International Journal of Chemical Studies

P-ISSN: 2349–8528
E-ISSN: 2321–4902
IJCS 2018; 6(2): 594-603

Received: 07-01-2018
Accepted: 10-02-2018

Akanksha Pahwa
Dairy Technology Division, ICAR-National Dairy Research Institute, Karnal, Haryana, India

Honey Kumar
Department of Food Science and Technology, Punjab Agricultural University, Ludhiana, Punjab, India

Correspondence
Akanksha Pahwa
Dairy Technology Division, ICAR-National Dairy Research Institute, Karnal, Haryana, India

Influence of cold plasma technology on food packaging materials: A review

Akanksha Pahwa and Honey Kumar

Abstract
In the past cold plasma technology has found wide applications in material processing and it finds widespread applications in food industries as a novel technology. Cold plasma was originally developed for usage in electronics along with improving various functional properties like printing and adhesion properties of polymers. When the ionized gas is released on the polymer, effects of ablation, cross linking and activation are produced on its surface, which results in enhancing surface energy and hence improvement of various functional properties like adhesiveness, prinitibility and wettability of polymers Furthermore, cold plasma has resulted into surface decontamination of the packaging materials and improved barrier properties of polymer. New trends aim to provide antimicrobial surface and thus set up active packaging. The present review provides an overview of principles of action of cold plasma technology, equipment and summarises recent advances in the modification of polymeric food packaging materials.

Keywords: Plasma, packaging, dielectric, antimicrobial

Introduction
In recent years, there has been growing interest in the modifying packaging materials using techniques like simple flame, corona treatments, UV, gamma-ray, electron beam irradiations, ion beam, plasma, and laser treatments (Ozdemir *et al.* 1999) [47]. Cold plasma technology is one of the most novel technologies which find widespread potential as surface modification technique in the field of food packaging. Cold plasma is produced by using electricity and a carrier gas. As a result of which, electrical discharges are produced and subsequently ionization of atmospheric air is carried out (Bevilacqua *et al.* 2018) [6]. The ionized species are then directed onto polymer surfaces either by reacting with the activated surface or forming cross-links with the surface polymer chains (Misra *et al.* 2011) [38]. In this way, degradation of the polymeric material is considerably reduced (Pandiyaraj *et al.* 2008a) [48]. Factors like the type of gas used for plasma generation which determine the proportion of active species in the discharge (Lerouge *et al.* 2000) [34] and general conditions of application, it is possible to activate a polymeric surface by inserting or creating active species (Ataeefard *et al.* 2009) [3]. Nowadays, polymers find wide applications in modern industry. However, polymers are hydrophobic, low surface energy materials, which do not adhere well to other materials. Therefore, many functional properties like wettability, adhesion, printability and biocompatibility of polymers are affected (Pandiyaraj *et al.* 2008a) [48]. For this reason polymer films need some additional treatment like plasma treatment to raise the surface activity, for better functional properties (Tendero *et al.* 2006 [60] and Wolf *et al.* 2010) [69]. Surface treatments can serve different purposes such as surface functionalization, surface cleaning or etching, and surface deposition (Oh *et al.* 2016) [46]. One of the most important application of CPT i. e. surface functionalisation has been used to improve barrier characteristics of food packaging polymers and to impart antimicrobial properties (Ozdemir *et al.* 1999) [47]. Decontamination of packaging materials using plasma technology is currently an area of major research in the field of plasma technology (Pankaj *et al.* 2014a) [50]. Sterilization of packaging materials is brought about by gas plasma reactions without adversely affecting the bulk properties of the packaging materials (Muranyi *et al.* 2007 [43] and Dong *et al.* 2017) [16]. Van de Veen *et al.* (2015) [64] reported that the effect of cold plasma on bacterial spores is more than the conventional techniques like heat, chemicals and UV treatment. Thus, cold plasma technology is an effective, economical, environmentally safe technique (Schutze *et al.* 1998) [55].

Plasma Chemistry

Atmospheric cold plasma (ACP) refers to non-equilibrium plasmas generated at near ambient temperatures and pressure. They are composed of free electrons, radicals, positive and negative ions, but are low in collision frequency of gas discharging compared to equilibrium plasma (Han *et al.* 2016) [23]. Electrons and photons are usually designed as "light" species in contrast to the other constituents defined as "heavy" species (Moreau *et al.* 2008) [41].

Fig. 1 depicts the chemical structure of surface when exposed to plasma. Plasma can be produced by subjecting a gas to an electric field (between two electrodes), either of constant (direct current field) or alternating amplitude (usually high frequency field). Fig. 2 depicts the principles of plasma generation. Several forms of energies like; thermal, electric or magnetic fields and radio or microwave frequencies can be used to attain plasma state (Wan *et al.* 2009) [66], which increase the kinetic energy of the electrons resulting in increased number of collisions in the gas forming plasma products which include various ionic species (Misra *et al.* 2011) [38]. d'Agostino *et al.* (2005) [12] reported that plasmas can be classified on the basis of the conditions in which they are produced into low temperature, non-equilibrium glow discharge or high temperature, equilibrium thermal plasma. Thermal plasmas are obtained at high pressure (≥105 Pa) and need substantial power (up to 50 MW). The gas temperature is nearly the same for all the components of the plasma which can be very high (5 to 20 ×103 K) and present local thermodyanamic equilibrium between the electrons and the heavy species Non-thermal plasmas are obtained at lower pressures and use less power. They are characterised by an electron temperature much higher than that of the gas and consequently do not present a local thermodynamic equilibrium. Such plasma can be generated by electric discharges in lower pressure gases (Moreau *et al.* 2008) [41]. A third category of plasmas are categorized as non-thermal plasmas because they are formed near atmospheric pressure and ambient temperature (Tendero *et al.* 2006) [60].

The various methods used for plasma generation includes the corona discharge; dielectric barrier discharges (DBD), radio frequency plasma (RFP) and the gliding arc discharge (Thirumdas *et al.* 2015) [61]. The ions and electrons from the plasma are produced at an electrode by means of a radiofrequency (RF), microwave (MW) or dielectric barrier discharge (DBD) power source, and a biasing power source is applied to another (packaging holding) electrode to create a significant ion bombardment component during plasma treatment (Breen *et al.* 2011) [9].

Microwave Discharges

Microwave discharges (MD) are the electrical discharges generated by the electromagnetic waves with frequencies exceeding 300 MHz. MDs are extensively used for generation of quasi-equilibrium and nonequilibrium plasma for different applications (Lebedev, *et al.* 2010). Microwaves are guided along the system and transmitted energy to the plasma gas electrons (Tendero *et al.* 2006) [60]. Lebedev *et al.* (2010) described that the microwave plasma generator consisted of microwave power source (usually the magnetron generator), element protecting the magnetron from the reflected power (any nonreciprocal device, e. g. circulator), standing wave ratio meter, matching circuit and microwave-to-plasma applicator. A microwave emitter is inserted into the reactor in which the gas is confined. The antenna transmits energy to the gas that is then converted into plasma. Moreover, as shown later by Moisan *et al.* (2001) [39], the effect of microwave plasma requires synergy between UV and chemical components of the plasma.

Dielectric barrier discharges (DBD) plasmas

Dielectric barrier discharge (DBD) is one of the most common methods for generation of non-thermal plasma. In DBD, plasma is generated between two parallel metal electrodes out of which, at least one of them is covered by a dielectric layer which restricts the discharge current to avoid an arc transition (Pankaj *et al.* 2014a) [50].

