

Study on Antistatic Modification of Polyurethane Elastomer Surfaces by Grafting with Vinyl Acetate and Antistatic Agent

Xiangdong Zhou, Pengsheng Liu

Institute of Chemistry, Xiangtan University, Xiangtan 411105, China

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ABSTRACT: Under UV light, vinyl acetate (VAc) was grafted onto polyurethane (PU) elastomer membrane, using benzoyl peroxide as photoinitiator. After surface alcoholysis reaction, hydroscopic hydroxyl formed on the surface of PU, and under catalysis of $MgCl_2$, the antistatic agent combined with hydroxyl by chemical linkage, so that the antistatic durability of PU improved. The ATR-FTIR spectrum, X-ray photoelectron spectroscopy, and SEM characterized the grafted copolymers and verified the occurrence of grafting copolymerization. The effect of grafting degree of VAc on

the antistatic ability of PU surface was also investigated in this study. Experimental results showed that after modification the surface electric resistivity of PU elastomer reached the nearly $10^8 \Omega$ class, with little change in spite of a washing-fastness experiment, although its mechanical ability was slightly decreased. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3617–3624, 2003

Key words: polyurethanes; elastomers; surfaces; modification; graft copolymers

INTRODUCTION

The polyurethane (PU) industry has entered a stage of stable progress and advanced technology exploitation. The widely used PU elastomer, characterized by high performance, has not only good wearability but also high intensity, hardness, and considerable tenacity.¹ It is a good electric insulator, and its volume resistivity ranges from 1×10^{10} to $1 \times 10^{12} \Omega\text{-cm}$ and surface resistivity, from 1×10^{11} to $1 \times 10^{13} \Omega$; however, it often produces static electricity, which is potentially disastrous upon discharge.² Thus the antistatic problem of PU elastomer has been the focus of much research since the 1960s, and some antistatic or conductive packings have been under constant development. Today, this research has attained some achievements and has thus been partly industrialized,^{2–4} although it still lacks comprehensive and systematic investigations, with scant progress and only few reports.

A number of studies in the literature^{1–7} have reported that present methods of avoiding or suppressing static electricity in PU elastomers mainly include (1) adding an antistatic agent; (2) loading carbon black, metal powder, metal oxide, or inorganic salt; or

(3) mixing with a hydrophilic polymer or conductive polymer. All these approaches increased the antistatic ability, although by adopting method (1) the antistatic durability was poor and by adopting methods (2) or (3) its mechanical property and uniformity were poor.

This investigation thus concentrated on ways to improve the antistatic durability of PU to which an antistatic agent has been added: that is, by photografting vinyl acetate (VAc) onto the surface of a PU membrane,^{8,9} then introducing hydroxyl by alcoholysis of VAc, and finally by catalysis of $MgCl_2$, PU elastomer combined with TN by chemical linkage. Thus, the antistatic durability of PU surface was improved.

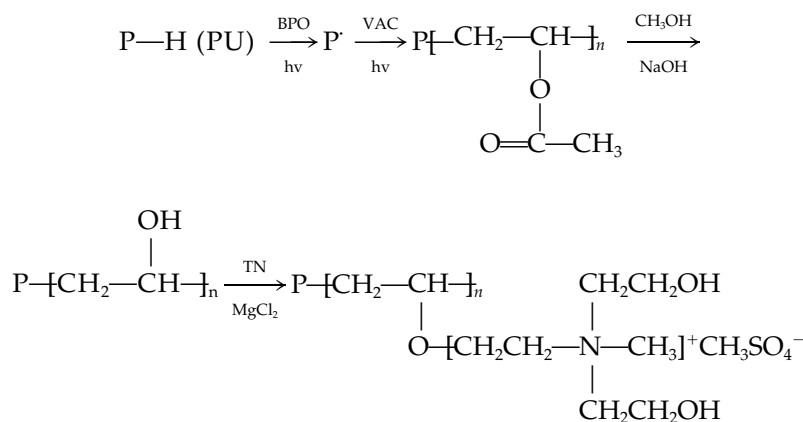
EXPERIMENTAL

Materials

PU membrane (10 cm \times 10 cm \times 0.3 mm; surface electric resistivity: $7.61 \times 10^{11} \Omega$) was a self-produced laboratory product. Vinyl acetate (VAc) and benzoyl peroxide (BPO) were both AR grade. Antistatic agent TN (N-methyl-N,N,N-trihydroxyethyl ammonium, monomethyl sulfate) and dimethylformamide (DMF) were both CP grade. Sodium chloride, iodine, sodium carbonate, benzene, toluene, xylene, alcohol, and methyl alcohol were all AR grade, without purification before use.

Principle of grafting reaction

Correspondence to: X.-D. Zhou (zxd_8@163.com).



