

Preparation of SBS-*g*-VP Copolymer Membrane by UV Radiation Without Degassing

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ABSTRACT: The solvent-cast film of styrene–butadiene–styrene triblock copolymer (SBS) was prepared, and the grafting of 4-vinyl pyridine (VP) to the SBS membrane was induced by ultraviolet radiation without degassing to obtain the SBS-*g*-VP copolymer membrane. The chemical composition of the graft copolymer membrane was studied by infrared spectroscopy. In addition to those absorption peaks associated with pure SBS, the SBS-*g*-VP graft copolymer also showed a peak of absorption at 820 cm⁻¹, which appeared in the spectra of homopolyvinylpyridine. The degree of grafting and the mechanical properties of SBS and SBS-*g*-VP were measured. Contact angle, water content, and protein adsorption of fibrinogen and albumin experiments were also performed to evaluate the blood biocompatibility of the SBS-*g*-VP membrane. It was found that the degree of grafting exhibited an approximate linear increase with VP concentration at 0°C. The degree of grafting increased sharply with VP concentration above 30% v/v at 10°C. The degree of grafting increased with VP concentration and then leveled off when the temperature was at 30°C. The rate of grafting followed Arrhenius law. The activation energy obtained was 3.25 kcal/mol. PolyVP has a glass transition temperature (T_g) at about 240°C, and hence, it performs as a hard rigid plastic at room temperature. Therefore, the SBS-*g*-VP graft copolymer showed the plastic performance with increasing degree of grafting. The surface tension of SBS-*g*-VP was determined by using Kaelble's equation and the contact angle data. It was found that the surface tension and water content of SBS-*g*-VP membrane increased, whereas the contact angle decreased with grafting degree. Albumin and fibrinogen adsorption increased with time and reached a steady-state level after 20 and 40 min, respectively. The maximum desorption appeared in 30 min for albumin, but it took more time to reach maximum desorption for fibrinogen. The amount of protein adsorption decreased with the increasing of grafting degree, and the amount of protein adsorption eventually leveled off. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 109–116, 1997

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INTRODUCTION

The applications of polymers for biomaterials have become increasingly important in the last decade. Since surface modification is an effective means to alter biological interactions to a polymeric material, it offers a number of advantages in biomedical fabrication. General methods for polymer surface modification include roughening, oxidation, coating, blending, ion implantation, and graft polymerization.¹

Surface modifications through covalent graft polymerization without any bulk deterioration are most desirable for biomaterials. A series of studies of the surface modification of polymers for medical applications (such as lubricious surface,^{2,3} blood-compatible surface,^{4,5} tissue-bonding surface,^{6,7} and physiologically active surface^{8,9}) by graft polymerization methods have been reported by Ikada et al.¹⁻⁹

Numerous investigators have found that foreign surfaces rapidly adsorb plasma proteins when exposed to blood,¹⁰ so it is essential to have an understanding of protein-polymer interaction for the development of antithrombogenic material. Hari et al.^{11,12} had prepared hydrogel-grafted surfaces by a γ -irradiation method and studied the protein-polymer interaction and morphology of platelets onto the surfaces.

In our previous study,¹³ hydroxyethyl methacrylate (HEMA) was grafted onto a membrane of styrene-butadiene-styrene triblock copolymer (SBS), a microphase-separated polymer,¹⁴ by a γ -ray irradiation method. From measurements of the contact angle and the blood-clotting time, both the wetting and the nonthrombogenic properties of SBS-*g*-HEMA were better than those of SBS. In a prior study,¹⁵ 4-vinyl pyridine (VP) was grafted to SBS particles by a γ -ray irradiation method. It was found that SBS-*g*-VP also retained the suitable mechanical properties of SBS and exhibited better blood compatibility than SBS as measured by the Lee-White clotting test.

