

GRAFT COPOLYMERIZATION OF ACRYLAMIDE ONTO POLYPROPYLENE FILMS BY PLASMA TECHNIQUE

WANG Shicai (王世才), YE Mu (叶牧),
LU Lizhen (卢丽珍) and CHEN Jie (陈捷)
(Changchun Institute of Applied Chemistry, Academia Sinica)

ABSTRACT

The graft copolymerization of acrylamide onto polypropylene (PP) film was carried out by using a capacitively coupled rf plasma apparatus with external plate electrodes. The relationship between the surface structure of the Ar plasma-treated PP films and the extent of grafting of acrylamide on the films was studied through observing the effects of discharge power and exposure time on the relative content of free-radical on the film surface. Meanwhile, the wettability and surface energy of the PP film were measured.

INTRODUCTION

Cold plasma treatment could remarkably improve the wettability, adhesion and abrasion resistance of the material surface without affecting the internal properties of polymers due to its stronger bombardment on the surface and weaker penetration^[1-3]. Material surface can be simply plasma-treated with some non-polymerized gases such as Ar, He, O₂ and N₂. However, the modified surface is easier to return to its original state. In order to increase durability of the modified properties plasma graft copolymerization was used. In the present paper, PP films were preirradiated in Ar glow discharge, then graft copolymerization was carried out in an aqueous solution of acrylamide. The effects of some variables on plasma-grafting and the structures and properties of the grafted PP films thus obtained were studied.

EXPERIMENTAL

Acrylamide, 98.5% pure, was purchased from Tianjin 1st Chemical Plant and argon 99.99% from Fushun Oxygen Plant.

PP film were treated by using a capacitively coupled rf plasma equipment with external plate electrodes, as shown in Fig.1. Prior to treatment, PP films were soaked in acetone for 24 hours and then dried in vacuum. 10% aqueous solution of acrylamide in a side tube outside electric field was deaerated twice by liquid N₂ freezing and degassing. After finishing Ar plasma treatment of the PP film, the reaction system in vacuum was filled with Ar to ambient pressure. Then the aqueous solution of acrylamide was poured into the reactor to immerse the treated PP film. After that the reactor was heated in a water bath at 50°C for 24 hours. At last, the sample was taken out and soaked in the 50°C distilled water for 28 hours, and then dried in vacuum to remove the homopolymers of acrylamide.

The quantity of the monomer grafted was determined by the weight difference. IR measurement was taken on a Perkin-Elmer 599B Infrared Spectrograph and ESR measurement on a

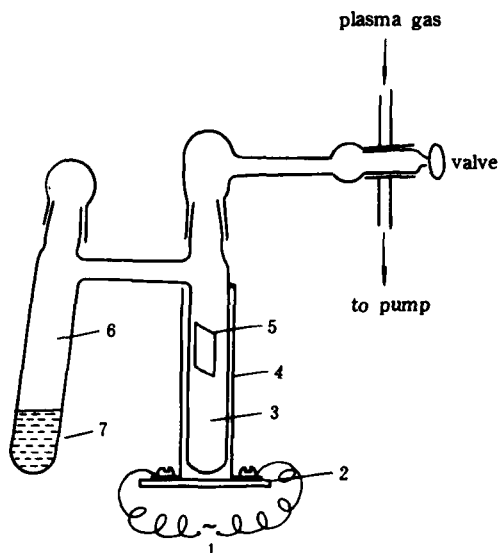


Fig.1 Schematic diagram of the plasma reaction apparatus

1. RF Generator, 2. PTFE plate, 3. Reactor, 4. Plate electrodes, 5. PP film, 6. side tube, 7. Aqueous solution of acrylamide. JES-FE 3AX Electronic Spin Resonance Spectrometer. The surface morphology was observed by a JEA-840 Scanning Electron Microscope and the contact angle was determined by a G-II Contact Angle Meter of Erma Optical Works Co., Japan.

RESULTS AND DISCUSSION

When PP films were exposed in Ar plasma at different power with a pressure of 6.67Pa for 10

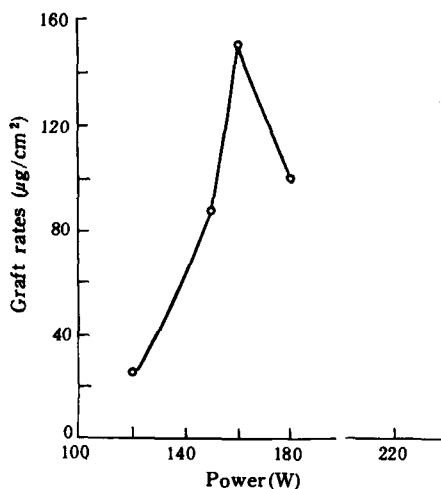


Fig.2 Graft rates of acrylamide on PP films at different powers

Pressure, 6.67Pa, exposure time, 10 sec.

