

## SURFACE MODIFICATION OF POLYESTER FILM BY SILANE TREATMENT FOR INORGANIC LAYER ADHESION IMPROVEMENT

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### Abstract

*In this work, surface of polyester films was modified via chemical solution by using a silane coupling agent (3-Aminopropyl)trimethoxysilane (APT MOS) acting as an adhesion promoter. Indium Tin Oxide (ITO) has been deposited on AryLite substrate by sputtering procedure. Infrared spectroscopic analysis has been performed in order to study the reaction between amino group present on the organo-silane backbone and carboxylic group of polymeric substrate. Nano-scratch test of ITO layer of untreated AryLite exhibit critical load associated to surface fractures, delamination and blistering. This is a clear evidence of a poor adhesion at the interface between substrate and inorganic films. Critical load for ITO detachment from treated samples was not observed, as a consequence of a different failure mechanism, due to surface modification. The results showed that adhesion of ITO on AryLite has been improved by substrate silane surface treatment.*

### 1 Introduction

The use of plastic film substrates for organic electronic devices promises to enable new applications.

Plastic substrates have several advantages, such as ruggedness, robustness, ultra lightness, conformability and impact resistance over glass substrates, which are primarily used in flat panel displays (FPDs) today [1]. However, high transparency, proper surface roughness, low gas permeability and highly transparent electrode conductivity of the plastic substrate are required for commercial applications [2,3,4].

Polyesters, both amorphous and semicrystalline, are a promising class of commercial polymers for optoelectronic applications.

Despite the best premises, the adoption of polymers for electronic applications has been slowed by their limited compatibility with semiconductor fabrication processes, at least during the first stage of the transition towards all-polymeric functional devices. In particular, the relatively high linear expansion coefficient,  $\alpha$ , and low glass transition temperature,  $T_g$ , of most polymers limit their use to temperatures above 250°C. Therefore, the high-temperature process leads to considerable mechanical stress and difficulties in maintaining accurate alignment of features on the plastic substrate.

At the present stage, inorganic materials are used as buffer, conductive and protective layers for functional organics and high performance polymer substrates.

Several high-T<sub>g</sub> polymers (T<sub>g</sub> >220°C) with optical transparency, good chemical resistance and barrier properties have recently been developed for applications in organic display technology, and these latest developments have motivated the present research. Ferrania Imaging Technologies, has developed amorphous polyester material, AryLite, with high glass transition temperature (T<sub>g</sub> ≈ 320°C) and good optical transparency [5].

Taking into account that for a number of these functions transparent coatings are required, Indium Tin Oxide (ITO) layer has been deposited on AryLite substrates by sputtering procedure. ITO thin films are widely used as transparent and conductive electrodes for various displays and photovoltaic devices.

In a multilayer structure, the adhesion between organic/inorganic layer plays an important role in determining the reliability of the optoelectronic devices.

AryLite shows a low surface energy and a chemical inertia. As a matter of fact, the effort is focused on the improvement of adhesion between polyester substrate and inorganic layer.

Adhesion properties can be varied by modifying the surface, by means of several chemical and/or physical processes [6].

In this study, the surface of polyester film was modified via chemical solution. Afterward, samples have been treated with (3-Aminopropyl)trimethoxysilane (APTMO) that function as an adhesion promoter between organic substrate and ITO layer. In particular, SiOH silane functional groups are suitable for coupling with ITO layer.

Contact angle and roughness measurements, surface free energy calculation and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) were used to monitor the effects of silane treatments on the physical and chemical characteristics of pristine and modified polyester surfaces. Infrared spectroscopic analysis has been performed in order to study the reaction between amino group present on the organosilane backbone and carbonilic group of polyester substrate.

Conventional characterization techniques are not appropriate for the measurement of mechanical and adhesion properties of thin functional layers on substrate. Nano-indentation and nano-scratch testing are alternative approaching methods. Both techniques have become important tools for probing the mechanical properties of small volumes of material at the nano-scale. Indentation measurements have been used to evaluate the hardness and Young's modulus of films. The film adhesion was determined by the nano-scratch test.

