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Plasma Modification of Polyolefins

Synthesis, Characterization and Applications

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Contents

Plasma Modification on Polyolefin: Necessity and Significance

P. S. Sari, Arunima Reghunadhan, Jiji Abraham, and Sabu Thomas

Abstract The commercial polymers classified under the name polyolefins have been used everywhere. These materials has a long chain structure. Most of the polyolefins need surface modification or compatibilization in order to enhance their dispersion and properties. Plasma modification is one such in which the surface is exposed to plasma, created by different types of gases such as oxygen, carbon dioxide, argon. Etc. Some more techniques such as dielectric and inductive coupling exist for plasma generation. The present chapter is explaining the basics of polyolefins, their structure, properties, need for the modification and the basics of plasma modification.

Keywords Plasma · Polyolefin · Surface modification · Structure · Properties

1 Polyolefins: An Overview

Olefins, or alkenes, are hydrocarbon molecules with at least one double carbon–carbon bond. Polyoleifin is produced by the polymerization of the monomer olefin or alkene. The most common method for the synthesis of alkene is the cracking of crude oil especially steam cracking. First polyoleifin was produced at the end of nineteenth century as a side product during the thermal decomposition of diazomethane [1]. Later several technological advancements came, several scientists and companies introduced many novel methods for the synthesis of polyoleifins. Two majour breakthroughs in the synthesis of polyoleif [1] ins such as Catalytic polymerization and

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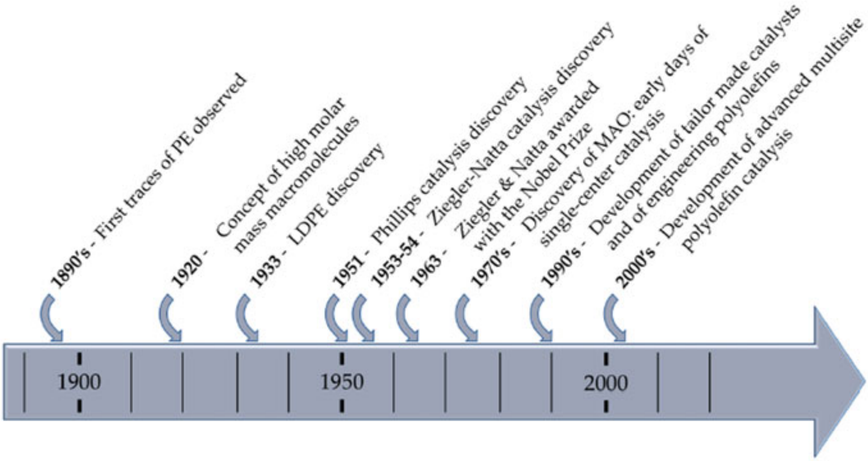

Fig. 1 Major advances in polyolefins development (Adapted from [3])

polymerization using zeigler natta catalyst were introduced in 1950 [2]. Usually Polyoleifins are prepared by free radical process or coordination catalysis. Polyolefins include polyethylene low-density (LDPE), high-density (HDPE), and linear low-density polyethylene (LLDPE), polypropylene (PP), and polybutene (polybutene-1 and polyisobutylene), crosslinked polyethylene (XLPE) etc. Figure 1 highlights the chronology of the development of the polyolefin production and the recent advances leading to performance polyolefins available today [3].

Polyoleifins global demand is increasing day by day. The polyoleifin business accounts for the 63% of the global polymer production [4]. This is because of their lost cost of production, light weight, chemical resistance and a wide range of mechanical properties are possible by copolymerization, blending and introducing additives, etc. Figure 2 represents the global demand of PP, HDPE and LDPE.

2 Classes of Polyolefins

Figure 3 represents the most important polyolefins such Polyethylene (PE), Polypropylene (PP) and Polybutene (PB).

2.1 *Polyethylenes*

Polyethylene is the simplest and, most commonly used polyolefin, its general formula is $(–CH_2–CH_2–)_{n.}$ It is a thermoplastic however, it can become a thermoset plastic when modified. Polyethylene is formed by the polymerization of

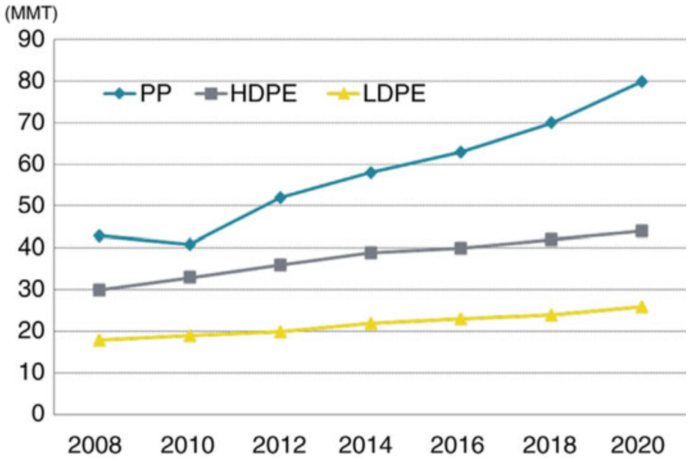

Fig. 2 Polyolefins global demand (Reproduced with permission from [4])

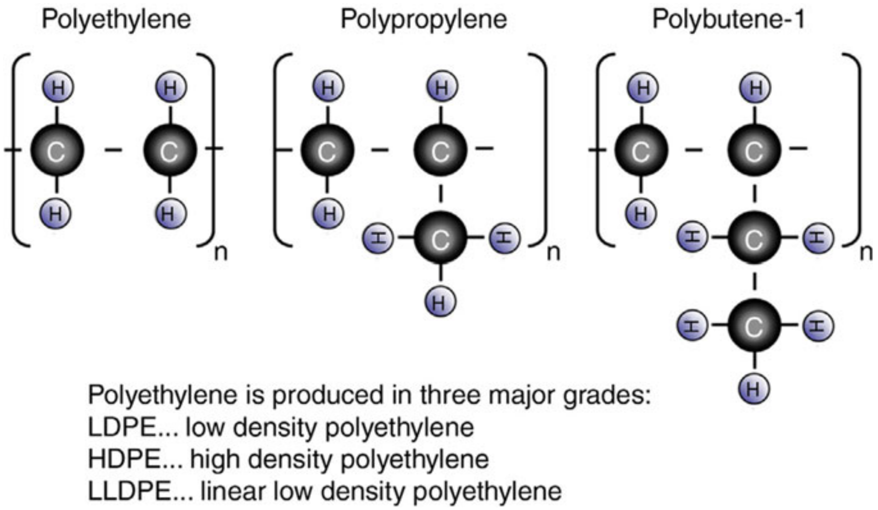

Fig. 3 Skeletal structure of some Polyolefins (Reproduced with permission from [4])

ethylene (ethane, C_2H_4). Ethylene can be prepared either by hydrogenation of acetylene or by dehydration of ethanol. Polyethylene can be produced by any one of the following methods: Radical polymerization, anionic addition polymerization, cationic addition polymerization or ion coordination polymerization. There are 3 majour types of polyethylene: High-density polyethylene (HDPE), Low-density polyethylene (LDPE), Crosslinked polyethylene (XLPE).

2.1.1 High-Density Polyethylene (HDPE)

- High Density Polyethylene (HDPE) is a thermoplastic with linear structure and no or low degree of branching.
- HDPE is known for its large strength-to-density ratio and density can vary from 930 to 970 kg/m^3
- Since the branching of HDPE is very limited, its tensile strength is high as compared with LDPE.
- HDPE, which is characterized by limited branching of the polymer chain, Linear molecules pack together well during crystallization, making HDPE much denser and rigid or more "crystalline" structure (90% crystalline).
- Crystalline melting temperature is 105–115 °C
- It is also harder and more opaque and can tolerate higher temperatures.
- It has also got high stiffness and chemical resistance, Commercial HDPE is soluble in hot xylene, but this highly crystalline polymer is insoluble in most solvents at room temperature.
- Most of HDPEs have number average molecular weights of 50×10^3–250×10^3.
- Glass transition temperature Tg below room temperature
- Its mechanical properties permit its use as both a plastic and a fiber.
- Because of the absence of polar groups, HDPE is an excellent electric insulator and has dielectric constant of 2.3 at 60 Hz and higher frequencies.

2.1.2 Low-Density Polyethylene (LDPE)

- Low Density Polyethylene (LDPE) is a thermoplastic with branched structure.
- Its density range is 0.917–0.930 g/cm^3
- Intermolecular force of attraction is very low in LDPE which leads to the low Tensile strength of LDPE is less as compared with HDPE.
- Its molecules are not closely packed so the crystallinity is around 40% only.
- Because of the presence of branches LDPE is more flexible and more ductile than HDPE.
- LDPE has a lower coefficient of expansion ($10 \text{ X } 10^{-5}$ cm/cm. ºC) and a lower heat deflection temperature (40 ºC) than HDPE.
- The dielectric constant of LDPE is 2.2.
- Gas permeability of LDPE is more as compared with HDPE because of its branched structure.

2.1.3 Linear Low-Density Polyethylene (LLDPE)

- LLDPE contains large number of short branches
- Strength is similar to HDPE but more flexible as compared with HDPE
- Narrow molecular weight distribution (Polydispersity index)

- Increased crystallinity, higher tensile and impact strength and greater puncture resistance compared to LDPE because of the absence of long side chains [5].

2.1.4 Ultra-High-Molecular-Weight Polyethylene (UHMWPE)

- It has extremely long chains
- The longer chain serves to transfer load more effectively to the polymer backbone by strengthening intermolecular interactions
- This results in a very tough material, with the highest impact strength of any thermoplastic presently made [6].

2.1.5 Crosslinked Polyethylene (XLPE)

- Cross linked polyethylene (XLPE) is prepared by the addition of crosslinking agents to polyethylene either by physical or chemical process.
- Crosslinks can be introduced by moisture, radiation, catalyst or chemicals
- Crosslinks converts this materials into infusible and insoluble polymers which have enhanced impact strength as well as improved creep, abrasion and stress crack resistance.
- Its density is around 0.92 g/cm^3
- It is widely used as an insulating material.
- XLPE is used in many commercial applications due to its high operational temperature, high dielectric strength, reliability, low dielectric loss, good dimensional stability, solvent resistance, and long life [7].

2.2 Polypropylene (PP)

Polypropylene is the second most widely produced and used plastic in the world. PP is a linear hydrocarbon polymer containing little or no unsaturation, More than 300 grades of PP are available with a wide range of mechanical properties. Polypropylene was discovered in 1954 and gained a strong popularity very quickly due to the fact that PP has the lowest density among commodity plastics. PP is normally tough and flexible, especially when co-polymerized with ethylene. The presence of a methyl group attached to alternate carbon atoms on the chain backbone introduce the possibility of several stereoisomers of PP namely (Fig. 4).

(a) isotactic (iPP)—all CH_3 groups are positioned on the same side of the polymer chain, highest crystallinity
(b) syndiotactic (sPP)—CH_3 groups are positioned on alternating sides of the polymer chain, medium crystallinity
(c) atactic (aPP)—No regular arrangement for CH_3 groups, not crystalline, a soft, transparent, viscous liquid [8].

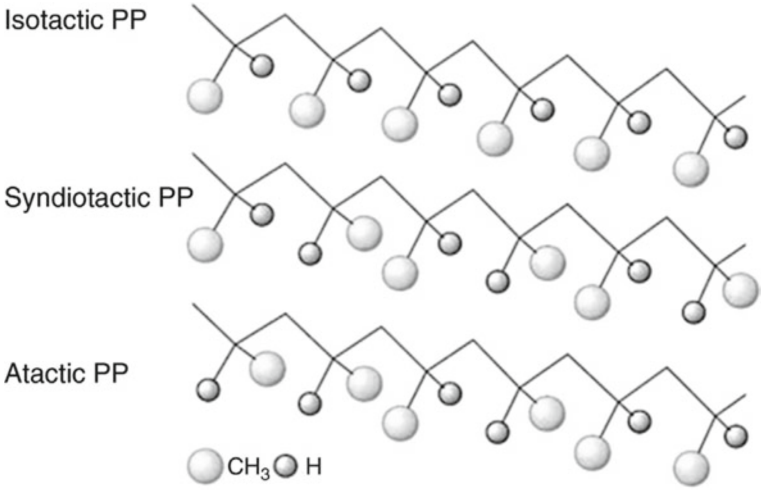

Fig. 4 Different configurations of polypropylene (PP)

2.3 Ethylene Propylene Diene Monomer (EPDM)

- It is a synthetic rubber made from ethylene, propylene and diene monomers
- This polymer has got saturated hydrocarbon backbone [9].

3 Properties of Polyolefins

- Density range is from 0.90 to 0.96 g cm^{-3}
- Low moisture regain
- Good tensile properties, good abrasion resistance and excellent resistance to chemicals, mildew, micro-organisms and insects
- They can be either crystalline or amorphous and behave as thermoplastics, thermoplastic elastomers, or thermosets.

The use of polyolefins is increasing day by day because of their availability, low cost, good mechanical characteristics and light weight. One of the major challenges on the use of these materials is its limited biodegradability. There are several methods available to modify polyolefins into biodegradable nature, including Oxo-biodegradation, Prodegradant technology, etc. As a result, these materials are degraded to non-toxic end products after their disposal to environment.

4 Applications of Polyolefins

Polyolefins are used in a wide variety of applications, including grocery bags, containers, toys, adhesives, home appliances, engineering plastics, insulators to electric cables, squeeze bottles, Agricultural, irrigation and domestic water line connection. automotive parts, medical applications, and prosthetic implants.

4.1 Use of Polyolefin in Medical Fields

- Non-implantable materials—wound dressing, bandages, plasters, etc.
- Extracorporated device—artificial kidney, liver, and lung
- Implantable materials—sutures, surgery meshes, vascular grafts, artificial joints, artificial ligaments
- Healthcare/hygiene products—bedding, diaper, surgical gowns, wipes, etc.
- Disposable syringes are the most common medical application of polypropylene. Other applications include medical vials, diagnostic devices, petri dishes.

4.2 Use of Polyolefin Fibres in Filtration

- These fibers are used in industrial liquid filtration process because of their excellent chemical resistance and inertness
- These can be used for filtration of sewage because of complete resistance to attack by micro-organisms.

4.3 Use of Polyolefin in Transportation

- Polypropylene is widely used in automotive parts because of its low cost, outstanding mechanical properties, and moldability. Other key features of automotive applications of PP include a low coefficient of linear thermal expansion and specific gravity, high chemical resistance and good weatherability, processability, and impact/stiffness balance.
- PP applications in the automotive, marine and air transportation systems are mainly in resin forms for injection molded parts: instrument panels, door panels, arm rests, headliners, sun visors, and mirror housings.

4.4 Packaging Applications

Good barrier properties, high strength, good surface finish, and low cost make polypropylene ideal for several packaging applications, flexible packaging and rigid packaging.

5 Importance of Plasma Modification on Polyolefins

Plasma modification is an attractive tool applied to many materials such as glass, metal, polymers, ceramics, etc. Polyolefins even though are widely accepted for their properties; they lack the fair adhesion and have inertness compared to many other polymers. As a well-known fact, the polyolefins contain a large degree of conjugation and they are non-polar in nature. In order to make them more applicable and to improve adhesion and decrease the inertness the surface modification of the polyolefins is suggested and this could be done with plasma [10]. During plasma modification of the surface of polyolefins, more and more hydrophilic groups can be included by oxidation and which will enhance their applicability. Plasma modification has been employed for polyethylene terephthalate, polybutylene terephthalate, polyether ether ketone, etc. other than polyolefins. A number of properties can be changed by means of plasma and some of them are adhesion, barrier properties and permeability, biocompatibility, color, dielectric constant, dyeability, hardness, toughness, reactivity and refractive index [11–14].

Plasma modification or treatment is commonly used for the surfaces to convert them between hydrophilic and hydrophobic. It means that the surfaces which were hydrophobic can be converted to hydrophilic and vice versa. The surface modified materials possess enhanced adhesion to be used in coating industry. Plasma modified materials have been exploited by many fields such as in the biomedical field for cleaning contaminated surfaces, they have been important in the increase of bonding in aerospace industry, the sensitive components in the microelectronics can be protected by means of plasma, ink-based industries tried plasma modification for enhancing the surface adhesion and to improve the wetting, and so on [15–17].

5.1 Plasma Modification: Basics and Categories

Plasma is a state of matter, generally considered as gaseous, which is a combination of ions and electrons. The plasma is generated by electrifying the gases so as to produce both cations and anions which are free to move. In brief, plasma can be a partly ionized gas consisting of neutral ions, ions present in both ground and excited states, atomic ions, neutral atoms, electrons, molecular ions, etc. [18–20].

Plasma can be of two types: cold and thermal. Thermal plasmas are ones in which all of the species found in the plasma have the same temperature. Thermal heating, which can exceed temperatures of over ten thousand of degree, provides the energy required to ionize and unlock the gas. The solar corona is a well-known natural example. Plasma spray, plasma torches, waste destruction, and welding are only a few of the uses for these plasmas. Cold plasmas don't have a distinct temperature. The temperature of electrons in these types of plasmas is much higher (around 30,000 °C), allowing them to cause other entities and produce ionized particles, excitation of present spices, and molecule dissociation [21].

The process of plasma modification of the surface includes the insertion of the surface to be modified into a vacuum chamber (Fig. 5). After that a small quantity of a desired gas such as oxygen, argon, etc. will be introduced in the chamber. The chamber is introduced with an electric field which ionizes the gas filled in the chamber. The ionization produces plasma ions, that will interact at molecular level with the surface and thus gets modified. The pressure, type of plasma and level of modification can be tuned until we obtain the materials with desired properties.

The experimental set up consist of a vacuum chamber, an electric power supply and a gas delivery system as shown in Fig. 6. The chamber is referred to as plasma generator and the excess gas will be driven out through an exhaust system. The additional assembly is demanded depending on the plasma to be generated. When the frequency of the field given is within or below the radiofrequency region, then

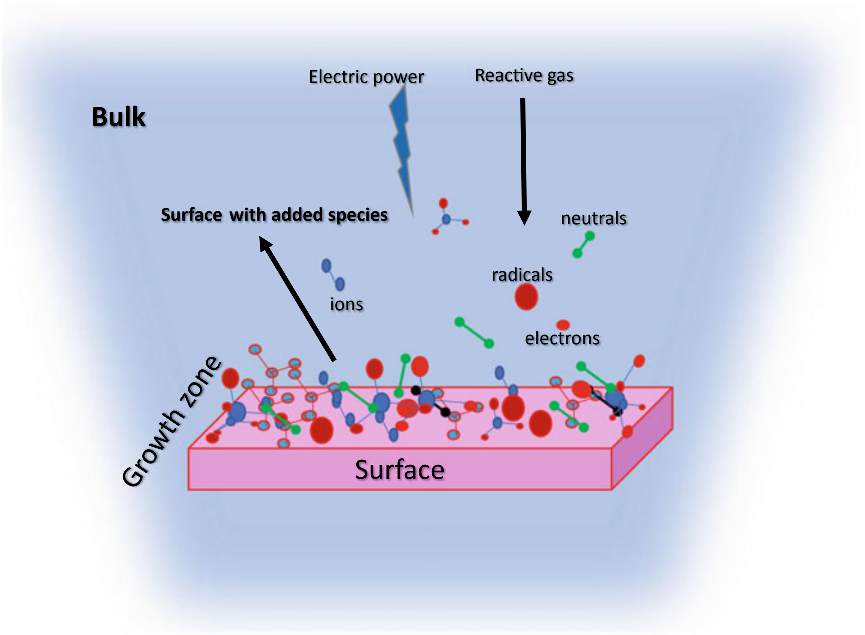

Fig. 5 Schematic representation of plasma modification

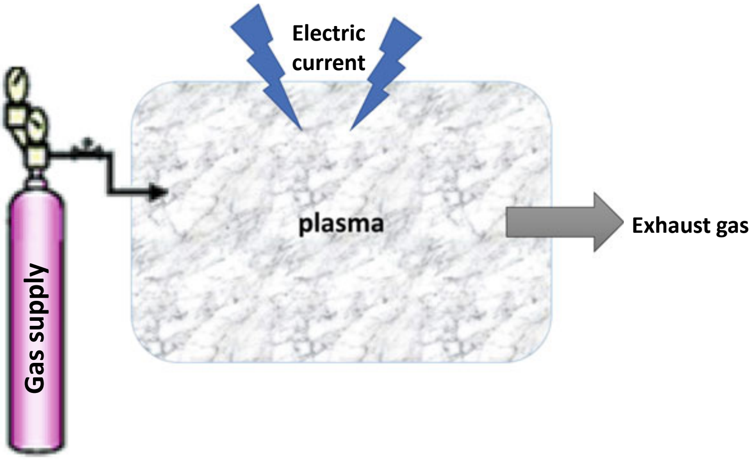

Fig. 6 Schematic representation of the plasma generation

the experimental setup will have electrodes. When the given frequency matches the radio frequency, then inductive coupling assembly or electrodes can be used. If the used frequency is in the microwave region, then no electrodes are required, but the impedance matching should be ensured [22].

The plasma modification used for surface can be of several types.

(1) **Etching or ablation**: it causes the substrate layer to be removed. It is primarily formed by positive ions in the plasma and can be used to achieve precise patterning.
(2) **Plasma deposition**: also recognized as Plasma Enhanced Chemical Deposition (PECD), happens when plasma produces reactive spices that can react with one another on the substrate's surface to form thin films.
(3) **Plasma functionalization**: in this situation, plasma species react with the substrate surface at predetermined locations rather than within themselves. It enables new functionalization while preserving the original surface structure.

The three processes are represented in the schematic Fig. 7

The plasma can be generated from different discharge sources and some of the techniques can be as follows:

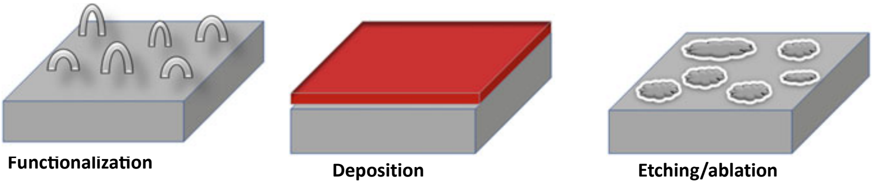

Fig. 7 Different changes on the surface by the application of plasma

(a) Corona discharge

When an electrically charged conductor is surrounded by a fluid such as air, the electric discharge will be produced by the ionization of the fluid. This discharge is termed as corona discharge and occurs in very high—voltage systems. The reason behind the hissing sound in the high voltage electric lines owe to the corona discharge. This effect occurs due to the fact that even though we consider air as an insulator, it is not so. It contains may ionic species. When an electric field is introduced in the space between the electrodes which is filled with air, the free ions will experience it. The ions will be energized and increase their mobility to flow to the counter electrode. During the flow towards the electrode collisions occur between charged and charge less particles so that the energy transfer occurs to create more charged species. Sufficiently high electric field will produce dielectric breakdown on air and an arc will be resulted. This is termed as Corona discharge [23]. So simply Corona is a stream of charged particles such as electrons and ions that is accelerated by an electric field. Corona discharge method of surface modification is employed in the case of plastics for enhancing the adherence properties. Corona discharges are in more than a few forms dependent upon the polarity of the field and the electrode geometrical conformation. The different types of corona discharge are schematically represented in the following figures (Fig. 8).

(b) Microwave discharge

They are also termed as wave heated discharges. Microwave discharge is considered as a non-electrode technique. It is quite useful in the generation of plasma having both low- and high-level absorption. They possess certain advantages over the other plasma generation techniques. They have wide operational pressures, easily controllable electro dynamic properties, opportunity of plasma generation both in small and large compartments, plus the free space, option to treat large volumes of gas and plasma generation lacking any contamination of gas phase or treated samples by products of the electrode erosion.

(c) Gliding arc discharge

Gliding arc method lies between thermal and non-thermal discharges. They are able to produce highly dense plasma, electric power and functioning pressure with top level of electron temperature, low-slung gas temperature and option to stimulate selective chemical procedures deprived of any quenching. The peculiar chemical characteristics and heightened reactivity of the heavy activated species (atoms, radicals, and excited molecules) created in the plasma have sparked widespread interest in gliding arc discharges.

(d) Dielectric barrier discharge

This type of discharge consists of non-thermal plasma discharge at atmospheric pressure. The dielectric barrier discharge is well-known for its ionization of molecules such as ammonia, carbon dioxide, hydrogen sulfide, etc. In this technique, the electrodes are separated by a dielectric insulating barrier. Normally, one of the electrode will be covered by a dielectric material. Fine and visible

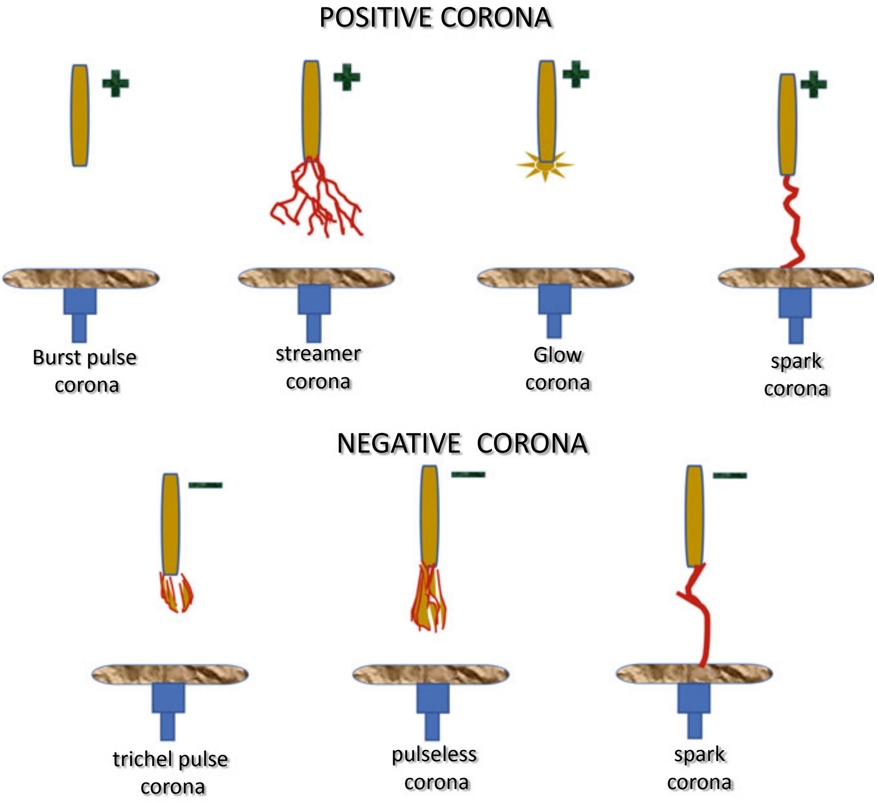

Fig. 8 Schematic representation of different types of corona

filaments will be between the two electrodes and the filaments are generally columns of conducting plasma.

6 Characterization of Plasma Modified Surface

The effects caused by the plasma treatment on polymer surface can be investigated by analyzing the chemical and physical changes occurred in the polymer surface, as well as practical consequences of these changes. Plasma modification generates functional groups on the sample surface. Spectroscopic techniques like x-ray photoelectron spectroscopy (XPS, also known as electron spectroscopy for chemical analysis, or ESCA), and Fourier transform infrared spectroscopy (FTIR) are generally used to probe this chemical modifications. Eventually the hydrophobic / hydrophilic nature has been altered so that contact angle measurement or wettability studies are expedient techniques to probe plasma modified surfaces. Chapter 6 gives more detailed information about the spectroscopic analysis of plasma activated polymeric materials. Microscopic techniques are the effective tool to monitor the morphological features of the plasma activated surfaces. It helps to obtain information about the surface topography and composition in a micrometer scale. Other characterizations relevant to practical consequences like mechanical properties, moldability, adhesion to metal, biocompatibility etc. have been explained in detail in the respective chapters (Chaps. 5, 8–10).

7 Conclusion

Polyolefins are the major classification of macromolecules that have plenty of applications from packaging to biomedical because of its exceptional characteristics. However, its inert nature put some barriers in their usage. Plasma modification is found to be an effective, efficient and economical way to make polyolefin surfaces more active and improve adhesion with other materials. Furthermore, exposure to plasma alters the surface of the material only and without affecting its bulk properties, which enhances its popularity among academicians as well as industrialists.

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Different Techniques Used for Plasma Modification of Polyolefin Surfaces

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Abstract Polyolefins are well-known and the most commonly used polymers worldwide. Advantages like outstanding mechanical properties, chemical resistance, low cost, and processability are neighboring with some drawbacks like relatively high gas and vapor permeability, low surface energy. This chapter introduces surface plasma modification as an environmentally friendly, fast, and versatile technique. Details regarding different plasma reactor designs, generation methods, working parameters suitable for treating polyolefins are presented. Furthermore, plasma activation, grafting, and etching are described as the most commonly used techniques for surface energy modification to enhance polyolefins' biocompatibility, printability, adhesion to materials, and other parameters. For instance, plasma activation cross-linking of the polymer chains can be achieved, which leads to gas and vapor permeability improvement. Choice of working conditions allows controlling the degree of cross-linking, the type, and the concentration of the incorporated functional groups on the surface. Plasma polymerization is introduced as a technique for coating deposition with different properties and functionality depending on the operating parameters and monomer selection. Improvement of barrier layer performance and modification of the surface energy are the main applications of plasma polymerization of polyolefins.

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1 Introduction

Polyolefins are a family of synthetic polymers prepared by the polymerization of olefin monomers. Olefins are acyclic and cyclic hydrocarbons that contain one or more carbon–carbon double bonds without an aromatic character [105]. Figure 1 shows some examples of polyolefins.

Polyolefins are the most commonly used polymers worldwide due to their low cost, processability, chemical resistance and mechanical properties (ranging from elastomeric to very rigid materials) [16]. By varying the processing parameters and the possible implementation of copolymerization and cross-linking, the desired properties can be obtained. Among the different polyolefins, polyethylene (PE) and polypropylene (PP) are most widely employed. For commercial purposes, isotactic PP (methyl side-groups located on the same side of the backbone) is most often considered due to its superior mechanical properties, originating from a higher degree of crystallinity. In contrast to PP, commercial PE can be classified based on its cross-linking degree, density and molecular weight. The most extensively used types are: (1) low-density PE (LDPE), which is the original commercial PE containing significant branching, resulting in a lower polymer chain packing density and therefore a low material density; (2) high-density PE (HDPE), being a highly linear polymer in which the polymer chains are tightly packed together, leading to a higher density and a more crystalline character and (3) linear low-density PE (LLDPE), being a similar linear polymer with short chain branches thus triggering similar densities as LDPE [120].

The application range of polyolefin-based materials is very broad, ranging from the biomedical field to the automotive industry and from packaging equipment to toys. In the biomedical field, the use of PP as hernia repair meshes, sutures and disposable items like syringes are good examples [123]. Ultra-high-molecular-weight PE (UHMWPE) has particularly gained considerable attention in this field given its improved mechanical properties engendered by the intermolecular interactions between the long chains. These properties make UHMWPE a suitable bearing material in joint replacements, for instance. LDPE, LLDPE, HDPE and PP are most commonly used for packaging of food, drinks and other consumer goods [120]. PP has also become the most employed thermoplastic material in the automobile

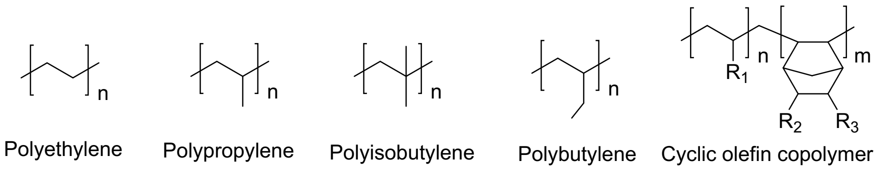

Fig. 1 Examples of polyolefins

industry [24]. Furthermore, cyclic olefin polymers (COPs) and cyclic olefin copolymers (COCs) have attracted much attention for microfluidic and biosensor applications [127]. This widespread use evidence that the aforementioned properties of polyolefins are highly advantageous for various applications. Nonetheless, some polymer characteristics are a disadvantage for certain purposes. Generally, these disadvantages can be divided in 2 main categories. The *first category* is the hydrocarbon nature of these polymers conferring them with a low surface energy. This makes printing on and adhesive bonding to the polymer difficult. Depositing a coating on the substrate is also challenging. Moreover, the polymer composition hampers cell adhesion and therefore subsequent cell performances such as proliferation, differentiation and migration. On the other hand, polyolefins are not completely inert, which is a problem for biomedical applications that demand either a good cell interaction or complete inertness [101, 146]. The *second category* is the relatively high gas and vapor permeability of the polymers, which is a major limitation for packaging applications given the resulting restricted shelf-life of the packed food or other goods. Typically, polyolefins have a moderate to good resistance against water vapor but are highly permeable to oxygen. The origin of this permeability is not completely clarified, but it is hypothesized that density and crystallinity play a role [152].

Several modification strategies have been developed to address these 2 problems. These strategies can be mainly divided based on the different underlying problems. The introduction of polar functional groups on the polymer surface is the main method to address the chemical inertness of polyolefins (problem 1). This can lead to a better adhesion in the aforementioned applications. A distinction can be made between bulk and surface functionalization, as illustrated in Fig. 2. Bulk functionalization can introduce functional groups on the polymer chains with a homogeneous distribution on the surface and in the bulk of the resulting material. This can be either done by modifying the polymerization process (a) or by functionalizing the polymer after polymerization (b). In the co-polymerization functionalization (a), monomers

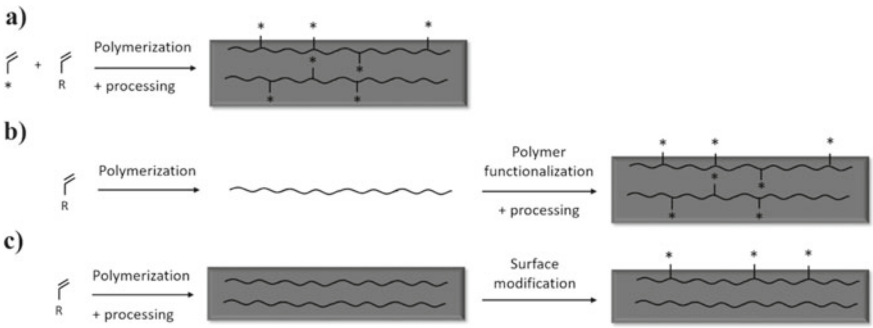

Fig. 2 Difference between bulk functionalization (**a** and **b**) and surface functionalization (**c**). **a**: functionalization by co-polymerization with a functional monomer. **b**: post-polymerization functionalization of the polymer chains before processing the material. Both techniques lead to functional groups in the bulk and on the surface of the material [16]. **c**: surface functionalization. * can be the desired functional group or a functional group that can be converted to the desired functional group

with the desired functional group are introduced in the polymerization process so that the resulting polymer has these groups build-in. In the post-polymerization functionalization (b), the C-H bonds in the polymer chain are preferably broken, which leads to the generation of reactive radicals on the polymer chain. Reactions with these sites lead to a functionalization of the polymer. In the surface functionalization (c), only the outer layer of the polyolefin will be modified, leaving the bulk of the material untouched. This method is advantageous for most applications, as the bulk properties that are most often desirable are not affected. Moreover, for most purposes, the interactions with the material usually take place at the surface. Additionally, the bulk modification needs an optimization of the well-established industrial material processing steps, while the surface modification is performed afterwards and is independent of these processing steps. Therefore, surface modifications provide an interesting and often sufficient strategy for material improvements.

In order to address the gas and vapor permeability (problem 2), a number of different strategies can be applied. The most important ones are the blending with low permeable materials to form nanocomposite materials and the modification of the surface by adding a barrier layer on top of the surface or changing the permeability of the surface itself by polymer cross-linking [152]. It is clear that the first technique has the same disadvantages as the bulk functionalization technique in comparison to surface treatments, as changing the bulk can, on the one hand, alter the advantageous polyolefin properties and, on the other hand, requires an optimization of the material processing. However, applying a barrier layer on the surface requires a good adhesion, thus making the chemical inertness a problem that also needs to be solved for addressing the gas and vapor permeability problem of polyolefins.

In view of the above, it can be concluded that the surface modification of polyolefins aiming at improving their properties is an interesting approach. In particular, increasing the surface energy is of uttermost importance. This can be done by a variety of different techniques. Similar to the polymer functionalization (Fig. 2), all surface modification techniques aim at breaking the C–H or C–C bond and introducing other functionalities on the polymer chain. One of the techniques to break C–H/C–C bonds is the use of γ- or UV-irradiation. The created radicals can react with oxygen, which leads to the generation of oxygen-containing functional groups like alcohols, hydroperoxides and ketones [85]. Another technique for the oxidation of polyolefin surfaces is flame treatment, in which radicals are created in the combustion process. This leads to the generation of carbonyl, carboxyl and hydroxyl groups on the surface. Both techniques lead to an increased surface energy, which is beneficial for applications in which a good adhesion is required [43]. A third technique is the chemical treatment of the polyolefin surface. This can be done by using oxidizing agents like chromic acid or aqueous solution of ammoniacal ammonium persulfate in the presence of Ni^{+2} ions, for example, which leads to the introduction of polar groups such as $>C = O$ and $–COOH$ [36]. A fourth technique is the use of plasma surface modification, which will be the main topic of this book chapter. In comparison to the abovementioned techniques, plasma surface modification has a number of advantages. Compared to the irradiation techniques and the chemical treatments with typical treatment times in the order of hours, plasma modification is a fast technique with treatment times ranging in the order of seconds to minutes [163]. Furthermore, plasma modification is a solvent-free technique, which makes it more environmentally friendly than chemical treatments. Flame treatment is also a fast and solvent-free technique, but care should be provided to prevent polymer melting, which is not a problem with optimized plasma surface modifications. The latter technique can also treat surfaces that cannot be reached with flame treatment, enabling the modification of 3D porous objects. Plasma surface modifications of polyolefins thus provide a platform with a number of advantages over other modification strategies and are therefore found in a variety of applications and research fields. Besides changing the surface energy, plasma surface modifications are also used for improving the gas and vapor permeability of polyolefins, making it a more widely applicable technique. On the other hand, there still remain some challenges as plasma treated surfaces are prone to ageing effects and the selectivity of the treatment is limited. This book chapter will give a general overview of the different plasma surface modifications of polyolefins. The focus will be on the general concepts of these techniques with references to the application potential. Therefore, the following sections will first introduce the concept of plasma and different plasma classifications (Sect. 2) and the methods to generate plasma for polyolefin surface modification (Sect. 3). This will provide the basis for a general description of plasma-surface interactions and different plasma surface modification techniques applied to polyolefins (Sect. 4).

2 Plasma Definition and Classification

2.1 What is Plasma?

The word "plasma", which was first introduced by Langmuir, can be defined as an environment where energetic, charged and neutral carrier assemblies move in random directions and exhibit a collective behavior [89]. The net electrical charge in this mixture of oppositely charged particles is approximately zero. Plasma is commonly referred to as the fourth state of matter and constitutes the most common state in the universe as stars, nebulae and Aurora consist of it. On earth, natural plasmas like lightning and Aurora Borealis are rare, and most common plasmas are man-made. In contrast to celestial plasmas that are generated by the addition of thermal energy, the most conventional method of plasma generation on earth is a gas breakdown, using an electric field. Even a neutral gas has some charged particles, that are generated by phenomena such as space radiations, which can accelerate in the presence of an electric field, thus hitting other species. At the right conditions, this can create new charges with the ability to collide with other molecules and atoms. This produces new electrons, negative and positive ions and radiation, leading to the generation of an avalanche of charged species until a steady state condition is reached. Besides the aforementioned species, usually a plasma also contains excited species and radicals. The produced radiation is mainly situated in the visible and ultraviolet (UV) range

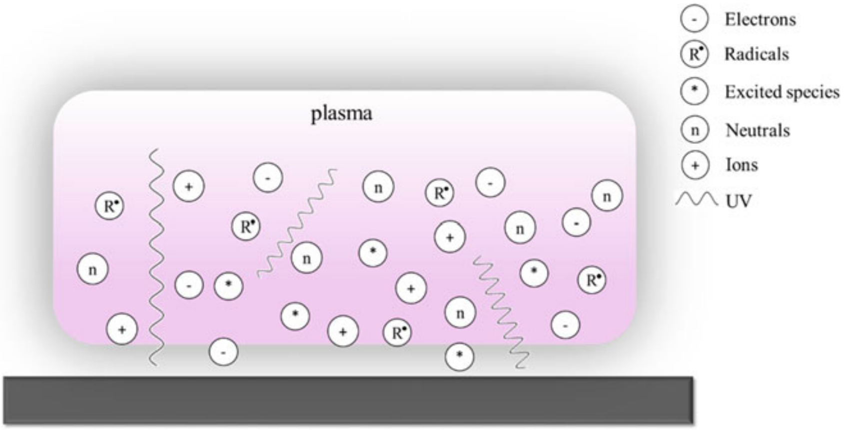

Fig. 3 Plasma components interaction with a substrate

and is generated as a result of inelastic collisions between atoms/molecules and energetic electrons. This process can lead to excitation of the atom/molecule ($A + e \rightarrow A^{*} + e'$), among others, which can subsequently induce emission of the energy stored in this excited state via radiation in a range of different wavelengths. This results in the luminosity of plasma ($A^{*} \rightarrow A + h\nu$). Furthermore, charges can be lost by homogenous recombination ($A^{+} + e^{-} \rightarrow A^{*}$) and/or diffusion to the wall of the discharge ($A^{+} \rightarrow A$).

In plasma surface modification, the plasma particles are brought in contact with a substrate (e.g. polyolefin) by placing it in the (vicinity of a) discharge. These energetic species can interact with this substrate as schematically presented in Fig. 3, resulting in the alteration of its surface properties. The interactions between the plasma species and the surface mainly depend on the respective amount and energy of these different particles. This is influenced by a number of plasma characteristics of which the ionization degree, plasma equilibrium, working pressure and discharge driving frequency are the most relevant for polyolefin surface modifications. These characteristics will be discussed in more detail in Sect. 2.2, which will form the fundamental basis for explaining the different plasma source configurations (Sect. 2.3) and plasma modification techniques (Sect. 2.4).

2.2 Plasma Classification

2.2.1 Plasma Ionization

The degree of ionization α is defined as $\alpha = N^{+}/(N + N^{+})$, in which N^{+} is the number of ions and N the number of neutral particles. It is a dimensionless number and can be denoted as a percentage. The ionization degree determines the amount of charged particles in the plasma and is, therefore, a measure of the interaction between a plasma and the electric and magnetic fields. An ionized gas can be identified as plasma when the degree of ionization is at least 10^{-6} [26]. Plasma is called weakly ionized if $10^{-6} < \alpha < 10^{-1}$. For this type of plasma, the collisions happen more often between neutrals and electrons than between ions and electrons. A weakly ionized plasma can be called a "low-temperature plasma" or more often "*cold plasma*", due to considerably low electron temperature which controls the degree of ionization in the plasma. Plasma can be referred to as "*hot plasma*" when it is almost or fully ionized ($\alpha \approx 1$).

2.2.2 Plasma Thermodynamic Equilibrium

Plasmas can be also classified in terms of their thermodynamic equilibrium, which is based on the relative temperature of ions, electrons and neutrals. Three different classes can be defined: *thermal equilibrium*, *local thermal equilibrium* and *non-thermal equilibrium.*

In *thermal equilibrium plasmas*, all components are in thermodynamic equilibrium with each other ($T_{electron} = T_{ion} = T_{gas}$). Such an environment can be created in high temperature and high-density plasma due to frequent collisions between fast electrons and heavy species (ions and neutrals). Typically, these plasmas also have a high degree of ionization. Some examples are lightening, the solar core and thermonuclear fusion plasmas. The temperature of these plasmas is too high for the treatment of polyolefins. Therefore, they are not further discussed.

In *non-thermal* or *non-equilibrium plasmas*, the temperature of electrons, which typically is in the range of 2 to 10 eV, and the temperature of ions are significantly different ($T_{electron} >> T_{ion} = T_{gas}$). The reason for this difference is that electrons gain much more energy from the applied power due to their considerably lower mass in comparison to ions. Moreover, the energy transfer from electrons to ions and neutrals is not efficient in this type of plasma because of conservation of momentum. Typically, these plasmas are weakly ionized and are therefore most often cold plasmas, however more highly ionized non-thermal plasmas also exist. Examples of non-thermal plasmas are the Earth's ionosphere and most of the "technological plasmas". The application range of non-thermal plasmas is broad and covers analytical chemistry, environmental engineering and biomedicine, among others. These plasmas are most suitable for the treatment of heat sensitive materials such as polyolefins.

Besides the two mentioned classes of plasma, there are also *local thermal equilibrium plasmas* which are in quasi-equilibrium. This means that the plasma is not far from full equilibrium, yet it is not fulfilled in all volume. Nevertheless, within the area, local thermodynamic equilibrium exists, and the electron, ion and neutral temperatures are in the same range (0.4 – 1 eV). The ion temperature is considerably higher than the one of non-thermal equilibrium plasma while the electron temperature is much lower. This type of plasma can be used for surface modification techniques like chemical and physical vapor deposition as well as plasma spraying. However, these techniques are generally not used for direct continuous polymer treatment as the overall plasma temperature will damage the surface.

2.2.3 Plasma Pressure

Plasma density is directly proportional to plasma pressure and both can be described together as one parameter. Working pressure determines plasma appearance, energy, temperature and other characteristics which are essential for surface modification applications. A *low pressure plasma* works at sufficiently low pressures (typically lower than 1 Torr), at which the collision between heavy particles is correspondingly low, which favors its non-thermal equilibrium character. Equally important, when the pressure is very low, high voltage and current are required to ignite and sustain the discharge due to the same reasons mentioned above. However, a *low pressure plasma* provides a controlled environment in which parameters like power, temperature and gas flow can be tuned for obtaining the desired surface reactions. As a result, a homogeneous and selective interaction between plasma and the substrate is feasible. At really low pressures, the lack of charged particles decreases the coupling efficiency of electromagnetic energy into the plasma, which makes it impossible to use high-frequency power sources like radiofrequency (RF) and microwave (MW) discharges (see Sect. 2.2.4).

For *atmospheric pressure plasmas* (APPs), the electron mean free path is significantly decreased in comparison to *low pressure plasmas* because of the increase in pressure. Correspondingly, the number of collisions drastically increases as well, which rises the temperature of the plasma. Therefore, an APP has a lower degree of ionization, a lower electron temperature and a higher particle and electron density as compared to low pressure plasmas. The particle density is in the order of 10^{12}–10^{14} particles cm^{-3} for low pressure plasmas and 10^{15}–10^{18} particles cm^{-3} for APPs. The first APP was developed as a high temperature arc-based source [51]. However, a stable homogeneous low-temperature plasma is required for the treatment of polyolefins, as the instability of the APP and the possible transition to a thermal arc are major issues because of the material's thermal sensitivity. By the beginning of the 1990s, non-equilibrium APPs began to overcome this problem by limiting the time of each glowing duration. This can either be done by utilizing a pulsed power supply as an energy source, or by alternating the polarity of electrodes with a high frequency. Another approach to control the transition to arc and thermal equilibrium is using a dielectric barrier which is discussed in detail below [87]. Furthermore, discharge gas selection and flow rate can have a significant influence on the stability of APPs. For instance, helium (He) is a well-known gas for producing a stable plasma due to the small atom size and hence a longer mean free path. Moreover, increasing the intensity of the electric field by implementing sharp points at the edge of the powered electrode (e.g. corona discharge) is another adjustment performed for obtaining low-temperature plasmas at atmospheric pressure. APPs are more widely accepted for industrial purposes because of the convenient implementation in industrial processes, the lacking need for expensive and huge vacuum equipment and the lower complexity of the reactors.

In between the pressure range of *low pressure plasmas* and APPs, *medium pressure plasmas* can be defined. This is a less frequently explored pressure range. However, this range is also interesting because obtaining a large plasma volume is more easy at medium pressure than atmospheric pressure. Furthermore, no expensive vacuum equipment is needed [32, 108, 110].

2.2.4 Plasma Excitation Frequency

As mentioned before, one of the most common methods to transform a neutral gas into a plasma discharge is by utilizing an electric field. According to the temporal behavior of the electric field, discharges can be classified as *direct current (DC)*, *pulsed DC*, *alternating current (AC)*, *RF* and *MW discharges*. Depending on this temporal behavior, different plasma chemistries can be obtained and utilized in a variety of processes. In order to predict possible surface plasma treatment of polyolefins, it is crucial to describe the main characteristics of each class of plasma excitation frequencies.

When a potential difference of zero frequency is applied between a cathode and an anode, the gas breakdown happens by a *DC discharge*. In this type of plasma, secondary electrons emitted from the cathode play a crucial role as they collide with the background gas and finally reach drift velocity along the tube axis. DC discharges have attracted enormous interest because of their time-independence in the macroscopic scale, which makes them more straightforward compared to RF discharges. At higher pressure, the transition to the arc is more probable because of an increased current density, which contributes to a higher temperature and instability of the plasma. This drawback limits the application of DC discharges in case of plasma treatment of polyolefins. Furthermore, plasma can be contaminated by sputtering the cathode surface, and the electrodes can only be made of conductive materials. Usually, the voltage can vary between a few hundred Volts to a few kV based on the application and the current is in the order of mA. There are possibilities to overcome the transition to arc, such as minimizing the radial size or using a dielectric barrier or a corona discharge source configuration.

Another option to avoid the transition of a DC discharge to an arc is to apply the electric field in a discrete form of *pulses* from microsecond to millisecond while keeping the amplitude of voltage and current high. The relatively short pulse duration contributes to the formation of non-equilibrium plasmas. The charged particles notice the relatively short pulses before the spark creation. The main advantages of using pulsed DC discharges are minimized etching and damage of the treated substrate surface and the possibility of working at a higher power by controlling the duty cycle.

AC discharges have electromagnetic field oscillations in the range of kHz. This discharge type is appropriate for overcoming the charge-accumulation problem that occurs when non-conductive materials are placed between the electrodes (as in dielectric barrier discharges (DBDs), see Sect. 3.4). In fact, the alternating voltage between electrodes in each half cycle will produce opposite charge accumulation. The advantage of oscillating power supplies over DC discharges is that they interact with plasma by displacement currents, rather than true currents. Therefore, no contact between the electrodes and plasma is needed. The absence of the connection between the discharge and the electrodes improves the reliability, reproducibility, and lifetime of plasma reactors and the produced species. The influence of frequency on the treatment of polyolefin substrates has been previously studied and the investigations have suggested that an increase in frequency can improve the surface modification [1, 82].

Low-frequency plasmas (up to 450 kHz) are widely used due to the simplicity of the power source. However, this discharge type has a slower reaction rate and a higher transition to arc probability as compared to higher frequency plasma sources. *RF discharges* can be utilized to overcome these limitations. RF discharges are obtained when the gas is subjected to an oscillating electromagnetic field with frequencies in the range of MHz. The main distinction that identifies RF plasmas from lower frequency plasmas is the dynamic behavior of electrons and ions: only electrons can follow the changes in the radiofrequency electromagnetic field, while heavy ions remain almost stationary. This is opposite to a low frequency plasma where both charged species move according to the electromagnetic field. Moreover, since the quenching time of reactive plasma species is longer than half a period cycle of an RF source, the stability considerably increases. Hence, RF discharges have some advantages, such as the less pronounced electron and ion bombardment of the electrodes, negligible thermal output, better discharge stability, higher electrical efficiency due to the lower electrode loss and higher electron kinetic temperature which results in the increased number of radicals, chemical reactions and ionization processes inside the plasma. This results in a large density of reactive species at a reduced temperature in comparison to lower frequency discharges [129, 164]. All these advantages make RF plasmas suitable for surface modification of polyolefins.

MW plasmas can be generated and sustained by electromagnetic radiation in the frequency range of 300 MHz–300 GHz. The typical frequency is 2.45 GHz, which corresponds to a wavelength that is comparable to plasma reactor dimensions (12.24 cm). In comparison with other power generators, MW generators require lower gas flow rates and powers in order to ignite a plasma. More dissociation of species also occurs in this system, which may lead to deposition and etching.

3 Plasma Source Configurations

Feasibility, in combination with some attractive properties for technological and industrial demands, has led scientists to broaden the applicability of plasma sources by using different configurations. Since the main focus here is directed towards a partially ionized low-temperature plasma for polyolefin surface modifications, the description is limited to the main plasma source configurations used for this purpose.

3.1 Corona Discharge

A corona discharge can be initiated by a local breakdown of gas in atmospheric pressure when the current density is comparatively low. A sufficiently high electric field in close proximity to the edges or small radii of curvature in a plasma reactor usually gives rise to a corona discharge development. Due to the electrode geometry and configuration, ionization occurs locally around tips or sharp points in the absence of insulating surfaces. It is also possible to ignite such a discharge without the presence of a grounded electrode. In this case, the surrounding environment acts like one. Typically, corona discharges contain a drift region positioned between the ionization region near the tip of the powered electrode and the grounded (low-field) electrode. This large drift zone can enhance the excitation or recombination of species such as ions, electrons and neutrals. However, due to inelastic collisions, this region is depleted from reactive components, and consequently, only a free radical chemistry happens there. Increasing the current leads first to the production of a burst corona, which is characterized by simple avalanches. The discharge can change to a regime where the charge density is high enough to trigger the streamer mechanism by further increasing the current. This highly branched non-uniform streamer, which occurs due to inhomogeneity in a corona discharge, can go beyond the active zone but cannot propagate infinitely. In fact, if there is enough applied potential through the conductive channel, it can lead to a longer streamer that might have better applicability. The presence of free transient electrons in such streamers makes them capable of dissociating and exciting neutrals. By increasing the current even further, it is possible to have extreme secondary emission that produces a self-sustained discharge which is quite similar to a glow discharge. If the secondary emission is really efficient, the discharge can make the transition to spark and arc [21]. For the treatment of heat sensitive materials, the latter is, however, undesirable. An alternative approach is the use of a corona discharge with a shortened lifetime. It has been shown that a pulsed power supply with a pulse duration between 100 and 300 ns provides an operating time small enough to prevent the transition from streamer to spark and leads to an increase in the ionization degree [52]. Consequently, a more ionized environment can improve the efficiency of the surface treatment. Figure 4 depicts different electrode configurations that produce structurally different corona discharges [35]. Nevertheless, in corona configuration, introducing plain polyolefin film gives a superficial resemblance to DBDs as the polymer can act as a dielectric barrier. This case is not valid for polyolefin textiles and fibers.

The generation of a corona discharge with low power and low temperature at atmospheric pressure opens a wide range of possible applications including treatment of polyolefin materials. The utilization of corona in the surface treatment of polymer is commercialized. Polyolefins have been ensured to be easily and successfully treated with corona discharge resulting in a significant surface oxidation. The main advantages of this plasma are the simplicity of the design, the generation of significantly small discharge currents and the possibility to work in atmospheric pressure and using ambient air as the reagent gas. However, the last feature is beneficial

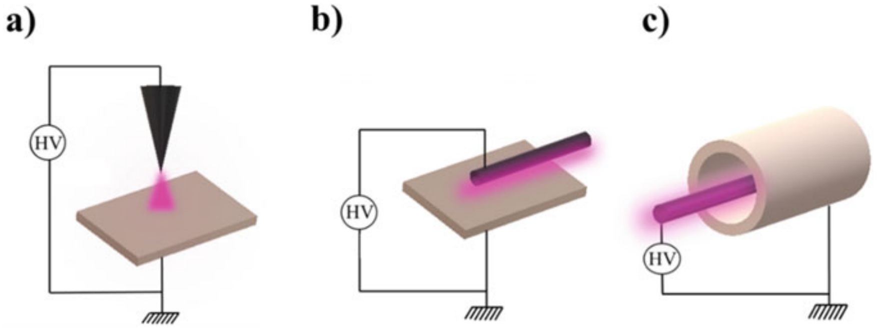

Fig. 4 Different configurations of a corona discharge. **a** point to plane; **b** wire to plane and **c** wire to cylinder

only for applications that are dealing with surface oxidation while for other types of treatment, this aspect can be a necessary restriction. This limitation can be solved by working with specific gases and in defined ambient conditions. However, this is not economically efficient and hazardous substances can only be used with designated suction systems [95].

3.2 RF Discharge

As mentioned before, high-frequency discharges have become more attractive due to the high density of excited species in low-temperature plasmas which makes such sources suitable for the surface treatment of polyolefins [93, 165]. The principal division in RF plasma sources depends on how the energy is coupled to the system. Figure 5 shows the two coupling mechanisms, namely capacitive or inductive coupling.

An *Inductively coupled plasma (ICP)* is characterized by a magnetic field of an induction coil or inductor in which the discharge is located. The coil can have a spiral or helix shape and can be positioned inside or outside the plasma volume. In most of the ICP arrangements, a quartz tube is used to separate the coil and the discharge in order to prevent plasma flow through the coil (see Fig. 5a). ICPs can reach a high electron density while the ion energy remains low. The main advantage of ICPs is the possibility to control the ion energy fluence, which is responsible for the nanoscale surface topography, the hydrophilic behavior and chemical properties of polyolefin as illustrated for argon (Ar) treatment of LDPE [143]. Additionally, the high electron density in these systems can be used for plasma polymerization purposes.

A *capacitively coupled plasma (CCP)* accomplishes the power coupling by oscillating electric fields. In this configuration, the plasma is formed between two separated parallel metal electrodes, which resembles a capacitor configuration. Another essential component in CCP systems is the network to match the impedance of the

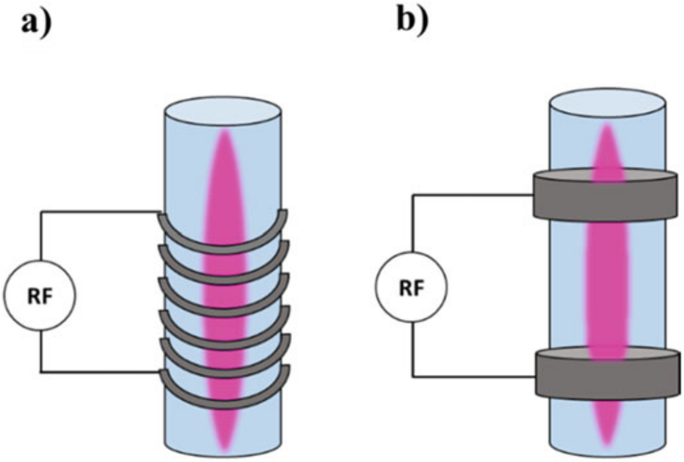

Fig. 5 Schematic representation of different RF plasma sources. **a** ICP and **b** CCP

generator and the reactor. This matching network reduces the power reflection and loss from the generator to the reactor. The ion energy that falls onto the polymer sample in CCP is small; thus, the possibility of polymer damage is low. Nevertheless, in order to control the ion bombardment of the substrate, dual frequency CCPs have been developed, resulting in faster treatment in case of PP [2, 77]. Furthermore, the structural modification of PP using CCP plasma has been investigated. The crystallite size of PP is prone to be modified depending on the CCP plasma operational condition [2].

3.3 MW Discharge

MW-induced plasma is mostly generated in a magnetron. In these systems, the electromagnetic wave is carried by a hollow shaped conductor waveguide to the reactor. A coaxial cable can also be used as a carrier, but this is performed less frequently, and therefore, this description focusses on waveguides. The waveguide carries high-frequency energy of a magnetron with lowered energy loss, only allowing the propagation of TE and TM wave modes into the waveguide. A few different examples of experimental set-ups will be mentioned below.

For instance, it is possible to couple the waveguide to the plasma by using a quartz tube positioned perpendicularly with respect to the waveguide where the axial high electric field exists. The discharge gas is passing through this tube which propagates the plasma. Figure 6a indicates the typical MW plasma coupled with the waveguide.

Electron-cyclotron resonance (ECR) MW reactor (Fig. 6b) is another configuration using MW power. In this configuration, plasma is formed through the interaction

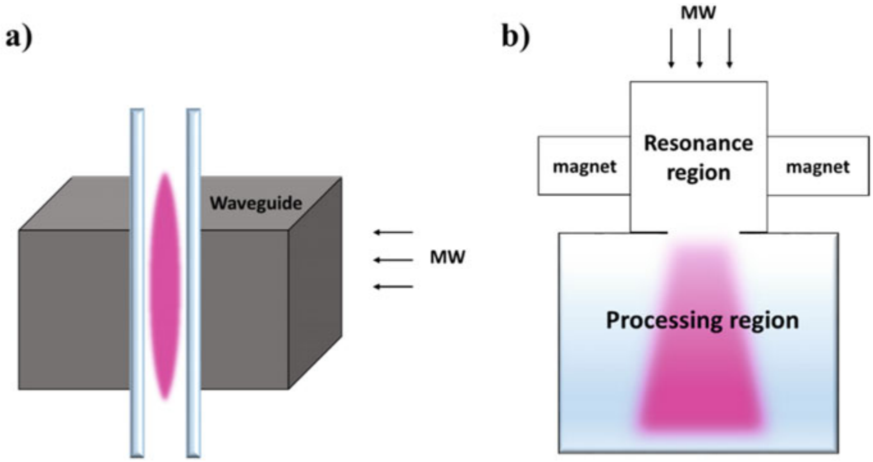

Fig. 6 Schematic representation of **a** typical MW-induced plasma with coupled waveguide and **b** ECR microwave reactor

between the MW electric field and magnetic field created by a solenoidal electromagnet. A superposition of these two fields under resonant condition brings a higher power to the plasma. Therefore, the reactor consists of a resonance region and a process part where the polyolefin sample is being treated [27]. This type of MW configuration is suitable for situations in which a higher degree of ionization and ion energy is of great importance.

MW induced plasma sources have been widely used for the surface modification of polyolefins [70, 96, 137]. One of the advantages of MW plasma sources is the possibility to work without any electrodes, making it easier to handle and preventing electrode contamination. Besides, the ignition under different discharge gases without transition to an arc mode is almost always possible. Both MW and RF discharges are known for their high radical density because a high power input can be used. This allows the reduction in treatment time to a few milliseconds, which is crucial and eligible for industrial applications [6]. However, the spatial limitation for some MW source designs is a disadvantage which makes the use of arrays necessary for applications where the treatment of large areas is required.

3.4 DBD

Besides using a pulsed mode corona discharge to prevent spark formation at higher voltages, a dielectric barrier between the electrodes can be employed. A DBD is a gas breakdown between two separated electrodes with at least one electrode insulated with a dielectric. This non-conductive material can be glass, ceramic or a specific polymer which prevents the generation of sparks and current propagation by the

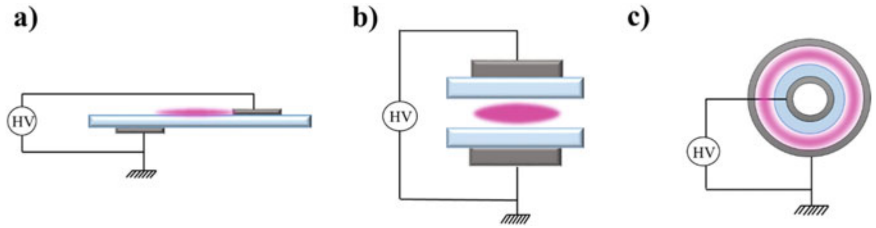

Fig. 7 Examples of **a** surface, **b** planer and **c** cylindrical DBD

formation of streamers. Furthermore, a dielectric barrier can control the amount of energy and charge of filamentary microdischarges and distribute them over an extended region, thus producing a homogeneous large-scale plasma. Generally, this plasma can be sustained by an AC, pulsed DC or high-frequency (from lower RF to MW) source in order to avoid charge accumulation and microdischarges due to direct currents. DBDs are perfect examples of how dielectric barriers can considerably suppress the large current density and limit the discharge current to avoid the transition to an arc.

