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〈Research Paper〉

Surface Modification of Ultra High Molecular Weight Polyethylene Films by UV/ozone Irradiation

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Abstract— Ultra High molecular weight polyethylene(UHMWPE) films were photooxidized by UV/ozone irradiation. Reflectance of the irradiated films decreased in the low wavelength regions of visible light, indicating destructive interference of visible light due to roughened surface. The UV treatment developed the nano-scale roughness on the UHMWPE films surface, which increased by two-fold from 82.6 to 156.6nm in terms of peak-valley roughness. The UV irradiation caused the oxygen content of the UHMWPE film surface to increase. Water contact angle decreased from 83.2° to 72.9° and surface energy increased from 37.8 to 42.6mJ/m^2 with increasing UV energy. The surface energy change was attributed to significant contribution of polar component rather than nonpolar component indicating surface photooxidation of UHMWPE films. The increased dyeability to cationic dyes may be due to the photochemically introduced anionic and dipolar dyeing sites on the film surfaces.

Keywords: *UHMWPE, UV/O$_3$ irradiation, photooxidation, surface energy, dyeability*

1. Introduction

Ultra High molecular weight polyethylene (UHMWPE) is a unique high performance polymer with outstanding physical and mechanical properties. Most notable properties are its chemical inertness, lubricity, impact resistance, and abrasion resistance. These characteristics of UHMWPE have been exploited since the 1950´s in a wide range of industrial applications, including pickers for textile machinery, lining for coal chutes and dump truck, runners for bottling production lines, as well as bumpers and siding for ships and harbors. Over 90% of the UHMWPE produced in the world is used by various industries[1,2].

Linear polyethylene can easily crystallize to achieve a maximum degree of crystallinity of 60-80% for the short-chain branched (2 CH$_3$/1000 C atoms) HDPE and 40-65% for the long-chain branched (10-35 CH$_3$/ 1000 C) LDPE with an average molar mass in technical applications of about 1 and 0.2-0.5x10^{5}g/mol, respectively. In comparison, UHMWPE is a linear polyethylene with an average molecular weight greater than 4x10^{6}g/mol. The UHMWPE with its extraordinary large chain length (molar mass: 2-6x10^{6}g/mol) and high entanglement density may result in a maximum degree of crystallinity of up to 60%, which is some what lower than that for the commercial HDPE[3].

The UHMWPE powder or flake resulting directly from synthesis is a highly crystalline (60-75%[10], depending on the resin type) material that is referred to as 'nascent' crystallized or crystallized at birth. The high crystallinity and melting temperature exhibited by the nascent UHMWPE powder were attributed to the presence of an extended-chain crystal morphology[10-12].

The UHMWPE has the characteristics of notably high abrasion resistance, high impact strength, low friction, excellent toughness, ease of fabrication, biocompatibility and bio-stability. However, the critical disadvantage of UHMWPE is its low adhesive and dyeing property, which can be improved by the surface modification of UHMWPE. The surface modification of polyethylene has been

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known for decades to improve abrasion resistance of the polymer for industrial applications.

Synthetic polymers often require high degree of multifunctional properties as well as inherent properties, which are closely related with surface properties such as wettability, antistaticity, antimicrobial property, biocompatibility, and so on. Therefore, various surface modification methods are in use to change relatively inert polymer surfaces. UV irradiation has become increasingly popular due to enhanced lamp intensity and versatile applications comparable to corona, plasma, electron beam, and gamma-irradiation treatment[4].

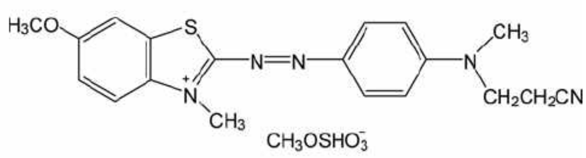
UV/O_3 has been a highly successful method for the surface modification of thermally sensitive polymers and fibers because the UV/O_3 treatment can be carried out continuously under atmospheric pressure using simple and inexpensive equipment[5,6]. Moreover, eco-friendly UV/O_3 treatment of polymer surfaces requires no addition of other chemicals and does not produce pollutants. When the polymer is exposed to ozone in the presence of UV light, the surface energy of the polymer can be increased through the scission of covalent bonds and concomitant photooxidation by the ozone or oxygen on the polymer surface without the negative impact on the bulk properties[7].