Preparation of PU elastomer films

PU membranes were first cut into circular samples with a diameter of 8 cm and then subjected to Soxhlet extraction using ethyl alcohol as solvent for 8 h to remove impurities and oligomers in advance, and subsequently washed with distilled water to remove impurities on the surface. Finally, the samples were dried under vacuum for 24 h at 60°C and then stored in a dry apparatus.

Photografting polymerization procedure

Photografting polymerization was carried out with the apparatus whose light source was a 450-W high-

pressure mercury lamp. The distance from the UV lamp to the film was about 15 cm. The reactor was placed in a controlled water bath. The atmosphere in the reactor was controlled by filling with N₂ and the reaction temperature was controlled by a thermocouple meter. At the first stage, the PU membrane was immersed in a BPO/toluene solution (30 g/L) and subjected to UV-irradiation for a given time under stirring at 50°C. The photooxidized membrane was rinsed with water to remove excess BPO and dried at room temperature in vacuum. At the second stage, the photooxidized membrane was immersed in the solution consisting of VAc and toluene in proportion and covered with sheet glass. The graft copolymerization

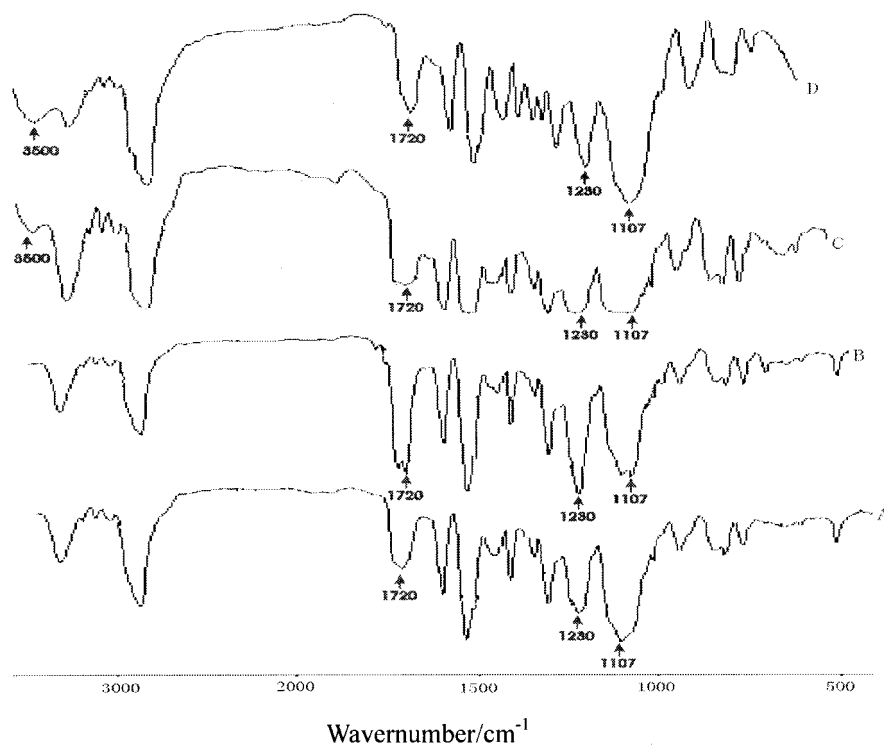


Figure 1 ATR-FTIR spectra of (A) PU, (B) PU-g-PVAc, (C) PU-g-PVAc after alcoholysis, and (D) PU-g-PVA-g-TN.

