NANOMECHANICAL FRACTURE-TESTING OF PHENOL-FORMALDEHYDE THIN FILMS

D.A. BOISMIER†, M.K. KRIESE and W.W. GERBERICH
Center for Interfacial Engineering, University of Minnesota, Minneapolis, MN, USA
†Industrial Fellow: Hutchinson Technology, Inc., Hutchinson, MN, USA

ABSTRACT

The interfacial fracture behavior of a 9.1 μm thick phenol-formaldehyde polymer thin film has been investigated with three nanomechanical test methods, namely indentation and scratching of films with a conical indenter and probing of fine lines with a wedge-faced indenter. These tests each allow calculation of the critical strain energy release rate G associated with the interfacial fracture energy Γ. Indentation testing was the primary method, in which the displaced volume of indentation generates stresses of 20–80 MPa, which induced circular delaminations of 15–95 μm radii corresponding to fracture energies of 1.1–18 J/m^2. Scratch testing was indentation with simultaneous translation, with the furrow resulting in stresses of 3.7–7.1 MPa, inducing circular delaminations of 40–60 μm radii corresponding to fracture energies of 0.7–2.7 J/m^2. Line testing involved probing against the end of a developed line at a constant depth to initiate and propagate interfacial cracks 250 μm long corresponding to fracture energies of 1.1 J/m^2. There is reasonable agreement among the test methods, though each method has complexities that need to be further investigated, and these aspects are discussed. Additionally, each test measures fracture energy associated with a different stress state at the crack tip, and this situation is expected to require different critical strain energy release rates for fracture.

KEYWORDS

interfacial fracture, indentation, scratch testing, nanomechanics, polymer thin films

INTRODUCTION

Thin films have become a key technology in a wide range of industries for an equally wide range of engineering purposes. However, in the great majority of applications the film must remain adhered to be of use. One can define the adhesion in various ways, but perhaps the simplest are the true work of adhesion and the practical work of adhesion. The first refers to the thermodynamic work W_A required to create two new surfaces at the expense of the interface, and is merely a summation of surface energies. However, in most practical cases of de-adhesion, there is additional inelastic damage, such as plasticity and microcracking, that occurs in regions of the substrate and film near the interface (Evans et al., 1990). In either case, a property of interest is the energy associated with the fracture, and in particular the energy per unit area of de-adhered film, referred to herein as the interfacial fracture energy Γ.

While there are many tests that semi-quantitatively measure the practical adhesion of thin films that are extremely useful for functional or comparative purposes (Jindal et al., 1987; Rickerby, 1988; Steinmann and Hintermann, 1989; McCabe et al., 1994), there are significantly fewer

applicable to direct quantitative assessment. Such direct assessment is needed in order to fully understand and effectively utilize thin films. In the work described herein, three such quantitative tests are applied to the measurement of the practical work of adhesion of a phenol-formaldehyde polymer thin film, used for photoresist applications. Each test involves a different ratio of shear to normal stresses, or mixity ψ, at the adhered film/substrate boundary, or interface crack tip. This factor is defined as

$$\psi = \tan^{-1} (\tau_{xy} / \sigma_{yy}) \hat{r} \quad (1)$$

where τ_{xy} and σ_{yy} are shear and normal stresses at a distance $\hat{r}$ in front of the crack. Here, $\hat{r}$ is some characteristic distance related either to the specimen microstructure or geometry, since the stress field ahead of the crack-tip is an oscillatory function of the elastic mismatch across the interface (Rice, 1988; Rühle et al., 1990; Hutchinson and Suo, 1992). However, in most cases the value of $\hat{r}$ can change an order of magnitude and only affect the mixity by a few degrees. While there is ample evidence that interfacial fracture energy is a function of mixity (Evans and Hutchinson, 1989; Evans et al., 1990; Jensen et al., 1990; Wang and Suo, 1990; Liechti and Chai, 1991) its influence is primarily evidenced only over large changes, and hence detailed analysis of the characteristic dimension is not included in this work. Rather, it is large changes in ψ that are relevant. Additionally, the theoretical analyses used in this work do not explicitly account for the characteristic dimension.

