

Non-thermal plasma assisted polymer surface modification and synthesis: A review

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Abstract: This article reviews the applications of plasma to polymer surface modification and polymer synthesis. Plasma treatment causes changes in morphology, structure and properties of polymers. When polymers are treated using plasma, certain monomers with functional groups can be copolymerized with backbone chain or be loaded on the surface, which would help couple reaction of existing polymer chains, graft monomers onto polymers, immobilize proteins, carry antimicrobial drugs, and enhance cell attachment. Hence, non-thermal plasma process creates unique properties on polymers which allow improved and expanded applications of polymers in food packaging and biotechnology.

Keywords: plasma, modification, synthesis, NTP, polymers, functional groups

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1 Introduction

Polymers are used in the manufacture of a broad spectrum of products for a wide range of applications that are beyond our imagination. The functionality, performance, and ultimately the applicability of a polymer, depend on the physical and chemical properties of the polymer^[1-3], which are in turn dictated by its

chemical composition and structure. One unique and interesting feature of many polymers is their surface properties, which are so crucial to their functionality, performance, and applicability that a large number of studies have been focused on the characterization and modification of the surface properties^[4-7].

Many of the functional groups on the surface of polymers interact with the surroundings and objects in contact with them^[8,9]. These interactions are the basis for many applications involving coating, attachment, grafting, embedding, etc.^[3,8,10-13] Modification of the surface properties will change the interactions and thus improve and create new functionality and applications. Polymer surface modification can be achieved using physical and chemical methods, in which existing functional groups are altered or new functional groups are introduced. However, many of these methods have some disadvantages including nonspecific reactions, unpredictable surface etching, etc^[14].

Over the past decades, non-thermal plasma (NTP) technology has emerged as a new surface modification method with unique advantages and great potential. The

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use of NTP to introduce functional groups on inert polymer surfaces was first reported in the early 20th century^[15]. NTP is electrically energized matter in a gaseous state which is not in thermodynamic equilibrium, and can be generated through electric discharge in a gaseous environment. Plasma is considered the fourth state of matter^[15]. Non-thermal plasma, as opposed to thermal plasma which is characterized by high temperatures ranging from 4 000 K to 20 000 K, can work at low temperatures through the interactions between its energetic particles (around 10 eV) and polymer surface. Therefore non-thermal plasma works effectively without causing thermal damages to polymers. NTP treatment of materials is usually carried out at low temperatures and low gas pressures in which an electrical discharge ionizes the gases present around the polymer being treated. The ionized particles, such as ions, electrons, radicals, and excited molecules, are then introduced onto polymer surfaces either by reacting with the activated surface or forming cross-links with the surface polymer chains^[15-17]. The ability of NTP to activate reaction groups and promote cross-linking indicates that NTP can also assist polymer synthesis.

The variety of plasma species is largely dependent on the composition of the gases through which electrical discharges take place. By choosing the composition of the gases, one can selectively introduce functional groups onto polymer surface. Inorganic gases such as air, Ar, H₂, He, O₂, CO₂, N₂, NH₃, F₂, and SO₂ and organic monomers such as CH₄, C₂H₄, C₂H₆, C₂F₄, or C₂F₆ are commonly used in plasma surface treatment. The distinct advantages of NTP surface modification and synthesis of polymers include:

- It does not affect the bulk properties of polymers because plasma-induced changes are limited to the surface layer to a depth of typically 0.005 μm to 0.05 μm.
 - It induces uniform changes regardless of the geometry of the polymers.
 - It is fast because of high treatment intensity.
 - It is environmentally friendly because it does not require the use of chemical solvents.
 - It is safe to temperature sensitive polymers.
- Non-thermal plasma is therefore particularly suitable

for surface modification of heat sensitive biopolymers such as biopolymers—poly (ethylene-co-vinyl acetate), polymethylpentene^[18,19,22], which makes non-thermal plasma treatment a very attractive tool for introducing desirable functional groups on the surfaces of biomaterials used for immobilizing cells, proteins, enzymes, etc., with improved material and blood compatibility^[18,20-21,23]. In addition, plasma surface modification does not require the use of water and chemicals, and is thus considered cost-effective and environmentally benign.

