

## Achieving Mechanically Durable Coatings:

*General Discussion & Applications to Polymer Substrates*

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Engineering thin-film coatings to withstand abrasive and impact forces involves complex physics and chemistry problem solving. Hardness, internal and external bond strengths, and surface abrasive wear resistance, are physical properties determined by materials and deposition processes. An additional parameter is the relationship of the surface chemistries of the multi-layer interfaces and layer thicknesses.

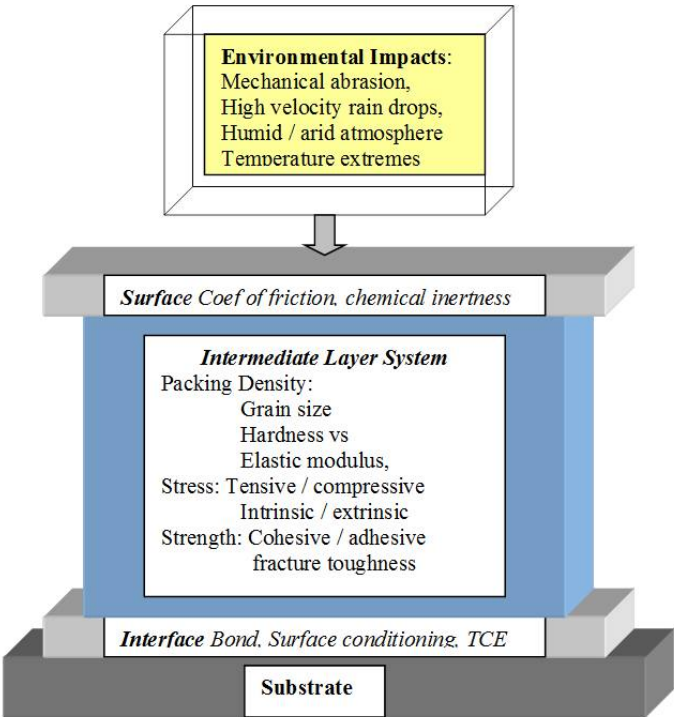
Coating of polymer surfaces poses special considerations imposed by temperature limitations and compositional, thermal expansion coefficient, and hardness differences compared with coating materials and deposition processes. We begin the discussion with a model that illustrates the construction and composition of a multi-layer coating designed for durability.

### Mechanical Properties Related to the Physical Durability of Thin Films

The mechanical hardness and wear resistance of coatings have been topics of extensive discussion in previous [Coating Material News](#) issues.

The model presented in *Figure 1* illustrates the multiple and inter-related components that influence and determine the hardness, strength, and wear properties of mechanically durable thin films. The model applies to any substrate material. Later we apply it to polymer surfaces.

*Figure 1. The functional locations of important mechano-chemical interfaces that produce mechanically durable coatings.*



Engineering a mechanically hard and durable coating begins at the substrate surface and involves the phenomena of nucleation and the characteristics of the film's nanostructure that promotes dense adherent growth. Nucleation density, and the establishment of interfacial bond strength, are functions of substrate surface energy. The kinetic and chemical energies of the arriving adatoms influence mobility on the surface and the initiation of surface bonds. High surface kinetic energy promotes 2-D coverage of the surface in advance of 3-D growth, thereby insuring a dense compact nanostructure as opposed to columnar growth with its characteristic large void volume.

Often a surface conditioning layer must be added to prepare the surface for chemical bonding, as discussed above for polymer compositions. When applying coatings to materials of dissimilar chemistry, specific metal oxides can be applied in thin layers to the substrate to form a chemically reactive interface bond. Specific fluoride compounds or mixtures are required to promote strong interface bonds on Infrared (IR) substrate materials such as Ge, ZnSe and ZnS. Another consideration that interferes with strong physio-chemical bonding is contamination. This must be removed prior to coating deposition.

Oil-free cryopumps are efficient at removing water from the coating atmosphere; note that low water content promotes chemical bonding. In addition to the chemical considerations, thermal expansion differences impose extrinsic stresses, and together with the internal stress of the multi-layer structure, need to be included in the total system stress analysis.

The Intermediate Layer System of the model in *Figure 1* provides the mechanical and optical properties required. The Intermediate Layer System is composed of sub-layers that, as a system, provide sufficient hardness and fracture toughness, and appropriate elastic modulus, to provide compliance for distributing and damping the Rayleigh shock loading caused by an impacting particle. This system will consist of multi-layers of alternating hard and elastic material components chosen to produce the durability required. Coatings materials that are hard often display high cohesion, but low adhesion. Similarly, they might possess a high degree of hardness, but be brittle or have high internal stress. Strong adhesive bonding between all layers of the AR coating is critical to achieving durability.

