

수산기 밀도 구배를 가지는 고분자 표면

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Characterization of Hydroxyl Group Gradient Surfaces Prepared by Water Vapor Plasma Treatment

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요 약 : 플라즈마 방전 장치를 이용해 PE, PP, PET, PMMA, PS 등의 고분자 시료 표면에 수증기 분위기하에서 플라즈마 노출시간을 서서히 변화시켜 주었다. 이와같은 처리에 의해 고분자 시료 표면에서 친수성과 수산기 표면 밀도가 점진적으로 변한다는 것이 물 접촉각 측정과 ESCA분석 결과에 의해 확인되었다. 표면의 성질이 점진적으로 변하는 고분자 시료는 고분자 표면과 생체와의 상호반응 연구 및 의약품 고분자로 응용하기 위한 최적 조건 정립에 매우 효율적이다.

Abstract : Various polymer surfaces, low density polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polymethyl methacrylate (PMMA), and polystyrene (PS), were gradually exposed to water vapor plasma along the sample distances. This treatment produced a continuous change in wettability and also hydroxyl group density on the polymer surfaces, as evidenced by water contact angle measurement and electron spectroscopy for chemical analysis (ESCA). The hydroxyl group gradient surfaces can be used to optimize protein, blood, or cell interactions with polymer surfaces.

INTRODUCTION

Many studies have focused on surface modification of polymeric materials. The systematic study of the effect of one surface parameter on surface properties of the polymeric materials requires many different samples, each with a different value of the surface parameter of interest. Such a study is often tedious, laborious, and time-consuming because the large number of samples must

be prepared to characterize the complete range of the desired surface property. It may also cause the strong possibility of a methodological error because each sample is prepared separately. In order to reduce the number of samples and experimental error, it is desirable to produce the gradient surface of required properties on one sample.

"Gradient surface", where a surface property is changed on one sample in a gradient over a distance, was first produced by Elwing, et al.¹⁻⁵ They

developed a method to make a surface energy gradient (or wettability gradient) along a silicon plate. A gradient of methyl groups was formed by diffusion of dimethyl dichloro silane ($\text{Cl}_2(\text{CH}_3)_2\text{Si}$) through xylene on a flat hydrophilic silicon dioxide (SiO_2) surface. The surface so formed had methyl groups at one end (hydrophobic and thus nonwetable) and hydroxyl groups at the other (hydrophilic and wettable) with a gradient of increasing wettability in between. Hlady, et al.⁶ also prepared a wettability gradient on a silica surface using a similar method to Elwing, et al's. Unfortunately, these approaches to prepare wettability gradient surfaces are limited to inorganic substrates like silicon, silica, quartz or glass.

Recently, we developed a new method to prepare the wettability gradient on the surfaces of polymeric materials.⁷⁻⁹ The wettability gradient on the polymer surfaces was produced via radio-frequency plasma discharge treatment by exposing polymer sheets continuously with oxygen plasma. The polymer surface was oxidized gradually with increasing plasma exposure time and thus created the wettability gradient on the sample surface. Similar works to prepare the wettability gradient on polymer surfaces were also carried out by Pitt, et al.^{10, 11} using radio frequency plasma discharge of ammonia, oxygen, and sulfur dioxide.

In this study, we prepared "hydroxyl group gradient" on the polymer surfaces by water vapor plasma treatment. There is an evidence from our previous work¹² that the water vapor plasma treatment is an effective way to produce the hydroxyl group functionality on the polymer surfaces. The polymer surface was continuously exposed to the water vapor plasma and produced a hydroxyl group gradient on the sample surface.

The hydroxyl groups on polymer surfaces may play an important role for cell adhesion and growth^{12, 13} and they can be easily modified for chemical attachment of bioactive species on the surfaces. Thus, the hydroxyl group gradient surfaces can be used to investigate protein, blood, or cell interactions in terms of the hydroxyl group

functionality or the bioactive species grafted onto the polymer surfaces via hydroxyl groups.