Dielectric barrier discharges (DBD) plasmas was first introduced by Siemens in 1857 to create ozone. This was achieved by subjecting a flow of oxygen or air to the influence of a dielectric-barrier discharge (DBD) maintained in a narrow annular gap between two coaxial glass tubes by an alternating electric field of sufficient amplitude (Kogelschatz, 2003).

DBD discharges are based on the use of a dielectric barrier in the discharge gap which stops electric currents and prevents the formation of sparks and are accompanied by local overheating (Moreau *et al.* 2008) [41]. Therefore, DBDs are referred to as barrier discharges or silent discharges The most important characteristic of DBDs is that non-equilibrium plasma conditions can be provided at elevated pressure, for example atmospheric pressure. In DBDs this can be achieved in a much simpler way than with other alternative techniques like low pressure discharges, fast pulse high pressure discharges or electron beam injection (Kogelschatz *et al.* 1997) [29]. In a common coaxial configuration, the dielectric is shaped in the same form as common fluorescent tubing. It is packed at atmospheric pressure with either a rare gas or rare gas halide mix and the glass walls act as the dielectric barrier. Due to the atmospheric pressure level, such processes require high energy levels to be sustained. Common dielectric materials include glass, quartz, ceramics and polymers (Liang *et al.* 2011).

DBD discharges usually operate at frequencies between 0.05 and 500 kHz. They are applied for example, in ozone generation, CO_2 lasers and as UV source in excimer lamps (Fridman *et al.* 2005) [18]. Typical electrode configurations of planar and cylindrical dielectric-barrier discharges are given in Fig. 3. DBDs are characterized by the presence of one or more insulating layers in the current path between metal electrodes in addition to the discharge gap(s).

DBD has the advantage that the presence of the dielectric prevents electric puncture of the plastic foils in case of pinholes. It is therefore used to treat polymer surfaces in order to promote wettability, printability and adhesion (Kogelschatz, 2003). Wang and He (2006) [68] studied that surface wettability of polypropylene (PP) was improved in atmospheric pressure dielectric barrier discharge. Dixon and Meenan (2011) reported that low treatment dose of 0.01 J/cm^2 resulted in significant increase in surface energy and hence wettability, which led to improved adhesive bonding and printability. Fig. 4 depicts the dielectric barrier plasma discharge.

The gliding arc discharges

Production of plasma by gilding arc discharge is carried out in a large reactor, in which two or more metallic electrodes are placed with a large potential difference of 9kV, in open conditions. Fig. 5 depicts photo image of the gliding arc in the parallel flow reactor. The gap between the electrodes is injected with a gas (generally humid air). The arc that forms at the shorter inter-electrodes distance is blown and breaks into a plasma plume. A new arc immediately reforms for a new cycle (Moreau *et al*. 2008) [41]. It can be applied on surfaces of bulky objects, and allows fast processing. Gliding arc discharges can provide a high degree of non-equilibrium, high electron temperature and high electron density simultaneously, and thus potentially enable selective chemical process with high productivity (Kusano *et al*. 2008) [31]. Kusano *et al*. (2008) [31] studied the effect of atmospheric pressure gliding arcs on glass fibre reinforced polyester plates for improvement of adhesion properties with vinylester resin. The effect of treatment highly depended on the temperatures of the electrodes and the discharge. Kamgang-Youbi *et al*. (2007) [25] reported that a spectroscopic investigation of the gliding arc discharge in humid air revealed that the main species formed in the non-thermal phase are the radicals OH and NO.

Corona discharge plasmas

Partially ionized gas discharges that occur between a sharp electrode (called a corona source), typically a needle or a wire, and a blunt electrode (called a collecting electrode or counter electrode) such as a plate or a cylinder are commonly referred to as corona discharges (Tirumala, 2013) [62]. When a negative high voltage is applied to the wire, the discharge is a negative corona. The positive ions are accelerated towards the wire where secondary electrons are emitted and accelerated into the plasma: this moving front of high-energy (about 10 eV) electrons followed by a tail of lower energy electrons (about 1 eV) is called a streamer (Bogaerts *et al*. 2002) [7]. A typical positive corona discharge between a needle and a plate is shown in Fig. 6

Magnitude of the electric field should be greater than a certain critical value (*Ec*) for ionization of the interstitial gas molecules. Unlike a glow discharge between parallel plates, where the field is uniform, in a corona discharge, the magnitude of the electric field is greater than certain critical value near the sharp corona source. As a result, ionization of gas molecules occurs in only *ionization zone*, and the corona discharge is thus said to be locally ionized plasma (Tirumala, 2013) [62].

Applications of Plasma technology in Food Packaging

As already discussed, if a substrate has a low surface energy, its functional properties are poor, then a surface treatment is required to increase its energy. Recently, atmospheric pressure plasma (APP) has been applied to the deposition, coating, synthesis, metallurgy, and etching of thin film etc (Gomez *et al*. 2009). Moreover, the highly reactive free radicals (OH, H_2O) and H_2O_2 produced during APP process play a major role in the inactivation of bacteria (Gweon *et al*. 2009) [22].

Food Packaging Surface Sterilisation

Sterilization is currently an active field of research because gas plasma allows fast and safe sterilization of packaging materials such as bottles, lids and films-without adversely affecting the main properties of the packaging materials (Muranyi *et al*. 2008) [44]. Sterilisation methods such as dry heat, steam, UV light and chemicals like ethylene oxide and hydrogen peroxide have been traditionally used for medical instruments and implants as well as packaging materials in food industry (Muranyi *et al*. 2010) [45], but certain limitations associated with such conventional sterilisation techniques like the generation of liquid effluents, which add to the overall cost of the process have motivated the search for new approaches (Schneider *et al*. 2005) [54].

Sterilization of packaging materials can be carried out using various techniques like high pressure, high power ultrasonics, pulsed ultraviolet light, pulsed electric fields and the most novel technique involving plasma of gases. Techniques, like high hydrostatic pressure, are chemically safer but require expensive equipment (Wan *et al*. 2009) [66]. A practical sterilization method for packaging materials must fulfil characteristics like fast microbiocidal effect, compatibility with packaging material, no chemical residues, harmless for personnel, free of hazardous solvents and economic efficiency (Ansari and Dutta, 2003 [2] and Misra *et al*. 2015) [37]. Gas plasma can be used for sterilization of heat-sensitive packaging material (Wan *et al*. 2009 [66] and Morent *et al*. 2011) [42]. Muranyi *et al*. (2007) [43] investigated microbial inactivation efficiency of a newly developed cascaded dielectric barrier discharge (CDBD) set-up against various microorganisms on polyethylene terephthalate (PET) foils. *Aspergillus Niger* was the most resistant test strain with an inactivation rate of about 5 log10 in 5 s. In another study, Muranyi *et al*. (2008) [44] have identified an increase in relative gas humidity as a key factor to achieve a minimum of 2log10 inactivation in *A. Niger* and *B. subtilis* for 1 s treatments.