In this review, we will focus on two areas where non-thermal plasma has already seen significant applications or will have potential impacts: (1) surface modification, and (2) synthesis/polymerization.

2 Polymer surface modification

The purpose of surface treatment is mainly to improve certain mechanical and performance-related properties. For example, appropriate wettability, hardness, adhesion, permeability, friction factor, bacterial repellence, surface conductivity, and biocompatibility are uniquely important for the industrial, medical and biological applications of polymers. There are successful examples where non-thermal plasma was able to introduce functional groups such as -COOH, -OH, -COOR, >C=O and -NH₂ onto the surfaces of some polymers for various applications^[16-17,25-28].

2.1 Improving material biocompatibility

For biological applications, polymeric materials are often required to have biocompatibility, which can be achieved by introducing amino group (-NH₂), carboxyl group (-COOH), hydroxyl (-OH) or other active groups onto the polymer surface. Usually ammonia, nitrogen, hydrogen and gas mixture or other gas admixture are used to provide a certain concentration of -NH₂, -COOH, -OH on polymer surface because these groups are biocompatible and polar which are active and excited to react with other organ molecules.

Inagaki et al.^[29] studied the effects of process parameters by amino functionality introduction onto an amorphous carbon sheet using an ammonia plasma. They estimated the introduced amino functionality to be

at a level of 1.3–1.4 amino-N/100C-atoms, which is very good for improving the compatibility of carbon sheet. Wang et al. used the plasma of nitrogen and hydrogen gas mixture to modify polystyrene (PS) and inspected surface free energy of PS, degradation degree and amino functionality introduction. The hydrogen and nitrogen plasma induces the formation of NH₂ radical and therefore controls the dissociation of nitrogen molecules^[30]. That means they can adjust and control the plasma treatment parameters and functional groups quantity and properties. Martin Kral et al. focused on the amino group introduction using a microwave surface wave plasma (SWP) in the nitrogen/hydrogen gas mixture and also studied the influence of electron temperatures, ion saturation currents and plasma potentials on results. To characterize the treated polyethylene surface, X-ray photoelectron spectroscopy (XPS) along with the amino derivatization technique has been employed. The correlation between the hydrogen gas addition and the nitrogen group introduction onto the polymer surface has also been evaluated. The results showed that plasma treatment can improve the PE properties successfully. The highest concentration of the amino group, about 2.0 in amino-N/100C atoms, was obtained soon after the onset of the ammonia plasma (treatment time > 5 s)^[31]. So Martin Kral et al.^[31] not only studied the plasma parameters effects on functional groups formation, but also the plasma function mechanism on the reaction, such as the effect of electron temperatures and ion saturation currents on results.

When artificial polymer surfaces are exposed to protein-containing solutions, protein adsorption usually takes place. However, the protein adsorption may lead to serious problems, so the study of protein-resistant materials has been a very active research field during the past decades. There has been much effort to minimize protein adsorption due to its importance in the areas of blood-contacting devices, coatings to minimize biofouling, separation membranes, contact lenses, protein drug-contacting materials, etc.

In order to improve the surface properties for meeting the requirements in protein resistant materials area, Akihisa Ogino et al.^[32] modified the chitosan structure

using plasma treatment at low temperature and investigated the effects of plasma treatment on chemical structures, surface morphology, and blood clotting property. The plasma treatment of chitosan can activate the clotting factor which in turn will improve the blood clotting process. In Akihisa Ogino's study, the chitosan film surface was modified through Ar, O₂, NH₃ and NH₃/He mixed gas plasmas treating. According to XPS analysis, the NH₃ plasma treatment with Ar plasma pretreatment of chitosan led to a significant increase in N/C ratio from 6.8% to 14.7%. The selectivity of amino group functionalization (–NH₂/N) also increased after plasma treatment with Ar plasma pretreatment. The surface treated with O₂ plasma was largely modified compared to the original surface. A comparison of morphology parameters between the plasma modified chitosan surface and the original chitosan surface indicated that there were a lot of changes on the surface of the samples treated with O₂ plasma. Experimental results of blood clotting property of plasma-treated chitosan showed that the blood clotting time of the sample treated by NH₃ and He plasma with O₂ pretreatment was reduced to 55.2% of that of untreated one. The results proved the possibility of low-temperature plasma modification of the chitosan surfaces that can contribute to activation of blood clotting process. So blood clotting can be greatly improved using this method^[33].

