WHAT IS GAS PLASMA AND SHOULD YOU CARE?

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ABSTRACT

Plasma surface treatment of plastics is definitely not new, nor is it commonplace. What is a plasma and what can it do is the subject of the following paper. A plasma is an excited gas, not unlike the aurora borealis. The excited particles that comprise the plasma bombard materials placed within their environment causing permanent change to their surface properties. By the judicious selection of process gas(es) and process parameters, the surface can be reengineered to fit specific needs. This paper presents quantitative analytical data on the chemical changes to the surface of polyethylene subjected to a plasma.

BACKGROUND

Tourists flocking to Alaska in the winter months have been turning Alaska's tourism business into a year-round opportunity. What would bring people to Alaska and out into below zero freezing wintry nights? The beauty of aurora borealis1, the northern lights, one of nature's plasma displays. The phenomenon begins with eruptions of hot gases from the Sun's surface releasing electrically charged particles into space. The electrons quickly travel toward Earth. As they enter Earth's atmosphere, approximately 200 miles above our surface, they ionize our atmospheric gases. The colors of the ionized gases differ with altitude; the colors we typically observe are from 60 miles and closer with the off blue light of nitrogen. The aurora borealis dances with streaks of bright green-yellow from oxygen and brilliant red of the rare gases. The aurora borealis; one of nature's plasma shows.

On Earth how do we create a plasma and avoid the potentially destructive temperatures of the sun? One method is to "excite" a gas in an electromagnetic field. Electromagnetic field is science speak for a volume or area affected by either an electric or magnetic field. For our work, it is an alternating field where the magnetic poles or the anode and cathode electrodes keep alternating. Molecules trapped within this oscillating field attempt to flip flop in unison with the alternating current. At some point the flip-flopping becomes so great, or excited, that electrons are shed and the molecule is ionized, thereby establishing a plasma. The rate of flip-flopping is measured in hertz. The hertz is named for Heinrich Hertz, a German professor who was the first to broadcast radio waves and measure them. A hertz is a measure of cycles or the frequency of oscillation. In the work presented herein a 13.56 MHz generator is used to create the plasma. MHz is short hand for mega-hertz. A megahertz is 1 million cycles per second. Now you can appreciate why the molecule flies apart.

These molecules that have lost their electrons are not very happy and are referred to by physicists as unstable or metastable particles. They are voracious hunters of the fragments they need to become whole again. These unstable and metastable particles may attack anything in their environment in an attempt to become whole again. It is this behavior that allows the modification of material surfaces that are placed within a plasma atmosphere. When these activated species become whole again they fall back (return) to their base state and emit their excessive energy as photons. Each gas has a unique color for specific pressure regimes (altitude sensitivity).

Typically the modification is limited to the top few molecules. Even when plasma is used to deposit a coating, the deposited coatings are very thin, measured in hundreds of angstroms. An Angstrom is very thin. To put it into perspective, an Angstrom is less than what one side railing of an aircraft carrier rises when a fly lands on a railing on the opposite side. Thus, it is easily appreciated why plasma treatment, whether surface functionalization or plasma deposition of a coating, has no impact on the bulk properties. But, why should you care?

It is often very desirable to alter the surface properties of a material to best suit its application. For example, plastic culturing dishes and flasks are preferred for their breakage resistance. However, for cultures to grow they must adhere to the container's surface. Plasma is employed to alter (functionalize) the plastic surface providing wettability (hydrophilicity), as well as, biological compatibility.

Many plastics are very difficult to paint, decorate, or to bond with adhesives and glues. Functionalizing the surface to provide both compatibility, as well as reactivity, to the paint, ink or adhesive is readily accomplished via plasma surface treatment. Paints, inks or adhesives applied to plasma functionalized plastics achieve extraordinary permanence and stability. Plasma is routinely used to treat medical devices to enhance the permanency of adhesive bond strength and/or critical markings.

Depending on the gas or liquids used to create the plasma, the surface of a plastic can be re-engineered to provide specific chemical functionality. In the series of experiments that follow, the choice of a co-reactant provides subtle, but very real changes, to the functional groups created on the surface of polyethylene.

RESULTS & DISCUSSION

Polyethylene was plasma treated in a 64-Liter plasma reactor manufactured by Europlasma. The chamber is evacuated by a 27 CFM 2 stage rotary vacuum pump. Gases are controlled with mass flow controllers and liquids are injected into the gas manifold by a precision Eldex® piston pump. The gases are introduced into the evacuated chamber and maintained at a reduced pressure by the vacuum pump and throttle valve. After the gas pressure is stabilized, the gas is energized with rf energy from a 13.56 MHz generator which has a controllable output from 0 - 550 watts. The polyethylene was treated in each case for 3 minutes.

ESCA, Electron Spectroscopy for Chemical Analysis, quantitatively determines the elemental composition of approximately the top 100 Angstroms of the materials surface. The surface of polyethylene, which has no bound oxygen functionality, can be readily re-engineered in a gas plasma to provide not only a highly oxidized surface, but a surface in which the oxygen functionality can be readily controlled by the composition of the process gas used to create the plasma. Equally important, the created oxygen functionality is covalently bound, thus providing environmental stability. These functional oxygen moieties can participate with other reactive groups present in adhesives, paints, inks or coatings to provide covalent bonds enhancing the performance and permanency of such material combinations.

ESCA Results:

The surface of plasma treated polyethylene is irradiated at a low angle with X-rays which interacts with an inner-shell electron of an atom causing photons to be emitted from the material’s surface. The kinetic energy of the emitted photoelectron is characteristic of the binding energy of a particular shell of an atom and is unique for each element. The elemental composition is thus determined and is expressed in atomic percent units for the elements detected.

