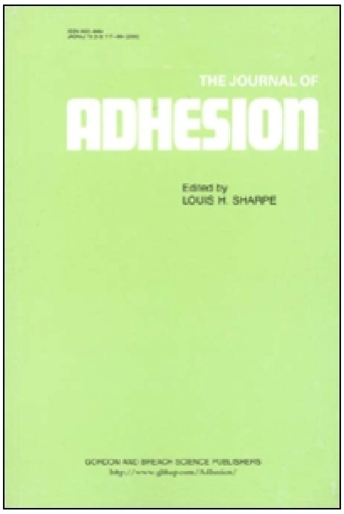

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Plasma Treatment for Improved Bonding: A Review†

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The nature of low-pressure glow-discharge plasma, plasma equipment, and the effect of plasma on materials is reviewed. Examples are given of the improved adhesive bonding of polymers after plasma treatment (2–10 times improvement in lap-shear) and of the surface cleaning and chemical modification that occurs during plasma treatment.

KEY WORDS Plasma; bonding; surface treatment; polymers; photochemistry; free radicals.

INTRODUCTION

The physics definition of a "plasma" is an ionized gas with an essentially equal density of positive and negative charges. It can exist over an extremely wide range of temperature and pressure. The solar corona, a lightening bolt, a flame, and a "neon" sign are all examples of plasma.

For the purposes of this paper, the discussion will be limited to low-pressure (0.1 to 1 Torr) plasma, or glow discharge, such as is found in the "neon" sign or a fluorescent lightbulb. In those two applications the desired result is to produce light. However, for the plasma treatment of materials for bonding, the extremely energetic chemical environment of the plasma is utilized to make chemical changes in the material surface to which the adhesive can bond.

It has been known for at least 50 years that plasma could effect desirable changes in the surface properties of materials. However, the practical application of plasma required the development of commercially available, reliable, and large plasma systems. Such systems are now available and the application of plasma to industrial problems has been increasing rapidly for the past ten years.

In plasma treatment of materials, all significant reactions are based on free radical chemistry.[1] The glow discharge is efficient at creating a high density of

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free radicals, both in the gas phase and in the surface of organic materials, even the most stable polymers. These surface free radicals are created by direct attack of gas-phase free-radicals, ions, or by photodecomposition of the surface by vacuum-ultraviolet light generated in the primary plasma. The surface free-radicals then are able to react either with each other, or with species in the plasma environment.

Free radicals created by low-pressure gas plasma have four major effects on organic substrates: surface cleaning; ablation, a form of dry micro-etching; crosslinking; and surface activation. These four effects occur concurrently and, depending on processing conditions and reactor design, one or more of these effects may predominate. In all cases, these processes affect only the top few molecular layers (about 100 Å) so they do not change the appearance or bulk properties of the material. The net result of these effects is a major improvement (2 to 10 times) in processes that require adhesion, such as bonding, printing, painting, and concurrently, wettability.

Many different gases and plasma operating parameters are used in the surface treatment of different materials. Studies are being performed on the effect (in terms of bondability) of these different plasmas on various polymers. It has been found that, for best results, different polymers may require different plasma treatment. In some cases it has been found that a plasma which gives excellent bonding on one polymer may give very poor bonding on a similar polymer. For example, the best process for perfluoroalkoxy (PFA) gives poor bonding to fluorinated ethylene/propylene polymer (FEP).

This paper will discuss the nature of plasma, plasma equipment, its effect on materials, and the results of that treatment on bonding; as well as a brief discussion of other applications, and problems that require further study.

NATURE OF PLASMA

By definition, plasma is an ionized gas that is spacially neutral. That is, there are an equal number of positive and negative charges in a given volume. In the plasmas being discussed here, most of the positive charges are positive ions and most of the negative charges are electrons. Because of the huge mass difference between these species, the ions are almost stationary in the plasma and most of the current is carried by the electrons. However, the ions nearest the electrodes, or material surfaces, can be accelerated by the sheath voltage to 10's of electron-volt energies. These accelerated ions can cause bond breaking and generate free-radicals in the material surface. The plasma gas contains a few parts per million of ions, a few percent (2% to 20%) of free radicals,[2–4] and large amount of extremely energetic vacuum-ultraviolet light.

In plasma treatment of materials, all significant reactions are based on free-radical chemistry. The glow discharge is very efficient at creating a high density of gas-phase free radicals by dissociating molecules through electron bombardment and photochemical processes. Most of the radicals will be in the ground state. However, the free-radicals can also exist in electronically excited states that carry a great deal more energy than the ground state radicals. The lowest excited state for the oxygen radical is 220 Kcal/mole above ground state.[5] This is sufficient to break any organic bond.

Therefore, when these gas-phase radicals (or ions) impinge on an organic surface, either a polymer or an organically contaminated surface, they have sufficient energy to break bonds in that surface. This results in abstraction of atoms or molecular fragments. These can react further in the plasma to form volatile species that are removed by the vacuum system. The abstraction causes a progressive ablation of the organic surface and the formation of residual free-radicals in that surface. These can either react with themselves to produce cross-linking of the surface or they can react with the plasma gas, even the ground state molecules, to form new chemical species in the surface. If the plasma is an inert gas such as argon, the surface will contain a large number of stable radicals that will persist until exposed to some reactive gas.[6–7]

