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Polypropylene surface modification by active screen plasma nitriding

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ABSTRACT

Here we describe the use of low energy plasma immersion with active screen as a convenient approach for polypropylene (PP) surface modification. Employing a stainless steel cathodic cage coated with carbon in order to prevent the sputtering of iron from the grid and its deposition onto the polymer sample, the physical chemical properties of PP surface could be effectively modified through the plasma-induced incorporation/formation of nitrogen- and oxygen-containing species. The areal densities of these elements depended on the plasma excitation source, as determined by Rutherford backscattering spectrometry (RBS). Newly formed C–O, C–N, and C=O/O=C–O/N–C=O bonds along with C–C linkages from the PP backbone were identified at the near surface region of the specimens by X-ray photoelectron spectroscopy (XPS). The insertion of such polar reactive functionalities was further confirmed by a substantial decrease in the water contact angle upon plasma treatment. Scanning electron microscopy (SEM) analysis revealed that while no major changes in the morphology occur upon DC plasma treatments as compared to untreated samples, the use of pulsed plasma consistently leads to the formation of cracks at the surface. The herein reported approach is an attractive tool for environmental friendly low-cost surface engineering of novel materials.

1. Introduction

Control of surface properties is paramount in materials science due to the fundamental fact that the interactions with the surrounding environments occur through this interface [1], which often needs to be engineered so as to meet very specific requirements for practical applications. Diverse surface treatment techniques aimed at control of wettability [2,3], biocompatibility [4], adhesion, and tribological characteristics (friction, lubrification, and wear under shear), have thus been continuously and successfully developed in both academy and industry [1,5].

In the case of polymeric systems, there is a huge interest in modifying surface properties [6,7], which sometimes hinder a better exploit of their usually attractive bulk properties (e.g.: strength to weight ratio, transparency, thermal stability, easy processing) [5,8,9]. The strategies undertaken in this direction resort, in most cases, on methods that consist in a combination of chemical and physical processes such as selective segregation (i.e.: preferential enrichment of one of the components of a polymer blend to the surface), etching, oxidation, flame, plasma, electron beam, and UV irradiation technologies [5,8,10]. Certainly, a wide range of chemistries apply to surface functionalization of polymers [6], but the inherent use of large quantities of solvents, reactive species and stringent conditions contrasts with the demand for green (environmental friendly) processes, hence limiting the industrial use of wet chemical processes.

Plasma treatments definitely offer many advantages over conventional approaches, since they are characteristically dry processes, that do not generate chemical waste, while allowing for facile control of superficial chemical composition of polymers simply by adjusting the stoichiometry of the gas inlet during the processes [5,7,9]. The highly energetic species generated in plasma can induce multifaceted structural rearrangements not only in the upper molecular layers of a polymer surface but also deep into several hundreds of nanometers. In general, the plasma can interact with the polymers in two ways: through the formation of cross-linkages between adjacent polymer chains, and chain scission. The former usually improves the surface properties while the latter causes polymer degradation. The resulting interfacial chemical composition and structure will depend on the plasma parameters (ion implantation) such as the gas composition and the energy of the implanted species [6–8,11]. Previous work showed, for instance, that three-dimensionally cross-linked surface layer with much improved hardness and wear resistance can be obtained by properly selecting ion implantation parameters for the treatment of polymeric materials [12].

Due to the electrical insulating characteristics of most polymers and to their relatively low thermal degradation temperature, surface modification technologies based on conventional DC plasma cannot

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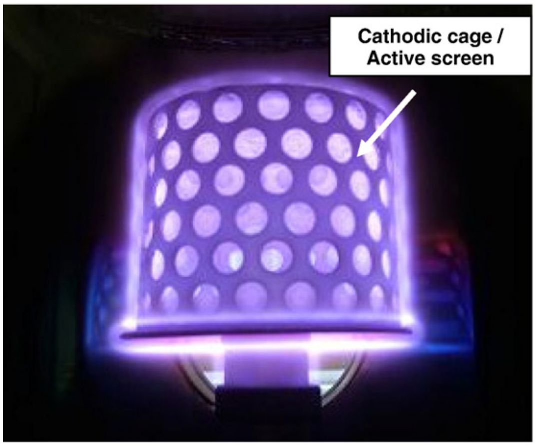

Fig. 1. Digital photograph showing the carbon-coated stainless steel cathodic cage used in this work.

be applied. In this context, the active screen plasma process emerges as a candidate for the modification of polymeric surfaces. In this technique, the cathode of the system surrounds the polymeric sample, which is held in a floating potential. The cathode is a grid usually called “active screen”. Around the grid, there is a high density of excited and electrically neutral gaseous species that may diffuse from the plasma to the polymer surface. Moreover, the typical energy of these active species is lower than the energy of the ions accelerated toward the cathode, thus reducing overheating that can potentially cause melting or thermal degradation of polymers. Further details of the technique can be found elsewhere [13,14]. In a pioneer investigation, Li and Bell [15] evidenced the great potential of plasma nitriding of ultrahigh molecular weight polyethylene for improved hardness and wear resistance.