For biomaterials, blood protein adsorption but also desorption, and cells adhesion or proliferation on polymeric materials are of great importance and unavoidably. Therefore the polymer surface should be biocompatible^[3]. Lee et al.^[34] studied the wettability gradient prepared through the corona discharge treatment of protein and cell interactions with polymeric materials. They prepared wettability gradient surfaces by treating PE polymer sheets with corona with power changed gradually along the sample length. The behaviors of the adsorption and desorption of albumin, the adhesion and proliferation of CHO cells on the wettability gradient surfaces prepared showed clear difference, and that surface wettability is an important factor affecting protein adsorption/desorption and cell adhesion/proliferation.

Also, the results demonstrated that the cells were not spread well on the surface not treated by corona plasma, while they were completely spread and flattened on the surface treated using corona after 24 h culture. The number of CHO cells grown on the wettability gradient surface after 48 h culture was twice more than that after 24 h culture. The cells grew better and better on the hydrophilic sections than those on the hydrophobic ones. The maximum growth of the cells appeared on the sections with moderate hydrophilicity at a water contact angle of 50° - 55° [35,36].

From the above research results, it is noticeable that plasma treatment improves material surface features though introducing some amino, hydroxyl, and other functional groups on the material surface which help enhance material biocompatibility and haemocompatibility. Also, the surface properties could be controlled through adjusting plasma treatment parameters and reaction conditions. And it is feasible to use different gases or their mixtures in the plasma arrangement environment to incorporate different functional groups onto biomaterial surface using different plasma treatments.

2.2 Increasing surface wettability

Dielectric barrier discharge (DBD) technique was used to modify PE films in order to improve surface energy, adhesion and wettability [3,36]. Dielectric barrier discharge, which is characterized by the configuration of at least one of the electrodes covered with an insulating layer, is proved to be a promising technology in the modification of surface properties of polymers. Usually, the mean electron energy in DBD plasma is in the range of 0–10 eV, while the chemical binding energy of polymers is less than 10 eV. Therefore, energetic particles in DBD can break down the chemical bonds of single molecular or polymers. In addition, modifying the surface properties of polymers without expensive vacuum system is another advantage of DBD. The study found that DBD treatment of the PE films reduced the water contact angle from the original 93.2° to less than 70° after treatment time of 1 s. The contact angle continues to decrease with increasing treatment time, but the change occurred at a lower speed, suggesting that the

changes on the surface of the treated PE samples mainly happen within the first several second treatment time and in a very thin layer. And the surface free energy increases from 27.3 to 51.89 J/m^2 with the treatment time changing from 0 to 50 s and the change tendency is similar to that of oxygen atomic concentration. This indicates that the change in surface free energy is mainly determined by the introduction of polar molecules on the treated PE surface. The DBD treatment of the films resulted in a higher surface free energy and lower water contact angle, and hence better wettability of polymers [10,21,32] and enhanced biocompatibility cell growth, and proliferation.

2.3 Modifying food package materials

Plasma treatment represents another choice of film and surface modification. It produces uniform, usually cross-linked and branched, high molecular weight networks on the surface of different materials very easily. Also, the benefit of this method is to improve the surface chemistry controllability which could be used in the retention of highly reactive functional groups, and provide non-fouling surface for implant biomaterials. High surface densities of active functional groups can be bonded together via strong covalent bond formation between substrates. Further, it can provide superhydrophobic or hydrophilic surface and antibacterial polymers [37-39].

Food quality and safety are major concerns in the food industry as bacterial and fungal contamination of ready-to-eat products is closely related to human health. The major possibility of food spoilage originates from microbial contamination on the food surface; so the antimicrobial packaging materials will be a better way of solving the food surface contamination problem. Using appropriate plasma based surface treatment, some monomers or polymers with functional properties can be loaded on the Polyethylene (PE) and polypropylene (PP) surface, so PE and PP would have some special functions, including oil and water repellency and wettability, antibacterial and other chemical functionalities.