Figure 7 illustrates three different electrodes configurations [17]. Other arrangements of electrodes and dielectric barriers can be subcategorized into these three configurations. In a volume DBD (Fig. 7b), the plasma filaments need to cross the gas gap without any contact with the dielectric. In a surface DBD (Fig. 7a), filaments always develop in direct contact with the dielectric. A cylindrical DBD (Fig. 7c) is another example of a potential volume DBD configuration. However, to the best of our knowledge, it is not used in polyolefin surface modification. The sample position varies for the different plasma source geometries. In volume DBDs, a sample can be positioned in the plasma active zone between the two electrodes. In surface DBDs, a sample can be placed next to the powered electrode. DBDs are suitable sources for polymer surface modification because of their simplicity of operation, the possibility to work in a wide pressure range at low temperature and the ability to have homogeneous surface modifications. Furthermore, this plasma type is easily up-scaled and has an extensive processing range [17, 19, 79]. All these listed benefits make DBDs a suitable and preferred option for industrial applications.

3.5 Trends in Plasma Source Technology

Unambiguously categorizing individual sources becomes less straightforward nowadays. In recent years, driven by the research intention to develop stable homogeneous plasma sources at ambient pressure, the majority of plasma sources described in literature today are a combination of features belonging to the above-described categories. One of the examples of non-equilibrium plasma sources working at atmospheric pressure is a microplasma. Based on Paschen’s law, the electrode separation should be small enough to obtain a lower breakdown voltage at high pressure. Therefore, a microplasma provides an improved stability by minimizing the dimensions to the sub-millimeter range. This results in a higher electron temperature accompanied by a lower gas temperature. Moreover, the accumulation of heat is hardly happening as a result of a comparatively high surface to volume ratio. This makes microplasmas suitable for the treatment of heat sensitive polyolefins [37]. Another example of a plasma source working at high pressure is the plasma jet. It is a system with a planar or coaxial geometry and a small discharge gap operating at atmospheric or elevated pressure. Usually, it blows a stream of noble gases outside of the source which allows the plasma to propagate outside the electrode arrangement. The geometry of the configuration and carrier gas flow can highly control the jet plume shape and the way it spreads. A plasma jet seems to be homogeneous at first glance while it actually consists of intermittent high-speed bullets [99]. The applied electric field has a particular influence on the way these bullets propagate in the environment. A plasma jet has the exclusive ability to work in almost the total frequency range (from MW to DC). Another feature of this plasma source is the ability to provide a vast range of temperatures, which makes it applicable for polymer treatments. A thermal plasma jet may turn to an arc and is called a “plasma torch”. A non-thermal plasma jet is found to work under different configurations, as Laroussi and Lu described (Lu et al., 2012). Figure 8 schematizes the four categories of jets: the DBD plasma jet, DBD-like jets, single electrode jet, and dielectric-free electrode jet.

DBD jets have become popular in many science areas, ranging from material processing to medical applications, due to the variety of features they offer and the possibility to pick a desirable one for each purpose. For instance, a plasma jet can be generated with up to a 100 mm length and a diameter in the range of few millimeters

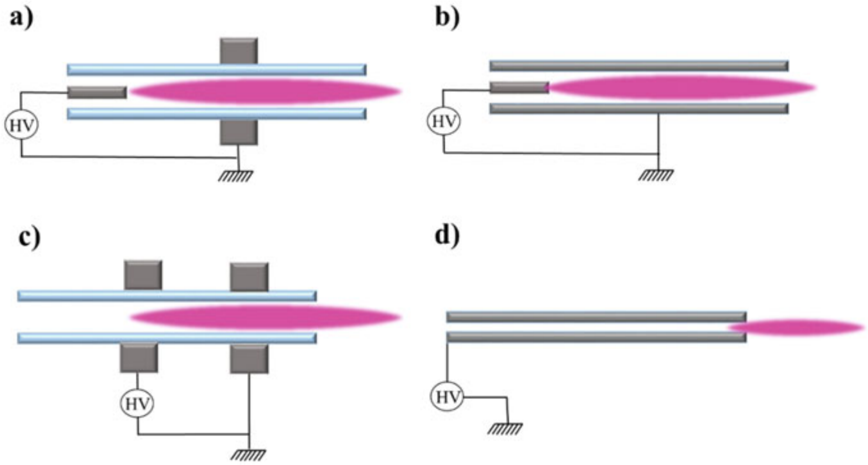

Fig. 8 Different configurations of a plasma jet: **a** DBD-like; **b** dielectric-free; **c** DBD and **d** single-electrode

while keeping the gas temperature close to the room temperature due to the low power density delivered to the system.

As mentioned before, the cost reduction due to the exclusion of vacuum devices and the design simplicity is advantageous and makes the source popular for the surface treatment of polyolefins [98, 132, 153]. Another advantage is the possibility for a remote operation, in which the sample is placed in the proximity (up to few tens of millimeter) of the plasma jet. Therefore, the treatment is not performed in a confined space and contact between the substrate and the plasma jet is not necessary, leading to polymer modification in non-contact mode [11]. As a consequence, the substrate can be processed by long-lived plasma species carried by the gas effluent. The treatment with this type of active species may prevent damage to the polymer surface since the modification condition is mild. Moreover, the miniaturized dimension makes the processing of complex structures like porous 3D scaffolds, tubular structures and delicate materials more feasible [122]. Lastly, it has been shown that samples treated with a plasma jet are more effectively modified compared to volume DBD-treated samples because of an increased surface degradation during the latter treatment. Samples modified with a DBD are more exposed to charged particles and UV radiation as compared to plasma jet-modified samples. Under this condition, polymer chains are more prone to breaking thus causing degradation of the polymer [83]. However, a plasma jet can only modify the region where reactive species formed by the discharge are present. This gives rise to a restriction residing in non-homogenous surface modifications by this discharge type. Nonetheless, this limitation can be solved by implementing multiple arrays of jets and/or a displacement of the plasma jet(s), similar to MW-induced plasma [61].

4 Plasma Surface Modification Techniques

As previously mentioned, plasma is a mixture of atoms/molecules, electrons, ions, excited species, radicals and radiation in the UV–visible range. The presence of reactive species like electrons, ions, excited species, radicals and UV radiation makes plasma a suitable environment for interaction with a surface. Even the surface of polyolefins, which are considered to be quite inert, can be modified by plasma species. The reason behind this phenomenon is that the range of dissociation and fragmentation energy of the bonds in polyolefins (and polymers in general) is low in comparison to the energy of the plasma species. Furthermore, as plasma only interacts with the uppermost layer of the surface, the bulk properties can be preserved while altering the surface properties.

Hence, plasma treatment can be an excellent alternative for surface modification of polyolefins, as it is capable of breaking chemical bonds, which can lead to different surface modifications. The different potential surface interactions are etching (ablation), cross-linking, functionalization, grafting of specific functional groups and plasma polymerization, as displayed in Fig. 9. During etching, plasma interacts with the surface to form volatile products that are removed from the surface.

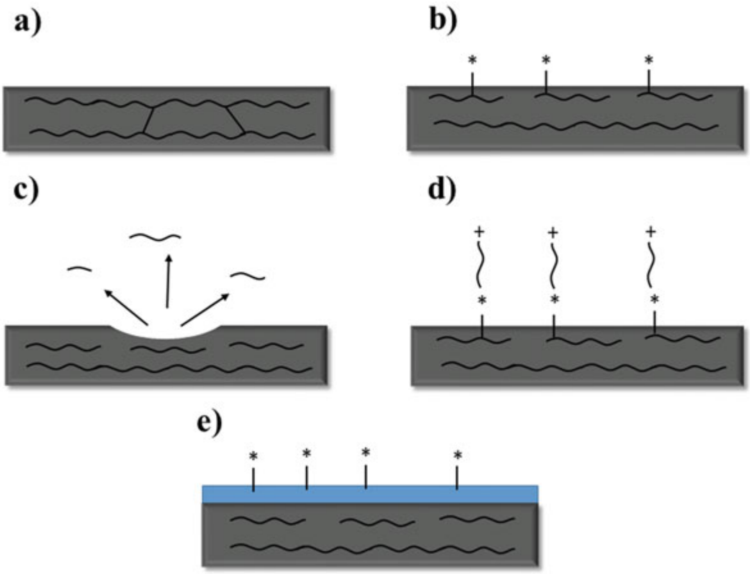

Fig. 9 Different mechanisms occurring during plasma surface modification: **a** cross-linking; **b** functionalization; **c** etching; **d** grafting and **e** polymerization

Cross-linking occurs when radicals on the polymer chains recombine. Functionalization refers to the formation of functional groups on the surface, while grafting uses functionalization for the addition of other functional groups to the surface. Plasma polymerization is used to deposit a coating on the surface. Cross-linking, functionalization and grafting are processes that are all typically described by the term “plasma treatment”. Depending on the selection of the plasma parameters like the gas composition, power and pressure, the desired surface modification can be obtained [95]. The following sections will give a more detailed overview of plasma etching, plasma treatment and plasma polymerization.

It should be noted that most of the presented studies have been carried out under low-pressure and high-frequency plasma environment, despite the need for expensive and complex vacuum equipment. This choice is made because these plasmas are highly controllable systems with well selected active species, as discussed in Sect. 2.2.3. Atmospheric pressure plasmas are a suitable alternative for polyolefin modification, because of the aforementioned absence of vacuum chambers and pumping time. However, the temperature of the reactive environment should be maintained sufficiently low to prevent thermal damage of polyolefins. Nonetheless, a considerable number studies have employed non-thermal plasmas successfully [20, 103, 107, 119].

4.1 Plasma Etching

Etching refers to the removal of a boundary layer of material from the surface by either dynamic physical or chemical processes. Plasma etching is a non-equilibrium process performed in non-thermal plasma and has some unique features as it is chemically selective and usually anisotropic. This process involves the removal of material and the formation of gas phase products by bombarding the surface with high energy ions, neutrals or their combination produced by a high-density plasma (e.g. capacitively coupled plasma). Plasma etching of polymer surfaces can be performed over a broad range of pressures and frequencies. However, in order to avoid damage to the material, the power should be optimized to the used substrate and plasma. This process is associated with a functionalization of the surface. This functionalization is preliminary and is followed by etching and formation of gaseous products.

For a successful etching of polyolefin surfaces, plasma discharge gases like O_2, F_2, Cl_2 and Ar can be used. During such plasma impact, volatile products like CO_x, CCl_x and CF_x will be generated in the plasma reactor [35]. However, it should be noted that polyolefins are less susceptible to plasma etching than polymers comprising oxygen-containing groups. Plasma etching can improve the adhesion properties of polyolefins by increasing their surface roughness and imparting anchor effects. However, the functionalization can also influence the adhesion properties during etching processes [142]. Plasma etching will not improve the permeability properties, although cross-linking effects can positively influence this parameter as will be discussed in Sect. 4.2. It is worth mentioning that the combination of an RF source and a plasma jet has also triggered the etching of polyethylene, as shown in a study conducted by Fricke et al. This research has provided information on the removal of microorganisms and therefore the decontamination/sterilization of the surface [50].

Application-oriented studies that are focused on the plasma etching of polyolefins are somewhat limited. However, some more fundamental studies focusing on the etching rate exist. This parameter is controlled by several process characteristics, such as the discharge gas, gas flow rate and reactor composition. The former characteristic is studied by Kwon et al., who have shown that an Ar RF plasma has a lower etching rate than a mixture of Ar with O_2, because O_2 can rapidly remove the oxidized or broken bonds on the top layer of polyolefin films [84]. The comparison between N_2 and O_2 ICP discharges for plasma etching has demonstrated a higher etch rate and an increased roughness in case of oxygen treated samples, but similar trends in etching rate for both discharge gases [64]. On the other hand, modifying the gas flow rate enables the control of the etching rate. It is assumed that this rate increases rapidly by increasing the gas flow rate until it reaches a maximum value that depends on the discharge gas. A further increase in the gas flow rate leads to a decrease in the etching rate [22]. An example of the etching rate control via the reactor composition is the use of a grounded metal screen in the reactive region (Faraday cage). This has enabled the elimination of ions from the reaction region in the RF plasma etching of PE by fluorine gas, which resulted in a larger fluorination depth [4]. The etching rate can influence the structure of polyolefins after plasma treatment. In the case of

PE, after plasma exposure, a lamellar structure of crystal or amorphous phases can be associated with a different etching rate. This structure does not even change after ageing [41, 168].

4.2 *Plasma Treatment*

4.2.1 Plasma Activation

This approach implies the introduction of different functionalities and/or the modification of already present functionalities on the chemically inert surface by a gas discharge, without introducing monomers. For this purpose, different gases can be used. A first distinction can be made between noble gas plasmas and other discharge gas plasmas. Theoretically, the former type of plasmas can only generate free radicals on the surface by dissociation and fragmentation of the surface bonds, as the generated plasma species will not be incorporated on the surface. Other discharges cannot only generate free radicals as the formed plasma species can also couple to the surface and induce functional group formation. In both plasma types, the remaining free radicals will react with ambient air, leading to the incorporation of oxygen-containing functionalities onto the treated surface. Furthermore, the coupling of free radicals leads to cross-linking in the polymer matrix, which competes with the degradation and functionalization of the polymer. In polyolefins, free radicals can be either created by C–C or C–H bond dissociation, as depicted in Fig. 10, which employs PE as an example. The former process leads to a functionalization with a degradation while the latter process leads to only a functionalization. Because of the excess of energy in plasma and the similarity between C–C and C–H bond dissociation, plasma parameters should be carefully tuned to obtain the desired surface modification. The functional group density after plasma activation increases with respect to the treatment time and reaches an equilibrium after a certain time [7, 151].

As mentioned before, plasma surface modification has certain advantages over other techniques, as it can cause less thermal and chemical damage to the surface

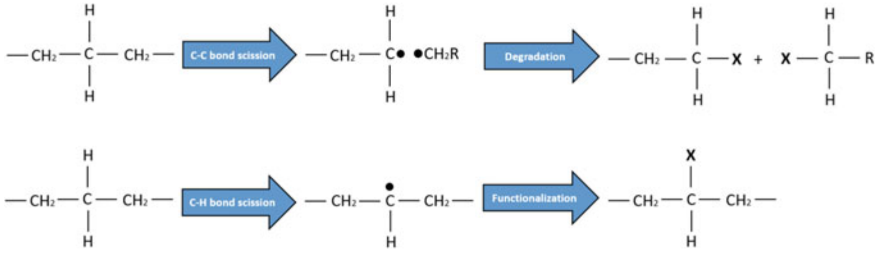

Fig. 10 Polyethylene C–C and C–H bond dissociation and the consecutive reactions

under appropriate conditions, uses a significantly smaller time interval and is solvent-free. However, there are also some disadvantages of using plasma for surface activation. Firstly, completely selective surface reactions are almost impossible to achieve, which leads to surfaces that have no unique functionality. Secondly, the level of surface functionalization by plasma is smaller than by wet chemical methods that have been well studied for a long time for such purposes [18, 28]. Thirdly, plasma activated surfaces are prone to ageing. This is an effect of surface adaptation in which the surface tends to minimize the surface and interface free energy and returns to a lower energy state. Reorientation of the plasma-induced polar groups toward the interface can explain this phenomenon [140]. However, these problems pose no limitation for most polyolefin applications, as the surface energy modification is most often sufficient and the ageing can be circumvented by performing post-plasma modifications directly after the treatment.

A wide variety of plasma process parameters can influence the activation process, like the plasma power and treatment time, which can be described together as energy density, the pressure and the discharge gas. Švorčík et al. have even indicated that the chemical structure of the substrate could influence the treatment, as LDPE and HPDE have shown different properties in terms of wettability, creation of conjugated double bonds, ageing rate, degree of cross-linking, incorporated oxygen percentage and surface roughness when both were exposed to the same Ar plasma [168]. With respect to the influence of plasma pressure, Shenton et al. have compared atmospheric pressure and low-pressure RF plasma surface modification of polyolefins [139]. These two types of plasma can induce a similar treatment effect on the surface, but with a different degree. Also the involved processes differ, as electron and ion bombardment and VUV and UV photons may all play a significant role in a low-pressure plasma, while it is unlikely that these species contribute to the surface modification at atmospheric pressure.

A wide variety of discharge gases is used for the surface modification of polyolefins. In the following sections, these gases are discussed in more detail. These different gases are researched both for fundamental and application-based reasons. For the latter reason, some gases are studied for the improvement of the surface free energy and adhesive bonding, while research also focuses on addressing the problem of gas and vapor permeability as discussed in the introduction. Typically, the introduction of polar functional groups via a wide variety of gases solves the former problem, since it increases the surface free energy and improves adhesion and wettability of the polymers [39, 98]. During the activation process, the previously described process of plasma etching may also take place, which leads to a roughness increase of the surface. On the other hand, the gas and vapor permeability are examined after a plasma-induced cross-linking effect.

Ar and He Plasma

As mentioned before, Ar and He plasmas are theoretically unable to incorporate new functionalities onto the surface and thus a surface functionalization proceeds through reactions between the generated surface radicals and the ambient air. This results in the incorporation of multiple oxygen-containing functionalities such as peroxide, carboxyl, hydroxyl and carbonyl groups on the polyolefin surface. It should, however, be noted that impurities in the discharge chamber like water vapor or air could lead to similar surface oxidation during the plasma process. This leads to a lower amount of free radicals on the surface before exposure to ambient air. The introduction of oxygen-containing groups alters the surface free energy, which determines the degree of wettability and adhesive capability [53]. For example, UHMWPE performance in shoulder prostheses can be enhanced by surface activation through Ar and He DBD plasma at atmospheric pressure. It was demonstrated that oxygen incorporation on the surface increases the adhesive interactions between UHMWPE and bone cement. Moreover, an increase in the cell adhesion has been reported through this plasma activation process [155].

Besides surface functionalization, Ar and He plasma are also of interest for the cross-linking of the surface because the radical formation is not competing with the functionalization, as compared to other gases that are mentioned in Sects. 4.2.1.2–4.2.1.4 [33, 62, 86, 169]. The cross-linking effect of He plasma can be applied as a pre-treatment of the substrate to prevent ageing of a subsequent treatment. For instance, plasma pretreatment has been performed prior to NH_3 treatment that is used to improve adhesion with aluminum deposited by metallization. The result showed that the adhesion degradation is minimized when applying this pretreatment [147]. Lin et al. have illustrated that Ar plasma activation with an RF source could reduce n-hexane permeation through HDPE bottles [94].

Nitrogen-Containing Plasma

Nitrogen-containing plasmas like nitrogen, ammonia and N_2/H_2 plasma can incorporate nitrogen functionalities like amines, imines and amides [37, 39, 45, 104, 159]. Also surface radicals can be introduced, leading to a similar oxidation as mentioned in the previous section. The introduction of these oxygen-containing functional groups can lead to an increase in the wettability [48]. In general, nitrogen-containing plasmas enhance the surface free energy which is desired for applications like dyeability, printability or biocompatibility [95]. For example, Hollahan et al. have used an ammonia-based RF plasma to introduce amine groups on different polymers like PP to improve blood compatibility. The ammonia is dissociated in the plasma, forming NH_2 radicals, which can combine with carbon radicals on the polymer surface to form amine groups [67]. Furthermore, N_2 pulsed arc plasma has shown potential in ion implantation of Cu and Ag antimicrobial reagents on PE surfaces, providing a considerable antibacterial performance against *E.coli* and enhancing cell growth [166, 167].

Nitrogen-containing plasmas do not always incorporate nitrogen functionalities. Sanchis et al. have used a nitrogen RF plasma to increase the wettability of LDPE for improved adhesion to polyolefin foams for automotive industry applications. This treatment only resulted in oxygen functionalities on the surface. The amount of these functionalities was similar to the amount introduced by the oxygen plasma. However, the mechanism of oxygen incorporation was different, as the oxygen plasma exposure resulted in direct functionalization, while the nitrogen plasma exposure introduced oxygen-containing functional groups via post-plasma reactions with ambient air [130].

Oxygen-Containing Plasma

Oxygen-containing plasma comprises a variety of possible discharge gases like CO_2, CO, O_2 and air. Although air mainly contains nitrogen, it can be classified in this category because it primarily produces oxygen-containing functional groups since oxygen is by far more reactive than nitrogen. Moreover, nitrogen-containing intermediates increase the atomic oxygen formation. *Air and oxygen plasmas* in vacuum have revealed a variety of oxygen containing functionalities [121]. A low-pressure RF plasma ignited in oxygen or air and applied for HDPE treatment, for example, was found to successfully increase its surface micro-hardness and incorporate carbonyl, carboxyl, ether and peroxide groups on the modified surface, which improved its wettability [92]. Multiple studies have focused on increasing adhesive bonding to polyolefins by air and/or oxygen plasma. A recent investigation has indicated that the shear strength of adhesive-bonded joints of two PP films made after low-pressure air or oxygen RF plasma treatment is significantly higher than the shear strength obtained from joints with only-degreased surfaces [102]. Furthermore, Murthy et al. have observed that the bond strength between glass reinforced PP and HDPE panels can be significantly increased after treatment with an air plasma jet, which could be directly associated with the increase in surface energy of both surfaces [131]. Also air DC discharge plasma has shown the ability to increase the adhesive bonding of HDPE and PP to steel as a secondary structure in assemblies for the automotive industry. In this case, the lap shear, tensile strength and surface free energy reach maximal values after which they decrease again, indicating a specific optimal plasma treatment for this particular experimental condition [14]. Other studies on an air DBD and air plasma jet, however, indicated that the surface oxidation and associated wettability reached an equilibrium after a certain treatment time [31, 75].

CO_2 and CO plasma can add oxygen-containing groups on the treated surface of polyolefins due to the presence of oxygen-containing reactive species in the reacting chamber. Apart from the alcohol, ketone and carboxylic acid functional group incorporation, substrate degradation and cross-linking can occur. This stabilizes the modified surface, as was illustrated with PP [5]. Utilizing a MW discharge at low pressure can produce carboxylic acid groups on the surface. Moreover, it was demonstrated that the degradation via chain scissions has a heterogeneous effect since it mainly affected amorphous zones [106]. An addition of H_2O to a CO_2 MW plasma did not improve the surface functionality, as HDPE treated in the CO_2/H_2O plasma demonstrated a lower percentage of carboxylic acid on the modified surface [115].

Halogen-Containing Plasma

Haloform plasmas are often reported to introduce a mono-sort of halogen groups. This designation is based on the ability of these plasmas to introduce mostly one type of chemical bonds, which is distinct from other plasmas. Namely, C-X bonds are mainly incorporated on the polyolefin surface, in which X is a halogen atom. *CF_4plasma* is one type of a haloform plasma that typically enhances the surface hydrophobicity [30, 76]. The fluorination mainly happens due to the substitution of H by F atoms in the polyolefin chain, leading to the formation of CF, CF_2 and CF_3 groups on the surface. It has been demonstrated that VUV radiation enhanced the surface treatment efficiency in RF glow discharges. Fresnais et al. have used a MW discharge to ignite a mixture of CF_4 with oxygen, which was proven to preserve the hydrophobic characteristics together with a lower surface roughness of the treated LDPE substrate [49]. One of the application examples of plasma fluorination is the enhancement of the PP surface properties to prevent fuel permeation through the walls of such polymeric containers. Although the wet chemical treatment can be used to achieve the same aim, it shows deeper altering effects in terms of the thickness of fluorinated surface (5000 nm) compared to a plasma functionalization (10–100 nm). Nevertheless, the barrier efficiency remains the same in both approaches [57]. Also SF_6 plasmas have the capability to fluorinate polyolefins, as demonstrated by Amorim et al. The treatment introduced, besides fluorine-containing functionalities, a significant amount of oxygen and a small amount of sulfur to the PP surface. However, it still resulted in a decreased surface wettability [3]. Other examples of mono-functionalization processes are *bromoform and chloroform plasmas,* which can produce a single surface functionality with high yields [56, 78, 162]. One of the necessary conditions to achieve a mono-sort functionalization is performing the treatment in low-pressure plasma reactors since they provide an excellent control over the discharge parameters and thus the final surface modification. Results indicated that the bromination by using a RF plasma is very selective and has less undesired side products. Moreover, the post-plasma oxidation in this functionalization was small compared to the fluorination process [55].

Hydrogen Plasma

Hydrogen plasma differs from others because of its particularly intense broadband emissions in the VUV region (below 170 nm). These photons are also the main reason why the primary outcome of such plasma treatment is cross-linking and the formation of double bonds. These changes in the polyolefin structure increase the surface density, which results in the reduction of the permeability of the surface layer [13, 68, 124].

4.2.2 Plasma Grafting

Plasma grafting is the second type of plasma treatment in which the activation step is used to covalently bind molecules on a surface. Plasma grafting can be performed via post-plasma grafting or syn-irradiation grafting (direct grafting). In the former approach, the sample is first functionalized by a plasma activation step. Within this approach, a distinction can be made based on the surface chemistry used for grafting. In the first post-plasma grafting technique, Ar or He plasmas are most commonly used to introduce radicals onto the surface. Typically, these radicals will react with the ambient air after the treatment, leading to the formation of peroxide and hydroperoxide groups, as mentioned before, although the radicals could also be used to start a radical polymerization reaction directly by introducing the monomer in the gas phase after the plasma is turned off. The latter strategy is, however, not frequently used. The aforementioned peroxide and hydroperoxide groups are then used as initiating sites for grafting polymerization. The monomer can be added in the gas phase or the substrate can be immersed into a monomer solution, after which polymerization is initiated by an increase in temperature or by UV radiation, for example [37]. This process leads to covalent bonding of a particular functional group to the surface with a composition similar to the typical polymerization, as the monomer is not introduced during the plasma exposure. Polyolefins are good candidates for this process, as the response to the plasma surface oxidation is fast and leads to the introduction of the desired chemical functionalities. Figure 11a illustrates the first type of post-irradiation plasma grafting, which is sometimes referred to as plasma-induced graft (co)polymerization [141]. The grafting quality depends on the initial radical density, the monomer quantity and reactivity and the reaction time [73, 125]. This

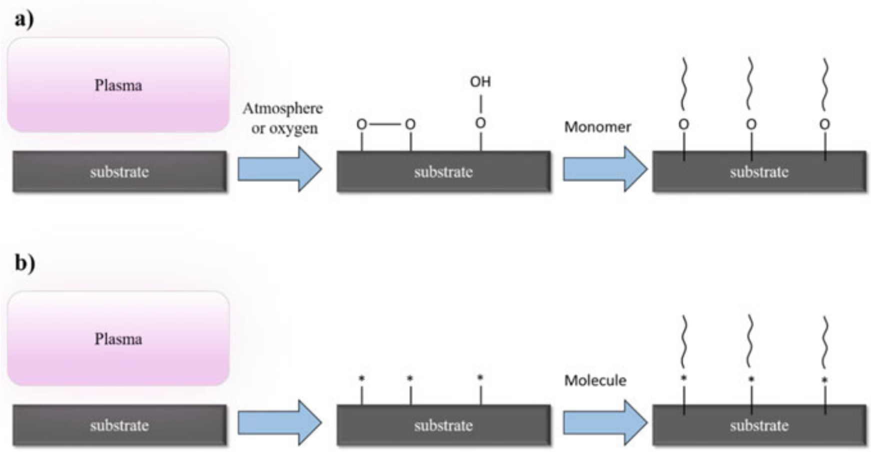

Fig. 11 Schematic representation of the post-irradiation plasma grafting steps. **a** plasma-induced graft (co) polymerization onto plasma-generated (hydro) peroxides and **b** grafting of molecules on plasma-generated functional groups (*)

technique can be performed with a wide variety of monomers like acrylic acid and different acrylates, such as glycidyl methacrylate, methyl acrylate, and 2-hydroxy ethylacrylate [73]. Polyolefins functionalized with the help of post-irradiation plasma grafting are mainly researched for biomedical applications. For instance, polyethylene has been grafted with styrene via CCP Ar plasma for the enhancement of the surface biocompatibility [58]. This study has concluded that the chemical nature of the monomer grafted onto the polymer is more critical than the oxidation induced by the plasma. Biomolecules can also be immobilized on plasma grafted polyolefins. An example is the immobilization of chitosan on plasma grafted acrylic acid making use of oxygen RF plasma on PP-based sutures via a carbodiimide-mediated reaction. Additionally, different antimicrobial agents have been coupled to the suture which leads to drug release properties and an enhanced antimicrobial activity [134].

As mentioned before, a distinction in post-plasma grafting can be made based on the surface chemistry used for grafting. Besides using (hydro) peroxides or radicals for initiating polymerization, other plasma-induced functional groups can be used to immobilize molecules, as illustrated in Fig. 11b. This resembles the immobilization after plasma grafting as described above. A frequently used functional group for molecule immobilization is a primary amine. As mentioned before, nitrogen-containing plasma can activate the polyolefin surface and introduce NH_2-groups [46, 159]. For example, Ghasemi et al. have immobilized the enzyme trypsin on ammonia plasma treated polyethylene films via a glutaraldehyde linker. The aldehyde functionality of the linker can react with a primary amine on the surface and the enzyme, forming an imine which is subsequently reduced by sodium cyanoborohydride leading to a chemically stable secondary amine [59]. Another employed strategy is the use of CO_2 plasma for the introduction of carboxylic acid groups. Vartiainen et al. have immobilized glucose oxidase and chitosan on N_2/CO_2 plasma-treated PP for antimicrobial packaging applications and have compared it with N_2/NH_3 treatment. The N_2/CO_2 DBD plasma treatment was reported to generate carboxylic acid functionalities on which the bioactive molecule can be immobilized via a carbodiimide-mediated reaction. Glutaraldehyde was again used as a coupling agent for the N_2/NH_3 plasma treated polymer, but without the reduction step. The density of primary amines was higher than the density of carboxylic acid groups, and the enzymatic activity and amount of immobilized chitosan were both higher for the N_2/NH_3 plasma treated PP [156, 157]. Plasma treated polyolefins can also be modified via less conventional chemical reaction pathways. Habib et al. grafted the antioxidant ascorbic acid (ASA), which also has antibacterial characteristics, on LDPE after air plasma treatment [63]. They suggested that the post-plasma grafting reaction proceeded via deprotonation of ASA by alkoxyl radicals, which originated from the decomposition of (hydro) peroxides on the plasma treated surface, after which the ASA-radical can interact with double bonds that were also formed during the plasma treatment. As such, ASA can be covalently grafted onto the LDPE surface, imparting the material with antibacterial properties towards *Escherichia coli and Staphylococcus aureus.*

Syn-irradiation grafting is the other main plasma grafting approach. During this process, a monomer or molecule is adsorbed onto the substrate and subsequently

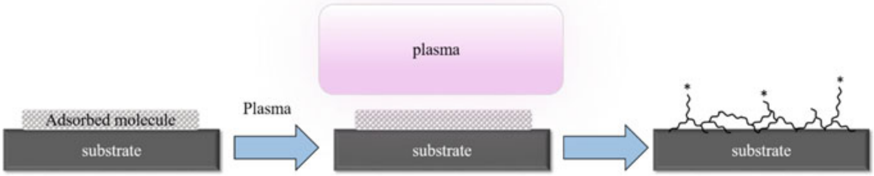

Fig. 12 Schematic representation of syn-irradiation plasma grafting steps. (*) is the desired chemical group

exposed to plasma. During the plasma exposure, radicals are generated in the adsorbed molecule layer, which leads to a coupling of the molecules to the surface and between each other. Most often, a monomer is used, which leads to the formation of a cross-linked polymer layer. Figure 12 shows the steps of syn-irradiation plasma grafting. An example of a simple monomer syn-irradiation plasma grafting step is the study of Prachar et al., in which tetraethoxysilane (TEOS) has been adsorbed onto the surface of PP via CCP air plasma exposure. The induced silicon functionalities have led to a permanent hydrophilicity of the substrate [126]. Bigger molecules can also be grafted via this method [117]. An example is the immobilization of dyes on PP, LDPE and HDPE for the fabrication of colored materials [34]. In this type of process, the preservation of the monomer or molecule is of importance to obtain the desired surface functionality. This needs an optimization of the plasma parameters, as side reactions can occur during the plasma exposure. These side reactions increase the heterogeneity, which is usually not desired in the process of grafting. Therefore, post-plasma grafting is more favorable than syn-irradiation plasma grafting to have higher homogeneity and specificity, as the grafted molecules will only resemble the conventional polymer completely in the former technique. Syn-irradiation plasma grafting, however, forms a more straightforward method, as the wet chemical treatment step is limited to a dipping or spraying procedure.

4.3 Plasma Polymerization

The term “plasma polymerization” is often employed to describe a variety of processes in which the introduction of precursors into a plasma results in the deposition of a coating [100]. Plasma-enhanced chemical vapor deposition (PE-CVD) is the most frequently used type of plasma polymerization for polyolefin surface modification. Therefore, this specific technique will be discussed in more detail in the following paragraphs. Also, all the examples of plasma polymerization that will be explained in detail in this section refer to PE-CVD processes. PE-CVD is a coating technique in which an organic monomer in the vapor phase is introduced in a plasma, leading to the conversion of the monomer into reactive fragments and subsequent polymerization. This can occur in the gas phase or on a substrate placed in the plasma, which usually results in the deposition of highly cross-linked films [71]. Typically, ions created in the plasma phase can bombard the surface and the coating, leading to an etching of the growing film [37]. The monomer can be, but does not need to be, a molecule that can polymerize via conventional polymerization techniques. In the former case, the resulting plasma polymer will not resemble a polymer obtained via these conventional techniques because of fragmentation of the monomer structure and the aforementioned cross-linking process [100]. There is also a difference between plasma polymerization and plasma grafting. The former technique applies a coating that is based on the monomer structure onto a substrate, although the monomer functionality is not completely preserved. The latter technique, however, leads to covalent grafting of molecules to the substrate that preserves the monomer/molecule structure [37].

During the plasma polymerization process, the monomer (alone or with a carrier gas) is fed into the plasma discharge or afterglow. Similar to plasma activation, plasma polymerization can be performed at low pressure, intermediate pressure and atmospheric pressure [100, 154]. The plasma process and the resulting coating is influenced by a number of other parameters besides the pressure, like the chemical structure of the monomer, the monomer flow rate, the carrier gas flow rate and the plasma power. The most important factor that affects the plasma polymer properties is the energy applied per monomer molecule. Yasuda proposed a parameter, W/FM (with W: power (W), F: monomer flow rate (mol/s), M: molecular mass of the monomer (kg/mol)), to represent the energy input per unit mass of monomer [148]. Increasing the energy applied per monomer molecule (or increasing W/FM) leads to a higher precursor fragmentation. This is considered to be beneficial for the stability of the coatings, which is in some applications of significant importance. However, more fragmentation will usually lead to a loss of the initial monomer composition in the resulting coating as well. This can be an unwanted effect, as the preservation of the monomer functionality is crucial for some purposes [148]. To improve the monomer functionality retention, a pulsed treatment cycle can be used. During the on-periods of the pulses, which are usually in the order of microseconds, monomer activation and generation of reactive site on the surface occur, while polymerization can take place during the off-periods, usually in the order of milliseconds, in which the influence of UV-, ion-, or electron-induced damage to the growing film is limited. This leads to higher retention of the monomer functionality, while stable coatings can be obtained [12]. Plasma polymerization can be performed in a wide number of source configurations of which DBD, RF and MW are the most frequently used.

The following sections will give an overview on different monomers used for PE-CVD on polyolefin substrates. This technique is applied for solving both general problems related to polyolefins. However, some coatings are mainly studied because they can increase the barrier performance of polyolefins, like silicon-oxide coatings (Sect. 4.3.1) and carbon-hydrogen coatings (Sect. 4.3.2), while other coatings are mainly applied to modify the surface free energy, like COOH- and amine-rich coatings (Sects. 4.3.3–4.3.4). Section 4.3.5 will shortly discuss less studied coatings and the last section will discuss grafting on plasma polymerized coatings.

4.3.1 Silicon-Oxide Coatings

Plasma polymerization of organosilicons has been widely applied on polyolefins for the creation of silicon-oxide (SiO_x) coatings [72, 102, 113, 114, 133]. These coatings have attracted interest because of their wide application range in several fields as they impart good scratch resistance, thermal stability, reduced friction, adjusted wettability, flame retardance and gas–vapor barriers. For polyolefin applications, the latter characteristic is the most important. Organosilicon precursors are characterized by their sufficient volatility near room temperature, affordability, relative non-toxicity and non-flammability [109, 113, 136, 161]. Moreover, a large variety of potential reactants are commercially available such as hexamethyldisiloxane (HMDSO), tetramethyldisiloxane (TMDSO), tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS). Particularly, HMDSO is preferred over other monomers in the broad majority of studies involving organosilicon plasma polymerization due to its highly organic character, high vapor pressure and ability to deposit siloxane coatings at low temperature [88, 109]). Since polyolefins are widely used in the pharmaceutical and food packaging sectors, the enhancement of their gas-barrier properties is critically required for a better product conservation. In this sense, polyolefins started, a few decades ago, to constitute one of the main substrates in the studies of HMDSO and other organosilicon plasma polymer coatings. It is worth mentioning that among all polyolefins, PP is by far the most considered in such studies because of its more prominent position as packaging polymer given its transparency, low specific weight brilliance and low density at considerably low costs [80, 136]. HMDSO plasma polymerization will deposit coatings resembling polydimethylsiloxane (PDMS) at low powers, which compromises the barrier performance. This behavior was compensated by increasing the oxygen to HMDSO monomer ratio, which reduces the organic amount within the plasma-polymerized coatings. This leads to more inorganic quartz-like deposits generally exhibiting higher barrier performance [81]. The challenge with the inorganic coatings is to have a crack-free coating as this will lower the barrier performance. Moreover, because of the use in food and pharmaceutical packaging applications, the necessary autoclaving also tends to induce cracks on the SiOx coatings. This can be enhanced by first depositing a PDMS-like coating or by using a vertical gradient in the coating from PDMS-like to SiO_2-like by progressively increasing the oxygen to HMDSO ratio. In this way a combination of favorable thermal, adhesive and mechanical properties on the one hand, and adequate barrier performance on the other hand is reached [80]. More recently, an atmospheric pressure plasma jet deposition of silica barrier coatings on PP was proposed by Scopece et al. as an alternative to the traditional high cost vacuum systems. One of the major downsides of the atmospheric plasma processes is the formation of powder during deposition. This can compromise the durability and quality of the generated coatings. Moreover, the formation of cracks was also observed on the coatings as a result of a thermal fatigue phenomenon after the repetitive heating and cooling steps induced by the repetitive plasma jet passages. Despite these drawbacks, the gas barrier performance of PP was improved by a factor of 2. Increasing the deposited coating thickness or applying multiple coating layers were shown to exhibit an additive gas barrier character [136].

4.3.2 Carbon-Hydrogen Coatings

Next to the silicon-oxide coatings, carbon-hydrogen coatings have also been deposited on polyolefins via plasma polymerization to enhance their gas-barrier properties [9, 69, 94, 145]. This polymerization can be performed using any gaseous hydrocarbon monomer. However, for an easy processability, methane (CH_4), acetylene (C_2H_2) and ethylene (C_2H_4) are generally selected. The properties of the obtained amorphous coatings are mainly influenced by the cross-linking degree and to a lower extent by the use of saturated or unsaturated monomers. Methane is characterized by considerably reduced deposition rates compared to ethylene and acetylene [66]. Lin et al. have conducted a comparative study between methane and acetylene plasma polymerizations done by an RF discharge to coat the inner surface of HDPE bottles. When using methane as precursor, free radicals were generated by the hydrogen detachment solely, which yields plasma polymers with low number of trapped free radicals. However, acetylene polymerization led to the formation of di-radicals and as such, the production of plasma polymers with considerably higher number of free radicals. As a consequence of this high free radical concentration, large amounts of oxygen-containing functionalities were incorporated onto the surface, even though the base monomer had no oxygen. Therefore, the O/C ratio of the acetylene-derived plasma coatings was 6 times higher than that of methane plasma-polymerized surface. Under optimal parameters, a significant reduction in gas permeation is detected when using acetylene in comparison to methane but also to trimethylsilane, acrylic acid plasma polymerizations and Ar plasma activation. This is mainly due to a combination of surface tightness and an increase in polar functional groups on the surface [94]. When increasing the input energy, the internal stress within the hydrocarbon network intensifies leading to the generation of diamond-like carbon (DLC) coatings [66]. DLC films consist of amorphous carbon with graphite structure comprising sp^2 bonds and diamond structures comprising sp^3 bonds. Moreover, DLC coatings are characterized by their lubricating properties, toughness, abrasion resistance, biocompatibility and chemical stability. In addition to their prominent role as gas-barrier, DLC films are also used to enhance the adhesive properties of polyolefins. In fact, the low adhesion of polyolefins is a limiting factor occasionally preventing them from being widely used particularly in the biomedical applications demanding an enhanced adhesion [69, 145]. Takahashi et al. have indeed shown that the low-adhesive surface of LLDPE and HDPE could be substantially improved after applying a DLC coating resulting from an acetylene plasma polymerization done via a RF plasma device. However, other polyolefins such as LDPE, isotactic PP and syndiotactic PP did not show higher adhesive properties because of the low adhesion between DLC and the 3 polyolefins. This adhesion can be improved by a number of different strategies like plasma etching or activation prior to plasma polymerization. For example, Baba et al. used H2O and O2 plasma prior to acetylene plasma polymerization [9].

4.3.3 COOH-Rich Coatings

Besides the use of plasma-coated polyolefins in many technological fields necessitating barrier and protective coatings, other particular plasma coatings are also continuously being developed for other purposes. The major field for COOH-rich coatings is the enhancement of the cytocompatibility of polyolefins for their use in the biomedical field. These functionality can also be introduced by plasma activation of polyolefins, because of the carbon-hydrogen nature of these polymers. As already mentioned in the introduction, the main downside restricting the use of unmodified polyolefins in the biomedical domain is their inadequate biocompatibility stemming from their hydrophobicity and low surface energy [111, 128, 135]. Therefore, among other plasma polymers, COOH-rich coatings are the most frequently deposited on polyolefin substrates in order to improve cell-surface interactions [29, 128]. In fact, COOH groups substantially enhance polyolefin surface wettability and favor the interactions with some cellular receptors thus stimulating several signaling pathways and metabolic processes. Consequently, COOH-dense coatings support the adhesion, proliferation and differentiation of a broad variety of cell types [15, 23, 29, 65, 112, 128, 138]. Moreover, COOH functionalities are sensitive to changes in the pH of the milieu in which they are submerged making them promising candidates in drug-delivery applications involving the release of a drug in a pH-specific environment [111]. Plasma deposition of carboxylic films on polyolefins was mainly performed using the unsaturated acrylic acid (AA) or maleic anhydride (MAA) monomers at low, medium and atmospheric pressures with a high retention of COOH groups [74, 112, 149]. However, the main issue of plasma-polymerized COOH films is their low stability in aqueous environments. If deposited with unsuitable plasma working parameters, the coating can rapidly dissolve, not only abolishing the coating effect but also drastically acidifying the surroundings. This acidification constitutes a major drawback in the biomedical applications as it yields harmful effects on tissues and cells, similar to what is perceived during infection [29, 38, 47, 111]. Therefore, several studies have tackled the stability of plasma-polymerized COOH–rich coatings on polyolefins while maximally preserving the high density of COOH by two approaches: (1) enhancement of the adhesion between the coating and the substrate via a surface pre-polymerization treatment and (2) improvement of the coating cohesion strength via increasing the cross-linking by carefully selecting the plasma parameters [111, 112, 128, 135]. Typically, these type of coatings contain next to carboxyl functionalities a wide variety of other oxygen-containing functionalities like alcohols, ethers and ketons [135]. Most studies investigate this plasma polymerization on flat polyolefin surfaces, but Nistico et al. subjected hernia-repair PP meshes to an RF pulse discharge plasma polymerization of AA to confer adhesive properties and therefore, reduce undesired displacements of the meshes [118].

4.3.4 Amine-Rich Coatings

Besides COOH-rich coatings, amine-rich coatings are also regularly studied for polyolefin surface modifications for biomedical applications [10]. These coatings have a more favorable wettability in comparison to untreated polyolefins and protonated amines can introduce localized positive charges on the surface if placed in aqueous solution at physiological pH. This can lead to electrostatic interactions with negatively charged cells and proteins [8]. Different precursor gases like organic amines (e.g. allylamine), (3-Aminopropyl) triethoxysilane (APTES) and mixtures of acetylene/ethylene and nitrogen or ammonia are used to deposit amine-rich coatings [8, [40, 54, 60, 150, 158]. Typically, these coatings possess a complex nitrogen-rich chemistry that includes, among others, nitriles, imines and primary and secondary amines. Furthermore, oxygen can interact with the surface after exposure to ambient air, leading to the formation of amides and conventional oxidation products like peroxides. Traces of oxygen-containing species in the discharge can also lead to this type of functional groups in the plasma polymer [8, 150]. Different studies have shown that amine-rich coatings can improve cell adhesion. The plasma polymerization of allylamine on UHMPE in a medium pressure DBD indicated a good cell viability in comparison to the bare polymer, for example [8]. The cell-interactivity of a plasma polymerized ethylene/N_2 mixture was used to synthesize micropatterns for controlled cell culturing on PP. The coatings were deposited with an atmospheric pressure DBD and the patterns were fabricated using a mask [60]. Another application that is researched is the use of amine-rich coatings on COPs. As mentioned in the introduction, COPs and COCs are emerging as biosensor devices and plasma polymerization of functional coatings can be interesting. APTES is plasma polymerized in a RF plasma source to add primary amines on the substrate, which can be used for covalent attachment of target molecules like active antibodies or DNA molecules [158].

4.3.5 Other Plasma-Polymerized Coatings

This section gives a short overview of plasma polymers with other functional groups than the aforementioned functionalities. Alcohol functional groups can be introduced via plasma polymerization of allyl alcohol. Besides hydroxyl groups, ether, epoxy, carboxyl and carbonyl groups can be found in these coatings [42, 116]. Nihlstrand et al. have performed adhesion tests between the coating, deposited by a RF plasma source on different thermoplastic polyolefins or polyolefin rubber, and lacquer. At appropriate plasma parameters, excellent lacquer adhesion could be observed. Increasing the power led to a lower amount of hydroxyl groups and a decreased adhesion performance. The variation in the adhesion performance is attributed to VUV emission during the plasma deposition, which leads to radical creation in the near-surface region of the substrate. This can cause chain scission reactions which can lower the cohesive strength of the substrate [116]. Friedrich et al. have tested the peel strength of an aluminum layer deposited on plasma polymerized allyl alcohol on PP by an RF plasma source and have compared it with plasma polymerized allylamine and acrylic acid. It was observed that the adhesion between the coating and the aluminum increased in the following order: allylamine << allyl alcohol < acrylic acid [54].

Plasma-polymerized poly (ethylene glycol) films are of interest for biomedical applications in which complete surface inertness is required, as these coatings can resemble the native polymer which is known for its antifouling behavior. As mentioned in the introduction, polyolefins are not completely inert in biological environments, which can for example lead to inflammatory responses when implanted. Choi et al. have deposited these coatings on PE in a RF plasma reactor and have performed in vivo evaluations. After 4 weeks of implantation, it could be observed that the coated substrates caused a lower degree of inflammation, fibrous tissue proliferation and toxicity as compared to the bare PE, illustrating the superior biocompatibility and minimum toxicity of these type of coatings [25].

Fluorocarbon plasma polymers are another type of coatings applied on polyolefins. Different precursors can be used like trifluoromethane/ethylene mixtures and octafluorocyclobutane [144, 160]. A hydrophobic fluor-rich coating with CF-, CF_2- and CF_3-bonds is usually obtained [144]. Walker et al. have observed that plasma polymerization of a trifluoromethane/ethylene mixture in a MW source results in PE with increased barrier performance to toluene [160].

4.3.6 Grafting on Plasma Polymers

Similar to plasma grafting on polyolefins, plasma polymerized coatings can also be used for immobilization purposes. A variety of studies has used plasma polymers for grafting, but only a limited amount has focused on polyolefin surfaces. An explanation for this limited interest can be due to the fact that the introduction of functional groups by plasma activation for subsequent immobilization is sufficient by itself for the intended applications, leading to a lacking need for grafting on plasma polymers. Another explanation could be that this grafting technique is mainly of importance in the biomedical field, where materials like titanium, polyethylene terephthalate and biodegradable polymers are preferred substrates. An example of grafting on a plasma polymer is the study of Lim and coworkers who have used acrylic acid plasma polymerization for protein immobilization on a HDPE facial implant [90]. The carboxyl groups on the surface reacted with the primary amine groups of a bone promoting signaling protein via a carbodiimide-mediated reaction. Another example has involved a RF plasma source to deposit plasma polymerized acrylic acid coatings on LDPE. A similar chemistry was used for subsequent attachment of heparin and highly-sulphated hyaluronic acid via a spacer molecule to avoid thrombus formation on the surface [44]. Amine-containing precursors were employed in other studies, like the work of Lee and co-workers. They have used allylamine and cyclopropylamine as precursors in a DBD plasma polymerization process for the immobilization of laccase enzymes on amine-functionalized non-woven PE/PP fibers, which can be used for dye removal from wastewater [91]. Glutaraldehyde has acted as a linking molecule, reacting with the primary amines on the surface and of the enzyme. The same strategy was also employed by Liu and co-workers to immobilize horseradish peroxidase on PP, using a plasma polymerized allylamine layer deposited with a RF plasma source. These surfaces could be useful for multiple biotechnological applications such as biosensors [97].

5 Conclusion

Polyolefins are of the most frequently used polymers because of their favorable properties. However, given their low surface energy and relatively high gas and vapor permeability, material adjustments are required for some applications. Surface modifications provide an interesting type of these adjustments, as, in addition to several advantages, they are performed independent of the well-established material processing steps. Among different surface modification approaches, plasma-based techniques are very attractive due to their fast, environmentally friendly and widely applicable aspects. A variety of different plasma reactor designs exists, of which corona discharges, DBDs, RF sources, MW sources and plasma jets are the most used for the surface treatment of polyolefins. Depending on the used plasma parameters, different plasma-surface interactions can be obtained. Plasma activation and grafting are two techniques that can introduce a variety of functional groups on the surface, with the latter providing more selectivity over these groups. Together with plasma etching, these techniques can all be used for surface energy modification. This enhances the printability, dyeability and biocompatibility of the polyolefin surface and increases the adhesive bonding to materials. Plasma activation can also induce a cross-linking of the polymer chains, which can lead to an enhancement of the gas and vapor permeability. Tuning the working conditions for plasma activation can modify the type and density of the incorporated functional groups on the surface and the degree of cross-linking. On the other hand, plasma polymerization leads to coating deposition. Depending on the monomer and other working parameters, coatings with different functionalities and properties can be obtained. Some coatings are very useful for improving the barrier layer performance. These coatings are significantly better and more useful than plasma activation for this purpose. Other coatings are applicable for modification of the surface energy, which has the same intent as plasma activated and grafted polyolefins. In general, it can be concluded that plasma modification of polyolefins is an interesting approach for the improvement of these materials, which widens their applications range.

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Plasma Modified Polyolefine: Physical Changing and Applications

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Abstract A cluster of electrons, ions, neutrals, and photons excited by electrical filed through a gas medium called plasma. According to the plasma medium chamber, plasma is classified into Low-pressure- plasma (LPP) and Atmospheric-pressure-plasma (APT). While polymer attracted a lot of attention, modified methods to change its defectiveness are developed. Plasma modification has common effects which could change in respect of plasma forming gas. In the first part of this chapter, we discussed polymer surfaces are studied in detail. In the second part, the Polyolefin family plasma modification and its classification. Besides, plasma reactions by polymer surfaces are studied in detail. In the second part, the Polyolefin family and its two members, Polypropylene (PP) and Polyethylene (PE) were introduced. In the third section, to scrutinize plasma forming gas effect on the modified surface, the plasma treatment of PP and PE discussed with a detailed. Great attention has been given to their applications in various fields, such as modifies base for new catalysts. Summarization is collected in the fourth section, to give a new vision to researchers.

1 Introduction

Since plasma introduction in the 1960s, plasma has been used in industrial applications [1]. In the 1980s, the plasma using broadened into surface treatment, to be more exact in fields of metals and polymers [2]. Plasma has a dominant role in surface treatment, and a huge range of materials has been modified by plasma. Although, plasma effect surface properties related to plasma type, but plasma treatment has a common effect on surface properties, for instance changing wettability, adhesion and surface energy, protection and anti-wear, and creating functional groups [3]. The outlooks of very good results, as experienced in the polymer field, are exciting attempts to apply plasma processing vastly to polymer's surface modification. Undoubtedly, many advantages are provided by plasma treatment as exclusive effective tools to achieve desirable surface properties in a broad range of polymer. In recent years, the polymer

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has increased greatly used in diverse industries as well as consumer products [2]. On account of polymer's properties, traditional engineering materials have been able to replace polymers [1]; however, polymers and other engineering materials have basic differences that created a broad range in research to modify polymers to reach ideal properties. Polymers can be categorized by their properties, i.e. their degree of entanglement and critical surface tension. Among this group of materials, Polyolefines excited attention because of its properties such as lightweight, recyclable, and inert type of thermoplastic [4], these unique properties made it the best choice for a wide range of applications. Nevertheless, having some inadequate properties such as poor wettability, polymers are ignored in some applications. To overcome this problem, various surface modification methods have been developed [5]. Modification surface properties without altering bulk properties are the main subject in polymers modification [6]. Polypropylene (PP) and Polyethylene (PE) have become the most attractive polyolefin family. PP and PE are used in industry, medical science, and catalyst fields as substrate. In practice, most industrial materials are made by blending PP and PE with other polymers. Producing new polymers does not sound wisely; in contrast altering surface properties is a very useful way to improve PE and PP usage.

2 Surface Modification Techniques

In order to improve polymers' surface properties, there is a wide range of techniques offered a good opportunity for using polymers in the industry [7]. Admittedly, each of these methods has its own prospects and performance for tailoring surface, to accomplish a feat choosing adequate technique is necessary. Physico-chemical, Mechanical and Biological methods are three classifications of modification methods, for more details see Ref. [5]. Reaching this method needs to know how is they exactly worked. In this chapter, we aim to focus on plasma modification classified into the physicochemical method.

3 Plasma Technology

3.1 Fundamental Background

It is useful to start by defining what plasma is. Plasma considered a fourth of state matter and the physical definition of plasma is a collective of ions, electrons, neutrals, radicals, and excited molecules [8] (Fig. 1). A gas typically is an insulator, applying extremely voltages across a chamber filled with gas or a mixture of gases leads to breaking down and turning into conduct electricity, the resulting ionized gas is often called plasma or electrical discharge. The degree of ionization of a plasma

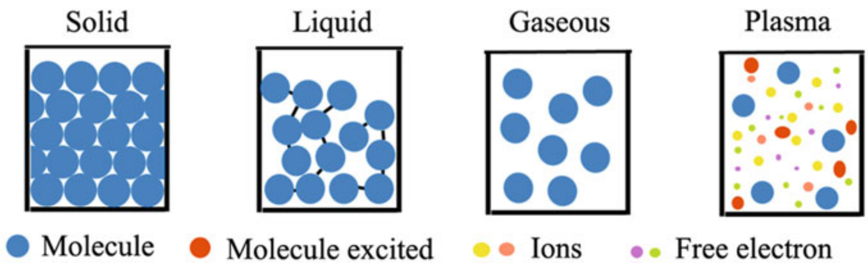

Fig. 1 The schematic of matter state (Modified reprinted from Ebnesajjad et al. [19])

is subjected to atoms that have lost (or gain) electrons, or in thermal plasmas is controlled by temperature. A collection of positive and negative charges provides plasma definition, the 'self-generated' electric filed has an important role in plasma effects. Not all ionized gas can be classified as plasmas; in fact the main characteristic of plasma is collective behavior [9]. Plasma treatment involves a number of physicochemical processes depending on the type and nature of plasma forming gas. Consequently, altering surface properties, especially in polymeric materials, is related to plasma type. Different types of gases such as argon (Ar), oxygen (O_2), nitrogen (N_2), fluorine (F_2), carbon dioxide (CO_2), Ammonia (NH_3), and water can alter the surface properties required by several applications.

3.2 *How to Apply Plasma*

With regard to susceptibility materials in plasma reaction, a better knowledge of elementary plasma processes is necessary. Not only the right parameters manage to control the plasma reaction, but they also could cover poor selectivity in creation species. Plasma parameters are listed in two groups as called internal and external parameters [10]. Internal parameters (such as type of plasma's species, energy, and directional distributions) and external parameters (such as reactor geometry, applied power, and gas pressure and flow) are governed plasma excitation type and interaction with the sample.

3.3 *A Brief Review on Plasmas*

A lot of studies on polymer modification have been reported previously in a number of literatures [11, 12]. Plasma is acknowledged a uniquely effective way to tailor polymer surface and engineering materials. Plasma processing shows some major advantages: it is a clean, dry, and very fast process, having low temperature, non-equilibrium nature, and their environmentally friendly nature, and it affects only the surface of samples [13]. The knowledge nature of plasma could very informative to understand the interaction between polymers' surface and plasma. According to the desired, the power supply can generate plasma [2, 14]; there are four classifications of plasma as follows:

Direct-Current.

Low-frequency (LF, 50–450 kHz).

Radio-frequency (RF, 13.56 or 27.23 MHz).

Microwave (MW, 915 MHz or 2.45 GHz).

It is worth mentioning prolonged applying time and higher microwave power cause irreversible damages in polymer treatment.

3.4 Condition for Sustained Plasma

Plasma is created by means of applied voltage in the gas environment, as mentioned above. Although, applying voltage is an important parameter, but this should have been surpassed breakdown voltage for the gases. If this potential is applied, the gas loses its dielectric properties and turns to the conductor, as a consequence sustainable plasma is achieved [15].

3.5 Why RF Plasma is Common?

As mentioned above, four different types of power supply are used in plasma generation, but the most popular excitation frequencies are in the range of RF frequency. Having clear boons such as simple setup, typical pressure gas process, and low breakdown voltage make it a common power source [10]. In the case of breakdown voltage, this value is lower than other power supply and depending on gas and pressure.

4 Plasma Categories

Broadly speaking, plasma can be classified into thermal and non-thermal categories. Thermal plasma is characterized by near equality between electrons, ions, and neutrals. Producing a high flux of heat, thermal plasmas commonly employed in certain areas, for instance in plasma treatment of waste materials. Plasma torches, plasma spray, and arc jets are three typical examples of thermal plasma sources. In contrast non-thermal plasma is produced near room temperature, also it referred to as 'cold' plasmas of non-equilibrium plasmas. The non-thermal plasma has unique

Table 1 Different example of plasma type

Plasma	Example
High temperature plasma	Laser induced plasma
Thermal plasma	Arc plasma, Plasma torches, plasma spray
Non thermal plasma	Glow, Corona, Plasma needle, Dielectric barrier discharge etc.

characteristic features that turn it important sources in a wide range of applications. A strong thermodynamic, non-equilibrium nature, low gas temperature, presence of reactive chemical species, and high selectivity attract a lot of attention for polymers treatment [13, 15, 16]. Different kinds of plasmas and their common example [17] is given in Table 1.

5 Plasma-Pressure Classified

Apart from plasma's temperature category, further plasma classification is applied in respect of gas pressure including Low-pressure plasma treatment (LPT), and Atmospheric pressure plasma (APP) [18].

Each of these treatment techniques has its own advantages and handicaps [19] that are summarized in Table 2.

Given that the benefits and drawbacks, many authors tend to use APP over LPT because needing an expensive vacuum chamber can be eliminated [20]. On top of that, the APP's lower operational cost and ease of use are clear beneficial factors.

Table 2 Summarization of advantage and drawback of LPT and APT in respect of parameters

Application properties	Low pressure plasma		Atmospheric pressure plasma	
	Advantage	Disadvantage	Advantage	Disadvantage
Plasma generation	Distribution of plasma is almost equal in vacuum chamber	Pricy vacuum chamber, limitation plasma application	Needless of vacuum equipment, Generation plasma directly in sample holder	Treatment Area is too small, Needing more nozzle to broaden treatment area
Bulk materials	Non uniform treatment cause of rotating method	The rotary drum volume is restricted	Surface can be modify directly	Sample have placed accurately on the holder
Polymers treatment	Etching process can be initiated	Needing big pump to achieve right pressure	Short time process Endless polymer can be modified	Having high temperature plasma jet Plasma parameters have be chosen precision to avoid degradation

Despite overpriced LPT, to better control chemical interaction, one might choose LPT treatment in polymer science.

6 Laser-Assisted for Producing Plasma

The laser turns to useable devices in a wide range of applications because of its adaptable parameter and low contaminate production [7]. Laser ablation in liquid (LAL) [21], laser surface modification [22–24], laser induced plasma (LIP) and laser-induced plasma spectroscopy (LIPS) are the famous forms of laser applications in researching fields [21, 25, 26]. In this section, we only focus on the LIP and LIPS application [27]. LIP formation is a rapid process that attracted a lot of attention, laser pulse delivers energy to the surface of the target and leads to excited, ionization, and vaporized materials from the surface of materials [25]. Three different regions are created in the process and called a hot core, mid and cold outer region. There is a diverse type of interaction between materials and laser, the LIP is produced because of laser energy absorption. LIP can be combined by optical emission spectroscopy for plasma diagnostics, known as LIPS [28]. Spectral lines of atoms and ions are used to study quantitative and qualitative analytical information about the sample. This technique is confined owing to difficult set-up and pricy equipment. Nevertheless, simultaneously production and detection plasma is a unique characteristic; a schematic illustration is presented Fig. 2.

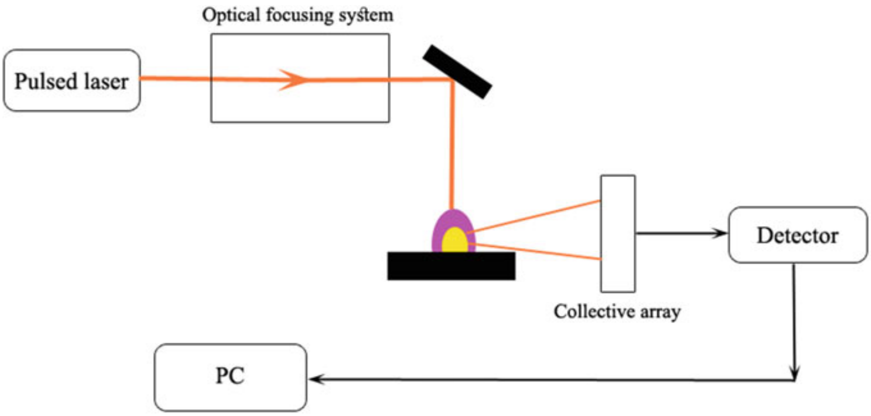

Fig. 2 The schematic photo of LIPS (Modified reprinted from Murtaza et al. [26])

7 Atmospheric Plasma Modification

As mentioned before, cold plasma technologies are appropriate for polymer modification, it worth mentioning it is applied at near room temperature [20]. Atmospheric cold plasma (ACP) can be divided as their excitation frequency and electrode configuration. The characteristic of atmospheric types of plasma sources' properties [15] is listed in Table 3.

