

Cold Plasma: A novel Non-Thermal Technology for Food Processing

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Received: 6 August 2014 / Accepted: 19 November 2014 / Published online: 27 November 2014
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Abstract In the past cold plasma is used for sterilization of sensitive materials and now it is extended to food industries as a novel technology. For years cold plasma processing has been viewed as useful for microbial inactivation while maintaining quality of fresh produce. However, this process is not effective for in vitro model food systems for inactivation of microbes or enzymes which are present in intact tissues, as it is a surface phenomenon. Cold plasma technology is also used to inactivate endogenous enzymes which are responsible for browning reactions particularly polyphenoloxidase and peroxidases. Several research investigations showed a reduced growth of microorganism via different mode of actions by etching phenomenon, cell disruption by electrophoration etc. Plasma technology is considered as modern non conventional technique which is used for the preparation of modified starches, altering its physical and chemical properties. Overall application of cold plasma for microbial destruction on different food substrates like fruits, meat products, cheese etc. was discussed. Besides this, it is also used to alter the germination rate of seeds. It is an eco-friendly process which is used in the preservation of food and other potential applications as an alternative to common techniques.

Keywords Cold plasma · Microbial inactivation · Reactive species · Surface modifications

Introduction

Matter on earth exists mostly in three distinct phases (gas, liquid and solid) but when universe is considered as fourth

state of matter which abundantly exists. So, Plasma is hence referred to as the fourth state of matter, next to solids, liquids and gases. The term ‘Plasma’ was first employed by Irving Langmuir in 1928 to define this fourth state of matter which is partially or wholly ionized state of gas and discovered plasma oscillations in ionized gas [1]. The change of phase from solid to liquid and further to gas occurs as we increase the energy input likewise increasing the energy input beyond a certain level in gas state causes ionization of molecules which yields the plasma state [2]. d Agostino et al. [3] reported that plasma can be obtained either in low temperature, non-equilibrium glow discharge or high temperature, equilibrium thermal plasma.

Based on the properties of plasma, it is used in various fields like textile, electronics, life sciences, packaging etc. [4]. The application of plasma technology as a surface cleaning tool has been commercially adopted for the removal of disinfection chemicals applied to medical devices manufactured from heat sensitive plastics [5]. In the biomedical sector plasma technology is used for cold sterilization of instruments and prostheses as well as many thermo labile materials used in the biomedical technology sector for its particular advantages, including its moderate or negligible impact on substrate materials and use on nontoxic compounds [6]. Conventionally, sterilization methods such as heat, chemical solutions are used for the surface disinfection of fruits, seeds, and spices etc., which are often time-consuming and damaging or have toxic residues [7]. Van de Veen et al. [8] reported that the effect of cold plasma on bacterial spores is more than the conventional techniques like heat, chemicals and UV treatment. The objective of this review are first, to present recent knowledge on effect of cold plasma on microbial inactivation and structural modifications of packaging materials as many reviews has been published on these topics. Secondly, the effect of cold plasma on endogenous enzymes, seed germination, starch modifications and limitations for its potential application in

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food sector as novel technology. One of the important challenges associated with cold plasma technology is ensuring high microbial inactivation while maintaining sensory qualities that ensure their fresh appearance.

Plasma Chemistry: Process & Categories

In plasma processing ionization is always considered as first important element followed by other factors like reaction rate, rate constants, the mean free path, the electron energy distribution [9]. Plasma chemical process can be divided into two categories based on reactions i) homogeneous gas-phase reaction (for example generation of N_3 from N_2) and ii) heterogeneous reaction where plasma comes in contact with the solid or liquid medium. The heterogeneous reaction is further classified into three sub categories. In the first sub category, material is removed from the surface termed as etching or ablation; in the second sub category, material is added on the solid surface in the form of thin film observed during plasma polymerization by a process called plasma enhanced chemical vapour deposition and in third sub category there is no material added or removed but the substrate surface is modified physically and chemically during exposure to plasma [3]. Different types of possible mechanisms that the gas used for plasma generation may act on the substrate during the plasma processing are shown in (Fig. 1).

