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Notes

Surface Modification Studies by Atomic Force Microscopy for Ar-Plasma Treated Polyethylene

Eun-Deock Seo

Division of Chemical Engineering, Kyungnam University, Masan 631-701, Korea

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Abstract : Atomic force microscopy(AFM) was used to study the polyethylene(PE) surfaces grafted and immobilized with acrylic acid by Ar plasma treatment. The topographical images and parameters including RMS roughness and Rp-v value provided an appropriate means to characterize the surfaces. The plasma grafting and immobilization method were a useful tool for the preparation of surfaces with carboxyl group. However, the plasma immobilization method turned out to have a limitation to use as a means of preparation of PE surface with specific functionalities, due to ablation effect during the Ar plasma treatment process.

Keywords : surface modification, AFM, plasma treated PE.

Introduction

The glow discharge plasma medium consists of atomic and molecular species as well as ions and electrons. These highly reactive species not only provide a low cost means for polymeric surface modification without altering the bulk properties of the material at ambient temperature but also allow the production of organic polymer films from monomers that cannot be polymerized by conventional means.[1] The films are generally chemically inert, mechanical tough, thermally stable, and have great applications in many aspects.[2-10] This process, more importantly, can be ideal for selective and surface-specific modification method. Abundance of free radicals can be created on the outer surface upon short exposure to plasma, and can initiate the grafting of vinyl monomers onto polymers.[1] Recently, a method called plasma immobilization, by which it is possible to introduce specific functional groups at polymeric surface, was developed by Hoffman and coworkers[11] and have received increasing attention. The applicability of the immobilization method has been demonstrated by researchers[11-15] as a powerful tool for surface-specific modification method. For example, carboxylate, sulfate, amine, and poly(ethylene oxide) groups were introduced at polymeric surfaces including PE and PP by above-mentioned researchers.

However, there is possibility that the functional groups can be destroyed during the immobilization process due to ablation characteristics of plasma treatments, which cause adverse effects for the preparation of specific functionality.

In our previous study,[16] we reported that ablation had an important role to decrease hydrophilic surface properties for the immobilized PE surfaces with acrylic acid by Ar plasma.

The objective of the study is to investigate surface topographical changes due to ablation effect of Ar plasma on the acrylic acid-immobilized surface by means of AFM.

It has been of interest to get an information on polymeric surfaces without serious or any damages on it. SEM technique has commomly been used to study of the effect of plasma treatments on polymer surfaces. However, SEM studies have limited depth resolution, which does not enable the detection of morphological features of much less than a micrometer. In addition to this, the high voltage required for larger magnifications with high resolution causes damage to the polymer surface.

AFM is a particularly powerful tool in the study of surface topography because it can be provide high-resolution three dimensional images of the film surface without any sample pretreatment, especially enough information on the film surface at the nano level in the height direction.[17]

Experimental

Materials. Low-density polyethylene(PE) without additives was supplied as chip by Hanhwa Co., Korea. These chips were hot-pressed and molded as a sheet. Ar gas(purity 99.9%) was purchased from Union Gas. Acetone(spectral grade) and acrylic acid(AA) were purchased from Sigma Chem. Co.. Acetone was used without further purification but AA was used after vacuum distillation.

e-mail : seo2659@kyungnam.ac.kr

Apparatus. A capacitatively coupled glow-discharge system[18] with a 13.56 MHz radio-frequency generator(Auto electronic, maximum power of 300 W), mass flow controller (MFC, MKS), pressure transducer(MKS Baratron), tubular reactor(76 cm long Pyrex glass tube with 5 cm diameter) and two-stage rotary pump(Welch) were used for activating the PE surface, and for grafting and immobilization of AA.

Atomic Force Microscopy(AFM). In order to obtain the images of Ar plasma-modified surfaces, AFM measurement (Auto Probe CP Research System equipped with commercial etched silicone tip) was carried out at ambient pressure, room temperature, 40% RH, and at scanning rate of 0.7 Hz in contact mode. The mean spring constant of the tip was 0.4 N/m, the length was 180 μm, and the tip end was about 10 nm in diameter. RMS surface roughness was determined as the standard deviation of Z values within given areas (10 μm $\times$ 10 μm). The PE samples of 1 cm $\times$ 1 cm size were attached to sample holder with double-sided carbon tape.

