Mechanical integrity of thin films on polymer substrates

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1. INTRODUCTION

The functional performance of nanosized oxide and nitride films on polymer substrates is dictated by the fracture properties of these extremely thin and brittle films, controlled by a complex interplay between process induced defects and residual film stresses, cohesive film properties and adhesion to the substrate (Figure 1) [1]. Successful design and process optimization of such composite materials relies on accurate analysis of the properties of the interfacial region, and, more specifically, of the stress transfer features of the interface. Stress transfer theories were developed in the 1950s, parallel to the development of adhesion tests. Since these early efforts, a broad diversity of models and test methods have emerged, but only a few are applicable in case of strong elastic contrast between coating and substrate, germane to stiff coatings on soft polymer substrates.

The following presents the key experimental techniques developed to determine the properties of such layered composite materials and reviews the classic mechanical analyses of films on substrates, based on failure statistics and interfacial stress transfer. These approaches are vital to process and material optimization, which is discussed based on a case study of transparent conductive oxide films on polymer substrates developed for flexible display applications [2, 3].

![Figure 1. The durability of thin film/polymer layered composites is determined by the internal stress (coating and interfacial region), the coating cohesive strength and related crack onset strain, and the coating/substrate adhesion.](image)

2. ADHESION TEST METHODS FOR THIN FILMS ON POLYMER SUBSTRATES

A broad diversity of methods have been developed to measure the adhesion of coatings on substrates [4]. Among these, three types of techniques are commonly used to investigate thin films on polymer substrates, namely the peel test, the indentation and related scratch techniques, and the tensile or fragmentation test, as summarized in Table I.

2.1. The peel and scotch tape tests

In the peel test, the thin coating is peeled from the substrate of well-defined width, at a specified angle, usually 90° or 180°, using a backing material such as ethylene acrylic acid (EAA). This technique and
derivatives have been largely used to test the adhesion of thin films on polymers (e.g. refs [5-7]). Nonetheless, the peel test is at best of semi-quantitative nature, since several dissipation processes other than those present at the coating/substrate interface contribute to the peel energy. Moreover, the peel strength often exceeding the measurement limit, with thin films that cannot be peeled off due to high adhesion levels [8]. The fundamental limitation of the peel test is in fact the introduction of third body, the adhesive backing, in the system, which seriously complicates the determination of absolute value of coating adhesion. The scotch tape test or cross-hatch test (ASTM D3359-78) consists in cutting the coating using a sharp razor blade or a cutter in a cross hatch pattern, then applying the scotch tape by pushing strongly with a nail, and removing the scotch quickly with a snatch. The sample is subsequently evaluated by visual inspection of the surface. In case of adhesion failure an adhesion classification value can be defined according to ASTM D3359-78.

2.2. Indentation and scratch tests

Nanoindentation was developed for the specific purpose of thin films characterization [9]. However, in case of soft polymer substrates, current models do not accurately account for compliance and yield effects, and often lead to considerable underestimation of coating properties such as Young's modulus. In the present work, a comparative assessment of thin ITO coatings on stiff glass and soft polymer substrates is reported in Figure 2. The Young's modulus of the ITO was determined from the indentation behavior.

Table 1. Main features of adhesion test methods for thin coatings on polymer substrates

<table>
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<tr>
<th>Adhesion test method</th>
<th>Avantages</th>
<th>Drawbacks</th>
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| Peel/scotch tape tests | • Simple, fast and cheap | • Qualitative  
  • No information on failure mechanism  
  • Third-body interaction (adhesive-surface) |
| Indentation/scratch tests | • Direct measurement on coating  
  • Load-displacement data  
  • AFM  
  • Numerous data points per sample  
  • Fast and easy automation | • Indirect information on the failure mode  
  • Third-body interaction (tip-surface)  
  • Only comparative method in case of polymer substrates, due to current lack of appropriate analysis of test results |
| Fragmentation test | • No third-body interaction  
  • Direct observation of failure processes  
  • Measurement of coating cohesion and adhesion  
  • Sensitive to interfacial region  
  • Enables continuous electrical measurement (conductive coatings) | • Time consuming and difficult automation  
  • Discontinuous ("stress and stop") measurements  
  • In-situ SEM required for coatings less than 50 nm thick |
using the Doerner and Nix model [10]. A realistic value, found to be equal to 116 GPa was obtained in case of rigid glass substrate. In contrast, the Young's modulus of ITO was found to be as low as 22 GPa on a soft PET substrate, although the microstructure and electrical properties of the latter coating were comparable to those of the coating on glass [2]. More, tensile tests carried out using a thin PET substrate (12 μm thick, in order to enhance the influence of the thin coating) coated with ITO enabled alternative determination of the ITO Young's modulus, found to be equal to 119±5 GPa, i.e., in good agreement with the value obtained using a glass substrate.

