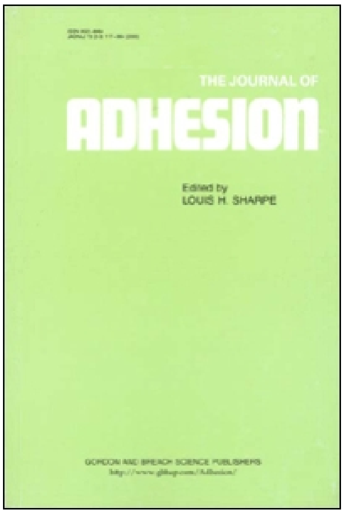

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Ko, Chan U. and Wightman, J. P.(1988) 'Experimental Analysis of Moisture Intrusion into the Al/Li-Polysulfone Interface', The Journal of Adhesion, 25: 1, 23 — 29
To link to this Article: DOI: 10.1080/00218468808075439
URL: http://dx.doi.org/10.1080/00218468808075439

J. Adhesion, 1988, Vol. 25, pp. 23–29
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Printed in the United Kingdom

NOTE

Experimental Analysis of Moisture Intrusion into the Al/Li-Polysulfone Interface

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(Received June 10, 1987; in final form August 25, 1987)

KEY WORDS Al/Li-polysulfone interface; moisture intrusion; STEM/XPS analysis; oxide to hydroxide transformation; spin cast polysulfone films; coatings.

INTRODUCTION

Aluminum-polymer bonds in hot-moist environments are subject to degradation due to moisture intrusion into the bonded joint and the resulting conversion of the surface oxide to the hydroxide.[1–3] In order to analyze moisture intrusion, work has been done on diffusion and/or solubility characteristics of humid air or water in polymer materials.[4–11] These investigations have been concerned with the actual solution and transport behavior of water in resins, especially the influence of morphology, temperature, or concentration, which affects the moisture absorption and desorption of homogeneous materials. However, such testing cannot give information on the effect of water at the substrate/adhesive interface but it can be used to screen water-sensitive adhesives.

Since the surface oxide on aluminum readily converts to aluminum hydroxide upon exposure to a high-temperature and high-humidity environment, the conversion can be used to study the mechanism of moisture intrusion into the bondline. This is the first instance in which this oxide-to-hydroxide transformation is used as an indicator for moisture intrusion into the aluminum oxide-polymer interface.

EXPERIMENTAL

Materials

The Al/Li sample used in the study was Alcoa 2090 alloy having the following nominal weight percentages of minor elements: $Li = 2.2$; $Cu = 2.7$; $Zr = 0.12$. Polysulfone (PSF) used as a thermoplastic adhesive is UDEL P-1700 (Union Carbide). The Al/Li substrates were anodized in phosphoric acid (PAA)[12] prior to coating with polysulfone.

Surface analysis

The Al/Li substrate surfaces were analyzed after dissolution of PSF in chloroform by scanning transmission electron microscopy (STEM) for surface morphology and by X-ray photoelectron spectroscopy (XPS) for surface composition. A Philips EM-42OT electron microscope was used for the STEM work. Thin Al/Li samples were used and coated with about a 2 nm of a Pd–Pt alloy. XPS analyses were made on a PHI 5300 ESCA system using a Mg anode.

Coating procedures

Two methods were used to coat the Al/Li substrate with polysulfone. In Method A, small quantities of 0.125, 3, and 10 wt % solutions of PSF dissolved in chloroform were solvent cast on the PAA samples of Al/Li. Solvent evaporation from different concentration solutions should give a varying thickness of PSF on the anodized Al/Li oxide surface. The film was assumed to be thicker in the center and thinner on the edge due to the way in which the solution was deposited on the sample. The samples were placed in a hot-moist environment (71°C-100% R.H.) for 115 hours. After environmental exposure, the samples were placed in chloroform for 4 hours at room temperature to remove the PSF. STEM photomicrographs were taken of the underlying oxide surface. While this method was useful in placing varying thicknesses of PSF on the anodized Al/Li surface, the method described below was more successful for this study.

