Cold Gas Plasma Treatment
For Re-engineering Films

by Stephen L. Kaplan, 4th State, Inc.

With cold gas plasma treatment you may not have to trade one critical quality for another when treating your film or web.

It is fair to say that the selection of a plastic is usually a compromise or a balance of bulk versus surface properties. If the surface of a plastic can be altered down to a depth of just a few molecules, it can make a profound difference in the plastic's suitability for a broad range of applications.

Using a cold gas plasma reactor to redesign the surface by just a few angstroms is an economical and environmentally safe method to change the basic polymer film in many manufacturing applications.

The engineering properties of plastics (abrasion resistance, heat tolerance, strength, and cost) are the primary reasons for selecting a resin. However, secondary engineering characteristics are assuming more critical importance.

In the case of films, designers often must select specially formulated and expensive polymeric materials, or combinations of materials. to provide an appropriate balance of properties. In some cases the polymer that exhibits the desired surface properties lacks the primary engineering attributes.

Often, the requirement is to provide a barrier against gas or liquid permeation through the film, necessitating the use of a costly multilayer construction when a simple coating, properly adhered to the surface, would be a more cost-effective and desirable route. Entire product concepts have been abandoned due to the inability to cost-effectively balance the primary engineering requirements of the bulk structural component with the secondary requirements of chemical inertness, bondability, or barrier characteristics. Whether the engineering problem involves the bonding of two polymers by lamination or multilayer extrusion, the adhesion of applied coatings, or the deposition of barrier coatings to polymer surfaces, gas plasma treatment may offer significant advantages.

Treatment Techniques

Any process that changes the polymer must not change the bulk properties, or the plastic may lose its primary physical and chemical characteristics. Prior to gas plasma treatment, various techniques were developed for such partial re-engineering, including: mechanical abrasion, acid etch (or other chemical/solvent treatment), and corona discharge.

Abrasion is usually accomplished by sand, grit, or bead blasting where a stream of particles is shot at the plastic by high-pressure air. This technique, while appropriate for molded components, is not truly amenable to film or webs (although, premium films such as Kapton® have been known to be "pumiced" to improve adhesion). Also, abrasive blasting is a dirty process.

While cleaner than mechanical abrasion, solvent or chemical etch is often only marginally effective at promoting adhesion. Removal of and drying of the solvents/chemicals adds further process steps and usually constitutes a toxic waste disposal problem and cost.

Corona treatment is a very cost-efficient treatment method, but it is not effective on many substrates. This very-high-voltage electrostatic discharge technique can also thermally damage the treated material. Because of the high heat generation, treatment is conducted at high speeds. While it is cost-effective, the residence times are insufficient to permit penetration of the active species that effect change into the fiber bundles or interstices of non-woven webs and fabrics. And, since corona discharge systems depend on ionizing free air, the process may not produce consistent results from day to day, season to season, and location to location. Electrostatic discharge produces ozone as an effluent, which must be properly processed, adding to the cost of the treatment process.

Controllable, Reproducible

As early as 1969, claims were made for improved bondability of high density polyethylene, nylon, and polypropylene by exposing their surfaces to a cold plasma of partially-ionized gas 1.2.

Even better, the surface modification did not affect the character of the base material beneath the surface. Bond strength was shown to have improved after such treatment to the extent that failures most often occurred in the unmodified base polymer rather than at the interface. The process was found to be controllable with excellent reproducibility and without any noxious byproducts.

Over the past quarter century, the technique of re-engineering polymer surface properties through exposure to a gas plasma has been extended to virtually all polymers. Producible effects run the gamut from highly wettable surfaces exhibiting superior adhesion characteristics and chemical reactivity to completely unwettable, inert surfaces.

More sophisticated plasma processes permit dissimilar polymers to be "grafted" onto the bulk polymer chain, or the deposition in-situ of a micro-thin coating via plasma polymerization. Plasma polymerization provides pinhole-free films that adhere tenaciously to the substrate.

The Cold Plasma Process

Cold plasma is a partially ionized gas composed of ions, free electrons, and various neutral particles. The process is initiated by placing the polymer in a closed, evacuated chamber (Figure 1). The selected gas to be ionized is then released into the chamber under a partial vacuum and subjected to an electromagnetic field (radio frequency field). Within the rf field, the gas molecules are excited into a "soup" of free electrons and neutral atoms in a metastable state with a broad distribution of energy levels. It is the response of these reactive species with the polymers placed in the plasma that results in the chemical and physical modification.