In industrial applications, surface graft polymerization is a time-consuming and expensive degassing process, which usually involves purging with an inert gas or repeated cycles of freezing and thawing. It will be economical if the oxygen removal process can be omitted for surface graft polymerization on a large scale.

Recently, Uchida et al.^{16,17} reported a method for surface graft polymerization of ionic monomer onto poly(ethylene terephthalate) by ultraviolet (UV) irradiation without degassing. In another

Table I Physical Properties of TPE 416

Butadiene/styrene ratio	70/30
Block polystyrene (%)	30
Volatile matter (%)	0.40
Ash (%)	0.25
Specific gravity	0.94
Gel (%)	0.08
Melt flow (180/5 kg), g/10 min	1.1
Hardness (type A)	74

study,¹⁸ we reported the grafting of dimethyl aminoethyl methacrylate (DMAEMA) onto the SBS membrane by UV photografting without degassing, the method of which is different from that in the study of Ikada et al.^{16,17} It was found that the tensile strength of the SBS-*g*-DMAEMA graft copolymer membrane could increase with the increase of DMAEMA grafting, whereas the amount of absorption of albumin and fibrinogen decreased with increasing grafting.¹⁸

In this article, the grafting of VP onto the SBS membrane by UV photografting without degassing is reported. The effect of radiation condition on the degree of grafting was studied. The effect of grafting on the mechanical properties of the SBS-*g*-VP graft copolymer membrane was also evaluated. The contact angle and water absorption of the SBS-*g*-VP graft copolymer membranes with different amounts of grafting were determined. By using the equation of Kaelbe and Moaain,¹⁹ and the contact angle data, the surface tension of the SBS-*g*-VP graft copolymer membrane was determined. In addition, the absorption of fibrinogen and albumin in the membrane experiments was also determined to evaluate the biocompatibility of the SBS-*g*-VP graft copolymer membrane.

EXPERIMENTAL

Materials

SBS

SBS, TPE 416, was obtained from Taiwan Synthetic Rubber Co, and its characteristics are listed in Table I. VP was distilled under 5 mmHg/54°C to eliminate impurities and was stored under nitrogen gas. Before purification, potassium hydroxide was added to remove water and stabilizer.

Reagents

Benzene was extracted several times with 80 mL of concentrated sulfuric acid per liter of benzene, until it became colorless. Chloroform, methanol, ethanol, formamide, glycerin, ethylene glycol, and β -thiodiglycol were all reagent grade and were distilled before use.

Film Casting

SBS was dissolved in chloroform to form 10% (w/v) solutions and was poured onto a clean teflon surface. After evaporation, membranes with a smooth surface and known thickness were obtained.

Preparation of SBS-*g*-VP Graft Copolymer Membrane

The SBS membrane, which was prepared by a film casting method, was immersed in a 4-VP-methanol-water solution and then immediately irradiated at different temperatures by UV light without degassing. Benzoin ethyl ether was used as a photoinitiator. After photografting, the membrane of SBS-*g*-VP was extracted with hot methanol for at least 48 h to remove the homopolymer, followed by drying in a vacuum oven; then, the sample was weighed. The amount of grafting was calculated by the equation

$$\text{grafting (mg/cm}^2\text{)} = (W_f - W_i) \div A \quad (1)$$

where A is the surface area of the membrane, and W_f and W_i are the final and initial weights of the membrane after and before UV photografting modification, respectively. A pure SBS and a clean SBS-*g*-VP graft copolymer were characterized by a Perkin-Elmer model 567 infrared spectrometer.

Measurement of the Tensile Strength and Strain Curve

Films of each polymer type were cut into strips of 50×5 mm, and tensile strength and elongation were measured with an Instron (model 1122) at room temperature with a crosshead speed of 50 mm/min.

