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A CALORIMETRIC EVALUATION OF THE PEEL ADHESION TEST

A Dissertation Presented

by

JAY L. GOLDFARB

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the degree requirements for the degree of

DOCTOR OF PHILOSOPHY

September 1992

Department of
Polymer Science & Engineering

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A Calorimetric Evaluation of The Peel Adhesion Test

A Dissertation Presented

By

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ABSTRACT

A CALORIMETRIC EVALUATION OF THE PEEL ADHESION TEST

SEPTEMBER 1992

JAY L. GOLDFARB, B.S., UNIVERSITY OF MASSACHUSETTS

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Directed by: Professor Richard J. Farris

Peeling of pressure sensitive tapes and polymeric coatings bonded to aluminum substrates was analyzed from a thermodynamic perspective with the intent of determining how the energy expended in separating the bonded materials is consumed. The mechanical work expended and the heat dissipated during peeling were simultaneously measured using deformation calorimetry. The surfaces exposed by peeling were analyzed by electron microscopy and electron spectroscopy. The thermodynamic state of the peeled materials was analyzed using solution calorimetry. The thermodynamics of tensile drawing for polymeric materials identical to those deformed during peeling was studied using solution calorimetry, differential scanning calorimetry, deformation calorimetry and thermomechanical analysis.

When polyimide coatings were peeled from aluminum substrates with a peel angle of 180° , almost all of the mechanical energy was consumed by propagating the bend in the peeling coating. The fraction of the peel energy dissipated as heat was $48 \pm 1.3\%$ and nearly all of

the remainder was stored as latent internal energy in the peeled polyimide. When the bend is propagated through aluminum, which has a limited capacity to store latent internal energy, $100\pm 2.7\%$ of the mechanical energy is dissipated as heat.

When pressure sensitive adhesive, PSA, backed with poly(ethylene terephthalate), PET, tape was peeled, the mechanical work was consumed by propagating the bend in the PET backing and by deforming the PSA layer. The fraction of the mechanical work of peeling which was dissipated as heat varied from 69-86% depending on the peel rate and the backing thickness. It was determined that the fraction of the peel energy, not dissipated as heat, was stored as latent internal energy in the PET backing. The energy stored in the backing is indicative of the total mechanical energy expended in deforming it. Studies of PET tensile deformation showed that 25-50% of the energy under the stress-strain curve is stored in deformed material.

When a crack is introduced in a coating containing residual tensile stresses, a shear stress, which acts to delaminate the coating, is concentrated near the intersection of the crack and the coating-substrate interface. Stress driven delamination occurs with little bending deformation as compared to peeling and requires considerably less energy. For coatings with residual tensile stresses, a superior adhesion test was developed based on calculating the stored elastic energy released when the stressed coating delaminates surrounding a cut-through. Photographs of delamination in cut coatings were taken and the coatings were modeled using linear elastic finite element analysis to calculate the stored elastic energy released in the delaminated region surrounding the cut-through.

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CHAPTER 1

INTRODUCTION

1.1 Adhesive Bond Testing

Polymeric Materials are used extensively as structural adhesives, matrix resins, binders, printing inks and protective coatings. In these applications, the ability of the polymer to form a strong adhesive bond to another often dissimilar material is crucial. Evaluating adhesive bond strength is a critical step in designing a structure or system involving adhesive bonding. The peel test is one of several simple mechanical tests which are used extensively to measure adhesion. In a peel test, the force required to pull a flexible film away from a substrate, to which it is bonded, is measured. In the absence of energy dissipation due to plasticity or viscoelasticity, the energy required to separate the film from its substrate is a direct measure of the adhesion. However, for many commercially important systems, including thin films which strongly adhere to rigid substrates and films which are bonded with soft rubbery adhesives, dissipative mechanisms dominate the peel behavior. When a thin film is peeled from a rigid substrate to which it adheres strongly, the peel force is sufficient to cause inelastic deformation of the film near the point of detachment where the film is subject to severe curvature. When films bonded with soft rubbery adhesives are peeled, failure in the adhesive layer is accompanied by liquid-like flow. Under these conditions, almost all of the work expended in peeling is consumed by dissipative processes

accompanying deformation of the test sample. Energy dissipation plays an important role in the strength of adhesive bonds. The performance of an adhesive bond is controlled not only by its fracture energy, but also by the rate at which energy is dissipated in resistance to externally applied loads. The extent and magnitude of the dissipation will depend on the testing method. In peel tests, energy dissipation can occur throughout the bulk of the test sample and bond strengths can be measured which are outrageously high when compared to values obtained by other testing methods. An accurate measure of adhesive bond strength is obtained only when energy dissipation is confined to a region where deformation concomitant with separation of the bonded materials occurs.

Not all of the mechanical work which is consumed by dissipative mechanisms during peeling appears as heat. If all other mechanisms of energy dissipation other than heat flow are negligible, for example, acoustic and light emission, conservation of energy requires that work done on the sample during peeling, which does not appear as heat, has raised the internal energy of the test specimen. Energy is consumed in creating the surfaces exposed by peeling, raising the internal energy of the test specimen. This is the energy required to reversibly separate the bonded materials, commonly referred to as the thermodynamic work of adhesion. The energy of the test specimen may be raised by a substantial amount when glassy polymeric films are deformed during peeling. Peeling causes molecular rearrangements in regions of the film exposed to bending strains similar to that which occurs when the film is subjected to homogeneous tensile or compressive deformation. These deformations are frozen into the deformed film leaving it in a high energy thermodynamic state. Elastomeric adhesives are generally

incapable of internally storing any of the energy of deformation after the stresses imparted by peeling are removed.

A strong relationship does exist between the nature of the interface and the peel energy because the peeled materials can be subject to stresses (and thus to energy losses) only if the interface is strong. At best, the peel test may provide a qualitative comparison of the adhesion between systems which have similar dissipative characteristics during peeling.

The adhesion of coatings, applied as liquids, is a consequence of solidification on the substrate. When a liquid coating solidifies on a rigid substrate and can no longer flow, further shrinkage results in internal tensile stresses in the plane of the coating. High processing temperatures and differing thermal expansion coefficients of coatings and substrates result in large thermal stresses when laminates are cooled to room temperature. Strong, high modulus films are often used as coatings and these can develop high residual stresses during processing. Interfacial delamination is one of the most significant failure modes of these films. If the internal tensile stresses exceed the cohesive strength of the solid coating, cracking may occur which can result in coating-substrate delamination propagating from the crack. The elastic energy stored in stressed coatings will be released if the coating delaminates. Stressed coatings are particularly vulnerable to stress cracking and delamination in the vicinity of substrate surface features where stress concentrations may exist. Structures containing stressed coatings are also vulnerable to failure by delamination when they are cut or punched.

A thin film or coating bonded to a substrate and under a state of residual biaxial tensile stress will delaminate from a cut-through if the elastic energy from the residual stress is high compared to the adhesion. Since delamination is likely to initiate from a crack in the film, tests to determine the interfacial resistance to delamination provide important data for design and performance prediction.

Standard adhesion tests such as the peel, pull-off, blister and scratch tests may be poor at predicting interfacial resistance to delamination. Cut tests use spontaneous delamination caused by residual tensile stresses in the film to measure the adhesion energy. The difference in the elastic energy in the cut film before and after delamination divided by the delaminated area is a measure of the adhesion energy. Adhesion energies determined by cut tests may be two orders of magnitude smaller than those measured for identical systems using peel testing.

1.2 Dissertation Overview

There are two primary objectives of this work: Decomposing the energy expended in peeling adhesively bonded layers and determining how it is consumed. Developing a new test to measure the delamination strength of stressed coatings adhering to rigid substrates. To accomplish the first goal, it was necessary to adapt the technique of deformation calorimetry to peel testing. Using this technique, the heat and work of peeling can be measured simultaneously. While it is well known that dissipation plays a major role in adhesive strength, this work contains the first

physical measurements of heat dissipation during peeling. Peeling was studied for two reasons. Its simplicity made it particularly well suited to the experimental techniques involved and it is used extensively in industry to characterize adhesive bond strength. It is hoped that this work will further the understanding of the peel test and adhesive bond failure mechanisms. Peeling of two major classes of adhesive systems was studied. In one system, rigid polymeric coatings, polyimides, were applied as liquids and solidified on metal substrates. In the other system, pressure sensitive adhesives, styrene-isoprene block copolymers with modifying additives, were applied as liquids to backing films, solidified and bonded to substrates using pressure. Various combinations of rigid and flexible layers were peeled in the calorimeter to determine the thermodynamic behavior of the bonded materials during peeling. Light microscopy, electron microscopy and x-ray photoelectron microscopy were used to study the surfaces exposed by peeling. Thermal analysis techniques and solution calorimetry were utilized to measure stored latent energy in polymers deformed by peeling and tensile drawing.

The effect of residual tensile stresses in polymeric coatings on the peel behavior was investigated for tapes bonded to rigid substrates, while in tension, and for polymeric coatings containing residual stress. A new adhesion test was developed to measure the interfacial resistance to delamination at a cut-through in a stressed coating adhering to a rigid substrate. This test is a direct measurement of the adhesion energy for a mode of failure which is important in the commercial use of coatings and it is free of the excessive dissipation associated with peeling.

Before presenting the results of this work, a review of adhesive bond formation, destruction and testing will be presented in Chapter 2 and a review of the theory and operation of the deformation calorimeter and the deformation thermodynamics of solids will be presented in Chapter 3.

CHAPTER 2

BACKGROUND

2.1 Introduction

As a means of joining materials, adhesives offer many competitive advantages over other joining methods such as riveting and welding. These advantages include the ability to join dissimilar materials such as fabrics and elastomers, improved stress distributions in joints and the elimination of stress concentrations at rivets. In addition, adhesive bonding is often the most convenient and cost efficient joining technique.

Despite the widespread use of adhesive technology in industry, our fundamental knowledge of the nature of the attractive forces which cause adhesion and their relation to measured adhesion strengths remains incomplete. To account for the strength of adhesive bonds, the adhesion scientist needs to consider aspects of surface chemistry and physics, the mechanics of fracture and the mechanical behavior of the joined materials. The first part of this chapter contains a brief summary of these topics and their role in determining the measured adhesion strength. In the second part of this chapter, the peel adhesion test is discussed in detail.

2.2 Formation of Adhesive Bonds

The establishment of intimate molecular contact is a necessary, though sometimes insufficient, requirement for the creation of strong adhesive bonds. In order to assess the ability of a given adhesive/substrate pair to meet this requirement, it is necessary to consider wetting equilibria and the kinetics of the wetting process.

To achieve intimate contact, the liquid adhesive must wet the substrate surface thoroughly. The dynamics of wetting are determined by the surface tension of the adhesive, the free surface energy of the substrate and the viscosity of the adhesive. Surface tension and surface energy are direct measures of the intermolecular forces. Surface tension exists and work is required to create surfaces because of the attraction of the molecules in the bulk for the surface layer which tends to reduce the molecular density in the surface region. The most common type of physical surface attractive forces are the van der Waals forces which can be attributed to dispersion forces arising from internal electron motions which are independent of dipole moments and polar forces arising from the orientation of permanent electric dipoles which have an induction effect on other polarizable molecules. The dispersion forces are weaker than the polar forces, but they are exhibited by all materials. Another type of surface force is the hydrogen bond formed as a result of the attraction between a hydrogen atom and a strongly electronegative element such as oxygen or nitrogen.

Wetting is quantitatively defined by reference to the contact angle of a liquid drop resting on a solid surface. The tensions at the

three phase contact point are the liquid-vapor tension, γ_{lv} , the solid-liquid tension, γ_{sl} , and the solid vapor tension, γ_{sv} . The Young equation relates these tensions to the equilibrium contact angle, Θ .