![Young's modulus vs indentation depth](image)

**Figure 2.** Comparison of Young's modulus of ITO coatings derived from nanoindentation tests carried out on a PET substrate (left) and on a glass substrate (right).

These results demonstrate that models developed to analyze the results of the indentation test are not valid in case of strong mechanical contrast between stiff coating and soft substrate with low yield stress. The conclusion here is that indentation method remains useful to obtain coating elastic properties, providing the test is carried out using a stiff substrate. An interesting alternative is tensile testing, using as substrate a thin polymer film.

In the scratch test [11], a stylus is drawn across the coating under increasing vertical load. The critical load at coating failure is often taken as a semi-quantitative measure of adhesion [12, 13]. Similarly to the indentation technique, the models developed to analyze the critical normal force (see review of Bull, Rickerby, et al. [14]) do not seem appropriate in the case of soft and ductile polymer substrates. Indeed, the main drawback of indentation tests is, again, the introduction of a third body, the stylus, in the system, which yields a complex triaxial stress field in the polymer substrate, resulting from the ploughing effort of the indenter. If the test is unable to provide an absolute value of coating adhesion [15], it is nevertheless very useful for comparative purposes and coating optimization. Progress in numerical analyses of the stress field and in standardization methods should improve further the usefulness of such techniques [16, 17].

**2.3. The fragmentation test**

In contrast to the above methods, the fragmentation test proved its relevance to determine the adhesion of thin films on a broad variety of polymer and metal substrates [1]. In this technique usually carried out in situ in a microscope, the evolution of crack patterns in the brittle coating is monitored as a function of the uniaxial tensile load applied to the substrate. With specially-designed clamps, changes in the electrical resistance of conductive coatings can moreover be measured under well defined loading conditions. The adhesion is then related to the density of coating cracks, measured in the saturation stage of the fragmentation process, i.e., when no more cracks are formed as the strain is increased. A detailed analysis of the test results is given in Section 3.
Correlations were reported between the results of fragmentation and scratch tests [15], and, more specifically between the crack density at fragmentation saturation, and the critical normal force measured during scratching [18]. This is a solid indication that both techniques detect an intrinsic property of the coating/substrate assembly, usually considered to be either the interfacial toughness, or the interfacial shear strength (IFSS), that will be detailed in the next Section.

2.4. The three stages of coating fragmentation

The phenomenology of coating fragmentation comprises three main stages [19], as sketched in Figure 3 in form of a crack density vs applied strain curve:

- The first stage is termed random cracking (Figure 3A). Crack interaction being negligible, the rate of crack generation is governed solely by the coating strength distribution and the crack location is determined by the defect distribution in the coating. The stress state in a coating fragment is equal to the equivalent far field stress, except along some critical distance from the edges, where stress relaxes to zero.
- The second fragmentation stage is termed mid-point cracking (Figure 3B). It corresponds to crack spacing becoming small with respect to twice the critical length. As a result, the maximum stress in a fragment cannot reach the unperturbed far-field level, which leads to a marked reduction of the fragmentation rate. The first two stages are in fact intimately correlated [20]. Transverse buckling failure of coating fragments is often observed during this second stage, due to lateral contraction of the substrate resulting from Poisson's ratio effects.
- The third and final stage begins with the delamination of the coating, and the fragmentation rate virtually stops (Figure 3C).

![Figure 3. The three stages of coating fragmentation. A: random cracking. B: mid-point cracking, and initiation of transverse buckling. C: delamination.](image)

3. STRESS TRANSFER THEORIES

The fragmentation of the thin coating during loading the substrate is controlled by the constitutive behavior of the coating/substrate interface, which is analyzed as follows.

3.1. Mechanical equilibrium

When a coated substrate is loaded in tension, the tensile stress applied to the substrate is transferred to the coating, through shear stress at the interface. Figure 4 sketches the geometry relevant for the unidimensional analysis of the stress transfer phenomenon.
The simplest case considers unidimensional stress transfer and neglects internal stresses. The stress distribution at the interface and in the coating is calculated from the equilibrium of a small coating element subjected to a tension force parallel to the interface, as depicted in Fig. 4. The force equilibrium of an infinitesimal coating element of thickness $h_c$, length $dx$ and width $W$ requires:

$$\left(\sigma_c(x) + d\sigma_c(x)\right) \cdot h_c \cdot W - \sigma_c(x) \cdot h_c \cdot W = \tau(x) \cdot dx \cdot W$$  \hspace{1cm} (1)

where $\sigma_c(x)$ represents the axial tensile stress in the coating and $\tau(x)$ the interfacial shear stress. The mechanical equilibrium derived from Eq. 1 provides the fundamental stress transfer equation, where the coating stress is the integral of interfacial shear over a stress transfer length, also termed critical length, $l_c$:

$$\sigma_c(x) = \frac{1}{h_c} \int_0^{l_c} \tau(x) \cdot dx$$  \hspace{1cm} (2)

The resolution of Eq. 2 implies defining interface properties, i.e., a constitutive form for shear stress $\tau$. The maximum value of the shear stress $\tau$ represents the interfacial shear strength (IFSS), a characteristic of coating adhesion. In the past 50 years, considerable effort was devoted to stress transfer theories. The following describes one classic model, which enables determination of IFSS from experimental data.