Measurement of Water Absorption

The SBS-*g*-VP membranes with various amounts of grafting were dried in a vacuum oven at 30°C for 24 h to determine their dry weight (W_d); the surface area (A) was also determined. Water content was tested by immersing the membranes in distilled water. The wet weight (W_w) with different immersion times was determined by wiping off the surface water with a piece of filter paper. The absorbed water content was then calculated by

$$\text{water content (mg/cm}^2\text{)} = (W_w - W_d) \div A \quad (2)$$

Measurement of the Contact Angle and the Calculation of Surface Energy

After the clean SBS-*g*-VP graft copolymer membranes with various degrees of grafting were prepared, a drop of solvent (such as water, β -thiodiglycol, ethylene glycol, glycerin, and formamide) was placed on the surface of the membranes with a pipette, and the contact angle between the solvent drop and the membrane was subsequently measured. A few more drops of solvent were added until the contact angle was constant. The results of the contact angle measurements are shown in Table II.

By combining the above contact angle data

Table II Contact Angle of SBS-*g*-VP Copolymer Membrane with Different Test Liquids

Grafting (mg/cm ²)	Water (degree)	β -Thiodiglycol (degree)	Ethylene Glycol (degree)	Glycerin (degree)	Formamide (degree)
0	104 ± 2	73 ± 1	72 ± 1	82 ± 1	78 ± 2
1.7	76 ± 4	62 ± 4	65 ± 1	69 ± 2	71 ± 2
2.1	72 ± 0.5	42 ± 2	60 ± 1	58 ± 2	46 ± 1
3.6	64 ± 0.5	36 ± 2	44 ± 4	42 ± 4	42 ± 2
4.9	59 ± 1	26 ± 3	32 ± 2	41 ± 2	32 ± 4

Table III Surface Tension Properties of Test Liquids

Test Liquid	γ_{IV} (dyne/cm)	α_1	β_1
Water	72.8	4.67	7.14
Glycerol	63.4	6.10	5.12
Formamide	58.2	6.28	4.32
Dithioglycol	54.0	6.20	3.94
Ethylene glycol	48.3	5.41	4.36

Data from ref. 5. γ_{IV} , liquid–vapor tension; α_1 and β_1 , square root of the respective (London) dispersion and (Keesom) polar parts of γ_{IV} .

with the solvent surface tension data of Table III, the surface energy of the SBS-*g*-VP graft copolymer membranes with various grafting degrees was calculated by the method proposed by Kaelble and Moacanin.¹⁹ The results are tabulated in Table IV.

Measurement of the Adsorption of Albumin and Fibrinogen

Albumin has thromboresistant ability, whereas fibrinogen promotes the platelet to adhere onto the biomaterial surfaces. In this study, the measurement of the adsorption of albumin and fibrinogen was conducted to evaluate the blood compatibility of the SBS-*g*-VP graft copolymer membranes.

SBS-*g*-VP graft copolymer membranes with various amounts of grafting were absorbed with albumin and fibrinogen, respectively, at 30°C for 1 h. The concentrations of albumin and fibrinogen were 1.0 and 0.1 mg/mL, respectively. Detailed measurements of the absorption of albumin and fibrinogen were performed following the procedures described in the literature.²⁰

RESULTS AND DISCUSSION

The Study of Grafting Behavior

Characterization of SBS-*g*-VP by Infrared Spectroscopy

Shown in Figure 1(a–c) are the absorption spectra of pure SBS block copolymer, homopolyvinylpyridine, and SBS-*g*-VP graft copolymer, respectively. In addition to those absorption peaks associated with pure SBS block copolymer, the SBS-*g*-VP graft copolymer also shows a peak of absorption at 820 cm⁻¹, which appeared in the spectra of homopolyvinylpyridine.^{21,22} Since the unreacted VP and its homopolymer have been extracted with hot methanol, the appearance of this absorption band would indicate that VP has been grafted onto the SBS triblock copolymer.

