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Argon/Oxygen Plasma Surface Modification of Biopolymers for Improvement of Wettability and Wear Resistance

Binnur Sagbas

***Abstract*—**Artificial joint replacements such as total knee and total hip prosthesis have been applied to the patients who affected by osteoarthritis. Although different material combinations are used for these joints, biopolymers are most commonly preferred materials especially for acetabular cup and tibial component of hip and knee joints respectively. The main limitation that shortens the service life of these prostheses is wear. Wear is complicated phenomena and it must be considered with friction and lubrication. In this study, micro wave (MW) induced argon+oxygen plasma surface modification were applied on ultra-high molecular weight polyethylene (UHMWPE) and vitamin E blended UHMWPE (VE-UHMWPE) biopolymer surfaces to improve surface wettability and wear resistance of the surfaces. Contact angel measurement method was used for determination of wettability. Ball-on-disc wear test was applied under 25% bovine serum lubrication conditions. The results show that surface wettability and wear resistance of both material samples were increased by plasma surface modification.

***Keywords*—**Artificial joints, plasma surface modification, UHMWPE, vitamin E, wear.

I. Introduction

POLYMERS are widely used in biomedical applications such as orthopedic prosthesis, micro-fluidics, drug delivery systems, micro-reactors for biological reactions etc. because of low cost, biocompatibility and reliability [1]. UHMWPE is the most preferred polymer in the orthopedic prosthesis application area such as total knee and hip joints. However, wear problem of this material has not been solved yet. Structural and surface modifications such as radiation cross-linking of UHMWPE and addition of α-tocopherol (vitamin E) in to the UHMWPE structure as a natural antioxidant have been applied. Although better wear resistance was obtained from these applications, adequate material properties for enhancing service life of the prosthesis cannot be achieved yet. Therefore, studies have been going on for improvement of tribological properties of the UHMWPE [2]-[4].

Plasma surface treatment of the polymers is one of the most effective and economical technique to modify the surface properties of the polymeric materials without changing bulk material [5]. It is possible to selectively modify the surfaces to enhance wide variety of surface properties such as surface wettability, functionality, hydrophilicity, hydrophobicity, surface roughness, scratch resistance, wear resistance, physical, chemical and mechanical properties by applying proper plasma method and gasses to the polymer surfaces [6}-[8]. Therefore, plasma surface modification has become increasingly popular method to improve the functionally required properties of biomaterials instead of developing new materials with expensive and time consuming processes [9].

Liu et al. studied on argon and oxygen plasma surface modification of UHMWPE and they concluded that both plasma surface treatment applications improved the wettability, surface hardness, anti-scratch and wear resistance of UHMWPE [10], [11].

In another study Noeske et al. searched effect of atmospheric plasma jet on adhesion property of a series of polymers included High-Density Polyethylene (HD-PE). They reported that adhesion property of the plasma treated polymers increased by oxygen functionality of the surfaces [12]. In previous study [13], argon plasma surface modification was applied to surface of UHMWPE textile. It was reported that the peel strength of the UHMWPE increased and contact angle decreased from 80° to 28° [13].

Plasma is the fourth state of matter and composed highly excited, ionic, atomic, molecular and radical species. Plasma gasses are excited in to these energetic levels by microwave, radio frequency, corona and dielectric barrier [8]. Much functionality will arise near the surface while the plasma applied to the polymer with proper plasma density and treatment time. In activation process, firstly hydrogen atoms are abstracted from the polymer chains by breaking the bond with the plasma energy. So radicals are created at the midpoint of the polymer chains and these radicals then built up new bonds with each other by crosslinking and with species that are activated by plasma gas [5], [9]. Type of the applied plasma gas is one of the most important parameter to obtain required surface activation. Also if gas mixture is used, the ratio of gasses in this mixture is important as well. Plasma induced activation of polymer surface, without changing bulk properties generally divided in two groups according to the nature of plasma gas, as reactive or inert. Oxygen (O_2) is most common active gas for plasma treatment. Besides, carbon dioxide (CO_2) and ammonia (NH_3) are generally used as active plasma gasses. Argon (Ar) and Helium (He) are the inert gasses that used for plasma treatment [14]-[18].

