The Challenge of Plasma Processing – Its Diversity

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Abstract

Cold gas plasma is used in many industries from aerospace to life sciences for permanent re-engineering of the molecular surface properties of polymers, elastomers, metals and ceramics to provide unique surfaces that do not affect the bulk properties of the material. Examples of applications are: corrosion resistance, etching, enhanced wear resistance, biocompatibility, adhesive bonding, altered wetting properties such as creation of either hydrophobic, oleophobic or hydrophilic surfaces, and providing unique vapor barrier or gas transport properties.

The challenge with plasma surface treatment is that the choices and capabilities are expansive. Plasma surface treatment is not one process, but an entire tool box. Surfaces created by plasma gas modification include: functionalized, passivated, coated, charged or neutral, acidic or basic.

Methods to create plasmas are also varied from continuous wave to pulsed plasma; use of simple inert gases or complex monomers; to unique chamber designs.

This paper provides an overview of the myriad plasma processes employed to address the different requirements for materials in medical device applications.

Introduction

Cold gas plasma is a powerful tool allowing customized re-engineering of materials to impart unique surface properties, without affecting the bulk properties. The effect of plasma on a material is determined by the chemistry of the reactions between the surface and the reactive species present in the process gas employed. A multitude of gases can be used. Each gas produces a unique plasma composition resulting in different surface properties. Liquids may also be introduced as vapors, expanding by many orders of magnitude the potential for unique surface alterations and coatings.[1]

Surface alterations include:

- atomic-level cleaning
- functionalization
- adhesion enhancement
- cross-linking and
- biocompatibility.

Applications include (but are not limited to):

- creation of pin-hole free thin films via PECVD (plasma enhanced chemical vapor deposition) for wear resistant coatings or gas/liquid barriers
- grafting of monomers for protein attachment
- cross-linking to prevent molecular rotation and/or migration and loss of additives
- enhanced adhesion for paint, ink, adhesives and deposited metallic films
- cleaning to remove weak boundary layers or processing oils, and
- rendering surfaces hydrophobic or hydrophilic.

Once the process conditions are developed, plasma offers customers a repeatable, reliable, easy, workplace safe, permanent modification with low costs, unlike competing surface modification techniques such as corona, atmospheric plasma and wet chemistries.

Applications discussed herein focus on the challenges of custom re-engineering polymers and metals to create unique surface properties. There is no universal process. For example, a plasma utilizing oxygen will give completely different results than a plasma created with tetrafluoromethane. This paper addresses the challenges of proper gas and parameter selections to yield the desired results.

Method

Cold gas plasma modifications are achieved via a vacuum process. The components to be treated are placed in a vacuum

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chamber with air removed via a vacuum pump to base pressures on average from 35 to 100 mtorr. Process gas(es) are introduced into the chamber and allowed to reach equilibrium, typically from 100 to 500 mtorr.

Radio-frequency energy supplied to electrodes within the chamber excites the gas(es) into plasma. Plasma, the 4th state of matter, is a gas comprised of modest concentrations of electrons, ions, as well as other excited meta-stables. These excited species have sufficient energy to rupture chemical bonds of the component (substrate). These ruptured bonds are thermodynamically unstable and reach out into the plasma to combine with gas fragments to normalize its energy, thereby molecularly re-engineering the surface of the material placed into the plasma.

Cold gas plasma processes are low energy processes and the species created have little penetrating energy, thus the modification is limited to the surface typically no deeper than a few molecular layers. Ultra-thin temperature sensitive materials can be easily modified in cold gas plasma without deteriorating the bulk properties of the material being treated. As practiced in non-semiconductor applications, cold gas plasma is recognized as both a worker and workplace safe clean air technology.[1]

Gas Selection – not just air, oxygen and argon

A multitude of gases and liquids can be used independently or in combination with other gases to create specific modifications (Table 1). The challenge is to choose gases and/or liquids that will yield desired properties for the customer's specific application.