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\Theta \quad (2.1)$$

For a planar surface, the equilibrium contact angle can be measured from the profile of a Sessile drop. For complete wetting, the contact angle approaches 0° . Generally, complete wetting requires low viscosity liquids with surface tensions lower than the surface energy of the solid. Surfaces may be classified as low or high energy. Organic compounds including polymers have low surface energies which rarely exceed 100 mJ/m^2 . Metals, metal oxides and ceramics have high surface energies which typically exceed 500 mJ/m^2 .¹ The free surface energies of polymeric solids cannot be measured directly. The first approach to characterizing this class of surfaces was developed by Zisman who established that a rectilinear relationship frequently existed between the cosine of the contact angle and the surface tension of the wetting liquid.² Zisman defined a critical surface tension of wetting for solid polymers, γ_c , as the value of γ_{lv} extrapolated to the point where the contact angle of a liquid on the solid surface approaches zero degrees. Thus, liquids with surface tensions less than or equal to γ_c will spread on the surface. Values of γ_c are close to the surface energy but not necessarily equal to it.

The free surface energy of a solid polymer can be estimated from liquid contact angle data or by extrapolation from the liquid state using the temperature dependence of the surface tension. A review of several different methods using liquid contact angle data is given by

Hata et. al.³ Fowkes proposed a method where the surface free energy of a solid, γ , could be represented by the sum of the contributions from dispersion forces, γ^D and a polar forces, γ^P .⁴

$$\gamma = \gamma^D + \gamma^P \quad (2.2)$$

The geometric mean relationship can be used to relate the dispersion and polar components of the surface energy of a solid, γ_s^D and γ_s^P , to the contact angle of a liquid resting on its surface. The dispersion, γ_{lv}^D , and polar, γ_{lv}^P , components of the liquid surface tension have been tabulated for many common solvents. The geometric mean relationship is

$$1 + \cos\theta = \frac{2(\gamma_s^D)^{\frac{1}{2}}(\gamma_{lv}^D)^{\frac{1}{2}}}{\gamma_{lv}} + \frac{2(\gamma_s^P)^{\frac{1}{2}}(\gamma_{lv}^P)^{\frac{1}{2}}}{\gamma_{lv}} \quad (2.3)$$

The contact angles of two different liquids are measured on a solid surface and two simultaneous equations in the form of equation 2.3 are solved for the components of the solid surface energy.

The adsorption theory of adhesion proposes that secondary forces acting across the interface are the primary basis of adhesion, providing that intimate molecular contact is established at the interface. The most common of these forces are the van der Waals forces. The thermodynamic work of adhesion, W_A , is the energy required to reversibly separate the adhesively bonded surfaces and is defined as

$$W_A = \gamma_s + \gamma_{lv} - \gamma_{sl} \quad (2.4)$$

where γ_s is the surface free energy of the solid substrate, γ_{lv} is the surface tension of the liquid adhesive and γ_{sl} is the interfacial free energy. This equation applies to a solid/liquid interface, but by

assuming that the surface energy of a liquid does not change drastically upon isothermal solidification, it may be applied to solid/solid interfaces. From equation 2.4, it would appear that maximizing γ_s and γ_{lv} would maximize W_A . However, the surface tension of the liquid adhesive must be lower than γ_c of the substrate for complete wetting to occur and the adhesive must be of a low viscosity so that it can readily flow into cavities in the substrate. In addition, the interfacial free energy γ_{sl} , should be as low as possible. The thermodynamics of wetting for a given adhesive/substrate combination may exhibit significant changes depending on the relative humidity during bonding or the presence of other contaminants which can be absorbed on the surfaces. High energy surfaces are particularly vulnerable to absorption of contaminants resulting in a significant reduction in surface energy.

In cases where the adhesive bond fails at the interface, it is logical to attempt to relate the bond breaking strength to the thermodynamic work of adhesion. Relating the thermodynamic work of adhesion to adhesive bond strengths measured by mechanical tests is complicated because these measurements contain indeterminate contributions from dissipative energy losses in the adhesive and substrate. Although the intrinsic adhesion forces acting across the adhesive/substrate interface may effect the bond strength, they are usually completely obscured by other contributions.

Studies by Andrews and Kinloch have shown a relationship between the thermodynamic work of adhesion, energy dissipation and the adhesive failure energy.^{5,6} They studied the adhesion of a rubber adhesive to a variety of rigid substrates showing that the peel energy was the sum of the energy dissipated viscoelastically within the rubber and the

intrinsic adhesion energy.⁵ The amount of energy dissipated in the rubbery adhesive was dependent on the rate of peeling and the temperature. At very low rates, the peel energy approached the thermodynamic work of adhesion calculated from surface energy data. At higher rates, the peel energy was orders of magnitude greater than the thermodynamic work of adhesion, but it was found experimentally and shown theoretically that the dissipation is proportional to the thermodynamic work of adhesion. In this case, the adhesion was primarily due to secondary forces acting across the interface. Therefore, the intrinsic adhesion is equal to the thermodynamic work of adhesion. The following relationship between the adhesion energy measured in peeling, W_p , and the thermodynamic work of adhesion, W_a , was proposed.

$$W_p = W_a \Phi_v(\omega, T, e) \quad (2.5)$$

Φ_v is The dissipative loss function dependent on the peel rate, ω , the testing temperature, T , and the strain level in the adhesive layer, e . This type of relation is not generally applicable to all adhesive/substrate combinations. It has only been demonstrated for the simple case of interfacial failure involving the rupture of secondary forces and a model viscoelastic adhesive.

The inability to directly measure interfacial interactions remains an obstacle to developing a comprehensive understanding of adhesion. Four mechanisms of adhesion have been proposed. They are mechanical interlocking, the diffusion theory, the electronic theory, and the adsorption theory. The adsorption theory, discussed in the preceding section, is the most widely accepted and is universally applicable to

all adhesive/substrate combinations. Some or all of the remaining mechanisms may contribute to the adhesion of a given adhesive/substrate combination. The primary effect of all of these mechanisms is to enhance the forces which create dissipative energy losses when the adhesive bond is destroyed.

The theory of mechanical interlocking proposes that the adhesive becomes mechanically locked into substrate surface irregularities. The attainment of good adhesion to smooth surfaces shows that this theory is not generally applicable. However, there are some important cases where mechanical interlocking makes a significant contribution to the adhesion. Two notable examples are: adhesion to oxide treated copper circuit board cladding and adhesion of uncoated fabrics to rubber adhesives. In both of these cases, the intrinsic adhesion between the adhesive and substrate is due to secondary van der Waals forces which is of direct importance to mechanical interlocking because it determines the interfacial shear strength. The principle effect of surface roughness is probably to increase the energy dissipation during bond separation. A larger volume of material will be plastically deformed during the destruction of a bond to a rough substrate as compared to a chemically similar but smooth substrate.

The diffusion theory of adhesion attributes the adhesion of high polymers to mutual diffusion of the polymer molecules across the interface. This mechanism only applies to polymer/polymer interfaces. Furthermore, the molecules must have sufficient mobility and be mutually soluble which eliminates highly crosslinked materials, highly crystalline materials or materials with significantly differing

solubility parameters. Interdiffusion is an important mechanism of adhesion for solvent and ultrasonic welding of plastics.

The electronic theory of adhesion proposes that electric charges at interfaces act as a mechanism for adhesion. If the adhesive and substrate have different electronic band structures, there is likely to be some electron transfer across the interface to balance Fermi levels which will result in the formation of a double layer of electrical charge at the interface. This theory is primarily due to Deryaguin and co-workers.⁷

Intrinsic adhesion arising from secondary bonding alone may result in high bond strengths, but the additional presence of primary bonding across the interface is of considerable importance for many adhesive/substrate combinations. Sophisticated analytical techniques such as Laser-Raman spectroscopy, secondary-ion mass spectroscopy and x-ray photoelectron spectroscopy can be used to detect and identify primary bonding at an interface..

The extent to which the above mechanisms contribute to the adhesion strength depends upon the particular adhesive/substrate combination. Typical bond energies for the bond types discussed in this section are shown in Table 2.1. The total contribution of these mechanisms would be the energy required to break an adhesive bond in the absence of contributions from dissipative mechanisms. In most cases, it is the dissipative contributions that dominate the measured adhesion energy. The chemistry and physics of the interface plays an important role in determining the extent of the energy dissipation because the materials can only be subject to energy losses if the interface is strong enough to support the development of stresses in the bonded

materials in response to externally applied loads. Although the adhesive failure energy is due to the interfacial bond between the adhesive and substrate, it is extremely sensitive to the mechanical properties of the bonded materials and the nature of the stresses produced by the applied loads in a particular adhesion test.

Table 2.1 Bond types and typical bond energies.¹

Type of bond	Bond energy kJ/mol
Ionic	590-1050
Covalent	63-710
Metallic	113-347
Permanent dipole interactions and hydrogen bonds involving fluorine	Up to 42
Hydrogen bonds excluding fluorine	10-26
Dipole-dipole excluding hydrogen bonding	4-21
Dipole induced dipole	Less than 2
Dispersion forces	0.08-42

2.3 Mechanics of Adhesive Failure

Many mechanical tests have been developed to evaluate the strength of adhesive bonds. The American Society for Testing and Materials, ASTM, issues an extensive list of standard adhesion tests. Adhesion tests include tensile tests of butt joints, shear tests of lap joints,

peel tests for flexible materials, cantilever beam tests, blister tests and others. An extensive tabulation of ASTM adhesion tests is given by Kinloch.⁸ Three types of stresses are commonly referred to when considering adhesively bonded structures: normal stresses, shear stresses and cleavage stresses which are tensile stresses acting normal to the plane of separation resulting from a bending moment. In the standard tests, one or a combination of the three stress modes may be applied to the adhesive bond. Many of these tests will give fracture energy when properly analyzed. The fracture energy is independent of specimen geometry but does depend on loading mode, testing rate, temperature and the presence of active liquids or vapors. When evaluating adhesives for design purposes, tests should be chosen which best approximate service conditions.

High adhesive strengths are obtained from materials which have large deformation energies within the stress limit set by the interfacial bond strength. The adhesion energy is very sensitive to the total volume of material undergoing deformation which is controlled by the distribution of stresses in the joint which is dependent on the testing method, the joint design and the material properties. Very high adhesion energies will result when local stress concentrations are minimized and the stresses in the joint are distributed over a large volume of the bonded materials.

The adhesive failure energy of soft rubbery adhesives is predominantly consumed by viscoelastic dissipation and depends strongly on the rate of separation of the bonded materials and on the temperature. The rate and temperature dependence of the peel force of a cloth-backed styrene-butadiene copolymer peeled from various rigid

substrates was studied by Gent and Petrich.⁹ The bond strength varied with rate and temperature in exactly the same way as the viscoelastic response of the polymer adhesive varied with temperature and deformation rate. Generally, a rise in peel strength with peel rate to a maximum was observed followed by a decrease at a given temperature. As the temperature increased, the maxima in peel force shifted to higher peel rates. The peel force-peel rate relation at one temperature could be superimposed on that at another by a displacement, corresponding to a single multiplying factor, along a logarithmically scaled rate axis. The multiplying or shift factors were obtained from the Williams, Landell and Ferry relation¹⁰ and used to reduce peel rates at various temperatures to equivalent rates at a reference temperature effectively producing a master curve of peel force versus peel rate. Two major transitions in peel strength were observed as the peel rate changed. The transition in peel strength at low rates of deformation is associated with the transition from liquid-like to rubber-like behavior of the polymer. The transition in peel strength at high rates of deformation is associated with the transition from rubber-like to glass-like behavior of the polymer.

2.4 The Mechanics of Peel Adhesion Testing

The peel test is a standard mechanical test which is used extensively to measure adhesion. In a peel test, a flexible film is pulled away from a substrate to which it is bonded with the angle between the detached film and substrate, usually 90° or 180° . In the

absence of energy dissipation due to plasticity or viscoelasticity, the energy required to separate the film from its substrate is a direct measure of the adhesion. However, for many adhesive/substrate combinations including thin films which strongly adhere to rigid substrates and films which are bonded with soft rubbery adhesives, dissipative mechanisms dominate the peel behavior. For thin films, strongly adhering to rigid substrates, work is expended in bending the film to bring stress to bear on the interface. The peel force is usually sufficient to cause inelastic deformation near the point of detachment where the material is subjected to severe curvature.¹¹ When films bonded with soft rubbery adhesives are peeled, cohesive failure in the adhesive layer is caused by liquid-like flow.⁹ Under these conditions, the peel energy will significantly exceed the true adhesion. The peel test is extremely sensitive to energy dissipative mechanisms.