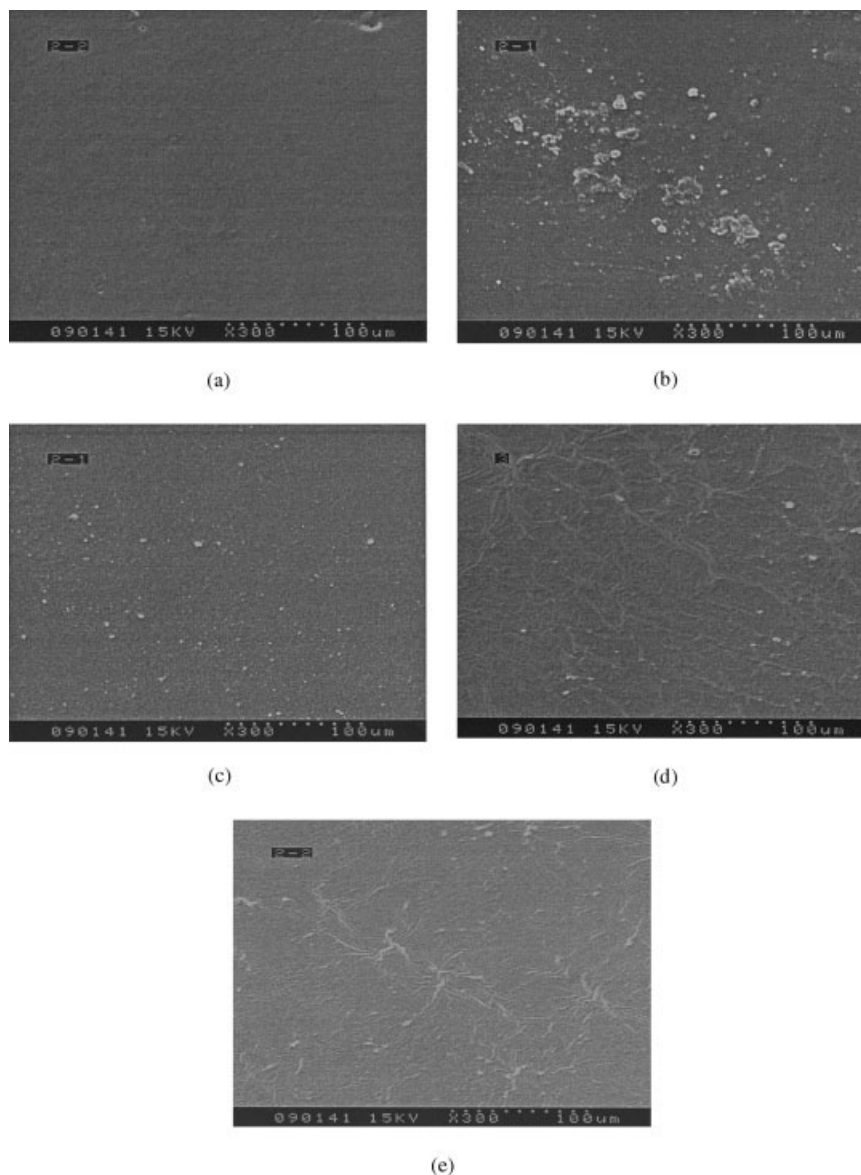


Figure 2 SEM micrographs of (a) ungrafted PU film, (b) PU-g-PVAc film, (c) PU-g-PVAc film after alcoholysis, (d) PU-g-PVA-g-TN film, and (e) PU-g-PVA-g-TN film after washing-fastness experiment.

was carried out under UV-irradiation for a given time at 50°C.

Subsequent handling of PU elastomer films

After irradiation, the film was removed; Soxhlet-extracted with ethanol for 24 h; washed repeatedly with hot water and distilled water to remove VAc homopolymer, BPO, and unreacted monomer; and finally dried in a vacuum oven at 60°C to a constant weight (W_g). In the experiment, we determined the quantity of ethanol used to remove PVAc according to the solubility of PVAc in ethanol, following the same earlier procedures. The experiment results stated that its solubility was almost 0.6625 g at room temperature

and it took 4 h to reach solubility. If all the VAc in the photografting polymerization reaction solution were changed into PVAc, the quantity of ethanol necessary to remove the PVAc could be counted. Actually, the quantity of ethanol added to the Soxhlet apparatus was 1.5 times as much as the determined theoretical value. Thus, all the PVAc homopolymer should be removed by Soxhlet extraction.

The degree of grafting ($G\%$) can be defined as¹⁰:

$$G\% = \frac{W_g - W_0}{W_0} \times 100$$

where W_g and W_0 denote the weights of the grafted and ungrafted PU films, respectively.