Table 1. Sample gases and liquids used to create plasmas

Gas Samples	Liquid Samples
Oxygen	Methanol
Argon	Water
Helium	Allyl Amine
Nitrogen	Ethylenediamine
Ammonia	Acrylic Acid
Hydrogen	Acetone
Nitrous Oxide	Hydroxyethylmethacrylate
Carbon Dioxide	Ethanol
Air	Toluene
Methane	Diaminopropane
Ethane	Butylamine
Ethylene	Gluteraldehyde
Acetylene	Hexamethyldisiloxane
Tetrafluoromethane	Tetramethylsilane
Hexafluoroethane	Polyethylene glycols
Hexafluoropropylene	Diglymes
	Silanes (Amino, Carboxy, Hydroxyl, Mercapto, Vinyl)

Equipment Selection

Appropriate equipment choice is key to ensure optimum throughput. 4th State's lab is equipped with batch systems from 1.5 to 80 cf. Systems have removable shelves, trays, fixtures or tumbler baskets. Batch systems are ideal for modification of powders, molded articles, glass and polymer slides, catheters, titer plates and porous frits for example.

Continuous profile systems allow for modification of fiber, tubing, yarns and thin films in an air-to-air mode with or without subsequent processing. And roll-to-roll equipment allows for modification of films, membranes, woven and non-woven fabrics and foils up to 60 inches wide with up to 19 inch outer diameters.

The Challenge

The technology challenge is identifying conditions that impart desired properties on the material for a customer's specific application. Generally, there is no universal process for plasma modification.

Any oxidation process (flame, corona, acid etch) or many plasmas will increase surface energy but the functionalities created can be very different. Most alternative methods will increase surface energy temporarily but will not provide specific reactivity needed for subsequent processing. Nor will most methods provide permanent surface stability. Cold gas plasma can provide specific functionality and long-term stability.

Understanding the material selection and application is advisable to ensure optimum results. A sales person's job involves investigation. Ultimately, the first question is "what does the customer want the surface to do." A common request is to render the surface "hydrophilic." This could be relatively simple if the customer truly wants only a water wettable surface. In most cases the customer is trying to impart specific surface functionality for subsequent bonding or trying to wet the surface to a reagent or other fluid. If so, the next investigative questioning involves trying to understand what functional groups are required.

Understanding of the subsequent environment helps guarantee success. Different surface preparations may be favored if the materials are to be exposed to repeated use, autoclaving, sterilization or require extended shelf life. If a biocompatible coating is required, the customer should know what surfaces are acceptable for their application. For example, is a fluoropolymer coating preferred over a hydrocarbon coating?[†]

[†] The customer is responsible for determining acceptability of any modification for their use. 4th State does not sell bottled FDA approved solutions nor warrants the effectiveness of a treatment for the customer application.

Additional questions are necessary to understand potential incoming material issues that may affect outcome of plasma processing. For example, is the material cast, extruded, sintered or machined? What processing agents or mold releases are used? Is there lot control? Is representation of lot variation available?

Once information has been gathered a matrix of processing experiments is recommended. Chemistries and variables are chosen from our knowledge base.

Applications

Hydrophilicity and/or Surface Functionalization

Hydrophilicity is defined loosely in the industry and wettability to water is often used inaccurately as a quantitative guide. There is general confusion between wetting and chemical functionality.

The sales person's question is "do you want the surface to wet to water, only?" Even though they may respond "yes", they often require specific binding properties for the attachment of reagents, markers, proteins or inks. Making a surface wettable to water does not guarantee that it will bind to these examples.

Our challenge is finding the optimum processing conditions that promote the desired wettabilty or binding. The composition of the gas dramatically influences the surface properties.

4th State has demonstrated that reliance on the contact angle measurement alone is not an accurate guide for wettability, unless the application solely uses distilled water, which is unlikely. And generally, there is a misconception that 70 dynes/cm equals water wetting. A study was conducted on polyethylene (a hydrophobic polymer) by varying power-pressure matrices with three chemistries that are known to create functional oxygen groups. Dyne solution surface energy tests and contact angle measurements with distilled water were taken for each sample immediately and 48 hours after processing.