EXPERIMENTAL

Substrates

Commercial polymer film free of additives (low density PE, PP, PET, and PMMA) and PS plate (bacteriological grade cell culture dish, Green Cross Medical Co., Korea) were used as the polymeric substrates for the gradient surfaces. The polymer samples (5.0 cm × 7.0 cm size) were ultrasonically cleaned twice in ethanol for 30 min each and then dried at room temperature. They were stored in a vacuum oven until use. The cleanliness of the sample surfaces was verified by ESCA.

Preparation of Gradient Surfaces

The polymer samples were treated in a radio-frequency glow discharge (RFGD) apparatus made by our laboratory for the purpose of gradient surface preparation (Fig. 1 & 2). The power supply of the RFGD generator was 200 volt, 160 mA at 100 kHz. The plasma treatment was performed in a bell-jar type reactor chamber with a constant water vapor pressure, 0.1 torr. The cleaned polymer sample was located on the round electrode plate in the reactor chamber. It was covered with a movable mask made of glass, which is connected to a motorized drive. The chamber was degassed for 10 min, and then purged with water vapor for 10 min at the rate of 100 ml/min from the container immersed in a constant temperature (40 °C) water bath (Fig. 1). Then the plasma was generated in the reactor chamber for a given time. At the same time as the RF power was turned on, the movable mask on the polymer sample was translated at a constant speed using the motorized drive to permit a continuous exposure of the sample surface to the plasma (Fig. 2). The distance and the speed of mask translation (and thus the plasma exposure distance and time) were carefully controlled. The plasma generated in the chamber was visually uniform and stable during the plasma discharge pro-

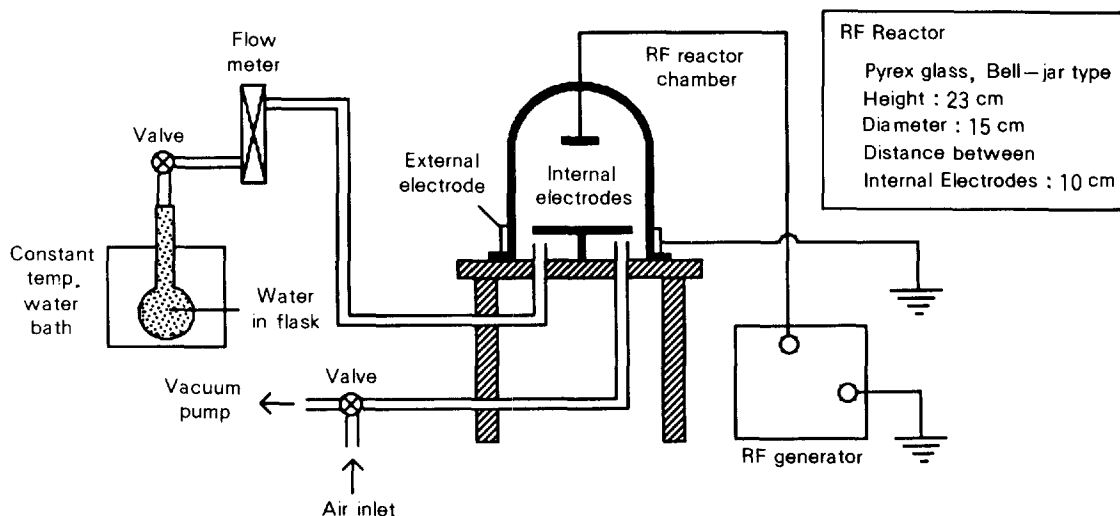


Fig. 1. Schematic diagram of water vapor plasma discharge apparatus.

