

Plasma Treatment of Polymeric Materials

9.1 INTRODUCTION

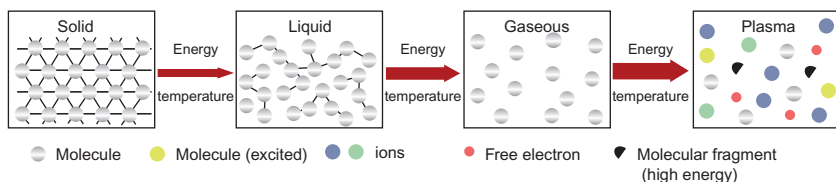
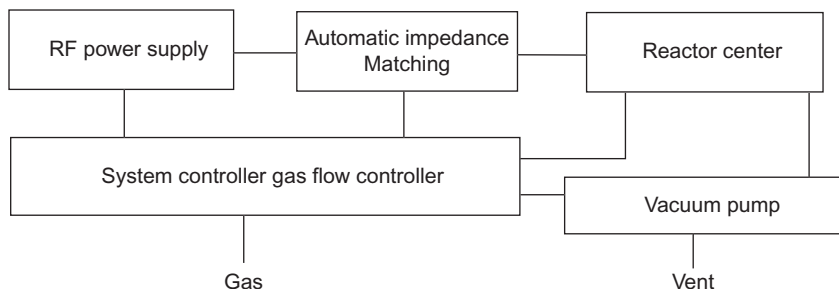
Plasma (glow discharge) sometimes refers to the *fourth* state of matter. It is produced by exciting a gas with electrical energy. It is a collection of charged particles containing positive and negative ions (Fig. 9.1). Other types of fragments, such as free radicals, atoms, and molecules, may also be present. Plasma is electrically conductive and influenced by a magnetic field (Fig. 9.2). Plasma is also intensely reactive, which is precisely the reason that it can modify surfaces of plastics [3]. It can be used to treat parts to make their surfaces harder, rougher, more or less wettable, and more conducive to adhesion.

Plasma is comprised of a partially ionized gas containing an equal number of positive and negative charges, as well as some non-ionized gas particles. A *glow discharge* is defined as plasma formed by the passage of electric current through a low-pressure gas like a fluorescent lamp. Glow discharge is globally neutral, but contains regions of net positive and negative charge. Most thin polymeric film processes utilize glow discharges, but “plasmas” and “glow discharges” are often used interchangeably [4]. *Plasma density* is the number of species/cm³, which is in the range of 10⁷–10²⁰. Typical glow discharges and arcs have an electron and ion density ~10⁸–10¹⁴.

Plasma treatment has its origins in the 1857 invention of dielectric barrier discharge (DBD). Werner von Siemens subjected oxygen or air to an alternating electric field of sufficient amplitude in a narrow annular gap, which resulted in dielectric barrier discharge. The process generated ozone, which became the first application of DBD [5]. The electrodes were placed outside the plasma chamber; thus they did not come into contact with the plasma front. DBD can take place in air, or in vacuum as long as trace amounts of one or more gases is injected into the plasma chamber.

Plasma treatment is probably the most versatile surface treatment technique [6,7]. Different types of gases such as argon, oxygen, nitrogen, fluorine, carbon dioxide, and water can produce the unique surface properties

Basics of the plasma process: States of matter

**FIGURE 9.1** Plasma is the fourth state of matter.**FIGURE 9.2** Schematic diagram of a plasma system [1,2].

required by various applications. For example, oxygen–plasma treatment can increase the surface energy of polymers, whereas fluorine–plasma treatment can decrease the surface energy and improve the chemical inertness. Crosslinking at a polymer surface can be introduced by inert gas plasma. Modification by plasma treatment is usually confined to the top several ten nanometers and does not affect the bulk properties. The main disadvantage of the low pressure (vacuum) plasma process is that it requires a vacuum system, which increases the cost of operation.

Corona treatment and low pressure and atmospheric pressure plasma treatment methods are all based on the dielectric barrier discharge phenomenon. All three processes have commercial applications which extend far beyond enhancement of adherability of surfaces. The relative cost and complexity of operating the three DBD-based treatment processes are shown in Fig. 9.3. The requirement of trace gases increases energy consumption, and special electrodes in atmospheric pressure plasma treatment (APT) render this technique more costly and complex than the standard corona treatment. The vacuum (low pressure) plasma method is more expensive than APT not only because of the higher capital cost of equipment but also by the requirement of extremely low pressure. The latter renders vacuum plasma treatment less productive and somewhat limited to higher value parts. More recently the industry's efforts have been focused on reducing costs and simplifying

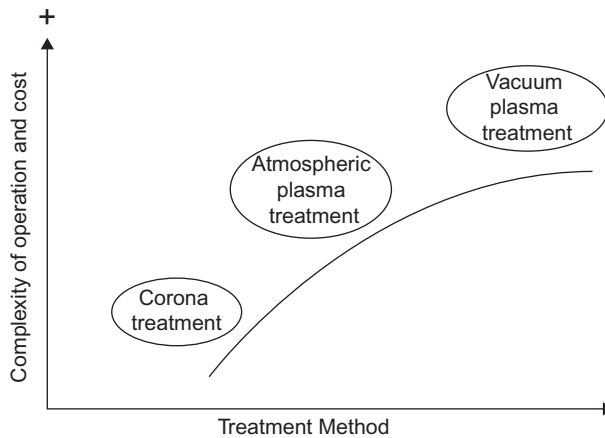


FIGURE 9.3 Complexity of operations and cost of treatment methods based on dielectric barrier discharge.

the low pressure plasma technique [8–10]. Good examples of cost analysis presented by the industry are available to readers as guidance for economic comparison of different plasma processes [11].

9.2 PLASMA REACTION WITH POLYMER SURFACES

Reactions of gas plasmas with surfaces polymers can be subdivided into three groups as per the following [12,13]:

1. Surface reactions include (a) reactions between the species in the gas phase and surface atoms and chemical groups and (b) reactions among the surface species that produce functional groups and crosslinking at the polymer surface. For example these reactions occur when a polymer surface is treated with plasma using gases such as ammonia, carbon monoxide, carbon dioxide, fluorine, hydrogen, nitrogen, nitrogen dioxide, oxygen, and water.
2. If the gases can act as monomers then plasma polymerization occurs at the surface forming a thin film on the surface of a polymer via polymerization of an organic monomer such as CH_4 , C_2H_6 , C_2F_4 , and C_3F_6 . The polymerization reaction scheme is rather complex because it involves reactions between gas-phase species, reactions between gas-phase species and surface species, and reactions between surface species.
3. Plasma treatment removes material from the polymer surfaces by chemical reactions and physical etching at the surface to form volatile products, and thus it can clean and etch polymer surfaces. Oxygen-containing plasmas are used to remove organic contaminants from polymer surfaces, e.g., oligomers, anti-oxidants, anti-block agents or mold-release agents.

Etching differs from cleaning only in the amounts of materials that are removed from the surface. Oxygen plasmas and oxygen- and fluorine-containing plasmas are frequently used for the etching of polymers [7].

There are different types of gas plasma depending on the properties of the gas; they include:

1. **Inert gas plasmas** – Helium, neon, and argon are the three inert gases used in plasma technology, although argon is the most common because of its low cost.
2. **Oxygen-containing plasmas** – Oxygen and oxygen-containing plasmas are most common for modifying polymer surfaces.
3. **Nitrogen-containing plasmas** – Nitrogen-containing plasmas are widely used to improve wettability, printability, bondability, and biocompatibility of polymer surfaces.
4. **Fluorine-containing plasmas** – When a plasma gas contains fluorine gas, surface reactions, etching, and plasma polymerization may take place simultaneously.

In general, plasma treatment increases the surface energy of polymers thus reducing wetting contact angle. The *depth of surface modification* mainly depends on the power level and treatment time. For plasma-treated polymer samples, the depth of the surface modification could be several tens of nanometers based on studies carried out using variation of angle-resolution in X-ray photoelectron spectroscopy (XPS) [14]. Concentration of functional groups created on a polymer surface by plasma treatment may vary depending on the *environment* and *temperature* over time. The underlying reason for surface chemical and physical changes of polymer surfaces is the extra mobility surface chains have over those in the bulk. The added mobility at the polymer surface lets the surface polymer molecules reorient in response to different environments [15]. Surface studies have demonstrated that the cause of decrease in the surface energy when the treated surface is placed in a low-energy medium such as air or vacuum is the rotation of the polar groups in the bulk or the migration of low-molecular-weight fragments to the surface to reduce the interfacial energy. Increasing the size of polar groups by grafting, an increase in crystallinity and crosslinking [16] have been found to be effective remedies for the prevention of physico-chemical surface changes of plasma treated polymers.

Another important factor that affects the speed of *aging* a plasma-treated polymer surface is temperature. A lower storage temperature reduces the rate of aging. Figure 9.4 shows the change of the water advancing contact angle on an oxygen-plasma-treated polypropylene surface as a function of aging time at different temperatures [17]. The rapid change of the contact angle at high temperatures supports the hypothesis that the changes in the surface are caused

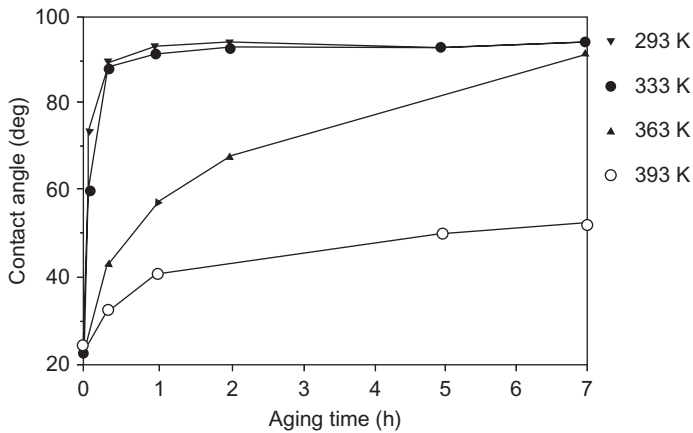


FIGURE 9.4 Advancing contact angle of water on oxygen—plasma-treated polypropylene as a function of aging time at different temperatures [17].

by polymer chain motion, reorienting the polar groups into the bulk. XPS studies of the chemical composition of the surface have shown little change after exposure to elevated temperatures. This is clearly an indication that any changes occur in layers thinner than the sampling depth of the XPS method [7].

9.3 LOW PRESSURE PLASMA TREATMENT (LPT)

In 1966, Schonhorn and Hansen [18] reported on a highly effective treatment for the surface preparation of low-surface-energy polymers for adhesive bonding. The techniques consisted largely of exposing the polymer surface to inert gas plasma at reduced pressure generated by electrodeless glow discharge (i.e., radio-frequency field). For polyethylene, only very short treatment times were necessary (approximately 9 seconds), while larger contact times were required for other polymers such as PTFE [19]. Plasma gases used (O_2 , He, N_2) can be selected to include a wide assortment of chemical reactions. In the process, atoms are expelled from the surface of the polymer and new chemical groups are formed thus can produce a strong, wettable, and crosslinked skin [20].

Low-pressure plasma treatment can be applied to a variety of plastic parts, even powder additives like pigments and fillers. In practice, this type of plasma treatment is not widely used in the industry because it is conducted in a vacuum process (10^{-2} – 10^{-3} mbar pressure), and is thus both expensive and inconvenient. Nevertheless, plasma treatment has been well researched and the academic literature is replete with papers.