Application of different plasma gasses may result different surface chemical structure so different surface mechanical properties. Different functional groups such as C–O, C=O,

B. Sagbas is with the Yildiz Technical University, Besiktas, Istanbul, Turkey. (phone: +90 212 383 2806; fax: +90 212 383 3024; e-mail: bsagbas@gmail.com).

O=C–O can be obtained on the polymer surface by oxygen plasma [11]. Addition of inert gas to active gas based plasma provides an increase in oxygen functionality by enhancing radical formation so more effective surface activation may be achieved [5], [9], [11].

In [19], the effects of argon plasma surface modification on tribological properties of UHMWPE and VE-UHMWPE were investigated. In this study, it is aimed to define effect of argon+oxygen gas mixture plasma on surface properties of the same materials. In literature, there is limited number of studies about argon+oxygen plasma treatment on VE-UHMWPE, so it is expected to contribute literature results by sharing present study.

II. Materials and Methods

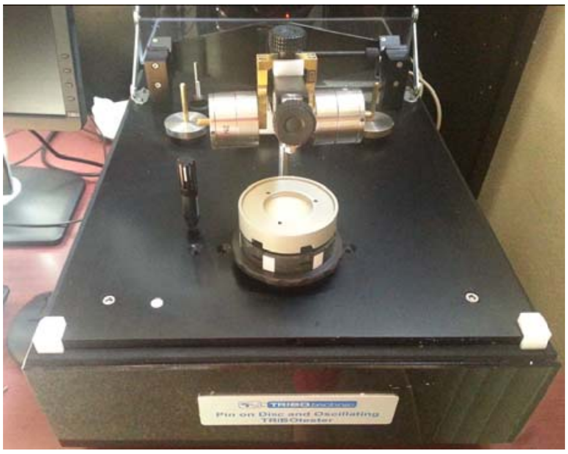
UHMWPE and VE-UHMWPE were commercially obtained from MediTECH Medical Polymers, Vreden, Germany as in 1000 mm length rods. Disc samples were machined from these Chirulen 1020 and Chirulen 1020 E rods in 40 mm diameter and 4 mm thickness in accordance with ASTM G99-05 [20]. Disc samples were polished by using 1000, 1200 and 2000 grid sand papers for reducing the surface roughness. The average surface roughness of the samples was about 0.62 µm. The polished samples were cleaned 15 min. in ultrapure water, 30 min. in ethyl alcohol and at the end 15 min. ultrapure water respectively in an ultrasonic bath, at 30 ^{o}C. The samples were coded as UHMWPE-0 for untreated conventional UHMWPE, UHMWPE-1 for argon+oxygen plasma treated conventional UHMWPE, VE-UHMWPE-0 for untreated VE-UHMWPE and VE-UHMWPE-1 for argon+oxygen plasma treated VE-UHMWPE. Some properties of UHMWPE and VE-UHMWPE can be seen in Table I.

TABLE I
Mechanical Properties of UHMWPE and VE-UHMWPE

Variable	Unit	UHMWPE	VE-UHMWPE
		Average	Average
Density	Kg/m^3	936	937
Young's Modulus	MPa	660	683
Poisson's Ratio	-	0.46	0.46
Molecular weight	g/mol*10^6	5.17- 5.41	5.17- 5.41

The argon+oxygen plasma surface modification process of UHMWPE and VE-UHMWPE samples were carried out in the Europlasma Surface Cleaner microwave plasma system at 35 ^{o}C with 300 W power 30 min processing time under 340 mTor working pressure and the ratio of plasma gas mixture was 1:1.

Ball-on-disc wear tests were done by Tribo Technic Pin-on-Disc and Oscilating Tribotester under 10 N load and 340 m sliding distance. Al_2O_3 standard balls in 6 mm diameter were used as counter face. 25% Bovine calf serum (Sigma-Aldrich) was used as lubricant. 0.3% sodium azide and 5 mM EDTA were added into the lubricant for avoiding bacterial contamination. The viscosity of the lubricant was measured with an NDJ-1 Rotary Viscometer as 0.002 Pa s. Wear track profile area was measured by Veeco Dektak XT Bruker Stylus Profiler for determining wear amount of the disc surfaces.