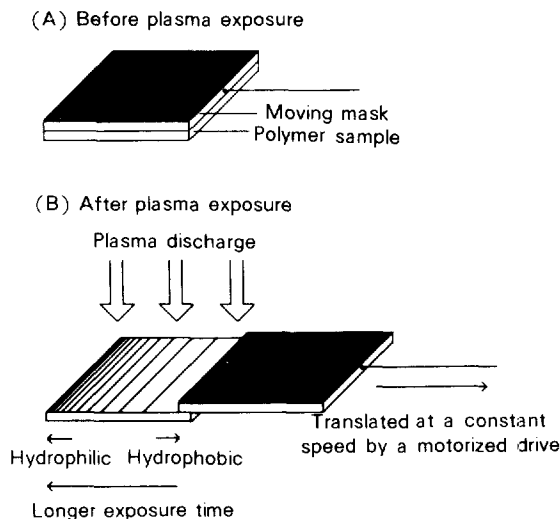


Fig. 2. Schematic diagram showing preparation of gradient surface by plasma discharge treatment.

cedure. After the RF power was turned off and the reactor chamber was degassed again for 10 min, the surface-treated sample was taken out from the chamber and the surface properties were characterized.

Characterization of Gradient Surfaces

The prepared gradient surfaces were characterized by the measurement of water contact angle

and ESCA analysis. The water contact angle, which is an indicator of wettability of the surfaces, was measured using a contact angle goniometer (Model 100-00, Rame-Hart, Inc., U. S. A.). $3\mu\text{l}$ drops of purified water (MPI Ultrapure water system, U. S. A.) were applied onto the sections of the plasma treated surface along the gradient. More than three different gradient sheets were measured for each polymer substrate. The degree of reproducibility for the different samples was within ± 4.0 degree.

The gradient surfaces were also characterized by ESCA (ESCALAB MK II, V. G. Scientific Co., U. K.) equipped with Al K α at 1487 eV and 300 W power at the anode. Survey scan and carbon 1S core level spectra were taken and corrected for scattering cross sections (sensitivity factors of carbon 1S and oxygen 1S : 0.25 and 0.66, respectively : deconvolution of the carbon 1S spectrum ; 30 scans with a analyzer energy of 20 eV and full width at half maximum (FWHM) of each peak, about 1.5 eV).

RESULTS AND DISCUSSION

The water vapor plasma treated surface did not show any noticeable change to the bare eye, but

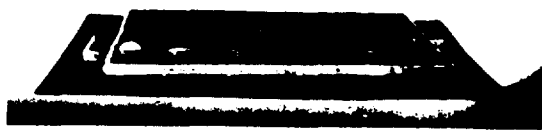


Fig. 3. Demonstration of wettability gradient formed on water vapor plasma treated PS surface.

the wettability of the surface gradually increased along the sample distance with increasing plasma exposure time (Fig. 3).

Water contact angle changes on the gradient surfaces are shown in Fig. 4(A) and (B). The contact angle is usually considered to be a sensitive probe of changes in surface properties, since the angle is largely determined by the nature of the surface layer of the substrate. The contact angles on the polymer surfaces sharply decreased with increasing plasma exposure time. However, after about 10 sec, no further significant changes were observed for all samples (Fig. 4(A)). Thus, we chose the maximum plasma exposure time of 10 sec to create effective gradients on the polymer surfaces as shown in Fig. 4(B). The decrease in contact angle (thus, increase in wettability) along the sample distance is probably due to the oxygen-based polar functionalities attached to the polymer surface by the plasma treatment.

The changes in chemical structure of the polymer surfaces by the water vapor plasma treatment were investigated using ESCA. Although ESCA does not provide absolute quantification, it is very sensitive to the small changes of the surface composition. Fig. 5 shows the survey scan spectra of PE gradient surface produced by the water vapor plasma treatment. The survey scan spectrum provides information about the elemental composition of surfaces for all elements present (except H and He). The elements are identified from their binding energies, which are unique for each element. The control PE surface (untreated section of the gradient surface) showed only carbon peak at the binding energy of 285 eV, as expected (Fig. 5(A)). The plasma exposed sections of the gradient sur-