Vacuum ultraviolet photochemistry

There have been many studies of the optical emission from plasmas.[2] However, there are almost no data in the literature on plasma emissions for wavelengths shorter than 1800 Å, or where the plasma system is considered a vacuum-ultraviolet (VUV) photochemical reactor. One notable exception is the excellent paper by Clark and Dilks[8] in which they show the relative effects of VUV and gas-phase free-radicals or ions on the depth of reaction in the surface of polymers. Their data, and the experiments reported there, show that the modern plasma reactor is essentially the same light-producing device as those used by researchers in vacuum-ultraviolet spectroscopy.[9]

Significantly, the materials being processed in the plasma are immersed in the light-producing medium, with no intervening window. Therefore, these surfaces are exposed to, and absorb, photons that are many times their bond strength. For example, almost all of the observed radiation from an oxygen plasma is from the first excited state of the oxygen radical at 1302 Å. A photon at this wavelength has an energy of 220 Kcal/mole. This is approximately double the bond strength of a C—C or C—H bond. Therefore, it is found that a significant portion (about 50%) of the organic surface reactions occurring in a plasma reactor are caused by vacuum-ultraviolet photochemistry.

There have been several studies that have shown that some of the effects of plasma may be caused (at least in part) by ultraviolet light generated in the plasma. In these studies the parts were separated from the plasma, usually by LiF windows, and yet it was possible to get cleaning, wetting,[10] crosslinking,[11] fluorination,[12] and free-radical generation[7] in polymer surfaces.

These studies are being extended to investigate the spectral and spacial distribution of VUV radiation in plasma reactors, the effect of operating parameters, and the effect of VUV radiation on processing.

The emission spectra are being measured using an Acton Research Corporation

Model VM-502 Vacuum Monochrometer.[13] This 0.2 meter instrument is equipped with an osmium grating, and mirror, to maximize short wavelength performance. It is operated in the windowless mode with a turbomolecular pump. To date, measurements have been made on the emission spectra, from 200 Å to 4500 Å, of 40 plasmas. Many cases have been found of species interactions and of significant spectral changes in mixtures of plasma gases. For example, the radiation, at 1302 Å, from oxygen radicals in He/5% O_2 (or Ar/5% O_2) is 10 times more intense than it is in pure O_2. This difference is not due to absorption of the 1302 Å radiation by O_2 since O_2 is transparent in this spectral region.[13,14,15] It is more likely due to enhanced dissociation of O_2 by collision with excited He species. This is supported by our observation that the helium emission at wavelengths shorter than 2900 Å is almost completely quenched by the presence of 5% O_2. The dissociation energy of O_2 is 2420 Å (5.1 ev).[16-17]

The analyses of these data show that very energetic photons are present in all the plasmas studied and that this radiation can pass through the plasma to the surfaces to be treated.

Table I gives some examples of the 1/*e* depth (the depth for 63% absorption of radiation) for various wavelengths and materials. These calculations assume a pressure of 0.3 Torr, and pure gases, which is not the case in real plasmas, but they do indicate that the VUV radiation from the primary plasma can propagate through the secondary plasma with very little attenuation.

In some reactor configurations the zone where the plasma is generated—the "primary plasma"—is separated from the surface being treated by a zone where there is little or no electric field. This is called the "secondary plasma" because it is generated by secondary reactions between the free radicals, ions, or VUV light, and ground state molecules in the gas. Secondary plasma is used primarily in systems designed for semiconductor applications where it is important to have a minimum of electric field and, consequently, a minimum of ion energy.

The absorption depths of VUV radiation in polymers are extremely small. When photons are absorbed in this shallow depth there is a high probability that

TABLE I
Absorption depths in materials at various wavelengths

Incident radiation				
Radiating Species	He	Ar	H	O
Wavelength-Å	590	1048	1215	1302
Photon Energy—ev	21.0	11.8	10.2	9.5
Photon Energy—Kcal/mole	484	273	235	220
Absorbing material				
O_2[15]	—	—	11,620 cm	280 cm
Ar[9]	3.2 cm	(NA)	(NA)	(NA)
NH_3[18]	6 cm	9 cm	15 cm	10 cm
Polyethylene[19]	154 Å	105 Å	169 Å	167 Å
Polymide[20]	118 Å	182 Å	476 Å	667 Å

bonds will be broken, releasing molecular fragments into the boundary layer over the polymer. These fragments can then react with radicals from the bulk plasma, or absorb additional radiation for further photodecomposition, or react with ground state gas molecules. The residual surface radicals can also react with any gas species diffusing from the boundary layer.

These data show that the flux of VUV photons from the primary plasma can cross the secondary plasma zone, with essentially no attenuation, be absorbed in an extremely shallow layer of the polymer surface, and cause surface radical reactions with the boundary layer gas. In this case the driving force for the reaction is from the surface radicals, not the gas-phase radicals.

The data in Table I also indicate that there are differences in the absorption spectra of polymers. This may make it possible to tailor the plasma emission spectra to maximize the photochemical effect on different materials.

These conclusions are supported by the results in Reference 8 in which it was reported that the top-most surface reactions (tens of angstroms) are dominated by direct reactions with ions and free radicals while the reactions in depth (100's Å) are dominated by VUV. But, both forms of energy transfer result in the formation of the same types of free radicals in the material.

PLASMA EQUIPMENT

Figure 1 is a block diagram of a typical plasma system. It consists of 5 modules or functions: vacuum system, power supply, matching network, reactor center, and controller.

