

Relationships between structural properties of vapour-deposited metallic films on to polymer and their relevant adhesive performance

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The use of ultrasonic vibrations to characterize the adhesion of ultra-thin metal layers on polymer films is reported. The aim of the study was to analyse and relate the microstructural characteristics of the metallic film to the ultimate practical adhesive properties of the metal–polymer system as measured by an ultrasonic test. The sample studied was formed by thermal deposition of an aluminium layer on to a poly(ethylene terephthalate) film: Al/PET. The adhesive strength of Al/PET laminates was studied in relation with the deposition rate of the metal, its thickness, the structure of the grains and the amount of metal oxide formed at the interface, as probed by transmission electron microscopy (TEM) and secondary ion mass spectroscopy (SIMS). From these results, a correlation between the microstructure of the interface, the bulk morphology of the metallic layer and the overall adhesive performance of the (Al/PET) laminates is proposed.

1. Introduction

An interesting problem when studying the adhesion of thin metal–polymer films is to understand how the overall adhesive behaviour of such systems is influenced by the structure and morphology of the metallic layers. For thermally evaporated systems, the morphology of the metallic film greatly depends on the conditions of metallization [1–4]: residual gas pressure, deposition rate of the metal, substrate temperature, etc. For a given substrate with functional groups and nucleating sites, the problem is to study the relation existing between the final morphology of the metallic film and its physical and chemical structure near the interface. In the case where this relation exists, the bulk morphology of the metallic film could be considered as depending on the nature of the interfacial bonds. Thus, a parametric study of the adhesion of Al/PET systems is developed, including the deposition rate of the metal, the thickness and the morphology of the metal layer and the structure of the metal or metal oxides at the interface. The results of the ultrasonic adhesion test are then correlated with those obtained from (TEM) and (SIMS) to draw the parametric laws which govern the adhesion of such thermally deposited metal–polymer films.

2. Principle of the ultrasonic test

The principle of this test, the technical characteristics of the device and its application have been extensively

presented in two earlier papers [5, 6]. As shown in Fig. 1, the method consists in generating longitudinal vibrations along a metallic rod (the acoustic amplifier) by means of a piezo-electric transducer supplied with a high-frequency current generator. Because the metallized polymer film is attached to the free end of the rod, the metallic layer is subjected to mechanical vibrations until complete or partial ejection of the metallic particles occurs.

The force f , applied to an elemental volume of the metallic film having an interfacial cross-section, s , is given by

$$f = a \times (\rho hs) \quad (1)$$

where ρ and h are, respectively, the density and thickness of the metallic film, and a is the acceleration of the ultrasonic vibrations defined by

$$a = \omega^2 u \quad (2)$$

with $\omega = 2\pi\nu$, where ν is the frequency of vibrations, and u represents the amplitude of deformation resulting from the mechanical vibrations.

The expression for the stress, σ , applied to an elemental volume of interfacial contact area, s , is then obtained as

$$\sigma = (f/s) = \rho h \omega^2 u \quad (3)$$

while the energy, E , absorbed in separating the interface is

$$E \propto (\omega^3 u^2 \rho hs)t \quad (4)$$

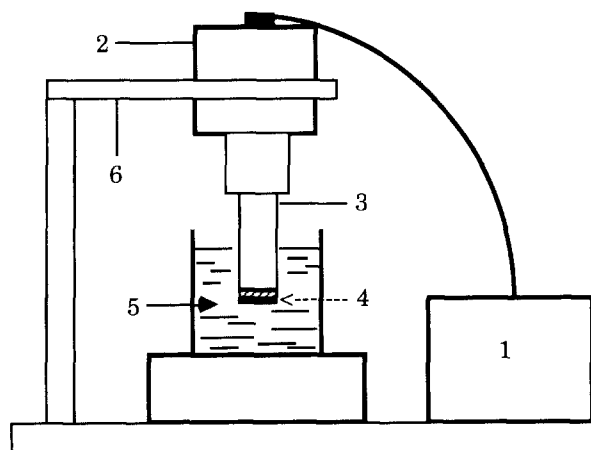


Figure 1 Experimental apparatus for the ultrasonic adhesion test. 1, Generator of frequency; 2, piezo-electric transducer; 3, acoustic amplifier; 4, sample: metal-polymer laminate attached to the free end of the acoustic amplifier; 5, test liquid (water); 6, ultrasonic device holder.