The brief description of ACP discharge type, used in the polymeric material, is illustrated in the succeeding sections in detail and shown in Fig. 3 [20, 29–31].

Table 3 Atmospheric plasma properties in different plasma type

Parameters	Corona discharge	Dielectric barrier discharge	Atmospheric pressure plasma jet
Method and type	Sharp electrode	Electrodes are cover by dielectric barrier	RF capacitvely coupled
Excitation	Pulsed DC	AC or RF	RF 13.5 MHz
Breakdown voltage (kV)	10–50	5–25	0.05–0.2
Gas	Depending in users	N^{2+}, O^{2+} and NO^+ Rare gas/Rare gas halides	Helium, Argon

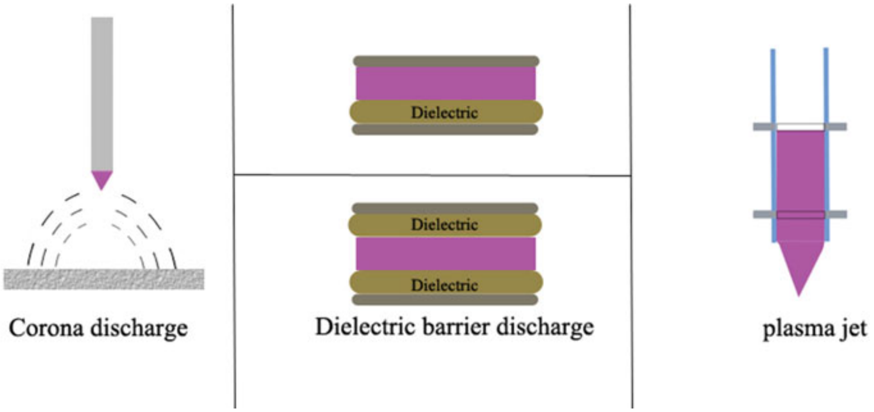

Fig. 3 Electrodes illustration of corona discharge, dielectric barrier discharge and plasma jet (Modified reprinted from Coutinho et al. [31])

7.1 Corona Discharges

Two electrodes of different shapes could generate Corona discharge, this is consisting of a sharp electrode such as a point or edge and a flat plate electrode. If the applied voltage between two electrodes is suitable, a strong electric field will be generated near the sharp electrode. As a result, plasma is generated near the electrode. According to a sharp electrode's potential corona discharge is called the negative or positive corona. Since the discharge volume is too small, this method is applicable for small area modification. Supplementary to this, a further handicap is non-uniformity causes a non-homogenous modification on materials' surface [20].

7.2 Dielectric Barrier Discharges

In Dielectric Barrier Discharge (DBD) plasma produce by an alternating current applied between two parallel metal plane electrodes. Through Fig. 4, either one or

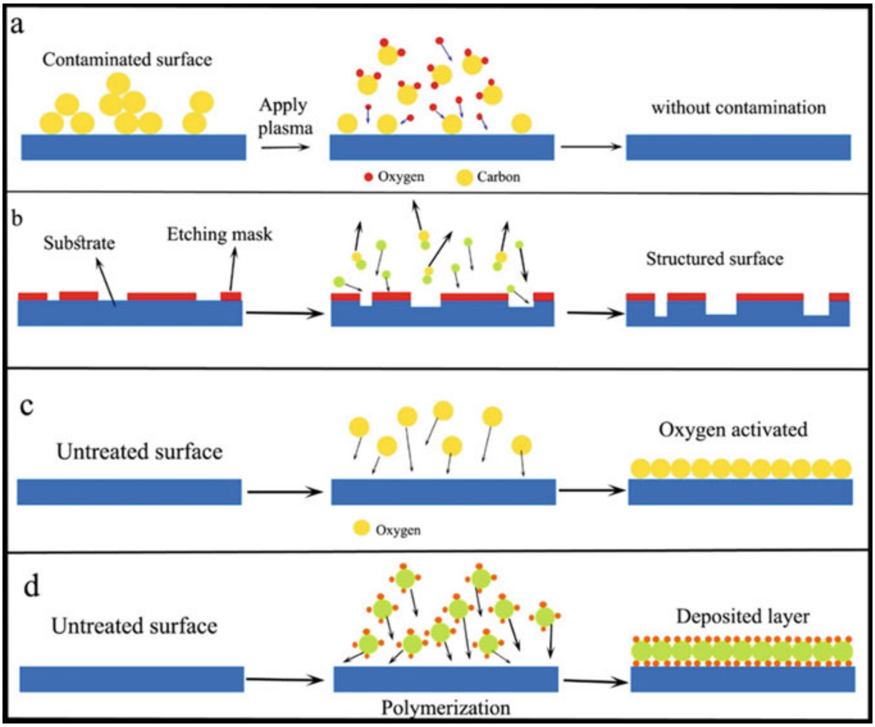

Fig. 4 The schematic of plasma cleaning (**a**), plasma etching (**b**), plasma activation (**c**) and plasma coating (**d**) (Modified illustrated from Nageswaran et al. [36])

two electrodes are covered with dielectric layers. Despite corona discharge, DBD could treat a broad area range of surfaces by a homogeneous discharge over the surface. The main impractical characteristic of DBD is the high ignition voltage [20].

7.3 Atmospheric Pressure Plasma Jet

Two concentric capacitive coupled electrodes through a gas or a gas mixture produce Atmospheric pressure plasma jets (APPJs) by means of RF power supply, frequency of 13.56 or 27.12 MHz, at a voltage lower than 100 V to a few kV. According to APPJs the ionized gas exits through a nozzle, having small plasma dimensions and high penetrability makes it more useful for modification micro-structured pores materials. At the same time, this feature is an unfavorable quality because it turns into an inapplicable method for a uniform treatment of a large surface area [20].

8 Application Types of Plasma Technology in Polymers

Plasma treatment is probably the most interesting way to modify polymer surface, as mentioned before plasma just affects the polymer's surface. The explanation for this could be that treatment by plasma is usually restricted to several ten nanometers, achieving bulk is impossible. Different types of gases can generate exclusive surface properties; in respect of the gas, plasma interaction, and effect on a polymer surface could be different [19]. Surface energy is increased by oxygen-plasma, in contrast, decreased by fluorine-plasma [19]. In fact, plasma reaction with polymer surfaces possesses important factors in polymer tailoring to achieve goals; therefore, investigation of plasma effect on polymers could be informative. The surface modification method of polymers can be divided into groups as follows: (i) cleaning or etching (removal of material from the surface) [32, 33], (ii) surface activation (producing functional groups and cross-linking) and (iii) deposition of thin films [34–36]. A short description are given below:

Plasma cleaning: Plasma cleaning produces a pure surface, ready for further processing, without any harmful agents. Oxygen plasma is used for the elimination of natural and oil contamination. If the substrate consists of easily oxidized materials, Argon and Helium are used instead of oxygen [19].

Plasma etching: materials are removed from the surface, converted to the gas phase, and eliminated by the vacuum system. Surface area, surface energy, and wettability are increased because of removing contamination [19].

Plasma activation: the absence of polar and reactive functional groups on the surface of materials, especially polyolefin family, is a clear drawback. One of the most effective ways to work it out is using plasma treatment [19].

Plasma coating: formation of a thin film on the surface of the substrate without changing color, odor, and appearance is achieved by means of plasma coating [19].

A schematic of Plasma treatments is shown in Fig. 4.

Reaction of gas plasma with surface polymers in respect of their effects can be divided into groups as follows [19]:

1. Etching and cleaning surface could be achieved by forming and removing unstable products by means of chemical reactions and physical etching.
2. Generating functional groups and crosslinking at the polymer surface can be enriched by reactions between the component of gas and surface atoms and chemical groups.
3. Plasma polymerization occurs if plasma's gas act as a monomer. In fact, polymerization of an organic monomer leads to the formation of a thin film on the surface of the polymer. This is correlated with the reactions between gas-phase species and gas-phase species-surface species [37].

These effects and many others rely on the type of plasma and plasma gas. Plasma surface treatment was done by unpolymerized gas. In respect of gas reaction, there are two kinds of technique, undoubtedly their effects on polymer's surface are different [38]. A short evaluation of their mechanism is given here:

Reactant gas:

The most commonly used in the plasma gas reaction is oxygen and ammonia. The unique characteristic, special chemical activity, of the O_2, N_2 leads to combine directly with the macromolecular chain; consequently, the chemical composition of polymer surface will be changed.

Unreacted gas:

Despite reactant gas, this category including Ar, He, and H do not combine directly by polymer surface. The high energy particles collide with the surface; therefore, a large number of free radicals were produced on the polymer's surface. Consequently, a thin layer crosslinks formed in this treatment method.

9 Introducing of Plasma Gas

In the previous section plasma surface reaction with polymers in respect of plasma gases were introduced. Through Sect. 7, the gas plasma plays an important role in the treatment and interaction between plasma and polymers. A short view of plasma gas used in polymer surface modification investigated here [37].

9.1 Inert Gas Plasmas

Inert gases, also designated to “noble gases” are Helium, Neon, Argon, Krypton, Xenon, and Radon. These gases never react with any other atom to a molecule because the maximum energy level of their atoms is complete with electrons. The most common of using inert gas is cleaning the substrate, and causing physical modification before applying reactive gas. Out of the group of inert gases, Argon is progressive for plasma treatment. Actually, Argon is a cheap gas and its ion is heavy enough to cause eligible effects in physical etching [39]. Besides, an inert gas can assist as a diluent parameter when the reactive gas flow rate is low.

9.2 Oxygen-Containing Plasma

According to Sect. 7, oxygen is a reactant gas. If oxygen introduces in the plasma chamber, two processes will occur etching of the polymer surface and formation of functional groups. As a result, oxygen containing functional groups are made on the surface, for instance C–O, C = O, O–C = O, C–O–O, and CO_3, which are highly oxidizing reactive agents [40]. Creating polar groups have a many benefits, especially in changing polymer’s surface energy and wettability, which have a vital role for using polymeric materials in industry and medical science. Designated oxygen plasma leads to achieving favorable surface with a good performance. This type of plasma gases is commonly used because of its low cost and wide availability.

9.3 Nitrogen-Containing Plasma

Nitrogen-containing plasmas are widely used to improve polymer surface properties. For instance, wettability, functional group, printability, and biocompatibility of polymer surfaces will be changed via Nitrogen plasma treatment. Surface amino binding sites of polymer surfaces was provided by means of ammonia and nitrogen plasmas. Besides, different nitrogen-containing plasmas have been used for producing different functional groups on a polymer surface. On top of that, a common phenomenon took place during and after plasma treatment, oxygen operations are always developed in nitrogen-plasma-treated polymer surfaces. Not only during modification free radicals can react with oxygen, but also free radical, which remain on the surface, will react with oxygen when the modified surface is placed at the atmosphere [41].

9.4 Fluorine-Containing Plasma

When Fluorine gases applied in plasma equipment, surface reactions, etching, and plasma polymerization can occur at the same time [42]. CF_x radicals introduces as polymerization booster and recombining type during etching. The operating parameters and the chemical nature of polymer can affect reactions' order [37].

10 Surface Properties

As mentioned above, plasma treatment affects the surface of polymers in respect of the gas plasma. The surface properties definition is necessary and classified as follows:

10.1 Functional Groups

The structural units within organic compounds are termed functional groups defined by particular bonding arrangements between atoms [43]. According to their charge or polarity, they are usually divided as hydrophobic or hydrophilic; the non-polar methane molecule and the carboxyl group are examples of hydrophobic and hydrophilic groups, respectively.

10.2 Roughness

Surface roughness is an item of surface texture, relying on the deviation from the normal vector. The rough surface is defined by large deviations, while on the other hand the smooth surface has small deviations [44]. It plays a crucial character to survey how the materials will interact with the environment or other materials.

10.3 Surface Energy

Free surface energy is defined as energy associated with the intermolecular forces between interfaces of two media [45]. When a surface has high surface energy, strong interaction can be presented with that surface [46]. Some materials with low surface energy, e.g. most plastics, are difficult to coat.

Table 4 Classification of materials in respect of water and oil contact

Contact angle	Water	Oil
<90º	Hydrophilic	Olephilic
<150º	Hydrophobic	Olephobic
>150º	Superhydrophobic	Superolephobic

10.4 Wettability

Wettability is the unique surface property determined the wetting phenomenon of materials [47]. According to contact angles of water on the surface, the materials are classified into hydrophilic and hydrophobic [48]. This classification is listed in Table 4. This item not only defined as water contact-angels, but also defined as other solvents. The hydrophilicity and surface energy of solid surfaces with liquid was strongly dependent on the surface geometry and the chemical composition [49–51]. Besides, the water contact angel (WCA) is influenced by roughness of surface, as roughness increases the WCA could increase or decrease in respect of hydrophobic and hydrophilic surface [48, 52].

10.5 Adhesion

Adhesion is an important characteristic of the tendency of particles or surfaces to adhere to one another [47]. The intermolecular forces is the chief factor for cling materials to each other, i.e. the adhesion occurs between two different substances.

11 Polyolefin

Polymers, a good candidate, can be used in a wide range of applications due to their unique characteristic. Polyolefin, which is a kind of polymer with the formula C_2H_{2n}, produced from olefin (alkene) as a monomer; such as the most important polyolefin, polypropylene (PP) and polyethylene (PE) are subdivided into several grades. Most polyolefins are made by polymerization using a catalyst; whereas PP and PE are produced from propylene and ethylene as a monomer, respectively. Molecular weight and degree of crystallinity are two considered factors to characterize polyolefin. Polyolefins, which have appropriate chemical stability, are not attacked by acids or salt solutions. Thereafter, they are wonderful electrical insulators and very sensitive to the action of ultraviolet rays (UV) in the presence of oxygen [53]. Despite these properties polymers are sometimes restricted by their poor surface properties such as wettability, surface energy, and etc. To overcome this problem several modification methods to turn polymers into valuable materials have been used. The surface modification of polymer is a useful way to obtain functional groups and change their surface properties. Surface's functional groups, structure, and morphology affect the surface energy and thus wettability of polymers [19]. Plasma treatment is a useful method to improve some properties of polymers.

12 Polypropylene

Polypropylene (PP) is a thermoplastic material made by polymerization of propylene monomers into long chains. It is sensitive to hydrocarbons and has a good barrier to moisture and gases [54]. PP can be categorized into two main branches: homopolymer and copolymer.

12.1 Homopolymer

Homopolymer polypropylene (HPP) is the most eminent polypropylene. Since it contains crystalline and noncrystalline regions, it is a two-phase system. Tacticity, which declares how methyl group is oriented in polymer chains, is the only property to make a difference among types of HPP [55]. According to tacticity, HPP can be classified into three main groups as follows:

Atactic polypropylene (aPP): Having irregular methyl group arrangement represents to be an amorphous polymer. The aPP is soft, sticky, and gummy and is mostly used where stickiness is desirable. It has a low melting temperature and high elasticity.

Isotactic polypropylene (iPP): it has desirable mechanical, physical, and thermal properties. This material has a high melting temperature and degree of crystallinity and its methyl group is arranged on one side of the carbon chain.

Syndiotactic polypropylene (sPP): it is less crystalline than isotactic polypropylene and has alternating methyl group arrangement.

12.2 Copolymer

Polymerization one or more different monomers that contain fewer olefins such as ethylene gives definition to the copolymer. Copolymers can be divided into two category:

Random copolymer: by copolymerizing propylene and a small amount of ethylene, random copolymers are made. The copolymerized ethylene in this type of PP changes the properties of the polymer chains. The melting temperature is about 145 ºC.

Impact copolymers: it contains both homopolymer and random copolymer while ethylene content is larger. The melting temperature is as same as the homopolymer cause rubber constituent does not affect the melting temperature.

Table 5 Advantages and drawbacks of PP

Advantage	Disadvantage
Good impact strength	Degraded by Ultraviolet
Low cost	Difficult to bond or paint
Low coefficient of friction	High thermal expansion
High temperature resistance	Flammable
Excellent moisture and chemical resistance	Oxidizes easily Poor weathering resistance
Low density	Low stiffness
Recyclable	Poor wettability

12.3 Polypropylene Applications

Since the properties of PPs cover a broad range, the applications of PP are used widespread. The most important applications are Fibers and fabrics, foam, film, sheets, blow molding, and injection molding. The PP has some advantages and handicaps listed in Table 5.

13 Polyethylene

Polyethylene is a thermoplastic material that is tough and flexible; in addition, it has high electrical and chemical resistance. It can be melted and formed into a shape that can then be melted and formed again into other shapes. PE does not usually have a special melting point (T); with regards to variety in molecular weight, crystallinity, and chain branching, it contains a range of melting temperatures. The melting point is between 120 °C and 140 °C. According to the semicrystalline nature of PE, the physical properties of solid polyethylene are determined [5]. Polyethylene can be categorized into Cross-linked polyethylene (XLPE), Ionomers, ethylene–vinyl ester copolymer, linear low-density polyethylene (LLDPE), Very low-density polyethylene (VLDPE), Low-density polyethylene (LDPE), High-density polyethylene (HDPE) and Ultra-high molecular weight polyethylene (UHMWPE) [56].

Linear Low-Density PE (LLDPE): This material is produced by the copolymerization of ethylene with 1-alkenes and it cannot be produced by free-radical polymerization. Density is in the range of 0.915–0.930 g/cm^3. The short branches of ethyl, n-butyl, and n-hexyl groups in LLDPE are the results of common comonomers such as Butene-1, Hexene-1, and Octene-1, respectively [56, 57].

Low-Density PE (LDPE): this polymer is produced by free-radical polymerization of ethylene. It contains substantial concentrations of branches and high amorphous content. The branches consist of ethyl and butyl groups together with some long chain branches. In order to improve processability, it can be blended with LLDPE and HDPE. The density is about 0.915–0.930 g/cm^3 [56].

High-Density PE (HDPE): this kind of PE consists of unbranched molecules and short chains which increase intermolecular forces and tensile strength. It cannot be produced by free-radical polymerization. HDPE is one of the most versatile plastics, and its density is typically 0.94–0.97 g/cm^3 [56].

13.1 Polyethylene Applications

As mentioned above, PE was divided into groups in respect of their structural properties. PE is used in a diverse range of applications including Packaging Applications, Fibers and Textiles, Water pipes, and other applications. Besides different shapes of PE were made in biological and bio media filters and used in catalyst activity as substrate [58]. Its plasticity and low water absorption are a unique structure especially in water pipes and fitting. Table 6 depicts the advantages and drawbacks of PE.

14 Plasma Performance

Many researcher have been used plasma treatment for altering surface properties of PP and PE. Probably, the most important plasma parameter in polymer treatment is the type of plasma gas being used. The surface properties are the main subject in plasma treatment fields; therefore, a brief review of plasma treatment of PP and PE in respect of surface modifying was presented in details.

The APPT was conducted for boosting surface wetting and energy (γ_s) of LDPE, HDPE and PP [4]; the WCA, the attenuated total multiple reflection technique (ATR-FTIR), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) analysis were used to study changes. The APPT was applied at frequency of 17 kHz and power source of 20 kW, and air plasma was generated and belched through a circular outlet onto the surface of samples. The results of ATR-FTIR and XPS suggest that polar groups, i.e. carboxyl, carbonyl, amid, and hydroxyl,

Table 6 Several bones and drawbacks of PE

Advantage	Disadvantage
Low density Water resistance Good impact absorption Heat resistance Chemical resistance	Large amounts of energy is needed to produce PE High thermal expansion Poor weathering resistance Difficult to bond Flammable Poor temperature capability Low stiffness Poor wettability

was introduced on the all samples, as well as SEM shows the plasma flux led to changing morphology and etching effect. Changing surface morphology steadily remained after some months for all samples, LDPE after plasma treatment shows a smooth surface, and in contrast HDPE and PP possess lamellar and rounded areas morphology; respectively, due to etching effect. Changing properties affect surface wettability and energy, the γ_s reach to 96% after 31 day of aging, confirmed the APPT could applied for commercial points. The altering surface properties of PP by air dielectric barrier discharge was surveyed by atomic force microscopy (AFM), XPS and contact angel (CA) [59]; the AFM analysis shows increasing roughness and creating nano-scale depression followed by plasma treatment, increasing processing time led to enhance roughness. Introducing oxygen-functional groups, carbon and oxidized-species because of plasma treatment was confirmed by XPS analysis, besides CH_3 functionalities was appeared because of plasma treating; after 2 min plasma exposure the CA of PP was decreased about 50°. In order to produce Gallic acid (GA) coated LDPE, the radiofrequency plasma (13.56 MHz) was deployed [60]; LDPE film was subjected to 0–90 W and 15–150 s to optimized treatment condition, subsequently it was immersed in GA solution. The tensile strength indicate that power source of 30 W and 60 s treatment time are the optimum condition; after being subjected of plasma the smoot surface of film was changed to a rough structure elevating surface area, consequently efficiency of coating was increased. PP is an inert polymer with low hydrophilicity properties, to address this handicap PP surgical mesh was modified by O_2 plasma to change surface energy [61]. It was subjected to different plasma modification time, the results show that prolonged irradiation time led to degradation polymer's chain, meticulously examination suggest that 30 s is considered as optimum time. Increasing oxygen functional groups after plasma treatment was approved by The ATR-FTIR analysis. Deposition poly(2-methacryloyloxy phosphorylcholine) (PMPC) on activated PP was achieved by UV irradiation to increase hydrophilicity. Absorbance of bovine serum albumin (BSA) protein was deployed to assess influence of plasma treatment on application, and the figures show that the amount of adsorbed BSA was decreased which is an obvious bones to prevent protein absorption, cell adhesion and proliferation.

To scrutinize the plasma gas effect on polymers, in next sections plasma modifying PP and PE in respect of the plasma gas are discussed.

14.1 Plasma Modification of PP

PP has some restricted properties that excited a plethora of attention for modifying its surface by means of plasma treatment and chemical treatment. Table 7 presents a summarization of plasma modification of PP and its influence on PP's properties.

Table 7 Examples of application of different gas plasma treatment for PP

Plasma-forming gas	Investigated properties	Modified properties of PP	Refs.
Air	Surface roughness	Surface morphology Elemental composition wettability	Cui and Brown [59]
	Functional groups		
	Wettability		
Air, N_2, O_2 and NH_3	Wettability	Hydrophilicity (depend on type gas and time)	Bhat and Upadhyay [62]
		Surface crosslinking (N_2 plasma)	
	Crosslinking	Bonding strength	
Argon and Oxygen	Surface morphology	Formation free radicals	Lee et al. [63]
		Rough topographies	
	Functional groups	O-containing groups	
	Wettability	Wettability	
Argon	Surface morphology	Formation polar groups	Gomathi et al. [20]
	Functional groups	Oxygen-containing groups	
	Wettability	Wettability	
He and He-O_2	Surface morphology	Surface roughness	McCord et al. [64]
	Functional groups	Oxygen and Nitrogen containing groups	
	Tensile strength	Increasing tensile strength in He-O_2 plasma	
Oxygen	Surface morphology	Increasing friction, formation microcraters and roughness	Yousefi et al. [65]

(continued)

14.2 *Plasma Modification of PE*

As mentioned before, modifying PE to improve its surface properties is one of the foremost fields. Increasing or decreasing wettability, changing surface morphology, and introducing functional groups are reached by means of plasma treatment. Table 8 shows many literatures has been done by plasma treatment.

Table 7 (continued)

Plasma-forming gas	Investigated properties	Modified properties of PP	Refs.
	Functional groups	Oxygen containing polar groups	
	Adhesion	Increasing interfacial adhesion	
Oxygen	Functional groups surface energy	Oxygen containing groups and Carboxyl group	Choi et al. [66]
		Surface energy	
Oxygen	Surface morphology	Increasing roughness	Hua et al. [67]
	Functional groups	Introducing carboxyl and hydroxyl groups	
Oxygen and Hexamethyldisiloxane	Wettability	Hydrophilicity	Mahlberg et al. [68]
	Surface morphology		
	Adhesion	Topography (spherulitic to a nodular structure)	
	Surface energy	Surface energy and adhesion	
Oxygen	Functional groups	Hydroxyl, carbonyl and carboxylate groups	Shahidzadeh-Ahmadi et al. [69]
	Wettability	Hydrophilicity	
SF_6, CF_4 and C_2F_6	Surface morphology	Oxygen containing groups	Nihlstrand et al. [70]
	Functional groups	Hydrophobicity	
	Wettability		
Oxygen and nitrogen	Functional groups	Oxygen containing groups	Harth and Hibst [71]
	Surface morphology	Roughness	
	Wettability	Wettability	
Argon and Argon/Water vapor	Functional group	Oxygen containing groups (Argon/Water vapor more than Argon)	Sarani et al. [72]
Oxygen and Argon	Surface morphology	Size of nodules and roughness	Mirabedini et al. [73]
	Functional group	Oxygen containing group	
	Wettability	Wettability	
	Surface energy	Surface energy	

(continued)

Table 7 (continued)

Plasma-forming gas	Investigated properties	Modified properties of PP	Refs.
N_2:H_2 and NH_3:H_2	Elemental containing deposition film process	Hydrogen and Nitrogen percentage	Jung et al. [74]
		Thickness of deposited film (depend on power)	
Nitrogen or oxygen (mixed with CF4)	Adhesion between PP and Aluminum alloy	Improving adhesion under nitrogen treatment	Lin et al. [75]
		Wettability	
	Elemental investigation	Rough structure	
	WCA	Nitrogen and oxygen prcentege	
Helium	Wettability	Improving hydrophilicty and surface energy	Palaskar et al. [76]
	Surface energy	Introducing oxygen functional groups	
	Adhesion	Adhesion strenght	
Compressed dry air	Wettability	Increasing wettability	Jelínek et al. [77]
	Elemental composition strength of the epoxy adhesive	Oxygen and nitrogen containing groups	
Oxygen	Wettability	Hydrophilicity	Sanbhal et al. [78]
	Functional groups	Hydroxyl groups	
	Morphology	Roughness	
Air	Morphology	Surface etching, formation of	Pandiyaraj et al. [79]
	Functional group	COOH groups	
	wettability	Increasing surface wettability	

14.3 Comparison Plasma-Forming Gas

Comparing literature shows applying different gas types leads to modify defectiveness and provide an eligible surface. Plasma applying on PP and PE has common results, for instance improving wettability, oxygen functional groups content, and adhesion. However, the modified percentage of these properties is related to the gas type and plasma treatment time. Actually, reactant gas has a huge effect in early exposure time compared with unreacted gas. This is owing to the fact that, reactant gas directly alters the surface, in contrast unreacted gas modifies surface by means of

Table 8 Examples of application of different gas plasma treatment for PE

Plasma-forming gas	Investigated properties	Modified properties of PE	Refs.
Oxidative (oxygen and air)	Surface morphology	Hydrophilicity	Lehocký et al. [80]
	Wettability	Surface micro-hardness	
		oxygen based functionalities	
Argon	Surface morphology	Surface morphology (subjected to power and exposure time)	Švorcík et al.[81]
	Functional groups	Oxidized structures	
	Wettability	Wettability	
Argon (LDPE)	Surface morphology	Spherulites structure incorporated Oxygen (about 25 nm)	Švorcík et al. [82]
	Functional group	Oxygen based groups	
	Wettability	Wettability (depend on exposure time)	
	Depth of incorporated oxygen		
Argon (HDPE)	Surface morphology	Lamellar structure	Švorcík et al. [82]
	Functional group	Surface roughness incorporated oxygen (about 25 nm)	
	Wettability	Oxygen based groups	
	Depth of incorporated oxygen	Wettability (depend on exposure time)	
Nitrogen, Nitrogen–Hydrogen and Nitrogen–Ammonia	Surface properties	Smooth surface	Šíra et al. [83]
	Wettability	Wettability	
	Functional groups	Oxygen and ammonia based group	
Fluorine (In the absence of an aluminum cage)	Depth of fluorination	Depth of fluorination (40 Å)	Anand et al. [84]
	Functional groups	CF_2 rapidly generated	
Fluorine (In the presence of an aluminum cage)	Depth of fluorination	Depth of fluorination (60 Å)	Anand et al. [84]
	Functional groups	CF_2 interspersed with some CF_3 groups	
		Chemical species in the surface and subsurface	
Dry air	Adhesion	Adhesion and surface energy	Noeske et al. [85]

(continued)

Table 8 (continued)

Plasma-forming gas	Investigated properties	Modified properties of PE	Refs.
	Surface energy	Oxygen and Nitrogen containing groups	
	Functional groups	Decreasing carbon	
Oxygen	Wettability	Wettability	Sanchis et al. [86]
	Adhesion	Polar specie	
	Surface morphology	Surface roughness (surface degradation/etching)	
Nitrogen and ammonia	Wettability	Hydrophilicity	Bretagnol et al. [87]
	Elemental percentage	Introducing C–N, C–O groups	
		Incorporated new nitrogen (larger by Nitrogen plasma)	
Nitrogen	Nitrogen appearing	Attaching Nitrogen atoms	Foerch et al. [88]
	Surface properties stability	Reaching a steady situation after 20 s	
Argon	Pore structure	Widened pore structure	Jeon et al. [89]
	Wettability	Hydrophobic to hydrophilic	
	Functional group	Appearing hydroxyl group	
	Adhesion	Increasing adhesion PE substrate and the ceramic coating layer	
Oxygen	Wettability	Decreasing WCA and Oxygen permeability	Glaser et al. [90]
	Functional group	Introducing oxygen containing groups	
		Improving stability and adhesion of chitosan layer	
Oxygen	Interfacial strength	Strong interfacial interaction between natural fiber and polymer matrix	Sari et al. [91]
	Wettability	Improving hydrophilicity by adding functional groups	

(continued)

Table 8 (continued)

Plasma-forming gas	Investigated properties	Modified properties of PE	Refs.
	Mechanical properties and moisture resistance	Good stability by plasma treatment and mild bleaching of natural fiber	

formation free radicals and post treatment [62]. Some studies show that mixing gas by other components adversely affects surface modification, i.e. slowed up surface modification, this effect leads to taking more exposure time and power, simultaneously [83]. Broadly speaking, plasma treatment can increase surface energy in parallel with wettability [73]. The depth of surface modification relies on the power supply, exposure time, and sample holder [84]. Introducing functional groups could be dependent on the gas type and temperature during radiation. Surface chemical and physical change could be cleared by the extra mobility surface change [19].

15 Application of Plasma Modified-PP and PE

Nowadays, having controlled penetration of chemical component, microporous polymeric membranes have extremely used in industry such as filtration and battery separators [92]. In this section we aim to introduce recent plasma modified-PP and PE membrane's application in industry and researches; the main motivation of this section is providing the definition of membrane and its application in environmental research to give a clear comprehension to researchers.

15.1 What is the Membrane?

Membrane is usually used as a fence to separate two phases and make a barrier to restrict unwanted particles from transportation [93]; therefore it provide multitudinous opportunity, especially in environmental remediation and energy storage due to the shortage of potable water and fossil fuels [94]. Physical separation is one of the most important merit of membrane technology because chemical additive utilization and phase changing could be eliminated [95]; besides membrane offers more challenges for producing more efficiently products to catch up with demands [96]. Among materials, polymers are pioneered due to their unique properties.

15.2 Polymeric Membrane

With aim to reduce cost and time in industry process, the membrane are used in a broad range of technology. The membrane technology excited a plethora of attention because of low cost, low energy consumption and environmentally adaptation [97, 98]. The polymeric membrane properties are related to fabrication process and materials itself [99]; nevertheless, there are some polymers have been used as polymer membrane materials, which their physical and chemical properties strongly affect their performances, including: polyvinylidene fluoride (PVDF) [100, 101], polysulfone (PS) [102], polypropylene (PP) [103], polyethylene (PE), polyimide and polyamide [104]; here we just pay attention to PP and PE membrane's applications.

15.3 Membrane's Surface Property

Membranes' performances are extremely affected by crystallinity, porous structure, and surface features like wettability, surface charges and roughness [105, 106]. Crystallinity of polymer define as polymer chain's order, there is some results suggest that crystallinity acts as an unfavorable property for separation process, increasing crystallinity leads to decreasing filtration coefficient [107–109]. In some application like wastewater, sea desalination, and batteries hydrophobicity is a major barrier because hydrophobic membrane does not adhere to hydrophilic substrates [110–113]; despite of good mechanical and chemical stability the fouling was occurred in using hydrophobic membrane for aqueous solutions like oil droplets, which has natural organic matter [98]. Designing the desirable membrane could achieve by modification hydrophobic surface without changing bulk properties to create hydrophilic surface [114]. According to reports, electrostatic charges of a porous membrane have a critical role for fouling prevention; the membrane prone to fouling when its and fouling's charges are opposite [115].

15.4 Applications

Nowadays, addressing energy shortage and environmental pollutant have been considered as pioneer issue which is carried out on different methods and materials [32, 116, 117]. Polymeric membranes possess exclusive properties turn them to valuable material in many application; therefore, a purposeful discussion for introducing applications is necessary. Some applications briefly presented as follows:

Lithium-ion batteries: according to run-away energy consumption, there is a great demand for rechargeable battery; among these type of system lithium-ion batteries excited a lot of attention in portable devices [118]. A lithium-ion batteries consist three functional parts including anode, cathode, and electrolyte; the most important section is restricting physical contact of electrodes while they act as reservoir to prevent ionic transport, which has made presence of separator necessary [119]. A good separator has some features including: chemically and electrochemically stable under redox reaction and anti-corrosion behavior, as well as it should be completely wetted by electrolyte [120].

Gas separation: increasing carbon footprint, air pollution and greenhouse gases require industrialists to deal with this dilemma, using gas separator is one way to address this issue [121]. Considering inert nature of separators to prohibit producing new component or pollution must be envisaged as a sensitive matter; the new polymeric separator was extensively utilized in separation technology duo to cost-effectiveness and versatility [122].

Wastewater treatment: not only wastewater poses a threat on living creatures, but also it could be dumped into the natural water bodies, which accelerate scarcity of water [123]. The problem causes by wastewater leads researchers to focus on treatment ways, membrane technology has been regarded as an attractive physical treatment methods which is controlled by porosity size [124].

As mentioned before, one of the most application of plasma is tailoring surface properties of materials; therefore in the subsequent section application of plasma modified-PP and PE are presented.

15.4.1 Surface Modification of Separator

Polyolefin membrane due to their inherent hydrophobic properties needs to be changed by plasma to turn them a practical separator [125]. Plasma modifies surface of polymer without changing the bulk properties; in many fields, adhesion and wettability are the important parameters and researchers has made efforts to improve separator's performances especially in industry and environmental cleaning [1]. The plasma modified membrane application was categorized in term of PP and PE and presented in following.

- Plasma modified-PP: A major obstacle for filtering is fouling, which is lead to increasing energy using to overcome persistence of fouling and stable flux, to overcome such a thing in wastewater treatment using hydrophilic membrane is popular. An adsorptive membrane was constructed by graphene oxide-PP (GO-PP) and subjected Ar discharge plasma for different exposure times [126]. Although, increasing plasma modification's time leads to decreasing porosity, the results suggest that adsorbing of Congo red particles strikingly increased, it is probably down to stable interaction between Congo red particles and oxygen-containing groups on the surface made by plasma modification. Polypropylene hollow fiber macroporous membranes was irradiated by H_2O plasma to decrease fouling behavior, the WCA was obviously decreased by increasing modification's time meaning that hydrophilicity groups were developed on the surface of membrane; the results show plasma modification contribute to improve antifouling characteristic dramatically [127]. The performance of ion-exchange membrane is rely on surface properties, the nitrogen, air and oxygen plasma-modified PP membrane was used as separator in electrochemical study to assess influence of wettability, pore size and the type of functional group on conductivity; the total measured electric current was compared with bare-PP and results show that it was risen about its two, seven and nine fold by applying nitrogen, air and oxygen plasma, respectively. The enhancement of conductivity come courtesy of increasing oxygen-containing group, pore diameter and hydrophilicity after subjected to plasma [128]. A commercial PP membrane was modified by atmospheric pressure glow discharge plasma jet (APGD-PJ) along with the acrylic acid (AA) monomer to use in lithium-ion battery as a separator with different exposure time [129]. PP was modified by Ar/O_2/AA and the result of WCA show decreasing about 38%, from 112° to 70°; using He/O_2/AA plasma eventuated in increasing wettability about 66%, the WCA was decreased from 112° to 39°, causes by polar groups creating on the surface. Also pore size was assessed as a function of exposure time and shows a dramatic decreasing in 10 min modification time for both treatment route. Comparison of WCA and pore-size in term of irradiation's time represented 10 min is suitable for improving surface properties of PP membrane. The electrolyte uptake of PP was increased about 250 and 300% by introducing Ar/O_2/AA and He/O_2/AA plasma, respectively; therefore membrane can be fully wetted by electrolyte rely on increasing wettability. Discharge capacity and coulombic efficiency of bare-PP and modified-PP was compared and resulted obvious increasing, like for instance coulombic efficiency was increased from 98.5% to 99% and 99.5% for Ar/O_2/AA and He/O_2/AA plasma, respectively. Surveying discharge capacity of bare-PP and modified-PP shows increasing capacity and coulombic efficiency due to the enhancement of surface properties.

- Plasma modified-PE: To address fouling, a widespread handicap of membrane, PE microporous membrane was modified by plasma graft polymerization and its fouling was investigated against glucose and dextrans. The molecular weight cut-offs (MWCOs) was monitored as a function of grafting amount, indicated MWCOs was decreasing from 5.8×10^5 to 5×10^3 by increasing grafting amount, the results demonstrated grafted polymer chains contribute to decrease pore size for grafting amount of lower than 0.1 mg cm^{-2}, oppositely they filled porosity for grafting amount of larger than 0.1 mg cm^{-2}; as a consequence MWCOs was dramatically decreased [130]. PE film was modified by CH_4 plasma for investigating water vapor diffusivity and permeability, consequently hydrophobicity and roughness was increased. Studying water vapor transport was demonstrated fluorination of surface reducing water permeability at the feed side due to increasing hydrophobicity [131]. Oxygen plasma was applied to modify PE membrane used as separator for lithium-ion battery by introducing functional groups and increasing wettability. To be more accurate, WCA measurement shows decreasing contact of electrolyte from 62° to 0° affirmed the separator can completely wetted by electrolyte when PE was treated for 10 min; FTIR and XPS results present increasing oxygen functional groups because of reaction between polymeric radicals and oxygen containing active site. Electrochemical method was carried out to study discharge capacity and resistance, the results confirm oxygen plasma treated, even after 1 min irradiation time, dramatically increased electrochemical stability and decreased interfacial resistance; besides cycling performance after 100 cycle with 0.1 C-rate were compare and present it was grown about 2% by applying 1 min oxygen plasma [132].

16 Summery

This chapter offered a brief review of plasma treatment to modify polymer surface, description of plasma types, and plasma-forming gas. It is universally accepted, changing polymer properties by means of cost-effective and adaptable methods is very important for industrial usage. To address this issue plasma technology is one of the most attractive methods because of its tremendous properties. Plasma could change surface properties with cleaning, etching, polymerization, and coating. Introducing functional groups can achieve by plasma activation, directly affected surface energy. Changing surface properties such as wettability and adhesion, the main aim in modifying the surface, act an important role in accomplishing adequate surface. To scrutinize plasma-forming gas effects on polymers, we provide an overview of plasma modification on two types of polyolefine family, PP, and PE. Tailoring PE and PP surface by means of plasma technology excited a lot of attention because of its diverse properties. Changing plasma-forming gas could introduce different types of functional group, which is responsible for altering surface properties. Besides, plasma modification could adversely affect the modified surface. Then knowledge of plasma-forming gas properties, right exposure time, depth of modification, and gas application can conserve the surface of materials. The above-described examples of application plasma in the tailoring of PP and PE, show that plasma not only success in modifying surface properties and structural characteristic but also success in extending plasma modification for the industry. In practical point of view, plasma modified-polyolefin has exceeding application in elimination pollutant from water and air, enhancing performance of energy storage devices and filtration environmentally-damaging agents.

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Plasma Texturing of Polymers

Jean-François Coulon, Dominique Debarnot, and Fabienne Poncin-Epaillard

Abstract This review explores the different processes usually applied in the field of nanotechnology for texturing polymeric materials. These technics mostly focused on dry and eco-friendly routes allow to create a multitude of patterns on the polymer surfaces bringing to the material specific and unique properties. Among these technics, plasma chemistry explored alone or combined with lased, beam, sputtering technologies… appears to be well adapted to thermosensitive materials for the preparation of original textured surfaces close to biomimetic surfaces as an example. This overview focuses as well as on the fundamental aspect of the texture creation than to its application in various industrial domains.

1 Introduction

Nanoscience and nanotechnology related to microelectronics, have brought about considerable new applications in the field of materials. Indeed, the change of scale passing from the micrometer to the nanometer has strong consequences on the final properties of a material widening the industrial fields and it could even open up new sectors of applications. These materials with enhanced properties are mostly based on the duplication of a pattern on double or multiple scales. This concept is originated from the observation of nature and more generally on biomimetism. Indeed, the nature offers many examples combining adapted surface chemistry and repeating pattern which give rise to remarkable properties like the water drop repelling, the ability to change the light reflecting or some extraordinary hooks on vertical or movable surfaces. The development of nanotechnology has made it possible to replicate the

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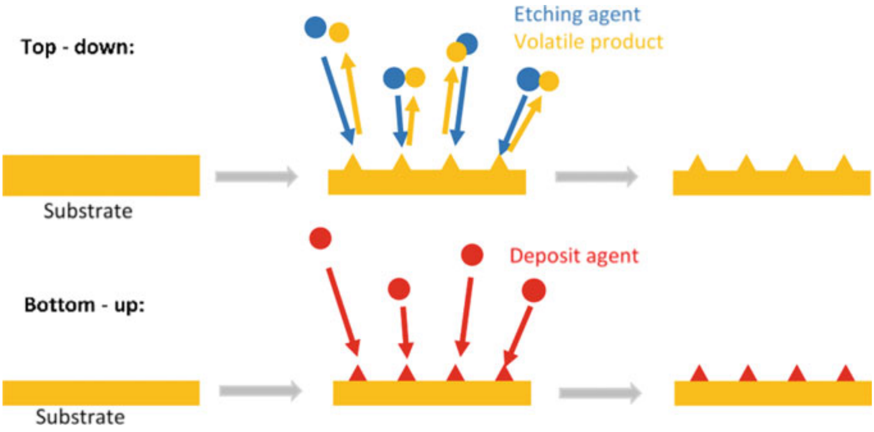

Scheme 1 Top-down and bottom-up routes

patterns observed in nature, hence texturing is the process which let us obtain a regular pattern on a surface.

Among the procedures deployed for texturing, two main routes are described. The first known as top-down for which the localized removal of material makes it possible to provide the pattern while the second known as bottom-up provides a textured material according to a precise topographic diagram (Scheme 1).

The surface chemistry can also contribute and can be simultaneous with this texturing step. Few processes allow both mechanisms and most of them require two or more steps to introduce expected texture and chemistry; some preparations also include the use of masks. An exception is focused on plasma technologies. In this chapter, we will describe how we can texture a polymer surface during its functionalization in one or two steps thanks to the plasma chemistry.

2 One-Step Top-Down Plasma Texturing

Micro, nano, double scale-texturing of polymers offers the possibility to drive important surface properties such as wettability, (bio)adhesion or anti-(bio)adhesion applied in various domains such as medical devices, biology, metalization, optics and electronics. In recent years, plasma-induced self-assembly of polymer nanostructures without any mask has emerged as a simple, scalable and rapid etching technique to pattern micro and nanostructures. This elaboration of polymer nanofiber arrays is correlated to plasma etching and the nanostructures are dependent on both plasma parameters and polymer characteristics. The general statement concerning the nanofeatures growth claims that the selectivity in etching is due to the difference of the density through the material, intrinsic for a given material.

2.1 Control of the Texture Thanks to the Plasma Properties

The plasma parameters act upon the reactive species nature, their relative concentration in the plasma and upon the associated energy deposited on the surface which has to be modified. Basically, the efficient plasma parameters are the gas pressure, the gas flow rate and the chemistry of the input gas composition as well as the power, the duration and the frequency of the discharge. The literature reports on almost all types of polymers (PC, PMMA, PET, PEEK, PS, silicone, elastomers …) which have been plasma-modified to present textured surface when subjected to different plasma phases (mainly O_2, CF_4, Ar and their mixtures….) [1–19]. The subsequent pattern is depending on plasma parameters. As an example, the higher the energy of the plasma is (like the duration or the power of the discharge), the more numerous and deeper the surface features are. Indeed, the PET when directly treated by an oxygen plasma shows a nano-fibrillar pattern [2] which density depends on the duration and on the discharge power. Without requiring masks, this route induces a similar surface topography than that one obtained with a filter in a two-step method, i.e. an optical lithography step followed by a plasma etching or a plasma deposition step [4]. The SEM pictures (Fig. 1) show that the density and the dimensions of the nanofibers increase with hard plasma conditions as the power. However, if the plasma parameters are too drastic (here 200 W), the fibers collapse. Such a behavior is significant of the fiber growth mechanism corresponding to local melting of polymeric chains, crystallization and aggregation of oxidized PET oligomers. These oxidized oligomers are repulsed by the untreated sub-layer chains because of their more hydrophilic character. The hydrophilic character can be prevented if such

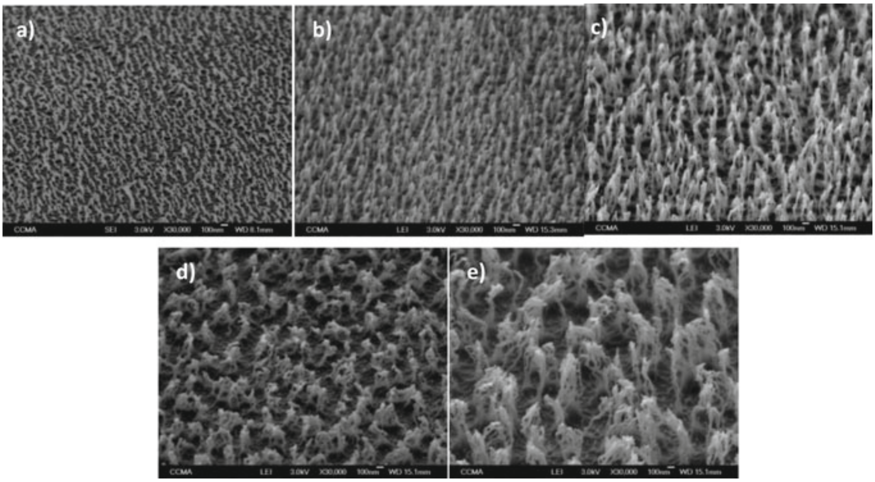

Fig. 1 Dependence of the texturing of PET on O_2 plasma parameters [2] (P = 70 W, p = 0.02 torr, t = 15 min, FO_2 = 15 sccm (**a**), 50 sccm (**b**); P = 100 W, p = 0.02 torr, t = 15 min, FO_2 = 50 sccm (**c**); FO_2 = 50 sccm, p = 0.08 torr, t = 15 min, P = 100 W (**d**), 200 W (**e**))

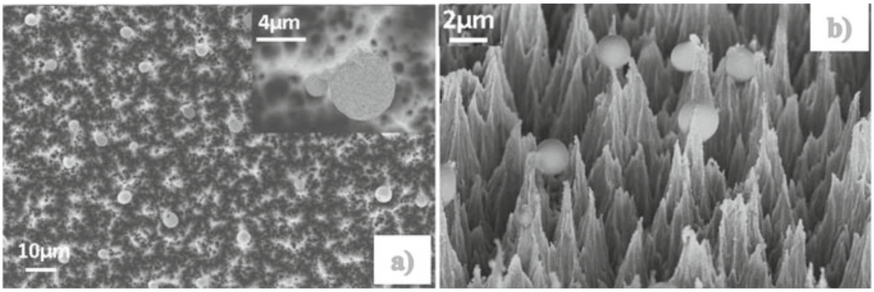

Fig. 2 Plasma-etched PTFE (O_2 plasma **a**: $t = 30$ min, $P = 300$ W; **b** tilted of 45°, magnification 10000x, $t = 30$ min, $P = 200$ W) [15]

a surface is then plasma-fluorinated to get- depending on the plasma parameters- the true Cassie–Baxter surface ($\Theta_{H2O} = 157 \pm 2°$, $H_\Theta = 1.6 \pm 0.6°$, mean distance between two features ≈70 nm) or the sticky superhydrophobic surface ($\Theta_{H2O} = 156 \pm 5°$, $H_\Theta = 65 \pm 4°$, mean distance between two features ≈145 nm) as also noticed in [20].

Similar etching plasma phases fed with CF_4/O_2 mixtures [7] allow to achieve superhydrophobic and slippery surfaces whose morphology and distribution are plasma-dependent. The denser the plasma phase is, the higher the nanofeatures height is. However, their density is decreasing leading to a progressive reduction of the Cassie–Baxter character. The fluorinated polymers also lead to patterned surfaces in specific plasma conditions, whose micro and nano-features exhibit a pyramidal shape with a well-finished spherule on the apex [15]. At lower RF power and process time, only pyramids can be observed. Their creation was explained by the deposition onto the surface of a cluster of metal sputtered from the electrodes, building up a nano-mask followed by an aggregation (filaments, oblate forms, bead shapes) of the polymeric species and the metal atoms (Fig. 2).

If the duration and the power of the plasma discharge increase, the surface temperature can be locally high enough to soften the matter and to reorganize the surface structure. However, the obtained surface topography is very close to that one obtained by a simple thermal annealing of PTFE. Such surface topography alteration has to be interpreted rather as a low effect of self-masking from the incorporated metallic cluster than as a crystallite growth and a stress relaxation of the PFTE [21] (Fig. 3). In the case of the thermal annealing of PTFE, the annealing time above the melting temperature (Tm) and the cooling time between Tm and the glass transition (Tg) could both govern the creation of two types of texturation leading to a super-hydrophobic state.

To summarize, depending on the plasma parameters mostly the power and the duration of the discharge, the pattern of various polymers (thermoplastic, thermoset, elastomer, polysiloxane) can tune the hierarchical surface topography at different scales (µm, nm and both of them). However, the measured roughness is usually

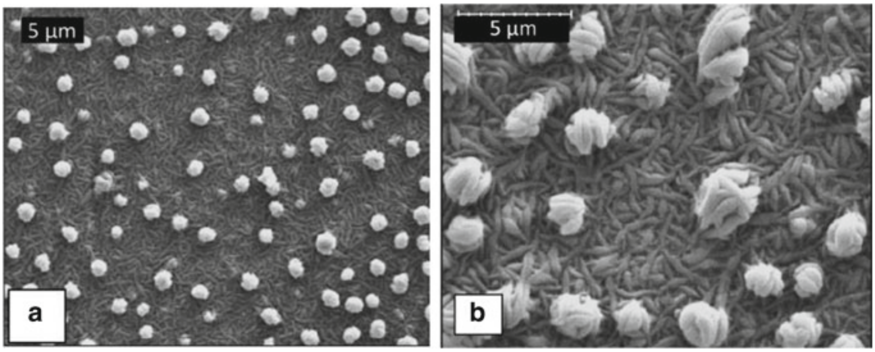

Fig. 3 Thermal texturing of PTFE with two patterns **a** wart creation depending on the annealing time at 350 °C **b** dendrite creation depending on the cooling time between Tm and Tg [21]

described as a mean value that is much too restrictive in order to provide the understanding of the subsequent specific surface behavior (either superhydrophobic or superhydrophilic). In order to separate out the roughness double scale, Fast Fourier Transform filtering analysis based on scaling theory was performed on AFM images of CF_4 plasma-textured polybutadiene [22]. Using this approach, the micro and nano roughness were respectively determined and their summation matches well with the average roughness value usually determined for such a double-scale surface. Besides, as expected, although all three morphologies are hydrophobic, only the double-scale composite surface displays a low contact-angle hysteresis thus making it superhydrophobic surface.

The double-scale pattern was not observed for PDMS whatever the plasma conditions. Indeed, the regular double-scale pattern is replaced by a wrinkling design with a high nano-scale amplitude and with a periodicity of about 100 nm [1]. Increasing the plasma treatment duration, the roughness increases while the periodicity decreases until reaching a plateau, resulting in an enhanced surface area. Such behavior was interpreted as a consequence of the thin silica-like layer creation at the PDMS top surface and its strain due to simultaneous ion-enhanced etching, oxidation during O_2 plasma treatment (Fig. 4).

The plasma gas composition is well known to produce a large variety of interactions in the gas phase and at the interface of any solid material. Depending on the chemical nature of the gas phase, these reactions are classified as chemical or physical ones. At a first glance, the former generates new functional groups at the material surface while the latter leads to higher energy brought to the surface. This higher energy can lead to sputtering processes which may induce the texturation. One would assume that the texturing of polymeric surface requires only physical interactions, and therefore neutral gases such as argon could be sufficient. However, the appearance of a pattern is not only synonymous of ablated matter. As well as the physical interactions between plasma and surface can also lead to surface chemical modifications, the chemical interactions between plasma and surface can give birth to

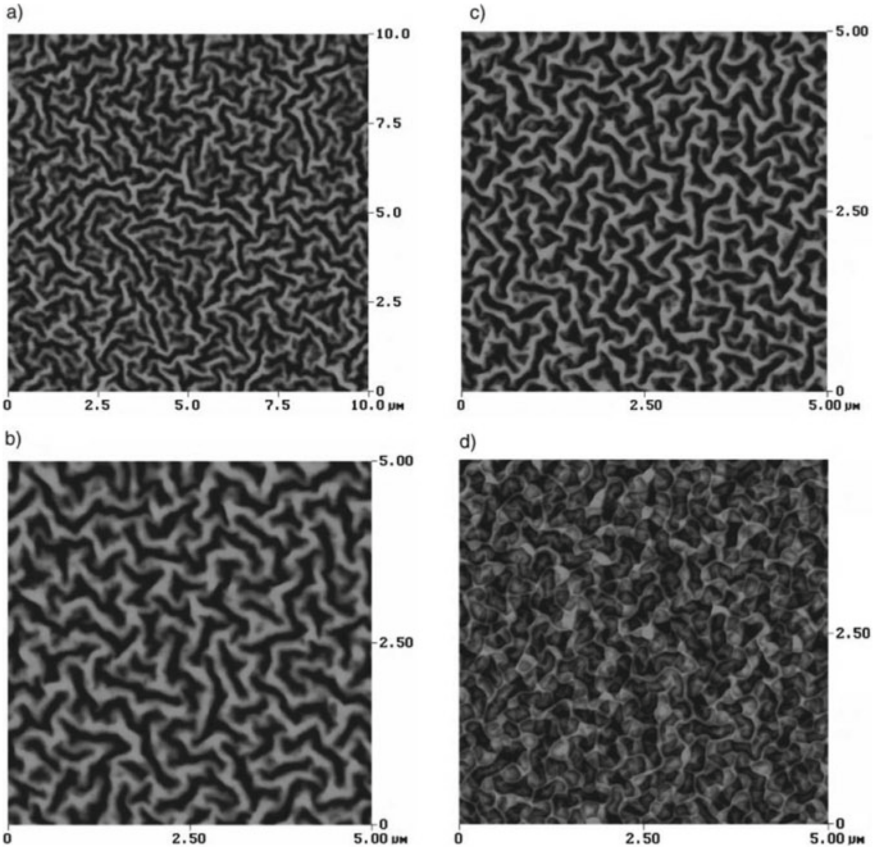

Fig. 4 AFM images of PDMS treated in a RIE O_2 plasma for **a** 30 s, **b** 60 s, **c** 420 s and **d** 600 s. Roughness (rms) and periodicity (λ) values for each surface are as follows: **a** rms = 23 nm, λ = 579 nm, **b** rms = 46 nm, λ = 338 nm, **c** rms = 37 nm, λ = 366 nm, **d** rms = 28 nm, λ = 461, 331, 149, 133 nm [1]

topographical modifications too. Thus, the achieved pattern in the case of polymers could also proceed via aggregation, rearrangement, chain reptation or functional groups turn over. These polymer chemistry phenomena are enhanced by the chemical affinity and, therefore reactive plasmas can also produce patterns on polymeric surfaces [1, 3, 20, 23–27]. Furthermore, whatever the plasma chemical composition (O_2 or Ar), the same trend for the roughness and for the periodicity of the texture for a plasma-treated PDMS surface is observed [3]. The only difference is noticed with a maximum value which occurs at 2 min for Ar treatment against 7 min for O_2 plasma [1]. This result may be surprising since both plasma phases have different chemistry; the Ar plasma mostly induces sputtering while the latter one mostly produces the oxidation. This may suggest that the PDMS surface properties are prevalent rather than the plasma properties. In an opposite manner, if O_2 and CF_4 plasma phases strongly induce a chemical process, it appears that on PC, the CF_4-to-O_2 feed ratio significantly alters the shape and the distribution of the generated structures. O_2 plasma leads to taller structures with wire-like aspect and more homogeneous distribution. The duration as observed previously alters mainly the dimension [23]. Besides the competitive reactions of surface functionalization and degradation, the interactions between plasma species and polymeric surface induce cross-linking reactions in inert atmosphere such as Ar or He with a subsequent mechanical stress appearing between cross-linked surface and the bulk matrix. And if after the long Ar plasma treatment (30 min), the polymeric film is kept under high pressure and temperature, that causes the creation of multiscale hierarchical wrinkles with nano-textured features [26] (Fig. 5).

The sputtering reaction can be emphasized by applying a bias voltage onto the substrate during the plasma exposure, whatever the excitation mode and the other plasma parameters. Such an experimental procedure significantly induces an anisotropic ion flux towards the surface to be treated [24, 25]. Without any external bias applied to the substrate, the texturation pattern does not appear on the plasma treated PEEK surfaces [24] or is less pronounced in the case of fluorinated poly(ethylene propylene) (FEP) showing rounded peaks, synonymous with few degradation and texturation [25]. When a bias voltage is applied, the surface texture is observed in both cases and can be reinforced by adding reactive gases such dioxygen or even dinitrogen (Fig. 6). Furthermore, fluorinated polymer shows sharp

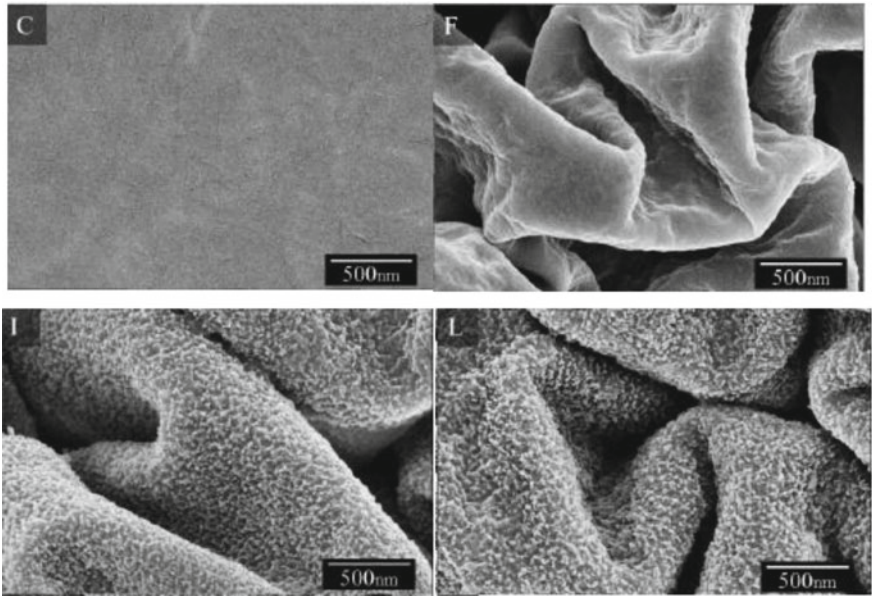

Fig. 5 SEM pictures of shrunk Ar plasma-treated polyethylene/polypropylene blend (**C**: blank; **F**: 1 min, **I**: 30 min, **L**: 60 min) [26]

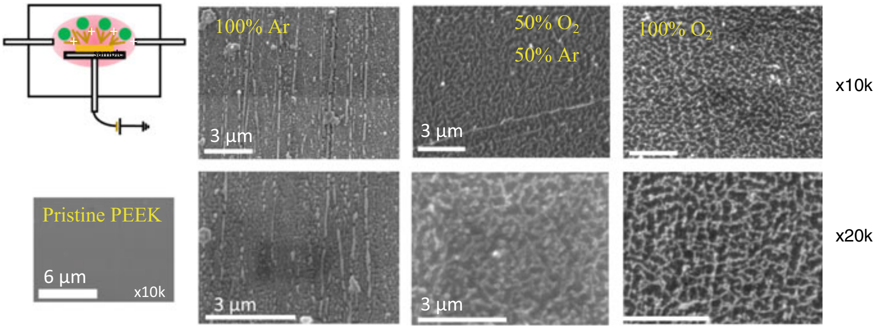

Fig. 6 SEM pictures of plasma-treated PEEK with a bias voltage of −200 V. (Ar/O_2 $P = 1500$ W, $t = 15$ min, $F = 10$ sccm) [24]

features leading to a Cassie–Baxter surface (high WCA and high CA hysteresis) while the rounded form belongs to the Wenzel type surface if we consider only the classical root mean square average RMS [2].

Atomic force microscopy reveals the dimensions of these features (Fig. 7). With pure Ar plasma, the topography of the surface is governed by surface ripples which provide regular lines spaced by one or two hundred nanometers and up to 100 nm height. This kind of texturing is assumed to be mainly due to a thermal macroscopic rearrangement of the surface following the high ion energy impacting the surface. In such plasma conditions, one has to take care not to extend too much the bias to avoid the surface degradation of the polymer. With pure dioxygen, an isotropic pattern is thereby well defined and composed of homogenous but quite separated features of about tens of nanometer height. This texturation is correlated to different etching mechanisms of the polymer due to its difference in crystallinity.

2.2 Control of the Texture Thanks to the Polymer Properties

The first property of a polymer to be textured is its own topography. The interaction between incoming reactive plasma species and the polymer is related to the incident angle of the species. Their deepest penetration occurs when the species fluxes are normal to the polymer surface but the presence of protusion and the roughness of the surface may alter their own path and the further etching of the polymer. Du et al. [27] gave an illustration on the impact of the roughness of the substrate on the deviation of species fluxes and the subsequent pattern growth. Different impact locations of the ions on the surface are distinguished: ionic impact on a flat area, on the top of the protusion, both with a normal incidence, or on the sidewall of the protusion. The two former ions have penetration length longer than that of the latter one. Such a scheme could explain the formation of the observed nanowires.