Surface Modification Procedures. The PE samples(4.7 cm $\times$ 2.0 cm $\times$ 0.3 cm) were cleaned first with acetone in Soxhlet extractor before being placed in the center of the Pyrex chamber. The chamber was pumped down to 5 mTorr to remove air, moisture and acetone that may have adsorbed on the PE surface and reactor wall. The plasma system pressure was adjusted with the aid of MFC and valves.

The grafting procedure was carried out as follows; activation of PE surface was conducted first by Ar gas plasma at 240 mTorr, 40 W for 1, and 2 min. AA was then fed into the reactor for 30 sec at room temperature. After completing grafting in plasma chamber the PE samples were washed with acetone in Soxhlet extractor to remove AA that was not grafted but simply adsorbed on PE surface, then dried at room temperature *in vacuo*.

The immobilization procedure was carried out in similar procedure to the grafting procedure; after activation of PE surface by Ar gas plasma at 240 mTorr, 40 W, acrylic acid was introduced into the reactor and then AA was immobilized on the PE surface by Ar plasma treatment for 1, and 2 min at 40 W of discharge power. The sample was washed with acetone in Soxhlet extractor to remove unreacted AA, and then dried at room temperature *in vacuo*. In fact, the immobilization in this study is a combination of grafting of AA by surface radicals and subsequent chemical bonding of physically adsorbed chains on PE surface, i.e., additional anchoring of AA on PE surface occurs during the immobilization.

Results and Discussion

AFM Images for Ar Plasma Treated PE. The surface functionality of polymeric materials have become an attractive subject in the study of biocompatibility in recent years. For example, researchers[19-21] reported that the surface functionality of polymeric surfaces plays an important role to improve cell-, tissue-, and blood compatibility. In this sense, plasma grafting and immobilization techniques to prepare polymeric matrials with specific functionalties are appropriate means as mensioned earlier.

The positive roles of carboxyl functional group in improving adhesion strength and wettability of PE which were subjected to plasma grafting and plasma immobilization, has reported in previous study.[16] By analysis of ATR-IR spectrum, adhesion strength, and contact angle measurement, however, the immobilization method has appeared to destroy the carboxyl group and to be detrimental for improving adhesion strength and wettability. These behaviors originated from ablation by Ar plasma treatment. Since adhesion strength and wettability, in general, may be significantly influenced by the physical state of surface or interface, it is necessary to get as detailed informations as possible on physical changes of the surfaces by ablation.

For evaluation of topographical changes due to Ar plasma treatment, AFM images were taken from PE surfaces prepared at different treatment times.

Figure 1 shows, although not immediately evident at a glance, a distinct change in the surface structure before and after Ar plasma treatment. Surfaces are getting smoother as the treatment time increases. Comparing A with D, for example, image A shows steep peaks and deep valleys, but image D consists of round-shaped features. The extent of these changes in this work can be measured by instrumental analysis of related data such as RMS roughness values, which are not far from the true value, but, in general, this method remains rather qualitative. One way to account for the reason of this is that the surfaces of PE samples in this work are not flat enough for analysis of AFM since PE is too soft to polish like a mirror surface.

In Figure 2, RMS roughness values are presented as a function of plasma treatment time. As can be seen in Figure 2, its values decrease with increasing the treatment time, and after that the surface gets a bit rougher; the value at 5 minute is positioned at a little bit higher than the very foregoing value. The reason of this higher value seems to be related, again, with the surfaces of PE samples in this work, which are not flat enough for analysis of AFM. Mahlberg *et al.*[17] reported a similar phenomenon in their study on oxygen plasma treated PP and lignocellulosics. Further studies are needed near future, but smooth and round-shaped features and decrease in RMS roughness, nevertheless, are due to ablation of PE surface by Ar plasma treatment. It has been well known by work of Yasuda[1] that ablation of materials by plasma can occur by two principle processes. One is physical sputtering and the other is chemical etching. The sputtering of materials by an inert gas such as Ar is a typical example of physical sputtering by a momentum-exchange process. Accordingly, it is evident in this work that ablation takes place by Ar plasma and it plays an important role to alter