Cell death by plasma takes place by three basic mechanisms. These are: etching of cell surface by reactive species like nitrogen and oxygen based species such as atomic oxygen, ozone, nitrogen oxide and hydroxyl (Laroussi and Leipold 2004 [33] and Moon and Choe, 2009). Present in plasma discharge, volatilization of compounds and intrinsic photodesorption of ultraviolet (UV) photons and the destruction of genetic material. Several reactions like lipid peroxidation of poly-unsaturated fatty acids, oxidation of amino acids and DNA oxidation takes place in bacterial cells (Dobrynin *et al*. 2009 [15] and Wan *et al*. 2009) [66]. These active species have short life in the gas phase thereby disappearing in milliseconds after they are produced and can also dissolve in liquids (Laroussi and Leipold, 2004) [33]. The short chains of charged fatty acids have a lower ability to rotate within the membrane and increase the fluidity of the membrane which can result in distraction of structural membrane integrity (Korachi and Aslan, 2013) [30]. Deilmann *et al*. (2009) [13] found that plasma radiation consisting of hydrogen, nitrogen, and oxygen in the wavelength range 230 nm≤280 nm is very efficient for reduction of *B. atrophaeus* spores. Active packaging and antimicrobial surfaces are novel technologies for food preservation. Active packaging can be defined as a mode of packaging in which the package, the product and the environment interact to enhance the shelf-life, safety or sensory properties of the product, while maintaining its quality (Suppakul *et al*. 2009). Bioactive functional compounds like lysozyme, nicin, vanillin, sodium benzoate, glucose oxidase or antimicrobial peptides can be immobalised into the packaging material by plasma treatment and produce antimicrobial and active packaging (Pankaj *et al*. 2014b) [51]. Patsy *et al*. (2003) [52] studied that selective attachment of nisin as a surface coating material on packaging film can inhibit bacterial growth and extend shelf-life of foods. Nisin-activated antimicrobial packaging can diminish the negative interactions of antimicrobial compounds with food (Karam *et al*. 2013) [26]. Patsy *et al*. (2003) [52] investigated the effect of film type and treatment conditions on the binding of nisin to ethylene acrylic acid copolymer films with surface energy =32 dyne/cm. The results revealed that the antimicrobial activity tended to increase in response to the increased nisin concentration of the coating solution and increased coating time from 30 s to 2 h. higher nisin coating concentration also promoted the binding of nisin to films with saturation level observed at 250 µg/mL. Moreover, lower coating pH of 3 led to higher binding of nisin to film surfaces and increased antimicrobial activity.

Plasma functionalization of polymer surfaces

Surface functionalization involves addition of functional groups or to the packaging material surface in order to improve antimicrobial properties and enhance mechanical properties (glazing, adhesion, sealability, wettability, dye-up-take, *etc*.) (Ekezie *et al*. 2017) [17]. alternately, the technique may be used to deposit coatings on the surface of polymers by employing layers of deposition barrier. Fig. 7 depicts the schematic illustration of the concept of the plasma polymerization process.

Plasma-induced grafting

Polymer surfaces can also be modified by "plasma-induced grafting", which is a combination of plasma functionalization and conventional chemistry. It is based on attaching functional monomers onto surfaces and can be carried out in three main steps as described and shown in Fig. 8. Firstly, polymers are first exposed to the plasma to activate the surface and produce radicals (Bogaerts *et al.* 2002) [7]. Futher, upon exposure to atmosphere, most of the formed radicals are oxidized leading to oxygen and peroxide groups. Then, the polymer is dipped in the monomer solution under inert atmosphere and the solution is heated (Kato *et al*. 2003) [27].

Grigoriu *et al*. (2013) [19] studied that polyvinyl alcohol (PVA) coating attached with monochlorotriazinyl-β-cyclodextrin (MCT) which provides cavities that can provide chemicals specific for particular antimicrobial coating. The results revealed that substances like ferulic acid, allantoin which has been included in the cavities of MCT attached on coated layer illustrate satisfactory antimicrobial activity against four microbial strains (*Escherichia coli, Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Candida albicans*). Oh *et al*. (2016) [46] studied the effects of CPT using various plasma-forming gases on the physical properties of defatted soybean meal (DSM)-based edible film (DSM film). After treatment with cold plasma, the tensile strength, elongation, and moisture barrier property of DSM film increased by 6.8%, 13.4%, and 24.4%, respectively. Ulbin-Figlewicz *et al*. (2014) prepared chitosan based edible films by casting from lactic acid solution with water solution of lysozyme in three various concentrations (0, 0.5 and 1%). Dried films were then modified by exposition on cold helium plasma treatment for 0, 5 and 10 min. The prepared films were tested against growth of *Listeria monocytogenes, Yersinia enterocolitica* and *Pseudomonas fluorescens*. The results revealed that films incorporated with 1% lysozyme enhanced the inhibition efficiency of chitosan based films against gram-positive (*L. monocytogenes*) and gram-negative (*P. fluorescens*) bacteria.

Surface wettability, often characterised by water contact angle, which is the angle at which a liquid drop meets the surface and is measured optically. The contact angle is influenced by both surface energy, roughness and is inversely proportional to wettability of a packaging material (Lai *et al*. 2006) [32]. Song *et al*. (2016) [56] treated PLA films with CP for 40 min at 900 W and 667 Pa using oxygen as the plasma-forming gas. The physico-chemical and biodegradability properties of the films were evaluated during storage for up to 56 days. The results revealed that CP-induced hydrophilicity, printability increased following CPT and remained stable throughout the storage period. Moreover, photodegradation, thermal, microbial and biodegradable properties of the films were significantly improved by CPT.

Adhesion is a manifestation of attractive forces among atoms. There is a general agreement on the fact that attractions due to hydrogen and Van der Walls bonding are responsible for adhesiveness between polymers. Low surface energies of PE and PP and the presence of ester groups in the backbone of PET restrict their adhesion to other materials. Therefore, plasma treatments can be used to increase adhesion characteristics to minimize leakage, reduce the risk of microbial contamination, and assure package integrity (Ozdemir *et al*. 1999) [47]. Dixon and Meenan (2012) [14] studied that DBD treatment of PE, PP and PET, which resulted in a reduction in contact angle of approximately 35-45° from the untreated level. While, DBD treatment of PS resulted in a reduction of 54-75°. For optimum adhesion, the surface energy of the polymer should be larger than that of the material to be bonded with. Similarly, for effective wetting by a liquid, the surface energy of the polymer should exceed the surface tension of the liquid (Guimond *et al*. 2002) [21]. Fig. 9a shows the surface of the untreated PP film which is very smooth. After the plasma treatment, the surface of the PP film shows rough morphology (Fig. 9b-e) (Pandiyaraj *et al*. 2008b) [49]. Pandiyaraj *et al*. (2008b) [49] found that glow discharge plasma at pressure 0.2 mbar and power input 10W resulted in improvement of hydrophilicity and adhesion of PP and PET films. From Fig. 10, it can be seen that the surface roughness factor increased with increased in treatment time led to increase in surface roughness factor. The roughness factor depicted an almost saturate trend at longer exposure times. Ataeefard *et al*. (2009) [3] found that treatment of LDPE surface layer with Ar or O_2 plasma treatment led to formation of oxidized structures The results of contact angle, surface free energy, SEM and AFM, revealed that Ar plasma is more effective than O_2 plasma, as in addition to production of functional polar groups, it enhanced surfaces roughness.

Barrier Properties

Barrier properties of food packaging material can be improved by exposing the material with cold plasma (Dielmann *et al*. 2009). Typical examples of polymeric materials used for food and beverage packaging materials are polypropylene (PP), polyethylene (PE), or polyethylene terephthalate (PET). Though these polymers have numerous advantages over conventional packaging materials (glass, metals, paper) including high flexibility, strength, stiffness, mechanical resistance and optical transparency, their main limitation is high oxygen, CO_2 or water vapour transition rate (Marsh *et al*. 2007) [36]. Karam *et al*. (2013) [26] reported that the basic techniques for deposition of barrier coatings are based on low-pressure plasma-enhanced chemical vapour deposition (PECVD), which refers to the deposition of thin polymer films by vapour phase deposition through reactions of the plasma with an organic monomer gas. The technique uses volatile precursors (e. g. hexamethyldisiloxane, tetramethoxysilane, divinyltetramethyldisiloxane, allyltrimethylsilane, acetylene or methane), which become excited and partially decomposed in the plasma, that leads to the growth of a film on a substrate, which results into improved chemical and physical properties (Chu *et al*. 2002) [10].

