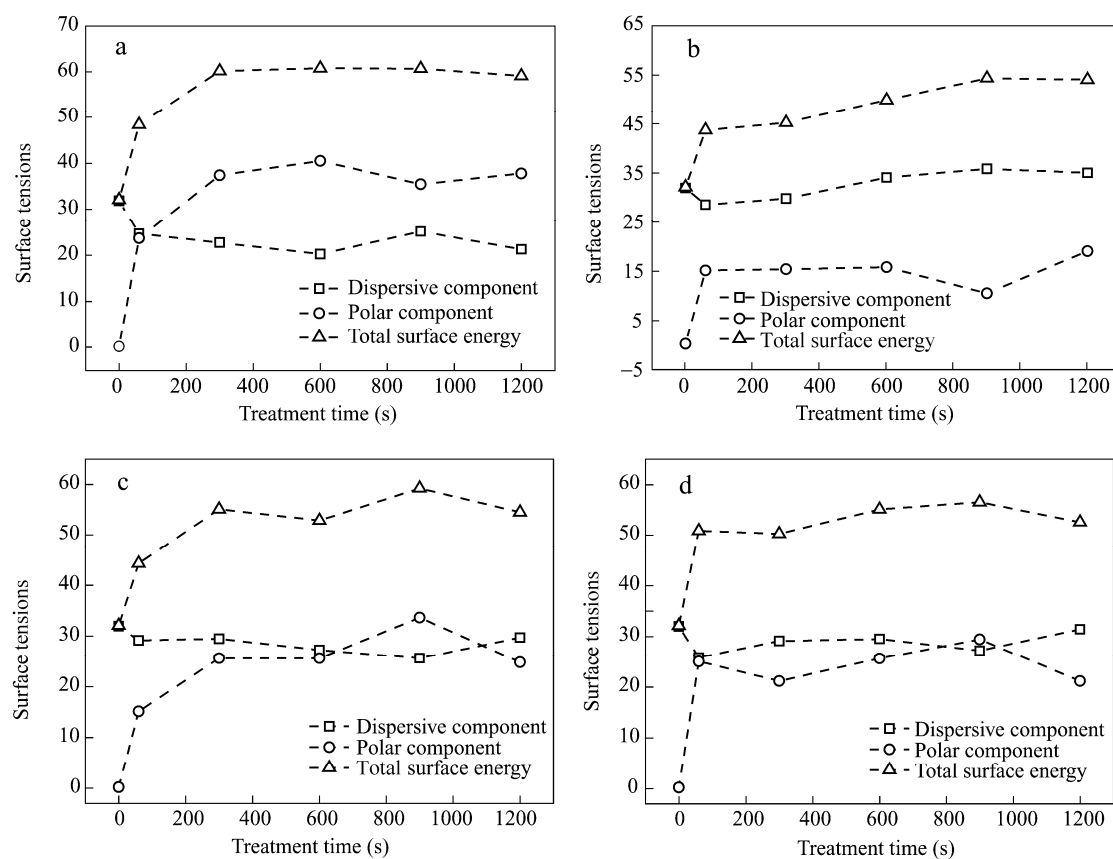


Fig. 8 Relationship of surface tensions with treatment time and at different discharge voltage: (a) 30 V, (b) 50 V, (c) 70 V and (d) 90 V

Prolonged excitation does not cause further changes for surface tensions of the treated films. This means that most of the surface reactions changing the character of the surface occur during the first moment of plasma treatment. The surface becomes highly wet-table with the polar component of surface tension equal to the dispersive one (Fig. 8).

Figure 9 shows that the variation of surface tensions with discharge voltage under different treatment time of plasma is the same as the variation of surface energy with treatment time of plasma.