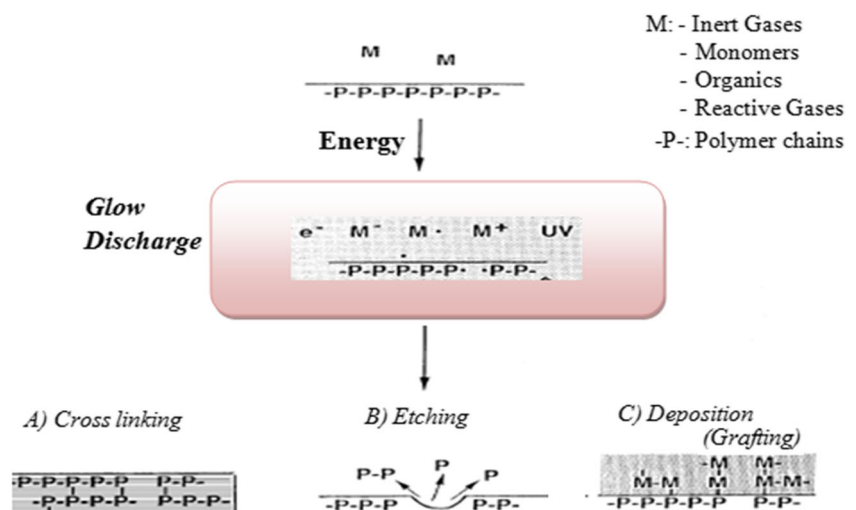
Plasma can be produced by subjecting a gas to an electric field (between two electrodes), either of constant (direct-current field) or alternating amplitude (usually high frequency field). Plasma state can be attained by the application of energy in several forms including; thermal, electric or magnetic fields and radio or microwave frequencies, which increase the kinetic energy of the electrons resulting in increased number of collisions in the gas forming plasma products like electrons, ions, radicals and radiation of varying wavelengths including that in the UV ranges. The various approaches used

for plasma generation includes the corona discharge, dielectric barrier discharges (DBD), radio frequency plasma (RFP) and the gliding arc discharge [10]. Cold plasmas, including low-pressure DC and RF discharges (silent discharges), discharges from fluorescent (e.g., neon) illuminating tubes, DBDs may be found both at low pressure or atmospheric pressure [11]. The dielectric barrier discharges (DBDs), historically also called ‘silent discharges’. They also operate at approximately atmospheric pressure (typically 0.1–1 atm). An A.C. voltage with amplitude of 1–100 kV and a frequency of a few Hz to MHz is applied to the discharge, and a dielectric layer (made of glass, quartz, ceramic material or polymers) is again placed between the electrodes. When a potential difference is applied between cathode and anode, a continuous current will flow through the discharge; giving rise to direct current (D.C) glow discharge. Capacitively coupled (CC) radio-frequency (RF) discharges are produced when alternating voltage is applied between the two electrodes, so that each electrode will act alternately as the cathode and anode. The frequencies generally used for these alternating voltages are typically in the radiofrequency (RF) range (1 kHz–10³ MHz; with a most common value of 13.56 MHz). Non thermal gas discharges at atmospheric pressure are of interest for the food industries as they don’t subject the food system to extreme conditions.

Evolution of Plasma’s Research or Application

Going back to history in 1960’s for the first time sterilization property of plasma was introduced, and a patent was filed in the year 1968 [12]. It was reported that the destruction of 10⁶ spores in inner surface of vials occurred in less than second using argon plasma by pulsed RF field atmospheric plasma. A series of patents were even filed by Ashman and Menashi [13], Boucher [14], and Bithell [15] reported that electrical discharge in particular gases can lead to complete sterilization.

Fig. 1 Types of modifications caused by cold plasma on substrates



Boucher [14] in his patent explained the role of UV radiations on microbial inactivation along with plasma. It was reported that UV photon can penetrate to the depth of only one micrometer, where as plasma penetrated to the depth of 10 micrometer was observed which is helpful for the destruction of sporulated bacteria. Jacobs and Lin [16] used H₂O₂ as sterilizing agent and applied plasma to remove the residues of chemical on the sterilized products. The first work with plasma was made from oxygen which was proposed in 1989 and its lethal activity was defined as it interferes with the biological matter. Nelson and Berger [17] reported that O₂ plasma showed efficient biocidal action on *B. subtilis* and *Clostridium sporogenes* as these two were considered as the most resistant bacteria. Plasmas generated at 200 W were sufficient to reduce the population of *B. subtilis* more than 3.5 log₁₀ in 5 min [18]. From then the utilization of plasma for sterilization was commercialized.

Plasma treatment can effectively inactivate a wide range of microorganisms including spores [19–21] and viruses [22]. Feichtinger et al. [19] reported that cold plasma technology preferred as alternative source for surface sterilization and disinfection process which can act on both vegetative cells and spores with shorter periods of time. The chemical composition of plasma contains free radicals, highly reactive species and radiations are often generated in varying range from UV to visible. It is believed that the role of different constituent depends on the gas and operating pressure. The destruction of microbial DNA by UV irradiation, volatilization of compounds from spore, so-called “etching” of the spore surface by adsorption is because of reactive species like free radicals [23].