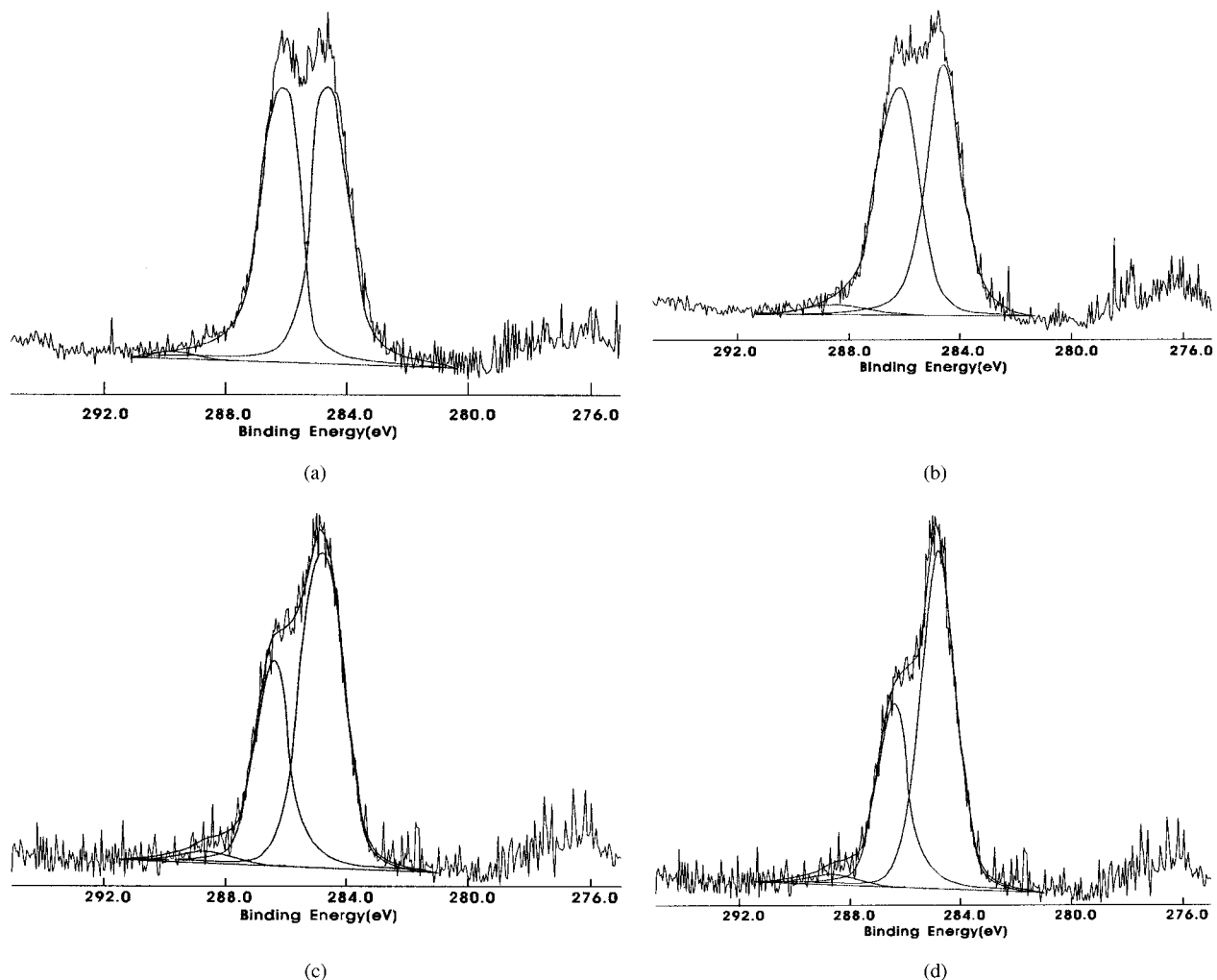


Figure 3 ESCA spectra for C1s of (a) PU film, (b) PU-g-PVAc film, (c) PU-g-PVAc film after alcoholysis, and (d) PU-g-PVA-g-TN film.

Alcoholysis

The PU-g-PVAc film was dipped into the methanol solution containing 2.5% NaOH under electromagnetic stirring at 30°C for 1 h and at 45°C for an additional 1 h.¹¹ The film was then removed from solution, repeatedly washed with distilled water, and dried to constant weight in a vacuum oven at 60°C.

Grafting reaction of antistatic agent

The grafting experiment was performed in a glass beaker. A solution consisting of antistatic agent (TN) and distilled water was added first, followed by a certain amount of MgCl₂. The grafting reaction was carried out by placing the beaker in a water bath under electromagnetic stirring at 60°C for 2 h. After the grafting reaction, the grafted sample was removed from the solution and placed in a dry box that was set at the desired temperature for 4 h. The grafted mem-

brane was rinsed with water to remove excess TN and MgCl₂, and dried at room temperature in vacuum.

Washing-fastness experiment of antistatic property of modified PU

The experiment was performed in a vessel under electromagnetic stirring. The antistatic modified PU membrane was immersed in a water solution containing 10 g/L washing powder and 2 g/L sodium carbonate. The vessel was placed in a water bath that was set at 60°C for 8 h. After this, the sample was removed and then subjected to Soxhlet extraction using ethanol as solvent for 8 h to remove impurities and additives in advance, and subsequently rinsed with a copious amount of water and then dried in vacuum at 50°C for 24 h. Finally, the surface electric resistivity of modified PU was measured.

