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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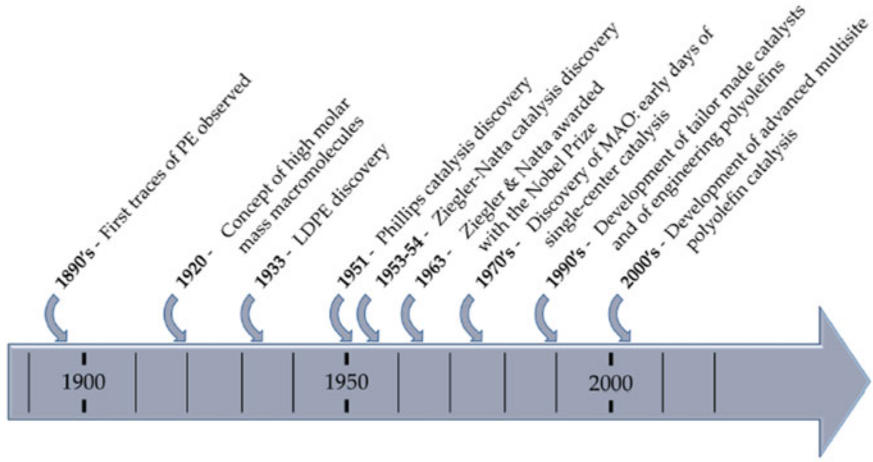

Fig. 1 Major advances in polyolefins development (Adapted from [3])

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

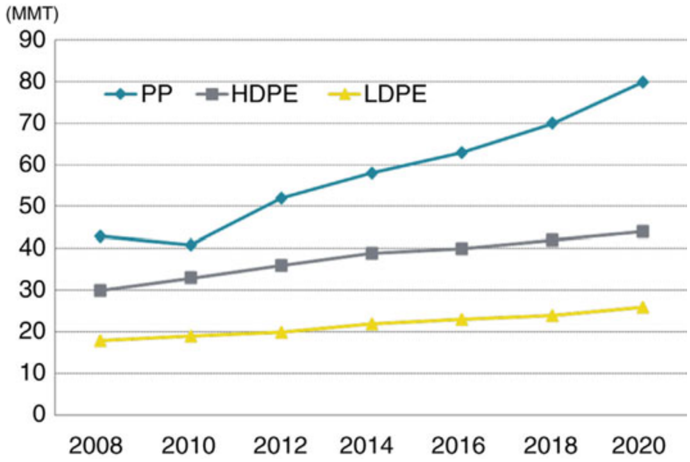

Fig. 2 Polyolefins global demand (Reproduced with permission from [4])

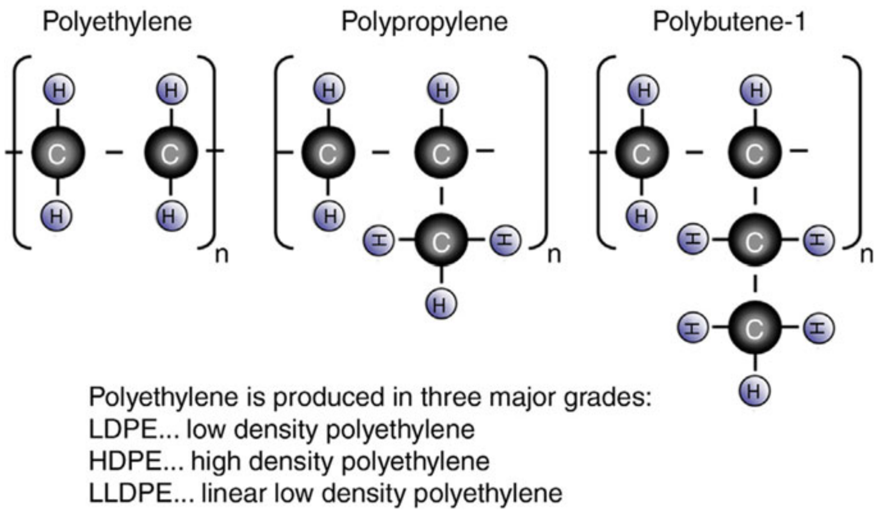

Fig. 3 Skeletal structure of some Polyolefins (Reproduced with permission from [4])

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 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].