The plasma used for treating material surfaces is called *cold plasma*, which means its temperature is room temperature. Cold plasma is created by introducing the desired gas into a vacuum chamber (Fig. 9.5), followed by

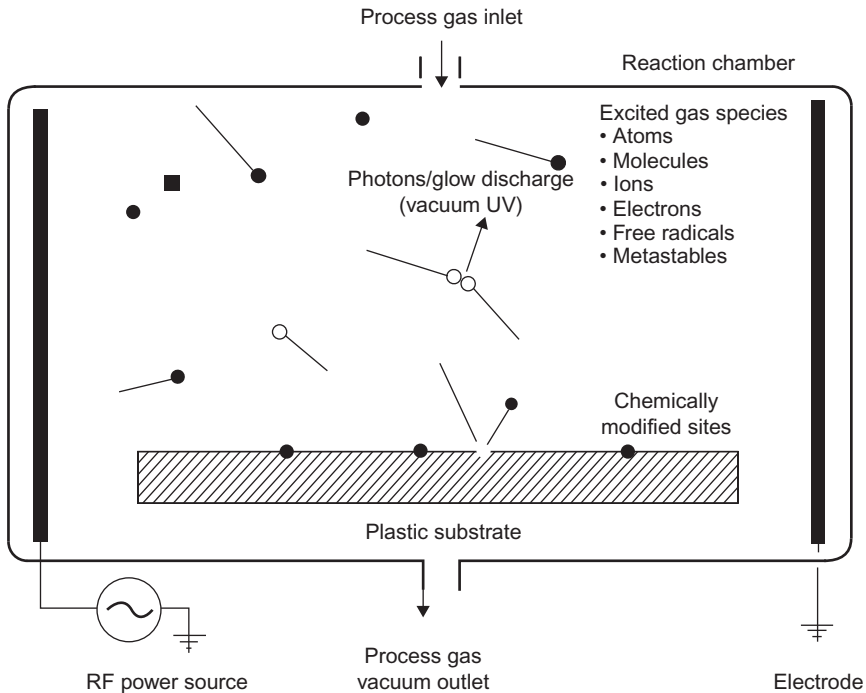


FIGURE 9.5 Schematic of the surface modification of plastic in gas plasma reactor.

radio frequency (13.56 MHz) or microwave (2450 MHz) excitation of the gas. The energy dissociates the gas into electrons, ions, free radicals, and metastable products. Practically any gas may be used for plasma treatment although oxygen is most common. The electrons and free radicals created in the plasma collide with the polymer surface and rupture covalent bonds, thus creating free radicals on the surface of the polymer as shown in [Figure 9.6](#). The free radicals in the plasma may then recombine to generate a more stable product. After a predetermined time or temperature is reached, the radio frequency is turned off. The gas particles recombine rapidly and the plasma is extinguished. The most important components of a system are the vacuum chamber, the vacuum pump, and a high-frequency generator for plasma creation. The principal process of a low-pressure system can be most simply explained by [Figures 9.7](#) and [9.8](#).

9.3.1 Applications of Low Pressure Plasma Treatment to Polymers

Plasma-treated polymers typically form adhesive bonds from two to four times stronger than bonds formed by traditional chemical or mechanical

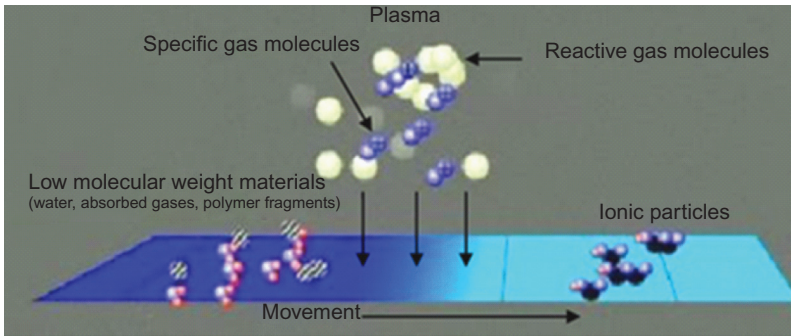


FIGURE 9.6 Schematic of surface modification of plastics in gas plasma [21].

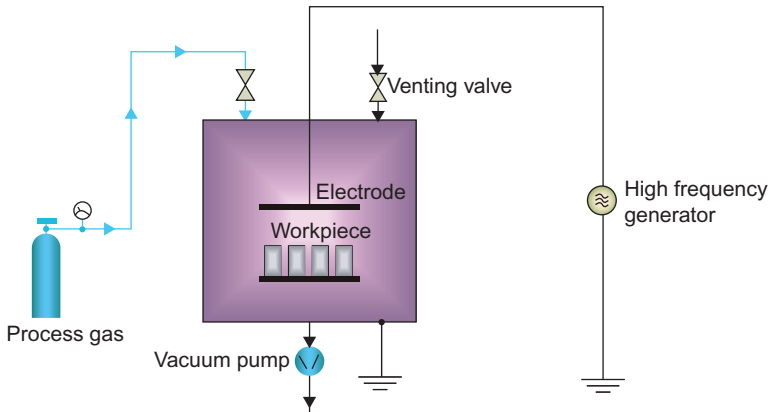


FIGURE 9.7 Basic schematic diagram of kHz and MHz low pressure plasma systems. (Courtesy of Diener Electronic, www.plasma.de/en/index.html) [22].

preparation. Researchers at Picatinny Arsenal conducted and reported on a study of a number of polymers, using activated gas plasma treatment [23]. A different study covered other plastics (Valox[®] polybutyl terephthalate polyester, polyethersulfone, polyarylsulfone, polyphenylene sulfide, ECTFE fluoropolymer, nylon 11, nylon 6/12, and nylon 12) [24].

Table 9.1 presents the lap shear joint bond strength of high density polyethylene as a function of gas used in the vacuum (low pressure) treatment and the width of the plastic film (Figures 9.9 and 9.10). The narrower bond area yields higher bond strength than the wider one (13 mm). Tables 9.1, 9.2, 9.3, and 9.4 show the effects of varying the process conditions of vacuum plasma treatment on the lap shear joint bond strength for a number of plastics. Clearly, plasma treatment is not equally efficient in rendering different plastics adhereable.

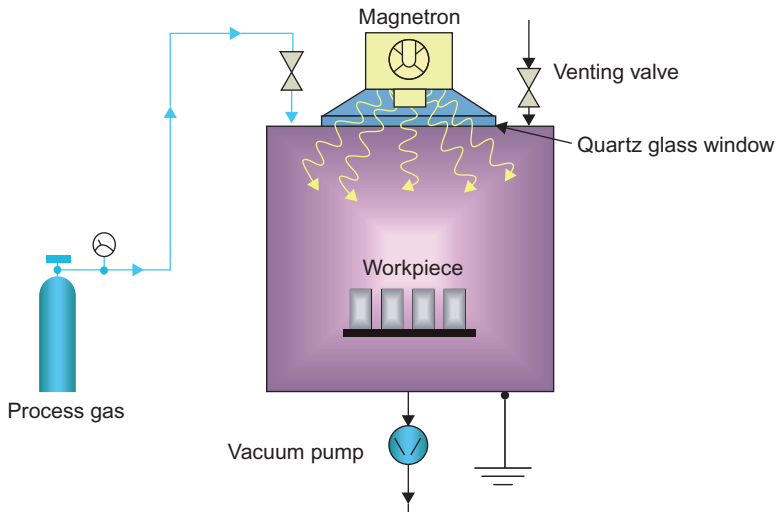


FIGURE 9.8 Basic schematic diagram of microwave plasma systems with metal chamber. (Courtesy of Diener Electronic, www.plasma.de/en/index.html) [22].

TABLE 9.1 Effect of Plasma Treatment on Lap Shear Joint Strength (kg/cm) of High-Density Polyethylene Sheet (1.6 mm Thick) [23]

Treatment Type (Duration)	13-mm Wide Lap Shear	6-mm Wide Lap Shear
Oxygen (30 min)	80	245
Oxygen (1 min)	84	248
Helium (1 min)	84	242
None – solvent wiped	9.3	–



FIGURE 9.9 Schematic of adherends (blue) and Adhesive layer (black) in Single-lap Joint Shear Test (per ASTM methods D1002 for metal/metal, D3164 for plastic/metal and D3163 for plastic/plastic adherends).

A significant amount of investigation has been conducted on the surface modification of fluoropolymers. Plasma treatment of polytetrafluoroethylene has been the subject of numerous and extensive studies and developments both in academia and in the industry because of the difficulty of obtaining



FIGURE 9.10 Lap joint shear test specimen in a tester device.

TABLE 9.2 Effect of Plasma Treatment Duration on Lap Shear Joint* Strength (kg/cm) and Failure Mode of Polyethylene (3.2 mm Thick) [23]

Treatment Type	Duration (min)	Bond Strength (MPa)	
		High Density	Low Density
None – solvent wiped	–	2.2 (A, PE)	2.6 (A, PE)
Oxygen	0.5	13.7 (A, PE)	–
Oxygen	1	9.2 (A, Al)	10 (C, PE)
Oxygen	30	16.8 (A, Al)	10.1 (C, PE)
Helium	0.5	6.4 (A, PE)	9.6 (C, PE)
Helium	1	9.4 (A, PE)	9.5 (C, PE)
Helium	39	21.6 (C, PE)	9.1 (C, PE)

* Notes:

Bonded to etched aluminum coupons using a crosslinked epoxy (a blend of Epon[®] 828 and Versamid[®] 140, 70/30 parts by weight).

A = adhesive failure, C = cohesive failure (see Ch. 5 for definitions of bond failure).

PE = polyethylene, Al = aluminum, PC = polycarbonate, PP = polypropylene.

acceptable adhesive bondability in addition to the strong desire to eliminate sodium etching.

A number of studies have been made on the vacuum plasma treatment of polymers [7], [25–27]. Chan et al. [7] have reviewed the low pressure (vacuum) plasma surface technology in a comprehensive study published in 1996.

TABLE 9.3 Effect of Plasma Treatment Duration on Lap Shear Joint* Strength (kg/cm) of Polycarbonate and Polypropylene Sheet [23]

Treatment Type	Duration (min)	Bond Strength (MPa)	
		Polycarbonate (1.6 mm Thick Sheet)	Polypropylene (0.12 mm Film)
None – solvent wiped	–	2.8 (A, PC)	2.6 (A, PP)
Oxygen	0.5	5.5 (A, PC)	12.9 (A, PP)
Oxygen	30	6.4 (A, PC)	21.2 (A, PP)
Helium	0.5	4.6 (A, PC)	3.1 (A, PP)
Helium	30	5.8 (A, PC)	1.4 (A, PP)

*Notes:

Bonded to etched aluminum coupons using a crosslinked epoxy (a blend of Epon[®] 828 and Versamid[®] 140, 70/30 parts by weight).

A = adhesive failure, C = cohesive failure (see Ch. 5 for definitions of bond failure).

PE = polyethylene, Al = aluminum, PC = polycarbonate, PP = polypropylene.

Most of the development efforts since the early 1990s have, however, been focused on atmospheric pressure plasma treatment because of its advantageous economics and relative ease of operation.

In a study in 2006 low density polyethylene was treated by low pressure plasma using oxygen. Increasing the exposure time increased the surface energy (γ_s) and its polar component (γ_s^p) while the dispersed component (γ_s^d) decreased (Table 9.5) rather unsurprisingly. The majority of the increase in surface energy was gained during the first minute of exposure.

