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Preparation and characterization of durable antistatic polyurethane elastomer by preirradiation grafting on its film

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Polyurethane (PU) film gave birth to free radical by ^{60}Co-γirradiation under nitrogen atmosphere, and then the film was dipped into water-ethanol solution of β-hydroxyl ethyl ester methacrylic acid (HEMA). After HEMA grafting with PU on the surface, PU-g-PHEMA (i.e. the grafted copolymer of HEMA onto PU) film was dipped into antistatic agent (TN). The PU-g-PHEMA-g-TN (i.e. the grafted copolymer of TN onto PU-g-PHEMA) film that has durable antistatic property on its surface was synthesized by PU-g-PHEMA film grafted with TN under catalysis of $MgCl_2$. The grafted copolymers were characterized by ATR-FTIR spectroscopy, Electron Spectroscopy for Chemical Analysis (ESCA), and Scanning Electron Microscopy (SEM), etc. The electrical property, thermal property, and mechanical behavior of PU after antistatic modification were tested. The results showed that after antistatic modification the surface electric resistivity of PU elastomer reached nearly 10^8 Ω class, with little change in a washing-fastness experiment, while its mechanical ability and thermal characteristic were slightly decreased. The result of WAXD indicated that the regular construction degree of the grafted PU declined, the grafting chains distributed randomly on the surface of PU.

1. 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 1×10^8 to 1×10^{10} Ω-m and surface resistivity, from 1×10^{11} to 1×10^{13} Ω; 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 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, although it still lacks comprehensive and systematic investigations, with scant progress and only few reports [2–4].

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 [8–10] to improve the antistatic durability of PU to which an antistatic agent has been added: that is, In nitrogen atmosphere, polyurethane (PU) film gave birth to free

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radical under ^{60}Co-γ irradiation and the film was dipped into water-ethanol solution of β-hydroxyl ethyl ester methacrylic acid thereon. PU-g-PHEMA film was gained by PU grafted with PHEMA, and PU-g-PHEMA-g-TN film having durable antistatic property on its surface was synthesized after PU-g-PHEMA film grafted with antistatic agent under catalysis of $MgCl_2$. Thus, the antistatic durability of PU surface was improved.

2. Experimental

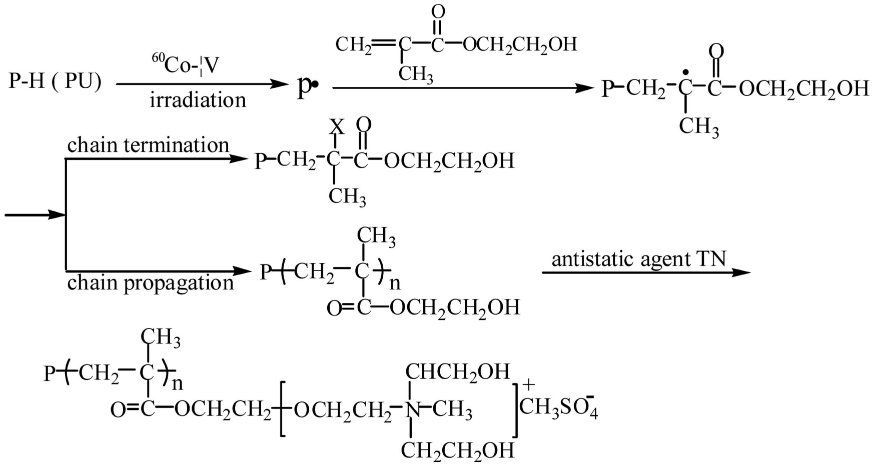
2.1. Materials

PU membrane [10 cm × 10 cm × 0.3 mm; surface electric resistivity: 7.61×10^{11} Ω; weight-average molecular weight (average M_w): 94417; hard segment content (wt%): 40%; soft segment content (wt%): 60%] was a self-produced laboratory product and β-hydroxyl ethyl ester methacrylic acid (HEMA) was 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.

