

Effects of Ar-Plasma Treatment in Alkali-Decomposition of Poly(ethylene terephthalate)

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Abstract: The ablation effects of Ar-plasma treatment and alkali-decomposition behavior in NaOH solution of polyethylene terephthalate (PET) film were investigated. The modifications were evaluated by analysis of atomic force microscopy topographical changes, and by the measurement of decomposition yield in conjunction with heats of formation and electron densities of acyl carbon calculated by Parameterization Method 3 method. It has shown that the alkali-decomposition is hampered by plasma treatment and its decomposition yield is closely related with plasma treatment conditions such as exposure time to plasma. Plasma-treated PET films exhibited lower decomposition yield, compared to that of virgin PET. Increasing plasma exposure time contributes positively to decrease the decomposition yield. It has also shown that the topography of PET surface was affected by the base-promoted hydrolysis as well as Ar-plasma treatments. These behaviors are attributed to the decreased nucleophilicity of acyl carbon damaged by the ablation of Ar-plasma.

Keywords: plasma treatment, surface modification, alkali decomposition, AFM, PET.

Introduction

Many researches have been performed to modify only the surface characteristics without altering the bulk properties of materials and numerous researchers have already reported the surface modification through plasma treatment,¹⁻⁴ and irradiation with ionizing and UV radiation.^{5,6}

Surface properties of materials are of great importance in biomedical applications. It is generally recognized that the adhesion and proliferation of cells on polymeric materials depended largely on the surface characteristics such as wettability, chemistry, charge and topography.⁷⁻⁹

The glow discharge plasma medium can be ideal for selective and surface-specific modification method. However, upon short exposure to plasma, the surface functional groups of materials can be destroyed and abundant radicals are created during the process due to ablation characteristics of plasma treatments, which can cause positive or negative effects to prepare surfaces with specific functionality. After Yasuda,¹ ablation of materials by plasma can occur by two principal processes. One is physical sputtering, and the other is chemical etching. The sputtering of materials by an inert gas such as argon (Ar) is a typical example of physical sputtering, which is essentially a momentum-exchange pro-

cess. The energy of impinging Ar⁺ is transferred to the colliding atom and dislodges the atom from the crystalline structure, transferring its energy to a neighboring atom. This energy transfer process continues until one of the atoms is knocked out into the vapor phase. In our previous study,^{10,11} we reported that ablation played an important role to decrease hydrophilic surface properties and surface topographies for the immobilized poly(ethylene) (PE) surfaces with acrylic acid by Ar plasma.

In this study, ablation effects on topographical changes of poly(ethylene terephthalate)(PET) surfaces by Ar plasma treatment and alkali decomposition treatment in NaOH solution via base-promoted hydrolysis are reported by analysis of the atomic force microscopy (AFM) image in conjunction with semi-empirical quantum mechanical calculation by Parameterization Method 3 (PM3) method. PET is not only an important material for conventional uses such as fiber, food package, and information storage but also for specific biomedical uses with good stability against body fluid and high radiation resistance for sterilization.¹² Therefore, it is necessary to understand the role of radical which originated from Ar plasma treatment on the alkali decomposition behavior of PET as an simulated interaction with body fluid. AFM is a particularly powerful tool in the study of surface topography because it can provide high-resolution three dimensional images of the film surface without any sample pretreatment, especially enough information

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on the film surface at the nano level in the height direction.¹³ Semi-empirical quantum mechanical calculation by PM3 method can also give insight to evaluate the experimental results theoretically and quantitatively.

Experimental

Materials. PET film (100 μm thickness) without additives was supplied by Kolon Co., Korea. Ar gas (purity 99.9%) was purchased from Union Gas (Korea). Acetone (spectral grade) as a solvent was purchased from Sigma Chem. Co. (U.S.A.) and was used without further purification.

Apparatus. A capacitatively coupled glow-discharge system¹⁴ with a 13.56 MHz radio-frequency generator (Auto electronic, Korea, maximum power of 300 W), mass flow controller (MFC, MKS, U.S.A.), pressure transducer (MKS Baratron, U.S.A.), tubular reactor (76 cm long Pyrex glass tube with 5 cm diameter) and two-stage rotary pump (Welch, U.S.A.) were used for Ar-plasma treatment on the PET surface.