Table 2 represents the matrix and Figures 1 and 2 show contact angle and dyne surface energy values. Contact angle and dyne values correlate for the most part. However, samples 9 and 12 exhibit poor hydrophilicity yet the dyne values are high. Further testing was conducted with permanent marking pens. The pen ink beads on the untreated control yet writes (unbroken clean line) and permanently marks samples 9 and 12, which are not water wettable. Dyne solutions are not water. They are solvent mixtures. Functional groups of the plasma treated samples interact to varying extents with the hydroxyl, ether and amine groups of the solvents.[2]

It proves that conventional ideas on the relationship between contact angle and surface energy do not apply to plasma treated surfaces. Unless your application only involves the use of distilled water, be careful how you attempt to correlate performance to standard surface characterization techniques.[2]

Table 2. Polyethylene Wetting Study

Process	Chemistry	Power	Pressure
1	Proprietary	LOW	LOW
2	Proprietary	HIGH	LOW
3	Proprietary	HIGH	HIGH
4	Proprietary	LOW	HIGH
5	O2	LOW	LOW
6	O2	HIGH	LOW
7	O2	HIGH	HIGH
8	O2	LOW	HIGH
9	O2/CF4 A	LOW	LOW
10	O2/CF4 A	HIGH	LOW
11	O2/CF4 A	HIGH	HIGH
12	O2/CF4 A	LOW	HIGH
13	O2/CF4 B	LOW	LOW
14	O2/CF4 B	HIGH	LOW
15	O2/CF4 B	HIGH	HIGH
16	O2/CF4 B	LOW	HIGH

A and B are different gas mixtures. Contact angle measurement: Projection contact angle apparatus with distilled water. Surface Energy measurement: dyne/cm solution. 33-66 dyne/cm varying solutions of ethyl cellosolve (ethylene glycol monoethyl ether) and formamide; 70 dyne is formamide and water.

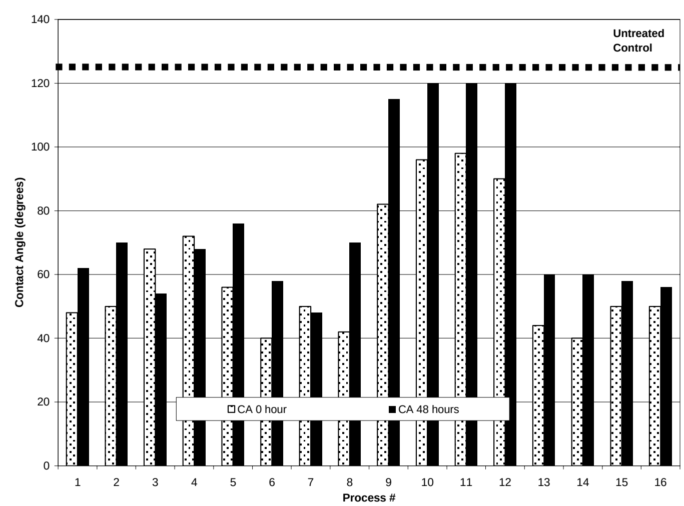
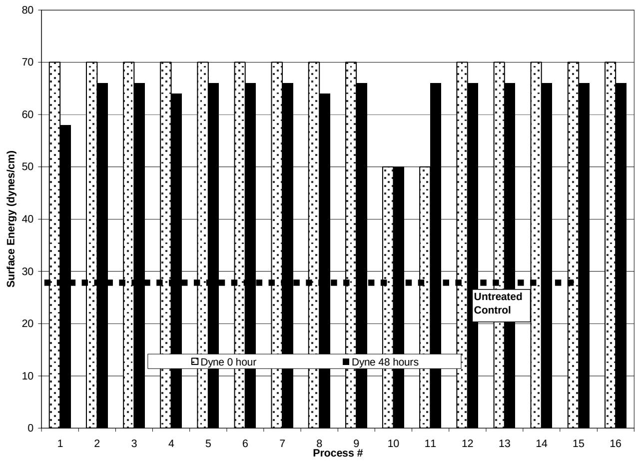


Figure 1. Contact angle measurements for Table 1 Processes



Note that technicians test kit only included values from 50 to 70 dyne/cm. Values reported at 50 dyne may be lower.