In a 1995 study [28], films of low density polyethylene, polypropylene, and polyethylene terephthalate were treated by low pressure microwave plasma using oxygen, hydrogen, and hexamethyldisiloxane mixed with oxygen and ethylene. The latter gases were monomers intended to plasma-polymerize on the film surfaces. The treated films were bonded to aluminum block with an epoxy adhesive on both sides and pulled, as seen in Figure 9.11, to measure bond strength.

Figure 9.12 shows that the bond strength of polyethylene treated by O₂ plasma increases strongly from the low value of 0.4 N mm⁻² for the untreated polymer by a factor of 20.5, up to 8.2 N mm⁻² after a plasma treatment of only 6 seconds [28]. The value of 8.2 N mm⁻² is nearly the maximum bond strength reached for polyethylene and is not significantly influenced by a longer treatment than 900 seconds. At treatment time of 1800 seconds, a bond strength declination to the value of 6.4 N mm⁻² is observed. In the case of polypropylene the improvement in the bond strength with oxygen plasma took place over a longer time and a slight decline of the bond strength is obtained for polypropylene for longer treatment times. Polyethylene terephthalate's

TABLE 9.4 Effect of Plasma Treatment Duration on Lap Shear Joint* Strength (kg/cm) of Various Plastics [23]

Treatment Type	Duration (min)	Bond Strength (MPa)				
		Polystyrene (0.25 mm Thick Film)	Polyethylene Terephthalate (0.25 mm Transparent Film)	Polyvinyl Fluoride (25 μm Transparent Film)	Cellulose Acetate Butyrate (15.2 mm Thick Sheet)	Nylon 6 (76 μm Thick Film)
None – solvent wiped	–	3.9 (A, PS)	3.6 (A, PET)	1.9 (A, PVF)	7.5, 4.5 (A, CAB)	5.8 (A, N)
Oxygen	0.5	–	–	9.4 (A, Al/PVF)	7.8 (A, CAB)	11.2 (A, Al)
Oxygen	1	–	–	–	3.1 (A, CAB)	10.5 (A, Al)
Oxygen	30	21.5 (C, PS)	9.4 (A, PET)	9.8 (A, Al/PVF)	9.5 (A, CAB)	24.1 (A, Al)
Helium	0.5	–	–	9.9 (A, Al/PVF)	9.6 (A, CAB)	9.4 (A, Al)
Helium	1	–	–	–	4.1 (A, CAB)	9.5 (A, Al)
Helium	30	27.7 (C, PS)	11.4 (A, PET)	9.3 (A, Al/PVF)	–	27.3 (A, Al)

* Notes:

Bonded to etched aluminum coupons using a crosslinked epoxy (a blend of Epon[®] 828 and Versamid[®] 140, 70/30 parts by weight).

A = adhesive failure, C = cohesive failure (see Ch. 5 for definitions of bond failure).

Al = aluminum, PS = polystyrene, PET = polyethylene terephthalate, PVF = polyvinyl fluoride, CAB = cellulose acetate butyrate, N = nylon 6.

TABLE 9.5 Surface Energies (Polar and Dispersive Component) for Low Pressure O₂ Plasma-Treated LDPE Surfaces as a Function of the Exposure Time [15]

Exposure Time (min)	γ_s^p (mJ m ⁻²)	γ_s^d (mJ m ⁻²)	γ_s (mJ m ⁻²)
0	3.7	24.2	27.9
1	59.8	2.6	62.4
2	59.6	3.3	62.9
5	63.3	2.6	65.9
10	62.9	2.2	65.1
15	66.7	2.0	68.7
20	67.0	1.6	68.6
25	68.1	1.3	69.4
30	67.0	1.8	68.8

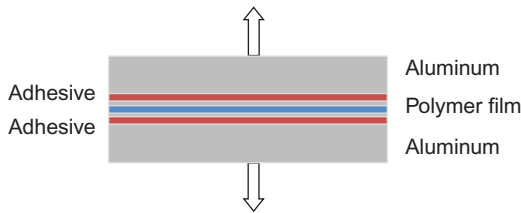


FIGURE 9.11 Schematic of test device for bond strength measurement of plasma treated polymer films.

bond strength of 5.1 N mm⁻² is measured and is increased by only 20% to 6.2 N mm⁻² by plasma treatments between 2 and 900 seconds. At a treatment time of 1800 seconds the bond strength declined to 4.3 N mm⁻². The improvements in adhesive bond strengths of polyethylene and polypropylene by oxygen plasma is due to the formation of hydroxyl, carboxyl, carbonyl, and ester groups in the surface layer of those polymers.

Surface modification of polyethylene terephthalate (PET) was investigated [3] by using low-pressure CF₄ plasma in a roll-to-roll double-sided treated system. The surface properties of the modified polymers are characterized by X-ray photoelectron spectroscopy (XPS) and water contact angle. Treated for a longer time and higher RF power (12 min, 600 W), the wettability of the PET surface shows two opposite extremes. The contact angle on one side of the PET film is super-hydrophilic, 7.56°, and the other side is hydrophobic, 108.63°. The XPS analysis measurement results also show different functional groups on the two sides of PET surfaces. The CF₃ in C (1 s) spectrum can enhance the hydrophobic surface, in spite of the fact that

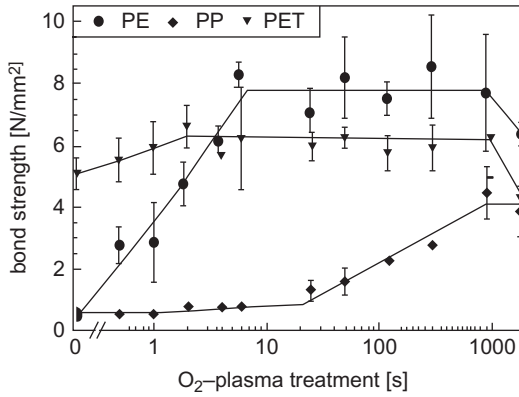


FIGURE 9.12 Peel strength of polymer films treated by O₂ plasma as a function of exposure time [28].

the relative intensity of CF₂ increases to 23.45%. Moreover, the surface dynamics of PET denote the concentration-dependent characteristics; that is, the F/C ratio decreases upon the concentration of hydroxyl ion increasing after dipping the sample into different [OH⁻] solutions.

Medical-grade polydimethylsiloxane (PDMS) elastomer was treated by low-powered plasma using four different gases: O₂, Ar, N₂, and NH₃. Changes to the surface chemistry after the treatment and the stability of those changes during aging in phosphate buffered saline (PBS) or in air for up to 1 month were investigated by Williams et al. [29]. Chemical analysis of the surface was conducted by X-ray photoelectron spectroscopy and dynamic contact angle and surface morphology were analyzed by optical microscopy and atomic force microscopy. Surface topography of untreated and plasma-treated specimens was examined using AFM operated in “tapping” mode. A typical AFM micrograph of Ar-treated PDMS is shown in Fig. 9.13. It can be seen that mild etching of the surface has occurred, producing surfaces that were more dimpled or pitted than the virgin surface.

All plasma treatments resulted in an increase in wettability, because of changes in chemistry combined with modest etching [29]. Furthermore, the primary site of attack of the plasma species appeared to be dependent upon the type of gas. The two main chemical changes observed after aging were due to reactions with the storage media and relaxation processes, resulting in further changes in wettability. The influence of the surface modifications on the blood compatibility of the materials was investigated by assessing contact phase activation using a partial thromboplastin time assay. It was demonstrated that the O₂ and Ar plasma treatments diminished the performance of the silicone but the N₂ and NH₃ treatments enhanced the activation of the coagulation cascade.

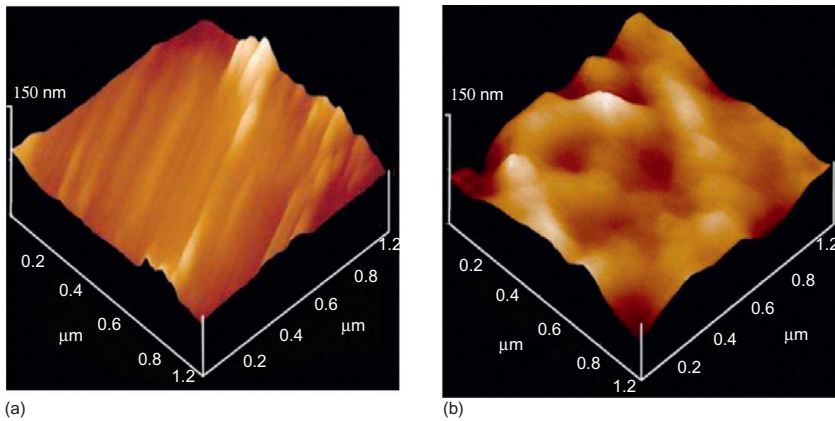


FIGURE 9.13 AFM micrographs of (a) untreated; and (b) Ar plasma-treated PDMS, scan angle ϕ 30° [29].

Low-pressure glow discharge plasma with O_2 and N_2 was used to treat the surface of LDPE films to improve wettability to adhesives and to increase bond strength in a LDPE to form laminates with polyolefin foam. The main application of film/foam laminate is in the automotive industry. Typically a reactive polyurethane adhesive is used to bond the LDPE film to the polyolefin foam. Treatment by oxygen-plasma generated polar groups directly, compared to nitrogen plasma for which surface functionalization occurred after the plasma treatment upon exposure of the samples to wet air. That is when reactions with oxygen and water vapor take place producing polar chemical groups. Increase in surface roughness by plasma generated abrasion (etching) increases the surface area of bonding thus improves adhesive bond strength. The laminates exhibited good durability under aging conditions required for automotive testing (Figs 9.14 and 9.15) at different temperatures and relative humidities.

9.3.2 Application of Low Pressure Plasma Treatment of Fluoropolymers

Table 9.6 contains data that compares the results of plasma treatment and sodium etching for four fluoropolymers. Peel strengths of untreated and treated samples were measured by bonding them into T-peel specimens using the flexibilized epoxy adhesive Scotch-Weld[®] 3553 (available from 3M Corp.). The laminates were cured for several hours at $70^\circ C$ and peel tested at a 12.5 cm/min pull rate. Polytetrafluoroethylene does not accept plasma treatment as well as PFA and FEP, as indicated by its relatively low peel strength. Plasma treatment does not impart sufficiently strong adhesive bonds

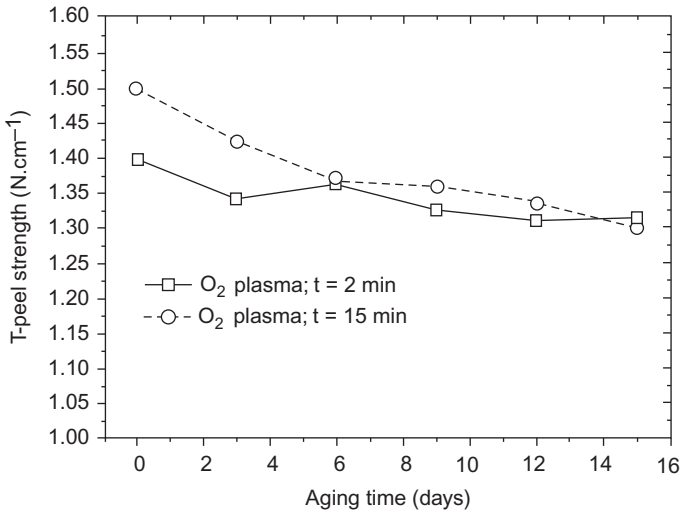


FIGURE 9.14 Aging effect on T-peel strength of oxygen plasma-treated LDPE films (conditions: 38°C and 95% relative humidity) [30].

