

### ***Effects of Electric Discharge Surface Treatment on the Diffusion Characteristics of Polymers***

The surface characteristics of polymers can be altered by exposure of the polymer to the plasma formed in a low-pressure electric discharge. If the discharge is sustained in an inert gas such as argon, the polymer surface exposed to this discharge is crosslinked. This process is widely known as CASING (crosslinking by activated species of inert gases).<sup>1</sup> If, on the other hand, the inert gas is replaced by an organic or organometallic vapor, a highly crosslinked polymer film is deposited on the substrate surface. Such films are very thin (of the order of several hundred angstroms to a few microns), pinhole free, and generally insoluble in common solvents.<sup>2</sup> The purpose of this communication is to examine the effects of these two types of electric discharge treatment on the diffusion of low molecular weight substances through polymers.

The first application which was considered was the reduction of the effusion or leaching of low molecular weight substances from polymers used for prosthetic implants. The literature<sup>3</sup> indicates that the release of materials such as plasticizers, antioxidants, initiators, residual monomers, and degradative products can cause harmful effects to the body of the host. Five polymers were chosen for treatment. Four of these were commercial samples of polypropylene (Calgard Co.), poly(ethylene terephthalate) (Hughes Plastics Co.), poly(vinyl chloride) (Ellay Rubber Co.), and poly(dimethylsiloxane) (Dow Corning Corp.) and were used as received. The other sample, poly(methyl acrylate), was polymerized by ultraviolet radiation using benzoin as the photoinitiator. Dioctyl phthalate, 10%, was added as plasticizer, and 1% ethylene glycol dimethacrylate was added as crosslinking agent. All monomers were purchased from the Borden Chemical Co. Prior to treatment, samples were cleaned by washing in Haemo-sol solution (Meinecke Co.), rinsed with distilled water, and dried in a vacuum oven. The discharge apparatus used was the same as that described previously.<sup>4</sup>

The determination of the leaching or removal of low molecular weight materials was carried out by sealing the sample in an ampoule containing a simulated body fluid known as pseudoextracellular fluid (PECF).<sup>5</sup> This solution has the composition of a body fluid minus the proteins. The ampoule was then autoclaved at 115°C at a pressure of 31 psia for 62 hr. Upon cooling, the ampoule was broken and the solution was filtered. The solution was then shaken with carbon tetrachloride to extract the dissolved organic liquids. The amount of extracted material was determined by infrared spectroscopy.

Figure 1 shows the effect of CASING produced by an argon discharge on the fraction of impurities ( $\phi$ ) that can be leached out by PECF;  $\phi$  is defined as the amount of impurities leached from the treated polymer divided by that leached from the untreated polymer. In all instances, the percentage of low molecular weight moieties released by the material is reduced by CASING, and the extent of reduction is increased with increasing exposure time  $t$  to the plasma. The effectiveness of this reduction depends on the polymer. Poly(methyl acrylate) showed a 31% reduction after being subjected to discharge for 60 min at a pressure of 1.5 torr and power of 80 watts. Similar treatments were much less effective for polypropylene and poly(ethylene terephthalate).

Exposure of a polymer to an inert gas alters the polymer surface by inducing crosslinking but does not affect the chemical nature of the polymer. A more drastic surface modification would be the deposition of a layer of polymer with a different chemical composition. This can be achieved by feeding ethylene gas into the glow discharge. As shown in Figure 2, deposition of a thin film of highly crosslinked polyethylene is more effective than CASING in preventing impurities from being leached out of poly(methyl acrylate) and poly(ethylene terephthalate). The effectiveness of the treatment depends on the discharge operating condition. At 100 watts and 2.0 torr, a 60-min treatment produced a 95% reduction in impurities extracted by PECF, whereas at 80 watts and 1.8 torr, the same treatment is only 50% effective. The reason for this difference may perhaps be attributable to the formation of a more uniform film over the

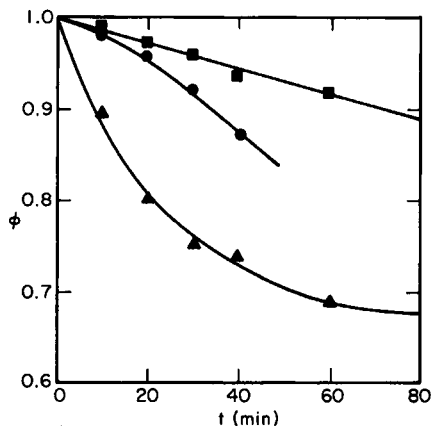


Fig. 1. Fractions ( $\phi$ ) of impurities released from polymers treated by CASING in argon, plotted as a function of the duration of treatment ( $t$ ). Squares: polypropylene; circles: poly(ethylene terephthalate); triangles: poly(methyl acrylate).