Figure 2. Dyne values for Table 1 processes

Gas mixture is important. Figure 3 illustrates results for polyethylene plasma treated in processes in which two gases were mixed at the noted percentages. The 50/50% mix provided a stable surface wettable to 70 dyne/cm over the 5 day period where other mixtures failed.

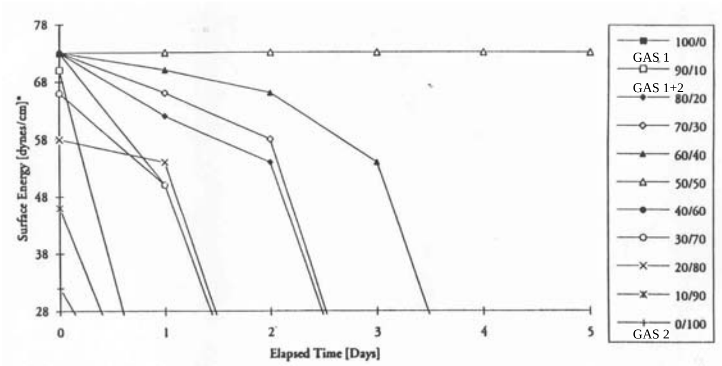


Figure 3. Change in surface energy based on gas mixture

Subtle changes in gas chemistry and process parameters can have a very dramatic impact on wetting, surface chemistry and stability as illustrated in Figs. 1, 2 and 3. It is important that the customer not draw conclusions solely on the surfaces ability to wet to water (unless that is the sole application). The plasma challenge is two fold: (1) having a sufficient understanding of the application to define the optimum surface; and (2) identifying a plasma process to create that surface.

PECVD Coatings

Plasma enhanced chemical vapor deposition (PECVD) enables the creation of thin films on polymers, elastomers, metals, ceramics and glass. The selected gas or monomer undergoes fragmentation and reacts with itself to combine into a polymer (polymerization), allowing the deposition of unique pinhole-free films. Applications include:

- decreased gas/liquid permeation
- wear-resistant coatings
- fluoropolymer coatings for water or chemical resistance
- lubricious coatings, decreasing the coefficient of friction (COF)
- transitional/interface layers
- retarding of additive migration and/or molecular rotation
- functionalized coatings for drug delivery or subsequent attachment chemistries.

PECVD coatings allow the engineer flexibility in choosing any material and applying a specific coating for desired properties. For example, if a fluoropolymer is selected not because of its thermal stability but because of its hydrophobic or chemical inertness, plasma technology offers the ability to create a stable fluoropolymer coating on any desired substrate. A fluoropolymer coating on a different polymer may offer considerable cost savings and/or mechanical design advantages.

Table 3 illustrates that not one process fits all.

Table 3. PECVD coating examples

Coating	Chemistries
Wear resistance	TEOS · HMDSO · Acetylene · TMS
Surface Inertness	HMDSO · TEOS · Fluoroalkanes · Fluoroalkenes · Acetylene · Ethylene · Methane · Propane · Ethylene
Hydrophobicity Oleophobicity	Fluoroalkanes · Fluoroalkenes · Fluoro organic compounds · Organosilanes · Siloxanes
Lubricity, decreased COF	Ethylene · Butadiene · Siloxane
Permeation Control	Ethylene Oxide · Butadiene · HEMA
Biocompatibility	PEGs · Ethylene Oxide · HMDSO
Functionalization	Allyl Amine · Acrylic Acid · HEMA

PECVD Coatings on Elastomers

Elastomers offer a particular challenge because of the mobility of the elastomer chains and the complexity of rubber formulations which typically contain more additives than engineering plastics. A successful plasma process addresses both of these issues by depositing a thin coating possessing the desired surface properties. The plasma parameters are chosen to stabilize the elastomer surface yielding a permanent modification.