As expected, the practical adhesion of the joint is shown to be directly proportional to the duration of vibrations. For a given metal-polymer interface, this last relation allows us to determine the influence of the morphology and thickness of the metallic film as shown by the dependence on phs . This has been done for different metal-polymer laminates by comparing the duration of vibrations needed to perform separation.

Under our experimental conditions of frequency and amplitude, the energy supplied by the ultrasonic device is not sufficient to allow the separation of the Al/PET interface in air. Therefore, the method was combined with a decrease in the separation energy when performing the test in certain liquid media (water, for instance) already applied in different studies in our laboratory [7].

3. Experimental procedure

The metallized samples were prepared by thermal evaporation of high-purity aluminium rods on to 100 μm thick poly-ethylene terephthalate-films (Du Pont Luxembourg Mylar® PET). The thickness of the deposited aluminium was measured *in situ* with a quartz microbalance installed in the evaporation chamber of a Jeol metallizer. The adhesion behaviour of the metallized samples was studied as a function of the deposition rate and final thickness of the metallic film which determine some intrinsic properties of the metallized laminates (amount of metal oxide, structure and morphology). During the entire experiment, the residual gas pressure in the evaporation chamber was maintained at a constant level of 2×10^{-4} torr (1 torr = 133.322 Pa).

The deposited aluminium layers were observed and analysed either by transmission electron microscopy (TEM) or dynamic secondary ion mass spectroscopy (SIMS). For TEM examinations, the aluminium films were carefully removed from the substrate by dissolving PET in trifluoro-acetic acid [8]. The removed aluminium films were then collected on microscopic

grids, rinsed in distilled water and dried before TEM examination. The SIMS analyses were performed directly on metallized laminates to investigate the chemical composition of the aluminium film as revealed by the profiles of the Al/O ratios through the thickness. Optical microscopy was also used, principally to observe and follow the ejection of aluminium grains during ultrasonic testing. The optical microscopic observations of the tested samples at increasing testing times were used to determine the complete metal-polymer separation. Owing to the granular structure of the metal, this separation was considered to be achieved when no aluminium particle was observed at a magnification of $\times 500$ on optical micrographs. This criterion was finally used to compare the adhesive strength of the Al/PET laminates as a function of the structural and morphological parameters of the aluminium film.

4. Results and discussion

4.1. Influence of the morphology of the metallic film

The influence on adhesion of the deposition rate of the aluminium layer has been studied for a constant final film thickness of 100 nm. The following deposition rates were used: 0.2, 1.3, 6 and 11 nm s^{-1} . The deposition rate corresponds to the volume of metal deposited on to the substrate per units of time and substrate area; the volume of the metal is obtained from the weight measured by the quartz microbalance. The practical adhesion of the laminates as measured by the duration of the ultrasonic vibrations is presented in Fig. 2 as a function of the thickness of the metal layer, at a constant metal deposition rate of 1.3 nm s^{-1} . The main interest of these results concerns the principle of the ultrasonic test and its experimental justification. From Equations 1-4, the energy or force transferred to the metal layer on each cycle of vibration is proportional to its mass or thickness, when the tested area, the density of the metal and the nature of the metal-polymer interface are assumed to be constant. Accordingly, the duration of ultrasonic vibrations needed to separate the (Al/PET) interface is expected to decrease with the thickness of the metal layer. The experimental results presented in Fig. 2 confirm these

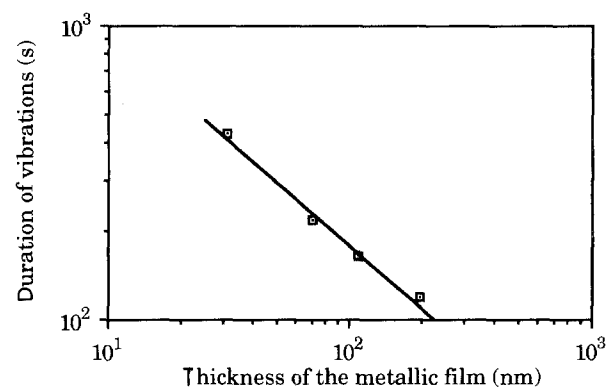


Figure 2 Ultrasonic adhesive strength of Al/PET laminates as a function of the metallic film thickness.