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 silicone tip, Thermomicroscopes, U.S.A.) was carried out at room temperature, 40% RH, and at scanning rate of 0.5 Hz in noncontact mode. The mean spring constant of the tip was 17 N/m, the length was 85 μm . Root-mean-square (RMS) surface roughness was determined as the standard deviation of Z values within given areas (1 $\mu\text{m} \times 1 \mu\text{m}$). The PET samples of 1 cm \times 1 cm size were attached to sample holder with double-sided carbon tape.

Surface Modification Procedures. Ar-plasma treatment was carried out as follows. The PET samples (4.7 cm \times 2.0 cm \times 100 μm) as a film were cleaned first with acetone in Soxhlet extractor before being placed vertically in the center of the Pyrex chamber (tubular plasma reactor). The chamber was pumped down to 5 mTorr to remove air, moisture, and acetone that may have adsorbed on the PET surface and reactor wall. The plasma system pressure was adjusted with the aid of mass-flow-controller (MFC) and valves. The activation of PET surface was conducted for 1, 3, and 5 min at 240 mTorr, 40 W. After this, PET film was taken out of the Pyrex chamber and then immersed in NaOH solution immediately to avoid unnecessary reaction of its surface radicals with oxygen, nitrogen, water vapor and etc. in the air. Alkali-decomposition treatment by base-promoted hydrolysis was carried out using round-bottomed flask equipped with condenser in which PET film was immersed in NaOH solution (10 g NaOH /1 L H₂O) for 3 hrs at 95 °C. This was followed by washing with water and vacuum drying. The extent of decomposition of PET by base-promoted hydrolysis was defined as decomposition yield. The decomposition yield was calculated as follows,

$$\text{Decomposition yield}(\%) = \frac{w_i - w_f}{w_i} \times 100 \quad (1)$$

where w_i and w_f are weight of PET film before and after the treatment, respectively.

Calculation of Heat of Formation and Electron Density.

To evaluate heat of formation, ΔH_f , and electron density of the damaged molecular structure by Ar-plasma, semi-empirical quantum mechanical calculation by PM3 method was carried out on ethyl benzoate as an model compound of PET. The parameters adopted in the calculations were UHF (unrestricted Hartree-Fock) wave function and its multiplicities are doublet (one radical) or triplet (diradical) state for open system and RHF (restricted Hartree-Fock), singlet state for closed system. For geometry optimization Polak-Ribiere optimizer was used with convergence limit of 0.001.

Results and Discussion

Decomposition Yield. It is well-known that exposure of a polymer to plasma of inert gases generally results in physical ablation and formation of radicals of the polymer^{1,15} as was already mentioned in introduction part. Consequently, polymer chains of PET are expected to be damaged by ablation, which could affect physical and chemical properties of PET film, for example, decomposition behavior in NaOH solution and topographies of surface of PET. Data for decomposition yields of PET films are listed in Table I. The data show the effect of plasma treatment on decomposition clearly. The decomposition yield is shown to be slightly dependent on discharge condition. Compared to the virgin PET film (0 min in Table I), decomposition yields of plasma-treated PET films (1, 3, and 5 min) fall off gradually but evidently. From this observation, it is concluded that Ar plasma treatment on PET film hinders the decomposition reaction, although its values are not sufficiently large. The reason for low decomposition yields seems to be originated from somewhat hydrophobic property of PET film, small contacting surface area of PET with NaOH solution, dense packing of polymer chain,^{15,16} and low temperature, which cause to slow down the penetration of NaOH solution into PET.

