Surface Modification and Hydrophobic Recovery (Aging) of Polyolefin Exposed to Plasma

Taís Felix, Valdir Soldi, and Nito Angelo Debacher

Abstract The hydrophobic characteristic of polymers is considered a limiting property for its applications. To some extent, this has been overcome by techniques such as non-thermal plasma, which, even with a few seconds of application, can increase the surface energy and hydrophilic character of polymers. However, this technique is associated with advantages and disadvantages. Surface degradation related to oxidation and crosslinking are considered irreversible changes, in most cases, while the hydrophobic character is quickly restored, presenting a challenge to researchers all over the world. As a reversible behavior, efforts have been made to understand this particular characteristic of the hydrophobic recovery (or the aging effect) of polymers. The application of non-thermal plasma on polymeric surfaces has also been used in biomedicine as a sterilization device to control the growth of biofilms, as well as to increase the biocompatibility of prosthetic surfaces. This chapter discusses some particular characteristics of polyolefins exposed to plasma.

1 Introduction

The environment generated by non-thermal plasma discharges is rich in highly reactive particles such as ions, electrons, radical species and UV radiation [1]. This enables the technique to be used to improve surface interactions and chemical changes in gas and liquids as well as in organized structures like condensed matter, exceeding the limits of conventional chemistry.

There is great interest in the improvement of current plasma techniques, mainly due to the low cost of implementation and low generation of waste associated with the process. These factors lead to very promising applications and, currently, there are

T. Felix (✉) · V. Soldi · N. A. Debacher
Chemistry Department, Federal University of Santa Catarina, Santa Catarina, Florianópolis
88040-900, Brazil

V. Soldi
Instituto Brasileiro de Tecnologia Do Couro, Calçado e Artefatos, IBTec, Novo Hamburgo, Rio
Grande Do Sul 93334-000, Brazil

many researchers addressing the application of non-thermal plasma in the degradation and reforming of polluting gases, the treatment of effluents, sterilization and the functionalization and degradation of surfaces [2–8]. Thus, some surface characteristics, such as the roughness, wettability and chemical composition, can be changed in response to a set of reactions promoted by the plasma.

In particular, properties conferred by non-thermal plasma (NTP) to polymeric materials have been investigated not only considering the wide range of applications identified for polyolefins, but also due to the relative simplicity and eco-friendly characteristic of the technique. Immediate effects on polymeric surfaces characteristic of plasma techniques include etching, crosslinking and chemical functionalization. However, there are also long-term effects, such as structural and conformational changes, and hydrophobic recovery (HR) or aging, but these do not restrict the feasibility of using polymers, given their attractive mechanical properties [9].

The direct application of NTP under atmospheric pressure conditions is an important tool used in sterilization processes applied to tissues in patients undergoing post-surgical treatment, wounds, catheters, and tools, etc. In general, the efficiency of sterilization to eliminate bacteria and viruses, without compromising the surface of the base or causing toxicity to living tissues, is obtained by applying an NTP with a low power dielectric barrier discharge for a few seconds [10].

In addition to sterilization, exposure to plasma can improve the quality to polyolefins and, in particular, polypropylene for application as a biosensor through the immobilization of anti-biofilm molecules or as separation membranes in hemodialysis. Recently, the co-immobilization of biomolecules on the polypropylene surface after activation by plasma has also been investigated [11]. Polyethylene can also be used for cardiovascular or orthopedic prostheses after exposure to plasma, which makes them more biocompatible than conventional materials and prolongs their mechanical resistance [12].

The usual techniques for the evaluation of polymeric surfaces exposed to plasma are image analysis and the evaluation of the chemical environment and structural changes. The magnified images provided by microscopy (optical, scanning and transmission electron, atomic force microscopy) provide structural information and are considered fundamental for this type of investigation.

High-resolution field emission gun scanning electron microscopy (FEG-SEM), for instance, provides important information on the surface erosion produced by plasma attack. However, the operation temperature of the light source needs to be known in order to avoid interference in the surface roughness.

The chemical environment can be analyzed by qualitative techniques such as infrared (vibrational) spectroscopy (IRS), based on the ability of the surface to absorb, emit and scatter radiation after applying electromagnetic radiation.

Among the quantitative techniques for the determination of chemical groups, X-ray photoelectronic spectroscopy (XPS) is a notable non-destructive technique used to analyze the binding energies of the core levels with intensity precision. This provides valuable information regarding the composition and chemical structure of polymeric surfaces and is considered a mandatory technique for surface analysis before and after exposure to plasma [13]. A technique associated with transmission

electron microscopy (TEM) is energy-dispersive X-ray spectroscopy (EDX), used for elemental analysis, from which qualitative data on the chemical composition of the surface can be obtained.

In thermogravimetry analysis (TGA), the physical properties of the polymer, related to the degradation temperature under an oxidizing or inert atmosphere, can be determined. Degradation events provide information on the thermal stability, degree of crystallinity and oxidation reactions, which can be used to evaluate the presence of crosslinking and fragments associated with plasma exposure. Simultaneously, derivative thermogravimetry (DTG) allows the initial and final temperatures of thermal degradation to be defined and the area proportional to the mass variation to be estimated.