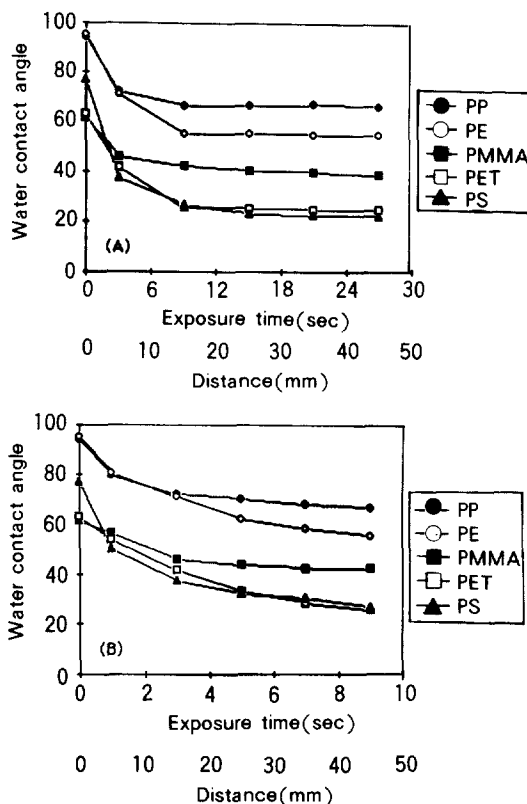


Fig. 4. Water contact angles of gradient surfaces as a function of water vapor plasma exposure time or position from the untreated hydrophobic end; plasma exposure time, (A) up to 30 sec and (B) up to 10 sec.

face showed oxygen peaks at the binding energy of 532 eV by the oxygens incorporated onto the surface (Fig. 5(B)-(E)). As the plasma exposure time on the surface increased, the oxygen peaks increased due to the increased incorporation of oxygens onto the surface. However, we could see little differences between the surfaces exposed to the plasma for 10 sec and 30 sec (Fig. 5(D) and (E)). Fig. 6 shows oxygen atomic % on the gradient surfaces, determined by the normalized area ratio of the oxygen and the carbon peaks. The oxygen contents on the gradient surfaces increased with increasing plasma exposure time. PET and PMMA surfaces could not directly compare with PE, PP, and PS surfaces because the control PET and PMMA surfaces have a large amount of

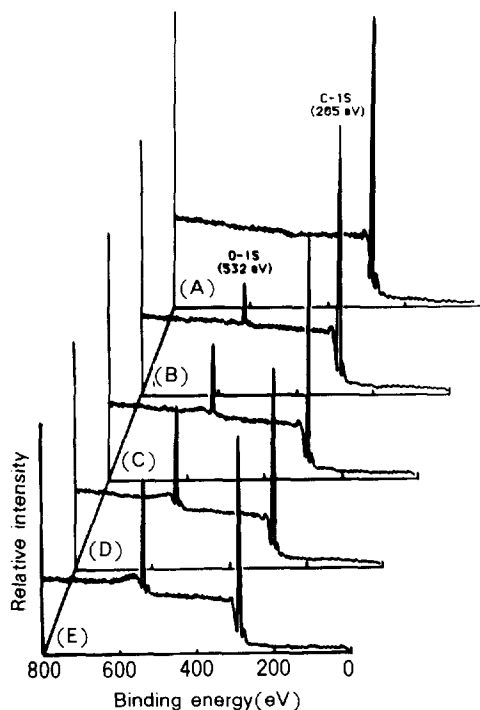


Fig. 5. ESCA survey scan spectra of water vapor plasma treated PE gradient surface ; plasma exposure time, (A) 0 sec (control), (B) 1 sec, (C) 3 sec, (D) 9 sec, and (E) 30 sec.

oxygen in their structures (34.3 and 31.5 atomic %, respectively, as determined by ESCA). Their oxygen contents also increased after the water vapor plasma treatment.