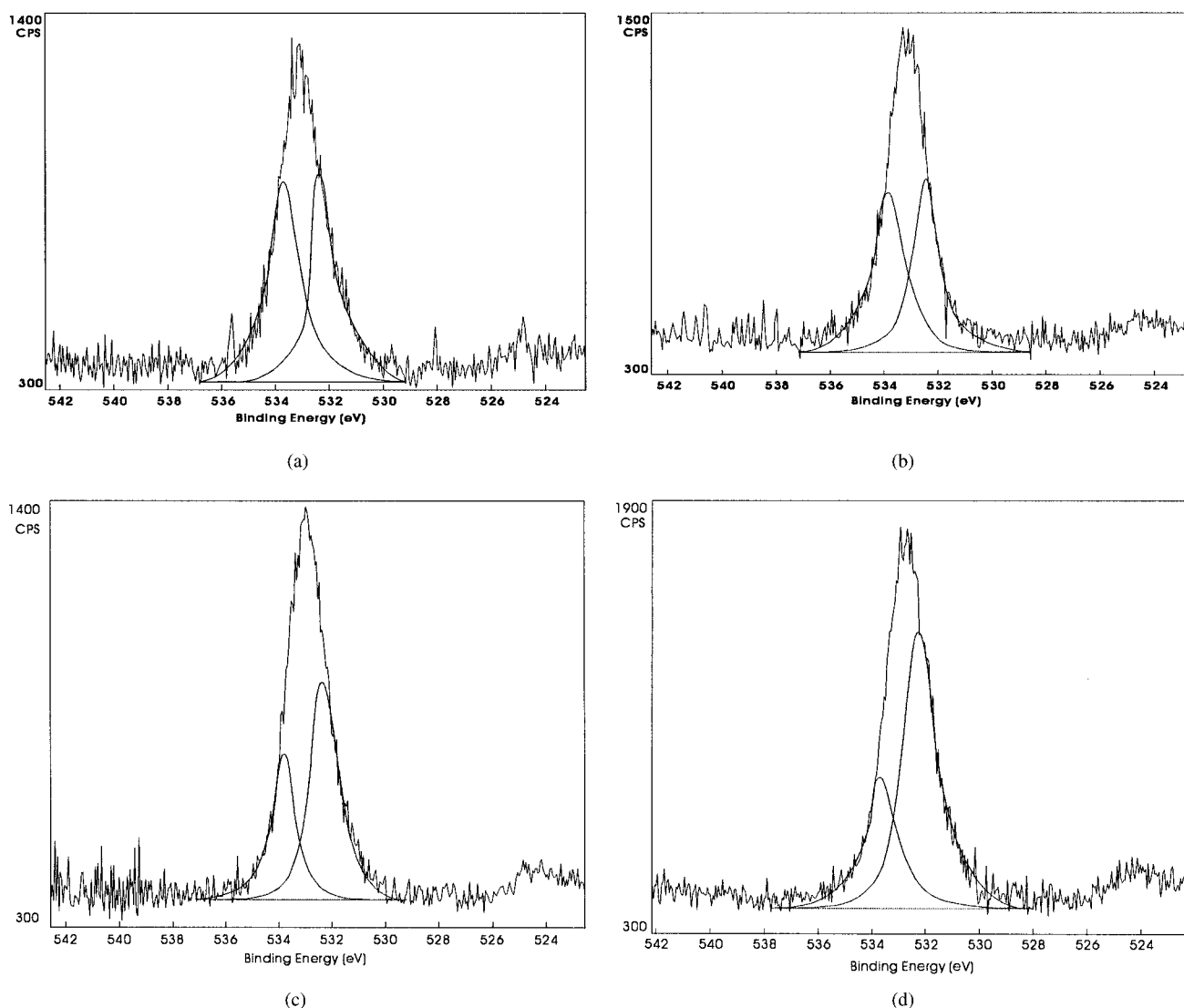


Figure 4 ESCA spectra for O1s of (a) PU film, (b) PU-g-PVAc film, (c) PU-g-PVAc film after alcoholysis, and (d) PU-g-PVA-g-TN film.

Characterization

Electrical surface resistivity

Under RH (relative humidity) of 65% and 25°C, the electrical surface resistivity of PU film was measured by an electrical high-resistivity meter (ZC36; Shanghai Precision Scientific Instrument Co., Ltd., China).

ATR-FTIR spectroscopy

ATR-FTIR spectra were obtained by using a Nicolet Magna-IR560 spectrometer (Nicolet Analytical Instruments, Madison, WI) equipped with a specific ATR attachment. The incident angle of infrared light was set at 45° with respect to the plane of the ZnSe crystal so that 12 internal reflections in total took place throughout the crystal. The 108×-scanned interfero-

grams were collected at 4 cm⁻¹ resolution and the scanning scope was 4000–400 cm⁻¹.

The PU membrane for ATR-FTIR was prepared by spreading a THF solution containing a 20% base PU onto a glass plate, after which the solution was rolled back and forth with a glass rod, so that we could obtain a very thin membrane (thickness < 30 μm). The plate was placed in vacuum box at 60°C to evaporate the solvent, then washed with copious amounts of distilled water and dried under vacuum to constant weight.

SEM

The surface morphological structure of specimens was studied using a scanning electron microscope (SEM S-570; Hitachi, Ibaraki, Japan).

