Improved Adhesion of Silicone Rubber to Polyurethane by Surface Grafting

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ABSTRACT: Polyurethane (PU) has widespread applications in implantable devices because of its excellent mechanical and biocompatible properties, whereas weak biostability limits its long-term implantation. The introduction of silicone rubber (SR) onto the PU surface is an effective method for improving the biostability of PU, but the adhesion of these two polymers is unsatisfactory. In this study, the surface modification of PU via grafting through the introduction of vinyl and Si—H groups onto the PU surface was attempted to improve the adhesion of PU to SR. Fourier transform infrared, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy were employed to investigate the graft reaction on the PU surface. The interfacial and surface morphology was characterized with scanning electron microscopy. Different PU/SR interfaces after oscillation and shear were compared as well. The results indicated that the PU surface was activated by diisocyanate, which generated free isocyanate groups for the further grafting of vinyl and Si—H groups. When addition-type, room-temperature-vulcanized SR was poured onto the PU surface, the vinyl and Si—H groups on the PU surface underwent an addition reaction, which improved the adhesion of PU and SR by connecting them with chemical bonds. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1245–1253, 2011

Key words: adhesion; polyurethanes; surfaces

INTRODUCTION

Polyurethane (PU), which is prepared through the step polymerization of isocyanate and polyols, possesses a structure of alternating soft and hard segments. The segmented microstructure in PU molecules accounts for its excellent mechanical properties and favorable biocompatibility, and this is manifested in a wide variety of biomaterial applications and especially in implantable devices, such as artificial blood vessels,[1,2] heart valves,[3–5] nucleus prostheses,[6,7] and tissue engineering materials.[8,9] However, experience with the implantation of PU has demonstrated the susceptibility of this class of materials to long-term degradation. In some cases, the direct contact of PU with the *in vivo* environment has led to environmental stress cracking, hydrolyzation, biodegradation, and calcification.[10,11] Therefore, the improvement of PU biostability is a requirement for a long product life and has sparked research interest in recent years; silicone is widely used to overcome typical biooxidation problems such as silicone grafting,[12] the incorporation of siloxane as part of the soft segment,[13–17] the construction of block copolymers with silicone,[18] and the introduction of silane coupling agents.[19] These approaches could successfully alleviate the oxidation degradation of PU, whereas siloxane segments might lead to significant compromising of the mechanical properties and biostability of PU because of migration to the surface.[20] The grafting of polysiloxane to a PU surface can slightly affect the mechanical properties of PU,[21] but the silicone coating is too thin and soft to protect PU effectively over the long run and especially when it must endure continuous friction.

Silicone rubber (SR) is another type of biomaterial adopted for medical implantation. In addition to being recognized as generally nontoxic and biocompatible, it has good biostability,[22] which is in great demand for PU. The combination of these two materials (e.g., in the preparation of a coating of SR on a PU surface) could compensate for each material's disadvantages and improve the biostability of PU. The polar nature of PU, which indicates immiscibility with nonpolar polymers, accounts for the unsatisfying interfacial adhesion with nonpolar SR in practice.[23,24] Hence, improving the adhesion of SR to PU surfaces has great significance.

In this study, improved adhesion of SR to PU surfaces was achieved through the grafting of vinyl and Si—H groups with a diisocyanate [4,4′-methylenediphenyl diisocyanate(MDI)] as a spacer. The isocyanate groups that attached to PU were then coupled through an addition reaction with allyl alcohol

terminated with vinyl groups. Finally, poly(methyl hydrosiloxane) (PHMS) was grafted onto PU surfaces through hydrosilylation between vinyl and Si—H groups. The surface properties of PU were investigated with attenuated total reflection/Fourier transform infrared (ATR–FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and energy-dispersive X-ray spectroscopy (EDS). The interfacial morphology of SR and PU was observed with scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The PU employed was a thermoplastic polycarbonate urethane (786E) supplied by Bayer Material Science Co., Ltd., with MDI and 1,4-butanediol serving as the hard segment and polycarbonate diols serving as the soft segment. MDI was commercially available with a purity greater than 97%. Allyl alcohol was purchased from Tianjin Yungogong Co., Ltd. Triethylamine was used as a catalyst to effectively promote the reaction between isocyanate groups and urethane —NH— and was used without further purification, whereas chloroplatinic acid was adopted for the addition reaction with vinyl groups. The raw materials [room-temperature-vulcanized SR, vinyl-terminated polydimethylsiloxane (PDMS–Vi) as the base polymer, PHMS as the curing agent, and a platinum complex as the catalyst] were provided by Shenzhen Kejunchi Co., Ltd. The viscosity and hydrogen content of PHMS were 45 cS and 0.75%, respectively. Tetrahydrofuran (THF), toluene, and isopropyl alcohol were dried with molecular seizes overnight, and this was followed by distillation before use and the usual treatment.

Methods

Preparation of the PU films

The PU membranes were obtained by the solvent-casting method. Pellets of PU were dissolved in THF to form a clear solution (10 wt %). The diluted solution was cast onto a glass plate, and this was followed by drying in an oven at 37°C for at least 48 h to remove most of the solvent; it was then heated in a vacuum oven at 80°C for another 24 h to remove the residual solvent. The films were purified by extraction with ethanol for 24 h, and this was followed by vacuum drying at 50°C overnight. The PU films were then punched into squares, which were approximately 1 cm^2 in area and 0.5 mm thick.