If sliding or impacting forces against the coating exceed the adhesive strength at layer interfaces, the film can fracture or detach. If the impacting force exceeds film cohesive strength, the film can be damaged. Ductile coatings are more likely than brittle coatings to maintain integrity (remain crack-free) and maintain adhesive bonds; therefore, layers with the appropriate elasticity modulus are integral components of our design. We know from published studies that to be mechanically resistant to high-velocity impact events, the protective coating design must include both hard and elastic layers [2]. Layers that possess high elastic moduli absorb and distribute the energy of the reflected Rayleigh waves that, if concentrated, can cause structural damage. The structural design of the coating will therefore include hard layers interspersed with layers of high moduli. Film modulus is determined to a large degree by film micro- and nanostructure. The deposition process and material composition are variables that require engineers to alter the film elastic modulus as required. The important properties, adherence, hardness, strength, and elasticity, would be balanced to produce the most durable coating.

Film thickness and shape of the substrate need to be considered for the protective coating of non-flat surfaces such as exposed lenses and domes. Durable films have thicknesses between 5 and 20  $\mu\text{m}$ , dependent on modulus and hardness balance as well as adhesive strength. Deposition chamber configuration will determine the angle of impingement of the materials on curved substrates, a parameter that influences the density and thickness uniformity of the film.

Finally, high resistance to abrasive wear requires an outer face with low coefficient of sliding friction. Abrasive wear resistance decreases rapidly with minor (microscopic) surface defects that are either inherent in the coating or that might be caused externally by micro-scratches or micro-particulate impact. The coating must be microscopically smooth and physically hard to resist micro-scratching during handling procedures and field operation. Surface defects will increase the coefficient of sliding friction, thereby permitting impacting objects to couple energetically and abrade or scratch the surface thus promoting coating fracture. Here again, a dense, hard, smooth film layer microstructure, such as that produced by high-energy deposition processes and advanced materials, is essential.

When high resistance to abrasive wear forces is needed, several interrelated ingredients are necessary beyond the requirement for a strong bond between substrate and coating. The coating layers must be physically dense to prevent the diffusion of moisture to the interface where it can weaken the adhesive bond strength or alter internal stresses. This generally requires that the film layers be amorphous in structure and without grain boundaries instead of polycrystalline, i.e. it must possess a packing density near that of the bulk form. The high kinetic energies present in the sputtering plasma and bombarding ions (IAD) increase the packing density of the layer and promote amorphous microstructure by discouraging crystalline microstructure. Deposition by ion beam sputtering (IBS) produces high quality dense layers but can result in stresses that exceed adhesion energies, and terminate in film failure (cracking and deadhesion). High surface energy is present denoted by high substrate temperature; for temperature-sensitive substrates, high adatom energies which are provided by energetic ions, promote dense microstructure. Special materials such as mixtures are able to be deposited at low temperature and grow with high packing density but low intrinsic stress.

Combining these essential components is the key to producing durable coatings with maximum abrasion and wear resistance, in addition to a high damage threshold to impacting forces.

#### **Coating Plastics to Achieve Adhesion and Scratch Resistance**

Optical polymers have wide optical applications because of their ability to mold complex shapes with precision surfaces at high volume. Plastic optical components are found in eyewear, instruments, cell phones and advertising displays, laminated windows, reflectors for automobile lighting, solar collectors, and many others. Injection-molded or form-cast polymer parts are now mass-produced as economical and light-weight replacements for glass parts.

The substitution of polymeric materials has required modification of traditional coating processes to be compatible with the lower temperature limitations of polymers compared with glass. As a consequence of softness, it is necessary to improve the abrasion and scratch resistance of coated polymer surfaces. Deposition processes and materials used to coat optics at lower temperatures have consequently been developed to respond to those needs.

### Adhesion Promotion for Polymers

Glass compositions consist of a high percentage of silicate compounds, therefore strong chemical bonds are formed between glass surfaces and typical silicate coating materials such as  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{LaTiO}_3$ , etc. Strong adhesive bonds are formed at the reactive interfaces between glass and oxygen-reactive metals such as titanium, nickel, and aluminum. Intermediate compounds, often sub-oxides of the metal, are formed that promote good adhesion. A metal layer 5 to 10 nm thick is sufficient, and will convert to a transparent suboxide with energetic bonding forces. The exact thickness of metal is dependent on system parameters such as partial pressure of oxygen present and the energy of the plasma present. Strong adhesion is related to high layer strength.

The majority of coating types applied to polymeric surfaces are anti-reflective (AR) and reflective metals. Durable coatings on commercial products such as ophthalmic AR coatings require scratch resistance as well as good adhesion. Designs, materials, and deposition processes have been developed to provide both functions to the level that such coatings appear in everyday applications. For some applications (e.g., eyewear), a polymer chemical hard coat is first applied to protect the polymer surface. The optical coating is deposited on top of the hard coat, and must itself be durable to withstand common handling and exposure. Metallization of plastic objects is often on the second-surface coating of the polymer, where the backside of the metal can be protected with a mechanically durable overcoat. In this case, the dominant challenges are the adhesion of the metal and the scratch-resistance of the incident side of the polymer substrate.

