WORK OF ADHESION MEASUREMENTS

BY A PERIODIC CRACKING TECHNIQUE

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INTRODUCTION

In a recent study, Chow et al.[1] introduced a technique* for determining the energy associated with interfacial separation of a two-layer composite which consisted of a polymeric substrate and a brittle film overcoat. The technique is based on a model which assumes a perfectly elastic composite. In the present study, it is shown that as long as only the film component of the composite is brittle, the technique is also applicable to the composites where the substrates may display plastic deformation prior to adhesive failure of the film. Strain measurements, instead of load, eliminate the difficulties introduced by the plastic behavior of the substrate. Experimental work was performed on systems containing brittle amorphous selenium films on aluminum and Mylar substrates. These systems with selenium films were of interest due to their usage in photoreceptor technology.

THE MODEL

The two-layer composite model used in this study is illustrated in Figure 1. Here, the substrate (layer 1) is subjected to the action of an external stretching force, F, per unit width in the z-direction. This load is then transmitted to the surface film (layer 2) through the interface. A strain energy is stored within the composite as a result of this stretching. A portion of this strain

* A specific title for the technique was not used by Chow et al., however, it is now proposed that "periodic cracking technique" is an appropriate title since periodic surface cracks of calculable spacing are almost always seen in the surface film during testing.

energy may be released through adhesive failure of the surface film. A crack then develops at the interface, and the composite fails adhesively. This adhesive failure may be preceeded by a periodic cracking of the surface film if the crack strain of the film is reached before the adhesive failure strain. This depends on the geometry and the material properties of the composite. However, regardless of a periodic cracking which may take place prior to adhesive failure, the analysis presented below is valid both for a sample that is uncracked (Fig. 1(a)) or for only a portion of a composite lying between two surface cracks (Fig. 1(b & c)).

If the strain energy is denoted as U_e and the energy required for crack formation as U_f, the total energy of the system

$$U = U_e + U_f. \tag{1}$$

The energy required for crack formation may be defined in terms of the work of adhesion per unit area, γ, and the crack length, a (Fig. 1), as $U_f = \gamma a$. When the critical stretching force, F_{cr}, is reached, an unstable equilibrium exists, and thus

$$\partial U/\partial a = \partial(\gamma a + U_e)/\partial a = 0, \text{ and} \tag{2}$$

$$\gamma = -\partial U_e/\partial a. \tag{3}$$

This work of adhesion per unit area, γ, is the difference between the sum of the surface energies of the two layers and the interfacial energy between them. In mechanical measurements, the effect of other factors, such as local plastic deformation, is also reflected in this term during actual tests. Therefore, the work of adhesion values are always higher than the ones obtained by thermodynamic techniques.

Equation (3) expresses the relationship between the work of adhesion and the strain energy, U_e. The elastic strain energy per unit width of the composite is

$$U_e = \frac{1}{2} \int_x \int_y \sigma_{ij} e_{ij} dxdy, \quad (i,j = x,y,z) \tag{4}$$

where σ_{ij} and e_{ij} denote the stresses and the strains, respectively.

The solutions of the stress and the accompanying strain fields for an elastically deforming composite of the geometry given in Fig. 1 have been obtained by Chow et al.[1] In their analysis a plane-strain state of stress is assumed, and the normal stress, σ_{yy}, is assumed to be negligible compared to the tensile (σ_{xx}) and the shear (σ_{xy}) stresses due to thin composite geometry. Furthermore, in numerical analyses carried out on Mylar substrates and amorphous selenium films, the shear stress contribution to the strain energy is found to be negligibly small compared to the tensile stress contribution.[1]

