

## Preparation and Characterization of Amine-modified Gradient Polyethylene Surfaces

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A gradient polyethylene (PE) surface was created through corona treatment, in which the corona power increased along the 5-cm length of the PE. The gradient PE surface was treated by amines with varying molecular weights. TOF-SIMS results exhibited the gradient surface images and intensities before and after amine modification on the corona-treated PE surface.

In the biomedical fields, surface modification of biomaterials can be performed by employing physical or chemical immobilization of bioactive molecules and can offer the potential to examine biocompatibility in biological system.<sup>2</sup> Simultaneous control over the position and density of bioactive molecules on a surface could constitute a powerful means to investigate the biologic interaction on a surface.

Meanwhile, modification of an uniform surface has some limitations because evaluation of the binding of bioactive molecules onto the biomaterial surface routinely requires several experiments.

A gradient surface is a surface on which a continuously varying chemical composition exists along its length.<sup>3</sup> If bioactive molecules are introduced to a gradient surface, relating the intensity or concentration of the bioactive molecules on the gradient surface to the chemical gradient would allow the gradient surface to become a useful method for further practical biomedical applications.<sup>4</sup>

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a surface analytical tool that is capable of detecting elemental and molecular species with a spatial resolution of  $< 1 \mu\text{m}$ .<sup>5</sup> In addition, the TOF-SIMS is ideal for imaging of molecules on surface.<sup>5</sup>

The aim of our research is to develop a simple and generally analytically applicable method of the gradient polyethylene (PE) surface and the polyamine groups present on the gradient PE surface using TOF-SIMS.

Recently, we reported the preparation of a gradient surface by radio-frequency corona discharge using knife-type electrodes and its biomedical applications.<sup>6</sup> The corona discharge power was increased gradually by operation of an automatic motorization drive.<sup>7</sup> This method is a useful candidate for introducing oxygen-containing functional groups, because it can be very easily performed under atmospheric conditions.

Several types of oxygen-containing functional groups, such as hydroxy, ether, ketones, aldehydes, carboxylic acid, and carboxylic esters were formed by successive reaction between aerial oxygen and carbon radicals formed through corona treatment of PE. To confirm the gradient formation of functional group on PE surface according to corona treatment, the PE surfaces were examined by TOF-SIMS methods.

By TOF-SIMS measurement of corona-treated PE surface,

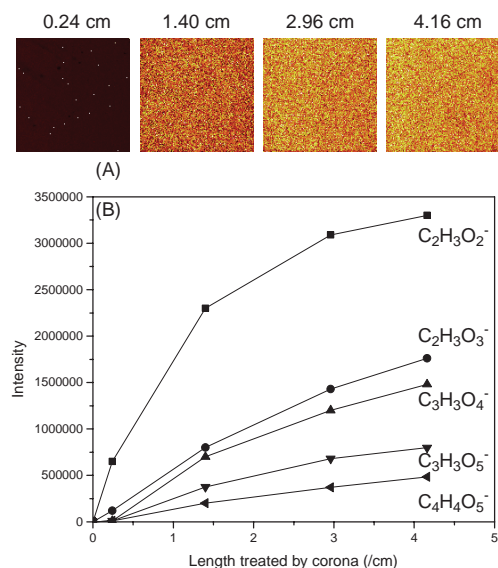
many ion peaks assignable to carboxyl groups were observed, due to fragmentation of the gradient surface PE.<sup>8</sup> Figure 1a exhibited TOF-SIMS chemical images of characteristic secondary negative ion,  $\text{C}_2\text{H}_3\text{O}_2^-$  as an example, relating to specie containing the carboxyl group.<sup>9</sup> It exhibited gradient change of TOF-SIMS chemical images along the PE length. TOF-SIMS intensities of the peaks,  $\text{C}_2\text{H}_3\text{O}_2^-$ ,  $\text{C}_2\text{H}_3\text{O}_3^-$ ,  $\text{C}_3\text{H}_3\text{O}_4^-$ ,  $\text{C}_3\text{H}_3\text{O}_5^-$ , and  $\text{C}_4\text{H}_4\text{O}_5^-$ , gradually increased along the PE surface length as the corona power increased (Figure 1b), indicating that a gradient of the carboxyl group was formed on the corona-treated PE surface. In addition, this result indicated that corona treatment introduced carboxylic acid group which can serve as reaction sites.

