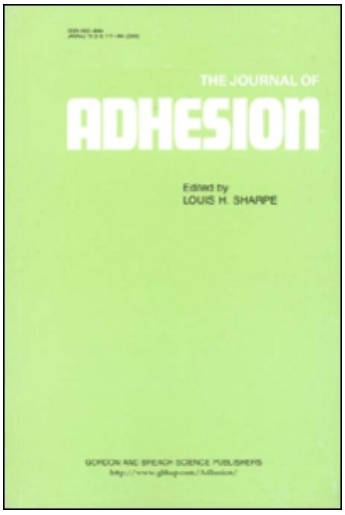

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A Self-Delamination Method of Measuring the Surface Energy of Adhesion of Coatings

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A self-delamination technique is presented to assess the surface energy of adhesion of coatings. By measuring the debond area resulting from a circular hole cut in a film adhered onto a substrate, the surface energy may be determined if the tensile modulus, Poisson's ratio and residual stress level of the film are known. This method is useful for coating thicknesses greater than a critical thickness for self-peeling. Using this technique, the surface energy for a polyimide film (cured up to 220°C) on a glass plate was determined to 3.2 Nm^{-1}.

KEY WORDS Coatings; surface energy; adhesion; polyimide film; spontaneous peeling; analysis.

INTRODUCTION

Thin coatings adhered to rigid substrates may be considered to be under plane stress conditions. This signifies that there are no stresses across the interface except at edges. Cuts or cracks in the coating create such free edges. The stresses acting across the interface near these cuts or cracks may then lead to delamination of the coating.

A usage criterion for coatings on substrates is difficult to define. Merely reporting the stiffness of a material or the adhesion strength

of a coating does not fully describe the coating. Stiff, high modulus films are generally preferred over softer coatings. However, these stiff materials can develop large residual stresses that may result in failure of the coating such as delamination or cracking of the film. A reliable assessment of a coating compares the mechanical properties and residual stress to the adhesion of the coating.

An energy balance approach has been successfully used to relate the adhesion of a coating to internal stress.[1–4] Typical experiments involve T-peel or pull-off tests. From these measurements the surface energy of adhesion may be determined, taking into account the effect of residual stress in the film. This stress actually decreases the force needed to remove a coating since it increases the energy of the system. If the stress is sufficiently large compared to the coating dimensions there may be enough energy to crack or self-delaminate the film.[5] Without any external constraints, the coating can completely delaminate.

A method has been developed that takes advantage of the spontaneous delamination by constraining the extent of debonding. This allows a unique method of measuring the surface energy of adhesion of coatings.

ANALYSIS

It has been indicated that spontaneous peeling of a coating from its substrate provides a measurement of the surface energy of adhesion.[1,2] A simplified analysis relates the interfacial surface energy, γ, to the stress: $\gamma = t_{cr}\sigma_0^2(1-\nu)/E$, where t_{cr} is the critical thickness required for debonding at a constant residual stress, σ_0, E is the tensile modulus and ν is Poisson's ratio. Existing methods to measure surface energy require a series of coatings of various thicknesses above and below the critical thickness to assess the surface energy. By inducing an internal geometrical constraint, a method has been developed to measure γ with the condition that $t > t_{cr}$. The constraint is due to a circular hole (radius 'a') cut in the material. The circular cut releases the radial stresses at the hole but there are still hoop stresses in the material and radial stresses away from the hole. If $t > t_{cr}$, the inner circular piece will completely debond while the material on the outer portion of the cut will only

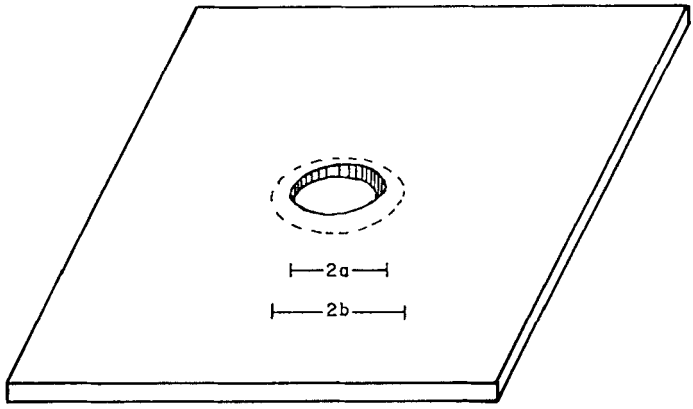

FIGURE 1 Illustration of delamination due to presence of circular cut in a coating on a rigid substrate.

partially debond to a radius 'b" (see Figure 1). The analysis for the determination of γ for this problem is given below. For a homogeneous, isotropic medium the constitutive relation between stress and strain that includes thermal effects can be expressed using indicial notation as

$$E(\epsilon_{ij} - \delta_{ij}\alpha\,\Delta T) = (1 - \nu)\sigma_{ij} - \nu\,\delta_{ij}\sigma_{kk} \tag{1}$$

where

σ_{ij} = stress,
ϵ_{ij} = strain,
δ_{ij} = Kronecker delta,
E = tensile modulus,
ν = Poisson's ratio,
α = thermal expansion coefficient,
ΔT = change in temperature.