The geometrical configuration of the peel test is shown in Figure 2.1. Stresses induced in a flexible layer during peeling have been analyzed by Bikerman¹², Kaelble¹³ and others. Kaelble analyzed stresses, normal to the bond plane, in a film being peeled from a rigid substrate. The film and substrate are assumed to be linearly elastic and the stresses are assumed to be constant across the width and the thickness of the adhesive layer. Beam bending relations are used to obtain the stress distribution. Two types of stresses can potentially cause failure during peel. These are cleavage (tensile forces normal to the bond plane) and shear. Shear dominates at very small peel angles, but these tests are more like lap shear than peel. At a peel angle of 90°, neglecting bending strains, only cleavage forces exist. Kaelble

Figure 2.1 Schematic diagram of the peel test.

has shown that the cleavage stress σ at a distance x from the point of rupture is

$$\sigma = \sigma_b [\cos \beta x + K \sin \beta x] \exp(\beta x) \quad (2.6)$$

where σ_b is the cleavage stress at the bond boundary where $x = 0$. The term β has units of reciprocal length and may be considered a measure of stress concentration. This factor is described by the equation

$$\beta = \left[\frac{E_a b}{4E I t_a} \right]^{1/4} \quad (2.7)$$

where E_a is the elastic modulus of the film, E is the elastic modulus of the substrate, t_a is the film thickness, b is the bond width and I is the moment of inertia of the peeling strip cross section ($bt_a^3/12$). The factor K is dimensionless and describes the relation between the local forces and moments of force associated with the stress distribution of equation 2.6.

$$K = \frac{\beta m}{\beta m + P \sin \theta} \quad (2.8)$$

$P \sin \theta$ is the summation of the bond normal forces and m , the moment of these forces about the bond boundary. Gent and Hamed have shown that the theory of small bending deformations used to derive 2.6 is only valid when $K \leq 1$.¹⁴ A profile of the stresses predicted by equation 2.6 is shown in Figure 2.2. The cleavage stress is highly localized at the point of detachment where the flexible member undergoes a sudden change from maximum bending to zero curvature. Equation 2.6 predicts that the cleavage stress reaches a maximum at the bond boundary and decays to compression on the bonded side of the bond boundary before returning to zero in the bulk film. The force normal to the thickness in the detached film is zero. Whether such a stress distribution really exists

Figure 2.2 Distribution of normal stresses in the flexible layer in the bonded film ahead of the advancing peel front.

is open to debate but it has been proven that a region of compression exists on the bonded side of the peel front.¹³ The assumption is made that the normal force in the adhesive layer is constant through the layer thickness and across the width of the joint. This assumption is not correct as evidenced by the tendency for failure in peel joints to occur close to the interfaces which is indicative of higher stresses near the interfaces as compared to the bulk of the adhesive layer. Force equilibrium also requires that the normal force at the top free surface of the film is zero. This analysis also does not consider materials such as pressure sensitive adhesives, which form filaments spanning the zone of separation similar to crazing. They will have a normal stress on the detached side of the bond boundary which may contribute substantially to the peel force.

Large deformation finite element analysis has been used to study the stress and deformation fields near the crack tip in peeling.¹⁵ The substrate was modeled as a linear elastic solid and the peeling strip as an elastic-plastic material, copper. The resulting stress distribution has some of the features predicted by Kaelble. Singular normal and shear stresses are developed at the tip of the interfacial crack. The resultant stress state near the crack tip is hydrostatic tension. These stresses are localized near the interface and do not extend throughout the thickness of the film. The singular crack tip stresses decrease rapidly and the interfacial stress changes from tensile to compressive at a distance of one third film thickness into the bonded film. A zone of compressive yielding extends approximately three film thicknesses into the bonded film. Both the normal and shear interfacial stresses approach zero at a distance of six film thicknesses into the bonded

film. For copper, the near tip plastic dissipation is limited to a very small region near the crack tip and bending is the predominant mode of deformation. This may not hold true in all cases because the stress distribution will be affected by the material properties of the film and substrate.

Kaelble determined the tension force of the peel test by integrating the result of the stress distribution within the bond that exists at the propagating boundary. The peel force, P , is given by

$$\frac{P}{b} = \frac{t_a K^2 \sigma_b^2}{2E_a (1 - \cos \theta)} \quad (2.9)$$

Finite element analysis shows that the assumptions used to derive this result are inadequate and this type of analysis is not commonly used to interpret peel test data.¹⁵ An energy balance approach, which avoids the necessity of developing a detailed stress analysis, has been more widely applied to analyze peel test data.

The primary objective of developing an energy balance for peeling has been to separate the energy consumed by plastic and viscous dissipation and thereby determine the intrinsic adhesion from peeling data. The dissipation and inelastic deformation come from two sources. One is the near tip stress which Kaelble attempted to analyze. The other is the plastic deformation caused by bending strains imposed on the film during peeling. For peeling thin, stiff films, strongly adhered to rigid substrates, plastic deformation induced by bending usually predominates. Therefore, energy balance approaches to peeling have concentrated on estimating the energy consumed by plastic and viscous processes due to propagating the bend in a film. Dissipation

due to near tip stresses is considered to be a part of the fracture energy.

Gent and Hamed calculated the energy required to propagate a bend in an ideal elastic-plastic strip using elementary beam bending theory.^{16,17} An ideal elastic-plastic solid follows a linear stress-strain relation until a yield stress is reached. It then deforms at constant stress. It is assumed that the yield behavior in tension and compression are equal. As a section of adhesive strip traverses the bend, it passes from an undeformed state in the bonded region through a maximum bending deformation where the radius of curvature at the neutral axis is a minimum. All of the elastic energy in the bend is recovered when the film is straightened and any plastic work required to straighten the detached film as it moves into regions of lesser curvature is neglected. The total energy, W , expended in plastic deformation during peeling of a unit length of adhesive layer is

$$W = 2 \int_{e_y R}^{\frac{t}{2}} \sigma_y (e - e_y) dx \quad (2.10)$$

where t is the layer thickness, R is the minimum bending radius, e_y is the yield strain and σ_y is the yield stress. The strain in the film, e , at a distance x from the neutral axis is given by $e = x/R$. The Measured peel forces for Mylar polyester films bent to various maximum curvatures during peeling were found to be in good agreement with the calculated values. The experimental arrangement employed resembles ASTM test method D 3167-73T where the Mylar strip was bent around a freely rotating roller as it was peeled from the substrate. The roller

diameter controlled the curvature of the film. The yield stress and yield strains used to calculate the plastic work expended in peeling must be determined for the correct strain rate. The strain rate in peeling, $\dot{\epsilon}$, is approximately

$$\dot{\epsilon} = c/t \quad (2.11)$$

where c is the rate which the peel front advances on the substrate and t is the film thickness. Strain rates for peeling very thin films are too high to duplicate in tensile tests. Therefore, material properties at these rates are obtained by extrapolation from tensile data taken at lower rates.

Kim has developed a more detailed analysis of bending dissipation during peeling and applied it to ideal elastic-plastic, strain-hardening and linear viscoelastic materials, all on elastic substrates. His analysis also includes the effects of reverse plastic bending required to straighten the peeled film.^{11,15,18,19,20} Figure 2.3 shows the zone in the immediate vicinity of the bond boundary during peeling. The points O and A through F lie on the film. The points are also plotted on the corresponding moment curvature diagram where $M/M(\max)$ is the bending moment divided by the maximum bending moment and K/K_e is the curvature divided by the critical curvature at which inelastic deformation begins. At point O, the bonded film has no curvature and is stress free. From O to A the film is in the elastic bending stage. At point A, the critical curvature is exceeded and the film is inelastically bent to its curvature at point B, the bond boundary. The bending moment in the film is elastically unloaded from point B to D, but, the film has residual curvature and plastic reverse bending is required from D to E. From E to F, the elastic stress from the reverse

Figure 2.3 Configuration of steady state peeling and the corresponding moment-curvature diagram.

plastic bending is unloaded and the film returns to zero curvature at point F so that it may be pulled in the direction of the applied force. Note that the detached film, the dashed line, will recoil upon unloading due to residual strain imparted by plastic deformation. The energy consumed in steady state peeling by bending the film is due only to the plastic or viscous work. The elastic bending energy is returned to the system upon unloading. The work consumed by plastic deformation per unit advance of peeling, ψ is

$$\psi = M_o K_e \int_{l_p} m(k) dk \quad (2.12)$$

where l_p is the loading path O-A-B-C-D-E on the moment curvature plane, M_o , the ultimate limit bending moment, and K_e , the elastic limit curvature defined as

$$M_o = \sigma_o t^2 / 4 ; m = M / M_o \quad (2.13)$$

$$K_e = 2\sigma_o / Et ; k = K / K_e \quad (2.14)$$

where σ_o is the yield stress and t the thickness of the film. Material constitutive equations are used to derive moment-curvature relations for each part of the loading path. Slender beam theory is employed and force equilibrium and moment-balance are determined. The moment-curvature relations are used in conjunction with the equilibrium equations to determine the moment and curvature distributions in a film during steady state peeling. The moment and curvature distributions can be used in equation 2.12 to calculate the bending dissipation. Closed form solutions are given for an ideal elastic-plastic material. Numerical integration is used for strain-hardening or viscoelastic

materials. The key factor which determines the dissipation is the maximum curvature of the peeling film which is a function of the base angle between the film and substrate at the crack tip. This angle will depend on the properties of the film and substrate as well as on the adhesion strength. Values for the base angle can be calculated for elastic substrates. However, in actual situations, the substrate may yield, resulting in larger base angles.

Kim, Loukis and Aravas have extended Kim's original analysis to materials obeying linear viscoelastic constitutive relations.^{19,21} A differential equation is derived describing the moment-curvature relation for the unattached part of a viscoelastic film. Boundary conditions are applied such that the film curvature of the detached film reaches zero away from the crack tip and the base angle is zero. There is no closed form solution and determination of the moment curvature relation and the resulting shape profile and moment distribution of the detached film requires sophisticated numerical techniques. Once determined, these can be used to compute the viscous dissipation in the film. The method is used to analyze the peeling of a polyimide film, with an experimentally determined stress relaxation function, from a rigid substrate. A relationship between the peel force, the viscous dissipation, the peel rate and the film thickness is derived.

The numerical results are questionable because the relative contribution to the peel energy from viscous energy dissipation is unreasonably small. Viscous work only accounts for 10% of the peel energy. The calculated bending radius for the polyimide film is very large, approximately 15 times the film thickness. These calculations are very sensitive to the value chosen for the base angle. The film and

substrate are subject to stress and deformation in the bonded region near the crack tip. Thus, a base angle of zero degrees is an unreasonable boundary condition and a key weakness in the models. The base angle needs to be experimentally measured.