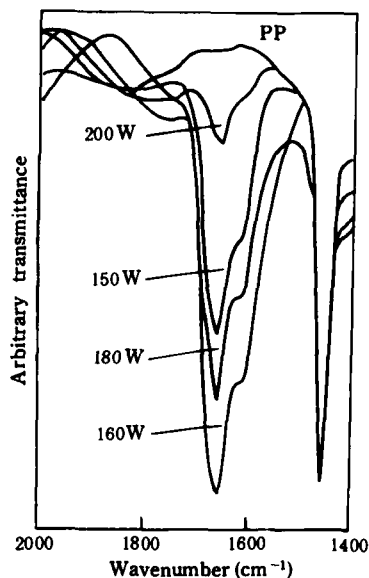


Fig.3 IR spectra of the acrylamide grafting PP films at different powers

Pressure, 6.67Pa, exposure time, 10 sec.

seconds, the graft rates (graft amounts at unit area) of acrylamide on PP films and the IR spectra of the grafted films were shown in Figs.2 and 3 respectively. In the IR spectra, absorption bands at 1650 and 1600cm^{-1} correspond to $\nu(\text{C}=\text{O})$ and $\delta(\text{NH}_2)$ vibration of the amide groups respectively^[4]. The absorption intensity changed with the discharge power, and the changing tendency was in agreement with that of grafting shown in Fig.2. It can be seen that when discharge power was increased to above 180W , the grafting was difficult to be performed. At a power of 200W , only a small IR absorption peak of amide groups could be seen.

In the Ar plasma PP films were exposed at the power of 120W or 180W and a pressure of 6.67 Pa for different durations, the grafting of acrylamide on PP films and the IR spectra of the grafted films were shown in Figs.4 and 5 respectively. At a power of 180W , it can be observed that grafting increased with the increase of the exposure duration as such exposure was within a limit of 20 seconds. The corresponding IR spectra show a similar tendency. When glow discharge lasted for more than 30 seconds, however, no grafting was detected, a similar result was also seen at a power of 120W . The grafting showed a maximum at an exposure duration of 30 seconds, but no grafting occurred when the films were exposed for longer than 40 seconds. The conclusion is that if higher power is used the exposure duration should be shortened in order to get a maximum grafting.

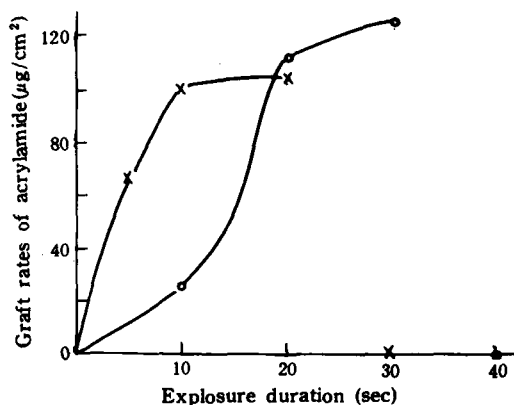


Fig.4 Grafting of acrylamide on PP films at different exposure durations

Pressure, 6.67Pa , power, (x) 180W , (o) 120W .

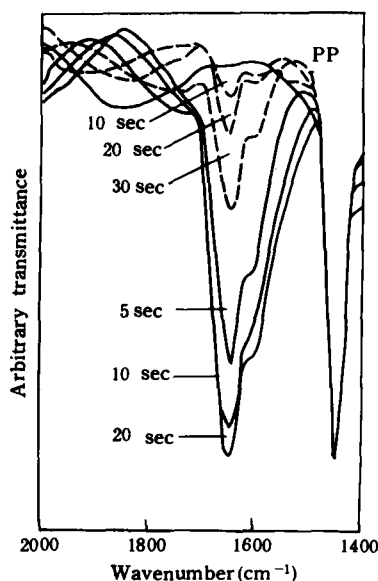


Fig.5 IR spectra of the acrylamide grafting PP films at different exposure durations

Pressure, 6.67Pa , power, --- 120W , — 180W .

