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### Gas Plasma Treatment of Polymer Surfaces

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## Gas Plasma Treatment of Polymer Surfaces

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### ABSTRACT

The modification of polymer surfaces by gas plasma treatment is reviewed. The two regimes of major interest are radio-frequency at low pressure (about 1 torr) and corona discharge at atmospheric pressure. The reactions produced by plasmas at polymer surfaces are due to both radiation and chemically active species created by electron bombardment. The major changes produced are in wettability, molecular weight, chemical composition, and surface morphology. The mechanisms of plasma polymerization and the properties of polymers produced by this technique are described. Finally, a brief outline is given of the industrial applications of plasma techniques.

### GAS PLASMAS AND THEIR GENERATION

Gas plasmas consist of partially ionized gases containing equal concentrations of positive and negative charge carriers, produced by very high temperatures or strong electric or magnetic fields [ 1]. Plasmas used for the treatment of polymer surfaces are comparatively low temperature gases (less than 1000 K) produced by corona or radio-frequency (RF) glow discharges. They have average electron energies

of 1-10 eV. Glow discharges produce electron densities of  $10^9$  to  $10^{12}$   $\text{cm}^{-3}$  and gas temperatures in the region of 700 K. The corresponding figures for corona discharges are approximately  $10^6$   $\text{cm}^{-3}$  and 400 K [2]. The discharges also produce radiation in the infrared-visible-ultraviolet region.

A variety of chemical species is produced by the interaction of free electrons and radiation with neutral gas molecules, including excited molecules, free radicals, and ions. These cause a wide range of reactions at the surfaces to which they are exposed. Although the intensity of activity at the surface is high, only a very thin (less than a few  $\mu\text{m}$ ) surface layer is affected. Plasma treatment is therefore a valuable means of modifying polymer surfaces without affecting the bulk properties of the polymer [3].

The main reactions between gas plasmas and polymers are:

1. Direct reaction of activated gases (e.g., surface oxidation by oxygen plasma)
2. Formation of free radicals and their subsequent reactions
3. When organic compounds are injected into a plasma, the initiation of polymerization reactions which occur both at the surface and in the gas phase (plasma polymerization)

There are two regimes of interest in plasma chemistry: low pressure (about 1 torr) and atmospheric pressure. Corona discharge treatment of solid surfaces is the only major technique used at atmospheric pressure [4]. The corona is generally struck between a stressed electrode(s) and a grounded roller over which the material to be treated is passed. Either the grounded roller or the electrode is covered with a dielectric layer of sufficient dielectric strength to prevent an arc forming in the gap. An arc, if formed, would have sufficient energy to punch through or severely damage the polymer being treated. Most practical systems are ac powered, typically at about 10 kHz, for ease of supply and reduced electrode corrosion. They operate at high voltage, in the region of 10 kV RMS and fairly high power levels (1-10 kW). A diagrammatic representation of the corona discharge treatment of polyethylene film is given in Fig. 1. The major control parameter is the current.

A number of techniques are used to produce low pressure glow discharges [1]. Direct current and low frequency (50 Hz) discharges can be used to carry out plasma reactions in contact with the high voltage electrodes. There are two disadvantages: contamination of the electrodes and the difficulty of introducing high power into the system.

Microwave discharges are also used but are difficult to initiate and sustain at low pressures and tend to be very nonuniform within the cavity. At higher pressures ( $> 1$  torr) the gas temperature can rise so high that it causes decomposition of the reactants. The most common low pressure technique uses RF discharges. Direct coupling between the electrode and the plasma is unnecessary, coupling being