### 3.2. Perfectly plastic interface model

Stress concentrations at fragment edges are bound by yield stress of the interface, or interface decohesion. This was accounted for by Kelly and Tyson [21], who assumed a perfectly plastic behavior of the coating/substrate interface, i.e., a constant IFSS. In spite of its simplicity, the assumption of a constant IFSS in the stress transfer zone is very robust in case of stiff coatings on soft substrates [22]. This results from the fact that the stress in the brittle coating is much larger than the typical IFSS values, so that the size of the stress transfer zone is proportional to the coating stress. In that sense, calculated IFSS value from fragmentation data reflects some effective shear property of the interfacial region. For ductile polymer substrates, a constant IFSS assumption is often preferable to alternative elastic models due to the plastic flow of the polymer in the strain range of coating fragmentation. Based on this approach, the resolution of Eq. 2 leads to the following determination of the IFSS [23]:

$$\tau = 2 \cdot h_c \cdot \sigma_{\max} \cdot \left(\frac{l_c}{l_c}\right)$$  \hspace{1cm} (3)

where $\sigma_{\max}$ represents the size-dependent tensile strength of the coating, characteristic of its defect-controlled cohesion, and $l_c$ is the critical stress transfer length defined as the minimum coating length in
which the maximum allowable coating stress, $\sigma_{\text{max}}$, is achieved. The determination of $\sigma_{\text{max}}$ and $l_c$ from fragmentation data follows.

### 3.3. Weibull analysis of coating tensile strength

The tensile strength $\sigma_{\text{max}}$ of brittle materials is defect controlled and exhibits size-dependent effects, which can be accounted for by the Weibull weakest-link model [24]. In case only one population of defects (e.g., volume defects) control the strength of the material, the Weibull model is written as a two-parameter equation:

$$\sigma_{\text{max}}(l) = \sigma_0 \left( \frac{l}{l_0} \right)^{-1/m} \Gamma \left( 1 + \frac{1}{m} \right)$$

where $l$ is the size of a coating element (i.e., fragment length), $l_0$ is a normalization factor, $\Gamma$ is the gamma function, and $\sigma_0$ and $m$ are the Weibull shape and scale factors, respectively. For thin coatings, these two factors are usually derived from a linear approximation of the initial part of the fragmentation diagram, where the average fragment size is reported as a function of applied strain, in logarithmic coordinates [25].

### 3.4. Critical stress transfer length

The length $l_c$ is obtained using a stochastic failure approach from the crack density at saturation, $\text{CD}_{\text{sat}}$, measured in the 3rd stage of the fragmentation process: $l_c = 1.496 / \text{CD}_{\text{sat}} - 1.5 / \text{CD}_{\text{sat}}$ [26].

### 3.5. Role of internal stresses on coating toughness and interfacial shear strength

Internal stresses were reported to change to a considerable extent the properties and adhesion of thin films on substrates [27, 28]. The main sources and measurement methods of coating stress are detailed in ref. [1]. The axial stress in the coating resulting from tensile loading the substrate adds to the initial axial internal stress in the oxide layer. Upon fragmentation, the average coating stress relaxes. At saturation, one obtains:

$$\sigma_{\text{max}}^*(l_c) = \sigma_{\text{max}}(l_c) + 0.67 \sigma_i$$

where $\sigma_{\text{max}}^*(l_c)$ and $\sigma_i$ represent the intrinsic tensile strength of the coating at critical length and of the internal stress, respectively, and the term 0.67 comes from stress relaxation at fragment edges. As a consequence, any change in internal stress level, $\Delta \sigma$, will result in a proportional change in apparent IFSS, $\Delta \tau = -\left( 1.34 \frac{h_c}{l_c} \right) \cdot \Delta \sigma_i$ [28]. The minus sign comes from the convention that tensile stresses are positive and compressive stresses are negative. The intrinsic toughness of the coating can then be evaluated, using the analysis of thin films on compliant substrates [29]:

$$G_c = \frac{\pi \cdot h_c \cdot \sigma_{\text{max}}^2}{2 \cdot E_c} \cdot g(\alpha; \beta)$$

where $\sigma_{\text{max}}$ represents the coating stress at crack initiation, equal to the product of coating Young's modulus and strain to failure, accounting for internal stresses [30], and $g(\alpha; \beta)$ is an elastic function of the Dundurs elastic mismatch parameters $\alpha$ and $\beta$ [31].
4. CASE STUDY OF ITO COATINGS ON POLYMERS