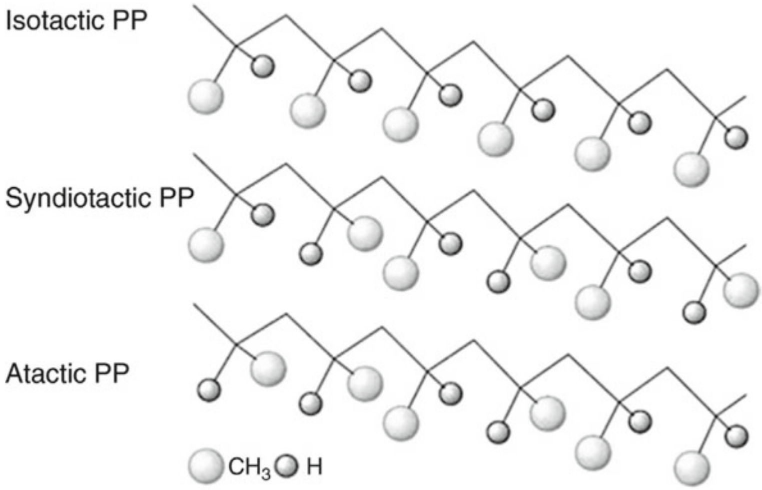

Fig. 4 Different configurations of polypropylene (PP)