Topography of PET Film. It is of interest to examine the effect of alkali-decomposition treatment on the topographies of PET surfaces. Four different AFM images are shown in Figure 1 in which A is for virgin PET while B is for the PET treated in NaOH solution but not treated in Ar-plasma. C and D are for PETs treated by Ar-plasma for 3 and 5 min,

Table I. Decomposition Yield (%) of PET Film Treated by Ar-Plasma at 240 mTorr, 40 W

Treatment Time	0 min	1 min	3 min	5 min
Decomposition Yield (%)	1.88	1.59	1.50	1.39

respectively, and followed by alkali-decomposition treatment in NaOH solution. Comparing A with B, it is evident that a significant change took a place in the surface structure. A shows relatively flat and uniform surface while B shows soft ridges of hill. The broad and smooth wavy structure originates from alkali-decomposition reaction and the number of ridges on the surfaces are influenced by plasma treatment time.

A comprehensive explanation of this result is not possible without introducing swelling phenomenon of PET surface due to alkali decomposition reaction in NaOH solution. This observation is also applicable to the cases of C and D. However, the distribution of ridges is influenced by the plasma treatment time. At longer exposure time, the size of ridges decreases but their number is increased.

For more detailed and quantitative comparison, the RMS roughness values for A, B, C, and D are presented in Figure 2 along with their histogram. The RMS roughness values give direct evidence for the swelling of PET film. The value for B is up to 4 times that of A. It is of interest to compare C and D with B since it can provide an information on the effect of Ar-plasma treatment in conjunction with alkali decomposition treatment. A short time exposure to Ar-plasma (for 3 min) reduces RMS roughness value from 6.343 to 4.600. Longer exposure (for 5 min) reduces RMS roughness value markedly from 6.343 to 1.787, which is nearly the

same as that of virgin PET (1.497). From the facts shown in Figures 1 and 2, it seems reasonable to conclude that Ar-plasma treatment plays a negative role in decomposition of PET, that is, the decomposition reaction is hampered due primarily to Ar-plasma treatment. As far as we are aware, this observation has not been discussed in the literature.

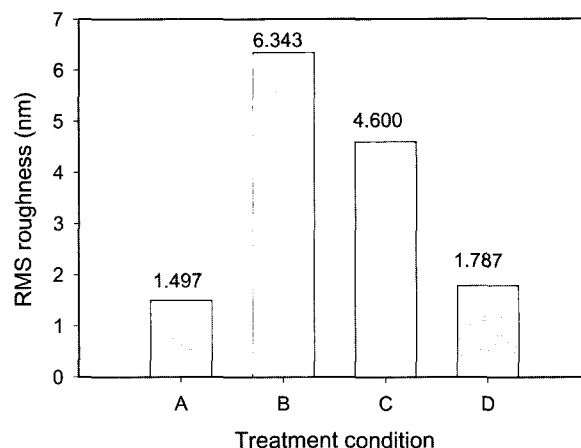


Figure 2. RMS roughness values of PET films treated at various conditions. A: virgin PET. B: PET treated in NaOH solution. C: PET treated by Ar-plasma for 3 min and then in NaOH solution. D: PET treated by Ar-plasma for 5 min and then in NaOH solution.