Vacuum system—Low pressure plasma systems operate at 0.1 Torr to 1 Torr (13 Pa to 133 Pa) with a continuous gas flow into the reactor. Therefore, the vacuum system must be able to maintain this pressure/flow regime. However, the moderate vacuum level does not require sophisticated pumps. Two-stage mechanical pumps are satisfactory. The pump package is usually sized to allow pumpdown in less than 1 minute and to maintain an inlet gas flow of 50 cc/min to 1000 cc/min, depending on the size of the reactor. The most expensive part of the vacuum system is the perfluorinated lubricant required if an oxygen plasma is to be used.

Power supply—This furnishes the electrical power necessary to generate the plasma. The power required ranges from 50 watts to 5000 watts, depending on the

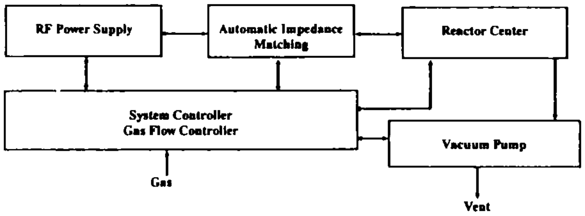

FIGURE 1 Schematic diagram of a plasma system.

size of the reactor. The larger generators are usually cooled, either with air or water.

Plasma reactors have been built utilizing a wide range of frequencies, from DC to microwave. DC plasmas are difficult to use because they require a current limiting resistor to prevent arc formation. This resistor must be changed for each different gas and operating condition. Also, ion bombardment becomes a significant factor in DC plasmas.

Low frequency plasma (50 Hz to 500 KHz) is sometimes used because the generators are somewhat less expensive and because they do not require precise impedance matching. However, in our studies of low frequency we have found that the plasma extinguishes each half cycle and that the reaction rates are significantly slower than at radio frequencies.

Radio frequency plasmas (13.56 MHz—an FCC assigned frequency) are easily generated with equipment that is stable and reliable and has been commercially available for many years. At this frequency it is necessary to use an impedance matching network to match the impedance of the plasma to the output impedance of the generator (usually 50 ohms, resistive). These can be tuned either manually or automatically with servo-driven devices. At 13.56 MHz the plasma is very stable and reactive because the quench time of the plasma species is much longer than the time between half-cycles of the excitation.

Microwave plasma (2450 MHz) may be even more reactive than RF plasma, but there is still some dispute over this. The microwave generator may be less expensive than RF generators. However, if the cost of the peripheral equipment such as wave guides, power meters, dummy load, circulator, stub tuners, and applicator is included, the total system cost appears to be about the same as an RF system. The decision between RF and microwave will probably hinge on process considerations and on the availability of an applicator that is tolerant of large impedance variations in the plasma.

Impedance matching network—This is usually an adjustable transformer or a manual, or servo-driven, pi-network that transforms the impedance of the plasma to the required output impedance of the generator. A match is necessary to prevent excessive reflected power from damaging the generator, and to know how much power is being dissipated in the plasma. The impedance of a plasma can vary from a few ohms to several thousand ohms and can be very reactive, depending on the gas, reactor design, and the operating conditions. The use of a matching network makes it possible to use one plasma system with many different gases and operating conditions.

Power dissipation in a plasma—Plasma systems usually include two power meters, one to show the power towards the reactor (the "forward" power) and the other to show the power being reflected back towards the generator by an impedance mismatch (the "reflected" power). When there is proper impedance match, the reflected power is <1% of the forward power and all the electrical energy is being absorbed by the plasma.

A recurring problem in specifying plasma processes, or in transferring a plasma process from one type or size of reactor to another, is in defining the "power density." This can be defined in at least three ways: (1) watts per unit area of electrode or shelf, (2) watts per unit volume of primary plasma or, (3) watts per unit volume of the entire reactor. Each of these is deficient in some way. Therefore, it is usually not possible to predict the best process parameters for transferring a process from one reactor to another. It is necessary to start with a reasonable set of parameters and to optimize the process experimentally in the new reactor.

Reactor center—This is the "heart" of the plasma system. It is a pressure vessel designed to support the pressure/flow conditions of the plasma, couple the electrical energy into the plasma, and contain the material for processing. There are four generic types of reactor chambers: quartz or metal, and batch or continuous.

Quartz chambers are essential in the semiconductor industry because of the requirement for extreme cleanliness and particle-free operation. In that industry plasma is used to strip photoresist from wafers and to etch patterns into the layers on the wafers. Quartz chambers may be used in industrial applications, however, their extreme cleanliness is rarely required, and there is always the danger of breakage if metal parts or fixtures are used. The maximum practical size of a quartz reactor is about 12 inches (30 cm) diameter.

Aluminum is the metal of choice for metal reactors. It has excellent thermal and electrical conductivity and it is not readily attacked by any plasma except the heavy halogens (Cl, Br, I). It has been fabricated into cylindrical reactors (known as "barrel" reactors) and into rectangular reactors with shelf or cage electrodes. It is also possible to make a special shape electrodes for special applications. The only size limitations on metal reactors is the practicality of fabricating large vacuum vessels. Stainless steel should be avoided in plasma reactors.

Most commercially available plasma systems are designed for batch operation. That is, they are designed to be loaded with a batch of parts, evacuated, plasma treated, purged to atmospheric pressure, and the parts removed. This has been satisfactory for most applications. However, as polymers are being used in more sophisticated applications, such as composite structures, the requirement for continuous processing of wire, yarn, film, and fabric, is increasing. Therefore, plasma systems are being developed for continuous processing. These can be either cassette-to-cassette or air-to-air.

In cassette-to-cassette systems the source and takeup spools are both in the vacuum chamber. This is the typical configuration in the vacuum-deposition coating industry where very low pressures are necessary to get good coating.