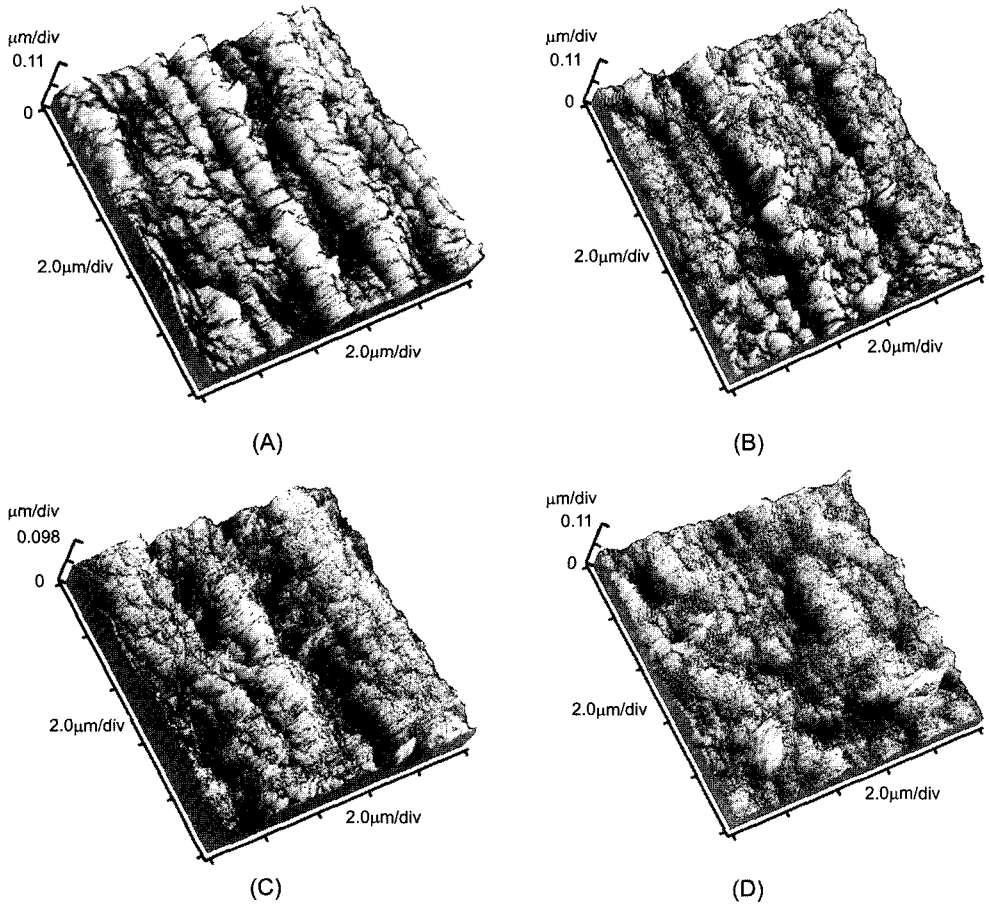

Figure 1. AFM images. (A) virgin PE. (B), (C), and (D) are Ar-plasma treated PE for 1, 3, and 5 min, at 240 mTorr, 40 W, respectively.

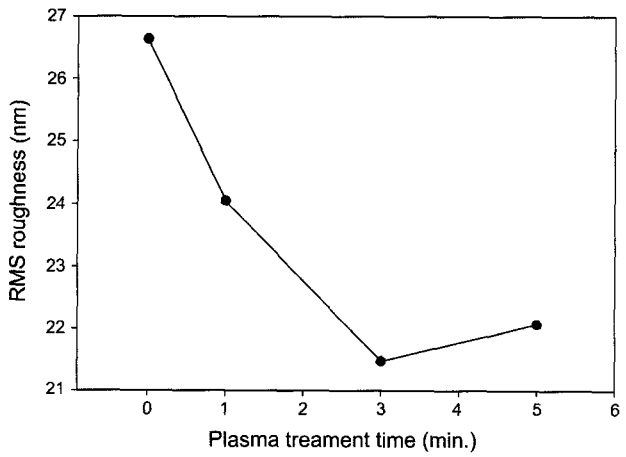

Figure 2. RMS roughness as a function of treatment time for PE surface, treated Ar plasma at 240 mTorr, 40 W.

physico-chemical properties of PE surface.

