Surface Grafting of Poly(vinylamine) onto Poly(ethylene) Film by Corona Discharge-Induced Grafting

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ABSTRACT: Poly(vinylamine) (PVAm) was grafted on a poly(ethylene) (PE) film surface via the surface graft polymerization of *N*-vinylformamide (NVF) and *N*-vinylacetamide (NVA) and the subsequent hydrolysis of those grafted polymers. The surface was characterized by X-ray photoelectron spectroscopy (XPS), contact angle, moisture absorption, and the leakage of electrostatic charge from the films. PNVF and PNVA were introduced onto the surface of the PE film successfully, in spite of the fact that the initiator for polymerization was a peroxide group. The grafted amounts of PNVF and PNVA were dependent on the grafting time. A PVAm-grafted surface was obtained via the hydrolysis of the grafted PNVF. The grafted-PNVA was not hydrolyzed under mild hydrolysis. The obtained PVAm-grafted surface appeared to be useful for various applications, such as protein immobilization or chemical modification. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1583–1587, 1999

Key words: graft polymerization; corona discharge treatment; *N*-vinylacetamide; *N*-vinylformamide; poly(vinylamine)

INTRODUCTION

Surface modification via surface graft polymerization has been widely studied in many fields. Various kinds of surface properties (such as static electricity, photoreactivity, and thermosensitivity) were realized using adequate monomers. In order to obtain a cationic surface, acrylic acid or acrylamide derivatives (e.g. dimethylaminopropylacrylamide, dimethylaminoethylmethacrylate, and diethylaminoethylacrylate) have been used.¹ On the other hand, when using cationic

surfaces for subsequent modification, (i.e., for the protein immobilization or chemical modification of amine groups), the grafted polymers in question need have a primary amine group. However, there are only a few monomers which can be used in these applications. Allylamine was one of the monomers that was used for further modification via primary amine groups. A novel methodology is needed in order to prepare other kinds of grafted poly(primary)amine. Poly(vinylamine) (PVAm) is one of the possible polymers in this regard; however, it is difficult to use in the preparation of the surface-grafted PVAm. Certain studies have examined the preparation of PVAm, such as the hydrazinolysis of poly(N-vinylphthalimide),² the Schmidt reaction of poly(acrylic acid),³ and the Hofmann degradation⁴⁻⁷ of poly(acrylamide).⁷ These methods were not suitable for obtaining

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surface-grafted PVAm. The other methods are the hydrolysis of poly(N-vinylacetamide),⁸ or poly(N-vinyl-tert-butylcarbamate).⁹

The authors have been studying the synthesis and the characterization of a series of vinylalkylamides and their polymers. Poly(N-vinylformamide) (PNVF) and poly(N-vinylacetamide) (PNVA) are effective precursors in the preparation of PVAm. In this study, N-vinylformamide (NVF) and N-vinylacetamide (NVA) were used as starting monomers to prepare surface-grafted PVAm. NVF or NVA were surface-graft polymerized on poly(ethylene) (PE) film, then the grafted PNVA or PNVF were hydrolyzed to form grafted PVAm, respectively. Researchers have found that the polymerization of NVA and NVF is sensitive to initiators, solvents, and temperature.⁸ The effectiveness of the corona discharge method on the grafting of NVF or NVA onto PE films was also analyzed. The characterization of grafted PVAm was also done via the static contact angle, the hygroscopicity, and the antistatic properties of the films.

EXPERIMENTAL

Materials

A blown-processed linear low-density PE film (J-REX.ELLD A208FS, 100- μ m thick) donated by Japan Olefins Co. (Tokyo, Japan) was used after purifying by Soxhlet extraction in distilled methanol for 48 h. NVF and NVA were donated by Showa Denko Co. Ltd. (Tokyo, Japan) and Mitsubishi Chemical Co. Ltd. (Tokyo, Japan), respectively, and used without further purification. Other chemicals were purchased from Nacalai Tesque (Kyoto, Japan) and used as obtained.