## 2 Materials and testing methods

### 2.1 Thermo-Mechanical properties of AryLite

AryLite exhibits excellent T<sub>g</sub> (324°C) (Figure 1) and good optical transparency. The lack of crystalline phase is a consequence of the aromatic and rigid nature of the polymer backbone which hinders conformational rearrangements into a regular crystalline structure. On the other hand the rigid backbone is responsible of reduced elongation at break and the lack of crystalline reinforcement results in poor elastic and ultimate properties (Table 1).

Glass transition temperature T <sub>g</sub> [°C]	324
Initial degradation temperature T <sub>id</sub> [°C]	489
Young's Modulus E [GPa]	2.81±0.26
Elongation at break ε <sub>r</sub> [%]	10.24±2.36

**Table 1** - Thermo-mechanical properties of Arylite.

The initial degradation temperatures ( $T_{id}$ ) have been measured by using thermogravimetric analyser at a scanning rate of 10°C/min in N<sub>2</sub> purging flow.  $T_{id}$  is associated to 3 % weight loss. Thermal and mechanical behavior of polyester indicate that AryLite is a good candidate for optoelectronic application (Table 1).

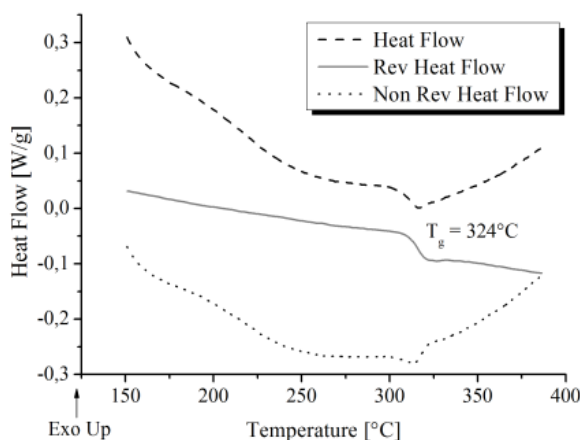


Figure 1 - Modulated Differential Scanning Calorimetry of AryLite.

## 2.2 Surface treatments

Polymer films were preliminary immersed in an alcohol/water (1/1, v/v) solution for 2 h in order to clean the surface and then rinsed with a large amount of distilled water. They were dried under reduced pressure for 12 h at 25 °C.

AryLite samples have been functionalized with (3-Aminopropyl)trimethoxysilane (APTAMOS). Untreated AryLite samples have been used as substrate for the sake of comparison.

Prior to AryLite surface treatments, the SiOR groups of the silane were transformed to active SiOH groups for the subsequent condensation reactions. The transformation is realized by hydrolyzing the silane in a aqueous solution. 7.5 wt % silane solution were prepared by adding the silane to a mixture of 70:30 ethanol and distilled water. The pH of the solution was adjusted to 5.5 by inclusion of a few droplet of acetic acid. The solution was stirred for 10 minutes and the system was kept 1 h at room temperature for hydrolysis reaction and silanol formation. Subsequently the films were dipped into the solution for 30 minutes at room temperature. These silane-treated specimens were rinsed with distilled water to eliminate the unreacted silane and dried under reduced pressure at 25°C overnight.

Reaction path is reported in Figure 2. The reaction proceeds through a nucleophilic attack of NH<sub>2</sub> nitrogen atom to the carbon atom of carbonilic group generating an amide group.

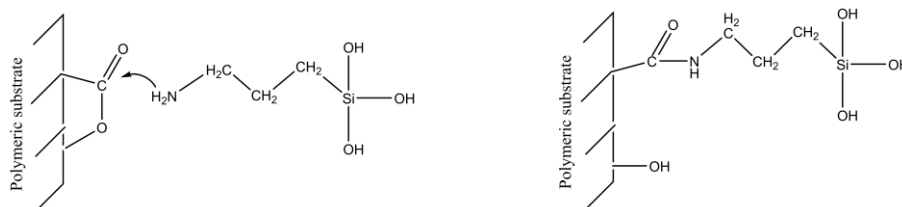


Figure 2 - Scheme of nucleophilic addition of NH<sub>2</sub> group to the polyester carbonilic group

## 2.3 Spectroscopic analysis FTIR-ATR

Infrared spectroscopic analysis has been performed to verify the reaction between amino group located on the organo-silane and carboxylic group of polymeric substrate.