PU surface grafting

A three-step surface modification reaction was used to graft vinyl and Si—H groups onto the PU substrate, as shown in Figure 1. The reagents for the grafting reaction were dried extensively to minimize the reaction between MDI and traces of water as much as possible.

The reactions were carried out in a 500-mL reaction flask equipped with a condenser and a thermometer. Briefly, a solution of MDI in toluene (200 mL, 2 wt %) containing 2 wt % triethylamine as a catalyst was heated to 60°C under a stream of nitrogen. To functionalize the PU surface, squares of PU were added to the stirred solution. After 2 h at 60°C, the isocyanate-terminated polyurethane (PU–NCO) films were removed from the reactor and rinsed with toluene twice. They were then immersed in 200 mL of 2 wt % allyl alcohol containing 2 wt % triethylamine in toluene and were reacted for 2 h at 60°C; this was followed by rinsing with toluene as described previously. To introduce Si—H groups onto the PU surface, the hydrosilylation reaction was performed afterwards. The vinyl-terminated polyurethane (PU–Vi) films were added to a 200-mL toluene solution containing 10 wt % PHMS and 0.5% (w/v) chloroplatinic acid as the catalyst. The last step of the reaction was performed for 3 h at 110°C. The silicon hydride terminated polyurethane (PU–SiH) films were removed from the reaction vessel and extracted in toluene for 6 h to remove residual PHMS; this was followed by thorough washing with ethanol and drying *in vacuo* at 50°C for 24 h.

Preparation of the SR coating

The SR was cured through a reaction between the base polymer PDMS–Vi and the curing agent PHMS (PDMS–Vi/PHMS mass ratio = 25 : 1) in the presence of a platinum complex (ca. 0.2 wt %) serving as the catalyst. All reagents were homogeneously mixed in a beaker via stirring under ambient conditions. After adequate blending, the mixture was poured onto the surfaces of PU films (both blank and surface-modified). The addition curing reaction of SR on the PU surface was continued for 24 h at 37°C *in vacuo*, as shown in Figure 2. The SR thickness (gravimetrically obtained) was approximately 1 mm.

Characterization

ATR–FTIR measurements were carried out on a Nicolet 6700 FTIR apparatus (Nicolet Instrument Corp., United States) equipped with an ATR accessory with a Ge crystal; more than 32 scans were collected for each sample. The spectra were recorded with a resolution of 4 cm^{-1}. XPS was performed with a PHI Quantern SXM X-ray photoelectron spectrometer with an aluminum-anode monochromatic source. Survey scans (0–1000 eV) were taken to identify constitutive elements, and low-resolution scans of the peaks provided atomic
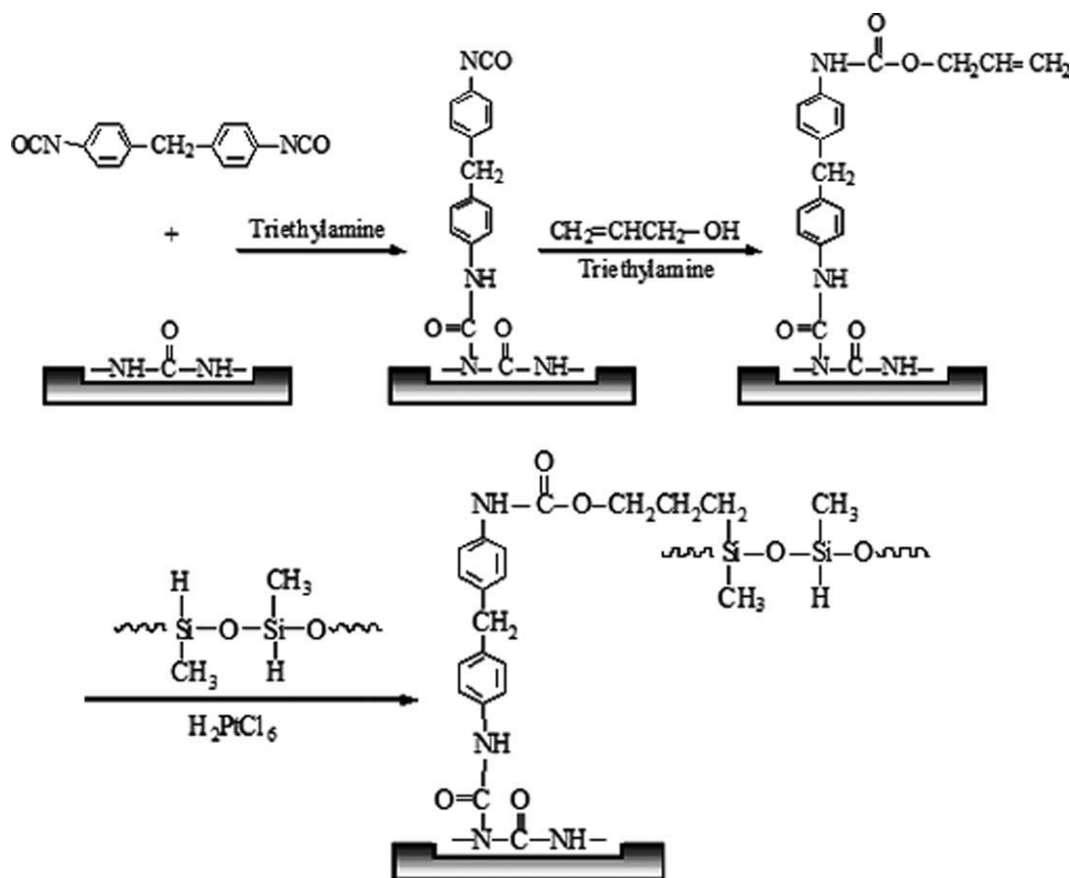
Figure 1 Three-step reaction for grafting on PU surfaces.