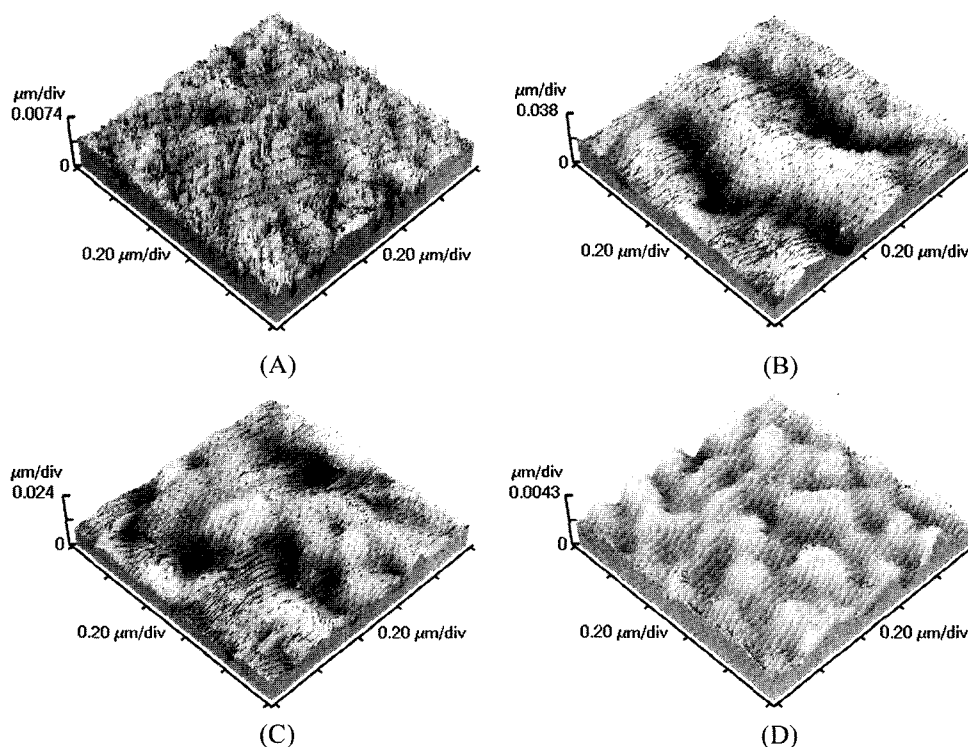


Figure 1. AFM images of PET films treated at various conditions. (A) virgin PET. (B) PET treated only by alkali decomposition in NaOH solution. (C) PET treated by Ar-plasma for 3 min and then in NaOH solution. (D) PET treated by Ar-plasma for 5 min and then in NaOH solution.

Nucleophilicity and Decomposition Yield. One way to account for the experiment facts, from what have been discussed above, is to examine the decomposition reaction in molecular level. Esters not only undergo acid hydrolysis, they also undergo base-promoted hydrolysis. The accepted mechanism for the base-promoted hydrolysis of an ester involves a nucleophilic substitution at the acyl carbon as shown in Figure 3. Accordingly, the ease of the decomposition reaction depends on accessibility of hydroxide ion to acyl carbon via nucleophilic substitution mechanism.

From this fact, decreased RMS roughness values and lowered decomposition yields of C and D are assumed to be directly related with the ability of nucleophilic attack of hydroxide ion at acyl carbon. To discuss the effects of Ar-plasma treatment on the ability of nucleophilic attack, it is reasonable to focus on two viewpoints; one is the change in enthalpy accompanied by plasma treatment, the other is the change in nucleophilicity, that is, electron density of acyl carbon. For this purpose, heats of formation and electron densities for the anticipated radical molecules, as shown in Figures 4 and 5, were calculated by PM3 method in which ethyl benzoate was taken as an simulated model compound for PET's repeating unit.

Among the reactions, Eq. 1 in Figure 4 is anticipated as the most probable and populated route due to relatively lower

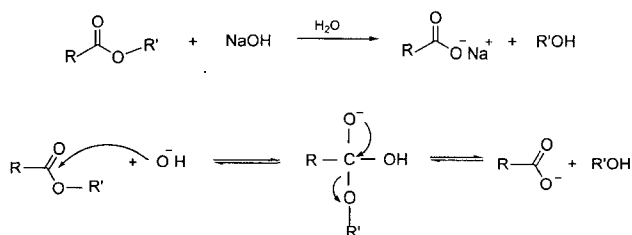


Figure 3. Decomposition reaction and its mechanism of ester in NaOH solution.

enthalpy than those of others as well as the consideration of the Boltzmann distribution. On the other hand, Eq. 2 in Figure 4 is the least probable route in the light of the viewpoints mentioned above. In addition, since carbonyl group itself is damaged, the nucleophilicity of acyl carbon is no longer effective to the nucleophilic attack by hydroxide ion. So, this situation seems not to occur as far as the nucleophilic substitution reaction is concerned.

To evaluate nucleophilicity of acyl carbon, electron densities of ethyl benzoate and its radicals, depicted in Eq. 1, 2, 3 and 4, are illustrated in Figure 5. As is expected, the positive charges of acyl carbons (underlined in Figure 5) are significantly lowered. For example, that of ethyl benzoate (A) is +0.427, while those of B (radical of Eq. 1), C (radical of Eq. 2), and D (radical of Eq. 3) are +0.018, -0.091, and +0.418, respectively. Consequently, it is difficult for the hydroxide ion to attack the acyl carbon, and their decomposition yields, as a result, should be lowered.