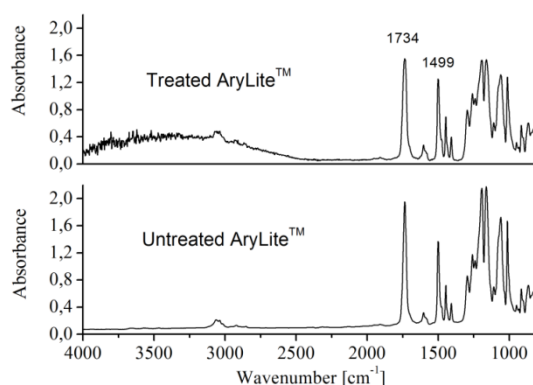
In Figure 3 normalized ATR spectra of untreated AryLite and AryLite treated with APTMOS solution have been plotted.

In order to make a comparison between the treated and untreated samples the intensity of each peak was rationed [7] against the absorbance of the invariant band at 1499  $\text{cm}^{-1}$ . These peaks are due to C-H in-plane bending of the benzene ring.

In the FTIR-ATR spectra, silane-treated specimens show a wide peak between about 2500 – 4000  $\text{cm}^{-1}$ . This is attributable to the presence of SiOH groups [8].

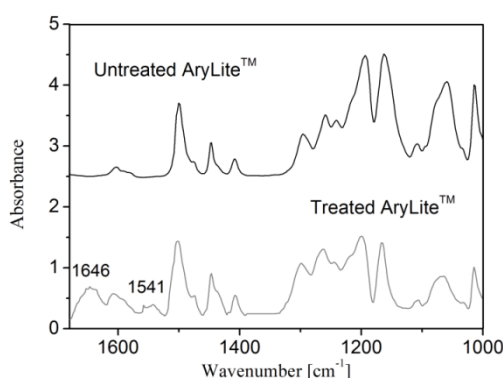
Treated sample spectra show a decrease of C=O ester linkage at 1734  $\text{cm}^{-1}$  and a decrease of C–O ester stretching vibrations in the region 1300 – 1000  $\text{cm}^{-1}$  after silane treatment [9,10].

This is attributable to nucleophilic addition of the amine group ( $\text{NH}_2$ ) to the carbonilic group. Following this reaction path, the organosilane APTMOS has been grafted on the AryLite substrate.



**Figure 3** - ATR spectra of AryLite before and after surface silane treatment in the range 4000-700  $\text{cm}^{-1}$ .

In fact, a chemical reaction could happen between amine group ( $\text{NH}_2$ ) of silane and carbonilic group of polymer substrate. The reaction produce an amide group ( $\text{O}=\text{C}-\text{NH}$ ). This hypothesis has been supported by a spectroscopic study. Figure 4 shows double peak of amide group located at about 1640-1540  $\text{cm}^{-1}$ .



**Figure 4** - FTIR spectra of polyarilate before and after silane treatment in a dichloromethane solution

#### 2.4 Evaluation of surface free energy (SFE)

AryLite is an hydrophobic film with a water contact angle of 92 degrees. Samples treated with silane show a decrease of water contact angle of about 30 degrees. It has been demonstrated that silane treatment is effective in increasing the hydrophilicity of samples.

Surface free energy of the polymer substrates was calculated using the methods proposed by Owens *et al.* [11] which divide the total surface free energy ( $\gamma$ ) in 2 parts: dispersive ( $\gamma_s^d$ ) and polar ( $\gamma_s^p$ ). The dispersive component accounts for all the London forces such as dispersion (London–van der Waals), orientation (Keesom–van der Waals), induction (Debye–van der Waals) and Lifshitz–van der Waals (LW) forces. The polar component is affected by hydrogen bonding components.