Cold plasma can be successfully employed for microbial destruction on fresh products to increase shelf life. In recent investigation of Misra et al. [24] reported that decrease in total mesophilic count was 12–85 %, yeast and mould count by 44–95 % in cold plasma treated strawberries. Raw milk was treated for destruction of *E. coli* using low temperature plasma by Gurol et al. [25]. They observed 54 % reduction of *E. coli* after the treatment of 3 min. Application of air plasma and SF₆ on nuts (pea nuts, hazel nuts and pistachio) found that 50 % reduction in total aflatoxins using air plasma and 20 % reduction using SF₆ [26]. Fernandez et al. [27] reported that treating with plasma for 15 min can achieve 2.72, 1.76 and 0.94 log-reductions of *S. Typhimurium* on lettuce, strawberry and potato respectively. The efficiency of microbial inactivation depends upon the surface of treating produce, plasma device, gas composition, and mode of exposure. Produces like potatoes, strawberries took more time for complete destruction of microbes due to grooves and uneven surfaces [27, 28]. Vannini et al. [29] applied the gas plasma for the decontamination of *Salmonella Enteritidis* and *Listeria monocytogenes* from table eggs. The maximum reduction was observed to be 4 and 5 log reduction of *Salmonella Enteritidis* and *Listeria*

monocytogenes respectively. The efficiency of microbial reduction was improved with increase in humidity of air. Experimental results of several authors suggested that the efficacy of cold plasma on particular microorganism depends upon the treated surface. For example, the destruction of *Listeria monocytogenes* was high in sliced cheese when compared to sliced ham [30]. It is also reported that there is more than 8 log reduction after exposure to 150 W for 120 s in sliced cheese and in sliced ham after exposure to 120 s there is 0.25 to 1.73 cfu/g reduction in microbial growth. *Citrobacter freundii* loads in apple juice were reduced by about 5 log cycles after a plasma exposure of 480 s using argon and 0.1 % oxygen plus a subsequent storage time of 24 h reported by Surowsky et al. [31]. Recent findings in the area of cold plasma for the inactivation of microorganisms on food surfaces are shown in Table 1.

Functionality of Plasma

Effect of Plasma on Microbial Cells

The effect of plasma treatment on microbial cells is mainly due to the plasma ions and cell interactions. The reactive species in plasma have been widely associated with the direct oxidative effects on the outer surface of microbial cells. The effect of plasma is highly dependent on the presence of water, highest effect was observed in moist organism compared to lowest in dry organism [45]. The potential application of plasma in inactivation is based on the fact that plasma reactive species damage the deoxyribonucleic acid (DNA) in the chromosomes. Wiseman and Halliwell reported that the results of radiobiology proved that the mechanism of plasma on a cell is through formation of ROS directly in the vicinity of a DNA molecule inside a cell nucleus. The ROS of interest in plasma processing are hydroxyl radicals, hydrogen peroxide, and the superoxide anion [46]. The application of plasma results in formation of malondialdehyde (MDA) in microbial cells, which participates in the formation of DNA adducts resulting in damage to cells [45]. In particular, reactive species interacts with water, leading to the formation of OH* ions [47] which are most reactive and harmful to the cells (Fig. 2). It is worth mentioning that the OH* radical is most important; these radicals formed in the hydration layer around the DNA molecule are responsible for 90 % of DNA damage. Hydroxyl radicals can then react with nearby organics leading to chain oxidation and thus destruction of DNA molecules as well as cellular membranes and other cell components [45].

Although it is likely that several active species are reacting with cells, it is well documented that reactive oxygen species such as oxygen radicals can produce profound effects on cells by reacting with various macromolecules. The microorganisms are more susceptible to singlet state oxygen leading to deformation of cells [48]. The lipid bi-layer of microbial cell is

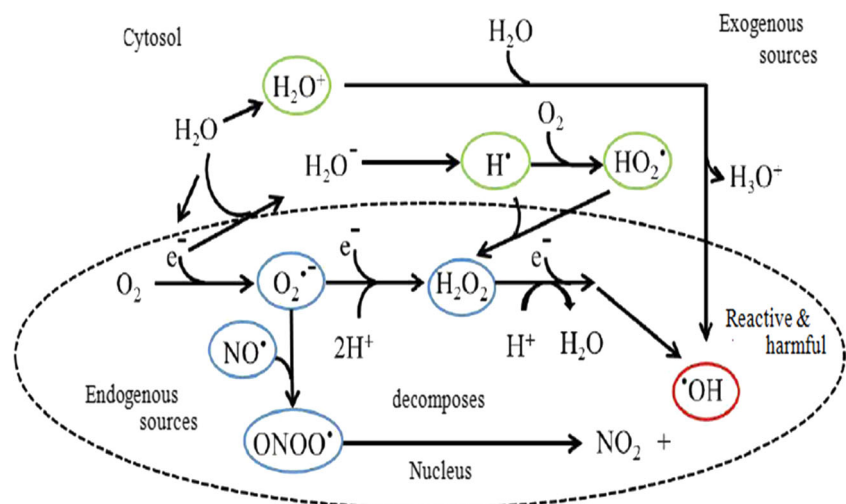
Table 1 Recent finding of microbial inactivation using cold plasma

