

MODIFICATION OF POLYMERIC MATERIAL SURFACES WITH PLASMAS*

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INTRODUCTION

As adaptable as polymeric materials are in their many applications in our daily lives, there is the need to tailor the surfaces of polymers to provide yet even more flexibility in their uses. Plasma treatments offer an unprecedented spectrum of possible surface modifications to enhance polymers, ranging from simple topographical changes to creation of surface chemistries and coatings that are radically different from the bulk polymer. Furthermore, plasma treatments are environmentally friendly and economical in their use of materials.

Plasma processing can be classified into at least four categories that often overlap. These are: (1) surface preparation by breakdown of surface oils and loose contaminants; (2) etching of new topographies, (3) surface activation by creation or grafting of new functional groups or chemically reactive excited metastable species on the surface; and (4) deposition of monolithic adherent surface coatings by polymerization of monomeric species on the surface. Key features of these processes will be briefly discussed, with a rudimentary introduction to the chemistries involved and examples. Focus is placed on capacitively-coupled rf plasmas, since they are most commonly used in polymer treatment.

SURFACE PREPARATION

In many industrial and scientific processes, extremely clean surfaces are crucial. By "clean" it is usually meant that the bulk material is also the material that makes up the actual surface, not foreign, loose or otherwise mechanically unstable debris. For metal surfaces, plasma treatment can strip off surface oils and contaminants leaving the surface truly "cleaned" down to the base metal (see the article by Rie *et al.*, in this issue of the MRS Bulletin). This is possible since metals are typically quite resistant to attack from many plasma chemistries. In the case of polymers, the use of the word "cleaning" takes on a slightly different context since polymers are readily attacked by plasma environments. Thus polymer surfaces are not just "scrubbed" down to the base polymer but are actually altered chemically and topographically.

Production of high-strength composites requires surfaces of fiber and plastic insert parts to be stripped of low molecular weight, poorly attached, surface polymer residues before matrix resins are applied.¹ Plasma "scrubs" surfaces of unwanted materials largely by a combination of sputtering by energetic ions and UV photolysis of covalent bonds of the surface contaminants' molecular structure. For example, the surface of polyethylene is typically contaminated with low molecular-weight, wax-like, incompletely polymerized oligomers of ethylene, the monomer for polyethylene. These poorly adherent fragments must be removed before printing inks or adhesives can be applied. Since the fragments are on the surface and they are more easily and quickly degraded into volatile compounds than the base polymeric structure. Therefore, the base polymer structure remains essentially intact and minimally etched if short treatment times are used. Repetitive cleavage of low molecular weight polyethylene surface contaminants produces gases that can be pumped from the system, leaving a stable surface suitable for strong attachment of adhesives:

Noble feed gases such as Argon are used since they tend to initiate cleavage without grafting to the surface. Treatment times are typically short so as to reduce further unwanted chemistry.

Excessive treatment results in attack of the base polymer which ultimately "ashes" the entire polymeric part resulting in its destruction. A typical cleaning procedure for polyethylene would be to treat with Argon at a pressure of 0.01 to 0.4 Torr, with a power density of $\sim 0.5 \text{ W/cm}^2$ at 13.56 MHz rf on parallel-plate electrodes. Once contaminants are removed, a more stable polymer surface is exposed to the plasma environment so as to facilitate further reaction such as etching, grafting or direct application

of the desired surface coating. More aggressive processing can be achieved by using reactive gases or by use of electrical biasing to increase the energetics of the bombarding ions. However, etching into the base polymer begins to occur, which leads us logically to the next topic.

ETCHING

To obtain highly adherent coatings on polymeric surfaces, more than surface cleaning is often required. Plasma can provide "micro-roughened" surface topographies unattainable by physical abrasion methods. One factor that contributes to the improved adhesion exhibited after plasma treatment is simply an increase in surface area of the polymer surface so as to provide a larger contact surface interface to the coating. This can be achieved either by the opening of micropores, by the ablative removal of contaminants on the surface that cover or block the porosity, or through micro-roughening. Micro-roughening occurs with crystalline polymers or alloys through the process of differential ablation whereby the crystalline and amorphous regimes or different components within the alloy ablate at different rates.² Scanning electron micrographs shown in Figure 1 illustrate differential etching due to crystalline differences in the polymer structure in which Spectra® ultra-high-molecular-weight polyethylene has been etched in 0.1 Torr oxygen at 0.01 W/cm² power density.