In the present work, we report a convenient approach for polymer surface modification that makes use of low energy plasma immersion with an active screen [14]. Operating in presence of a carbon-coated cathodic cage [16] under either continuous or pulsed plasma excitation, the proposed undemanding (mild conditions) plasma treatment system can be easily scaled-up for complex sample geometries. Although no medium and high energy ion acceleration step was used to conduct ions from plasma into the sample, surface modification and functionalization of polypropylene (PP) was effectively achieved using this method. PP is a widely used material whose characteristic surface energy is low as can be anticipated from its chemical structure, thus implying in, for instance, poor adhesion towards paintings [17], and membrane fouling [18]. Therefore, original approaches to modify the PP surface properties are exceedingly welcome. Besides, this surface modification/functionalization approach can be possibly extended to other polymers.

2. Experimental section

2.1. Plasma-induced surface modification

Polypropylene (PP; Braskem H503 without additives; $d = 0.907$ g/mL; average $M_w = 470{,}000$ g/mol) was injection molded (injection temperature = 225 °C; mold temperature = 4 °C), and cut into 10 mm × 10 mm × 3 mm specimens, whose degree of crystallinity was 49%, as measured by differential scanning calorimetry (DSC) and X-ray diffraction (XRD). These samples were firstly ultrasonically cleaned in acetone for 30 min.

Surface modification by active screen plasma nitriding was subsequently performed using a cylindrical stainless steel vacuum chamber (∅ = 280 mm) equipped with an active screen that worked as a cathode (∅ = 80 mm; height = 65 mm; see Fig. 1). The distance between the samples and the cage was ~55 mm. The chamber was pumped to a base pressure of 3.5 Pa, and during treatment the pressure was maintained at 35 Pa by adjusting the N_2 flow. Current densities of 0.15 and 1.5 mA cm^{-2} were achieved exciting the plasma with a DC (~−440 V) and a pulsed (40 μs at −780 V) source, respectively. Treatments duration varied from 15 to 75 min for the DC plasma and from 3 to 15 min for pulsed source. In order to avoid heating the samples at temperatures higher than 100 °C, they were leaved to rest for 5 min in N_2 flow every 3 min of pulse plasma treatment.

2.2. Physical–chemical characterization

The chemical composition of the near surface region of the samples was determined by Rutherford backscattering spectrometry (RBS). The areal densities of the chemical species incorporated during treatment were determined within an estimated 10% uncertainty [19]. The chemical environment of these species was accessed by X-ray photoelectron spectroscopy (XPS) using an OMICRON-EA125 station and a Mg Kα (1253.6 eV) radiation source. Scanning electron microscopy (SEM) imaging experiments were carried out using a Philips XL-30 microscope in order to characterize the surface morphology before and after plasma treatment.

3. Results and discussion

Conventional plasma nitriding processes have been extensively applied for surface treatments aiming at the improvement of hardness and wear resistance of metals and alloys. However, the use of such convenient techniques in soft matter modification is still rather unexplored. Most likely, this is due to the insulating nature of most of the polymer systems, which cannot therefore be adequately polarized so as to function as cathode. Other strategies have thus been devised in order to overcome such problem, and enable surface engineering via undemanding plasma processes. Among other approaches, the recent development of active screen techniques where the plasma is

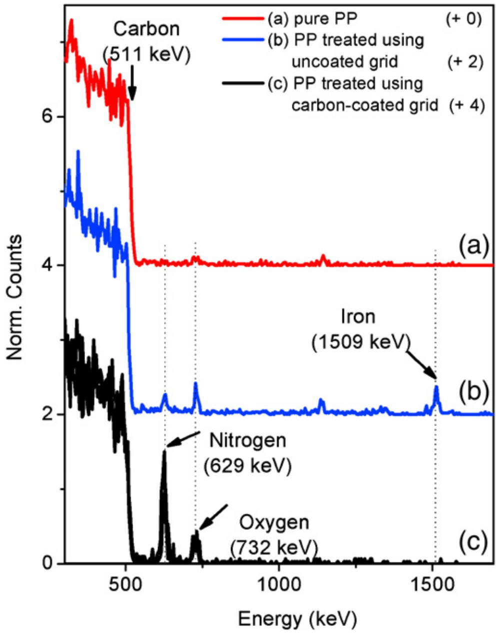

Fig. 2. RBS spectra for untreated PP, and 15-min DC plasma-treated PP using uncoated and carbon-coated stainless steel cathodic cage working as active screen, as indicated. The spectra were obtained with a 2 MeV He$^+$ beam in normal incidence and the backscattering yield measured at 165°. The energies corresponding to He backscattered at the surface by C, N, O, or Fe are identified.