When we compared carbon 1S core level spectra of PE surface treated with the water vapor plasma and that treated with oxygen plasma at the same condition,¹² we could see that the functional groups produced on the surfaces by both plasma treatments are quite different (Fig. 7). The control PE surface showed only alkyl carbon peak (C1) at 285 eV (Fig. 7(A)). The oxygen plasma treated surface showed new peaks to high binding energy, indicating the formation of carbon-oxygen functionalities (Fig. 7(B)). The peaks of the high binding energy region correspond to carbon atoms with a single bond to oxygen (C2) at 286.6 eV (e. g. hydroxyl, ether, or other groups), carbon atoms with two bonds to oxygen (C3) at 287.9 eV (e. g.

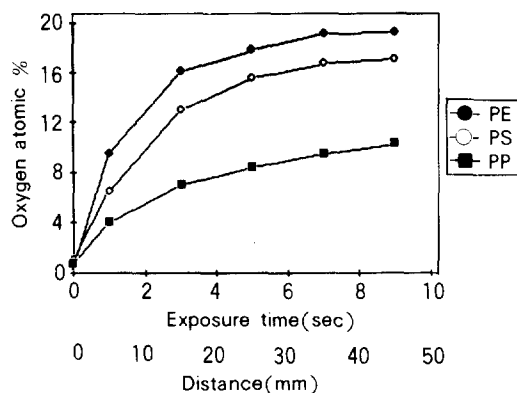


Fig. 6. Oxygen contents of gradient surfaces as a function of water vapor plasma exposure time or position from the untreated hydrophobic end.

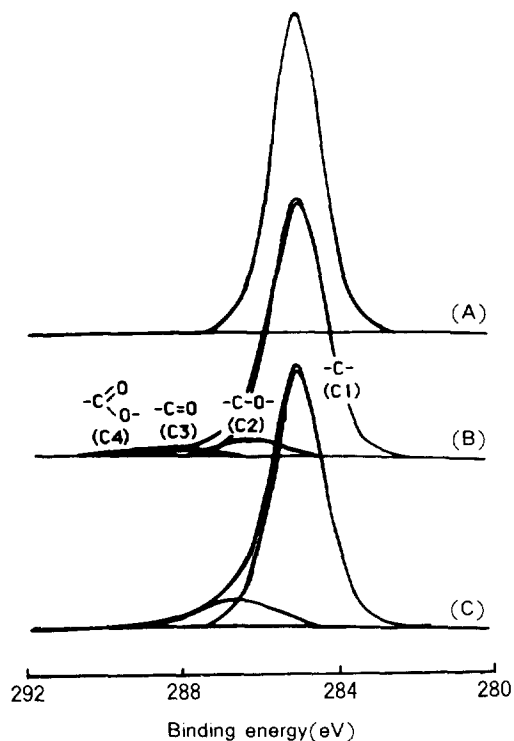


Fig. 7. ESCA carbon 1S core level spectra of PE surface ; (A) control, (B) O₂ plasma treated (9 sec), and (C) water vapor plasma treated (9 sec).

ketone or aldehyde groups), and carbon atoms with three bonds to oxygen (C4) at 289.1 eV (e. g. carboxylic acid or ester groups), as labeled in Fig.

7(B). The spectrum of the water vapor plasma treated surface showed that almost all carbon components produced on the surface are C2 (Fig. 7(C)).

Fig. 8 shows the carbon 1S core level spectra of the PE gradient surface prepared by the water vapor plasma treatment. We could see increased C2 component on the surface with increasing plasma exposure time. Fig. 9 shows the contents of C2 component on the gradient surfaces, determined by the area ratio of C2 and C1 peaks. C2 contents on the gradient surfaces increased with increasing plasma exposure time for all three polymer samples.