expectations well. On the other hand, Fig. 3 illustrates some more intrinsic properties of the metallized film. This figure represents the quantitative dependence of the metal–polymer adhesion with the deposition rate of the metal layer. Because of the structural and morphological dependence of the metallic films on their processing conditions, especially on metal deposition rate, it was natural to look for the true relevant parameters controlling the adhesion of the (Al/PET) laminates. Figs 4 and 5 show transmission electron micrographs of the aluminium layers corresponding to the lowest and highest deposition rates (0.2 and 11 nm s^{-1}). As revealed by these examinations, the drastic microstructural differences arising from the two deposition rates give a first explanation of the respective environmental adhesive or cohesive performance of these joints. The higher deposition rate is characterized by coarse grains, the lateral mean dimension of which ($120 \pm 10 \text{ nm}$) are of the same order of magnitude as the thickness of the metal layer ($100 \pm 3 \text{ nm}$). As is generally assumed, this type of structure results in a less dense and cohesive film contrary to the slow deposition rate, leading to a fine-grained morphology. The mechanical consequence of these differences is illustrated in Fig. 6. For the slowly deposited metallic film, the structure of the grain boundaries is complex and irregular, and fracture propagation is constantly deviated along these broken

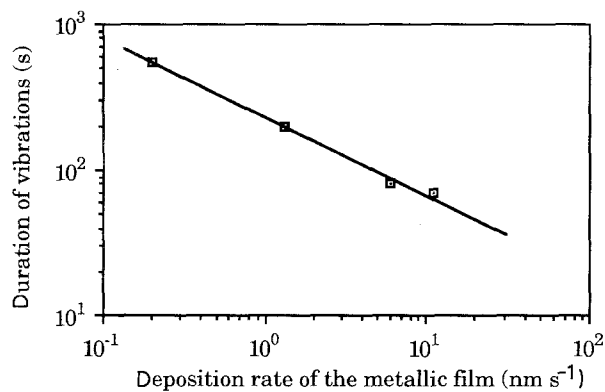


Figure 3 Ultrasonic adhesive strength of Al/PET laminates as a function of the deposition rate of the metallic film.

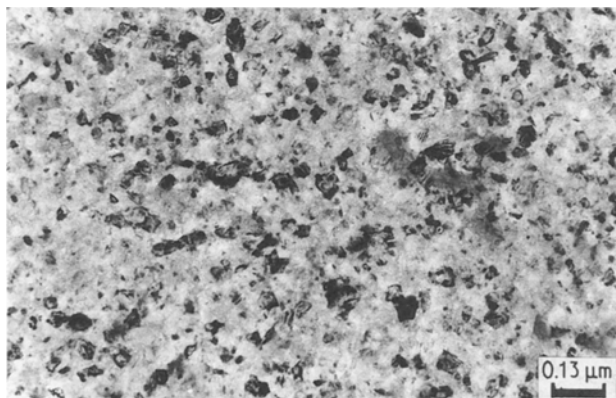
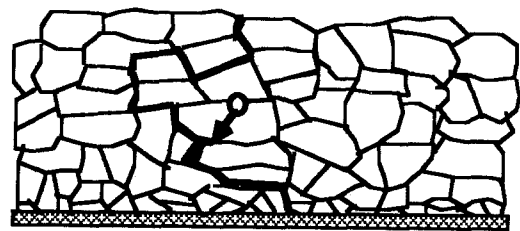


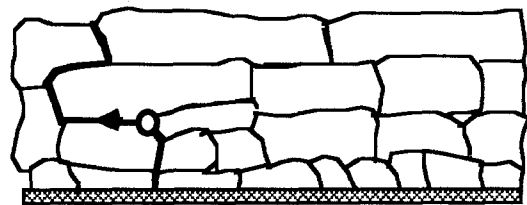
Figure 4 Transmission electron micrograph of thermally evaporated aluminium films. Deposition rate = 0.2 nm s^{-1} .



Figure 5 As Fig. 4, but with a deposition rate = 11 nm s^{-1} .



(a)



(b)

Figure 6 Schematic representation of the dependence of mechanical vibration efficiency on the grain structure of the metallic film. (a) Fine-grained morphology, (b) coarse-grained morphology.

contour lines. In other words, the mean path of a fracture initiated at a given point in the metallic layer will be considerably magnified before it leads to the ejection of a cluster of grains. The decrease of the ultrasonic durations with the metal deposition rate and thickness (Figs 2 and 3) could thus be partially explained by the above morphological and mechanical considerations.