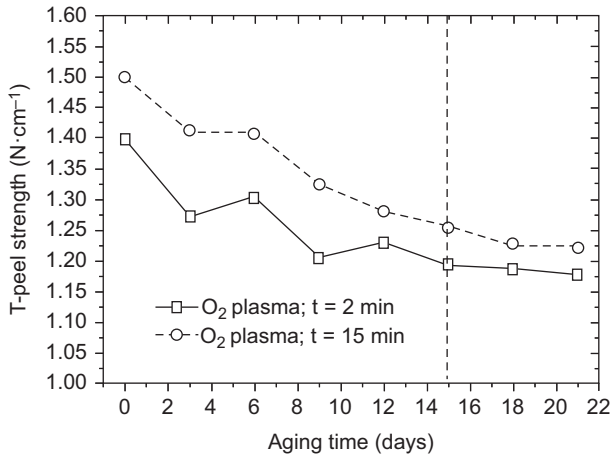


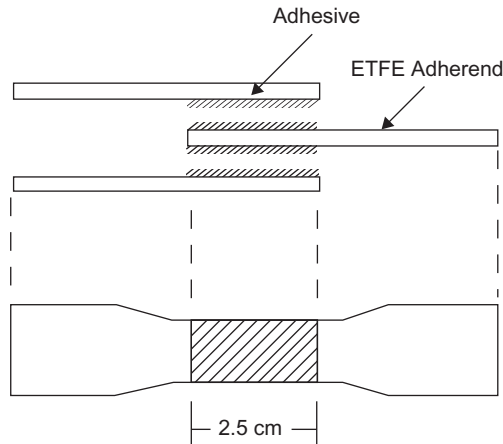
FIGURE 9.15 Aging effect on T-peel strength of oxygen plasma-treated LDPE films (conditions: 70°C and 55% relative humidity) [30].

in polytetrafluoroethylene, the most common fluoropolymer. Bond strength of plasma treated PTFE is at best less than half that obtained by sodium etching [33]. Sodium etching was the *only* effective method of modifying the surface of PTFE.

TABLE 9.6 Peel Strength of Adhesive Bonded Fluoropolymers [31,32]

Treatment	Material			
	PTFE	FEP	ETFE	PFA
Untreated	Negligible	0.1	Negligible	0.04
Sodium etched	5	8.2	—	6.4
Plasma treated	2.2	10.4	15.8	8.3

PTFE = Polytetrafluoroethylene, FEP = Fluorinated ethylene propylene copolymer.
 ETFE = Ethylene tetrafluoroethylene copolymer, PFA = Perfluoroalkoxy copolymer.

**FIGURE 9.16** Schematic of the double-lap shear test specimen.

A study of adhesion improvement of ETFE by plasma treatment using oxygen, ammonia, and oxygen-plus-SF₆ gases has been reported [34]. Joints were made using commercial epoxy adhesives by a double-lap shear configuration (Fig. 9.16). The bond strength of the plasma-treated ETFE significantly exceeded the bond strength of the sodium-etched polymer specimen (Table 9.7). A range of values was obtained for bond strength with different adhesives.

An alternative plasma treatment technique is the glow discharge method that can be done at atmospheric pressure. Fluoropolymer films were treated by glow discharge in helium atmosphere [36]. Strips of the treated and untreated films were bonded to 0.2 mm thick aluminum foils using a urethane adhesive cured at 100°C for 15 minutes. The treatment conditions and bond strengths of the samples are given in Table 9.8. Glow discharge was effective for the

TABLE 9.7 Bond Strength of Plasma-Treated ETFE Using a Double-Lap Shear Test and Epoxy Adhesives [35]

Treatment Type	Bond Strength (MPa)
None	0.07
Tetra-Etch [®] *	0.78
Plasma (O ₂ + SF ₆)	1.49–2.31
Plasma (O ₂)	1.47–1.83
Plasma (NH ₃)	1.40–1.72

*Tetra-Etch[®] by WL Gore & Associates, Inc.
 ETFE = Ethylene tetrafluoroethylene copolymer.

TABLE 9.8 Effect of Atmospheric Glow Discharge Treatment in Helium Gas on Bond Strength [36]

Fluoroplastic	Untreated (g/cm)	Treated (g/cm)
PFA	0	600
FEP	0	640
ETFE	0	430
PVDF	100	830

Treatment conditions: gas flow rate = 5 l/min, discharge frequency = 5 kHz. Treatment time = 60 sec.

PFA = Perfluoroalkoxy copolymer, FEP = Fluorinated ethylene propylene copolymer.
 ETFE = Ethylene tetrafluoroethylene copolymer, PVDF = Polyvinylidene fluoride.

treatment of a number of fluoropolymers. This technology has been commercialized.

A 1990 study [37] of plasma treatments of PTFE with air, oxygen, argon, and water vapor process gases created modified surfaces that were more polar and had a higher surface energy. A plasma treatment duration of 15 seconds (Fig. 9.17) was sufficient; this is considerably shorter than the treatment times in other reports. X-ray photoelectron spectroscopy (XPS) data showed the plasmas treatment with the gases used, mainly led to the loss of a considerable fraction of the fluorine atoms. In all cases the amount of oxygen uptake was much less than the amount of fluorine loss, indicating that the radicals generated by fluorine abstraction reacted with other radicals rather than oxygen-containing species from the plasma. The authors concluded the absence of an optically measurable level of conjugated double bonds suggested that double bond formation was less important than cross-linking of the surface for radical dissipation. The main effect of plasma

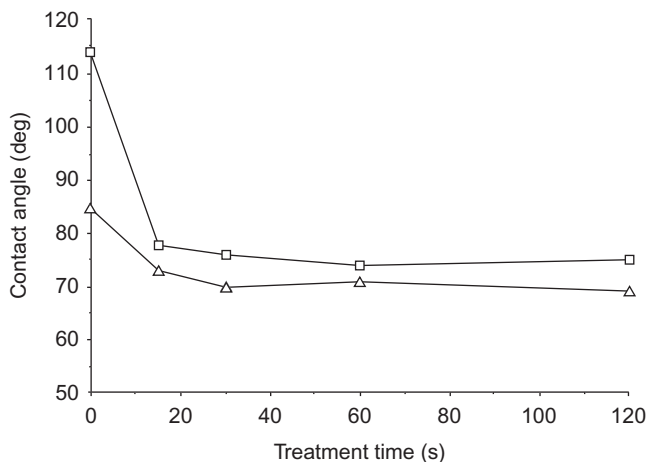


FIGURE 9.17 Contact angles of PTFE surfaces modified by treatment in a water vapor plasma, as a function of treatment duration. Distilled water (□) and methylene iodide (△) [37].

treatments of PTFE is not oxidative as is the case for most other polymers, and depends little on the plasma process gas used.

In a study [38], low-pressure plasma treatments of PTFE films using sulfur dioxide (SO_2) as the process gas were performed to impart functional groups containing sulfur and oxygen to the polymer surface. Plasma process parameters including gas flow rate, power, and treatment time were varied to determine the optimal plasma conditions for the desired surface modification. Wettability of the plasma-treated PTFE surface increased as demonstrated by a decrease in contact angle. Surface analysis by XPS showed decrease in fluorine content of the surface accompanied by the presence of oxygen and sulfur on the surface. The insertion of sulfur groups on the PTFE surface was not completely successful. The investigators followed up with another study.

In this study [39], PTFE films (100 μm thick) were first treated with low pressure plasma application using hydrogen as process gas. The second step was either a plasma treatment with SO_2 or by the immersion of the H_2 treated films in fuming sulfuric acid, containing SO_3 . The contact angle of the treated samples decreased from the original 110° to 53° for H_2/SO_2 plasma and to 74° (H_2 plasma/ SO_3), respectively. The sample “ H_2/SO_2 plasma” showed only at the outer surface layer oxygen and sulfur traces as shown by XPS, while no evidence for the presence of functional groups in inner layers could be observed by attenuated total reflectance-Fourier transform infrared spectroscopy. Otherwise, the sample “ H_2 plasma/ SO_3 ” yielded exactly the contrary results: the observed bands in the infrared spectra assigned to associated OH and to SO_3 (at $3000\text{--}3700\text{ cm}^{-1}$ and $1,056\text{ cm}^{-1}$ respectively) are very strong but the O/C and S/C ratios given by XPS were not high

enough. It was concluded from the different depths of surface penetration of both XPS and infrared spectroscopy that these two modification methods are able to insert functional groups into the polymer surface at different surface layers.

In another study, short-time plasma pre-treatment of polytetrafluoroethylene PTFE [40] with a low pressure microwave plasma was investigated. The source was Plasmodul[®] (Fig. 9.18), which allows the pre-treatment of PTFE substrates with ammonia plasma (NH_3). The newly developed plasma source Planartron[®], which is derived from Duo-Plasmaline, was used for improving the adhesion properties of PTFE by generating oxygen and nitrogen plasmas. PTFE foils were modified on both sides by plasma treatment for typically 30 seconds. After bonding the films to an aluminum substrate using an epoxy adhesive, the bonding strength was measured directly by pull off tests. In Fig. 9.19 the bond strength is plotted vs. the exposure time in ammonia plasma. The figure shows that a short-time plasma treatment in the range of 15 seconds results in maximum bond strength (3.5 N mm^{-2}) that is more than one order of magnitude higher compared to the untreated PTFE bond strength of 0.25 N mm^{-2} .

Next, PTFE films, pretreated with NH_3 plasma, were treated with N_2 plasma using the Planartron[®] device (Fig. 9.20) by placing the substrates at



FIGURE 9.18 Plasmodul[®] device with gas inlet system, plasma source, reaction chamber, and diagnostic ports [40].

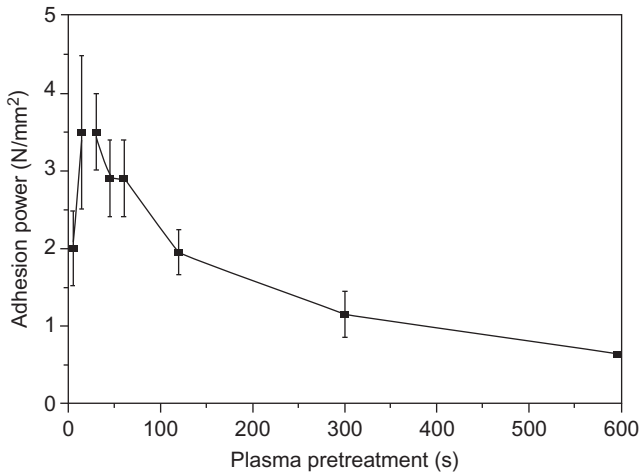


FIGURE 9.19 Bond strength versus plasma exposure time of PTFE treatment in Plasmodul[®] using NH₃ gas [40].



