Cold Gas Plasma in Surface Modification of Medical Plastics

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Abstract

Cold gas plasma may be applied to medical and life science material surfaces for the permanent re-engineering of polymers, elastomers, metals and ceramics to provide unique surface properties without affecting the bulk properties. Examples of applications include: surface amination, coating and/or ink adhesion, biocompatibility, or wettability to fluids or reagents. Plasma is an excited gas comprised of metastable molecular fragments that are able to polymerize or covalently graft to a surface. Considerations in creating a plasma include power delivery, gas or vapor composition, or unique chamber configuration and design. Plasma systems exist that enable both facile batch processing or in-line treatment of sheet and fiber.

Introduction

Surface interactions play a critical role in biological and polymeric systems. It is at these interfaces that chemistries will undergo reaction or elicit a specific environmental response. Plasma is a means by which to modify the chemistry at a surface. This allows for greater versatility with a substrate and less emphasis on the material selection. The plasma is used as a catalyst for the modification of a wide range of materials. In their energized state, molecular fragments will effectively restructure the topmost layer of a solid.

A myriad gases or vapor may be used independently or in concert with other gases or liquid species to create specific modifications to a surface (Table 1). Careful consideration is made to select chemistry that will yield a desired property for a specific application or function.

Table 1. Sample gases and liquids used to create plasmas in low pressure

Gas Chemistry	Liquid Chemistry
Oxygen	Methanol
Argon	Water
Helium	Allyl Amine
Nitrogen	Ethylenediamine
Ammonia	Acrylic Acid
Hydrogen	Acetone
Nitrous Oxide	Hydroxyethylmethacrylate
Carbon Dioxide	Polyethylene glycols
Air	Hexamethyldisiloxane
Ethylene	Diaminopropane
Hexafluoropropylene	Diglymes
	Silanes (Amino, Carboxy, Hydroxyl, Mercapto, Vinyl)

As practiced, cold gas plasma modifications are achieved via a vacuum process. The components to be treated are placed in a vacuum compatible chamber that is vacated to a base pressure of on average 35 to 100 mtorr. Process gas(es) are then introduced into the chamber to a desired system equilibrium.

Radio-frequency energy supplied to electrodes within the chamber excites the gas(es) into plasma. Plasma, the fourth 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 their 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 of solid materials. This is typically no deeper than a few molecular layer. Porous media, such as sintered polyethylene membranes, polyolefin non-wovens, and foams are readily modified as the species sustain enough energy for modification of the interstitial surfaces. Temperature sensitive materials such as low molecular weight olefins, and individual fibers may 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 safe workplace clean air technology.[1]

Applications in Medical Plastics

<u>Surface Functionalization</u>

Cyclo olefin, glass, methyl methacrylate or lower cost polypropylene, polyethylene and polyester micro fluidic devices and sensor surfaces may require a specific binding property or a capacity to react with a fluid. Functional groups such as amine, hydroxyl and carboxyl (to name a few) will evoke system specific responses such as binding to proteins, nucleotides, or adhesives. Plasma begins by removing organic surface contaminants by reducing them to volatile compounds. The nascent surface is subsequently reacted to process specific plasma chemistry. The intensity and duration of a plasma process is deterministic in the surface functionality and density that result. If the density of a functional moiety is either too high or too low this may hinder an intended surface reactivity. Table 2 illustrates the percentage of elemental

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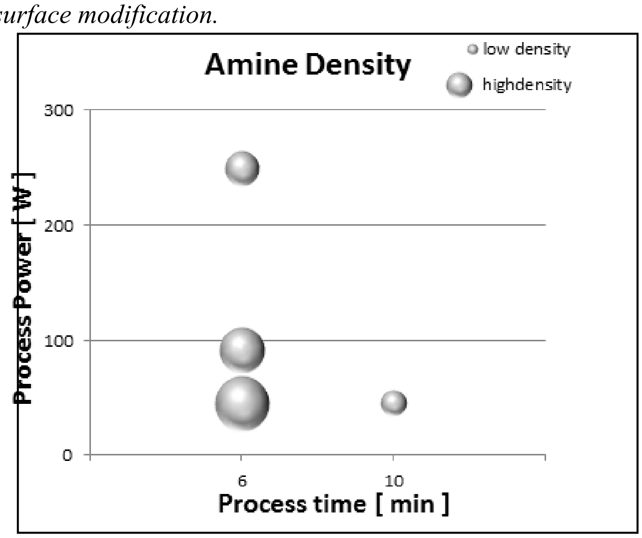
nitrogen detected on a gold surface as measured by XPS before and after plasma functionalization.[2] This amine is covalently bound to the surface meaning it is permanently incorporated onto the surface. This is exemplified by the persisting nitrogen composition post solvent wash. Figure 1 demonstrates different amine densities resulting from varying plasma process intensity and exposure. It is noteworthy that plasma processing isn't a linear phenomenon and therefore judicious selection of power, pressure, and time may be necessary. More power and more time does not always translate to denser species loading. Plasma operates within regimes that may be either addition or ablation dominant.