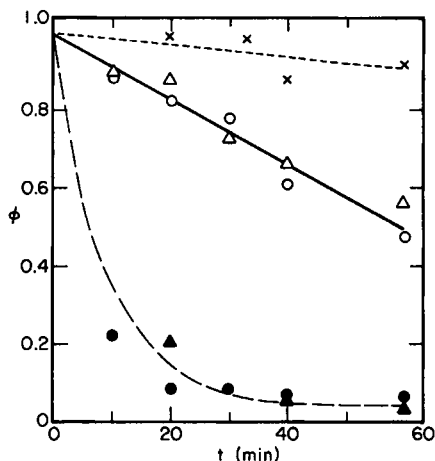


Fig. 2. Fractions ( $\phi$ ) of impurities released from polymers treated by glow discharge in ethylene plotted as a function of duration of treatment ( $t$ ). Crosses: poly(vinyl chloride); filled circles: poly(ethylene terephthalate); filled triangles: poly(methyl acrylate) plasticized with dioctyl phthalate. All treated with ethylene plasma at 2.0 torr pressure and 100 watts power. Open circles: poly(ethylene terephthalate); open triangles: poly(methyl acrylate) plasticized with dioctyl phthalate, treated at 1.8 torr and 80 watts.

entire sample surface under the former set of conditions. It has been shown in a previous publication<sup>4</sup> that under certain conditions of plasma polymerization, a powder or an oil rather than a film will be deposited on the substrate. Such conditions cannot, of course, be expected to produce effective diffusion barriers to the low molecular weight moieties present in the polymer.

Figure 2 also shows that the nature of the substrate is important in the deposition of plasma-polymerized ethylene. For instance, the effect is nearly the same for poly-

(methyl acrylate) and Mylar. However, similar treatment produces practically no reduction in the percent of extractable material for poly(vinyl chloride). The role of the nature of the substrate has been previously noted in the literature.<sup>6</sup> However, its mechanism remains obscure at this time.

Another possible application of glow-discharge surface treatment is the erection of a diffusion barrier to gases. Poly(dimethylsiloxane), for instance, is highly permeable to gases. The permeability of these gases through the polymer membrane can be controlled by either CASING or ethylene polymerization. We have determined the permeabilities of oxygen through silicone rubber membrane by using a permeation cell. Nitrogen was used as the carrier gas, and the amount of oxygen permeated was

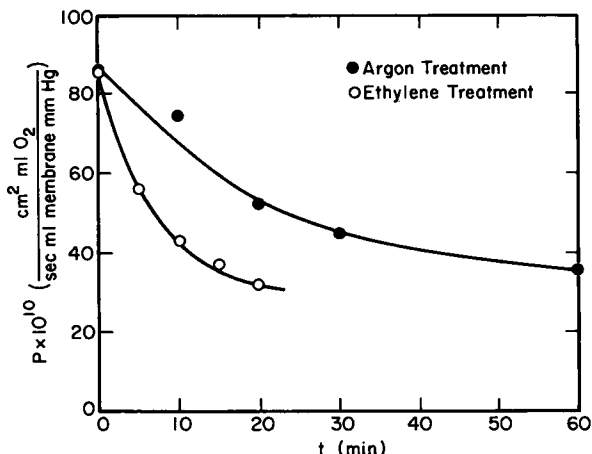


Fig. 3. Permeability coefficient ( $p$ ) of oxygen through poly(dimethylsiloxane) treated by argon and ethylene plasmas at 2.0 torr pressure and 100 watts power plotted as a function of duration of treatment ( $t$ ). Filled circles: argon treatment; open circles: ethylene treatment.

measured with a Servomex Type OA-150 oxygen analyzer. As seen in Figure 3, the permeability coefficient of oxygen through silicone rubber decreases with increasing exposure time to the plasma. Again as expected, the deposition of a thin layer of polyethylene film was more effective than CASING in argon.

In conclusion, these preliminary data show that glow-discharge surface treatment appears to be a potentially useful tool in changing the diffusion characteristics of liquids and gases through polymers. Its effectiveness depends on the nature of the plasma, the type of the surface treated, and conditions of the discharge.

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