The surface reaction between the carboxylic acid group on a corona-treated PE surface and various amine compounds was carried out. The carboxylic acid on the PE surface was activated with *N*-hydroxysuccinimide (NHS) and *N,N*-dicyclohexylcarbodiimide (DCC). The activated PE surface reacted with the amine group such as 1,9-nonanediamine (ND) and polyethyleneimine (PEI) of different molecular weights (600, 1200, 10,000, and 60,000 g/mol), resulting in the formation of an amide bond.<sup>7</sup>

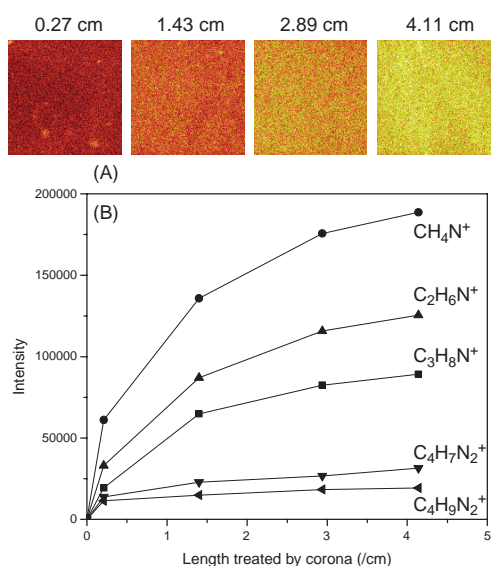
TOF-SIMS measurement was carried out with gradient PE surface modified by five different MW of amine compounds. TOF-SIMS chemical images of characteristic secondary positive ion,  $\text{C}_2\text{H}_6\text{N}^+$ , relating to specie containing the amine of PEI (MW 600 as example) on surface exhibited gradient changes along the PE length (Figure 2a).<sup>10</sup>

Figure 2b shows plots of the length treated by corona versus the TOF-SIMS intensities of the amine characteristic secondary positive ions obtained from amine-modified PE surfaces. The intensity of secondary positive ions,  $\text{CH}_4\text{N}^+$ ,  $\text{C}_2\text{H}_6\text{N}^+$ ,  $\text{C}_3\text{H}_8\text{N}^+$ ,  $\text{C}_4\text{H}_7\text{N}_2^+$ , and  $\text{C}_4\text{H}_9\text{N}_2^+$ , exhibited gradual increasing along the PE length.

Among several positive ions containing amine, the intensity of  $\text{C}_2\text{H}_6\text{N}^+$  secondary positive ion as an example was collected from PE surfaces modified by ND and PEI with different molecular weights. The plot for intensity of  $\text{C}_2\text{H}_6\text{N}^+$  ion versus the length treated by corona was shown in Figure 3. There is a correlation between the intensity of  $\text{C}_2\text{H}_6\text{N}^+$  secondary positive ion and the amine molecular weights on PE surface. We also confirmed a similar correlation for various secondary positive ions, although it showed slight different trends according to ion species.<sup>11</sup> The gradient of the amine surface density became distinct when the lower PEI compounds were used for making the amine modified PE surface. PE surfaces modified by PEI with molecular weight over 1200 resulted in the saturation of amine density after approximately 1.5 cm along the surface. We assume that this is probably due to increase surface coverage of branch PEI or saturation of the amine repeating units in PEI combined to PE surface by one covalent bond. Nevertheless, it was evident



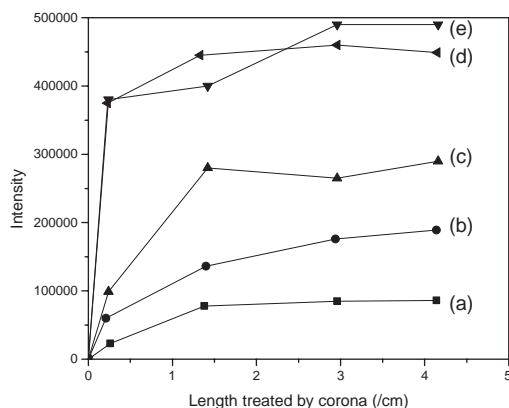
**Figure 1.** (A) TOF-SIMS images of negative ion ( $C_2H_3O^-$ ) obtained at different positions of a corona-treated PE surface and (B) plot of TOF-SIMS intensities of characteristic carboxyl secondary negative ions versus length treated by corona. The image analysis area was  $500 \times 500 \mu m^2$ .