concentrations. High-resolution $C1_s$ scans were also taken to determine the contributions of different functional groups containing carbon atoms. Measurements were performed at a takeoff angle of 45° (normal to the surface).

The surface morphology of the PU films was studied with an SM-6301F scanning electron microscope from Japan Electron Optical, Ltd. The polymer samples were highly nonconductive. To avoid charging of the surface, a conductive layer of gold was coated onto the PU films with a JFC-1100 sputter coater with a 5-kV beam voltage. The distributions of atoms on the surfaces of the PU films were investigated with SEM and EDS (Inca 300, Oxford).

For tensile strength testing, the sample sheet was cut into dumbbell shapes according to the ASTM D 683 testing method with a GT-TS-2000 testing machine (Taiwan GOTECH, Ltd.). The test was carried out at a crosshead speed of 500 mm/min. Three specimens were tested in each case. All tests were performed at the ambient temperature of 25 ± 2°C. For fatigue testing, the sample sheet was cut into rectangles (ca. 30 mm × 6 mm × 0.5 mm), which were vibrated 10,000 times at a frequency of 5 Hz with a TA Instruments DMA 2980 at the ambient temperature of 25 ± 2°C.

RESULTS AND DISCUSSION

It is well known that isocyanate can be easily reacted with compounds containing active protons such as alcohol, amine, acid, and water. The aim of this research was to design a new type of grafting with active groups on the PU surface via an MDI spacer that could react with PDMS–Vi or PHMS when SR was cured and therefore improve the adhesion of SR to the PU surface. The target was achieved with two processes. In the first process, for the formation of vinyl- and Si—H-grafted PU surfaces, the PU substrate was initially activated by diisocyanate and then modified by allyl alcohol and PHMS. In the second process, the addition curing of SR took place on the PU surface, and vinyl or Si—H groups also reacted to strengthen the combination of PU and SR with chemical bonds.

PU surface grafting

ATR–FTIR

The allyl alcohol and PHMS grafted onto the surfaces of PU films were verified with ATR–FTIR, and the spectra of PU, PU–NCO, PU–Vi, and PU–SiH are shown in Figure 3. The spectrum of PU [Fig. 3(a)]
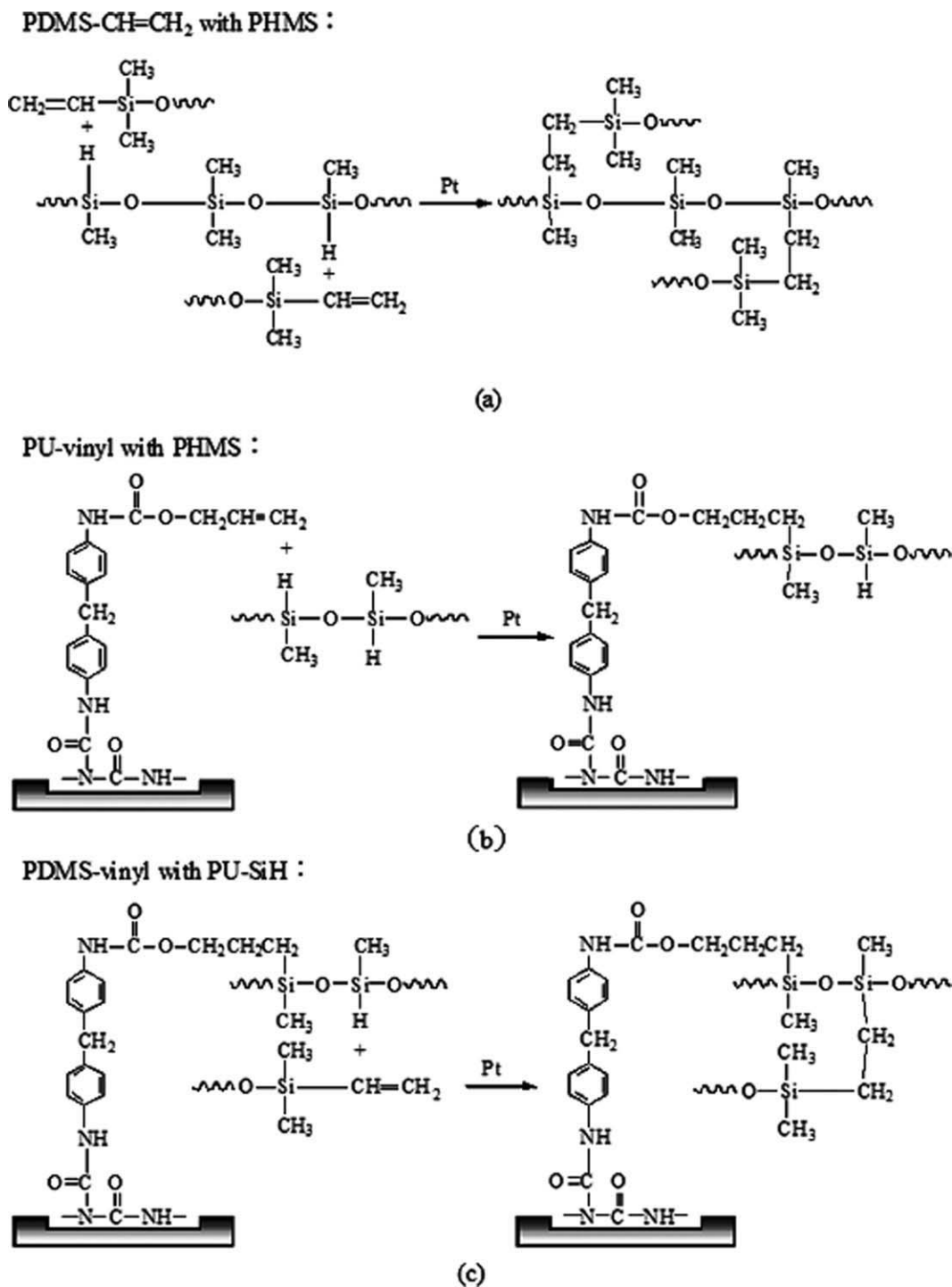
PDMS–CH=CH₂ with PHMS :