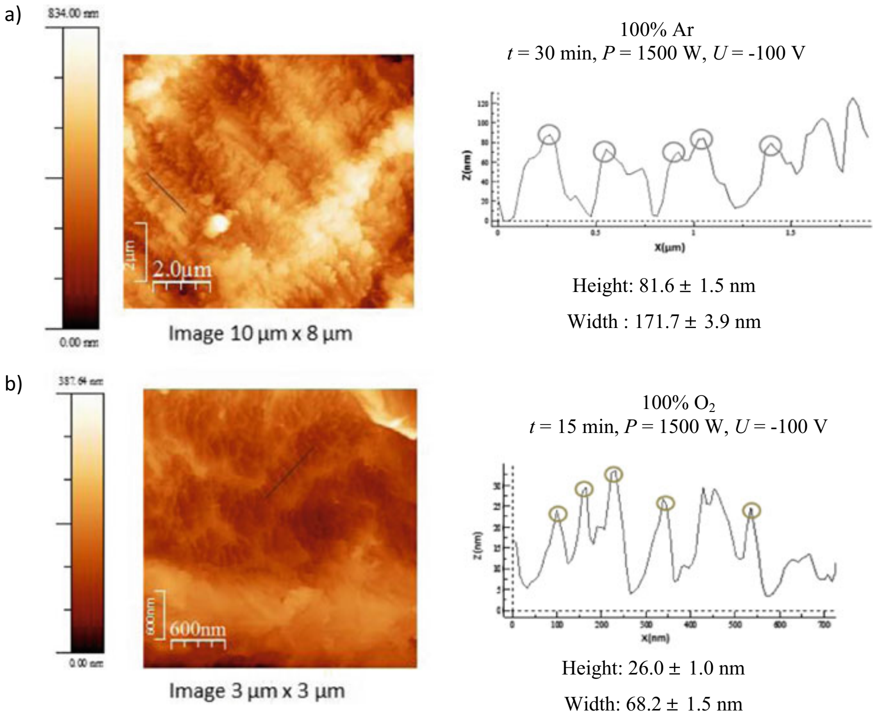

Fig. 7 AFM images and profiles for **a** pure Ar and **b** pure O_2 plasma-treated PEEK—Bias voltage of −100 V [28]

Another possibility of selectivity due to the polymer itself arises from polymer impurities or metal deposition on the surface. Polymeric materials are never pure compounds and depending on their further application different charges, either inorganic or organic are added to the polymeric matrix. In addition, depending on the plasma chamber design and on the excitation mode of the plasma, some metallic particles from the chamber walls or electrodes can be ejected and randomly included in the polymer matrix. Finally, the polymer substrate contains metallic and hard particles that modify the etch rate and the substrate pattern [10–13, 15, 18, 19, 29]. Indeed, during the O_2 plasma treatment of PMMA [12], nanoparticles such as antimony, aluminum, fluorine, sodium, potassium, silicon … are self-generated and act as etch masks to form vertically aligned nanowires. It must be pointed out that with such a process, no control of the particle deposition is achieved. Furthermore, if a composite material is plasma-treated as for example carbon nanotubes/polydimethylsiloxane [29] its surface becomes patterned, rough and superhydrophobic. Such a behavior can be interpreted as a selective etching of PDMS that reveals the hydrophobic carbon fiber.

Polymers are heterogeneous materials not only on the chemical aspect but also on the structural property, since most of them are semicrystalline polymers. In the

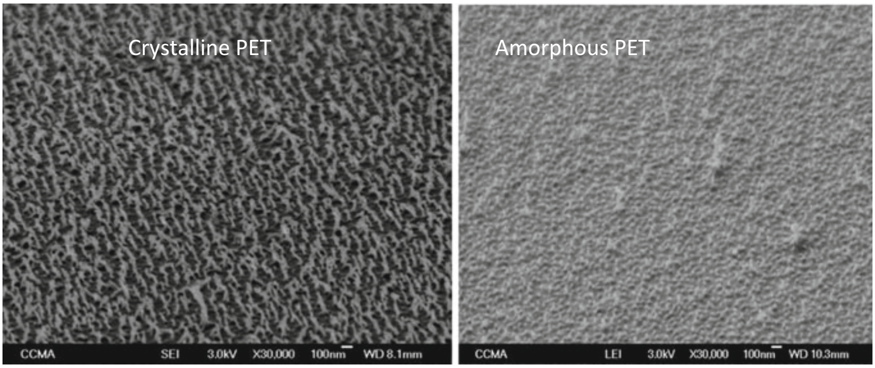

Fig. 8 Dependence of the textured plasma-treated PET on its crystallinity [2]

case of PET, the crystalline matrix when plasma-treated leads to a pattern whose decorative motives are sharper, like nanopillars, nanofibers [2] (Fig. 8).

The crystalline domains have higher density and thus are etched with a lower rate than amorphous ones. The type of crystallites and its proportion should influence the polymer patterning as shown in the literature [2, 30, 31]. For amorphous polymers, the selectivity is achieved by the creation of surface crystallites through chain motion, nucleation or germination upon exposure to the plasma [2, 7, 9]. Differential scanning calorimetry (DSC) measurements of pristine and plasma treated samples have confirmed the aforementioned predictions, through the presence of crystallinity in amorphous polymers after being exposed to the plasma.

In the case of PEEK, its crystallinity rate could directly impact its ability to be textured. Indeed, the total surface/etched surface ratio is the crystallinity rate as measured by DSC and FTIR [32]. The amorphous parts of the PEEK polymer are etched before the crystalline ones leading to those features producing the global texturation (Fig. 9). Therefore, the texturing efficiency could need to take care of- or at least to have the knowledge of the surface crystallinity rate. One can argue that the process used to produce the samples may then have a great importance towards the crystallinity rate of the surface and thus towards its ability to be textured the right way depending on the application. If the surface temperature can exceed the glass transition during the plasma treatment, the atomic structure of the polymer may rearrange and its crystallinity rate can increase. This is particularly possible with an atmospheric plasma torch which supplies a higher temperature on the surface during treatment. In the case of an amorphous specimen, if processed with a high speed of cooling, the plasma treatment may produce a reorganization of the surface leading to a re-crystallization, and this has been observed up to several hundred micrometers deep under the surface. At the opposite, the polymeric crystallinity rate is not altered by the plasma torch when the pristine material is already at its maximum crystallinity rate which is about 38% for the PEEK.

Polymers are stretchable materials, therefore the patterning process is also studied when polymers are stretched, specifically the PDMS, since this polymer induces a

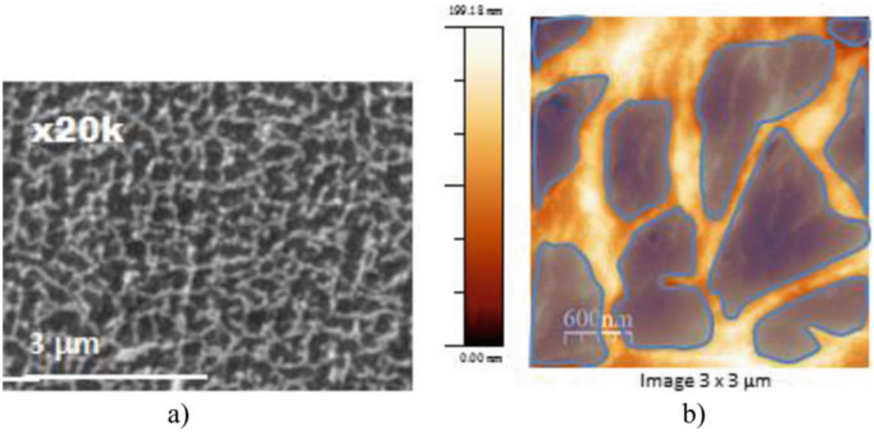

Fig. 9 Texturing PEEK by the selective etching of its amorphous parts in 100% O_2 plasma and with a bias voltage of −200 V **a** SEM image **b** AFM—Dark areas ≈70% of the total area were assigned to the amorphous phases—White upper areas ≈30% were assigned to the crystalline parts [32]

different pattern, a wrinkling one. The purpose of such experiment is associated to the incorporation of a nanoscale roughness on the wrinkle walls during the strain and then, after the strain has released this nano-scale feature is hidden, and finally a mechanical-responsive material is prepared [33–35]. The morphology of wrinkle patterns, specifically their wavelength and amplitude is controlled by the strain release after the O_2 plasma step. This can be repeated several times in order to obtain different sizes of wrinkle patterns with a wavelength in the range of 50 nm to 10 µm and an amplitude in the range of 20–400 nm (Fig. 10) [33].

All the methods described above concern plasma etching of industrial bulk polymers, while only few applications to plasma-deposited films were found [36]. The issue with plasma polymers is the absence of linear chains which makes them difficult to form crystalline domains. Thus, no selectivity of degradation is possible due to crystallization. Plasma-polyaniline films treated by argon plasma show nanostructured surfaces whose density and dimensions depend on the operating conditions. The creation of the nanodots is mainly ion-dependent according to the ion energy and the ion flux. In addition, when the substrate is polarized, sputtering effects become important such that sputtering and ion-induced diffusion become competitive mechanisms. It is interesting to note that some of these parameters do not have the same influence on thin film than on bulk polymers [36]. For example, for conventional polymers, the rise of processing time and of discharge power leads to increase the height of nanofibers and therefore of the surface texturation. This observation suggests that the creation of the grains on plasma-polymer surface does not have the same origin as on bulk polymer.

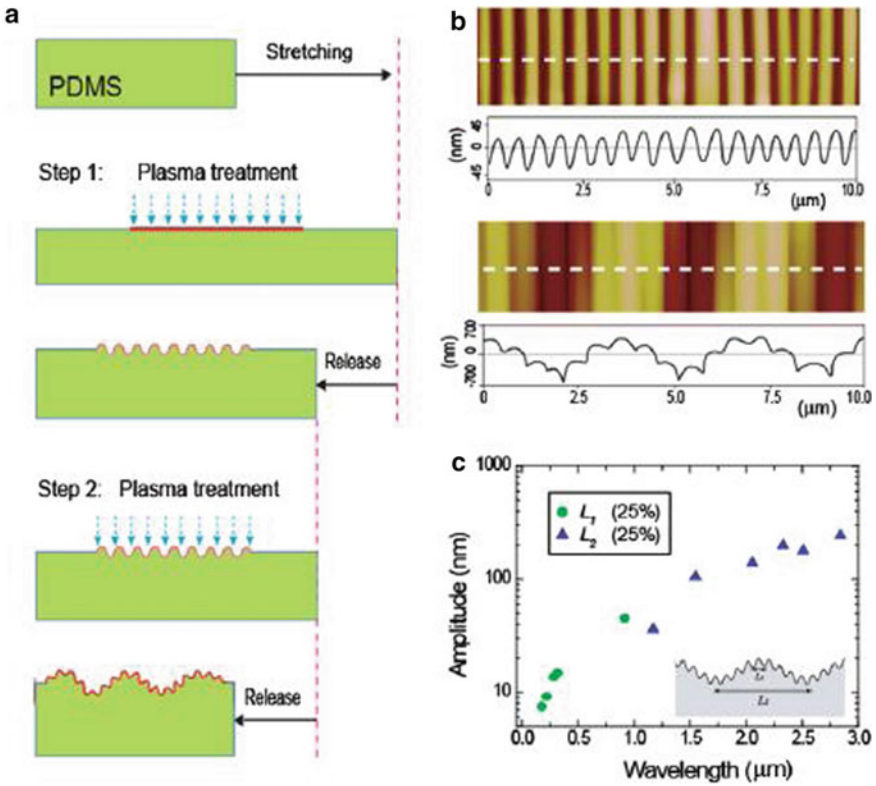

Fig. 10 PDMS multi-step plasma treatment for the creation of hierarchical wrinkles. **a** Schematics of the experiment. **b** AFM images of hierarchical wrinkle patterns created by a two-step plasma treatment [33]

3 One-Step Bottom-Up Plasma Texturing

Over several decades, plasma polymerization of a wide range of compounds has been fully recognized as an important process for the formation of new thin layers deposited on most substrates, using a simple one-step procedure. The possibility of obtaining different morphologies of plasma polymers prepared without templates, at atmospheric pressure or at low pressure, in a continuous or pulsed mode has been studied for only few years [7, 30, 31, 37–39]. The most relevant works describe either the creation of nanoribbons, nanowires whose size is comprised between 15–20 nm [7, 30, 37] or nanodots, nanopillars [31, 38, 39]. Despite the consequent enhanced properties due to the patterning, these structures are not entirely normally aligned to the surface as observed with the top-down process.

However, Zaitsev et al. [38, 39] demonstrate how to obtain well-defined one-dimensional polymer structures while preserving the monomer chemical structure. The process (two-step or three-step process) is based on the gradual decrease of the

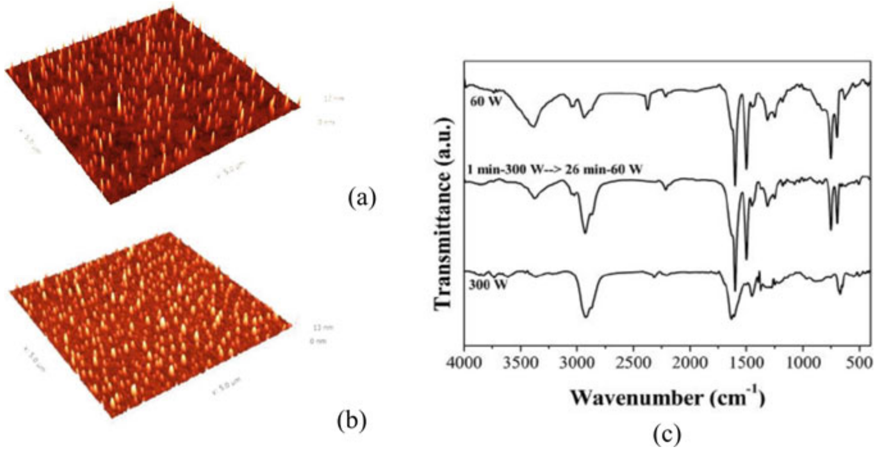

Fig. 11 Plasma polyaniline prepared in different conditions. **a**, **b** AFM images. **c** FTIR spectra [38]

discharge power during the deposition. A high power is first applied during a short time in order to form polymer nuclei followed by a low power step for a long time allowing the obtention of a well-ordered polymer structure. Figure 11 illustrates the chemical structure and the morphology of the obtained plasma polymer using aniline as monomer. The polymerization of aniline at 300 W during 1 min leads to a textured surface (Fig. 11a) but without retention of the monomer structure (Fig. 11c, 300 W). On the contrary, the low power (60 W) aniline polymerization gives a smooth surface with a low monomer fragmentation (Fig. 11c, 60 W). By combining these conditions in a two-step process, plasma polyaniline presents a textured surface (Fig. 11b) with retention of the aniline structure (Fig. 11c, middle spectrum).

This polymer structuring can be associated with the partial dewetting of plasma polymer chains as already observed with other coatings techniques (spin-coating, annealing of thin layers…) [40]. This dewetting namely the diffusion of reactive species on the substrate surface strongly depends on the temperature of this surface which is time and power dependent. Figure 12 presents the dependence of the polymer roughness on the surface temperature. This figure shows that the dewetting occurs within a range of surface temperature comprised between 40 and 50 °C. In this range of temperature, the film roughness drastically increases and nanodots appear while below this temperature range, the plasma polymer is rather smooth.

Above this range, the temperature is too high and leads to a liquid-like state of the film. In this state, the film is unable to form any nanostructures and thus a smooth uniform film is obtained. Such operating conditions thus degrade chemical structure of both precursor and growing polymer and a multi-step process including low discharge power can be applied if the chemical structure of the precursor must be preserved [39].

Similar structures have been obtained with fluorinated plasma-polymers [7, 37, 41]. All single step methods combine the fluorinated chemistry with a textured surface

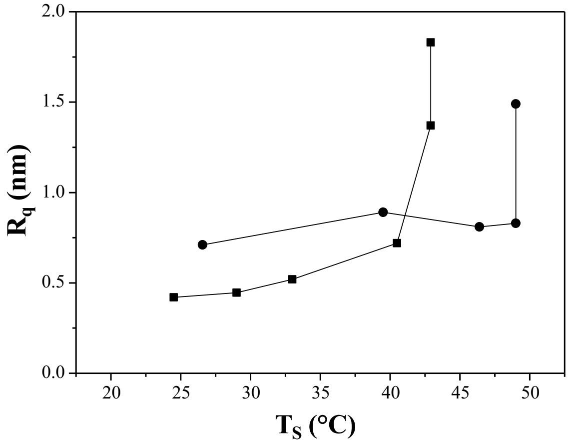

Fig. 12 Dependence of plasma polyaniline roughness Rq on surface temperature Ts [38]

whose elemental pattern deals with micrometer-long ribbon-shaped nanostructures rather than nanopillars under pulsed fluorinated plasmas. The ribbon-like structure is achieved at low duty cycle, long modulation period and duration [37]. The proposed growth mechanism deals with successive steps as the creation of nucleation centers, the nucleus alignment into a spiral mimic, the attachment of further spheric nuclei, and termination with further nucleation sites on the ribbon surface.

4 Plasma Texturing Combined with Other Methods

4.1 Plasma Texturing Combined with Laser Irradiation

Laser texturing followed by plasma modification or deposition offers the possibility of synthesis of hierarchically patterned surface with locally heterogeneous properties [24, 42, 43]. While the plasma treatment leads to nanotopography, the laser treatment induces microstructures over the polymeric surface as observed with laser-irradiated and plasma-oxidized PEEK. The laser treatment leads, through a thermal or a photodegradation mechanism according to the wavelength of the laser beam, to the microstructuring ablation from the surface. The formed dot arrays separated by the interspacing of several hundred interspacing in two axes are in the shape of microcraters with a diameter around 20 µm and depths around 600 nm. After the plasma treatment, the polymeric surface bears 1D nanostructures with a diameter around 30–40 nm and a length of few micrometers (Fig. 13 [42]). This dual treatment leads to a unique topography composed of both nanofibrous surface structures and microcraters.

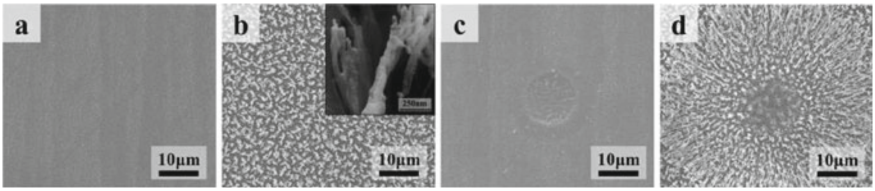

Fig. 13 SEM images of prepared surfaces: **a** non-treated, **b** plasma-treated, **c** laser-treated, and d plasma and laser-treated [42]

4.2 Other Combined Routes of Texturing

Most of the combined techniques coming from the microelectronic background are dealing with the plasma treatment of polymeric films in the presence of masks or templates that induce the creation of the first level of the required roughness scale [34, 44–46]. This review is not focused on this route. However such a process allows to prepare onto strained PDMS singular surfaces pattern, hierarchically wrinkled one with the well-defined wavelength/amplitude, organization, orientation, but also location as described in [34]. Indeed, the strained areas in contact to O_2 plasma form a hard zone because of the SiO_2-like layer growth while the unexposed areas remain soft zones with different mechanical behaviors after the strain releases.

Plasma deposition in presence of nanoparticles injected alone or included in an aerosol droplet in the plasma phase sometimes so-called atomized spray plasma deposition create hierarchical hybrid plasma polymer [45, 47–49]. The plasma deposition of the organic precursor onto these nanoparticles suspended in gas phase allows to prepare textured hydrocarbon surface when the plasma-coated particles precipitate onto a substrate. Thus, if the initial particles have different sizes, the final surface shows a dual-scale roughness that achieves for example the superhydrophobic, surperhydrophilic property. The increase of the plasma parameters (duration, concentration of aerosol droplets) has a significant effect on the chemical and morphological structure of the thin films which ultimately leads to superhydrophobic with low contact angle hysteresis due to the hierarchical multiscale roughness of the coating. This approach brings a major advantage to coat any substrate materials including polymers or metals, which enlarges the possible range of applications of this process.

In order to produce smart materials for wide applications such as in biomimetics, hierarchical structures can also be prepared by combining the micro-imprint technique followed by plasma etching [50–52]. Two scales of roughness are obtained, the first one at the microscale thanks to the molding of photocured polymers or blends so-called negative stamps and then, the embossed film is simply exposed to an oxygen plasma to produce the hierarchical structure (Fig. 14.). A plasma-deposit could also induce the final structure.

Some examples of the colloidal lithography including the spin coating of PS nanoparticles on both silicon or polymeric substrates are illustrated in [46, 53, 54].

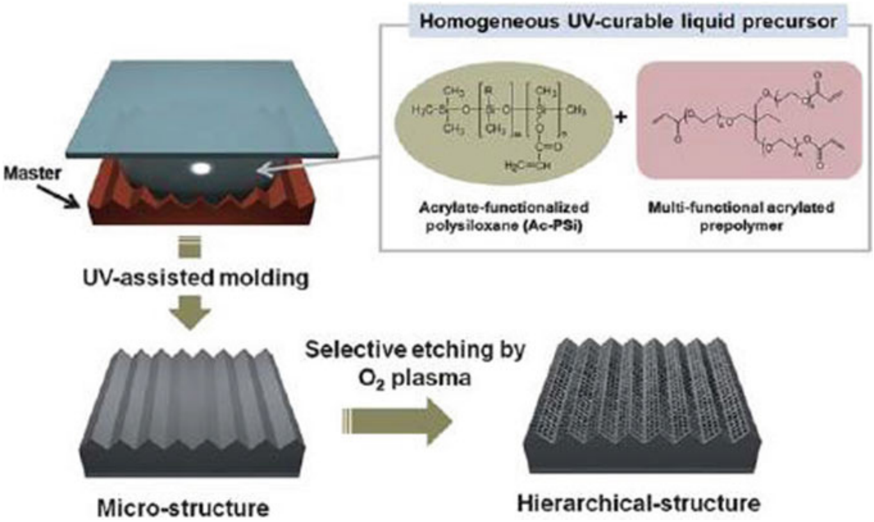

Fig. 14 Route of synthesis of hierarchical structure from imprint and plasma etching [50]

With this two-step process, the atmospheric plasma treatment induces not only the “cauliflower-like” nanotexturing of the PS spheres but also the etching of the underlying polymer (Fig. 15). After etching/nanotexturing, Ellinas et al. [54] gave evidences of a hierarchical triple-scale roughness with microscale ordered columns, and dual-scale (hundred nano/ten nanometers) nanoscale texture on the particles (top of the column) and on the etched PMMA surface.

The colloidal lithography has the major disadvantages that the scale of the first roughness depends on the colloid size, on the chemical nature of the commercial product and further on its availability that limits its application. The so-called breath-figure technique leads to well-organized structures bearing micropores obtained via the condensation of water vapor onto the surface of the evaporating polymeric solution. The structure and the morphology of the produced film are controlled by several factors such as temperature and relative humidity as well as chemical nature, concentration, viscosity, density, surface-free energy, and solubility parameters of the casting solution and therefore; a large variety of micropatterns of many types of polymeric materials are successfully synthesized [55]. Then, the double scale of roughness is achieved by plasma etching or deposition.

5 Applications of Plasma-Texturing of Polymers

If the hierarchical textured surfaces whatever the chosen preparation route are also chemically functionalized, the material properties will be extended from superhydrophilic to superhydrophobic character including both Cassie–Baxter and Wenzel

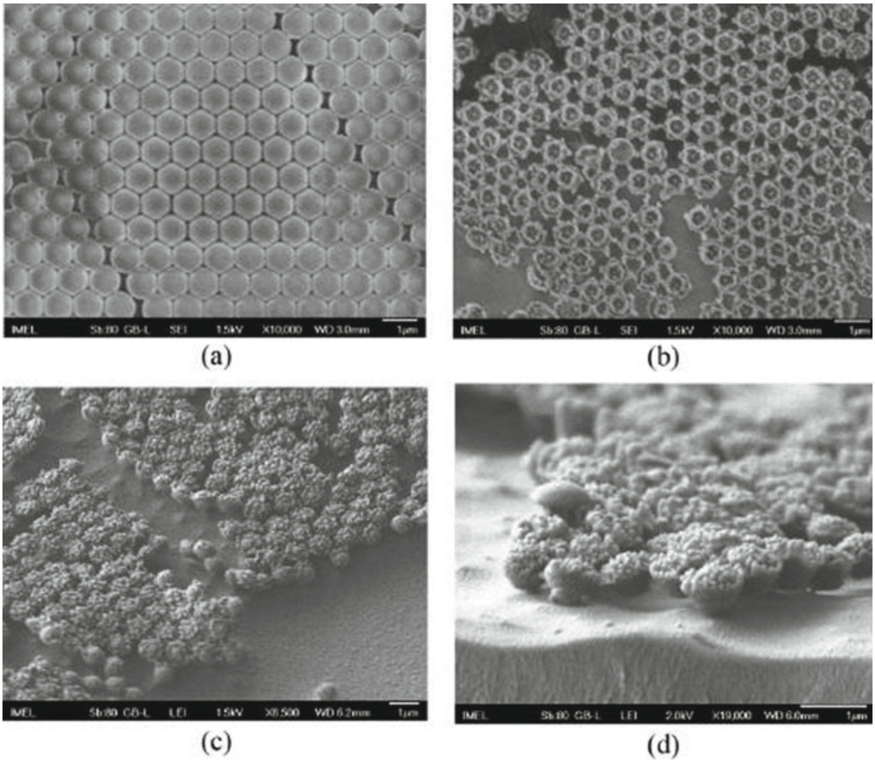
(a) (b)
(c) (d)

Fig. 15 SEM images of colloidal PS nanoparticles coated on PMMA and etched with atmospheric pressure He/O_2 plasma: **a** untreated surface (d = 1 μm), **b** plasma treated surface for 8 min, **c** plasma treated surface for 8 min (tilted surface), **d** plasma treated surface for 8 min (tilted surface at higher magnification) [46]

types depending on the pattern and the functional groups. Such singular behavior that can be summarized as the resulted effect of an increased specific surface area with a more concentrated chemical group; such behavior was explored for various application domains such as optics [2, 23, 25, 43, 53, 56], electronics [45, 57], sensors [3, 58–60], medical devices [2, 41, 61–68] and metal-polymer assemblies [24, 42, 44, 69–74].

5.1 Application of Plasma-Texturing of Polymers for the Optic and Electronic Fields

Depending on its scale, the geometrical pattern of textured material induces broadband anti-reflective properties compared to that of plane and smooth surface. Antireflective material was prepared from nanotextured PC [2, 23] since the reflectance of normal incident light was reduced if the nanofeatures are not able to collapse, i.e. are not too tall meaning that the plasma-treatment duration is too short. A regular pattern obtained from fluorinated plasma-treatment of polycarbonate glazing commonly used in automotive application, improves its anti-reflective property by simulating the so-called “moth eye” effect. The reflectance/transmittance measurements showed that this approach is able to increase the anti-reflective property of the polycarbonate without drastically damaging its transmittance [56]. The plasma patterning in conjunction with colloidal lithography on PS has attracted considerable attention in recent years as a means to reduce Fresnel reflection in photovoltaic solar cell materials. The resulting paraboloidal hierarchical structures suppress average reflectance to below 0.5% across a spectral range of 500–1000 nm [53].

Besides the direct optical behavior of patterned surfaces, the combination of both extreme wetting states to micro, nanopatterns opens up interesting applications, as the example of the fog-collecting [43], anti-fogging and anti-icing properties [25] of materials applied in optic domains. Microfluidic channels were manufactured thanks to a three-step fabrication [43]. In the first step, a double-hierarchical superhydrophilic surface structure was generated on glass using femtosecond laser. In the second step, a superhydrophobic fluorinated plasma polymer was deposited. In the last step, the coating was selectively removed by laser ablation to uncover superhydrophilic spots. The fog-collection efficiency is due to the combination of water attraction and water repellency: the superhydrophilic areas act as drop accumulation zones, whereas the surrounding superhydrophobic regions allow a fast water transportation. The patterned superhydrophobic surfaces are water repellent and therefore could act as anti-icing or de-icing surfaces [25]. However, it appears that a strictly repetitive pattern is required for increasing the freezing delay time, even if depending on the polymer structure and on the plasma chemistry, sharp or rounded features are prepared. Therefore, the combined technique including nanoimprint allowing a more regular pattern increases the freezing delay time.

The combination of template-assisted self-assembly of nanocrystals with plasma polymerization allows synthesis of nanocrystals with tailoring properties explored in electronic field [57]. Same methodology was also preconized for the preparation of mechanically stable silicon anodes [45].

5.2 Application of Plasma-Texturing of Polymers for the Sensor Field

Chemical sensors play a major role in various fields (medical diagnosis, environmental monitoring….). Improving the sensor characteristics specifically induces the detection of lower concentrations of the targeted molecules. To realize this goal, one of the proposed methods is focused on the increase of the specific surface area of the sensing layer. Indeed, these textured sensors were developed since their surface nanostructures, and associated roughness, lead to a larger surface contact and therefore to the improvement of sensor performances. As most of these sensors operate at ambient temperature, if the superhydrophobic character is added, their very low surface energy also avoids moisture adsorption while they are more attractive for organic molecules [3, 58].

Another example of texturing effect is given with plasma-polyaniline. Polyaniline is known to be sensitive to ammonia gas. The absorbance variation measurements (at $\lambda = 430$ nm) can be used to characterize plasma-polyaniline under gas. Figure 16 presents the evolution of absorbance of the polymer elaborated by the two-step process and submitted to 4618 ppm of ammonia. First, the absorbance of the layer is constant under air and then decreases in presence of ammonia until a plateau is reached. When ammonia flux is turned off, the regeneration of the polymer begins.

In the two-step process bottom-up process (Cf. Sect. 3), the duration and the power of the first step have been varied in order to study the sensitivity of the obtained layers (Fig. 17) [60]. The power and the duration of the second step are kept constant at 60 W and 26 min respectively. The horizontal line in the figure represents the sensitivity of a smooth layer elaborated in one step at 60 W during 26 min, this sample is the reference. Figure 17 shows the improvement of the gas sensitivity at the shortest first step duration regardless of the power compared to the smooth surface. Moreover, the

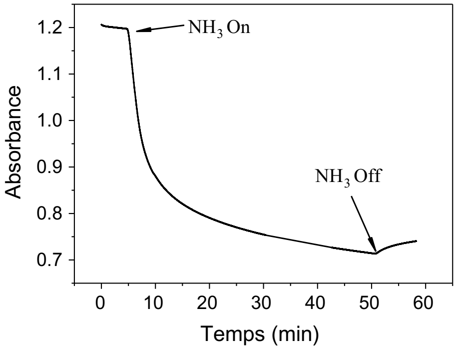

Fig. 16 The absorbance variation of plasma-polyaniline elaborated by the two-step process ($t = 1$ min, $P = 240$ W, $t = 26$ min, $P = 60$ W) and submitted to 4618 ppm of ammonia [59]

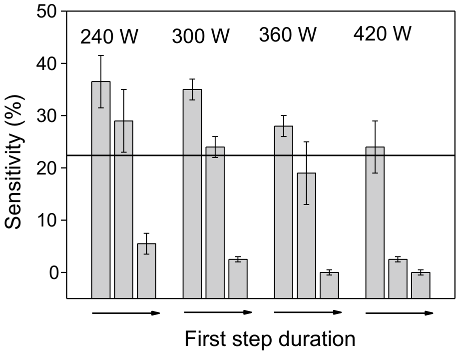

Fig. 17 Sensitivity to ammonia of plasma polyaniline layers elaborated at different powers ($P = 240$ W, 300 W, 360 W or 420 W) and deposition duration ($t = 1$ min, 2 min or 3 min) of the first step [60]

Table 1 Specific surface of plasma-polyaniline elaborated by the two-step process at different duration and powers of the first step

First step power (W)	240			420		
First step time (min)	1	2	3	1	2	3
Specific surface ($\mu m^2/\mu m^2$)	1.009	1.076	1.006	1.114	1.085	1.078

sensitivity decreases with the rise of the power and the duration of the plasma. These results can be explained by the specific surface of the nanostructured film and by the chemical structure of the layer.

The specific surface (Table 1) of all the layers elaborated by the multi-step process is higher than that of layers synthesized in one step at 60 W which is 1 $\mu m^2/\mu m^2$. The best sensitivity is obtained for layers elaborated at 240 W during 1 min for the first step. It appears that a small increase in the specific surface significantly improves the layer sensitivity to gas. However, the specific surface increases with power whereas ammonia sensitivity decreases. Moreover, at a given power, the sensitivity decreases with the rise of the deposition time to become, in some cases, lower than that of the smooth layer. Therefore, the chemical structure of the plasma polymer also plays an important role. The results prove that a dense layer is formed at high power or duration where the ammonia molecules can hardly diffuse, hence a decrease in sensitivity with the rise of input power or deposition duration.

5.3 Application of Plasma-Texturing of Polymers for the Biomedical Field

Recently, hierarchical surface patterns consisting of a mixture of micro- and nano-sized structures have been investigated in terms of their effect on bioadhesion of bacteria and proteins and on cellular responses [61–63, 65–68]. Thus, such surface patterning has a great academic interest for studying the biofilm formation, the competitive adsorption of proteins on surfaces with heterogeneous wettability and clarifying the relationships between protein adsorption and cell orientation, spreading and migration.

The superhydrophobic hierarchical surfaces were investigated for the purpose of anti-adhesion of bacteria. However, their bio anti-fouling potentiality is still unclear. Indeed, Tarrade et al. [2] shows that whatever the surface morphology of virgin PET, plasma-fluorinated surfaces (smooth and hydrophobic, Wenzel or Cassie–Baxter superhydrophobic ones), their bacteria adhesion behavior is almost the same as compared to the untreated surface (Fig. 18). The only noticed difference is on the biofilm compacity, that formed on the two superhydrophobic PET is weaker than that of virgin and hydrophobic PET. These results were explained by mechanical anchoring of the bacteria if any pili can grow from the bacteria material as shown on SEM images (Fig. 19).

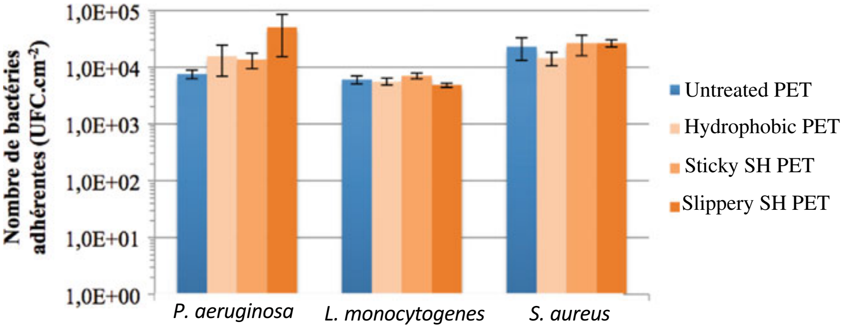

Fig. 18 Bacteria adhesion on different patterned PET surfaces [2]

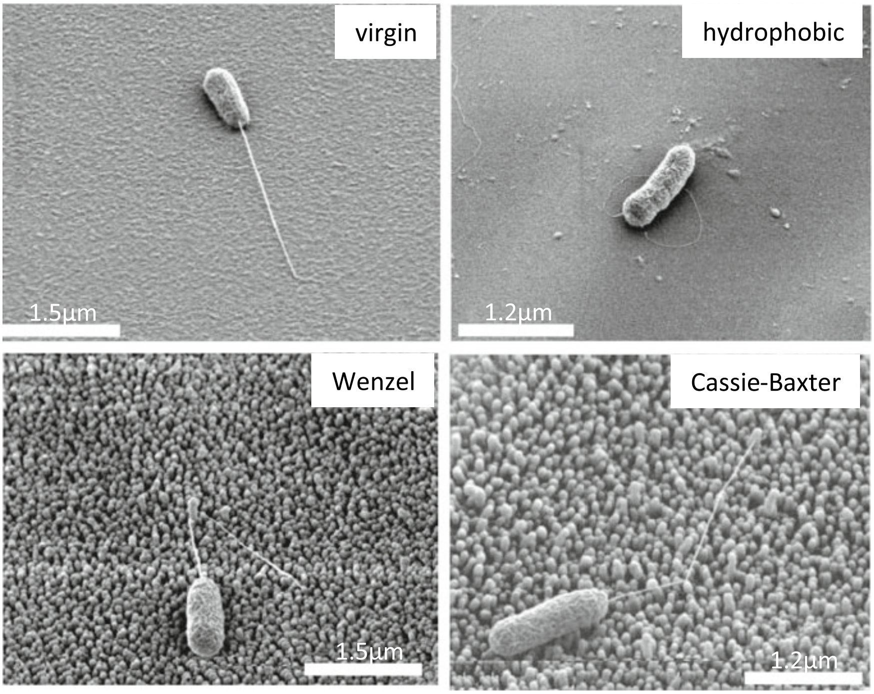

Fig. 19 SEM pictures of bacteria adhesion on different PET surfaces [2]

Such results are contrary to those obtained with hierarchical CF_4 plasma-treated PP which exhibits a 99.6% reduction of *E. coli* adhesion compared to untreated PP [64]. Such a different behavior could be interpreted as different bacterial behavior or a different surface pattern. The PP one appears to bear less nanostructures resulting in a higher air incorporation in the polymeric matrix. In addition, superhydrophilic surfaces in contact with water spontaneously form a water monolayer that acts as a weaker boundary layer for the biomolecules adhesion as observed with POE films. But same PP plasma-oxidized and textured in a same manner as the previous one [64] and thus completely wetted with water is more adhesive for bacteria. The additional nanostructuring reduces the surface anti-biofouling properties.

Such hybrid patterns have been described being among those having the greatest influence on the proliferation and differentiation of cells. A heterogeneous polymeric surface with a regular pattern could be achieved with a partial plasma modification leading to an area whose hydrophilic or hydrophobic character is opposite to untreated zones [61]. But depending on the scale of the hierarchical roughness, the textured surface may not match ideally the nanostructure off cell adhesion complexes. Therefore, this requires the fine-tuning of nanoarchitecture of plasma layers for the biomolecule immobilization and cell adhesion [65] since the cell adhesion and growth vary in function of the roughness of coatings [41]. Patterning should have a broader definition extended to the microporosity. Indeed, when the microporosity comes from the electrospinning while the nanoroughness is obtained thanks to the plasma-treatment of the polymeric fiber, such patterned microfibers enhance dramatically the oblast cell attachment [63].

5.4 Application of Plasma-Texturing of Polymers for the Metal Adhesion

For texturing, laser is a very well-known technology which gives rise to a well-defined and large-scale texture that can be applied to polymers in order to allow or improve the adhesion of metal coatings [70–75]. When PEEK surface was textured by an infrared 1026 nm radiation (224 femtosecond impulse), a pattern made of regular triangles with 60 μm side length induces one of the most efficient increase in adhesion for an aluminum or a copper thin film [74]. Such a laser etching can extend the practical adhesion strength of a metal onto a polymer greater than the best conditions found with an O_2 ECR plasma. Obviously, those processes are not comparable in terms of surface mechanisms. The first one being mainly an anchoring mechanism (laser texturing) while the second one is assumed to be mainly a chemical mechanism (ECR plasma without extra bias voltage applied to the sample—called low-energy ECR plasma). These conditions of plasma texturing with a vacuum ECR plasma were already more effective in terms of adhesion than those provided with an air plasma torch which nevertheless enhanced the metal adhesion (Fig. 20).

Currently, the laser ablation process leads to a two-scale alteration of the polymer (Fig. 21). Inside the etched trenches, a random and small-scale texture appears to be assigned to polymer redeposits. These redeposits were considered sufficiently cohesive to the polymer bulk as they were not removed by the subsequent alcohol rinsing of the samples before metal deposition. These redeposit could significantly take part to the enhancement of the adhesion. By the way, the rupture of the interface when the metal-polymer assembly was mechanically tested is mainly cohesive. The

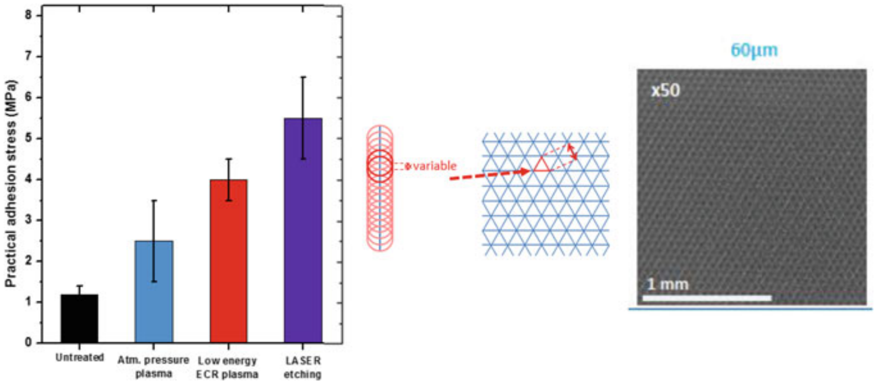

Fig. 20 Improvement of the adhesion of a metal thin film deposited on PEEK after the surface has been laser textured in comparison with plasma modified PEEK surfaces and with the untreated sample (left) and the features of the laser spot line and geometry which was selected (right) [75]

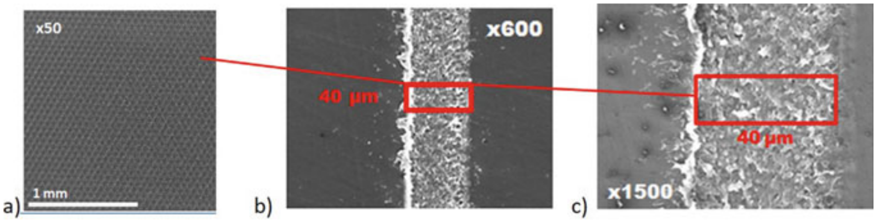

Fig. 21 SEM images of femtosecond impulse laser-treated PEEK surface showing **a** first scale and **b**, **c** second scale of texturing [75]

rupture strength of the coating did not reach the value which is calculated if one considers the specific surface increase supplied by the triangles pattern creation. The polymer redeposits are thus assumed to limit the enhancement of the adhesion which could have been reached otherwise.

Even if Yu et al. [69] shows that the surface roughness significantly affects the performance of gecko mimetic adhesives, the dual modification (plasma and laser combined treatments) allows to enhance the Al adhesion [24, 42].

Indeed, the double scale roughness positively impact the mechanical anchoring of deposited metal layer. However, this assessment is only verified if the metallic layer is perfectly covers the undulating surface topography as shown in [42] since the roughness values of the two-step modified surfaces before and after the deposition remain very close to each other. Besides the possible reinforcement of the mechanical anchoring, the chemical bonding must be taken into account. Gravis et al. [24] studied the competitive effect of the roughness and the surface chemistry on PEEK modified either by plasma (at atmospheric pressure or at reduced pressure) or by a laser beam on Al adhesion. Currently, the surface chemistry of PEEK can be tuned in terms of hydrophilic bonds (mainly C=O and COO) leading to an increase of its surface-free

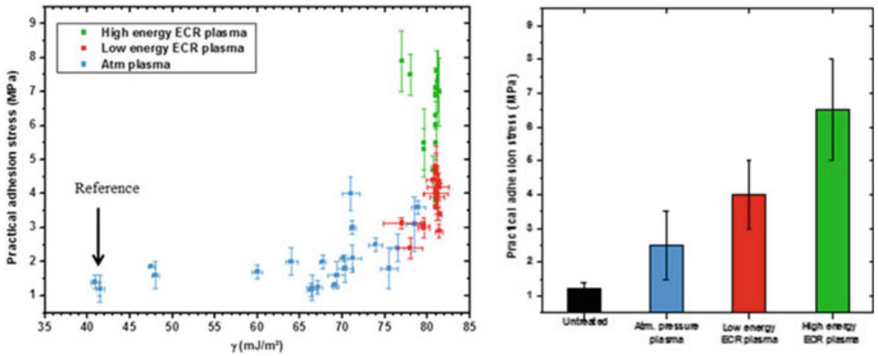

Fig. 22 Comparison between an atmospheric plasma, a low energy ECR plasma and a high energy ECR plasma treatment on the surface-free energy (□) and on the practical adhesion on PEEK surfaces [24]

energy therefore leading to an increase of the adhesion between a metal coating and the polymer (Fig. 22). An ECR plasma treatment can add a texturing effect to the polymer surfaces especially if an external bias voltage is applied to the samples (called high energy ECR). In that case, one can overlay the advantage of the chemical functionalization of the surface to the advantage of the anchoring effect to extend the result in terms of adhesion as shown on Fig. 22.

In conclusion, on polymer-metal adhesion, Fig. 23 provides an overview on the balance that one can select between the chemical (functionalization) and the texturing (mechanical anchoring) effects on a polymer surface as supplied by plasma and laser technologies. Polymer texturing is playing a major role towards the anchoring effect which can be filled out with the chemical modification of the surface with only one process in the case of plasmas.

Surface patterning for adhesion purpose is also developed for the metallic ink used in inkjet printing; the aim is not only to improve the adhesion of metallic ink but to limit its spreading during the printing (Fig. 24).

That means to balance the hydrophilic/hydrophobic character of the substrate and to control the wettability equilibrium. For such a purpose [44], a multiple-step plasma treatment including deposition, oxidation and etching of a polyimide surface leads to micro-patterned surface with hydrophilic and superhydrophobic Wenzel-type domains. Such a treated surface bears fine lines of adhesive Ag ink.

6 Conclusion

The aim of this review was to illustrate the versatility of plasma nano-texturing. Nano-features with high aspect ratio can be prepared either by etching or deposition whatever the type of polymer and plasma. Even more, a regular pattern is obtained

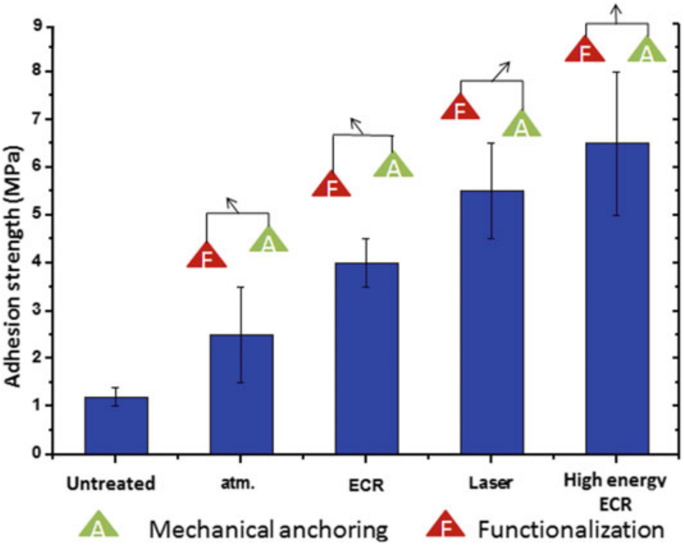

Fig. 23 Competitive balance between mechanical anchoring and surface chemistry of PEEK in the case of different plasma treatments or laser texturing

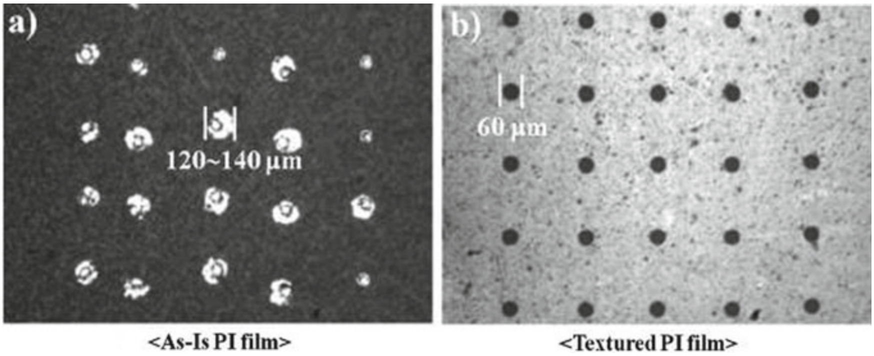

Fig. 24 Optical microscope images of Ag dot pattern formed by an inkjet printing system on the polyimide surface before (**a**) and after (**b**) texturing using atmospheric pressure plasmas [44]

without any mask layered on the polymeric substrate. Furthermore, plasma nanotexturing has a low environmental impact, it can be combined to other dry technics. The texturing mechanism was illustrated through different applications.

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Plasma Modification of Polyolefin Blends and Composites

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Abstract Polyolefins are very important commercial polymers. They represent a broad class of materials which include different grades of polyethylene(PE), poly(propylene), polystyrene, polybutylene, and so on. This chapter is discussing about the blends and composites of different types of polyolefins. They are the class of thermoplastics from which a large percentage of blends and composites are made. The polyolefin-polyolefin blends and composites are itself a large category. In addition to that they have been added to other thermoplastics like PVC, PTT, PC, etc. and elastomers such as natural rubber, SBR, NBR, EPDM, etc. and thermosets like epoxies. Generally they hold a degree of immiscibility with most of the other polymers and in order to enhance miscibility and decrease the interfacial tension, fillers and compatibilizers are preferred. Other than these, the surface functionalization is preferred in most of the cases. Plasma modification is one such method to introduce surface functionalities in an otherwise non-polar material. High voltage electric current will be applied to gases such as oxygen, argon, ozone to make them ionized. The resultant state contains a large number of different species such as ions, atoms, molecules, electrons, neutral species, etc. These plasma are effective in modifying the surface of polyethylenes. The blend components are either pre-treated or post treated with plasma to enhance the interfacial adhesion.

Keywords Polylefin · Blends · Compatibilization · Interface · Plasma

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1 Introduction

Poly olefin plays a significant role in modern industry and it constitutes the most widely used plastics today, especially polyethylene and poly propylene. Polyolefin can be regarded as the as the most widely produced commodity plastics also and its production exceeds several million tonnes. The usage as well as researches on polyolefin based blends and composites have increased drastically because of their new applications in medical, packaging, automobile, electronic and industrial fields [1–5].

The blending of polyolefin with other polymers leads to the improvement of its native properties as well as leads to the cost effect products having high end use. Polyolefin based blends possess many advantages such as low density, low cost ease of processing and improved chemical, physical and mechanical properties. Polyolefin blending requires the knowledge of miscibility, crystallinity and other features components. Polyolefin can be studied under two distinct headings such as polyolefin-polyolefin blends and polyolefin-non polyolefin blends. Polyolefin blends are usually prepared by in- reactor blending or non reactor blending [6]. The former method involves the blending of polyolefin different polyolefin in the polymerization reactor and the latter involves the mechanical blending of the premade polyolefins with other polyolefin or non poly olefins in compounding extruders. The hydrophobic nature of the polyolefin usually leads to the poor miscibility which in turn results in phase separation and that can be solved by the use of suitable compatibilzer. The compatibilzer reduces the interfacial tension between the polymers and strengthen the interface.

Polyolefin composites are the polyolefin materials containing at least one non polymeric reinforcement of organic or inorganic origin. The reinforcement may be micro or nano in size, natural or synthetic, which includes glass fibers, natural fibers, carbon based nanomaterials, clay minerals, magnesium hydroxide, aluminium hydroxide, calcium carbonate, titanium dioxide, silica [7–11] etc. In the next section, we have discussed briefly about the fiber reinforced polyolefin blends and composites.

2 Fibre Reinforced Polyolefin Blends and Composites

Fiber reinforced polyolefin blends and composites are on of the most popular type of materials in which the continuous thin fibers are embedded in the polymer matrix. Fiber-reinforced polyolefin blends and composites offer not only high strength to weight ratio, but also provides exceptional properties such as high durability; stiffness; damping property; flexural strength; and resistance to corrosion, wear, impact, and fire. A great number of research and developments has been done with different fibers on the effects in the origin, type, surface modification, loading and orientation [12–15]. In the recent years natural fibers attains more attraction among the researchers owing to the availability, cost effectiveness, environmental friendliness etc.

Recently, polypropylene-high density polyethylene-coir coconut fiber (PP-HDPE-CCF) biocomposites were prepared as alternative materials for the design and manufacturing of sustainable products. The addition of CCF generates an increase of the tensile and flexural modulus up to 78% and 99% compared to PP-HDPE blend. This stiffening effect is attributed to the decrease in the polymeric chain mobility due to CCF and the higher mechanical properties of the CCF compared to the polymeric matrix [16]. Old Newspaper Recycled Fibers-Reinforced Polypropylene Composites were prepared by adding Maleic anhydride as a coupling agent in order to increase the strength of the interface between the matrix and the reinforcements. The prepared composites exhibit increased the impact strength of the composites and decreased the water uptake. Impact strengths of 21.3 kJ/m^{3}were obtained for a coupled composite with 30 wt % reinforcement contents, which is a value higher than that obtained for glass fiber-based materials [17, 18]. Even though the natural fibers have many advantages, they suffer from lower modulus, lower strength and relatively poor moisture resistance when compared the synthetic fibers. Glass fibers (GF) are also used as reinforcement agent used in polyolefin based blends and composites. The effect of fiber content on the stress relaxation of polypropylene/glass fiber composites was conducted with and without coupling agents was studied [19]. Another interesting study demonstrates the preparation and properties of glass fiber-reinforced polypropylene composites using different fiber loading and different comaptibilizers. Toughness, crystallization ability and heat resistance were all enhanced when compared to the pure polymer matrix [20]. It has been reported that the strength and toughness increases three times and the interfacial strength duplicates in PP/GF composites prepared with *in-situ* polymerized fibers [21].

Intermixing of natural fiber with stronger and more corrosion resistant synthetic fibers such as glass fiber can lead to the synergetic effect. Literature review reveals that the addition of a small amount of glass fiber enhance the durability of bamboo-fiber reinforced polypropylene [22]. Recycled low density polyethylene composite materials having hybrid coconut/glass fiber as reinforcement were fabricated to enhance the desired mechanical properties for car bumper as automotive structural components [23].

3 Interfacial Adhesion in Polyolefin Blend System

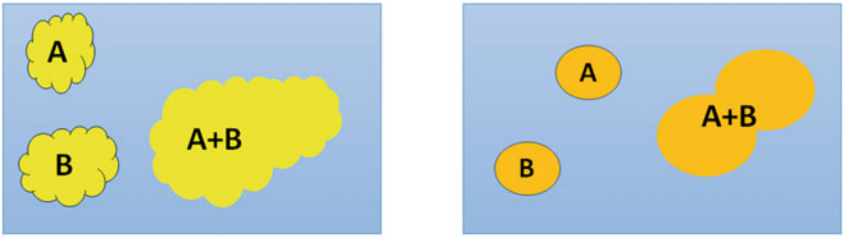
Polymer blending is a cost effective and easier way to develop materials for high performance applications. Generally, blends are of three types-miscible, immiscible and partly miscible. The miscibility has a direct connection with the morphology and properties. Miscibility is also dependent on the interfacial tension, viscosity and process conditions and technologies. A huge percentage of the reported works in blends contain polyolefins.

Polymer blending is a cost effective and easier way to develop materials for high performance applications. Generally, blends are of three types-miscible, immiscible and partly miscible. The miscibility has a direct connection with the morphology and properties. Miscibility is also dependent on the interfacial tension, viscosity and process conditions and technologies. A huge percentage of the reported works in blends contain polyolefins. On analyzing the miscibility of the liquid mixtures, it was noted that at the interface between low molecular weight liquid in an immiscible liquid mixture, there exists a tension-the interfacial tension. When polymer blends are mixed, shear or elongation processes distort the minor phase into long fibrils or thin films, which are then broken down into minute particles. Lesser interfacial adhesion prevents shear stress from moving from one phase to the next, hence higher interfacial tension implies lower interfacial adhesion [24].

Intermolecular forces, chain entanglements, or both are used to establish adhesion through interfaces between phases or materials is considered as interfacial adhesion. When two separate materials are fused, merged, or mixed, interfacial adhesion occurs. Typically, to improve interfacial adhesion, a mixture of materials with similar properties, such as hydrophilic fillers and hydrophilic matrices or hydrophobic and hydrophobic materials, must be used, resulting in a close bond between the two. Instead, when hydrophobic and hydrophilic materials are combined, there must occur some problems. Interfacial adhesion is an important parameter to define the dimensional stability of materials. The schematic representation of the above statement is given in Fig. 1. It is clearly indicated that when A and B are of different nature a distinct interface exist between them.

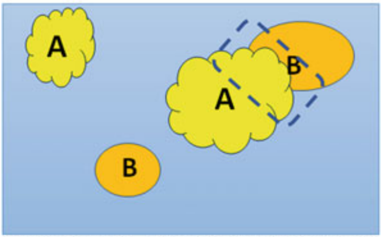
Interfacial interactions are generally characterized using microscopic techniques and poor interfacial adhesion results in poor mechanical properties. In the case of blends and composites, the demand is always to enhance the miscibility. Generally miscible and partially miscible blends make the processing easier. When it comes to the immiscible blend system, different methods have been employed to enhance the interfacial adhesion. These methods are generalized by the term compatibilization and the materials which enhance the interaction are called compatibilizers. A variety of materials are being incorporated in different immiscible systems as compatibilizers—fibers, metal oxides, clays, nanoparticles, biopolymers, etc. The mechanism of compatibilization is very simple, the material added for this will have affinity towards both the phases and thus forms bond between the two. Even though they are immiscible, due to the common dissolved materials, they tend to interact with each other through the new added phase/material. There are different ways to implement compatibilization. Other than compatibilizers, introducing functionalities which can react with the immiscible phases are efficient in improving the adhesion.

Normally the polyolefin- polyolefin blends appear to be miscible, but a huge number of reports are available on the miscibility of these blends. Polyolefin based blends and composites are very important in the application point of view. Among the polyolefins, polyethylene and polypropylene are used more widely. The adhesion in polyolefin blends is enhanced by means of fillers. The following discussion will



Interaction of hydrophilic materials A and B

Interaction of hydrophobic materials A and B

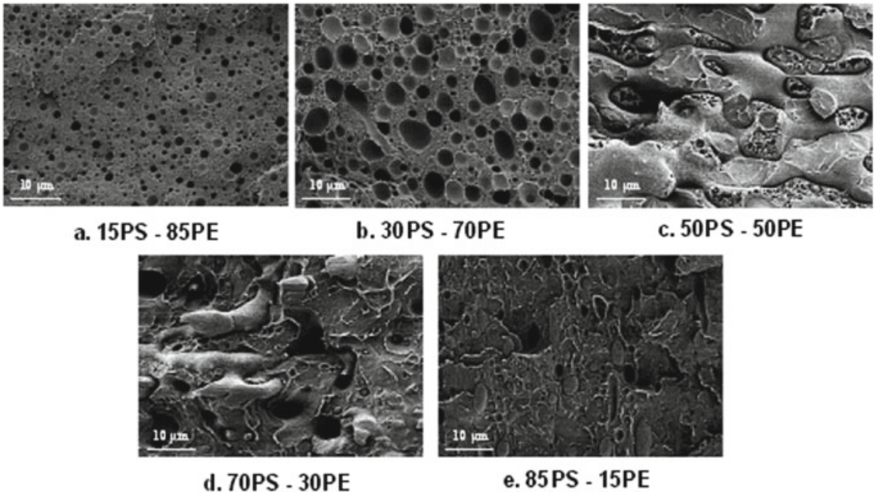


Interaction of hydrophilic A+ hydrophobic B
The interface is also indicated

Fig. 1 Schematic representation of the interfacial interaction of like and unlike materials

be about the different types of modifications implemented so far in the case of most common polyolefins. Polyethylene, the common plastic material in applications worldwide, can be blended with polystyrene. The polymers interacted through graft polymerization. The high molecular weight polymer servs as a compatibilizing agent. Even with a catalytic amount of the polymers better interfacial adhesion and reduced particle size were resulted [25]. Even with the addition of compatibilizing agents, the processing conditions will change the adhesion and morphology (Fig. 2). One such example is the study done with PE/PS and PP/PS blends with and without compatibilizing agents and with different mixing strategies such as single-screw, twin-screw and an internal mixer. The studies on morphology revealed that the single-screw extruded materials gave better adhesion [26].

With the change in interfacial interactions, the morphology also changes. By examining the morphology, the miscibility and reduction in interfaces can be predicted. Also the effect and interaction of the compatibilizer can also be analyzed [28]. When compared to the other polyolefins, the polycarbonate shows more adhesion towards the PE phase. The improvement in adhesion resulted in the enhancement of mechanical properties and this was owed to the debonding mechanism of the blend system. The debonding relieves the triaxial tension in front of the crack tip, followed by shear banding of the PC matrix. The fact was a surprise as there were no visible reactive functionalities in PE and PC but an assumption can be made that the mixing was done in the brabender and this will cause the breakdown of PE polymer(oxidation) into finer PE particles and these particles can penetrate into the



a. 15PS - 85PE
b. 30PS - 70PE
c. 50PS - 50PE
d. 70PS - 30PE
e. 85PS - 15PE

Fig. 2 Morphology of different composition blends if polyethylene and polystyrene (Reproduced with permission from [27])

polycarbonate chains by making available suitable reaction sites [29]. The compatibilization can also be done by certain chemicals like dicumyl peroxide [30]. The interfacial adhesion can also be enhanced via the addition of co polymers with both polar and nonpolar functionalities. The otherwise immiscible NBR and polyolefins can be made compatibilized by the aforementioned way. The added copolymer along with the melt mixing enhances the compatibilization action.

Another common procedure is the filler addition. With the inclusion of different fillers, the blends which are immiscible or in compatibilized can be made compatible. In their study, Pracella et al., investigated the effect of different types of natural fibers in polyolefin systems. In the report, they have included the composites of isotactic polypropylene (PP), polystyrene (PS), poly (ethylene–vinyl acetate) (EVA) as matrices and cellulose fibers, hemp or oat as natural fillers. Bi-functional monomers (glycidyl methacrylate, GMA; maleic anhydride, capable of inducing chemical interactions between the components during melt mixing) were used to modify both polymers and fibers. As compatibilizers, reactive polyolefin copolymers (PP-g-GMA, SEBS-g-MA, PS-co-MA, etc.) were utilized [31]. The addition of fibers could not improve the morphology, but the reactive functionalities could. The improved interfacial adhesion is revealed from the SEM micrographs of the composites given in the Fig. 3.

Effect of addition of ethylene-based compatibilizers in the immiscible polybutylene terephthalate (PBT) with very low-density polyethylene (VLDPE) was studies and results suggest significant improvements in the mechanical properties through modification of phase morphology and interfacial adhesion [32]. Surface functionalization can also be suggested as a route to improve interfacial adhesion. Chlorinated polyethylene can act as a compatibilizer for the poly-(vinylchloride)/polyolefin

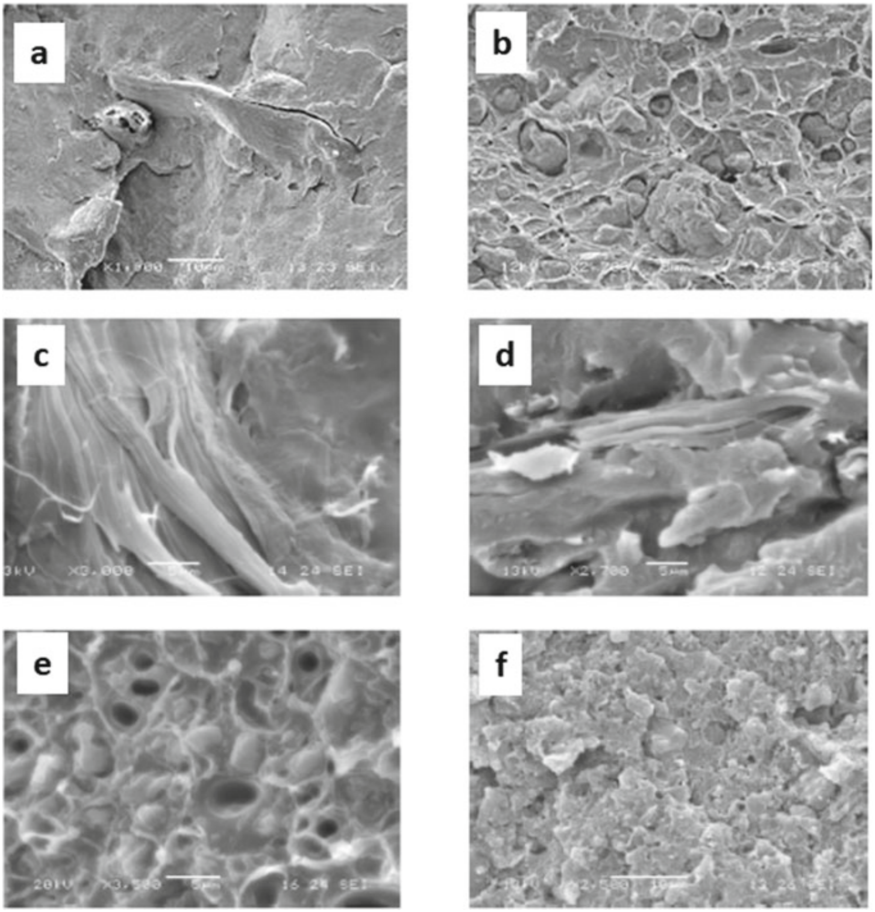


Fig. 3 SEM micrographs of polyolefin composites. **a** PS/Cellulose **b** PS/oat **c** cellulose modified with grafted polymer **d** PS-co-MA/cellulose **e** PS/oat/PEG **f** PS/Calcium carbonate/graft polymer (Reproduced with permission from [31])

elastomer blend system. According to the findings, the improvement in interfacial adhesion between the PVC and the POE is significantly greater with the blocky chlorinated PEs than with the randomly chlorinated Pes [33]. The studies on the composites and blends of polyolefins with and without functionalization and fillers are still a hot topic of research. The publications are beyond the limit and above the scope of this chapter. The interfacial properties can also be enhanced by an advanced technology called plasma modification.