Abdou et al. [35] conducted research to modify the surface of nonwoven PP and cotton fabrics to put antimicrobial potential onto them. The bactericidal

activity was evaluated based on the killing rate by the viable cell counting technique against *Clavibacter michiganensis* and *Pseudomonas solanacearum*. Two types of materials, nonwoven PP and cotton fabrics, were treated with plasma and then were dipped into chitosan, CM chitosan, and CM chitin solutions. The results showed the antifungal activity of PP fabrics treated with plasma then with chitosan, CM chitosan and CM chitin that were against some fungal pathogens. The effectiveness was found to depend on the type of fabrics, treatment conditions, and the tested fungus. The results revealed that the untreated PP fabrics had no inhibitory effect at all against all the tested fungal species. The plasma treated fabrics showed slight effectiveness on the other hand, fabrics treated with plasma then with chitosan showed pronounced antifungal efficacy against all the tested fungal species. Hence, plasma treatment of polymer packaging materials can be a choice to prevent contamination of food surfaces^[35,36].

3 Polymer synthesis

Plasma assisted polymerization refers to a process in which monomer in vapor state passes through an NTP reaction chamber and converted into reactive fragments, then which grow to longer molecular--polymers. The polymers formed in a plasma environment may not necessarily have the same structure and composition as they are produced using conventional polymerization

methods. Polymers made using this technique may have superior properties, such as high ion conductivity, low fuel permeability, high thermal and chemical stability, and excellent optical properties which provide them with great potentials as promising polymer electrolyte membranes for polymer electrolyte membrane fuel cell, optical information storage, optical signal processing, antistatic materials, sensors etc. Therefore NTP may be used to synthesize polymers with unique structure, composition, and thus special properties.

3.1 Synthesis of electrolyte materials

Polymer electrolyte membrane plays a bi-function role in conducting protons or hydroxide ions and separating fuels and oxidant, largely determining the performance of the corresponding polymer electrolyte membrane fuel cell. Therefore, the development of polymer electrolyte membranes with efficiently conducting protons and blocking fuel permeation is a promising way to improve the electrochemical performance.

A few studies^[39-43] show that the polymer electrolyte membranes synthesized directly via plasma technique have some special ion conductivity which is suitable for fuel cell membrane. However, the plasma assisted polymerization is a very complicated process involving degradation of monomers and the formation of polymers. Therefore, the whole plasma synthesis process should be well controlled in order to obtain membranes with desirable properties.

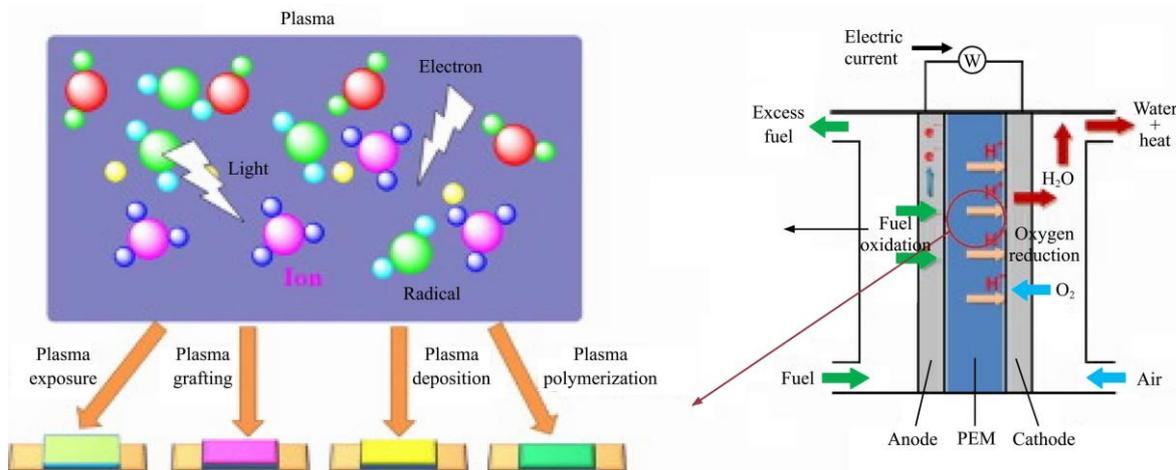


Figure 1 Fabrication of polymer electrolyte membranes through plasma

Meng et al^[41] studied multi-composition of the polymer nanoball carrying sulfonic acid groups, silicon oxide and pyridine groups with the diameter of 25 nm