MATERIALS & TEST APPARATUS

A phenol-formaldehyde based polymer film was roll-coated onto a cold-rolled austenitic stainless steel substrate. Film thickness was 9.1 μm as measured by microprofilometry. Some films were lithographically developed into line structures 20–50 μm wide. The test apparatus is a nanomechanical indenter (Wu, 1991) with practical resolutions of 0.05 mN normal and tangential load, 5 nm vertical displacement and 100 nm horizontal x-y displacement. Polished diamond tips were used with the instrument to probe the film and induce interfacial fracture. Optical microscopy was used to analyze the failed films; this was greatly assisted by the fact that the film is translucent and regions that had failed contrasted distinctly with those still adhered.

In order to properly use the quantitative tests of adhesion discussed below, the elastic properties of the film and substrate must be known. A film modulus of 3 GPa was determined by normal probing of the film with a spherical tip indenter. Analysis of the unloading behavior yields the elastic modulus (Pharr and Oliver, 1992). Typical probe depths used for elastic modulus determination were 2–14% of the film thickness. Elasticity corrections were made for the presence of the stiffer substrate and to the area of contact (King, 1987; Pharr and Oliver, 1992). In all cases, it was assumed that both film and substrate were isotropic, and that the film had no residual stress.

TEST METHODS & RESULTS

Each of the three test methods used to measure the practical work of adhesion is discussed separately below. For each test technique, cracks are initiated and propagated along the interface, which is presumably weaker than either material, though a precise analysis of the point at which kinking away from the interface occurs requires a knowledge of the mode mixity ψ. (He and Hutchinson, 1989; He et al., 1991) However, for the work described, interfacial fracture was the predominant mode. Figures 1 through 3 show representative micrographs of the de-adhered film after testing for each method, along with a test schematic. By using analytical expressions for the strain energy release rate G for each test, one can determine the interfacial fracture energy. The results for all tests are shown in Fig. 4, where the critical strain energy release rate is shown as a function of fracture area.

Indentation Test

The indentation test was the primary assessment method of adhesion due to its ease of use and reproducibility, and has been studied by a number of researchers (Chiang et al., 1981; Evans and Hutchinson, 1984; Rosenfield et al., 1990; Drory and Hutchinson, 1994; Weppelmann et al., 1994; Bahr and Gerberich, 1996). Physically, a spherical indenter with 18 μm tip radius was driven perpendicularly into, then out of, the film at 50 nm/sec. In the model used for this work (Marshall and Evans, 1984; Rossington et al., 1984) the indenter displaces a volume of film and initiates an interfacial crack. This volume of displaced material is assumed to plastically flow radially into the surrounding film. The surrounding elastic film thus exerts a plane-stress compressive stress σ_o to restrain the outwardly flowing material around the indenter, such that for films free of residual stress,

$$\sigma_o = E V_o / 2\pi (1-\nu) t a^2 \quad (2)$$

where E and ν are the elastic modulus and Poisson's ratio of the film, V_o is the indentation volume at maximum probing depth, t is the film thickness and a is the radius of the de-adhered film. The strain energy of the system can decrease by propagation of the interfacial crack as

$$G = (1-\nu^2) \sigma_o^2 t / E \quad (3)$$

Since the applied G rapidly decreases with increasing crack size, indentation-induced propagation occurs in a stable manner, and hence the crack size upon tip removal corresponds to the critical release rate, i.e. the interfacial fracture energy Γ. Modeling the film as a clamped circular plate yields a mixity value ψ of 55°, noting that the stresses calculated with equation (2) do not exceed those required to cause buckling of the film as modeled, though mixity would drop to –35° from such an occurrence (Hutchinson and Suo, 1992).