4.1. Materials

Transparent conductive oxide coatings such as indium tin oxide (ITO) used as hole injection layer on glass substrates in flat displays are being considered for flexible displays based on polymer substrates [3]. The thermo-mechanical properties of ITO and polymers differ to a considerable extent, and extensive process optimization is required before reliable coatings are produced. In the present work, the influence of ITO thickness, substrate type, and annealing on the mechanical properties and adhesion of the coating is investigated using the fragmentation technique. The ITO films, of thickness of 30, 100 and 130 nm were prepared from ITO targets by means of DC magnetron sputtering on two types of polymer substrates: a 175 μm thick poly(ethylene terephthalate) (PET) film, and a 100 μm thick aromatic polyester film (A-Poly). As-grown ITO on the aromatic polyester was also annealed for 2 h at 200°C under vacuum.

As-grown ITO coatings were systematically under compression as indicated in Table II, a result of thermal stresses generated upon cooling the coated polymer at the end of the deposition cycle. Compressive stresses were found to increase during annealing, where crystallization of ITO takes place. Such an increase was unexpected since the coating shrinks during crystallization, and would in fact result from annealed-induced shrinkage of the polyester.

4.2. Fragmentation analysis of the ITO coatings

Figure 5 depicts the progressive cracking of the 130 nm thick ITO coating on PET during tensile loading. The three stages of fragmentation described in Section 2 are evident. Cracks initiate on coating defects such as pin-holes and grow stable perpendicular to the loading direction until their length reaches several 100 times the thickness of the coating. This observation appears to be a fundamental feature of stiff coatings on compliant substrates, and confirms recent numerical studies [32]. At a threshold strain, which roughly corresponds to a 10% increase in coating electrical resistance [33], the cracks propagate unstable, forming a dense network of parallel cracks. The issue of crack initiation vs crack propagation is discussed elsewhere [2].

![Figure 5. Three main fragmentation stages of a 130 nm thick ITO coating on a PET substrate, with indication of strain levels. The tensile load was applied parallel to the scale bars.](image-url)
The fragmentation process turns out to be very sensitive to the thickness of the coating, the type of polymer substrate or annealing treatment (Figure 6), and therefore enables coating, substrate and process parameters to be optimized, based on the analysis of the test results. The mechanical properties of the thin ITO films on polymers derived using the theoretical treatment described in the previous section, are reported in Table II. Improvement of ITO mechanical properties may be obtained through:

- Decreasing the ITO thickness, with resulting increase in strain to failure, although this might imply increased electrical resistance of the layer;
- Annealing, which clearly improves coating toughness and adhesion;
- Internal compressive stress, with direct increase of strain to failure, although this could trigger coating buckling in case the coating is compression loaded.

Figure 6. Influence of ITO thickness (a), polymer substrate (b) and post-deposition annealing (c) on the evolution of the density of tensile cracks in ITO coatings as a function of applied strain. Lines are guides for the eye.
5. CONCLUSIONS

The mechanical integrity and adhesion of thin functional coatings on polymer substrates have been reviewed, with attention paid to process-induced internal stresses. Among the different adhesion test methods, the fragmentation test, free of third-body interactions, is best suited to investigate the cohesive and adhesive properties of thin coatings on polymer substrates. Analysis of the fragmentation process based on a perfectly plastic interface model and a statistical description of coating cohesion enables realistic description of coating cohesive and adhesive properties. In addition, the following factors are critical for proper determination of coating toughness and adhesion:

- Coating elastic properties. Accurate determination of these properties is a challenging task when thickness lies in the nanometer range, and in case of soft polymer substrate. A recommendation is to measure these properties by means of tensile tests using a thin substrate, or by means of nanoindentation, using a stiff substrate.
- Process-induced internal stresses. These stresses directly impact the coating and interface properties, and must be included in the analysis to eventually enable optimization of process cycles.
- Coating thickness. There exists an optimal thickness, which combines functional and mechanical performance: thinner films usually possess higher critical failure strain, but might have reduced functional performance, including electrical conductivity or barrier properties.
- Initiation and propagation of coating cracks. The loss of functional performance of coated polymer components is generally controlled by the propagation of coating cracks. However, very small and stable cracks may already have initiated before longer cracks are detected, and are likely to grow under fatigue loading, or as a result of visco-elastic, time-dependent processes such as creep, typical of polymer materials.
- Interfacial adhesion in multilayered structures. Multilayer structures are usual in industrial applications. Processing the various layers imply redistribution of internal stresses, with potential impact over interfacial adhesion. The best situation is when the adhesive strength of each of these interfaces is higher than the bulk shear strength of the base polymer material. This is possible with high enough density of chemical bonds between the various materials.

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