Microorganism	Substrate	Plasma source	Exposure time	Log reduction	Reference
<i>S. enteritidis</i> (01)	Table Egg	RBD prototype	90 min	4–5	[32]
<i>L. monocytogenes</i>					
<i>E. coli</i> , <i>C. jejuni</i>	Chicken skin	Pulsed gas plasma discharge	24 s	up to 8	[33]
<i>Listeria innocua</i>	Chicken meat	He-O ₂ plasma	4 min	> 3.5	[33]
<i>E. coli</i> , <i>S. typhimurium</i>	Bacon	APP	90 s	2–3	[34]
<i>L. monocytogenes</i> , <i>L. monocytogenes</i>	Sliced Ham	APP	120 s	up to 1.73	
	Sliced cheese	APP	120 s	> 8	[35]
<i>S. typhimurium</i>	Lettuce		15 min	up to 2.72	
	Strawberry	CAP	15 min	1.76	[27]
<i>E. coli</i> , <i>S. Stanley</i>	Red apples	Gliding arc CP	3 min	up to 3.7	[36]
Yeast/mouls	Strawberries	DBD	5 min	up to 3	[24]
<i>E. coli</i>	Apple juice	Needle/plate system	–	7	[37]
<i>E. coli</i>	Almonds	Dielectric discharge	30 s	1.8–5	[38]
<i>S. aureus</i> , <i>E. coli</i> , <i>C. albicans</i>	Orange juice	DBD	25 s	>5	[39]
<i>A. parasiticus</i> Hazelnuts, peanuts, pistachio nuts		Low pressure plasma	20 min	5	[26]
<i>G. liquefaciens</i> , <i>P. agglomerans</i> , <i>S. cerevisiae</i>	Mango & melon skin	APJ	25 s	1–3	[40]
<i>E. coli</i>	Mango & melon skin	APJ	5 s	up to 3	[40]
<i>A. parasiticus</i> , <i>Penicillium</i>	Grains and cereals	SF ₆ CP	15 min	3	[41]
<i>L. sakei</i> ,	Cold-smoked salmon	DBD	–	1–5	[42]
<i>S. typhimurium</i>	Tomatoes	DBD	300 s	3.8	[28]
<i>A. hydrophila</i>	Lettuce	COP	5 min	5	[43]
<i>A. flavus</i>	Pepper powder	microwave-CPT	20 min	2.5	[44]

DBD-Dielctric barrier discharge, APJ-Atmospheric plasma jet, CP-cold plasma, COP-Cold oxygen plasma, APP-Atmospheric pressure plasma

more susceptible to atomic oxygen as the reactivity of atomic oxygen is much higher than the molecular oxygen, which can degrade lipids, proteins and DNA of cells. The damage of the double bonds in lipid bi-layer cause impaired transportation of molecules in and out of cell. The bombardment of reactive oxygen species (ROS) on the surface of bacterial cell also disrupts the membrane lipids [49–51].

During application of plasma, microorganisms are exposed to an intense bombardment by the radicals most likely provoking surface lesions that the living cell cannot repair sufficiently fast this process is termed “etching”. Plasma etching is based on the interaction of relative energetic ions and activated species with the molecules of the substrate. The accumulation of charges imparts an electrostatic force at the outer

Fig. 2 Dissociation of water molecule into reactive species

surface of cell membranes which can cause cell wall rupture called as electroporation as the same principle occurring in pulsed electric fields [52–55]. During application of plasma treatment where plasma initiates, catalyzes, or helps sustain a complex biological response, compromised membrane structure (e.g. peroxidation) or change in membrane-bound proteins and/or enzymes leads to complex cell responses and may affect many cells as the affected cell signal others [45]. Dolezalova and Lukes [56] demonstrated with their experiments that peroxidation of cell membrane lipids by cold plasma was an important pathway of bacterial inactivation. It is also reported that the amount of malondialdehyde and membrane permeability of *E. coli* to propidium iodide increased with increasing bacterial inactivation by plasma.

Action of Plasma on Endogenous Enzymes

The plasma can be applied not only to microorganisms, but also to simpler biological compounds, like enzymes [45]. Fruits and vegetables mostly spoil due to the enzymatic browning which is considered as secondary loss during post harvest handling and during storage. The endogenous enzymes particularly polyphenoloxidase and peroxidase are the major causes for enzymatic browning as they oxidize phenols at the expense of H_2O_2 leading to off flavours [57]. Different methods used to prevent the enzymatic browning are heating, blanching, commercial sterilization [58, 59]. Enzymes are inactivated through oxidation reactions mediated by free radicals and atomic oxygen [60]. The other non conventional techniques used in inactivation of endogenous enzyme are the pulsed electric field [61, 62], irradiation [63], high pressure processing [64].

Dobrynin and his colleagues observed there is decrease in enzymatic activity of trypsin (zero at 4 Jcm^{-2}) after the application of plasma [45]. They reported that the plasma was able to change the 3D structure of proteins in trypsin enzymes due to cleavage of peptides bonds. In our investigation we found that the activity of polyphenoloxidase in cold plasma treated guava (*Psidium guajava*) pulp and whole fruit was reduced by 70 % and 10 % in 300 s at 2 kv respectively. In recent investigations of Pankaj et al. studied the kinetics of inactivation of tomato peroxidase enzymes fitting in different kinetic modeling like first-order, Weibull and logistic models [65]. They observed that there is a decrease in the enzymes activity at different voltages using atmospheric air dielectric barrier discharge plasma.