In Method B, thin polymer films were spin cast on PAA Al/Li samples secured to a custom-made spinning platform. The PAA Al/Li substrates were flooded with a polymer solution of known concentration and spun at an average speed of 1500 rpm for five seconds. This method of sample preparation was assumed to give about the same thickness of PSF at the edge and the center of sample. PSF film thicknesses could not be measured ellipsometrically on the anodized Al/Li sample. A 0.3 wt% PSF solution cast under the same conditions on a smooth, reflective Ferrotype plate gives a film thickness of about 30 nm. The samples were placed in the same hot-moist environment for 15 hours. After environmental exposure, the samples were placed in chloroform at room temperature for 4 hours to remove the PSF and subsequent examination of the underlying oxide surface by STEM followed.

RESULTS AND DISCUSSION

In Table I, the binding energies and atomic fractions are listed for Al/Li substrates after removal of the PSF coating from the 10 and 0.125 wt% solutions. The XPS results are equivalent for the two samples. For these samples, the 0 1s photopeak assigned to aluminum oxide is at 531.8 eV and the Al 2p photopeak at 73.9 eV are present on both surfaces. The atomic fractions of 0 and Al are high, indicating aluminum oxide and confirmed by the very low concentration of the S 2p photopeak from PSF. Therefore, the chloroform removed virtually all the PSF from the substrate surface.

The STEM photomicrographs in Figure 1 on PAA Al/Li sample before (Fig. 1a) and after (Fig. 1b) placing in chloroform for 4

TABLE I
XPS Analysis of 10% PCF and 0.125% PSF onto PAA surface, placed in 71°C & 100% R.H. environment for 115 hours and then dissolved in chloroform to remove PSF

	PAA Al/Li		10% PSF on PAA		0.125% PSF on PAA	
Photopeak	B.E. (eV)	A.F.	B.E. (eV)	A.F.	B.E. (eV)	A.F.
C 1s	284.6	0.23	284.6	0.22	284.6	0.21
O 1s	531.3	0.49	531.7	0.59	531.9	0.62
Al 2p	74.2	0.24	73.8	0.18	74.0	0.16
S 2p	—	NSP	167.6	0.005	168.2	0.003
P 2p	133.9	0.03	133.4	0.005	—	NSP
O/Al		2.04		3.28		3.88
P/Al		0.13		0.028		0

hours show no physical change of the oxide due to chloroform exposure. Since the removal of the PSF adhesive from the oxide surface does not change the topography of the surface, the mode of moisture intrusion into the bondline can be studied by placing PSF coated PAA Al/Li samples in a hot-moist environment then dissolving away the PSF and observing the topography at the edge and center of subsequent underlying surface. The main two modes of moisture intrusion into the Al-PSF bondline are by i) diffusion through the polysulfone and ii) transport along the aluminum oxide–polysulfone interface, a process which is also known as wicking.[13]

The STEM photomicrograph shown in Figure 2a for the 0.125 wt% PSF sample is representative of both the edge and center of the sample which shows hydration products and is *prima facie* evidence of oxide conversion. The STEM photomicrograph in Figure 2b for 10 wt% PSF taken from the edge shows signs of hydration (pore filling).[14] But, at the center of the sample there is no sign of hydration (Figure 2c). This difference between Figure 2b and 2c indicates some diffusion of water molecules to the interface. Figures 2a–c were photographed taken of samples prepared by Method A. The problem with Method A is that the PSF thickness at the edge and at the center may differ. Therefore, samples were then prepared by Method B in which the PSF thickness from edge to center was assumed to be fairly uniform. On a 0.125 wt% PSF surface prepared by Method B after 15 hours of environmental exposure, hydration products were observed on both the edge and