Water contact angle (WCA) analysis is carried out to evaluate the free surface energy, wettability and adhesive properties related to polar and dispersive components and, therefore, the hydrophilic characteristics. However, the roughness and smoothness of the surface need to be taken into account since they influence the contact angles.

The subjects discussed in this chapter are closely linked but, to allow a better understanding, they are divided into two topics. The first addresses the degradation of polymeric surfaces exposed to non-thermal plasma with an emphasis on polyolefins and the second is related to the definition of hydrophobic recovery (or aging), its characteristics and some unpublished research results highlighting its effect on polyolefins.

2 Surface Modification of Polyolefins Treated by Plasma

In general, polymers are versatility materials due to their mechanical properties. They can therefore be used in almost all technological areas in their pure form, as polymeric blends or associated with other materials in composites or nanocomposites [14–17].

There are two essential characteristics that define most of the properties of a polymer: the chemical structure and the molar mass distribution pattern [18], since these directly determine the cohesive forces, the packing density and the molecular mobility of the chains. Indirectly, these characteristics play an important role in the morphology and the relaxation phenomenon. The different chemical structures, compositions and functional groups of polymers determine their resistance to chemical attack. Under a plasma ionizing radiation atmosphere, for example, aromatic and conjugate structures are more resistant to photon absorption or the collision of excited or charged particles. On the other hand, aliphatic chains undergo hydrogen abstraction, forming $C^\bullet$ radicals, which easily result in oxidation sites, double bonding and crosslinking [9]. Figure 1 shows the main degradation reactions that occur under non-thermal oxygen plasma.

The susceptibility to etching and the successive reactions that occur on the polymer surface are directly related to the mechanical and chemical resistance of the polymeric
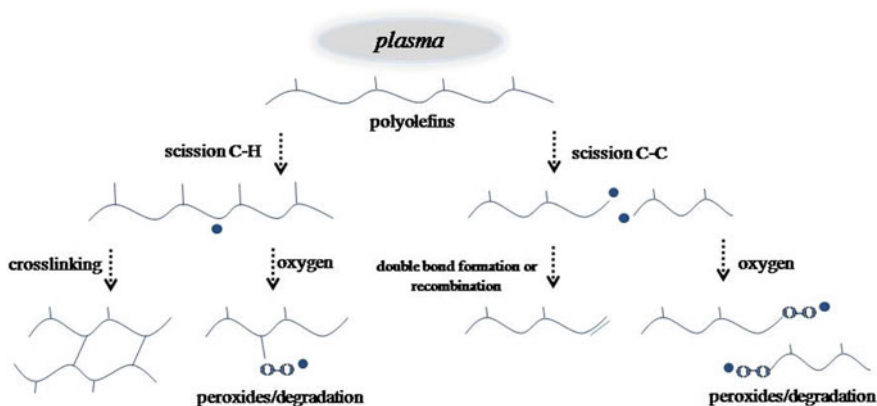
Fig. 1 Main degradation reactions that occur under non-thermal oxygen plasma (adapted from [8])

matrix. Polymers with high resistance to oxidation, molar mass, density and hardness generally show high resistance to degradation. Plasma can cause the erosion of several micrometers of a surface, depending on the hardness of the material and also on the exposure time and distance between the electrodes. Figure 2 shows in detail the erosion of a polymer surface caused by non-thermal oxygen plasma [19, 20].

Figure 3 shows the spectra obtained from the X-ray photoelectronic spectroscopy (XPS) analysis of high-density polyethylene (HDPE) samples, unexposed and exposed to non-thermal oxygen/argon plasma (NTP). Note the increase in the groups containing oxygen (C-O) and a considerable decrease in the intensity of the C1s peak (C–C) in relation to the unexposed sample [21].
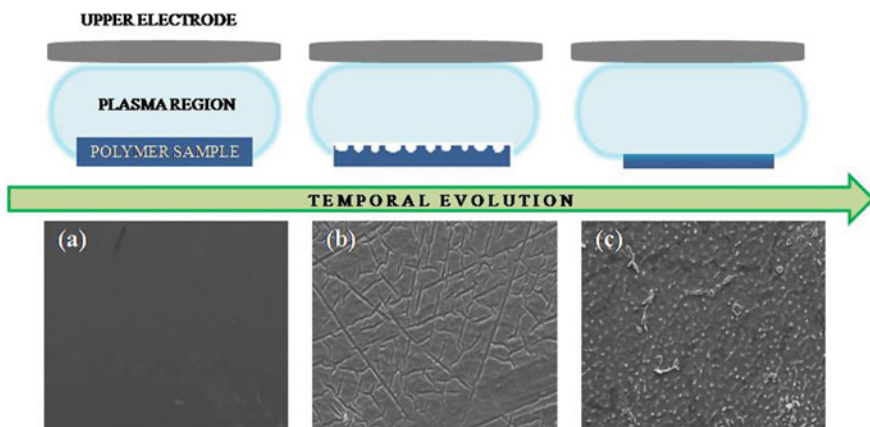