The Effect of Monomer Concentration and Irradiation Time on Grafting

Figure 2 shows the relationship between the VP concentration of various VP–methanol–water solutions and the amount of grafting at various irradiation temperatures. It was found that the amount of grafting exhibited an approximate linear increase with VP concentration when the photografting temperature was 0°C. The amount of grafting increased sharply with VP concentration above 30% v/v when the photografting was conducted at 10°C. The amount of grafting increased with VP concentration and then leveled off when the photografting temperature was 30°C. As has been reported previously,²³ the amount of grafting of irradiation-induced graft copolymerization is affected by the molecular chain mobility, which is related to the solubility of molecules in the graft polymerization system. When the photografting temperature was raised from 0 to 10°C, the viscosity in the system increased, which resulted in dif-

Table IV The Water Adsorption and Surface Tension of SBS-*g*-VP Membrane

Grafting (mg/cm ²)	Water Adsorption (wt %)	γ_{sv}^d (dyne/cm)	γ_{sv}^p (dyne/cm)	γ_{sv} (dyne/cm)
0	0.2	14.9 ± 1.4	6.5 ± 0.6	21.4 ± 0.8
1.7	1.8	20.1 ± 0.8	7.3 ± 2.1	27.4 ± 1.4
2.1	2.2	27.5 ± 1.4	9.6 ± 0.2	37.2 ± 1.1
3.6	3.6	28.8 ± 2.4	14.2 ± 0.7	43.0 ± 1.7
4.9	3.7	29.3 ± 0.1	17.2 ± 0.6	46.5 ± 0.7

γ_{sv} , liquid–vapor tension; γ_{sv}^d , liquid–vapor tension of London dispersion; γ_{sv}^p , solid–vapor surface tension of Keesom polar.

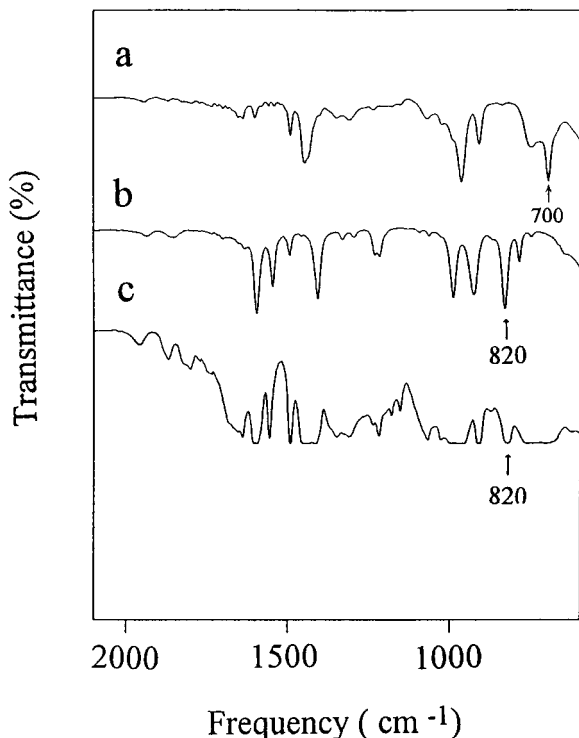


Figure 1 Infrared spectrum of (a) SBS, (b) poly(4-vinylpyridine), and (c) SBS-g-VP.

difficulty in determining the active centers of the propagation chain end in the grafted polymer chain with VP concentration above 30% v/v. With an increase in temperature from 10 to 30°C, the viscosity in the test system increased rapidly due

