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New UV/ozone treatment improves adhesiveness of polymer surfaces

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TECH PAPER

TREATING HYDROPHOBIC POLYMERS WITH ULTRAVIOLET LIGHT AND OZONE GREATLY INCREASES POLYMER SURFACE ENERGY.

For most polymers, the outermost surface is hydrophobic due to a preponderance of nonpolar bonds and is difficult to wet. Many of the paints, adhesives, and printing inks used to coat polymer products are hydrophilic. They do not form strong chemical interactions with a hydrophobic polymer surface, and cannot properly adhere. Thus, there is a real commercial incentive to develop methods capable of modifying the outermost surface of the polymer in order to improve its adhesion.

Modification processes usually involve the incorporation of oxygen, and/or nitrogen into the surface of the polymer. This enables the formation of stronger interactions between the surface and the coating, improving adhesion without affecting bulk properties.

The main gas-phase techniques for modifying polymer materials involve excited state chemistry processes such as plasma glow discharge, corona discharge, or flame treatment. Plasma glow discharge is currently under intense study and a number of commercial processes have been introduced in Japan and Europe. However, the processes are expensive and complex because they require a high vacuum to create the plasma (ionized gas) needed for operation. Therefore, plasma glow discharge is applied only to high value-added materials.

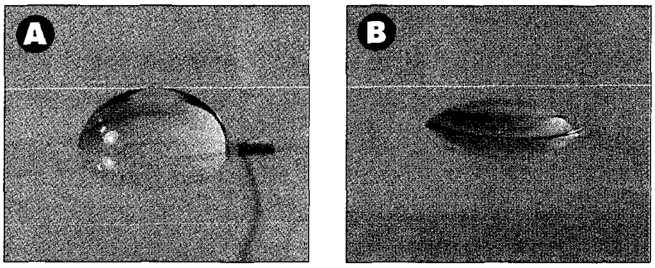
By contrast, corona discharge is an ambient air process which does not require a vacuum. However, the process is difficult to apply to 3-D objects. Flame treatment is a low-cost process, but it can be uneven when used on 3-D objects and unsuitable for materials that are sensitive to high temperatures.

Recently, an alternative surface modification process that also uses excited state chemistry has been developed in Canada (Ref. 1). This process exposes the polymer surface to both ultraviolet light (UV) and ozone to increase the number of oxygen-functional groups. This UV/ozone (UVO) approach appears to overcome many of the negative features of other surface treatments, especially for 3-D objects.

The UVO process has been tested on polypropylene (PP) and polyethylene terephthalate (PET) substrates. Both materials show relatively rapid and reproducible uptake of surface oxygen functional groups with UVO exposure. Attachment of oxygen groups greatly changes the surface energy and can lead to improved adhesion of paint and other materials. Results show that the UVO technique can change the surface properties of polymers economically.

How does UVO work?

The major process development has been targeted at the treatment of 3-D plastic components. These are suspended or tumbled inside a reactor chamber at room pressure and temperature, while exposed simultaneously to UV (mercury) light and various concentrations of ozone (O_3) gas. The chamber is usually cylindrical, with mercury lamps lining its periphery, such that all surfaces of the components



Water droplet A is on untreated polypropylene; droplet B is on polypropylene that was treated for 10 minutes with UV/ozone. The significantly lower contact angle in B demonstrates the increase in surface energy and wettability. [Photo, Ian Craig]

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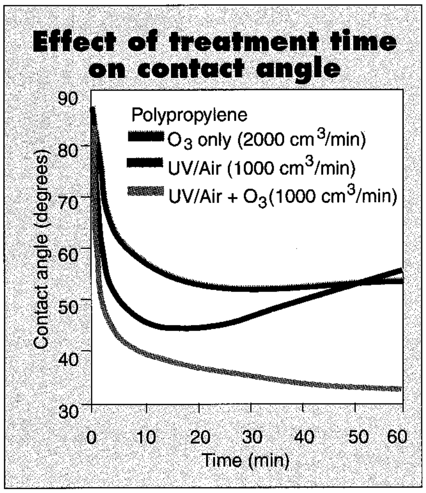
receive some exposure. Most of the ozone gas is supplied by an attached commercial generator which uses an electrical discharge to create O_3 in an airstream. Ozone level is varied by adjusting the air flow and is monitored spectroscopically. Air exiting from the reactor contains ozone and can be exposed to an "ozone killing" lamp which converts O_3 to normal oxygen.