The gas species being ionized is not the only factor that determines etching parameters. The polymer composition and microstructure also plays a key role. Typical reactive gases used are O₂, CF₄, SF₆, and mixtures of these with each other or with noble gases. Higher power densities of order 1 W/cm² and often electrical biasing are used to increase ion bombardment energies. Biasing is achieved by using deliberately mismatched electrode areas, *i.e.*, one electrode of the diode pair is much larger than the other, giving a "self bias," Alternatively, a steady-state rf bias may be directly applied to a target electrode that may be configured either as a solid plate beneath the polymeric material, or as an highly-transparent screen on top.

SURFACE ACTIVATION AND GRAFTING

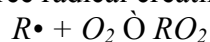
Plasma activation is the alteration of surface characteristics by the substitution or addition of new chemical groups from active species created in a plasma for groups normally present in the base polymer. For example, conventional polyethylene can be made more useful by transforming its surface with simple plasma treatments as shown in Figure 2. Such groups become "handles" that can perform new roles. For example, hydroxyl and carboxylic acid groups can be grafted to polyethylene to make the once hydrophobic surface hydrophilic. Amide and amine groups could alternatively be grafted to make surfaces receptive to dyes for coloration.

Process gases such as O₂, N₂, He, Ar, NH₃, N₂O, CO₂, CF₄, and air or some combination of these gases are generally used in activation treatments. The activation mechanism is believed to be the creation of free radicals on the polymeric material's surface molecules and then subsequent coupling of these free radicals with active species from the plasma environment. Depending on process gas, a large variety of chemical groups can be incorporated into the surface (*e.g.*, hydroxyl, carbonyl, carboxylic, amino or peroxy groups).

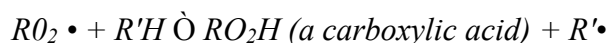
To better understand the complexity of some of the chemistry involved, consider the case of an oxygen plasma. The following oxidation reaction scheme is a logical pathway to produce oxygenated groups grafted on a polymeric surface. First, hydrogen is abstracted from the polymer backbone, R, by atomic oxygen present in the plasma leaving the polymer with a free radical site:



Then, molecular oxygen can couple to the free radical creating a peroxy radical:



The peroxy radical can then abstract hydrogen from a neighboring polymer backbone or other source and rearrange into a carboxylic acid group or an ester:



Not indicated in this reaction scheme are the possible formation of alcohols, ethers, peroxides and hydroperoxides. The byproducts, typically CO₂, H₂O and low molecular weight hydrocarbons, are readily removed by the vacuum pumps.

Additional co-reactants can produce new surface chemistry or accelerate the reaction kinetics. For example, in an oxygen plasma, the breaking of the carbon-carbon and carbon-hydrogen bonds are the rate limiting steps. When tetrafluoromethane is introduced as a co-reactant, the O₂/CF₄ plasma yields excited forms of O, OF, CO, CF₃, CO₂, and F. Fluorine and fluorine containing species are more effective in breaking the carbon-carbon and carbon-hydrogen bonds (than oxygen species), thereby accelerating the reaction rate. Oxidation by fluorine free-radicals is known to be as effective as oxidation by the strongest mineral acid etchant solutions, with one important difference: the plasma byproducts do not require special handling. As soon as the plasma is shut off, or the excited species exit the rf field, the species recombine to their original stable and non-reactive form, usually within a few seconds.

As an example of a commercial application, we consider paint adhesion to polymers, an important need in automotive manufacturing. For the painting of plastic surfaces, cleanliness alone is not necessarily sufficient to assure enduring paint adhesion. Rather, grafting of new surface chemistry is needed.

Polymers, such as polyolefins and polyolefin alloys, e.g., Thermoplastic Olefins (TPO), are especially difficult to paint due to their "waxy" surface and require pretreatment to provide paint film adhesion. The most common pre-treatment for TPO prior to painting has been either application of oxy/acetylene flames directly onto the surface (flaming) or the application of chemical adhesion promoters. Flaming, while effective to a degree, is not practical with more sophisticated panel designs which have recesses, louvers, or deep accent grooves. Adhesion promoters, typically low-solids (<5%) solution of chlorinated olefins in solvent, generally provide a higher level of effectiveness than flame treatment. Solvent-based adhesion promoters are not environmentally friendly since they contain a large proportion of volatile organic compounds. Water-borne adhesion promoters have not yet proven to be as effective and are more costly. Plasma treatment outperforms these commercial pre-treatment processes or combinations of processes^{3,4}. Paint adhesion has actually been shown to exceed the strength of the TPO base material, which has never been demonstrated with any other pretreatment process. Material was treated with an air feed gas at 0.2-0.4 mTorr, rf energy density from 0.01 to 0.1 W/cm² and treatment time from 30 to 60 sec. Plasma treatment provided a 1400 to 1800% improvement in peel strength vs the control, while the failure mechanism shifted from adhesive between the paint-substrate interface to cohesive within the TPO substrate