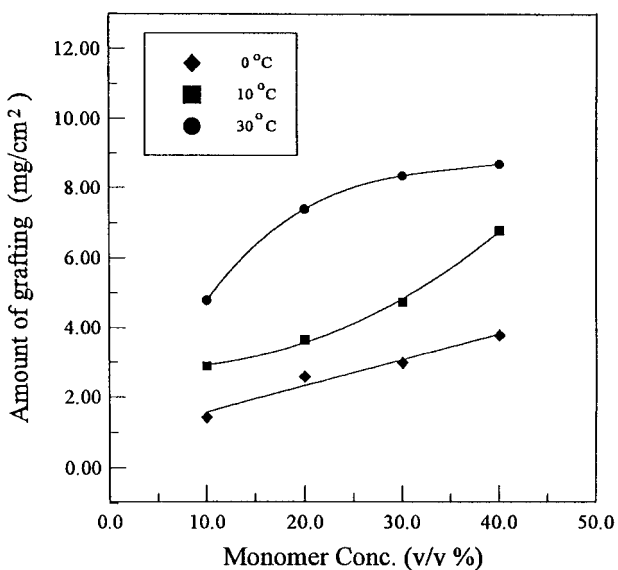


Figure 2 Effect of VP concentration on grafting at (◆) 0°C, (■) 10°C, and (●) 30°C.

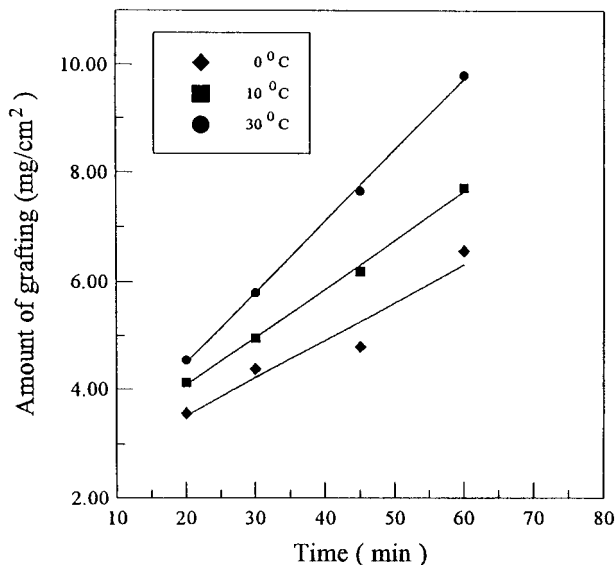


Figure 3 Effect of irradiation on grafting of VP onto SBS at (◆) 0°C, (■) 10°C, and (●) 30°C.

to the formation of homopolymer. Because there was competition between the homopolymerization and the grafting polymerization, at the high-viscosity condition, the VP monomer was trapped in the homopolymer and was homopolymerized before they could diffuse to the surface to undergo graft copolymerization. The amount of grafting therefore leveled off when the VP concentration was above 30% v/v.

Figure 3 shows the relationship between the amount of grafting and the irradiation times for various photografting temperatures. The amount of grafting increased linearly with the irradiation times. The rate of grafting, which is defined as the increase of the amount of grafting per minute, is plotted in Figure 4 against the photografting temperature. The rate of grafting followed the conventional Arrhenius law of $R_p = k_p \exp(-E_p/RT)$, which is evident in Figure 4. The activation energy (E_p) obtained by the Arrhenius plot was 3.25 kcal/mol.

The Properties of SBS-g-VP Graft Copolymer

Tensile Strength and Strain

Figure 5 displays the relationship between the tensile strength and strain for the SBS-g-VP graft copolymer with various amounts of grafting. The tensile strength of SBS-g-VP was higher than that of SBS. With an increasing degree of grafting, the tensile strength increased but the strain de-

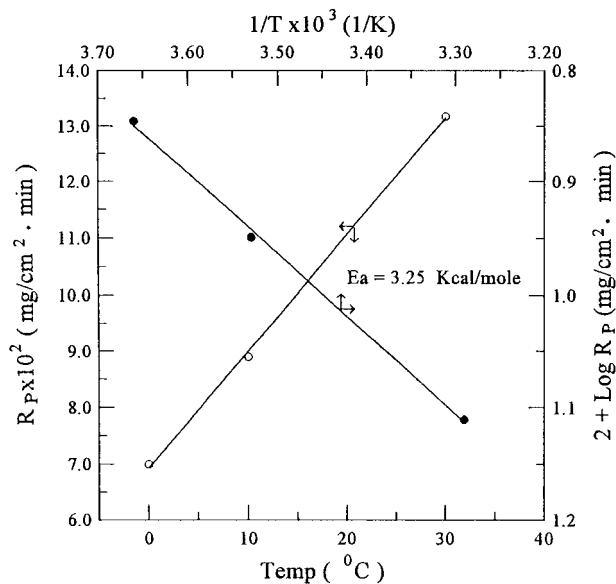


Figure 4 Effect of temperature on the rate of grafting of VP onto the SBS membrane.