was made through plasma assisted polymerization of 2-vinylpyridine and trifluoromethanesulfonic acid cooperating with direct current (DC) plasma sputtering of

methyl ethenyl silicone rubber in a low-frequency after-glow capacitively coupled plasma (CCP) discharge apparatus. The results showed that the size and composition of the nanoball can be controlled by altering the partial pressure ratio of trifluoromethanesulfonic acid and 2-vinylpyridine. Pyridine groups on the polymer backbone act as a medium through the basic nitrogen for transfer of protons between the sulfonic acid groups of proton exchange membrane, and water retention can be improved by silicon oxide formed in polymer nanoball. Thus, the polymer nanoballs could be a proton transport facilitator for polymer electrolyte membrane fuel cells.

Matej Micusik et al.^[39] also obtained electrically conductive fibres and textiles to be applied on antistatic materials, sensors, electromagnetic shielding materials using plasma polymerization. In the research, they chose polypyrrole (PPy) as the test material among the wide variety of conductive polymers due to its high electrical conductivity, environmental stability, and the ease of its chemical synthesis. Polypropylene (PP) grafting vinyltrimethoxysilane by means of a radiofrequency plasma discharge was done. It has double bond on the structure of vinyltrimethoxysilane ($\text{CH}_2=\text{CH}-\text{Si}(\text{OMe})_3$), which is easily opened and then polymerized with other materials. (as shown in Figure 2). Their study was focused on the influence of pyrrole-functionalized silane (SP) on the washing fastness of a Polypyrrole (PPy) layer and, consequently, on the overall conductivity of the textiles after washing.

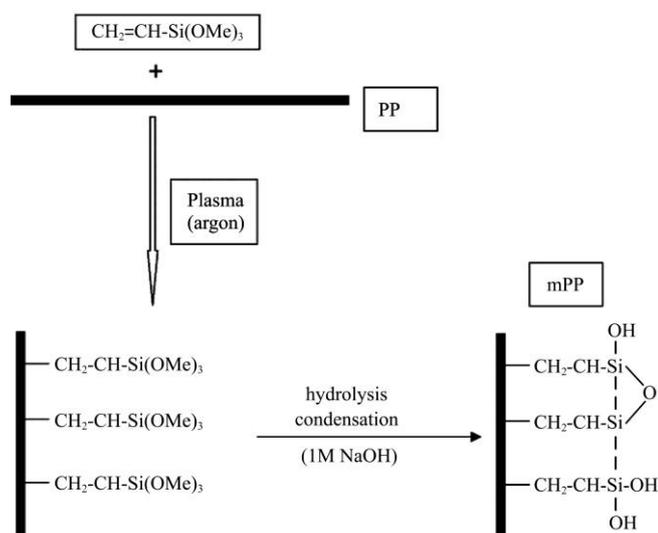


Figure 2 Polymerization of PP with VTMS and plasma discharge

3.2 Synthesis of optical materials

Optical materials are receiving considerable attention in the application for laser diodes optical information storage, optical signal processing and optical computing etc. Plasma treatment has been used to improve optical response by delocalizing electronics.

Polynitrile is a typical conjugated polymer which was found to have large third-order susceptibility, hyperpolarizability and reproducible electrical bistability. Plasma polymerization of nitrile is a good technique to deposit on the film and obtain conjugated carbon-nitrogen bond. Zhao X Y et al.^[38] researched conjugated polybenzotrile films produced through plasma synthesis. After plasma treatment, the films, which are of high quality, homogeneous, adherent, pinhole free, could be applied in electronic devices, optical wave-guides, thin film lenses, reverse osmosis membranes, photovoltaic membrane and sensors. In their work, plasma polymerization was used in the preparation of plasma-polymerized benzotrile (PPBN) thin films, which were directly deposited onto calcium fluoride (CaF_2) plates and potassium bromide (KBr) pellets placed in the reaction chamber under glow discharge. The results showed that the polymerization of benzotrile monomer took place mainly through the opening of carbon-nitrogen triple bonds by the free radical polymerization process. Smooth and homogeneous plasma-polymerized polybenzotrile films with strongly delocalized electrons along the backbones could be obtained at the relative lower discharge powers. In the case of higher discharge powers, some obvious folds were formed on the surface of PPBN films owing to the higher film deposition rate. The extremely fast and larger nonlinear response of PPBN film was observed, which shows that PPBN film is a promising material for applications such as fast optical switches and modulators.