FIGURE 9.20 Schematic view of the Planartron[®] source. The antenna structure is placed under a quartz plate. This arrangement is especially designed for use in Plasmodul[®] [40].

distances of 2 and 0 cm from the plasma source. **Figures 9.21 and 9.22** show the bond strength versus the exposure time in nitrogen plasma for 2 and 0 cm distances. **Figure 9.21** shows that the bond strength of PTFE treated with nitrogen plasma at a 2 cm distance in a Planartron[®] source increases from 0.25 N mm^{-2} for the untreated material to 5.9 N mm^{-2} after 50 seconds of plasma treatment. At longer treatment times the bond strength decreases to 2.6 N mm^{-2} (after 200 seconds). The maximum bond strength of PTFE film, treated with N₂ at a distance of 0 cm, was reached in 5 seconds at 5 N mm^{-2} . This represents a factor of 20 compared to the untreated

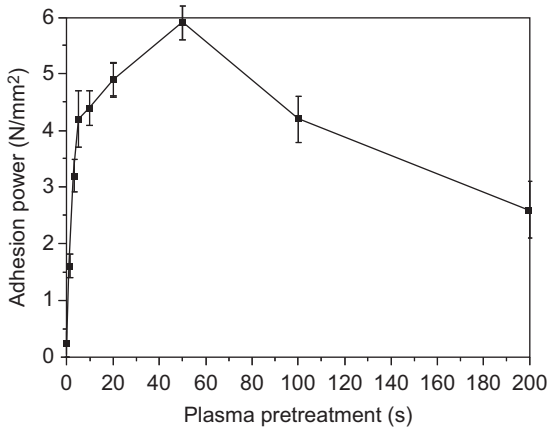


FIGURE 9.21 Bond strength versus plasma exposure time for PTFE treated with N₂ plasma at a distance of 2 cm [40].

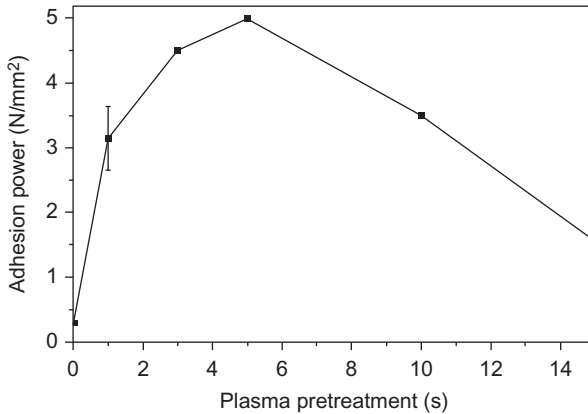


FIGURE 9.22 Bond strength versus plasma exposure time for PTFE treated with N₂ plasma at a distance of 0 cm [40].

material. Increasing the plasma exposition time again leads to a strong decrease in bond strength. It is remarkable that, already after a treatment of 5 seconds, the same bond strength is achieved as treating the PTFE for 20 seconds at a distance of 2 cm from the source. This type of development has reduced the cost of low pressure plasma treatment. A number of companies including Diener Electronic (www.plasma.de/en/index.html, Ebhausen, Germany), Henniker Plasma (www.plasmatreatment.co.uk, Warrington, UK), and Acton Technologies (www.actontech.com), Pittston, PA, USA offer treatment services.

A 2003 article [41] described the etching of polymer surfaces by low pressure plasma treatment. The topography of the surface is measured by atomic force microscopy (AFM). The as-received PTFE, Fig. 9.23(a), consisted of a dense assembly of 200–300 nm thick and 0.5–1.5 μm long cigars. These cigars arranged themselves on a micrometric rough surface. The PTFE films used had been produced by a cast process, where in a number of very thin layers were successively deposited and then fused all together. Figures 9.23b and 9.23c show the PTFE surface after a soft and a pronounced He plasma treatment, respectively. If the micrometric structure remains unchanged for both ion energies, an etching of the fine structure is clearly visible. The cigars become thinner by plasma treatments.

Effective PTFE surface treatment by low pressure plasma treatment (LPT) has been achieved thanks to combined academic and industrial research and development efforts. The new treatment processes have lower cost though are still more expensive than other methods. Companies such as Diener Electronic (www.plasma.de/en/index.html, Ebhausen, Germany), Henniker Plasma (www.plasmatreatment.co.uk, Warrington, UK), and Acton Technologies (www.actontech.com, Pittston, PA, USA) offer LPT for PTFE treatment.

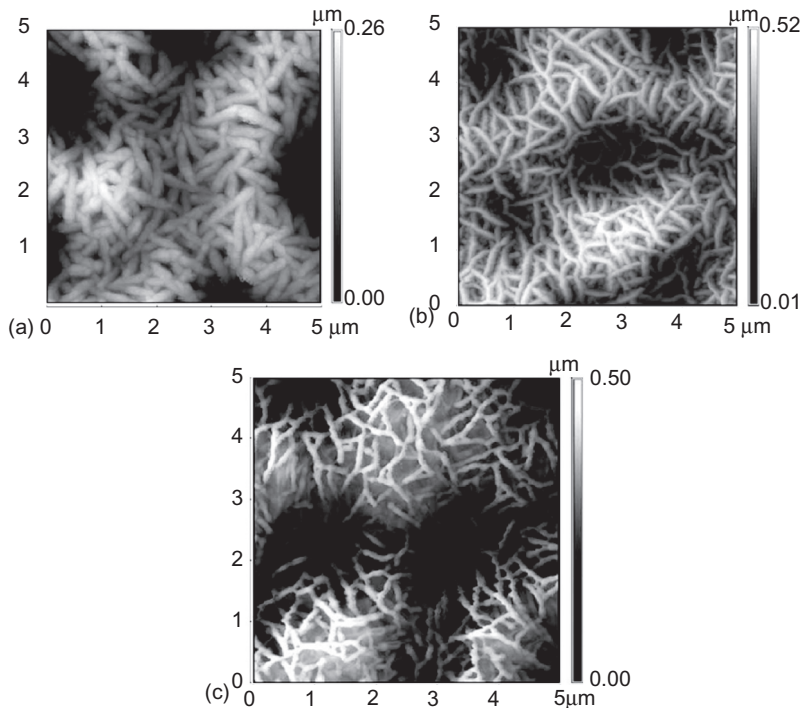


FIGURE 9.23 AFM profile of PTFE surfaces (a) untreated, (b) helium-plasma treated at a DC bias of 100 V for 2 min, and (c) helium-plasma treated at a DC bias of 200 V for 5 min [41].

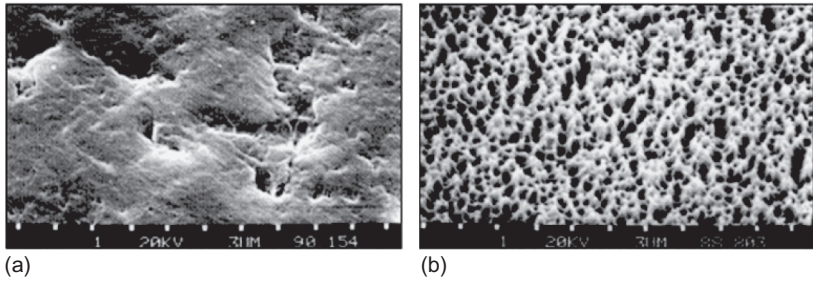


FIGURE 9.24 Scanning electron micrograph of PTFE: (a) before plasma treating and (b) after plasma treating.

Figure 9.24 shows the topical view of PTFE surface as-is and after low pressure plasma etching. The benefit of etching is increased surface roughness, which leads to an increase in available adhesive bonding surface area.

Many academic research papers on PTFE surface modification [42–49] have focused on the effect of LPT using different gases and compounds, grafting, plasma process variables, surface wettability, and analysis of surface composition and topography. These studies are useful in shedding light on the state of the modified PTFE surfaces versus the as-is sample. Indeed some of the articles report on good quality research work [48]. The studies seem to stop short of completing the rational research cycle because little has been reported about the effectiveness modification with respect to bondability of the treated surfaces or in other applications. Wettability improvement and impartation of polar functional groups on PTFE surface are prerequisite requirements of bonding using adhesives. In the end, however, the actual demonstration of successful bonding to the treated surfaces is the true measure of success of surface modification. If the surface treatment is not aimed at adhesive bonding and at other targets such as biocompatibilization, then the effectiveness of the modified surfaces to that end must be elucidated.

A study of low pressure plasma treatment of PTFE surface was made using scanning probe microscopy (SPM) [48]. The gases used were air, helium, and acrylic acid (AAc). The SPM image of the untreated PTFE film [Fig. 9.25(a)] shows a smooth surface, without any particular features on the surface. The PTFE films treated for 60 s in He plasma showed sphere-like aggregates which are formed on the surfaces [Fig. 9.25(d) and (e)]. Furthermore, the topography of the He-plasma-treated surface at 100 W [Fig. 9.25(e)] had higher sphere features than He-plasma-treated surface at 70 W [Fig. 9.25(d)]. However, less sphere-like structures were formed on surfaces treated with air plasma [Fig. 9.25(b) and (c)]. The morphologies of AAc-plasma-treated surface at 100 W [Fig. 9.25(f) and (g)] were similar to those for the He-treated surface [Fig. 9.25(e)], and only the surface treated with AAc-plasma for 60 s [Fig. 9.25(f)] was with lower sphere features and

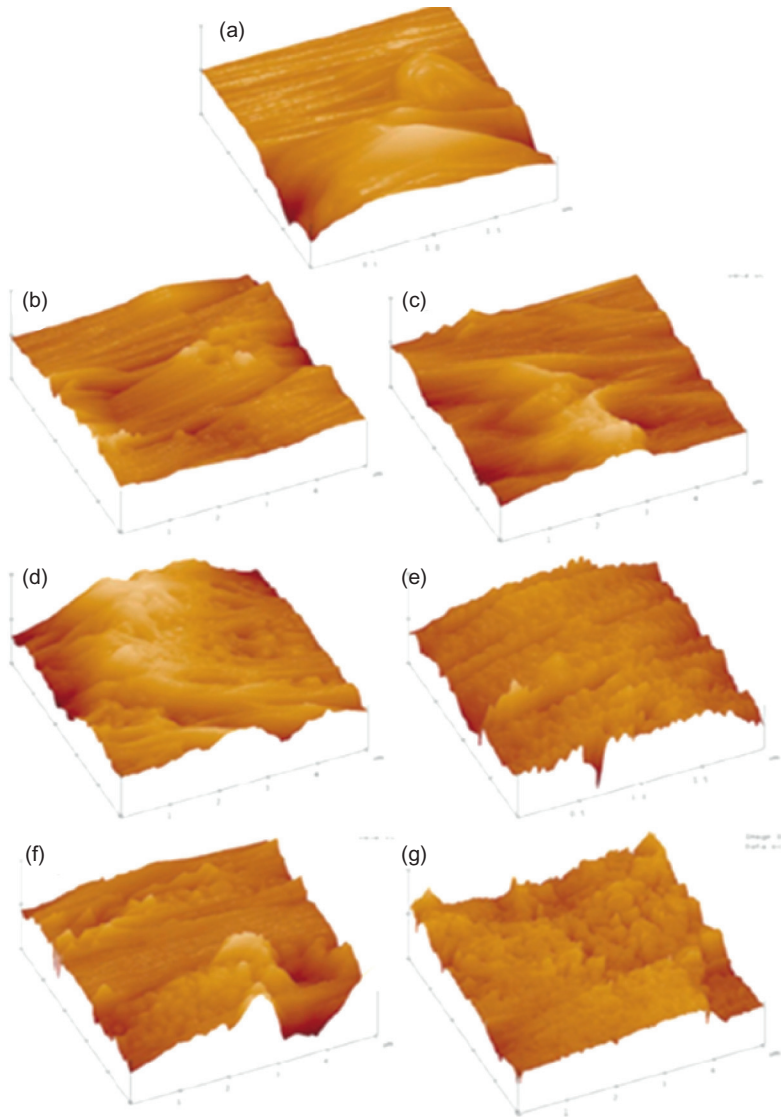


FIGURE 9.25 SPM images of untreated and treated PTFE surfaces: (a) untreated; (b) treated with air plasma at 70 W for 60 s; (c) treated with air plasma at 100 W for 60 s; (d) treated with He plasma at 70 W for 60 s; (e) treated with He plasma at 100 W for 60 s; (f) treated with AAc plasma at 100 W for 60 s; (g) treated with AAc plasma at 100 W for 120 s [48].

the surface treated for 120 s [Fig. 9.25(g)] had more intensive sphere-like peaks. As can be seen from Figure 9.25, for the same conditions, the PTFE films treated in air, He, or AAc plasma showed that the average roughness increased with a even higher power (100 W) or an even longer plasma

exposure time (120 s). Also, the difference among the samples treated with air, He, or AAc plasma is noticeable: the sample treated with He plasma showed much rougher surface for the same treatment time and power, which was probably due to a different etching rate that was higher in the case of He plasma than in the case of air or AAc plasma. The formation of the rough surface after plasma treatment was mostly caused by the chemical erosion by atoms and physical erosion by ions in the plasma.