Fig. 2 Erosion on a polymer surface after exposure to non-thermal oxygen plasma: **a** untreated surface; **b** and **c** after 20 and 30 min of exposure, respectively [19]
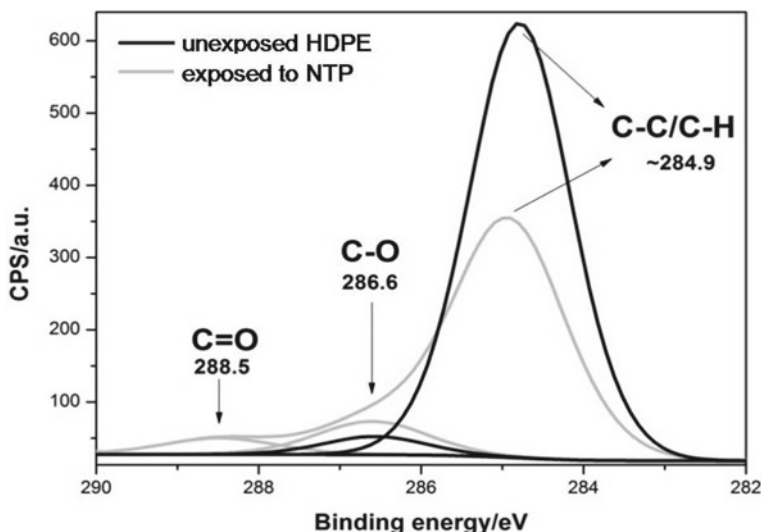
Fig. 3 C1s peaks of high-density polyethylene unexposed and exposed to Ar/O$_2$ NTP for 60 s (8 mbar, 80 W) [21]

Many low molar mass fragments are formed through the oxidation mechanism. In some cases, spectra obtained by XPS can be used to quantitatively estimate the degree of double bonds formed (C=C), and mass spectrometry provides information on crosslinking based on an increase in the average molar mass. The new interaction groups generate an increase in density in the polymer and consequently a new orientation, reducing the distances between the fragments of larger chains. Thus, the formation of crosslinking using plasma derived from inert gases has been used to induce stiffness of the polymer surface, a technique known as CASING (crosslinking by activated species of inert gases), since 1967 [22, 23].

The crosslinking phenomenon can start within the first few seconds of plasma application, depending on the polymer matrix. Studies on polystyrene have shown that after 180 s of exposure to O$_2$ plasma the crosslinking reached 80% of the original sample, increasing the molar mass distribution from 80,000 g/mol to more than 18,000 g/mol. In addition, the density of low-density polyethylene increased from $\rho = 0.75$ g/cm^3 to $\rho = 0.79$ g/cm^3 [24]. Chalykh et al. [25] showed that polypropylene, despite losing its biaxial orientation after a few seconds of exposure to plasma, produced a completely different orientation after long exposure as a result of the intersection of the chains. This new conformation is called "chemi-crystallization", and it is also associated with higher density and, consequently, higher resistance [25].

For all polymers, the surface differs from the bulk of a sample with respect to the physical–chemical characteristics, such as surface tension ($\gamma_{S/A}$)- or surface energy, which can result from polar and dispersive energies, this being closely related to the fraction of the exposed macromolecule, consisting of side/end groups of the chains, polar groups or branches. The occurrence of crosslinking, oxidation and degradation,
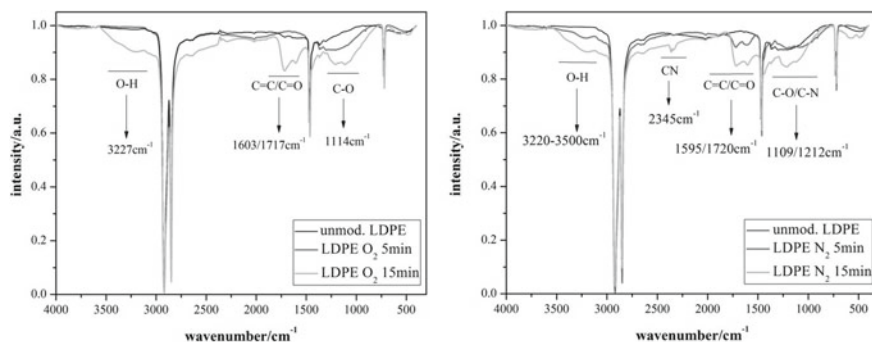
Fig. 4 Sample spectrograms of low density polyethylene unexposed and exposed to O_2 NTP (left) and N_2 (right) plasma treatment, (1 torr, 8 W) [20] (unpublished results)

therefore, may also be dependent on the macromolecular orientation on the surface [26]. Crosslinking occurs in the superficial layer reaching a few micrometers of thickness (Fig. 4) [24]. In this case, the main species responsible for this crosslinking originate from UV radiation and $C^{\bullet}$ radical sites, which are continuously supplied by the oxidizing source [1].

