Applied Surface Science 279 (2013) 285–292

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Effect of atmospheric oxidative plasma treatments on polypropylenic fibers surface: Characterization and reaction mechanisms

Roberto Nisticò[a,*], Giuliana Magnacca[a], Maria Giulia Faga[b], Giovanna Gautier[b], Domenico D'Angelo[c], Emanuele Ciancio[c], Roberta Lamberti[d], Selanna Martorana[d]

[a] University of Torino, Department of Chemistry and NIS Centre of Excellence, Via P. Giuria 7, 10125 Torino, Italy
[b] CNR-IMAMOTER, Strada delle Cacce 73, 10135 Torino, Italy
[c] Clean-NT Lab, Environment Park S.p.A., Via Livorno 60, 10144 Torino, Italy
[d] Herniamesh S.r.l., Via F.lli Meliga 1/C, 10034 Chivasso, Italy

ARTICLE INFO

Article history:
Received 4 January 2013
Received in revised form 27 March 2013
Accepted 19 April 2013
Available online 26 April 2013

Keywords:
Hernia-repair biomaterials
Plasma treatment
Polypropylene fibers
Surface modification
Oxidation mechanism

ABSTRACT

Atmospheric pressure plasma-dielectric barrier discharge (APP-DBD, open chamber configuration) was used to functionalize polypropylene (PP) fibers surface in order to generate oxidized-reactive groups such as hydroperoxides, alcohols and carbonyl species (i.e. ketones and others). Such a species increased the surface polarity, without causing material degradation.

Three different types of plasma mixture (He, He/O_2, $He/O_2/H_2O$) under three different values of applied power (750, 1050, 1400 W) were investigated. The formed plasma species (O_2^+, O single atom and OH radical) and their distribution were monitored via optical emission spectrometry (OES) measurements, and the plasma effects on PP surface species formation were followed by X-ray photoemission spectroscopy (XPS). Results allowed to better understand the reaction pathways between plasma phase and PP fibers. In fact, two reaction mechanisms were proposed, the first one concerning the plasma phase reactions and the second one involving material surface modifications.

1. Introduction

Surface chemistry finds many applications in polymer science. Plasma treatments [1–4] have recently gained much attention comparing with high energy radiations [5–7] for their ability to modify material surfaces without compromise their intrinsic chemico-physical and mechanical properties. E-beam [5] or γ-rays [6] (the most commonly used high energy radiation treatments), in fact, are especially utilized in sterilization processes, but both methods modify the chemico-physical structure of the original polymeric material, thus the mechanical properties are also altered. In particular, when the treatment is carried out in the presence of oxygen, the process starts with the formation of macroradicals (caused by C—H bonds breaking), leading to polymer oxidation [5,8]. Moreover, many authors [5–8] proposed that all the oxidized species begin to form at the same time, without preliminary hydroperoxides production (as in the Bolland cycle, which is valid for hydrocarbons in solution at high temperatures but not necessarily for solid polymers) [9].

Plasma treatments also present the advantage to be eco-friendly, together with the peculiarity to induce limited modification on the materials surface [2]. Plasma is a distinct state of matter consisting of electrically neutral gases and ionized species. Already present in nature (for example, in polar aurora and solar wind), an artificial plasma can be generated by ionizing a gas, which origins charged particles (positive and negative ions, electrons and/or radicals). Industrially, the gas ionization can be induced by a strong electromagnetic field, applied with a microwave generator, which causes bonds dissociation of reactive molecular species present in the gas mixture.

Plasma are characterized by different parameters, some of which are described in the following.

- The degree of ionization (α) is defined as:

$$\alpha = \frac{n_i}{n_i + n_a} \quad (1)$$

where n_i is the ions number and n_a is the neutral atoms number [4]: it corresponds to the fraction of atoms experiencing ionization phenomena. It is essentially controlled by the temperature.
- The plasma temperature provides information about the thermal kinetic energy per particle. Very high temperatures are usually needed to sustain ionization, whereas low temperatures allow ions and electrons to recombine into neutral species, reconverting the plasma in a gas.

* Corresponding author. Tel.: +39 011 6707533; fax: +39 011 6707855.
E-mail address: roberto.nistico@unito.it (R. Nisticò).

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http://dx.doi.org/10.1016/j.apsusc.2013.04.087

Table 1
Plasma treatment conditions applied on PP fibers.

Samples	Plasma components	Nominal power (W)	Effective power (W)	Time per side (s)	Effective energy density (J/cm^2)[a]
PP01	He	1400	840	15	31
PP02	He/O_2	750	450	15	17
PP03	He/O_2	1050	630	15	24
PP04	He/O_2	1400	840	15	31
PP05	$He/O_2/H_2O$	750	450	15	17
PP06	$He/O_2/H_2O$	1050	630	15	24
PP07	$He/O_2/H_2O$	1400	840	15	31
PP08[b]	–	–	–	–	–

[a] Calculated considering: the effective power applied, an exposure time of 15 s and a total surface area relative to five electrodes of 400 cm^2 overall.
[b] Original not treated sample.

