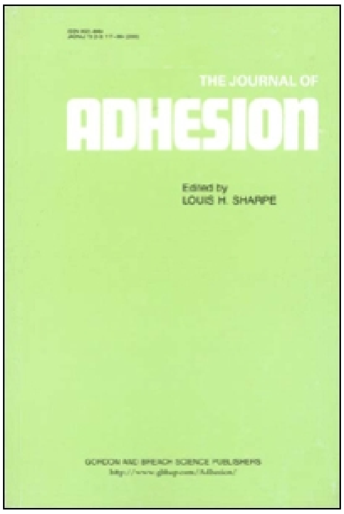

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PET Treatment in Different Solvents: Influence on the Adhesion After Metallization

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In order to correlate the adhesion of Al/PET laminates with the number of nucleation sites, gold replicates have been observed by TEM on PET immersed in various solvents before metallization. The question of the relationship between the morphology of the aluminum films evaporated onto these treated polymers is also addressed. Treatments in water, acetone, ethanol, and methanol result in a decrease of the number of nucleation sites and of the adhesion of the subsequently-evaporated aluminum films. Chloroform behaves differently and produces the reverse effect. The special behavior of $CHCl_3$ is tentatively attributed to the substitution of some surface hydrogen atoms by chlorine atoms, giving rise to new active centers on the PET surface. The decrease of the adhesion in all the other cases may be determined by the decohesion of the PET skin resulting from the diffusion of solvents.

KEY WORDS polyethylene terephthalate; nucleation; solvent treatment; solubility parameter; metallized polymers; adhesion; peel test; aluminum metallization; morphology of evaporated aluminum films.

INTRODUCTION

Metallized polymers are commonly used for audio and video recording tapes, electronic devices, and in the packaging industry. Knowledge of the properties of the metal-polymer interface is important, particularly to enhance control of the interface chemistry and to promote adhesion. Metallization of polyimide (PI)[1,2] and polyethylene terephthalate (PET)[3,4] (Mylar™ Du Pont de Nemours trade mark) have been studied in order to correlate the adhesion of metal/PET wafers with the microstructure of the metal films and the surface of the PET before metallization. The aim of this work is to determine the number of nucleation sites on the PET treated surface and to correlate this quantity with the mean grain size of the metallic thin film. Cross section transmission electron micrographs have also been obtained in order to analyze the metal/PET interface.

Part of this work was presented at the "Journées de l'adhésion," Giens, October 1991.

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EXPERIMENTAL

PET samples were immersed for one hour in different solvents (acetone, methanol, ethanol, water, and chloroform) at room temperature. After drying, the PET sample was fixed on a sample holder in the metallization chamber. Metallizations were performed in an evaporation chamber at a pressure in the low 10^{-6} mbar range. A heat-shielded Knudsen cell was used for the metal considered here. The metallic vapor flux was monitored with a quartz balance and kept constant at 3 nm/min. The distance between the Knudsen cells and the surface of the polymer was about 50 cm allowing a uniform deposition rate on the entire surface of the substrate. Furthermore, it was determined that the radiation of the cells does not affect the temperature of the substrate. Typically, the thickness of the evaporated metal film was around 50 nm.

Gold replicates were made on virgin PET. The gold clusters were evaporated from a molybdenum boat at a pressure around 10^{-4} mbar. After a controlled-thickness gold deposition (less than a monolayer), 20 nm of carbon were deposited on the PET/gold wafer. The PET was then dissolved in a trifluoroacetic acid solution and the gold/carbon specimens were then observed by TEM in order to calculate the size and the density of the gold clusters.

The adhesion strength of the Al/PET wafers were measured by a 180° peel-test previously described.[5] It is worth noting that the upper limit of this measurement is 500 J/m^2 due to the mechanical properties of the bulk polymer. The mean grain size was deduced from a statistical examination of TEM plane view micrographs. The metal polymer interface was observed by TEM (Jeol 200 CX microscope at 200 kV) on ultra thin samples prepared by mechanical polishing and ion milling.