Polyolefins (e.g., polypropylene (PP) and the class known as polyethylene (PE)) are inert and only certain processes, such as those involving oxidation, can increase their free surface energy, making them, for example, printable. In this regard, the application of oxygen plasma to polymer surfaces, either at low or atmospheric pressure, is advantageous, since it provides partial hydrophilization of the surface through functional groups derived from oxygen. An increase in the wettability and adhesive properties of surfaces considered inert is the result of oxidative degradation processes initiated/supported by the plasma. Fig. 5 shows the variation in the roughness, monitored by atomic force microscopy (AFM) as a function of the time of exposure to plasma of three different areas of the sample. The average roughness values for each of the three areas were determined with the aid of the *WSxM* software [27]. As mentioned above, variations in the etching resistance are observed for PP and PE. The microscopy results in Figs. 5, 6 and 7 show that, under the same conditions, erosion on the surface increases for both the PP and PE samples. However the visual aspect of this erosion as well as the size "depth" of the peaks and valleys differ [21].

The 3D images in Fig. 6, for PP, show the changes in the surface topography during the period of exposure to plasma, with successive stages of elevation (light dots) and relaxation (darkened regions). This suggests that the erosion caused by exposure to plasma occurs as fragments are removed layer by layer. For polyolefins, a first stage of erosion occurs after 20–30 min of exposure followed by a second stage. However, the HDPE shows a homogeneous evolution, with only one stage of roughness formation being observed, probably due to its high-density structure. In general, the superficial fraction of the samples that erodes in the first 20–30 min of exposure to plasma appears to be distinct from the bulk of the polymeric sample, presenting
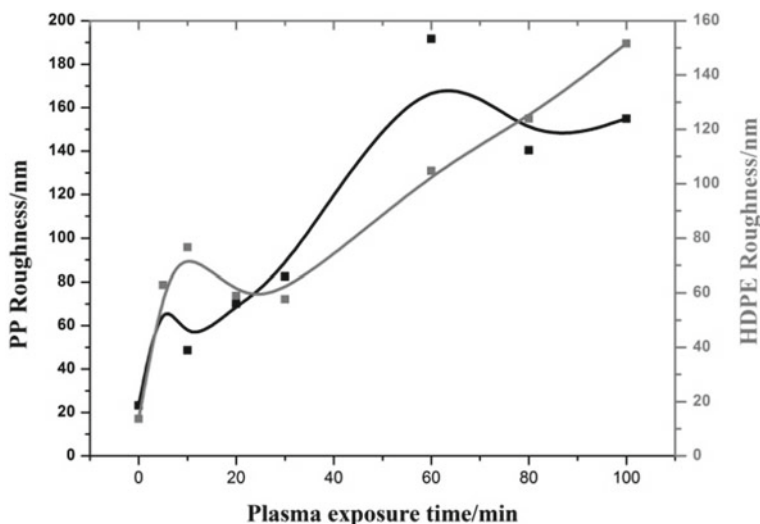
Fig. 5 Average roughness (nm) as a function of the plasma exposure time (min) obtained by AFM, in three different sample areas (5 mbar, 65 W) [21]
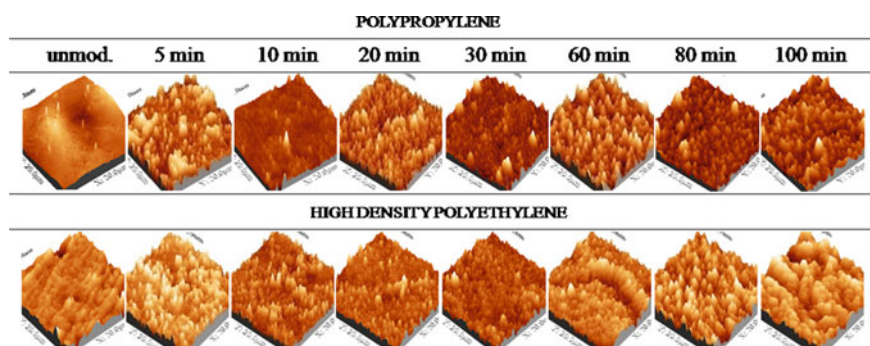

Fig. 6 Atomic force micrographs as a function of plasma exposure time (5 mbar, 65 W) [21]

less resistance to attack, which could be related to the superficial stress caused by the sample preparation. The thickness of the layer that will undergo erosion can vary by a few hundred nanometers, depending on the exposure time and experimental conditions of plasma application.

The erosion of the polymer surface exposed to plasma is also a function of the gas used in the process, the working pressure, the applied power and the exposure time. Friedrich et al. [24] demonstrated that the erosion rate for high and low density polyethylene samples (HDPE and LDPE), in an oxygen atmosphere at 8 Pa and 300 W, was 6 mg.cm^{-2} s^{-1}. Under the same conditions, poly(methyl methacrylate) (PMMA), with functional groups in its structure, showed a higher degradation rate,
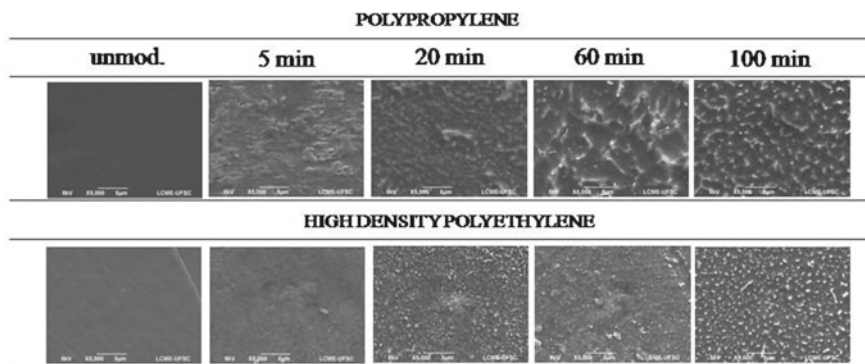
POLYPROPYLENE

