PLASMAtech, inc
Plasma Surface Modification of Polymers

Material selection of polymer components and disposables is determined by various factors such as physical/optical properties, cost, biocompatibility, etc. However, due to the hydrophobic (non-wetting) characteristics of many polymers, challenges can occur when bonding, coating or printing are required. Low pressure gas plasma is an environmentally- and user-friendly solution for modifying or functionalizing the surface of materials without changing bulk properties or appearance. While variable results can occur with so-called atmospheric plasma or corona treatments, low pressure plasma processes are absolutely repeatable since treatment occurs in a precisely controlled environment.

Plasma Defined
Solid, liquid and gas phase states are recognized as the physical states of matter. Yet the most commonly occurring is a fourth state of matter, as plasma is often called. Examples include the sun and polar lights. Matter is composed of atoms containing atomic nuclei (ions) and electrons. What differentiates the physical states of matter is the bond between these two particles. Plasma is the least orderly aggregate of electrons and ions and the dissolution of the bond between these as a plasma is formed result in the qualitative difference between a gas and a plasma.

Creating Plasma
A plasma is a partially ionized gas generated by applying an electrical field to a gas under at least partial vacuum. For surface engineering purposes, the plasma is generated by introducing gas into a vacuum chamber and exposing to an electromagnetic field. The resultant plasma consists of ions and free electrons, free radicals, excited state species, photons, and neutrals. When a gas is ionized in this manner, both the ions and electrons experience the same force and are accelerated. Collisions occur between these particles which transfers kinetic energy from one to the other. Since energy transfer in two body collisions favors the lighter particle (electrons in the case of plasma), the electrons soon have much greater velocity (i.e. temperature) than the ions. Radicals formed through the interaction of charged particles react differently depending on the gas type and the molecules on the substrate surface. Almost any gas can be used to generate a plasma. Specific gas chemistry depends upon the material to be treated and the desired surface characteristics to be achieved.

In the case of surface treatment of polymers, oxygen is one of the common gases used. The modification consists of oxidation (oxygen absorption by the upper most atomic layers) of the polymer by active oxygen radicals resulting in a considerable increase in the number of functional polar regions on the substrate surface. This results in increased surface energy rendering the surface hydrophilic (i.e., improved wetting) and is beneficial as a pre-treatment prior to bonding, coating or printing.

Processing Conditions
One of the most important characteristics of low pressure plasma is that reactions requiring hundreds of degrees C at atmospheric pressure typically take place between ambient and 50° C. This phenomenon is due to the fact that despite low gas temperature, high electron temperatures (about 20,000 to 50,000 K) are present due to the increased free path length. Temperatures are even further reduced when microwave plasma is utilized instead of the more conventional RF plasma approach. This allows very heat-sensitive plastics like balloon catheters or heat shrink tubing to be processed.

Since treatment occurs under vacuum in a precisely controlled environment, variable results that can result with atmospheric treatment such as corona or so-called “air plasma” are not an issue. Use of automated and precision metering components such as mass flow controllers, PLC control, error monitoring, and batch process data recording ensure absolute process repeatability.

Since plasma is a dry process, there are no disposal or personnel safety issues commonly associated with wet chemistry or other conventional methods such as flame treatment. The vacuum pump exhaust generally consists of minute amounts of gases such as H_2O and CO_2 and is easily neutralized and vented outside the work area. Inherent cleanliness and the ability to automate and control all critical functions of the processing make the technology especially attractive for cleanroom manufacturing environments.

Plasma in Practice

Just one example of the many applications for polymer surface modification in the medical device industry is treatment of polystyrene lab ware for increased (or selective) cell attachment. Typical of polymers with a carbon backbone, polystyrene has innately low surface energy making the surface hydrophobic or non-wetting. Figures 1 and 2 show XPS survey spectrum of untreated and plasma treated polystyrene respectively.

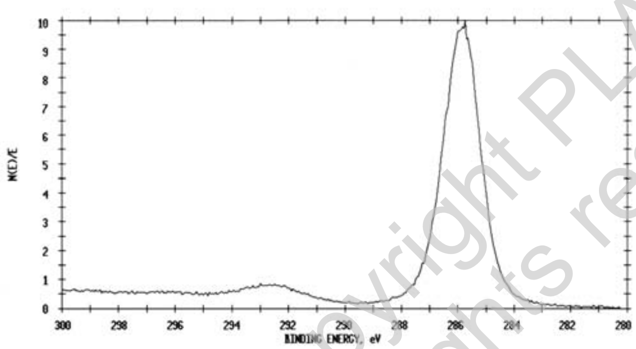

Figure 1. XPS spectra of surface of untreated PS. The surface consists primarily of carbon as represented by the tall peak.

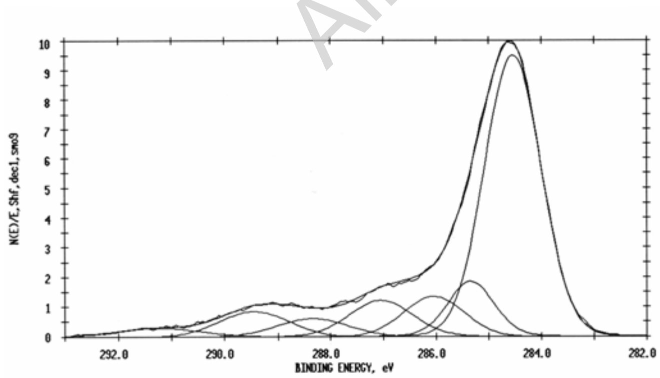

Figure 1. Surface of PS after short exposure to oxygen-containing plasma.

After a short exposure to an oxygen plasma, the surface chemistry is significantly altered. In the case of lab ware, adding these functional groups increases the polarity of the polystyrene surface to permit cell attachment. As opposed to polar groups associated with oxygen-containing plasma, by using alternate gas chemistry the surface can be specifically tailored with other chemical functional groups (amine, carboxyl, hydroxyl, etc.).

Component	Functional groups	Untreated	Plasma Treated
C-C, C-H	Aliphatic + aromatic carbon	100	71.4
C-O	Ether, alcohol	---	8.8
C=O	Ketone, aldehyde	---	8.7
O-C=O	Ester, acid	---	4.8
O-(C=O)-O	Carbonate	---	6.3

Table 1. Functional chemical groups on surface of untreated and plasma treated polystyrene

While there can be shelf-life issues caused by the underlying base material migrating back to the surface, polystyrene treated with low pressure plasma typically remains hydrophilic for many months.

While this is just one example of surface modification with low pressure plasma, plasma technology is extremely versatile and conducive to cleaning, treating or coating virtually all polymers. Contact PLASMAtech for more information.

PLASMAtech offers a full line of state-of-the-art equipment for all types of plasma surface engineering including standard treatment and thin film deposition (PECVD). Contract processing services and R&D customized solutions are also available in our GMP-compliant lab.

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