Adhesion of metals to polymers presents a complexity because of the chemical dissimilarity and often incompatibility between the polymer and the coated materials. Adhesion and scratch resistance require initial surface conditioning and intermediate chemical interfaces to form strong chemical bonds. A published study explored adhesive-promoting layers, and surface conditioning for different polymers that are often used for metallized products [1]. This study showed the importance of the specific metal adhesion layer and surface pretreatments on adhesion and fracture energies for common polymers. Injection-molded samples of acrylonitrile-butadiene-styrene (ABS), polycarbonate (PC), polypropylene (PP), and polyethylene terephthalate (PET) were coated and tested. The energies required to peel the coating from the surface and to fracture it were then measured. Metal layers were Cu, Ti, Cr, and Al, all sputter-deposited to 50 nm thickness. A 10  $\mu\text{m}$  layer of copper was electrodeposited on the adhesion metals for the peel test. The results using the four metals on ABS ranked the sequence of bond failure energies as follows:

$$\text{Al} > \text{Cr} > \text{Ti} > \text{Cu}.$$

The aluminum bond was 1.75 x stronger than the copper bond for ABS, and so forth. Process variables and internal stress levels involving cohesive vs adhesive strengths and surface preparation influence the results, as we shall see.

Strong adhesion requires modifying the surface chemistry to promote the creation of reactive groups on the metal – plastic interface. The researchers tested the role of the polymer type when coated with a Cr adhesion layer. The results are ranked:

ABS > PET-G > PC > PET > PP.

PET-G and PET have different compositions. ABS more easily forms metal-oxide bonds due to its functional C=O bonds and benzene rings. A measure of the effectiveness of this reactive chemistry is the water contact angle (see CMN V18 I4 (2008)). A low contact angle indicates high surface free energy (hydrophilic wetting), and correspondingly good adhesion. Atmospheric plasma pretreatment of the surface of PP with He/N<sub>2</sub> reduced the contact angle more than plasma pretreatment with He/O<sub>2</sub>. Sputter etching of PP surfaces with argon ions immediately before deposition produced slightly better adhesion and fracture-results than plasma etching. The reason may be that there is the possibility of surface textural modification during installation in the coating system after the atmospheric procedure. We will examine in detail the physics that determine the mechanical properties of thin films.

### Improving the Scratch Resistance of Polymers

Polymeric materials are soft and therefore require a coating to improve their resistance to abrasive damage. However, the model would apply to any material that requires an optical coating. Mechanical properties such as: modulus of elasticity, fracture strength, and hardness of the substrate and its coating, determine the ability to resist scratching up to specific forces. Resistance to scratching is tested by moving contact with an indenter point at different force loads. The Rockwell indenter of 200 μm is typically used. The force at which the coated surface develops transverse cracks is termed the critical load that induces failure. Aside from the structural properties mentioned, the coef of sliding friction of the coating affects the coupling of the applied force into the system. Compared to glass surfaces, plastics are many times softer, suffer larger plastic deformation, and have a higher coef of sliding friction. Plastic surfaces also must be hardened in order to endure abrasive wear imposed by cleaning and sand erosion. Scattered light increases with exposure, and this can be measured with the Taber abraser test, sometimes referred to as a 'haze meter.' Thin layers of metal oxides are applied to overcome the properties of the bare polymer surface, by producing a new surface with more durable mechanical properties.

Window and display applications that use polymers, such as those mentioned in the previous section, are generally coated with thick sputter-deposited protective silica, SiO<sub>2</sub>, layers. A study determined that the scratch and wear resistance of polycarbonate varies for different thickness of AC magnetron sputtered SiO<sub>2</sub> [2]. The critical load at which transverse cracking (spalling) occurred was ~3 N for thickness 0 to 1 μm. A thickness of 2 μm was required to increase the critical load to 5-6 N. Increasing the thickness to 4 μm doubled the critical load for the onset of cracking. Scatter (haze) decreased from 60% for the uncoated PC surface to 40% for a thickness of 1 μm, and to 15% for 2 μm SiO<sub>2</sub> thickness, and only slightly decreased for greater thickness.

**Future Challenges**

The rapid development of coating deposition technology and specialty coating materials prepares the industry to take on new challenges. We have presented some of the special considerations that must be taken into account for coating of polymer surfaces. Issues such as adhesion, durability and scratch resistance have greater weight when working with polymeric surfaces compared to glass. Materion Advanced Materials offers a [range of wear resistant thin film deposition materials](#) that offer superior protection against abrasion, corrosion and more.

**References**

1. Ferreira, O. Dos Santos, A. Stevens, and C. Schrauwen, Thin Solid Films, V517, 3070 (2009).
2. Boentoro, W., A. Pflug, and B. Szyszka, Thin Solid Films V517, 3121 (2009).

Some past discussions in Newsletter Archives of [Coating Materials News](#) (CMN) that may be of interest include: adhesion in V7, Issue 7 (1997); types of polymers and processes in V15 I4 (2005); general coating treatment in V10 I4 (2000). Further background is provided in the article on surface cleaning: V18 I4 (2008). The third topic discusses the growth of titanium dioxide layers on polycarbonate. CMN V17, I1 (2007), CMN V16 I1 (2006), CMN, V18 Issue 2 (2008), CMN V15, I1 (2005) and references contained therein.

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