2.2. Principle of grafting reaction

2.3. Preparation of durable antistatic PU elastomer films

2.3.1. Pretreatment 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.

2.3.2. Grafting of HEMA onto surface of PU

PU membrane was put into irradiation apparatus filled with some alcohol-water solution and oxygen in the apparatus was driven away by filling with nitrogen after 12 h. The membrane was subsequently irradiated by ^{60}Co-γ irradiation (dose = 60 kGy) for certain time and then was transferred to other container filled with definite alcohol-water solution of HEMA at room temperature in atmosphere of N_2. After a given time, the film was removed; Soxhlet-extracted with ethanol for 24 h; washed repeatedly with hot water and distilled water to remove HEMA homopolymer and unreacted monomer; and finally dried in a vacuum oven at 60°C to a constant weight. Grafting level of HEMA is quantified by degree of grafting (G_1). The degree of grafting (G_1) can be defined as [11]:

$$G_1 = 100(W_2 - W_1)/W_1(\%)$$

where W_1 and W_2 denote the weights of the PU and PU-g-PHEMA films, respectively.

2.3.3. 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 $MgCl_2$. 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 membrane was rinsed with water to remove excess TN and $MgCl_2$, and dried at room temperature in vacuum. Grafting level of TN is quantified by degree of grafting (G_2). The degree of grafting (G_2) can be defined as [11]:

$$G_2 = 100(W_4 - W_3)/W_3(\%)$$

where W_4 and W_3 denote the weights of the PU-g-PHEMA-g-TN and PU-g-PHEMA films, respectively.

2.4. 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 kg/m^3 washing powder and 2 kg/m^3 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.

2.5. Experiment to remove TN of PU-g-PHEMA-g-TN film

The experiment was performed in a three-necked bottle fitted with condenser. The PU-g-PHEMA-g-TN film was immersed in excessive 57% (wt%) hydroiodic acid (HI) added firstly, and then heated to form backflow at 120°C for 2 h under nitrogen atmosphere. After this, the sample was removed from the solution and subsequently rinsed with a copious amount of water and then dried in vacuum oven at 60°C to a constant weight. Finally, SEM of the film was measured.

2.6. Characterization

2.6.1. 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 interferograms 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%(wt%) 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.

2.6.2. Scanning electron microscope (SEM)

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

2.6.3. Electron spectroscopy for chemical analysis (ESCA)

ESCA spectra were conducted on ESCA LAB Mark II spectrometer (Scientific Instrument Services, Inc., Ringoes) employing Al-K⟨alpha⟩ excitation radiation. The charging shift was referred to the C1s line emitted from the saturated hydrocarbon. Every sample in ESCA test was circular membrane with a diameter of 8 mm, and thickness of 0.3 mm. Quantitative surface analysis and curve-fitting were carried out using the manufacturer's standard software. The error range of percentage of element (At.%) and percentage of species (area%) are from ± 10% to ± 20%.

2.6.4. 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). Measurement range of the meter is from 1×10^3 Ω to 1×101^7 Ω, error range is from ± 0.5% to ± 2%. Each sample was tested three times and got average value.

2.6.5. Tensile testing

The sample sheet was cut to the size required by the ASTM D 638–58 T. The tensile strength and rupture elongation were performed with a testing instrument (RGT-5 A; Shenzhen Reger Instrument Co., Ltd., China) at room temperature with a crosshead speed of 30 mm/min. Tensile strength (MPa), error ± 0.5%; rupture elongation (%), error ±3.5%. Each sample was tested three times and got average value.

2.6.6. Thermogravimetry (TG) analysis

TG was performed on a Perkin-Elmer TGA-7 thermal gravimetric analyzer, error ± 1%. The mass of each sample was about 5–6 mg. The carrier gas was nitrogen with a flow rate of 5×10^{-5} m^3/min. The temperature was raised from 50°C to 450°C at rate of 10°C/min. The TG curves were recorded.

2.6.7. Variable-temperature wide-angle X-ray diffraction (WAXD)

Variable-temperature wide-angle X-ray diffractograms were recorded on a Rigaku Dmax-rc X-ray diffractometer with CuK⟨alpha⟩ radiation (40 kV, 100 mA), which had been fitted with a high-temperature sample chamber. The film for WAXD measurement was placed into a platinum holder and then heated to desired temperature at a rate of 5°C/min. Before commencing the data collection, the sample was held for 2 min at that temperature. WAXD error < ± 2.5%.