Kazminova *et al*. (2013) [28] investigated properties of a-C: H and SiOx thin films deposited by PECVD using Ar/n-hexane and HMDSO/O2 gas mixtures on PET foils. Significant improvement of barrier properties of PET foils was observed after their coating with a-C: H film having the thickness of about 12 nm. In case of SiOx coatings, highest barrier character towards water vapour for thickness of SiOx coating about 40 nm.

Poly (ethylene terephthalate) (PET) is a thermoplastic polymer resin of the polyester family (Marsh *et al*. 2007) [36]. Boutroy *et al*. (2006) [8] carried out the deposition of hydrogenated amorphous carbon (a-C: H) films of thickness 100nm on PET surfaces. It involved combination of acetylene gas precursor and microwave plasma to obtain a high deposition rate. The combination of acetylene gas precursor and microwave plasma was used to obtain a high deposition rate of 60 nm/s. The results revealed that a permeation rate of O_2 was reduced by 50 folds. Deilmann *et al*. (2009) [13] studied the improvement of barrier properties through deposition of thin layers of SiOx on PET foils by PECVD.

Recently, biodegradable polymers such as poly (lactic acid) (PLA), chitosan and arabinoxylans (AXs) have gained interest as conventional polymers lead to serious environmental problems of waste disposal (Marsh *et al.* 2007) [36]. Peroval *et al*. (2003) grafted omega-3 (ω3) fatty acids onto arabinoxylan polymeric chains by using cold plasma technology. The results revealed a decrease in water vapour permeability (WVP) for the film treated with the α-linolenic acid-rich oil. Contact between food and plastic packaging may cause reciprocal transfer between the material and the surrounding medium. Various processing aids like plasticizers may migrate from the packaging material or can be extracted by the foodstuff. This phenomenon of migration affects packaged food and a decrease in the chemical and physical properties of the plastic material (Guillard *et al.* 2010) [20]. Audic *et al.* (2001) [4] studied the effect of plasma-induced surface cross linking of poly (vinyl chloride) (PVC)-based flexible films to limit its migration from packaging into fatty foodstuffs. The results revealed that, the Argon plasma appeared to be the most efficient as 5 min of treatment caused decrease in overall migration from 15.8% to the lowest observed value (3%). Another technique to reduce migration was to substitute low molecular weight plasticizers like di-2-ethylhexyladipate (DEHA) with higher molecular weight compounds like elastomeric ethylene-based terpolymer (EE), completely or partially. After treatment with Ar plasma, a significant reduction in migration from all plasticised PVC films was observed. Pankaj *et al.* (2014b) [51] reported that very limited migration was expected from PLA films into food after DBD plasma treatment and below the 10 mg dm^2 amount of migrant limit is indicated in the current European Legislation.

Ageing

Ageing is defined as the loss of beneficial attributes derived from cold plasma processing of polymers over time. Ageing leads to deterioration of the beneficial surface properties (Banik *et al.* 2002) [5]. Factors responsible for ageing are type of polymer and the process conditions which include thermodynamic properties of the surface and the environment (Akishev *et al*. 2008) [8], rearrangement of surface layer as movement of polymer chains may take place from the bulk of the polymer to the surface or vice versa. Major drawback of plasma applications is hydrophobic recovery (Jokinen *et al*. 2012) [24]. Banik *et al.* (2006) investigated the effect of plasma treatments, involving argon and oxygen in a ratio of 9:1 on HDPE. The results showed that the plasma treatment was found to lower the aging effect more because of an increased degree of cross-linking in addition to oxidation. Similarly, higher crystalline surface resulted into higher structural regularity and lower free volume in the polymer matrix, therefore, resulting into decreased ageing effect. Guimond *et al.* (2002) [21] investigated ageing of the BOPP and compared for the two types of DBD treatments, namely air corona, and N_2 atmospheric pressure glow discharge (APGD). The results revealed that the increased surface energy is found to decay with increasing storage time after treatment. Ataeefard *et al.* (2009) [3] studied Ar and O_2 plasma treated samples which were subjected to several aging processes to determine the durability of different plasma treatments. By comparing, Ar plasma treatment revealed fewer trends to reduce its contact angle in the aging process because it maintains its greater roughness. Thus, the mechanism of ageing and approaches to delay the hydrophobic recovery is a subject of active research.

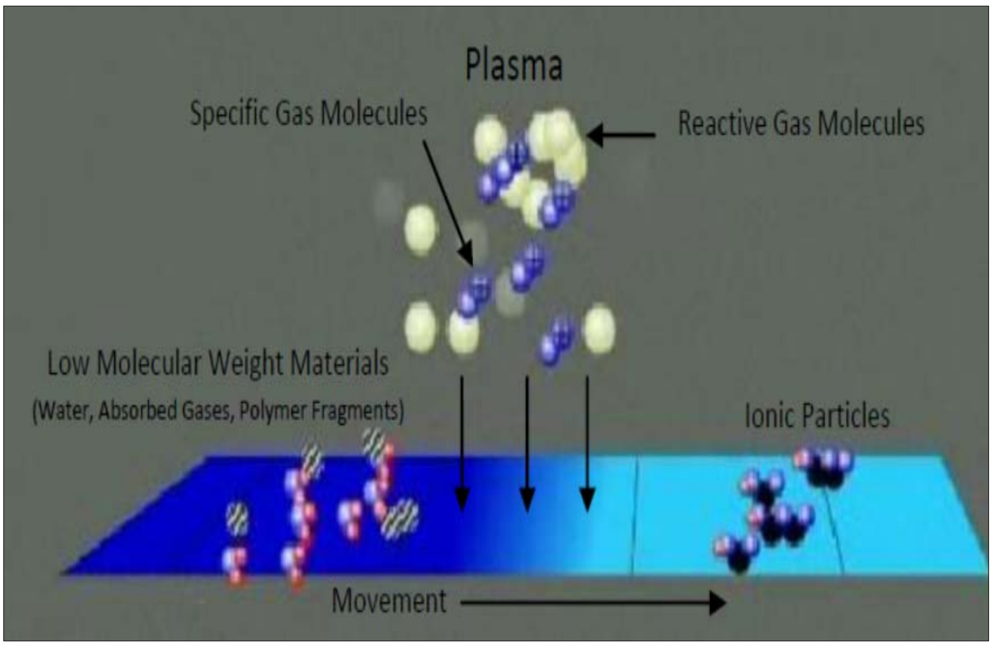

Fig 1: Chemical structure of surface when exposed to plasma (Taylor, 2009) [59]