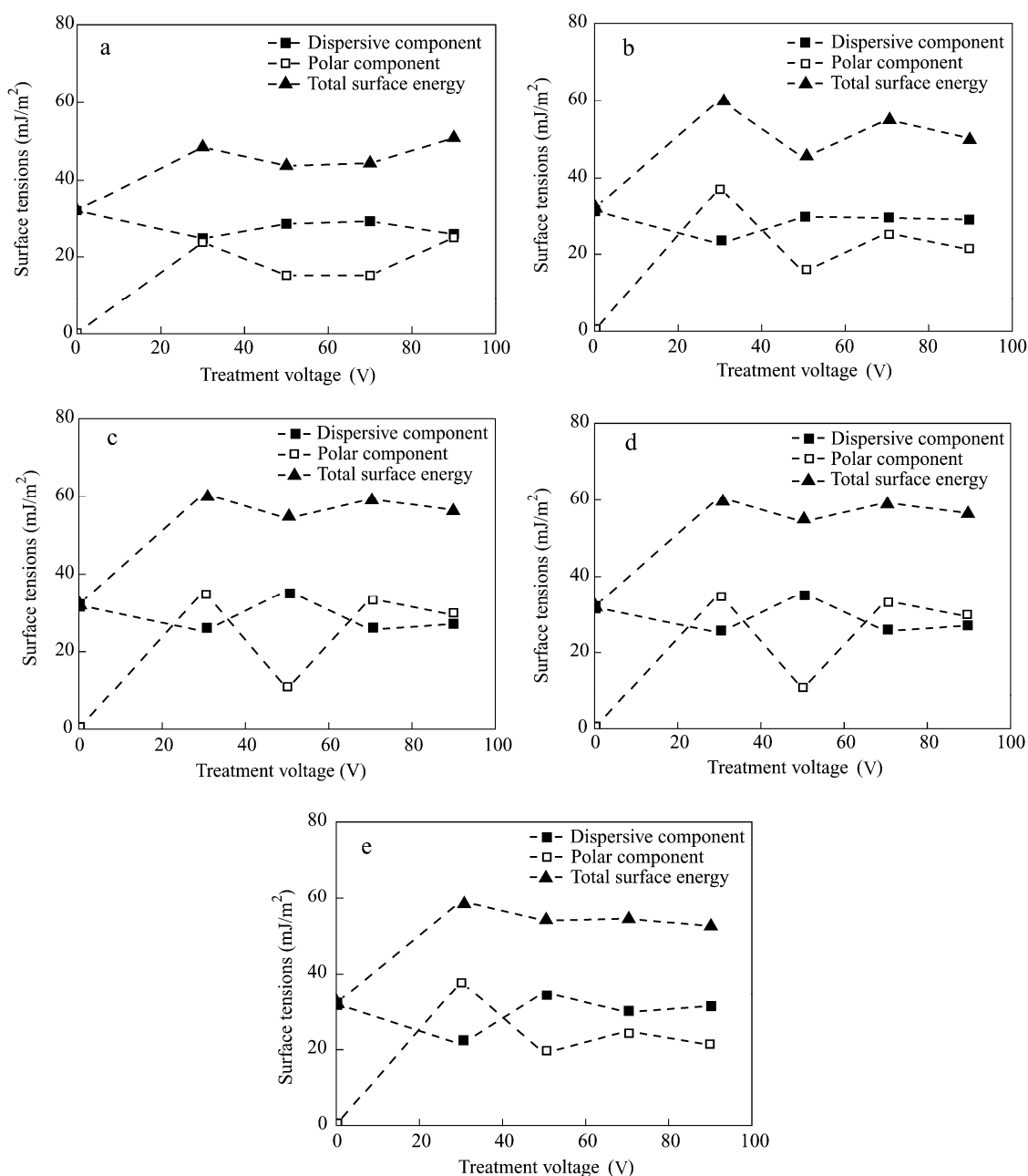


Fig. 9 Relationship between treatment voltage and surface tensions at different treatment time: (a) 1 min, (b) 5 min, (c) 10 min, (d) 15 min and (e) 20 min

Surface free-radical of studies

The polymer surface bombardments by species in the plasma create free-radical sites. Therefore, this free-radical of surfaces could be measured by chemical method using DPPH. Figure 10 shows the relation of the concentrations of free radicals, C_{fr} , with plasma treatment time on the surface of *i*PP films. C_{fr} increases quickly with increase in treatment time of plasma, and then levels off, showing that most of the surface free-radicals form during the first moment of plasma treatment.