In air-to-air systems there are several sequentially pumped chambers on either side of the reactor chamber, which are connected by some form of "die." These make it possible to bring material continuously from atmospheric pressure to reactor pressure, and back to atmospheric pressure. In this type of system the major engineering problem is the design of these dies.

In both types of continuous systems the maximum processing speed ("line speed") is determined by the required residence time in the plasma to get the proper treatment. The present data show that, for reasonable power densities and existing equipment, clean polymers (*e.g.* polyethylene, polyimide, and polyamide) can be treated in <10 seconds residence time. This gives a line speed of 500 ft/min or more. Graphite yarn takes more time to process because it is usually desired actually to etch the surface of the fiber rather than just to change its chemistry. Processing speeds for graphite are usually <100 ft/min. However, multiple tows of yarn can be processed, in parallel, so that the net processing speed can be much greater.

There are also discrete-continuous machines. These are systems where discrete parts, or racks of parts, enter the reactor on one side and exit on the other. Typical applications would be the treatment of automobile bumpers or golf balls.

System controller—This is the "brain" of a plasma system. It controls all the process variables: type of gas, pressure, gas flow rate, power level, and processing time. It may be as simple as discrete relays, timers, and needle valves or it might be a microprocessor based system with sophisticated displays, fully automated process control, multiprocess capabilities, and data-output, and alarm systems.

EFFECT OF PLASMA ON SURFACES

Four major effects of plasma on surfaces are normally observed. Each is always present to some degree; however, one effect may be favored over another depending on substrate chemistry, reactor design, gas chemistry, and processing conditions. The effects are: cleaning of organic contamination from the surfaces; material removal by ablation (micro-etching) to increase surface area or to remove a weak boundary layer; crosslinking or branching to strengthen the surface cohesively; and surface chemistry modification to improve chemical and physical interactions at the bonding interphase.

Surface modification alone, or in combination with any or all the competing reactions, provides a means to improve the strength of adhesive bonds dramatically.

Cleaning—Cleaning of surfaces is one of the major reasons for improved bonding to plasma treated surfaces. Most other types of cleaning procedures leave a layer of organic contamination that interferes with adhesion processes.

For example, it is known that as little as $0.1\,\mu g/cm^2$ (a single molecular layer) of organic contamination on a metal surface can interfere with bonding.[21] This amount of contamination is the residue, on $1\,cm^2$, of less than $\frac{1}{2}$ drop of liquid containing 10 ppm non-volatile organics. It is extremely difficult to obtain solvents or water with less than 10 ppm non-volatiles so, almost by definition, a surface will remain contaminated after any cleaning process that ends with a liquid rinse.

Plasma is capable of removing molecular layers from polymers and all organic contamination from inorganic surfaces, as shown by Auger analysis of the surface.[22] This results in hyperclean inorganic surfaces and polymer surfaces that are really the polymer and not the surface of some contamination on the polymer. Therefore, these surfaces give very reproducible bonds and, in many cases, make stronger bonds than normally "cleaned" surfaces.

Ablation—Ablation is important for the cleaning of badly contaminated surfaces, for removal of weak boundary layers formed during the fabrication of a part, and for the treatment of filled or semicrystalline materials. Amorphous polymer is removed many times faster than either crystalline polymer or inorganic material. Consequently, a surface topography can be generated with the amorphous zone appearing as valleys.[23] This change in surface can improve mechanical bonding as well as increase the area available for chemical interactions. This is one of the mechanisms that gives improved bonding to graphite yarn.

Crosslinking—Crosslinking occurs in polymer surfaces exposed to plasmas which are effective at creating free radicals in the polymer, yet do not provide stable moieties at the radical sites. Noble gas plasmas, such as helium and argon, are crosslinking plasmas if they are used in the total absence of oxygen or other free radical scavengers. The electronically excited atoms, and the VUV light, attack the polymer surface and break C—C and C—H bonds, leaving radicals in the surface. Once free radicals are created in this environment they can only react with other radicals and are, therefore, very stable.[7] If there is any flexibility in the polymer chain, or if the radical can migrate on the chain, there can be recombination, unsaturation, branching, or crosslinking. The latter effect may improve the heat resistance and cohesive strength of the surface. It may also act as a barrier layer, hindering diffusion across the interphase. The term CASING (Crosslinking via Activated Species of Inert Gas) has been applied to this treatment.[24]

Surface chemistry modification—The most dramatic and widely-used effect of plasma is the surface modification of polymers, where the surface layer of a polymer is altered to create chemical groups capable of interacting with an adhesive.[25–28] The inherently low surface-energy of untreated polymers hinders the wetting and interaction with adhesive systems. Typically, plasma is used to add polar functional groups which dramatically increase the surface energy of polymers.