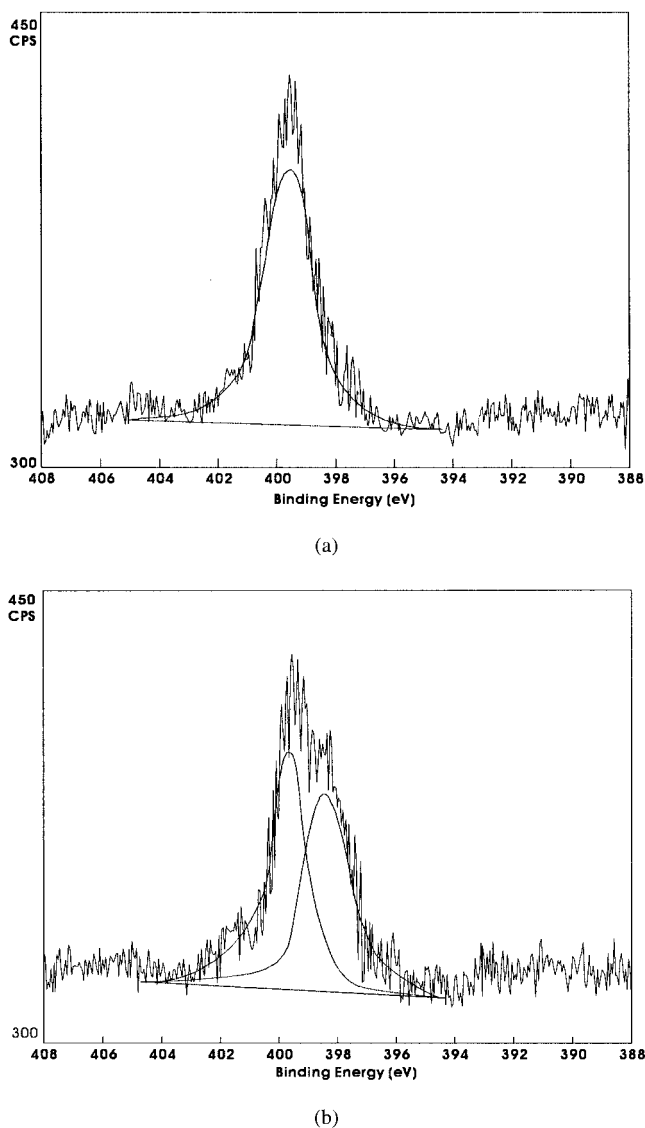


Figure 5 ESCA spectra for N1s of (a) PU film and (b) PU-g-PVA-g-TN film.

Tensile testing

The sample sheet was cut to the size required by the ASTM D 638-58T. The tensile testing was performed with a testing instrument (RGT-5A; Shenzhen Reger Instrument Co., Ltd., China) at room temperature with a crosshead speed of 30 mm/min.

Electron spectroscopy for chemical analysis (ESCA)

ESCA spectra were conducted on a ESCA LAB Mark II spectrometer (Scientific Instrument Services, Inc., Ringoes) employing Al-K α excitation radiation. The charging shift was referred to the C1s line emitted from the saturated hydrocarbon.

RESULTS AND DISCUSSION

Characterization of graftomer

Analysis of ATR-FTIR spectroscopy

The change of chemical structure of the surface of membranes before and after grafting was investigated by ATR-FTIR spectroscopy. Figure 1 shows their ATR-FTIR spectra. Compared with Figure 1(A) (spectrum of base membrane), the characteristic peak of carbonyl (1720 cm^{-1}) and C—O (1230 cm^{-1}) in Figure 1(B) (spectrum of film after grafting with VAc) had a distinct increase, which indicated that some of the VAc had been grafted onto the PU. Compared with Figure 1(A) and (B), the characteristic peak of —OH (3500 cm^{-1}) in Figure 1(C) had a distinct increase, which indicated that a number of —OH had been introduced by alcoholysis. From Figure 1(C) and (D), the characteristic peak of —OH vibrated even more strongly in Figure 1(D), which indicated that antistatic agent (TN) had been grafted with PVA onto the surface of PU, attributed to more —OH in TN. The stronger vibration of the characteristic peak of C—O—C (1107 cm^{-1}) also proved the grafting of TN.

Analysis of SEM micrographs

SEM micrographs are illustrated in Figure 2. Looking at Figure 2(B), one may observe numerous unevenly distributed grainy PVAc grafted onto the surface of PU membrane, which might be caused by different degrees of grafting attributed to the nonhomogeneity of lamplight, although they are decreased in size in Figure 2(C) because the PVAc had been partly alcoholized. Figure 2(D) and (E) show that a layer of compact antistatic agent membrane had formed on the PU surface after grafting TN. After the washing-fastness experiment, the layer hardly changed, which proved the grafting modified the PU with a characteristically good durable antistatic property.

Analysis of ESCA spectra

C1s. The C1s ESCA spectra are shown in Figure 3. The C1s spectrum of the control membrane gave three component peaks with the binding energy at 284.7, 286.3, and 288.6 eV, respectively [Fig. 3(A)]. The peak at 284.7 eV could be attributed to the saturated carbons. The C1s peak corresponding to the carbonyl of the urethane groups was observed at 288.6 eV. The peak at 286.3 eV could be attributed to the carbonyl carbon of the ester group.¹² In the C1s spectrum of the PU-g-PVAc membrane, the strength of the binding energy at 286.3 and 284.7 eV was higher than that of the control membrane. This indicated that the amount of ester groups on the surface increased, which came from PVAc [Fig. 3(B)]. Compared with the PU-g-PVAc