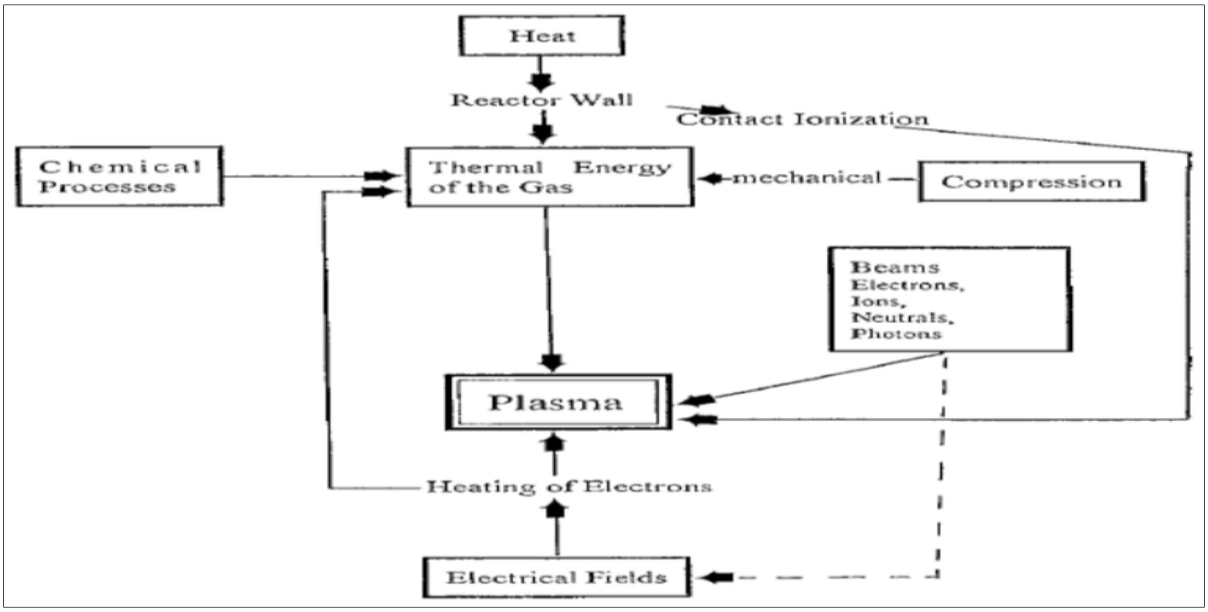

Fig 2: Principles of Plasma generation (Conrads and Schmidt, 2000) [11]

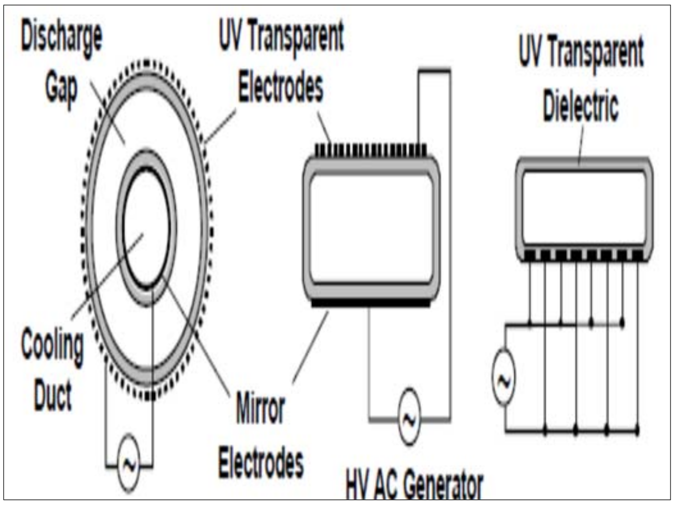

Fig 3: Sealed cylindrical and planar dielectric-barrier discharge excimer lamp configurations **(**Kogelschatz *et al.* 1997) [29]

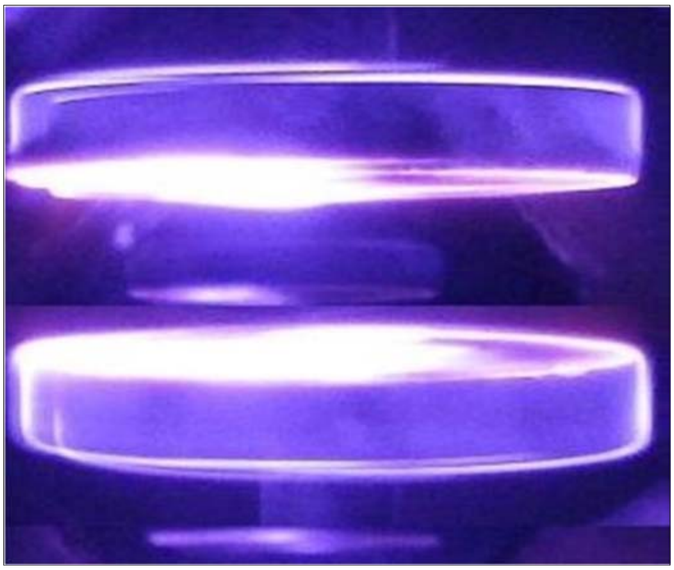

Fig 4: The dielectric barrier plasma discharge (Korachi and aslant, 2013) [30]

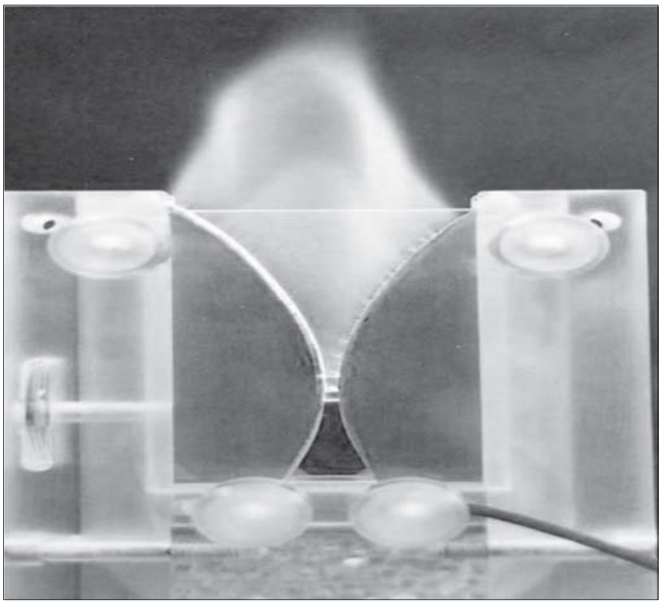

Fig 5: Photo image of the gliding arc in the parallel flow reactor (Fridman *et al*. 2005) [18]

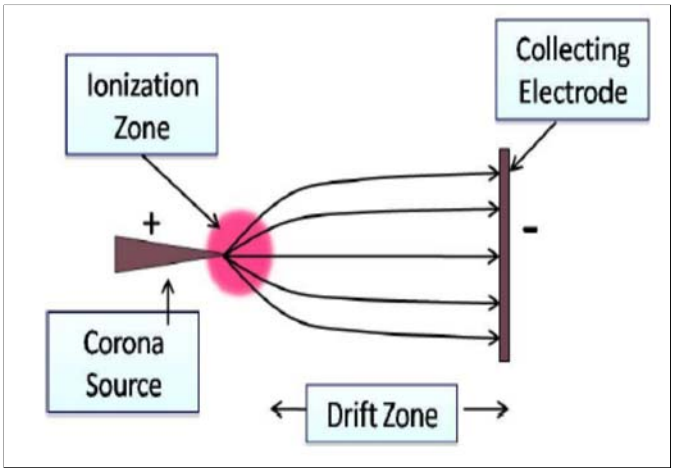

Fig 6: Schematic of a positive corona discharge (Tirumala, 2013) [62]