Sample Treatment	**C**	**N**	**O**	**F**	**Na**	**P**	**Cl**
CO2 / CH3OH	85	--	15	--	--	--	--
O2 / CH3COCH3	80	0.4(?)	20	--	--	0.2 (?)	--
CO2 / N2O	80	1.4	16	2.7	0.4	--	0.1 (?)

Note: A question mark (?) indicates that a weak signal, which may or may not have been real, was detected at a binding energy which was characteristic of that element. "--" indicates no signal was detected for that element.

High Resolution ESCA data: Binding energies were corrected to the binding energy of the -(CH2)n_ signal at 284.6 eV. Atom percentages were calculated from the high-resolution data. Peak assignments were based on the binding energies of reference compounds.

Sample Description	**C1**	**C2**	**C3**	**C4**
CO2 / CH3OH				
Binding energy (eV)	284.6	286.0	287.5	288.9
Atom Percent	69.0	8.9	3.4	3.1
O2/ CH3COCH3				
Binding energy (eV)	284.6	286.0	287.3	289.1
Atom Percent	66.0	4.3	3.7	6.2
CO2 / N2O				
Binding energy (eV)	284.6	286.1	287.1	288.6
Atom Percent	69.0	3.6	2.8	4.5

Peak Assignments:

C1 = C-R (R=C, H)

C2 = C-OR (hydroxyl)

C3 = O=C-R (carbonyl)

C4 = O=C-OR, O-CO-O, C_F (?) (carboxylic acid)

Untreated polyethylene has no functional oxygen, consisting of just carbon and hydrogen. The three plasmas examined all readily oxidize the polyethylene surface, but, as can be seen in the above ESCA data, the hydroxyl content of the polyethylene can be varied from 3.6 to 8.9 atomic percent oxygen by judicial selection of a co-reactant.

Polyethylene is normally employed to package reactive adhesives such as cyanoacrylates, since it is normally inert to the cyanoacrylate group. However, at 8.9% hydroxyl oxygen content the cure reaction is readily initiated and such a modified surface can easily be adhesively bonded. Other adhesives or paints may favor carboxylic oxygen.

In addition, the surface energy of the polyethylene from all of these three treatments is greater than 70-dyne centimeters and readily wetted with distilled deionized water. Water is self-spreading. The adhesive strength is improved not only by the chemical reactivity between the adhesive or coating and the polyethylene, but also by the ability of the adhesive to penetrate into the smallest crevice or pore in the polyethylene surface thus providing significant increase in the surface area. Increased surface area directly translates to increased adhesive strength. However, the improvement in adhesive bond strength obtained with gas plasma treatment far exceeds that which could be attributed to increased surface area alone. The utility of plasma is universal across all polymers, albeit the optimum selection of gas or process parameters may differ from one polymer to another.

Oxygen and oxygen containing compounds are not the only useful gases for plasma treatment. Ammonia is routinely employed to provide amine and amino functionality to a variety of plastics and fibers.

Functionalization is also known as activation or etching, but it is not the only process used for plasma surface treatment. More complex gases such as hexamethyl disiloxane may be employed which, when excited into a plasma, fragment and rearrange and/or combine to deposit unique materials3 onto the surface. This process is called plasma enhanced chemical vapor deposition. Depending on the process parameters, common monomers such as ethylene employed as the plasma gas will deposit a coating that may resemble products obtained from conventional polymerization or be totally unique. Regardless, since the reaction is carried out in a closed chamber and the process parameters are totally controllable, the process is inherently reproducible and reliable. Such PECVD coatings are routinely employed to create gas and chemical barrier coatings on conventional polymers.

CONCLUSION

Without plasma technology our world of subminiature electronics would not exist. Plasma processing is synonymous with semiconductor manufacture used in the etching of both the conductive and dielectric layers of the semiconductor active device, as well as in the removal of photoresist patterning between the successive layers. Although plasma processing has been used for several decades to enhance the performance and permanence of adhesive bonds and paints to plastics and rubbers, it is still in its infancy as a general process technology within the plastics industry. Plasma has been specified since the early 1960's in numerous military specifications such as the adhesive bonding of silicone rubbers and ultra high molecular polyethylene to other plastics and metals. It has been, and continues to be, widely used to alter the surface wettability of medical disposables such as culture dishes, flasks, and multi-well trays for the past two decades. It is widely used in the electronics industry to improve the weatherability of encapsulated electronic components.

As practiced in the plastics industry, plasma is workplace and environmentally clean and safe. It is recognized by the State of California as environmentally friendly and as a recommended alternative to solvents and wet chemical processes.

As can be seen in the above discussion, the surface of polyethylene can be reengineered to provide specific surface energy and chemical functionality. This reengineering is possible with any polymer from the most simple polyethylene to the most advanced liquid crystal polymers.

Why should you care? Because, if you adhesively bond, paint, decorate or mark materials, plasma may be a process that will improve your product. If you use an expensive polymer only because of its surface properties, plasma may be a process that can allow considerable cost savings by allowing the use of an alternative and less expensive material. If you are having difficulty achieving the bond strength or permanency of bond strength you desire upon environmental exposure, plasma may be a process to eliminate such concerns. In general, if you have a problem that is surface sensitive or related, you should be familiar with the power of plasma treatment.

REFERENCES

(1) see typical aurora borealis displays, as well as auroral activity, by visiting the University of Alaska Geophysical Institute web site at: www.gi.alaska.edu/