The methods developed by Kim, Aravas and others are well suited to analyze peeling of metals, but are inadequate for most polymeric materials. The form of the viscoelastic solutions makes interpretation of the results difficult and requires complicated numerical analysis to obtain quantitative results. Beyond this inconvenience, there are several serious problems with the model. The axial and shear forces which cause additional strains are neglected in the model. In polymer peeling, the extensional strains in the film may be large. Therefore, simple bending theory will only be applicable for thick films or small peel forces. The elementary plane strain beam bending theory used by Kim and Aravas is a good approximation if the minimum radius of curvature is not less than four to five times the film thickness. However, peeling experiments on thin strongly adhering polymer films show that the minimum radius can be in the range of one to four film thicknesses. The near tip stresses in peeling may not be confined to a small region near the crack tip in softer materials such as polymers. Dissipation caused by these stresses is neglected by the bending models and is considered part of the fracture energy. For cases where a significant part of the peel energy is consumed by near tip dissipation, finite element analysis should be used. A numerical finite element solution of the elastoplastic peel problem has been given by Crocombe and Adams who calculated the stress distribution ahead of the interfacial crack.^{22,23}

Complete stress analysis is almost impossibly difficult for peeling of strain-hardening or viscoelastic materials. Plastic yielding of the flexible adherand in bending has been considered in detail. A great deal of information can be gained from these studies, for example, they have provided explanations of the effects of test conditions such as the thickness of the adhesive layer and the peel angle. Direct measurements of the energy dissipated during peeling would eliminate the need for such complex analysis. Regardless of the method of obtaining the dissipation, measurements or calculations, peel energy data may never be useful for determining intrinsic adhesion. The accuracy of the intrinsic adhesion determined from the peel energy is only as good as the accuracy to which the dissipation is known. In most cases of practical interest, the peel energy is greater than two orders of magnitude larger than the intrinsic adhesion, completely obscuring it. Alternatively, the intrinsic adhesion energy may be estimated from peeling by extrapolation of the peel energy to experimental conditions where dissipation is negligible, for example, extremely low peel rates. Accurate extrapolation of small numbers from data containing large numbers requires points close to the origin. The large magnitude of the peel energy at easily accessible experimental conditions and inaccuracies associated with measuring small peel forces make this a difficult proposition.

2.5 Energy Balance for the Peel Test

The work done on the peel test sample by the applied force per unit area peeled, ΔW , can be equated to the internal energy change per unit area peeled, ΔU , of the sample and the heat flowing from the sample per unit area peeled, $-\Delta Q$.

$$\Delta W = \Delta U - \Delta Q \quad (2.15)$$

Neglecting the destruction and creation of chemical bonds, the internal energy change of a body undergoing fracture can be partitioned as

$$\Delta U = \Delta U_{\text{surface}} + \Delta U_{\text{elastic}} + \Delta U_{\text{stored}} \quad (2.16)$$

The change in surface energy is equivalent to the thermodynamic work of adhesion, W_A , which is the energy required to separate the interface reversibly.

$$\Delta U_{\text{surface}} = W_A \quad (2.17)$$

When energy dissipation occurs, the measured peel energy greatly exceeds the thermodynamic work of adhesion

$$\Delta W = W_A + \Psi + \Delta U_{\text{elastic}} \quad (2.18)$$

Ψ is the work consumed by dissipative processes. Some of the work consumed by dissipative processes dissipates as heat and the remainder is stored as physical changes in the deformed material.

$$\Psi = \Delta U_{\text{stored}} - \Delta Q \quad (2.19)$$

The total energy consumed in separating the bonded layers is the sum of the work done by the external force and the elastic energy in the adhesive layer. The elastic energy is due to the presence of residual

tensile stresses in polymeric adhesives and coatings which are solidified under dimensional constraints. For example, a coating on a rigid substrate is dimensionally constrained in the plane of the substrate and will develop shrinkage stresses in the plane. The stresses are eliminated by debonding and the energy concomitant with these stresses is released, reducing the effective adhesion.²⁴ The total elastic strain energy in the film is

$$U_{ELASTIC} = \frac{1}{2} V_0 \left(\sigma_{ij} e_{ij} \right) \quad (2.20)$$

Where σ_{ij} is the Cauchy stress tensor and e_{ij} is the Cauchy strain tensor, V_0 is the volume of the film and $i, j = 1, 2, 3$. The strain energy for a linear elastic isotropic solid can be written in terms of the stresses.

$$U = \frac{V_0}{2E} \left[\sigma_{xx}^2 + \sigma_{yy}^2 + \sigma_{zz}^2 - 2\nu \left(\sigma_{xx}\sigma_{yy} + \sigma_{xx}\sigma_{zz} + \sigma_{yy}\sigma_{zz} \right) + 2(1+\nu) \left(\sigma_{xy}^2 + \sigma_{xz}^2 + \sigma_{yz}^2 \right) \right] \quad (2.21)$$

E is the elastic modulus and ν , the Poisson's ratio. For a coating in equilateral biaxial tension, there are two non-zero stress components; $\sigma_{xx} = \sigma_{yy} = \sigma_1$. If a coating of thickness t is peeled and the detached portion is completely unloaded, the change in elastic energy per unit area peeled is

$$\Delta U_{ELASTIC} = -\frac{t\sigma_1^2}{E}(1-\nu) \quad (2.22)$$

The energy balance per unit area for separating an adhesive layer, bonded in equilateral biaxial tension, from a rigid substrate is

$$\Delta W = -\frac{t\sigma^2}{E}(1-\nu) + \Delta U_{\text{surface}} + \Delta U_{\text{stored}} - \Delta Q \quad (2.23)$$

where ΔW , ΔU and ΔQ are the work, internal energy change and heat dissipated per unit area peeled.

A principle objective of this work is to experimentally measure ΔW , ΔQ and the total internal energy change of peeling, ΔU , using deformation calorimetry and to analyze the peeled materials so that the source of the internal energy change of peeling can be determined.

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CHAPTER 3

DEFORMATION CALORIMETRY AND DEFORMATION THERMODYNAMICS

3.1 Introduction

In the deformation of a material, work is applied. If the deformation is irreversible, some of this work is stored in the material and some is dissipated as heat. The stored work does not always consist of elastic energy, which can be recovered upon removal of the load. The deformed material may be frozen in a state in which its internal order is different from that of the undeformed material resulting in a change in the internal energy of the material. These internal energy changes differ from those resulting from temperature changes, which disappear when the temperature returns to its initial value, or from the application of an elastic load, which disappear when the load is removed, because the material remains in a high energy state indefinitely. Internal energy changes of this type are therefore referred to as latent internal energy changes. Deformation calorimetry is a technique which can measure the heat and work associated with deforming a solid material. If processes for transferring energy out of a sealed system other than heat flow, for example, acoustic and light emission, are negligible, the internal energy change associated with the deformation is also measured. For irreversible deformation, the internal energy change is a valuable addition to the more common mechanical measures of deformation, the stress and strain. In some cases, it may be possible to relate the internal energy change to

differences between the properties and structure of the deformed and undeformed materials. The machine used in this work is not a commercial instrument. Deformation calorimetry is not a common technique and there are only a few such machines in the world. In the first part of this chapter, an overview of deformation calorimetry, a description of the instrument used in this work, the computational algorithms used to interpret the experimental data, and the results of calibration experiments are presented. The second part of this chapter contains a review of the thermodynamics of solid deformation. Several simple cases are considered including the elastic deformation of a Hookean solid, plastic deformation of metals and polymers and heat effects associated with fracture. All of these processes may occur simultaneously during a peel test and their study is useful for interpreting peel test data from the deformation calorimeter.

3.2 Deformation Calorimetry

One of the first people to recognize that thermal effects accompanied deformation of materials was Joule who determined the work required to stir a liquid and at the same time measured the temperature change of the liquid.¹ In this way, Joule was able to determine the mechanical equivalent of heat. Joule also noted that a steel bar became cooler upon rapid elastic stretching and warmer upon rapid elastic compression. These experimental observations were later explained by Lord Kelvin who first postulated the equations of thermoelasticity.² By the late 1800s, it was well established that heat flows accompany

deformation of solids. Furthermore, it was discovered that a thermodynamic equation of state existed for solids relating the stress, strain and temperature in a manner very similar to that which relates the pressure, volume and temperature of a gas.

In gases, the thermal effects accompanying rapid changes in volume and pressure are striking. In contrast, thermal effects associated with elastic deformation of solids are small, requiring extremely high accuracy in calorimetric measurements. For example, adiabatic elastic deformation of metals will result in temperature changes on the order of a fraction of a degree Celsius. There are practical limits on the size of sealed calorimeter chambers which limit sample size. For direct determination of heat effects, the heat produced in the sample must reach the calorimeter quickly. Therefore, calorimeter samples must be very small and are typically limited to several inches in length and must possess small cross sectional areas. As an example of the magnitude of the heat effect for a calorimeter sized sample, consider the elastic tensile loading of a 10 cm long by 0.4 mm diameter steel wire with 50 Newtons force producing a stress of 400 MPa, 50-75% of its yield strength. This would require 5 mJ of work and result in a heat flow of 15 mJ into the wire. While the heat of deformation is small, its magnitude is actually larger than the work of deformation and is certainly significant from an energetics point of view. Typically, the work and heat of deformation are of the same order. When equated to heat, the energy expended in doing mechanical work seems disproportionately small. This is why it takes so much exercise to burn off the energy in food which is measured in thermal units. Elastic deformation of calorimeter sized samples, will usually result in work

and heat between 1 and 50 millijoules. If irreversible deformation occurs, for example, plastic or viscous processes, the energy will be significantly larger, 10 to 500 millijoules.

Calorimetric methods of studying deformation may be divided into one step and two step methods. In the one step methods, known as deformation calorimetry, the heat and work are measured simultaneously and directly. In two step methods, the sample is deformed while the work is measured. A post deformation procedure is then used to measure the difference in the thermodynamic states of the deformed and undeformed solids by comparing the heats of converting both samples to a common reference state. Common methods of conversion include dissolution, chemical reaction and annealing in a differential scanning calorimeter. These methods are of no use for studying reversible deformation since the deformed and undeformed samples are thermodynamically identical. Such techniques have been used with efficacy to determine the stored energy of plastic deformation for metals.³ While two step methods can only differentiate between initial and final values of thermodynamic quantities, deformation calorimetry, a one step method, can determine the thermodynamic state at intermediate stages in the deformation process.

Several different types of deformation calorimeters have been built. Duvdevani designed an instrument which measured temperature changes in a gas flowing over the sample.⁴ Several Tian-Calvet type instruments have been designed. In these calorimeters, thermocouples sense gas temperature differences between a sample cell and a reference cell. The measured temperature difference is theoretically related to the heat flux.⁵ The Tian-Calvet principle and construction design has

been used by Godovskii et al.,⁶ Sergeyev et al.⁷ and Miller and Hohne.⁸

One of the most prolific investigators in deformation calorimetry is F.H. Muller.^{9,10} Muller and Engelter developed a calorimeter which senses pressure changes in a gas at constant volume surrounding a sample. Pressure changes are due to heat being absorbed or emitted by the sample as it deforms. The heat flux caused by the deformation process is equated to the electrical energy required to heat an identical reference chamber so that the gas pressure in both the sample and reference chambers remains identical. Endothermic processes are difficult to measure, requiring pre-heating of the chamber. Strict proportionality must be maintained between the gas pressure and heat flow at all times during the process to be measured. Therefore, all of the heat in the sample must be transferred to the gas quickly. Similar devices were built by Morbitzer et. al.¹¹ and Foster and Benner.¹² All of the deformation calorimeters have mechanical drives capable of placing a controlled deformation on the test specimen and are equipped for measuring the mechanical work.

3.3 Experimental Apparatus

The deformation calorimeter used in this work is derived from the Muller-Engelter device. It was originally designed and built by Farris and Lyon.¹³ This instrument directly measures the heat of deformation in contrast to the Muller-Engelter device which calculates heat using an electrical compensation device. A schematic diagram of the deformation calorimeter is shown in Figure 3.1. The instrument operates by

Figure 3.1 Schematic diagram of the deformation calorimeter.
 1) Sample, 2) Sample cell wall, 2A) Sample cell base, 3) Reference cell, 4) Load cell, 5) Sample cell pull-wire, 6) Sample cell retaining nut, 7) Pressure transducer, 8) Load cell amplifier, 9) Reference cell pull-wire, 10) Pressure transducer amplifier, 11) Computer data acquisition system, 12) Thermal bath.

measuring pressure changes in a gas surrounding the sample, which is contained in a sealed chamber, relative to a sealed reference chamber. The entire apparatus is contained in a constant temperature bath. The sample and reference chambers are connected to a mechanical testing device using tungsten pull-wires which pass through gas tight mercury seals. One end of the sample is attached to the base of the sample cell and the other end is attached to the bottom of a pull-wire. The pull wire in the reference chamber is dead weighted. The reference chamber is identical to the sample chamber so that no relative pressure change results from the small volume changes due to motion of the wires. The sample volume is small compared to the total volume of the chamber so that volume changes due to Poisson's effects do not significantly effect the gas pressure. Any change in gas pressure is due to the emission or absorption of heat by the sample. The area under the time dependent differential pressure between the calorimeter cells is found to be proportional to the total heat absorbed or emitted during a process.