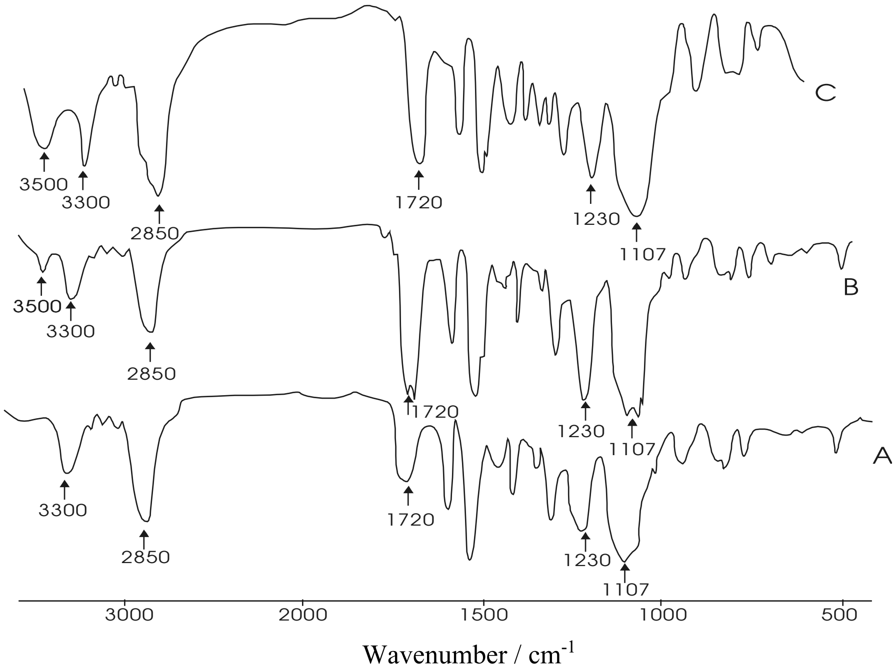


Figure 1 ATR-FTIR spectra of (A) PU, (B) PU-g-PHEMA ($G_1 = 8.5\%$), (C) PU-g-PHEMA-g-TN ($G_1 = 8.5\%$, $G_2 = 15.4\%$).

3. Results and discussion

3.1. Characterization of graftomer

3.1.1. 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. Fig. 1 shows their ATR-FTIR spectra. Compared with Fig. 1(A) (spectrum of base membrane), the characteristic peak of –OH (3500 cm^{-}1) and carbonyl (1720 cm^{-}1) as well as C–O (1230 cm−1) in Fig. 1(B) (spectrum of film after grafting with HEMA) had a distinct increase, which indicated that some of the HEMA had been grafted onto the PU. Compared with Fig. 1 (A) and (B), the characteristic peak of –OH vibrated even more strongly in Fig. 1 (C), which indicated that antistatic agent (TN) had been grafted with HEMA onto the surface of PU, attributed to more –OH in TN.

3.1.2. Analysis of SEM micrographs

SEM micrographs are illustrated in Fig. 2. Looking at Fig. 2(b), one may observe numerous unevenly distributed grainy PHEMA grafted onto the surface of PU membrane, which might be caused by different degrees of grafting attributed to the nonhomogeneity of ^{60}Co-γirradiation. Fig. 2(c) shows that a layer of compact antistatic agent membrane had formed on the PU surface after grafting TN. However, Fig. 2(d) shows that the antistatic agent membrane had been disappeared by action of hydroiodic acid, which should be caused by breakage of ether linkage between HEMA and TN. This indicates that TN had been grafted with PHEMA onto surface of PU by forming ether linkage.

TABLE I Percentage of elements of PU and grafted PU

	Percentage of elements (At.%)		
Element	PU	PU-g-PHEMA ($G_1 = 8.5\%$)	PU-g-PHEMA-g-TN ($G_1 = 8.5\%$, $G_2 = 15.4\%$)
C	79.5	80.9	79.1
O	18.6	17.6	18.5
N	1.9	1.5	1.8
S	0	0	0.6