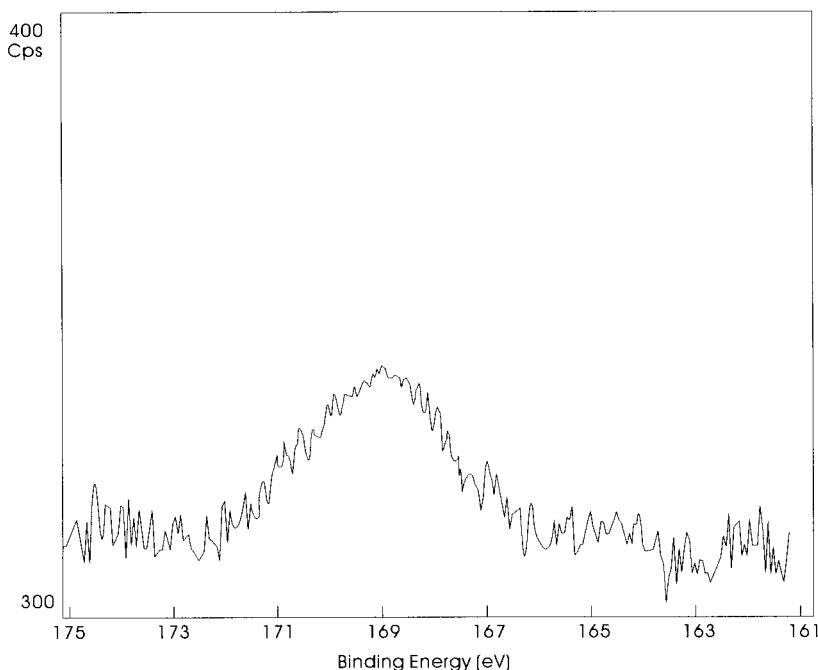


Figure 6 ESCA spectrum for S2p of PU-g-PVA-g-TN film.

membrane, the strength of the binding energy at 286.3 eV in the PU-g-PVAc membrane after alcoholysis [Fig. 3(C)] became smaller, which indicated that the amount of ester groups on the surface decreased because of the alcoholysis of PVAc. It may also be seen from Figure 3(D) where the strength of binding energy at 284.7 eV increased higher than that of the PU-g-PVAc film after alcoholysis, which implied that TN grafted onto PU. It could be concluded from the C1s spectra differences among the control membrane, grafted membrane, and PU-g-PVAc after alcoholysis that graft copolymerization and alcoholysis occurred.

O1s. The O1s ESCA spectra are shown in Figure 4. The O1s spectrum of the control membrane [Fig. 4(A)] could be considered as the contribution of oxygen in the ester and urethane groups. There were two peaks with the binding energy at 532.4 and 533.8 eV, respectively, which was attributed to the oxygen of the C—O bond and C=O bond in the ester and urethane groups, respectively. Figure 4(B) shows the O1s spectrum of the PU-g-PVAc membrane. The curve at 532.2 and 533.9 eV obviously increased, which was attributed to the oxygen of the C—O bond and C=O bond in the ester and urethane groups, respectively. It was the result of the PVAc unit grafted onto the PU membrane. As compared with the PU-g-PVAc membrane [Fig. 4(B)], the strength of the binding energy at 533.9 and 532.2 eV in the PU-g-PVAc membrane after alcoholysis [Fig. 4(C)] and PU-g-PVA-g-TN [Fig. 4(D)] became smaller and higher, respectively, which indicated that the amount of ester groups on the surface decreased and hydroxyl increased because of alcohol-

ysis of PVAc and antistatic agent TN grafted onto the PU membrane, respectively.

N1s. Figure 5 shows the N1s ESCA spectra of PU membranes. The control and PU-g-PVA-g-TN membranes showed the peak with the binding energy at 400.4 eV, which was attributed to the nitrogen in urethane. The N1s spectrum of PU-g-PVA-g-TN membrane [Fig. 5(B)] gave an extra peak with the binding energy at 399.3 eV, which was attributed to the nitrogen in TN.

S2p. The S2p ESCA spectrum of PU-g-PVA-g-TN membrane is shown in Figure 6. The S2p spectrum gave a peak with the binding energy at 169 eV, which could be attributed to the sulfur of the sulfate radical in TN.

Effect of grafting degree of VAc on surface electric resistivity of PU

The experimental results are presented in Figure 7, which indicates that the grafting degree of VAc had a dramatic effect on the surface antistatic property of PU. The surface electric resistivity decreased with the increasing of grafting degree of VAc, but it increased after the washing-fastness test: the higher the grafting degree, the less the surface electric resistivity increased. The antistatic ability of modified PU was enhanced with better durability when the grafting degree of VAc increased. At the same time, Figure 7 also shows that the surface electric resistivity of modified PU might decrease to the $10^8 \Omega$ class and could