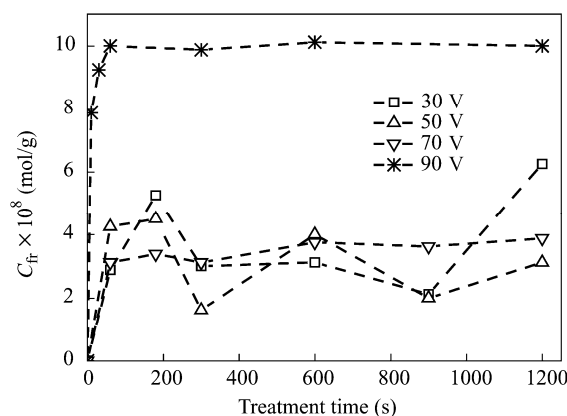


Fig. 10 The relation of concentration of free radicals with plasma treatment time on *i*PP surface

Graft Copolymerization of St onto Activated Surfaces of *i*PP

Above-mentioned study shows that there are a lot of activated groups and free-radicals on *i*PP surfaces after Ar plasma treatment. Thereby, the grafting copolymerization of monomers onto the surface should be induced by the activated surfaces of high surface energy.

Figure 11 shows the FTIR spectra of an unmodified *i*PP and the grafting product of St onto *i*PP activated surfaces at reaction temperature of 100°C, reaction time of 2 h. The IR spectrum of *i*PP-g-St exhibits a strong absorption band at 698 cm⁻¹ which can be assigned to wagging of C—H in the benzene ring, and the small absorption bands at 1603, 1706, 1755 and 1804 cm⁻¹ are skeletal vibrations of benzene rings, showing the existence of the grafting copolymer, *i*PP-g-St.

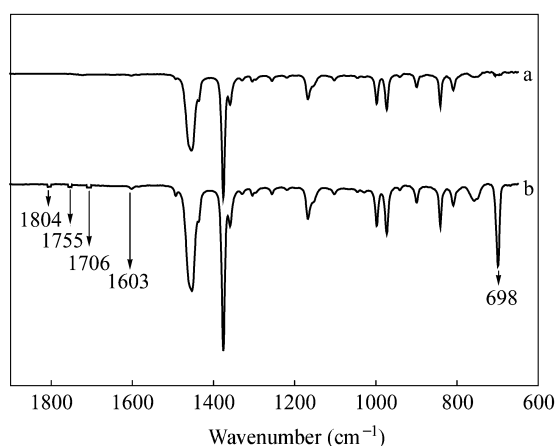


Fig. 11 FTIR spectra of *i*PP (a) and *i*PP-g-St (b)

Data for grafting copolymerization of St onto *i*PP are shown in Tables 2 and 3. The relation of the grafting percentage, G_g , of St on *i*PP surfaces with discharging voltage of plasma is shown in Table 2, showing G_g

increases with an increase in the discharging voltage of plasma at treated time of plasma of 15 min and the reaction temperature of 100°C and 120°C, respectively. The grafting percentage at the reaction temperature of 100°C is less than the grafting percentage at 120°C. The relation of grafting percentage of St on *i*PP with treatment time of plasma for *i*PP surface is shown in Table 3, showing G_g is almost invariable with an increase in treated time. Also the grafting percentage at the reaction temperature of 100°C is less than the grafting percentage at 120°C.

Table 2. The relation of grafting percentage of PS on *i*PP surface with discharging voltage of plasma*

Discharging voltage (V)	Grafting percentage (%)	
	100°C	120°C
30	1.42	2.27
50	1.92	2.41
70	2.38	3.01
90	2.65	4.32

* Treatment time of plasma is 15 min.

