

Comparative Studies on Hydrophilic and Hydrophobic Segments Grafted Poly(vinyl chloride)

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Abstract Poly(vinyl chloride) (PVC) is one of the mostly produced plastics in the world and is widely used in single-use medical devices. However, the additives that are often necessary for PVC arouse concerns of its safety, thus quests the modifications of PVC itself. In this study, poly(ethylene glycol) (PEG) and polydimethylsiloxane (PDMS) segments were grafted onto PVC backbone in similar ways, and the chemical structures of the modified PVCs were characterized by Fourier transform infrared spectra, X-ray photoelectron spectra, thermogravimetric analysis and differential scanning calorimetry. Moreover, the water contact angle, protein adsorption, platelet adhesion, cell attachment and proliferation on different material surfaces were studied and compared. It was found that both PEG and PDMS grafting yielded improvement on biocompatibility compared with bare PVC, while hydrophobic PDMS grafted PVC showed more effective on cell attachment and proliferation than that of hydrophilic PEG grafted PVC.

Keywords Poly(vinyl chloride); Poly(ethylene glycol); Polydimethylsiloxane; Grafting; Biomedical properties

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INTRODUCTION

Poly(vinyl chloride) (PVC) has been widely applied and heavily studied for many years because of its high performance and relatively low cost, especially used for manufacturing disposable medical devices^[1]. The two main medical applications for PVC materials are flexible containers and tubing^[2]. Generally speaking, PVC materials are quite chemically stable, thus in real hospital practices, PVC medical devices can be easily sterilized without affecting their properties such as flexibility and resistance to tears, scratches and kinks. As a result, the risk of healthcare related infections can be largely reduced by the use of PVC-based devices comparing to traditional and reusable medical devices. The advantage of PVC-based medical devices has been evidenced by the fact that over 40% of plastic-based disposable medical devices used in hospitals are made from PVC^[3].

However, the heat resistance of PVC is rather poor^[1]. At 140 °C, PVC starts to decompose and at 160 °C, it starts to melt. A commonly used strategy to ensure the successful manufacturing of PVC-based devices, heat stabilizers and plasticizers are often added. Additionally, some other additives, such as ultraviolet stabilizers, lubricants, processing aids, fillers, pigments *etc.*, although not absolutely necessary, are added to yield desired properties.

Unfortunately, many studies have shown that additives, especially the plasticizers, may contribute to health complications^[4, 5]. In fact, there has been a call for reducing the use of PVC in some particular situation, for example, in blood-contact medical devices and in devices designed for neonates^[5].

In order to reduce the necessity of additives and to improve the performance, studies on modifications of PVC have emerged. The grafting on PVC chain is one of the most important routes and for example, it has been proven to yield self-plasticization and improvement on the materials' hydrophilic performance^[6–13]. Poly(ethylene glycol) (PEG)^[8, 9] is one of the most intensively studied materials that have been grafted onto PVC backbone. It is not surprising at all considering that PEG is the most widely used material for biocompatible surface grafting modifications on polymers due its well-known biocompatibility. By grafting PEG onto PVC^[9], the hydrophilicity of PVC is largely increased and thus blood compatibility. Contrary to PEG, polydimethylsiloxane (PDMS) is a typical hydrophobic biocompatible polymer which has also been used for various medical applications. There are many studies on grafting PDMS onto polymer surfaces to improve the material functions^[14]. However, it is unclear whether the hydrophilic grafting or the hydrophobic grafting benefits the biomedical properties of PVC more.

In this study, we employed the bulk chemical grafts of PEG and PDMS onto PVC backbone to prepare the modified PVC with hydrophilic and hydrophobic properties, respectively.

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Comparison studies of modified PVC membranes were carried out, especially on the properties including hydrophilicity, protein adsorption, platelet adhesion, cell attachments and proliferations.

EXPERIMENTAL

Materials

PVC for solid-medicine package with polymerization degree of 800 was kindly provided by Yangzhou Qionghua Group (Yangzhou, China) and used as received. PEG ($M_n = 700$ Da) was purchased from Sinopharm Chemical Reagent Co. (Shanghai, China) and dried by refluxing with benzene (which was previously dried by refluxing with Na for several hours and distilled off.) for at least 4 h. Then benzene was distilled off at normal pressure, and the residual PEG was vacuum dried for 48 h in P_2O_5 desiccators before use. Aminopropyl terminated PDMS with molecular weight of 1000 Da (DMS-A12) was obtained from Gelest Inc. (Morrisville, PA, USA). Isophorone diisocyanate (IPDI) purchased from Sigma-Aldrich (Milwaukee, WI, USA) was used as received. Tetrahydrofuran (THF) and petroleum ether (AR grade, Sinopharm Chemical Reagent Co., Shanghai, China) were dried over 4Å molecular sieve for at least 24 h and distilled before use. The other chemicals, such as ethanolamine (EA), ethanol, hexane, and cyclohexane (AR grade, Sinopharm Chemical Reagent Co., Shanghai, China) were used without further purification.

