UV-Grafted Gradient Surface Polyurethane Membrane

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ABSTRACT: Gradient surfaces of polyurethane (PU) membranes were created by UV grafting approach in a graded temperature field. Acrylic acid was selected as grafting monomer to improve the hydrophilicity of the surfaces. The Fourier transform infrared spectroscope (FTIR) spectra and scanning electronic microscope (SEM) were used to characterize the gradient. The results showed that the graft yield increased gradually from the lower temperature end to the higher temperature end. As a result, the hydrophilicity of the gradient surfaces displayed a gradual change along the same direction. Water contact angle measurements also proved this point. The graft reaction rate was investigated as a function of positions along the PU membrane. The average grafting yield of PU membrane increased with the extending of UV light irradiation and increase of photo initiator dosage. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 769–774, 2009

Key words: gradient surface; UV grafting; polyurethane; surface modification; hydrophilicity

INTRODUCTION

Surfaces whose properties change gradually in one or several directions are called gradient surfaces. Gradient surfaces have been paid much attention in the studies on combinatorial materials and high throughout experimentation methods because of their ability to explore systematically a multiparameter phenomenon and accelerate substantially data acquisition speed and efficiency.[1,2] Interactions of gradient surfaces with invading species can change gradually across the surface. As a result, the species can select the different positions according to the variable interactions.[3] Surface energy, one of the most important properties of the materials' surfaces, affords a powerful means to design the gradient surface. In 1978, Greenspan[4] discussed theoretically the possibility of droplet movement driven by the gradient surface energy. In 1992, Chaudhury and Whitesides[5] proved that a drop of water could move uphill on a surface tilted from horizontal plane by 15 degree from hydrophobic to hydrophilic end. Subsequently, Daniel et al.[6] observed the fast drop movement on the gradient surface. This effect can be used to enhance the heat transfer in heat exchangers and heat pipes.

Surface grafting is an effective and important means to obtain gradient surface. In the previous researches, "grafting to"[2] and "grafting from"[7–9] processes have been employed successfully to create gradient surfaces polymer materials. UV irradiation is a convenient and effective method to obtain the grafted polymer surface. In addition, the properties of substrate polymer can not be reduced. The strength of UV, time of irradiation, temperature, and concentration of monomer or initiator will affect obviously the graft yield.[10–14] The gradual variation of these factors across the surface may result in a gradient surface. However, the gradient of strength of UV and temperature may be easier to create. Herein, we will report the UV grafting of polyurethane (PU) membrane under a temperature gradient.

PU membranes with good biomedical compatibility and mechanical property are widely used in biomaterial and separation fields.[15,16] Generally, surface modification of PU membrane is performed to enhance the surface properties by grafting approch.[17–20] However, these surface modifications were carried out to form a uniform surface. If the gradient surface is introduced to PU membrane, some new and useful applications may be found. In this article, we described a method to prepare PU membranes with gradient surfaces by UV grafting. The gradient surfaces were characterized by FTIR and SEM. Also, the changing trend of water contact angle along the gradient surface was investigated.

EXPERIMENTAL

Materials

Tolylene diisocyanate (TDI) is supplied by Bayer poly (oxypropylene) glycol(PPG: $M_n = 2000$) is supplied by

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the third plastic plant of Nanjing. 3, 3-dichloro-4,4-dianilino methane (MOCA), used as chain extender, is produced by Xiangyuan refined chemical industry limited company, Jiangsu provenience. Acrylic acid (AA), analysis reagent, supplied by Tianjin Kaitong chemical reagent limited company was used without treatment. Acetone, analysis reagent, is produced by Guangdong Xilong chemical industry limited company. Benzophenone (BP) produced by Shanghai chemical reagent company, was used without further purification. PU prepolymer was prepared in our laboratory.[21]

Preparation of PU membrane

The PU prepolymer and MOCA were mixed by vigorous stirring with molar ratio $NH_2/NCO = 0.9$. The mixture was poured onto a clean glass plate after the air bubbles were eliminated under vacuum condition. The PU membrane with the thickness of 0.5 mm was obtained after curing for a month at ambient temperature.

Preparation of gradient surface

The PU membrane prepared was cut into rectangular pieces with the width of 1 cm and length of 3 cm. The rectangular membrane was put on the designed stage, whose temperature at two ends can be controlled. When the temperature of the two ends was stable, the mixture of AA, BP, and acetone was poured onto the membrane. Then, the quartz was put on the membrane making the mixture form a homogeneous liquid layer. Subsequently, the 450 W mercury lamp was turned on to offering UV light irradiation. After the grafting, the PU membranes were washed by acetone for several times firstly. Then, the membranes were put into distilled water at 60°C for 24 h. During this period, the water was renewed at intervals. The PU membranes with gradient surface were obtained after drying at 40°C. The experimental setup was shown in Figure 1. The conditions to prepare the gradient surfaces were listed in Table I.