HIGH DENSITY POLYETHYLENE

Fig. 7 SEM micrographs as a function of plasma exposure time (5 mbar, 65 W) (5000x / 5 μm scale) [21]

around 11 mg.cm^{-2} s^{-1} [24]. Oxygen plasma produces a more uniform and progressive erosion of the surface when compared to other gases, independent of the polymer structure. The etching rate for a sample of polyethylene terephthalate (PET), exposed to O$_2$/NTP was 6.4 mg.cm^{-2} s^{-1}, while for He and N$_2$/NTP, under the same experimental conditions, the corresponding values were 1.8 mg.cm^{-2} s^{-1} and 0.8 mg.cm^{-2} s^{-1}, respectively [28].

There are negative and positive aspects associated with the techniques used to increase the adhesion or free surface energy, the hydrophilicity and the biocompatibility of polymer surfaces.

As shown in Fig. 8, under identical conditions of NTP exposure, PEEK and PET show similar WCA values and differ only in terms of roughness and *Enterococcus faecalis* adhesion. Despite the original structural and composition differences, these results suggest that the roughness of the surface plays an important role in the microbiological adhesion.

Of the existing methods, those that have the least effect on the physical properties (transition temperature, viscosity, etc.) and mechanical properties (strength, toughness and rigidity) are preferred. In general, the erosion due to plasma exposure is limited to a few micrometers of the interface and the process preserves the bulk of the polymer, which is not the case with conventional chemical erosion processes. The erosion of the surface, in general, improves the quality of polyolefins in a controlled and versatile way.

3 Hydrophobic Recovery (Aging) Effect

The NTP plasma technique is notable for increasing the polar component of polymer surfaces, a term related to polar interactions and hydrogen bonds, which directly contributes to increasing the surface energy [30, 31]. The increase in the polar
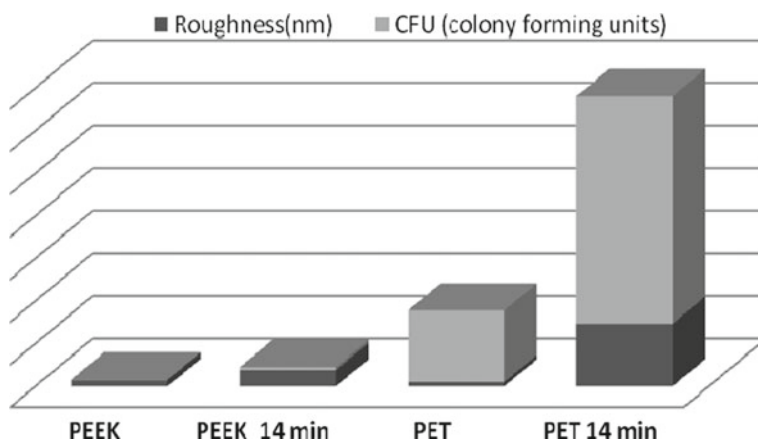
Fig. 8 Roughness (nm) and CFU (*Enterococcus faecalis)* of unmodified PEEK and PET after 14 min exposure to NTP (argon 1.5 L.min^{-1}, 74.6 kPa). WCAs measured after NTP exposure were 33.32° and 33.68°, respectively [29] (unpublished results)

component, however, is short lived due to the effect of physical aging or hydrophobic recovery (HR) [32–36]. This effect is observed through the gradual recovery of the original wettability properties of the surface, which can last for a few minutes or for months, and it can be partially or totally restored to the initial hydrophobic conditions.

The change in the water contact angle (WCA), shown in Fig. 9, has been widely used as a primary tool to observe the hydrophobic recovery of polymer surfaces. Contact angle measurements performed immediately after the application of plasma to polymer samples, in general, show a sudden decrease in hydrophobicity of up to 80% of the initial value [37, 38], followed by an exponential increase over time, reaching a new level of stabilization that does not always match the original contact angle [39–42]. In addition, morphological modifications resulting from
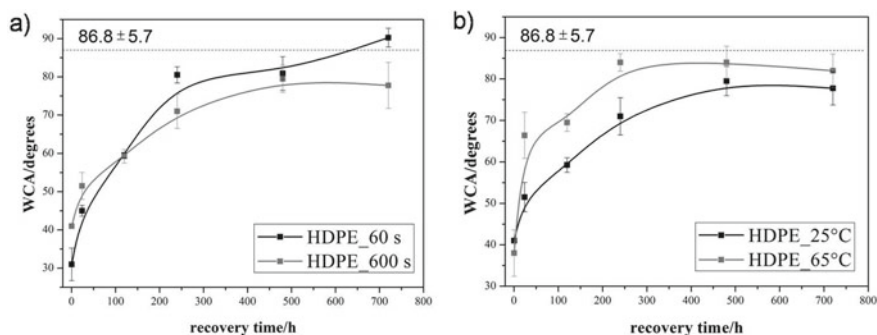

Fig. 9 WCA profiles (degrees) as a function of restoration time (h) for high-density polyethylene: samples **a** exposed to plasma for 60 s and 600 s; and **b** aged at 25 °C and 65 °C [21]

these hydrophilic $\rightarrow$ hydrophobic changes promoted by the plasma have been the subject of studies by several authors using different polymeric matrices [43–47].