In order to obtain  $\gamma_s^d$  and  $\gamma_s^p$  of a solid, contact angle data for a minimum of two known liquids are required. If two liquids are used, then, one must be polar and other is non-polar.

In this study two test liquids were used as a probe for surface free energy calculations: distilled water and diiodomethane.

Silane treatment binds OH groups on the polymeric surface. This phenomenon increase polyester surface polarity and surface free energy [12] (Table 2). The increase in surface polarity causes an increase in molecular forces between substrates and hence an increase in adhesion strength [13,14,15].

In Table 2 are reported SFE of untreated AryLite and treated AryLite calculated by using geometric mean method.

	Surface Free Energy [mJ/m <sup>2</sup> ]			
	$\gamma$	$\gamma_s^d$	$\gamma_s^p$	<b>P</b>
<b>Untreated AryLite</b>	29.97	27.80	2.17	0.07
<b>Treated AryLite</b>	30.19	17.10	13.09	0.43

**Table 2** - Surface free energy and polarity of AryLiteTM films before and after surface treatment

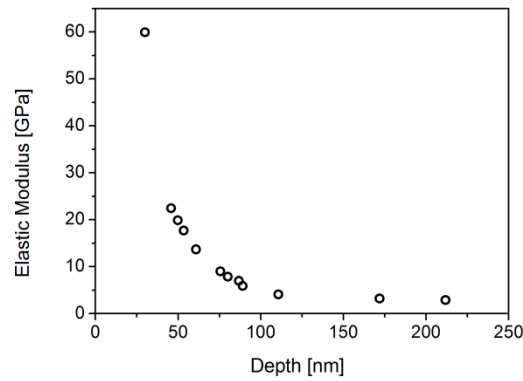
### 2.5 ITO deposition

Deposition of the ITO thin films was performed by dc-magnetron sputtering (MP-1, Huettinger Electronic) from an oxide ceramic target 90 wt % In<sub>2</sub>O<sub>3</sub> and 10 wt % SnO<sub>2</sub>. AryLite substrates were placed at 55 mm in front of the target to obtain ITO deposition without intentional heating. A flow of Ar and 10% v/v O<sub>2</sub> were introduced through independent mass flow controllers after the vacuum chamber was evacuated below 7x10<sup>-5</sup> mbar. The process total pressure was kept at 8.5x10<sup>-3</sup> mbar and the sputtering power employed during deposition was 100W. The respective deposition rate is about 0.5 nm/s and the ITO film thickness was controlled to be about 100 nm.

### 2.6 Nanoindentation and nanoscratch analysis

Nano-indentation and nano-scratch techniques have been used in order to investigate the mechanical surface properties of inorganic layer and the adhesion properties between organic substrate and inorganic layer. The apparatus used in this work was NanoTest Platform by Micro Materials Ltd.

Elastic modulus is calculated from the load vs. displacement data obtained by nano-indentation on coating at twenty different indentation depths ranging from 20nm to 600nm. The experiments were performed with an initial load of 10  $\mu$ N at loading and unloading rate of 10  $\mu$ N/sec. The hold time of 30 sec at peak load was kept constant. Additional hold at 90% unload in all tests was set for thermal drift correction. Three-sided pyramidal diamond Berkovich tip with a radius of about 100 nm has been used.