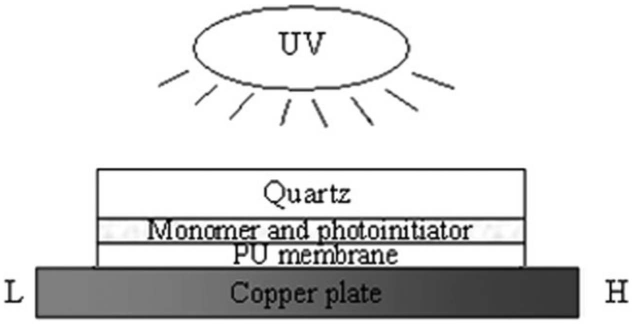

Figure 1 Scheme of surface photografting with temperature gradient.

Characterization of gradient surface

FTIR

The FTIR spectra were collected by the attenuated total reflection (ATR) technique using a NICOLET 5700 FTIR apparatus. The spectra were obtained with 4.0 cm^{-1} resolution and 32 times scanning.

SEM

The morphologies of gradient surface were observed by Quanta 200 scanning electron microscope. Images from different parts along the gradient surface were obtained to show the change trend of the morphologies.

Water contact angle

The water contact angle of the gradient surfaces was measured using a JJC-1 contact angle goniometry (Changchun 5th optic instrument factory, China). For each sample, the measurements were carried out along the gradient direction. The water contact angle reported were the average values of at least 10 replicates.

Grafting yield

The grafting yields were calculated according to the equation[21]:

TABLE I
Conditions of Preparing the Gradient Surfaces

Sample	Higher temperature (°C)	Lower temperature (°C)	BP (wt % of AA)	Weight radio of AA and acetone	UV irradiation time (minute)
S1	60	38	1	0.5	5
S2	60	38	1	0.5	10
S3	60	38	1	0.5	20
S4	60	38	2	0.5	10
S5	60	38	3	0.5	10

$$\text{Graft yield }(\%) = \frac{W - W_0}{W_0} \times 100\%$$

where W_0 and W were the weight of the ungrafted and grafted PU membranes, respectively.

RESULTS AND DISCUSSION

Under UV light irradiation, the initiator BP absorbed UV light and was excited. The excited BP molecules can abstract hydrogen atoms from PU membrane leading to generation of free radicals on the surface.[22] These radicals can act as grafting sites for vinyl functional monomers. Then AA monomers were grafted to the surface by a free radical polymerization mechanism. The temperature may have a positive effect on the radical polymerization. Therefore, the graft yield gradient was expected to be obtained in a graded temperature field.

The ATR spectra were collected from the higher temperature end (H) to the lower temperature end (L) to investigate the grafted PU membranes. Figure 2 gave the ATR spectra of sample S3 and S5. The obvious change can be observed at 1724 cm^{-1} and 1100 cm^{-1}, which attributed to the stretching vibration of carbonyl (C=O) and ether (C—O—C) groups, respectively. The carbonyl absorbance peaks became gradually stronger and stronger from L to H. Moreover, the peaks moved gradually from 1724 to 1715 cm^{-1}, which attributed to the carbonyl stretching vibration of PAA. However, the absorbance peaks at 1100 cm became gradually weaker and weaker from L to H, which was caused by the poly(acrylic acid), PAA, coverage on the surfaces. On the whole, the ATR spectra from L to H exhibited more and more characteristics of the infrared spectra of PAA, which was shown at the bottom in Figure 2. These facts reflected strongly that more and more AA were grafted on the surface from L to H. The increase of graft yield was attributed to the increase of temperature. Although increasing temperature can enhance grafting rate and homogeneous polymerization rate of AA at the same time, the grafting was influenced more. As a result, the graft yield varied with the temperature. And the graft yield gradient was created under a temperature gradient.

The gradient surface morphologies were investigated by SEM. Figure 3 displayed the morphology gradient from L to H. Obviously, the ungrafted surface was smooth. On the grafted surfaces, the dendritic PAA was observed clearly. With the increase of temperature, the graft density increased gradually and the surface was covered more and more.