The sample and reference cells are 20 cm in length and made of stainless steel, having an inner diameter of 1.905 cm and an outer diameter of 3.175 cm. The calorimeter cells are accessed by unscrewing a retaining nut which seals an O-ring fitted cap to the cell bottom. Each cell is connected to one side of a Celesco P7D variable reluctance differential pressure transducer, having ± 0.1 Psi (± 690 Pa) range, with stainless steel tubing which passes through the constant temperature bath. All fittings are silver soldered to the tubing and connect to threaded fittings on the calorimeter cells and pressure transducer using O-ring seals. A Celesco CD-10 AC amplifier provides excitation current to the transducer and supplies a ± 10 Vdc output at

maximum differential pressure. The noise level in the output signal is ± 3 mv. The minimum detectable pressure change, at a signal to noise ratio of two, is 0.8 Pa which is 0.1% of full scale. The pressure sensing system was typically operating at 1-5% of full scale. With this sensitivity, a differential pressure change is detectable when a flashlight is directed at one of the calorimeter cells. Due to convection effects at heating rates greater than about 15 mW, thin flexible polyester baffles are positioned inside the sample chamber at 4 cm intervals. This ensures that the pressure response is independent of the axial position of the sample.

The mechanical testing system consists of a specially designed tensile testing device having a screw-driven crosshead with a gear transmission capable of ten linear velocities from 0.027 to 27 cm/min. The movable crosshead is equipped with an Interface 5 kg load cell which measures the force on the sample. A Data Instruments Model #201 amplifier provides excitation current to the load cell and produces a ± 5 Vdc signal at the maximum load. The noise level in the output signal is ± 5 mv. A Trans-Tek linear variable displacement transducer (LVDT), having a total linear range of approximately 15 cm, is also mounted on the movable crosshead. The LVDT is excited with a 15 Vdc regulated power supply and has a positional accuracy of approximately ± 0.1 mm. All of the electronic transducers are connected to a computer which is equipped with a 12 bit auto-ranging analog/digital converter to digitize and store the data. Software was written to collect and analyze the signals and plot the results. The work is calculated from the force-displacement data and the heat is calculated from the pressure-time data.

3.4 Theory of Operation

The differential pressure response of the calorimeter to an electrically input heat pulse is shown in Figure 3.2. Initially, 120 seconds of baseline data was collected before a resistive heating wire was supplied with power. The power was turned off at 140 seconds. Within 60 seconds, the differential pressure returns to zero, reestablishing the baseline. Studies using electric heating wires showed that the measured, time varying differential gas pressure, ΔP , at time t was related to the heat flow in the calorimeter cell, $\partial Q/\partial t$, through the linear hereditary integral, or convolution integral^{13,14}

$$\Delta P(t) = \int_0^t K(t-\xi) \frac{\partial Q}{\partial \xi} d\xi \quad (3.1)$$

where ξ is the time variable of integration and the kernel function, $K(t)$, depends only on the apparatus and is not dependent on sample properties or any particular thermal history. Assuming that equation 3.1 adequately represents the relationship between the calorimeter pressure response and the heat flux, it can be proven, regardless of the form of the kernel function, that the total heat of a process taking place in the calorimeter is proportional to the area under the pressure-time curve. The derivation is summarized here and a detailed derivation is given by Lyon and Farris.¹⁵ Taking the Laplace transform of equation 3.1 results in

$$\Delta \bar{P} = s \bar{Q} \bar{K} \quad (3.2)$$

Figure 3.2 Deformation calorimeter differential pressure response to electric heating versus time for two different power inputs.

where top bars denote Laplace-transformed functions and s is the transform variable. Applying the appropriate limit theorem,

$$\lim_{s \rightarrow 0} \overline{\Delta P}(s) = \left[\lim_{s \rightarrow 0} s \overline{Q}(s) \right] \left[\lim_{s \rightarrow 0} \overline{K}(s) \right] \quad (3.3)$$

results in

$$\int_0^{\infty} \Delta P(t) dt = \frac{Q(\infty)}{C} \quad (3.4)$$

where $Q(\infty)$ is the total heat from the process. The constant C is the thermal capacitance of the calorimeter and is given by

$$C = \left[\int_0^{\infty} K(t) dt \right]^{-1} \quad (3.5)$$

Equation 3.4 states that the total area under the pressure-time response curve, taken from the start of the process and continuing until some time after the process, where the differential pressure between the calorimeter cells has returned to zero, reestablishing the pressure baseline, is proportional to the total heat of the process. The constant C is the only parameter needed to determine the heat from an experimental process. Likewise, if a known quantity of heat is generated within the calorimeter cell, the constant C can be determined from the area under the pressure time curve.

While equation 3.4 allows the computation of the total heat flux of a process, it is often desirable to analyze the pressure-time response curve in such a way as to reconstruct the thermal history of the process allowing the determination of the instantaneous heat flow at any time during the deformation process and of the total heat up to that time. There is a brief lag time between the occurrence of a thermal

event in the sample and its detection by the pressure measuring system. Therefore, the total area under the pressure time curve at any time before the differential pressure has returned to zero is not directly proportional to the total heat up to that point in the process. In order to reconstruct the thermal history of a process, the kernel function in equation 3.1 must be known. Experimentally, the transient pressure response has been found to be well described by the single exponential kernel function

$$K(t) = (1/C\tau)e^{-t/\tau} \quad (3.6)$$

in which τ is the experimentally determined time constant for the system. In general, the form of the kernel function and the value of the time constant will depend upon the sample properties and geometry. Using this function, equation 3.1 can be inverted to give

$$Q(t) = C \int_0^t \Delta P(\xi) d\xi + C\tau \Delta P(t) \quad (3.7)$$

More accurate solutions can be found by fitting the pressure response to a kernel function with more than one exponential term. It should be emphasized that specific knowledge of the kernel function is not required to obtain the total heat for a process. This knowledge is only necessary to obtain the thermodynamic state of the sample at intermediate stages in the deformation process.

An average time constant for the calorimeter, $\bar{\tau}$, can be defined as the mean value of the continuous time variable if the kernel function $K(t)$ is considered as a weighting function such that the usual definition of the mean applies.¹⁵

$$\bar{\tau} = \frac{\int_0^{\infty} tK(t)dt}{\int_0^{\infty} K(t)dt} \quad (3.8)$$

The value of the mean time constant can be determined from the pressure-time response for a single square wave heating pulse beginning at $t = 0$ with a duration of t_0 .

$$\bar{\tau} = \frac{\int_0^{\infty} tP(t)dt}{\int_0^{\infty} P(t)dt} - \frac{t_0}{2} \quad (3.9)$$

This result was derived by Lyon and Farris.¹⁵

The deformation calorimeter can determine the heat of deformation for a wide variety of samples. However, there are some limitations to the technique. The sample must have a relatively small thermal mass so that heat is transferred quickly to the gas. A sample of large thermal capacity will act as a heat sink and conduction through the sample will occur more rapidly than the heat is transferred to the gas. The sample volume must be very small compared to the sample chamber so that the instrument does not measure volume changes of the sample like a gas dilatometer. Significant changes in sample volume will be manifested as permanent shifts in the pressure baseline of the instrument. Finally, the sample must not absorb or emit gas during deformation or the baseline will shift or drift in response to a pressure change caused by a change in the number of moles of gas in the chamber.

3.5 Electrical Calibrations

Calibration of the calorimeter was performed at atmospheric pressure and 293 Ω by electrical resistance heating of 0.255 mm diameter Nichrome wires having a linear resistance of 0.224 Ω/cm . Initial calibrations were performed with 10-15 cm lengths of straight wire placed along the centerline of the sample chamber and connected to a terminal, set in the base of the cell, and a terminal on the bottom of the pull-wire. The sample cylinder was purged with dry nitrogen before calibration. Calibration results have been shown to be independent of axial position.¹³ A regulated power supply with a timing circuit was used to deliver square wave pulses of power with durations, Δt , of 20.2, 40.7 and 61.3 seconds. Variable current settings were available and the heating rate, or power input, was calculated as I^2R where I is the current and R is the resistance of the wire heating element in the calorimeter. The current was measured during heating using a digital voltmeter and the resistance of the heating wires was measured using a four probe conductivity meter. The total heat input for a constant current is $Q = \Delta t I^2 R$.

Figure 3.3 shows four calibration curves obtained from the calorimeter using different heating elements. The slope of the line connecting the pressure-time integral versus heat input data is equal to the reciprocal of the calorimeter constant, C . Two of the calibrations were done with wire heating elements having 2.2 and 1.6 Ω resistances. The other two calibrations were done with wire heating elements bonded to polymer coated metal strips with epoxy adhesive. One of these elements consisted of a 3.2 Ω wire epoxied to a polyimide coated brass

Figure 3.3 Calibration curves for the deformation calorimeter at 25°C.

strip, 5 mm wide, 100 mm long and 0.76 mm thick. The other element consisted of a 3.0Ω wire epoxied to a polyimide coated aluminum strip 5 mm wide, 80 mm long and 0.1 mm thick. In each case, the polyimide layer was approximately 50 microns thick. The dimensions and thermal properties of strips bonded to the heating elements were deliberately chosen to approximate the properties and dimensions of peel test samples used in the calorimeter. Power inputs ranged from 1.5-20 mW spanning the complete range observed in peel experiments. A minimum heat flow of 84 microwatts is required to produce a pressure deflection equal to twice the signal-to-noise ratio and the minimum detectable heat is about 0.42 mJ.⁶ The precision of the instrument, the standard deviation of the mean calibration constant, is $\pm 3\%$. The value for the calorimeter constant, $C = 14.46 \pm 0.5 \text{ mJ/V}\cdot\text{s}$, as defined in equation 3.4, was determined using the following procedure. The best value for each heating element is chosen from a least squares fit of the integrated pressure-time versus heat input data, where the regression line is forced through the origin since zero heat output must correspond to no area. Each point on Figure 3.3 represents a single calibration experiment. For each heating element, the standard deviation of the mean is then calculated from the distribution of calibration constants obtained from the individual calibration experiments. The most probable value, $\bar{x}$, of C , based on experiments done with these four heating elements is taken to be an average of the values determined by least squares, x_i , weighted by $1/s_i^2$ where s_i^2 is the standard deviation of the mean for all of the experiments done with a single element.

$$\bar{x} = \frac{\sum x_i / s_i^2}{\sum 1/s_i^2} \quad (3.10)$$

The standard deviation for the most probable value is computed from the following formula.

$$\frac{1}{s_m^2} = \sum_i \frac{1}{s_i^2} \quad (3.11)$$

The statistical procedures are reviewed in a book by Young.¹⁶

The calorimeter time constant, τ , was determined from equation 3.9. The average time constant for heating wires is 7 ± 1.5 sec. The time constant is highly dependent on the sample geometry and thermal properties. The time constants for the systems consisting of wires on polyimide coated aluminum and brass strips were 60 and 80 seconds respectively. When these values for τ were used to calculate $Q(t)$ for a peeling experiment, the heat calculated at the end of peeling was only a fraction of that calculated when the entire $\Delta p(t)$ peak was integrated, an illogical result. In a peeling experiment, the mechanical work of peeling is nearly linearly proportional to the peeled area. The heat must also be approximately linearly proportional to the peeled area. The single relaxation time model used to derive equation 3.7 must be inadequate for these samples and heats calculated using time constants given by equation 3.9 are invalid for peel test samples.