(a)

PU-vinyl with PHMS :

(b)

PDMS-vinyl with PU-SiH :

(c)

Figure 2 Curing process of SR on PU films: (a) PDMS—CH=CH₂ and PHMS, (b) PU—CH=CH₂ and PHMS, and (c) PDMS—CH=CH₂ and PU–SiH.

shows that the —NH— stretching and deformation vibration appeared at 3326 and 1599 cm^{-1}. The urethane —NHCOO— carbonyl stretching vibration was split into peaks at 1740 (free carbonyl) and 1700 cm^{-1} (bonded carbonyl). Peaks at 1077 and 1104 cm^{-1} represented asymmetric stretching vibrations of the C—O—C band. Methyl and methylene stretch-

ing vibrations could be found between 2865 and 2968 cm^{-1}. The peak at 1415 cm^{-1} represented the deformation vibration of methyl, whereas that at 1430–1489 cm^{-1} indicated that of methylene.

After the reaction with MDI, a sharp band at 2280 cm^{-1} (the characteristic asymmetric stretching vibration of —NCO groups) appeared in the spectra of
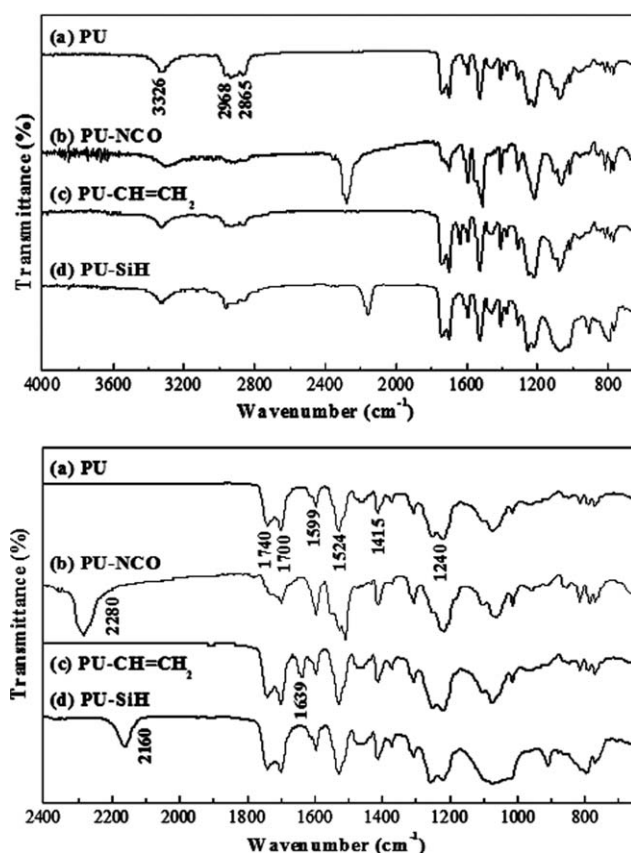
Figure 3 ATR–FTIR spectra of (a) blank PU, (b) PU–NCO, (c) PU–vinyl, and (d) PU–SiH.

PU–NCO [Fig. 3(a)]. Meanwhile, the intensity of the peaks at 1740 and 1700 cm^{-1} decreased because of the coverage of MDI at the PU surface.

In the second reaction step, vinyl groups were allowed to react with the free NCO groups at the surface. The peak at 1639 cm^{-1} should be assigned to the stretching vibration of —CH=CH$_2$ in PU–Vi [Fig. 3(a)]. The disappearance of —NCO absorption and the strengthened intensity of —NHCOO— carbonyl absorption indicated that the reaction was complete and that new urethane bonds had formed.