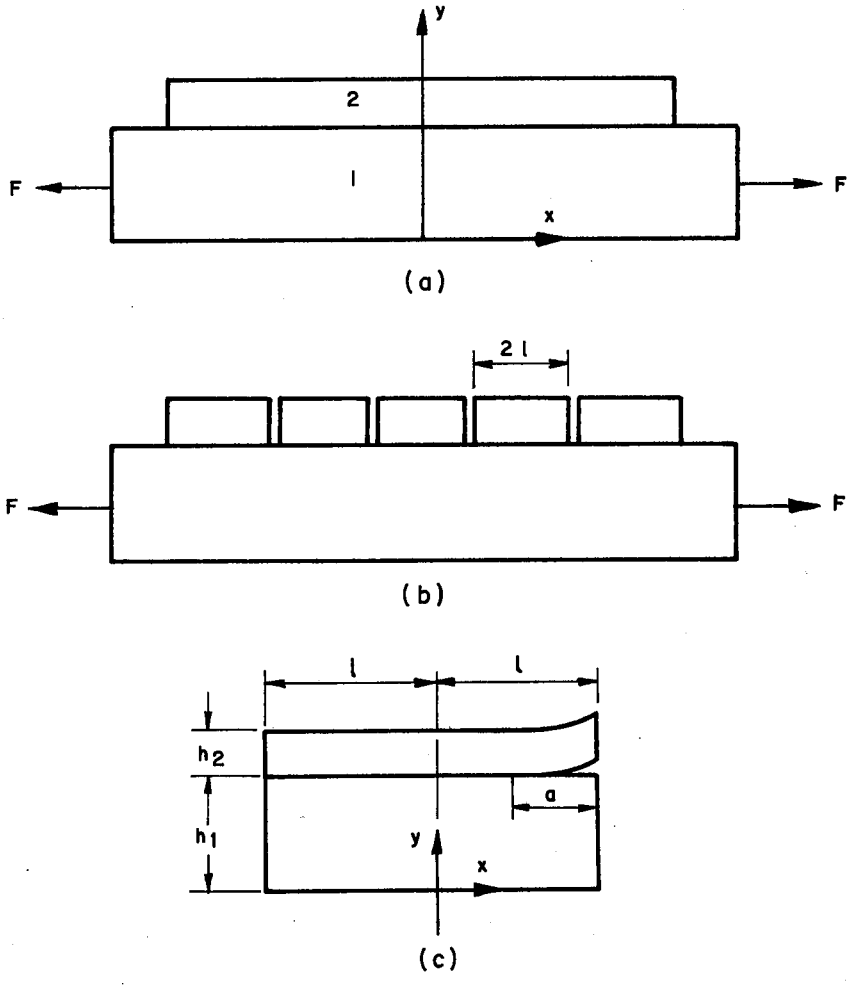

Fig. 1. Two-layer composite model used in the formulation of the periodic cracking technique.[1]

Therefore, the shear stress term is neglected in eq. (4). The resulting work of adhesion equation is then

$$\gamma = (\bar{C}h/2)(F_{cr}/C_1h_1)^2\delta(1 - \delta)^2(1 + \delta/4D^*) \qquad (5)$$

where $C_i = Ei/(1 - \nu_i^2)$, the elastic constant of the ith layer, (i = 1,2); ν = Poisson's ratio; E = Young's modulus; $\bar{C} = (C_1h_1 + C_2h_2)/h$,

the mean elastic modulus; $h = h_1 + h_2$, the thickness of the composite; $\delta = C_2h_2/\bar{C}h$, a non-dimensional parameter; $D^* = [C_1h_1^3 + C_2h_2^3 + 3\delta(1 - \delta)\bar{C}h^3]12\bar{C}h^3$, the non-dimensional flexural rigidity of the sample; and F_{cr} = the critical stretching force where adhesive failure occurs. Eq. (5) relates F_{cr} to the materials properties and the geometry of a given system. The validity of this equation at different geometries was tested by Chow et al.[1] with amorphous selenium films on polymer substrates, and excellent agreement was obtained between experimental and calculated values. The same method was utilized in the measurement of work of adhesion in similar systems in a later study.[2]

Simplified Adhesion Formula

A simplification of eq. (5) is possible if the flexural rigidity of the substrate, $D_1 = C_1h_1/12$, is much higher than that of the overcoat, $D_2 = C_2h_2/12$. The simplified form of eq. (5) is then

$$\gamma = \frac{1}{2} (F_{cr}/\bar{C}h)^2 C_2h_2 \tag{6}$$

which may be obtained from eq. (5) by taking $C_1h_1 >> C_2h_2$. Physically, eq. (6) represents a substrate that transmits the tensile load to the overcoat without itself being bent. This situation is approached for thin films on high modulus substrates such as metals.

It should be noted that the term $(F_{cr}/\bar{C}h)$ of eq. (6) is the strain that the composite has undergone at the critical load. This term is defined as the critical strain, e_{cr}, and when it is substituted into eq. (6)

$$\gamma = \frac{1}{2} e_{cr}^2 C_2h_2. \tag{7}$$

Eq. (7) does not contain any material properties of the substrate; therefore, for an overcoat of given thickness on different substrates, the work of adhesion may now be measured as a function of only the critical strain where adhesive failure takes place.