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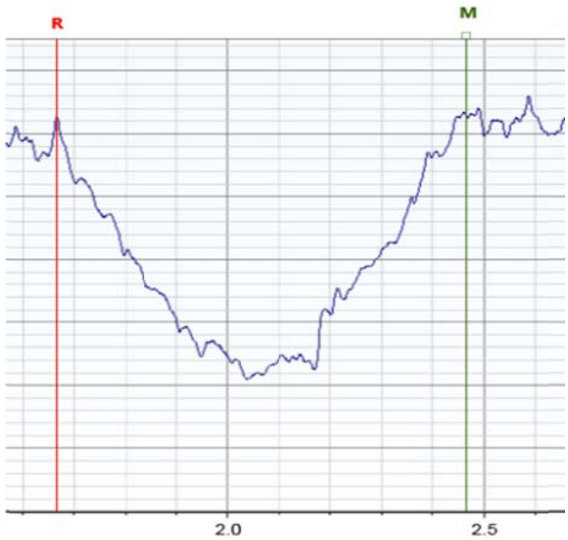

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Fig. 1 (a) Tribo Technic Pin-on-Disc and Oscilating Tribotester, (b) Wear track profile

By using cross-sectional area of wear track and its radius the wear volume was calculated. Then by using (1), wear factor (k) of each disc sample was determined.

$$k = \frac{V}{NS} \tag{1}$$

k; wear factor (mm^3/N.m), V; wear volume (mm^3), N; applied load (N), S; friction distance (m) [21]-[23].

The morphology of wear tracks of both plasma treated and untreated samples were analyzed by scanning electron microscopy (SEM). Worn surface of the samples were examined by Bruker Contour GT-K Optical Profiler. The surface wettability of treated and untreated UHMWPE and VE-UHMWPE samples were measured by a contact angle measurement system in air. The droplets of de-ionized water were applied on the sample surface by hand with a syringe. Contact angle measurements were taken from at least three different regions of the surface and then the average value of the results calculated.

III. Results and Discussion

Wear test results such as average friction coefficient and wear factor are listed in Table II. Average friction coefficient of untreated UHMWPE-0 sample (written as PE0 in Table II) recorded as 0.044 while this value becomes 0.064 after plasma treatment of UHMWPE-1 (PE1). Friction coefficient of untreated VEUHMWPE-0 (VEPE0) is 0.070 while for plasma treated VEUHMWPE-1 (VEPE1) is 0.075. Friction coefficient of UHMWPE-1 increased after plasma treatment while friction coefficient of VEUHMWPE-1 does not change.

TABLE II
Ball-on-Disc Wear Test Results

	PE0	PE1	VEPE0	VEPE1
Av. Friction Coefficient	0.044	0.064	0.070	0.075
Wear Factor (10^{-5} mm^3/N.m)	4.77	4.16	3.93	1.96

Wear factor of UHMWPE-0 is 4.77, after plasma treatment, reduces to 4.16. For VEUHMWPE-0 wear factor is 3.93, after plasma treatment this value decreases to 1.96. Comparison of wear factors for all samples can be seen in Fig. 2.

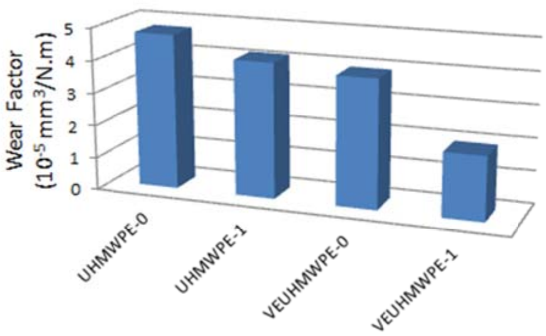
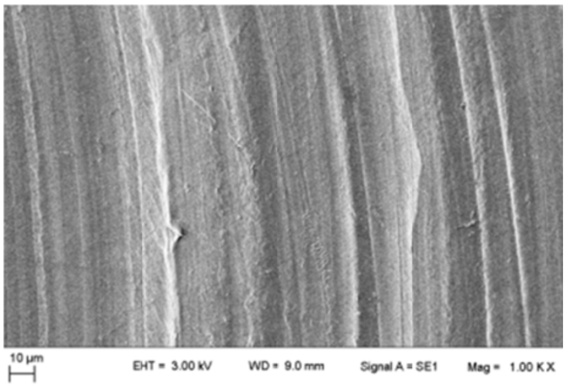


Fig. 2 Wear factor of untreated and plasma treated disc samples

Worn surface SEM and optical profiler images can be seen in Figs. 3 and 4. Wear scars and wear is so clear on the images of untreated VEUHMWPE-0 samples. The surface of plasma treated VEUHMWPE-1 is very smooth in SEM image in Fig. 4, also the wear track is not so clear in the image that taken by optical profiler.