The hypothesis of Meiqiang et al. [66] showed there is increase in the activity of lipase and dehydrogenase enzymes in the hypocotyls of tomato root cells. They concluded that there is no detrimental effect of magnetized plasma on the tomato growth and yield but treatments should be optimized. The relative lipase activity was increased from 1 to 1.4 with the increase in treatment time from 0 to 50 s using helium RF atmospheric pressure discharge [67]. They also reported that

there is increase in activity of lipase with increase in plasma treatment time due to changes in the molecular structure of lipase protein which were confirmed by circular dichroism [CD] and fluorescence spectrum. The changes in activity of antioxidant enzymes was studied in the body tissues of plasma treated Indian meal moth larvae by Aziz et al. [48] It was reported that the activity of catalase, lipid peroxide and glutathione S-transferase enzymes was observed significant increase and no change in glutathione peroxidase activity.

Effect on Starch Granules and its Modification

Modified starches are prepared to alter its functional properties to increase its efficiency to use as food additives in several food preparations. Tensile strength and mechanical properties were observed to be improved in starch films with the use of modified starches. For the preparations of modified starches, the natural polymers available are sensitive to chemicals particularly to strong acids for etching of surface. So, they use weak chemicals to convert smooth hydrophobic surfaces to rough hydrophilic surfaces. Pashkuleva et al. [68] reported that cold plasma technology is an alternative technique for dry etching for surface modification and surface cleaning of biopolymers. They also reported that introduction of oxygen containing groups like hydroxyl, carboxyl, and carbonyl groups increases surfaces hydrophilicity. According to previous reports starch can be modified by using cold plasma. Most probably starch is modified by two main mechanisms, depolymerization and cross linking of starch granules. The depolymerisation of starch granules can occur at amylopectin side chains or break down of glycoside bonds which are close to side chains. Lii et al. [69] reported that glow plasma could induce the graft-polymerization of ethylene onto sweet potato and rice starches, while the homopolymerization of ethylene on the granules took place for cassava, potato, corn, and waxy corn starches. The plasma treatment has a significant effect on the crystallinity of the solid starch granules [70]. It was also reported that there is a high degree effect on the supra-molecular region and a higher decrease in the molecular weight of plasma treated starch granules.

The cross linking agent joins two starch molecules by the removal of hydrogen bonds forming stronger covalent bonds. Previous studies reported that modification of starches can also be prepared by exposing starch to plasma at different varying condition of pressure and time. Zuo et al. [47] reported that the starch modification can be occur using plasma as per the mechanism shown in Eq. (1). The two starch molecules are cross linked by the release of water molecule. The water molecule formed will be disassociated to hydrogen and hydroxyl ion with no residue of chemical compound.



Lii et al. [69] reported that reaction of plasma treated starch with iodine reagent showed an increase in shift in wavelength in UV-VIS band this shows that there is an increase in availability of amylose for the reaction with iodine. There is decrease in pH of plasma treated starch solution due to cross linking of starch molecules resulting in formation of carboxylic acid [69]. Due to the oxidation, the surface of starch granules are covered by irregular deposits like subtle occurs by a process called etching [71]. The effect of plasma on crystalline structure of starch was explained by [72], it was observed slight decrease in crystallinity after exposure to ethylene plasma. According to Mirabedini et al. [73] changes in crystalline structure is due to the physical damage caused by the bombardment of high energetic particles formed during the plasma generation breaking down the chemical bonds.

The ultimate goal of cold plasma is to create more hydrophilic surfaces of the starch films. Szymanowski et al. [74] studied the changes in properties of potato starch film using RF plasma produce from methane gas to use as filler in polyethylene composite films. The plasma treatment can be used to reduce the capillary elevation by de-agglomeration of starch granules. In untreated samples agglomeration of starch granules was observed, but in treated samples starch granules were separated attributing to decrease in capillary elevation. Andrade et al. [75] worked on the plasma polymerization of maize starch film to reduce its water absorption using cold glow butene plasma. Lares and Perez [76] reported that due to rearrangement of intermolecular bonds of starch resulting in disintegration causing lower water absorption capacity. Misra et al. [77] studied the effect of atmospheric plasma on the dough rheology of wheat flour. They reported that there is increase in viscous and elastic moduli of strong wheat flour after the plasma treatment. With the application of cold plasma the secondary structure of proteins were affected by changing the number of beta sheets and alpha helix.