Table2. XPS measurement of amine incorporation onto a gold surface. The modification is permanently bound to the surface and persists after a solvent wash

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

Figure 1.The relative amine density on a surface as related to process power and duration of a plasma surface modification.



Device Hydrophilization

As markets improve the accessibility of medical and diagnostic devices to their consumers, product evolution drives material selection towards the use of commodity polymers such as polypropylene and polyethylene. Many of these plastics however lack the surface polarity that typically makes a surface compatible with an aqueous solution or biological reagents.

In industry there is often confusion relating wetting, surface energy, and chemical functionality. One general misconception is that 70 dynes/cm is synonymous with a hydrophilic surface. Dyne solutions are not water. They are solvent mixtures. Functional groups of the plasma treated samples may interact with the hydroxyl, ether, and amine groups of the solvents.[3] A study was conducted on polyethylene (a hydrophobic polymer) by varying exposures of power and pressure using three plasma chemistries known to add oxygen moieties to a surface. Figure 2a and 2b present measurement made over a 48 hour interval on the polyethylene surface using both a surface dyne solution and a contact angle using distilled water. In most cases greater hydrophilicity is accompanied by a high surface dyne level, however, samples 9 and 12 exhibit poor hydrophilicity yet the dyne values are still high. Reliance on the contact angle or dyne solution alone is not an accurate guide for wettability.

Figure 2a. Contact angle measurements conducted on polyethylene after exposure to various plasma processes.

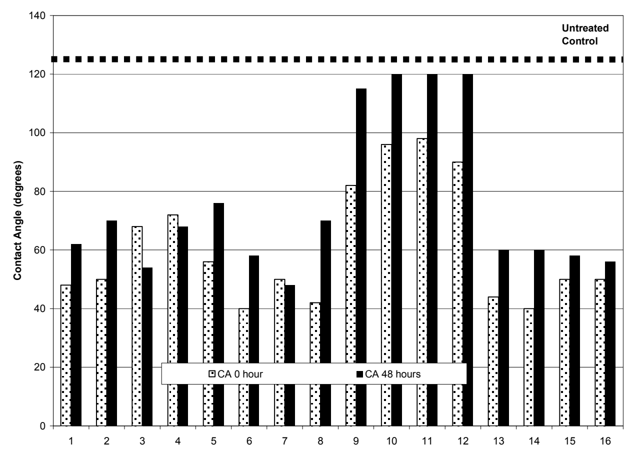
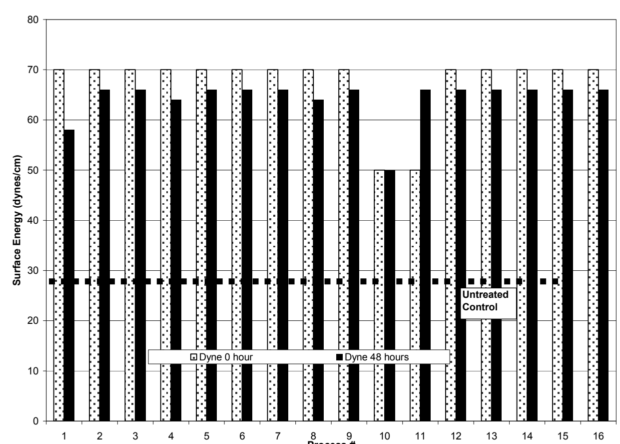


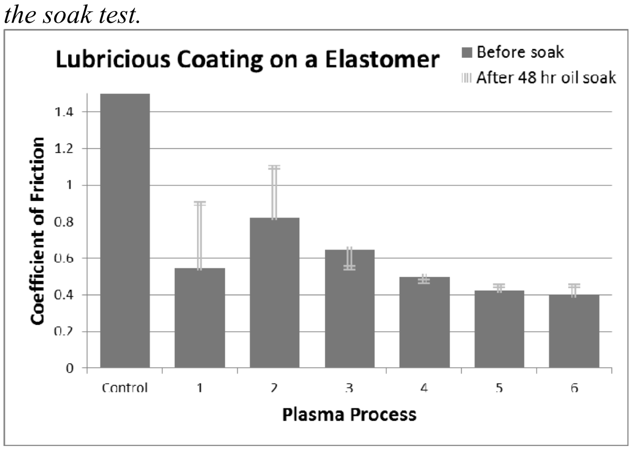
Figure 2b. Surface dyne level as measured on polyethylene after exposure to various plasma processes.