It is well-known that the polymerization of acrylamide is a radical addition reaction. Therefore in the graft copolymerization acrylamide could only be initiated by the free-radicals on the surface of PP films. The ESR spectrum of the Ar plasma-treated PP film was shown in Fig.6. The relative radical contents of PP films were represented by the area ratios of the ESR peaks. By comparing the results of PP films shown in Figs.7 and 8 with those shown in Figs.2 and 4, it can be seen that the condition giving a maximum relative radical content led to a failure of grafting. In order to explain the above result, an experiment was made in which the free radicals on plasma-treated PP films were subjected to attenuation at ambient temperature. As shown in Fig.9, after exposure of PP film for 30

seconds it showed a higher relative radicals content with few attenuation. On the contrary, at an exposure time of 10 seconds, more radicals attenuated although their relative concentration was lower. Obviously, acrylamide could not be initiated by those slowly attenuated radicals due to their stability. It is convinced that crosslinking causes combination of a radical with its adjacent one. The higher the power raised, the higher the crosslinking degree would be. Such process reduced the amounts of active radical on the film surface and led to a loss of the their ability of initiating acrylamide. In addition, the original regular structure of polymer surface could be broken to some extent in glow discharge. The steric effect of molecular branching could also impede the reaction of surface active sites with acrylamide in larger volume.

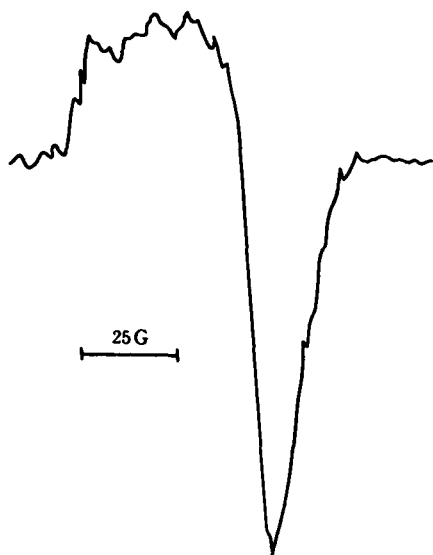


Fig.6 ESR spectrum of the Ar plasma-treated PP film
Power, 180W, exposure time 10 sec.

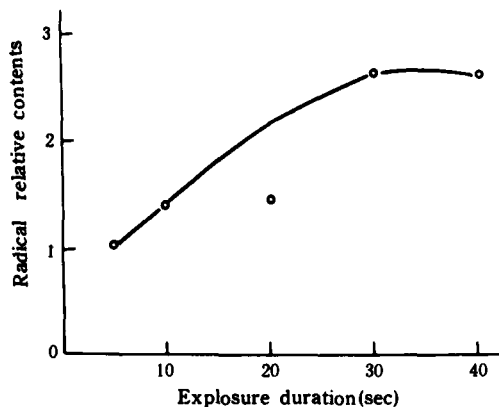


Fig.8 Relative contents of radical on PP films treated at different exposure durations
Pressure, 6.67Pa, power, 180W.

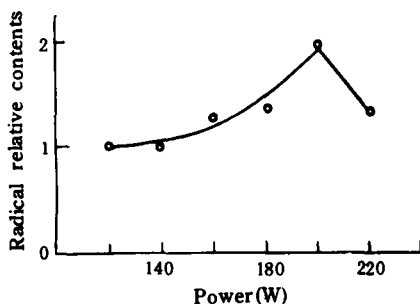


Fig.7 Relative contents of radical on PP films treated at different powers
Pressure, 6.67Pa, exposure time, 10sec.

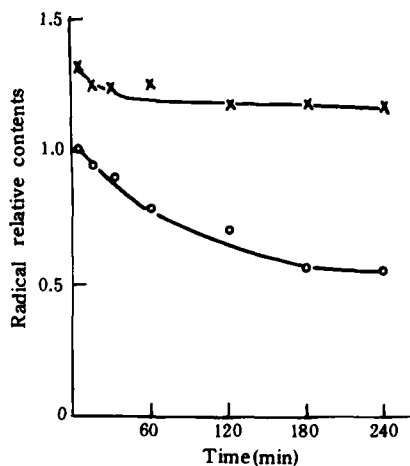


Fig.9 Radical attenuation of PP films treated at different exposure durations
Pressure, 6.67Pa, power, 180W.
exposure duration, (○) 10sec., (×) 30sec.

The SEM photographs of the blank (A), Ar plasma-treated (B) and acrylamide-grafted (C) PP films were shown in Fig.10. It can be observed that there are evident differences in surface morphology among these three PP films.