In the last reaction step, we aimed to construct Si—H groups on the PU surface; the addition reaction between vinyl and Si—H groups was the main approach. The wide absorption band between 1000 and 1200 cm^{-1} for PU–SiH [Fig. 3(d)] was the char-

acteristic stretching vibration of Si—O—Si. Excessive PHMS ensured that there were no vinyl groups but some Si—H groups left on the PU surface, and this corresponded to the disappearance of absorption of vinyl groups at 1639 cm^{-1} and the appearance of a stretching vibration at 2160 cm^{-1}. This evidence confirmed the presence of vinyl and Si—H groups grafted onto the PU surface.

Actually, when PU was immersed in the solution for the whole grafting process, it swelled a lot, and this made it possible for MDI and allyl alcohol to diffuse into the swollen PU and undergo a reaction in the bulk or subsurface similar to that on the surface. Even so, because of the swelling capacity of PU and the diffusivity of the spacer, the reaction inside PU still had far fewer possibilities versus that on the surface and, consequently, made little contribution to the subsequent reactions. Hence, in this study, much more importance was attached to the surface properties of PU, which positively outweighed the changes in the bulk that could be minimized.

XPS

Table I summarizes the atomic percentages of blank and modified PU surfaces measured by XPS, and from the XPS spectra (Fig. 4), the elemental compositions of the surfaces were calculated. In comparison with blank PU, the nitrogen content of PU–NCO increased from 1.31 to 6.86%, and the N/C ratio increased from about 0.02 to 0.10, as expected; this resulted from the surface activation of MDI. Moreover, the silicon content of PU–SiH was shown to be 17.66%, and it had a relatively high Si/C ratio of approximately 0.34; this verified the successful grafting of PHMS chains to the PU surface. It was worthwhile to determine that a small increase in O/C for PU–SiH was attributable to the polysiloxane structure of PHMS. In addition, the change in the surface free energy of the PU films could be reflected by the water contact angle, which showed results similar to those of our previous research.[25]

Details from XPS spectra for blank and grafted PUs (Fig. 4) were illustrated as well. The C1$_s$ peak could be fairly resolved into three component peaks: a hydrocarbon (—C—C—C—) peak (C1) at about 282.50 eV, an ether (—C—O—C—) peak (C2) at about

TABLE I
Elemental Compositions of the PU Surfaces According to XPS

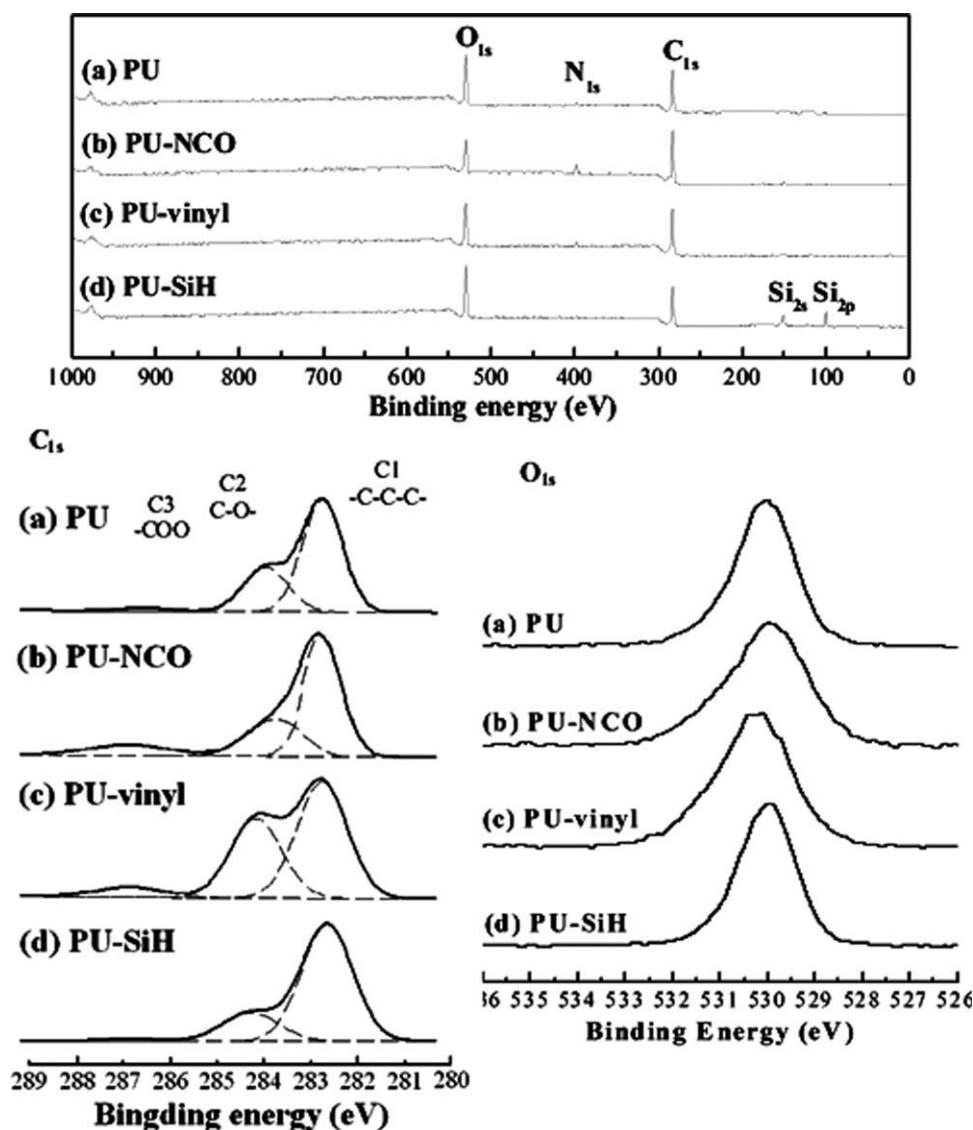| Sample	Atomic percentage				Atomic ratio		
	C$_{1s}$	O$_{1s}$	N$_{1s}$	Si$_{2p}$	N$_{1s}$/C$_{1s}$	O$_{1s}$/C$_{1s}$	Si$_{2p}$/C$_{1s}$
PU	69.51	29.18	1.31	—	0.019	0.42	—
PU–NCO	68.77	24.37	6.86	—	0.10	0.35	—
PU–vinyl	65.22	32.40	2.38	—	0.036	0.50	—
PU–SiH	52.68	29.23.	0.43	17.66	0.0082	0.55	0.34