X-ray photoelectron spectroscopy spectrums of untreated and plasma treated UHMWPE and VEUHMWPE samples are given in Figs. 5 and6 respectively. Oxygen containing groups such as C-O, C=O, O-C=O on the sample surfaces can be seen in these curves. Binding energy about 284.8 eV indicates C-C bonds while 286 eV means C-O-C and 288.5 eV shows O-C=O bonds [11]. With this reference information, there is no any detectable change on the high resolution C1s peak of the argon+oxygen plasma treated UHMWPE-1 sample in Fig. 5. Liu et al. [11] applied oxygen plasma to the UHMWPE surface and they reported that oxygen functional groups were formed after plasma treatment.



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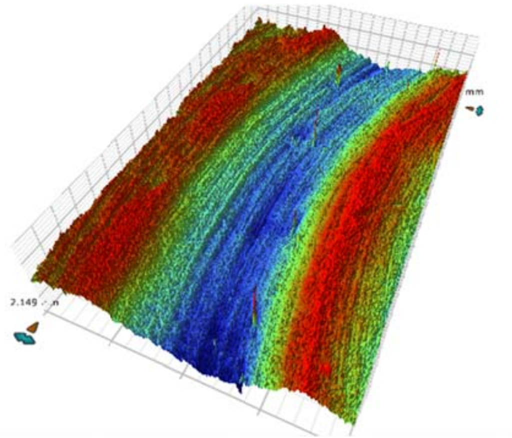

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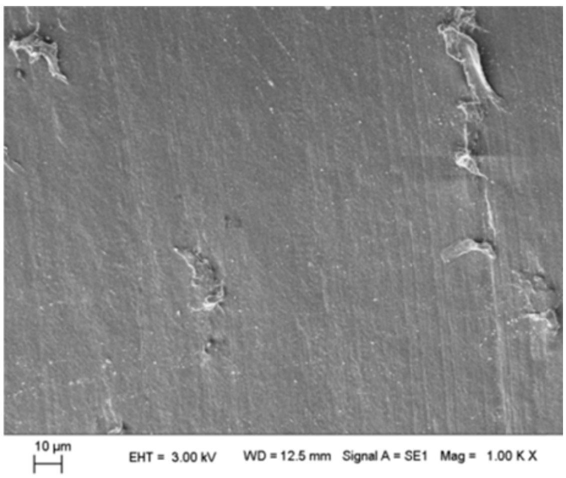
Fig. 3 (a) SEM and (b) optical profiler images of untreated VEUHMWPE-0 worn surfaces



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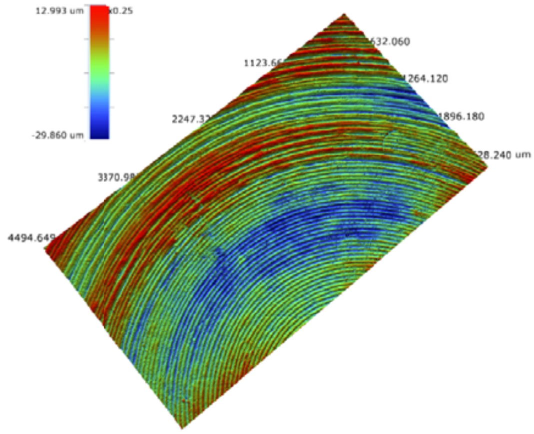

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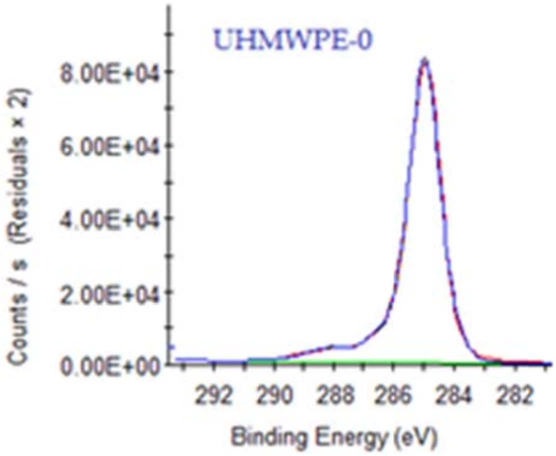
Fig. 4 (a) SEM and (b) optical profiler images of plasma treated VEUHMWPE-1 worn surfaces