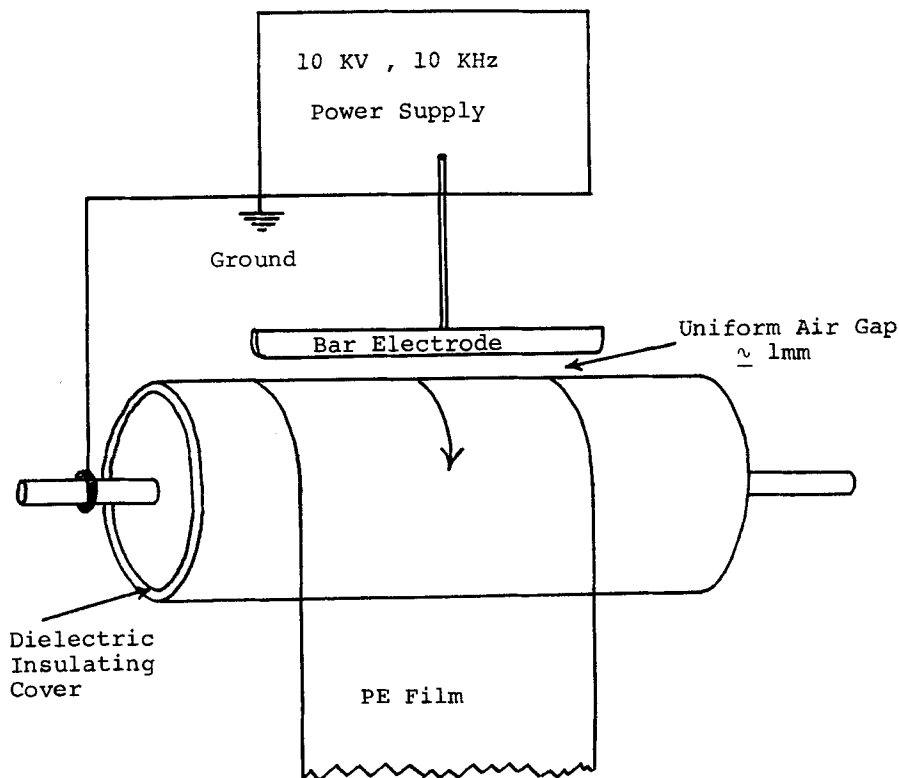
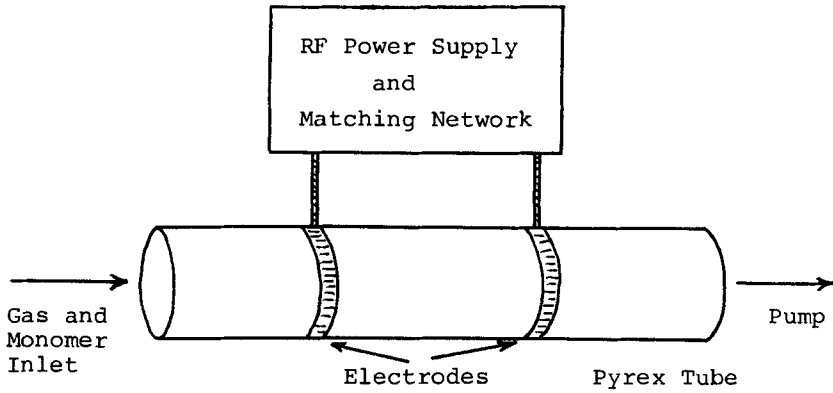


FIG. 1. Corona discharge treatment of polyethylene film.

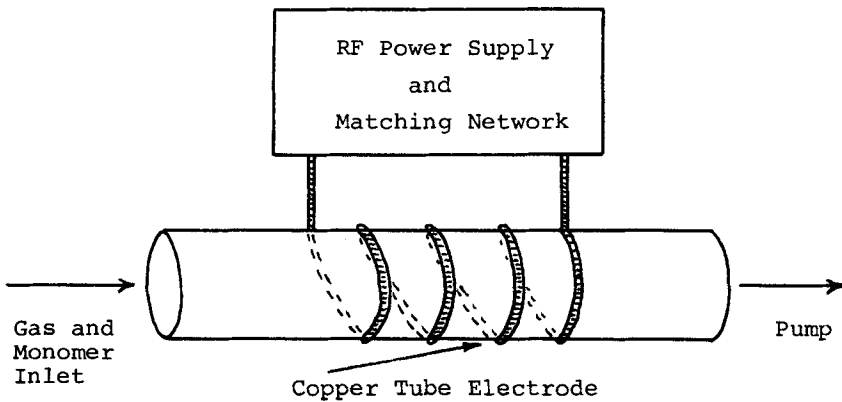
either capacitive or inductive through the walls of the reactor (Fig. 2). Inductive coupling, typically being several turns of 0.25 in. copper tubing, is preferred because of the ease of matching the load to the power supply. RF plasma reactions are not strongly frequency dependent so that frequencies in the range 2-60 MHz can be used, with 13.56 MHz being common because of the ready availability of power supplies [1]. For laboratory use, power of the order of several hundred watts is sufficient. The three interrelated control parameters are power input, gas bleed rate, and system pressure [5].

#### CHEMICAL AND PHYSICAL PROCESSES AT PLASMA-TREATED SURFACES

The treatment of a polymer by a plasma produces major changes in wettability and adhesion due to altered chemical composition, molecular



(a)



(b)

FIG. 2. Capacitive (a) and inductive (b) coupling for electrodeless formation of a plasma.