It is noteworthy to discuss electron densities of acyl carbon for E, F, and G in Figure 5. Their values are nearly the same or somewhat even higher, compared to that of ethyl benzoate. Judging from this result, the most probable route for producing radical seems to be Eq. 4 in Figure 4. However, it is not hopeful for Eq. 4 in Figure 4 to be the main route for precursor of decomposition reaction due to high heat of formation and consideration of the Boltzmann distribution. Consequently, Eq. 1 and 3 in Figure 4 seem to be main route of alkali-decomposition reaction although there are still something that await further studies. It is evident, nevertheless, that the decreased nucleophilicity of acyl carbon by ablation hinders the alkali-decomposition reaction, and that this reduces, in turn, the extent of swelling (RMS roughness value) of PET surfaces which were subjected to Ar-plasma.

This work could be applicable to plasma sterilization¹⁸ of biomaterials and the field of PET recycling^{16,17} as a fundamental data.

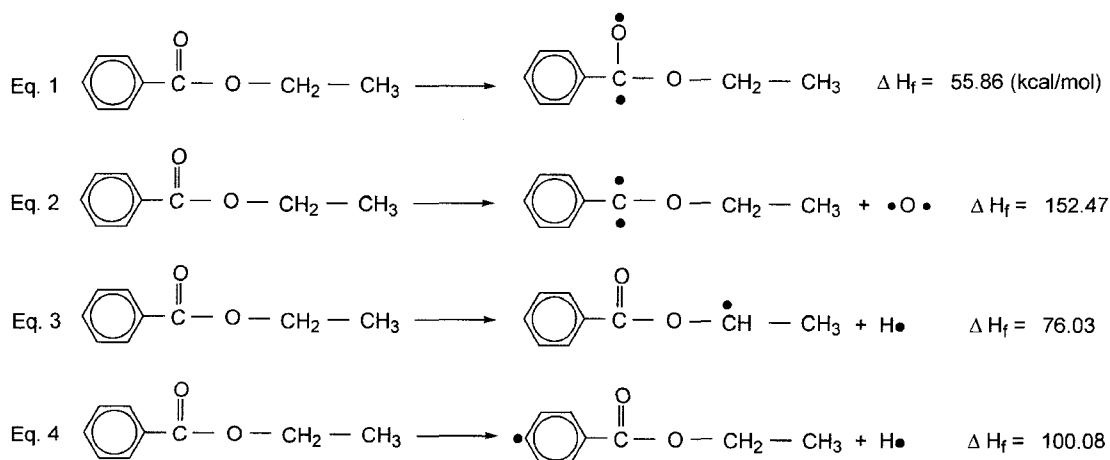


Figure 4. Heats of formation calculated semi-empirically by PM3 method.