For example, Figure 2 shows the low-angle ESCA analysis of a polystyrene surface before, and after, treatment with a water vapor plasma.[29] There have been several other reports of these ESCA analyses.[2,30] This demonstrates the spectacular change in chemistry of the treated surface that is typical of most polymers exposed to an oxygen-containing plasma. This surface will be very polar, completely water wettable, and receptive to reactive adhesives. It is

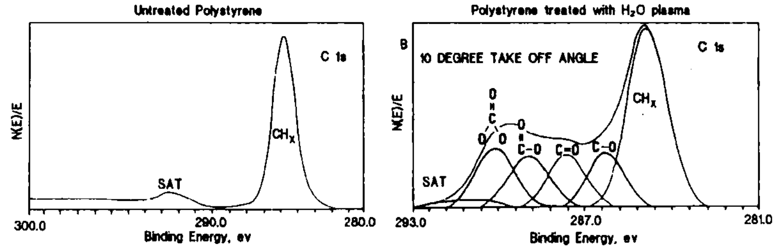

FIGURE 2 Effect of plasma on a polymer surface.[29]

believed that, during curing, the adhesive can react with the surface oxygen species and covalently bond to the plasma treated interphase. Depth profiling has shown the plasma treatment affects only the top 20 Å to 200 Å of the polymer. Therefore, it is important that the surface be cleaned before plasma treatment and that the treatment time be long enough to remove any weak boundary layer. This shallow depth of treatment is the reason why proper plasma treatment does not affect the optical, physical, or mechanical properties of the bulk part.

It is believed the plasma treatment will leave 5% to 20% of the surface carbons with some form of organic oxygen species.[31] However, studies of the fluorination of polymers have shown almost complete replacement of the surface H with F or CF_x.[32–33] More work needs to be done in this area.

Plasma can also be used to modify the surface of inorganic materials. For example: silver oxide can be reduced to silver metal with an Ar or Ar/H_2 plasma; molybdenum and chromium can be removed using a CF_4/O_2 plasma; Al_2O_3 can be converted to AlF_3 using a CF_4-containing plasma; and metal surfaces can be nitrided using a N_2 plasma.[1]

Many different gases or gas combinations are used in plasma processing, depending on the type of surface modification that is desired.

Oxidizing gases

O_2, air, H_2O, N_2O are used to remove organics by oxidation and to leave oxygen species in the polymer surface.

Reducing gases

H_2 or H_2 mixtures replace F or O in surfaces and can also remove organics on materials that are sensitive to oxidation. The contamination is converted to volatile low molecular-weight species that do not polymerize or re-deposit on adjacent surfaces.

Noble gases

Ar or He are used to generate free radicals in surfaces, either to cause crosslinking, or to leave active sites for later reaction with a purge gas. These gases are also used as diluents for other gases to increase the ultraviolet light and to increase the dissociation of the other gas. They should not be used alone for cleaning because there is no mechanism for converting the molecular fragments to permanently volatile compounds. Therefore, there will be polymerization or redeposition of the fragments.

Active gases

NH_3 will leave amino groups in the surface that are believed to react covalently with adhesives such as epoxies.

Fluorinated gases

CF_4, SF_6, and other perfluorinated gases will replace H with F or CF_x in polymer surfaces that do not contain a significant amount of oxygen, either adsorbed or in the molecular structure. This gives a very low-energy surface that has good chemical inertness and is very hydrophobic. The presence of oxygen in the boundary layer is a problem because it competes with the fluorination reaction to form polar oxygen-species in the surface.

Polymerizing gases

A large amount of work has been done on the direct polymerization of layers onto substrates.[34-36] Many different gases have been used and in some cases good coatings have been obtained. From an engineering standpoint, the major problem is that the deposition occurs on all exposed surfaces, not just on the desired substrate. Therefore, the inside of the reactor builds up a thick coating of deposited material and must be cleaned periodically.

If a very thin coating is required, the part can be treated in an inert gas plasma (such as argon or helium) which leaves free-radicals in the surface of the polymer. After plasma treatment, and before coming into contact with air, the part can be exposed to a gas that can react with the surface free-radicals to graft the desired functionality into the surface. This can be considered a version of free-radical initiated polymerization.

RESULTS OF PLASMA TREATMENT OF SURFACES

Wettability of polymers—The most obvious result of the plasma treatment of a polymer is the improved wettability of the surface. For most untreated polymers the surface energy is 25 to 50 dynes/cm, with a contact angle of 95° to 60°. After plasma treatment with an oxidizing gas the contact angle decreases to less than 40°, with some surfaces being so wettable that the contact angle cannot be measured. Table II shows data for some materials.[37] The surfaces also become wettable by many adhesives. If the adhesives do wet the surface there is usually a reduction of voids in the bond line and much better bonding. However, there is not always a good correlation between wetting and bonding.

Figure 3 shows typical lap-shear bond strength *vs.* contact angle. These data are for polyphenylene sulfide (PPS) (Ryton® R-4) bonded with an epoxy adhesive (Dexter-Hysol® EA 9330) using 1/2 in by 1/2 in overlap. Most of the data show the correlation that would be intuitively expected. That is, as the wetting improves the bonding improves. However, the data for 4% O_2/96% CF_4 show that you can get excellent bonding with very poor water wetting. This surface has not been analyzed with ESCA so the reason for this result is not known.

It should also be stressed that it is possible to have excellent wetting and yet

TABLE II

Typical polymers commonly treated in low-pressure gas plasma for surface modification (partial list)