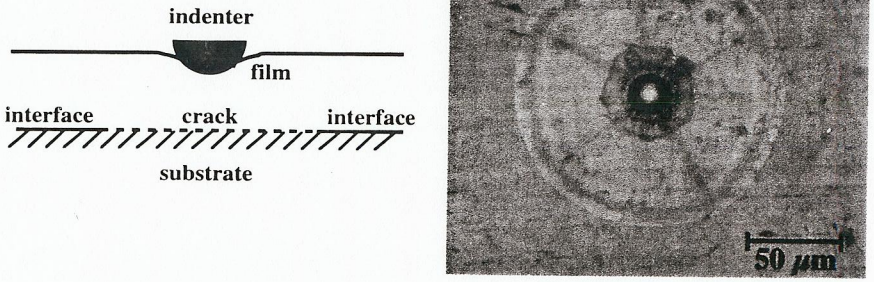

Fig. 1. Indentation test. As shown in schematic, the indenter nucleates and propagates an interfacial crack. The optical micrograph shows the residual deformation from the indenter, the total delaminated area and radial cracks produced with deep indents.

From Fig. 1 it is apparent that the crack radius is rather simple to identify as the fracture was repeatably circular. The indentation volume wasn't directly measured, but rather was calculated from a knowledge of the shape of the indenter tip as a function of indentation depth h. Calculation involves a proper accounting for both pileup during indentation and recovery during tip removal of the elastic response of the film and substrate. Failure to do so in either case results

in overestimation of V_o, the volume of the tip that is actually embedded into the film to induce lateral compression. While no pile-up was evidenced, elastic recovery was accounted for by the same methods used in the evaluation of the film modulus (King, 1987; Pharr and Oliver, 1992). As Fig. 1 shows, radial cracking was induced in the brittle film and it is unclear whether this occurred upon loading or unloading; if it occurs on loading it is still unclear whether it appropriate to subtract the volume of the open radial cracks from the indentation volume. The polymer film also exhibits limited viscoelastic behavior which becomes increasingly evident at deeper indentations.

Despite these complications, realistic and reproducible values of 1.1–18 J/m^2 for Γ were obtained. As depth of penetration increases from 24 to 94% of the film thickness, the radius of interfacial fracture increases from 15 to 95 μm. As shown in Fig. 4, interfacial fracture energy is highest for the shallowest indents, dropping to some minimum and rising back to an apparent constant value of 2.2 J/m^2; the applied stress behaves similarly as dictated by equation (2). While it remains unclear why such behavior is evidenced, it is expected that changes in mechanism of the crack-tip fracture process would influence the practical work of adhesion. Evidence for such changes is connected with the radial cracking, which occurred for even the shallowest indents, and prior to the minimum in Γ. It then extended near the edge of the delamination, but after this point the delaminations outpaced the radial cracking.

Scratch Testing

Scratch testing has been widely used for both semi-quantitative and quantitative evaluation of film adhesion (Rickerby, 1988; Steinmann and Hintermann, 1989; Sarin, 1993; Venkataraman et al., 1993; Nsongo and Gillet, 1996). For this test, a 90° conical indenter with a 1 μm radius tip is driven both horizontally and vertically into the film, schematically shown in Fig. 2, which introduces stresses that initiate and propagate interfacial fracture. The model used to analyze the polymer film for this work (Venkataraman et al., 1993) shown in Fig. 2, relates the energy of the stress-strain field induced by the indenter to the area and geometry of interfacial fracture A_d. Using the Boussinesq solution of the average τ_{xz} stress field (Johnson, 1985), the model for the spallation of film due to point normal and tangential forces P_n and P_t results in

$$\tau_{xz} = \tau_{xz,1} + \tau_{xz,2} \tag{4a}$$

$$\tau_{xz,1} = -\frac{3P_n t^2 \sin\alpha}{\pi A_d}\left[\frac{B}{3t^2(t^2+B^2)^{1/2}} - \frac{B}{3(t^2+B^2)^{3/2}} + \frac{a}{3t^2(t^2+a^2)^{1/2}} - \frac{a}{3(t^2+a^2)^{3/2}}\right] \tag{4b}$$

$$\tau_{xz,2} = \frac{3P_t}{2\pi A_d}\left[\frac{\sin 2\alpha}{2} + \alpha\right]\left[\frac{t}{(t^2+B^2)^{1/2}} - \frac{t}{(t^2+a^2)^{1/2}} + \frac{t^3}{3(t^2+B^2)^{3/2}} - \frac{t^3}{3(t^2+a^2)^{3/2}}\right] \tag{4c}$$

where the parameters a, B, α and A_d are defined in Fig. 2. By assuming that all other τ_{ij} and σ_{ij} stresses are of the same order as τ_{xz}, then one can find the strain energy release rate via

$$G = 2\sum\left[\frac{\tau_{ij}^2}{2\mu}t + \frac{\sigma_{ij}^2}{2E}t\right] \tag{5}$$