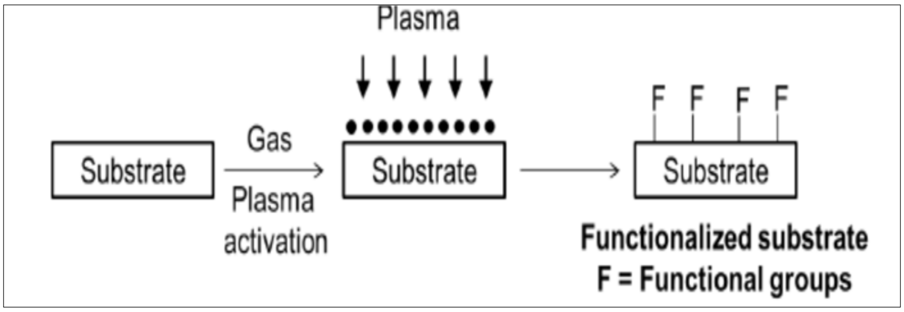

Fig 7: Schematic illustrating the concept of the plasma polymerization process (Karam *et al*. 2

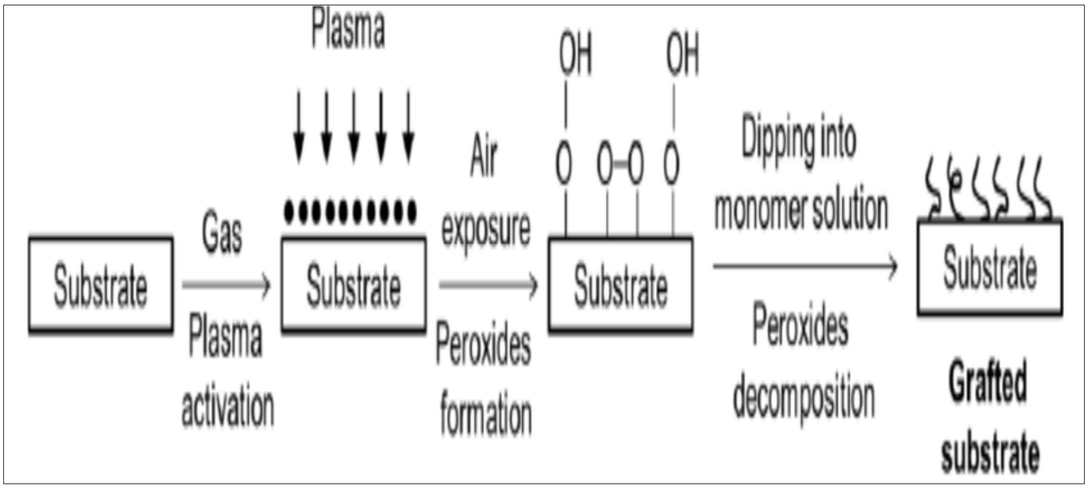

Fig 8: Schematic illustrating the concept of the plasma-induced grafting process (Karam *et al*. 2013) [26]

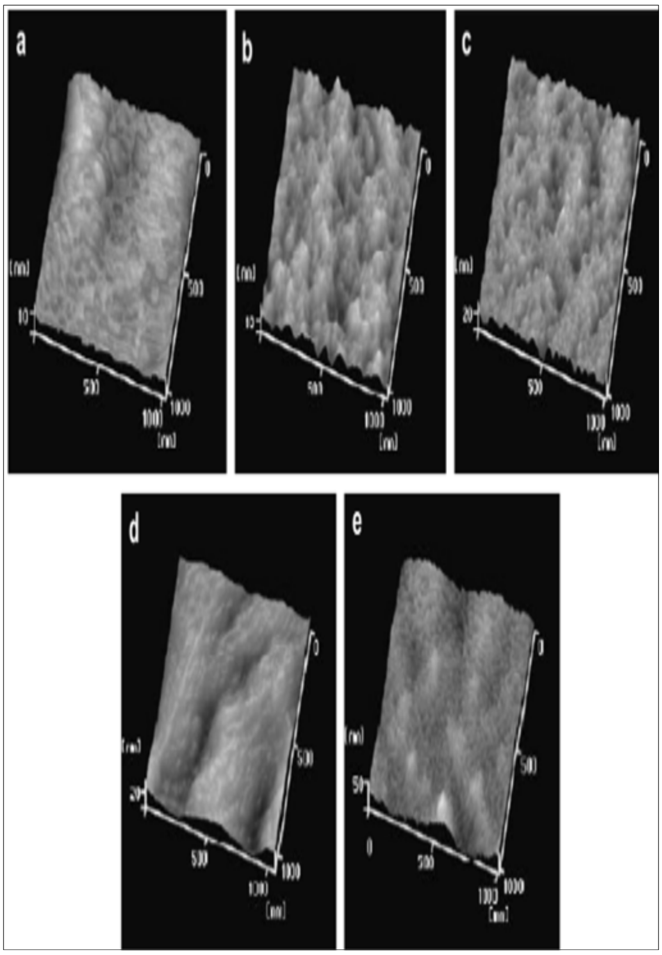

Fig 9: AFM topographic representation of PP film surface for different exposure times: (a) untreated; (b) 5 min; (c) 10 min; (d) 15 min; (e) 20 min (Pandiyaraj *et al*. 2008) [48]

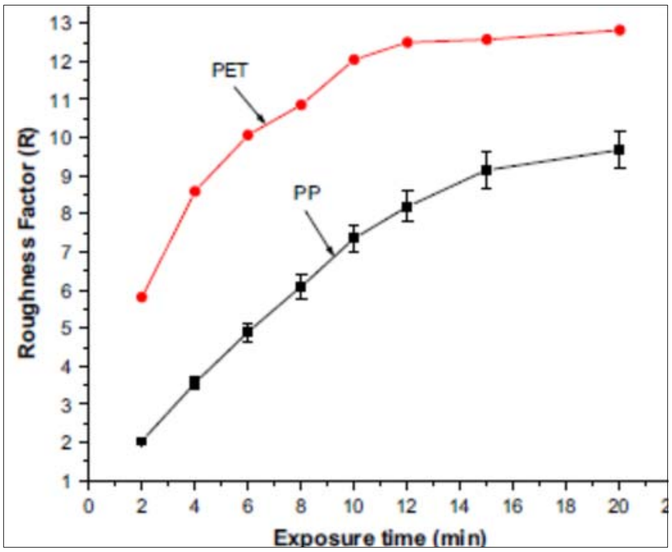

Fig 10: Roughness factor (R) as a function of exposure time (Pandiyaraj *et al*. 2008 b) [49]

Conclusion

Cold plasma technology has established a great potential to provide significant improvements in the food packaging sector. This review has discussed a few of the most potent applications of cold plasma technology. Plasma sterilization is highly advantageous as it is economical, provides high efficacy, preservation, does not introduce toxicity to the medium, is suitable for heat sensitive materials and is environmentally safe method. Cold plasma treatment can be brought about by various surface modification techniques, such as plasma functionalization and plasma induced grafting which subsequently aids in attachment of bioactive agents. Deposition of bioactives and antimicrobials with the help of cold plasma technology can make significant contribution to the emerging field of edible films and active packaging of foods. Besides sterilization, barrier properties of packaging material can be improved by plasma-enhanced chemical vapour deposition. However, ageing is a significant limitation for most of the plasma applications. Future studies should be directed towards approaches to delay ageing and assessment of the efficacy of antimicrobials after immobilisation into the packaging material by plasma treatment.