This study is to investigate the effects of UV irradiation on surface properties of UHMWPE reflectance, AFM, surface energy. ESCA and ATR were used to characterize chemical compositions of the UHMWPE surface. Cationic dyes were used to assess the dyeability of the modified UHMWPE film.

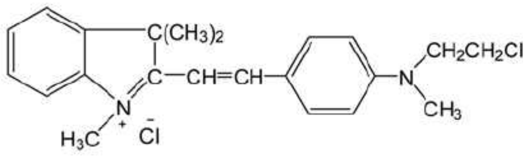
2. Experimental

2.1 Materials and Chemicals

UHMWPE powders with a number-averaged molecular weight (M_n) of 5,000,000 and a density of 0.94g/ml at 25°C, supplied by Aldrich Chemicals Co. were used for the study. Cationic dyes of Rifa Cationic Pink FG (C.I. Basic Red 13) and Rifa Cationic Blue FRL (C.I. Basic Blue 162) were used for the dyeing of UHMWPE films(Fig. 1).



(a) C.I. Basic Blue 162



(b) C.I. Basic Red 13

Fig. 1. Molecular structure of cationic dyes.

2.2 Preparation of UHMWPE Films

The mold was pressed between two heated brass plates at 250°C for 30 minutes under a pressure of 50MPa. The mold was allowed to cool under pressure to ambient temperature. The thickness of the films was adjusted to c.a. 400μm.

2.3 UV/O_3 Treatments

The UV/O_3 treatment of UHMWPE surface was performed in a UVO-cleaner (Jelight Co., USA) with a maximum lamp intensity of 24 mW/cm^2. Hg lamp was chosen to maximize surface modification effect due to more intense emission in shorter wavelength region compared with doped lamps. The main UV spectral emission ranges from 230 to 320 nm and the maximum emission occurs at 250, 280, and 310 nm. UV energy was controlled by adjusting UV irradiation time, which was determined by a UV radiometer (EIT Inc., USA).

2.4 Surface Characterization

Reflectance of the modified UHMWPE films was measured with a reflectance spectrophotometer (Coloreye 3100, Gretag Macbeth). Nano-scale surface morphology was imaged using a scanning probe microscopy (XE-100, Park System Co., Korea) in a noncontact mode on 10×10 μm area. A Jasco FT-IR 300E spectroscopy with an ATR accessory was used for the functional group analysis of the modified films. The subtracted spectra were obtained by subtracting the absorbance of the modified samples by that of the untreated after standardization. ESCA (Electron Spectroscopy for Chemical Analysis) was performed on the surface of the UHMWPE films using a X-ray photoelectron spectroscope (K-Alpha, ThermoFisher).

2.5 Contact Angle Measurement and Surface Energy Calculation

Static goniometer attached with a CCD camera (Phoenix 300, SEO Co. Ltd., Korea) was used to measure contact angles of water, diiodomethane and glycerin on UV irradiated samples by sessile drop method under constant temperature and humidity condition (20°C, 65% RH). Three or more contact angle measurements were averaged to calculate the surface energy of the UHMWPE film. Surface energy was calculated according to the method of van Oss *et al.*[8] using the contact angles of the three liquids. When a liquid wets on a solid surface, Young's equation and work of adhesion (W_a) are as follows:

$$\gamma_L(\cos\theta) = \gamma_L - \gamma_{SL}$$

$$W_a = \gamma_S + \gamma_L - \gamma_{SL}$$

Where γ_S, γ_L, and γ_{SL} are interfacial energies of solid/air, liquid/air and solid/liquid interfaces respectively. The total surface energy (γ_S^{TOT}) of a solid surface is the sum of the Lifshitz van der Waals component (γ_S^{LW}) and the Lewis acid-base component (γ_S^{AB}) of which the latter is the geometric sum of the electron-withdrawing parameter (γ^+) and the electron-donating parameter (γ^-).

$$\gamma_S^{AB} = 2\sqrt{\gamma^+\gamma^-}$$

Therefore the total surface energy of a solid can be calculated by the measured contact angles (Θ) of the three liquids according to the following quation.

$$W_a = \gamma_L(1+\cos\theta) = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + 2\{\sqrt{\gamma_S^{-}\gamma_L} + \sqrt{\gamma_S\gamma_L^{-}}\}$$

2.6 Assessment of Cationic Dyeability

The irradiated UHMWPE films were colored using an infrared dyeing machine with two cationic dyes of C.I. Basic Blue 162 and C.I. Red 13 at 2 % shade under pH 5.5 at 60°C for 1 h. After dyeing, the dyed films were thoroughly rinsed with running water and dried. Both color yield (K/S) and % exhaustion were evaluated at the maximum absorption wavelength by the reflectance spectrophotometer and a UV/VIS spectrophotometer (Agilnet 8453) respectively.