9.4 ATMOSPHERIC PRESSURE PLASMA TREATMENT

Atmospheric pressure plasma treatment (APT) systems have been developed out of necessity and for a number of reasons:

1. To take advantage of the capability of plasma technology.
2. In response to a number of shortcomings of 3D corona treatment systems discussed in Chapter 6 (see a comparison of atmospheric pressure plasma and a 3D corona treater given in [Table 9.9](#)).
3. To offer an alternative process to low pressure plasma methods which are costly and complex due to the vacuum requirement (see [Table 9.10](#) for a comparison).

APT techniques are versatile and have found a number of important applications based on the properties of the plasma [\[51,52\]](#). Some of these uses include:

1. Spectroscopic analysis.
2. Gas treatment: gas cleaning and synthesis.
3. Surface treatment: surface cleaning and etching, surface activation, surface coating.
4. Powder treatment.
5. Toxic waste treatment.
6. Plasma enhanced chemical vapor deposition.

Although the same physical phenomenon of electrical breakdown of gases at atmospheric pressure (electrical discharge) is used, the methods of creation and application of this discharge are completely different for 3D corona and atmospheric pressure plasma treatment techniques [\[50\]](#).

The plasma system is designed to create ([Fig. 9.26](#)) a uniform plasma cloud that completely surrounds small objects or spreads into the boundary layer of the surface. It can also be placed in the internal cavities, channels, etc. The same plasma system may treat the internal surfaces of a 50 μm capillary and cover a 50 mm diameter (and higher) surface area. One design of such a machine is based on the well known physical phenomenon [\[53\]](#). The strength of the electrical field considerably increases in the vicinity of small radius objects. Applying a high voltage signal to a sharp edge body (e.g., a needle) causes electron leakage from the edge to the gaseous

TABLE 9.9 Comparison of an Atmospheric and a 3D Corona-Treater [50]

	Atmospheric Plasma	3D Corona
Average power	100 W	1000 W
Plasma carrier	Argon	Air
Plasma currents	Low (mA)	High (>10 mA)
Main direction of the energy transfer	From the electrode to the substrate surface	Between the electrodes parallel to the substrate surface
Plasma frequency	High (20,000 Hz)	Low (60 Hz)
Noise level	Low	High
Ozone generation	Low	High
Plasma flow temperature	Low (room)	High (>250°F)
Substrate exposure	Unlimited	Limited to thermal damage
Coverage from single head on the flat surface	Up to 3" diameter circle or up to 5" × 1" strip	Up to 2" × ¼" strip
Ability to treat patterned surfaces	Unlimited	Limited
Ability to treat inner surfaces	Unlimited	Very limited
Ability to introduce special additives into the plasma for chemical surface modification	Limited	Very limited
Overall flexibility	High	Low
Overall efficiency	High	Low

environment (e.g., air). These free electrons, accelerated by the strong electrical field, have enough energy to ionize neutral gas molecules and produce other free electrons and ions.

These electron avalanches do not develop into an arc, but gradually decay as they move away from the edge, creating a uniform glowing cloud near the electrode. Since there is no well-defined second electrode, the currents in the plasma cloud are extremely low (100 μ A) and plasma occupies a finite volume near to room temperature. The overall power to initiate and maintain this glow discharge usually does not exceed 100 watts. The low-temperature plasma cloud may be applied directly onto the surface of the treated material, or be considerably extended with the use of inert gases such as helium, argon, etc.

This kind of plasma is very effective since most of the micro-discharge trajectories end up on the surface of the treated material. A specially designed high frequency, low current power supply significantly increases

TABLE 9.10 A Comparison* of Advantages and Disadvantages of Low Pressure and Atmospheric Pressure Plasma Treatment Methods [8]

Applications properties	Low pressure plasma		Atmospheric plasma	
	Advantages	Disadvantages	Advantages	Disadvantages
Generation of plasma – generally –	Plasma is evenly distributed inside the plasma chamber. Chamber volume can vary from 2 to 12,000 liters	Complex vacuum technology. In-line plasma applications are limited	Plasma treatment is possible directly at the conveyor belt. In-line suitable. No vacuum necessary	The treatable area is limited to approx 8–12 mm (plasma generation principle). More nozzles are required to treat larger surfaces
Treatment of metal	Oxidation-sensitive objects can be treated with plasma. (e.g., H ₂ process gas)	Microwave plasma can transfer the energy to the object, which then overheats. kHz do not cause overheating	When aluminum is treated with plasma, very thin oxide layers (passivation) can be created	Plasma treatment of oxidation-sensitive objects is limited
Treatment of polymers and elastomers	PTFE can be activated with plasma. (Etching process.) Advanced plasma processes for elastomer- and PTFE gaskets have been developed and are in use	For several materials (e.g., silicon) a bigger pump is required to reach the necessary process pressure	“Endless objects” (e.g., tubes or cables) can be treated with plasma. Very short process time	The plasma jet has a high temperature of 200–300°C. Process parameters have to be well-aligned to the surface to avoid burning the material. (thin materials)
3D Objects	All items in the plasma chamber are treated uniformly. Also cavities can be treated from inside. (e.g., water tanks, ignition coil)	None known	Local surface treatment is possible (e.g., gluing groove)	Complex robotic technology is necessary. Treatment of surfaces with deep grooves is limited

(Continued)

TABLE 9.10 (Continued)

Applications properties	Low pressure plasma		Atmospheric plasma	
	Advantages	Disadvantages	Advantages	Disadvantages
Bulk material	The rotary drum procedure enables uniform plasma treatment of bulk material. The quantity and volume can vary	Only one third of the rotary drum volume can be used	The objects can be treated directly in-line	The objects have to be positioned very accurately on the conveyor belt
Electronic/ semiconductors	Plasma treatment of electronic devices, printed circuit boards, and semiconductors is state of the art	None known	Plasma treatment of metal or indium tin oxide contacts is possibly directly before the bonding process. (e.g., LCD—TFT, chip production)	The high temperature of the plasma jet and the reduced ability to treat surfaces with deep grooves may limit the usage of atmospheric plasma in the electronics industry
Coating process	The coating layers are identical und uniform. Many PECVD and PVD processes have been developed and are in use	Plasma chamber can be contaminated by coating material	No industrial uses known yet	No industrial uses known yet

**Diener Electronic Company offers both low pressure and atmospheric pressure plasma treatment systems.*

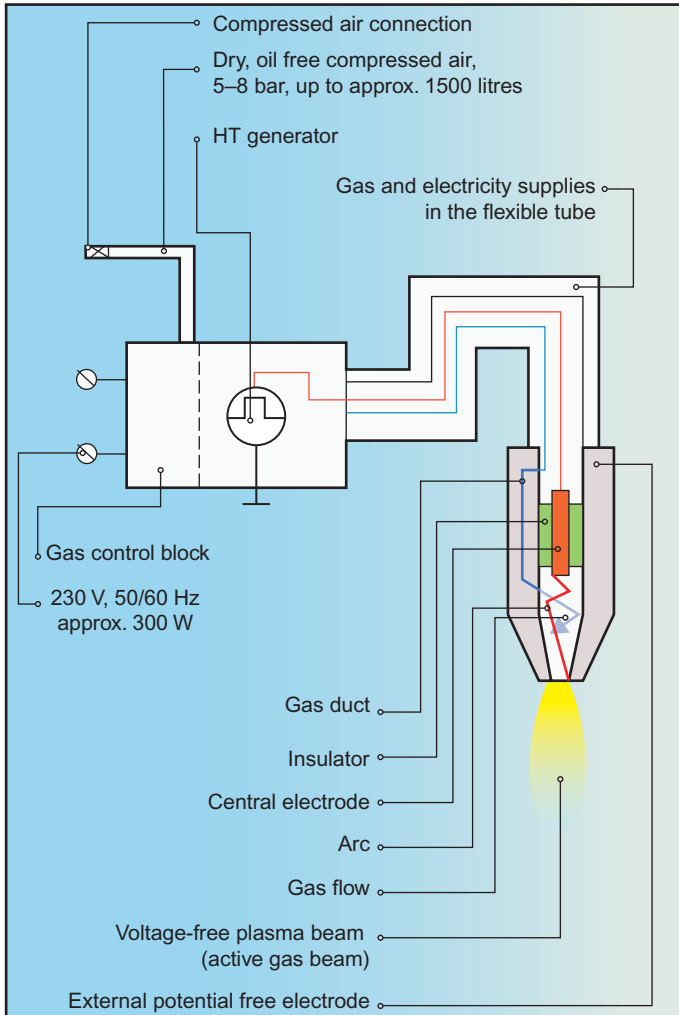


FIGURE 9.26 Schematic diagram of functional principles of an atmospheric pressure plasma system. (Courtesy of Diener Electronic, www.plasma.de/en/index.html) [8].

the efficiency by multiplying the number of micro-discharges in the cycle. The system is practically noiseless, produces very little ozone when operating in the open air, and generates no ozone when inert gases are used. A small amount of reactive gases may be added into the flow to obtain plasma with unique properties; this is frequently required for chemical surface modification. Thin film deposition by plasma polymerization may also be accomplished on the treated surface by adding monomers (C_2H_4 , C_2H_2 , etc.) into the plasma cloud. Some of the applications of APT for treating polymer

surface are described in the rest of this section. Typical contact angle and adhesive bond strength before and after atmospheric pressure plasma treatment are listed in Table 9.11. The values in the table are subject to appreciable variability depending on the treatment process and measurement of contact angle and bond strength.

Early studies [55,56] demonstrated the effectiveness of APT for the treatment of polymethylmethacrylate (PMMA) and PTFE. For PMMA, helium and its mixtures with oxygen, argon, and nitrogen were used for the surface treatment, which produced bondable surfaces (Fig. 9.27) in relatively short exposure times. Similar results were obtained for PTFE as shown in Fig. 9.28, although a longer treatment time was needed to enhance the bondability of PTFE significantly.

Polyvinyl fluoride (PVF), poly[tetrafluoroethylene-co-hexafluoropropylene] (FEP), and poly[tetrafluoroethylene-co-perfluoroalkyl vinyl ether] (PFA) films were treated by atmospheric plasma treatment method to increase their adhesive strength [57]. The adhesive was Araldite, which is an epoxy resin sold by Ciba Geigy Company. The process gases included helium and its mixtures with argon, oxygen, and nitrogen. Adhesive strength was measured by a 180° peel test. Sodium-etched PFA and FEP film were tested in addition to untreated samples. The bond strengths of sodium-etched samples were called the “control”.

This study found that the O₂/He plasma-treated films had the highest peel forces although their contact angles were highest and their amounts of incorporated oxygen or nitrogen atoms were least. He plasma treatment also showed better effects on the overall results.

