PLASMA TREATMENT OF POLYMERS TO IMPROVE ADHESION OF METALS OR DIELECTRICS

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1. Introduction

The use of polymers in high-technology and in consumer-product applications is growing steadily on account of the many attributes offered by these synthetic engineering materials. Those attributes include high strength-to-weight ratio, resistance to corrosion, relatively low cost, recyclability, and others; however, polymers also have certain inherent drawbacks, which can render manufacturing operations difficult. One such hurdle is the low surface energy of polymers and their resulting poor adhesion [1-3], where the term "adhesion" may be defined as the mechanical resistance to separation of a system of bonded materials. Because adhesion is largely a surface property, it is possible to modify the near-surface region of polymers by a variety of methods, thereby improving their adhesion without affecting desirable bulk properties.

Such methods include mechanical roughening; wet-chemical treatments with solvents, strong acids or bases, etc; exposure to flames, energetic photons, ion beams and other types of ionizing radiation, and corona discharges [1-3]. The present contribution deals with a relatively "new" method, exposure to low-pressure "cold" plasmas, which has numerous (technologically important) advantages over the above-mentioned techniques [4-6].

2. Interaction of Plasmas with Polymer Surfaces

Low-pressure glow discharge plasmas, regardless of the type of feed-gas used, comprise a complex mix of charged and neutral particles, and photons: The primary species, hot electrons, fragment or ionize feed-gas molecules via inelastic collisions, thereby creating ions, excited molecules, and molecular fragments (radicals) which are generally far more chemically reactive than the initial ground-state molecules. Energetic photons (emitted by certain excited species) can contribute an important photochemical component to this already complex plasma chemistry.

Plasmas interact strongly with polymer surfaces, largely through two main types of phenomena:

a) Plasma "etching", or removal of material from the treated surface via the formation of volatile reaction products; and
b) surface modification; here, surface-specific properties (eg adhesion) can be drastically altered via other processes, discussed below.

Processes (a) and (b), in turn, give rise to four main types of effects, namely

(i) cleaning (removal of adsorbed contamination on the polymer surface),
(ii) ablation, or etch-removal of polymer molecules, which can lead to micro-roughening;
(iii) cross-linking or branching of near-surface molecules, which can cohesively strengthen the sub-surface layer, and
(iv) modification of surface-chemical structure, that is, creation of new chemical functionalities; these can include different hetero-atoms, originating from the feed gases, for example O, N, F, Si, etc.

All these processes are present to some extent, and they often interact in synergy; however, one or the other can be made to dominate, depending upon the polymer, gas chemistry, reactor design, and the process parameters chosen by the operator.

3. Adhesion Enhancement to Polymers through Plasma Treatment

Figure 1 schematically depicts a layer on a plasma-treated polymer surface, where this overlayer may be an adhesive, another polymer (eg a layer of paint), or a vacuum-deposited thin film (metal, dielectric, ...). This diagram illustrates the important concept of an "interphase" [7], a region intermediate to the two contacting solids (bulk polymer and overlayer), that is distinct in structure and properties from both. The four effects described in section 2 above can be considered to have contributed in a synergetic manner to creating the depicted situation, and thereby to the overall mechanism of enhanced adhesion. For lack of space, we list below only a few selected aspects of this picture [4-6]:

(i) The creation of new (eg polar) surface moieties results in increased wettability of the treated polymer by a liquid adhesive or a paint.
(ii) The altered surface chemistry facilitates reaction of the overlayer with surface species during curing, to form covalent chemical bonds with the plasma-treated surface.
(iii) Surface acidity (or basicity), for example via plasma-induced oxidation or amination, respectively, can give rise to strong acid-base interactions with a deposit.
(iv) In the case of evaporated metals, the formation of M – O – C or M – N – C (M = metal) chemical linkages can give rise to very strong, permanent bonds which can resist extremes of temperature and corrosive environment.
(v) Intense ultraviolet (UV) or vacuum UV (VUV, $\lambda < 200$ nm) radiation from certain plasma constituents (eg hydrogen) can mechanically stabilize the interphase by crosslinking, to depths which can exceed hundreds of nm. For example, strong adhesion of Cu to He/N_2 – plasma treated Teflon PFA has been attributed to this effect.

There now exist commercial plasma reactors which exploit the processes described above in the treatment or pretreatment of a wide variety of polymers. These include flexible webs (polymer films, or textiles); filaments, yarns or fibres (for example those used in the manufacture of polymer-matrix composites); large plastic objects such as automobile bumpers, dash assemblies, and the likes; and treatment of large numbers of small plastic parts or particulates. The reader is referred to the literature for details about this large and increasing inventory of low-pressure plasma processes [6].

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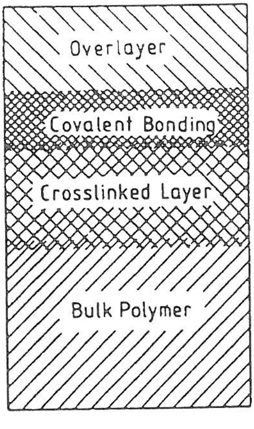

Figure 1 Schematic diagram of the interphase structure between an adhering overlayer and the plasma-treated polymer base