Surface Graft Polymerization

The surface graft polymerization procedure is shown in Figure 1. The equipment used in the corona treatment was developed by us, and we referred to that of Blythe et al.¹⁰ A circular parallel-plate electrode cell was constructed with stainless electrodes having a diameter of 17 cm. A pair of 2-mm-thick glass square plates (20×20 cm²) was used as insulator. They were placed being adjacent to each of the electrodes, with two glass blocks as spacers to maintain a fixed air gap of 1 mm. The PE films were cut to strips of 1×4 cm² and were placed on the lower glass plate. Any

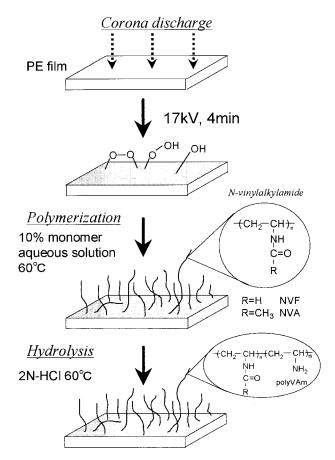


Figure 1 Schematic representation of amphiphilic polymer graft and hydrolysis experimental procedures.

trapped air was squeezed from underneath. A corona discharge treatment was done on the PE films in dry air under atmospheric pressure at 20°C. The gap voltage was 17 kV (10.6 W). The dose rate was calculated as 46.7 mW/cm². Films were treated for 4 min per side that was determined to give the maximum peroxide concentration to PE film surface.^{11,12} The corona-treated PE film was then immersed in a 10 wt % aqueous solution of NVF or NVA in a glass ampoule within 10 s, respectively. After a vigorous degassing of the contents (monomer solution and films), the ampoule was sealed and kept at 60°C for 3, 6, 12, and 24 h in order to achieve graft polymerization. The films were rinsed with water and stirred for 24 h in order to remove the homopolymers that had formed, and they were air-dried and stored in a desiccator before use. The grafted amounts were determined by gravimetry.

Characterization

The hydrolysis of surface-grafted PNVF or PNVA was done in 2N HCl at 60°C for 6 h. X-ray photo-

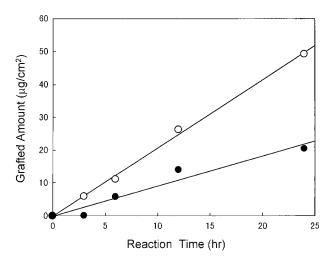


Figure 2 Time dependence of the grafted amounts of PNVF and PNVA: (\bigcirc) NVA; (\bigcirc) NVF.

electron spectroscopy (XPS) was performed on a ESCA 1000 (Shimadzu Co. Ltd., Kyoto, Japan) using a MgK α X-ray source. The static water contact angles were measured at 20°C using the sessile drop method, and 10 readings were averaged. The moisture absorption of the films was estimated by weight gain when the bone-dry film was maintained at 20°C under 65% RH for 50 h. The electrostatic propensity was evaluated by the half-life measuring method¹³ with a slight modification on a Static Honestmeter S-5109 (Shishido Electrostatic Ltd., Tokyo, Japan). After charging the film with 10 kV for 30 s, the period of time in which the charge potential attenuated to $\frac{1}{2}$ of the initial potential was observed at 20°C under 65% RH. Throughout the measurements, the filmfixed turntable was rotated at 1000 rpm. $^{\rm 14-20}$ In this study, as the charge potential did not attenuate to $\frac{1}{2}$ of the initial potential even after 120 s, the percentage of leakage after 5 min was calculated by estimating the electrostatic propensity.