RESULTS

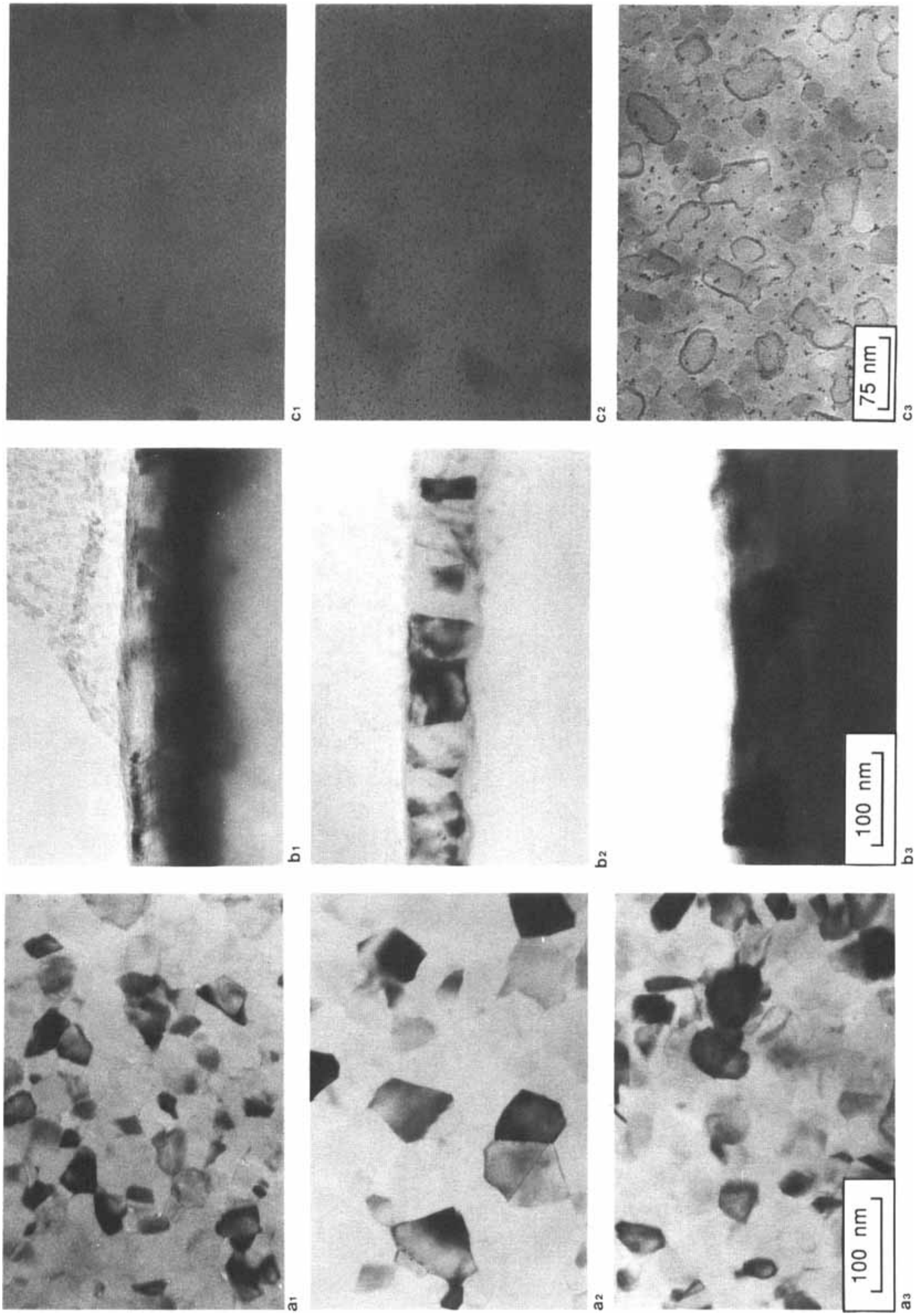
TEM micrographs are presented in figure a, b, and c for $CHCl_3$-treated PET (1), CH_3COCH_3-treated PET (3), and non-treated PET (2), and in figure d for $CHCl_3$-treated PET (1), CH_3COCH_3-treated PET (2), and CH_3CH_2OH-treated PET (3).