3. Results and Discussion

3.1 Reflectance and AFM Analysis

The UV/O_3 treatment effect on subtracted reflectance of the UHMWPE films was shown in Fig. 2. Higher UV energy resulted in slight yellowing and decreased reflectance at the short wavelength region. The decrease in reflectance may be due to the destructive interference of roughened UHMWPE surface caused by the photoscission of covalent bonds of polymer backbone under UV irradiation. Also the ozone generated under UV light can oxidize the polymer surface. The pronounced decreased in 380 nm may be related to the height of surface roughness which can scatter short wavelength of visible spectrum[9]. AFM analysis was carried out to observe nano-roughness of the modified surface. Fig. 3 and Table 1 are AFM

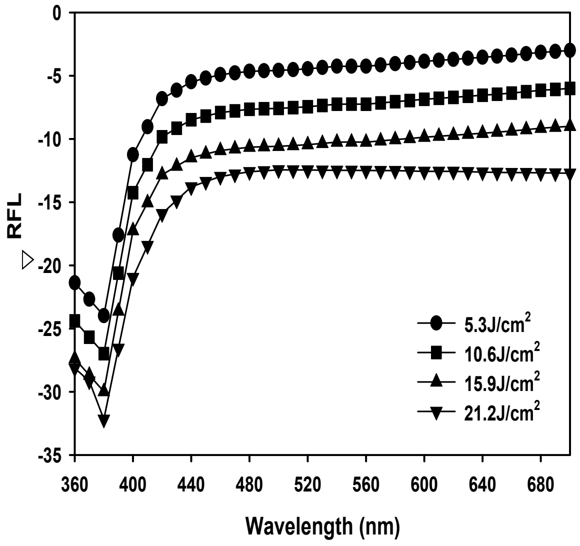
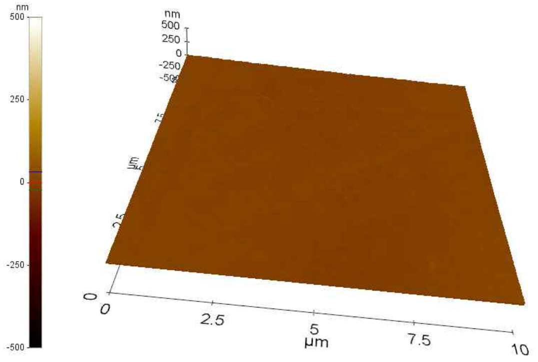
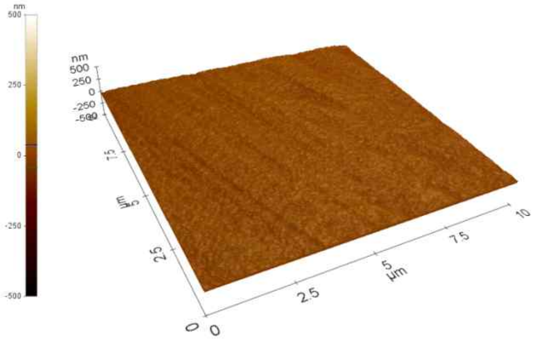


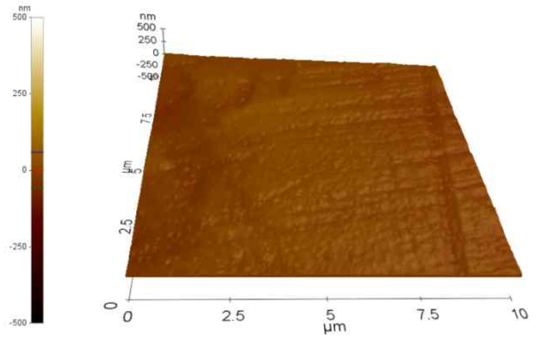
Fig. 2. ATR spectra of UV-irradiated UHMWPE films.



(a) Untreated



(b) 5.3 J/cm^2



(c) 15.9 J/cm^2

Fig. 3. AFM images of UV-irradiated UHMWPE films.