References

1. Akishev Y, Grushin M, Dyatko N, Kochetov I, Napartovich A, Trushkin N, *et al*. Studies on cold plasma-polymer surface interaction by example of PP- and PET-films. Journal of Physics D: Applied Physics. 2008; 41(23):235-203.
2. Ansari IA, Datta AK. An overview of sterilization methods for packaging materials used in aseptic packaging systems. Food and Bioproducts Processing. 2003; 81(1):57-65.
3. Ataeefard M, Moradian S, Mirabedini M, Ebrahimi M, Asiaban S. Investigating the effect of power/time in the wettability of Ar and O_2 gas plasma-treated low-density polyethylene. Prog. Org. Coat. 2009; 64:482-488.
4. Audic JL, Poncin Epaillard F, Reyx D, Brosse JC. Cold plasma surface modification of conventionally and nonconventionally plasticized poly (vinyl chloride) based flexible films: Global and specific migration of additives into isooctane. J. Appl. Polym. Sci. 2001; 79(8):1384-1393.
5. Banik I, Kim KS, Yun YI, Kim DH, Ryu CM, Park CE. Inhibition of aging in plasma-treated high-density polyethylene. J Adhes. Sci. Technol. 2002; 16(9):1155-1169.
6. Bevilacqua A, Petruzzi L, Perricone M, Speranza B, Campaniello D, Sinigaglia M *et al*. Nonthermal Technologies for Fruit and Vegetable Juices and Beverages: Overview and Advances. Comp. Rev. Food Sci. Food Safety. 2018; 17(1):2-62.
7. Bogaerts A, Neyts E, Gijbels R, Van der Mullen J. Gas discharge plasmas and their applications. Spectrochim. Acta Part B At. Spectrosc. 2002; 57(4):609-658.
8. Boutroy N, Pernel Y, Rius JM, Auger F, Von Bardeleben, Cantin HJ *et al*. Hydrogenated amorphous carbon film coating of PET bottles for gas diffusion barriers. Diamond and Relat. Mater. 2006; 15(4):921-927.
9. Breen A, Milosavljevic V, Dowling DP. Influence of gas type on the thermal efficiency of microwave plasmas for the sintering of metal powders. Plasma Chem. Plasma Process. 2011; 31(5):771-785.
10. Chu PK, Chen JY, Wang LP, Huang N. Plasma-surface modification of biomaterials. Mater. Sci. Eng. R. Rep. 2002; 36(5-6):143-206.
11. Conrads H, Schmidt M. Plasma generation and plasma sources. Plasma Sources Sci. Technol. 2000; 9(4):441.
12. d'Agostino R, Favia P, Oehr C, Wertheimer MR. Low-Temperature Plasma Processing of Materials Past, Present, and Future. Plasma Processes Polym. 2005; 2(1):7-15.
13. Deilmann M, Halfmann H, Steves S, Bibinov N, Awakowicz P. Silicon oxide permeation barrier coating and plasma sterilization of PET bottles and foils. Plasma Processes Polym. 2009; 6(S1):S695-S699.
14. Dixon D, Meenan JB. Atmospheric dielectric barrier discharge treatments of polyethylene, polypropylene, polystyrene and poly (ethylene terephthalate) for enhanced adhesion. J Adhes. Sci. Technol. 2012; 26:2325-2337.
15. Dobrynin D, Fridman G, Friedman G, Fridman A. Physical and biological mechanisms of direct plasma interaction with living tissue. New J Phys. 2009; 11(11):115-020.
16. Dong S, Gao A, Xu H, Chen Y. Effects of dielectric barrier discharges (DBD) cold plasma treatment on physicochemical and structural properties of zein powders. Food Bioprocess. Technol. 2017; 10(3):434-444.
17. Ekezie FGC, Sun DW, Cheng JHA. Review on recent advances in cold plasma technology for the food industry: current applications and future trends. Trends Food Sci. Technol. 2017; 69:46-58.
18. Fridman A, Chirokov A, Gutsol A. Non-thermal atmospheric pressure discharges. J. Phys. D: Appl. Phys. 2005; 38(2):R1.
19. Grigoriu AM, Luca CO, Horoba E, Dunca S. Antimicrobial Polymer Films Functionalized with Cyclodextrins. Rev. Chim. (Bucharest). 2013; 64(6):606-611.
20. Guillard V, Mauricio-Iglesias M, Gontard N. Effect of novel food processing methods on packaging: structure, composition, and migration properties. Crit. Rev. Food Sci. Nutr. 2010; 50(10):969-988.
21. Guimond S, Radu I, Czeremuszkin G, Carlsson DJ, Wertheimer MR. Biaxially oriented polypropylene (BOPP) surface modification by nitrogen atmospheric pressure glow discharge (APGD) and by air corona. Plasma Polym. 2002; 7(1):71-88.
22. Gweon B, Kim DB, Moon SY, Choe W. Escherichia coli deactivation study controlling the atmospheric pressure plasma discharge conditions. Curr. Appl. Phys. 2009; 9(3):625-628.
23. Han L, Boehm D, Amias E, Milosavljevic V, Cullen PJ, Bourke P. Atmospheric cold plasma interactions with modified atmosphere packaging inducer gases for safe food preservation. Innov. Food Sci. Emerg. Technol. 2016; 38:384-392.
24. Jokinen V, Suvanto P, Franssila S. Oxygen and nitrogen plasma hydrophilization and hydrophobic recovery of polymers. Biomicrofluidics. 2012; 6(1):016-501.
25. Kamgang JO, Briandet R, Herry JM, Brisset JL, Naïtali M. Destruction of planktonic, adherent and biofilm cells of Staphylococcus epidermidis using a gliding discharge in humid air. J Appl.Microbial. 2007; 103(3):621-628.
26. Karam L, Jama C, Dhulster P, Chihib NE. Study of surface interactions between peptides, materials and bacteria for setting up antimicrobial surfaces and active food packaging. J Mater. Environ. Sci. 2013; 4(5):798-821.
27. Kato K, Uchida E, Kang ET, Uyama Y, Ikada Y. Polymer surface with graft chains. Prog. Polym. Sci. 2003; 28(2):209-259.
28. Kazminova A, Shelemin A, Pert M, Olylian O, Biederman H. Barrier coatings on polymeric foils for food packaging. In Proceedings of the 22nd Annual Conference of Doctoral Students-WDS, 2013.
29. Kogelschatz U, Eliasson B, Egli W. Dielectric-barrier discharges. Principle and applications. J de Phys. IV. 1997; 7(C4):C4-47.