creased. This observation can be interpreted by considering the glass transition temperatures (T_g) of the VP and the SBS components. Polyvinylpyridine has a T_g at about 240°C, and hence, it performs as a hard rigid plastic at room temperature. On the other hand, SBS is a thermal plastic rubber with a T_g of the polybutadiene block at about -94°C.²¹ Therefore, the SBS-*g*-VP graft

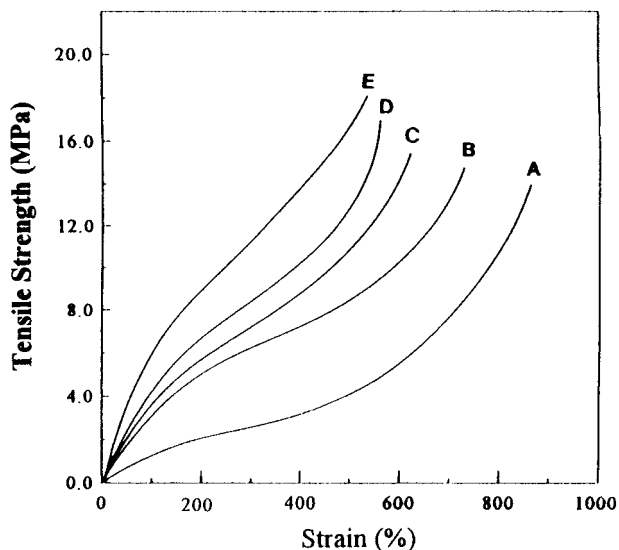


Figure 5 Stress-strain curve of SBS-*g*-VP membranes with different degrees of grafting: (A) 0 mg/cm², (B) 1.7 mg/cm², (C) 2.8 mg/cm², (D) 3.6 mg/cm², and (E) 4.9 mg/cm².

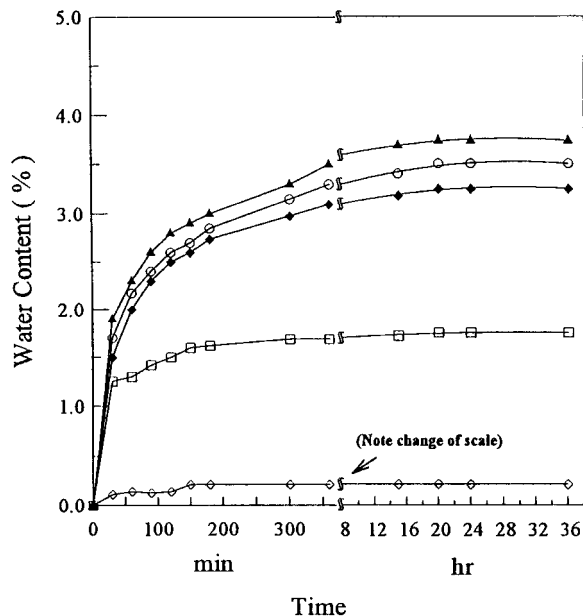


Figure 6 Water adsorption of SBS-*g*-VP membrane with different degrees of grafting: (\diamond) 0 mg/cm², (\square) 1.7 mg/cm², (\blacklozenge) 2.1 mg/cm², (\circ) 3.6 mg/cm², and (\blacktriangle) 4.9 mg/cm².

copolymer showed the plastic performance with an increase in VP grafting.