TABLE 9.11 Wetting Contact Angle Before and After Atmospheric Pressure Plasma Treatment [54]

Plastic Type	Wetting Contact Angle (°)		Lap shear Adhesive Bond Strength (MPa)	
	Before	After	Before	After
Polypropylene	87	22	2.55	9.51
Low Density Polyethylene	87	22	2.55	10.00
High Density Polyethylene	—	—	2.17	21.55
Polyamide (nylon)	73	15	5.86	27.58
Polystyrene	—	—	3.93	27.58
Polyimide	79	10	—	—
Polycarbonate	75	33	2.83	6.40
Ethylene-tetrafluoroethylene copolymer	92	53	2.83	22.06

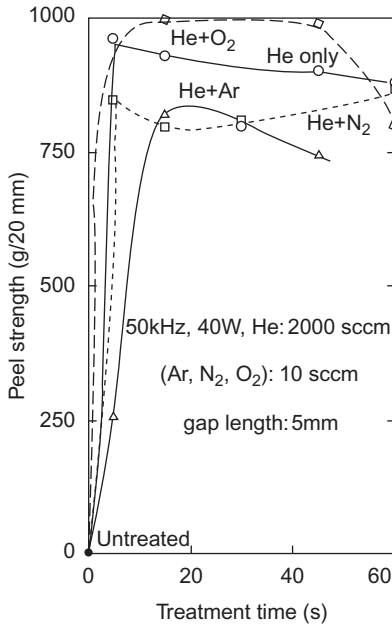


FIGURE 9.27 Peel strength of PMMA as a function of atmospheric pressure plasma treatment time [55].

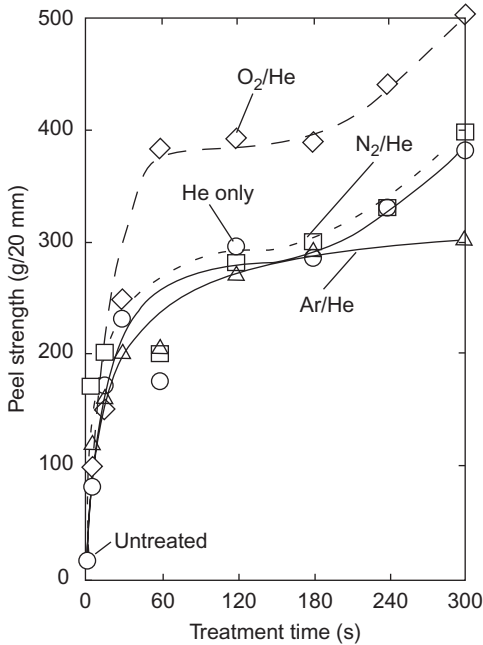


FIGURE 9.28 Peel strength of PTFE as a function of atmospheric plasma treatment time [57].

PVF treatment yielded the highest peel strength at >2 kg/mm (exceeded limits of test apparatus) compared to untreated film at 1.06 kg/mm. Surface roughness of treated PVF films increased significantly whilst treatment virtually did not affect FEP and PFA surfaces. Peel strength of treated FEP and PFA surfaces as a function of treatment time can be seen in Figs 9.29 and 9.30. Note: “control” in these figures refers to the sodium-etched film. Peel strength of APT-treated FEP film was close to or higher than the peel strength of sodium-etched film in contrast to FEP which had lower values. The maximum peel strength of FEP and PFA treated by plasma were approximately 180 (FEP) and 80 (PFA) times stronger than the forces of untreated films, whose values were 0.004 and 0.006 kg/mm. The best peel strength results for PFA were close to that of sodium-etched film.

Softal and Air Liquide companies have developed an APT technology marketed under the trade name Aldyne[®]. Air is substituted with a nitrogen-based gaseous mixture in the discharge area. In this process nitrogen-based chemical functional groups are grafted onto the surface, which generates both high level improvement in wettability and adhesive bond strength. For example, surface energy of biaxially oriented polypropylene is raised to 60 dynes/cm and up 72 dynes/cm for polyethylene terephthalate [58].

Plasma treatment has been applied [59,60] to textiles with the objectives of increasing or decreasing hydrophilicity, and improving dyability and printability of cotton, wool, and synthetic polymers. Atmospheric pressure plasma

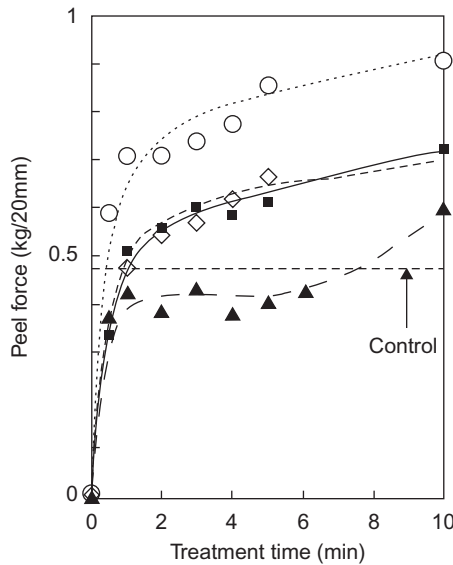


FIGURE 9.29 Variation of the peel strength of FEP film. Treatment gases were: ■ = He, ○ = O₂/He, ◇ = N₂/He, and ▲ = Ar/He [57].

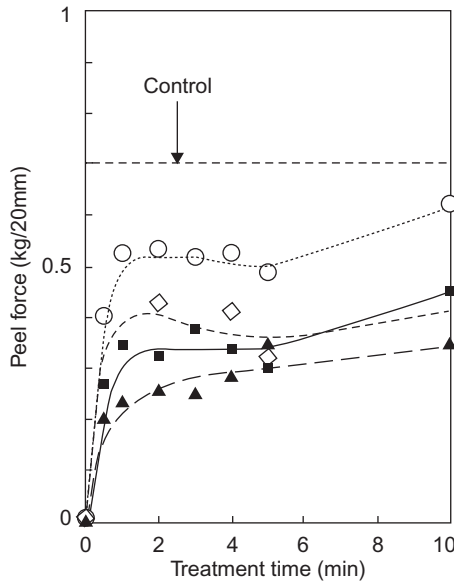


FIGURE 9.30 Variation of the peel strength of PFA film. Treatment gases were: ■ = He, ○ = O₂/He, ◇ = N₂/He, and ▲ = Ar/He [57].

treatment has been investigated as a possible means to treat textile fabrics because it represents the lowest cost plasma technique. For example, wool responded well to O₂-, air-, NH₃- gases which converted its surface from hydrophobic to completely hydrophilic. Another example was successful conversion of hydrophilic cotton surface to hydrophobic.

In another study [61] atmospheric pressure plasma, using a process gas of N₂/O₂ mixture, was applied to a polypropylene spun-bonded fabric. Chemical composition of the fabric before and after plasma treatment was analyzed by Fourier transform infrared spectroscopy. The spectra showed that oxygen- and nitrogen-containing groups were generated on the surface of the plasma-treated fabric. The scanning electron microscope was used to observe the surface morphology of the substrate. Physical properties like moisture and vapor transport, pore size distribution, and tensile strength were evaluated to understand the effect of the plasma treatment on spun-bonded polypropylene. It was evident from the capillary flow porometer results that pore size increased after plasma treatment, resulting in enhanced moisture vapor transport rate. No significant decrease in breaking strength of fabric was observed after the plasma treatment.

Commercialization of APT in the textiles industry has encountered difficulties [62]. The porous and uneven surface characteristics of fabrics make obtaining satisfactory results more difficult than with polymer films. The difficulty of inclusion of the treatment process in existing textile factories, and capital and operating costs of APT, remain barriers to its adoption in the industry.

Okubo et al. [63] modified PFA, PTFE, and polychlorotrifluoroethylene (PCTFE) by using atmospheric pressure argon and acrylic acid vapor plasma. The results of the T-type peeling test show that the peeling strength of the treated PTFE film is approximately over 100 times greater than that of the untreated film. It was confirmed from X-ray photoelectron spectroscopy and scanning electron microscope analyses that no chemical connections with F atoms existed on the surface and a hydrophilic layer was formed due to the plasma graft polymerization process.

9.4.1 In-line Plasma Treatment of Wire and Cable

Some atmospheric pressure plasma treatment methods allow inline surface modification of almost any wire insulation material [64,65]. Examples include polyamides, polyesters, and the most difficult fluoropolymers to treat. Following treatment, a surface can accept inkjet printing for marking purposes. Table 9.12 shows a comparison of the marking durability on ethylene tetrafluoroethylene copolymer (ETFE) and fluorinated ethylene propylene copolymer (FEP) for untreated (U), flame treated (Fl), and plasma treated (Pl) conditions. Some wires have been crosslinked by irradiation (IR) to enhance cut-through resistance of the insulation. Wire suppliers have been identified in each case and all ink was UV curable.

Table 9.13 shows the results of scrape abrasion testing on a Tefzel[®] ETFE insulation, both with and without plasma treatment. Clearly, plasma has a positive effect, enhancing the marking's resistance to removal by scrape abrasion. Contact angle data and calculated surface energy data can be found in Tables 9.14 and 9.15.

Enercon Industries has researched the in-line treatment effectiveness of different atmospheric surface activation systems on various polymer substrates. The study focused on the in-line effectiveness of the treatment methods because the processing of jacketed wires and cables is typically in-line (continuous) and printing of inks and coatings takes place immediately after the treatment. Table 9.16 shows a comparison for atmospheric pressure surface modification aimed at raising the surface energies of non-polar jacketing substrates. The data indicate that the APT process was effective in increasing the surface energy of PTFE and FEP, which are quite difficult to treat.

9.5 SURFACE TREATMENT OF BIOPOLYMERS

In the early 1980s, the plasma polymerization and plasma treatment of polymer surfaces of plasma polymers and/or plasma treated polymer surfaces in biomedical applications were contemplated seriously [66]. Some of the applications envisioned included improving the biocompatibility of polymer surfaces such as blood and tissue compatibility and controlled drug release by selective surface modification. Others were aimed at the improvement of

TABLE 9.12 Marking Durability of Flame and Plasma Treated Fluoropolymer Insulated Wires [64]

Insulation Type	ETFE			ETFE			IR ETFE			IR ETFE			FEP					
Wire Spec	M17 5000-14TE1U00			M37 500 10TO2T14			M17 500 24102T23			M13-101364			WS191991-20-1			MIL-C 17G		
Wire Vendor				Thermax CDT, Belden Company			Teledyne Thermatics			Judd Wire			Delta Wire			Thermax CDT, Belden Company		
Treatment Testing	U	Fl	Pl	U	Fl	Pl	U	Fl	Pl	U	Fl	Pl	U	Fl	Pl	U	Fl	Pl
Rub (finger)	F	P	P	F	F	P	F	P	P	F	P	P	F	P	P	F	F	F
Rub (eraser)	F	P	P	F	F	P	F	P	P	F	P	P	F	F	P	F	F	P
Alcohol	F	P	P	F	P	P	F	P	P	F	P	P	F	F	P	F	F	P
1,1,1-Trichlor	F	P	P	F	P	P	F	P	P	F	P	P	F	P	P	F	F	P
Freon [®] TMC	F	P	P	F	P	P	F	P	P	F	P	P	F	P	P	F	F	P
Water +	F	P	P	F	P	P	F	P	P	F	P	P	F	P	P	F	F	P
Acetone	F	F	P	F	P	F	F	P	P	F	F	P	F	F	P	F	F	P
Episolve 301	F	P	P	F	P	P	F	P	P	F	P	P	F	F	P	F	F	P
Masking tape	F	P	P	F	F	P	F	P	P	F	P	P	F	P	P	F	F	P
Thermal shock	F	P	P	F	F	P	F	P	P	F	P	P	F	F	P	F	F	P
ISO oil	F	P	P	F	P	P	F	P	P	F	P	P	F	P	P	F	F	P
Pen (40 dyne/cm)	F	P	P	F	P	P	F	P	P	F	P	P	F	P	P	F	F	F
Cold shock	F	P	P	F	P	P	F	P	P	F	P	P	F	F	P	F	F	P

Notes: U: untreated, Fl: flame-treated, Pl: plasma-treated. F: fail, P: pass.