RESULTS AND DISCUSSION

Surface Graft Polymerization

The amounts of PNVF and PNVA grafted onto the films are plotted as a function of the graft polymerization time in Figure 2. It can be seen that the graft polymerization amount increases almost linearly with the polymerization time. This time dependence of the grafted amount was due to the reactivity of the peroxide group that had formed on the PE surface.¹¹ The grafted amounts of

PNVF and PNVA after 24 h were 20.4 and 49.2 μ g/cm², respectively. The effects of initiators on the polymerization of NVF or NVA have already been reported.^{8,21} Based on the results of those studies, NVF and NVA have been thought not to be polymerized by peroxide-type initiators; however, the results of the study show that PNVF and PNVA could be polymerized by the peroxide-type initiators that are generated on the PE surfaces.

Characteization of Film Surface

Table I shows the static water contact angles of the surfaces of the films. After surface graft polymerization, the contact angles of the PE film decreased from 83.0 to 59.2° (PNVF-grafted) and 72.1° (PNVA-grafted), respectively. As PNVF and PNVA are amphiphilic polymers, the static contact angle of PNVF and PNVA surfaces are not as low as other hydrophilic-polymer-grafted surfaces, such as poly(acrylamide) (under 20°), it was, however, clear that PNVF was more hydrophilic than PNVA. Figure 3 shows the moisture absorption of the surface-grafted films. The moisture absorption of PNVA grafted film was saturated after 1 h, and the amount of moisture absorption per unit mass of the graft chains (MAP) was $0.82 \,\mu g/\mu g$. The moisture absorption of PNVF was saturated after 3 h, and the MAP was 2.23 $\mu g/\mu g$. The grafted amount of PNVF were less than that of PNVA (as mentioned above); however, the maximum amount of the adsorbed moisture of PNVF-grafted films was larger than that of the PNVA-grafted films. The MAP of the hydrolyzed-PNVF-grafted film was 7.75 μ g/ μ g. This indicates that their moisture absorption capacity was enhanced by the hydrolysis of the PNVF chains. On the other hand, the hydrolyzed-NVAgrafted film gave the same results as the NVAgrafted film (data not shown). This lack of change

$Sample^{a}$	Contact Angle ^b
PE NVA NVF	$egin{array}{rl} 83.0 \pm 1.8 \ 72.1 \pm 2.8 \ 59.2 \pm 1.4 \end{array}$

^a PE is an untreated polyethylene film; NVA, the PE film grafted with NVA (grafted amount = 11.1 μ g/cm²); NVF, the PE film grafted with NVF (grafted amount = 11.5 μ g/cm²).

 $^{\rm b}$ Values are means of 10 measurements \pm standard deviation.

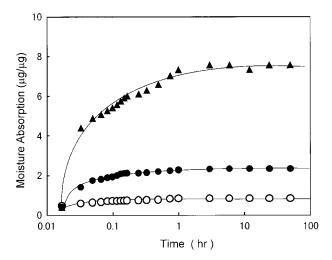


Figure 3 Moisture absorption behavior of the grafted films: (\bigcirc) the PE film grafted with NVA; (\bigcirc) the PE film grafted with NVF; (\blacktriangle) the PE film grafted with NVF and then hydrolyzed.

seemed to be caused by the fact that PNVA grafted on PE film was not hydrolyzed. The details are discussed in a latter section.

XPS wide scans of the films are shown in Figure 4. The surface of the corona discharged film has C_{1s} and O_{1s} peaks, as is evident from the strong O_{1s} band due to the oxidized carbon groups. The surface of the PNVF-grafted film shows $C_{\rm 1s},~O_{\rm 1s},$ and $N_{\rm 1s}$ peaks. The $N_{\rm 1s}$ peak comes from the nitrogen atoms in PNVF. This confirms that PNVF was introduced onto the surface of the PE film. When comparing the N_{1s} and C_{1s} peak ratios of the PNVF-grafted film, however, it becomes clear that the surface is not fully covered by PNVF chains. The stoichiometry of N_{1s}/C_{1s} was about 0.06, whereas the theoretical value was 0.5. This lower N_{1s}/C_{1s} is due to the low grafted amount of PNVF. The hydrolyzed PNVF grafted surface still gives an O_{1s} peak. PNVF was reported to be fully hydrolyzed under these experimental conditions (2N HCl, 60° C). The O_{1s} peaks seemed to be due to the PE substrate. The XPS spectra of PNVA showed almost the same results (data not shown). In order to obtain 100% hydrolyzed PNVA (PVAm), a strong level of hydrolysis was necessary (6N HCl, 90°C, 6 h). If this level of hydrolysis was used to hydrolyze the surface grafted polymers, the grafted polymers will be removed from the surface because of the breakdown of the PE substrate; therefore, a milder hydrolysis level was used in this study. Further research in order to obtain highly hydrolyzed surfaces is now in progress. The narrow scan of the