Mixity in this model is not rigorously analyzed, since the assumption is that all stresses are of "equivalent order," which thus yields a value of ±45° depending on relative signs, but is implied to be no more accurate than ±25 to ±65°. The effect of elastic mismatch across the interface also is not included. Therefore, no value of mixity can be taken with great confidence.

Probing rates were 500 nm/sec horizontally and 40 nm/sec vertically into the film. As shown in Fig. 2, the failed area is semicircular, such that 2α is 180°; delamination beyond 180° is theorized to occur prior to the fracture event. The test was fairly repeatable, yielding areas of fracture of 40–60 μm in radius, corresponding to interfacial fracture energies of 0.7–2.7 J/m^2. As shown in Fig. 4, there is a consistent trend of increasing toughness with decreasing interfacial fracture area.

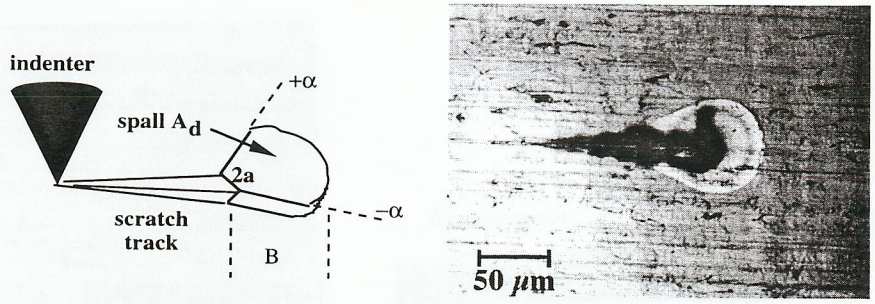

Fig. 2. Scratch test. The schematic shows the fractographic parameters needed to calculate interfacial fracture energy as the conical indenter drives a deepening furrow into the film, inducing fracture at a characteristic load. The optical micrograph exhibits these parameters.

Line Scratch Testing

The line scratch test method is a specialized version of the scratch test, in which a wedge-shaped indenter tip drives at constant depth into the end of a lithographically developed line of the film as depicted in Fig. 3. This probing initiates an interfacial crack, and then compresses the cracked portion of the line. The compressive strain energy can be lowered by continued interfacial cracking or buckling of the line. It is thus possible to relate either the tangential load P_t or displacement δ to the strain energy release rate and measure interfacial fracture energy Γ (deBoer and Gerberich, 1996a; deBoer and Gerberich, 1996b; deBoer et al., 1996) by modeling the non-adhered end of the line as a simple beam in compression. For a line of width b and thickness t,

$$\sigma = P_t / bt = \delta E / a(1-\nu^2) \tag{6a}$$

$$\sigma_b = P_t / bt = \pi^2 t^2 E / 3a^2(1-\nu^2) \tag{6b}$$

$$\delta_b = \pi h / \{2\Gamma(1-\nu^2) / 9Et\}^{1/4} \tag{7}$$

where the subscript b refers to the buckled state, a is the length of line no longer adhered and δ_b is the critical displacement for the onset of simple Euler buckling. These parameters can then be related to the strain energy release rate by

$$G = \sigma^2 t (1-\nu^2) / 2E \tag{8a}$$

$$G_b = \pi^2 t^3 E (4\delta a - \pi^2 t^2) / 6a^4 (1-\nu^2) \tag{8b}$$

For the polymer film tested, there was no precrack, and since crack length must be known, only the final length could be used, which was assumed to be the spallation lengths shown in Fig. 3. This model has numerous advantages, such as a plane-strain stress-state that is significantly

removed from any inelastic phenomena occurring near the indenter tip. Secondly, the mixity angle starts at 55° and upon buckling steeply drops to –30° or more, theoretically allowing measurement at any value in between. However, the test is best suited to lines that have precracked portions at one end, as a crack initiation event can result in an overdriven situation. When a precrack exists, the maximum load corresponds to the onset of stable crack growth; in situations where a true precrack is not present, but merely a weakly adhering interlayer, the maximum load is an upper bound.