The effect of UV irradiation time and concentration of initiator BP on the graft yield were investigated. Just as shown in Figures 4 and 5, the graft yield increased with the increase of irradiation time and concentration of BP in our experiments. The sample S3 exhibited the highest graft yield, 28.3%. In addition, extending the UV irradiation time seems more effective than increasing the dosage of BP to enhance the graft yield according to the experimental results. The graft yield reported here was an average value of the whole membrane because it changed gradually along the membrane. However, it was helpful to study the relationship between gradient properties and graft yield.

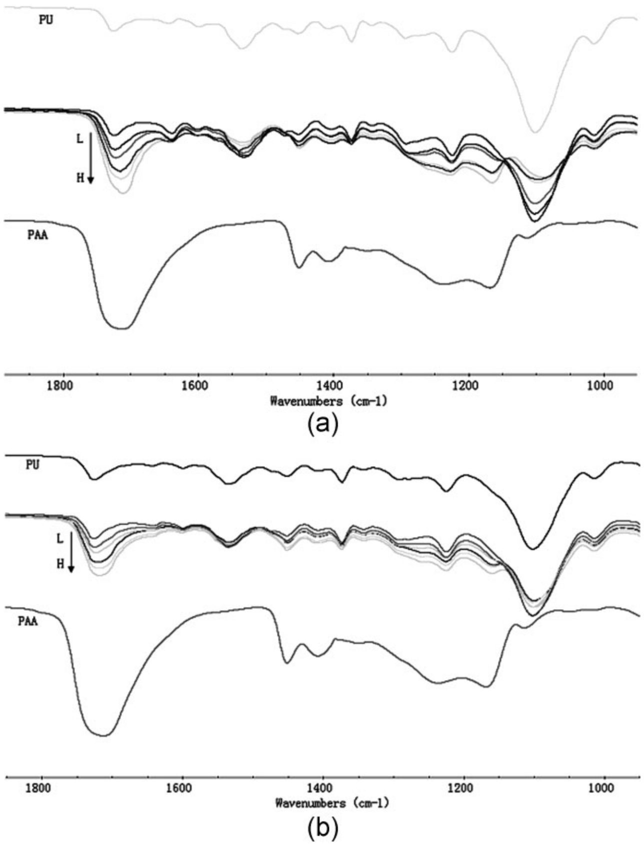

Figure 2 ATR spectra of gradient surfaces from L to H (a) S3, (b) S5.

The temperature is an important factor to affect photograft reaction. Both the photoreduction of initiator and grafting reaction rate will be affected by the change of temperature. The surface grafting reaction could begin earlier in higher temperature position than in the lower one. Moreover, the grafting reaction rate will increase with the increasing temperature according to Arrhenius equation. As a result, the graft yield of the PU membrane could be expected to change gradually from lower to higher temperature positions on the surface.

Equation (1) gives the rate constant as a function of temperature. The activation energy of graft reaction can be obtained according to eq. (2).[23] If the temperature changes gradually and linearly from L