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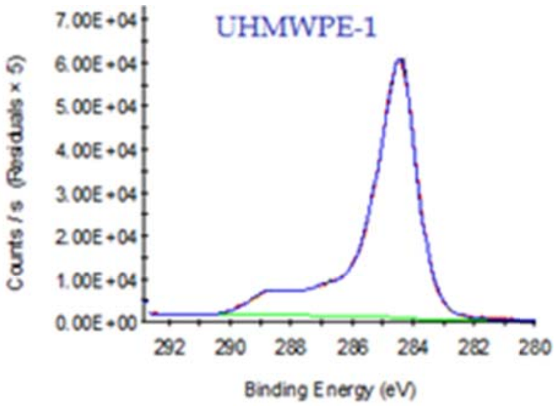
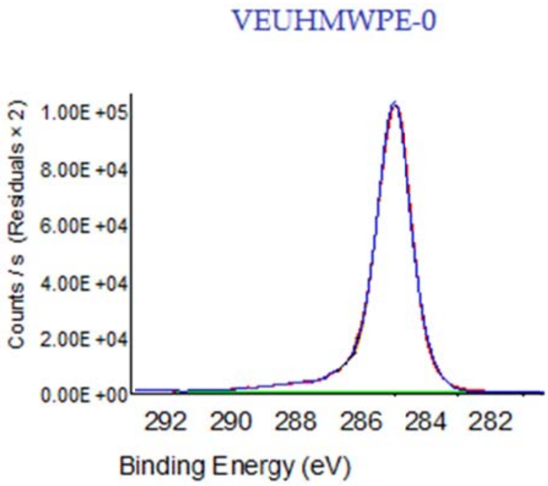


(b)

Fig. 5 X-ray photoelectron spectroscopy spectrum of UHMWPE: (a) High resolution XPS C1s peaks of UHMWPE-0 (untreated sample) and (b) UHMWPE-1 (plasma treated sample)

In Fig. 6, it is possible to see a shoulder on the high resolution C1s peak of the argon+oxygen plasma treated UHMWPE-1 sample which cannot be seen on untreated sample. Binding energy about 288.5 eV indicates O-C=O functional groups. Beside this C–O/C–OH group can be seen at 286.5 eV. Therefore it can be concluded that some oxygen based functional groups formed on VEUHMWPE-1 surface after argon+oxygen plasma treatment.



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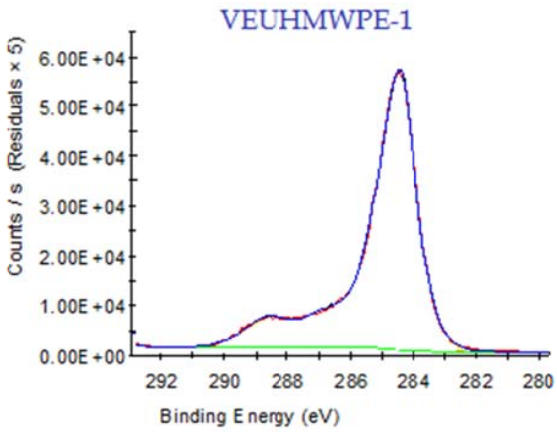
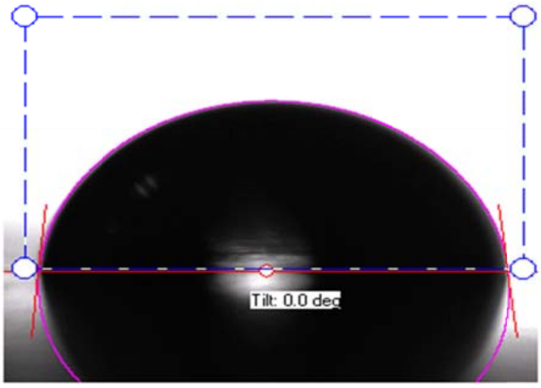


(b)

Fig. 6 X-ray photoelectron spectroscopy spectrum of VEUHMWPE: (a) High resolution XPS C1s peaks of VEUHMWPE-0 (untreated sample) and (b) VEUHMWPE-1 (plasma treated sample)

Polymers are generally hydrophobic and converting these surfaces to hydrophilic is important for obtaining improved adhesion strength, biocompatibility and wettability properties [5]. For determining effect of argon+oxygen plasma treatment on the surface wettability, the contact angel of plasma treated and untreated samples were measured by a contact angle measurement system in air. Image of dropped water on UHMWPE can be seen in Fig. 7.



