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Plasma Polymerized Thin Films for Surface Engineering

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Gas plasma is a versatile, green technology used for surface engineering of materials. When non-polymerizing gases such as oxygen or argon are utilized, surfaces may be cleaned at an atomic level. Polymers can also be modified by rearrangement of the upper most molecular layer and incorporation of chemical functional group. Rather than simply cleaning or modifying the surface of a material, polymerizable gases can be used to create a "new" surface by depositing a highly cross linked nano-coating. Plasma enhanced chemical vapor deposition (PECVD) coatings are permanent and do not affect bulk properties of the base material. Processing under precisely controlled conditions and without use of solvents or reactive chemicals ensures consistent results and an environmentally safe workplace.

Plasma Technology

Plasma is a partially ionized state generated by introducing gas into a vacuum chamber and exposing it to an electromagnetic field. When the electric field is applied, active species such as ions and radicals are formed by collisions between free electrons and gas phase molecules. For surface modification or cleaning, a surface is exposed to plasma species created by *non-polymerizable* gases (e.g., argon, oxygen, etc.). In cleaning applications, the surface reacts with active plasma species resulting in organic contaminants being lifted off at low temperatures. This results in an ultra-pure, atomically clean surface.

Non-polymerizing gases are also used to modify the surface of polymers by addition of functional groups to increase the surface energy and improve wetting; or conversely, to render the surface hydrophobic (non-wetting). Unfortunately treatment on polymer surfaces can have limited shelf life. This is due primarily to a tendency of labile molecules in the bulk material to migrate back to the surface, thus degrading the plasma surface treatment.

PECVD Coatings

As opposed to the above examples, rather than simply modifying or cleaning a surface, *polymerizable* gases can be used to create a new surface. During PECVD, the active gas species react with themselves as well as with the surface to form a coating. Since the polymerization occurs at an atomic, non-molecular level, the films are tightly adherent and conformal to the substrate surface.

The thickness of film required to obtain the desired properties depends on the application, and in some instances can be as thin as several hundred Å and are typically in the nanometer range. Superior to other coating or conversion processes, plasma polymerized thin films can be deposited directly onto a plasma pre-cleaned substrate without exposure to the atmosphere. This continuous multi-step process provides excellent adhesion of the plasma polymerized coating to most metal and polymer substrates. As opposed to many other coating techniques, no drying or curing is required.

Types of Coatings

Almost any compound with vapor pressures higher than several tens of Torr may be polymerized with PECVD technology. Film properties can include excellent wettability (hydrophilic), low surface energy (hydrophobic), low coefficient of friction/lubricious, low gas/liquid permeability, chemical resistance, high/low conductivity – or some combination of properties. The versatility of the technology permits tailoring coating characteristics to specifically address unique or especially challenging applications.

Primer or Interface Layers. Creation of a tie or interface layer to permit bonding or over molding of incompatible materials provides many advantages in industrial applications. For example, suppliers of over molded metal parts often encounter issues with silicone or elastomer adhesion to metal. Surface preparation may include caustic chemical etchants or toxic conversion coatings such as chromium or phosphoric acid to ensure a good bond to the base metal substrate. A thin film polymerized coating deposited directly onto the metal acts as a tie layer providing a surface that is highly receptive to direct over mold or bonding agents - and again, without any additional chemical or mechanical surface preparation to the base part. The resultant bond performance is excellent with results that can meet or exceed those achieved with conventional surface preparation methods.

Reduced Coefficient of Friction. High coefficient of friction (i.e., surface "sticktion" or tackiness) of rubber and elastomeric components can be problematic. For example, seals and orings used in assemblies may have a tendency to drag or stick. Problems can also occur when automated high speed handling and insertion equipment is used due to parts "clumping." Depositing a lubricious coating can dramatically reduce coefficient of friction. By using plasma systems designed specifically for high volume bulk parts coating, the process is both efficient and cost-effective.

Hydrophobic/Oleophobic. PECVD coatings can be repellent or non-wetting. Depending on the surface tension of the liquid media to which the substrate will be exposed, characteristics may be hydrophobic (water repellent) or oleophobic (oil repellent). Examples include hydrophobic coating on fabric to prevent material wicking and oleophobic coatings on seals or closures.