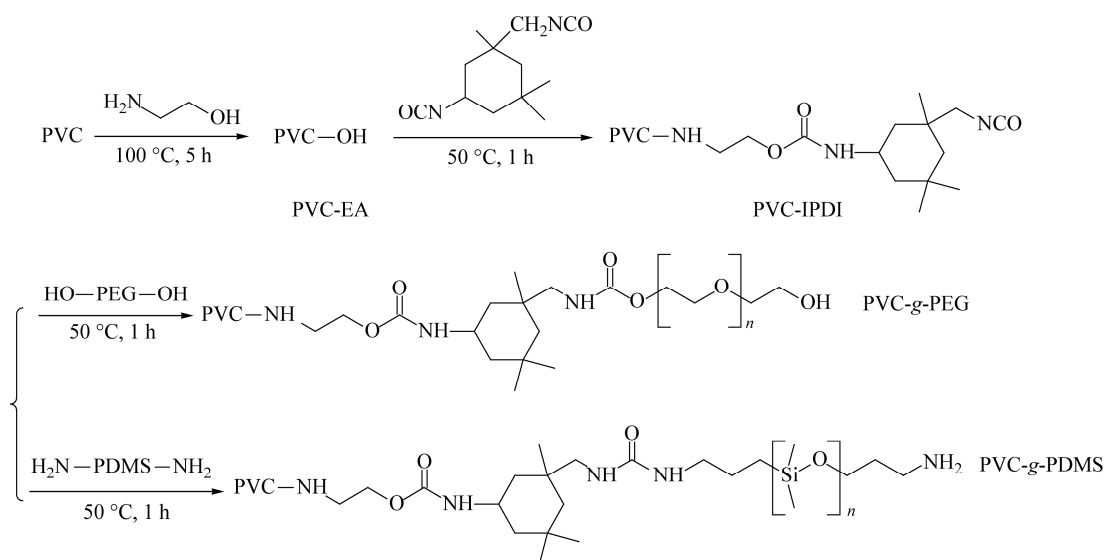
Platelet-rich plasma (PRP), prepared on a Baxter CS-3000 Plus blood cell separator with 10^6 platelets/ μ L, was supplied by Jiangsu Province Blood Center (Nanjing, China) and used within 24 h after collection. The mouse fibroblast cells L929 were supplied by Lifeline Cell Technology (Distributed by Beijing Qingyuanhao Biologics, Beijing, China). VEGF LS-1020 culture medium was purchased from Thermo Fisher Scientific China Branch (Shanghai, China). Carboxyfluorescein diacetate succinimidyl ester (CFDA-SE) was purchased from Dojindo Molecular Technology (Shanghai, China).

Preparations of Grafting PVC Samples

In order to prepare the grafting samples^[9], 50 g of PVC powder was stirred in 160 mL of EA and 40 mL of distilled water at 100 °C for 5 h and filtered, washed with distilled water once, and then extracted in Soxhlet extractor with ethanol for 12 h to remove the excess EA and then vacuum dried for 2 h to give the refined product labeled as PVC-EA. Then, 10 g of PVC-EA was dissolved in 120 mL of anhydrous THF and heated to 50 °C with 5 mL of IPDI and a drop of stannous octoate ($Sn(Oct)_2$) was charged as catalyst. After been stirred for 1 h under N_2 atmosphere, the solution was added drop-wise to 500 mL of petroleum ether to precipitate the products. After being filtered out, the crude products were washed with 100 mL of petroleum ether and the washing was repeated for 3 times to give the PVC-IPDI used in the following experiments. At last, 5 g of PVC-IPDI was re-dissolved in 60 mL of anhydrous THF, 5 g of refined PEG or PDMS and a drop of $Sn(Oct)_2$ were added. The mixture was stirred at 50 °C for 1 h and then dropped into 500 mL of petroleum ether. The filtered products were extracted with ethanol for PEG while hexane for PDMS in Soxhlet extractor for 24 h. After dried in vacuum, the grafted PVCs were obtained and labeled as PVC-g-PEG and PVC-g-PDMS, respectively. The synthesis route is illustrated as Scheme 1. Raw PVC, PVC-g-PEG and PVC-g-PDMS were dissolved in THF respectively at the concentration of 5 wt%, and the solutions were casted on glass and dried at 40 °C to give the sample films.

Instrumentations

Fourier transform infrared spectra (FTIR) were recorded on a Nicolet Nexus 870 FTIR spectrometer (Thermo Nicolet, USA) from 4000–400 cm^{-1} with a resolution of 2 cm^{-1} at room temperature. Size exclusion chromatography (SEC) of samples was performed at 25 °C on a SEC system composed of a Waters 515 HPLC pump (Waters, US) and a Wyatt Optilab rEX refractive index detector (Wyatt, US). The columns were Styragel HR3, HR4 and HR5 (300 mm $\times$ 7.8 mm) in series from Waters. HPLC grade THF was used as



