Adhesion and Scratch Resistance of Coatings on Plastics

Introduction

This issue discusses three topics, two having to do with the coating of polymeric materials for optical applications; the third is related to an alternate material to ITO as the transparent electrode for solar cells.

Progress on these topics is occasionally updated in Coating Materials News (CMN) issues since polymer substrates are being used with greater frequency in displays, solar panels, laminated window glazing, reflectors for illumination, and *other optical applications. 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 coating processes to accommodate lower abrasion resistance compared with those of glass surfaces. Processes for applying optical coatings with improved adhesion and scratch resistance at lower temperatures have been developed. Previous discussions in CMN deal-* *ing with the coating of polymer surfaces may be obtained on the Technical Publications selection at www.cerac.com. Some past discussions include: adhesion in V7, I7 (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).*

Adhesion Promotion for Polymers

The majority of adhesion issues involving polymers are with AR and metallization coatings. Durable coatings on commercial products such as ophthalmic AR coatings require scratch resistance as well as good adhesion. Therefore, such coatings are designed and processed to provide both functions. Chemical hard coats protect the polymer lens surface, but the optical coating on top of the hard coat must itself be durable to handling and exposure. Metallization on plastic objects is often a second-surface coating where the coating can be protected with a mechanically durable overcoat, and in this case adhesion is the dominant challenge.

Adhesion between metals and polymers is difficult because of the chemical incompatibility of the two materials. In the case of glass (silicate) surfaces, intermediate compounds, generally suboxides, can be formed to promote adhesive bonding. Polymer surfaces require not only intermediate chemical interfaces, but initial surface conditioning to form strong chemical bonds. A recent study explored adhesive-promoting layers, surface conditioning, for different polymers that are often used in metallized products [1]. Injection molded samples of Acrylonitrile-butadine-styrene (ABS), polycarbonate (PC),

polypropylene (PP), and polyethylene terephthalate (PET) were tested. The energies required to peel the coating from the surface and to fracture it were measured. Metal layers were Cu, Ti, Cr, and Al, all sputter deposited to 50 nm thickness. A 10µm layer of copper was electrodeposited on the adhesor metals for the peel test. The results using the four metals on ABS ranked the sequence of both failure energies as follows:

$$Al > Cr > Ti > Cu$$

The aluminum bond was 1.75 x stronger than the copper bond for ABS.

Improving the Scratch Resistance of Polymers

The mechanical hardness and wear resistance of coatings have been topics of extensive discussion in past CMN issues [2]. The model presented in the referenced issue illustrates the multiple and inter-related components that contribute to and determine the hardness, strength, and wear properties of mechanically durable thin films. Polymeric materials are soft, and therefore require a coating to improve their resistance to abrasive damage. Mechanical properties: 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 coefficient 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 coefficient of sliding friction. Plastic surfaces also must be hardened to 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 polymer such as those mentioned in the previous section are generally coated with sputter-deposited silica, SiO_2, layers.

A recent study determined the scratch and wear resistance of polycarbonate for different thickness of AC magnetron sputtered SiO_2 [3]. 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. Doubling 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 um, and to 15% for 2 um SiO_2 thickness, and only slightly decreased for greater thickness.

Titanium Dioxide Films on Polycarbonate

TiO_2 is a high-index material used for optical coating, photo catalysis, gas sensor, and electronic device applications. We have discussed these various applications, the evaporation material processing (starting composition), and deposition techniques in many CMN pages. Among the lessons learned is that the crystalline and nano-structural properties, and associated optical and mechanical characteristics, are strongly process dependent. The type and nature of the crystalline phase presented is dependent on the energy of growth, and IAD or high substrate temperature are parameters employed to achieve the desired result. Amorphous films are formed under low energy conditions, and can be transformed to the anatase phase with heat. Deposition on temperature sensitive polymers such as PC requires IAD.

A recent study describes the influence of ion anode voltage and film thickness on refractive index, porosity, and grain structure for evaporated films [4]. What we learn from this work is that ion anode voltage in excess of ~70 eV are required to realize an increase in index and simultaneous decrease in porosity. Increasing voltage to 110V produced denser and thicker layers, while maintaining the anatase structure. An interesting bit of spectral data is presented that illustrates the optical absorption of titania at wavelengths larger than 700 nm, and to at least 1500 nm. This absorption is the reason tantala or lanthanum titanate are used as the high-index layers in NIR and SWIR coatings [5].

Process variables and internal stress levels and cohesive vs adhesive strengths can influence the results, as can surface preparation, as we shall see.

The researchers tested the role of the polymer type when coated with a Cr adhesor 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. Stronger adhesion requires modifying the surface chemistry to promote the creation of reactive groups on the metal – plastic interface. A measure of the effectiveness of this chemistry is the water contact angle (see CMN V18 I4 (2008)). A low contact angle indicates high surface free energy (wetting), and correspondingly good adhesion. Atmospheric plasma pretreatment of the surface of PP with He/N_2 reduced the contact angle more than plasma pretreatment with He/O_2. Sputter etching of PP surfaces with argon ions immediately before deposition produced slightly better adhesion and fracture results than plasma etching. Perhaps the reason is that there is the possibility of surface modification during installation in the coating system after the atmospheric procedure.

This study showed the importance of the specific metal adhesor layer and surface pretreatments on adhesion and fracture energies for common polymers.

Improving the Properties of ZnO as a TCO

We have discussed the substitution of doped-ZnO for ITO in applications such as solar cells and displays in previous CMN issues [6]. Al-doped compositions known as AZO or ZAO have been studied. Recall that the lower cost relative to ITO, its high visible-Near-IR transparency due to a wide bandgap (3.3 eV), and its relatively low sheet resistance are advantages offered by doped ZnO.

We have seen that the addition of a dopant can result in the modification of the growth and structural properties of a host material. Associated with nano-structure are optical and mechanical properties. We review an interesting paper that reports the use of ZnO targets with 0-4 wt% of Al_2O_3 added and R. F. magnetron sputtered [7]. The authors suggest that the resistance of ZnO to an 'aggressive plasma' is an advantage that ZnO has in the application to amorphous silicon solar cell manufacture. In the study reported, the grain size of the sputtered films was observed to decrease from 160 nm at 0% to 41 nm at 4 wt% alumina concentration. The dopant apparently acts to inhibit grain growth and crystallinity (as indicated by x-ray diffraction). A strong influence of concentration on electrical resistivity is observed; with higher concentrations decreasing resistivity. A change of 5 orders of magnitude is reported over the 0-4% dopant range. Pure films of ZnO had a resistivity of 74 Ω-cm, and increasing the dopant to 4% decreased the resistivity to 2.2 E-3 Ω-cm. A 4 wt% film that is ~130 nm thick will have a sheet R of ~170 Ω/sq. Higher carrier density due to defect substitution or greater grain

boundary scattering might be responsible for the resistivity decrease. The absorption edge for ZnO is between wavelengths 400 and 300 nm. Higher doping shifts the edge to shorter wavelengths. Films with higher alumina content are more transparent throughout the Visible and Near IR. This work represents one example of the ability to manipulate and improve on the optical and structural properties of ZnO.

Coating Materials News

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