**Figure 2.** (A) TOF-SIMS images of secondary positive ion ( $C_2H_6N^+$ ) obtained at different positions of PEI (MW = 600) modified PE surface and (B) plot of TOF-SIMS intensities of amine characteristic secondary positive ions versus length treated by corona. The image analysis area was  $500 \times 500 \mu m^2$ .

from the TOF-SIMS analysis that the amine modification occurred gradually along the PE surface.

In conclusion, we prepared gradient PE surface and amine-modified PE surfaces with varying in the surface amine density. The gradient in amine density on PE surface may be related to the amount of amine groups that exist in the polyamine compounds. We confirmed that TOF-SIMS measurement can be used as useful analytical tool for evaluating molecules on the gradient surface.



**Figure 3.** Plot of TOF-SIMS intensities of secondary positive ion ( $C_2H_6N^+$ ) versus length treated by corona. Amine compounds used for surface modification were (a) 1,9-nonanediamine and PEI with molecular weight of (b) 600, (c) 1200, (d) 10,000, and (e) 60,000.

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#### References and Notes

- M. S. Kim, Y. H. Cho, contributed equally to this paper.
- a) B. D. Ratner, D. G. Castner, *Surface Modification of Polymeric Biomaterials*, ed. by B. D. Ratner, D. G. Castner, Plenum Press, New York, **1997**. b) M. Kobayashi, A. Takahara *Chem. Lett.* **2005**, *34*, 1582. c) L. Jiang, S. Cai, B. Liu, J. Xu, J. Zhang, J. Zhu, *Chem. Lett.* **2005**, *34*, 1212.
- a) T. G. Ruardy, J. M. Schakenraad, H. C. van der Mei, H. J. Busscher, *Surf. Sci. Rep.* **1997**, *29*, 3. b) T. G. Ruardy, H. E. Moorlag, J. M. Schakenraad, H. C. van der Mei, H. H. Busscher, *J. Colloid Interface Sci.* **1997**, *188*, 209.
- a) H. Huang, Y. Chen, *Chem. Lett.* **2006**, *35*, 372. b) S.-H. Choi, B. Zhang Newby, *Langmuir* **2003**, *19*, 1419.
- a) *TOF-SIMS: Surface Analysis by Mass Spectrometry*, ed. by J. C. Vickerman, D. Briggs, SurfaceSpectra Limited, Manchester and IM Publication, Chichester, UK, **2001**. b) S. V. Roberson, A. J. Fahey, A. Sehgal, A. Karim, *Appl. Surf. Sci.* **2002**, *200*, 150.
- a) S. K. Kim, Y. H. Cho, M. H. Cho, Y. N. Shin, M. S. Kim, G. Khang, B. Lee, H. B. Lee, *Tissue Eng. Regen. Medicine* **2006**, *3*, 58. b) J. H. Lee, S. J. Lee, G. Khang, H. B. Lee, *J. Colloid Interface Sci.* **2000**, *230*, 84. c) Y. Iwasaki, S. Sawada, N. Nakabayashi, G. Khang, H. B. Lee, K. Ishihara, *Biomaterials* **1999**, *20*, 2185. d) J. H. Lee, G. Khang, J. W. Lee, H. B. Lee, *J. Biomed. Mater. Res.* **1998**, *40*, 180. e) Y. Iwasaki, K. Ishihara, N. Nakabayashi, G. Khang, J. H. Jeon, J. W. Lee, H. B. Lee, *J. Biomater. Sci., Polym. Ed.* **1998**, *9*, 801.
- Detail experiment procedures are explained in the Supporting Information.
- High mass resolution SIMS spectra of negative ion of gradient PE surface is illustrated in the Supporting Information (Figure S1).
- TOF-SIMS chemical images of characteristic secondary negative ions are illustrated in the Supporting Information (Figure S2).
- TOF-SIMS chemical images of characteristic secondary positive ions are illustrated in the Supporting Information (Figure S3).
- TOF-SIMS intensities of several secondary positive ions are illustrated in the Supporting Information (Figure S4).