Figure 4   XPS spectra of PU surfaces: (a) blank PU, (b) PU–NCO, (c) PU–vinyl, and (d) PU–SiH.

284.20 eV, and a carbonyl (—NHCOO— or —NCO) peak (C3) at about 286.90 eV. The high-resolution C_{1s} data are shown in Table II. The C3 peak of blank PU was too small to allow accurate peak resolution. After activation of MDI, a C3 peak newly appearing at 286.9 eV and assigned to —NCO indicated further reaction. When allyl alcohol was grafted, a lot of urethane groups formed on the PU surface, and this accounted for the significant increase in C2 for PU–Vi. The O_{1s} peak of PU–NCO and PU–vinyl had wider binding energy ranges than the other two. This might be the combination of contributions of the ether (—C—O—C—) peak and the urethane oxygen (—N—COO and —N—COO). When the PU surface was introduced to PHMS, it was covered by a lot of long polymer chains. The newly formed polysiloxane oxygen (—Si—O—Si—) on the outer surface dominated the signal of O_{1s}, so a lot of information

on ester and urethane oxygen was missing, and a narrower range was exhibited in comparison with PU–NCO and PU–vinyl. According to N_{1s}, PU–NCO had the strongest peak intensity because of the introduction of diisocyanate; this was weakened and could not be allowed in PU–SiH. The peak newly appearing at a binding energy of 100.3 eV was assigned to Si_{2p} [Fig. 3(d)], and this was the

TABLE II
High-Resolution XPS $C1_s$ Data for the PU Surfaces

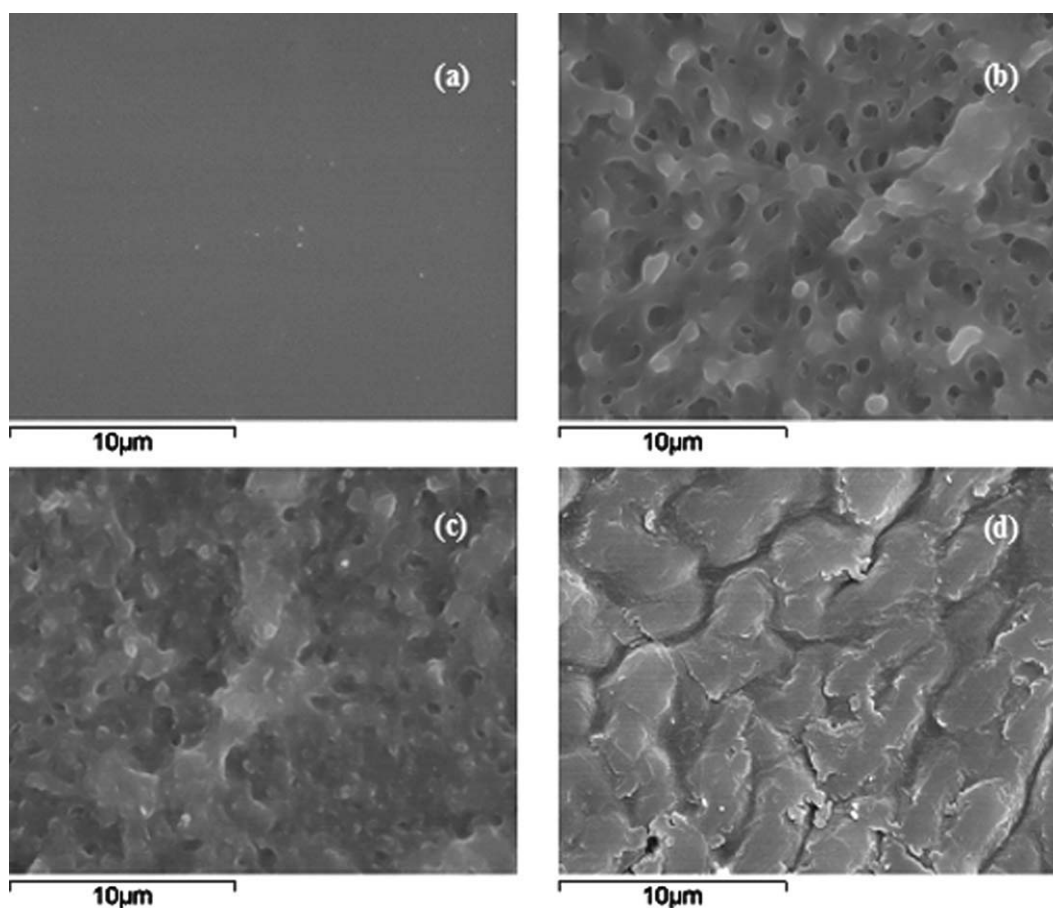| Sample	C1 (%)	C2 (%)	C3 (%)
PU	70.88	27.87	1.25
PU–NCO	64.94	29.21	5.85
PU–vinyl	57.16	37.21	5.63
PU–SiH	78.44	19.96	1.60