Scheme 1 Synthesis route to grafted PVC

eluent at a flow rate of 1 mL/min under 4.14 MPa pressures. THF and samples were filtered with pore size of 0.45 μm (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, US). The columns were calibrated using polystyrene standards with molecular weights ranging from 900 g/mol to 1.74×10^6 g/mol (with NMD 1.02–1.11). ASTRA software (Version 5.3.1.4) was utilized for data acquisition and analysis. The sample concentrations were 5 mg/mL. Differential scanning calorimetry (DSC) curves were recorded at a heating rate of 20 K/min in a N_2 atmosphere ranged from 20 $^\circ\text{C}$ to 130 $^\circ\text{C}$ with a Perkin-Elmer Pyris 1 thermal analysis system (PerkinElmer Life Sciences, Boston, MA, USA). Thermogravimetric analysis (TGA) was conducted with a PE Pyris 1 thermogravimeter (PerkinElmer Life and Analytical Sciences, Inc., Boston, MA, USA) in a N_2 atmosphere at a heating rate of 20 K/min from room temperature to 700 $^\circ\text{C}$. The X-ray photoelectron spectra (XPS) of samples were recorded on a VG Scientific ESCA Lab MK-II spectrometer (West Sussex, England) equipped with a monochromatic Mg-K α X-ray source. XPS peak software (v4.1) was utilized to analyze and deconvolute the XPS peaks. Peak deconvolutions were performed using Gaussian components after a Shirley background subtraction. The water contact angles of samples were recorded with a KSV CAM200 optical contact angle and surface tension meter system (KSV Instruments Ltd., Helsinki, Finland) at 20 $^\circ\text{C}$ with relative humidity of 60%. Each datum point was the average of 10 determinations and photographs were taken immediately after pure water (5 μL) was dropped onto the samples.

Protein Absorption Determination

Fibrinogen (Fbg) was radiolabelled with ^{125}I (Isotope Company of China, Beijing) using the iodine monochloride (ICl) method. Unbound radioactive iodide was removed by ion exchange chromatography on an AG-1-X4 resin column (Bio-Rad Laboratories, Hercules, CA, USA). For studies of protein adsorption from buffer, both labeled and unlabeled proteins were mixed (1/19, labeled/unlabeled) at a total concentration of 1 mg/mL. The clean modified PVC round pieces with 7 mm diameter and 0.2 mm thickness were first immersed in Tris buffered saline (TBS, pH = 7.4) for 12 h to achieve complete hydration prior to the adsorption experiments. The samples were then placed in the protein solutions, and adsorption was allowed to proceed for 3 h at room temperature. The sample surfaces were then rinsed 3 times, 10 min each time with TBS, wicked onto filter paper, and transferred to clean tube for radioactivity determination using a Wizard 3" 1480 Automatic Gamma Counter (Perkin-Elmer Life Sciences, Boston, MA, USA). Protein adsorption was expressed as mass per unit surface area ($\mu\text{g}/\text{cm}^2$).

Platelet Adhesion Investigations

20 μL of PRP was dropped onto the sample surface and kept for 30 min at room temperature. The samples were gently washed with phosphorus buffer solution (PBS, pH = 7.4, 0.1 mol/L) for 3 times and then dipped into 2.5% glutaraldehyde solution for 30 min to fix the platelets. After that, the samples with fixed platelets were dehydrated for 15 min in each of a series of ethanol/water solutions at the

concentration of 50%, 60%, 70%, 80%, 90%, 95% and 100% (V/V) and then dried in air at room temperature. All samples with gold coating (approx. 40 nm thickness) were observed by FEI Quanta 200 scanning electron microscope (SEM, FEI Co., Hillsboro, OR, USA) at an acceleration voltage of 20 kV.

Plasma Recalcification Time (PRT) Measurements

A series of dried test tubes ($\text{O}6 \text{ mm} \times 30 \text{ mm}$) was coated with solutions of PVC, PVC-g-PEG and PVC-g-PDMS in THF, respectively, and then dried in vacuum and kept in refrigerator at 4 $^\circ\text{C}$ for 24 h. Fresh rabbit blood (0.1 mL) containing sodium citrate and 0.1 mL of CaCl_2 solution (0.025 mol/L) were added into each tube. The time of the emergence of a milky white flocculate was recorded. The results were compared with those of blank tubes and the tubes coated with silicon oil. Six tubes were coated and determined for every sample and the 6-point average value was adopted as the result.

Cell Attachment and Proliferation

L929 cell density was counted and adjusted to 5×10^5 cells/mL. Four samples were placed in a glass culture dish as a group. The cells were finally seeded in complete cell culture medium and incubated for 4, 8, 16, 24, 72, and 120 h at 37 $^\circ\text{C}$ in a humidified 5% CO_2 atmosphere. After incubation, the cell culture medium was removed and the samples were washed 3 times in PBS and fixed with 4% paraformaldehyde solution for 15 min, then washed 3 times in PBS. All the cells fixed were stained with 20 μL of CFDA-SE solution (20 $\mu\text{mol}/\text{L}$) for 15 min in the incubator. Finally, the CFDA-SE solution was removed and samples were washed with distilled water. The adhesion and proliferation of L929 were observed with a Zeiss Axio Scope A1 fluorescent microscope (Zeiss, Germany) with magnification of 100.