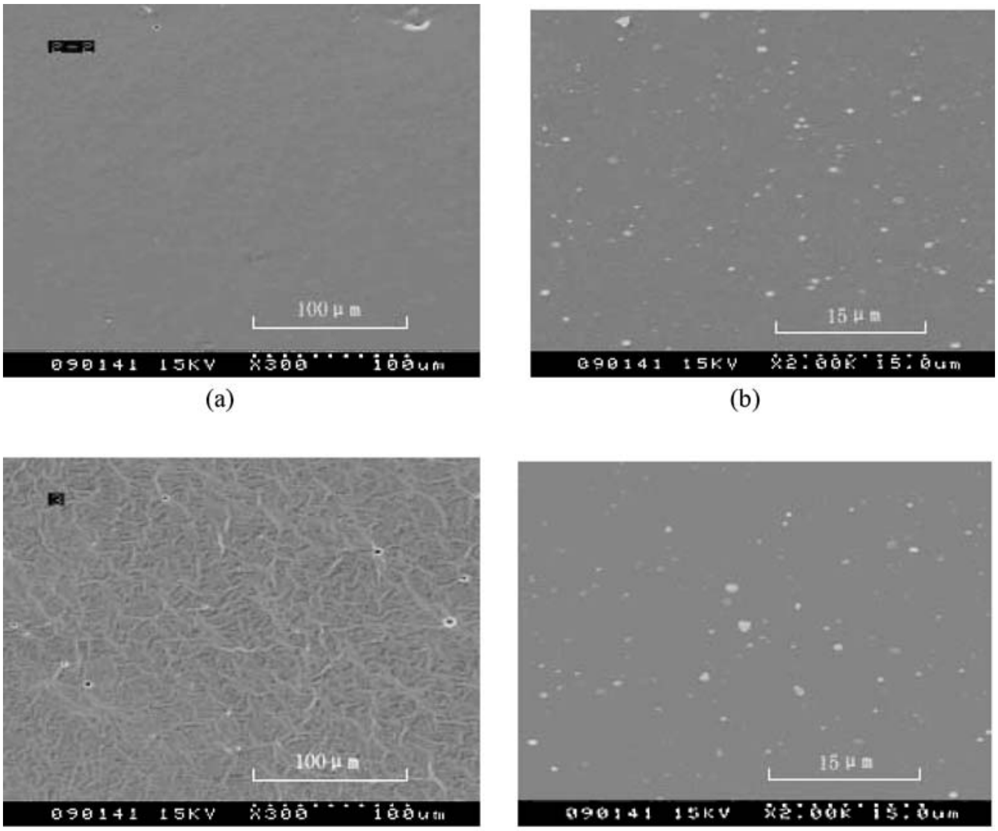
3.1.3. Analysis of ESCA spectra

The percentage of element (At.%) of PU and grafted PU obtained by ESCA quantitative surface analysis is shown in Table I.

3.1.3.1. C1s. The C1s ESCA spectra and the percentage of species (area%) from the C1s ESCA spectra are shown in Fig. 3 and Table II, respectively. The C1s spectrum of the control membrane gave three component peaks with the binding energy at 284.7, 286.3, and 288.6 eV,

TABLE II Percentage of species obtained from C1s curve fitting of PU and grafted PU

		Percentage of species (area%)		
Species	Binding energy (eV)	PU	PU-g-PHEMA ($G_1 = 8.5\%$)	PU-g-PHEMA-g-TN ($G_1 = 8.5\%$, $G_2 = 15.4\%$)
C—C, C-H	284.7	48	52	51
C-O	286.3	46	43	44
-NHCOO	288.6	6	5	5



(a) (b)

(c) (d)

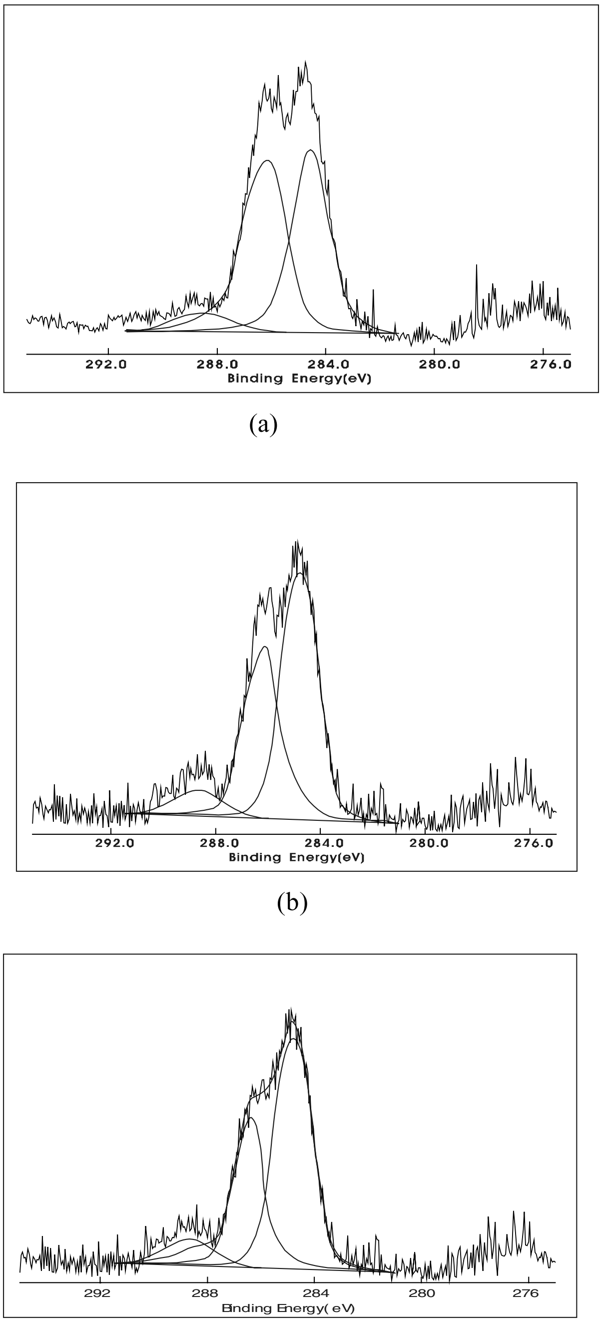
Figure 2 SEM micrographs of (a) ungrafted PU film, (b) PU-g-PHEMA film ($G_1 = 8.5\%$), (c) PU-g-PHEMA-g-TN film ($G_1 = 8.5\%$, $G_2 = 15.4\%$), (d) PU-g-PHEMA-g-TN film (TN had been removed).