4.2. Influence of the interfacial structure of the metallic film

In order to determine how the morphology revealed by TEM examinations is related to some interfacial features of the metal–polymer laminate, SIMS profiles were determined from three samples corresponding to different metal deposition rates. These results are expressed in terms of (Al/O) ratios through the metallic layer and are presented in Table I.

As one could expect, the aluminium layer is richer in oxygen at the interface with air and PET film than in

TABLE I Interfacial oxide ratio as a function of the deposition rate of the metal layer

	Metal deposition rate (nm s ⁻¹)		
	0.2	1.3	11
Interfacial (Al/O) ratio (counts s ⁻¹)	2350	3600	5500
Bulk metal (Al/O) ratio (counts s ⁻¹)	3200	4100	6600
Metal surface (Al/O) ratio (counts s ⁻¹)	2300	2150	2600

the bulk. The low (Al/O) ratio at the surface can be mainly attributed to the atmospheric oxidation as shown by the relatively constant value of about 2350 for the different deposition rates. If one considers that the contribution of the oxygen atoms from the surface of PET is constant whatever the Al/PET sample, the increase in interfacial aluminium oxide from high to low growth rates may be explained as follows. At low metal deposition rate, the free mean path of aluminium atoms before reaching the PET surface is very large and the probability of Al-oxygen atom interactions from the residual gas is increased. As a consequence, the oxygen incorporated in the metallic layer, especially in the first stage of film growth is more important compared to that trapped at high metal deposition rate. As discussed above, the fact that the metallic film morphology depends strongly on the deposition rate, as shown by the TEM examinations, appears to be a direct consequence of the existence of a sub-structure, defined by the interfacial oxide content (Al/O ratio) of the aluminium layer. On that account, the dependence of the adhesive strength of the Al/PET systems on the deposition rate of the metal reflects, in fact, the influence of these interfacial properties.

5. Conclusion

The adhesive strength of Al/PET laminates as measured by an ultrasonic test decreases when the deposition rate or the thickness of the thermally deposited aluminium layer is increased. According to TEM examinations, this behaviour is shown to be closely linked to the morphology of the metallic film, going from a fine- to coarse-grained structure when the

deposition rate or thickness is increased. The evidence that the morphology of the deposited aluminium film and the subsequent adhesive behaviour of the metal-polymer laminate are closely related to the microstructure of the interfacial metal layer was obtained by SIMS analysis. Finally, the chemical composition given by the metal oxide ratio, Al/O, and the microstructure of the metallic layer at the interface, constitute the main parameters controlling the overall behaviour of the vapour-deposited metal-polymer films. As mentioned earlier in Section 2, the adhesion measurements were performed in water. The principal role of this test liquid consists in a diffusion towards the metal-polymer interface and then a weakening of the existing interfacial bonds [7]. In order to understand these mechanisms better, further studies must be undertaken. With respect to these results and analyses, the ultrasonic vibration appears to be a valuable practical adhesion test.

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References

1. Y. DE PUYDT and P. BERTRAND, *Nucl. Instrum. Meth. Phys. Res.* **B39** (1989) 86.
2. M. J. VERKERK and G. VAN DER KOLK, *J. Vac. Sci. Technol.* **A4** (1986) 3101.
3. P. L. FERRAGLIO and C. D'ANTONIO, *Thin Solid Films* **1** (1967/68) 499.
4. J. F. SILVAIN and J. J. EHRHARDT, "Le Vide", les Couches Minces Supplément au no. 251, March/April 1990, p.18.
5. H. HAIDARA, M. F. VALLAT and J. SCHULTZ, *C. R. Acad. Sci. Paris Ser. II* **309** (II) (1989) 1653.
6. H. HAIDARA, M. F. VALLAT, J. SCHULTZ and P. LUTGEN, *Eur. Polym. J.* **26** (8) (1990) 907.
7. A. CARRE and J. SCHULTZ, *J. Adhesion* **18** (1985) 171.
8. J. F. SILVAIN, J. J. EHRHARDT, A. PICCO and P. LUTGEN, in "Metallization of polymers", edited by E. Sacher, J. J. Pireaux and S. P. Kowalezyk, ACS Symposium Series 440 (1990) p. 453.

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