Fortunately, the calibration experiments show that the total heat for a peel experiment can be calculated with confidence because the calorimeter constant, C is independent of the sample geometry and thermal properties. As an approximation, a time constant can be fit by trial and error such that the heat is approximately proportional to the

peeled area reaching a final value equal to that calculated from integrating the entire peak. Figures in this thesis which plot the heat versus the distance peeled are constructed using this concept, but all reported numerical results utilize the heat calculated from integrating the entire $\Delta p(t)$ peak.

Alternatively, the calorimeter can be calibrated electrically by applying constant heat flux and measuring the differential pressure response when the system reaches equilibrium.¹⁵ The system can also be calibrated by comparing thermal expansion coefficients calculated from the heat flow resulting from elastic deformation to values obtained by other methods. This is discussed in more detail in section 3.6. In section 3.6, deformation of an ideal rubber and ideal plastic are discussed. These also provide means of calibrating the instrument because the work and heat are equal for these processes.

The mechanical work measuring system is calibrated by moving a weight through a distance, measured with digital calipers. The accuracy of the instrument determined for 50 mJ of mechanical work, typical of a peeling experiment, is ± 0.6 mJ.

3.6 Thermodynamics of Solid Deformation

The first law of thermodynamics states:

$$dU = dQ + dW \tag{3.12}$$

where dU is the change in internal energy, dQ is the heat transferred to the system and dW is the work done on the system. The first law is

applicable to all processes, reversible or irreversible, and all states of matter. Since the deformation calorimeter is capable of measuring dQ and dW and calculating dU , it is worthwhile to consider the expected results for some idealized simple cases. These results provide additional methods of calibrating the instrument and are useful for understanding the behavior in more complex cases, such as the peeling experiments which are the primary subject of this thesis.

Thermal effects always accompany the application of stress to a material. It is well known that most of the energy expended in irreversible frictional processes, such as plastic and viscous deformation, is dissipated as heat. Plastic deformation can result in significant heating, for example, the head of a nail which has been subject to repeated blows with a hammer will be hot enough to cause pain when touched. It is less widely known that thermal effects are associated with reversible elastic deformation. Purely elastic processes also involve heating and cooling and the thermal effects, like the elastic deformations, are reversible. The isothermal stress-strain relation for a Hookean elastic solid in one dimension is

$$\sigma = Ee \tag{3.13}$$

where σ is the stress, e is the small strain, and E is the Young's modulus. The work of deformation, per unit volume, is obtained by integrating equation 3.13.

$$dW = Eede \tag{3.14}$$

The relationship between the thermoelastic heat, dQ , and an increment of uniaxial tensile or compressive force, df , at constant temperature and

pressure is given by the following formula which is derivable from thermodynamics.^{17,18}

$$dQ = -\alpha T l df \quad (3.15)$$

where α is the linear thermal expansion coefficient, T is the absolute temperature and l is the length of the sample. For a material obeying the Hookean constitutive relation expressed by equation 3.13, the heat flow per unit volume can be expressed in terms of an increment of tensile or compressive strain, de .

$$dQ = -\alpha T E de \quad (3.16)$$

A material with a positive thermal expansion coefficient cools when stretched and warms when compressed. Most metals, isotropic polymers and glasses have positive thermal expansion coefficients. Stretched rubbers and highly oriented polymers become warm when stretched. These materials have negative thermal expansion coefficients. Equations 3.14 and 3.16 can be combined to give an approximate expression for the internal energy change per unit volume of a Hookean elastic material at constant temperature and pressure.

$$dU = E de + \alpha T E de \quad (3.17)$$

This equation has been verified by deformation calorimetry of steel wires¹⁷ and glassy and crystalline polymers.^{10,17} In an ideally elastic system, all of the work done on the system would be reversibly transformed into internal energy. Deformation of such a system would not be accompanied by thermal effects. The classical theory of elasticity treats elastic deformation in this manner. Equation 3.17 shows that when elastic deformation is accompanied by thermal effects,

the internal energy of the deformed material will deviate from that of an ideally elastic system. The relationship between the work, heat and internal energy change for a linear elastic solid in uniaxial deformation at constant temperature and pressure is shown in Figure 3.4.

The general relation for the internal energy change of an elastic solid subject to a multiaxial state of stress is

$$dU = \frac{1}{2} \sigma_{ij} e_{ij} + \frac{\alpha E e_{ii}}{2(1-2\nu)} dT + C_e dT \quad (3.18)$$

where ν is the Poisson's ratio and C_e is the heat capacity at constant strain. For elastic deformation, contributions to internal energy changes can be identified with three sources corresponding to the three terms in equation 3.18. The first term is the elastic work. The second term contains e_{ii} , which is the volume dilatation and this is the term that causes coupling between elastic and thermal processes. Heat effects during the isothermal deformation of classical elastic solids are due to entropy changes resulting from volume dilatation. The third term is the change in internal energy resulting from temperature changes.

Entropy effects associated with volume dilatation are analogous to entropy changes associated with temperature. The heat capacity of a solid increases with temperature because the population of higher vibrational energy levels increases with temperature. As higher vibrational energy levels become active, interatomic distances increase resulting in thermal expansion. The vibrational entropy of a solid also increases as more vibrational modes become active. Analogously, increases in the vibrational entropy of a solid result from the volume

Figure 3.4 Heat, Q , work, W , and internal energy change, ΔU , versus strain, ϵ , for a linear thermoelastic solid.

dilatation accompanying uniaxial stretching. As the volume of a solid increases, so does the average distance between atoms increasing the available vibrational modes at a given temperature. For reversible processes, the second law of thermodynamics applies

$$dQ_{\text{rev}} = TdS \quad (3.19)$$

Therefore, a reversible increase in entropy must be accompanied by cooling in the solid so that thermal energy may be transferred in from the surroundings.

Additional heat effects associated with the reversible deformation of polymeric materials result from distortional strains. In contrast to simple solids, distortional deformation of polymeric solids may cause molecular rearrangements, changing the entropy of the solid. In the deformation of an elastomer, work is primarily expended in changing the conformation of the molecules. Tensile deformation places individual polymer molecules in extended states which are statistically less favorable than the undeformed states resulting in a decrease in the total entropy of the material. The elastic restoring force of elastomers is primarily entropic and elastomers can be considered entropic-elastic solids. For an ideal entropic-elastic material, all of the work done on the material would be used to change the entropy. Therefore, the heat given off by the material would equal the work done on it resulting in zero internal energy change. The internal energy of an ideal elastic-entropic system is only a function of temperature. An ideal gas is an ideal elastic-entropic system. By definition, $(\partial U / \partial V)_T = 0$ for an ideal gas. Another example of a purely entropic-elastic system is length changes, λ , of an ideal rubber where

$(\partial U/\partial \lambda)_T = 0$. The condition which must be satisfied for an ideal elastic-entropic system is that there is no change in interaction between the molecules during deformation. For polymers, there must be no change in intrachain or interchain interactions with deformation. The interactions in a polymeric solid will change if the volume changes. Elastomers have Poisson's ratios greater than 0.498, approaching the incompressible limit of 0.5, so that the volume dilatation is extremely small. However, limited volume dilatation does occur during the deformation of real elastomers, effecting molecular interactions and changing the internal energy of the system. At small strains, the thermoelastic behavior is dominated by volume dilatation and the elastomer will have a positive thermal expansion coefficient. At larger strains, the thermal expansion coefficient becomes negative as conformational entropy changes dominate the thermoelastic behavior. The theory of rubber elasticity, including the thermodynamics of elastomer deformation, is one of the oldest theories in polymer science and has been extensively reviewed.^{19,20} Derivations of theoretical models for the thermodynamics of elastomer deformation, based on calorimetric measurements have been presented by Godovsky,²¹ Kilian²² and Lyon and Farris.¹⁵

Materials where the thermoelastic effects are due to volume dilatation will have positive thermal expansion coefficients. Polymeric solids which contain molecules in highly extended conformations may exhibit negative thermal expansion coefficients in the direction of molecular orientation. Small deformations in this direction will result in large changes in entropy as the molecules are stretched toward fully extended conformations. The room temperature thermal expansion

coefficient of drawn HDPE in the draw direction becomes negative at draw ratios greater than 4.²³ Similar behavior is observed for other semi-crystalline polymers above their glass transition temperatures. The same type of behavior may also be observed for drawn amorphous or semi-crystalline polymers below their glass transition temperatures.²⁴

When a material is deformed beyond its elastic limit, yielding occurs and the elasticity and viscosity coefficients become functions of stress. The situation is further complicated for polymeric materials by temperature and rate effects. These complications make complete analytical descriptions of post-yielding behavior almost impossible for polymeric materials. Deformation calorimetry can provide valuable information about the post-yielding behavior of a material. The first law of thermodynamics is valid for irreversible and reversible processes and the energy balance must always be satisfied. Therefore, deformation calorimetry can be used to measure the internal energy change during deformation and the latent internal energy change, which is the difference in the enthalpy of the sample before and after deformation. The internal energy change is a valuable addition to the stress and strain behavior and provides a means of comparing the deformed and undeformed material as well as a means of checking the validity of constitutive equations. Generally, the change in entropy cannot be determined from deformation calorimetry alone. Internal changes to the structure and organization of the molecular chains may take place upon deformation resulting in a change in the structural entropy of the solid. Therefore, the measured heat, ΔQ , consists of two components, one corresponding to structural entropy changes which is reversible and

can be expressed as $-T\Delta S$ and one which corresponds to entropy generated by the irreversible nature of the process.

In the final deformed state, a material may not be in thermodynamic equilibrium. In solids, the effects of deformation may be frozen in depending on the temperature and rate. Different final states may be obtained by deformation at different rates and temperatures. There are a few simple cases where the work of deformation is entirely dissipated as heat and the deformed and undeformed materials are thermodynamically identical. These include pure flow processes such as the deformation of a Newtonian fluid and ideal plastic deformation. Some metals approach ideal plasticity, but non-ideal plasticity, manifested by strain hardening, has been observed in a number of metals resulting in small internal energy changes.²⁵ Ideal elastomers and ideal gases also exhibit no change in internal energy upon deformation, but these are thermodynamically reversible processes in contrast to the previous examples which are irreversible flow processes.

Glassy amorphous and all semi-crystalline polymers may exhibit large changes in internal energy with inelastic deformation. The macromolecular nature and complex morphologies of polymers lead to many possibilities for structural change upon deformation. Changes in chain conformation and orientation, bond angle deformation, crystallinity and changes in intermolecular interactions may all occur. A fascinating comparison may be made between typical cold drawing behavior of metals and rigid polymers. Table 3.1 shows the ratio of heat to work for the cold drawing of several metals and polymers. A heat to work ratio of one corresponds to ideal plasticity. The metals dissipated 92-98% of the work of deformation whereas the polymers only dissipated 45-70%.

Expressed on a per unit mass basis, the internal energy change accompanying polymer deformation is 10-100 times larger than that of most metals.

Table 3.1 Stored energy of inelastic drawing for various materials.

Material	Q/W %
Copper	92
Lead	98
Nickel	98
Silver	96
Iron	95
Aluminum	95
Polycarbonate (20°C, 1.8 min ⁻¹)	49
LDPE (20°C, 1.8 min ⁻¹)	70
PMMA (20°C, 1.8 min ⁻¹)	45
PET (25°C, 1.2 min ⁻¹)	67

Source: References; 24,25

Figure 3.5 shows the stress, heat, work and internal energy change versus strain for uniaxial drawing of poly(ethylene terephthalate) in the deformation calorimeter at 25°C and 1.2 min⁻¹. At small strains, the material deforms elastically and heat flows into the sample because it exhibits positive thermal expansion. After yielding, heat is dissipated by the material. Typically, the dissipation associated with plastic deformation is much larger than the thermoelastic heat flow and the overall heat effect will change from endothermic to exothermic after yielding for materials with positive thermal expansion coefficients. Drawn to a strain of 25%, the polymer dissipated approximately 66% of the work of deformation as heat. The remaining energy is stored in the

Figure 3.5 Work, heat and stress versus strain for PET films drawn in the calorimeter at $.02 \text{ sec}^{-1}$ and 25°C .

polymer as a latent internal energy. Adams conducted an extensive investigation of latent internal energy storage caused by drawing of semi-crystalline and glassy amorphous polymers.²⁴

Figure 3.6 shows the stress, heat, work and internal energy change versus strain for elastic extension of poly(ethylene terephthalate) in the deformation calorimeter at 25°C and 1.2 min⁻¹. At small strains, the material deforms elastically and the heat flowing into the sample can be calculated from equation 3.16. The total heat absorbed is proportional to the strain with the proportionality factor being αTE . Thermal expansion coefficients calculated from measurements of heat versus strain in the deformation calorimeter provide a method of calibrating the instrument. The reproducibility of the calorimetrically determined thermal expansion coefficients is fair with a standard deviation of approximately $\pm 15\%$. Thermal expansion coefficients of several materials calculated from deformation calorimeter data are compared to values obtained by other methods in Table 3.2.