Table 1. The roughness parameters of untreated and treated UHMWPE films

Treatment	Roughness (nm)		
	Average (R_a)	Root mean square (R_q)	Peak-to-valley (R_{pv})
Untreated	7.7	9.7	82.6
5.3 J/cm^2	10.2	14.3	100.3
15.9 J/cm^2	19.5	24.1	156.6

images and roughness data of untreated and irradiated UHMWPE films respectively. With increasing UV energy up to 15.9 J/cm^2, nearly two-fold increase in surface roughness values R_{pv} of treated film was observed from 82.6 to 156.6nm, indicating that UV irradiation break down and oxidize surface layer of UHMWPE films inhomogeneously depending on the crystalline nature of the surface. In other words, UV etching effect concentrated more on amorphous-rich region compared to more crystalline region resulting in peak and valley morphology.

3.2 ATR and ESCA Analysis

The UHMWPE films surface was analyzed by ATR analysis as shown in Fig. 4. Weak stretching bands of carbonyl and vinyl groups and asymmetric stretching of C-O newly appeared with UV/O_3 irradiation at 1724 and 1226 cm^{-1} respectively, indicating that the UHMWPE films have been oxidized to generate C-O and carbonyl groups. Chemical compositions of the modified UHMWPE surface were quantitatively characterized by ESCA

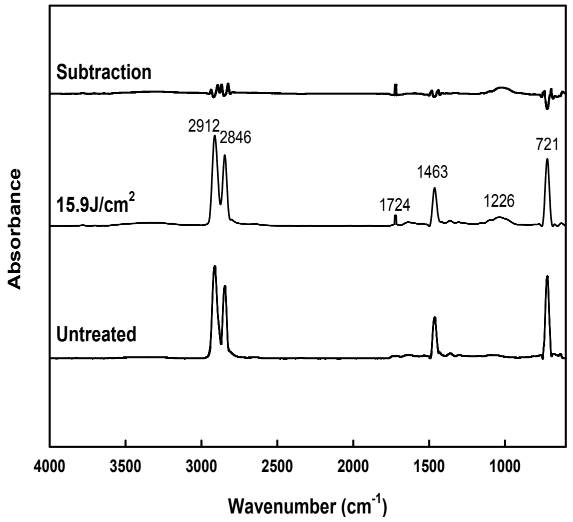


Fig. 4. ATR spectra of UV-irradiated UMHWPE films.

Table 2. Chemical compositions of UV-irradiated UHMWPE films

Treatment	C_{1s} (%)	O_{1s} (%)	O_{1s}/C_{1s} (%)
Untreated	82.1	4.9	5.9
5.3J/cm^2	83.7	8.3	10.1
15.9J/cm^2	63.7	19.1	30.2

analysis(Fig. 5). The corresponding elemental compositions were summarized in Table 2. The surface oxygen content increased, coupled with decreased carbon content with UV irradiation. The higher O_{1s}/C_{1s} atomic ratio substantiated the photooxidization effect of the UHMWPE surface by the UV/O_3 treatment.

3.3 Surface Energy

The surface energies of UHMWPE films were assessed with the contact angles of three liquids on the films (Fig. 6). The UV irradiated UHMWPE films became more hydrophilic, as indicated in the decreased water contact angle from 81.8 ° to 73.2 °. It may be resulted from the introduced hydrophilic polar groups on the photooxidized UHMWPE surface. Surface energy components were calculated and individual values were shown in Fig. 7. The total surface energy (γ^{TOT}) of the untreated UHMWPE film was 40.8 mJ/m^2 consisting of a

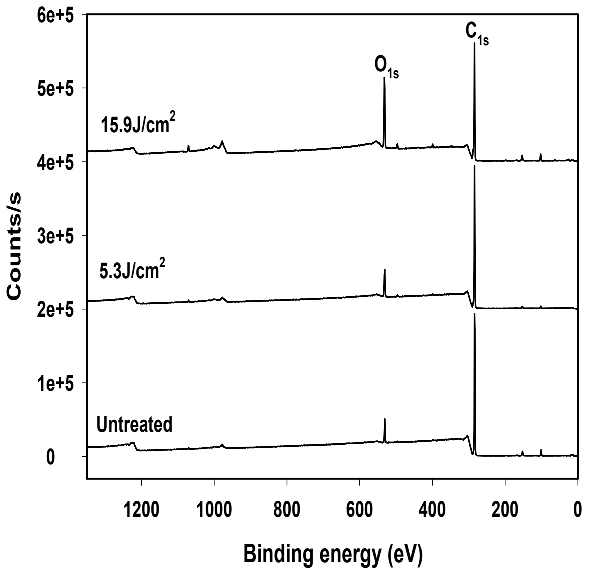


Fig. 5. Chemical spectrum of UV-irradiated UHMWPE films.