PECVD Coatings on Metals

Customers desire phobic coatings on metals to provide hydrophobicity, chemical resistance and decreased COF. Routine requests are received for coating metals such as stainless steel and Nitinol™. One surface does not provide an answer for each application. Some customers require resistance to IPA, DMSO, hydrogen peroxide, and nitric acid, where as another may require resistance to oils and inks. Similarly to the hydrophilic example, it is important to understand what the customer is trying to repel from the surface.

A common question from our sales investigator is “does a glass, fluoropolymer or polyethylene surface provide the require phobicity?” If the customer can provide guidance on desired surface coating, we have a starting point. As noted in Table 3, PECVD coatings can be created from fluorocarbons, hydrocarbons and siloxanes.

Functionalized Coatings on Inert Surfaces

Functionalized metals and glasses are desired for the attachment of reagents to improve biocompatibility, specific moieties for bioanalysis, attachment of DNA, proteins or drugs. The challenge with modification of inert metals is how to bond desired species to the material.

Two different methods are demonstrated below for creating amine functional sites on gold, an inert metal.

- Method 1 is the introduction of a transitional layer via PECVD to create binding sites for the desired functional groups (Table 4).[3]
- Method 2 is a direct deposition of an amine coating on to the gold surface (Table 5).[4]

Samples were plasma treated and thereafter exposed to a 10 min hexane ultrasonic wash followed by a 10 minute methanol wash.

Original studies conducted with gold show that a hydrocarbon tie layer was necessary, yet further research proved that a selected liquid could be polymerized yielding an amine rich surface. Depending on the customer application, one method may be preferred over the other. Some processes will favor direct addition of the functional group while other plasma processes will place the functional groups one, two or more carbon atoms removed. This represents another example of plasma’s processing diversity.

Table 4. Method 1 – PECVD hydrocarbon with amine functionalization (XPS Atomic Concentrations in %)

Sample	C	N	O	Na	Si	S	Cl	K	Au	F
Control	33.5	4.4	18.3	5.1		3.5	0.3	0.1	34.7	
Hydrocarbon	85.0		4.8						10.3	
Hydrocarbon + wash	76.6		10.9		1.9				10.1	0.6
Hydrocarbon + amine	74.5	17.8	7.6	0.1		<0.1			0.1	
Hydrocarbon + amine + wash	64.7	13.3	15.1		6.5				0.2	0.2

Table 5. Method 2 – Direct amine polymerized coating (XPS Atomic Concentrations in %)

Sample	C	N	O	Cl	Si	S	Cu	Zn	Au	F
Control	46.5	-	10.8	0.7	-	0.8	1.6	-	39.7	-
Amine	72.9	16.5	8.1	0.2	-	-	0.1	-	2.2	-
Amine washed	73.6	15.7	10.0	-	-	-	-	0.4	0.2	0.1

Summary and Conclusion

Plasma is a versatile tool that is capable of solving many surface modification challenges. A key to successful plasma applications is not relying on a single chemistry at set conditions nor a single measurement tool such as contact angle.

Examples show that there is no universal process for like and dissimilar materials. Screening studies are warranted to understand optimum conditions for the desired surface modification. And a representational measurement tool is warranted: characterization of surface properties should not rely on a single measurement tool (such as contact angle) but surface energy, reactivity and functionalization for example. Understanding of the customer’s application as well as the material selection is also valuable in ensuring plasma’s success.

Plasma gives the design engineer the freedom to separate mechanical, optical and fabrication techniques from the surface requirements. Freedom of choice usually results in significant cost savings.

Presenting a comprehensive overview of plasma’s potential in a brief presentation unfortunately minimizes the true capabilities of the technology. Just a few examples of what can be accomplished with only two techniques (functionalization and

PECVD coatings) are presented herein and in no means are inclusive or conclusive.

The challenge with plasma surface treatment is that the choices and capabilities are expansive. Plasma surface treatment is not one process, but an entire tool box.

References

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