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Organic ultrathin film adhesion on compliant substrate using scratch test technique

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ABSTRACT

Many adhesion test techniques have been developed to measure the adhesion energy of thin films but they are hard to implement in the case of submicron organic thin films deposited on a flexible substrate. Recently the feasibility and repeatability of the scratch test technique as a tool for testing the adhesion and the damage behaviour of ultra-thin films on polymer substrates has been demonstrated. However, direct comparison of the critical load between samples was not straightforward since different failure mechanisms were induced. In the present work, we have performed nanoscratch experiments on submicron thin films deposited on a flexible substrate. The use of a tip radius of 5 μm enabled a unique delamination mechanism to be induced by localizing and maximizing the stress closer to the interface. We have observed an increase of the critical load on samples processed with an adhesive plasma treatment prior to thin film deposition, confirming the effectiveness of this treatment. We have also performed mechanical ageing tests on specimens and proved that the scratch test technique is sensitive enough to monitor the degradation of the interface properties. Finally, we have discussed some existing energy models. Taking into account some limitations, Laugier's model gives an upper bound for the adhesion energy.

1. Introduction

A large amount of effort has been devoted to the design and development of printed electronics on flexible substrate to achieve low cost, large area flexible electronics [1]. The manufacturing process consists of the deposition of active thin layers and electrodes on a plastic substrate using different printing techniques like screen printing, flexography and inkjet printing. The electrical performance and stability in ambient air are quite high [2,3]. Since these devices are flexible, they will have to resist, during their useful life, a lot of mechanical strains and stresses. Consequently, the investigation of the mechanical properties of the interfaces and the evaluation and improvement of the adhesion are essential to ensure the stability and reliability of the devices.

Many adhesion test techniques have been developed to measure the adhesion energy of thin films but they are hard to implement in the case of submicron organic thin films deposited on flexible substrates. The peel test is used in a variety of configurations, in which a thin strip is pulled away at some angle from the underlying substrate. Although the peel test offers a simple test for measuring adhesion strength [4,5], in the case of organic thin layers the coating may tear due to the high stresses at the contact with the mechanical grips [6]. The pull-test allows a quantitative adhesion measurement, in which strain or energy can be extracted [7], but it still suffers from several problems like the adhesive compatibility [8]. Other specific adhesion test techniques have been developed, such as cross section indentation [9], four point bending [10], or blister adhesion test [11,12]. However, these methods require coating thicknesses of about several hundred micrometers, rigid substrates and difficult sample preparation, respectively. In a previous paper, we have tested the scratch test technique on thin organic layers printed on a flexible polyethylene naphthalate (PEN) substrate and demonstrated the feasibility, reproducibility and sensitivity of this technique [13]. However, direct comparison of critical load between samples was not straightforward since different failure mechanisms were induced.

The objective of this work is to improve the scratch test experimental conditions to get more quantitative results. We performed nanoscratches on a thin perfluoropolymer layer deposited on a PEN substrate, studied the influence of scratch speed on damage mechanism and discussed the effect of the tip radius. Mechanical ageing tests were then carried out to investigate the degradation of the interface properties. Finally, we discuss existing energy models and calculate the adhesion energy.

2. Experimental details

One type of sample is used in this work. It consists of a single thin layer deposited on a 125 μm thick Teonex® polyethylene naphthalate (PEN) semicrystalline polymer substrate. The substrate was obtained

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after a lamination process inducing anisotropic properties. Young's Modulus is specified by DuPontTeijinFilms™ at 5060 and 6240 MPa for parallel and perpendicular directions to the laminating direction respectively and the Poisson ratio at 0.4. An 800 nm thick perfluoropolymer dielectric layer [14] was deposited on the PEN by spin coating, at room temperature at 2000 rpm, using an SCS 6800 spin coater. The substrate size was 10×10 cm^2. Two deposition conditions were studied with and without plasma treatment prior to coating deposition. The plasma treatment, performed by means of a RIE Oxford Instrument Plasmalab apparatus, consists of a rapid reactive ion etch using O_2 and SF_6 gases, in order to improve the wettability of the PEN surface [15]. The layer presents a glass transition temperature above 100 °C preventing any change of structure during measurements. The layer thickness has been set to optimize the electrical performance of the OTFT [16].

The adhesion properties were evaluated at room temperature using a Nano Indenter® XP system. The scratch indenter was a diamond Rockwell C stylus with a spherical tip having a radius of 5 μm. The value of the Young's modulus and Poisson ratio were specified at 1050 GPa and 0.20 respectively [17]. The scratch length has been set to 1 mm. Two different speeds were tested: 10 and 100 μm s^{-1}. A typical scratch experiment is performed in three stages; an original profile, a scratch segment and a residual profile. In the original profile the surface morphology is obtained by pre-profiling the surface under a very small load of 100 μN. During the scratch segment the applied load was progressively increased from 0 to 30 mN. The penetration depth of the indenter under the sample surface is estimated by comparing the indenter displacement normal to the surface during the scratching with the topography of the original surface at each position along the scratch length. Finally a post-profile at a normal load of 100 μN is used to evaluate the residual scratch depth. Thus the variations of the indenter penetration and residual depth are recorded as a function of the normal load. A sensor enables the measurement of the tangential force allowing the estimation of the friction coefficient. For statistical purposes ten measurements parallel to the substrate lamination direction were performed at room temperature on each sample. After the test the critical load (Lc) where failure occurred in a particular mode was determined by post-mortem observation of the scratch track using optical and SEM microscopes. The error in the Lc determination depends on the sample preparation, the accuracy and the stability of the nanoscratch equipment and the exact location of the beginning of the damage. Since statistical errors represent the major contribution, the scattering given below corresponds to the standard deviation.