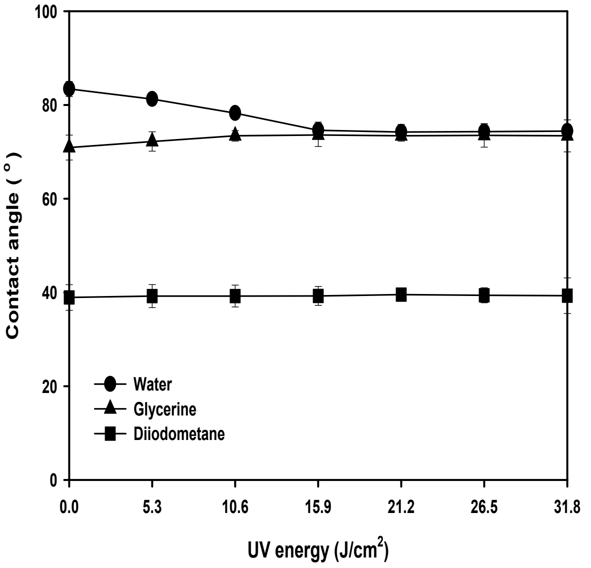


Fig. 6. Contact angles of UV-irradiated UHMWPE films.

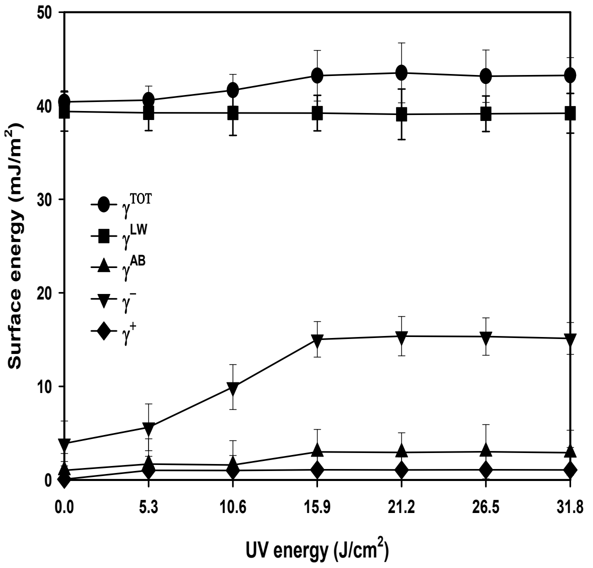


Fig. 7. Surface energy of UV-irradiated UHMWPE films.

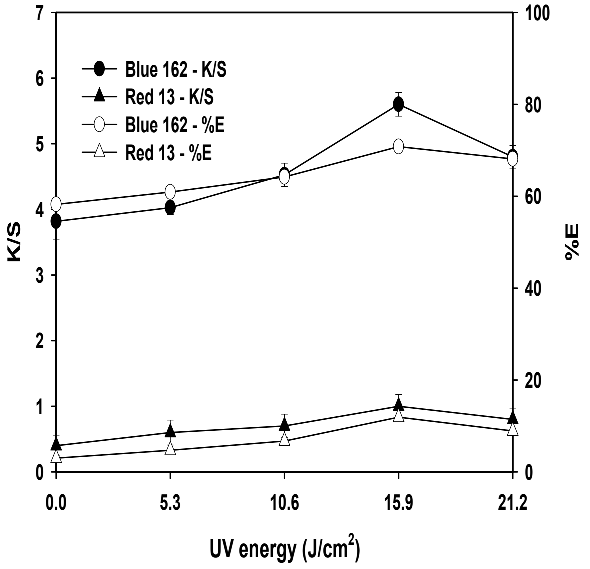


Fig. 8. K/S and exhaustion of UV-irradiated UHMWPE films.

nonpolar component (γ^{LW}) and a polar component (γ^{AB}) having 38.4 and 2.6mJ/m^2 respectively, where Lewis acid (γ^+) and base (γ^-) parameters are 1.8 and 3.7 mJ/m^2 respectively. While the nonpolar component of UV-irradiated films with a UV energy of 15.9 J/cm^2 decreased to 37.1 mJ/m^2, the γ^{TOT} increased to 43.2 mJ/m^2 with the significant increase in the γ^{AB} to 5.2 mJ/m^2, which mainly resulted from more substantial increase of γ^- to 16.4 mJ/m^2 rather than that of γ^+ to 2.5 mJ/m^2. The five-fold increase in Lewis base parameter of the UV irradiated UHMWPE films can be attributed to electron donating capability of the photooxidized hydrophilic groups such as C=O and C-O introduced by the UV irradiation.