POLYMERIZATION AND DEPOSITION OF SURFACE COATINGS

Polymerization is the creation of very large molecules by the joining of many small, linkable, molecules called monomers. Classical monomers, as used in wet chemistry polymerization, have reactive structures such as double bonds that allow them to bond to one-another when the appropriate conditions are present. The double bond in methyl methacrylate provides the linking site for forming the useful plastic, polymethyl methacrylate (N = a large number of repeat units, e.g., 100,000) resulting in the reaction

Uv light, free radicals or energetic ions from the plasma, initiate the polymerization process. The monomer methyl methacrylate, when used as the feed gas, will begin the polymerization process by linking repeatedly, increasing its molecular weight many thousand fold. This plasma polymerization has

been studied by Fourier Transform InfraRed Attenuated Total Reflectance (FTIR/ATR) spectroscopy in real time.⁵ The resulting polymer was directly grown onto a Ge crystal ATR optic element inside the plasma reaction chamber. The crystal was IR probed through a window in the chamber. A polymethyl methacrylate film was deposited at 65-W power, 0.2 Torr pressure and 30 sccm flow rate of monomer. Interestingly, the polymer as deposited continued to change its IR signature even after the plasma power was turned off. This is not uncommon in plasma induced reactions due to long-lived free radical species that continue to react.

In the above example, a known "polymerizable" monomer was reacted into a polymeric film.

Surprisingly however, plasma conditions can also create polymer films from materials that ordinarily do not form polymers by conventional wet chemistry techniques. Plasmas can fractionate feed gases that lack linkable sites into many new and reactive compounds that subsequently may polymerize. For instance, ethane (C₂H₆) in an rf plasma will deposit as a polyhydrocarbon that has a density approaching 1.6 g/cc.

The structure of plasma polymers can be varied by the use of co-reactants or the introduction of O₂, N₂, or NH₃ into the reaction chamber during polymerization. This technique is commonly employed to incorporate specific atomic species into the resulting polymeric material that may be missing in the primary monomer. Ammonia or acrylonitrile are used as the co-reactants during the deposition of films from a methane plasma to incorporate nitrogen.⁶ Similarly, hydroxyl and carboxylic acid functionalities can be incorporated by plasma co-polymerizing acrylic acid⁶ or ally alcohol with the primary monomer to provide oxygen and hydrophilicity.^{7,8}

Studies have developed correlations between the power input, the type of monomer feed gas used, and the gas flow rate to the density and type of active species in the plasma. These factors in turn determine the rate of deposition and the film structure.^{9,10} Depending on the monomer used, deposition rates typically range between 5 and 100 nm/min, at 100 W rf power levels and monomer flow rates of a few sccm.¹¹ Benzene is observed to have a relatively high deposition rate¹³ even though it lacks a conventional polymerization linking site, and, thus, would not form a polymer under usual wet chemical means. The properties of materials polymerized in this manner can be very different from polymers obtained from these same materials via conventional, wet

chemical polymerization methods (if indeed, such polymers can even be made by wet chemical means).

The physics and chemistry of plasma polymerization processes have been described in sufficient detail elsewhere for the interested reader.¹⁰⁻¹³

SUMMARY

The modification that occurs to a polymeric material by exposure to a plasma is largely determined by: (1) the process gas(es), (2) the exposure time to the plasma, (3) the energy and power densities, and, to a lesser degree, (4) the original composition of the surface. Types of modifications span from relatively simple surface morphological roughening or smoothing changes, to complex grafting of radically different functional groups or molecular moieties, to totally enveloping coatings that completely alter the surface properties of the bulk material. Free radical chemistry appears to be the dominant mechanistic pathway for achieving most surface modifications. In spite of the high complexity of the ensuing chemistry in a typical plasma, it is possible to tailor the process to perform specific targeted changes to polymeric surfaces.

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* Chapter IV of **Plasma Processing of Advanced Materials**, edited by George A. Collins and Donald J. Rej, MRS Bulletin, August 1996