Similar expressions may be written to include any non-mechanical displacements such as swelling.

For a thin coating on an infinitely flat, rigid plate, plane stress conditions may be applied; thus, there are no shear or normal stresses acting on the interface ($\sigma_{33} = \sigma_{13} = \sigma_{23} = 0$). Equation 1

may then be expanded in cylindrical coordinates as:

$$E(\epsilon_{rr} - \alpha\,\Delta T) = \sigma_{rr} - \nu\sigma_{\theta\theta}, \tag{2a}$$

$$E(\epsilon_{\theta\theta} - \alpha\,\Delta T) = \sigma_{\theta\theta} - \nu\sigma_{rr}, \tag{2b}$$

$$E(\epsilon_{zz} - \alpha\,\Delta T) = -\nu(\sigma_{rr} + \sigma_{\theta\theta}). \tag{2c}$$

Solving Eq. (2) for the principal stresses in the plane of the film gives:

$$\sigma_{rr} = [\epsilon_{rr} + \nu\epsilon_{\theta\theta} - \alpha\,\Delta T(1+\nu)]E/(1-\nu^2), \tag{3a}$$

$$\sigma_{\theta\theta} = [\epsilon_{\theta\theta} + \nu\epsilon_{rr} - \alpha\,\Delta T(1+\nu)]E/(1-\nu^2). \tag{3b}$$

Initially the coating is in uniform tension and there are no displacements in the plane such that $\epsilon_{rr} = \epsilon_{\theta\theta} = 0$. With these conditions Eqs. (3) become

$$\sigma_{rr} = \sigma_{\theta\theta} = -E\alpha\,\Delta T/(1-\nu). \tag{4}$$

As described above, when a circular hole of radius 'a' is cut in the film it may partially debond to a radius 'b'. The stress in the coating may be obtained by using the plane stress solution for a hollow cylinder under pressure:

$$u_r = A/r + Br, \tag{5}$$

(u_r = radial displacement, A, B = constants).

At $r = b$, the film remains bonded to the plate, therefore $u_r = 0$. With this boundary condition, on solving for A, u_r can be expressed as

$$u_r = B(r - b^2/r). \tag{6}$$

Using this to obtain the strains (ϵ_{rr}, $\epsilon_{\theta\theta}$) and inserting these into Eq. (3a) gives:

$$\sigma'_{rr} = \frac{E}{(1-\nu^2)}[B(1 + b^2/r^2) + B(1 - b^2/r^2) - \alpha\,\Delta T(1+\nu)]. \tag{7}$$

where the prime indicates the partially debonded case.

With the other boundary condition, $\sigma_{rr} = 0$ at $r = a$ (free surface), Eq. (7) becomes

$$\sigma'_{rr} = \frac{-E\alpha\,\Delta T\,b^2(1 - a^2/r^2)}{b^2(1-\nu) + a^2(1+\nu)} \qquad \text{for } a \le r \le b. \tag{8}$$

Similarly it can be shown that

$$\sigma'_{\theta\theta} = \frac{-E\alpha\,\Delta T\, b^2(1 + a^2/r^2)}{b^2(1-\nu) + a^2(1+\nu)} \qquad \text{for } a \le r \le b. \tag{9}$$

The stored energy in a material is defined over a volume element as

$$U = \int_V \tfrac{1}{2}\,\sigma_{ij}\epsilon_{ij}\,dV \tag{10}$$

which for a thin film, neglecting shear stresses, becomes

$$U = 1/(2E)\int_0^t \int_0^{2\pi} \int_{r_1}^{r_2} (\sigma_{rr}^2 + \sigma_{\theta\theta}^2 - 2\nu\sigma_{rr}\sigma_{\theta\theta}) r\,dr\,d\theta\,dz. \tag{11}$$

For the bonded case in the region from $r_1 = a$ to $r_2 = b$, the internal energy is found by using Eq. (4) in Eq. (11):

$$U = \frac{tE\pi(b^2 - a^2)(\alpha\,\Delta T)^2}{(1-\nu)}. \tag{12}$$

For the debonded case between $a \le r \le b$, by using Eqs. (5) and (9) for the stresses, Eq. (11) gives the energy as

$$U' = \frac{tE\pi(b^2 - a^2)(\alpha\,\Delta T)^2 b^2}{b^2(1-\nu) + a^2(1+\nu)}. \tag{13}$$

The difference between the two states is equal to the energy required to form two new surfaces over the debonded area:

$$U' - U = -\gamma\pi(b^2 - a^2) \tag{14}$$

with γ = surface energy of adhesion at interface.