3.4 Cationic Dyeability

The dyeability of treated UHMWPE films were assessed with C.I. Basic Blue 162 and C.I. Red 13 as shown in Fig. 8. The irradiated UHMWPE showed increased dyeability to the cationic dye.

The K/S as well as exhaustion increased with UV energy up to 15.9 J/cm^2 indicating the presence of electrostatic or polar interactions between the dyes and photooxidized UHMWPE surface. In present dyeing condition more negative surface potential of the modified may encourage stronger electrostatic interaction with cationic dyes compared with that of the untreated film.

4. Conclusion

UHMWPE films surface was modified by UV/O_3 irradiation, and surface properties were characterized by reflectance, ATR, ESCA, and surface energy. Upon UV/O_3 treatment, the surface roughness and the O_{1s}/C_{1s} atomic ratio obviously improved, resulting from the implantation of carbonyl and hydroxyl groups. The surface energy of the UHMWPE films increased substantially due to the significantly enhanced Lewis acid parameter with increase in UV energy, which promoted the acid-base interaction of the surfaces. Also UHMWPE films became hydrophilic as indicated by substantially decreased water contact angle. The dyeability of UHMWPE films to cationic dyes increased due to higher hydrophilic surface and strong electrostatic attraction between the cationic dyes and anionic dyeing sites of the UHMWPE.

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References

1. S. M. Kurtz, "UHMWPE Biomaterials Handbook", Academic Press, London, U.K., pp. 197-200, 2009.
2. A. Koh, V. Shim, and V. Tan, Dynamic Behavior of UHMWPE Yarns and Addressing Impedance Mismatch Effects of Specimen Clamps, *Int. J. Impact Eng.,* 37, 324-332(2010).
3. S. Kurtz, O. Muratoglu, M. Evans, and A. Edidin, Advances in the Processing, Sterilization, and Crosslinking of Ultra-high Molecular Weight Polyethylene for Total Joint Arthroplasty, *Biomaterials,* 20, 1659-1688(1999).
4. G. H. Koo and J. Jang, Hydrophilic Modification of Poly(ethylene oxide) by UV Irradiation, *Textile Coloration and Finishing*, 21, 16-20(2009).
5. H. S. Lee, Y. K. Jeong, and J. Jang, Surface Modification of Cellulose Acetate using UV/O_3 Irradiation, *Textile Coloration and Finishing*, 18, 281(2006).
6. G. H. Koo and J. Jang, Surface Modification of Poly(Lactic Acid) by UV/Ozone Irradiation, *Fibers and Polymers*, 9, 674(2008).
7. E. M. Kim and J. Jang, Surface Modification of Meta-aramid Films by UV/Ozone Irradiation, *Fibers and Polymers*, 11(5), 677-682(2010).
8. C. J. van Oss, R. J. Good, and M. K. Chaudhury, Additive and Nonadditive Surface-tension Component and the Interpretation of Contact Angles, *Langmuir*, 4, 884-891(1988).
9. J. Jang and Y. Jeong, Nano Roughening of PET

and PTT Fabrics via Continuous UV/O_3 Irradiation, *Dyes and Pigments*, **69**, 137-143(2006).

10. X. Wang and R. Salovey, Melting of Ultra High Molecular Weight Polyethylene, *J. Polym. Sci.*, **34**, 593-599(1987).
11. P. Smith, H. D. Chanzy and B. P. Rotzinger, Drawing of Virgin Ultra High Molecular Weight Polyethylene: an Alternative Route to High Strength/high Modulus Materials, Part 2 Influence of Polymerization Temperature, *J. Mater. Sci.*, **22**, 523-531(1997).
12. A. Bellare, H. Schnablegger and R. E. Cohen, The Melt Anisotropy of UHMWPE, *J. Polym. Sci.*, **21**, 821-830(2003).