4 Plasma Modification in Polyolefin Blends

The surface modification of polyolefins becomes necessary when cases arise where the mixed polymers are incompatible or the processing become difficult. The plasma modification is a superior technique where surface functionalities are introduced by the irradiation with suitable source. Plasma is created when enough energy is applied to a gas, causing the electronic structure of the atoms or molecules to reorganize, resulting in the generation of excited species and ions. The theory and other details are already mentioned in previous chapters. Corona discharge, which is produced by electrifying gases inside a chamber, is one of the favorite methods to introduce oxygen or other ions. It has been widely employed in the pretreatment of polyolefins [34]. But the reports on the plasma modification of blends and composites seems to be very less compared to the other modification methods (Fig. 4).

It has been shown that oxygen plasma can create a variety of oxygen functional groups at the surface of olefins, including C=O, C–O, OCO, COO− and CO_3^-. In a reported work, the polymer substrates made up of a polypropylene–polyethylene were investigated copolymer with a high percentage of PP and a mixture of ethylene–propylene rubber in the range of 15 to 60 mol%. For graft polymerization, plasma pretreatment was utilized to create reactive radicals and oxygenated groups on the polymer surfaces. It was concluded that plasma pretreatment endorsed the ethylene–propylene rubber component of the substrate, and that the ethylene–propylene rubber concentration was related to graft yield [35]. Low density polyethylene(PDPE)-casted polypropylene(CPP) films were modified by

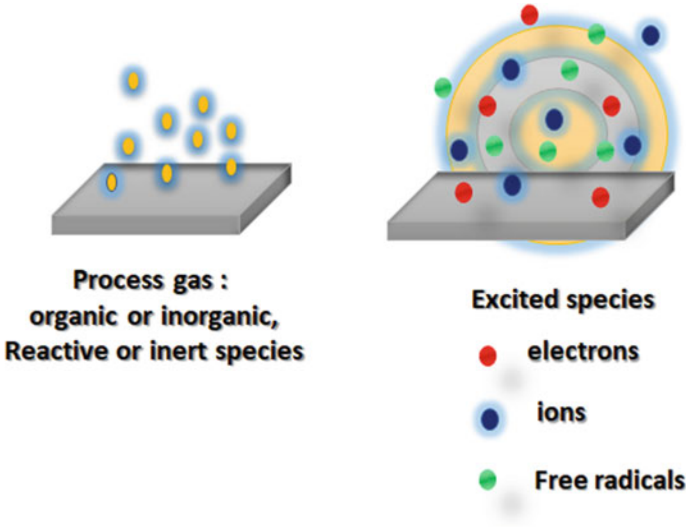


Fig. 4 Schematic representation of the effect of plasma irradiation on surface of a material

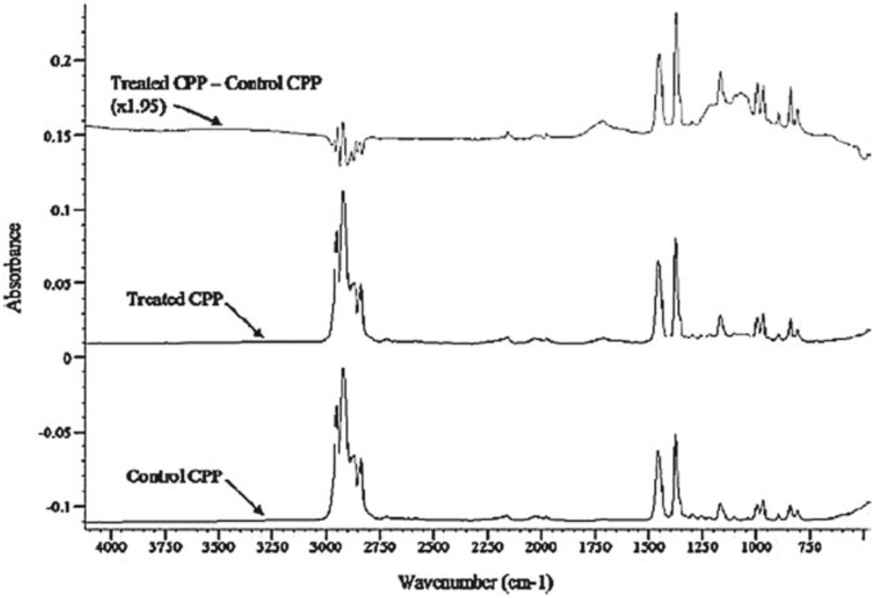


Fig. 5 ATR-FTIR results to confirm the introduction of surface functionalities (Reproduced with permission from [36])

capacitively-coupled radio-frequency oxygen plasma of field strength 13.56 MHz, essentially, to raise the quantity of active molecules attached to them [36] (Fig. 5).

In another report, to enhance the dispersion of the filler in the polymer matrix and decrease space charge buildup by modifying the charge trapping capabilities of these silica/PP/POE blends composites, the compatibility of silica with the PP/POE blends matrix must be increased.

A polypropylene (PP) blend used for automotive bumper fascia was subjected to surface modifications using a radio frequency Ar-plasma treatment. According to surface characterization, the Ar-plasmatreatment on a PP blend surface turns the wholly annular surface into a locally dimpled surface, resulting in improved wettability. The increased wettability and interfacial adhesion between the PP blend substrate and bumper coating layers can be attributed to the observed surface characterization and morphologies [37]. The ambient pressure air discharge is observed to change the morphology and structure of the PP base, as shown by the following results: the spherulitic characteristics of the pristine PP film's layer transform into arbitrarily shaped surface appendages as the processing time is increased; highly oxidized carbon species are present on the plasma-processed surface, and the contact angle is significantly decreased from 93.7° for the untreated surface to 53.8° post-treatment [38].

Plasma modification can be done to enhance the interaction between fillers and blend system in composites. The aim of one such modification on polypropylene/polyolefin elastomer blend was to optimize the compatibility of silica filler

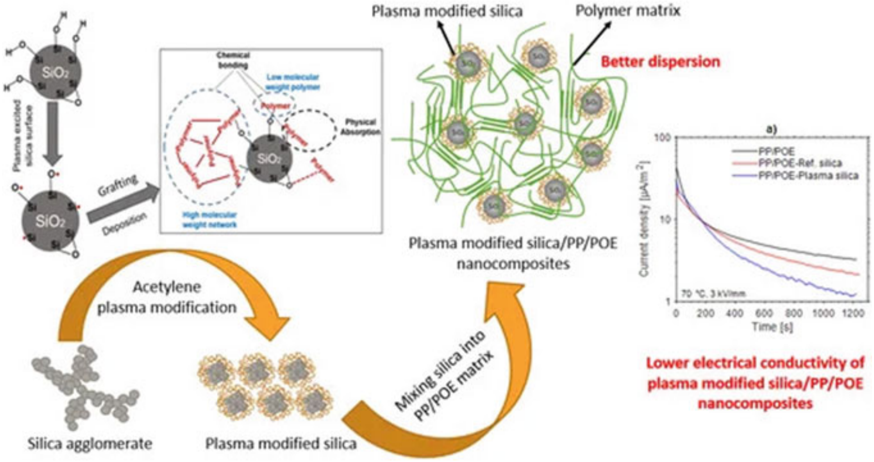


Fig. 6 Schematic representation of the process of plasma modification of silica particles to enhance the interaction with the PP/POE blend matrix (Reproduced with permission from [39])

with the PP/POE blends mixture in terms of improving filler dispersion in the polymer matrix and to inhibit space charge deposition by changing the charge sealing properties of such silica/PP/POE blends composites [39] (Fig. 6).

Wood fiber was modified using argon and air-plasma to enhance the compatibility with polypropylene(PP) and the surface characterization suggested enhanced oxygen/carbon ratio after the treatment [40]. PP/PS interface was modified by surface modification of polypropylene (PP) film is induced by CO_2 plasma [41]. The hexamethyldisiloxane (HMDSO)-radiofrequency plasma was employed on PP fabric to get the inorganic surface [42]. By analyzing a sample made of polypropylene (PP) decorative paper, the substrate, treated with low temperature plasma PP surface treatment, and coated with waterborne primer coating and topcoat material, to investigate the effects of plasma treatment on waterborne painting film adhesion. According to the findings, plasma treatment reduced the water touch angle on the surface of a PP decorative board material and increased the surface free energy and roughness. Besides that, plasma alteration can provide a large number of oxygen-containing active elements on the surface of the PP decorative material, which aids in the dissemination, adsorption, and adhesion of waterborne paints on the surface [43]. In recent years, the cold atmospheric pressure plasma jet (CAPPJ) has gotten a lot of attention for materials processing applications including surface alteration and biomedical applications. The surface properties of polypropylene were modified using a cold atmospheric pressure plasma jet maintained in pure argon [44]. Thus the plasma modification on blends can be used to enhance filler-matrix interaction, wettability, as coating on surface and for introducing functionalities.

Plasma modification has been successfully employed to improve the interfacial adhesion between nonpolar PE powder and polar polyamide prepared via rotational molding [45]. PE powders first treated with plasma [46] to impart fuctional groups such as hydrauxyl, which interact with CONH groups present in the polyamide. Multilayer rotomolded treated PE and polyamide blends have been produced and compared their properties with untreated PE polymamide blends prepared in same manner. They found that improved joint strength is a result of chemical bonding and mechanical anchoring. In another work, plasma modified PE powder has been incorporated as filler in natural rubber matrix and compared the properties with samples with unmodified PE [47].

5 Plasma Modification in Polyolefin Composites

Being nonpolar in nature, polyolefine find difficulty to prepare composite with important fillers like cellulosic fibers, glass fibers etc. which are highly polar because of the lack in interfacial adhesion. Plasma modification of polyolefin surface found to be innovative method to enhace the reactivity of the polymer surface by introducing several functional groups on it. Consequently these polar fuctional groups allow possible interaction with OH groups present in cellulosic fibers and glass fibers.

Adhesion between glass fibers and plasma treated PE has been anlysed by Novacek and also compared it with that of industrially using chemical bonding agents [46]. Previously, research is focused mostly on the modification of inorganic fillers and fibers by themselves or combined with chemical agents to enhance the interfacial strength. But this work measure the adhesion properties of the low temperature plasma-modified PE powder onto glass sheet surfaces in comparison with the commonly used chemical modifiers MAH and silane, and the examination of the dependence of the adhesion to the glass on the plasma treatment time of PE. Adhesion and mechanical properties were studied by Universal testing machine and the interface was closely examined using SEM. It was found that the maximum mechanical properties has been shown by the sample in which good interfacial adhesion has been observed.

As a continuation of the previous work, glass fibers composites based on unmodified and plasma modified polyethylene matrixes were successfully manufactured via rotational moulding [48]. Plasma treatment of PE powder improves the mechanical properties of the composites produced using treated powder comparing to the composites produced using untreated powder. Tensile strength increased by 10% as the fiber content increased up to 10 wt.%, Tensile modulus, increased as the fibers contents increased for all composites, composite prepared with treated powder showed even higher modulus.

The natural fibre composites gained major attention in this era because of the environmental concerns and their specific advantages over synthetic fibre composites. natural fibre composites there is usually limited interfacial bonding between the hydrophilic fibres and matrices which are commonly hydrophobic leading to limited mechanical performance. The used methods to enhance compatibility and interfacial adhesion in natural fibre composites are the use of compatibilizer and modifications of fibres or polymers. Plasma modified polyethylene (PE) was used as the matrix for coir fibre reinforced composites [49]. The use of compatibilizers, and chemical modification of fibre or polymer is a usual practice to improve the interfacial adhesion and to make the fibre and polymer matrix compatible [50–52]. Here, plasma modification of PE was introduced as a new method to improve the compatibility between hydrophobic PE and hydrophilic natural fiber. Plasma modified PE (PPE) and coir fibre composites have been manufactured using different preparation methods. The mechanical properties of the composites obtained from UTM were compared with unmodified PE/coir fibre composites. The newly prepared thermoplastic composites based on PPE and modified coir fibre showed lower water absorption due to better fiber/matrix interaction. We could observe different kinds of interfaces in the composites. In the plasma modified one, a good wetting of fibre by the matrix eliminated the possible microvoids. Finally, it is important to add that plasma modification of the polymer was found to be an effective technique to improve the compatibility between polyethylene and natural fibre.

Rotomoulding is an important pressureless processing method in the polymer industry which can produce stress free products. Use of composite material in rotomoulding is facing a lot of issues because of the filler aggregation and lack of good adhesion with polymer matrix. We successfully prepared plasma modified PE/natural fibre composites with improved properties [53]. We have created four different types of interfaces these include PE/natural fibre, PE/bleached natural fibre PPE/natural fibre, PPE/bleached natural fibre. Among all, PPE/bleached natural fibre showed the best balance of properties. SEM images given in Fig. 7, showed that a strong interfacial interaction between natural fibre and polymer matrix is possible with plasma modification of PE matrix. Plasma treatment modifies the surface of powder polymer to become more hydrophilic by imparting functional groups on it. This could improve the compatibility between the polymer matrix and natural fibre. Finally, it is important to add that plasma modification of PE coupled with mild bleaching of natural fibre is an excellent cost effect technique for the manufacture of rotomoulded natural fibre composites of PE having good mechanical properties and moisture resistance.

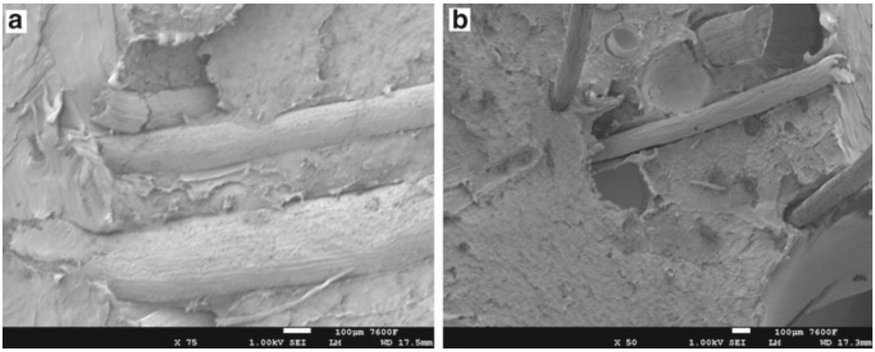


Fig. 7 SEM image of **a** PPE coir fiber composite and **b** untreated PE coir fiber composites

6 Applications of Plasma Modified Polyolefine Blends and Composites

The surface treated polyolefins and their blends and composites can be used in many fields such as biomedical, electrical, electronics, coatings, and so on. Environmental applications such as antifouling is important in water treatment. Plasma treatment can be utilized for introducing antifouling coatings on low density polyethylenes (LDPEs). Pandiyaraj and colleagues explained how they used atmospheric pressure non-thermal plasma (APNTP) assisted copolymerization with a mixture of acrylic acid and polyethylene to produce antifouling functional coatings on the surface of low density polyethylene (LDPE) films (ethylene glycol) [54]. Polyethylene is an important material in the fabrication of separators in lithium –ion based batteries. Many research works applied different types of plasmas to modify the surface of the films. Plasma modification is also meant to enhance the electrolyte retension and wettability, ionic conductivity and adhesion [55–60]. Similarly polypropylene membranes are also employed [61–63].

Plasma modified polylefine blends have been employed in biomedical applications such as in tissue engineering [64] Ultra-High-Molecular-Weight-Polyethylene (UHMWPE) is a promising material in the biomedical field [65]. Another important application of plasma modified polyolefin composites are in the field of antibacterials. PET/PP films were treated with ambient pressure plasma before being assembled with chitosan and various preservatives and used for antimicrobial food packaging [66]. For food packaging applications the barrier properties should be improved. This can also be done with plasma modification [67]. Most of the reported application of plasma modified polyolefins are for polyethylenes and polypropylene along with fillers for the above mentioned applications.

7 Conclusion

Polyolefine blend and composites have great importance many application. However the lower surface energy of polyolefin demand the use of chemical compatibilizing agents or chemical modifations to have enough interfacial adhesion, which is necessary for the required performance of blends and composites. The negative impact of using chemicals and solvents can be avoided by plasma modification of polymer, a new method to improve the interfacial adhesion. By this way polyethylene composites of natural fibers and glass fibers have been successfully manufactured which possess improved properties. Plasma modified polyolefin exhibited good bonding with other polymeric materials even with polyamide that are polar in nature.

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Spectroscopic Analysis of Plasma Modified Polymer Surfaces

Yuliia Onyshchenko, Ke Vin Chan, Nathalie De Geyter, and Rino Morent

Abstract The surface properties of polymers are essential for various industrial applications. Spectroscopy techniques like Fourier-transform infrared spectroscopy (FTIR), secondary mass spectrometry (SIMS), X-ray photoelectron spectroscopy (XPS), and nuclear magnetic resonance spectroscopy (NMR) are the most prominent for plasma modified polyolefin surface analysis. This book chapter provides a brief introduction to the principles of these spectroscopy methods, their uniqueness, usability, and limitations. The application of FTIR, SIMS, XPS, and NMR to the study of the surface physical and chemical properties of plasma modified polyolefins are described. Particular emphasis is devoted to the challenges arising from the chemical structure of polyolefins and handling the analysis.

1 Introduction

Polymeric materials have been used for a long time both in technology and industry, polymer films are now vital in various fields. Polyolefins like polyethylene (PE), polypropylene (PP), low-density polyethylene (LDPE), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), polyisobutylene (PIB) and polybutylene (PB) are prevalent in a wide array of applications: packaging, toys, automotive industry, biomedical and many others. The majority of these applications require the surface properties to be tailored with specific features. Nowadays multiple methods to modify the surface of polyolefins exist; however, plasma treatment is one of the best techniques since it leaves most of the bulk properties unaffected while impacting only the surface characteristics for a targeted application [1–4].

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Moreover, it is environmentally friendly, fast and efficient. Various plasma treatment types can be applied to modify different aspects of the surface. In general, plasma activation, etching, grafting and polymerization are the most recognizable and well-distinguished methods. With those mentioned above, any polymeric surface can undergo functionalization, cross-linking, etching or be coated with a layer of a plasma polymer [5, 6]. Since pristine polyolefins consist of only carbon and hydrogen, the incorporation of any new elements beside these two is noticeable on the modified surface. However, the same elements can be present in many combinations which complicates the determination process for the exact surface composition in terms of its functionality. For instance, the different oxygen-containing groups, introduced during surface oxidation processes, may be hard to distinguish during the analysis.

Before introducing various analytical techniques that are suitable for surface-sensitive analysis, an appropriate definition of the material surface should be provided. Theoretically, the surface of a given material is the outermost atomic layer facing the neighboring phase (gas, vacuum, liquid, solid). However, in practice, this theoretical definition is irrelevant since the complete termination of the surface extends into the solid beyond the outermost atomic layer. Thus, a solid surface defines as a layer of the order of 5–20 nm. After these few atomic layers, the effect of the surface termination decays until only bulk properties are observed. The analytical techniques are the surface-specific methods that can provide the information about the surface and can be split into two groups: (1) the ones operating only in the mentioned surface thickness context and (2) the ones typically used for the bulk analysis but applicable for surface analysis as well due to a good sensitivity or surface properties peculiarity.

The task of studying the surface properties is not as simple as it might seem. Firstly, a suitable analytical method among a wide variety should be chosen. This selection plays a significant role since every single technique is ideal for defining a specific surface property while leaving aside the other surface characteristics. Secondly, the sensitivity and the depth of analyzing area of a selected technique should match the degree and the depth of a surface modification to distinguish the surface changes from the bulk material. Some examples of the experimental techniques, together with types of sample surface information, are listed in Table 1. At this point, many methods will be deflected since they can cause degradation of the polymeric chain or some changes in the comparatively delicate surface of polymers and polyolefins in particular. Moreover, some analyzing techniques can induce a sample charging of a non-conductive substrate. Some other methods require high vacuum systems for exploitation which cannot bear the release of the volatile components from the analyzed samples. The possibility of the inspected substrate contamination or its surface properties being altered due to uncontrollable factors (for instance, exposure to the air or high chain mobility of the polymers) should also be considered. And last but not least, the interpretation of the obtained results should be in agreement with the method used to obtain it. The limitations of each specific instrument may lead to insufficient information regarding the change in the surface properties or cause misinterpretation of the results. In this case, it is advisable to apply a few analytical methods when analyzing a modified surface to help explain the results

Table 1 Some of the surface analysis techniques for polymer surface and interfacial study

Technique	Acronym	Outcome
Contact angle	CA	• Surface wettability
Optical microscopy	OM	• Surface image
Scanning electron microscopy	SEM	• Surface morphology and topography • Surface image
Transmission electron microscopy	TEM	• Cross-section view • Two-dimensional profile
Atomic force microscopy	AFM	• Cross-sectional view • Surface topography • Molecular imaging
Scanning tunneling microscopy	STM	• Surface topography • Molecular imaging
Static secondary ion mass spectroscopy	SSIMS	• Surface composition
Dynamic secondary ion mass spectroscopy	DSIMS	• Composition-depth profile
X-ray photoelectron spectroscopy	XPS (ESCA)	• Surface composition • Composition vs depth profile
Near-edge X-ray absorption fine structure	NEXAFS	• Surface composition • Group orientation
Photoemission electron microscopy	PEEM	• Surface composition • Group orientation
Infra-red attenuated total reflection	IR-ATR	• Surface vibrational spectrum
Ellipsometry	ELLI	• Film thickness • Refractive index profile
Auger electron spectroscopy	AES	• Surface composition • Compositional topography

correctly. Taking into account the complexity of the surface properties interpretation, the number of surface characterization techniques that can be used for plasma modified polymer surface analysis continues to grow [7–14]. Moreover, well-known long-time techniques get adapted and enhanced to become beneficial for analyzing delicate polymeric materials.

When limiting only to a surface analysis, which is one of the most important areas in the case of applying plasma for polymer modification, a few categories can be defined among the possible examining methods. The lateral and depth resolution are more important when compared to the other possible parameters and capabilities of different surface interpretation techniques. These parameters are fixed for each analytical method and restricted by (i) the type and the energy of particles that are

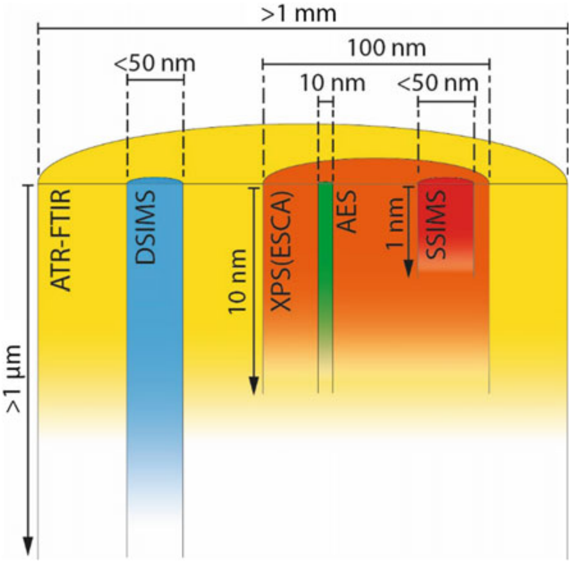


Fig. 1 A sketch diagram that demonstrates the typical values of the depth and the spatial resolution of some surface analysis techniques

used as a source; (ii) the incident beam diameter; and (iii) the escape depth of the exiting beam. Both of these resolutions should be kept in mind for each specific technique, especially if the area of the plasma-treated polymer is small and well-defined or when a good knowledge about the thickness and properties of thin plasma polymerized coatings on polyolefins is required. The depth and lateral resolution of some standard analytical methods are shown in Fig. 1.

This chapter focuses only on a single surface analysis method: spectroscopy. The other methods of surface analysis will be described in the other chapters of this book. FTIR, NMR, and solid-state NMR, XPS, SIMS and nanoSIMS will be discussed in the details in this part of the book. These analytical techniques are commonly used for identifying chemical functionalities of the polymeric surfaces or thin films. Therefore, the discussion will focus on the chemical properties, although there will be some links with physical and microanalytical outcomes when relevant.

This chapter is divided into two parts. The first part describes the working principles of the mentioned techniques, their limitations and the possible usage. Polyolefins represent one class of polymers, and thus most of the techniques can be discussed in relation with a broad range of polymers and only when a particular behavior is observed in the case of polyolefins it will be mentioned. The second part of this chapter includes examples of applying these techniques and the output results for the analysis of plasma modified polyolefins.

2 Working Principles of Various Spectroscopic Techniques

Good knowledge of the basic principles of each technique is crucial to understand and decide which of them is applicable in a particular situation. Moreover, this section provides the information on the type of data that can be obtained, limitations and advantages of each specific analysis. A universal principle of all spectroscopic techniques is the usage of two beams: one travelling towards the substrate under the study, and the other from it. An incident beam may consist of ions, electrons, or photons. The type of particles and their energy determines the limitations of depth they can reach inside the surface and also how this beam interacts with the sample. After the interaction with the surface area, a second beam is formed carrying information about its composition. This beam is then detected and analyzed by a spectrometer. The diversity of spectroscopic methods for surface analysis appears due to the different types of particles and the energy of the incident beam.

2.1 FTIR

Amongst the surface analysis instrumentations discussed in this chapter, FTIR spectroscopy is one of the most affordable and straightforward in operation. Fast measurements at ambient air without the need for extra sample preparation which is required for devices with high vacuum promote the popularity of this analytical method. The FTIR operation is simple in general and becomes slightly more sophisticated only with the usage of liquid nitrogen which is needed to chill the MCT (mercury cadmium telluride) infrared detector to improve the sensitivity. The infrared spectroscopy method provides information on the vibrational spectrum of the sample, which allows identification of the organic (and in some cases inorganic) materials. In the case of polymers, FTIR is a very indispensable technique since it assists chemical description and molecular structure determination.

The main working principles of FTIR are presented in Fig. 2. In general, FTIR

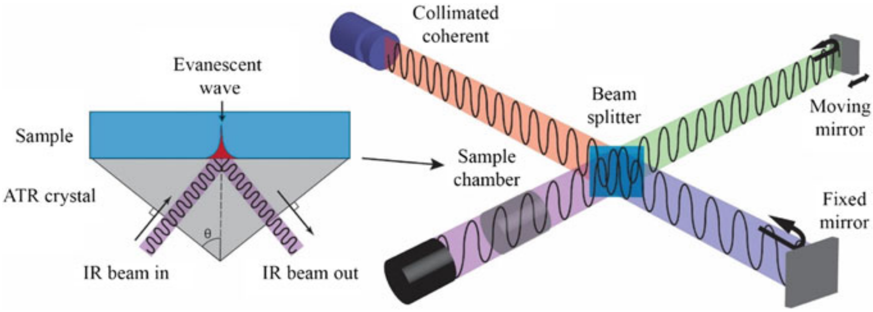


Fig. 2 Working principles of ATR-FTIR

spectrometer consists of a source, that generates light across the spectrum of interest, an interferometer, a cell with sample and a detector. At first, the light source sends a broad range of IR radiation to the Michelson interferometer. Inside the interferometer, the light passes through a beam splitter which divides and sends the incident light onto two orthogonal directions. Both beams meet again at the splitter after one is reflected from the stationary mirror, and the other one from the moving mirror, as shown in Fig. 2. The total path length of the second beam is varied by moving the corresponding mirror. Thus, when the two beams recombine again at the beam splitter, constructive and destructive interference (interferogram) occurs due to the difference in their path lengths. The resultant beam passes through the sample and, afterwards, is collected with the detector. The measured signal is the intensity of transmitted light as a function of the wavelength (position of the movable mirror). Fourier transformations are used to convert the obtained interferograms into a single-beam infrared spectrum. Usually, a few cycles are used to produce a final spectrum which increases the signal to noise ratio. The outcome (FTIR spectrum) is a plot of intensity versus wavenumber (cm^{-1}) which is the reciprocal of the wavelength. The result can be represented as a percentage of light transmitted or absorbed by a sample. Examples of FTIR spectra for PE and PP are presented in Fig. 3. In the case of polyolefins, the spectra look relatively simple and have a lot of similarities since they all contain C–H starching and C–H bending deformation regions.

One of the most common methods in IR spectrometry is the usage of multiple internal reflections or an attenuated total reflectance (ATR). This upgrade is often used to investigate the impact of plasma modification on the polyolefin materials. The infrared light passes through the crystal (KRS-5, Ge, ZnSe, etc.) and interacts with the sample surface that is in intimate contact with the internal reflection element, as shown in Fig. 2. The geometry of the IR transparent ATR crystal is made in such a way that the infrared light will experience at least one total internal reflection event where the evanescent wave forms.

The depth penetration of the IR radiation is assumed to be the distance at which the light decays to 1/e of its electric field amplitude at the interface. Accordingly, the penetration depth can be defined as following:

$$d(p) = \lambda / \left[2\pi n_1 \left(\sin^2\phi - n_{21}^2 \right)^{1/2} \right] \tag{1}$$

where λ is the wavelength, ϕ is the angle of incident, n_1 is the refractive index of the denser material (crystal), and n_{21} is the ratio n_2/n_{11} (n_2 is the refractive index of the sample). The incident angle must be higher than the critical value defined from the total refraction phenomena when an electromagnetic wave is incident at the interface between two different media:

$$\phi_c = \arcsin(n_{21}) \tag{2}$$

As can be observed from Eq. (1), the penetration depth linearly depends on the wavelength of IR radiation. This relation means that a longer wavelength penetrates

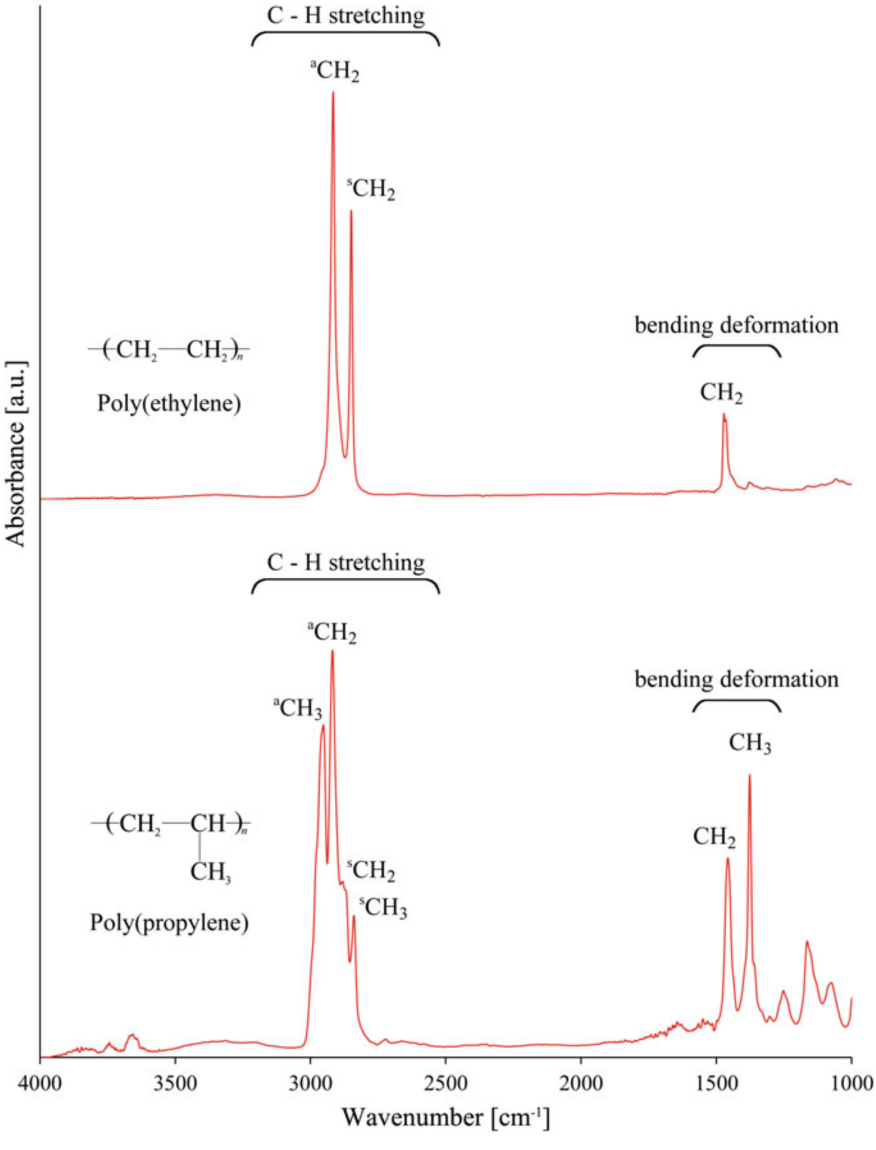


Fig. 3 Examples of FTIR spectra for PE and PP. “a” and “s” notations stand for asymmetric and symmetric stretching respectively

deeper and produces the enhanced absorption bands in comparison to the bands at lower wavelengths. The range of penetration depth varies from ~0.2 μm to more than 5 μm. Thus, the results obtained with FTIR spectrometry contain a strong signal from a material’s bulk, and it may be a challenge to identify changes derived only at the surface. However, in the case of polyolefins, it is sufficient to notice the impact of plasma treatment on the surface. For instance, new functional groups that are introduced on the surface upon the plasma modification have a strong absorption band in the FTIR spectrum due to the decrease of the signal from polymer itself after the macromolecular chain was broken during exposure to plasma.

The infrared radiation is chosen due to a large number of matches between the wavelength (frequency) of the IR spectrum and the specific vibrational frequency of the molecule present in the analyzed sample layer. When such an event occurs, the molecule structure will absorb the radiation at the resonance frequency and make a transition from an at-rest to an excited vibrational state. The amount (intensity) of absorbed radiation is proportional to the number of molecules with matching vibrational frequency while its wavelengths are characteristic of molecular structure. Therefore, FTIR can be considered a quantitative analysis. A broad spectrum of IR is needed to evaluate the functional groups of any given sample fully.

FTIR allows performing quantitative material identification as well as the quantitative concentration of the compounds. The latter process determines the concentrations accordingly to the surface area under the band that represents a specific compound after applying the required calibration. The rich database of IR spectra helps to interpret the FTIR spectra by comparing the obtained set of peaks with already known from the database or with spectra obtained from standard material. This comparison can also be used to identify the polymer and the various functional groups present in the sample under investigation. For example, absorption bands in the range of 4000–1500 cm^{-1} are typically due to the functional groups like –OH, C=O, N–H, CH_3 which can be often found on the plasma-treated polyolefins. Another broad region in wavenumber (1500–400 cm^{-1}) is known as the fingerprint region since well-defined absorption bands occur in this range due to intermolecular phenomena which highly specific to each material.

FTIR can also be used for depth profiles between 1 and 10 μm. As demonstrated with Eq. (1), the penetration depth depends on the IR wavelength and the incident angle at the total internal reflection. Typically for a single reflection ATR, the angle of incident is configured at 45°, which will result in a depth penetration of 2 μm–600 nm depending on the IR wavelength. Analysis at different depths can be performed by utilizing crystals made of various materials (different refractive indexes and IR transparent ranges) or with different geometry. The latter means the crystals with different angle θ, which is shown in Fig. 2. Despite the fact that FTIR is the least sensitive surface-specific technique among all discussed in this chapter, it is also least sensitive to surface contamination.

In conclusion it can be mentioned that FTIR:

- can identify the unknown material, molecules and functional groups;
- is capable of analyzing a highly insulating material;
- is capable of detecting the functional group concentration below 1%;
- can provide a chemical mapping of surface functionality with a lateral resolution around 10 μm;
- can analyze thick samples up to 10 mm;
- has a good signal to noise ratio;

- has a good database;
- possesses a good wavelength accuracy due to laser calibration.

2.2 SIMS and NanoSIMS

Secondary ion mass spectroscopy or SIMS has been utilized in many different fields of research such as astronomy, biology, chemistry, materials and semiconductors, etc. [15–18]. Furthermore, it has been used in the recent Rosetta comet space mission to study the composition of the cometary dust in 2014 [19, 20]. A broad range of SIMS applications induced the development of many accessories to extract more information from the sample. Depending on the sample type and its properties, the analysis can be performed without any prior preparation. The only requirement for the samples is that they should be compatible with an ultra-high vacuum. SIMS is typically used to qualitatively study the elements, isotopes and molecular species of the material. This analyzing technique is present in two variations: non-destructive and destructive.

Generally, a SIMS instrumentation consists of two core components: the focused primary ion beam and the mass analyzer. During measurements, the sample surface is bombarded with primary ions of the energy of 0.3–10 keV, as shown in Fig. 4. Upon collision between the primary ions and the surface, two possible events can happen: either the surface atoms elastically scatter the incident ion, or it can penetrate into the surface. The first scenario leads to a flux of reflected primary ions with energies that depend on the mass of the surface atoms that participated in the scattering process and thus containing the information about the sample surface. The second scenario results in the desorption of atoms and molecules in either neutral or positive and negative ionized states. Only a small fraction (<1%) of all the particles are ionized components from the bombardment event, which are the secondary ions. These ions

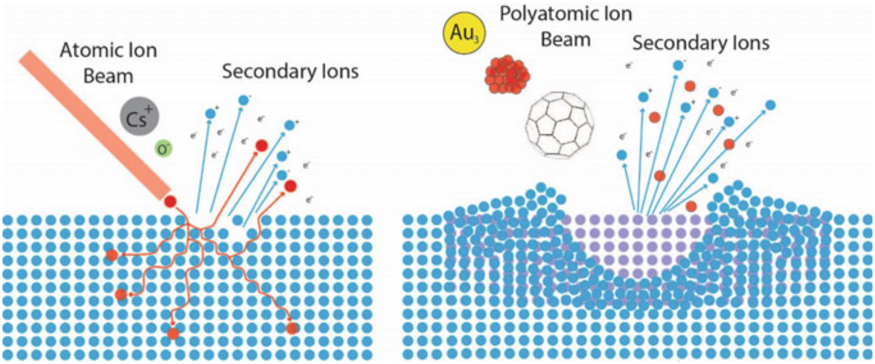


Fig. 4 Schematic illustration of the SIMS processes for different types of the ion beams

are guided into the mass analyzer to be sorted, detected and counted according to the mass to charge ratio.

Depending on the intensity of the primary ion beam, it can be categorized into either static or dynamic-SIMS. In static-SIMS, the primary ion beam incident on the surface is small ($<10^{-9}$ A/cm^2) which results in the secondary ions from the top layers of the sample without substantial damage. Therefore, this is usually considered to be a non-destructive mode, even though after several hours of measurements, a monolayer is sputtered, yet, the integrity of the surface maintains through the time needed for analysis. Conversely, during dynamic-SIMS, high primary ion currents ($>10^{-6}$ A/cm^2) cause an intensive production of secondary ions and surface erosion. This process exposes the materials below the sputtered layers to the primary ion beam. Thus, over time, a depth profile of the sample can be obtained, which allows investigating the depth penetration of plasma treatment into the polyolefins instead of only a surface analysis.

Both positive and negative ions can be used for mass analysis. Despite the higher number of the positive-ion spectra, negative-ion spectra are particularly useful for detecting chemical groups with electronegative elements, e.g. oxygen or halogens. A spectrum is plotted in terms of signal intensity (counts per second) as a function of atomic mass units (amu). Figure 5 shows positive ion mass spectra collected from the surface of pristine LDPE and PP. These spectra look similar since both polymers belong to the same family of polyolefins; however, the fragmentation pattern is typical for each polymer, and this information can be used as a sort of fingerprint for material identification. However, it should be emphasized that SIMS can be used for quantitative analysis only in some particular cases. The mechanisms of the formation and emission of secondary ions are not fully established, which increase the difficulty of quantitative analysis.

A high vacuum condition is required for SIMS to be operational during analysis to ensure that the primary and secondary ions can reach its target without colliding with the background gases. Many different sources can be used to produce the primary ion beam. Generally, all of them can be divided into two categories: either atomic or polyatomic. Such a division is essential due to the difference in the interaction between the sample surface and the primary ion beam. For atomic ion beams, all the kinetic energy is contained in a single atom. Due to the small size of the ion, very little material is sputtered upon impact. Furthermore, the ions continue to travel into the bulk sample while causing significant disruption to the molecular structure deeper in the material. On the other hand, due to the big size, polyatomic ion beam with the same kinetic energy as the atomic ion one has a smaller impact upon collision since the energy is distributed equally among the atoms on the sample surface area. Due to this soft sputtering, the disruption to the molecular structure of the bulk is also minimal. There exist ion guns based on noble gases (Ne, Ar, Xe) as well as liquid metal guns (Ga, In, Cs, Au, Bi). The latter provides better resolution while using a different type of ions for analyzing high- and low-mass molecules and elements. For example, high-mass areas (mainly molecules) are better examined by Au and Bi ions while for low-mass areas (mostly atoms) Ga ions are more applicable. However, it should be kept in mind that the primary ion beam can cause charging of the insulating

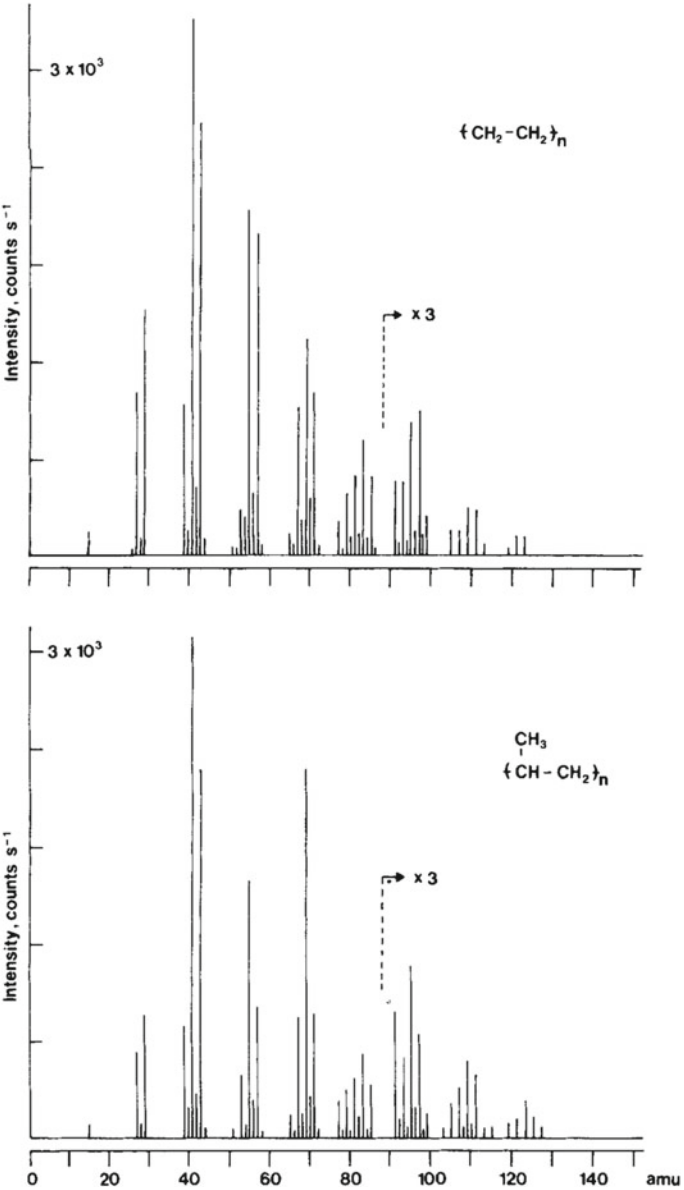


Fig. 5 Examples of positive ion mass spectra of LDPE and PP [23]

materials like polymers. This problem can lead to a signal loss, change in the relative peak intensity and disturbance in sensitivity. An electron gun (flood gun) can be used to overcome such problem and neutralize the positive charge induced on the material. This additional element floods the sample with the low energy electrons to achieve charge elimination but at the same time to avoid influence on the obtained results.

For polyolefin dynamic-SIMS analysis, the polyatomic ion beam is generally preferable because the large sputter volume leads to the secondary ion yield being significantly higher compared to the atomic ion beams which improve the signal to noise ratio. Sulphur hexafluoride (SF_6) and fullerene (C_{60}) molecules are the earliest to be adopted for use as the primary ion beam. However, the current state of the art ion gun technology is capable of forming ion clusters using Ar or Au, which yield superior results compared to molecules because it does not leave background chemical contamination during analysis. One of the latest cluster sources uses an Ar_{2500}^+ ion beam which has the most versatile capability for organic films depth-profiling [21, 22].

As mentioned above, only a small fraction of all the particles are secondary ions which can be detected in SIMS. Therefore, a mass spectrometer with high sensitivity is required for a static SIMS analysis. Various analyzers have been used in static SIMS such as magnetic and electrostatic sector analyzers which are more effective for very heavy species but with reduced transmission and finishing quadrupole mass analyzers which are relatively cheap and easy to use. However, recently one of the most popular is a time-of-flight (ToF) analyzer due to the parallel detection method and high transmission of 20–30% in comparison to a fraction of 1% for the other analyzers. Besides the fast data averaging, ToF–SIMS features a high mass resolution ($M/\Delta M$). The working principle of such an analyzer is simple: the secondary ions are accelerated into the tube, and by flying through it, they arrive at the detector at a different time depending on the mass.

For the nanoSIMS analysis, the spot size of the primary ion beam is typically ~ 100 nm. This means the polyatomic ion beam cannot be used here because of a spot size ≈200–500 nm. Instead, a reactive atomic ion beam of O^- and Cs^+ is used as depictured in Fig. 4. The selection of these two primary ions is determined by the promotion of positive secondary ions in the case of O^- and negative secondary ions during Cs^+ bombardment [24, 25]. Another variation of nanoSIMS is using a triple focusing time-of-flight (TRIFT) mass analyzer. Such a spectrometer consists of three 90º sector electrostatic analyzers. This design successfully eliminates metastable ions and increase the detection sensitivity. Moreover, the obtained spectra have a very low background signal. The nanoSIMS with TRIFT analyzer possess the following advantages: broad energy bandpass, significant angular acceptance, excellent resolution (depth-of-field). As a result, high mass resolution, together with high spatial resolution, can be obtained with described nanoSIMS equipment [26].

SIMS facilitates the acquisition of a spectrum from a small area of the analyzed substrate. A highly focused primary ion beam scans across a raster pattern over the sample surface. The resultant secondary ions are collected and analyzed at each point on a whole lateral zone and produced a grid pattern over the selected surface area. Usually, it is a 256 × 256 array where each pixel represents a high-resolution mass spectrum from the area of interest on the sample. This result can be analyzed pixel by pixel and provide detailed information on the elemental composition. Alternatively, by selecting only one mass peak of interest, the distribution of this element across all of the scanned area can be demonstrated [27]. This type of surface analysis is a compelling method which allows observing plasma-treated patterns on the polyolefins [28]. Uniquely when combining with nanoSIMS, this technique provides the opportunity to obtain molecular imaging and microanalysis with a high resolution.

In conclusion, SIMS is a very powerful technique for surfaces analysis with the multiple advantages. In particular it.

- can identify all possible elements, isotopes and molecules present on the surface;
- is capable of analyzing a highly insulating material;
- is suitable for surface analysis with a good sensitivity up to 0.5 nm depth;
- provides chemical mapping of elements or molecules present on the surface with an excellent lateral resolution down to 40 nm;
- has a good detection limit up to ppm-ppb (parts per million/billion);
- possesses structural information about the analyzed material;
- can analyze samples without causing damage;
- has a growing database.

2.3 XPS

X-ray photoelectron spectroscopy (XPS) is a perfect technique for investigating plasma-induced chemistry at polymer surfaces. Semi-quantitative information regarding the elemental composition and chemical bonding state obtained from samples surface (<10 nm) are the main reasons for the supremacy of this technique. Moreover, XPS, in combination with sputtering or angular-dependent XPS measurements, gives access to obtain a compositional depth profile of the plasma modified region. It is widely used in the study of surface science as a qualitative and quantitative technique with a long history of usage and well-developed data interpretation. The analysis can be performed immediately after the plasma treatment without any prior sample preparation, with the only prerequisite being that the sample should be able to maintain its stable solid physical state in a vacuum environment.

As mentioned in the name, XPS utilizes an X-ray beam on the sample, which causes the emission of photoelectrons with a range of kinetic energy. X-rays are generated through the bombardment of a metallic anode with high-energy electrons. The anode material is accountable for the energy of the emitted X-rays while the energy and electron current striking the anode tune the beam intensity. The X-ray source can produce either non-monochromatic or monochromatic radiation. The monochromatic sources are more in use nowadays due to better sensitivity. It is also essential to use such a source for polymer analysis since the radiation damage is minimal and the resolution of the obtained spectra allows us to determine the plasma-induced changes on the modified samples. The X-ray radiation (photons) interacts with the core-level electrons of an atom on the analyzed surface. The kinetic energy,

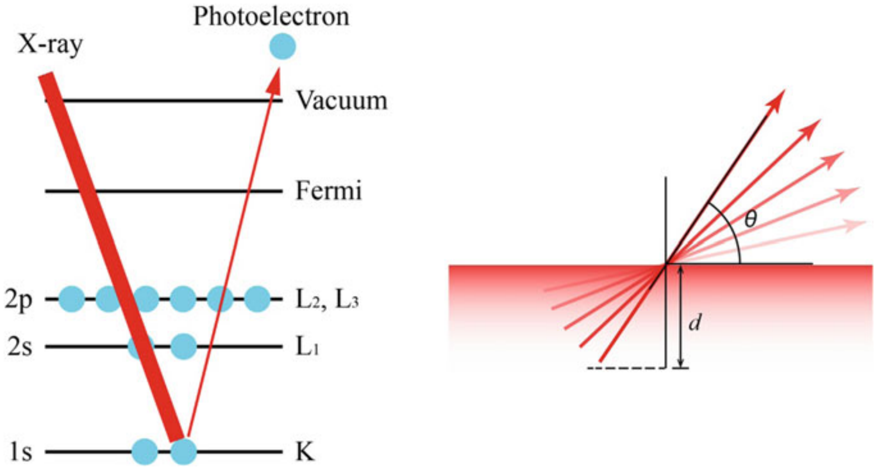


Fig. 6 Schematic representation of XPS working principles and angle-resolved depth-profiling

transferred to the electron from the photon, is sufficient for it to escape the surface of the sample, as demonstrated in Fig. 6. Such an electron is referred to as photoelectron. However, in order for the emitted photoelectron to reach the detector, an ultra-high ($<10^{-5}$ Pa) vacuum environment is required for the analysis. At these pressures, the mean free path of the particles is more than 1 km, which means the photoelectron will not experience any collisions as it travels to the detector. A high working pressure during the XPS measurements can be detrimental to the quality of the results.

A hemispherical analyzer is used to detect the number of photoelectrons at corresponding kinetic energies E_k. The binding energy of the core-level electron (E_b) can be calculated using the following equation:

$$E_b = hv - (E_k + \mathbf{\Phi}) \tag{3}$$

where hv is the X-ray photon energy and $\mathbf{\Phi}$ is the work function of the spectrometer (energy needed for an electron to transition from Fermi level to vacuum) which is about 4–5 eV. For the most commonly used monochromatic X-ray sources, the energy of photons is 1486.6 eV for Al K_α and 1253.6 eV for Mg K_α [29, 30]. The "missing" photoelectrons from the analyzed surface can cause the accumulation of a positive charge. This problem can be overcome by replenishing the electrons to the surface from the external source. In the case of polymers, which are insulators, surface charging will occur during the measurements and thus should be taken into account during the spectra analysis by charge-correction using internal references. For instance, for the polymers like polyolefins, C 1 s of aliphatic carbon is shifted to a position of 285.0 eV [31]. Each element in the periodic table has a specific electronic configuration which allows identifying the elemental composition of the analyzed sample by utilizing XPS. Moreover, the binding energy of the photoelectrons also

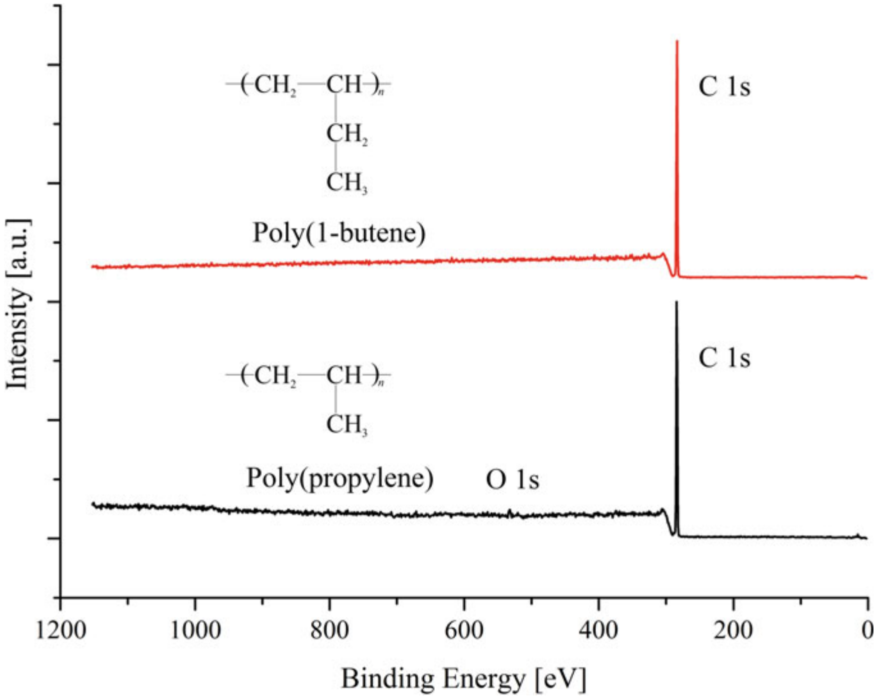


Fig. 7 Examples of XPS survey spectra of pristine PB and PP. The presence of O 1 s in PP spectrum is due to a low-level oxidation

depends on the electronic environment of the atom. In other words, when the atom is bonded to another atom, it can be detected through the changes in the measured binding energy, which is known as a chemical shift. This data can provide information regarding the chemical structure of the polymer, e.g. polymer oxidation.

Generally, an XPS spectrum is plotted with the number of electrons detected (Y-axis) to its corresponding binding energy (X-axis). The spectrum peak positions are a unique fingerprint for each element. Furthermore, the intensity of these peaks can then be used to determine the atomic concentrations by applying the sensitivity factors that are well known for each XPS device or can be determined experimentally. This allows performing quantitative analysis without any standards that, otherwise, might be required for other methods. Overlapping of peaks from different elements rarely occurs, however in this case valence band spectra help yield a definitive analysis, especially in the case of polyolefins. The latter mentioned spectra are useful for the molecular structure analysis, which is sometimes challenging to perform on core-level spectra. An example of an HDPE survey spectrum is shown in Fig. 7. As expected, only a single peak due to electrons originated from the C 1 s level is detected on the untreated surface of this polyolefin polymer. There is no sign of hydrogen on the spectrum since this element is the only one that cannot be detected with the XPS technique.

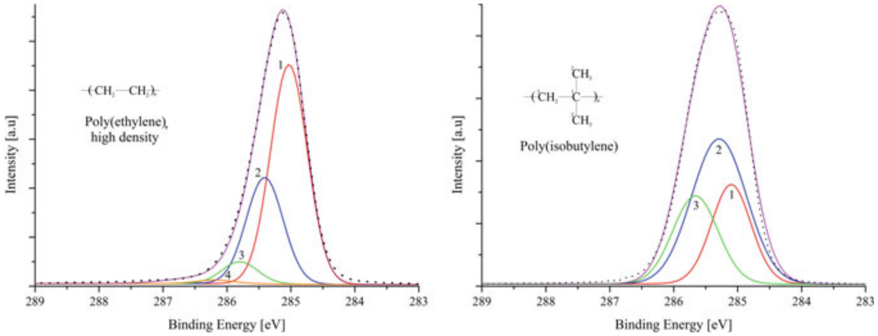


Fig. 8 High-resolution C1s spectra from pristine HDPE and PIB. Components 1–4 of HDPE curve fitting represent vibrational fine structure

As mentioned above, XPS is also capable of extracting information about the chemical states of the element. This is due to the electron bond polarization between neighboring atoms, which will cause small shifts in the resulting binding energy. The mentioned change in binding energy can be measured by performing high-resolution XPS analysis. The obtained spectrum undergoes the process of peak fitting, which qualitatively determine the component concentrations. One of the most important high-resolution peaks for polymers is C 1 s, especially for polyolefins since it is the main element of the polymeric chain. Only after plasma surface modification, other elements can be detected on the surface of polyolefins and thus new chemical shifts will appear in the individual spectrum of C 1 s. For instance, complimentary analysis of high-resolution O 1 s peak can be performed when the polyolefin surface is oxidized for additional confirmation and validation of various oxygen functional groups present on the plasma modified surface. Figure 8 shows examples of high-resolution C 1 s spectra for PP and LDPE with their deconvolutions.

The surface sensitivity of the XPS technique depends on the depth from which the photoelectrons can escape from the material even though X-ray radiation can penetrate deeply into a sample. The sampling depth can be elucidated by the following equation:

$$d = 3\lambda \sin\theta \tag{4}$$

where λ is the attenuation length obtained from kinetic energy of the photoelectron and θ is the take-off angle which is measured between the sample surface and the analyzer. Thus, by varying the observation angle mentioned in the equation above, it is possible to obtain the chemical information from different depths, as illustrated in Fig. 8. Angular-dependent XPS measurements can be used to nondestructively depth-profile the top region of the plasma modified polymers providing information on the elemental composition and chemical states as depth profile reconstruction [32, 33]. Typically, angle dependent XPS analysis at several take-off angles will provide a chemical depth profile up to 10 nm. This maximum depth is estimated based on the photoelectron's kinetic energy which is generally in the range of 200–1400 eV due to the energy limitation of X-ray sources that operate with $h\nu$ <1500 eV. Hence, for depth profiling deeper than 10 nm, a destructive approach is required when the top surface layers are gradually removed via sputtering to expose the material underneath. To accomplish this, the cluster ion sputtering is used, which is similar to that of dynamic-SIMS. The XPS analysis is performed after each sputtering step. The thickness of the sputtered layer can be controlled by adjusting the energy of the used ions, the surface area of sputtering and the type of the ions. Formerly, the monoatomic ion sources have been used for depth profiling and surface contamination removal. Though such sputtering has limitations for utilizing with soft materials like polymers, for instance, this process will induce damage to the material and change the chemistry of the polymer due to ion bombardment. Thus, new gas cluster ion sources are used for depth profiling of sensitive materials since they overcome the mentioned limitations. The most broadly available cluster beam is C_{60} which is basically 60 carbon atoms bonded together in one aggregation. The depth profile is then generated by alternating the sputtering cycles with XPS analysis [34, 35].

A good sensitivity and energy resolution of modern XPS apparatus allow performing the analysis on small areas (<100 μm). Thus, similar to SIMS, it is possible to perform chemical imaging with XPS as well. Such type of measurements reveals the distribution of the elements across a surface and demonstrates the areas with various chemical composition or functionality [36, 37]. The information obtained from the XPS imaging also helps to determine the limits of the contamination and estimate the variations in ultra-thin coating thickness. Mapping (serial acquisition) is a common approach to performing XPS imaging. The main idea behind it is the collection of the spectra from each small area of a defined rectangular array. In this way the size of XPS image is limited only to the equipment technical limitations and each "pixel" is obtained with the same parameters: X-ray beam energy, resolution, transition function of the lens.

Summarizing above mentioned information, XPS technique:

- can identify elements and chemical states present on the surface;
- is capable of analyzing a highly insulating material;
- is suitable for surface analysis with a sensitivity in the range of 1–10 nm in depth;
- provides elemental imaging and chemical states mapping (maximum resolution < 3 μm);
- allows quantitative analysis of the samples;
- has a rich database;
- does not cause damage to the samples during measurements (except sputtering);
- has a good detection limit 0.1% to 1%.

2.4 NMR and Solid-State NMR

Nuclear Magnetic Resonance (NMR) is a specific spectroscopic technique that analyzes the nuclei (Nuclear) behavior using a strong magnet (Magnetic) by analyzing the transitions between nuclear energy levels (Resonance) under electromagnetic radiation. This is one of the useful methods to deduce the structure of the molecules and the presence of the functional groups. In organic chemistry and biochemistry, NMR is used to study the chemical state, dynamics, interaction and environment of the molecules. The size of the molecules that can be studied can vary from small organic molecules, biological molecules of middle size to macromolecules like proteins and nucleic acids.

NMR is based on the physical phenomenon of the resonance transition between the magnetic quantified energy levels of the atomic nuclei in an external magnetic field that can occur due to electromagnetic radiation with a specific frequency. The resultant spectrum contains peaks at certain positions with a distinctive fine structure and particular intensity. This information facilitates the examination of the molecular structure qualitatively.