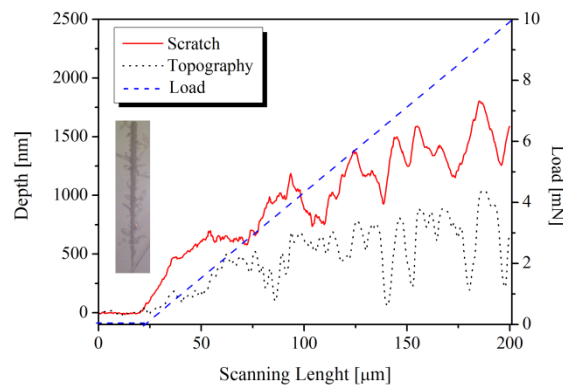


**Figure 5** - Young’s modulus of untreated AryLite coated with 100nm of ITO layer

As reported in Figure 5 Young’s modulus decrease with increase depth. Polymer substrates exhibit the same elastic properties approximately 3.5 GPa for depth higher than 200 nm. Beyond this limit the elastic modulus is not influenced from the presence of the ITO coating. This value is slightly higher than 2.9 GPa calculated by tensile test and reported in literature [16]. According to Zheng *et al.* [17] elastic modulus measured by depth sensing indentation are invariably higher than tensile test by a value of 5-20%. The difference between uniaxial and indentation results is probably attributable to the data reduction procedure used in analyzing the indentation data. If the polymer was creeping while unloading, this would tend to increase the slope of the unloading curve and hence the calculated elastic modulus.

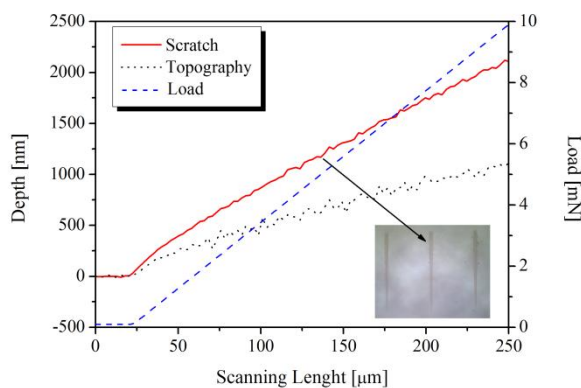
In nano-scratch studies a conical indenter is drawn over the sample surface with ramping up of the load until damage occurs. The load corresponding to this damage provides a measure of scratch resistance or adhesive strength of a coating and is called the “critical load” [18]. The definition of damage can be the onset of cracking around the scratching tip, spalling of the coating, or the formation of a channel in which all of the coating has been removed from the substrate. The critical loads are indicators of the scratch resistance of these samples.

Five scratches were made at each load at different areas of specimen. Untreated AryLite exhibit a Lc value of  $3.8 \pm 0.6$  mN (Figure 6); a 1  $\mu\text{m}$  conical indenter has been used resulting in evident and reproducible data. The failure begins abruptly by brittle fragmentation and spallation in the coating. Spalling coating failure modes [19] occurs as a result of the compressive stress field preceding the moving tip. Spallation is the result of total delamination and adhesive failure.



**Figure 6** - Scratch test curve of ITO layer of untreated AryLite with optical image in the plot inset (magnification 20x)

The scratch curve test of ITO coating reveal that no inflexion can be found in depth curves of silane-treated samples which means that the films cannot be delaminated in the scratch process. Indeed, critical load disappeared after surface modification treatment, there is no abrupt change in the displacement curves, implying that the coatings did not peel off during the scratch ramping load (Figure 7).



**Figure 7** - Scratch test curve of ITO layer of treated AryLite with optical image in the plot inset (magnification 20x).

A careful observation by optical microscopy has been made by comparing the topography pre-scan and post-scan to the scratch-scan for silane-treated and coated sample. The optical images reveal that the scratch is extremely smooth and shallow.

## Conclusions

In this paper polymer surface has been modified by chemical treatment in order to improve the adhesion properties. Coupling agent with amino functional group (APTMOs) has been grafted on polyester surface. A significant decrease of water contact angle have been measured for treated sample resulting in increased wettability and surface free energy of polymeric substrate. The increase of surface polarity enhance the adhesion of ITO subsequently deposited by dc-magnetron sputtering.

The improvement of adhesion is probably associated with the presence of SiO<sub>x</sub> grafted on the surface. Nano-scratch test of ITO layer of untreated AryLite exhibit surface fractures and delamination. This is a clear evidence of a poor adhesion at the interface between substrate and inorganic films. Treated samples did not show an abrupt change in the displacement curves, implying that the coatings did not peel off during the scratch ramping load scratch. The optical images reveal that the scratch is extremely smooth and shallow, implying that the coatings strongly adheres on substrate. These results showed that adhesion of ITO on AryLite has been improved by substrate silane surface treatment.