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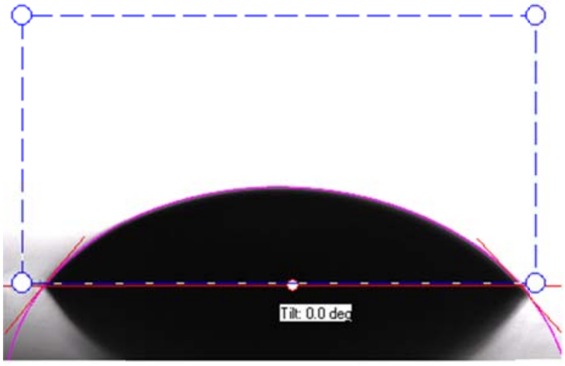

(b)

Fig. 7 Image of dropped water on (a) untreated UHMWPE-0, (b) argon+oxygen plasma treated UHMWPE-1

Average contact angel of untreated UHMWPE-0 was 77.44^o, this value became 47.87^o while argon+oxygen plasma applied to the surface of conventional UHMWPE. In previous study argon plasma treated UHMWPE sample's contact angle was 23.97^o [19]. Average contact angel of untreated VE-UHMWPE-0 sample was 83.26^o while this value became 62.84^o for plasma treated VE-UHMWPE-1. Argon+oxygen plasma treatment increased wettability of both material but not as much as only argon plasma treatment.

IV. Conclusion

Argon+oxygen plasma surface treatment was applied to the surface of UHMWPE and VE-UHMWPE samples. It is clear from the results that mixed gas plasma treatment does not affect the friction and wear properties of the conventional UHMWPE. These results are in accordance with XPS analysis results. In contrast, argon+oxygen plasma treatment increased wear resistance of VEUHMWPE-1 sample. This result can be explained with the formation of cross links between polymer chains and functional groups detected in XPS results. Wettability of both material samples increased after plasma treatment slightly. To make more definite conclusions and determine the optimal treatment parameters, the experiments and analysis are going on with different plasma treatment duration and plasma gasses.