For the sake of better understanding of the NMR working principles, a short explanation regarding a nuclear spin and nuclear energy levels in a magnetic field is provided below. Nuclei consist of the nucleons (protons and neutrons) which are comprised of subatomic particles: quarks and gluons. Each nucleon has the intrinsic quantum property of a spin and an intrinsic angular momentum. Similar to an electron, the spin of a nucleus can be described using the following quantum numbers: I for the spin and m for the spin in a magnetic field. The nuclei consisting of an even number of protons and neutrons have a zero overall spin while the nuclei with an odd number of nucleons have a non-zero spin. For the molecules with a non-zero spin, a magnetic moment μ can be defined as follows:

$$\mu = \gamma I \tag{5}$$

where γ is the gyromagnetic ratio [MHz/T], which is unique for each nucleus and represents a proportionality constant between the magnetic dipole moment and the angular momentum. The examples of nuclei with non-zero spin include ^{1}H, ^{2}H, ^{13}C, ^{31}P, ^{27}Al, ^{23}Na. ^{17}O, etc. These compounds can be used for NMR analysis. Generally, the bulk magnetization of a sample is equal to zero due to the random orientation of spins. However, in the external magnetic field, all spins align in parallel to it, resulting in a non-zero bulk magnetization. These two statements are demonstrated in the first two panels of Fig. 9. Spin orientation can be flipped after applying an exact quantum of energy that is matching the difference between the energy levels the number of which is predicted by m as $2m + 1$. For instance, for a nucleus with $1/2$ spin there are only two energy levels, the low energy level with the spins aligned in the direction of the external magnetic field B_0, and the high energy level occupied by the spins aligned against B_0. Thus, for each of the levels the energy can be defined as following:

$$E = -m\hbar\gamma B_0 \tag{6}$$

which leads to the energy difference between the energy levels:

$$\Delta E = \hbar\gamma B_0 \tag{7}$$

where $\hbar$ is the Planks constant. The last formula demonstrates the significance of the external magnetic field as it is directly responsible for the energy level difference. Usually, the magnetic field is in the range 1–20 T for most of the NMR equipment. The measurement requires a spin flip between the energy levels. When the energy difference between these levels corresponds to the energy of the electromagnetic radiation, the event of spin flipping occurs, as shown in the third panel of Fig. 9. Taking into account that γ is the order of 10^7, the required frequency of electromagnetic radiation is in the range of $10^8 - 10^9$ Hz. By defining the frequencies of the RF radiation that was absorbed during the transition between the lower energy level to the higher energy level, or the energy of the radiation during the returning to equilibrium state event (relaxation), the NMR spectrum is formed. Relaxation is known as a phenomenon of nuclei returning to their thermodynamical equilibrium state after being excited to higher energy levels. This process is followed by releasing the energy that was absorbed during the excitation event, as shown on the last panel in Fig. 9. The most common types of relaxation are spin–lattice (τ_1) and spin–spin relaxation (τ_2). The spin–lattice relaxation (or longitudinal relaxation) denoted as τ_1, is the time needed for the 37% of bulk magnetization (average spin) to recover and align along the axis of the external magnetic field from the perpendicular plane. In polymers, since the motion between the molecules is limited, the spin–lattice relaxation time is big. In the case of spin–spin relaxation, τ_2 is the time needed for the spins to lose coherence with one another, and usually $\tau_2 \leq \tau_1$.

As already stated, NMR is capable of defining the chemical shifts and the molecule structure. The structural assignment is possible due to the nuclear shielding that can be observed with this technique. The effective magnetic field at the nuclei can be affected by the electron shielding due to the chemical environment, which in turn can be noticed as the change in the resonant frequency of the energy transition. The secondary field caused by the charges around the selected nucleus shield it from the external magnetic field, which should be increased now to achieve a resonance with the RF radiation. In other words, a higher resonance frequency is needed for the nucleus with the higher electronegative environment. The change in the magnetic field is tiny, and this is the reason for the original x-axis units when plotting NMR spectrum: usually, units of parts per million (ppm) are used which express a small increment in the magnetic field due to the shielding. The y-axis is represented as the intensity of the signal. Another possibility to avoid using the resonance frequency as a parameter for comparison is to utilize tetramethylsilane (TMS) as the proton reference frequency or any other appropriate material [38, 39]. Examples of ^{1}H NMR spectra of LDPE and HDPE are demonstrated in Fig. 10, where the polymers

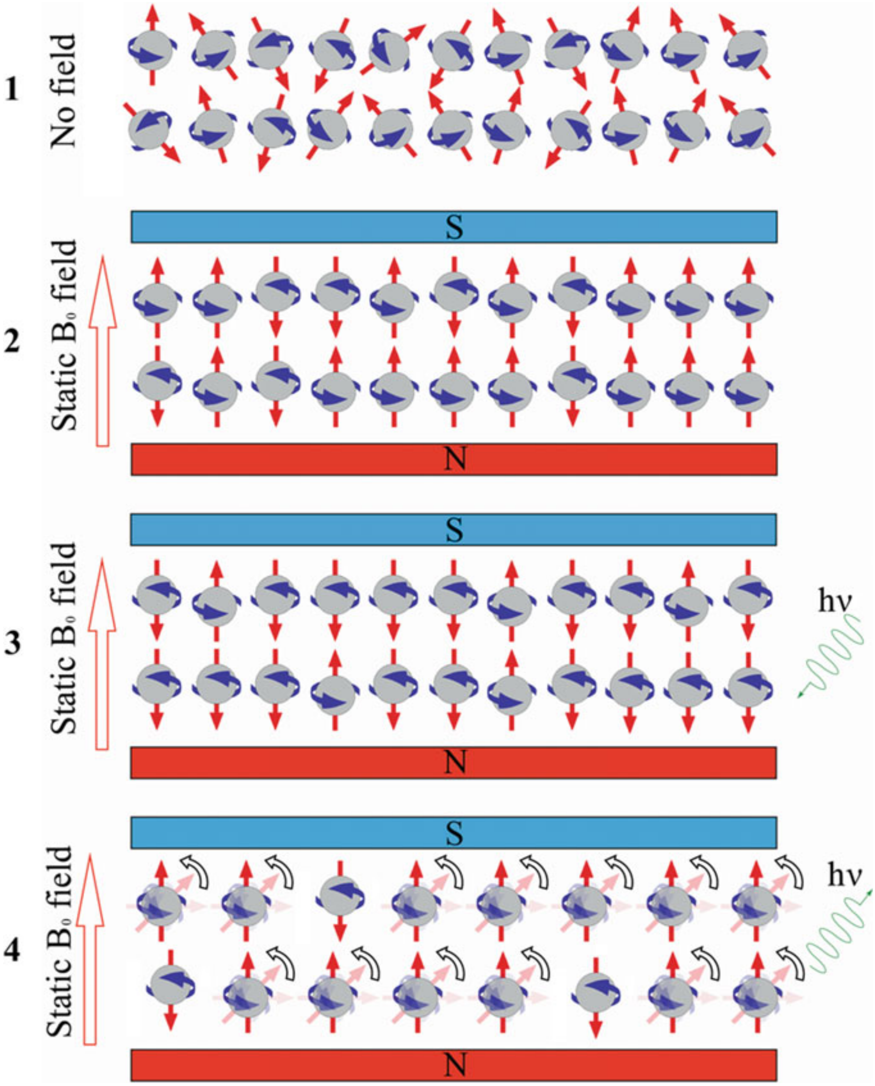


Fig. 9 Schematic representation of working principles of NMR

were dissolved in deuterated chloroform of 0.02 g/2 ml (w/v), and solution of devoid of dextrose and sodium citrate was used as a control sample.

One of the methods to obtain the NMR spectrum is monitoring the variation of the voltage induced by the precision of the magnetic moment in the RF-coil-receiver. As the magnetic moment realigns with the direction of the permanent magnetic field, the amplitude of the voltage in the RF-coil-receiver decreases exponentially; this behavior is known as the free induction decay (FID). Similar to FTIR, a Fourier

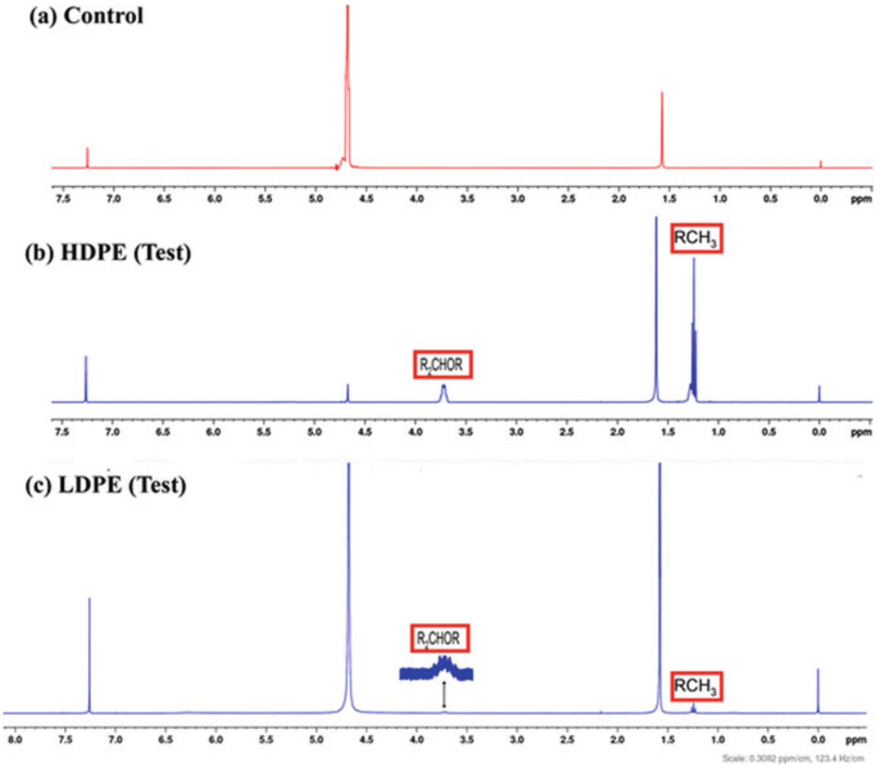


Fig. 10 Examples of 1H NMR spectra of **a** the control sample, **b** HDPE and c LDPE test samples [38]

transform is then applied to this time-domain function of the NMR signal to obtain the typical NMR spectra. Although the FID spectrum has a weak signal to noise ratio, it can be significantly improved by averaging the repeated scan cycles. Although more than 10 scan repetitions are needed for a high-quality spectrum during the usual ^{1}H NMR acquisition, it requires only approximately 15 min to complete the analysis.

^{1}H NMR is one of the most popular types that is used for various analysis. However, in some cases, like lack of C-H bonds, the proton NMR cannot provide sufficient data, or the obtained spectrum is overcomplicated without the detailed information. Carbon NMR can be used to overcome the mentioned difficulties. As mentioned above, the magnetic resonance can be applied only for nuclei with non-zero spin. Thus, ^{13}C isotope may be used for NMR. However, among all carbon, only 1.1% are present in the form of isotope under interest. While using ^{13}C NMR, the following should be kept in mind:

- the sample should be present in a higher concentration (for liquid samples),
- the carbon isotope is fifty times less sensitive in comparison to ^{1}H,
- the positioning of peaks differs from proton NMR,

- the relative intensity of the NMR signals does not have a direct correlation with the number of the atoms,
- the range of chemical shift can reach 220 ppm,
- it takes a longer time to obtain one spectrum.

For ^{13}C NMR the number of discrete peaks and their positions play the most important role [40, 41].

There are two types of NMR: liquid-state and solid-state. A liquid-state NMR (typically mentioned as just NMR) is considered to be a destructive analysis methodology in the context of this book chapter. For this method, a solid sample is dissolved in a solvent that can be selected from a long list of suitable compounds like chloroform, ethanol, methanol, toluene, acetone. Unfortunately, the majority of polyolefin are highly resistant to many solvents. Nevertheless, liquid-state NMR can be used to study the functional groups deposited as plasma polymers with use of polyolefin-based monomers which can be dissolved in a deuterated solvent. A solid-state NMR (or ssNMR) usually requires supplementary hardware for high-power radio-frequency radiation and magic-angle spinning (MAS) in comparison to solution NMR [42–44]. These additional components help to overcome nuclear spin interaction problems that arise for a solid-state sample such as chemical shielding, J-coupling and dipole–dipole interactions which are much stronger in comparison to a liquid sample. The listed interactions induce the broadening of ssNMR spectra. However, this disturbance to the spectra can be desirable since they contain information regarding the molecular structure and orientation. In a liquid-state NMR, these interactions are negligible due to the presence of Brownian motion and migration freedom in the solution. ssNMR employs a sample spinning at a substantially higher speed in the range of 15–20 kHz to minimize the broadening by chemical shift anisotropy (CSA) and dipolar couplings to other nuclear spins, in comparison to liquid sample spinning at approximately 20 Hz. Furthermore, as was mentioned above, a technique called the magic-angle spinning (MAS) is used, when the sample is spun at a magic angle of approximately 54.74° with respect to the direction of the static magnetic field. In this case, the sample is spinning at a certain angle with respect to the direction of the magnetic field to minimize the broadening of the signal to the degree of isotropic environment. This makes the ssNMR spectra narrower effectively increasing the resolution of the spectrum. Due to the high spinning speed, the sample-container has to be carefully prepared because any imbalance in the sample tube can damage the instrumentation or give poor NMR results. The preparation of the samples for ssNMR involves grinding the solid sample in powder and then firmly packing it into the sample holder (capsule) for even weight distribution. It means that in both cases, ssNMR and NMR, the sample is destroyed in terms of surface wholeness. Nevertheless, both of the methods are used for the polyolefin analysis. The NMR data can be useful when the treatment is homogeneous through all the polymer bulk or when the region of interest can be removed and diagnoses separately, like plasma polymerized coating. Examples of ^{13}C ssNMR spectra are demonstrated in Fig. 11. The spectrum of LDPE, as representative of polyolefins, has a simple structure due to the presence of carbon only in the form of CH_2. Thus,

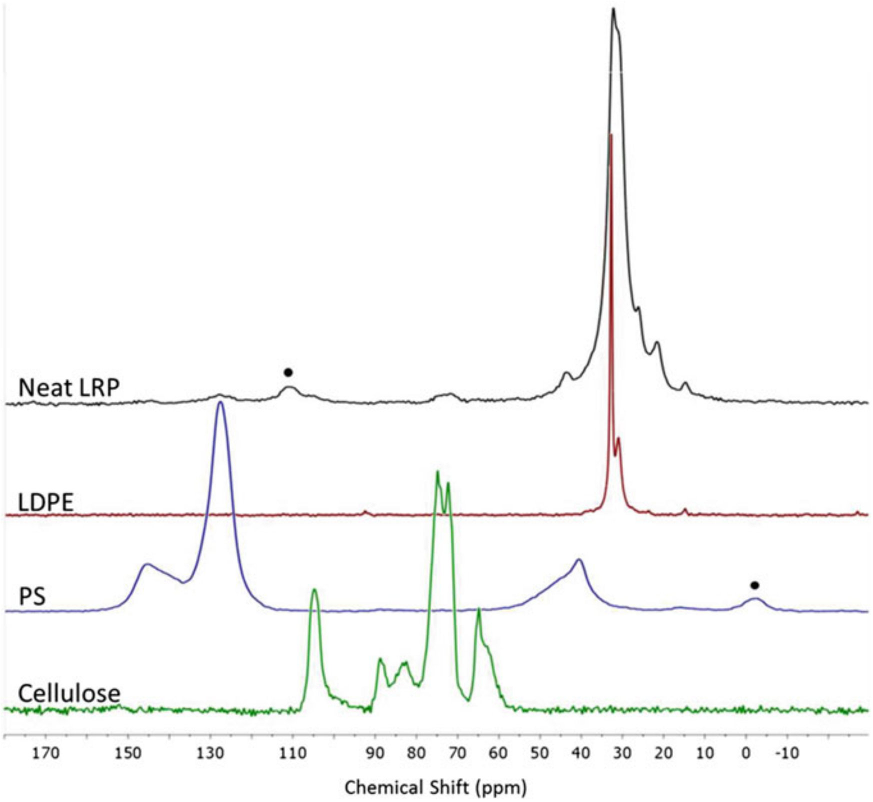


Fig. 11 Examples of solid state ^{13}C NMR spectra of landfill-recovered plastic (LRP), LDPE, PS and cellulose [39]. The dot marks spinning sidebands

it can be expected that after the plasma impact, when new chemical functionality is introduced to the polymer structure, it can be noticed in the NMR spectrum as new peaks.

Based on the provided information, it can be concluded that NMR:

- can identify the molecule structure and orientation;
- is capable of analyzing highly insulating material;
- provides the information about the composition of atomic groups within the molecule;
- gives information about adjacent atoms and molecule dynamics;
- allows quantitative analysis;
- can use different nuclei for analysis;
- has a rich database;
- provides an excellent resolution.

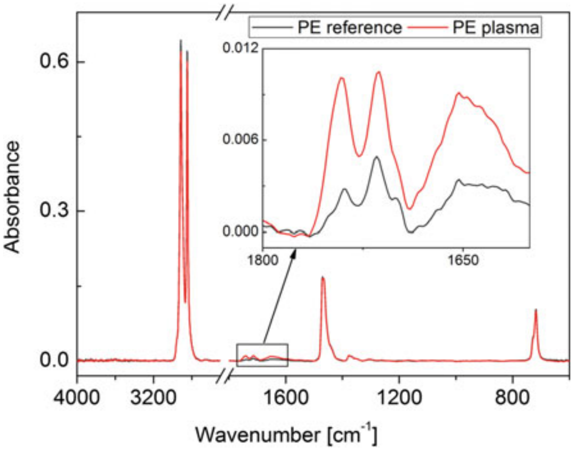
3 Surface and Interface Characterization of Plasma Treated Polyolefins with Different Spectroscopic Techniques

Polyolefins as an example of hydrocarbon polymers possess particular properties which differ from the other polymers due to the chain structure and chemical composition. Plasma treatment induces a new chemical functionality usually common for a specific type of plasma modification. Nevertheless, suppose the backbone of the polyolefin polymer is not destroyed during such an impact. In that case, the spectroscopic techniques described in this book chapter can provide the information on both the backbone material and the induced changes. It should be kept in mind that in order to thoroughly compare the results obtained from the same analytical technique and for the same material the working parameters and conditions should match as well as the nature of the polymer: average molecular weight, crosslinking degree and processing conditions. A significant resemblance in the polymeric chain among all polyolefins might make identifying each of them respectively challenging. Thus, primary and secondary chemical shifts shake-up satellites and valence band spectra provide supplementary information that can facilitate the determination of the composition and structure of a polyolefin sample. As demonstrated in the previous part of this chapter, each particular analyzing technique has a specific sampling profile, the depth and lateral resolution, sensitivity, etc.; hence, each of them can be the most suitable choice for one or another application. At the same time, a combination of several techniques can provide complementary data helping to interpret the properties of the testing surface. It is common to employ a few various analysis methods to obtain adequate information regarding the surface properties. In this part of the book chapter, results obtained with one of the discussed earlier spectroscopic techniques are often complemented with the other analysis, including the other spectroscopy methods.

The number of papers including FTIR, SIMS, XPS and NMR for polyolefins surface analysis is overwhelming. Thus, it is impossible to cover all the literature thoroughly. Some works are selected here to demonstrate the possibilities of each technique and their combinations.

As mentioned before, FTIR is one of the fastest and most convenient analyzing methods. This explains a wide variety of research that utilizes FTIR for analyzing the plasma treatment impact on polyolefins. Frequently, ATR-FTIR is a well-suited preliminary tool before moving forward to more expensive techniques. For instance, it was used to show that the increase of the exposure time and the discharge power leads to the higher incorporation of the oxygen-containing groups on LDPE under RF low-pressure argon and oxygen plasma [45]. As another example, FTIR was able to show the difference in the oxidation degree occurring on the sample surface of the corona-treated PE surfaces at the different distances from the knife-type electrode [46]. It was demonstrated that the oxygen-based functionalities (such as a single oxygen-to-carbon bond, the hydroxyl and ether groups) were formed by the rapid binding between the oxygen from air with unstable hydroperoxides and confirmed

Fig. 12 Changes in the ATR-FTIR spectra of PE after plasma treatment in comparison to untreated sample [52]



by the curve fitting of high-resolution C 1 s XPS spectra. A promising investigation on obtaining commercially available polyolefins, that are stable in time after modification by an atmospheric pressure air plasma torch, used XPS and FTIR to prove the stability of carboxyl, carbonyl, hydroxyl, amide, etc. groups after 31 days of ageing [47].

A few examples from above, have already revealed that XPS and FTIR are often used together since the output results complement each other very well due to a different depth of analysis [48–51]. Despite the fact that generally, the plasma modification is a surface-focused method, a small increase in the absorbance due to the induced functionality is sufficient in FTIR spectra to distinguish the plasma impact as shown in Fig. 12 [52]. It should be kept in mind that polyolefins are known as relatively poorly photostable polymers which results in the presence of oxygen on the surface of pristine polyolefin [52–55]. FTIR and XPS also can be used to confirm a successful grafting of glycidyl methacrylate (GMA), hyaluronic acid (HA), acrylic acid (AA), tetraethoxysilane (TEOS) etc. on plasma treated polyolefins [56–59].

A significant amount of information regarding various plasma-induced surface functionality on the modified polyolefin surface can be deduced from the curve-fitting of XPS high-resolution C 1 s peak since the same peak for a pristine polymer does not contain any features apart of C–C/C-H bonds [60]. For instance, a combination of high-resolution C 1 s peak fitting and SIMS analysis proved that CO_2 plasma treatment of PP could lead to degradation, cross-linking and functionalization in terms of alcohol, ketone and acid functions [61]. Another research demonstrated that a longer plasma treatment duration and a lower pressure result in higher incorporation of the oxygen functional groups which were determined form the curve-fitting of the detailed C 1 s spectra [62]. There are a few pitfalls for this method, as the difficulty of resolving functional groups that have a similar chemical shift and may even overlap or conformation of the polymer chain. As an example, Chvátalová et al. observed the wettability recovery 14 days after plasma treatment of PB-1 while no significant change in the XPS were detected [63]. Thus, the wettability recovery phenomenon was attributed to the gradual reorientation of the polymer chain into a more thermodynamically preferential state over a long period similar as was observed in [64, 65]. Unobvious results were reported by Kwon et al. by demonstrating higher oxygen incorporation when using Ar plasma comparing to Ar/O_2 plasma, as shown in Fig. 13 [66].

Apart from the XPS high-resolution determination of the chemical content, a quantitative chemical analysis of plasma modified polymer surfaces can be achieved by selective chemical derivatization. By consecutively applying either FTIR or XPS, it is possible to differentiate among different oxygen- or nitrogen-bearing functionalities and others [67]. As an example, the chemical derivatization a trifluoroacetic anhydride (TFAA) was used to semi-quantitatively determine the concentration of –OH groups after the O_2 plasma treatment of PP foil [68, 69]. In this work, the incorporation of the new element and formation of new functional groups after the TFAA derivatization can be seen on both XPS and FTIR spectra respectively. Friedrich et al. estimated the relative concentration of olefinic double bonds by measuring the concentration of Br attached to them on a PP sample after the low and atmospheric pressure plasma [70]. This derivatization is possible via a side reaction by H substitution; however, there should be no nitrogen-containing stabilizers on the plasma-modified surface. A similar reaction between Br_2 and argon plasma treated PP and PE samples was used for quantification of radicals and/or C=C double bonds formed after plasma impact by applying XPS and ATR-FTIR [71]. It was demonstrated that bromine reacts mainly with the radicals which are present in the majority on the plasma-treated top surface layers.

Due to the XPS angle resolved depth-profiling, it was possible to demonstrate that nitrogen and oxygen plasma treatment of LDPE and PP respectively is able to uniformly penetrate over 10 nm which is a maximum depth for XPS analysis [72, 73].

Plasma treatment of polyolefins may often result in crosslinking. One of the most suitable analytical techniques to evaluate the degree of crosslinking, branching and confirm the formation of new fragments due to the plasma impact is SIMS [74, 75]. For example, XPS and ToF–SIMS allowed to confirm the presence of specific nitrogen and oxygen fragments/groups on nitrogen plasma treated LDPE [76]. Practically, ToF–SIMS can be used to gain molecular information on the PP treated by plasma, as shown in Fig. 14 [77]. In another work, different glow discharges of CF_4 were used for surface fluorination of PE [78]. XPS and SIMS confirmed the presence of CF polar groups such as CF_2 and CF_3; however, SIMS analysis showed a surface saturation with fluorine after a shorter period of plasma treatment on the contrary to XPS. This contrast was attributed to the different depth of analysis of these two techniques. A unique capability of ToF–SIMS ultra-shallow molecular depth-profiling by Ar_{5000}^+ and Bi_5^+ gas clusters of LDPE samples modified by atmospheric pressure argon plasma torch was demonstrated by Cristaudo et al. [79, 80]. The authors were able to show that after Ar-D_2O post-discharge treatment, H–D substitution happened at the topmost surface layers as the fragments containing deuterium were reduced by a factor > 2 over a depth of 3 nm. The interaction of ammonia (NH_3) and deuterated ammonia (ND_3) plasma with PP and PE surface was demonstrated by studying the H–D exchange making use of ToF–SIMS and detecting the difference between

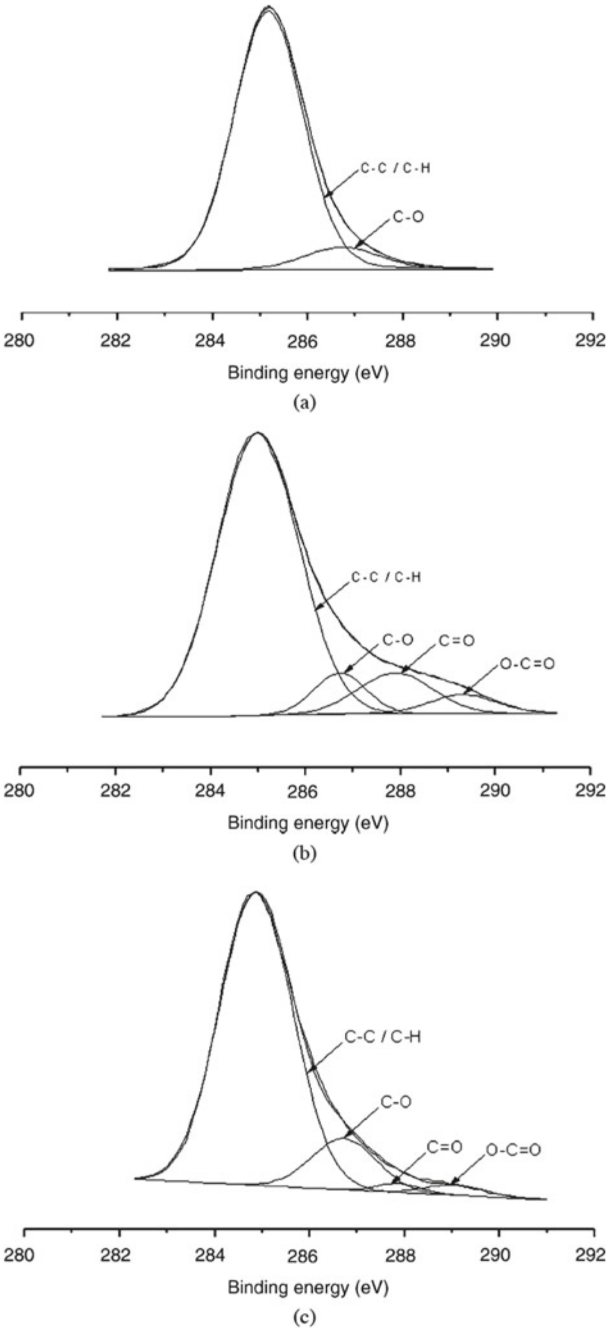


Fig. 13 XPS high-resolution C 1s peak curve fitting for **a** untreated, **b** Ar plasma-treated and **c** Ar/O2 plasma-treated PP film [66]

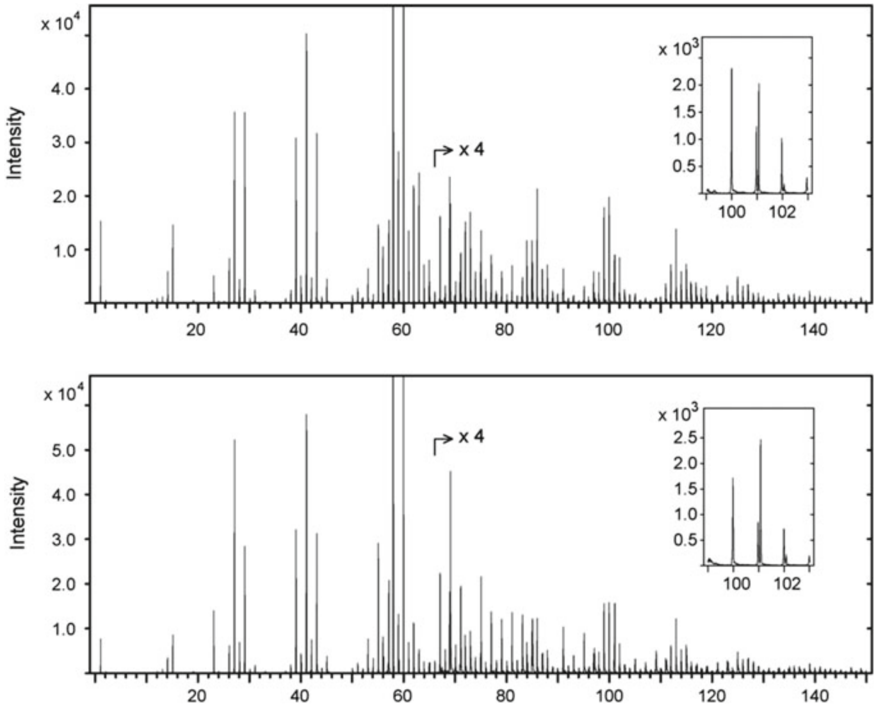


Fig. 14 Positive ion mass spectrum obtained SIMS for pristine PP (top) and air plasma treated PP (bottom) [77]

H and D peaks as shown in Fig. 15 [16]. This work revealed that due to the side chain methyl groups, PP is more sensitive to the exchange of hydrogen between plasma and polymer surface. Generally, in the mentioned research, apart from H–D exchange, grafting of N containing fragments were detected as well as a wide range of characteristic H/D mixed secondary fragment ions which suggests manifold and complex reaction pathways at the polyolefin surface during the plasma treatment. As a part of the previous work, Wettmarshausen et al. making use of ToF–SIMS and XPS demonstrated that the topmost surface of PE was highly doped with nitrogen which was present only in the minority (<10%) as primary amino groups [81]. What is more significant, these authors proved that the H–D exchange was occurring deep (>1 μm) into the polymer layers in a low-pressure NH_3 and ND_3 plasma by applying ATR-FTIR and NMR spectroscopy techniques.

As an example of a good agreement between XPS, FTIR and SIMS analytical techniques, employing the advantages of each of them, it was possible to demonstrate PP surface activation, degradation, functionalization and cross-linking by the nitrogen low-pressure plasma treatment [82].

Even though NMR spectroscopy requires a destruction of the sample structure, it provides supporting information regarding the presence of the different chemical

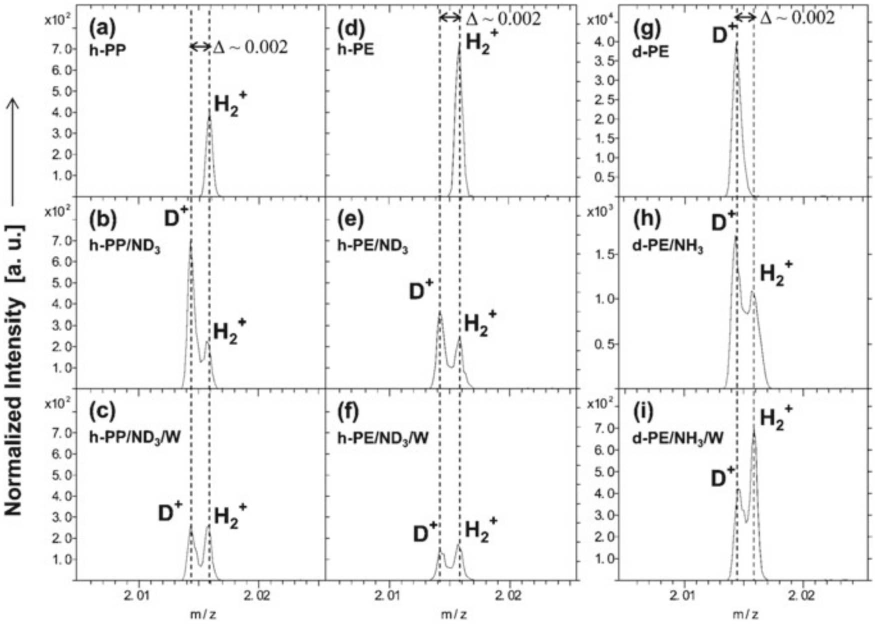


Fig. 15 Selection of positive ToF–SIMS spectra of PP and PE samples in untreated (top row), ND3 or NH3 low-pressure plasma-treated (middle row) and THF (cyclic ether tetrahydrofuran) post-plasma washed (W) states (bottom row). "h" stays for conventional polymers and "d" stays for deuterated samples [16]

functionality and cross-linking. In combination with other analytical techniques, NMR can significantly improve the explanation of the processes occurring on the polyolefin samples under the impact of plasma. For instance, this technique can help to answer the question of whether the molecular weight of the polymeric chain changes when the surface is modified by plasma. Boyd et al. found out that the formation of low molecular weight oxidized material happens due to the chain scission, which is accompanied by the oxidative attack which then agglomerates into globules at the surface [83]. This conclusion was drawn by combining the results from XPS, NMR and ToF–SIMS spectroscopic methods; in particular, ^{1}H NMR spectra for untreated and plasma modified PP sample shown in Fig. 16, clearly displays the presence of the low molecular weight oxidized material. A good agreement between results of FTIR and ^{1}H NMR analysis on the PP samples dissolved in $CDCl_3$ solution with tetramethylsilane was achieved by demonstrating the decrease in methyl groups and presence of a small doublet that corresponds to $=CH_2$ groups, which might be evidence of initiated crosslinking [84]. Besides the ability to study the functional groups' formation, NMR was applied to determine the crystallinity of PE molecular structure deposited via thermal decomposition with or without plasma assistance. FTIR and XPS results supported the ^{13}C ssNMR finding which showed that higher discharge power yields a more heterogeneous PE structure because it decreases the

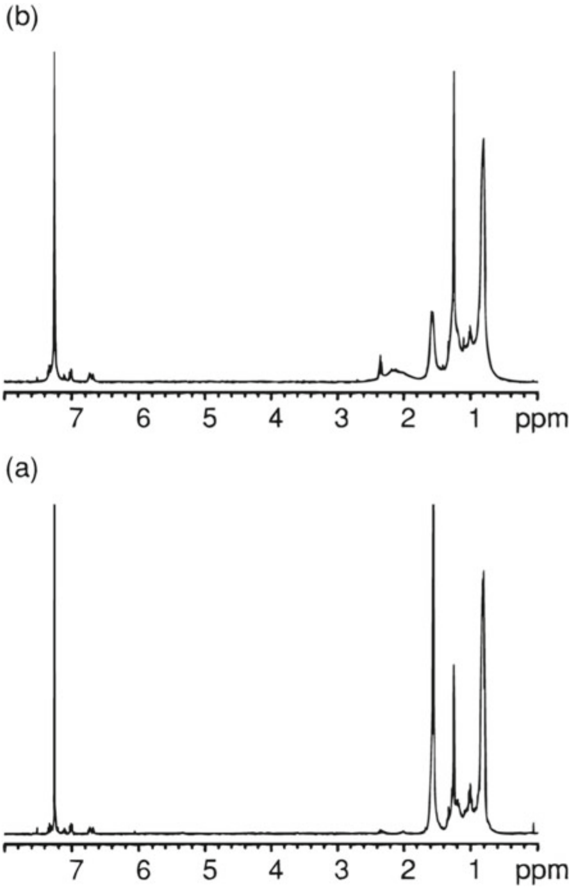


Fig. 16 FH NMR spectra of **a** untreated and **b** silent discharge treated*PP* [83]

highly crystalline structure of bulk PE while promoting the formation of the amorphous structure due to increased degree of cross-linking among plasma activated polymeric fragments [85].

From the examples discussed above, it is clear that the limitations and weaknesses of a single analysis technique can be compensated and overcome by using other analytical methods. Additionally, a combination of the multiple analyzing technique results provides a more meaningful explanation of the experimental data and further insights into the underlying complex interaction mechanisms between the plasma and the polyolefin polymers.

4 Conclusions

This chapter describes the working principles and possible applications of the most powerful spectroscopic techniques for plasma modified polyolefin surface analysis: FTIR, SIMS, XPS and NMR. Each method is unique in terms of the outcome information (quantitatively, qualitatively, depth profiling capability), the type of the analyzed constituent (elements, chemical groups, molecular structure, etc.), the physical constraints (depth of examined layer, spatial resolution, sensitivity).

The main advantage of FTIR spectroscopy is the possibility to identify, with good sensitivity and signal to noise ratio, unknown materials, defined molecules and functional groups on samples with a thickness up to 10 mm. SIMS is well-known due to its ability to both distinguish between elements, isotopes and molecules at the topmost surface (up to 0.5 nm) as well as to provide information regarding the material structure. XPS is capable of identifying both the elemental composition and the chemical states on the polymeric surface. The technique provides both qualitative and quantitative information about the upper layers of the surface (analyzing depth ~ 1–10 nm) without sample destruction. NMR can analyze different nuclei to provide data on the molecular structure and orientation. Quantitative results can be obtained.

The last part of this chapter clearly shows that these surface analysis techniques are highly complementary. Each method may be explicitly selected for a particular field of study; however, it is the combination of these methods that allows the best possible study of a polymeric surface. Nevertheless, the results obtained from any of the techniques used for the plasma treatment of a polymer surface should be critically treated. The detected chemical functionality of the surface does not solely depend on the plasma conditions during the treatment, but also on the time elapsed after the treatment, on the storing conditions of the sample between treatment and analysis, and the conditions during the analysis process.

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Comparison of the Effect of Excimer Laser Irradiation and Plasma Treatment on Polypropylene Membrane Surface

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Abstract Polypropylene membrane with the base of polyolefin exhibits promising applications such as packaging, medical tools, and especially in the filtration industry, due to its outstanding properties such as well mechanical features, recyclability, acceptable resistance to temperature and chemicals, and reasonable price. However, its applications are restricted by its hydrophobic nature. To amend the surface physical and chemical properties of polypropylene and broaden its usage, well-known methodologies such as laser modification and plasma irradiation have been investigated more than the other methods. Herein, in this chapter, the investigations on the surface refinement of polypropylene using laser and plasma are discussed. Furthermore, a comparison between the effectiveness of both methods (i.e. laser modification and plasma irradiation) is presented.

1 Introduction

The foremost way in the filtering industry is using membrane because, in general, it controls flux rate and allows some components of a mixture to pass through it while other components are abandoned. On the other hand, with depletion of water resources and clean water shortage, wastewater treatment concerns more than previous. Hence, membranes have been widely used in various industries ranging from wastewater treatment and fuel cells to filtration industry and even medicine as artificial organs [1, 2]. The permeability feature of the membrane is widely used in the separation and filtration industry. Since the main purpose in the filtration industry is to separate a particular material from a mixture, a membrane can provide this opportunity [3]. Thereafter, the controllability property of the permeation rate of the membrane has caused a lot of attention in medicine, especially in the field of drug delivery, because the main goal in drug delivery is to regulate the permeation rate, which in general a membrane can be very efficient. In this regard, some of the most

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successful uses of the membrane in the medical field are artificial kidneys based on hollow-fiber membranes, artificial lungs, and drug delivery.

According to the size of particles that should be separated, in general, membranes are classified into four major categories [3]. Likewise, membranes could be divided into two categories from the point of the membrane's structure view, isotropic and anisotropic membranes [3]. Isotropic membranes have a uniform structure throughout, and they can be subdivided into three types, microporous, nonporous, and electrically charged membrane. On the other hand, anisotropic membranes consist of layers with different chemically and or physically heterogeneous structure and permeability. Indeed, they have a skin/core structure in such a way that an extremely thin surface layer (i.e. the skin) supported on an open much thicker porous core [3]. There is quite an extensive diversity of techniques to fabricate membranes such as phase inversion, track etching, and stretching which in the following a brief description of these techniques will be outlined.

To begin with, phase inversion is one of the applicable techniques for membrane fabrication. It is a mixed way; a solution of liquid polymer from which a membrane is to be made is prepared in a selected solvent. The precipitation of the solution results in the formation of two phases of solid and liquid [3]. The solid which is a polymer-rich part forms the polymer matrix and the membrane pores are made of liquid. One of the major drawbacks of this method probably is solvent prediction since there is no straight strategy to select the appropriate solvent [3].

The track etching method is performed in such a way that the polymer sheet or foil is first exposed to the radiation of the metal ions. In the following, the exposed polymer foil is etched in an acid or alkaline medium. While the porosity of the membrane affects by the duration of radiation, the etching time, as well as temperature, determine its pore size [4]. As porosity increases, the membrane becomes fragile, so pore size is limited.

Stretching technique has been used in which the sketching of a polymer film or sheet is fundamental aspect [3]. This technique relies on having one of the following: filler particles, a mixed solvent, beta or hexagonal unit cell crystals, or a stacked lamellar structure [3]. For example, uniaxial stretching is used for a lamellar structure as follows: (1) creating a film by lamellar morphology, (2) annealing the precursor film, and (3) stretching at the desired temperature.

Having stunning properties, polymers excite large attention in membrane fabrication and are used in the wastewater industry with ease [5]. The performance of a polymeric membrane occasionally depends on several factors, including surface roughness, its material, the chemical properties of the polymer surface, and its structure [1, 6]. The membrane properties relate to its fabrication process and materials themselves. To date, to aim of reducing cost and time, synthetic-polymeric membranes have been used in various applications like reverse osmosis, wastewater treatment, microfiltration, and ultrafiltration. The polymeric membrane technology excited a plethora of attention because of its low cost, low energy consumption, and environmental adaptation. However, hydrophobicity of a membrane is an impractical characteristic, which causes inconvenience in different industrial sectors. The fundamental rationale for the hydrophobicity of a material is the lack of hydrogen bonding with water molecules. So, if we could increase the percentage of oxygen content, as a result, the hydrophobic membrane turns to a hydrophilic one [1, 7]. Wetting changes of a membrane could be scrutinized using water contact angle measurement.

The hydrophobic nature of some polymeric membranes (e.g. polypropylene) does not allow them to adhere to hydrophilic substrates and it shows a major barrier in wastewater, sea desalination, and separators in battery industries [1, 8–10]. Besides, a hydrophobic membrane could not contribute to the reversible process and it is a major drawback especially in dealing with aqueous solutions. Most synthetic-polymeric membranes, used commercially, are hydrophobic in nature [6]. The hydrophobic membrane has a high level of mechanical and chemical stability than the hydrophilic one which makes them appropriate candidates. Additionally, the previous studies suggested that in the case of hydrophilic membranes, a very thin layer of water could exist on the skin layer of it which contributes to reducing fouling components adsorption on it, and as a consequence increasing the antifouling characteristic of the membrane [1, 11]. Considering the aforementioned statements, a desirable membrane, which is mechanically tough and durable, antifoul, and chemically stable, could be achieved by modification of a hydrophobic polymeric membrane without changing its bulk properties [1, 5, 12, 13]. Hence, to date, several different methods for the functionalization of polymeric membranes have been introduced and applied. Techniques which are successfully used to improve a polymeric membrane are corona, chemical, UV irradiation, flame, plasma, and excimer laser [9, 10, 14]. The surface properties of polymeric membranes such as wettability, roughness, and chemical structure are determining factors in choosing a membrane for a particular application [15]. Accordingly, a few polymers having been used as polymeric membrane materials including cellulose, polyvinylidene fluoride, polysulfone, polypropylene, polyethylene, polyacrylonitrile, polyamide, and polyimide. Among the aforementioned polymers, We focus on polypropylene (PP) membrane.

2 Polypropylene Membrane

Polypropylene membrane with the base of polyolefin exhibits promising applications such as packaging, medical tools, separator in lithium-ion batteries, and especially in the filtration industry [16–19]. These vast applications are attributed to its outstanding properties such as well mechanical features, recyclability, acceptable resistance to temperature and chemicals, and reasonable price [1, 17, 20–22]. Yet, due to low surface energy, its hydrophobicity, and the lack of some functional groups, polypropylene exhibits several weak properties, which in turn limits its applications [1, 17, 19, 23, 24]. Of course, it should be added that there are solutions to this problem that significantly improve its poor features and broadens its usage more. Since it is the most widely used material in the filtration industry, its hydrophobicity causes proteins and other hydrophobic compounds to absorb into the membrane's pores which count as an undeniable obstacle in the filtering process [25, 26]. Admittedly, it usually leads to a reduction in liquid permeability and membrane useful life, increasing energy usage to overcome the persistence of fouling and have a stable flux [26]. In addition, we need to replace the used membrane after a while which makes the filtration process costly. The fouling phenomenon could be categorized into two types of irreversible and reversible fouling which the intrinsic properties of the membrane (i.e. membrane wettability) determine the type of fouling. To put it another way, the reversible fouling in which membrane can be revived happens when reversible organic matters are adsorbed on hydrophilic surfaces [26]. While in contrast, adsorption of the irreversible organic matter on a hydrophobic membrane results in irreversible fouling which only chemical cleaning can partly remove precipitate [1, 26]. The fouling phenomenon could be explained based on the bonding between membrane and hydrogen of water molecules.

PP serves as the most important polymeric membrane material due to its high stability and low price. PP never shows a disposal problem than other materials (like PVDF) due to not having halogen content. Besides, the PP membrane has a vital role in microfiltration and ultrafiltration processes. The hydrophobic nature of PP could be considered as a disadvantageous factor in industrial and wastewater processes. In wastewater treatment and bio-separation, hydrophobicity is a major handicap when it comes to the treatment of solutions consist of the organic matter content which causes irreversible fouling of the membrane, and membrane fouling leads to membrane deterioration. Under this condition, some strategies such as cross flushing and backwashing can partly recover the membrane [26]. In biomedical applications, the usage of polypropylene is restricted by its hydrophobicity because of biomolecules such as enzymes prone to adsorb on hydrophobic surfaces [6, 9, 15, 17, 27, 28]. This could lead to infection and membrane fouling and change in biomolecules performance [16]. Accordingly, to avoid irreversible fouling even in hydrophobic membranes, it seems that for membranes to increase the hydrophilicity offers a practicable solution. Membrane surface treatment can indeed be applied to modify surface wettability, improve biocompatibility, and chemical properties [9, 15].

3 Surface Modification Strategies

The main purpose of surface tailoring is modification outer layer of polymers aim to add some useful functional groups which improve adhesion, hydrophilicity/hydrophobicity, anti-fouling, and dye uptake [1, 6, 29]. Eliminating the drawbacks of polymers led scientists to utilize different methods, which have been categorized in physical, chemical, and biological methods [30–32]. These categories are described as follows.

3.1 Chemical

An accepted route to introduce desired effects is the wet chemical method, in which the surface of polymers was exposed to some chemical reagents such as chromic acid, nitric acid, and potassium hydroxide. Utilizing this technique for polypropylene and polyethylene resulted in generating some carbonyl groups, hydroxyl groups, and carboxylic acid groups on the surface of polymers. Introducing such functional groups contribute to improve the wettability and adhesion of the surface.

3.2 Biological

Thanks to lower cost and high purity, biological modification methods have been celebrated as a convenient route for use in medical applications. In this method biomolecules such as enzymes, antibodies, and proteins were loaded on the surface of polymers through physical or chemical attachment. Physical adsorption is the easiest way compared to chemical interaction; it must be considered that chemical attachment was occurred by covalent bonding which offers a more stable biomolecule material.

3.3 Physical

To eliminate chemical agents utilized in traditional chemical routes, which impose irreparable damages to the environment, methods based on physical principles have been developed. The physical methods have been justified based on their principles in two categories plasma and radiation-assisted such as corona discharge and laser, respectively. Introducing oxygen containing functional groups, which has been provided by physical treatment, endows the surface of polymers with suitable properties like adhesion, wettability, and printability.

Among different methods, the further sections are dedicated to justify physical methods in detail.

4 Radiation

The energy coming from a source and passing through a medium is named radiation. When an electron drops down from higher energy levels to lower ones, radiation could be created [30]. Diverse types of radiation could be classified into two major categories including ionizing and non-ionizing radiation, based on their source and power [30]. Ionizing radiations have high energy which able to create an ion by removing an electron from the matter [30]. On the contrary, non-ionizing radiations do not have enough energy to create ions during exposure [30]. To be more accurate, not having acceptable parameters, some materials cannot excite interest unless to be modified through an appropriate method. These methods are classified by their technology such as chemical, plasma, and laser methods. In polymer surface modification, plasma and laser modification techniques are commonly used to improve membrane properties. In exceeding sections, a brief description of plasma and laser is exhibited.

4.1 Plasma and Plasma Modification Technique

In a broad statement, a gas that consists of ions, electrons, molecular, and atomic components in the electromagnetic field is plasma [1, 15, 33, 34]. Plasma is formed by applying an electric field between powered and grounded electrodes through a gas medium [9, 35, 36]. The most important factor to produce plasma is breakdown voltage to split gas into its species. Non-thermal (usually named as cold plasma) and thermal plasmas are commonly used for polymers to functionalize [34, 37]. Plasma is classified according to electron density and type of power supply. Among all power supplies, radio frequency (RF) or microwave sources are most common [34]. When plasma treatment is implemented to a polymer, then drastic changes are simultaneously done on the top surface of the polymer such as cross-linking (including enhancement of its hydrophilicity and/or improving its adhesion), removing contaminants, etching [10, 17, 24, 34, 38]. Accordingly, the interactions of plasma and polymer can be divided into three categories, surface reaction, polymerization of plasma, and cleaning [13]. Surface reactions occur when surface and gas species react with each other; thus, functional groups are introduced on the polymer surface. Under this condition, reactions between surface species result in cross-linking [30]. Previous studies revealed that surface reactions are done when plasma modification is performed using carbon oxides, hydrogen, oxygen, water, neon, nitrogen and its oxides, and ammonia. Polymerization occurs when a monomer in plasma (such as C_2H_6, C_2F_4, CH_4, C_3F_6) is polymerized on the polymer surface [13]. In this condition, reactions including gas species and surface species, as well as between surface species might occur. A typical process occurring during the plasma modification is surface cleaning using etching the surface.

The performance of the plasma is that the gas-forming molecules prone to activation by the possible collisions with other species in the gas and then they hit the surface of the polymer [1]. In this method, the excited molecules of a gas are thrown to the surface of the polymer; so, physical phenomenon occurs in such a way that plasma irradiation causes heating the polymer surface resulting in the chemical bonds breaking. The necessary conditions for chemical reactions on the polymer surface are prepared. Consequently, plasma prepares the necessary environment for chemical groups to combine [9, 39].

Plasma could promote surface properties using the interaction between gas's species and material's surface and similarly via restructuring the surface of materials. The first one is achieved by oxidation and the second is done by degradation and formation of oxygen groups. It could be argued that nitrides and oxides are created from plasma irradiation [1]. Accordingly, the key factor in plasma functionalization to attain favorable properties is selecting the gas because the properties of the top layer of polymer which have been exposed to plasma strongly affected by the type of gas [1, 38, 40, 41].

Surface properties affect directly by plasma gas type and its nature (reactant or non-reactant). However, the most practical feature of plasma modification is altering the surface of matter while preserving the bulk properties [9, 13]. To date, many studies have been employed for the investigation of the effect of plasma on PP membrane [42, 43]. According to kinds of literature, plasma hydrophilization has been successfully performed on polymers and it has been confirmed that in some cases the water contact angle drops to less than 20° which is considerably low [1, 44, 45].

Besides, surface characterizations have confirmed the formation of polar groups during plasma exposure which is a sensible reason for hydrophilization and increasing water uptake [1, 24, 46]. Plasma modification is conducted on polymers with different active gases including oxygen, nitrogen, carbon dioxide, air, fluorine, argon, and ammonia, or a mixture of these gases [34, 44, 47–49]. To reduce the modification cost, oxygen and argon-containing gas are commonly utilized. On the other hand, plasma could apply at a broad range of pressure from atmosphere pressure to higher ones which the applied pressure strongly depends on the gas type and the main goal of modification [9, 34]. Low-pressure plasma results in more induced free radicals on the polymer surface according to the literature [9, 24]. Generally, it could be asserted that plasma modification is one of the few environmentally-friendly, dry, time-efficient methods which only affect the top layer of the polymer [9, 17, 24, 34].

Oxygen plasma treatment is a common method with the aim of fabricating suitable materials in many research fields. Oxygen is a reactant gas; it contributes to fabricate a desirable material by reacting with its surface. During oxygen plasma treatment, two processes may occur including itching and formation of oxygen functional groups. These mechanisms down to the highly aggressive features should be controlled by operation parameters. As a result, oxygen-containing functional groups such as C–O, C=O, O–C–O, C–O–O, and CO_3 are made on the surface due to oxygen plasma radiation [10, 34]. Changing the wettability of polymers relied on creating polar functional groups which possesses many benefits [46]. Wettability has a vital role in using polymeric materials in the industry and medical science. In general, oxygen-assisted plasma is commonly performed to increase surface energy to dramatically increase the hydrophilicity [10, 13]. Additionally, oxygen plasma leads to clean the surface from organic contaminants. While in contrast, fluorine-assisted plasma contributes to surface etching and/or surface energy reduction and, as a consequence, increasing hydrophobicity [10, 13]. In general, polymer's chemical structure does not affect the etching rate of a particular type of polymer. However, it can be stated that the etching rate in polymers with a lower melting point is higher than that of other ones [34]. The etching rate relates to the plasma gas which is used. For example, etching rate varies based on the assisted gas according to such sequence: O_2 > air > CO_2 > CF_4 > Ar [34]. Adhesive improvement of polypropylene has been reported due to the oxygen plasma modification. It was outlined that the formation of oxygen-containing functional groups (carboxyl, hydroxyl, and carbonyl) are responsible for adhesive improvement [50].

Previous studies suggest that the surface morphology of polymer, as well as its roughness, is altered by means of low-pressure argon-assisted plasma [23]. Indeed, some oxygen functional groups appear after argon plasma modification [23]. It has been reported that after the end of the plasma irradiation process, the plasma surface can include free radicals and active species, which, if the polymer surface is exposed to the atmosphere, will cause oxygen-containing functional groups [24, 51, 52]. Novák and co-workers have reported that oxygen functional groups have been generated after atmospheric plasma modification of the polypropylene fabrics which formation of these functional groups was confirmed employing XPS and FTIR characterization techniques [24]. Among the many types of polymers, polypropylene has been shown to be most effective in argon plasma radiation, so that its wettability is increased significantly [9]. In a recent study, Mansuroglu et al. examined the effect of argon and nitrogen plasma and also RF plasma power on polypropylene crystallinity [17]. It was found that new structures such as clusters and valleys, having different order, size, and shape, are created during the plasma irradiation which was attributed to its crystallinity [17]. Rezinckova et al. investigated argon-plasma surface modification of polypropylene [53]. In this study, it was revealed that argon-plasma treatment induces dramatic changes in terms of surface roughness and morphology on polypropylene [53]. In another research, the surface of the PP membrane was treated by argon plasma [49]. The authors inferred that outcome polypropylene samples have high oxygen concentration and, as a result, less water contact angle. However, the oxygen concentration of the polypropylene surface decreased with the aging process and its water contact angle increased again over time [49]. Nitrogen-containing plasma is often used to introduce amino groups and improve printability, biocompatibility, and wettability [10, 13]. Micro-porous polypropylene membrane was exposed to Ar and He plasma aiming to modify surface properties [54], a schematic illustration of experimental was represented in Fig. 1a. To study the influence of plasma treatment, the modified PP membrane was investigated by water contact angle, and the results confirm increase of hydrophilicity of the membrane which was further used as the battery separator. The uptake ratio of electrolyte for samples was assessed and the results show it was raisin from 300 to 600% after treatment; the increase was attributed to high polarity and pore structure. The electrochemical performances resulted, in respect of unmodified PP membrane, after treatment by Ar and He plasma capacity was increased about 48% and 50%, respectively. Figure 1 depicted the percent of electrolyte uptake as a function of modification time and the performance of the battery.

To investigate the influence of working gas on surface properties, polypropylene samples were tailored by low pressure plasma in the presence of oxygen and air as working gas [55]. The investigation of contact angle, surface chemistry and morphology, and roughness was used for this purpose. The results depicted creating

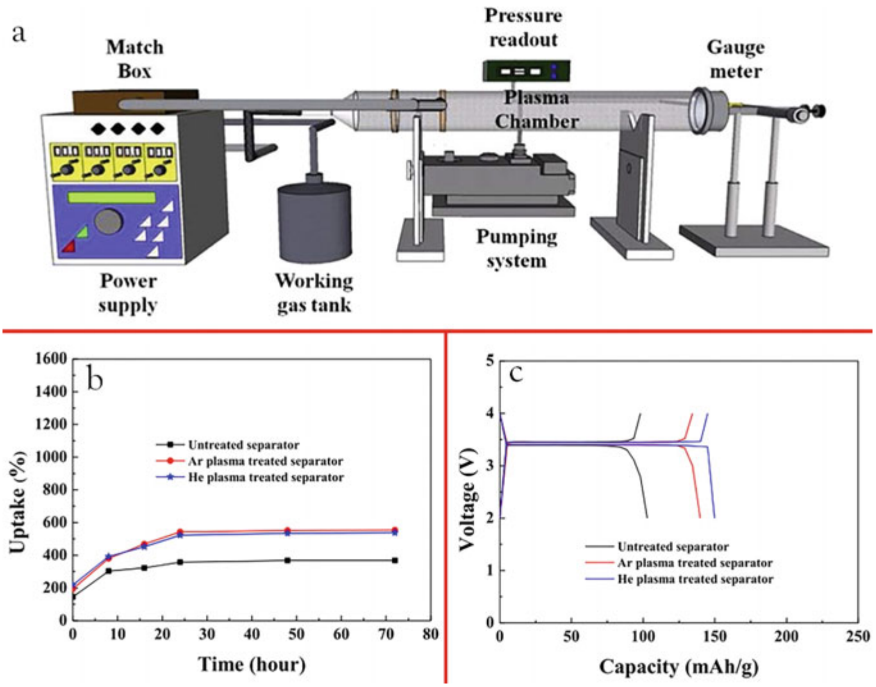

Fig. 1 **a** A schematic illustration of experimental setup, **b** the percent of electrolyte uptake, and **c** charge/discharge profile of battery. (Reproduced from Liang et al. [54])

polar species and introducing oxygen functional groups contribute to decrease water contact angle; and as a result, hydrophilicity was increased. The XPS analysis suggested that the increasing ratio of O/C is more significant than N/C. The AFM analysis shows that for 50 W treatment, roughness changing was considerable. For example, for 180 s of applying air and oxygen treatment for 50 W, the roughness was about 900 nm and 400 nm, respectively. The contact angle, surface roughness, and AFM analysis were presented in Fig. 2.

The effect of low-pressure radio-frequency (RF) methane (CH_4)/oxygen (O_2) mixture plasma was assessed by changing properties which occurred on microporous polypropylene (PP) membranes [56]. The deionized water contact angle was measured to study surface wettability and the results suggest that the angle was declined from 150° to lower than 30° and 70° in the glow and remote region, respectively, at the power of 15 W. The comparison of the surface energy of PP membrane shows increasing polar components, such as CO, contribute to increasing surface energy, which means wettability was increased. The FTIR spectra revealed that increasing hydroxyl (OH) and carbonyl (C=O) took place after plasma modification. Morphology investigation shows that the surface was altered after plasma irradiation; indeed, the smooth surface of the PP membrane became rough and porous after plasma modification. The XPS analysis, a supplement for FTIR, shows oxygen

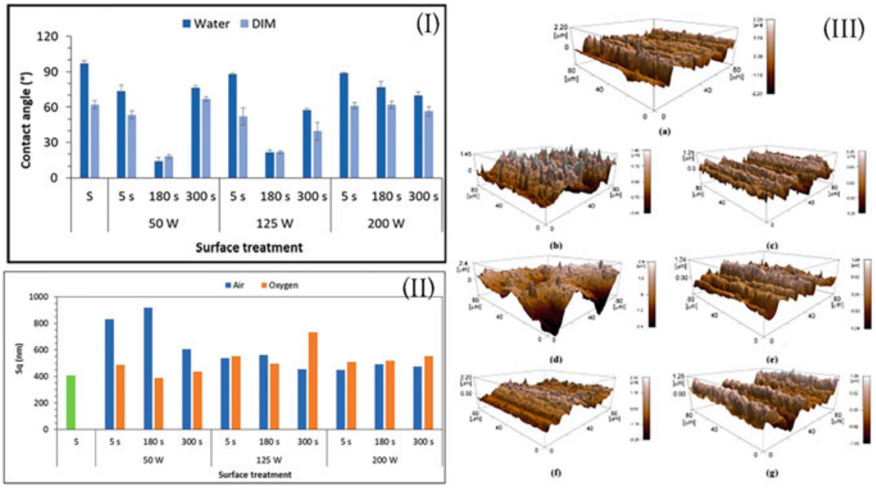

Fig. 2 (I) contact angel, (II) surface roughness, and (III) AFM analysis for **a** untreated and plasma treated PP substrates, in particular: **b** Air treatment 50 W-180 s; **c** air treatment 125 W-180 s; **d** air treatment 200 W-180 s; **e** oxygen treatment 50 W-180 s; **f** oxygen treatment 125 W-180 s; **g** oxygen treatment 20. (Reproduced from Hegemann et al. [5])

containing functional groups appeared for both glow and remote regions. Eventually, the comparison of glow and remote regions for CH_4/O_2 suggests that radical reaction could be promoted as well as etching effect could be restrained. Water contact angle, FTIR analysis, SEM, and the XPS spectrum of C1s were presented in Fig. 3.

The aging phenomenon is an important feature in plasma treatment, using additives or further steps were recommended as convenient ways to stable properties and prevent downfall [57]. In this respect, a single-step gliding arc plasma-based method was deployed to modify biaxially-oriented polypropylene (BOPP). The samples were exposed in different exposure times and extent of hydrophobic nature was surveyed for 5 weeks. The roughness was increased after modification and the results show a maximum of 40 s of exposure. The SEM analysis of untreated sample shows some spots which are disappeared after 10 s of treatment, these spots attributed to available additives in the commercial BOPP. Increasing treatment time led to appearing plasma etching, consequently, the porous structure was observed in 30 s tailoring with the size of less than 50 nm. The results did not show a regular attitude between pore size and exposure time. The water contact angle was investigated immediately after plasma treatment and the results suggest that it was declined from 90° to 55° for 120 s of treatment. The aging phenomenon was assessed by the water contact angle of samples after 3 h of sample storage. The results affirmed a fast decline of WCA from 55° to 37°; ironically, the hydrophilicity was increased, in other words in other cases after aging hydrophobicity was recovered. The WCA was observed for prolonged time, and the results were surprisingly illustrated steady hydrophilicity. To elucidate chemical composition, the ratio of O/C was measured and it was grown after sample storage from 1 to 5 weeks. The O/C growing probably due to the active

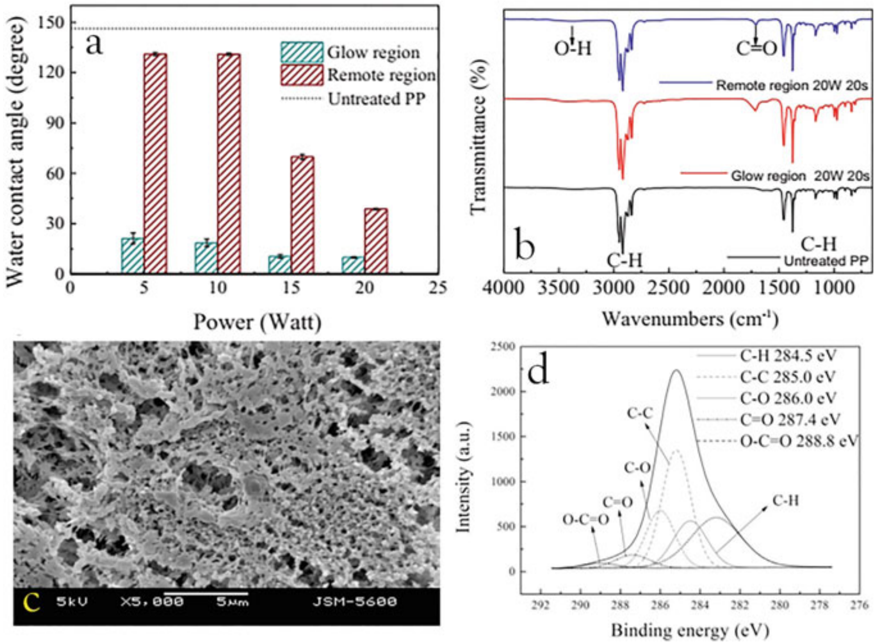

Fig. 3 **a** Water contact angle, **b** FTIR, and **c** SEM and **d** C1s spectrum of 5 W, 20 s glow/direct. (Reproduced from Juang et al. 2016)

surface area of BOPP which could react by atmospheric air. The results of studies on plasma modification of polypropylene are tabulated in Table 1.

