Research article

SURFACE and INTERFACE ANALYSIS

Received: 11 July 2012 Revised: 22 October 2012 Accepted: 23 October 2012 Published online in Wiley Online Library

(wileyonlinelibrary.com) DOI 10.1002/sia.5181

Surface characterization and radical decay studies of oxygen plasma-treated PMMA films

Ozge Ozgen,[a,b] Eda Ayse Aksoy,[c,d] Vasif Hasirci[a,d,e,f] and Nesrin Hasirci[a,d,f,g]*

Polymethylmethacrylate (PMMA) films were modified by RF oxygen plasma with various powers applied for different periods, and the effects of these parameters on the surface properties such as hydrophilicity, surface free energy (SFE), chemistry, and topography were investigated by water contact angle, goniometer, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy, and the types of the created free radicals and their decay were detected by electron spin resonance spectroscopy (ESR). SFE and contact angle results varied depending on the plasma parameters. Oxygen plasma treatment (100 W–30 min) enhanced the hydrophilicity of PMMA surface as shown by decreasing the water contact angle from 70° to 26°. XPS analysis showed the change in the amounts of the present functionalities as well as formation of new groups as free carbonyl and carbonate groups. The roughness of the surface increased considerably from ~2 nm to ~75 nm after 100 W–30 min oxygen plasma treatment. ESR analysis indicated the introduction of peroxy radicals by oxygen plasma treatment, and the intensity of the radicals increased with increasing the applied power. Significant decrease in radical concentration was observed especially for the samples treated with higher powers when the samples were kept under the atmospheric conditions. As a conclusion, RF plasma, causes changes in the chemical and physical properties of the materials depending on the applied parameters, and can be used for the creation of specific groups or radicals to link or immobilize active molecules onto the surface of a material.

Keywords: PMMA; oxygen plasma treatment; contact angle; SFE; XPS; ESR

Introduction

Low cost, good mechanical properties, and chemical passivity of PMMA make it one of the most commonly used polymers in industry.[1,2] In general, PMMA has a low polydispersity index, high molecular weight, excellent optical, electrical, mechanical properties, and environmental stability.[3] It is a polymer of choice for many industries such as biomedical, automobile, aircraft, etc. In the biomedical field, PMMA is extensively used for intraocular lenses, hard contact lenses, dentures, artificial kidney, and bone cement,[4,5] and it is also especially preferred for the production of micro-electro-mechanical systems, microarrays, biosensors, and in DNA hybridization, etc.[6] Still some modifications may be needed to enhance its surface properties. The techniques used for surface modification are many, such as, ozone treatment, chemisorption, gamma or UV irradiation, laser, ion beam, electron beam, flame, and plasma treatment.[7–9] Among these, plasma treatment is one generally preferred because of the capability of creating surfaces with different properties from a single sample by changing the applied plasma parameters such as power, exposure time, gas type, and flow rate.[10–12] In addition to its being environment friendly, dry, solvent free, economical, reliable, and reproducible, it consumes small amounts of chemicals, eliminates the need for sterilization, has low energy requirements, and these make plasma treatment very attractive for the industry.[13–16]

In plasma treatment, accelerated electrons collide with the gas in the plasma chamber resulting in the meeting of the surface with the energetic species like ions, electrons, radicals, and metastables. These energetic species undergo reactions with the surface of the sample and cause a variety of changes in the physicochemical properties of the surface depending on the plasma parameters and the reactor design.[17,18] Main routes of modification by plasma are crosslinking, degradation, formation of new functional groups, ablation, and etching. In the case of inert carrier gases, etching and/or crosslinking dominates, whereas in the use of reactive gases (oxygen, nitrogen, etc.), etching and/or functionalization are the main results.[19,20] Hence, even when the same substrate and the same gas are used, different surfaces can be obtained with plasma application using different parameters.

The focus of the present study was to investigate the influence of plasma parameters on the chemistry and physical properties of

* Correspondence to: Nesrin Hasirci, Department of Chemistry, Middle East Technical University, Ankara 06800, Turkey.
E-mail: nhasirci@metu.edu.tr

a Department of Polymer Science and Technology, Middle East Technical University, Ankara 06800, Turkey

b Department of Physics, Faculty of Engineering, Atılım University, Ankara 06836, Turkey

c Central Laboratory, Middle East Technical University, Ankara 06800, Turkey

d METU-BIOMATEN Center of Excellence in Biomaterials and Tissue Engineering, Ankara 06800, Turkey

e Department of Biological Sciences, Middle East Technical University, Ankara 06800, Turkey

f Department of Biotechnology, Middle East Technical University, Ankara 06800, Turkey

g Department of Chemistry, Middle East Technical University, Ankara 06800, Turkey