Barrier. Polymers, metals and ceramics may be coated for specific barrier properties. Typical applications include chemical, moisture or gas barrier on metals or polymers and coatings on rubber to prevent material leaching.

Hydrophilic. One of the more common applications for thin film technology is to increase the surface energy of polymer components, films or fabrics to create a wettable surface. As stated previously, the advantage vs standard plasma surface modification is that the treatment is permanent. Products treated include culture components for enhanced cell attachment or selected or specific binding; and treatment of films and membranes. Following is a comparison of plasma surface modification on polystyrene using non-polymerizable and polymerizable gases.

Polystyrene Treatment – O₂ vs PECVD coating

Polystyrene is an inexpensive polymer that is easily processed by techniques such as injection molding. It has the low surface energy characteristic of hydrocarbon polymers. Many disposables in the medical industry, for example culture components, benefit from having a surface that is highly (or selectively) receptive to various media. Traditional plasma treatment readily creates a spontaneously wettable surface, but the article has a limited shelf-life. A longer-lived high-energy surface can be created by deposition of a thin, highly cross-linked film. The films may be achieved with a variety of monomers resulting in a high energy surface.

Figure 1 shows contact angle as a function of elapsed time for polystyrene surfaces that were plasma treated with a non-polymerizing, oxidizing gas (O₂) or coated with a few nanometers of a plasma polymerized coating. To determine the stability of the PECVD coating, the mechanism of contact angle decay in the coated sample was further investigated using XPS analysis before coating and after 8 months aging.

After processing, both treatments show an initial contact angle of 0° (spontaneous wetting). After a few days, the surface energy of the O₂ treated surface has significantly decreased (i.e, higher contact angle).

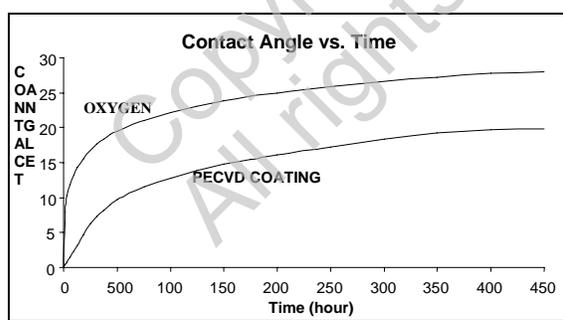


Figure 1 Water contact angle vs post treatment elapsed on PS treated with O₂ and plasma-polymerized coating.

Decay in surface energy of the coated sample is much slower, however, and the difference between the two treatments is even more apparent when the rate of decay in surface energy is analyzed (Figure 2).

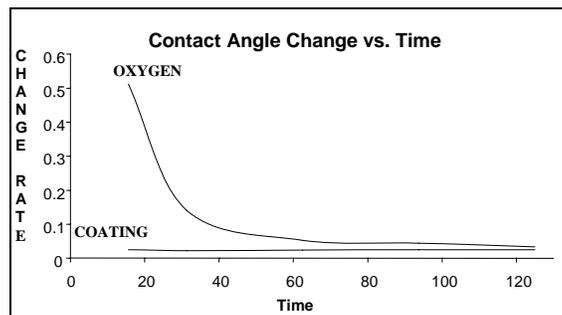


Figure 2 Rate of change in water contact angle vs elapsed time since treatment with O₂ and PECVD coating.

Whereas increase in contact angle over time observed on polymers treated with non-polymerizable gases is primarily due to molecular rearrangement, XPS results show that the change seen in the coated PS surface is due solely to adsorption of atmospheric contamination from the laboratory environment. XPS atomic concentrations revealed that the carbon signal strength decreased significantly as the sampling depth increased, showing that the carbon present on both the aged and unaged surfaces is truly adventitious and does not originate within the film or the polystyrene substrate. The percentage of carbon increases only slightly with 8 months again, but enough to account for the small increase in contact angle seen in Figure 1.

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 solutions are also available in our GMP-compliant lab.

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