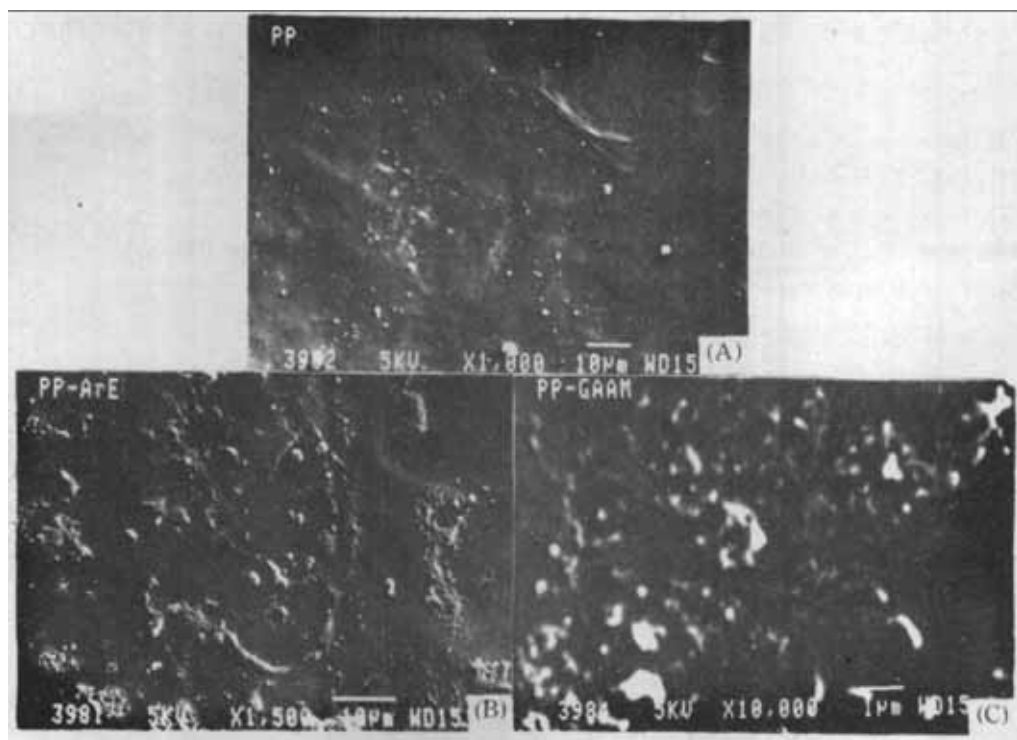


Fig.10 SEM photographs of PP films

The contact angles of H_2O and CH_2I_2 on blank (A), Ar plasma-treated (B) and acrylamide-grafted (C) PP films were determined. The surface energies of the films which were calculated by Owens and Wend's formula^[5] were listed in Table 1, in which γ_s^d and γ_s^h were dispersion force and the effect of polarity respectively. After Ar plasma-treatment, the contact angles of pp film either with H_2O or CH_2I_2 was reduced. Of course, the improvement of wettability mainly came from the effect of polarity. In general, active sites on polymer surface, generated by plasma bombardment, could react with oxygen to form some polar groups after exposing to atmosphere. It can also be seen in Table 1, the wettability of the acrylamide-grafted PP films was more efficaciously improved as

Table 1 Contact angle and surface energy of PP films

Samples	Contact	angle(°)	Surface energy (erg/cm ²)		
	H ₂ O	CH ₂ I ₂	γ_s^p	γ_s^d	γ_s
blank	95	44	0.44	37.10	37.54
Ar plasma-treated	82	36	3.01	38.68	41.69
acrylamide-grafted	69	25	13.02	25.62	38.64

compared with that of the Ar plasma-treated films. The incorporation of many amide groups onto surface leads to an increase of several times in polarity.

Keywords:

Graft copolymerization; Acrylamide polypropylene films; Plasma technique; Surface energy

REFERENCES

- [1] Hammermesh C. L. and Dynes P. J., *J. Polym. Sci., Polym. Letters Ed.*, **1975**, 13, 663.
- [2] Hall J. R., Westerdahl C.A.L., Devine A.T. and Bodnar M.J., *J. Appl. polym. Sci.*, **1969**, 13, 2086.
- [3] Hollahan J.R. and Wydeven T.J., Jr. *U.S.Pat.* 3, 847, 652, **1974**.
- [4] Deyan Shen, Application of IR to the studies of Polymers. Science Publishing house **1982**, p.91.
- [5] Owens D.K. and Wendt R.C., *J. Appl. polym. Sci.*, **1969**, 13, 1741.