A prototype UVO reactor has a reaction volume of 3.5 ft.^{3} and a bank of low pressure mercury vapor lamps with a total power of 200 W. The important UV wavelengths emitted by the lamps are 185 and 254 nm. A rotatable cage placed in the center of the reactor can hold up to 50 flexural bars at a time and tumble them to achieve maximum UVO exposure.



Effect of treatment time on contact angle

Based on experimental results from a small reactor, treatment times can be as short as 5 min. depending on the polymer. There is no significant pre- or post-treatment waiting period. Residual ozone is removed in a 60 sec. exposure to the "ozone killing" lamps.

Two different analytical techniques are used to measure the change in polymer surface chemistry. One of these, contact angle goniometry, indicates the change in surface energy by measuring the angle made by a droplet of water receding or advancing on the treated polymer surface. A hydrophilic (high energy) surface allows the droplet to spread due to the attraction caused by the higher number of oxygen functional groups attached to the surface. A reduction in the contact angle results as the treatment alters the surface (photos).

The second technique, X-ray photoelectron spectroscopy (XPS) directly measures the concentration of oxygen functional groups that have bonded to the surface as a result of the UVO surface treatment. Moreover, XPS can indicate the nature of the chemical bonds formed by the oxygen atoms.

UVO boosts surface energy

Changes to the near-surface chemistry of PP have been followed as a function of UVO treatment time. The contact angle changes rapidly in the first 5 minutes of UVO exposure (graph). During this time, the surface oxygen/carbon atomic ratio (O/C), as measured by XPS increases from 0 to about 0.05. This is equivalent to attaching an oxygen functional group to between 20-40% of all PP carbon atoms on the outermost surface. Similar results have been obtained with treated PET specimens. Since PET already has oxygen in the polymer structure, the *change* in O/C compared to the original composition increases dramatically with exposure to UVO for 2 min.

Ozone treatment, without UV radiation present, also results in surface functionalization, but the reaction times are longer. This treatment could still be practical for treatment of very large sample charges where time is more flexible. It is thought that the products of ozone-only reactions last longer than the groups generated at surfaces treated by UVO. Other surface chemistries for ozone-treated polymers may be possible to fabricate.

The stability of PP surfaces treated by UVO is very high. Relatively little change occurs in the receding contact angle on a PP surface that has been aged in air for a period of up to 28 days. Changes that take place in the surface chemistry during this period are not significant. In addition, the UVO modification of the polymer extends to depths of up to 1 micron. The extent of plasma treatment is usually shallower.

Additional ozone source

UVO has been used in the semiconductor industry to remove carbon contamination from wafer surfaces (Ref. 2). The technique produces ozone as a byproduct of the UV irradiation of oxygen in the vicinity of the target sample. The technology was not considered for modification of polymer surfaces because the reaction rates were too slow. The work reported here has shown that realistic reaction rates (order of minutes) can be achieved by adding an external source of ozone in addition to that produced in situ by UV radiation. The primary mechanism of surface functionalization appears to occur via atomic oxygen arising from the decomposition of ozone by UV radiation. The photodecomposition of ozone occurs primarily between 200 nm. and 308 nm. This is similar to some of the plasma-based processes (Ref. 3), but in the case of UVO, far fewer side reactions are present.

UVO technology for plastic surface modification appears to offer a number of advantages over related processes:

- ■ The equipment needed is simple and inexpensive
- ■ The equipment can be safely operated by nontechnical personnel
- ■ No chemical reagents are required
- ■ There are no residual polluting byproducts
- ■ The process has the potential to effectively modify the surfaces of 3-D objects.

While the reaction times are longer than those used with plasma, this can usually be overcome by batch processings. *–Edited by William A. Kaplan* ❑

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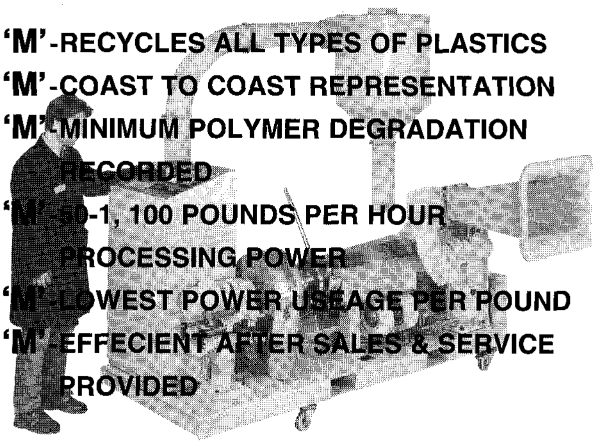

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