Effect on Phenolic and Antioxidant Compounds

Antioxidants are considered as first line of defence against free radicals. It is therefore of particular interest to elucidate and understand the basic interactions of plasma species with bioactive compounds, in order to avoid nutritional degradation or any other undesired effects in future applications. Antioxidants protect cells against the damaging effects of ROS, such as singlet oxygen, superoxide, peroxy radicals, hydroxyl ions and peroxynitrite etc. [78]. There are only a few literatures available on effect of plasma treatment on the phenolic compounds. Harborne & Williams [79] reported that several plant species are tolerant to UV radiations accumulating flavonoid metabolites in epidermal cells. During plasma generation the UV radiations formed may be responsible for the formation of phenolic compounds which are extracted from the cells of upper epidermis of leaves.

Recent investigations of Grzegorzewski et al. [80] using low-pressure oxygen plasma, that a time and structure dependent degradation flavonoids can be observed, due to plasma-immanent reactive species such as ozone or hydroxyl radicals. To evaluate possible protective effects of the plant's matrix against plasma-induced degradation of secondary plant metabolites Grzegorzewski et al. [81] worked on flavonols and phenolic acid of lamb's lettuce leaves which were exposed to the cold oxygen plasma. It was reported that there is increase in phenolic contents particularly protocatechuic acid and luteolin was observed doubled upon plasma treatment. The diosmetin content was found to be increased more than others, whereas there is no change in chlorogenic acid content. The use of cold plasma technique over the conventional sources like pasteurization for the treatment of sour cherry maraschino juice showed a higher percentage of phenolic acid and anthocyanin content reported by Garofulic et al. [82]

Effect on Seed Germination

Several authors found that early germination of seeds can be achieved by treating the seeds with plasma this is because of penetrating active particles through the seed coat and directly influencing cells inside. The increase in germination rate is due to changes on the surface causing ablations which increased the transmission of oxygen and moisture through the seed coat to the embryo affecting its germination rate. According to Fridman, the interaction of cells with plasma might have been resulting in DNA damage, cell wall fracture, can stimulate natural signal like production of growth factors, changing the protein structure, affecting enzymatic activity leading to breakdown of seed dormant stage casing which lead to increase in the germination rate of seeds [9]. Sera et al. [83] found that germination rate of plasma treated wheat was quick and germination occurred first in plasma treated seeds then in untreated seeds. The seed immersed into air plasma is subjected by attack of oxygen radicals and bombardment by low-energetic ions resulting in seed coat ablation and probably significantly contributes to germination enhancement. Germination studies of legumes was carried out by Filatova et al. [84] resulted increase in germination both at laboratory and field by 10–20 % and also lowered the fungicidal effect by 3–15 % and concluded that atomic oxygen and OH radicals generated in plasma to be the most probable sterilizing agents. The germination rate of safflower seeds was conducted by Dhayal et al. [85] using cold plasma. It reported that cold plasma is suitable for surface modification of seeds due to high ion energy particles causing etching of seed coat leading to increase in germination rate of seeds by 50 % after the treatment. Jiafeng et al. [86] successfully increased the germination rate of wheat by 6.7 % using helium plasma. They also conducted field experiments using plasma treated seeds and

observed the increase in growth of plant significantly compared to control plant growth.

Volin et al. [87] investigated on the effect of cold plasma chemistry technology to enhance the delay of seed germination by coating with CF_4 and octadecafluorodecalin. It was reported that the delay in germination of seeds greatly depended on the thickness of coating. It was also reported that they successfully studied the delay in germination of soy beans, peas, corn etc. The degree of delay was observed to be more in octadecafluorodecalin coated seeds compared to CF_4 . To improve the seedling growth and germination of spinach seeds were carried out by Shao et al. [88] using arc plasma. It has been reported that there is increase in germination rate by 137.2 % and germination vigour was increased by 217.6 % after the plasmas treatment.

Effect on Packing Material

Food packaging materials are responsible for protection of food materials from the outside environment during handling, transportation and distribution. Cold plasma is used in decontamination of packing material externally where chance of shadow effect is negligible as plasma flows all round the surface [89]. Plasma processing is well known to change or make surface modifications in the case of packing materials. It serves purposes for surface treatment such as cleaning, coating, printing, painting, and adhesive bonding [90]. Low-temperature gas plasma sterilization allows fast and safe sterilization of packaging materials such as plastic bottles, lids and films without adversely affecting the properties of the material or leaving any residues. Cold plasma can be used for sterilization of heat sensitive packing materials like polythene ethylene and polycarbonate as the temperature is low. Surfaces of polymers particularly for edible packaging films nature of surface should be more hydrophobic with lower surface energies [91].

Using plasma as the transport mechanism and the catalyst, one material can be deposited (in a very thin layer) onto the surface of another material; thereby transferring some of its qualities. Hedenqvist and Johansson studied the oxygen transport properties of the SiO_x coating on polyethylene terephthalate [PET], low and high-density polyethylene [LDPE, HDPE] and polypropylene [PP] films, obtained using cold plasma technology and compared experimental data with computer model and found diffusivity was less than normal material [92]. Plasma deposition of heat-sensitive materials such as vitamins, antioxidants and antimicrobials into the packaging material may be sought as potential alternatives in the emerging field of antimicrobial and active packaging. Applications of nanotechnology in packaging as become wide spread to improve the barrier properties of packing material and this can be achieved by cold plasma processing. Pankaj et al. [93] studied the surface topography of zein film using atomic force

microscopy [AFM]. The roughness of plasma treated zein film increased with a root mean square of 100 nm from 20 nm in untreated films this is due to surface etching occurred during plasma treatment. Table 2 shows the finding of changes in the properties of packing materials after the exposure to cold plasma.

