Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Surface & Coatings Technology 200 (2005) 14 – 20

SURFACE & COATINGS TECHNOLOGY

www.elsevier.com/locate/surfcoat

Processing of polymers by plasma technologies

F. Arefi-Khonsari[a,*], M. Tatoulian[a], F. Bretagnol[a], O. Bouloussa[b], F. Rondelez[b]

[a]*Laboratoire de Génie des Procédés Plasma et Traitements de Surface, Université Pierre et Marie Curie, ENSCP, 11 rue Pierre et Marie Curie, 75231 Paris cedex 05, France*

[b]*Laboratoire de Physico Chimie Curie, Institut Curie, 11 rue Pierre et Marie Curie, 75005 Paris, France*

Abstract

In this paper plasma processing of polymer films and particles is examined by coating and noncoating plasmas. OTS-SAM (octadecyltrichlorosilan self-assembled monolayers) grafted to silicon wafers were used as a model to mimic the structure of PE. The authors believe that the difference by a factor of three in the etching rate between SAM and PE films in ammonia plasma is the consequence of their quasi-crystalline arrangement, compared to the amorphous PE films. For the surface treatment of polymer particles a fluidized bed low pressure plasma has been used. With the help of LDA (Laser Doppler Anemometry) measurements the real time during which the particles were exposed to the plasma was determined. A coating plasma such as allylamine was used to obtain tailored material presenting amino groups on particles. The development of the quantitative chemical derivatization assisted by UV–Visible measurements showed that it was possible to incorporate up to a maximum of 110 nmol of amino groups per gram of powders under specific conditions. Moreover, by using appropriate blocking agents, this derivatization technique allows to differentiate between primary, secondary and tertiary amino groups.

Keywords: Plasma; Degradation; Ammonia; Allylamine; Beads; Stability; UV derivatization

1. Introduction

The plasma technique is a dry process which can tailor polymers in different forms: webs, fibers, particles, etc., in order to modify their surface properties without changing their intrinsic bulk properties. The examples of technological applications of plasma processed polymers are numerous in the field of automobile industry, microelectronics, decoration or packaging, biotechnological applications, biomedical applications, etc. [1].

There are two ways to modify the surface properties of polymers either by introducing new functional groups by surface grafting using noncoating plasmas or by deposition of organic or inorganic films with the desired properties using coating plasmas. In the first case, i.e. surface functionalization, the energetic particles and photons generated in a nonequilibrium plasma strongly interact with the polymer surface, usually via free radical chemistry. Three major effects are normally observed in this case: (1) functionalization, which can lead to covalent bonds suitable for attachment of other coatings; (2) cross-linking, which can cohesively strengthen the topmost surface layer; (3) surface ablation, which can also be used for surface cleaning (removal of organic contamination from the surfaces, i.e. dust, process residues, etc.). Surface ablation can also occur during plasma deposition of organic precursors (CAP, Competition between Ablation and Polymerisation) studied for the fist time by Yasuda et al. [2]. In fact scission of the chemical bonds in plasma-surface interactions can lead to ablation of deposited layer. This is an inevitable process which should be taken into account when processing polymers either by using coating or noncoating plasmas.

In the case of the surface treatment of conventional polymers, the different effects mentioned above are difficult to separate and analyse, due to their inherent structural and chemical complexity. Their structure is generally amorphous, with random orientation of the chains, as well as their chemical composition which is often not well defined.

---

* Corresponding author. Tel.: +33 1 46334283; fax: +33 1 46235813.
E-mail address: farzi-arefi@enscp.fr (F. Arefi-Khonsari).

0257-8972/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2005.02.184

This can be a consequence of functional additives, such as lubricants, anti-oxidants and light protective agents, and of non-polymerised residual monomers. Indeed such low molecular weight chains can migrate to the surface and modify it in a non-controlled manner and could interfere in the investigation of the chemical modifications introduced by the plasma. On the contrary, no such problems exist in the case of Self-Assembled Monolayers (SAM) on oxidized silicon wafers. That is why the first part of this paper will be devoted to the study of the ablative effect of an ammonia plasma on octadecyltrichlorosilane (OTS) self-assembled monolayers deposited on oxidized silicon wafers [3]. OTS-SAM layers provide a straightforward model for polyethylene (PE) films since their alkyl chains contain mostly methylene groups. Another advantage of SAMs on silicon wafers is their planar geometry that allows the use of optical ellipsometry to measure the layer thickness and its eventual modification during the plasma treatments; the sensitivity, in fact, is such that even a change of 0.1 nm can be detected.