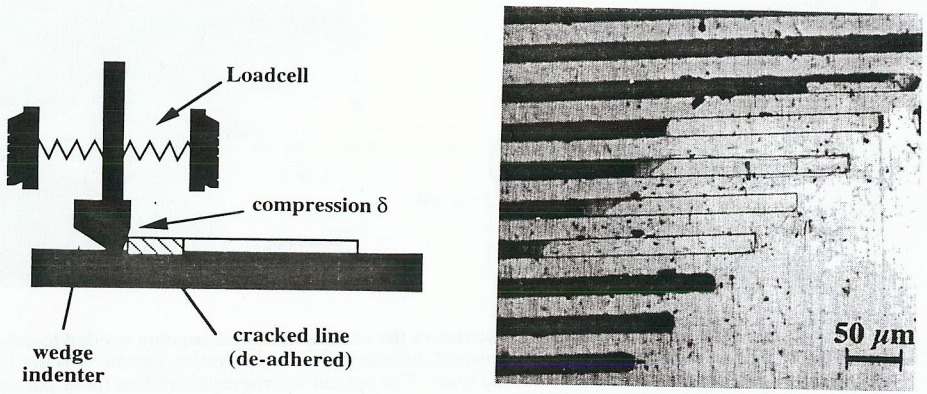

Fig. 3. Line-scratch test. The schematic shows how the wedge-indenter probes the end a developed line, compressing the portion that is cracked or de-adhered. Continued load and displacement extends the crack ; if the line is long enough it buckles as modeled by simple beam theory. The optical micrograph shows untested and tested lines, the latter having outlines to show original position. Here it is clear that spallation, i.e. cracking through the film, occurred at a shallow angle.

Two variants of this test were conducted on 9.1 μm thick films, namely one with the as-prepared specimens and one with lines whose ends had been vertically indented with the wedge to introduce a precrack. In both cases, an interfacial crack extended rapidly approximately 250 μm and spalled upon reaching some critical load. The critical load for the precracked line was one-fourth to one-tenth that of the as-prepared lines, resulting in an upper-bound calculation of 1.1 J/m^2 and strongly suggesting the overdriven condition for the as-prepared sample. Analysis of the final crack length, i.e. that at which spallation occurred, requires one to establish whether spallation was a result of crack kinking or merely excessive bending strain in the buckled line, as each case results in a different assessment of the interfacial fracture energy. Estimates of the toughness of the polymer film based on the radial cracking of the indentation tests are in excess of 50 J/m^2. Using this value, kinking analysis only sets an upper bound of the interfacial fracture energy of at best 30% of the film toughness (He and Hutchinson, 1989; He et al., 1991). Assessment of interfacial fracture energy utilizing the critical bending strain is complicated by the fact that the test apparatus is neither fixed grip nor fixed load, and hence results in a load drop concurrent with rapid crack propagation upon buckling. It is at this time impossible to associate a load or line-end displacement with the spallation event, which itself drops the load to zero.

DISCUSSION

The principal difference between the three test techniques is the stress state, characterized in this work primarily by the mode mixity parameter. The scratch test involves a single event occurring at a fixed and largely unknown value. In contrast, both the indentation and line scratch methods

initiate interfacial crack propagation at a value of 55° and upon buckling steeply drop to values of –30° or more as the crack advances in a stable manner. As the theoretical treatment of the latter two is more rigorous, little further attention to the scratch test is given, other than its use as an additional measurement confirming the order of magnitude of the polymer film's adhesion. It should be noted though that other researchers have found this technique to be in excellent agreement with other test methods (Moody et al., 1996).