Using Eq. (12) and (13) in eq. (14) and solving for γ gives:

$$\gamma = \frac{Et(\alpha\,\Delta T)^2 a^2(1+\nu)}{b^2(1-\nu)^2 + a^2(1-\nu^2)}. \tag{15}$$

Since $\sigma_{rr} = \sigma_{\theta\theta} = -E\alpha\,\Delta T/(1-\nu)$ Eq. (4) is the residual stress, σ_0, in the unbonded state, Eq. (15) simplifies to

$$\gamma = \frac{\sigma_0^2 t}{E}\left[\frac{a^2(1-\nu^2)}{b^2(1-\nu) + a^2(1+\nu)}\right] \tag{16}$$

From this expression the surface energy of adhesion may be determined if the tensile modulus, Poisson's ratio, coating thickness, residual stress in the film and the debonded area are known.

DISCUSSION

This technique was demonstrated using polyimide (PI) coatings on glass. These films were prepared by spin-coating a polyamic acid solution, PAA, [poly(N,N'-bis(phenoxyphenyl)-pyromellitamic acid)] in NMP onto glass plates. The thickness was altered by varying the spinning speeds. The PAA coatings were heat treated at 85°C for 30 min., 150°C for 30 min. and 220°C for 30 min. under nitrogen to remove solvent and thermally imidize the material.

A circular hole of radius 0.7 cm ('a') was cut in a coating of thickness 35 μm. Within seconds, the inner circular piece completely delaminated and the film on the outside of the circle partially debonded to a radius 'b' which, for this example, is 1.05 cm.

For the PI coating the tensile modulus was determined to be 3 GPa, Poisson's ratio assumed to be 0.4 and the residual stress estimated to be 30 MPa.[6] With these values the surface energy was calculated to be 3.2 Nm^{-1} using Eq. (16).

To illustrate that this method is independent of hole size, a circle of radius 0.55 cm was used. From the measured delamination ($b = 0.8$ cm) γ was found to be 3.4 Nm^{-1}.

For comparison, 180° peel tests were performed on these samples. Strips of the 220°C cured material were peeled off the glass in an Instron to obtain peel energies between 1 and 2 Nm^{-1}. This is good agreement considering the assumed values for σ_0 and ν. However, these values are two orders of magnitude less than adhesive energies for polyimides reported in the literature as determined by a blister method and a T-peel test.[7,8] The literature values were obtained for PI cured at 400°C on silicon wafers while our results were obtained for a 220°C cured PI film on glass. This method for determining the surface energy considers only initial and final states and does not incorporate any energy release rate.

Several other coatings were prepared using the same PAA material except that curing steps or thicknesses were varied. A

20 μm coating cured up to 220°C as before showed no signs of delamination with this method. This indicates that the critical thickness for self-peeling lies between 20 and 30 μm. However, on applying this technique to a 20 μm film cured only at 85°C for 30 min., slight debonding was observed and the surface energy was determined to be 1.1 Nm^{-1}. In comparison, thin films cured up to 400°C had a final thickness of 15 μm and showed no signs of delamination upon inscribing a hole in the material. After the 85°C cure step, the coating remains as poly(amic acid). Only after higher heat treatments is it thermally cyclized to the polyimide. Therefore, the difference in results between 85° and 400°C cure may be attributed to a chemical change in the material which alters the properties such as surface energy. Also, after imidization, the thickness has been reduced to a value below the critical thickness for self-delamination. It should then be possible to use this technique to follow the change in surface energy throughout the processing history.

The approach described above for obtaining γ is not restricted to circular cuts. Cuts of varied shape and size, for example, a straight slit, may be used for this technique. In this case, semi-circular debonding was observed on both sides of the slit. Although such geometries are easier to inscribe in the film the energy and stress analysis becomes more difficult, especially at corners.

Additional experimental work is required to assess the limitations of the analysis presented. The preliminary results do support the analysis discussed above. This analysis is based on a spontaneous self-delamination process in the system and does not consider rate effects.

Experimentally, to improve this technique, new methods of cutting holes in coatings without disturbing the stress state of the film are required. Since the inner piece of film completely debonds it should be possible to obtain the residual stress in the film using strain analysis techniques. These methods, such as Moire fringes or digital-image-correlation techniques, allow determination of small planar displacements of the film due to delamination.[9,10] With these displacements and mechanical properties of the coating, the residual stress may be obtained for the film for each individual delamination test.

SUMMARY

A method of assessing the surface energy of coatings has been presented. This method is applicable when the thickness of the coating is greater than a critical debond thickness such that there is sufficient energy in the film for self-delamination. This technique is ideal for coatings which experience several processing steps, since one coated plate may be used for several tests. It should be possible to repeat this method on the same film after each processing stage, providing a direct means of following the change in stress and adhesive strength throughout a coating's processing history. This technique was demonstrated using a polyimide film cured at 220°C for which a surface energy of $3.2\,Nm^{-1}$ was obtained. This technique may also be generalized for multilayered coatings.

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