3.3 Synthesis of biomedical materials

Polymers obtained by plasma polymerization usually show good biocompatibility when compared with biomaterials through conventional synthesis. Especially for polymer films, the thickness of these films (from several hundreds of Å to several μm) makes them suitable for the purpose of changing the surface properties of the

substrate without altering its bulk properties. Both the above features together indicate the possible biomedical use of plasma polymerization^[44,45].

Jafari R, et al.^[46] used plasma to polymerize acrylic acid on polyethylene. The purpose of this treatment was to immobilize DNA probes that would immobilize cells and generate the amine reactive N-hydroxy succinimide (NHS) active groups on material surface. This microarray produced from plasma polymerization acrylic acid (PPAA) has a high relative density of attached probe DNA molecules and signal-to-background ratio measured for target DNA hybridization (See Figure 3). During this process, the plasma power played an important role in the chemical composition and stability of the PPAA.

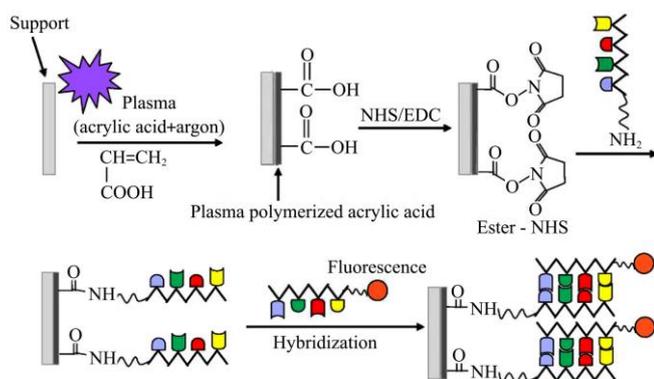


Figure 3 Scheme of the different steps for formation of DNA array on glass support

The XPS spectra showed that the high-binding energy structure is an indication of the existence of carbon-oxygen bonds. The spectrum peak is at 285 eV corresponding to C-C and C-H moieties, the peak at 286.5 eV to C-OH and C-O-C functional groups, the peak at 287.8 eV to O-C-O and C=O groups and finally the peak at 289.2 eV is due to COOH and/ or COOR groups.

On PPAA surface, the -COOH group has been activated by NHS/EDC solution to form activated ester groups (see scheme of Figure 3). Then the final step was to link the DNA probe to the activated ester groups. The amino-modified probes Amino-1S, Amino-2S and Amino-3S were arrayed in triplicate at a fixed concentration of 15 μM on three samples of each support. After hybridization, the average fluorescence signal intensities of spots clearly evidenced that probe

attachment was higher on PPAA slides.

Plasma synthesis has been explored for engineering and biomedicine applications. As the energy of plasma is higher than that of chemistry bonds, plasma can initiate different chemical reactions. This polymerization method has special advantages: fast reaction, polymers cross-linked, pin-hole free and better gas barrier properties, non-toxic, and better biocompatibilities. Polymers synthesized through plasma based processes can be used in cell culture, controlled release of drugs, biosensors, implanted biomaterials, non-fouling surfaces, and plasma-treated materials for bio-recognition materials^[47-50].

4 Summary

Applications of plasma in surface modification and synthesis have great potentials, especially in situations where special properties such as hydrophilicities, biocompatibilities, cell affinities, electrical and optical properties are needed. These properties are generally desirable for tissue engineering, and other biotechnology and engineering uses.

Plasma assisted polymer surface modification and polymerization have made significant progress in the past decades. However, current processes cannot provide precise control of polymer properties. The exact interaction mechanism between polymers and some bio-organisms is not known well. In the near future, better control over the polymer surface modification and polymerization, from thickness, composition, molecular structure to functional properties should be developed. New plasma equipment might appear to create new possibilities to apply on these processes. In addition, finding new gases or mixtures for plasma sources may be desirable to support plasma discharge.

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