Waste Water Treatment

Developing an innovative advanced oxidation process for treatment of waste water is a big challenge. As complete oxidation is required for the treatment of waste water and transfer of contaminants is not complete in methods like photocatalysis, ultrasonication, UV/ozone [101]. Physico-chemical effects of plasma generates the formation of oxidizing species: radicals (H^\cdot , O^\cdot , OH^\cdot) may diffuse into the liquids and molecules (H_2O_2 , O_3 , etc.), shockwave, ultraviolet light and electrohydraulic cavitation may degrade the pollutant in waste water or decomposes the pollutant into other compound [102]. In liquid and gas plasma can be created either directly in the liquid, or in the gas above the liquid, or, in case of hybrid reactors, both in liquid and in gas. The more efficient way which requires less energy for waste water treatment can be done by diffusing gaseous phase species into liquid [103]. Recent investigations of Non thermal plasma on oxidation of products in water phenols [104] organic dyes [105], degradation of pharmaceutical compounds [106], pesticides [107] and also mineralization of pollutants by using several catalysts are also reviewed extensively [103]. Extensive research for commercial design of non-thermal plasma waste water treatment equipment should involve in theoretical aspects of diversified fields of Engineering, Electronics and Applied Sciences. Plasma oxidation mechanism of degradation of parent pollutants, different other properties to optimise the plasma plant process and also the interaction of liquid and gas on liquid gas interface should be examined [108].

Limitations and Toxicology of Plasma Treatment

There are some limitations of plasma processing like increase in oxidation of lipids, reduction in colour, decrease in firmness of fruits, and increase in acidity etc. were reported. In our preliminary studies we successfully decontaminated the surface of walnuts and peanuts using cold plasma technology. In our research work for plasma generation we used Bell jar 5 radio frequency plasma reactor with 13.56 MHz frequency and atmospheric air was used as gas for plasma generation and pressure was kept constant at 0.5 mbar. We treated the peanuts and walnuts at three different powers and times and analyzed for peroxide value. The main important problem encountered is increase in peroxide value by 20 % in walnuts at higher

Table 2 Results of action of cold plasma on packing materials

Packing materials	Treatment plasma	Applied voltage	Results	References
Polypropylene	Air Corona	30 kHz, 1.7 j/cm ²	Decrease in contact angle, increase in adhesion	[94]
PET films	Glow discharge	10 W	Decrease in contact angle, increase in roughness, crystallinity and degradation yield	[95]
Potato starch film	Air plasma	–	Decrease in hydrophilic nature, Increase in tensile strength	[71]
PP film	Diode plasma discharge	8.3 W	Decrease in contact angle, increase in surface energy	[96]
PET film	Jet plasma DC discharge	35 W	Increase in hydrophobic nature	[97]
PET	Jet plasma	285 V	Increase in weight, decrease in contact angle and wettability	[98]
HDPE film	RF Ar:O ₂ Plasma	150 W	Decrease in crystallinity, contact angle, increase in roughness	[99]
LDPE	RF Argon plasma	25–100 W	Decrease in contact angle and ageing effect, increase in crystallinity	[100]
BOPP film	RF Air plasma	10–50 W	Decrease in contact angle, increase, roughness ageing effect	[73]

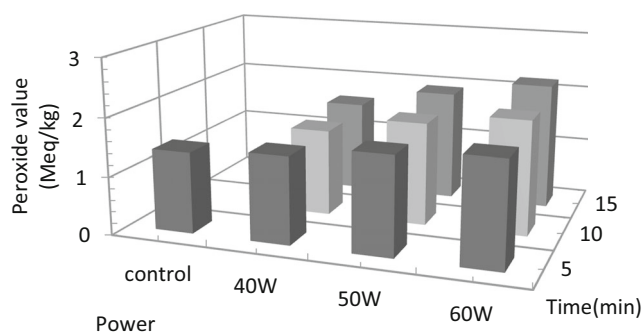
power and time of treatment. We observed similar results in the case of plasma treated peanuts samples (Fig. 3). This may be due to radicals are capable of oxidizing lipid molecules and resulted in increase in peroxide value. We noticed a decrease in L^* , a^* and b^* in treated samples. Similar kind of results was observed for strawberries treated with cold atmospheric plasma [24]. The discolouration and wilting effect of spinach leaves was observed after treating in atmospheric non equilibrium plasma for 5 min by [109]. Another main disadvantage of this technology, it is not possible to use for inactivation of endogenous enzymes which are present intact in the whole fruits because plasma effect is a surface phenomenon. The other disadvantage is that application of direct plasma causes decrease in firmness of fruits [24]. Kim et al. [110] reported that with the application of plasma there is decrease in pH of milk after 10 min treatment.