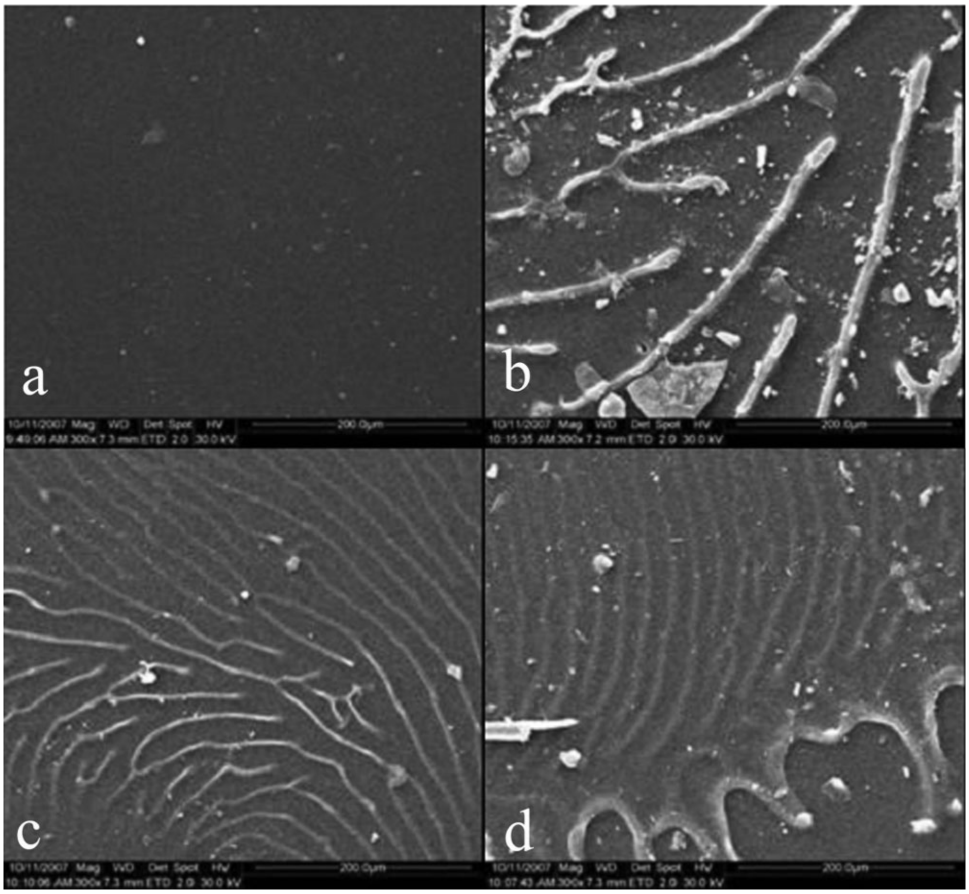

Figure 3 SEM images of gradient surface (a) ungrafted surface; (b), (c), (d) are images from L to H.

to H, the temperature at one position can be given by eq. (3).

$$k = Ae^{\frac{-E}{RT}} \tag{1}$$

$$E = E_p - \frac{E_t}{2} + \frac{E_d}{2} \tag{2}$$

where the E_p is the activation energy of chain propagation; E_t is activation energy of chain termination; and E_d is activation energy of hydrogen abstraction.

$$T = T_l + \frac{T_h - T_l}{l}x \tag{3}$$

where the T_l and T_h mean the temperature at the lower and higher temperature ends, respectively; x

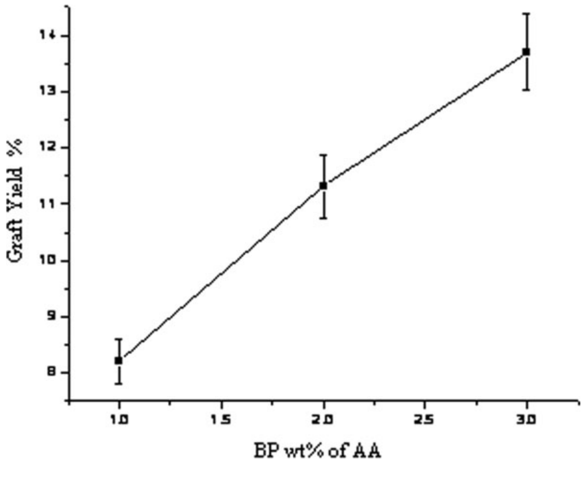

Figure 4 Average graft yield of gradient surfaces varies with the dosage of BP. The ratio of AA and acetone is 0.5; the UV irradiation time is 10 minutes.

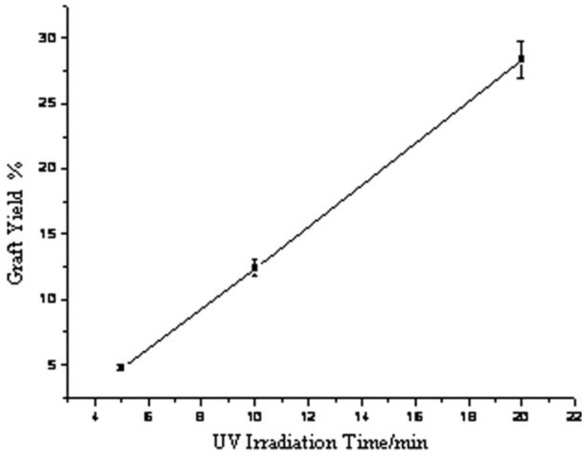

Figure 5 Average graft yield of gradient surfaces varies with the UV irradiation time. The ratio of AA and acetone is 0.5; the is BP wt % of AA is 1%.

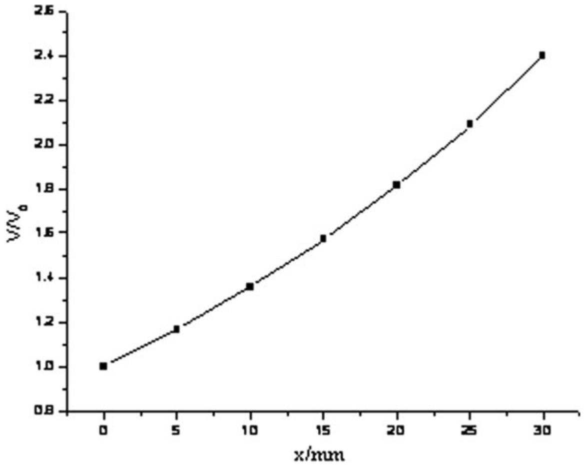

Figure 6 Graft reaction rate varies with the positions from the lower to higher temperature end V means the graft reaction rate at x; V_0 means the graft reaction rate at the L end.

is the distance to the L end; and l means the length of the PU membrane.