The calculations based on this model are for a perfectly elastic composite case. When such a composite fails adhesively at a critical force, F_{cr}, the strain energy released from the system is calculated as the γ value. This γ value is then equal to the area designated as (1) in Fig. 2 as the difference in the areas under the load-elongation curves of the composite and the substrate calculated up to the corresponding critical strain. The area (2) under the load-elongation curve of the film up to the same critical strain is similarly equal to this γ value if the assumption neglecting the bending contribution is a valid one. When experiments are done on elastically deforming composites, the utilization of either the critical load (eq. (6)) or the critical strain (eq. (7)) measurements results in identical γ values. However, in cases where adhesion of

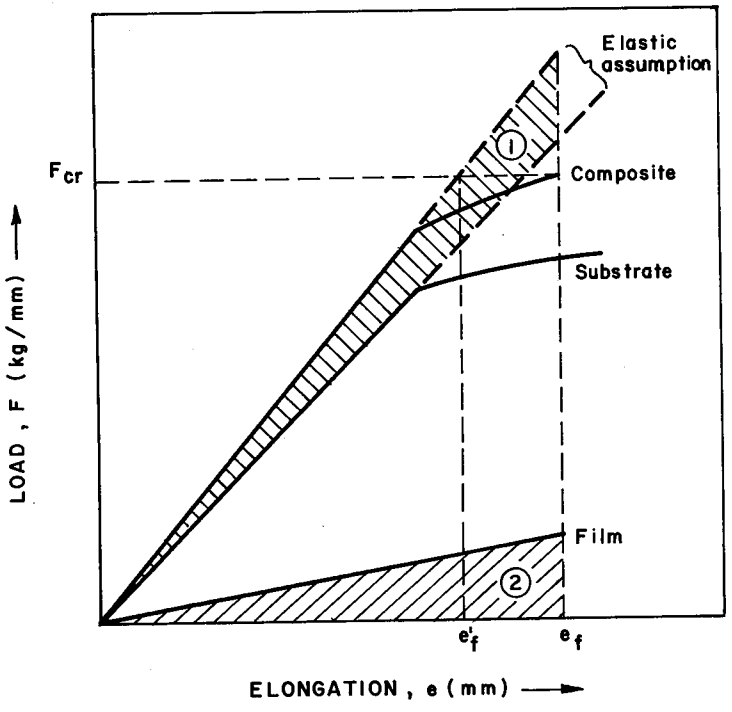

Fig. 2. Schematic load-elongation diagram of an elastoplastic composite.

brittle films on plastically deforming substrates is considered, the results differ from each other.[2] In such cases, if F_{cr} is used as the loading parameter from which the associated quantities such as the stresses and the strains are calculated, a virtual strain, e_f, instead of the real strain, e_f, enters into the calculations. Erroneously low adhesion values and a dependence of adhesion on the film thickness are then observed when experimental work is based on the measurement of F_{cr}.[2] These difficulties, however, are completely avoided when the calculations are based on the actual e_{cr} values.

EXPERIMENTAL

Mylar* and aluminum¶ strips of 15mm x 100mm in thicknesses of 0.0762mm and ∿1.5mm, respectively, were used as the substrates. The aluminum substrates were electropolished after a fine mechanical polishing in order to obtain smooth surfaces. Both the Mylar and aluminum substrates were cleaned ultrasonically and rinsed with reagent grade alcohol and acetone.

* A commercial grade polyester.

¶ Supplied by Etibank Aluminum Works, Seydişehir, Turkey. Code Etial-0, 99.0% Al.

A rectangular section of 10mm x 15mm in the middle of these substrates was then coated with selenium in groups of four or five in a high vacuum coating unit. A filament-wound alumina boat containing pressed selenium pellets was used as the evaporation source. Coatings were done at a deposition rate of ∿200 Å/sec on a substrate of ∿40°C in a starting vacuum of $<10^{-5}$torr.

In an effort to eliminate the effect of the presence of an oxide layer on aluminum surfaces, a double coating technique was used. A set up with two evaporation sources in the same coating unit was utilized to vacuum deposit fresh (unoxidized) Al onto the prepared Se surfaces just before (∿15 sec) Se deposition took place. Some Mylar substrates were similarly aluminized and coated with Se without breaking the vacuum.