		Initial surface energy (dynes/cm)	Initial water contact angle (degrees)	Final water contact angle (degrees)
Hydrocarbons				
PP	Polypropylene	29	87	22
PE	Polyethylene	31	87	22
PS	Polystyrene	38	72.5	15
ABS	Acrylonitrile/butadiene/styrene copolymer	35	82	26
—	Polyamide (Nylon)	36	63	17
PMMA	Polymethyl metharylate	36	—	—
PVA/PE	Polyvinyl acetate/polyethylene copolymer	38	—	—
—	Epoxy	36	59.0	12.5
—	Polyester	41	71	18
PVC	Rigid polyvinylchloride	39	90	35
PF	Phenolic	—	59	36.5
Fluorocarbons				
ETFE	PTFE/PE copolymer	37	92	53
FEP	Fluorinated ethylene propylene	22	96	68
PVDF	Polyvinylidene fluoride	25	78.5	36
Engineering thermoplastics				
PET	Polyethylene terephthalate	41	76.5	17.5
PC	Polycarbonate	46	75	33
PI	Polyimide	40	79	30
—	Polyaramid	—	—	—
—	Polyaryl etherketone	36	92.5	3.5
—	Polyacetal	36	—	—
PBO	Polyphenylene oxide	47	75	38
PBT	Polybutylene terephthalate	32	—	—
—	Polysulfone	41	76.6	16.5
PES	Polyethersulfone	50	92	9
—	Polyarylsulfone	41	70	21
PPS	Polyphenylene sulfide	38	84.5	28.5
Elastomers				
SR	Silicone	24	96	53
—	Natural rubber	25	—	—
—	Latex	—	—	—
PUR	Polyurethane	—	—	—
SBR	Styrene Butadiene Rubber	48	—	—
Fluoroelastomers				
FPM	Fluorocarbon copolymer elastomer	36	87	51.5

Note: The final surface energy of all these materials is greater than 73 dynes/cm after plasma treatment.

have very poor bonding. For example, a material having a thick layer of oil or wax can be made very wettable but it still cannot be bonded. The wettability is from a crosslinked skin on the oil or wax and there is no adhesion between that skin and the underlying material. It is the ultimate example of a weak boundary layer.

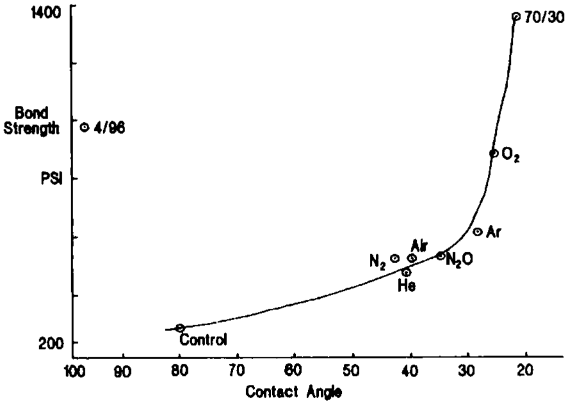

FIGURE 3 Bonding *vs.* wetting.

Effect of treatment time

A study was performed[38] in which samples of polyphenylene sulfide/40% glass fiber (Ryton® R-4) were treated in a plasma (70% O_2/29% CF_4/1% Ar) for various times. The contact angles for the treated samples were then measured. These data are plotted in Figure 4.

The data show that a decrease in contact angle, from about 72° to <10°, is caused by about 7 minutes of treatment. The increased wettability results from the removal of surface contamination (cleaning) and the incorporation of polar groups into the surface.

The gradual increase in contact angle after 7 minutes indicates that the surface is being over-treated. The increase may be attributed to a gradual exposure of glass filaments, a change in surface roughness, or fluorination of the polymer or glass.

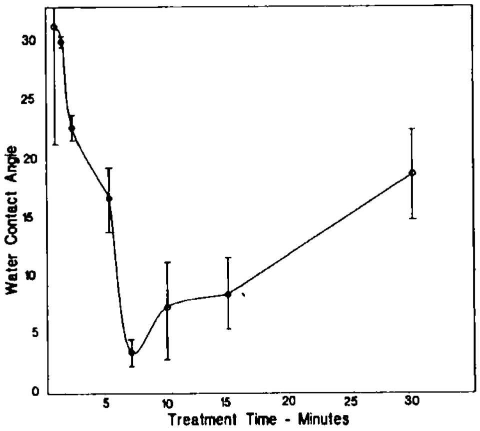

FIGURE 4 Wettability *vs.* treatment time.

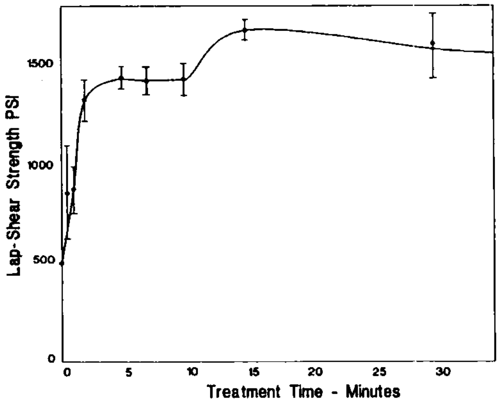

FIGURE 5 Bond strength *vs.* treatment time.

Samples of the treated parts were also bonded with an epoxy adhesive (Dexter-Hysol® EA 9330) and pulled to determine the bond strength.

Figure 5 is a plot of the lap shear strength *vs.* treatment time. It has been assumed that the initial surface does not contain any exposed glass fibers. Therefore, the short-time data in Figure 5 are assumed to represent the effect of plasma on the polymer-rich surface. These data indicate that the optimum treatment time for the polymer is between 5 and 7 minutes. The lap-shear bond strength improves by a factor of three (from 485 psi to about 1400 psi) as a result of this treatment. The data show a further increase in bond strength to about 1650 psi at 15 minutes of treatment time. It is believed that this is caused by bonding to glass-fiber surfaces that are gradually being exposed by the plasma ablation of the polymer. The slight decrease in bond strength at 30 minutes may not be statistically significant. It was noted that, at lap shear loads greater than about 1400 psi, the failure often occurred in the material rather than in the bond. The 1400 psi lap-shear load equals about 5800 psi tensile load in the cross-section.