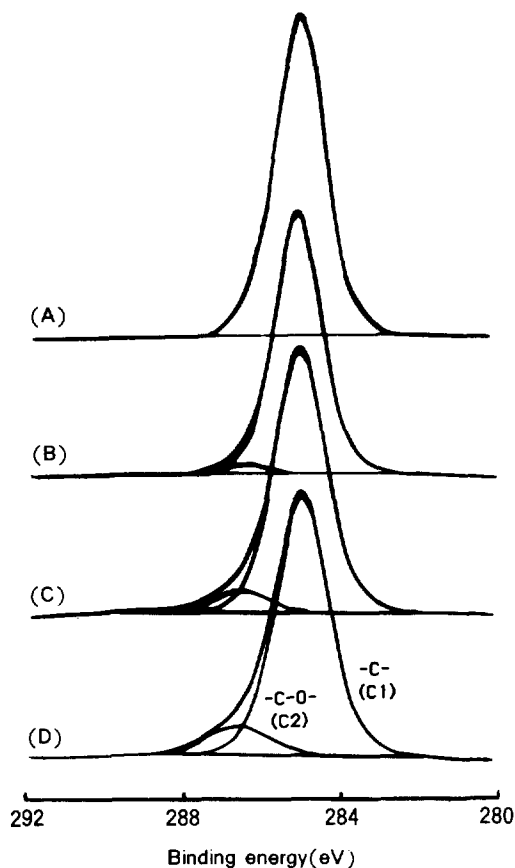


Fig. 8. ESCA carbon 1S core level spectra of water vapor plasma treated PE gradient surface : plasma exposure time, (A) 0 sec (control), (B) 1 sec, (C) 3 sec, and (D) 9 sec.

C2 component of the carbon 1S spectrum (286.6 eV) can correspond to hydroxyl, ether, or other functional groups. However, we expect that the hydroxyl groups are predominant on the surfaces treated with the water vapor plasma. One way to determine specific functional groups present on the surfaces is to label the functional groups with ESCA-sensitive elements. We used p-chlorophenyl isocyanate as the reagent to detect the hydroxyl groups present on the water vapor plasma treated surfaces (not gradient surfaces).¹² P-chlorophenyl isocyanate selectively reacts with the hydroxyl groups on the surfaces and also contains a ESCA-sensitive element, chlorine.¹⁴ From the results of ESCA analysis, we found that the chlorine atomic % on the surfaces is almost same as the atomic % of C2 component, which strongly indicates that C2 component present on the water vapor plasma treated surfaces mostly corresponds to the hydroxyl groups. Thus, we could confirm that the water vapor plasma treatment is a simple and effective way to introduce hydroxyl groups on the polymer surfaces.

We still continue to identify functional groups (hydroxyl, ketone, carboxylic acid groups, etc.) on the gradient surfaces produced by various plasma treatments using the technique of labeling the functional groups with specific ESCA-sensitive elements.

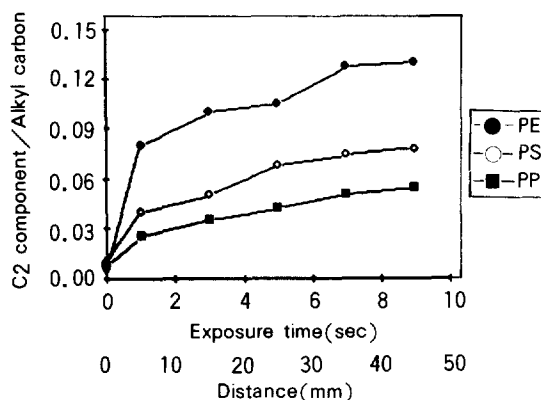


Fig. 9. C2 component contents of gradient surfaces as a function of water vapor plasma exposure time or position from the untreated hydrophobic end.

CONCLUSIONS

Hydroxyl group gradient surfaces were produced on various polymer substrates by gradually exposing the surfaces with the water vapor plasma. The hydroxyl groups are easily modified for immobilization of many bioactive species on the surfaces and also play an important role for protein or cell interactions. Thus, the hydroxyl group gradient surfaces can be used to investigate protein, blood, or cell interactions in terms of the hydroxyl group functionality or the bioactive species immobilized onto the polymer surfaces. Studies on the interactions of the hydroxyl group gradient surfaces with proteins or cells are on progress.

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