RESULTS AND DISCUSSION

Synthesis and Characterization of Modified PVC

FTIR was used to characterize the modified PVC. Figure 1(a) shows the FTIR spectra of bare PVC, the two modified PVCs and the intermediate products. The raw PVC spectrum was in accordance with the standard IR spectrum of PVC. In the PVC-EA spectrum, the absorption band at 3400 cm^{-1} was assigned to the hydroxyl groups (OH), suggesting that EA had been successfully grafted on PVC. The PVC-IPDI spectrum had an absorption peak at 2260 cm^{-1} , which was not seen in PVC-EA spectrum. This peak was assigned to the isocyanate groups (NCO). The peak at 1645 cm^{-1} was assigned to the carbonyl groups. The OH absorption peak of PVC-IPDI is weaker than that of PVC-EA, which also indicates that part of OH group has reacted with NCO group in IPDI. As a result of the reactions with PEG or PDMS, the PVC NCO peak at 2260 cm^{-1} disappeared. For PVC-g-PEG spectrum, OH absorption was stronger than that of other samples. The new peak at 1100 cm^{-1} was assigned to C—O—C vibration in the PEG segments. For PVC-g-PDMS, the double peaks at 1110–1000 cm^{-1} and 900–600 cm^{-1} are typical absorbance of —Si—O— vibrations. In summary, the transformations of FTIR spectra confirmed the successful modifications on PVC.

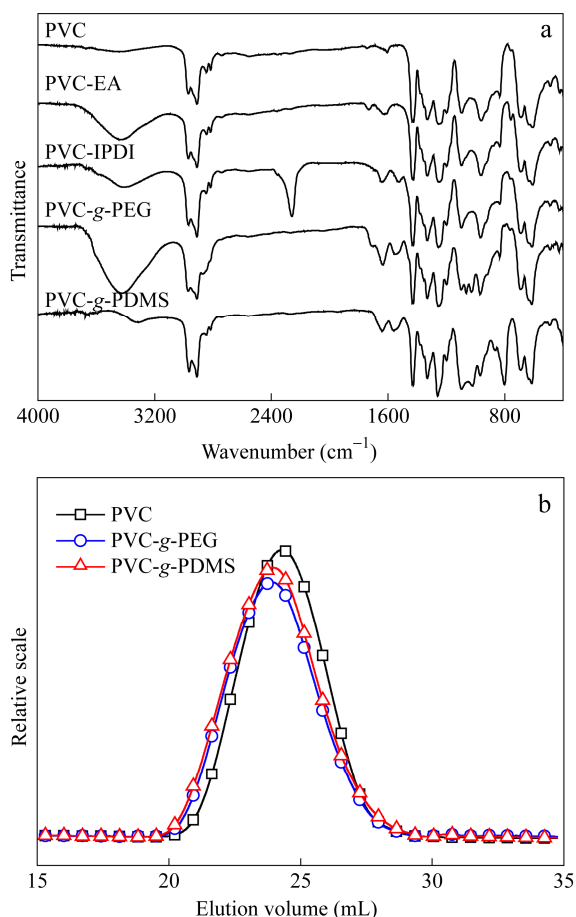


Fig. 1 FTIR spectra (a) and SEC traces (b) of bare PVC and grafted PVCs

Figure 1(b) shows the SEC traces of PVC and grafted PVC with 1 mL/min THF as eluent at 25 °C on a Waters model 515 gel permeation chromatograph. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) of bare PVC calculated from the curve are 4.95×10^4 Da, 1.21×10^5 Da, and 2.44 respectively. For PVC-g-PEG, the results are 5.4×10^4 Da, 1.34×10^5 Da, and 2.47; for PVC-g-PDMS, the molecular weights and PDI are 5.45×10^4 Da, 1.35×10^5 Da and 2.48. The increased molecular weights indicated the successful grafting of segments. Because of the substitution of Cl in PVC chain by PEG and PDMS segments with higher molecule mass, the molecular weights of the grafted products were increased accordingly. Assuming that the grafting reactions happen uniformly on PVC backbone and according to the increase of number-average molecular weights, the grafting ratio of PVC-g-PEG is 9.1% in mass, while for PVC-g-PDMS, the grafting ratio is 10.1% in mass. The calculated average numbers of grafting chains in every 1000 repeat units of PVC is 6 for PVC-g-PEG and 5 for PVC-g-PDMS.

The successful introduction of PEG and PDMS segments onto PVC backbone certainly will show effect on various properties of raw PVC. However, it is expected that the influence on other performances can be minimized except the projected hydrophilicity and hydrophobicity. Figure 2 shows

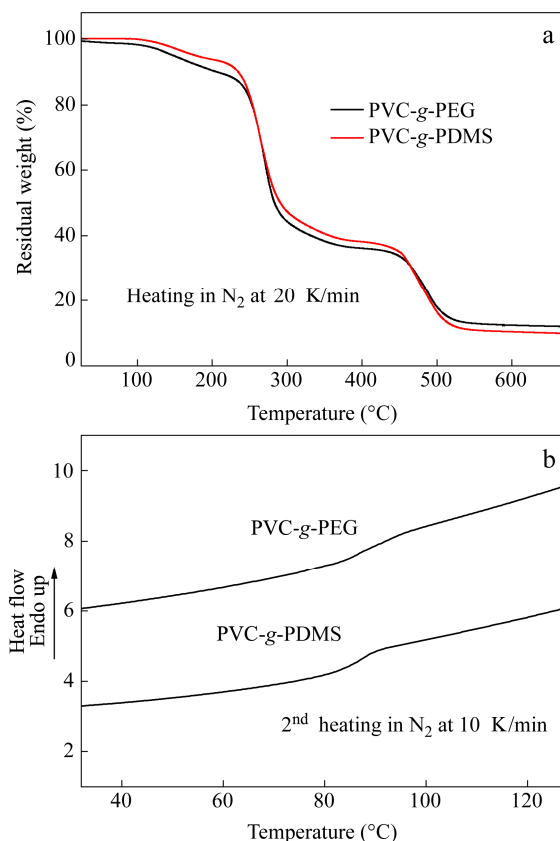


Fig. 2 TGA (a) and DSC (b) curves of PVC-g-PEG and PVC-g-PDMS

the TGA and DSC analysis results of the modified PVC. It was found that thermal decomposition behavior and glass transition temperature of the two modified PVCs were not significantly different, which means that the modification on PVC did not affect the thermal properties of PVC. Then the following comparison will focus on the surface properties and the biomedical properties.