respectively (Fig. 3a). The peak at 284.7 eV could be attributed to the saturated carbons. The C1s peak corresponding to 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. In the C1s spectra of the PU-g-PHEMA film and PU-g-PHEMA -g-TN film (Fig. 3b and Fig. 3c), the percentage of species [52 and 51 area%, respectively] of the binding energy at 284.7 eV was higher than that [48 area%] of the control membrane. This indicated that the amount of saturated carbon on their surfaces increased, which came from HEMA and TN. It could be concluded from the percentage of elements and the C1s spectra differences among the control membrane and grafted membranes that graft copolymerizations occurred.

3.1.3.2. O1s. The O1s ESCA spectra and the percentage of species (area%) from the O1s ESCA spectra are shown in Fig. 4 and Table III, respectively. The O1s spectrum of the control membrane (Fig. 4a) could be considered as 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. Fig. 4b shows the O1s spectrum of the PU-g-PHEMA film. Compared with Fig. 4a, the curve at 532.4 eV in Fig. 4b obviously increased (the percentage of species changed from 52–56 area%), which was attributed to the oxygen of the C—O bond in HEMA. As compared with the PU-g-PHEMA film (Fig. 4b), the strength of the binding energy at 532.4 eV in the PU-g-PHEMA-g-TN film (Fig. 4c) became higher (the percentage of species changed from 56–62 area%), which indicated that the amount of C-O bond increased because antistatic agent TN grafted onto the PU membrane.

3.1.3.3. N1s. Fig. 5 and Table IV show the N1s ESCA spectra and the percentage of species (area%) from the N1s ESCA spectra, respectively. The control and PU-g-PHEMA-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-PHEMA-g-TN membrane (Fig. 5b) gave an extra peak with the binding energy at 399.3 eV (percentage of the species is 46 area%), which was attributed to the nitrogen in TN .

3.1.3.4. S2s and S2p. The S2s and S2p ESCA spectra of PU-g-PHEMA-g-TN film are shown in Fig. 6. The S2s and S2p ESCA spectra gave a peak with the binding energy at 232 eV and 169 eV respectively, which



(a)

(b)