Irving Langmuir (1938) [48] reported the effect of hydrophobic recovery using stearic acid salts in water, having verified that hydrophilic groups (dipoles or ionic charges) are reoriented on the surface and cause changes in the properties of the films. He showed that in the liquid phase molecules of different polarities tend to undergo reorientation, minimizing contact with each other. Sharma and Yasuda (1981) carried out studies exposing more complex materials, such as polypropylene, to oxygen plasma and observed that the inserted hydrophilic groups do not rotate as rapidly. The decay phenomenon, related to reorientation of macromolecules occurs in the order of days to months ($>8^5$ s) [49].

The vast majority of studies found in the literature on the HR of polymers, relate the HR effect to the formation of hydrophilic groups and low molecular weight oxidized materials (LMWOM) by surface oxidation. These oxidized species have the ability to undergo reorientation or even leave the surface during aging. This restructuring, rotation and modification of the roughness morphology conferred by the plasma is commonly reported for polymers with a lower crystallinity index, since the fragmentation in amorphous materials is pronounced. With regard to the interface, the restructuring is related to the thermodynamic imbalances between the surface of the polymer exposed to the plasma and the surroundings. This energetic difference is the driving force for neutralization at the interface of charged species, radicals or volatile fragments in post-discharge reactions. There is another active mechanism in most of the material, which, despite receiving less radiation intensity and oxidizing species, responds to surface disturbances, such as crosslinking. The translational entropy associated with increased energy on the surface interferes, in the long-term, with the macromolecules close to the surface and can affect the HR [50].

In addition to the proposed mechanism of HR, based on the surface rearrangement, the release of dimers and trimers and the mobility of macromolecules and their fragments, there may be another effect in action based on the fact that polymeric matrices can retain charge as electrets [51, 52]. Polymers in general are known as insulating materials and are often used to insulate cables and electrical devices. In addition, when compared to inorganic materials, for example, of high molecular order, polymers are considered molecularly disordered and weakly linked with respect to their chains. This characteristic strongly affects the electrical properties, such as the glass transition temperature, related to the crystalline fraction.

The mobility capacity of polymer fragments, such as translation or rotation, is higher in polymers with high amorphous content. In a polymer with a high crystalline index, the amorphous fraction has less mobile segments and, therefore, shows a higher glass transition temperature. Molecules are continuously in motion and the crystalline fraction imposes restrictions on these movements. The high degree of translational and rotational disorder in polymeric materials results in the occurrence of states called traps (Fig. 10). These states and the energy they store after a load stimulus, have a temporal fluctuation. Therefore, charge storage will be dependent on the mobility of the polymer chains/fragments. The impurities present, chain ends,
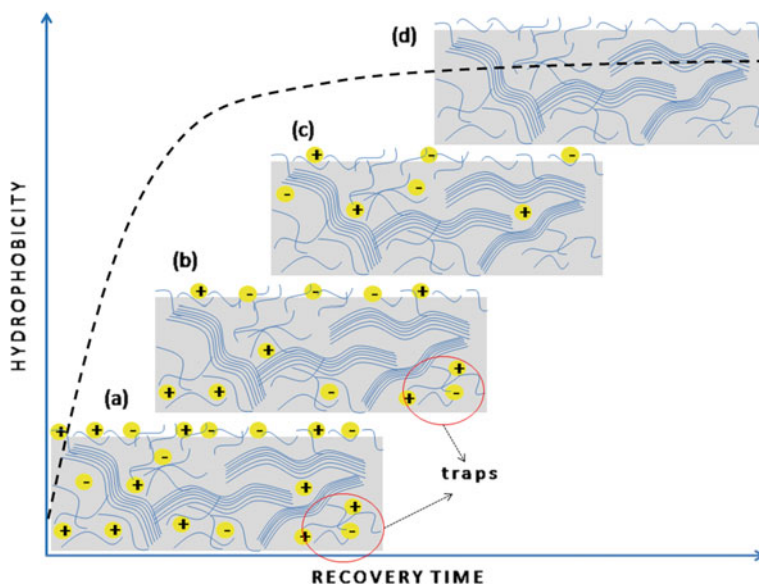
Fig. 10 HR dependence with charges induced by exposure to plasma as a function of time. **a** The charge-carrying fragments at the interface and subinterface, dipole orientation and charge induction; **b–c** start of thermodynamic relaxation in fragments of the amorphous fraction and at the interface, decay of energy in the traps and the compensation of charged species; **d** potential decay and HR [54] (unpublished results)

branches and interfaces of crystalline-amorphous fractions act as traps [51]. In a study by Tompkins and Fisher (2015), HDPE (with a higher degree of crystallinity) showed less initial variation in the post-plasma contact angle and at the end of 30 days the angle had a higher value compared to LDPE. Thus, the amorphous fraction in a polymer is an important factor for HR evaluation [53].