Scanning electron microscopy (SEM) was performed using a CARL ZEISS-Ultra 55 apparatus and elemental analyses were carried out by energy-dispersive X ray (EDX) using an OXFORD INCA system.

Fatigue tests have been performed at room temperature using a dedicated cyclic bending machine. The procedure was similar to that detailed elsewhere [18]. Cyclic stresses were performed at 15 cycles per minute by rolling the flexible specimen on a 5 mm radius cylinder, corresponding to a bending strain of 1.25%. Before the fatigue sequence, scratch tests were performed to determine the initial critical load. The mechanical stability of the interface was monitored by scratch test measurements done after 1000, 5000, 9000 and 10,000 cycles.

3. Results and discussion

3.1. Description of the damage mechanism: influence of the scratch speed and plasma treatment

The damage sequence, obtained at 10 μm s^{-1}, of the perfluoropolymer coating deposited on PEN with plasma treatment is presented in Fig. 1. There is a small amount of deformation observed under low load and stress level since only the wake of the indenter is observed. This is due to fully recoverable elastic deformation, time dependent viscoelastic deformation and a small amount of nonrecoverable plastic deformation resulting from compressive indentation [19]. When the load increases, lateral pads are more pronounced as seen in Fig. 1a. Then a large delamination of the coating is observed, which spreads into a diamond shape widely outside the scratch track (Fig. 1e and f). A plastic deformation of the substrate under the indenter is still visible at the beginning of the delamination area (Fig. 1b) but as the load increases, the scratch track on the substrate becomes blurred (Fig. 1c and d).

An EDX elemental analysis, presented in Fig. 2, was performed at the beginning of the delamination area. It reveals that fluorine, a constituent of the coating, is present outside the delaminated area (point 3) but is no longer detected inside (points 1 and 2), showing an adhesive damage at the interface between the coating and the substrate.

The penetration and residual depths are both plotted as a function of the scratch length in Fig. 3. At the beginning of the scratch, the indenter penetrates linearly into the material. When the load increases the penetration depth slope is steeper, showing the onset of delamination. The residual depth, determined at 100 μN normal load, takes into account the elastic recovery of the material. The first part of the track is clearly visible, the plastic deformation increases progressively up to the delamination occurrence (see arrow in Fig. 3). Then the residual depth is nearly constant at about 800 nm, corresponding to the coating thickness. This observation is in good agreement with the lower plastic deformation of the substrate shown at higher load on SEM pictures in Fig. 1c and d.

During the scratch, compressive stresses are generated ahead of the indenter and tensile stresses are induced behind the indenter [20]. Therefore it is possible to describe the delamination mechanism. A crack is initiated by tensile stresses at the coating surface on the rear side of the contact between the indenter and the coating [21]. This crack, in the case of a pure indentation test, is not able to propagate through the whole coating thickness due to the existence of compressive stresses on the opposite side of the coating [21]. However in the present case the crack opens due to the tip motion and friction effects and propagates towards the interface, initiating the delamination mechanism. Thus, the film is torn and as the indenter moves forward part of the coating is wedged between the indenter and the substrate. The coating is then compressed in front of the indenter and the shear stresses induce a delamination of the coating just ahead of the tip, so that the superficial layer accumulates in front of the indenter. Moreover, part of the removed coating may progressively accumulate under the indenter. As a consequence, the stress is reduced at the substrate surface. This is confirmed by the change of the slope which can be seen at a distance of about 800 μm on the penetration depth curve in Fig. 3. Hence the plastic strain of the substrate is very low.

Scratch test measurements were also performed at 100 μm s^{-1} on the above sample and at both speeds on the sample processed without plasma treatment. In each case the same damage sequence is observed. Consequently the critical load corresponding to the beginning of the delamination is considered as relevant to evaluate the adhesion properties. Mean critical loads, friction coefficients and adhesion energies (see Section 3.2) are reported in Table 1. The repeatability is quite good as indicated by the low standard deviations. Moreover the delamination appears at higher critical loads when a plasma treatment is done before the perfluoropolymer thin film deposition, indicating an improvement of the adhesion. The specimen processed without plasma treatment is more sensitive to the scratch speed. The influence of the scratch speed on mechanical properties was exhaustively studied in the case of polymer systems by Barletta et al. [22] for speeds ranging between 0.2 mm min^{-1} and 100 mm min^{-1}. They observed variations of deformation contributions, namely elasticity, plasticity and fracture expressed in terms of the three response model [23], as a function of the speed. They pointed out that elasticity is not sensitive to the speed over the entire range studied. Plasticity remains constant for scratch speeds between 1 mm min^{-1} and 20 mm min^{-1}. Above