Table 3.2 Thermal expansion coefficients calculated from thermal effects measured in the deformation calorimeter at 25°C.

Material	$\alpha \text{ } ^\circ\text{C}^{-1} \times 10^{-6}$ Calorimeter	$\alpha \text{ } ^\circ\text{C}^{-1} \times 10^{-6}$ Reference Value
Mylar PET	25	17*
Polyimide (PMDA-ODA)	51	47*
Aluminum	.30	24 ²⁶
Tungsten	3	4.5 ²⁶

* Measured in a thermomechanical analyzer

In this thesis, deformation calorimetry is used to study peeling which involves a combination of elastic, plastic, and viscous

Figure 3.6 Work, heat and stress versus strain for elastic tensile deformation of PET films in the calorimeter at $.02 \text{ sec}^{-1}$ and 25°C .

deformation. In addition to deformation, peeling results in fracture, exposing two new surfaces. There is an increase in internal energy due to surface creation which was discussed in Chapter 2. Additionally, surface creation may require the destruction of covalent chemical bonds resulting in a chemical energy contribution to the total internal energy change.

Griffith²⁷ described crack propagation as the conversion of the work done by the external force, W , and the available elastic energy stored in the specimen, U , into surface energy, γ . The criterion for crack propagation is

$$\frac{\partial(W-U)}{\partial a} \geq \gamma \frac{\partial A}{\partial a} \quad (3.20)$$

where ∂A is the increase in surface area associated with an increment of crack growth ∂a . The energy required to cause crack growth in a brittle material such as glass is approximately twice the surface energy. However, for the vast majority of materials, including metals and polymers, the fracture energy is much greater than the surface energy. There are two principle reasons for this discrepancy. First, the value of the surface energy only accounts for the rupture of weak secondary bonds such as van der Waals forces. Crack growth in metals and crosslinked, high molecular weight or crystalline polymers often requires the destruction of stronger primary bonds. Second and most significantly, fracture involves viscoelastic and/or plastic processes which are often concentrated in the vicinity of the crack tip, but may occur throughout the specimen. When tough materials fracture, almost all of the mechanical work is consumed by dissipative processes resulting in the production of heat.

In elastic fracture mechanics, deformation is assumed to be controlled solely by the elastic response of the material and the crack growth results in elastic energy release. This is balanced by the energy required to create the fracture surfaces and the dissipation process in the body, which is local to the crack tip, and on such a small scale that it does not effect the elastic response of the body away from the crack plane. The fracture toughness, G_{Ic} , considered a material property, is a combination of the crack tip specific dissipation and the surface energy. Fracture toughness can be measured by suitable mechanical experiments where the elastic energy release of the system can be determined.

When fracture proceeds through peeling, the dissipation is not always confined to a local scale which can be considered crack tip specific. The total mechanical work input is readily determined since the crack advances at a controlled rate. However, the definition of G_{Ic} does not apply because the inelastic deformation is not crack tip specific. For cases where the bulk material does not deform elastically J integral fracture analysis is used to define the fracture toughness.²⁸

Measurements of heat generation during rapid crack propagation through PMMA were made by Doll.^{29,30} To derive Q , the temperature rise was measured on the surface of fracture specimens close to the fracture plane using thermocouples. Heat outputs, estimated from the temperature data, contained errors of approximately 30%. The heat always increased with crack velocity. The heat output varied from about 0.2 kJ/m^2 at a crack velocity of 200 ms^{-1} to 5 kJ/m^2 at 700 ms^{-1} . The observed increase was rationalized in terms of the strain energy release rate and the extent of the plastic zone at the crack tip. The size of the

plastic zone predicted by Irwin-McClintock and Dugdale-Muskhelishvili models increases with energy release rate.^{31,32} Therefore, the heat output will increase with the energy release rate. When extrapolated to the critical energy release rate, the minimum energy input necessary to make the crack propagate, (at 140 ms^{-1}) the heat output accounted for only 57% of the released mechanical energy G_{Ic} . The difference is attributed to heat which is dissipated over sample sized dimensions and escapes detection or energy which is dissipated in the form of shock waves instead of heat. The possibility that some of the energy is used to raise the internal energy of the fractured specimen was not considered.

Thermal measurements of fracture also permit estimation of the temperature rise, ΔT at the crack tip. ΔT will depend on the thermal conductivity of the material, the size of the crack tip plastic zone and the magnitude of the heat dissipation. For tough polymers with low thermal conductivities, ΔT can be appreciable. If the heat is assumed to be confined to the plastic zone surrounding the crack tip, estimates by Doll for PMMA place ΔT at an amazing 230 K. Infra-red measurements on PMMA at crack velocities of 200 to 640 ms^{-1} showed a constant temperature rise of 500 K.³³ The increase in the heat output with crack velocity, while ΔT remained constant, implied that the plastic zone became more extensive at higher crack velocities. At these temperatures, melting and degradation should occur. Heat output also increased with the molecular weight for a series of PMMA.³⁰ There is an inverse relationship between yield strength and the size of the plastic zone which leads to larger plastic zones for softer materials.³⁰

In peeling, temperature increases won't be as high, because crack velocities are four orders of magnitude smaller. The heat should be conducted away almost as fast as it is generated resulting in a quasi isothermal process. The crack velocity in a steady state peel experiment is determined solely by the testing machine velocity in contrast to other fracture tests where the crack propagates at high velocity after a necessary load is applied to the specimen.

When the deformation of a polymeric material results in fracture, as in peeling, the possibility exists that changes in the internal energy of the system can result from the breakage and reformation of chemical bonds. When a polymeric sample undergoes fracture, new surface is created requiring the severance of either primary (covalent) or secondary, (van der Waals or hydrogen) bonds or both. Breakage of secondary bonds will be followed by reformation of similar bonds in the fractured sample producing no change in internal energy. In contrast, broken covalent bonds will produce reactive radicals which could recombine with many different species producing internal energy changes. The extent to which each type of bond is broken depends upon the polymer being tested and the testing conditions. Highly crosslinked polymers cannot be fractured without the breakage of primary bonds. In the fracture of thermoplastics, it may be possible for molecules to slide past one another by breaking secondary bonds only. Chain entanglements and crystalline regions in semi-crystalline polymers function as physical crosslinks in high molecular weight thermoplastics providing sufficient anchoring of the chains to require some breakage of primary covalent bonds during fracture. However, the density of chemical crosslinks in a thermoset polymer is much higher than that of the

physical crosslinks in a thermoplastic. Therefore, primary bond breakage is far more important in thermoset fracture. Regardless of the mechanism of failure, the strength of polymers is strongly influenced by the density of main polymer chains crossing the fracture plane.

Vincent attempted to quantify the breakage of main chain bonds during fracture by examining the relationship between the fracture strength of a series of polymers and the density of main chain bonds crossing the fracture plane.³⁴ He concluded that fewer than 1% of the main chain bonds were broken. For fibers and highly oriented polymers, the percentage of broken main chain bonds is much higher.

The most widely used technique to measure the breakage of primary bonds is electron spin resonance spectroscopy, ESR, which allows direct observation of free radicals produced when covalent bonds are broken. A review of ESR applied to polymer fracture is given by Kausch.³⁵ The level of sensitivity for this technique limits it to the study of highly oriented fibers and films where the density of free radical generation is high or milled polymers with high surface areas. Since free radicals are extremely reactive, it is necessary to work at low temperatures. Most tests are carried out in liquid nitrogen at 77 K. Free radicals have been observed during the fracture of highly oriented nylon, polyethylene, polypropylene and polyethylene terephthalate fibers.³⁵

Primary covalent bonds will be in a highly stressed state before breaking. Upon breakage, a large amount of elastic energy would be released. Some of this energy should be irreversibly dissipated as heat by frictional forces as the broken chains and those entangled with them slip by other chains into lower stress positions. The frictional dissipation would not change the internal energy of the material. If

there are no frictional forces restricting the recoil of the entropically stretched chain segments after the bonds break, no work is done by the chains during recoil. In this case, what happens to the elastic energy in the stretched chains when they recoil? The extension, scission and retraction of single chains during fracture could be considered as adiabatic stretching followed by free adiabatic recoil. An amount of work, ΔW , is done on the sample during stretching. If the process is adiabatic, the heat flow, ΔQ , is zero and the internal energy of the system increases by ΔW resulting in a temperature rise. During adiabatic free recoil, no work is done by the system and there is no heat flow. The temperature and internal energy of the system would not change during recoil. Successive adiabatic stretch, break and retract events would effectively act as an internal energy pump, progressively increasing the temperature and internal energy of the system. While the molecular events in a polymeric material undergoing fracture can be considered as adiabatic on a time scale commensurate with the deformation and fracture of single chains, the system is not truly adiabatic and will eventually attain thermal equilibrium with its surroundings dissipating the internal energy. Therefore, polymeric materials can dissipate mechanical energy in the absence of frictional forces.

Chain breakage should facilitate molecular reorganization within the polymer producing latent internal energy changes. It would be impossible to separate measured internal energy changes during fracture, measured in the deformation calorimeter, into chemical bond energy and molecular rearrangement components. However, the local stress at the molecular level which would cause secondary bond breakage is probably

small compared to that required for breaking primary covalent bonds. Therefore, the molecular rearrangement resulting from the breakage of a single primary bond would certainly be more extensive than that resulting from the breakage of a secondary bond. In Chapters 4 and 5, latent internal energy changes in the range of 2-10 J/g (Joules per gram) are measured for drawing, not fracture, of thermoplastics, where bond breakage is confined to secondary bonds. For comparison, the chemical energy needed to break primary bonds during the fracture of highly oriented Nylon 6 fibers has been estimated from ESR data to be 0.1 J/g.³⁵ The actual internal energy change energy will certainly be smaller after the free radicals recombine with other species. A free radical may recombine to form a bond identical to the one which was broken resulting in no change in the chemical energy of the material. For the scission of a main chain bond, it would seem likely that the latent internal energy change associated with reorganization of the material following breakage would obscure the change in chemical bond energy.

For crosslinked polymers, fibers or other highly anisotropic polymers, changes in chemical energy due to primary bond breakage will be a contributing factor to the total internal energy change of fracture. In other cases, where chain slippage and pullout is a relatively easy process, the chemical energy of broken primary bonds will not significantly contribute to the internal energy change of fracture. When primary bond breakage is significant, it is likely that the internal energy changes resulting from molecular rearrangements following breakage will obscure those due to the difference in chemical energy for breaking and reforming the bonds.

3.7 Summary

The technique of deformation calorimetry is capable of measuring the heat flow associated with mechanical deformation to an accuracy of $\pm 3\%$. A wide variety of samples may be used, but the samples must fit in a 20 cm long by 2 cm diameter cell and have a small volume compared to that of the cell. Heats of deformation for this size sample are small and the instrument is accordingly sensitive, with the capability of detecting heat flows of 82 microwatts.

Heat flows accompany reversible and irreversible deformation of solid materials. The deformation calorimeter is extremely useful for analyzing the irreversible deformation of polymeric materials. The energy frozen in the solid as a result of deformation, the latent internal energy, can be measured and provides a means of comparing the deformed and undeformed materials. For glassy and semi-crystalline polymers, the latent internal energy can be greater than half of the mechanical energy expended in deforming the sample. This is a consequence of the variety of molecular rearrangements which can occur within the solid during deformation.