individual XPS peaks were measured and analyzed by decomposing the peaks; however, there were no stoichiometrical relationships between them. This also appears to be due to the low grafting amount of PNVF. As the grafted layer of PNVF was so thin that the O_{1s} and C_{1s} spectrums included these from the substrate (corona-treated PE), the N_{1s}/C_{1s} ratios became very small. Angle-

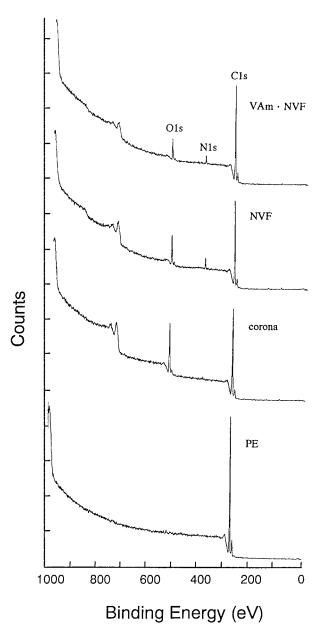


Figure 4 XPS wide scans of the film surfaces: (PE) an untreated PE film; (corona) the PE film treated by corona discharge; (NVF) the PE film grafted with NVF (grafted amount = 15.8 μ g/cm²); (VAm-NVF) the PE film grafted with NVF.

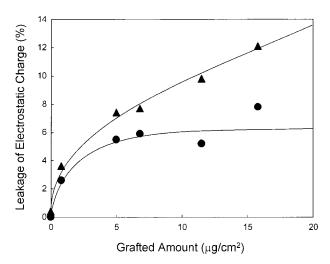


Figure 5 Leakage behavior of electrostatic charge for 5 min for the grafted films: (\bullet) the PE film grafted with NVF, (\blacktriangle) the PE film grafted with NVF and then hydrolyzed.

dependent XPS analysis is going to be measured in future research.

The antistatic property of surface-grafted film was studied for the further characterization of PVAm-grafted surfaces. The percentage of leakage after 5 min was measured on the PNVFgrafted films, and the hydrolyzed PNVF films, respectively. The results are plotted in Figure 5. Leakage of electrostatic charge (LEC) was significantly limited via grafting with PNVF. The antistatic property of the grafted PNVF was saturated over 5 μ g cm². The antistatic properties were still improved by hydrolyzing with the surface-grafted PNVF. LEC increased with an increase in the grafted amount of PNVF. This improvement in the antistatic property appears to be due to the presence of PVAm components. These results show that the grafting of PVAm onto the surface could improve the antistatic property, even if its grafted amount was low.

In conclusion, amphiphilic polymers (NVF and NVA) could be introduced onto the PE surface by the corona discharge treatment, though their grafted amounts were not so high. PVAm was successfully produced from PE-surface-grafted PNVF, while it was impossible to hydrolyze the surface-grafted PNVA. Using the primary amine groups of PVAm, thermosensitivity was already introduced.²² Moreover, the authors have estab-

lished the surface grafting of poly(*N*-isopropylacrylamide) via the corona discharge treatment method.¹² The next step of this study is to develop a novel functional surface combining the above technologies.

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