The adhesion tests were done by applying a tensile load[§] to the substrates at a rate of 0.5 mm/min. The strain was recorded using an extensometer capable of measuring 0.02% strain. The adhesive failure point of the specimens was observed either visually or with a low-power telemicroscope.

Specimens after adhesive failure were examined with a scanning electron microscope. The amorphous selenium film thicknesses were also determined with the SEM.

RESULTS AND DISCUSSION

The adhesion values listed in Table 1 were calculated using eq. (7) based on the material properties listed in Table 2. A comparison with the values calculated using eq. (5) was made, and a good agreement within experimental error was obtained indicating that the assumption ignoring the bending contribution was a valid one. The reported adhesion values are the averages of values obtained from four or five specimens prepared simultaneously. The deviation of the individual values from the mean was within the experimental accuracy (±10%) for most specimens.

SEM examination of these interfaces after failure showed that Mylar/Se composites failed through the interface (Fig. 3(a)). On the other hand, when Mylar/Al*/Se specimens were examined, the Al film was observed to remain on the Mylar surface (Fig. 3(b)). The Se part of the interface similarly showed the presence of a thin layer (∿0.1μm) of Al (Fig. 3(c)). The adhesive failure then took place not at the interfaces but through the aluminum layer between Mylar and Se. This observation supports the measured increase in the adhesion value from 5.1×10^3 to 13.0×10^3 ergs/cm^2 (Table 1) when the Mylar/Se system is modified with the introduction of an unoxidized interfacial Al layer. The work of adhesion values of both

§ Instron Universal Testing Machine, Model 1125, Instron Co., Canton, Mass.

Table 1. Adhesion Values of Selenium on Mylar and Aluminum Substrates

Composite	Layer Thickness, mm			γ, ergs/cm^2
	Substrate	Aluminum*	Selenium	
Mylar/Se	0.0762	-	0.0200	5.1×10^3
Mylar/Al*/Se	0.0762	0.0002	0.0020	13.0×10^3
Al/Se	1.450	-	0.0020	2.3×10^3
Al/Al*/Se	1.450	0.0002	0.0030	3.8×10^3

*Unoxidized aluminum deposited just before Se deposition.

Table 2. Mechanical Constants of Mylar, Selenium, and Aluminum

Material	E, kg/mm^2	ν	$C = E/(1-\nu^2)$, kg/mm^2
Mylar[1]	386.65	0.375	449.92
Selenium[3]	1019.30	0.324	1135.58
Aluminum[4]	7382.19	0.310	8167.04

the Mylar/Al and the unoxidized Al/Se interfaces would be $>13.0 \times 10^3$ ergs/cm^2. When Se is in contact with atomically clean Al, a thin layer ($\sim$15-20 Å) of aluminum selenide forms at the interface as a result of a reaction between Al and Se.[5] The formation of this aluminum selenide compound at the Al/Se interface would account for the high γ value of this interface. The high adhesive strength of the Mylar/Al interface, however, was not expected. Spectroscopic work on the chemical nature of the Mylar/Al interface would be useful in the clarification of the observations made in this study.

An increase in the work of adhesion of the Al/Se system is similarly detected from 2.3×10^3 to 3.8×10^3 ergs/cm^2 when the interface is modified with the presence of an unoxidized Al layer. SEM examination showed that the Al/Se system failed through the interface.