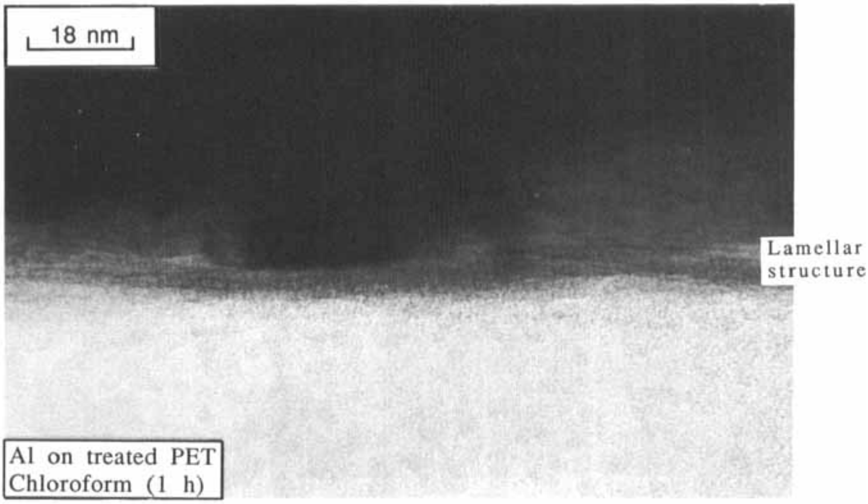
Table I shows the influence of the different solvents on the adhesion, the mean grain size of the metallic thin films, and the density of gold grains on the PET surface. In respect to the non-treated PET (control PET), all of the treatments tend to decrease the mean grain size of the aluminum films. The influence of the PET treatment is well related to the variation of the three measurements presented in Table I. In fact, for the treated PET, the increase of the gold clusters (see figure

FIGURE a Plane view TEM micrographs of Al thin films deposited onto $CHCl_3$-treated (1), CH_3COCH_3-treated (3), and non-treated PET (2).

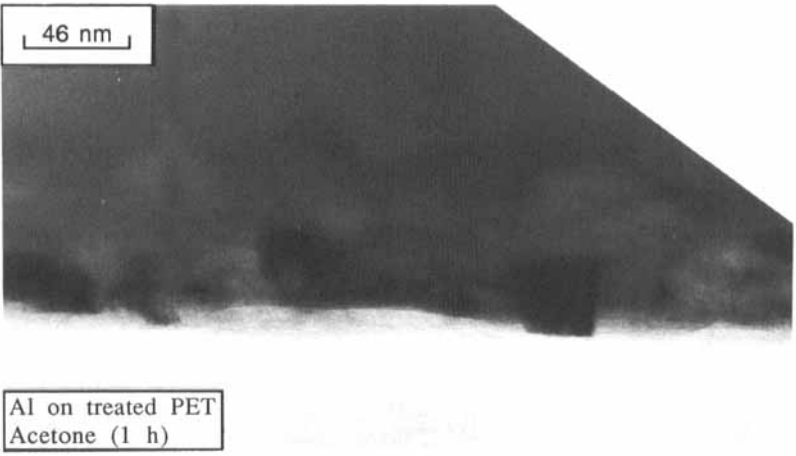
FIGURE b Cross section TEM micrographs of Al thin films deposited onto $CHCl_3$-treated (1), CH_3COCH_3-treated (3), and non-treated PET (2).

FIGURE c Gold TEM replicates micrographs done on $CHCl_3$-treated PET (1), CH_3COCH_3-treated PET (3), and non-treated PET (2).