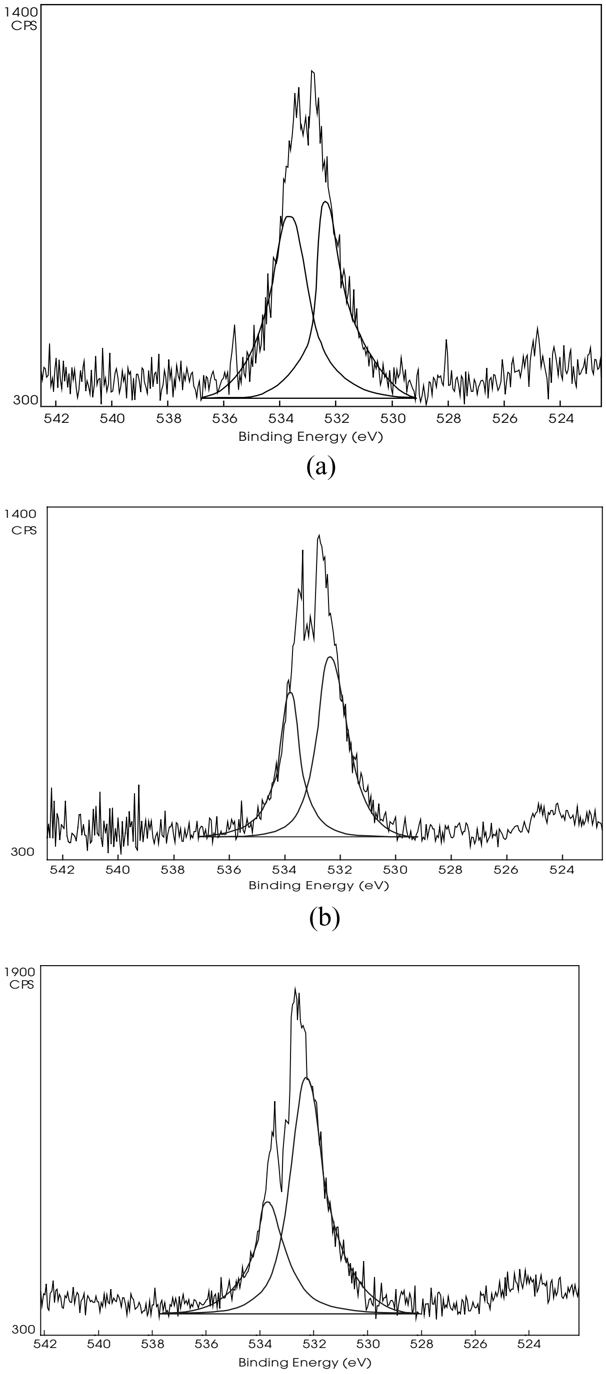
(c)

Figure 3 ESCA spectra for C1s of (a) PU film, (b) PU-g-PHEMA film (G_1 = 8.5%), (c) PU-g-PHEMA-g-TN film (G_1 = 8.5%, G_2 = 15.4%).

could be attributed to the sulfur of the sulfate radical in TN.

3.2. Effect of grafting of HEMA or TN on antistatic property of PU

The experimental results are presented in Table V, which indicates that the grafting of HEMA or TN had a dramatic effect on the surface antistatic property of PU. The surface electric resistivity decreased with not only the grafting of HEMA or TN, but also addition of TN into PU. However,



(a)

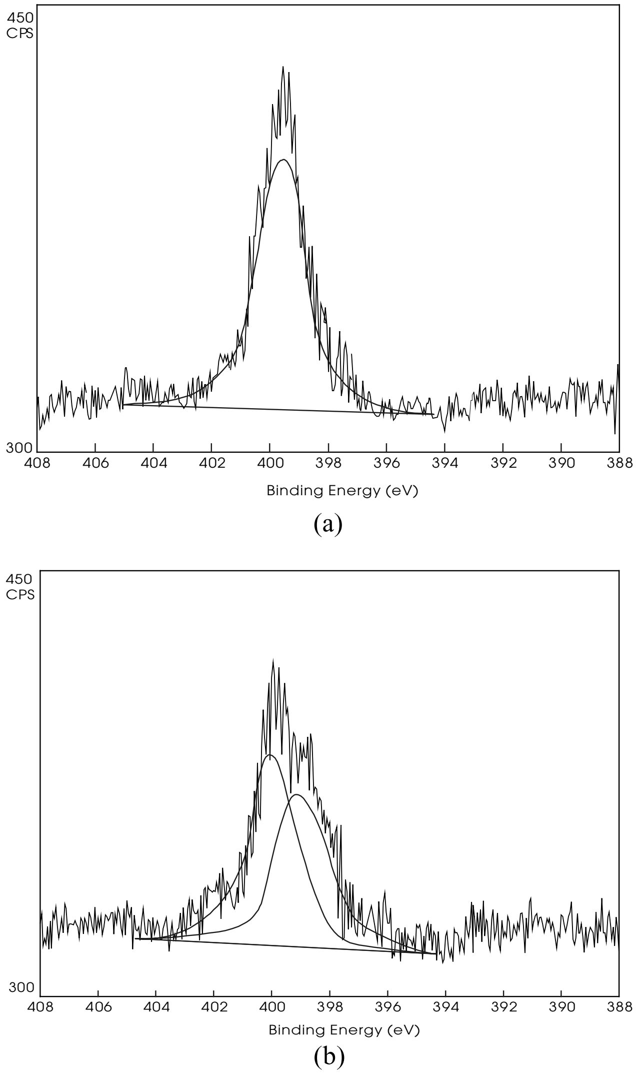
(b)

(c)

Figure 4 ESCA spectra for O1s of (a) PU film, (b) PU-g-PHEMA film (G_1 = 8.5%), (c) PU-g-PHEMA-g-TN film (G_1 = 8.5%, G_2 = 15.4%).