Lubricious Coatings and Anti-blocking

Without a surface treatment many categories of elastomers adhere to themselves or another surface when exposed to pressure, temperature, or humidity. Anti-blocking refers to the ability of a surface to not stick. In the medical device arena, anti-blocking agents such as waxes and oils are often unacceptable solutions in the management of adhesion. Such modifiers may be unapproved for device use due to the potential for elution into a working fluid or the disruption of organism function. Various low coefficient of friction surface treatments are available for deposition on polymeric substrates such as those used in seals, caps, catheters, and syringe plungers. These materials include but are not limited to silicones and thermoplastic elastomers such a Polyether block amide or polyurethane. Plasma polymerized coatings form densely crosslinked polymer networks that are covalently bound to a surface. Some of these coating chemistries have also been optimized for performance as flexible gas and/or liquid barriers[4]. Figure 3 demonstrates plasma processes which reduce static friction as deposited on a fluoroelastomer surface. Plasma treated components were then soaked in oil for 48 hours and the change in coefficient of friction was noted in orange. In particular process 4, 5, and 6 exhibit a threefold decrease in the coefficient of friction and minimal change after the oil exposure.

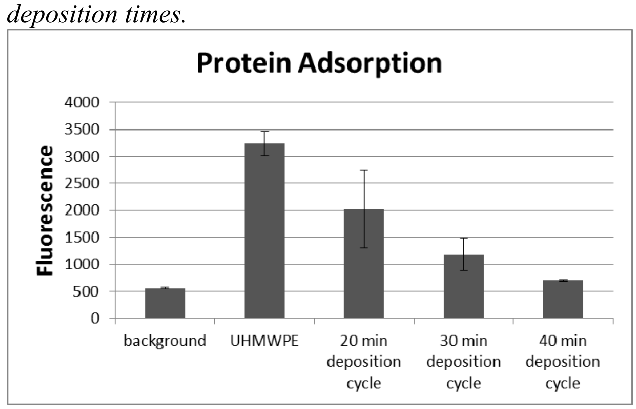
Figure 3. Friction reducing plasma surface treatments before/after oil soak. The coatings are leach free and some exhibit good compatibility in oil as demonstrated by the soak test.



Bioactive Surface

Dynamic interactions exist between surfaces and living organisms. Biocompatibility is loosely achieved if a device functions without eliciting an unfavorable response in a living system. Surface energy, ionic interaction, and intermolecular forces all play a role in the adsorption of proteins. In one example when a foreign object becomes implanted in the body the immune system may respond by marking the surface with communicative molecules. It has been demonstrated that cell attachment may be inhibited through protein resistant coatings. S. Kane *et al.* demonstrates the feasibility of plasma polymerized polyethylene glycol (PEG)-like hydrogels on the surfaces of implantable ultra high molecular weight polyethylene (UHMWPE) components[5]. Plasma introduces a streamlined controlled approach to functionalize and coat the surface without a time intensive or multi-step wet chemistry. Figure 4 compares the protein adsorption via optical fluorescence on a few variations of plasma deposition thicknesses. A positive correlation can be seen relating plasma coating thickness and protein resistance. The ether (C-O) content in the plasma coated hydrogel was measured between 82.1-83.2%. This nearly matches the 100% ether content of conventional bulk polymerized polyethylene glycol. Additionally the mechanical properties of the ultra-thin coating were assessed using atomic force microscopy. Unlike alternative hydrogels, the plasma deposited coating is covalently coupled to the polymeric surface and demonstrates improved pressure and wear resistance. The time required for processing a batch of parts is on average less than 20 minutes using a 5 cubic feet PTS 0500 plasma reactor.

Figure 4. Protein adsorption on the surface of PEG-like plasma polymerized coatings as related to increasing deposition times.



Conclusion

Plasma is a versatile tool that is capable of solving many surface modification challenges. This includes streamlining approaches where conventional multi-step wet chemistries are employed. 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. 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. It is important to note that presenting a comprehensive overview of plasma's potential in a brief presentation minimizes the true capabilities of the technology. With plasma surface treatment, the choices and capabilities are expansive. Plasma surface treatment is not one process, but an entire chemistry tool box.

References

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