4.2 *Laser-Assisted Polypropylene Modification*

Nowadays, laser systems which are common types of radiation have various functions in the field of medicine. On the other hand, lasers are considered as one of the effective tools to modify polymer surfaces [30]. Since conventional surface modification techniques usually could not introduce all the required properties on the polymer surface and may cause unwanted contamination on the surface, some alternative methods are proposed to improve surface properties [19]. In this respect, laser-based modifications that induce functional groups on polymeric surfaces were substituted for conventional methods [19]. Laser-based techniques are classified into three groups, laser patterning, laser structuring, and laser texturing [67]. As mentioned previously, laser surface modification is another method to tailor the surface properties of polypropylene. Nowadays, thanks to laser power and high precision, modification of polymeric materials using lasers attract a great deal of attention [27, 68, 69]. UV lasers are one of the most favorable laser systems which are utilized in many studies

Table 1 Several studies on plasma modification of polypropylene

Plasma	Water contact angle (°)	Ref. no.
O_2	15	[58]
CO_2	76	[59]
Air	35	[48]
N_2	86	[47]
NH_3	58	[60]
A mixture of CH_4 and O_2	8	[61]
Ar	–	[45]
N_2	–	[62]
A mixture of He and 0–1% O_2	70.1[a]–35[b]	[63]
Air	52.15	[64]
N_2	–	[65]
He/O_2	39	[21]
O_2	61.42–56.14	[66]
Ar	–	[9]
Ar/N_2	–	[17]

[a] 1.4 s treatment time
[b] 120 s treatment time

and most of the fields [10]. Laser modification is considered the simplest, one-step, and medium-cost technique to amend surface-chemistry and/or –morphology [70].

Micron patterns could be induced on the polymer surface using UV lasers with no damage to its bulk properties. Laser-based techniques of polymers modification, generally, are performed in two ways which are based on the alteration of the surface chemistry and/or surface deformation (increasing roughness). Consequently, surface morphology is altered which in turn leads to adhesion improvement. As clarified previously, the laser modification technique is based on the interaction of the laser beam and polymer [67]. This process begins with focusing the laser beam on the frontal surface of the target (e.g. PP membrane) [67]. Absorption of the laser beam on the polymer surface leads to polymer heating and/or vaporizing which in turn induces chemical and/or morphological changes [27, 71]. The laser beam and polymer surface could have photochemically or thermally interaction in the exposed area [71]. Because of the low absorption coefficient of polypropylene, it was asserted that the majority of the laser's energy penetrates the polypropylene [18].

In general, laser-based modifications could introduce oxygen-containing groups on a polymeric surface [19]. Riveiro and coworkers investigated the effect of the irradiation of a diode end-pumped Nd:YVO_4 laser source operating in its fundamental wavelength, second, and third harmonics on PP samples (1064, 532, and 355 nm, respectively) for biomedical application [27]. At first, the optical response of the PP samples was surveyed. They coated PP samples with a carbon thin layer to address the high transparency (40%–62%) of the PP samples to all of the emitting wavelengths and so to increase the PP sample's energy absorption. This group concludes that the studied laser wavelengths increase the average roughness of the samples to higher than 1 μm which is a minimum value to enhance the PP membrane's properties for biomedical purposes. Although the studied laser wavelengths led to an increase in the average roughness of PP samples and generation of hydroxyl and carbonyl functional groups, the wettability study suggested that PP samples which are exposed to the laser wavelengths of 1064 and 335 nm demonstrate better hydrophilicity. Indeed, the mechanical performance of PP samples was not significantly improved through laser irradiation. As the response of the human tissue depends on the surface properties of the material which is in contact with it, the laser-based surface modification, which enhances the surface energy and wettability and also changes the chemistry of the surface, could be an alternative approach. In an early work, Mandolfino et al. studied the adhesion enhancement of polypropylene surface deploying two laser systems operating at 1064 and 355 nm wavelength [19]. This study suggests that polypropylene surface treatment by the laser source of 1064 nm (infrared region) leads to surface damage [19]. While in contrast, surface treatment by laser source of 355 nm presents better results with no surface damaging. This research group scrutinized laser parameters such as frequency and overlapping value. The authors inferred that using low values of frequency and overlapping results in better adhesive performance and superior mechanical behavior [19]. Park et al. searched the variation in pore size concerning laser parameters such as processing time and laser fluence to reach favorable results [18]. It was revealed that as the laser fluence increases the pores increase, provided there is sufficient processing time [18]. A femtosecond Titanium: Sapphire laser source was used to tailor surface morphology of PP to enhance automotive applications and surface changes were surveyed by different characterizations [72]. Laser modification contributes to introduce micrometric sized dimple- and groove-like structures, which changed wettability without altering surface chemical features. The measurement of water contact angle shows an obvious raising of wettability; in the other words the angle of water was reduced from 80° to 35°. μ-Raman spectroscopy data confirmed oxygen-containing functional groups was increased on the surface of PP. In contrast, the intensity of C=O was declined but the structure of PP was almost maintained. The surface adhesion was investigated by standard ink and methods, and the results suggest that femto-second laser treatment improve painting features and illuminate others surface activation step. The experimental setup and water contact angle were represented in Fig. 4.

An ArF excimer laser was used to enhance the wettability of PP in water by replacing OH functional group by H atoms [73]. Indeed, C–H and C–H_3 bonds are the prominent important for PP chemical stability. The XPS results show that the increase number of laser shots led to increasing O1s concentration in the presence of water on the surface sample. Additionally, the IR-ATR analysis affirmed that after laser treatment the OH stretching bond appeared at the center of 3300 cm^{-1}, which turn the surface from hydrophobic to hydrophilic. The water contact angle was measured to elucidate the wettability of PP against the number of laser shot and the results exhibited increasing hydrophilicity because of decreasing water contact angle from 93° to 65° at 10,000 shots. The treated PP successfully bonded with an epoxy

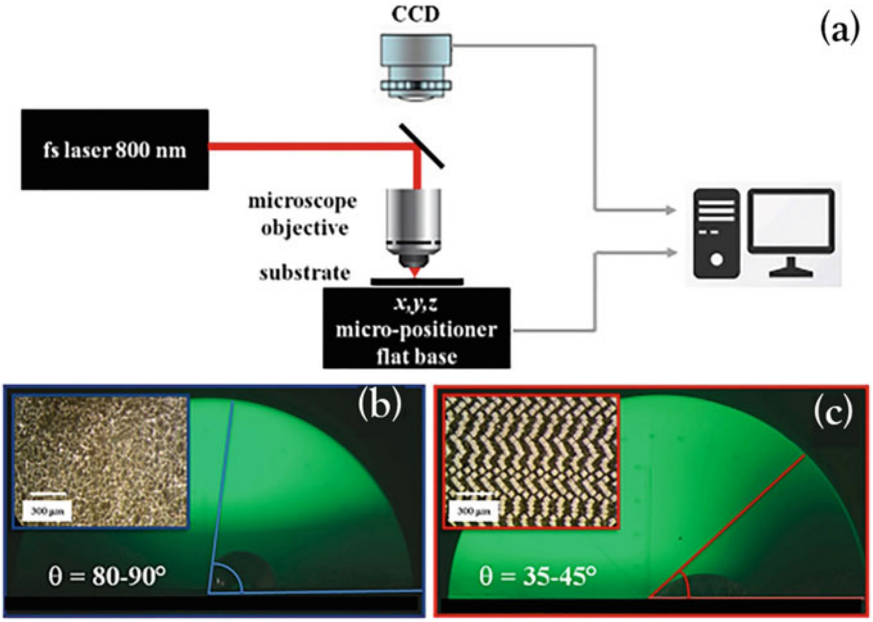

Fig. 4 **a** A illustration of experimental rout and water contact angel for **b** untreated PP and **c** treated PP. the insets show optical microscopic images. (Reproduced from Guarnaccio et al. [72])

adhesive and the tensile shear strength of treated PP was increased about seven times higher than the untreated sample. To overcome lack of wettability of PP surface, the ArF excimer laser was utilized in air medium with different fluences (50, 100, 150, 200 mJ/cm^2) [74]. The surface analysis was deployed to survey the effect of laser and water flux was measured to study storing capability of membrane. The AFM analysis affirmed decreasing of roughness from 48 to 17 nm. Furthermore, laser treatment changed the chemical composition confirmed by a peak located at 1720 cm^{-1} which is a signal of C=O functional group. According to XPS analysis, increasing of carbon bond and O/C was detected and formation of C–O and O–C=O, as well as increasing C=O, contribute to enhancement of wettability. WCA measurement was conducted and the results exhibited laser-modified by 200 mJ/cm^2 possesses the lowest WCA about 75°. Water flux was tested for different applied pressure and the samples treated by 50 and 100 mJ/cm^2 show an obvious increase compared to control sample. The experimental illustration of laser-assisted and water flux test, SEM image and percent of water flux as a function of pressure were illustrated in Fig. 5.

It should be underlined that laser-based techniques have not been extensively studied on polymers. Therefore, the optimum irradiation parameters (such as optimum fluence, wavelength, etc.) by which the better results (better surface morphology and chemistry) can be achieved have not been investigated in detail. Hence, several impacting factors remain unclear and investigation of these factors can stimulate researchers to more study about this technique [67].

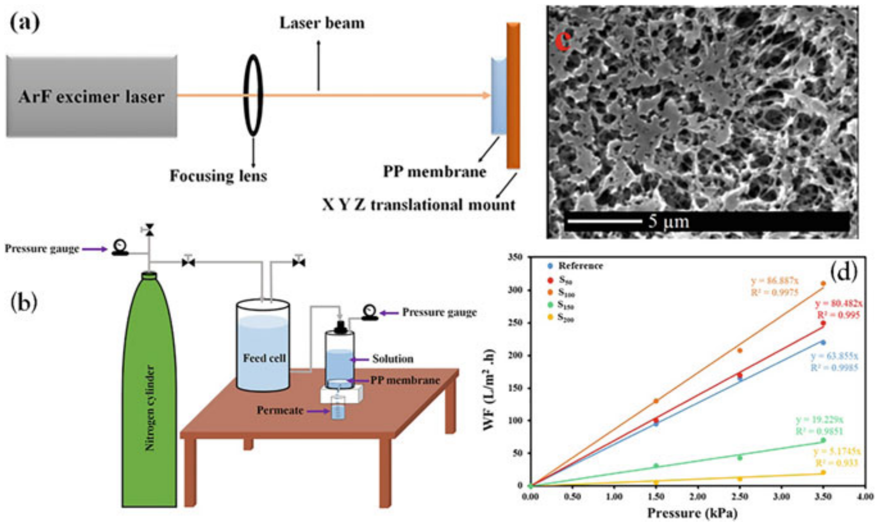

Fig. 5 **a** A schematic illustration of experimental details, **b** illustration for water flux experiment, **c** the SEM of PP morphology for 100 mJ/cm^2, and **d** water flux as a function of pressure. (Reproduced from Mohammadtaheri et al. [74])

5 Comparison of the Laser Treatment and Plasma Modification

Some polymers suffered from their low surface wettability or adhesion, which lead to hinder their application. Using laser and plasma are pioneering methods to modify the surface properties of polymers to achieve desirable products. A comparison discussion of their principles is necessary to get a clear view of the differences between plasma and laser. The interaction of plasma and polymer relied on the interaction of ions or charge carriers [10]. To be more direct, the species of the used gas in plasma could provide different reactions by polymer's surface and the radicals, which are produced during plasma treatment, could contribute to happen other reactions. If the duration of plasma treatment excided, etching may be taken place during it and the losing of material is relied on treatment duration and plasma power [75].

The interaction of laser and polymers is attributed to coherence light, and the influence of laser beam on polymer surface relied on laser properties, such as fluence, the applying wavelength, and power [76]. Laser has been produced in different wavelengths and the interaction of laser beam and polymer surface can be divided by the wavelength range, i.e. the wavelength of laser is of importance to predict the type of interaction in advance. The UV irradiation can break molecular bonding down to photolytic interaction, which is unattainable in IR range. Indeed, in the IR region, the molecular of polymer are excited and the energy state of polymer reached a higher level. Heat generation is the consequence of molecular excitation and leads to breaking bonds and providing an opportunity for thermal reaction. In the visible region, the majority of interaction is associated to absorbing agents, which are decomposed during irradiation [76]. If laser fluence is lower than ablation threshold, surface modification is accomplished without losing weight [77].

From the review of literatures, it is obvious that the argon and nitrogen plasma modification offer multitudinous opportunity to create desired roughness and wetting in the polypropylene [30]. For example, better conductivity for polypropylene is obtained using nitrogen-plasma modification which is well above the conductivity of the untreated one [30]. To now, introducing hydroxyl groups which was attained by plasma modification carried out extensively on polymers have provided superior adhesion and hydrophilicity [27]. Considering the significant potential of laser to alter the surface properties of polymeric materials is crucial [68, 69]. The laser modification technique enjoys advantages which are highlighted as follows. An environmentally friendly polymer modification method with medium cost could be achieved by laser ablation, which is provided high speed and simple process; it is worth mentioning it could apply to large scale with limited damages [27, 67, 78]. Eliminating contamination significantly could decrease by using laser, because laser provides non-contact process. Performing in one-step, laser facilitates surface modification in the absence of chemical components [67]. Accordingly, surface modification of roughness and chemical properties for functionalization of polymer surface is attainable with ease.

Admittedly, it should be considered the low absorption coefficient of polypropylene in the wavelength range of 400 nm to 1600 nm restricts operating lasers which is an obvious handicap [27, 79]. The transparency of polypropylene in the aforementioned wavelength rang has been reported and to tackle this repercussion different methods such as using fillers, carbon pigment, and dyes are utilized [80, 81]. The optical absorption coefficient has been significantly enhanced in the near infrared region [81].

Generally, any method used to modify the surface properties of polymers has advantages and disadvantages. In other words, it is not possible to create all the desired features using one method. We can mention some of these benefits and drawbacks of the plasma modification approach according to the provided descriptions. Restricting the bulk properties changes of the polypropylene, the selection of gas type to make accurate changes, eliminating chemical reagents used in conventional approaches, and the reaching uniformity of surface are classified as obvious merits [34]. In contrast, the shortcoming could be clarified including: providing high vacuum situation, the dependence of modification degree to plasma parameters, costly process, and the absence of ability to control the formation of functional groups during process. One drawback in the use of lasers for treating polymers is their high transparency to the laser wavelength resulting in the minimum absorption of the laser beam [27].

6 Summary

Polypropylene as a promising polymer has a vital role in the industry. Its implementations, however, are constrained by its impractical properties, such as hydrophobicity. Accordingly, plasma and laser modification techniques as two popular methods have been used to develop polypropylene's applications. Any method used to modify the surface properties of polymers has advantages and disadvantages. However, implementing environmentally-friendly and low-cost techniques is of particular interest. The present chapter provided a study on laser and plasma modification techniques of polypropylene membrane. These techniques were explained in terms of applying method and interaction and also compared on the base of effectiveness. In a conclusion, the laser modification technique is as effective as plasma modification with different active gases. The plasma modification technique is applied extensively on polypropylene and the formation of the polar functional groups is observed after the process. The reported results revealed that argon-plasma treatment induces dramatic changes in terms of surface roughness and morphology on polypropylene. Laser-based modifications could, in general, introduce groups containing oxygen on the polymeric surface. Surface treatment by laser source presents better results with no surface damaging and since this process is a non-contacting method, the outcome polypropylene presents better surface properties without additional contamination. Admittedly, the low absorption coefficient of polypropylene is the major handicap putting a limit on using laser sources. However, adding some fillers, carbon pigments, and dyes are recommended as good approaches to enhance absorption coefficient in the near infrared region. It seems that with more interest to use one-step modification techniques such as the laser method, the effect of processing parameters will be cleared which will be a significant achievement in the surface modification topic.

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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

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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

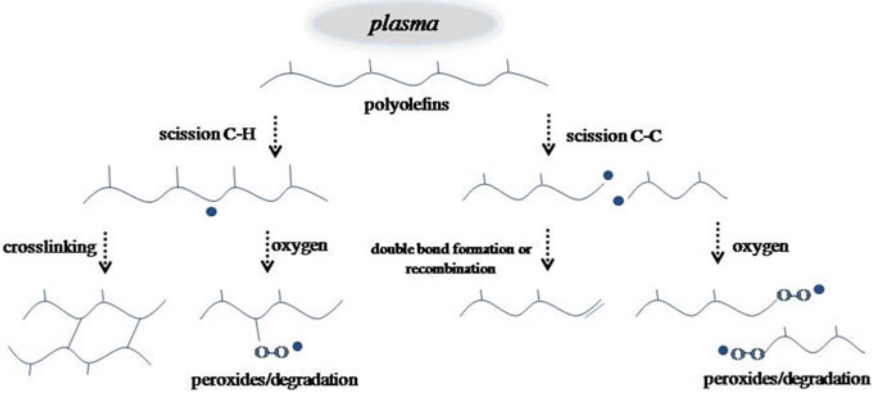


Fig. 1 Main degradation reactions that occur under non-thermal oxygen plasma (adapted from [8])

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].

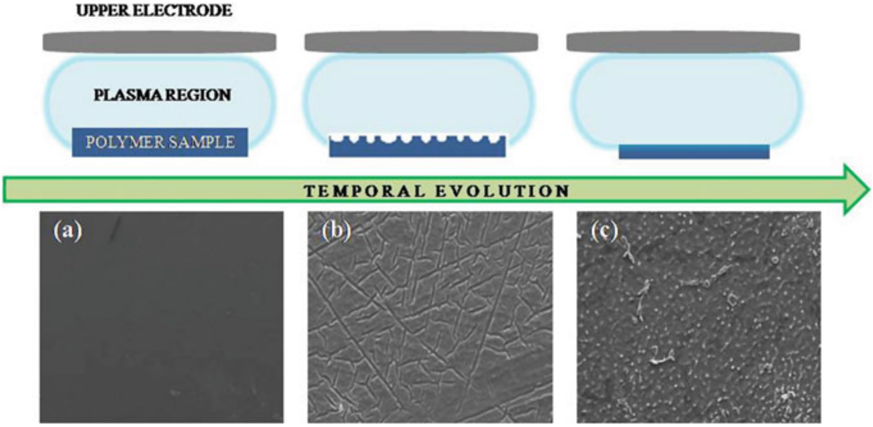


Fig. 2 Erosion on a polymer surface after exposure to non-thermal oxygen plasma: **a** untreated surface; **b** and **c** after 20 and 30 min of exposure, respectively [19]

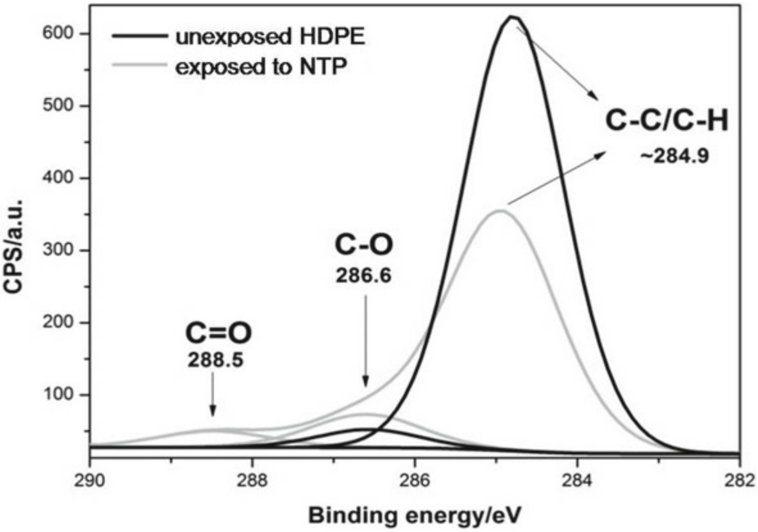


Fig. 3 C1s peaks of high-density polyethylene unexposed and exposed to Ar/O_2 NTP for 60 s (8 mbar, 80 W) [21]

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,

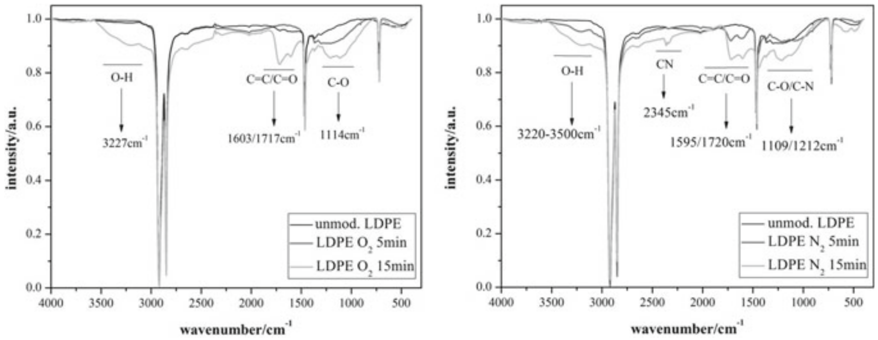


Fig. 4 Sample spectrograms of low density polyethylene unexposed and exposed to O_2 NTP (left) and N_2 (right) plasma treatment, (1 torr, 8 W) [20] (unpublished results)

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

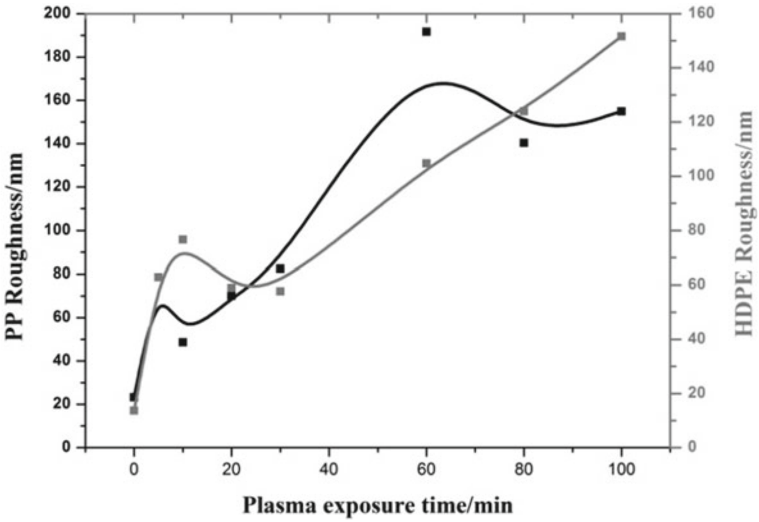


Fig. 5 Average roughness (nm) as a function of the plasma exposure time (min) obtained by AFM, in three different sample areas (5 mbar, 65 W) [21]

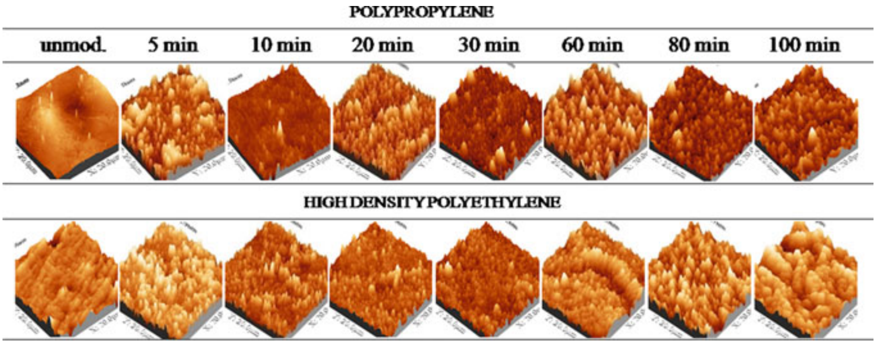


Fig. 6 Atomic force micrographs as a function of plasma exposure time (5 mbar, 65 W) [21]

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,

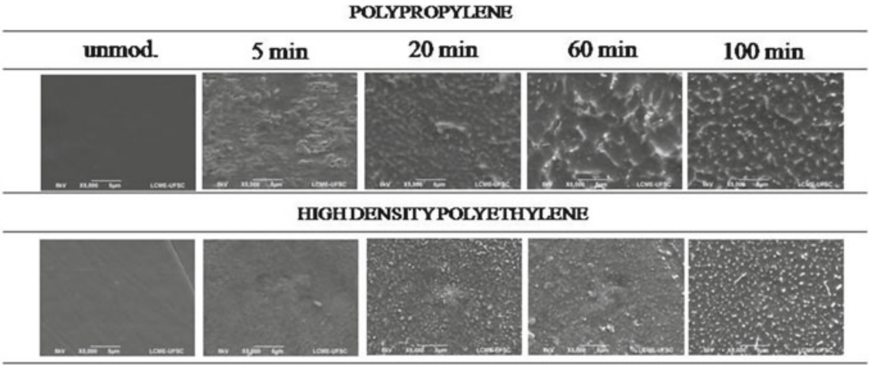


Fig. 7 SEM micrographs as a function of plasma exposure time (5 mbar, 65 W) (5000x / 5 μm scale) [21]

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

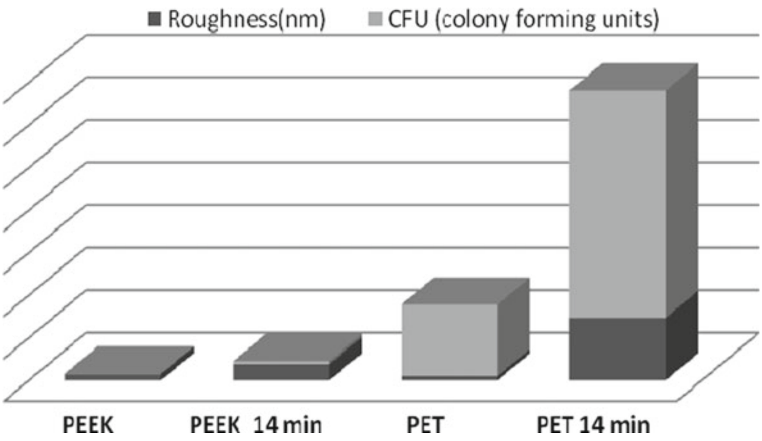


Fig. 8 Roughness (nm) and CFU (*Enterococcus faecalis)* of unmodified PEEK and PET after 14 min exposure to NTP (argon 1.5 L.min^{-1}, 74.6 kPa). WCAs measured after NTP exposure were 33.32° and 33.68°, respectively [29] (unpublished results)

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

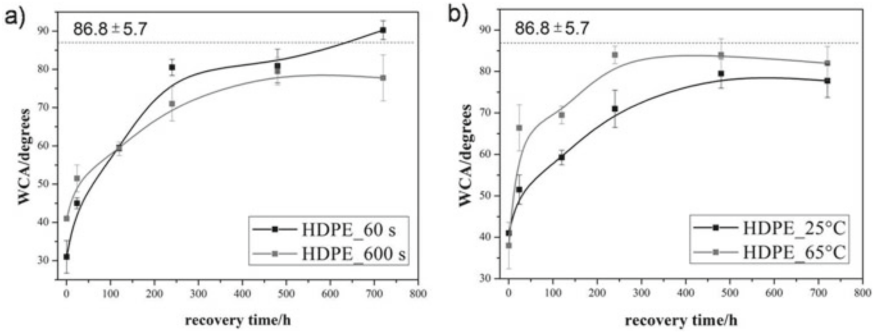


Fig. 9 WCA profiles (degrees) as a function of restoration time (h) for high-density polyethylene: samples **a** exposed to plasma for 60 s and 600 s; and **b** aged at 25 °C and 65 °C [21]

these hydrophilic → 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,

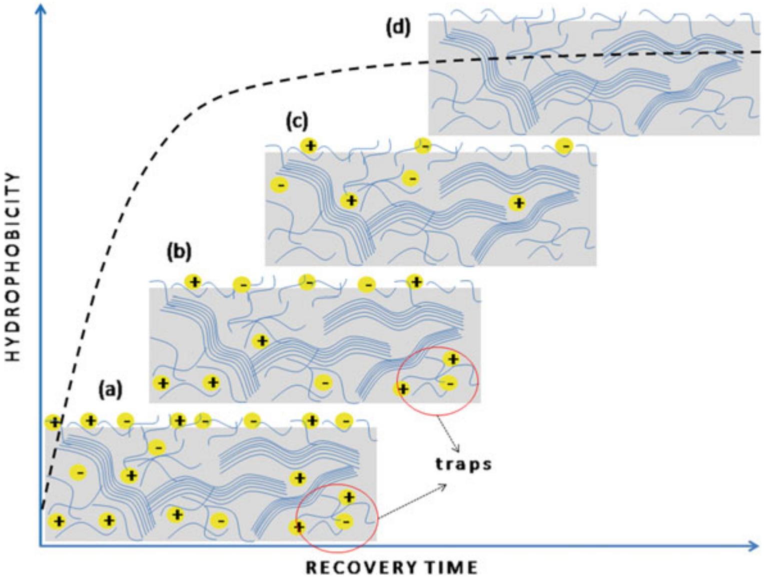


Fig. 10 HR dependence with charges induced by exposure to plasma as a function of time. **a** The charge-carrying fragments at the interface and subinterface, dipole orientation and charge induction; **b**–**c** start of thermodynamic relaxation in fragments of the amorphous fraction and at the interface, 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].

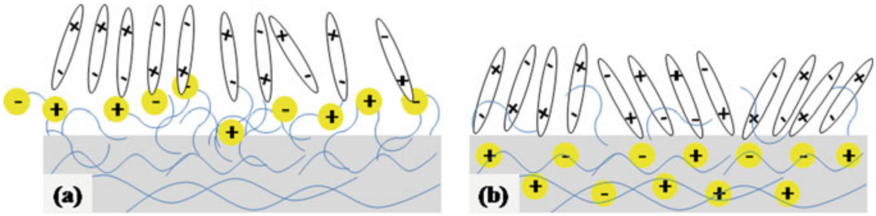


Fig. 11 Plasma-exposed surface: **a** charge-bearing fragments orienting liquid/vapor molecules from the immersion medium (adapted from [38]) and **b** charges trapped in shallow or deep traps, and oriented polar groups of the immersion medium on the surface

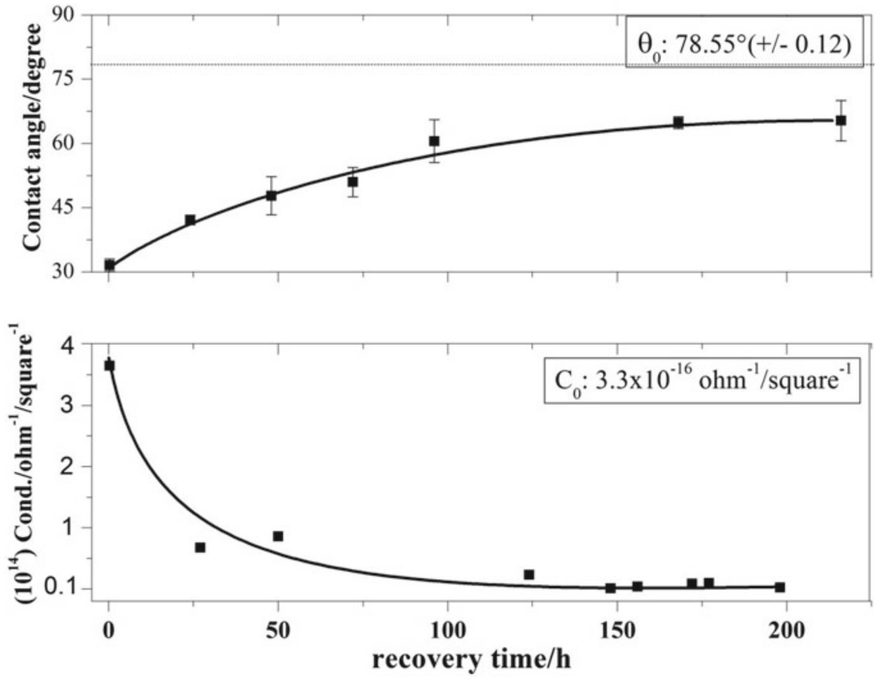
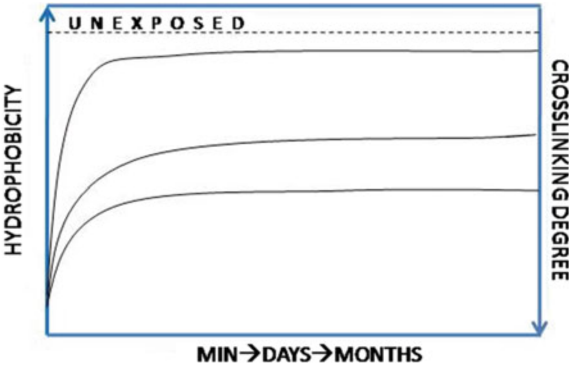


Fig. 12 The profiles for WCA and SEC as a function of time (h) for PET samples exposed to NTP at 8 W [54] (unpublished results)

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 non-thermal 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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Enhanced Fluoropolymer Surface Adhesion by a Plasma Hybrid Process—Metal Plating Technology and Its Application to Millimeter-Wave Devices

Masaaki Okubo

Abstract An improvement of the adhesiveness of PTFE/plastic using a plasma hybrid process, metal plating technology, and its application to millimeter-wave devices are described. Atmospheric-pressure plasma graft polymerization (also called “atmospheric-pressure plasma hybrid surface treatment”), which has been developed by the group of the author, is presented as an innovative surface treatment method to improve the PTFE adhesiveness and enable surface plating with minimal impact on the environment. First, the applicability of PTFE/plastics to millimeter-wave devices is briefly described, while next section presents the atmospheric-pressure plasma hybrid surface treatment that enables plating on PTFE. Next, methods to assess the effect of the surface treatment on PTFE metal plating are described. Final section describes several examples of improved strength of fiber-reinforced composite materials, which have a low dielectric constant similar to that of PTFE and can be used in radar domes. Some trial production results using this plasma hybrid surface treatment technology are also provided. Long-term durable adhesion properties of the surface are improved by this type of plasma treatments.

1 Introduction

Fluoropolymer plastic materials, such as polytetrafluoroethylene (PTFE, $-(CF_2-CF_2)_n-$), perfluoroalkoxy fluoroplastics (PFA, $-(CF_2-CF_2)_n-[CF_2-CF(OCF_2CF_2CF_3)]_m-$), and polychlorotrifluoroethylene (PCTFE, $-(CF_2-CFCl)_n-$), exhibit excellent physicochemical properties, including thermal durability, chemical resistance, electrical insulation, low transmission losses, gas barrier functionality, flame retardancy, and low friction. Therefore, a wide range of applications of these polymers are currently being developed. However, layering and metal plating with these materials is difficult, as they do not adhere easily to themselves or other materials. If layering and plating were possible, multiple applications in various fields could

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be realized. Examples of such applications include automobile-related electrical parts, such as car navigation systems and millimeter-wave radars, telecommunication devices, such as wireless and optical communication devices, and the millimeter-wave coaxial cables used in various fields, such as industrial device wiring and connection. The relative dielectric constant (ε_r) and dielectric loss tangent (tanδ) of PTFE are both low; hence, antennas and cables that use PTFE as the internal dielectric material present extremely low transmission losses. However, as PTFE is a low-adhesion material, the above issues remain during metal coating processes, such as copper film adhesion and metal plating on the PTFE surface.

On the basis of the background described above, the improvement of the adhesiveness of PTFE/plastic using a plasma hybrid process, metal plating technology, and its application to millimeter-wave devices are described here.

Atmospheric-pressure plasma graft polymerization (also called "atmospheric-pressure plasma hybrid surface treatment") [1–8], which has been developed by the group of the author, is presented as an innovative surface treatment method to improve the PTFE adhesiveness and enable surface plating with minimal impact on the environment.

In Sect. 2 of this chapter, the applicability of PTFE/plastics to millimeter-wave devices is briefly described, while Sect. 3 presents the atmospheric-pressure plasma hybrid surface treatment that enables plating on PTFE. In Sect. 4, methods to assess the effect of the surface treatment on PTFE metal plating are described. Finally, Sect. 5 describes several examples of improved strength of fiber-reinforced composite materials, which have a low dielectric constant similar to that of PTFE and can be used in radar domes. Some trial production results using this plasma hybrid surface treatment technology are also provided. Long-term durable adhesion properties of the surface are improved by this type of plasma treatments [9–29].

2 Applicability of PTFE/Plastics in Millimeter-Wave Devices

2.1 Plastic Properties: Dielectric Constant, Dielectric Loss Tangent, and Hydrophobicity

Figure 1 shows the dielectric constant (ε) and dielectric loss tangent (tanδ) of various plastics [30, 31]. Fluoroplastics, such as PTFE, PFA, and PCTFE, present the smallest dielectric constants and dielectric loss tangents among them. Liquid crystal polymers (LCPs) exhibit also similarly small values. In other words, these plastics exhibit low transmission losses when used as electronic substrates. The application of PTFE to millimeter-wave antennas is very promising and a particularly desired goal. As the era of next-generation 5G mobile telecommunication systems and automatic driving operations using millimeter-wave devices approaches, a paradigm change is also occurring in substrate materials for wireless communication devices, where the transition from conventional glass epoxy substrates and polyimide substrates to low-transmission-loss

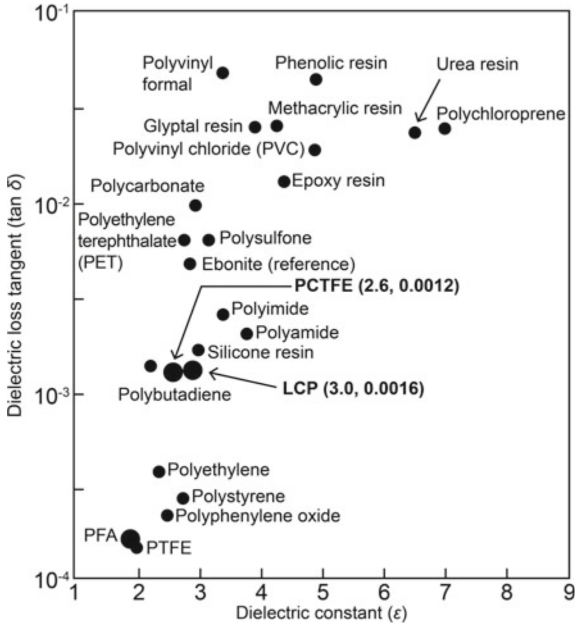


Fig. 1 Relation between dielectric constant and dielectric loss tangent of various plastics. Data are added to graphs in Refs. [3, 4]

materials, such as LCPs and fluoroplastics, is occurring at a fast pace [32]. The latter materials are hydrophobic and hence biologically compatible with the human body, which allows for their application in implantable electronic devices.

2.2 Small-Size/High-Performance Millimeter-Wave Band Antennas

Developed examples of antennas for automobile radars using PTFE and LCPs are introduced according to Ref. [33]. Fujitsu Ten Ltd. (Now, Denso Ten Ltd.) has been continuously developing radars for automobiles using the millimeter-wave band at 30–300 GHz. Important electrical parts are the flat tri-plate antennas installed in automobiles and simple microstrip antennas. The flat antenna is indispensable to simultaneously realize automobile mountability and scanning functions. Moreover, microstrip antennas, with their simple structure, are particularly effective for cost reduction. However, as microstrip antennas contain a plastic substrate, the transmission losses are high, which reduces their efficiency.

Figure 2 schematically shows an example of a microstrip antenna structure. The microstrip antenna contains a dielectric plastic substrate that is interposed between a conductive feeder line and grounded plate (copper foil). To achieve high performance of the antenna, a thin dielectric material with a low relative dielectric constant is required. The microstrip antenna is also called a printed antenna, and it is constructed

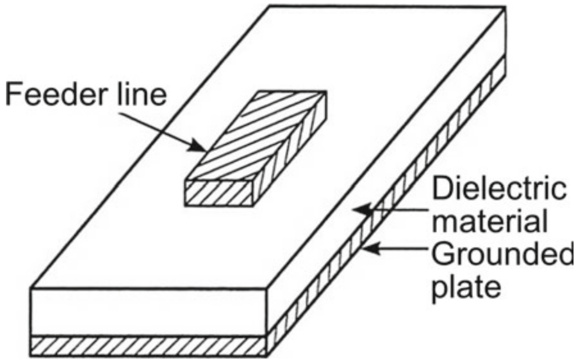


Fig. 2 Structure of microstrip antenna

with dimensions matching the resonance frequency. This antenna is also a narrow-band, wide-beam antenna.

The electrical properties, mechanical strength, environmental durability, etc. of the plastic substrates of microstrip antennas have been studied in detail. When the antenna is used in the millimeter-wave band, its electrical properties are particularly important. As stated previously, the principal electrical properties of the substrate are its dielectric constant and dielectric loss tangent. Since the frequency bandwidth becomes narrower with the increasing dielectric constant, a dielectric constant of approximately three or smaller is usually appropriate. Uezato et al. [33] provides a description of the target materials LCPs and fluoroplastic PTFE. The results there show that the losses are lower with PTFE. Therefore, the possibility of realizing high-efficiency antennas using PTFE as the substrate material is a reality.

PTFE is a poorly adhesive material, and unresolved issues remain when a copper coating is attached to its surface. A thin adhesive layer of hydrophilic polyacrylic acid (thickness ~100 nm) is obtained when the atmospheric-pressure plasma hybrid treatment described in the next section is performed. Consequently, the above-described microstrip antenna could be potentially constructed by adhering a metal film to the polymer surface or by performing electroless plating, followed by electrolytic plating. Once this type of antenna is built, little deterioration of the electrical properties is expected as the polyacrylic acid layer interposed between the metal and dielectric material is very thin.

2.3 Applicability to High-Frequency Coaxial Cables

PTFE can be similarly applied to waveguides that supply microwaves or the following described coaxial cable assemblies with a high frequency corresponding to millimeter waves. Since both LCP and PTFE materials display low ε_r and tanδ, coaxial cables that use both materials as internal dielectrics exhibit extremely low transmission losses. Coaxial cables are used in a broad range of fields, including wireless and optical telecommunication systems, wiring and connection of industrial devices, and

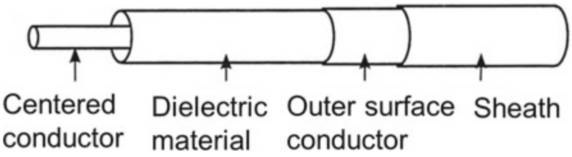


Fig. 3 Structure of coaxial electrical cable

automobile-related parts, such as car navigation systems and millimeter-wave radars [34]. In recent years, the applicable frequency bandwidth of coaxial cable assemblies has increased from several tens of GHz to several hundreds of GHz, and the bandwidth continues to widen. In response to these developments, high-frequency coaxial cable assemblies for millimeter-waves using porous PTFE as the dielectric material are already being commercialized [34].

The structure of an ordinary coaxial electrical cable is shown in Fig. 3. When poorly adhesive PTFE is used as the dielectric material, a copper coating or copper braided wire is used as the external dielectric material, but the dielectric material and metal do not adhere well to each other. Therefore, a surface treatment is needed. As shown in the figure, the cable is composed of a central conductor, such as a silver-plated copper wire; a dielectric material, such as porous PTFE; an outer-surface conductor, such as a silver-plated copper foil roll or silver-plated copper braided wire; and a sheath, such as fluorinated ethylene propylene (FEP). The processes listed below are normally used to yield excellent characteristics. Porous PTFE, the plastic material with the smallest tanδ and ε_r values is typically used. Furthermore, a uniform dielectric material is laid in the longitudinal direction on both the external diameter and void fraction using the paste press-out method. In addition, the outer surface conductor is formed in a spiral roll of silver-plated tape, where the tape width and roll pitch are strategically customized to ensure smooth signal flow. For low attenuation, silver-plated copper with low resistivity and porous PTFE with low dielectric constant and dielectric loss tangent are used.

However, as PTFE is a poorly adhesive material, certain problems remain to realize high-performance coaxial cables when a copper plating layer is deposited on its surface. Therefore, a thin adhesive layer of hydrophilic polyacrylic acid (thickness ~100 nm) can be laid on the surface of PTFE using the atmospheric-pressure plasma hybrid treatment described in Sect. 3. Upon adhering a metal film to the surface or performing electroless plating, followed by electrolytic plating, a high-performance coaxial cable can be built. Once this is accomplished, negligible deterioration of the electrical properties is expected, similar to the case of the microstrip antenna, because the polyacrylic acid layer inserted between the metal film and dielectric material is thin.

2.4 Applicability to Radomes

Section 5 describes the improvement of the strength of fiber-reinforced composite materials for aerospace applications through the atmospheric-pressure plasma graft

Fig. 4 Appearance of a radome at Osaka international airport

polymerization treatment. The word “radome” is a combination of two words: “radar” and “dome,” which are used to protect radar antennas from the natural environment, mainly from wind, rain, snow, etc., in airports or aircrafts themselves. Figure 4 shows an example of the outer appearance of a radome in an airport.

The use of a radome mitigates the effects of environmental conditions on the antenna system. Specifically, it provides wind speed, rain, and sunlight resistance. Therefore, deterioration of the antenna system over time can be minimized, without the need for adding reinforcements. Therefore, the antenna systems can be used safely over longer terms [35]. The materials used for radomes include glass fiber, PTFE, and fiber-reinforced composite materials, which allow radiowaves to pass through easily. Moreover, the electrical properties can be customized for the frequency band used. In addition, the land radomes placed at airports are actually buildings and have access doors, lightning rods, aircraft obstacle lights, etc.

Assuming that the radome is the final applied product, the section introduces several attempts to improve the strength of fiber-reinforced composite materials. Some trial production results using such plasma hybrid surface treatment are described. The treatment is performed to either make the fiber fabric hydrophilic or to modify the surface for improved adhesiveness. This research will contribute to broaden the applicability of organic fiber-reinforced composite materials with low dielectric constants (~3) and high radiowave permeabilities in aerospace structure materials.

3 Atmospheric-Pressure Plasma Hybrid Surface Treatment Toward Metal Plating of PTFE

3.1 *Effect of Plasma Surface Treatment and Plasma Graft Polymerization Treatment*

Figure 5 shows an overview of the electrode system of the surface treatment device using atmospheric pressure plasma. An unsteady current, e.g., pulses, is applied between the positive and negative sharp tip electrodes under argon flow, forming a plasma flow or jet. A film of the targeted material sample is passed through the gap over which the plasma jet is ejected, whereby the surface of the film is treated. In this case, only the single-sided surface impinged by the jet is treated. The use of this method, the so-called gliding arc-discharge plasma method, for surface treatment is relatively new, but several plasma-generation products that use it exist already in the market. In this method, because a plasma jet is used, it is possible to treat a three-dimensional or large object. However, to treat a large surface area, it is necessary to consider whether to move the torch according to the size or shape of the treated surface or to employ multiple torches. It is noted that, compared to surface treatment with argon-gas or air plasma alone classified as "plasma solo surface treatment", the present surface treatment under a monomer gas environment (e.g., acrylic acid) should be referred to as a "plasma hybrid surface treatment."

In the treatment system shown in Fig. 5, polymer, glass, and metal surfaces can be treated by a "plasma solo surface treatment" without a monomer gas environment, and the surface of these materials frequently becomes markedly hydrophilic with improved adhesiveness. This is because high-energy electrons (~1–10 eV) generated

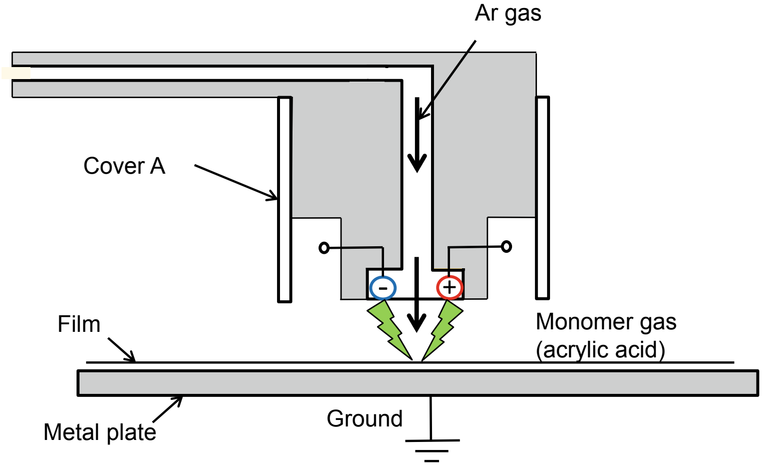


Fig. 5 Overview of electrode system of surface treatment device using atmospheric pressure plasma (Nozzle cover A is attached)

by electrical-discharge-induced atmospheric-pressure plasma induce the dissociation of the main and side chains on the material surface into radicals. Furthermore, the molecules of atmospheric gases, such as air and water, dissociate and generate radicals too. The electrons, radicals, and ions generated by the plasma are able to degrade organic materials such as the "dirt" (oils and fats) on the surface of materials. As a result, the surface becomes hydrophilic. However, owing to recombination reactions between radicals of the gas and on the surface, hydrophilic functional groups, such as hydroxyl (−OH), carbonyl (>C=O), and carboxyl (−COOH) moieties, are formed on the surface of the material. As a result of these phenomena, the surface becomes hydrophilic, the surface free energy increases, and it becomes easier to adhere or attach other materials to the surface.

However, if the treated materials are left in atmospheric air after the plasma solo surface treatment, the hydrophilic surface disappears almost completely within several days to one week, as the segments that include the functional groups burrow inside the plastic. In addition, plastic surfaces with low chemical reactivity, such as the surface of fluoroplastics like PTFE, barely become hydrophilic with such a plasma solo treatment.

Therefore, a treatment in which the effects of the plasma remain permanently without dissipating is highly desired. The "plasma hybrid surface treatment" has been proposed by the group of the author as such a method. Specifically, "plasma graft polymerization" is performed: monomers with unsaturated bonds (double bonds), such as acrylic acid CH_2=CHCOOH, are successively polymerized on the surface of the treated material activated by plasma irradiation, whereby a grafted functional film is formed. This permanent surface treatment method is typically used at reduced pressure below atmospheric pressure. However, the authors have also performed it with high efficiency using plasma at atmospheric pressure, establishing a new technology, "atmospheric-pressure plasma graft polymerization" [1–8, 36, 37]. A treatment system similar to that shown in Fig. 5 has been used for the present plasma treatment. Generally, permanent surface treatment methods in which a plasma treatment and a treatment with liquid chemicals, such as monomers or paint, are performed in parallel are referred to as "plasma hybrid surface treatments". The following text describes the principles, methods, and examples of atmospheric-pressure plasma graft polymerizations, a technology that can powerfully attach metal films to the surface of PTFE.

3.2 Principles of Atmospheric-Pressure Plasma Graft Polymerization and Adhesion Improvement

The principles of the present atmospheric-pressure plasma graft polymerization are summarized in the following reactions, using plasma graft polymerization of a hydrophilic monomer, in this case, acrylic acid, as an example of a double-bonded monomer.

Atmospheric-pressure plasma application (radical generation on the surface of fluoroplastics by plasma-induced electrons)

$$R - F \rightarrow R\cdot + F\cdot \tag{1}$$

$$R\cdot + CH_2 = CHCOOH \rightarrow R{-}CH_2{-}C\cdot HCOOH \tag{2}$$

Graft polymerization (hydrophilic layer formation)

$$R\cdot + nCH_2 = CHCOOH \rightarrow R{-}(CH_2{-}CHCOOH)_n{-} \tag{3}$$

where R represents the main chain of a fluoroplastic composed of C, H, O, and F atoms, and R·, F·, and R–CH_2–C·HCOOH are radicals with an unpaired electron. Although in reaction (1), cleavage of the C–C bonds in the main chain of PTFE is also possible, cleavage of the C–F bond occurs more frequently. The electrons generated by the atmospheric-pressure plasma (energy ~5 eV, electron number density ~10^{17} m^{-3}) collide with the monomer molecules, as well as the material surface, inducing the cleavage of covalent bonds and the formation of radicals. Finally, reaction (3) affords a hydrophilic graft polymerization layer of –R(CH_2–CHCOOH)$_n$ on the surface of the fluoroplastic R–F, which improves the adhesive properties of its surface.

In reduced-pressure plasma graft polymerization, which is the conventional technology, the energy of the generated electrons is relatively higher and the density is lower than the atmospheric-pressure plasma. Furthermore, to achieve a reduced-pressure environment, a vacuum chamber and vacuum pump are required for plasma generation. On the other hand, the authors have developed a method using atmospheric-pressure plasma by making use of high concentrations of generated radicals. This technology leads to high adhesion efficiency. Since the treatment can be performed at atmospheric pressure, it can be easily incorporated into manufacturing lines with high productivity. This treatment is also advantageous because it has a negligible impact on the environment, as it does not use harmful gases or solutions of heavy metals as in the case of the sodium-ammonia method.

3.3 Instrumentation Required for the Treatment

Figure 6 shows a schematic of the atmospheric-pressure plasma graft-polymerization treatment apparatus developed by the author's group, which can be used to treat an A4-size (210 × 297 mm) fluoroplastic film. Using this apparatus, the author has carried out sample treatment tests on a variety of polymers, metals, and glasses. The thickness of the sample is in the range of 300 μm–20 mm. The apparatus is placed inside the draft chamber shown in the figure with dotted lines. A single stainless evaporation vessel or double ones filled with the liquid acrylic acid monomer (FUJIFILM Wako Pure Chemical Industries, purity of 98 mass%) is placed on top of a plate heater equipped with a temperature regulator and a transformer as a steam generator inside the acrylic chamber. The monomer liquid is maintained at a constant temperature (~60 °C), and the monomer is vaporized inside the acrylic chamber, the

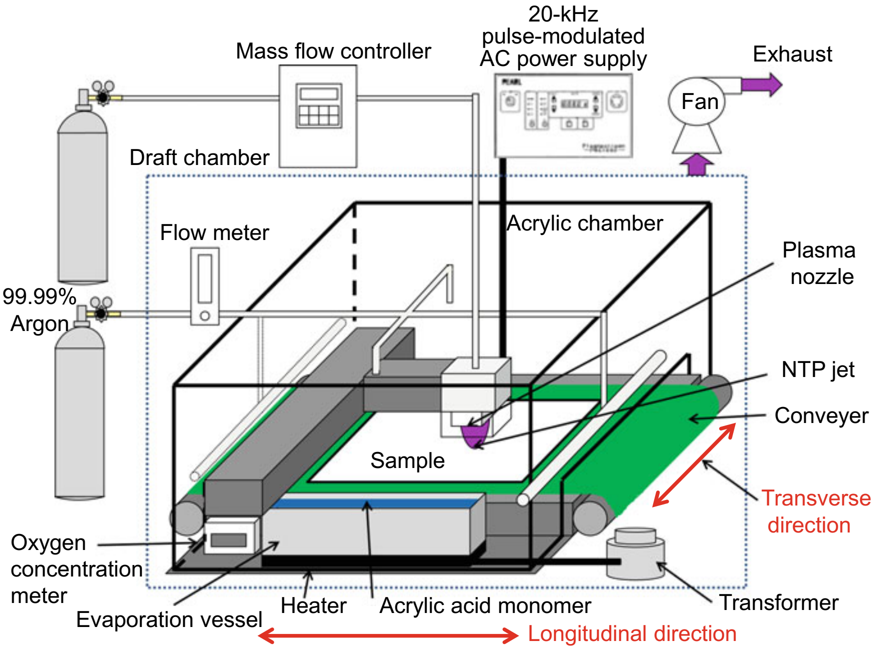
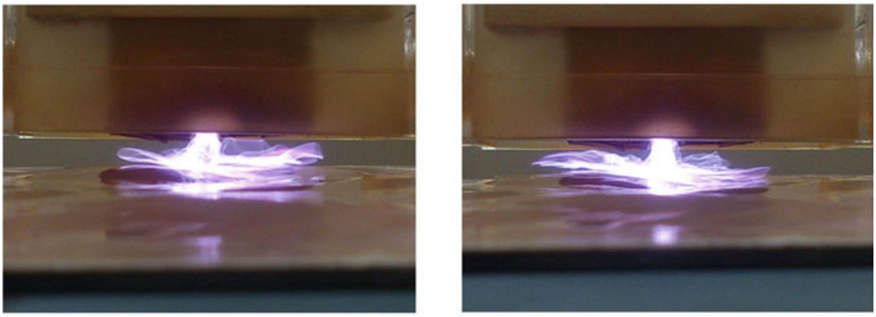
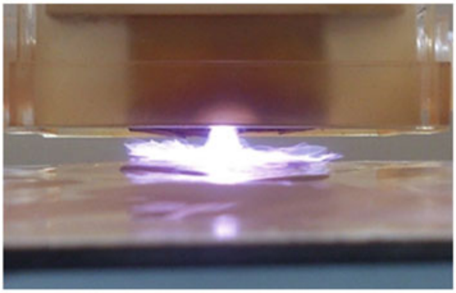


Fig. 6 Schematic of the atmospheric-pressure plasma graft-polymerization treatment apparatus

concentration of which is approximately 2000 ppm. Industrial argon with purity of 99.99% is used as the plasma-forming gas, and the argon flow in the plasma torch is regulated at a constant flow rate of Q. In later experiments, Q is changed from 30 to 50 L/min to know the effect of it. As shown in Fig. 5, a pair of sharp tip wire electrodes is located inside the plasma torch. When a pulse-modulated AC high-voltage (20 kHz and 24 kV) is applied, a gliding arc discharge is generated. The atmospheric-pressure low-temperature plasma jet formed by the s gas discharge the temperature of which is below 80 °C acts on the film sample surface on top of the conveyor to initiate the surface treatment. Graft polymerization is performed in an argon and acrylic acid steam environment, with the plasma radicalizing the flow while simultaneously cleaving the C−F bonds on the surface. The characteristic of this method is that the acrylic acid steam is ionized and a green colored plasma jet is generated. The plasma torch moves in the lateral direction as the sample is transported by the conveyor in the longitudinal direction. The whole surface of the A4-size film is treated. In order to place the plasma torch under a positive pressure argon environment, the argon gas also flows into the acrylic chamber. Moreover, to prevent air from flowing in through the entrance and exit of the film conveyor, gas injection-type curtains are generated at the entrance and exit. The total flow rate q of the flows in the chamber and gas flow curtains is 20 L/min. Furthermore, the chamber has to be thoroughly purged with argon gas before the experiment to remove any air inside the acrylic chamber.



(a) $Q = 30$ L/min (b) $Q = 40$ L/min



(c) $Q = 50$ L/min

Fig. 7 Photographs of plasma jets at varying flow rates of argon gas

3.4 Effect of Gas Flow Rate on the Treatment

Figure 7 shows photographs of the plasma jets at varying flow rates of argon gas. The figure shows a side-image during the film treatment. The gap between the torch and the film surface is 10 mm. As the flow rate increases, the plasma jet becomes longer. Observation of the plasma under these conditions reveals that the level of contact between the plasma and film surface is low at $Q = 30$ L/min and the highest at $Q = 50$ L/min. The adhesive properties are the greatest at $Q = 40$ L/min, as explained in more detail later. A stable and uniform monomer environment is formed by selecting the optimal flow rate, and stable, large adhesion is successfully achieved. The color change observed on the fluoroplastic surface during the sodium-ammonia treatment, i.e., the conventional surface treatment technology, does not occur in the present plasma treatment.

4 Surface Treatment Assessment and Technology for PTFE Metal Plating

4.1 Contact Angle Measurement

To evaluate the surface hydrophilicity of the treated fluoroplastic films, the contact angle can be measured with a measurement device (Kyowa Interface Science, CA-VE) after adding a 5 μL drop of purified water to the surface. Smaller contact angles indicate more hydrophilic surfaces. As an example, the contact angles of untreated films of PFA, PTFE, and PCTFE are large at 94°, 104°, and 91°, respectively; hence, those surfaces are hydrophobic. After treating those surfaces in a laboratory prototype plasma hybrid surface treatment apparatus, the contact angles decrease considerably, becoming 44° for PFA and 39° for PTFE (one second after dropping the water droplet). Interestingly, the contact angle rapidly decreases with time: in the case of PTFE, it drops to 17° in 2 min and reaches saturation at just 10°; that is, the surface becomes superhydrophilic.

4.2 T-type Peeling Test Method and Results

The surface of a highly pure PTFE sample is subjected to the previously described surface treatment. After adhering a 25-mm-wide stainless-steel plate to the treated sample using a 2-part epoxy adhesive (Konishi E-set), the adhesive strength is evaluated by performing a T-type peeling test. A peeling-test machine (digital force gauge plus electrical measurement stand ZTA-100 N + MX2-500 N, Imada Co., Ltd., Japan) is used in this T-type (90°) peeling test. A piece of a non-adhesive sample is placed in a clamp, the stainless-steel plate is fastened by a jig, and allowed to slide from left to right, while the tension angle is maintained at 90°. The peeling strength or adhesive strength is measured while the test piece is peeled by pulling upward at a peeling speed of 100 mm/min. The sample is layered in the following order: PTFE film/plasma graft polymerization layer/epoxy adhesive layer/stainless-steel metal plate. It can thus be confirmed that there is sufficiently large adhesive force between the plasma graft polymerization layer and epoxy adhesive layer and between the epoxy adhesive layer and stainless-steel metal plate layer. Therefore, peeling is observed to occur mainly at the interface of PTFE/graft polymerization layer.

The results of the T-type peeling test are described below. PTFE (thickness 0.2 mm) is treated by nonthermal plasma graft polymerization at an argon main flow rate of 30, 40, or 50 L/min, an acrylic acid temperature of 60 °C, and a head feed rate of 4 mm/s, and the T-type peeling test is then performed to measure the adhesive strength. The peeling test is typically performed six times at each flow rate. The results show that the maximum adhesive strength for a width of 25 mm is 45.3 N at 30 L/min, 65.0 N at 40 L/min, and 57.5 N at 50 L/min. Furthermore, the average

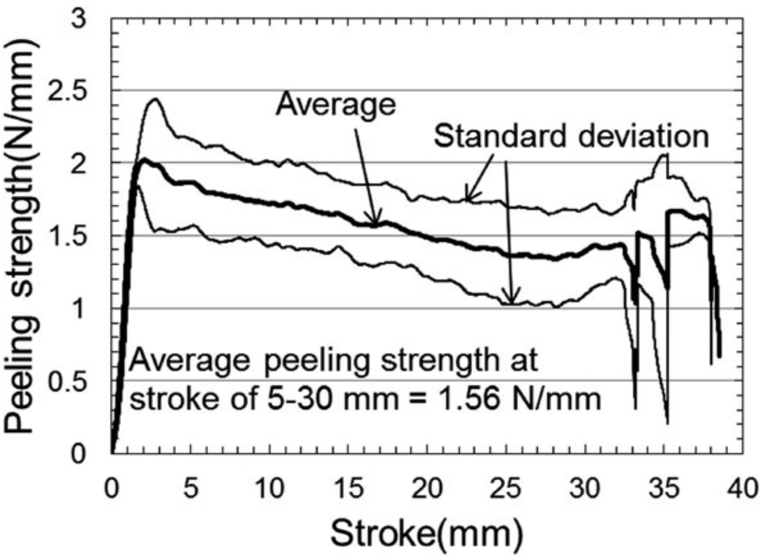


Fig. 8 Measurement results of the curve of stroke–strength at a flow rate of 40 L/min. Maximum average peeling strength for six samples is 2.0 N/mm

adhesive strength for a width of 25 mm is recorded as 20.3 N at 30 L/min, 45.3 N at 40 L/min, and 26.8 N at 50 L/min. In other words, the maximum and average adhesive strengths are both observed at 40 L/min.