MacDonald and Fallone (1993) studied the effects of X-rays on polyethylene terephthalate (PET) and polytetrafluoroethylene (PTFE) and observed that, after 50 days, for PET 40% of the original surface potential was restored, while for PTFE the corresponding value was 15%. They found that polymers with greater internal resistivity (greater electrical stiffness) conserve more surface potential. Thus, the current induced in the material and how it is stored is dependent on the chemical nature of the material and reflects in the electrical potential observed at the surface [55]. In addition, Borcia et al. [56] showed, through experiments with polysulfone (PSU), that the relationship between the changes in the contact angle ($\Delta(\theta)$) and the number of groups containing oxygen ($\Delta(O/C)$) is not direct. For the PSU, a difference of 31° was observed due to a 89% increase in the amount of oxygen, and for PET there was a difference of 32° due to a $\Delta(O/C)$ of only 13% [56]. Therefore, HR is not only associated with the displacement/disappearance of hydrophilic groups.

If the HR effect is also related to the surface charge, then the compounds or the ability of the environment to interact electrostatically will have an important effect

on this phenomenon. Bormashenko et al. [39] showed that liquids with a molecular dipole momentum (D) "compensate" for the charges on the surface of LDPE samples and delay the HR effect while liquids with zero dipole momentum do not "slowdown" the HR and the surface hydrophobicity is restored (Fig. 11). In addition, for samples kept in a vacuum the HR is suppressed, showing the opposite behavior to that observed in contact with air [39, 57].

Bormashenko et al. [58] studied polyethylene samples and suggested that the collision of ions accelerated by the plasma can modify the organic molecules in a small layer at the interface, by a magnitude of the order of the Debye length. Therefore, the momentary hydrophilization of polymeric surfaces would be related to the capture of ions by the solid and subsequent orientation of the dipoles induced by the electric field in an interfacial fraction of the surface [58]. This concept of charge "storage" after the cessation of the source of radiation or electrical induction is the principle of electrets and is observed in both conductive and insulating materials.

The crossover effect refers to the injection of charged species into the bulk, followed by a slow process of internal polarization, in response to the initial charging stimulus. The decay process appears to be dependent on the initial surface potential applied, duration of discharge, ambient temperature and relative humidity [59]. Other mechanisms responsible for the decay are the bulk neutralization, gas neutralization and surface conduction [60–62]. Although studies have shown that bulk neutralization is the dominant decay mechanism [62, 62, 63, 63], surface electrical conductivity (SEC) can be measured and used to observe the phenomenon. As an example, Fig. 12 shows the WCA and SEC profiles as a function of time and the two profiles are similar. PET samples were exposed to NTP and the contact angle and SEC were monitored during aging.

The WCA and SEC reach the stable regime at around 150 h, so the driving agent of HR is related to the surface conductivity.

The rate and extent of HR can be associated with factors such as temperature, time of exposure to plasma, plasma working gas and stored conditions after exposure [41, 42, 56, 63–65]. Studies show that hydrophobic recovery can be accelerated in LDPE samples by increasing the temperature, which, due to diffusion effects, accelerates the rearrangement of LMWOM and polar groups [64].
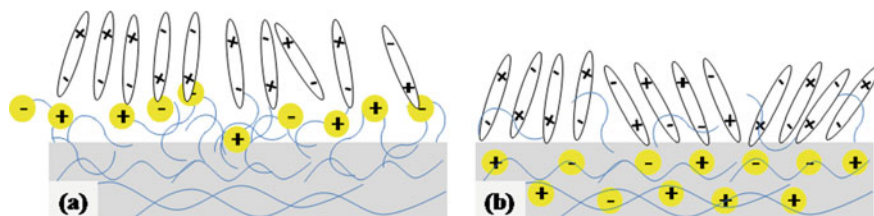