Based on the above three equations, it can be concluded that the graft reaction rate will increase gradually from L to H end. Therefore, the graft field of the PU membrane will show the same changing trend. Generally speaking, the value of $(E_p - \frac{E_t}{2})$ is about 20 KJ/mol in the radical polymerization reactions.[23] If assume $E_d = 28.5$ KJ/mol according to Ref. 10, the variation of graft reaction rate can be plotted as a function of x, as shown in Figure 6.

If the ungrafted PU membrane is homogeneous, the piece with the same sizes should have the same weight. We cut the grafted PU membranes into pieces with the same sizes and weighted them one by one from L to H end. The weight of each ungrafted piece can be obtained by dividing the value of W_0. Herein, the sample S3 and S5 were cut into six pieces with the width 5 mm. These pieces were marked, respectively, by Arabic numerals in turn from L to H end. The graft yield of each pieces were given and plotted in Figure 7, showing the gradual change from the first to the sixth piece.

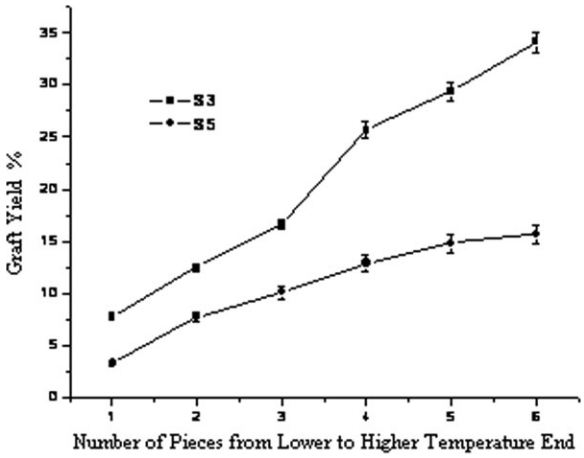

Figure 7 Average graft field varies with the positions from lower to higher temperature end.

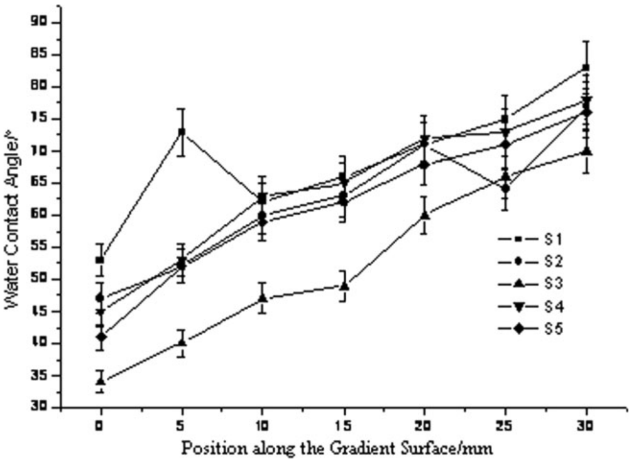

Figure 8 Water contact angle varies with the positions along the gradient surfaces.

The water contact angle along the surface was measured to investigate the wetting behavior gradient, which reflecting the surface energy gradient. The ungrafted PU membrane is hydrophobic. However, the PAA is hydrophilic. So the hydrophilicity of PU membrane grafted with AA will be improved correspondingly according to the graft yield. Figure 8 showed the gradual change of water contact angle from L to H of the PU membranes with gradient surfaces. The change of contact angle of sample S1 and S2 showed some fluctuations. However, on the whole, the average graft yields of these two samples increased gradually from L to H. The sample S3 $\sim$ S5 displayed continuous and gradual change of water contact angle. These facts mean that a good gradient surface can be created only when the graft yield comes to a certain level. Among the sample S3 $\sim$ S5, the differences of the water contact angle between the L and H end increased with the average graft yield.

CONCLUSION

UV surface grafting of PU membranes was performed in a graded temperature field obtain gradient surface. Both the FTIR and SEM proved the gradient of graft yield along the surface, increasing from the lower temperature end to the higher one. Consequently, the surface energy of the PU membranes changed gradually, leading to hydrophilicity gradient across the surface. The property of gradient surface was related to the average graft yield of the PU membrane. Only when the average graft yield comes to a certain level, can the hydrophilicity exhibit good continuity along the surface.

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