Surface Properties of PVC and Modified PVC

Surface chemical composition of the samples can be conveniently investigated by XPS with high sensitivity. Figure 3 shows the survey scans of PVC-g-PEG and PVC-g-PDMS membrane surfaces. Typical elemental intensive scans have also been presented and interpreted based on binding energy (BE). Both carbon (BE 285 eV) and chlorine (BE 200 eV) that came from the backbone of PVC were found in the survey scans of both PVC-g-PEG and PVC-g-PDMS, while the presence of oxygen indicated the successful introduction of the oxygen-containing structures that resulted from PEG and PDMS. The higher BE at 532.5 eV was assigned to $\text{Si}-\text{O}^*$ bonds while the lower BE at 531.8 eV was from the $\text{C}-\text{O}^*$ bonds. The results are in accordance with the chemical composition of PVC and match the previous reports^[9]. In the intensive scans of elements that resulted from the grafting, the signals in $\text{C}1s$ scan at 284.8 eV were attributed to the $\text{C}-\text{C}^*-\text{C}$ bonds, the signals at 286.5 eV were attributed to the C^*-Cl bonds, and the signals at 285.5 eV were attributed to the C^*-O bonds or the C^*-Si

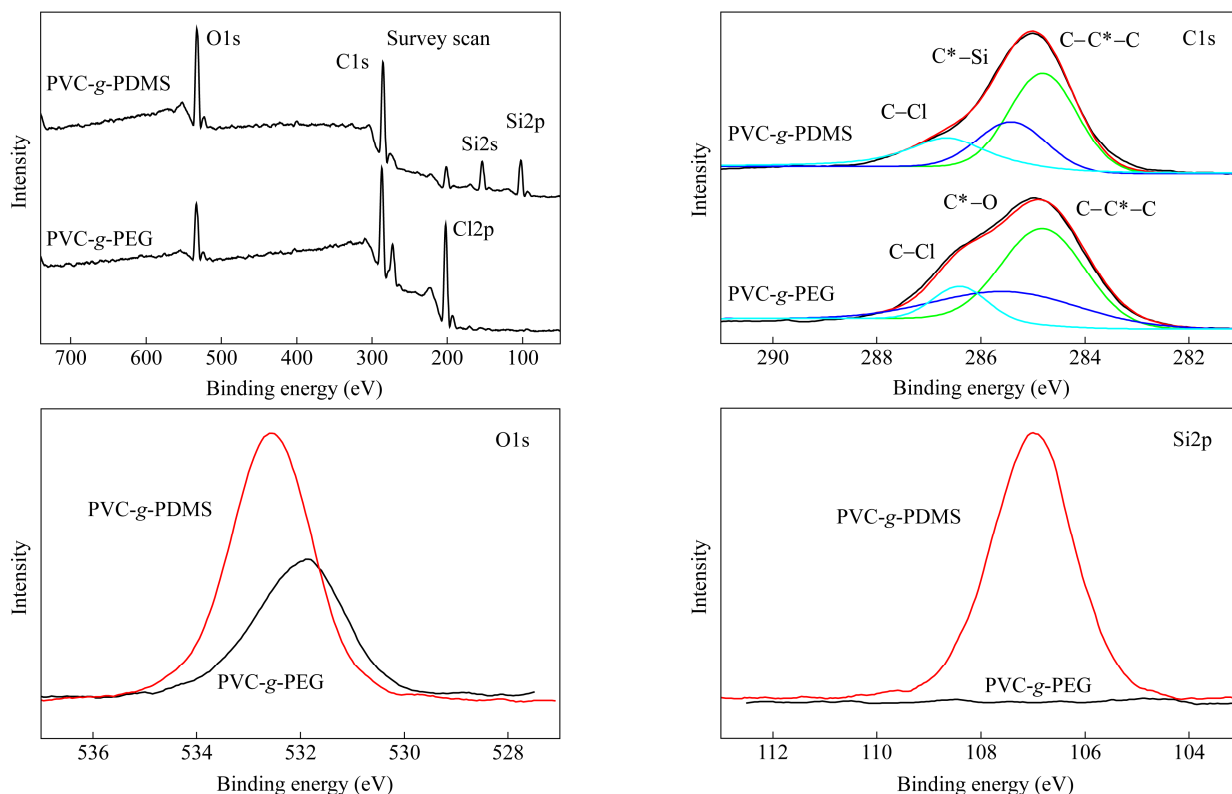


Fig. 3 XPS survey scan and intensive scans on C, O and Si of PVC-g-PEG and PVC-g-PDMS

bonds. The C^*-O and C^*-Si bonds were introduced by the chemical grafting of PEG and PDMS segments, which further confirmed the chemical grafting. In the intensive scan of Si, the Si2p signal can only be found in PVC-g-PDMS. It is obviously reasonable because of the different grafting segment structures: only can PDMS introduce silicon element into modified PVC samples.