Fig. 11 Plasma-exposed surface: **a** charge-bearing fragments orienting liquid/vapor molecules from the immersion medium (adapted from [38]) and **b** charges trapped in shallow or deep traps, and oriented polar groups of the immersion medium on the surface
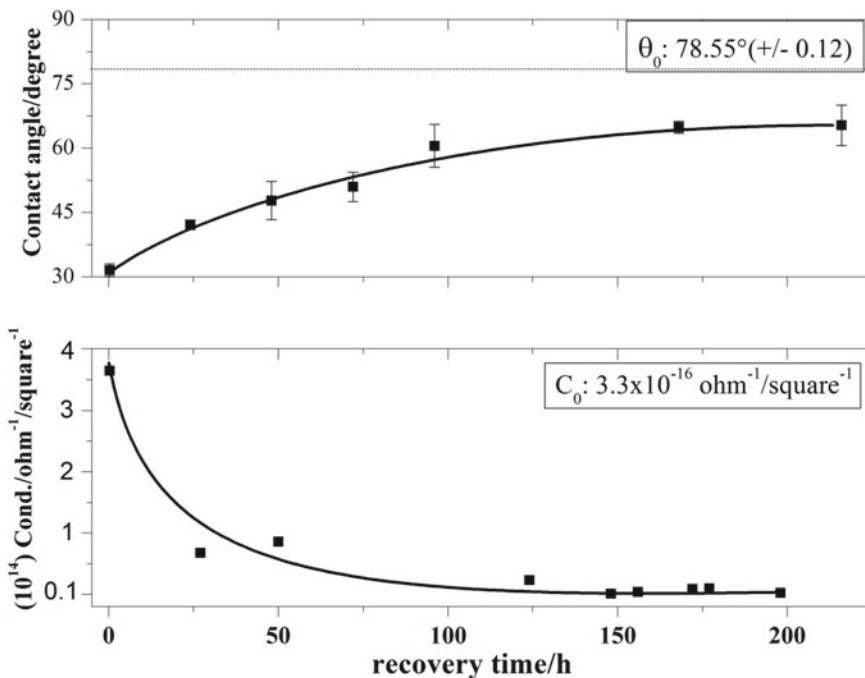
Fig. 12 The profiles for WCA and SEC as a function of time (h) for PET samples exposed to NTP at 8 W [54] (unpublished results)

The delay or attenuation of HR is determined applying experimental strategies, such as the use of hydrogen plasma or recurrent exposure to it, thus obtaining surfaces with a high degree of crosslinking, restricting the mobility of fragments associated with HR (Fig. 13) [66].

The HR also can be attenuated by coating the surface with a different polymer (or blends), and crosslinking by the plasma source itself. A well-known technique

Fig. 13 Profiles showing the variation in WCA over time. The intensity of RH is a function of the crosslinking promoted by the plasma (adapted from [49])
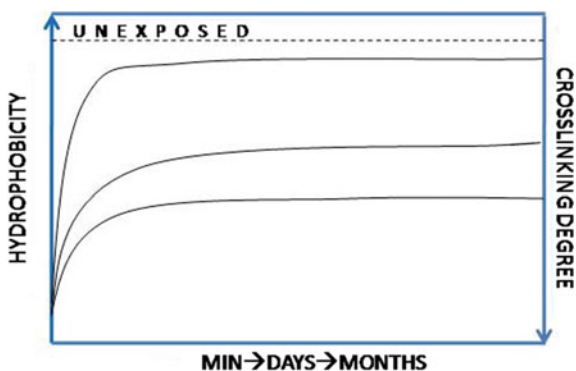
is the grafting of functional molecules using the surface with high free energy after exposure to plasma [67].

Despite all techniques developed to reduce or delay HR, this effect cannot be completely avoided. The decay of this energy is related to the ability to relax thermodynamically, reorganize its structures and disperse the induced charges, either in the amorphous fractions or in the crystal lattices. The presence of impurities, dopants, plasticizers and other additives as charges, also act as charge carriers [68].

In summary, it is possible to describe some factors related to the HR of polymers, including: (i) resistivity of the material; (ii) reorientation and neutralization of hydrophilic fragments on the surface; (iii) reorganization of fragments of macromolecules in the amorphous fraction of the material; and (iv) decay of the surface potential (relaxation) trapped in the material.

Therefore, the HR and the decay of the potential on the surface have a synergistic effect, resulting from energy in the amorphous fraction traps, contaminants or additives, plus the mobility/neutralization of fragments on the surface resulting from oxidation. If the recovery process is monitored based on the WCA, the total or partial restoration of the contact angle will also be dependent on the degree of roughness obtained after the etching/degradation process. The contact angle for rough surfaces needs to be corrected, since the equations commonly used consider perfectly smooth surfaces [21, 69, 70].

4   Conclusions

This chapter describes some characteristics of polymeric surface erosion by nonthermal plasma (NTP) and highlights that oxidation processes constitute the main result of the interaction of a polyolefinic surface with NTP. The amount of species derived from the oxidation, during and after NTP exposure, as well as the final morphological aspect of the surface, is dependent on the properties of each polyolefin. According to reported studies, the higher the degree of crosslinking, the greater the energy or exposure time required for erosion to be continuous and the process seems to occur layer by layer.

Hydrophobic recovery (or simply aging) is a common effect observed in polyolefins after exposure to NTP radiation and oxidizing species, regardless of the atmosphere used, time of exposure and electrical working conditions. This phenomenon can be attenuated using some experimental strategies; however, it cannot be completely avoided. Studies show that the mobility of the fragments formed and the structural rearrangement of the macromolecules help to explain the HR effect, but its behavior is far from been fully understood. For this reason, a new perspective of the HR effect, based on the storage of charges by traps, such as amorphous sites or clusters, impurities and additives, is described, in which the response can be observed from the electrical conductivity on the surface. Polymers, therefore, would act as semiconductors and the electrical response is explained by considering these versatile materials as simple electrets.

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