30. Korachi M, Aslan N. Low temperature atmospheric plasma for microbial decontamination. Microbial pathogens and strategies for combating them: Sci. Technol. Educ. 2013; 1:453-459.
31. Kusano Y, Teodoru S, Leipold F, Andersen TL, Sørensen BF, Rozlosnik N *et al*. Gliding arc discharge-Application for adhesion improvement of fibre reinforced polyester composites. Surf. Coat. Technol. 2008; 202(22, 23):5579-5582.
32. Lai J, Bob S, Jianming X, Sha Yan, Weijiang Zhao, Melvyn Folkard *et al*. Michael, Yugang Wang. Study on hydrophilicity of polymer surfaces improved by plasma treatment. Appl. Surf. Sci. 2006; 252(10):3375-3379.
33. Laroussi M, Leipold F. Evaluation of the roles of reactive species, heat, and UV radiation in the inactivation of bacterial cells by air plasmas at atmospheric pressure. Int. J Mass Spectrometry. 2004; 233(1-3):81-86.
34. Lerouge S, Wertheimer MR, Marchand R, Tabrizian M, Yahia LH. Effect of gas composition on spore mortality and etching during low-pressure plasma sterilization. J Biomed. Mater. Res. 2000; 51(1):128-135.
35. Liang Y, Jensen RE, Pappas DD, Palmese GR. toughening vinyl ester networks with polypropylene meso-fibers interface modification and composite properties. Polymer. 2011; 52(2):510-518.
36. Marsh K, Bugusu B. Food packaging-roles, materials, and environmental issues. J. Food Sci. 2007; 72(3):R39-R55.
37. Misra NN, Kaur S, Tiwari BK, Kaur A, Singh N, Cullen PJ. Atmospheric pressure cold plasma (ACP) treatment of wheat flour. Food Hydrocoll. 2015; 44:115-121.
38. Misra NN, Tiwari BK, Raghavarao KSMS, Cullen PJ. Nonthermal plasma inactivation of food-borne pathogens. Food Eng. Rev. 2011; 3(3-4):159-170.
39. Moisan M, Barbeau J, Moreau S, Pelletier J, Tabrizian M, Yahia LH. Low-temperature sterilization using gas plasmas: a review of the experiments and an analysis of the inactivation mechanisms. Int. J Pharm. 2001; 226(1-2):1-21.
40. Moon SY, Kim DB, Gweon B, Choe W, Song HP, Jo C. Feasibility study of the sterilization of pork and human skin surfaces by atmospheric pressure plasmas. Thin Solid Films. 2009; 517(14):4272-4275.
41. Moreau M, Orange N, Feuilloley MGJ. Non-thermal plasma technologies: new tools for bio-decontamination. Biotechnol. Adv. 2008; 26(6):610-617.
42. Morent R, De Geyter N, Desmet T, Dubruel P, Leys C. Plasma surface modification of biodegradable polymers: a review. Plasma Process. Polym. 2011; 8(3):171-190.
43. Muranyi P, Wunderlich J, Heise M. Sterilization efficiency of a cascaded dielectric barrier discharge. J Appl. Microbiol. 2007; 103(5):1535-1544.
44. Muranyi P, Wunderlich J, Heise M. Influence of relative gas humidity on the inactivation efficiency of a low temperature gas plasma. J Appl. Microbiol. 2008; 104(6):1659-1666.
45. Muranyi P, Wunderlich J, Langowski HC. Modification of bacterial structures by a low-temperature gas plasma and influence on packaging material. J App. Microbial. 2010; 109(6):1875-1885.
46. Oh YA, Roh SH, Min SC. Cold plasma treatments for improvement of the applicability of defatted soybean meal-based edible film in food packaging. Food Hydrocoll. 2016; 58:150-159.
47. Ozdemir M, Yurteri CU, Sadikoglu H. Physical polymer surface modification methods and applications in food packaging polymers. Crit. Rev. Food Sci. Nutr. 1999; 39(5):457-477.
48. Pandiyaraj KN, Selvarajan V, Deshmukh RR, Bousmina M. The effect of glow discharge plasma on the surface properties of Poly (ethylene terephthalate) (PET) film. Surf. Coat. Technol. 2008; 202(17):4218-4226.
49. Pandiyaraj KN, Selvarajan V, Deshmukh RR, Gao C. Adhesive properties of polypropylene (PP) and polyethylene terephthalate (PET) film surfaces treated by DC glow discharge plasma. Vacuum. 2008b; 83(2):332-339.
50. Pankaj SK, Bueno-Ferrer C, Misra NN, O'Neill L, Tiwari BK, Bourke P *et al*. Physicochemical characterization of plasma-treated sodium caseinate film. Food Res. Int. 2014a; 66:438-444.
51. Pankaj SK, Bueno-Ferrer C, Misra NN, Milosavljevic V, O'donnell CP, Bourke P *et al*. Applications of cold plasma technology in food packaging. Trends Food Sci. Technol. 2014b; 35(1):5-17.
52. Patsy P, Yousef AE, Shellhammer TH. Antimicrobial properties of nisin-coated polymeric films as influenced by film type and coating conditions. J Food Saf. 2003; 23(1):1-12.
53. Péroval C, Debeaufort F, Seuvre AM, Chevet B, Despre D, Voilley A. Modified arabinoxylan-based films. Part B. Grafting of omega-3 fatty acids by oxygen plasma and electron beam irradiation. J Agric. Food. Chem. 2003; 51(10):3120-3126.
54. Schneider J, Baumgartner KM, Feichtinger J, Kruger J, Muranyi P, Schulz A *et al*. Investigation of the practicability of low-pressure microwave plasmas in the sterilisation of food packaging materials at industrial level. Surf. Coat. Technol. 2005; (1-4):962-966.
55. Schutze A, Jeong JY, Babayan SE, Park J, Selwyn GS, Hicks RF. The atmospheric-pressure plasma jet: a review and comparison to other plasma sources. IEEE Trans. Plasma Sci. 1998; 26(6):1685-1694.
56. Song AY, Oh YA, Roh SH, Kim JH, Min SC. Cold oxygen plasma treatments for the improvement of the physicochemical and biodegradable properties of polylactic acid films for food packaging. J Food Sci. 2016; 81(1): E-86-E96.
57. Strobel JM, Strobel M, Lyons CS, Dunatov C, Perron SJ. Aging of air-corona-treated polypropylene film. J Adhes. Sci. Technol. 1991; 5(2):119-130.
58. Suppakul P, Miltz J, Sonneveld K, Bigger SW. Active packaging technologies with an emphasis on antimicrobial packaging and its applications. J Food Sci. 2003; 68(2):408-420.
59. Taylor W. *Technical synopsis of plasma surface treatments* (Doctoral dissertation, Dissertation for the Degree of University of Florida, Gainesville, FL), 2009.
60. Tendero C, Tixier C, Tristant P, Desmaison J, Leprince P. Atmospheric pressure plasmas: A review. Spectrochimica Acta Part B: Atomic Spectroscopy. 2006; 61(1):2-30.
61. Thirumdas R, Sarangapani C, Annapure US. Cold Plasma: A novel non-thermal technology for food processing. Food Biophys. 2015; 10(1):1-11.
62. Tirumala R. Corona discharges in asymmetric electric fields and its impact on ionic wind generation. University of Notre Dame, 2013.

63. Ulbin-Figlewicz N, Zimoch-Korzycka A, Jarmoluk A. Antibacterial activity and physical properties of edible chitosan films exposed to low-pressure plasma. Food Bioprocess. Technol. 2014; 7(12):3646-3654.
64. Van Bokhorst-van, de Veen H, Xie H, Esveld E, Abee T, Mastwijk H, Groot MN. Inactivation of chemical and heat-resistant spores of *Bacillus* and *Geobacillus* by nitrogen cold atmospheric plasma evokes distinct changes in morphology and integrity of spores. Food Microbiol. 2015; 45:26-33.
65. Villeger S, Ricard A, Sixou M. Sterilization of dental bacteria in a N_2-O_2 microwaves post-discharge, at low pressure: influence of temperature. Eur. Phys. J. Appl. Physi. 2004; 26(3):203-208.
66. Wan J, Coventry J, Swiergon P, Sanguansri P, Versteeg C. Advances in innovative processing technologies for microbial inactivation and enhancement of food safety-pulsed electric field and low-temperature plasma. Trends Food Sci. Technol. 2009; 20(9):414-424.
67. Wan J, Coventry J, Swiergon P, Sanguansri P, Versteeg C. Advances in innovative processing technologies for microbial inactivation and enhancement of food safety-pulsed electric field and low-temperature plasma. *Trends* Food Sci. Technol. 2009; 20(9):414-424.
68. Wang C, He X. Polypropylene surface modification model in atmospheric pressure dielectric barrier discharge. Surf. Coat. Technol. 2006; 201(6):3377-3384.
69. Wolf R, Sparavigna AC. Role of plasma surface treatments on wetting and adhesion. Eng. 2010; 2(06):397-2010.