PEG is a typical hydrophilic polymer while PDMS is a hydrophobic one. It is expected that modified PVC with PEG or PDMS would differ on their properties such as water contact angle, water adsorption and other surface properties. Figure 4(a) shows the water contact angle of bare PVC, PVC-g-PEG and PVC-g-PDMS membrane surfaces. The water contact angle of PVC-g-PEG decreased significantly from 105° , as for bare PVC, to 82° . However, for PVC-g-PDMS, the water contact angle significantly increased from 105° to 142° . For PVC-g-PEG, the decrease of water contact angle was mainly caused by the formation of hydration layer *via* electrostatic interaction and hydrogen bonding between PEG segments and water in air. For PVC-g-PDMS, the natural enrichment of silicon segment on surface resulted in the significant increase of water contact angle.

In addition to the surface hydrophilicity, the bulk water absorptivity of modified PVCs is expected to change due to the different grafts. In order to investigate the water absorptivity, three groups of bare PVC, PVC-g-PEG and PVC-g-PDMS membranes including 6 specimens in every group were soaked in distilled water for 24 h and then taken out. After the surface-adsorbed water was removed by blotting paper, the samples were weighed and recorded as the

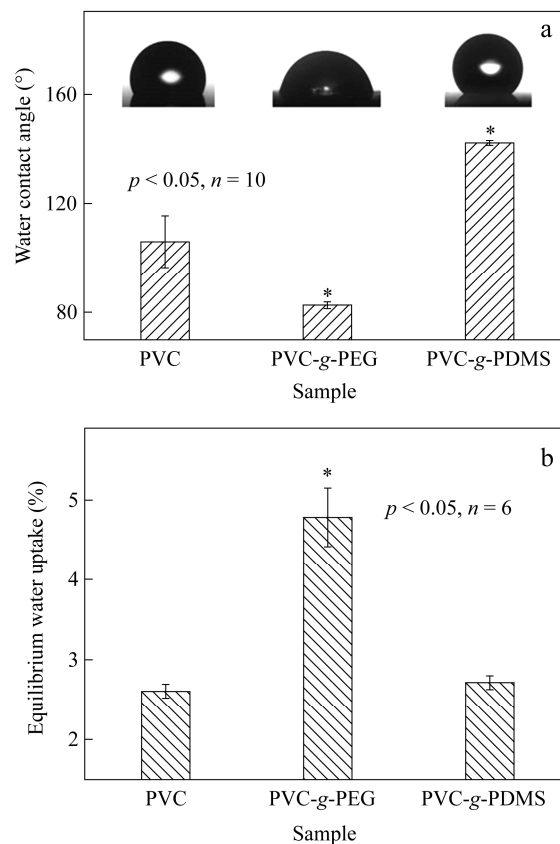


Fig. 4 Surface water contact angle (a) and water swelling (b) of PVC-g-PEG and PVC-g-PDMS (The insets in a show representative 5 μ L water drop images on different surfaces.)

equilibrium mass (w_s). Subsequently, the samples were dried in vacuum at 50 °C till reaching constant weight. The final masses were recorded as w_0 and the equilibrium water uptake was calculated according to $[(w_s - w_0)/w_0] \times 100\%$. The results are shown in Fig. 4(b). It was found that the PEGylated sample incorporated about 5% water while bare PVC and PDMS grafted PVC had only about 2.5%. It is obvious that the grafting of PEG on PVC chain changed the hydrophilicity of PVC, whilst the grafting of PDMS had no significant effects on the hydrophilicity of PVC.

Comparison of Blood Compatibility of Modified PVC

Both PEG and PDMS are well known biocompatible polymers. Grafting PEG or PDMS onto the surface of polymers such as PVC^[9, 15], polyurethane^[14] and poly(ether imide)^[12] has been reported to show enhanced protein adsorption, platelet adhesion and anticoagulation. Here in this study, such blood compatibility properties of our samples have also been investigated and analyzed.

Protein adsorption on the surface of materials is believed to be the initial event when materials come into contact with a biological environment. The adsorbed protein layer will affect the subsequent biological reactions including platelet adhesion and activation. Therefore, understanding of the interactions between proteins and material surfaces is of great importance, and the control of protein-surface interactions is an important aspect of biocompatible material designs. We examined the absorption of ¹²⁵I-labelled Fbg on the surfaces of pristine and modified PVCs. The results are shown in Fig. 5(a). The adsorptions of Fbg on PVC, PVC-g-PEG, and PVC-g-PDMS were 0.84, 0.71 and 0.63 $\mu\text{g}/\text{cm}^2$ respectively.

Both PEG and PDMS were effective to resist Fbg absorption on the PVC films and PVC-g-PDMS had slightly better anti-protein absorption properties.