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## References

- [1] Imparato A., Minarini C., Rubino A., Tassini P., Villani F., Guerra A., Amendola E., Della Sala D., Thin silicon films on polymeric substrates. *Macromol. Symp*, **228**, 167-176, (2005).

- [2] Choi M.C., Kim Y., Ha C. S., Polymers for flexible displays: From material selection to device applications. *Prog. Polym. Sci*, **33**, 581–630 (2008).
- [3] Mannifacery J.C., Szepessy L., Bresse J.F., Perotin M., Stuck R., In2O3:(Sn) and SnO2:(F) films–Application to solar energy conversion; part 1 – preparation and characterization. *Mater. Res. Bull*, **14**, 163, (1979).
- [4] Adhikari B., Majumdar S.. Polymers in sensor applications. *Prog. Polym. Sci*, **29**, 699–766 (2004).
- [5] Angiolini S., Avidano M. P-27: Polyarylite Films for Optical Applications with Improved UV-Resistance. *Organic Synthesis Lab. Polymers*, Ferrania Imaging Technologies, Technical Information. (2001).
- [6] Goddard J.M., Hotchkiss J.H., Polymer surface modification for the attachment of bioactive compounds, *Progress in Polymer Science*, **32**, 698-725, (2007).
- [7] Gu X., Raghavan D., Nguyen T., VanLandingham M.R., Yebassa D.. Characterization of polyester degradation using tapping mode atomic force microscopy: exposure to alkaline solution at room temperature. *Polymer Degradation and Stability*, **74**, 139–149, (2001).
- [8] Anderson D.R., Lee Smith A. *Analysis of Silicones*. Wiley-Interscience editor, New York (1974).
- [9] Bellamy L.J. *The infrared spectra of complex molecules*. John Wiley & Sons, 3rd ed., p.49, New York (1975).
- [10] Colthup N.B., Daly L.H., Wiberley S.E., Introp P. *Introduction to infrared and Raman spectroscopy*. Academic, 3rd ed., p 94. (1990).
- [11] Owens D.K., Wendt R.C. Estimation of the surface free energy of polymers. *J. Appl. Polym. Sci.*, **13**, 1741–1747 (1969)
- [12] Clint J. H, Adhesion and components of solid surface energies. *Current Opinion in Colloid & Interface Science*. **6**, 28-33 (2001)
- [13] Burnett D., Thielmann F., Ryntz R. Correlating thermodynamic and mechanical adhesion phenomena for thermoplastic polyolefins. *Journal of Coatings Technology and Research*, **4**, 2, 211-2151 (2007).
- [14] Comyn J. Contact Angles and Adhesive Bonding. *International Journal of Adhesion and Adhesives*, **12**, 3, 145–9(1992).
- [15] Lee I., Wool R.P.. Thermodynamic Analysis of Polymer-Solid Adhesion: Sticker and Receptor Group Effects. *Journal of Polymer Science Part B: Polymer Physics*, **40**, 20, 2343–53 (2002).
- [16] Abdallah A.A., Bouten P.C.P., den Toonder J.M.J., de With G. The effect of moisture on buckle delamination of thin inorganic layers on a polymer substrate. *Thin Solid Films*, **516**, 1063–1073 (2008).
- [17] Zheng S., Ashcroft I.A. A depth sensing indentation study of the hardness and modulus of adhesives. *International Journal of Adhesion & Adhesives*, **25**, 67–76. (2005).
- [18] Park H.S., Kwon D. An energy approach to quantification of adhesion strength from critical loads in scratch tests. *Thin Solid Films*. **307**, 156-162 (1997).
- [19] Burnett P.J. and Rickerby D.S. The relationship between hardness and scratch adhesion. *Thin Solid Films*, **154**, 403-416 (1987).