Figure 5 SEM photographs of the morphological structures of PU surfaces: (a) blank PU, (b) PU–NCO, (c) PU–vinyl, and (d) PU–SiH.

characteristic peak of —Si—O— and also confirmed the graft reaction of PHMS.

SEM

When functional groups were employed on PU surfaces, the morphological structures and shape variations of the PU films studied with SEM could be used to investigate the distribution of grafted groups and the extent of the graft reaction carried out on the PU surfaces. Figure 5(a) shows the morphology of the blank PU surface; Figure 5(b) shows the morphology of PU–NCO; and Figure 5(c,d) presents PUs grafted with vinyl and Si—H groups, respectively. In fact, the distribution and efficiency of the grafting reaction, which could be reflected by the roughness and its distribution for the PU surface, were consequently quite significant for the combination of the two substrates. Observations of these photographs can be summarized as follows. Blank PU showed the flattest surface both macroscopically and microscopically; in comparison, the surfaces of PU–NCO, PU–vinyl, and PU–SiH became rougher. The obviously porous structures of PU–

NCO [Figure 5(b)] were quite possibly caused by the corrosion of toluene, and this phenomenon appeared less often for PU–vinyl [Figure 5(c)] and disappeared for PU–SiH [Figure 5(d)]. Although it was partially affected by the corrosion of toluene, the rough and compact structure in Figure 5(c,d) could more obviously verify the process of the grafting reaction carried out on the PU surface. The successful grafting was confirmed by ATR–FTIR previously; here, it was not hard to deduce that the reagents for grafting were uniformly distributed on the PU surface, although roughness was exhibited.

The morphology of the PU surfaces was observed with SEM, whereas EDS was employed to elucidate the distribution of vinyl and Si—H groups on the modified PU surface. To analyze the extent of the grafting reactions, the contents of the elements carbon, oxygen, and silicon on different PU surfaces were examined, and they are listed in Table III. The obvious increase in the silicon content in PU–SiH further proved that Si—H groups had been successfully grafted onto the PU surface finally; this agreed with the results of the previous investigation with XPS.

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TABLE III
Elemental Compositions of the PU Surfaces
According to EDS

Sample	C (%)		O (%)		Si (%)	
	wt	mol	wt	mol	wt	mol
PU	73.21	78.47	26.79	21.53	—	—
PU–NCO	74.93	77.63	25.07	20.06	—	—
PU–vinyl	69.72	74.66	30.28	24.32	—	—
PU–SiH	48.97	61.29	28.16	26.43	22.88	12.27

Tensile properties

Table IV summarizes the tensile properties of PU films both before and after modification and shows the effects of the activation and graft reaction on the tensile properties of PU. From this table, we can observe that the mechanical properties of PU declined slightly after modification, whereas the rupture elongation increased to a small extent. This phenomenon might have been caused by small changes on the PU surfaces generated by small molecules during the grafting process. Nevertheless, the modified PU films still showed excellent mechanical properties, and this should be appreciated in applications.

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TABLE IV
Tensile Properties of the Blank and Grafted PU Films

Sample	Maximum strength (MPa)	Rupture elongation (%)
PU	18.18 ± 0.62	340 ± 20
PU–NCO	17.21 ± 1.24	380 ± 30
PU–vinyl	18.09 ± 0.83	350 ± 20
PU–SiH	17.54 ± 1.09	360 ± 30