The decrease of Fbg adsorption on surface was expected to result in the decrease of platelet adhesion. The representative SEM images of platelet adhere surfaces of PVC, PVC-g-PEG and PVC-g-PDMS are shown in Fig. 5(b) and the statistical analysis is shown in Fig. 5(c). It can be seen that a large number of platelets aggregated on surface of bare PVC. However, after grafting, the number of platelets adhered to PVC-g-PEG and PVC-g-PDMS dramatically decreased to 3% of that of PVC, suggesting excellent platelet-adhesion resistance enhancement by grafting. There was no significant difference between the platelets adhesion of the two modified surfaces.

Although protein adsorption and platelets adhesion are two key factors that are often used to evaluate blood compatibility, there are other factors that should be considered and examined. It is well known that protein adsorption and platelets adhesion in blood is far more complicated than that *in vitro* with solution which just contains a single type of protein or with artificial platelet-rich plasma. The whole blood is a concentrated, multi-protein-containing solution, and the protein adsorption and platelet adhesion from blood are regarded as a selective and competitive process^[16]. Fortunately, a macrocosmic examination and statistical analysis such as plasma recalcification time (PRT) test will provide more information on this concern.

PRT is a practical parameter that reflects the integrated results of blood-material interaction. It also indicates the anticoagulation property of a foreign material. Experimentally,

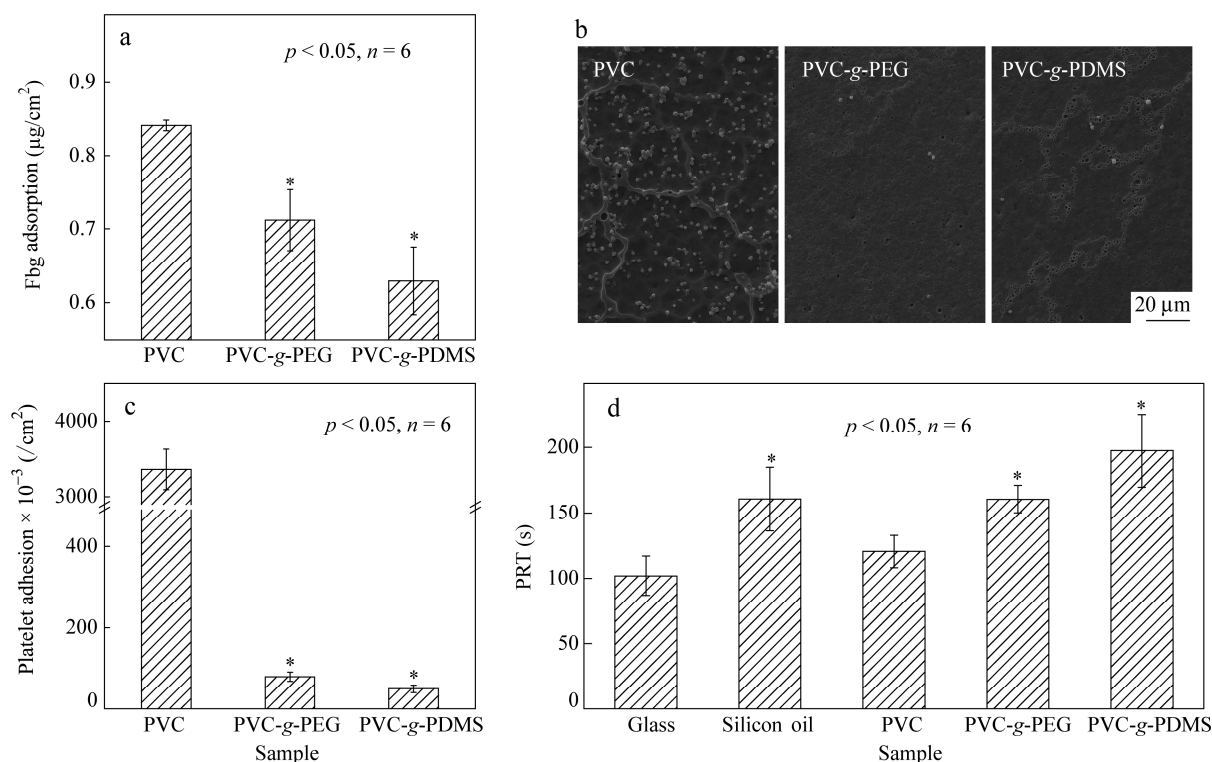


Fig. 5 Fibrinogen adsorption (a), SEM images of platelets adhered (b), statistic platelet adhesion (c) and plasma recalcification time (d) on bare PVC and modified PVC surfaces

PRT is the time that has elapsed before clotting occurs. In general, clotting occurs in a three-phase fashion. The first stage can occur *via* two different pathways: intrinsic and extrinsic pathways, and result in the formation of enzyme prothrombinase. This phase happens as a result of a cascade of protein coagulation factors interactions^[16, 17]. In this study, plasma recalcification profiles are used to mimic the intrinsic coagulation system *in vitro*. The PRT of PVC, PVC-g-PEG and PVC-g-PDMS in platelets poor plasma were compared with glass surface as the blank control group and silicon oil coated glass surface as positive group.