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

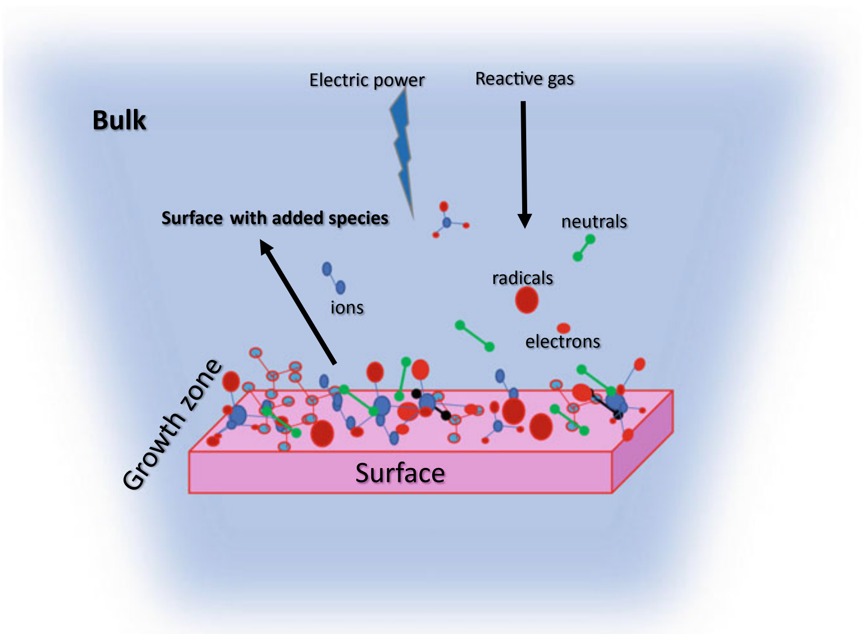

Fig. 5 Schematic representation of plasma modification

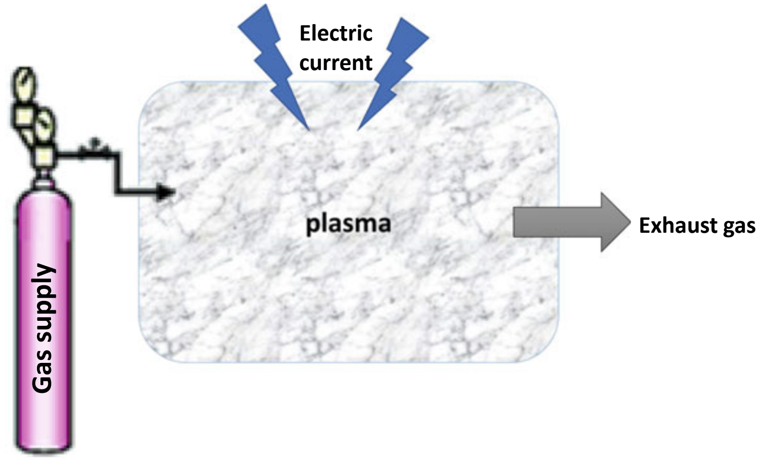

Fig. 6 Schematic representation of the plasma generation

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:

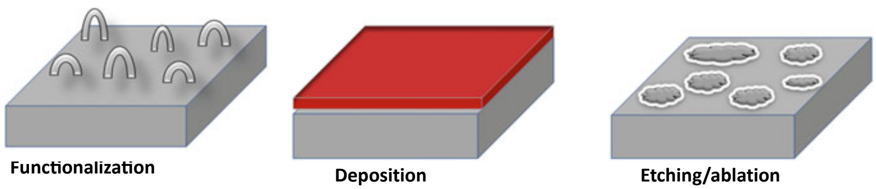

Fig. 7 Different changes on the surface by the application of plasma

(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

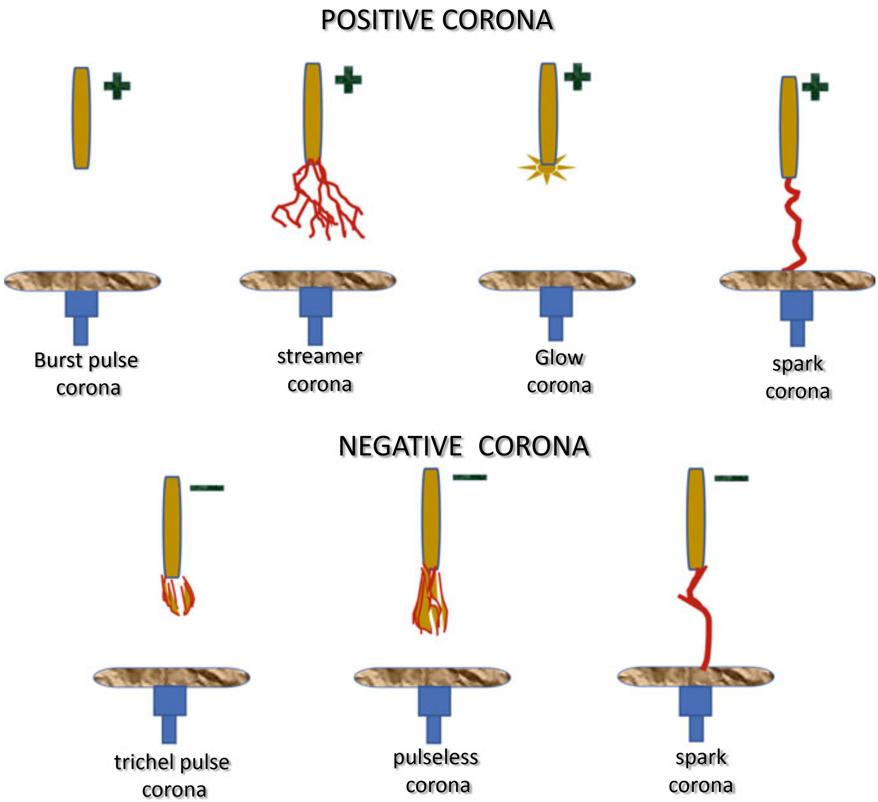

Fig. 8 Schematic representation of different types of corona

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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