Till now no investigation has been carried out on the formation of any toxic compounds after the application of cold plasma in food products. Any technology used for food processing should not affect allergenicity of food constituents. Besler et al. [111] reported that several processing technologies could alter allergenicity particularly antibody (IgE) related allergy to food. The allergic activity of proteins will be remained stable or lowered, but rarely increase is observed. Harborne and Williams [79] stated that plants produce stress

induced secondary metabolites when they exposed to adverse conditions like UV radiations in their epidermal layer to protect the cells. These secondary metabolites may induce pathogenesis induce related proteins some of which have high allergenicity [112]. Kasera et al. [113] investigated on the allergenicity of legume proteins using combined effect of cooking and irradiation. It was reported that there is reduction of IgE binding to both soluble and insoluble proteins and resulted in attenuating allergenicity of legume proteins. Lectins treated with gamma irradiations showed changes in the hydrophobic surface of proteins resulted in protein misfolding and aggregation to reduce or eliminate allergenicity [114]. These reports concluded that exposure with gamma irradiation can reduce allergenicity of proteins in lectins. Based on these results plasma treatment may have chances of reduction or no significant effect on allergenicity of proteins even after the plasma treatment. However, there is no such data available presently on the allergenicity of plasma treated food products. No studies have been conducted on formation of toxic compounds in plasma treated foods.

Impact on Environment and Economy

The aim of any food processing industries is to reach consumers demand for high quality foods raising their economic standards, with net profits. Over a past few years the food processing industries are focusing on the energy consumption and energy savings. This can be achieved only with the use of non conventional emerging technologies as the thermal preservation techniques requires large amounts of water and additional cost for waste water managements. Many authors reported that energy efficiency of non conventional technologies was high compared to thermal processing. Dalsgaard & Abbots reported that the principal type of energy used for traditional thermal processing is fossil fuel, whereas electricity is mainly used for refrigeration and generation of mechanical

**Fig. 3** Effect of cold plasma on peroxide value (PV) of Peanuts

power for pumps [115]. It is also reported that use of novel non-conventional technologies like PEF and HPP may partially reduce the use of cooling systems, which often represents approximately 50 % of total electricity consumption. In many developing countries food processing industries continuously evaluating the use of non conventional technologies, as most of these technologies are not only energy saving but also water saving (water scarcity was already occurred in many of world particularly in developing countries like India). Schluter et al. [116] reported that plasma treatment is also regarded as a potential alternative to other chemical or physical methods (HPP, PEF, and irradiation). Advantages of plasma processes are: high efficiency at low temperatures, precise generation of plasmas suitable for the intended use; just in time production of the acting agent; low impact on the internal product matrix; application free of water or solvents; no residues; resource-efficient. The main advantage of cold plasma technology in volatile organic compounds (VOC) removal from the food industries which are toxic and harmful are their relatively low energy consumption and generally moderate cost, compared to conventional air treatment methods, and more importantly, their ability to treat air containing low concentrations of VOCs at relatively low operating temperatures [117].

Conclusion

Cold plasma is a unique technology which is responsible for microbial destruction and surface modification of substrate as conventional preservatives techniques as some detrimental effects on nutritional quality. Plasma sterilization provides high efficacy, preservation and does not introduce toxicity to the medium. The most important is to select (choosing) a particular gases which already possess germicidal properties so that the efficiency of plasma sterilization can be increased. The cold plasma techniques are preservation treatments that are effective at ambient temperatures, thereby minimum thermal effects on nutritional and sensory quality parameters of food with no chemical residues. Plasma can be used for starch modification as additive and as filler component in packing materials. Although cold plasma technology is not yet used commercially on a large scale, the equipment should be readily scalable. However, research efforts must be taken to evaluate the expenditure for the treatment for large quantities of food commodities at industry level and also the quality, safety, wholesomeness of food commodities. Conclusion can be drawn that in future we hope plasma processing becomes common processing at food industries.

Future Scope

Cold plasma is used efficiently for sterilization and modifications of packaging polymers purpose but there is a huge

application in food processing. d' Agostino et al. [3] reported that there are 14 research areas where application of plasma technology can be increased which are determined by international research scientists. The amount of energy consumptions and stability depends up on the type of discharges used for treatment. Based on this parameters for the application of plasma should be optimized for maximum efficiency at low cost of operation. Many scientists successfully applied plasma on foods (solids and liquids) for the microbial inactivation but they did not explain its effects on the nutritional qualities and toxicology of treated foods. There is a necessary that application of plasma on foods should be recognized as GRAS after intense study and research (in vitro and in vivo) in this field. Future studies should be done on applications of plasma on food surfaces to change its physical and chemical properties with cost effective.

Acknowledgments This research was supported by Union grant commission [UGC], New Dehli, India.

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