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References

[1] D. Jackson, *Biopolymers: Applications and Trends,* William Andrew-Elsevier, USA, 2015, pp.291-405.
[2] S.M. Kurtz, UHMWPE Biomaterials Handbook, Second Edition, Elsevier Inc., Oxford, UK, pp.173-363, 2009.
[3] E. Oral, K.K. Wannomae, N.E. Hawkins, W.H. Harris, O.K. Muratoglu, "α-Tocopherol doped irradiated UHMWPE for high fatigue resistance and low wear", *Biomaterials*, vol.25, pp.5515-5522, 2004.
[4] E. Oral, S. D. Christensen, A.S. Malhi, K.K. Wannomae, O.K. Muratoglu, "Wear resistance and mechanical properties of highly cross-linked, ultrahigh–molecular weight polyethylene doped with vitamin E", *The Journal of Arthroplasty,* vol. 21, pp. 580-591, 2006.
[5] P.K. Chu, J.Y. Chen, L.P. Wang, N. Huang, "Plasma-surface modification of biomaterials", Materials Science and Engineering R, vol. 36, pp.143–206, 2002.
[6] K. Ellinas,K. Tsougeni, P.S. Petrou, G.Boulousis, D. Tsoukleris, E. Pavlatou, et al., "Three-dimensional plasma micro–nanotextured cyclo-olefin-polymer surfaces for biomolecule immobilization and environmentally stable superhydrophobic and superoleophobic behavior", *Chemical Engineering Journal*, Chemical Engineering Journal Vol.300, pp. 394–403, September 2016.
[7] E. Bormashenko, G. Whyman, V. Multanen, E. Shulzinger, G. Chaniel, "Physical mechanisms of interaction of cold plasma with polymer surfaces", *Journal of Colloid and Interface Science* vol.448, pp.175–179, February 2015.
[8] L.S. Barbarash, E.N.Bolbasov, L.V.Antonova, V.G.Matveeva, E.A.Velikanova, E.V. Shesterikov, et al., "Surface modification of poly-ε-caprolactone electro spun fibrous scaffolds using plasma discharge with sputter deposition of a titanium target", *Materials Letters,* vol.171, pp.87–90, February 2016.
[9] F. Khelifa, S. Ershov, Y. Habibi, R. Snyders, P. Dubois, "Free-Radical-Induced Grafting from Plasma Polymer Surfaces", Chemical Review, vol. 116, pp. 3975−4005, March 2016.
[10] H. Liu, Y. Pei, D. Xie, X. Deng, Y.X. Leng, Y. Jin, N. Huang, "Surface modification of ultra-high molecular weight polyethylene (UHMWPE) by argon plasma", *Applied Surface Science*, vol. 256, pp.3941–3945, January 2010.
[11] H. Liu, D. Xie, L. Qian, X. Deng, Y.X. Leng, N. Huang, "The mechanical properties of the ultrahigh molecular weight polyethylene (UHMWPE) modified by oxygen plasma", *Surface & Coatings Technology, vol.* 205, pp. 2697–2701, 2011.
[12] M. Noeske, J. Degenhardt, S. Strudthoff, U. Lommatzsch, "Plasma jet treatment of five polymers at atmospheric pressure: surface modifications and the relevance for adhesion", *International Journal of Adhesion & Adhesives*, vol. 24, pp.171–177, 2004.
[13] C.Y. Huang, J.Yi Wu, C.S. Tsai, K. H. Hsieh, J.T. Yeh, K. N. Chen, "Effects of argon plasma treatment on the adhesion property of ultra-high molecular weight polyethylene (UHMWPE) textile", *Surface and Coatings Technology,* vol.231, pp. 507–511, September 2013.
[14] P. Hojati-Talemi, L. Zou, M. Fabretto, R.D. Short, "Using Oxygen Plasma Treatment to Improve the Performance of Electrodes for Capacitive Water Deionization", *Electrochim. Acta*, vol. 106, pp. 494−499, 2013
[15] Y. L. Cheng, Y.K. Wang, P. Chen, S.B. Deng, R. Ruan, "Non-Thermal Plasma Assisted Polymer Surface Modification and Synthesis: A Review", *International Journal of Agricultural and Biological Engineering,* vol.7, pp. 1-9, 2014.
[16] S. Patra, S. Anjum, A.R. Ray, B. Gupta, "Effect of CO2 Plasma Exposure on Physico-Chemical Properties of Porous Polycaprolactone Scaffold", *Polymer Bulletin*, pp. 1-6, 2015.
[17] B. Akhavan, K. Jarvis, P. Majewski, "Development of Oxidized Sulfur Polymer Films through a Combination of Plasma Polymerization and Oxidative Plasma Treatment", *Langmuir,* vol. 30, pp.1444−1454, 2014.
[18] K. Sahagian, M. Larner, S. L. Kaplan, "Cold Gas Plasma in Surface Modification of Medical Plastics", Presented at SPE Antec Medical Plastics Division, April 23, 2013, Ohio, Publication pending.

[19] B. Sagbas , "Effect of argon plasma surface modification on tribological behavior of biopolymers",*Industrial Lubrication and Tribology*, Vol. 68 Iss: 4, pp. --, 2016, in press.
[20] ASTM G99-05(2010), Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus.
[21] L. Ma, V.M. Rainforth, D. Sun, J.A. Wharton, R.J.K. Wood, "A '3-body' abrasion wear study of bioceramics for total hip joint replacements", *Wear*, 267, 2122–2131, 2009.
[22] T. Pylios, D. E. T. Shepherd, "Wear of medical grade silicone rubber against titanium and ultrahigh molecular weight polyethylene", Journal of Biomedical Materials *Research Part B: Applied Biomaterials*, vol. 84B, pp. 520–523, 2008.
[23] B. Sagbas, Measurement, analysis and metrological evaluation of physical magnitudes and geometrical features that show alteration with regard to friction in hip prosthesis, PhD Thesis, Istanbul Turkey: Yildiz Technical University, 2013. 228 p.