The results of PRTs on different surfaces are shown in Fig. 5(d). It was observed that the PRTs for PVC-g-PEG and PVC-g-PDMS were significantly prolonged compared to those of glass surface and PVC, suggesting that the modified PVC had better anticoagulant property than glass. The anticoagulant property of PVC-g-PEG was similar to that of the pure silicon oil coated surface. PVC-g-PDMS showed the longest PRT (198 s) while it was 160 s for PVC-g-PEG and 120 s for PVC, all of which were significantly longer than that of blank control ($n = 6$, $p < 0.05$). The result agreed with the observation in protein adsorption and platelet adhesion, both of which suggested that the modified PVC with both PEG and PDMS had good anticoagulant property and PDMS showed better performance among the two.

Cell Attachment and Proliferation on Modified PVC

The modified PVC surfaces have exhibited excellent inhibitory effects on Fbg adsorption, platelet adhesion and coagulation, thus, the cell attachment and proliferation on the surfaces were expected to be improved as well. Using L929 as a representative cell line, the cell attachment and proliferation on PEG and PDMS grafted surface were studied and compared.

The initial *in vitro* response of L929 to different surfaces

was evaluated in terms of cell attachment, while the long-term L929 growth was investigated as proliferation. The L929 surface images after several incubation periods are shown in Fig. 6(a). For PVC-g-PDMS, in the initial stage (4–16 h), L929 attached to the surfaces and their pseudopodia formed but the cells distributed separately. The interaction between surface and cells is mainly adsorptive action. After cell planting for 24 h, a number of cells began to divide and many binucleate cells were found, indicating that the cells had entered mitotic phase. 72 h after cell planting, the cell number increased significantly and the cell-cell interactions started. Cells adhering on the surfaces continued to grow. In the 5th day, the cells almost covered the entire surface. However, for PVC-g-PEG, the attachment and proliferation of L929 were delayed. By the 5th day, the cells did not cover the surface to the same level as observed on PVC-g-PDMS.

The statistical results of L929 density calculated from every 6 visions on modified PVC membrane are shown in Fig. 6(b). The increase in the incubation time from 4 h to 16 h resulted in about 50% increase in L929 numbers that were attached to PVC-g-PDMS surfaces, and in the entire 5-day incubation, the proliferation of L929 increased near linearly. The cell proliferation was much slower for PVC-g-PEG surface but a linear increase in cell numbers has also been observed. In general, L929 proliferation rate, which is reflected by the slope of cell proliferation curves as shown in Fig. 6(b), on PVC-g-PDMS is significantly higher than that on PVC-g-PEG surfaces. In other words, the inhibition of cell attachment and proliferation by hydrophilic surface is more effective than that by hydrophobic surface. The hydrophobic modification, which resulted in rapid cell attachment and proliferation, is probably beneficial to implantable medical devices, while the hydrophilic modification is probably more suitable for devices that contact blood transiently, such as blood bags, blood transfusion tubes and *etc.*

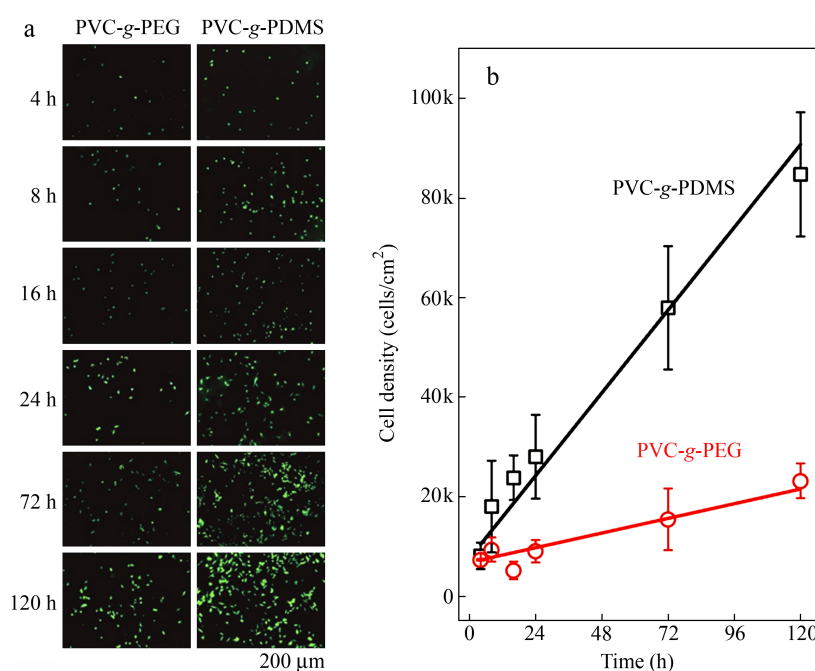


Fig. 6 Images (a) and cell density (b) of L929 attachment and proliferation on PEG and PDMS grafted PVC surfaces

CONCLUSIONS

By simple amination and then mediated by IPDI, hydrophilic PEG and hydrophobic PDMS segments ($M_n \sim 1000$ Da) were successfully grafted onto PVC backbone. According to the studies on chemical structures, physical properties, hydrophilicity performances, blood compatibilities and L929 cell proliferations, it was found that both PEG and PDMS grafting can improve the biocompatibility of PVC. As for the cell attachment and proliferation, the inhibition of cell attachment and proliferation by hydrophilic surface is more effective than that by hydrophobic surface.

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