TABLE III Percentage of species obtained from O1s curve fitting of PU and grafted PU

		Percentage of species (area%)		
Species	Binding energy (eV)	PU	PU-g-PHEMA (G_1 = 8.5%)	PU-g-PHEMA-g-TN (G_1 = 8.5%, G_2 = 15.4%)
C–O	532.4	52	56	62
C=O	533.8	48	44	38



(a)

(b)

Figure 5 ESCA spectra for N1s of (a) PU film, (b) PU-g-PHEMA-g-TN film ($G_1 = 8.5\%$, $G_2 = 15.4\%$).

the PU-g-PHEMA-g-TN film had best antistatic property and durability.

3.3. Effect of grafting modification on mechanical property of PU

Table VI 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 grafting with HEMA, which might be caused by damage of ^{60}Co-γirradiation during the process, but grafting with TN had little effect on mechanical property of PU.

3.4. Effect of grafting modification on thermal characteristic of PU

Fig. 7 indicates the effect of grafting modification on thermal characteristic of PU. Fig. 7 shows a gradual weight loss above 350°C in the curves (a, b, c), which could be attributed to degradation of PU. The curves (b, c) show that weight loss occurs at 310–350°C, which could be at-

TABLE IV Percentage of species obtained from N1s curve fitting of PU and grafted PU

		Percentage of species (area%)	
Species	Binding energy (eV)	PU	PU-g-PHEMA-g-TN ($G_1 = 8.5\%$, $G_2 = 15.4\%$)
—NHCOO	400.4	100	54
C—N	399.3	0	46

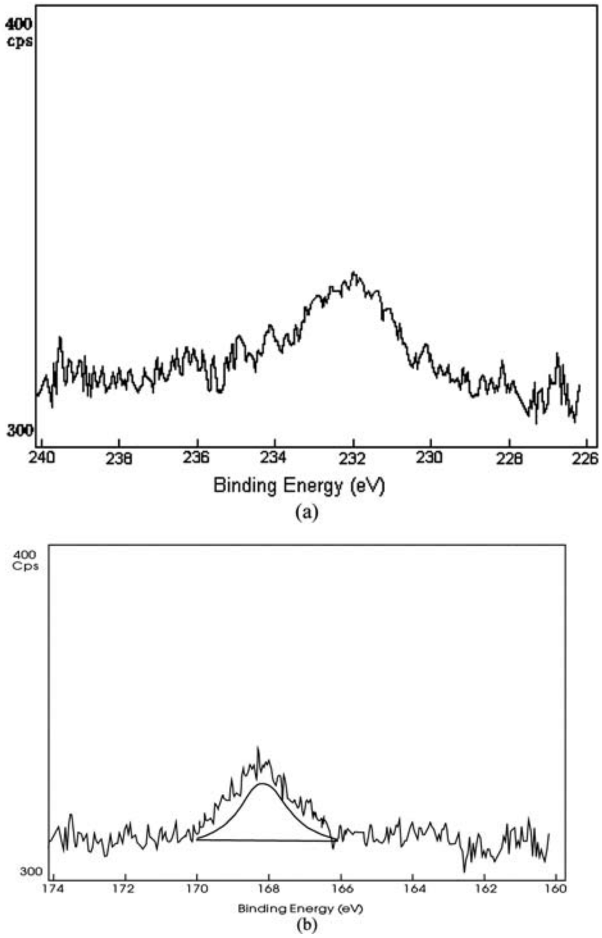


Figure 6 ESCA spectra for (a) S2s, (b)S2p of PU-g-PHEMA-g-TN film ($G_1 = 8.5\%$, $G_2 = 15.4\%$).