All wires were marked with UV-curable ink ● Rub (finger): 20 strokes of moderate pressure ● Rub (eraser) per MIL-M-91531, 4.62 ● Alcohol, trichlor, Freon[®] TMC (50% methylene chloride, 50% 1,1,2-trichlorotrifluoroethane), water (plus surfactant to promote wetting), acetone, and Episolve per MIL-STD 202 ● Masking tape: press onto marking, wait 30 sec, peel off and read marking ● Thermal shock per WS 19185 ● ISO oil: soak for 48 hr and rub once ● Pen: check the spreading on the surface of the wire ● Cold shock: 5 min at -40°F, bend and rub.

TABLE 9.13 Results of a Scrape Abrasion Test Performed at Raychem, Menlo Park, CA, on Tefzel[®] Spec 55 Insulated Wire for Marking Identification Made by M-100J Ink-Jet Wire Marker [64]

Line Speed	30 ft/min	60 ft/min	120 ft/min
UV exposure	1 s	0.5 s	0.25 s
Average # of cycles Plasma off	7	11	12
Average # of cycles Plasma on	58	>125	48

Testing Method: Motor driven, reciprocating cam mechanism, equipped with a reset counter and capable of a 3/8" stroke at 60 cycles per minute with a clamp for holding specimens. The contact surface is a smooth cylindrical steel mandrel, 0.025" in diameter. Applied weight is 500 g. One cycle corresponds to two strokes. Note: The tests were stopped after 125 cycles.

TABLE 9.14 Contact Angles (Degrees) Measurement for Plasma Treated FEP Insulated Wire (22759/11-20) [64]

Plasma Treatment Conditions	Water Surface Tension (72 dyne/cm)	Methylene Iodide Surface Tension (50 dyne/cm)	Xylene Surface Tension (30 dyne/cm)
No treatment	101 ± 5	75 ± 4	46 ± 4
Air plasma	94 ± 8	70 ± 3	32 ± 3
Argon plasma	90 ± 4	66 ± 5	23 ± 5
Argon and ammonia	82 ± 4	6 ± 6	20 ± 7

adhesion in medical devices and applying protective coating to their surfaces. Since those early days, much progress has been made in the use of both technologies in modification of biopolymer surfaces. The extensive research and development and progress made in the area of compatibilization of biomaterials warrants coverage in a book devoted to the subject matter.

In the 1990s, extensive research and development on a number of biomedical devices took place. Some of the results were applied to products in orthopedic and medical devices such as knee, teeth, bone, pedicel screw, surgical tools, and others [67].

Two types of applications have been pursued for the use of plasma treatment [68]. First, modification of synthetic polymers intended for use with biological materials such as implants. Some examples include vascular prostheses, heart valves, and blood-bags. Second, plasma treatment can be used for biomolecule-immobilization of heparin and heparin-like molecules, collagen, albumin, and

TABLE 9.15 Surface Energy Calculation Based on Contact Angle Measurement for Plasma-Treated FEP Insulated Wire (22759/11-20) [64]

Plasma Treatment Conditions	Harmonic-Mean Approximation			Geometric-Mean Approximation		
	Dispersive Component (dyne/cm)	Polar Component (dyne/cm)	Total (dyne/cm)	Dispersive Component (dyne/cm)	Polar Component (dyne/cm)	Total (dyne/cm)
	No treatment	17.3	5.4	22.7	14.3	2.6
Air plasma	20.5	7.2	27.9	17.7	3.9	21.6
Argon plasma	19.9	9.1	29.0	16.4	6.0	22.4
Argon and ammonia	23.0	11.5	34.5	19.3	8.4	27.7

TABLE 9.16 Effect of Surface Treatment Methods on Surface Energy of Polymers [65]

Polymer Name	In-line Surface Treatment Method	Energy Flux, W/m ² /min	Surface Energy (dynes/cm)	
			Before Treatment	After Treatment
PTFE	Atmospheric Gas-Phase Plasma	109	18.5	39
FEP	Atmospheric Gas-Phase Plasma	21.8	16–18	52
PVC	Flame Treatment	116.5	35	46

other molecules of biological origin to confer anti-thrombotic properties to polymer surfaces. Important research areas and specific examples of the use of plasma treatment with biomaterials are listed in [Table 9.17](#).

Surface properties of poly (D,L-lactide) (PDLLA) were modified [69] by combining plasma treatment and collagen modification. A mouse model was used as model cells to evaluate the cell affinity of PDLLA before and after modification. Effects of different modification methods, including low pressure plasma treatment using ammonia and oxygen, collagen coating, and a combination of plasma treatment with collagen anchorage, were investigated and compared. The results showed that the hydrophilicity and surface-free energy were improved and reduced, respectively, after each modification. Plasma pre-treatment could improve the roughness as it incorporated the polar groups and positively charged groups on to the sample surface; so the plasma pre-treated surface would benefit in anchoring more collagen tightly.

TABLE 9.17 Common Research Areas and Applications of Plasma Treatment in Biomaterials Engineering [67]

Blood-compatible surface	Vascular grafts, catheters, stents, heart-valves, membranes (e.g., for hemodialysis), filters (e.g., for blood cell separation), biomolecules immobilized on surface
Non-fouling surfaces	Intraocular lenses (IOLs), contact lenses, wound healing, catheters, biosensors
Tissue engineering and cell culture	Cell growth, antibody production, essays, vascular grafts
Sterilization of surgical tools and devices	Cutting tools of surgeon, tweezers
Biosensors	Biomolecules immobilized on surfaces
Barriers coatings	Drug-release, gas-exchange membranes, device protection, corrosion protection, reduction of leaches (e.g., additives, catalysts, plasticizers)

As a result, cell affinity of PDLA modified by combining plasma treatment with collagen anchorage was greatly improved. The modified materials could endure rinsing by PBS, which would facilitate further application when the modified materials were used as cell scaffolding in tissue engineering.

A medical grade segmented polyetherurethane (PEU) was treated with a low-powered low pressure gas plasma using O_2 , Ar, N_2 , and NH_3 as the treatment gases [70]. The influence of the surface modification to the polyurethane on the blood response to the polyetherurethane was investigated by measuring changes in the activation of the contact phase activation of the intrinsic coagulation cascade. The data demonstrated that the plasma treatment process caused surface modifications to the PEU that in all cases increased the polar nature of the surfaces. O_2 and Ar plasmas resulted in the incorporation of oxygen-containing groups that remained present following storage in an aqueous environment. N_2 and NH_3 plasmas resulted in the incorporation of nitrogen-containing groups but these were replaced with oxygen-containing groups following storage in the aqueous environment. In all plasma treatments there was a lowering of contact phase activation compared to the untreated surface, the N_2 and NH_3 treatments.

In this study [71] poly (lactide-co-glycolide) (PLGA) films were treated by oxygen plasma. The surface structure, topography, and surface chemistry of treated PLGA films were characterized by contact angle measurement, scanning electron microscope observation, atomic force microscopy, and X-ray photoelectron spectrum analysis. The cell (a mouse model) affinity of the oxygen-plasma treated films was evaluated under dynamic conditions

by use of the parallel plate flow chamber (PPFC). The results showed that the hydrophilicity increased greatly after oxygen plasma treatment. High quantities of $-C-O$ groups, such as hydroxyl and peroxy groups, could be incorporated into the surface of PLGA (70/30) by controlling appropriate plasma treatment conditions. Moreover, the oxygen plasma treatment resulted in formation of peaks and valleys on the sample surfaces, and the roughness increased with treatment time. Cells stretched very well and the ability to endure the shear stress was improved greatly after the PLGA (70/30) was modified by appropriate plasma treatment, i.e., under 50 W for 2 or 10 min. However, when the treatment time was increased to 20 min, the percentage of adherent cells on the roughest surface decreased because the content of polar groups incorporated onto the surface decreased. The results showed that improved cell adhesion was attributed to the combination of surface chemistry and surface morphology of PLGA during plasma etching.

Biopolymers have continued to become increasingly important in the industry because of sustainability and environmental considerations. Hydrophobicity of poly(L-lactide) scaffolds is a drawback in applications such as tissue engineering. A study of plasma treatment is a useful technique to enhance the hydrophilicity of this polymer. The effect of this technique on the modifying depth and degradation of poly(L-lactide) has been studied. In this program the influence of NH_3 plasma treatment on the modifying depth and degradation of tissue scaffolds was investigated [72].

Cell attachment and proliferation are particularly important for the materials used for tissue-engineering purposes [73]. Polymethyl methacrylate (PMMA) and its copolymers have biomedical applications in vascular grafts, drug-releasing systems, and intraocular or contact lenses. In a study, polymethyl methacrylate films were prepared by solvent casting and their surfaces were modified by low pressure oxygen-plasma treatment by applying power of 20, 100, and 300 W. The effects of surface chemistry alterations on hydrophilicity, work of adhesion, surface free energy, and cell adhesion were examined. The results demonstrated that there was an optimum value for hydrophilicity and surface free energy which enhanced cell attachment.

Radio frequency (RF) plasma treatment in O_2 was applied [74] to modify the surface of poly (L-lactic acid) (PLLA) and poly (D,L-lactic acid-co-glycolic acid) (PLGA) as biodegradable polymers. The surface structure, morphology, wettability, and surface chemistry of treated films were characterized by water drop contact angle measurement, scanning electron microscopy (SEM), optical invert microscope, differential scanning calorimetry (DSC), and ATIR-FTIR spectroscopy. The cell affinity of the oxygen-plasma treated film was evaluated by nerve tissue cell culture in stationary conditions. The results showed that the hydrophilicity increased greatly after O_2 -plasma treatment. The results showed that improved cell adhesion was attributed to the combination of surface chemistry and surface wettability during plasma treatment. Cell culture results showed that B65 nerve cell attachment and

growth on the plasma treated PLLA was much higher than for an unmodified sample and PLGA. Surface hydrophilicity and chemical functional groups with high polar component play an important role in enhancing cell attachment and growth.

The interaction of proteins and cells with polymers is critical to their use in scientific and medical applications [75]. In this study, plasma immersion ion implantation (PIII) was used to modify the surface of polytetrafluoroethylene (PTFE), enabling the covalent binding of a cell adhesive protein, tropoelastin, without employing chemical linking molecules. Tropoelastin coating of untreated or PIII treated PTFE simultaneously promoted and blocked cell interactions respectively, i.e., PIII treatment of the PTFE surface completely inverts the cell interactive properties of bound tropoelastin. This activity persisted over long-term storage of the PIII treated surfaces. The integrin binding C-terminus of tropoelastin was markedly less solvent exposed when bound to PIII treated PTFE than untreated PTFE, accounting for the modulation of cell adhesive activity. This presents a new methodology to specifically modulate cell behavior on a polymer surface using a simple one step treatment process, by adjusting the adhesive activity of a single extracellular matrix protein.

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