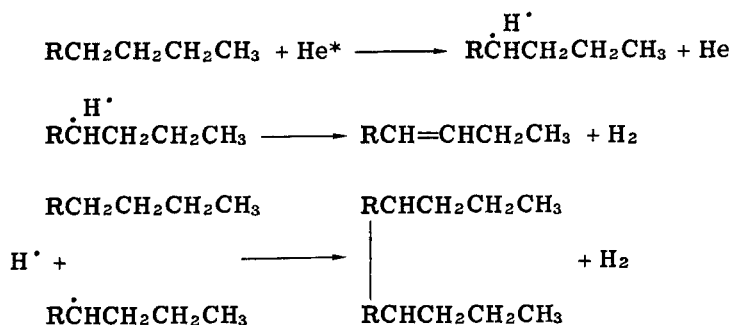
weight, and morphology in the surface layer. The effects of plasma treatment tend to be confined to thin layers variously estimated as being between  $50 \text{ \AA}$  and  $10 \text{ }\mu\text{m}$  in depth [6, 7].

The wettability of a polymer surface may be assessed in terms of contact angle or degree of adhesion of inks or surface coatings. The changes in wettability produced by corona treatment are frequently attributed to the formation at the surface of chemical functional groups such as carbonyl or amide groups [3, 6, 7]. Polyethylene films treated

by helium or argon plasmas also show good adhesive properties [6, 8, 9], but oxygen-containing functional groups could be formed in these surfaces through reaction with oxygen in the system or after they are exposed to the atmosphere through the reaction of atmospheric oxygen with free radicals formed during plasma treatment [7, 10]. It has been suggested that under conditions of commercial corona discharge treatment, improved adhesion is due mainly to changes in surface morphology [11]. However, surface morphology is not generally held to have a major influence on wettability [6].

When a polyethylene surface is treated by a corona discharge in air, the resulting concentration of oxygen-containing groups is much higher than that of nitrogen-containing groups, which suggests that oxygen species are much more active than nitrogen in modifying the polymer surface [12]. With a nitrogen plasma, significant amounts of nitrogen are incorporated into the polymer surface, probably in the form of amides [7, 12]. In an ammonia or nitrogen and hydrogen plasma, amino groups are formed on the polymer surface [13]. Thus the chemical composition of the polymer surface layer can be changed in various ways, depending on the nature of the gases present in the plasma. The polymerization reactions involving organic species introduced into the plasma will be considered later.

The molecular weight of the surface layer may be either increased or diminished. Generally, inert gas, nitrogen, and hydrogen gas plasmas lead to higher molecular weights due to cross-linking, whereas oxygen gas plasmas lead to lower molecular weights due to scissioning [6]. Schonhorn and Hansen [14, 15] found that polyethylene treated by inert gas plasmas exhibited increased cross-linking, unsaturation, and loss of hydrogen. The cross-linking led to greater cohesive strength of the surface layers and improved adhesive bonding. The following reactions were suggested:



Recent studies with electron spectroscopy for chemical analysis (ESCA) techniques tend to confirm that in inert gas plasmas, cross-linking is due to direct energy transfer from excited species, at least in the outermost few monolayers: at greater depth ultraviolet radiation may become a more important agent [16, 17]. The cross-linking

reaction reduces the crystallinity of the surface layers of polyethylene [18].

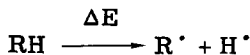
Corona treatment of polypropylene in an oxygen atmosphere creates both unsaturation and oxidation. Infrared spectroscopy studies indicate that carbonyl groups are the main oxygen-containing species formed [19]. Surfaces treated in a nitrogen atmosphere and subsequently exposed to air also acquire carbonyl groups, but at much lower concentrations [19]. With prolonged treatment the surface layers can be converted to volatile products [20]. Atomic oxygen is probably the most active species in this process [20, 21].

Changes in the surface morphology of plasma-treated polymer surfaces are largely due to an etching process. Polyethylene treated by corona discharge in air shows increased surface roughness under the electron microscope, with craters between 20 and 40,000 Å in diameter and about 1100 Å deep [11]. Etching can also occur, to a lesser degree, in non-oxygen containing plasmas such as nitrogen and helium [3]. In addition to chemical decomposition and volatilization, change in surface morphology can occur by localized melting and recrystallization. Change in the morphology of the surface is strongly influenced by the type of gas, discharge wattage, treatment time, and the chemical structure of the polymer [3, 22].

## PLASMA POLYMERIZATION

It has long been recognized that when most organic compounds are injected into a gas plasma they readily undergo polymerization. The mechanisms of plasma polymerization tend to be far more complex than those of conventional polymerization. The monomer may undergo considerable decomposition or fragmentation. For example, when acrylic acid is polymerized in a plasma the polymer shows a deficiency of carboxylic acid groups and is rather hydrophobic [23]. High concentrations of ions and free radicals are produced, and the active species in the polymerization can be free radicals [23, 24], ions [25], or ion radicals [26].