Measurement of Contact Angle, Water Absorption, and Surface Energy of SBS-*g*-VP

Figure 6 shows the relationship between the water absorption and the soaking time for the SBS-*g*-VP graft copolymer membranes with various amounts of grafting. As the VP grafting in the SBS-*g*-VP graft copolymer membrane increased, the water absorption in the SBS-*g*-VP graft copolymer membranes increased, while the contact angle decreased (Table II). These changes may be due to the existence of a portion of polyvinylpyridine in the SBS-*g*-VP membrane surface. As the degree of VP grafting increased, the role of the hydrophilic polyvinylpyridine domain in SBS-*g*-VP became more significant. These results could be confirmed by the observation that the surface energy of SBS-*g*-VP increased with the amount of grafting (Fig. 7). The surface free energy increase can be ascribed to the increase of the dispersion (γ^d) term and the polar (γ^p) term for the SBS-*g*-VP membranes (Table IV). Thus, the water absorption in the SBS-*g*-VP graft copolymer membranes increased with an increase of VP grafting, whereas the value of the contact angle decreased.

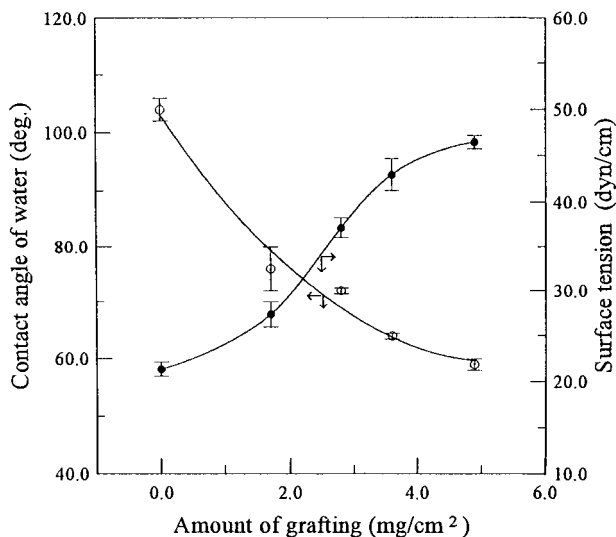


Figure 7 Effect of grafting on the contact angle and surface tension of SBS-g-VP membranes.

Measurement of the Adsorption of Albumin and Fibrinogen

Figure 8 shows the adsorption isotherms of albumin and fibrinogen on the SBS membrane. Albumin adsorption increased with time and reached a steady-state level after 20 min. Fibrinogen adsorption on the SBS surface showed the same pattern as albumin, but it took about 40 min to reach steady state, because the molecule of fibrinogen is larger than that of albumin. A larger amount of fibrinogen adsorption on the SBS surface is ob-

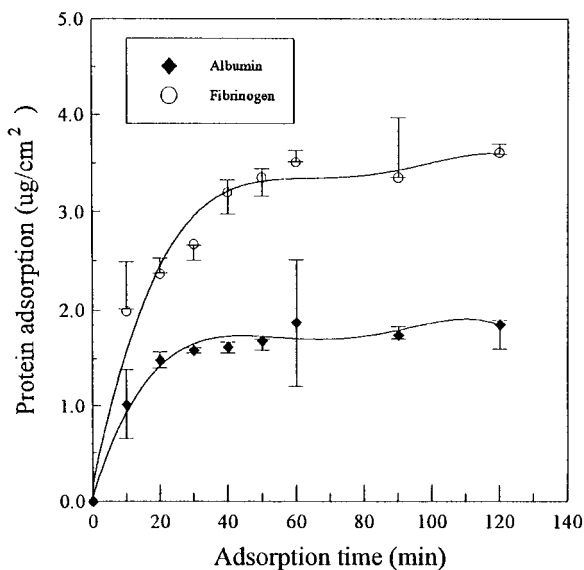


Figure 8 Adsorption isotherms of albumin and fibrinogen of the SBS membrane.