The second part of this paper will be devoted to the surface processing of polymer beads and particles in a low pressure fluidized bed reactor. In order to have a better understanding of the behavior of the particles in the fluidized bed, LDA (Laser Doppler Anemometry) was used to determine the concentration and velocity of the particles. Since polymer beads are characterized by their high specific surfaces rising up to few hundreds of m^2/g, higher reactivity can be expected for such materials. Consequently, innovating processes with high sensitivities can be developed by plasma treatments of powders and beads for the preparation of the interface required for the immobilization of molecules with a biological interest. In order to obtain tailored polymers presenting amino groups on particles, particularly interesting for immobilization of biomolecules, noncoating plasmas such as N_2 and NH_3 [4] and coating plasmas such as allylamine [5] were used in this reactor. In this paper, however, only results concerning plasma polymerization of allylamine will be presented. The development of a quantitative chemical derivatization technique assisted by UV–Visible measurements has provided the possibility to determine the total number of amino groups per gram of powders. Moreover, by derivatiziting with appropriate blocking agents, it has been possible to differentiate between primary, secondary and tertiary amino groups. Finally the stability of the deposited films upon washing will be discussed.

2. Experimental

The details of the experimental set up used for the plasma treatment of polymer films have been described elsewhere [6]. It consists mainly of a bell jar glass reactor with a non-symmetrical configuration of electrodes. Low frequency power (70 kHz), provided by an industrial generator from STT-France, was capacitively coupled to the hollow blade type electrode through which the gases were introduced. The polymer film (22×22 cm^2) was rolled on the grounded cylinder which rotates in front of the high voltage electrode. The power density used in this discharge was in the range 1–3 W/cm^3. The silicon wafers were fixed on the cylinder by a double-face scotch tape, while the flexible polymer films were simply rolled on the cylinder surface (length 22 cm and diameter 7.0 cm). Polyethylene (PE) films were obtained from BASELL and ATOFINA and used as received. The films were composed of three layers and had a total thickness of 150 μm. The outer surfaces are low-density polyethylene whereas the inner core is of high-density polyethylene (PE). Bi-stretched polypropylene (PP) films were provided from BOLLORES Technologies.

The fluidized bed reactor (FBR) used for the surface treatment of beads consisted of a cylindrical Pyrex glass tube of 30 mm internal diameter and 600 mm height. The details of the experimental set-up are explained elsewhere [4]. Low Density Polyethylene (LDPE) powders (density: 920 $kg.m^{-3}$; diameter: 350 μm) supplied by Goodfellow were fluidized by mixtures of allylamine/Ar that passed through a porous glass plate. A capacitively coupled system composed of two external electrodes (distance between the two electrodes: 6 cm) was placed at the same level as the fluidized bed. The plasma is maintained by radio frequency energy generated by a SAIREM generator (power range from 0 to 300 W) with a matching box.

In order to have a better understanding of the behavior of the particles in the fluidized bed, LDA (Laser Doppler Anemometry) was used to determine the concentration and the velocity of the particles. A 300 mW Ar* laser source with λ=514.5 nm was used. The principle of this technique and the system have been described in a previous work [7].

3. Results and discussion

3.1. Plasma processing of polymer films by noncoating plasmas

The bell-jar type reactor with the nonsymmetrical configuration of electrodes allowed for the first time to investigate the surface modification on polymers submitted to a low pressure plasma for very short treatment times (milliseconds to a few seconds) [8]. Surface treatment of polypropylene has been carried out in this reactor in plasmas of nitrogen, ammonia [9], as well as mixtures of helium and ammonia [10], in order to obtain stable adhesive properties to aluminum [11]. Ammonia plasma gave rise to a nitrogen uptake of the polypropylene surface which reached a plateau (N/C=10%) for treatment times as short as 0.1 s. d'Agostino et al. used pulsed RF discharges in ammonia and found high selectivities for short treatment times [12]. Recently Ohl et al [13] investigated 13.56 MHz and 2.45 MHz CW and pulsed discharges in ammonia and showed a high nitrogen uptake of polystyrene (PS) films at short treatment times, in