Figure 8 shows the measurement results of the curve of stroke–strength at a flow rate of 40 L/min [2]. The number of samples is six, and the three curves in the graph represent the average value and average value plus and minus standard deviation (±SD). The unit of N/25 mm on the vertical axis represents the peeling strength for a width of 25 mm, where N denotes the unit Newton. Although the variation in the data is somewhat large, a maximum adhesive strength of 2.0 N or more per 1 mm of width and an average adhesive strength of 1.56 N per 1 mm of width are observed. This adhesive strength is very high, and it could not have been achieved without using a sodium solution solvent surface treatment agent, which is the conventional technology. The best results for both the maximum and average adhesive strengths are obtained at a flow rate of 40 L/min. The reason for this is discussed below. First, when the flow rate is low, plasma jet injection and the activation of the monomer or PTFE surface are insufficient, resulting in low adhesive strength. When the flow rate is high, the monomer concentration is diluted or the plasma energy for the unit gas flow rate is low, causing a reduction in the adhesive strength. Thus, the peak strength is observed at $Q = 40$ L/min. Based on these results, we can conclude that PTFE adhesiveness is markedly improved by performing plasma graft-polymerization in a highly concentrated acrylic acid environment using a corona discharge plasma device.

The maximum peeling strength or adhesive strength (value for a width of 25 mm) achieved previously for PTFE—stainless steel materials is shown in Table 1. The

Table 1 Maximum peeling strength of T-type peeling strength for three-types of fluoropolymer plastics (Use of acrylic acid, value for sample width 25 mm, maximum values until April 1, 2018)

	Untreated	Ar plasma solo treatment	Plasma graft-polymerization treatment
PTFE	Lower than 0.3	6.7	65.0
PFA	Lower than 0.6	–	50.0
PCTFE	Lower than 0.6	–	35.5

maximum peeling strength is determined from the maximum load point in the elongation—peeling strength diagram. It is known that the adhesiveness of fluoroplastics, unlike other polymer materials, does not increase much after a plasma solo treatment. However, if the conditions are suitable, the adhesiveness increases to a certain degree, e.g., 6.7 N in the case of PTFE. The peeling strength for untreated PTFE, PFA, and PCTFE is up to 0.3, 0.6, and 0.6 N, respectively; hence, adhesion is difficult. Furthermore, upon plasma graft polymerization treatment, the peeling strength is very high, 65.0, 50.0, and 35.5 N, respectively. It is concluded from these results that the peeling strength or adhesive strength is sufficient to enable applications for fluoroplastic endoscopes, chemical liquid injection tubes, and electronic substrates.

4.3 Method of Copper Plating on PTFE and Results

Through trial and error, we have successfully used the sensitizing–activating method to perform electroless copper-plating on the surface of PTFE films treated by atmospheric-pressure plasma graft polymerization [3]. The specific procedures are described below.

(1) Sensitizing process: The plasma graft polymerized PTFE film is immersed for 5 min in a mixed aqueous solution containing 20–40 g/L $SnCl_2$ and 20–40 mL/L HCl, after which it is washed with purified water.

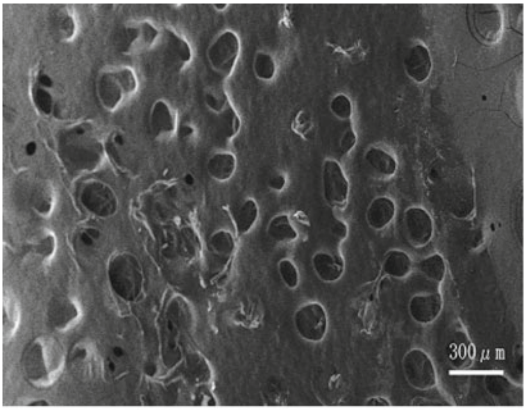
(2) Activation process: The film is immersed for 5 min in a mixed aqueous solution containing 0.25–0.50 g/L $PdCl_2$ and 2.5–5.0 mL/L HCl, after which it is washed with purified water.

(3) Alkaline cleaning process: To remove the tin on the film and metalize it with palladium, cleaning with an alkaline solution is performed. Specifically, the film is immersed in 10% NaOH at room temperature for 10 min and washed again with purified water. When the treated film is immersed in NaOH for an extended period of time, the polyacrylic acid polymerized layer begins to peel off and the process fails.

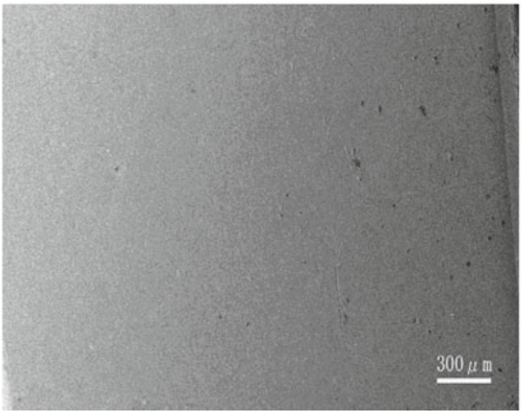
(4) Electroless plating process: After finishing the palladium metallization, the sample is immersed for 3 min in a copper-plating solution (concentration of $CuSO_4 = 3.5$ g/L, Rochelle salt $KNaC_4H_4O_6{\cdot}4H_2O = 34$ g/L, $Na_2CO_3 = 3.0$ g/L, $NaOH = 7.0$ g/L, and 37% formalin $HCHO = 13$ mL/L) under stirring.

Then, it is washed with purified water and dried. To increase the thickness of the metal plating, electrical plating can be performed after the electroless plating procedure.

Figure 9a and b show SEM images of copper plating on untreated and treated PTFE film surfaces (Nikon E − SEM2700 is used), respectively. Many holes with a diameter of 100–200 μm are observed on the surface of the untreated sample, as a result of the formation of bubbles caused by the hydrophobicity of the surface. In this case, uniform metal plating is impossible. Figure 9b shows the very smooth metal-plated surface obtained for the treated film, where none of the holes in Fig. 9a are observed.



(a) copper plating for untreated PTFE film



(b) copper plating for plasma graft polymerization treated PTFE film

Fig. 9 SEM images of untreated and treated PTFE film surface copper plating

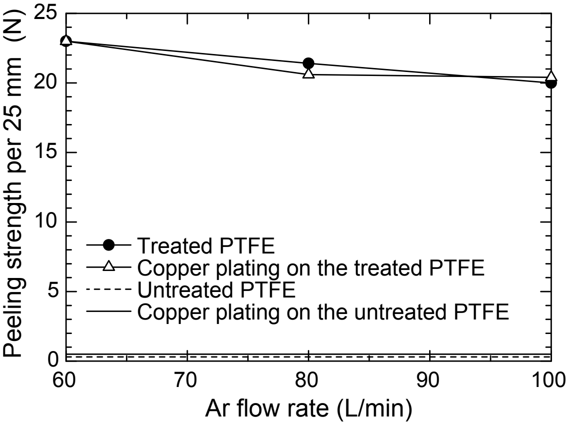


Fig. 10 Example of results for T-type peeling tests for metal plating layers on treated and untreated PTFE films (the effect of argon gas flow rates in plasma graft polymerization on the peeling strength)

Electroless copper plating can be performed on four types of PTFE-treated/untreated samples. Figure 10 shows the results when a stainless-steel plate is adhered to the surface of one of these samples during the previously described T-type peeling test. The horizontal axis shows the argon gas flow rate. The peeling strength or adhesive strength of the untreated sample is less than 0.5 N in the figure, while the maximum peeling strength or adhesive strength for a treated sample is 23 N. This value is large and approximately 50 times larger than that of the untreated sample. The thermal durability at 300 °C and 1 min of the copper plating was also confirmed.

4.4 Method of Nickel Plating on PTFE and Results

Through trial and error, we successfully used the catalyzer–accelerator method to perform electroless nickel plating on a PTFE film treated by the atmospheric-pressure plasma graft polymerization [6]. The specific procedure consists of the following processes.

(1) Activation process: The film is immersed in Kondilizer FR Konku (concentration = 50 mL/L), a chemical that improves the adherence of catalysts, for 5 min at 40 °C, after which it is washed with purified water.
(2) Catalyzer process: A catalyzation treatment is performed with a mixed colloidal solution of Sn^{2+} and Pd^{2+}. The temperature of the solution is 35 °C with a sintering time of 6 min. Then, the film is washed with purified water.
(3) Accelerator process: After immersing the film in an accelerator solution (an acidic solution with concentration of 200 mL/L) at a constant temperature for 5 min, it is washed with purified water.
(4) Electroless plating process: The film is immersed in an acidic nickel-plating solution (Top Nikoron TOM−S, concentration = 200 mL/L). The temperature of the liquid is 80 °C. After that, it is washed with purified water and dried. To

increase the thickness of the metal plating, electrical plating can be performed after electroless metal plating.

Figure 11 shows photographs of a sample in which the aforementioned process is used to perform nickel electroless plating on the surface of PTFE untreated and treated by plasma graft polymerization. Although no metal plating occurred on the

Fig. 11 Photographs of samples of nickel electroless plating on the surface of PTFE untreated and treated by plasma graft polymerization (sample width of 10 cm)

(a) untreated surface

(b) plasma treated surface

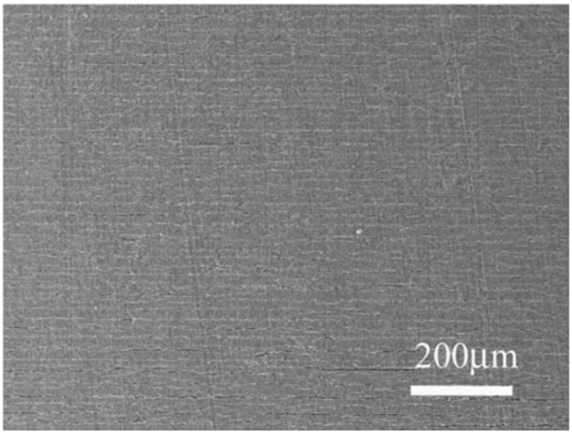


Fig. 12 Results of cyclic bending test of nickel plated PTFE (SEM image after test)

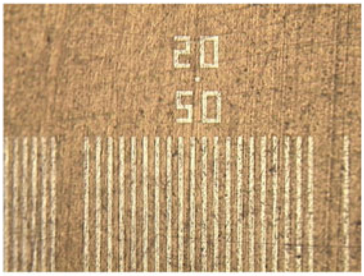
surface of untreated PTFE, a uniform plating film is formed after treatment. The peeling strength or adhesive strength reaches over 1 N per 1 mm width.

To test the flexibility of the metal-plated PTFE film, a repeated bending test is performed using a repeated bending tester. Accordingly, 100,000 rounds of bending at a bending angle of approximately 170° are performed on the metal-plated PTFE film sample. The sample is held by a rod for bending and two sample holding rods. Figure 12 shows a SEM image after the test at an argon flow rate of 40 L/min. The adhesiveness of the metal plating is fairly good with no peeling observed.

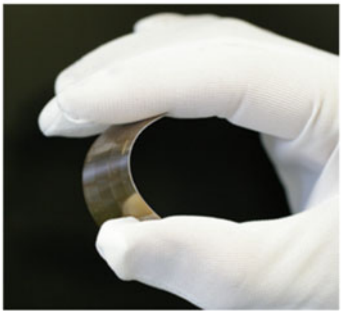
4.5 Microfabrication of Nickel Plating on PTFE

Pattern generation by photolithography on nickel-plated PTFE can be performed according to the following processes.

(1) The sample is attached to a Si wafer with a diameter of 4 inch.
(2) A positive-type resist (OFPR-800 50cP, Tokyo Ohka Kogyo Co., Ltd., Japan) is coated on the surface by a spin-coating process (first time: 500 rpm, 5 s; second time: 4000 rpm, 20 s). The thickness of the film on the Si substrate is typically 1.2–1.5 μm.
(3) Pre-baking of the sample is performed in an oven at 90 °C for 15 min.
(4) Mask exposure is performed at 18 mW/cm^2 for 20 s using an extra-high-pressure mercury lamp.
(5) The resist and nickel at the unexposed parts are dissolved using a developer liquid (tetramethyl ammonium hydroxide, NMD−3, 2.38%, Tokyo Ohka Kogyo Co., Ltd.) for 45 s.
(6) The wafer is washed with flowing purified water for 2 min. The resist is completely removed.
(7) After blowing with nitrogen gas, the wafer is dried in an oven at 90 °C for 10 min.



(a) Photolithographic pattern formed on nickel plated PTFE



(b) Confirmation of the flexibility of PTFE having a photolithographic pattern formed thereon

Fig. 13 Photolithography of nickel plating of PTFE by atmospheric pressure plasma polymerization

Figure 13a shows an example of this procedure. The numbers 20 and 50 shown in the photograph in the figure indicate that each line is drawn at a thickness of 20 μm and intervals of 50 μm. As shown in Fig. 13b, the PTFE on which the photolithography pattern is created exhibits flexibility, and applications such as flexible print boards or GHz-bandwidth high-frequency antennas may thus be expected.

5 Plasma Hybrid Surface Treatment of Fiber-Reinforced Composite Materials

5.1 Adhesion of Fiber-Reinforced Composite Materials

A surface modification/adhesion improvement assessment can be performed on fiber-reinforced composite materials with different dielectric constants, aiming for applications in radome structures [36, 37]. In this study, plain weave fabrics made of the following four types of organic fibers were used as samples: polypropylene (PP) fiber Innegra (Integrity Corporation), polyethylene (PE) fiber Dyneema

(Toyobo Co., LTD.), polyarylate (PAR) fiber Vectran (Kurary Co., LTD.), and poly *p*-phenylenebenzo bisoxazole (PBO) fiber Zylon (Toyobo Co., LTD.).

The device and apparatus are similar to those shown in Figs. 5 and 6. An A4 size (approximately 300 mm × 200 mm) sample is fixed to a conveyor belt of an atmospheric-pressure plasma graft polymerization apparatus, and while the plasma torch moves horizontally at a speed of 4 mm/s, a pulse modulated AC argon plasma jet (frequency 20 kHz; voltage 24 kV; pulse modulation frequency 60 Hz; pulse duty ratio 99%; gas flow rate 30 L/min) is sprayed on the surface. At that time, argon (flow-rate of 3 L/min) bubbling in an acrylic acid monomer solution heated to 45 °C is sprayed from the side of the jet and, as the surface of the test material is radicalized, the carbon bonds are cleaved, and graft polymerization occurs. After the torch makes a roundtrip, the test material is moved vertically 10 mm through the conveyor belt, and this is repeated to treat the entire A4 size surface.

First, to evaluate the adhesiveness, a peeling test is performed on each of the materials, Cyneema, Vectran, and Zylon, which are either treated or untreated by plasma graft polymerization. A 50-mm-long part of the test sample extracted at a width of 25 mm and length of 100 mm is adhered to an aluminum plate coated with epoxy adhesive (Konishi E-set) at a thickness of 250 μm, and the adhesive is cured by allowing it to rest at room temperature (~25 °C) for 24 h under a load of 5 N. Subsequently, the aluminum plate is peeled at a speed of 100 mm/min, and the peeling strength (adhesive strength) at that time is measured.

Subsequently, the vacuum-assisted resin transfer molding (VaRTM) method [38] can be used to trial-produce flat fiber-reinforced composite material test pieces using treated or untreated samples by the following method. For the thickness to be approximately 2 mm, the test materials are layered with 6 fibers (Innegra), 10 fibers (Dyneema), 8 fibers (Vectran), and 12 fibers (Zylon) and, after immersion in a matrix resin by vacuum aspiration, the materials are heated and the resin is cured. Epoxy resin (XNR6815/XNH6815, Nagase ChemteX Corporation) is used as the matrix resin. The resin curing temperature and time are 80 °C and 2 h. Three test pieces (length × width for peeling test: 250 mm × 25 mm, for compression test: 80 mm × 12.7 mm, for three-point bending test: 90 mm × 12.7 mm) are obtained by cutting the fiber-reinforced composite material test pieces. A peeling test (ASTM D3039), a compression test (SCAMA SRM 1R-94), and a three-point bending test (ASTM D790) are performed at room temperature using a material universal test machine (AUTOGRAPH DCS-10 T, Shimadzu Corporation) at speeds of 2, 1, and 1 mm/min, respectively.

5.2 Results and Discussion

The results of the peeling tests for the test materials are shown in Fig. 14. It is found that the peeling strength, σ_T, increases after nonthermal plasma graft polymerization of all the test materials. However, as shown in Fig. 15, σ_T tends to decrease in the peeling test for the fiber-reinforced composite material specimen. It is considered

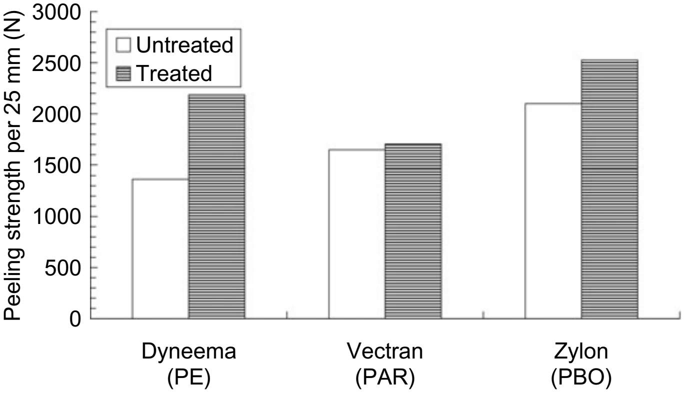


Fig. 14 Results of peeling tests for three types of fiber-reinforced composite material specimens [36]

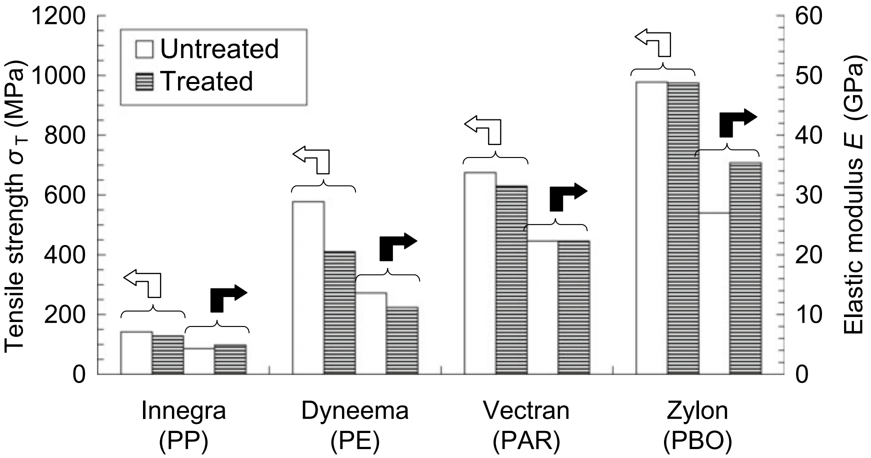


Fig. 15 Result of tensile tests for four types of fiber-reinforced composite material specimens [36]

that slight damage to the fiber surface during the plasma treatment may reduce σ_T. In particular, the Dyneema sample shows a lower heat resistance than that of the other tested materials, which is easily influenced by the temperature (~150 °C) during plasma irradiation; therefore, it is much smaller than that of the other tested materials. With regard to the elastic modulus, E, the relationship between the adhesion improvement by the plasma treatment and the fiber damage is different. In particular, the Dyneema sample, which has a lower heat resistance, presents a large degree of fiber damage; therefore, E decreases. In contrast, the Zylon material, which has a higher heat resistance, presents negligible fiber damage; thus, E is improved.

On the other hand, in the compression test, as shown in Fig. 16, the compression strength, σ_c, is improved in all the composite materials. It is considered that

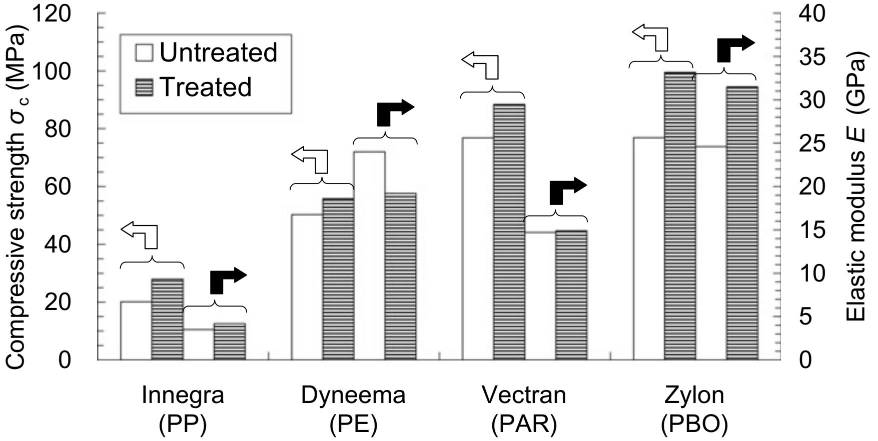


Fig. 16 Results of compression tests for four types of fiber-reinforced composite material specimens [36]

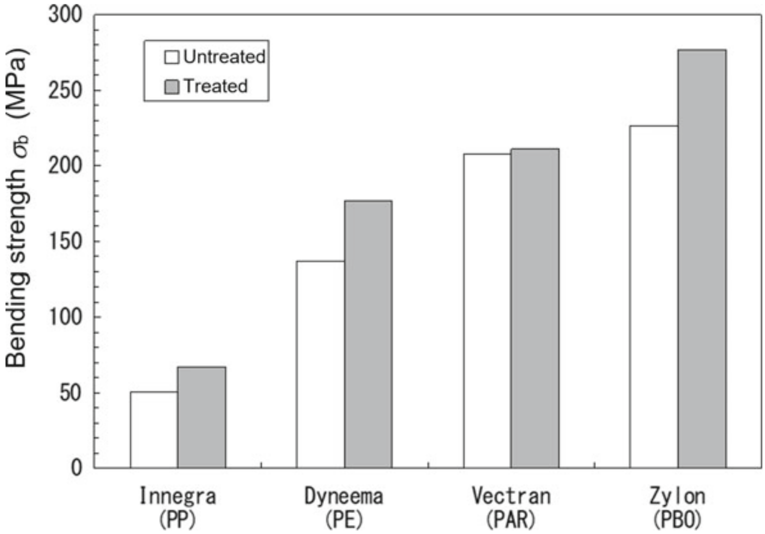


Fig. 17 Results of bending tests for four types of fiber-reinforced composite material specimens

σ_c is improved because of an enhancement of the adhesion after plasma graft polymerization. With regard to *E*, similar results to those of the peeling test are obtained. Furthermore, Fig. 17 shows a result of bending test for four-types of fiber-reinforced composite material specimens. In the bending test, an increase in the bending strength, σ_b, is observed. This increase is believed to be caused by an improvement of the compression strength, particularly during the plasma graft polymerization treatment.

6 Conclusion

The improvement of the adhesion and plating technology on PTFE and plastics treated by the plasma hybrid process, its application to millimeter-wave device, and its feasibility have been thoroughly discussed. The atmospheric-pressure plasma graft polymerization process developed by us has been employed for improvement of fluorocarbon plastic adhesion, followed by metal plating of PTFE. The fundamentals of plasma treatment, examples of electrode systems, the apparatus for plasma treatment, the effects of the surface treatment, plating methods on PTFE, and evaluation of the plasma composite surface treatment on fiber-reinforced composite materials have also been described.

With regard to surface modification of PTFE and improvement of adhesion, the adhesive strength obtained by the conventional technology, i.e., the sodium-based solution surface treatment method, can be significantly surpassed upon further optimization of the treatment conditions, improvement of wide electrodes, and other approaches. We believe that it would be possible to realize a targeted value of 5 N per 1 mm width, which is the standard value for the sodium solution method, while averting the color change of the fluorocarbon plastic.

Among our achievements, the peeling strength of 2 N per 1 mm of sample width or more, which is realized with a fluorocarbon polymer, is the highest among the various methods to improve the fluorocarbon polymer adhesion without surface color change. This highest peeling strength has been confirmed by researchers at a major company in Japan manufacturing medical devices made of fluorocarbon polymers. In the future, we will develop plasma hybrid surface treatments for electronic parts such as coaxial cables, antennas, and reinforcing fibers. We would like to increase the adhesive strength even further, the number of successful cases using this developed method, and promote and industrialize such plasma hybrid surface treatment. If the opportunity arises, we would like to be involved in collaborative research toward a wide range of applications. Furthermore, we intend to develop a roll-to-roll large-area treatment apparatus and pursue aerospace applications.

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Plasma Surface Modification of Polymers for Biomedical Uses

Phan Lan Thi and Moon Myoung-Woon

1 Introduction-Concepts of Material and Plasma Processing

Polyolefins-POs or polyalkene (–C_nH_{2n}–) are one of synthetic polymer class and are the most common used materials among polymers in industry, consumption. They are produced from olefinic monomers (called as alkene with the general formula of C_nH_{2n}). The most popular polymers in this class are polyethylene-PE with commercialized subgroups such as high-density HDPE, low-density LDPE, linear low-density LLDPE; and polypropylene-PP; ethylene propylene diene monomer (EPDM) rubber. The plastics from PE and PP are used everywhere in household appliances and industry due to the flexibility, durability, convenience, light weight and good look while EDPM usually uses for technical purposes such as seals, electrical insulation. Other important properties of polyolefins are biocompatibility and bioresorbability which pave the way of these materials to biomedical field. The remarkable uses of polyolefins in these important applications are hard tissue usage such as bone substitutes, control drug delivery and tissue adhesives. POs usually have a low energy surface but with the modification of plasma, POs could change the surface structure and properties. Among POs, PE and PP are the most widely used in biomedical applications.

Plasma is the 4th state of material where the molecules, particles, ions, electrons move freely. Many literature researches about plasma interaction from electron to particle collisions [1, 2] in large range of energy. The natural plasma is the aurora which could be seen frequently in North pole sky. Plasma used in laboratory is

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created by using a very high voltage for a low-pressure/atmospheric gases or gas mixtures. The voltage provides energy to electrons at outlet orbital, helps them break the covalent bonds between nuclears to go to vacuum, leaves molecules ionized. The dynamic energy provided by voltage potential for free electrons and ionized molecules causes many collisions with neutral molecules in the mater and lead to ionization cascade. Then the gas becomes ionized locally or fully. Plasma is a very well-known technique for surface modification as it could change the surface energy and surface morphology, which decide the wettability of surface: hydrophilicity or hydrophobicity, indicate the biocompatibility of the surface. In addition, plasma could change the surface structure by chemical or physical impacts. The ions with high kinetic energy gained from bias voltage between cathode and anode will bombard the sample surface molecule in the molecule/atom scale, cause the interactions in aspect of chemical or physical modification. There are many interesting surface modifications by using plasma [3] and finish in amazing applications such as water collection [4], oil and water separation [5], biomedicine [6], energy [7], battery [8], sensor [9], and so on.

In this chapter, we will focus on the current state of art of using plasma for polyolefin polymer surface modification in medical uses, mainly on PE and PP as they are the most popular polymers used in this field [10, 11].

2 Polyolefins in Interaction with Biomedical Media

Medical applications are important, sensitive and highly safe for any surface material due to the direct contact with human organs which is very complicated and vulnerable. The process of applying the material into human body must result in improvement of the patients' health status rather than result in sub-symptoms or toxic harms. Hence the whole process of applying material for medical use must be inspected carefully. In the aspect of using polymer to support the remedy for patient diseases, the first condition is the medical polymers must show specific properties without interactions with surrounding tissues or with the body as a whole. One of important factor is biocompatibility, with the meaning of the polymer could exist in contact with blood and enzymes without undergoing degradation or provoking the media around such as tissues, organs, immune systems or causing toxic, allergy.

Polyolefins such as polyethylene or polypropylene are very common and low-cost, which makes them some of most popular used polymers in the world. But they also own a natural hydrophobicity that limits their biocompatibility. However, with high molecular weight which generally have low toxicity, they are used in a wide range of medical applications including hip replacement implants, knee arthroplasty, dilators, introducers, packaging, film, and molded components. The use of them in biomedicine has last for long with many deep researches in term of mechanical, physical, and chemical properties that impacts their performance in the curing period.

Basically, polyolefin plastics are safe and stable. However, PE's biodegradation rate is slow, allows for the production of highly stable, high shape-fidelity and permanent implants. For the safety purposes in medicine in specific instants, the degradation rate could be improved if employed some methods during synthetic process to stimulate more rapid degradation, including the application of heat, light and oxygen exposure and modified carbon chains. The high-molecule-weight polyolefin polymers intend to degrade to low-molecular-weight fragment and even monomer, and then could be diffused safely to surrounding [12]. The PP is considered as one of the biocompatible, biostable polymer and used widely in clinical applications ranging from sutures to lead-bearing implants. They have excellent stiffness and strength when compared to PE [13]. Recently, a technology of additive manufacturing (3D printing) has intensively developed and innovated the uses of polymers for industry and biomedicine, polyolefins are in focus as attractive class of biomaterial with more complex shape and multimaterial in one go.

2.1 Polyethylene: Properties and Medical Applications

Polyethylene has been applied in surgery since 1950s, as one of optimal replacement of metallic implants at that time. The popular metals used in medicine such as titanium, stainless steel, have revealed the problems of toxicity and a lack of tissue adherence, leading to fractures and stress shielding. These materials are usually not recommended to soft tissue but for bone tissue [14]. In nanoscale, PE could be used as drug delivery as well [15].

PE is categorized by its density and branching, from ultra-high-molecular-weight to medium- and low- density types of PE. Each type has various range of thermal, mechanical, chemical, electrical and optical properties relevant for biological mimicry. PE synthesis has a breakthrough by eliminating the condition of high pressures and temperatures, simplifying the process to a catalytic system at mild condition, make this polymer production in large-scale and commercialized. Currently, the typical PE synthesis process begin with single monomer: ethylene which produced from petrochemical sources and represents a pair of connected methylene groups. The catalysis system could be metallocene molecule to control the polymerization process and structure of produced PE. This results in the formation of a number of varying density and molecular weight PEs, such as low density PE (LDPE), linear low density PE (LLDPE), medium density PE (MDPE), cross-linked PE (XPE), high density PE (HDPE), ultra-high molecule weight PE (UHMWPE) (Table 1).

PEs' biocompatibility is validated in a range of reviews [17–19] as well as in vitro and in vivo studies [20, 21], and is known to be non-biodegradable within biological time frames. The oxidation and the demanding in vivo mechanical and biochemical conditions experienced by PE medical devices can influence the chemical composition of the PE polymer chains, leading to the degradation, loss of mechanical strength and ultimately plant failure [22].

Table 1 Average properties of Ultra-High Molecular Weight Polyethylene (UHMWPE) and high-density polyethylene (HDPE). Reprinted with permission from [16]

Property	UHMWPE	HDPE
Melting temperature (°C)	132–138	130–137
Molecular weight (106 g/mol)	3.5–7.5	0.05–0.25
Specific gravity	0.925–0.945	0.952–0.965
Poisson's ratio	0.46	0.40
Modulus of elasticity (GPa)	0.5–0.8	0.4–4.0
Tensile ultimate strength (MPa)	39–48	22–31
Tensile yield strength (MPa)	21–28	26–33
Tensile ultimate elongation (%)	350–525	10–1200
Degree of crystallinity (%)	39–75	60–80
Impact strength (J/m of notch)	1070	21–214
Wear Rate (mm^3/10^6 cycles)	80–100	380–400

PE are used in medical devices as a cheaper, more light-weight alternative to traditional biomaterials such as metals. Small HDPE particles have been sintered into predefined shapes and size or relevant shapes for specific surgical applications. The implants are porous in size of 100–250 mm to facilitate the growing of tissue [23]. The low-pressure condition with catalyst for high-molecule-weight PE of 4 × 10^6 g/mol has been conducted as the initial material for preparation of the elements of endoprosthesis. The next candidate of PE type for endophrosthesizing pelvis bones is superhigh-molecular-weight polyethylene (SHMWPE) for excellent anti frictional properties and good ability of dry sliding [24].

2.2 *Polypropylene: Properties and Medical Applications*

PP is a thermoplastic polymer used in a wide variety of applications. It is produced via chain growth polymerization from monomer propylene with the chemical formula $(C_3H_6)n$ by processes of gas phase polymerization, bulk polymerization and slurry polymerization. The monomer propylene is a by-product, derived in steam-cracking process using naptha which is valuable fraction of crude oil. The second largest production of propylene is from the gasoline refining process [25]. PP is the commodity plastic with the lowest density of between 0.895 and 0.92 g/cm^3 and Young's modulus is between 1300 and 1800 N/mm^2. They are normally tough and flexible, have a good resistance to fatigue. As a partially crystalline, isotacticity, different molecule weight and molecular weight distribution, the melting point is in a range from 145 to 195 °C and somewhat less than that of polyethylene. They are usually made translucent when uncolored. This polymer is resistant to fats, organic solvents and apart from strong oxidants but could be degraded to benzene and toluene when exposures to temperatures above 100 °C. As a matrix material, PP is widely used because it has some excellent characters for composite fabrication.

PP used in medicine because of its high chemical resistance and stability, favorable mechanical performances. It has been used from lining the valves of artificial hearts and for ball joint prostheses. PP fibers, complex thread, have been investigated after 4 years of use in vivo in skin cellular tissue of rabbit. The fibers lose about 60% of their initial durability and 80% of their initial extension. The weight loss of samples were found to be 3.8%. The cracks on the surface appeared after 5 months in small size but developed to large cross crack located perpendicular to the axis of the fibers after 10 months. PP films also used in implantation under skin of white rats with and without stabilizer. The result showed that there is no change in mechanical properties of PP film with the use of stabilizer but the stress at rupture reduced 20% after 19 month of implantation without the use of stabilize [24].

3 Plasma Technology Processing for Polyolefinic Surface Modification in Biomedical Uses

a. Plasma technology processing for polyolefinic surface modification

There are many plasma technologies applied in surface modification. Basically, the differences are from energy sources, the non-equilibrium electrical ignited factor. The energy source for ionization could be from direct current- DC, such as DC plasma or alternate current- AC. In AC source, there are microwave plasma or radio frequency plasma. Also, there are laser treatment, plasma treatment or ion implantation, nanoparticle grafting if we consider deeper view in the aspect of energy source and the particle interacting with surfaces. The pressure of plasma chamber also make changes in structure of ionized precursor gases, such as atmospheric, low pressure or high vacuum. On the other hands, the temperature of plasma processing is also a fundamental for classifying the plasma categories, such as cold plasma if the processing temperature is at ambient (PE-CVD), or hot plasma if the processing temperature is hundreds to thousands degree (sputtering deposition, laser plasma, 10^4–10^5 K). The precursor gases used in plasma processing are one of important factors in the surface modification of substrate. They could be fluorocarbon gases, silicon-containing organic compounds (e.g. hexamethyldisiloxane -HMDSO) or grafting chemical group carried gases (e.g. NH_3, N_2, O_2). Each precursor gas brings their specific chemical and physical characters when interacting with polymer surface and innovates the surface in different ways.

Plasma treatment methods are known as a powerful process. They are used for cleaning, means that sterilizing tools and removing contamination on the surfaces, especially used widely in pharma and medicine due to the high demands in this field. They are also used for selective etching, to make different structure or used inert gases to modify the morphology of the surfaces. They could functionalize the surface by grafting chemical group on the surface using precursor reactive gases such as O_2, N_2, fluorocarbon, for self-cleaning, antireflection, adhesion, biocompatibility, and friction. They are also used for surface activation and polymerization [28].

The plasma modification for PE and PP have been investigated for long time and carefully. Plasma modification could change the properties of surface material, such as: nanostructuring, nanopatterning, surface morphology modification, surface energy [3]. For POs, the plasma for surface morphology and chemical modification, along with surface energy change are the most common targets for surface innovation and for widening its applications.

Plasma processing for PEs

As described in the Fig. 1, plasma is a cluster of active and various charged particles, species or radicals in gaseous state. These particles damage the polymer backbone to produce free species, increase the ability of polymer molecule diffusion and promote the etch-rate in the surface layer. The functional groups (–OH, C–O, –COOH) formed in plasma process changes the surface energy of polymers. The kinetic energy of plasma particles and the chemical reactions modify the surface morphology, create nanotexture, roughness or nanostructures.

PEs have a low surface energy, which limited the used of this materials in biomedical and clinical applications. Therefore, it is a necessity to increase the wettability of these materials. And plasma processing is competitively selective, which modify the surface of material rather than the bulk.

O_2 or N_2 plasma precursor gases are usually used for grafting chemical group for functioning the surface as the functional groups usually created and anchored on the surface material. A work by Hassan et al. [29] has demonstrated the innovation of surface roughness, stiffness and wettability of LDPE using two these gases by using radio frequency (13,56 MHz) glow discharge plasma reactor, 100 W, processing pressure of 3×10^{-3} mbar. The higher etch rate, significant changed morphology, higher friction coefficient and decreased hydrophilicity of PE surface were found for

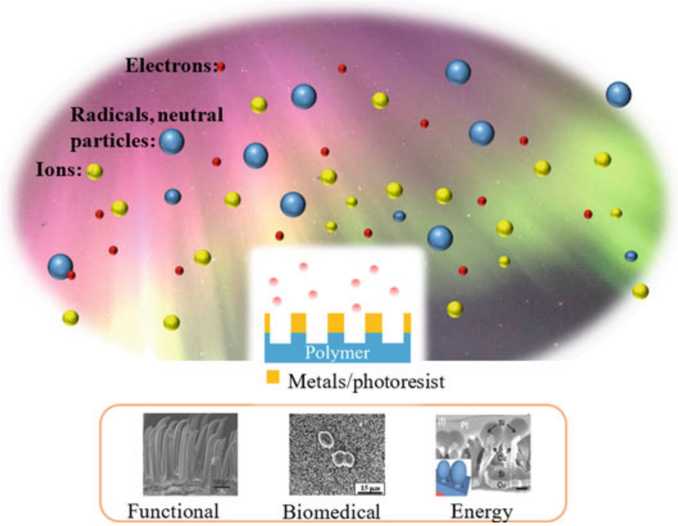

Fig. 1 Plasma and charged particles for polymer surface nanostructuring and applications. Reprinted with permission from [9]

O_2 gas plasma treatment, in comparison with that of N_2 gas. The UV–vis spectral analysis show that the optical properties are affected by plasma treatment. The new properties of PE surface after plasma treatment prove that gas plasma is an adequate tool for modifying surface properties effectively for specific applications. Another work using dielectric barrier discharge-DBD plasma in air (means the mixture of mainly O_2, N_2 and very little other gases) has been performed and resulted in free surface energy increase, from 27.3 to 51.89 J/m^2, correspond to transition of contact angle of 93.2° to 53.3° [30]. Also, the change in surface structure of PE was analyzed with different plasma gases to see the chemical modification of surface sample [31]. Aya et al. [32] presented a research of RF plasma using different gas such as air, nitrogen, oxygen, argon on LDPE and a qualitative, quantitative characterization to find the optimum treatment in the presence of air is 120 s exposure time, 80 W of nominal power. Another application of PE using surface Oxygen plasma processing described by So Yeon et al. [33] for lithium ion battery. The Oxygen plasma have been used to insert some functional group to improve the electrolyte wettability and retention of PE separators, resulted in the improvement of charge–discharge capability with lower interfacial resistance and stable cycling performance. The chemical modification on PE has been shown in the Fig. 2.

Plasma processing for PPs

Polypropylene is the most difficult polymer to treat due to the high chemical barrier responses. The structure of this polymer is responsible for its chemical inactivity. Therefore, PP usually used in composite to facilitate the processing effectivity [34]. However, the innovations of pristine PP surface are reported frequently using plasma processing to enhance both wettability and adhesive properties for better performance [35] and widening applications [36], satisfied the requirements in industry and material aspect. Low pressure plasma has applied on neutral PP and shift the surface properties to hydrophilicity and better adhesive [37]. A set of process variables (voltage, time, and air flow rate) was identified and optimized to conduct the test to increase PP's wettability and adhesion [38].

A further step of using Ar and O_2 plasma treated PP surface has achieved the higher adhesion of a-C:H:SiOx film deposition. The PP deposited diamond-like–layer (DLC) show the low thrombogenicity and no cytotoxic activity towards human leukocytes [39].

The inert gas plasma, Ar ion beam irradiation was also used in a work to make the modification of PP surface, forming the nano-embossed structure for the puspose of adhesion, wetting and biological compatibility. The 2D surface of PP film has changed to 3D of long nanofiber-like nanostructure in long treatment time under the bombardments of Argon atoms. Argon is known as an inert gas, therefore the Argon plasma usually takes effect on the surfaces and changes the surface structure by its kinetic energy rather than chemical reactions [40]. The surface transition morphology process has been shown in the Fig. 3.

The experimental result has been analyzed deeply after that by Chansoo et al. [41]. The group used molecule dynamic simulation to rebuild the whole process again and characterized the phenomenon occurred in bombardment between ion beam

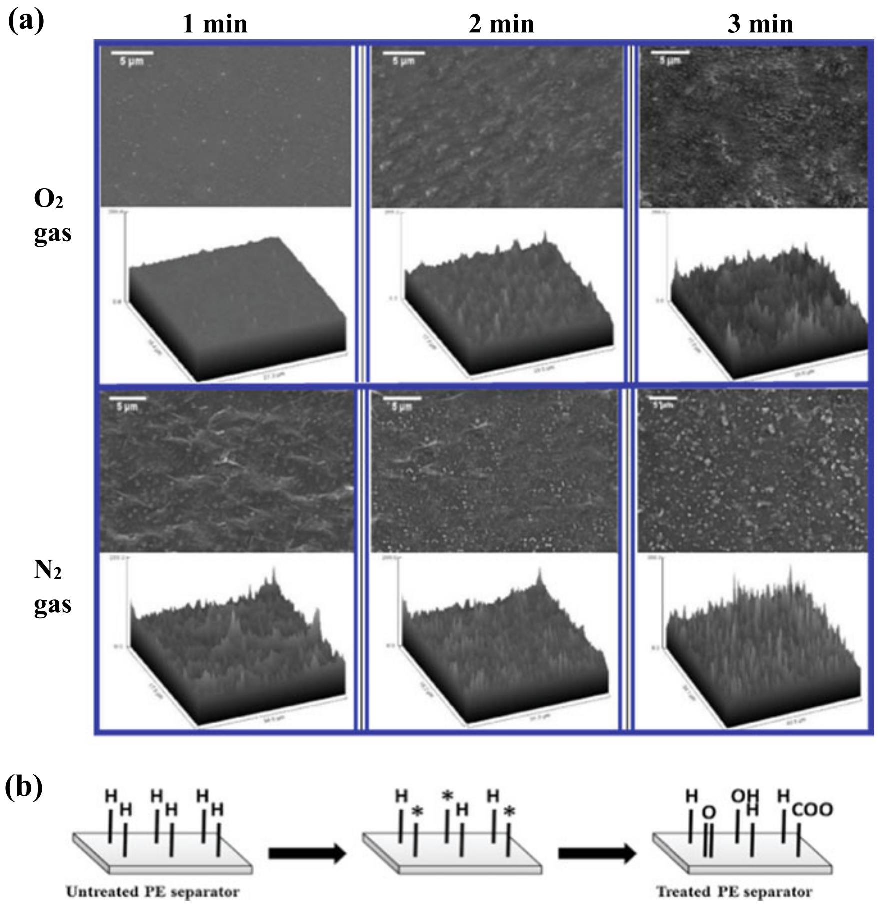

Fig. 2 **a** Surface morphology of N_2 and O_2 plasma treated LDPE surface samples with different plasma processing time. Each micrograph is accompanied by the corresponding 3D top-down view. Reprinted with permission from [29]. **b** Schematic representation of surface modification of the PE separator via oxygen plasma treatment. Reprinted with permission from [33]

and polymer surface. They used Reactive Force Field (ReaxFF) to mimic chemical covalent bonds, includes van der Walls potentials for describing the intermolecular interactions.

b. Plasma processing Polyolefinic surface in biomedical uses

The use of polyolefin in biomedicine is facilitated by many technologies. Among, the surface modification by plasma is very popular and paves a way of using this material into many important biomedical applications. As referred before, the use of polyolefins in biomedical was before 1950s. Up to now, the biomedical applications have covered from wettability modification, antibacterial/antifouling [42] to bioadhesives, bone generation and further.

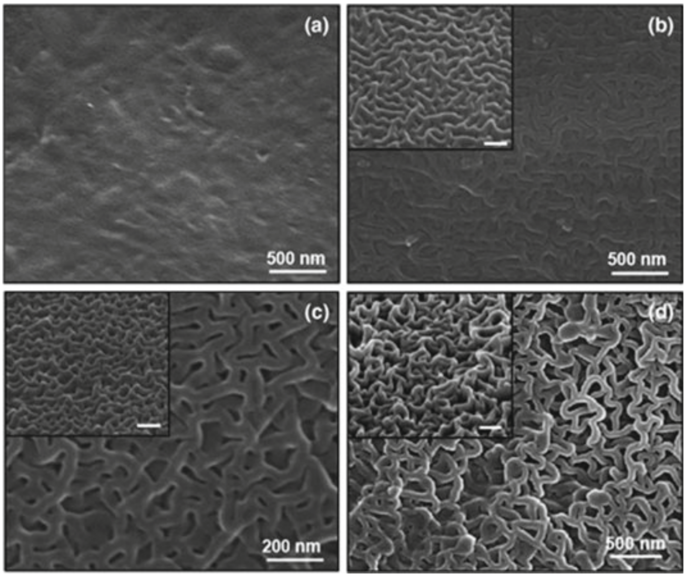

Fig. 3 SEM images of the PP surfaces **a** untreated, **b** 5 min, **c** 30 min and **d** 50 min treated with an Ar ion beam. The insets corresponding to the 50° tilted view. The scale bar length in the insets is 200 nm. Reprinted with permission from [40]

Wettability and surface energy of the substrates are among the most studied research topics, especially in bioapplication aspects since these factors strongly affect the success of surface treatment and are critical for the formation of secondary bonds in adsorption theory.

The natural hydrophobicity of polyolefin polymers makes barrier for using these convenient and economic materials in many applications as hydrophilicity is one of important properties for biocompatibility. This property is not available in as-produced PP or PE. Plasma is shown as the effective method to innovate POs surface for this function. In the work of Dvorakova et al.'s group [43], polypropylene, TUPLEX foil, 2 mm thickness, have been processed by DSCBD at power of 3.75 W/cm^2, 30 kHz in 0.5–20 s. Precursor gases are the mixture of propane, butane in N_2 gas 99,99% purity. The processed surface results in significant decrease of water contact angle from 92 to 9° due to a deposited plasma-polymer nanolayer. A highly reduced aging of surface modification also obtained to make the use of this surface a longer life cycle. The work is of interest for utilization in biological, as well as technical applications.

The surface property modification of polyolefin after plasma treatment is from the changes in chemical and physical of surface compound structures. This starts with the physical interaction between plasma species and the chemical elements on the polymer films. Si-XLPE is a type of crosslinked polyethylene compound contained vinylsilane inside structure. It uses predominantly in building pipework. The challenge arises with Si-XLPE blends, the poor surface wettability and adhesion limits their application. Mostofi Sarkari et al. [44] used plasma grafting method to graft GLYMO ((3-glycidyloxypropyltrimethoxysilane) as vapor precursor to modify the poor surface bonding properties. The result shows that plasma post-irradiation grafting yielded to higher grafting density and efficiency with more uniform distribution on the surface, in combination with a fall of water contact angle-WCA and growth of surface free energy-SFE. The better adhesive could have obtained by plasma. Silvana et al. [45] have applied Oxygen and Argon plasma (30 W, 12 Pa,1,3,5 min) on PE fiber (from Fibra, Connect, Construct) to get the adherence of fiber to polymeric matrices in dental applications, reinforcing the dental particulate composite. The material has been processed in 3 min to get the highest strength values in the group reinforced. The oxygenated functional groups and surface roughness have obtained after plasma treatment.

Antibacterial

Infection is a challenge. Absolute solution has not found yet as bacterial could be everywhere, both positive and negative types. A highly probability of infection is challenging the effort of improving the patient's health status, especially with the opening wounds. Using metal coating is a way to make antimicrobial surface [46], but modifying surfaces of POEs also are reported prominently [47].

PE is the most widely used polymer in many industrial applications but it prone to infections which became one of obstacle in biomedical uses. The solution proposed is additional surface treatment. Popelka et al. [48] have use cold plasma (Diffuse Coplanar Surface Barrier Discharge-DSCBD) of triclosan and chlorhexidine to treat the LDPE surface because of the substances containing **antibacterial** group and very low clinical toxicity in clinical test of these films. The bacterial included Escherichia coli and staphylococcus aureus have been used for testing the antibacterial activity and it show that the sample coated triclosan does meet the expected antibacterial requirements. For the same purpose of antifouling, LDPE films have been processed by atmospheric pressure non-thermal plasma—APNTP assisted polymerization of acrylic acid and polyethylene glycol in order to functionalized with chitosan-CHT for further enhancing its antifouling properties. The result shows excellent antifouling behavior of the surface modified LDPE films in-vitro in the test with blood component [49].

PP has good mechanical properties and is easy to manufacture at low cost. However, its surface needs to be modify, especially with its natural hydrophobiicity and lack of functional groups. A report on surface modification of PP for biomedical applications is coating polyglycerol-PG on the PP surface for more hydrophilic and biocompatible, resulted in grafting hyperbranched polyglycerols with very few amino fuctionalities. The work has been conducted and resulted in protein and bacteria resistance by using two steps of low-pressure plasma bromination and direct grafting of PG [51]. A similar approaching to innovate PP surface to impart antibacterial and hydrophilic surface properties, is plasma processing of grafting Methyl Diallyl Ammonium Salt, called immersion–pad-pressing–drying–plasma (IPDP) [50]. Ar and O_2 were used as carrier gases for the plasma treatment (radio frequency plasma treatment system RF-O-001, Helix Technology Inc., Taiwan) but also for activating

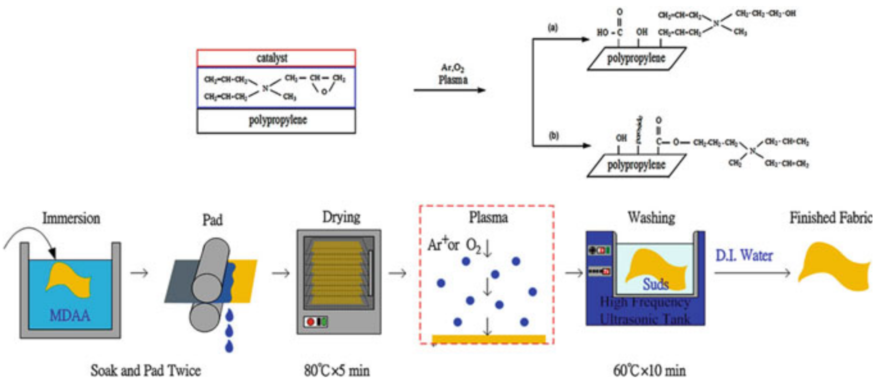

Fig. 4 Grafting Methyl Diallyl Ammonium Salt onto Polypropylene by immersion–pad-pressing–drying–plasma (IPDP), in which the plasma treatment and grafting reaction occur simultaneously. Reprinted with permission from [50]

the grafting salt onto the PP nonwoven fabric surface with the support of acid catalysts. The IPDP process was illustrated in the Fig. 4 with the plasma treatment and detailed grafting reaction. The tests showed higher graft ratios let to higher antibacterial and hydrophilic properties. The time required for the IPDP procedure was much shorter than that for the plasma grafting process with the far superior graft ratio, antibacterial property and hydrophilicity.

Bioadhesive is important characteristic of biomaterials, refers to the phenomenon where natural and synthetic materials adhere to biological surfaces. The fundamental mechanisms that govern bioadhesion are of strong interest from various researchers who aim to develop new biomaterials, therapies and technological applications. Biomedical used polymers such as low-density polyethylene-LDPE, high-density polyethylene-HDPE and ultra-high molecular weight polyethylene—UHMWPE were activated by Ar plasma discharge and then were studied using 2 distinct model cell lines, vascular smooth muscle cells-VSMCs and connective tissue cells-L929 (mouse fibroblasts), for vascular graft testing and standardized material cytotoxicity testing [52]. It was found that a positive effect of plasma processing on the adhesion of proliferation of VSMCs and L929 cells. The highest increase in number of adhered cell for both L/HDPE obtained at 120 s but UHMWPE take 240 s to show the best result. PE and polystyrene-PS also modified and grated to create artificial bioinspired nanostructured surface for tissue engineering using Ar plasma with polyethylene glycol-PEG grafting in further step [53]. The process formed a dramatic change in the polymer surface morphology, roughness and wettability. The plasma treated with PEG grafted surface were seeded with rat vascular smooth muscle cell (VSMCs). The biological test, performed in vitro, show increased adhesion and proliferation of cells.

Commercial hernia mesh is commonly made from PP due to its inertness, biocompatibility and flexible shape. Recently, some issues are pointed out like diminished long-term strength, foreign body rejection, and high adhesion to the abdomen wall,

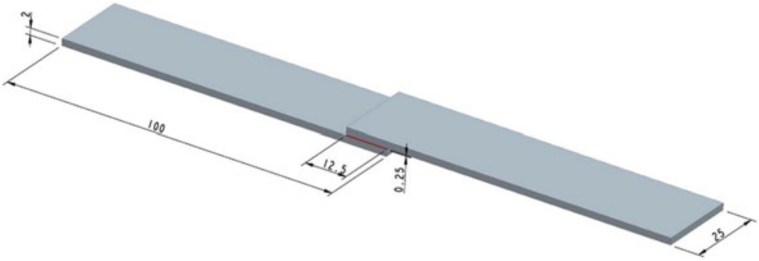

Fig. 5 Single overlap joint configuration according to test conditions followed the ASTM D3163 standard. Reprinted with permission from [26]

resulted in an integration of mesh into the body, leading to a rapid reduction in mesh mechanical properties and potential infection. A method developed by Houshyar et al. [54] using nanodiamond-ND in PP filaments and coating on the surface of plasma-treated PP-ND mesh showed that the dynamic modulus of the PP-ND mesh increased significantly, without compromising its flexibility. In addition, coating PP-ND mesh with hydroxylated ND lead to a reduction in nonspecific protein adsorption onto the surface of nanocomposite. This is an important factor for hernia mesh to prevent foreign body reaction, attachment of mesh to the abdominal wall and nearby organs. The in-vitro study with mammalian cells shows that coated PP-ND mesh with functionalized ND obtains a significant increase in the number of adhered cells with more elongated morphology in comparison with other PP mesh. The result suggests a promising candidate for hernia repair in the future. Another work on PP hernia mesh devices using cold O_2 plasma has conducted, considering the aspect of antibacterial and drug release properties [55] due to the danger in infection of implantation. The PP mesh has been fabricated with antimicrobial, stable drug coating layer to slow the drug release property during the hernia repair process. Bio-inspired polydopamine-PDA was coated on cold O_2 plasma activated PP mesh. The mesh was soaked in levofloxaxin afterthat and was tested for antimicrobial properties and drug release. The result was 6 day for excellent antimicrobial properties (and at least 24 h of drug release), while 2 day for that in case of non-plasma processed sample.

The adhesion characteristics of neutral popylropylene substrate after low plasma processing has been effectively innovated and used to create single overlapping bonded joins and evaluated the effect of the surface treatment on the mechanical characteristics of the joints (Fig. 5) [26]. The properties of this PP film has been described partly in Table 2, trade name of PPC 5560. The low pressure plasma-LPP, generated by a Tucano plasma device, powered by an RF generator operating at a frequency of 13.56 MHz, was used. Air and O_2 precursor gases were investigated. Air was for economic choice and O_2 was the strong activating gas toward polymers. The increase in wetting properties and surface free energy produces a remarkable increase in mechanical performance of polypropylene bonded joints with an epoxy adhesive. The power input acted as the most effective parameter. It can be concluded that plasma treatment proved to be an effective solution to obtain good shear strength of joints, especially with the use of oxygen.

Table 2 Specification of polypropylene. Reprinted with permission from [26, 27]

Properties	Value	Unit
Density @ 23 °C	0.905	g/cm^3
Yield stress (MPa)	25	MPa
Elongation at break (%)	6	%
Tensile modulus of elasticity (MPa)	1300	MPa
Melting point (°C)	165	°C

Tissue generation

In addition, the **bone regeneration** capacity of recombinant human bone morphogenetic protein-2 (rhBMP-2) immobilized HDPE Medpor surface has been investigated using acrylic acid plasma-polymerization (RF, 13.56 MHz, 20 W, acrylic acid flow rate 7sccm, working pressure 10mTorr in 5 min) [56]. The result surface shows hydrophilicity with high density of carboxyl groups after plasma polymerization, which facilitates the immobilizing rhBMP-2 by covalent bonds with 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide and N-hydroxysuccinimide. The HDPE Medpor surface activity has been cultured with MC3T3-E1 cells at a density of 3×10^5 cells/mL, resulted in the increase of MC3T3-E1 cell differentiation level (Fig. 6). The result demonstrated that plasma surface modification has the potential to immobilize rhBMP-2 and to bind bioactive Nano molecules in bone tissue engineering.

Food, beverage and drug container

As one of the most used material in food,beverage and drug storing industry, POs are very attractive for aplications in food storage technology. Reducing oxidation in environment of low oxygen and inert gas processing are key points to keeping food fresh and retaining valuable nutrients. A interesting bioapplication has been done using composite oxygen-barrier coating on the PP food container using plasma polymerized-hexamethyldisiloxane (pp-HMDSO) [57]. The 25 mm height and 0.55 mm thickness PP food container (Fig. 7) was process with 20 sccm

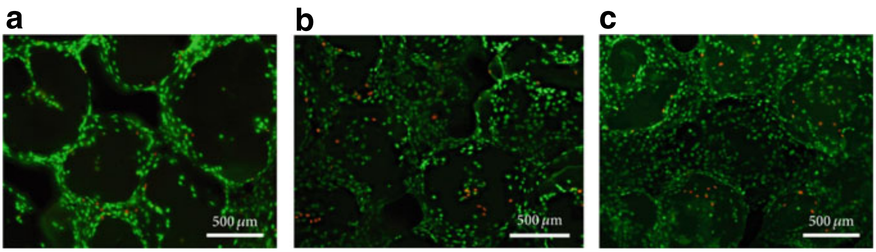

Fig. 6 Live/dead fluorescent stain images of MC3T3-El cells on **a** untreated, **b** AA plasma treated, and **c** rhBMP-2 immobilized Medpor surface for 3 days. Viable cells were stained green and dead cells stained red. Reprinted with permission from [56]

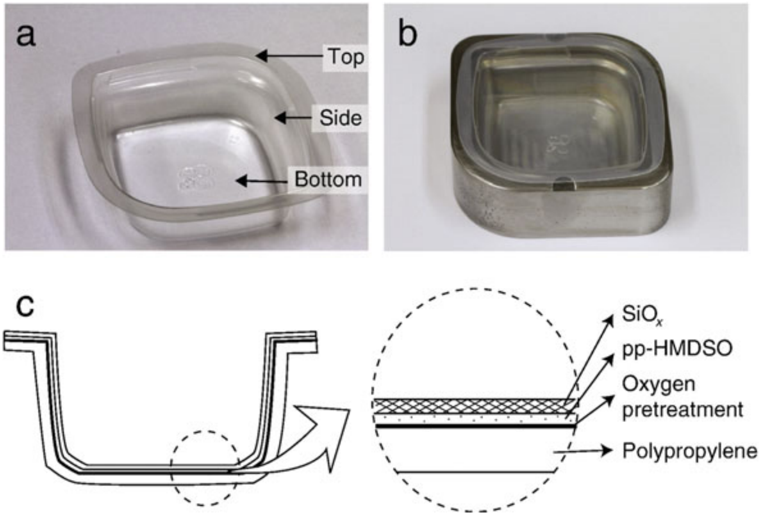

Fig. 7 **a** Polypropylene (PP) food container with a bowl shape and **b** a stainless steel mold filled with a PP bowl. **c** A schematic of a composite coating of pp-HMDSO/SiOx on a PP bowl pre-treated by oxygen plasma 57. Reprinted with permission from [57]

O_2 plasma in 1 min to enhance adhesion of PP surface. A pp-HMDSO interlayer was coated on the adhesive PP surface in the next step, using a precursor of HMDSO vapor at 2sccm. And a SiOx thin film was deposited using the mixture of HMDSO and O_2 gases with the ratio of 1/20 sccm/sccm, as shown in the Fig. 7c. It was found that there was an optimum thickess for pp-HMDSO and SiOx to reduce the scratches on the layers. The work decreased the oxygen transmission rate-OTR of PP container from 7.42×10^{-4} to a record rate of $2.6 \times 10^{-5} cm^3/m^2$ which could make the food storage much longer in safe condition. The work was one of endeavor of famous Korean food company CJ Cheiljedang to improve quality of their product to consumers.

4 Conclusion

The plasma for surface modification on polymer is very well-known in industry and research works for the convenient of processing method: simple and save time, surface evolution without change in bulk, the modification could approach to molecule or volatile particles level. Therefore, the change would be made in multi-level in size and dimensions from macro to micro or nano. The treatment of plasma on polyolefin has made a long step forward in popularizing this materials in biomedicine and bring benefits to human for health protection and disease cure. The most important properties that polyolefins need to change to integrate to medical uses, is hydrophilicity instead of hydrophobicity as that in original surface. And this could be change in many ways such as coating with a new layer by plasma polymerization (HMDSO, PG, acrylic acid, gases mixture.), plasma rare gas-ion processing, as discussed in the previous part. However, other supportive techniques should be considered such as thermal annealing, other precursor gas (Carbon Florour-CF gas) for plasma polymerizations to prevent the hydrophobic aging recovery of resulted surface of polyolefinic polymers.

Biomedicine will more intensively develop field in the coming future. Therefore, more functions on polyolefinic surface will be required to satisfy the human health challenges, that could be changed dramatically, as we see the side-effects of Corona virus pneumonia recently. The control of plasma technology should be more accurate and develop deeper to support polyolefins, as well as other polymers for new properties that brings benefits to society development. As the most used and consumed polymers in industry, medicine and living appliances, the innovation of plasma processing on POs bring many benefits and meaning to human's lives, especially in health care aspect. More functions could be attached to the POs using plasma processing to innovate the surface. But more smart materials (such as graphene, fibers, nanodiamond, nanomaterials) would be mixed with POs to form the composite for higher performance before treating with plasma. However, POs is a synthetic polymer and the uses of them should be governed well to decrease their harm to environment and species existences, for the sustainable development of human and earth.

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