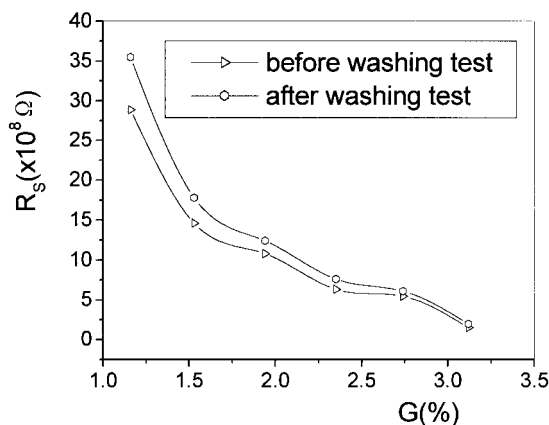


Figure 7 Effect of grafting degree of VAc on surface electric resistivity of PU film.

maintain the $10^8 \Omega$ class after the washing-fastness experiment.

Effect of RH on surface electric resistivity of PU

The effect of RH on surface electric resistivity of PU is illustrated in Figure 8, which indicates that the surface electric resistivity of PU was influenced by the RH of atmosphere. The surface electric resistivity increased with the decrease of relative humidity. Because the surface electric resistivity of antistatic material should be below grade $10^{10} \Omega$,¹³ the modified PU is still fit for antistatic materials even if under a lower humidity atmosphere.

Effect of grafting modification on mechanical property of PU

Table I indicates the effect of grafting antistatic modification on the mechanical property of PU membrane. From this table, one may observe that the mechanical property of PU declined slightly after modification,

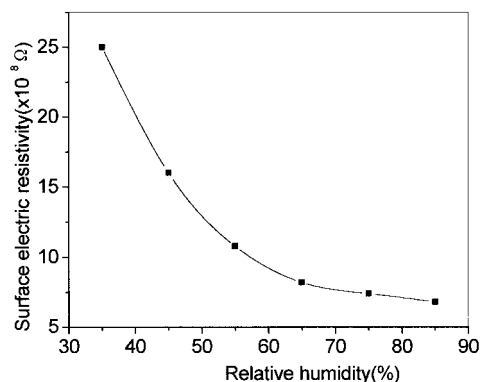


Figure 8 Effect of relative humidity on surface electric resistivity of PU film.

TABLE I
Effect of Grafting Modification on Mechanical Properties of PU Films

Type of sample	Tensile strength (MPa)	Rupture elongation (%)
PU	52.97	117.24
PU-g-PVAc	49.44	107.38
PU-g-PVAc after alcoholysis	46.50	100.51
PU-g-PVA-g-TN	44.28	97.29

which might be caused by the swelling generated by dissolution of the organic solvent and the oxidation damage of the photoinitiator during the process.

CONCLUSIONS

1. Polyurethane with a surface antistatic property was prepared by photooxidizing and grafting with VAc under UV-irradiation, and then an active hydroxyl ($-\text{OH}$) could be introduced to the surface of PU by VAc alcoholysis. In the end, the hydroxyl combined with antistatic agent TN by chemical linkage to form a compact antistatic membrane on the surface of PU under catalysis of MgCl_2 and appropriate temperature. Surface analysis (ATR-FTIR, ESCA, SEM) verified the occurrence of grafting copolymerization.
2. PU-g-PVA-g-TN film has both antistatic ability and durability superior to those of films modified by adding antistatic agent by the usual methods. The antistatic ability and durability of the grafted film increased with increasing of degree of grafting.
3. After antistatic modification, the mechanical property of PU declined slightly and its surface electric resistivity was influenced by the relative humidity of the atmosphere, although it could still meet the antistatic requirement.

References

1. Zhu, Y. *Polyurethane Ind* 1994, 4, 11.
2. Shanxi Institute of Chemical Industry. *Polyurethane Elastomer Manual*; Chemical Industry Press: Beijing, 2000; pp. 15–90.
3. Alex, P. U.S. Pat. 6,018,015, 2000.
4. Pcolinsky, M. P. U.S. Pat. 4,605,684, 1986.
5. Li, F.; Qi, L.; Yang, J. *J Appl Polym Sci* 2000, 75, 68.
6. Gerherd, B. U.S. Pat. 4,526,925, 1985.
7. Ruckenstein, E.; Sun, Y. *Synth Met* 1995, 75, 79.
8. Deng, J.; Yang, W.; Ranby, B. *J Appl Polym Sci* 2000, 77, 1513.
9. Deng, J.; Yang, W.; Ranby, B. *J Appl Polym Sci* 2000, 77, 1522.
10. Guan, J.; Gao, C. *J Appl Polym Sci* 2000, 77, 2505.
11. Markley, T. J.; Pinschmidt, R. K. *J Polym Sci Part A: Polym Chem* 1996, 34, 2581.
12. Bai, G.; Hu, X.-Z.; Yan, Q. *Polym Bull* 1996, 36, 503.
13. Zhao, C. *Antistatic Technology of Polymers*; Textile Industry Press: Beijing, 1996; pp. 8–10.