These data illustrate that there is usually an optimum treatment time for a polymer. In this case, a pure PPS polymer should be treated for 5 to 7 minutes. This will also give adequate treatment on a 40% glass-filled polymer. However, if the best bonding is desired, it will be neccessary to treat the glass-filled material for 15 minutes to achieve the additional 20% improvement in bond strength.

The decrease in bond strength at 30 minute treatment time in Figure 5 may be the beginning of "over-treatment." Many polymers show a decrease in bonding properties after the optimum treatment time. This may be caused by an accumulation of ash on the surface or some other undefined mechanism. The phenomenon is real but not well understood.

In general, there are economic as well as engineering benefits to using the optimum treatment time. Any processing time, after the optimum has been reached, is wasted production time and can result in reduced throughput.

Bonding improvement on polymers

A large number of studies have been performed over the last 20 years[39–44] that show improvement in bonding of most polymers after plasma treatment. It is not possible to reference all of these studies, therefore typical results will be given here. It should be stressed that these are not optimized results. With any polymer/adhesive system it is necessary to perform a parametric study to determine the best process. As a corollary, the value of plasma treatment in any given situation should never be determined by a single test because the wrong parameters may have been selected for that test. For example, a polyethersulfone/epoxy system can show a 2:1 difference in bond strength depending on which gas is used.[39]

Table III gives data on lap-shear bond-strength improvements for several polymers. In all cases there are very significant improvements which are realizable in a production environment.

Table IV gives typical data for peel-strength improvements for several polymers. These tests were all performed on thin film specimens using a variety of adhesvies.

TABLE III
Examples of lap-shear bonding improvement

	Control PSI	After plasma PSI
Polyimide (PMR®-15)/graphite	420	2600
Polyphenylene sulfide (Ryton® R-4)	290	1360
Polyether sulfone (Victrex® 4100G)	130	3140
Polyethylene/PTFE (Tefzel®)	very low	3200
HDPE	315	3125
LDPE	370	1450
Polypropylene	370	3080
Polycarbonate (Lexan®)	410	928
Nylon	850	4000
Polystyrene	570	4000
Mylar A®	530	1660
PVDF (Tedlar®)	280	1300
PTFE	75	750

TABLE IV
Examples of peel strength improvements

	Control LB/IN	After plasma LB/IN
Silicone (red, Durometer 50)	0.4	19
RTV silicone (D.C. type E)	very low	2.3
PFA	0.1	8.3
FEP	0.1	10.4
Tefzel®	0.1	15.8
PTFE	0.1	2.2
Polyimide (Kapton®)	4	16

Coating, printing, painting and potting

All of the prior data have referred to the bonding of two surfaces together with an adhesive. It should be remembered that the same principles apply if there is only one adherend surface, for example, in coating, printing, painting, and potting. In these applications plasma gives the same improvement in performance that is found with "normal" bonding. The surface of the part is cleaned and modified to improve wettability and reactivity to the coating. The following are several examples where plasma has been used for these types of applications.

Potting of components—A major manufacturer of discrete components produces several million potted parts per month. Before using plasma their defect rate, due to "leakers", was as high as 5%. After initiating plasma treatment, to improve the bond between the potting compound and the Valox® housing, the defect rate has dropped to less than 1/2%.

Potting of connectors/wires—Several manufacturers of cables (both round and flat) are using plasma to treat the insulation on the cable before potting the cable end into the connector. This provides both a better hermetic seal and a stronger physical connection between the cable and the connector. Plasma has been used successfully on jackets of polyester, silicone rubber, Kapton®, and Tefzel®.

Potting of high voltage transformer—The coil form for a high voltage fly-back transformer has deep narrow slots to separate the windings. The potting material must wick down to the bottom of these slots to ensure reliable, corona-free, operation. The form is made from Valox® and is plasma treated before winding. This treatment has virtually eliminated premature failure of these transformers.

Coating of aircraft power supply—A high-performance military aircraft uses a wing-mounted power supply to fire its missiles. The manufacturer of these supplies was unable to deliver the completed units because they could not pass the final environmental test, which included a "rain" test. They found the solution in plasma treating the complete power supply, minus only the outer cover. After treatment, the entire unit, including all exposed components, was fully wettable by the urethane dip coating.

Coating of implantable heart-pump—The inside of the human body is an extremely corrosive environment. Usually the protective coating on implanted devices is a polyurethane. One type of implantable heart-pump has exposed titanium and two different engineering polymers on the outside of the unit. The completed device was coated in four steps: (1) the entire unit was plasma treated to clean and chemically activate the surface, (2) it was coated with an epoxy system to give a pinhole-free coating, even around sharp edges, (3) the cured epoxy coating was plasma treated to activate its surface, and (4) the epoxy was given an overcoat of a polyurethane which formed a second pinhole-free layer that could resist the body fluids. It was found that this completed assembly could be put into boiling saline solution for two weeks with no corrosion. It has since been used successfully in human implants.

Coating plastic containers—It is sometimes desirable to mold a container out of a specific polymer because of its good handling or physical properties. However, the container may then have to be coated with a second polymer to improve its barrier properties or chemical stability. This can be facilitated by plasma treating the molded part to make it wettable and bondable by a barrier coat. An example of this is the internal coating of molded automobile gasoline tanks to reduce permeability.