Table 3. The relation of grafting percentage of PS on *i*PP surface with treatment time under Ar plasma*

Treatment time (min)	Grafting percentage (%)	
	100°C	120°C
5	1.65	2.25
10	1.71	2.36
15	1.92	2.41
20	1.94	2.39

* Discharge voltage: 50 V

The monomer of St can form homopolymers during the process of plasma induced grafting of St onto *i*PP, and the viscosity-average molecular weight, M_η , of the homopolymers of St bears a relation to discharging voltage and treatment time of Ar plasma on the surface of *i*PP, showing plasma generates radical sites on the surface of polymer which can initiate the conventional polymerization of St monomers. The relation of viscosity-average molecular weight, M_η , of the homopolymers of St with various discharging voltage and treatment time of Ar plasma at the temperature of 100°C and 120°C is shown in Tables 4 and 5, respectively. They show that M_η increases with an increase in the reacted time; M_η at the reaction temperature of 100°C is greater than that at 120°C.

Table 4. The relation of viscosity-average molecular weight of St homopolymers with discharging voltage of plasma

Discharging voltage (V)	Viscosity-average molecular weight $\times 10^{-5}$	
	100°C	120°C
30	4.8	3.8
50	5.1	4.0
70	4.1	3.2
90	4.0	3.0

* Treatment time of plasma: 15 min

Table 5. The relation of viscosity-average molecular weight of St homopolymers with treatment time under Ar plasma*

Treatment time (min)	Viscosity-average molecular weight $\times 10^{-5}$	
	100°C	120°C
5	4.2	3.4
10	4.6	3.6
15	5.1	4.0
20	4.7	3.9

* Discharge voltage: 50 V

The polymerization of St under definite temperature may occur, *i.e.* the thermal polymerization, and the homopolymers of St, PS_{tp}, are obtained. The relation of the viscosity-average molecular weight, $M_{\eta_{tp}}$, of PS_{tp} with reaction time is shown in Fig. 12. It is clearly seen that $M_{\eta_{tp}}$ is less than M_{η} under similar reaction conditions (see Fig. 12), showing that M_{η} is increased due to existence of the activated surfaces of *i*PP.

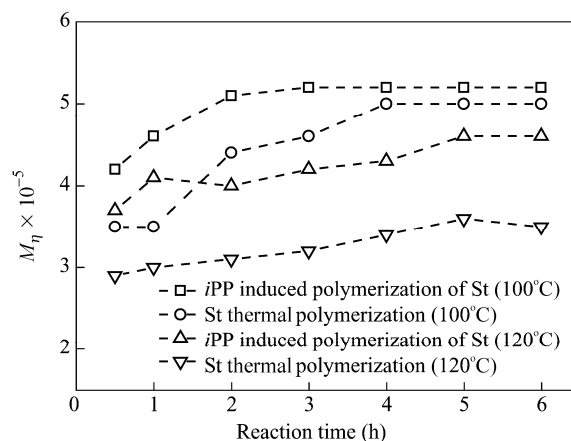


Fig. 12 The relation of viscosity molecular weight of St homopolymers, M_{η} , with reaction time

CONCLUSIONS

The *i*PP surface can be etched using low temperature Ar plasma. The pattern of *i*PP surface formed under glow discharge is the crystalline pattern of the *i*PP film surfaces. Ar plasma introduces on *i*PP surfaces many various activated groups comprising aldehyde and ketone because of the existence of few air in plasma reaction system. The surface tension, *i.e.* surface free energy, on *i*PP surfaces increases with increase in treatment time and discharge voltage of Ar plasma, and most of the free-radicals are formed on the *i*PP surface.

A lot of free-radicals and activated groups on *i*PP surfaces can induce the grafting copolymerization of St onto *i*PP and polymerization of St. At the same time, the contribution of thermal polymerization of St should also be considered.

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