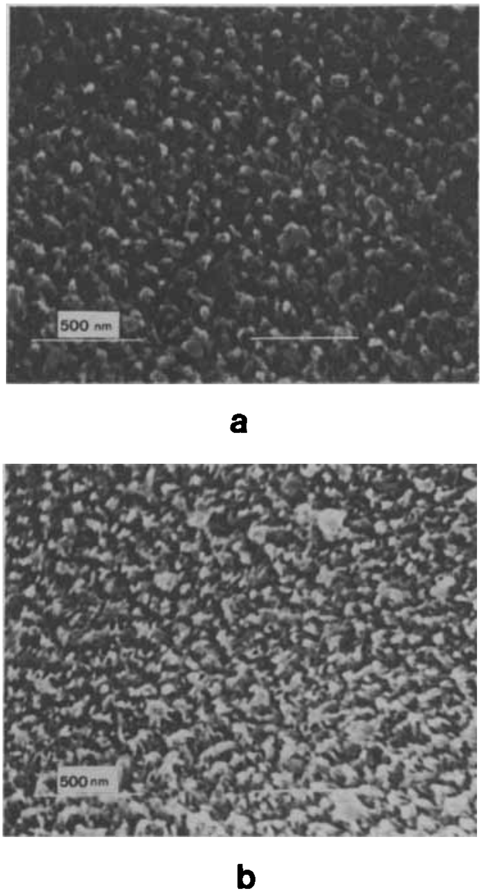

FIGURE 1 STEM photomicrographs of PAA Al/Li sample; (a) before 71°C and 100% R.H. environment, 50,000×; (b) after placing in chloroform for 4 hrs, 50,000×.

center of the sample similar to Figure 2a. The STEM photomicrograph shown in Figure 2d for 0.3 wt% PSF sample after 15 hours of environmental exposure, which is representative of both the edge and center, shows no sign of hydration products. This indicates that diffusion of water molecules to the polymer-oxide interface is primarily through the polysulfone coating and not by transport along the polymer-oxide interface.

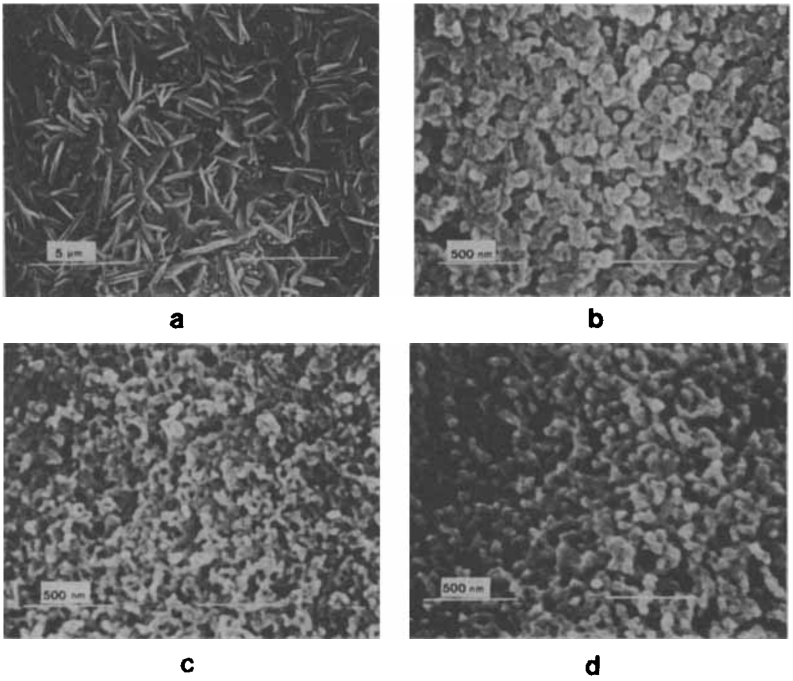

FIGURE 2 STEM photomicrographs of: (a) 0.125% PSF sample on edge and center, 6,400× (115 hr); (b) 10% PSF on edge, 50,000× (115 hr); (c) 10% PSF on center of the sample, 50,000× (115 hr); (d) 0.3% PSF on edge and center, 50,000× (15 hr).

CONCLUSIONS

STEM photomicrographs for the 0.125 wt% (115 hr environmental exposure) PSF sample on the edge and in the center both show hydration products. For the 10 wt% PSF (115 hr environmental exposure), the sample edge shows signs of hydration whereas the center of the sample does not. STEM photomicrographs of 0.3 wt% PSF (15 hr environmental exposure) samples from the center and the edge show no signs of hydration products. Water molecules diffuse into the polysulfone and thence to the interface.

Acknowledgement

The authors acknowledge the financial support of the Alcoa Technical Center and the Center for Innovative Technology. We thank Dr. Karl Wefers for helpful technical discussions and Steve McCartney for assistance in the STEM work. Enabling funds for the purchase of the surface analysis equipment came from the National Science Foundation and Virginia Tech.

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