The principal difference between the indentation and line scratch methods is the stress-state. As noted, the latter is a plane-strain stress-state and in the absence of additional film properties such as toughness and critical bending strain, is primarily limited to an upper bound value associated with a critical load. In contrast, the indentation method is one of plane-stress and produces stable cracking as the indenter drives into the film. Thus while the line scratch method establishes an upper bound to the interfacial fracture energy of 1.1 J/m^2, it does not necessarily invalidate higher values obtained with the indentation method, as there is less constraint in a plane-stress system. In addition, the line scratch value is based on an estimated 2–3 μm precrack, and the proximity of the load application to the crack-tip may be problematic. Further, the lithography treatment itself may induce a change in the properties of the film or its adhesion.

The key feature of the values of interfacial fracture energy as measured with the indentation method is the range of values, though it is clear in Fig. 4 that it is a smooth function of fracture area. Despite the difference in mixity and stress-state, the values measured with the scratch and line scratch methods suggest that values greater than 10 J/m^2 are likely inaccurate, and also suggests possible errors in assessment of the procedures for calculating indentation volume. Rather the apparent asymptotic value of 2.2 J/m^2 for deep indentations is more representative of the film's adhesion. For shallow indentations, there is the matter of crack nucleation, which would be expected to require more energy than propagation. As indentation depth increases, the an increasingly smaller fraction of the indentation volume is associated with nucleation. And as mentioned above, there may be a change of fracture mechanism as the crack tip becomes sufficiently removed from the loading point.

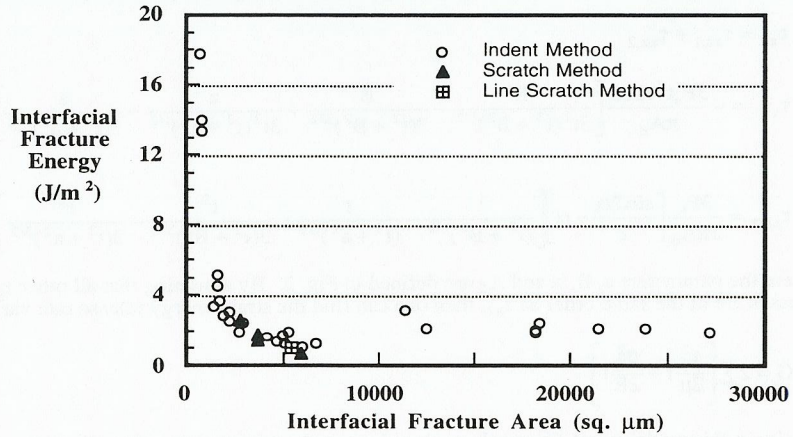

Fig. 4. The critical values of strain energy release rate (i.e. the interfacial fracture energy) are shown as a function of the area of fracture for each method, which is a circular delamination for the indentation test, a semicircular delamination for the scratch test and a length of spalled line for the line scratch test.

CONCLUSIONS

The work described herein demonstrates that there are several methods for direct quantitative evaluation of the adhesion of a thin polymer film. The three tests described herein, the indentation, the scratch and the line scratch methods, each induced interfacial crack propagation and yielded a fairly consistent measurement of 1–3 J/m^2 for a 9.1 μm thick phenol-formaldehyde polymer film. Interfacial fracture energy also appears to be a smooth function of fracture area. However, it is also apparent that each of the test methods requires fuller investigation. While the line scratch method is simple to conduct and analyze, the model is insufficiently rigorous for other than first order quantification. The line scratch method requires further analysis of the film properties to analyze post-buckling crack propagation, kinking and spallation, as well as a more in-depth analysis of the effects of the apparatus. It is also clear that a reliable method of generating sufficiently long precracks is necessary. The indentation method suffers from experimental difficulties associated with accurate assessment of the indentation volume, especially with regard to viscoelastic films. As this method is simple and repeatable, considerable ongoing work is being conducted to refine this method as well and would confirm the presence or absence of changes in fracture mechanism. Finally, since the true usefulness of adhesion measurement is that it enhances the ability to study the effects of processing and application on the functional performance of the film, such comparisons are also being conducted. As applications involve differing stress-states, the need for multiple tests with different stress-states is apparent.

Acknowledgments

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