AFM Images for Grafted, and Immobilized PE. AA and its polymeric chains which are deposited on PE surface through chemical bonding by these processes lead to significant topographical changes on the surfaces. AFM images of AA-grafted and AA-immobilized PE, and their related data are presented in Figures 3, 4, and Table I, respectively.

As expected, it can be seen that the values of Z scale, RMS roughness, Rp-v values, and areas are different depending upon the plasma treatment time and surface modification method. For the cases of grafting (A and B in Figure 3), the values of Z scale increase greatly compared to that of the virgin PE(A in Figure 1). In contrast to these observation, those of the immobilized cases decrease significantly although it is still higher than that of the virgin PE due to the deposition of the immobilized chains of AA and its polymeric thin film. These results can also be seen clearly by quantitative comparison of Rp-v values between these surface modification methods. Although Rp-v values measurement gives the maximum peak-to-valley distance within the scanned areas, and are not a direct measurement of the thickness of deposition of AA and its polymeric thin film, its values can be used as a parameter to indicate the extent of the deposition, at least, in qualitative aspect. The values by the grafting are 650.3 and 729.8 nm while the values by the immobilization are 375.8 and 326.4 nm for 1 minute-treated PE and 2 minute-treated PE, respectively.

It is also of worth to mention RMS roughness originated

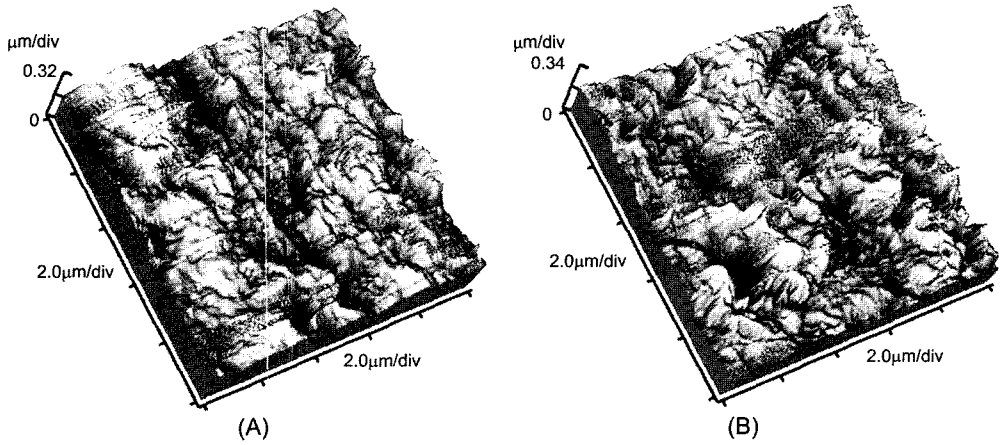

Figure 3. AFM images for AA grafted PE. (A) at 240 mTorr, 40 W for 1 min and (B) at 240 mTorr, 40 W for 2 min.