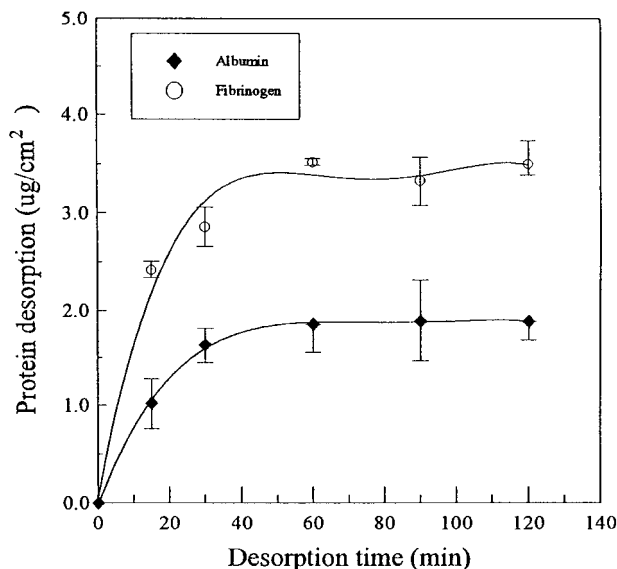


Figure 9 Desorption isotherms of albumin and fibrinogen of the SBS membrane.

tained compared with albumin adsorption. Figure 9 shows the desorption isotherms of albumin and fibrinogen on the SBS membrane. The maximum desorption appears in 30 min for albumin, but it took more time to reach maximum desorption for fibrinogen.

Table V shows that the amounts of adsorption of albumin and fibrinogen for pure SBS membrane are 2.55×10^{-11} and 1.03×10^{-11} mol, respectively. For the SBS-g-VP graft copolymer membrane with 3 mg/cm^2 amount of grafting, the corresponding values are 2.15×10^{-11} and 0.88×10^{-11} mol. It seemed that the amount of protein adsorption decreased with the increase in grafting amount and that the amount of adsorption eventually leveled off. This is due to the increasing number of hydrophilic functional groups on the membrane surface. These results were confirmed by the increase of the water absorption and surface energy of SBS-g-VP with the increase of grafting.

CONCLUSIONS

The SBS-g-VP graft copolymer membranes were synthesized by UV photografting without a degassing method. Because the grafting is affected by molecular chain mobility, the amount of grafting increased sharply with VP concentration above 30% v/v when the photografting temperature was 10°C. The amount of grafting increased

Table V Protein Adsorption of SBS-g-VP Membrane

Grafting (mg/cm ²)	Protein			
	BSA (μg/cm ²)	BSA (mol/cm ²) × 10 ¹¹	Fibrinogen (μg/cm ²)	Fibrinogen (mol/cm ²) × 10 ¹¹
0	1.76 ± 0.01	2.55	3.5 ± 0.1	1.03
1	1.58 ± 0.04	2.30	3.1 ± 0.1	0.91
2	1.55 ± 0.19	2.26	3.0 ± 0.2	0.88
3	1.48 ± 0.20	2.15	3.0 ± 0.3	0.88

with VP concentration and then leveled off when the photografting temperature was at 30°C.

The SBS-g-VP graft copolymer could exhibit the plastic performance with the increase of VP grafting. This is due to the presence of the VP graft, which has the performance of a hard rigid plastic.

From the measurements of contact angle, surface energy, and protein adsorption, it was found that the SBS-g-VP graft copolymer membrane exhibited better wetting and less protein adsorption than SBS. In order to decrease the protein adsorption, the SBS-g-VP graft copolymer membrane will be treated with CH₃I and then can complex with heparin to prepare a heparin-containing SBS-g-VP graft copolymer. A detailed study of the preparation and properties of the heparin-containing SBS-g-VP graft copolymer membrane will be reported in the future.

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