Moreover, plasmas can be classified in different categories, for instance thermal and non-thermal, hot and cold.

- Thermal plasmas contain both electrons and other particles at the same temperature, whereas non-thermal plasmas possess both ions and neutral species at a much lower temperature (normally room temperature, RT), whereas electrons are much hotter.
- Hot plasmas correspond to a fully ionized gas, whereas cold plasmas present only a small fraction of ionized gas species. It is noteworthy that both cold and hot plasmas contain electrons at very high temperature (thousands of degrees Celsius). Cold plasmas, and in general artificial plasmas, find applications in many technological fields, such as industrial metallurgy, surface treatments for coatings, microelectronics, oxidation surface treatment allowing the adhesion of materials and sterilization [10,11].

Aim of this work is to propose a reaction mechanism between an oxidizing plasma and the surface of the polypropylene (PP) material, based on optical emission and X-ray photoemission spectroscopies. Three types of plasma mixtures were selected: the first one constituted by pure He (non-directly oxidative plasma) and should be totally inert, while the other two are originated by He/O_2 and $He/O_2/H_2O$ gas mixtures, respectively, and are largely used for soft surface oxidation treatments. In order to verify the effects of the oxidizing mixtures, also three different values of powers were applied. Optical emission spectroscopy (OES) allowed to characterize plasma ionized species. X-ray photoemission spectroscopy (XPS) and also drop shape analysis (DSA) were the chemico-physical techniques selected for characterizing PP surface before and after plasma treatment. Radiation and plasma-induced polypropylene oxidation have been widely studied but many aspects are still unclear, thus the mechanism of plasma-induced reactions proposed in this paper should help in clarifying the effects of all the actors involved.

2. Experimental

2.1. Materials and plasma treatments

Monofilament sterilized polypropylene meshes for surgical applications were provided by Herniamesh® S.r.l. (Chivasso, Italy). Lightweight (~30 g/m^2) meshes probes were 6 × 11 cm, with 0.32 ± 10% mm of thickness, and fibers diameter of 80 ± 10% μm. Both sides of mesh probes were treated by Clean NT Lab (Torino, Italy) in an atmospheric plasma pressure glow dielectric barrier discharge (APP-GDBD), an open-air plasma apparatus following an already tested procedure [12]. Table 1 summarizes all the experimental conditions used in this work. Helium was selected as gas-carrier for all the experiments. Each treatment was conducted for 15 s per mesh side at three different power values.

2.2. Plasma apparatus

The system consists of an open-air atmospheric plasma pressure glow dielectric barrier discharge (APP-GDBD): two stainless-steel parallel plates of 80 cm × 23 cm × 3.5 cm are available for sample treatment and five electrodes of 80 × 1 cm, providing self plasma impedance adapting glow discharge, generate plasma phase. The type of discharge (filamentary or glow mode) is determined from the space between electrodes and composition of dielectric. The maximum attainable process power is 2500 W (corresponding to 3.75 W/cm^2). An energy loss of about 40% is expected. Table 1 reports both the nominal and the effective power applied for each experimental conditions. For the sake of simplicity figures and discussions will report the nominal power values. A rotary pump and a heating box were used to produce water vapor for the treatment. The unit is a lab scale roll to roll version of an industrial production size system (it allows to work in continuous) and allows developing dedicated functionalization processes directly scalable up and transferable to industrial production. The picture of the apparatus is reported in Scheme 1.

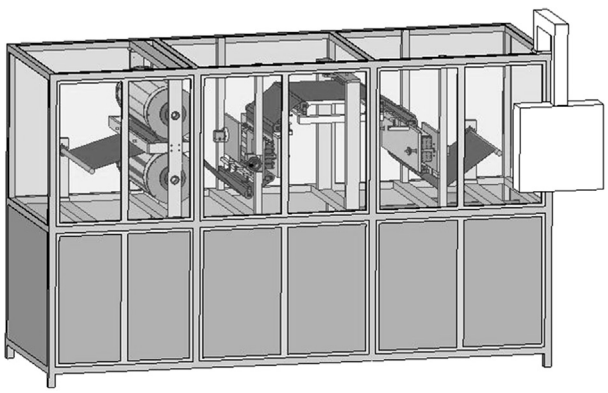
2.3. Methods

X-ray photoemission spectroscopy (XPS) studies were carried out by a Versa Probe 5000 from PHI electronics, using Summit as software. Spectra were analyzed using Multipak 9.0. Al Kα radiation (1486.6 eV), having a beam diameter of 100 μm, was used as X-ray source.

C 1s signals were analyzed. Each decomposed spectrum was obtained by normalizing each peak area to the experimental curve.

Optical emission spectroscopy (OES) was performed by using an Ocean Optic spectrometer LIBS2500 2plus-optic probe QP600-2-SR/BX, using integration times (optical scan) of 100 ms.

Drop shape analysis (DSA) was performed by using a Kruss DSA 100 with 25× optical zoom available. The experiment was done



Scheme 1. Experimental set-up relative to the lab scale roll to roll plasma apparatus.