Depotting—For several years plasma has been used successfully to remove the potting from integrated circuits and transistors. This is necessary to perform failure analyses on parts. It can be time consuming because, in filled polymers, the inorganic filler builds up a layer of powder over the underlying polymer as the polymer is oxidized away. This powder slows the removal rate of the polymer. The part must be periodically removed from the reactor and dusted off with a fine brush. If this technique is used properly it will remove the potting material without damaging the device.

Cleaning, wetting, and bonding of inorganics

The primary effect of plasma on metals, glass, and ceramics is to hyperclean them. The plasma is usually oxygen-containing to oxidize the organic contamination to CO, CO_2, and H_2O.

Figure 6 shows the typical results of plasma cleaning. The two pieces of 6061 aluminum sheet were both vapor degreased. The lower piece was also plasma cleaned in an O_2 plasma for 3 minutes. After the cleaning, a low viscosity epoxy

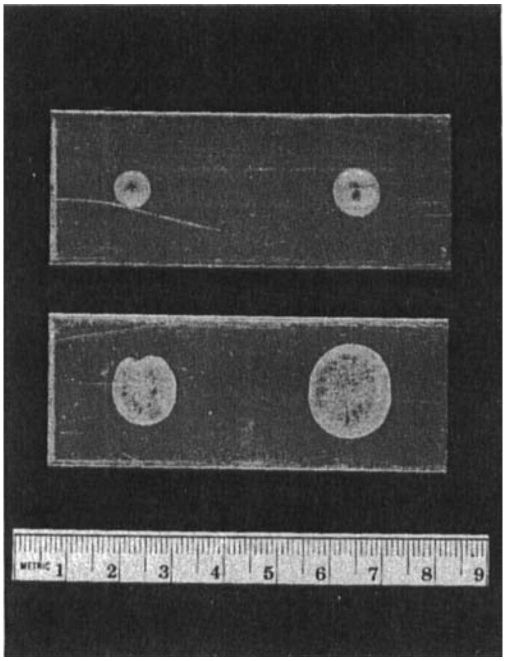

FIGURE 6 Adhesive wettability of aluminum (see text).

(Hysol® RE 2038 and Hysol® HD 3475) was dripped onto the surface: one drop on the left side and two drops on the right side in Figure 6. The difference in wettability of the metal by the adhesive is obvious. On the treated part, the same amount of adhesive covers about 4 times more surface area than on the untreated part. The practical results of this are better adhesion and less voids, skips, and pin-holes. This same improvement in wetting occurs on all inorganics that we have tested.

Materials that are sensitive to oxidation, such as silver or solder, can be cleaned using a plasma of Ar/H_2 or N_2/H_2. This mixture removes organics from the surfaces and converts them to low molecular weight species that are volatile and are removed by the vacuum system. This gives surfaces that show greatly improved soldering[45] and wire bonding and adhesion in hybrids.[46–49]

Optical components, especially intracavity laser components, are sometimes plasma cleaned to eliminate contamination that can degrade their performance.

PROBLEMS NEEDING FURTHER STUDY

Bonding to PTFE

Plasma treatment of PFA, FEP, and Tefzel® gives surfaces that can be bonded with epoxy. The resulting bonds are stronger than those obtained with sodium-etched surfaces. However, it has not been possible to get really good bonds to PTFE using plasma. This may be due to the inherent weakness of the PTFE structure under the surface.[50] This is an important problem because of the excellent properties and wide use of PTFE.

Limited lifetime of plasma treatment on silicones

Plasma treatment of silicones for bonding and printing is a routine and successful application. However, the treatment is transient, that is, the bonding or painting must be done within an hour or so of the plasma treatment to be successful. The reason for this short lifetime has not been determined. It may be due to thermodynamically-driven rearrangement of the surface molecules or it may be due to "bleeding" of some mobile species to the treated surface. This is important, especially for medical applications where the ability to make silicone permanently wettable would be a great improvement.

Covalent bonding

It has been proposed that one of the mechanisms for improved bonding to plasma-treated polymers is the chemical reaction between the residual surface species and the curing adhesive to form covalent bonds between the polymer and the adhesive.

If it could be demonstrated and, more importantly, if the mechanism could be elucidated, it should be possible to tailor the plasma/polymer/adhesive system to maximize the bonding, especially the hot/wet performance.

Hot/Wet performance

There is a great deal of data in the literature on the dry bond strength of plasma-treated materials. However, there are little or no data on the hot/wet bond strength of similar materials. Since hot/wet performance is often the limiting factor in the utility of bonding, this area needs to be investigated.

Degree of surface coverage

As was stated earlier, some work has been done in this area but there are still a lot of questions. Additional work needs to be done to learn how to maximize both the coverage and depth of penetration of organic oxygen species on a polymer.

SUMMARY

This paper has reviewed the nature of low-pressure plasma, the equipment necessary to generate it, its effects on materials (primarily polymers), and the results of plasma treatment in terms of improved bondability.

It is shown that the chemical effects are due to a combination of the attack by electronically-excited free-radicals or atoms, ions, and vacuum-ultraviolet photochemistry. These processes can hyperclean metal, ceramic, and glass and, in some cases, can chemically modify these surfaces.

Polymer surfaces are cleaned or ablated and may be chemically modified through crosslinking or through the addition of new chemical species to the surface atoms.

The treated surface is usually completely wettable by water, adhesives, and other liquids (such as solder on tin). These surfaces can give 2 to 10 times stronger bond strengths than untreated surfaces.

Data are given on the wettability of polymers, the relationship between bonding and wetting, the effect of treatment time on bonding and wetting, and the degree of improvement in bonding.

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