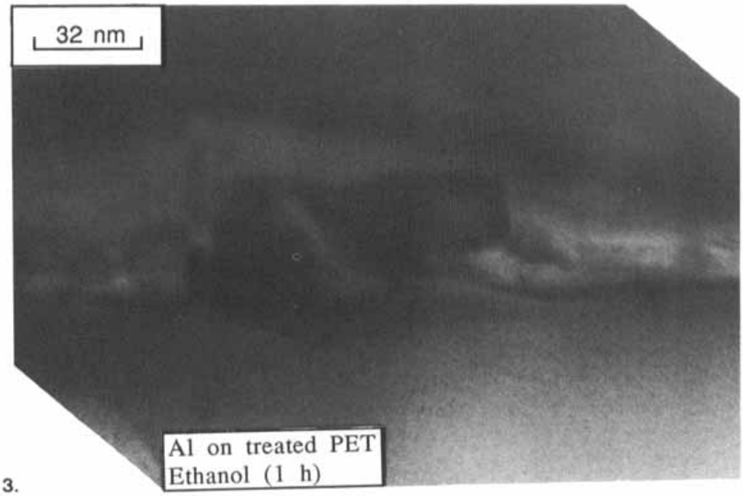

c1
c2
c3
75 nm
b1
b2
b3
100 nm
a1
a2
a3
100 nm


18 nm
Lamellar structure
Al on treated PET
Chloroform (1 h)

1.


46 nm
Al on treated PET
Acetone (1 h)

2.


32 nm
Al on treated PET
Ethanol (1 h)

3.

TABLE I
Influence of the different PET treatments on the adhesion, the mean Al grain size, and the gold cluster density.

Treatment	Adhesion J/m^2	Al mean grain size (nm^2)	Au grain density (nm^{-2})
Acetone	10	1700	$0.1\ 10^{-2}$
Methanol	20	1700	$0.1\ 10^{-2}$
Water	40	1500	$0.9\ 10^{-2}$
Ethanol	50	1500	$0.8\ 10^{-2}$
Control PET	80	3100	$1.0\ 10^{-2}$
Chloroform	400	1100	$2.5\ 10^{-2}$

c1, c2, c3, and Table I) is correlated to a decrease of the mean Al grain size (see figure a1, a2, and a3) and an increase of the Al/PET adhesion (Table I).

Figures b1, b2, and b3, and d show a series of cross sections for aluminum films evaporated on variously treated PET. The bottom and the upper parts are related respectively to the polymer and the epoxy used for the preparation of the cross section samples. Several features can be observed in these figures:

- the thickness of the film is around 60 nm for the Al films as expected from flux measurements,
- a sharp interface between the polymer and the metal films (except for the chloroform-treated PET) is observed; no cluster diffusion in the skin of the PET can be detected,
- a lamellar-like structure appears in the outer skin of the chloroform-treated PET (see figure d),
- the column-like morphology can be observed for all the metallic films. A column-like structure is defined when metal grains boundaries cross the entire thickness of the film.

DISCUSSION

The results of this study show that all of the PET treatments (except for $CHCl_3$) tend to decrease the mean grain size of the aluminum films and the density of gold grains on the PET skin. Because of the direct correlation between adhesion and gold cluster density, gold replicates can be considered as an image of the number of nucleation sites on the PET surface. Al adhesion strength seems to be directly associated with the number and the strength of the PET nucleation sites.