Improved adhesion of SR to PU surfaces

In most cases, the peel strength test is the most commonly used method for investigating the adhesion of two substrates; it provides direct data about the mechanical properties on a macroscale. In fact, the peel strength test was performed, but it did not reveal convincing results as expected because of the rather poor properties of SR without any filler for reinforcement. Mostly, the experiments had to be terminated with the randomly oriented destruction of SR instead of regular peeling at the interface. Therefore, the results were imprecise or, rather, of little significance. Despite the absence of quantitative results, this phenomenon could also reveal that the combination of the two subtracts was somehow
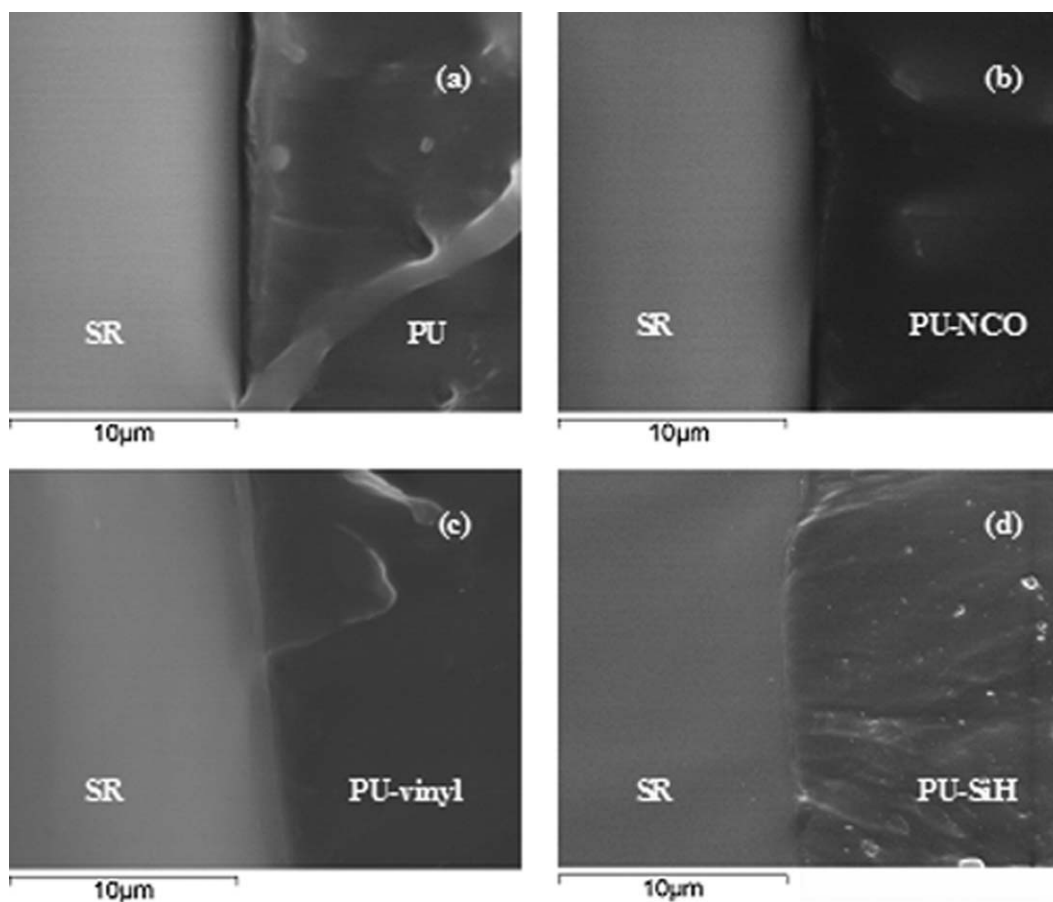
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Figure 6 SEM photographs of the interface morphological structures of SR and (a) blank PU, (b) PU–NCO, (c) PU–vinyl, and (d) PU–SiH.

stronger than the cohesion of SR to some extent. Furthermore, we tried to prepare smaller samples (ca. half of the standard sample in size); SR was relatively unlikely to be destroyed because there was less stress. During the hand operation of peeling, the SR samples with PU–vinyl and PU–SiH required for more effort and showed better endurance in comparison with blank PU and PU–NCO samples. To corroborate the quantitative conclusions, SEM was employed here to investigate the adhesion of SR and PU to different surfaces and illustrate the morphology at the interface on a microscale, which could also be considered convincing evidence.

The morphology of the interface of adhered PU films and SR is shown in Figure 6. The interface of SR and blank PU is sharply obvious, as presented in Figure 6(a). As previously mentioned, the PU film became rougher after activation by grafted MDI. Therefore, the adhesion of SR and PU–NCO saw little improvement, although the free isocyanate groups on the PU–NCO surface also could react with traces of water in SR. The result is illustrated in Figure 6(b). The improved adhesion of SR to PU–vinyl and PU–SiH was verified by Figure 6(c,d). The two immiscible materials were tightly connected, with their interface being less obvious than those of the previous two or, rather, exhibiting an intermediate zone. Microscopically, SR that adhered to the PU surface was connected with chemical bonds and not only physical adhesion and displayed distinct properties in comparison with blank PU and PU–NCO. In summary, the adhesion of SR to PU after the grafting of vinyl and Si—H groups was improved a lot.

To investigate the fatigue durability of the combined system of SR and PU, the adhered samples were vibrated 10,000 times at a frequency of 5 Hz; this was assisted by dynamic mechanical analysis. The interfaces of different PUs (blank and modified) with SR were observed by SEM as well. The results indicated slight peeling of SR on PU and PU–NCO surfaces, whereas PU–vinyl and PU–SiH were able to fix SR successfully and presented excellent surface adhesion.

CONCLUSIONS

Vinyl and Si—H groups grafted onto PU surfaces were used to improve the adhesion of chemically inert SR to PU. Surface characterization by ATR–FTIR indicated that the functional groups were successfully introduced onto the PU surfaces. The modified PU–vinyl and PU–SiH possessed active groups on the surfaces and showed a uniformly distributed morphology structure, which was also demonstrated by XPS, SEM, and EDS analysis. The vinyl and Si—H groups grafted onto the PU surface, which could react with SR, accounted for the remarkable improvement of the adhesion of SR to PU. The success in adhering these two immiscible polymers through the alteration of their surface properties demonstrates the feasibility of introducing active groups to modify polymeric surfaces. The applicability of this method to different SRs is a subject for further study.

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