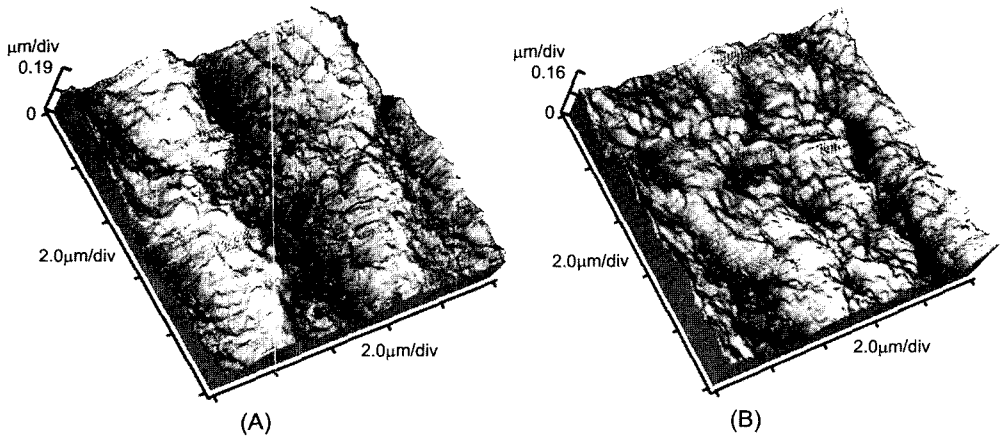

Figure 4. AFM images for AA immobilized PE. (A) at 240 mTorr, 40 W, for 1 min and (B) at 240 mTorr, 40 W, for 2 min.

Table I. AFM Parameters Representing Topographical Changes of PE Surfaces

RMS Roughness(nm)				
Virgin	Grafted		Immobilized	
26.64	(1 min)	(2 min)	(1 min)	(2 min)
	62.79	71.65	56.00	34.41
Rp-v values(nm)				
Virgin	Grafted		Immobilized	
217.3	(1 min)	(2 min)	(1 min)	(2 min)
	650.3	729.8	375.8	326.4
Area(μm^2)				
Virgin	Grafted		Immobilized	
101.3	(1 min)	(2 min)	(1 min)	(2 min)
	112.5	116.2	103.4	101.4

by difference in surface modification method.

As presented in Figure 5, entirely different trend was observed depending upon the modification method. The values for the grafted surface increase with the treatment time. On the other hand, corresponding values of the counterpart decrease markedly by the plasma treatment, which is far below the expected one. Area data listed in Table I show also similar behavior. Compared to the virgin PE, area of the grafted PE increase but those of the immobilized PE increase slightly or nearly equal to the virgin PE. The reason for these discrepancies is derived from the difference in the nature of surface modification process; in the grafting, the role of Ar plasma is only to produce surface free radicals. As a result, the AA grafted surface itself is not in contact with Ar plasma in the grafting process. While, in the immobilization process, the layer already covered with AA and its polymeric chains are subject to Ar plasma treatment. Consequently, a comprehensive explanation of these contrasting results are not possible without emphasizing the role of

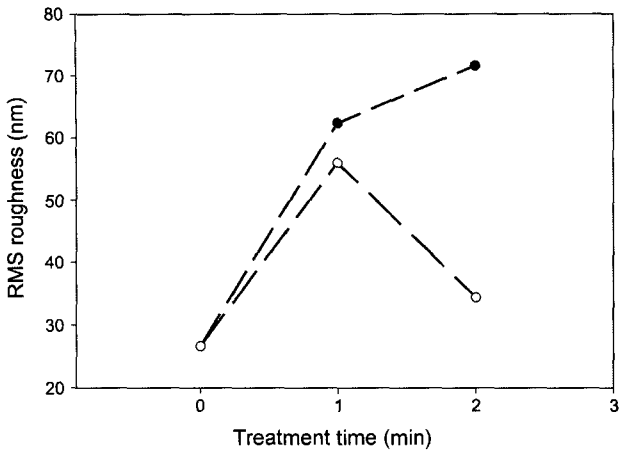

Figure 5. RMS roughness as a function of treatment time for grafted PE(●) and immobilized PE(○) surfaces.

ablation by Ar-plasma treatment, and it has become evident that the destruction of carboxyl group[16] during the immobilization process originates from the ablation of the polymeric chains immobilized onto the PE surface.

Surface modification by plasma immobilization has many leading-edge applications as was mentioned in the introduction part, but the resultant ablation effect by this immobilization method seems to limit its applications. In this sense, it is important to consider ablation effect in advance before carrying out studies on polymeric surface modification by plasma treatment, especially by plasma immobilization technique. In addition to this, the treatment time should be as short as possible to minimize the destruction of specific functional groups.

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