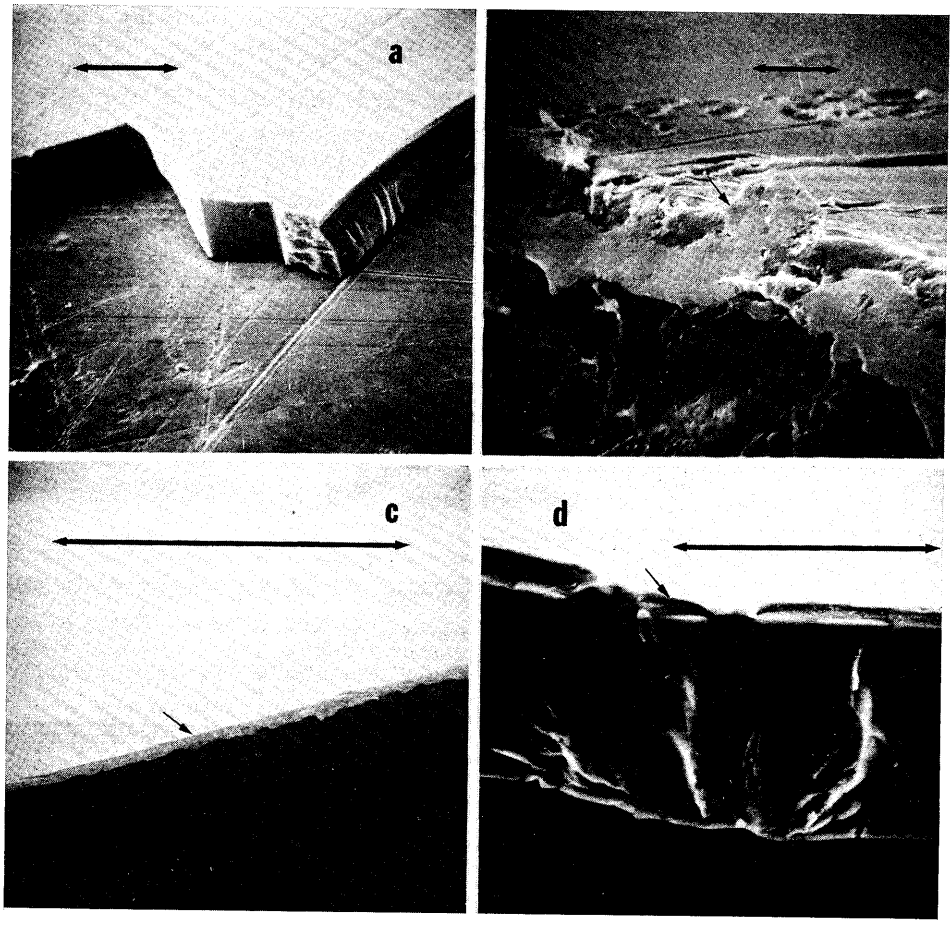

Fig. 3. SEM photographs of (a) amorphous selenium film on Mylar substrate, (b) aluminum film hanging over the edge of the Mylar substrate of the Mylar/Al*/Se composite, (c) other half of the aluminum film on the selenium portion of the Mylar/Al*/Se composite, and (d) aluminum film which remained adhered to the Se portion of the Al/Al*/Se composite. Aluminum films are indicated with the short arrows. The lengths of the magnification bars are 10 μm. (Photographs were taken on samples other than ones listed in Table 1. Therefore, the layer thicknesses differ.)

Both the Al and Se surfaces appeared clean at magnifications up to 10000X. Optical and SEM examination of the surfaces in the Al/unoxidized Al/Se system, however, showed that the fresh Al layer remained attached to the Se film (Fig. 3(d)). Adhesive failure took place through the Al/fresh Al interface. The adhesive strength of the fresh Al/Se interface is again increased due to the formation of an aluminum selenide compound at the interface.

CONCLUSIONS

The periodic cracking technique, which was formulated by Chow et al.[1] with the assumption of a perfectly elastic composite, is shown to be applicable to systems where the films must be brittle but the substrates may display plastic deformation. In such cases where the substrate deforms plastically, strain measurements, instead of load, must be performed in order to correctly calculate the strain energy stored in the film.

Experiments were performed on systems which contained amorphous Se on Mylar and aluminum substrates. In both systems, the adhesive properties were improved when an unoxidized layer of Al was introduced between the Se film and the substrates.

ACKNOWLEDGEMENT

Discussions with T. Ö. Oğurtanı were most helpful.

REFERENCES

1. T. S. Chow, C. A. Liu, and R. C. Penwell, Direct determination of interfacial energy between brittle and polymeric films. J. Polym. Sci. 14: 1305 (1976).
2. A. Davutoğlu, Determination of the work of adhesion by a periodic cracking technique, M. Sc. Thesis, Department of Metallurgical Engineering, Middle East Technical University, Ankara, Turkey (1980).
3. W. E. Snowden and İ. A. Aksay, Measurement of thick film adhesion by an impact separation technique, in, "Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems," J. A. Pask and A. G. Evans, eds., Plenum, New York (1981).
4. G. E. Dieter, "Mechanical Metallurgy," McGraw-Hill, Kogakusha, Ltd., Tokyo (1976).
5. İ. A. Aksay and K. S. Liang, unpublished work.