TABLE V The antistatic property and its durability of modified PU

		Surface electric resistivity (Ω)	
Type of sample	Degree of grafting (G) (%)	Before washing-fastness experiment	After washing-fastness experiment
PU film	-	7.61×10^{11}	7.61×10^{11}
PU-g-PHEMA film	$G_1 = 8.5$	6.33×10^{10}	6.35×10^{10}
PU-g-PHEMA-g-TN film*	$G_1 = 8.5$, $G_2 = 15.4$	3.52×10^8	3.56×10^8
PU/TN composite film*	–	5.46×10^9	1.12×10^{10}

*The content of TN in PU/TN composite was the same as in grafting-solution consisting of antistatic agent (TN)

TABLE VI Effect of grafting modification on mechanical property of PU

Type of sample	Degree of grafting (G) (%)	Tensile strength (MPa)	Rupture elongation (%)
PU film	–	5.35	119.0
PU-g-PHEMA film	$G_1 = 8.5$	4.52	105.4
PU-g-PHEMA-g-TN film	$G_1 = 8.5, G_2 = 15.4$	4.48	103.5

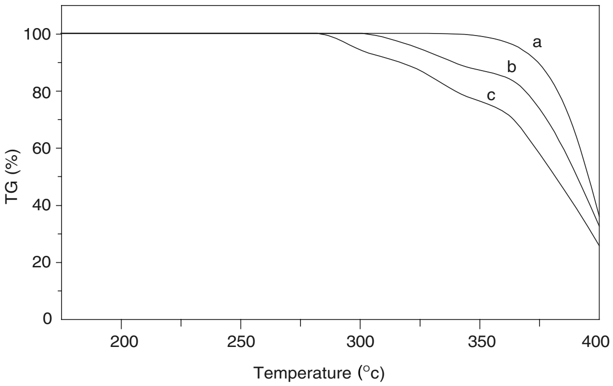


Figure 7 TG curves of (a) PU film, (b) PU-g-PHEMA film ($G_1 = 8.5\%$), (c) PU-g-PHEMA-g-TN film ($G_1 = 8.5\%, G_2 = 15.4\%$).

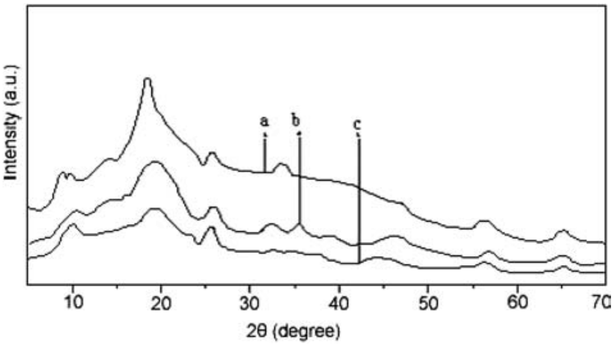


Figure 8 WAXD patterns of (a) PU film, (b) PU-g-PHEMA film ($G_1 = 8.5\%$), (c) PU-g-PHEMA-g-TN film ($G_1 = 8.5\%, G_2 = 15.4\%$).

tributed to decomposition of PU-g-PHEMA. In the curve (c), weight loss at 290–310°C could be attributed to degradation of PHEMA-g-TN in PU-g- PHEMA-g-TN.

3.5. Wide-angle X-ray diffraction (WAXD) analysis

Fig. 8 shows the wide-angle X-ray diffraction (WAXD) spectra of the PU film, PU-g-PHEMA film and PU-g-PHEMA-g-TN film. In the WAXD spectrum of PU film (curve a), there are two strong scattering peaks at $2\theta \approx 10^\circ$ and $2\theta \approx 20^\circ$. Compared with the two peaks at $2\theta \approx 10^\circ$ and $2\theta \approx 20^\circ$ in curve a, the peaks at $2\theta \approx 10^\circ$ and $2\theta \approx 20^\circ$ in curve b and curve c had a distinct increase, which indicated that the regular construction degree of the grafted PU declined, the mountain of crystallization became weak, so the grafting chains distributed at random on PU.

4. Conclusions

By adopting ^{60}Co-γray preirradiation-grafting, PU membrane produced free radicals under the condition of vacuum, then grafted on HEMA to be PU-g-PHEMA membrane. Finally, TN grafted onto PU-g-PHEMA membrane under the action of catalyst, so PU-g-PHEMA-g-TN elastomer with good and durable antistatic property was synthesized. Surface analysis (ATR-FTIR, ESCA, SEM) verified the occurrence of grafting copolymerization. The experimental results stated that the surface electric resistivity of PU-g-PHEMA-g-TN film might decrease to the 108 Ω class and could maintain the 108 Ω class after washing-fastness experiment, although the tensile strength and the elongation at fracture as well as the heat steady property of PU declined slightly after grafting with HEMA or TN. The result of WAXD stated that the regular construction degree of the grafted PU declined and the grafting chains distributed at random on PU.

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