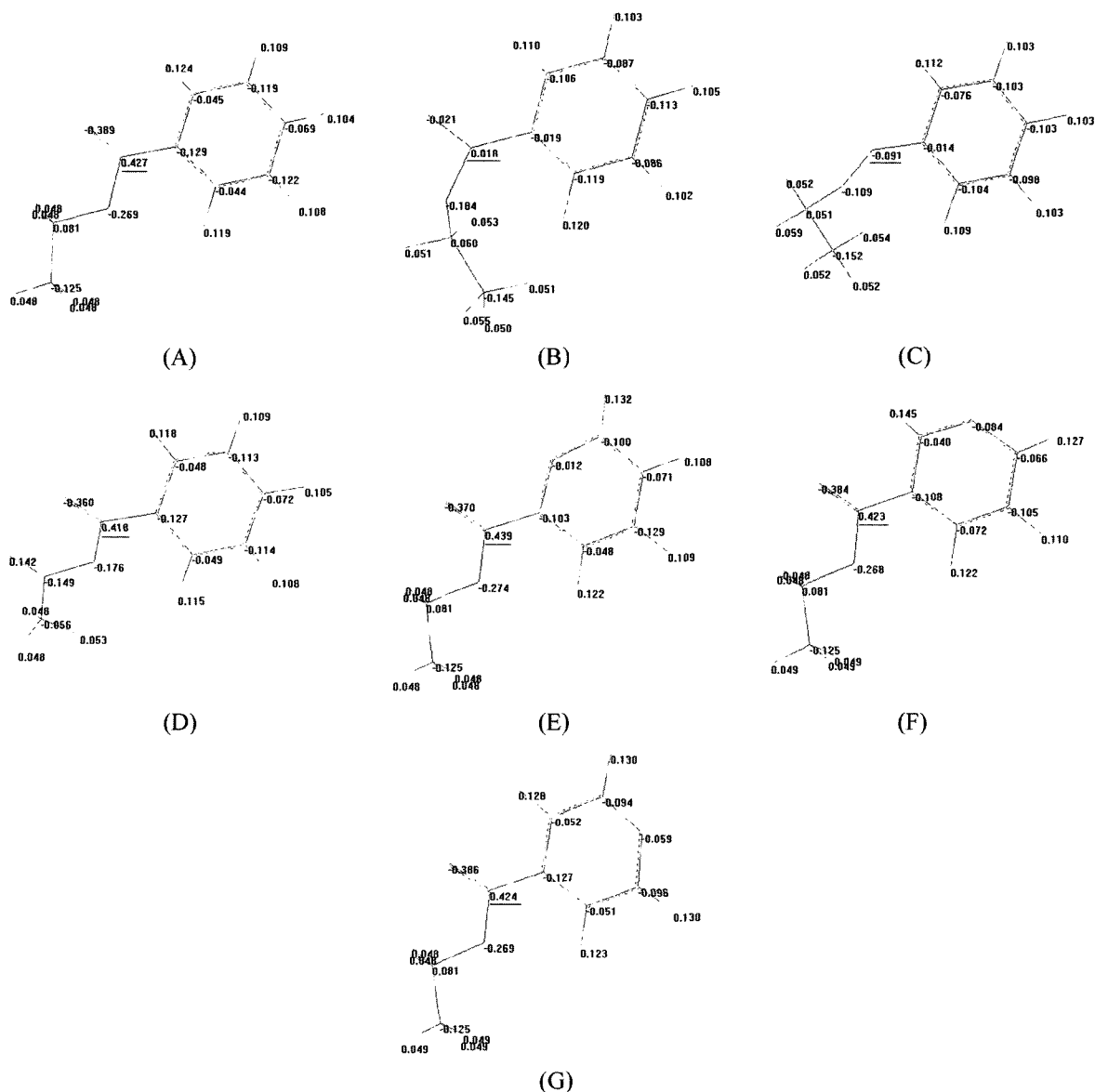


Figure 5. Electron densities of ethyl benzoate and its radicals produced by Ar plasma treatment. (A) ethyl benzoate. (B) radical (triplet state) at carbonyl group. (C) diradical at carbon of carbonyl group in which oxygen is eliminated by Ar plasma. (D) radical at ethyl group. (E) radical at phenyl ring (ortho position). (F) radical at phenyl ring (meta position). (G) radical at phenyl ring (para position).

Conclusions

Plasma treatment of PET films under Ar atmosphere and subsequent base-promoted decomposition treatment in NaOH solution leads to significant chemical as well as topographical changes on the surface. The roughness in the form of ridges at the surface was evident from the analysis of AFM images. The broad and smooth structure originated from the swelling of surface polymer chains. The number of ridges on PET surface were influenced by plasma treatment time while the extent of the swelling and decomposition yield decreased with increasing treatment time of Ar-

plasma. These observations were directly related with RMS roughness values of the surfaces. The effects of Ar-plasma treatment on topographies of the surface and on decomposition yield by alkali decomposition were correlated with ΔH_f and electron density of the damaged molecular structure of ethyl benzoate as a model compound of PET by Ar-plasma. The decreased decomposition yield was attributed to the decreased nucleophilicity of acyl carbon by ablation of Ar-plasma.

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