Free radicals can be formed by hydrogen detachment, e.g.,



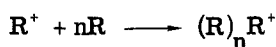
opening of cyclic structure and double bonds, opening of triple bonds such as  $\text{C}\equiv\text{C}$  and  $\text{C}\equiv\text{N}$ , and opening or fragmentation of aromatic structure [23].

For plasma-polymerized polystyrene a cationic polymerization scheme has been proposed [25]:

Initiation:



Propagation:



and cation radicals suggested as the predominant active species in the plasma polymerization of difluoroethylenes [26].

The predominance of free radical reactions is supported by electron spin resonance (ESR) studies which indicate a high concentration of trapped free radicals in the polymers [23, 24]. Many reactions can operate simultaneously in the plasma, and the mechanisms are strongly influenced by experimental conditions.

Two phases can be detected in a plasma-formed polymer, the minor phase consisting of soluble material (less than 2%) [5]. Gel permeation chromatography (GPC) studies of plasma-polymerized styrene indicate that the soluble fraction consists of very low molecular weight polymer [25]. Infrared spectroscopy, mass spectrometry, and thermal analysis data indicate that the major, insoluble fraction consists of highly cross-linked polymer, but with some degree of unsaturation. X-ray diffraction analysis gives no indication of crystallinity. Scanning electron microscopy studies suggest that polymerization takes place both on the surface and in the gas phase [25].

A more detailed picture of reaction mechanisms has been obtained in recent years by electron spectroscopy (ESCA/XPR) determinations of the chemical composition of plasma-polymerized films. Fluorocarbon polymers are particularly useful for such work because of the large shift in core-binding energies for the  $C_{1s}$  levels of

fluoropolymer systems [26, 27]. Differences between the surface and the bulk of the polymer can be established by this technique [17].

The polymerization of vinyl monomers initiated by plasma can continue after the plasma is removed, if sufficient monomer is present [23]. Solid-state polymerization can also be initiated by plasma [28, 29], producing polymers with a high degree of crystallinity.

Metals such as Mo and Cu can be incorporated into polymers during their formation in plasma. ESCA measurements indicate up to 40% Cu in the polymer [30, 31].

Polymerization can occur in any plasma. However, it is desirable not to have the plasma in contact with the electrodes, otherwise a polymeric deposit will build up on them. Most studies of plasma polymerization use RF glow discharge.

The major reactor parameters—power input, monomer flow rate, and system pressure—interact in a complex manner, and it has been proposed [32] that a composite parameter,  $W/FM$ , where

$W$  is discharge power

$F$  is monomer flow rate

$M$  is the molecular weight of the monomer



is more suitable for describing the conditions of plasma polymerization.

The rate of polymer deposition increases with discharge power and flow rate up to limiting values. The distribution of polymer deposition in the reactor is found to be nearly independent of monomer flow rate or system pressure, but is largely determined by the characteristic polymerization rates of the monomers. Acetylene tends to deposit polymer near the monomer inlet, whereas ethylene deposits polymer uniformly. The addition of carrier gas such as argon or nitrogen narrows the distribution of polymer deposition [33]. Discharge power has only a small effect on the pattern of polymer deposition distribution if the value of  $W/FM$  is maintained above a critical level to maintain full glow in the reaction tube [34].

It has recently been reported that plasma polymerization at frequencies between 50 Hz and 6 MHz is frequency dependent [35], and can proceed at a much higher rate than at the higher radio frequencies. There does, however, need to be direct contact between the electrodes and the plasma at lower frequencies.

Generally low pressures are used (less than 1 torr). However, the plasma polymerization of ethylene at atmospheric pressure has recently been reported [36]. These films were soft, had good adhesion, and low degrees of unsaturation and cross-linking.

The adhesion of plasma polymers to substrates is often poor, and depends on polymerization conditions. Generally it improves with increasing flow rate and distance from the electrode [37].

## APPLICATIONS

The major applications of plasma techniques are in improving the wettability and adhesion of polymers for surface coatings, inks, and dyes [6]. Self-adhesion can also be markedly improved by plasma treatment [8, 10].

Plasma techniques are becoming widely used in the electronics industry [38], particularly for microelectronics fabrication. Although most of the materials involved in these applications are inorganic, they are of interest to polymer chemists because polymers can be involved as resists, insulators, or semiconductors. Operations carried out by plasma techniques include photoresist removal [39], etching silicon compounds [40], and deposition of polymer films [41, 42]. The chief virtue of plasma techniques in microelectronics fabrication is that it permits automated, sequential, multi-step processing of complex devices [43].

Plasma treatment has been used to modify the properties of natural materials, for example in the shrinkproofing of wool [44, 45].

Other applications of plasma polymerization have included the production of protective coatings for metals and other reactive surfaces [46], fabrication of reverse osmosis membranes [47], coatings

for optical plastics [48], and the formation of radiation resistant coatings [49].

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