In a cold gas plasma system the electrons display a broad range of energies, with a mean energy level to around 5 electron Volts (I eV ˜11,600 deg K). Although energetic, the electrons embody only a tiny fraction of the thermal mass of the ions and neutral atoms within the plasma. As a result. the plasma remains relatively cool - around 300o deg K (23o deg C).

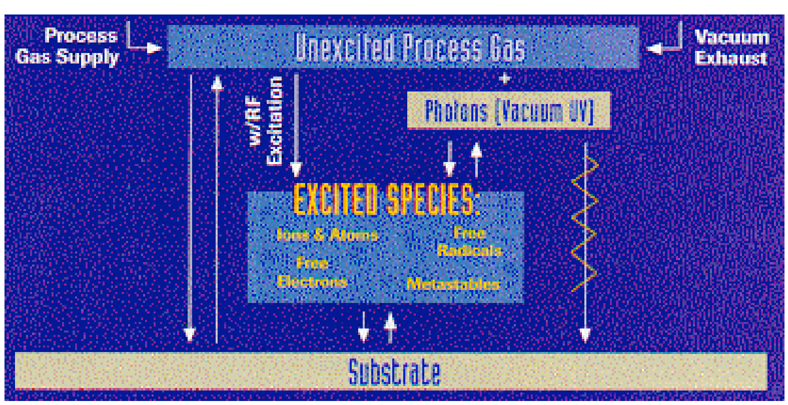

Figure 1.

Polymers In Cold Gas Plasma

For any gas composition, three simultaneous processes alter the outer molecular layers of the polymer: ablation, crosslinking, and activation. The effect of each depends on the chemical nature of the gas plasma and the polymer.

1. Ablation is literally "boiling off" of the outer molecular layer of the polymer surface by the bombarding energetic plasma particles. Charged particles (free radicals, electrons, and ions) and ultraviolet photons break the covalent bonds of the polymer backbone, resulting in fragmented polymer chains of a much lower molecular weight.

   As long molecules become shorter, the volatile oligomer and monomer byproducts ablate and are swept away with the outgoing vacuum pump exhaust. Ablation can be very effective in cleaning metal foils or fabrics as well as conventional polymer films, removing contaminants (such as mold-release or process oils), or in removing weak boundary layers.

2. Crosslinking is forming covalent bonds between adjacent polymer chains, ideally in an atmosphere such as argon or helium. The inert gas is ionized and the covalent polymer bonds are broken at the polymer surface, 10 to 40 Å deep.

   Since there are no free radical scavengers in an inert gas, one of three things can occur in the inert plasma: The dissociated molecule can simply revert to its previous state by recombining; it can react with an adjoining free radical within the polymer chain, forming a double or triple bond; or it can form a bond with a nearby free radical on an adjacent chain (this occurrence is crosslinking). Crosslinking may strengthen certain polymers, retard the migration of additives (blooming), and/or modify the permeation characteristics.

3. Activation results when different atoms or chemical groups from the plasma are added to the surface molecules of the treated plastic surface. As with ablation, surface bombardment by energetic particles breaks the polymer chain or extracts pendant groups or atoms such as hydrogen, forming free radicals.

Similarly, high-energy UV photons emitted by excited free electrons in the plasma have sufficient energy to break carbon-carbon and carbon-hydrogen bonds in the polymer chain, also creating free radicals on the polymer surface. Active species within the cold plasma react with these sites to obtain thermodynamic stability resulting in changed chemistry at the polymer surface

With activation, the surface energy of a polymer can be increased by employing an oxygen-rich process gas, or it can be decreased by employing a process gas with a high fluorine content. Selection of the gas and the process parameters permits the polymer surface to be specifically tailored to promote or prevent wetting and adhesion.

Activation and Reactions

The effect of a plasma on a given material is determined by the chemistry of the reactions between the surface and the reactive species present in the plasma. At the low-exposure energies typically present in glow-discharge plasma systems, the interactions occur only in the top few molecular layers. The majority of activation processes are related to preparing the surface for subsequent operations (such as printing or altering the surface wetting characteristics).

Gases, or mixtures of gases, used for cold plasma treatment of polymers include air, nitrogen, argon, oxygen, nitrous oxide, helium, tetrafluoromethane, water vapor, carbon dioxide, methane. and ammonia. Each gas produces a unique plasma composition and results in different polymer surface properties.