The improvement of the Al/PET adhesion due to $CHCl_3$ treatment has to be discussed in more detail. There was observed on this Al/PET $CHCl_3$ treatment i) an unusual lamellar morphology of the polymer skin (micrograph d1), ii) an increase of the Au cluster density, and iii) a decrease of the Al mean grain size. It is worth noting that fluorine treatment of the PET before metallization is known to induce a huge increase of the adhesion strength. In these conditions, fluorine atoms have been detected by various spectroscopies in the outer skin of the polymer. Clark *et* *al.*,[6] and Silvain *et al.*[4] have shown by XPS that in addition to the usual three Cls carbon peaks (C_I at 285.7 eV (—C—), C_{II} at 287.7 eV (—C—O—) and C_{IV} at 289.8 eV (—O—C=O)), four more carbons $C_{I'}$, $C_{II'}$, $C_{III'}$ and $C_{IV'}$) are present in the fluorinated PET at 300K. According to Chtaib's decomposition,[7] these carbons are assigned to $\underline{C}$—CF, $\underline{C}$F—C, $\underline{C}$F—CF$_2$, and $\underline{C}$F$_2$—C, respectively. However, the origin of the improvement is still an open question. We proposed that strong chemical interaction modification, including cross-linking, could be the origin of such a peculiar behavior. In that way, the role of $CHCl_3$ could be understood if a dissociative adsorption would be postulated leading to the production of atomic chlorine. The high reactivity of these atoms toward electron-acceptor groups could change the outer structure of the polymer. The unusual lamellar morphology of the PET skin (figure d1) could be an evidence of the modification. The modification of the glass transition temperature values of a polymer after immersion in a solvent has been shown by Hsiung *et al.*[8] For the PET, the values of the glass transition temperature after immersion in chloroform, acetone, ethanol and methanol are 60, 69, 70 and 75°C, respectively. The smaller value for the chloroform can be associated with an increase of the plasticity of the PET and, in that way, an increase of the cross-linking due the higher mobility of the polymer chains.

An alternative hypothesis could be the substitution of some hydrogen atoms in the surface of the PET by chlorine atoms, giving rise to new active centers favorable for Al nucleation. According to the XPS results on fluorinated PET, $\underline{C}$—CCl, $\underline{C}$Cl—C, $\underline{C}$Cl—CCl$_2$, and $\underline{C}$Cl$_2$—C carbon species could be expected. This latter explanation could be supported by gold decoration which strongly indicates an increase of the nucleation sites. Both explanations, cross-linking or new nucleation sites, are attractive and further experiments have to be performed to obtain a clear answer to this question. Nevertheless, it is believed that the first step of this process is a chemical reaction of the surface, probably through dissociative adsorption of chloroform and production of chlorine atoms. In a second step, and in the hypothesis of chain fragmentation, some selective dissolution of low molecular weight PET fragments could occur. Such a mechanism has been considered in particular with the ageing of PET after corona treatment.[9]

The experimentally-observed decrease of the adhesion of the other-treated PET/Al wafers is more puzzling. In the absence of a detailed surface reaction understanding, we are left with the proposal of some crude hypotheses that can only be considered as guidelines for further work. Among the possible hypotheses, the question of the decohesion of the polymer skin due to associative adsorption followed by solvent dissolution has to be addressed. Knox *et al.*[10,11] have shown the effect of the solvent solubility parameter on the polymer skin degradation; the increase of the solvent solubility parameter is correlated with an increase of the degradation of the polymer skin. For the PET, the solubility parameter of the chloroform, the acetone, the ethanol and the methanol[10] are respectively, 9.21, 9.77, 12.92, and 14.48. The increase of the solubility parameter has to be associated with the decrease of the measured adhesion coefficient. In that case, the dissolution of part of the polymer has also to be considered. Another attractive possibility would be the formation of nucleation active centers of different chemical nature. If, for chloroform, it is reasonable to assume that the Cl atoms play a role in the metal surface bonds then, by analogy, for the other solvents the OH groups are certainly the key factor of the surface properties. Furthermore, if we consider that the strength and the number of metal polymer bonds are, on the atomic scale, an important factor in the macroscopic adhesion strength, it is worth noting that a low number of nucleation centers are evidenced by gold decoration, after immersion in water, acetone, methanol or ethanol.

Finally, it has to be recalled that the metallization is performed under vacuum and pumping, and pumping on the polymer could also induce strong surface modification. In conclusion, this interesting behavior will be a strong stimulation to define the main parameters involved in the change of the adhesion due to the immersion in various liquid media.

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