For example, the surface energy that is analogous to wettability and chemical reactivity can be increased very quickly and effectively by plasma induced oxidation, nitration, hydrolyzation, or amination. Conversely, plasma induced fluorination depresses surface energy, producing an inert and nonwettable surface.

The Gas Plasma Reactor

The physical process of cold gas plasma surface treatment is as straightforward and easy to describe as the equipment is to operate. The reactor is a combination of a vacuum chamber with vacuum pump and purge plumbing, a source of electromagnetic energy (rf generator), process gas sources and regulators, and a system controller to orchestrate the process.

In the pilot line operated at this company, the roll product to be treated (up to 60 in. width and 19 in. package diameter) is loaded in the payoff chamber and threaded through the chamber to the take-up reel. The plasma treatment operation is then initiated and entirely controlled by the push of a single button.

The process steps are: 1) pump down to predetermined vacuum pressure (base pressure); 2) introduce a process gas and stabilization at a desired process pressure; 3) initiate the plasma by providing rf energy; 4) transport product through the system; 5) after treating the desired length, shut rf power and process gas delivery; 6) pump down to base pressure to eliminate residual process gas(es); 7) vent to atmosphere; 8) remove treated product. (See Figure 2.)

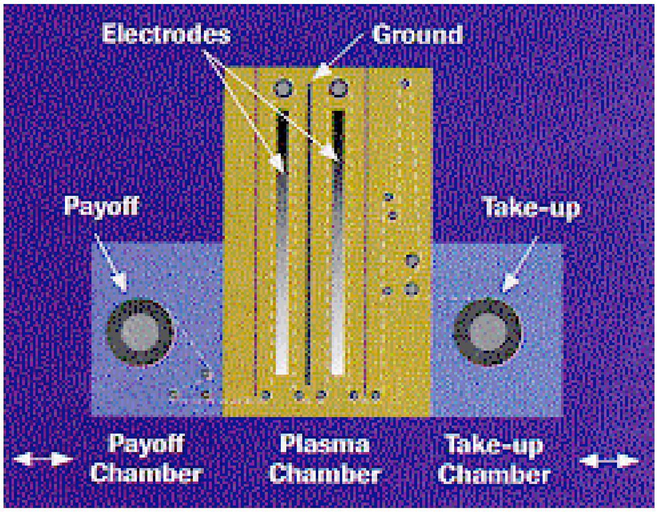

Figure 2

Some Examples

One of the more common plasma processes used to enhance adhesion among polymers involves treatment of the polymer surface in an oxygen-rich plasma.

An oxygen plasma surface modification increases the surface energy of the polymer, resulting in improved adhesive bondability of the modified surface. Engineering films are so treated to enhance the adhesion-and thus permanency of silk screened graphics as well as subsequently applied scratch-resistant coatings.

Gas plasma is also being used to improve me wetting by blood of membranes used in dialysis treatment, thereby increasing their efficiency.

Plasma film deposition, also referred to as plasma polymerization, offers an entirely new avenue for the surface engineering of polymers and inorganic substrates as well. When the process gas contains more complex molecules, these molecules are fractured into free radical fragments. These free radical fragments then become sites for initiating polymerization.

As the molecular weight of the polymerized molecule increases, it is deposited on the substrate placed within the reactor chamber. Plasma formed polymers have been created from a wide variety of monomers, from simple hydrocarbons such as methane, ethylene, and propylene, as well as their fluorinated analogs, to organosilicon compounds such as hexamethyldisiloxane and vinyltrimethylsilane.

Due to the complex nature of the fragmentation process, the resulting polymer structure is usually unlike any that can be produced from conventional polymerization mechanisms. Optimization of process parameters such as pressure and power provides a reproducible process capable of depositing a very uniform film, free of anomalies.

Economics vary widely with the process. Residence time in the plasma may vary over a considerable range. Since the process does not subject the substrate to temperature, long processes are possible.

Depending on the specific effect desired, throughput rates vary from 10 to 300 fpm. At a single day laboratory fee of $300/hr, the cost would thus vary from $0.01 to $0.10/sq. ft. Production contract treatment costs are substantially reduced. Cost of $3/1,000 sq. ft are possible if the customer purchases his or her own system.

On the environmental front, the state of California has certified plasma processes as typically practiced for the modification of polymers to be a "pollution prevention technology" that is both environmentally and workplace friendly.

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