The primary application for deformation calorimetry in this thesis is to peeling, which is discussed in detail in Chapters 4 and 5. Peeling is a combination of reversible deformation, irreversible deformation and fracture which leads to the creation of new surfaces. Surface creation may involve the breaking and reforming of covalent chemical bonds resulting in a permanent internal energy change and adding to the latent internal energy change caused by molecular rearrangement in the material.

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CHAPTER 4

PEELING OF POLYIMIDE COATED ALUMINUM

4.1 Introduction

Polymeric coatings are usually thin, flexible and strong enough to be peeled without breaking. Therefore, the peel test is used extensively for measuring adhesion in polymer coatings applications. Polyimides are an important class of high temperature polymers with good dielectric properties which are used as coatings or substrates for electronic circuitry or as interlayers between metals and semiconductors in multilayer electronic devices. Accordingly, the peel test is used extensively to test the adhesion of these materials by the electronics industry.

This chapter presents the results of investigations of the peel behavior of polyimide coated aluminum. Peel samples were fabricated with either the aluminum or polyimide reinforced such that plastic deformation through the bulk of the films due to bending could be confined to the polymer or metal layer being peeled. Deformation calorimetry showed that about half the mechanical energy required to peel polyimide from aluminum was dissipated as heat. In contrast, almost all of the mechanical energy expended in peeling aluminum from polyimide was dissipated as heat. The composition and topology of the fracture surfaces were investigated using x-ray photoelectron spectroscopy and scanning electron microscopy, confirming that the locus of failure is identical for peeling polyimide or aluminum. Most of the

energy not dissipated as heat when polyimide is peeled is believed to be stored as latent internal energy in the peeled polyimide film. The tensile drawing of polyimide films was studied because bending strains induced during peeling must cause molecular rearrangements in high strain regions of the film similar to those caused by homogeneous tensile or compressive deformation. As with peeling polyimide, deformation calorimetry showed that more than 50% of the energy used to draw polyimide films is stored as latent internal energy in the drawn material. The mechanisms of plastic deformation in polyimides are also considered in relation to the thermodynamic data.

4.2 Sample Preparation

The polyimide used in this study, PMDA-ODA, is not soluble and is thus applied as a poly(amic acid), Dupont Pyralin 2540, polymerized from pyromellitic dianhydride and oxydianiline, which is soluble in N-methyl-2-pyrrolidone, NMP. The peel test samples were prepared by spin coating a solution of polyamic acid onto 0.004" thick aluminum substrates using a Headway Research EC101 photoresist spinner. The aluminum substrates were etched in chromic acid, bonded to glass plates with a high temperature adhesive to prevent curling and solvent wiped with acetone prior to coating.

The spun-on films are then thermally imidized by baking in several steps.

Step 1: 80°C for 60 minutes in air

Step 2: 150°C for 30 minutes in air

Step 3: 250°C for 30 minutes in air

Step 4: 360°C for 30 minutes in nitrogen

The first step removes most of the solvent from the film. Subsequent heating above 110°C causes cyclohydration of the polyamic acid, converting it to polyimide. The final heating at 360°C is done under dry nitrogen to prevent degradation. After exposure to a final temperature of 360°C, the polyamic acid has been totally converted to polyimide. The structure of the fully imidized polymer is shown in Figure 4.1. To produce thick coatings, additional layers were applied on top of partially imidized polyamic acid coatings which had been taken through cure steps 1 and 2. For coatings spun at 1000 rpm, the thickness was approximately 15-20 μm (microns) per layer. Coatings were prepared having thicknesses ranging from 28 to 95 μm . Internal tensile stresses in the films limited the coating thickness to less than 120 μm , a thickness at which stress driven spontaneous delamination occurred during post curing cooldown. After the final curing step, the aluminum was easily separated from the glass plates and peel test samples were prepared by cutting strips from the polymer/metal sheets. When removed from the glass, the sample would curl into the polyimide side indicative of tensile stress in the polyimide layer.

Two types of calorimeter peel test samples were fabricated from the polyimide/aluminum sheets. A photograph of both is displayed in

poly-[N,N' bis-phenoxyphenyl pyromellitimide]

Figure 4.1 Structure of fully cured polyimide coating.

Figure 4.2. A rigid steel wire is bonded to the back of the aluminum strip of the top sample, which prohibited the aluminum from bending while the polyimide film was peeled from the aluminum. A rigid steel wire is bonded to the back of the polyimide film of the bottom sample, prohibiting it from bending while the aluminum was peeled from the polyimide.

4.3 Peel Tests in the Deformation Calorimeter

In Figure 4.3, force and differential pressure signals obtained from peeling a 63 μm thick polyimide film from a rigid aluminum substrate in the calorimeter are plotted versus the time which elapsed from the beginning of data collection. Initially, 120 seconds of baseline data was collected before the crosshead of the mechanical tester began moving upward at a constant rate of 5.42 cm/min. The pressure decreases initially, producing an endotherm with a minima at 123 seconds. The endotherm is due to stretching of the detached portion of the polymer film which has a positive thermal expansion coefficient. The onset of peeling is indicated by the yield in the force curve. As peeling commences, heat is evolved and the pressure in the sample chamber rapidly increases. The peeling proceeds in a steady continuous manner with relatively little fluctuation in the peel force. Peeling stopped at 140 seconds and the peeled film was unloaded, negating the effect of thermal expansion and releasing the nominal elastic energy in the peeled film. Figure 4.4 shows the work, heat and internal energy change calculated from the data in Figure 4.3. The rate of thermal

Figure 4.2 Calorimeter peel test samples.

Figure 4.3 Force and pressure signals obtained by peeling polyimide film from aluminum in the deformation calorimeter.

Figure 4.4 Work, (W), heat, (Q), and internal energy change, (ΔU), versus distance peeled calculated from the data in Figure 4.3.

dissipation and work expenditure appear to be constant during peeling, increasing proportionally with the peeled area. The total area peeled is 0.46 cm^2 ; the width of the sample multiplied by one half the crosshead displacement. In 180° peeling, the length of the peeled adherand is one half the displacement of the testing machine crosshead because the point of detachment advances in the direction of displacement as peeling proceeds. The work is equal to 660 J/M^2 or 7.5 J/g (joules per gram of peeled film). The heat dissipated is 310 J/M^2 or 3.5 J/g . The difference between the work done and the heat dissipated, 350 J/M^2 or 4.0 J/g , is the internal energy change of peeling. If mechanisms of energy dissipation other than heat flow are assumed to be negligible, for example, acoustic and light emission, then conservation of energy requires that the internal energy change has raised the energy of the peeled specimen. For peeling polyimide, approximately 50% of the mechanical energy consumed by peeling has gone into raising the energy of the peeled sample.

The precision of the calorimetric measurements is indicated by Table 4.1 which gives mean values of the work and heat, the number of measurements and the standard deviations, for several sets of measurements at different peel rates.

Table 4.1 Measurements of the work, W , and heat, Q , of peeling $63\text{ }\mu\text{m}$ polyimide films from rigid aluminum substrates in the deformation calorimeter.

Peel rate cm/min	Number of peels	$W\text{ J/m}^2$	$Q\text{ J/m}^2$
0.68	4	640 ± 50	-290 ± 50
2.71	5	660 ± 30	-330 ± 40
6.67	6	640 ± 40	-330 ± 50
13.4	3	620 ± 10	-300 ± 10

The standard deviations in the mean heat values range from 3-17% of the mean. While large, the source of these deviations is not necessarily the method of measurement, but variability in the peeling experiments as reflected by the standard deviations of the mean work values which are almost equal to those of the heat. The systematic errors of the work measurements are known to be smaller than those of the heat. The combined effect of all systematic errors inherent in the heat measuring technique is best evaluated from calibration experiments done with wire heating elements and the systematic errors in the work measuring technique are best evaluated from calibration experiments done by moving a weight through a known distance. The systematic errors in the heat and work measured with the deformation calorimeter, where the magnitude of the work and heat are similar to those in the peeling experiments, are estimated to be less than 5% and 1% respectively. The large standard deviations in the experimental populations are indicative of random errors due to the poor repeatability of peel experiments.

To determine the total heat flow of the peeling experiments, integration of the pressure time data was performed over the interval beginning with the motion of the mechanical tester and ending when the

differential pressure signal returned to its baseline value. The only correction applied to the pressure data before integration was subtraction of the pressure baseline, determined from 120 seconds of baseline data collected before the peeling experiment. This produced a horizontal, zero differential pressure baseline. In all of the experiments, data was collected for 5 or more minutes after the end of peeling to obtain additional baseline data. If, after baseline correction, the baseline before the start of peeling was not collinear with the baseline re-established after the end of peeling, the data was discarded. Some possible sources of baseline problems include electrical problems, gas leaks and absorption or desorption of gas by the sample. To minimize the chance of baseline problems and verify that the instrument was operating properly, the calorimeter was tested after loading each sample by pushing pull-wires into the sample chamber, the reference chamber and both chambers simultaneously. This procedure verified that the differential pressure transducer and electronics were working properly and that there were no gas leaks in the system. The mechanical work measuring system was also checked after loading each sample. The load cell was calibrated with 500 g and 1000 g weights and the force was set to zero, compensating for the dead weight of the pull-wire and the detached portion of the peel sample. Displacement calibrations were performed frequently with digital calipers and the integrated system was checked by measuring the work required to move a weight through a known distance. The heat measuring system was also recalibrated frequently using wire heating elements as described in Section 3.5.

An energy balance for peeling was developed in Section 2.5 and is given by equation 2.23. The results presented in this chapter will facilitate the decomposition of the mechanical energy of peeling into the terms in equation 2.23 which are believed to represent the major mechanisms of energy consumption during peeling. Up to this point, the peel energy has been partitioned into thermal dissipation and an internal energy change. The internal energy change is a large portion of the total energy of peeling. Additional experiments are necessary to identify the mechanisms responsible for the internal energy change and determine to what extent they contribute to the observed internal energy change. The internal energy change caused by peeling can be partitioned into changes in the elastic energy of the system, creation of new surfaces exposed by peeling and the latent internal energy stored in the peeled materials. The latent internal energy change can be attributed to two mechanisms: Some of the deformations induced by peeling are frozen into the materials leaving them in a non-equilibrium, high energy thermodynamic state. Creation of the new surfaces exposed by peeling may result in the rupture and reformation of covalent chemical bonds changing the chemical energy in the sample. In the energy balance given by equation 2.23, the latent internal energy change is expressed as a single term, ΔU_{stored} , because it is impossible to separate the mechanisms contributing to this term experimentally. In this chapter, experimental and theoretical evidence will be presented which, as quantitatively as possible, accounts for most of the internal energy change of peeling. In Chapter 5, peeling of a different system will be studied, for which quantitative results are readily obtainable.

The heat and work of peeling aluminum from rigid polyimide, as shown in the bottom sample in Figure 4.2, were measured using the deformation calorimeter at several peel rates. The thermodynamic data is tabulated in Table 4.2.

Table 4.2 Measurements of the work, W , and heat, Q , of peeling 100 μm aluminum films from rigid polyimide substrates in the deformation calorimeter.

Peel rate cm/min	Number of peels	W J/m ²	Q J/m ²
0.68	3	1050+/-100	-1000+/-90
2.71	5	800+/-70	-740+/-80
6.67	4	803+/-50	-830+/-90
13.4	4	900+/-90	-870+/-90

The thermodynamic data for peeling polyimide or aluminum does not show any significant rate dependence. The ratio of the highest to lowest peel rates is only 20. This small change in deformation rate would not significantly effect the viscoelastic response of a glassy, elastic polymer like polyimide unless the combination of testing rate and temperature caused the polymer to behave as if it were in the vicinity of its glass transition. It is justified to combine the thermodynamic measurements, done at different peel rates, to obtain a larger experimental population and therefore, more precise mean values for the thermodynamic quantities. The mean of the combined population was obtained by weighting the individual mean values from each peel rate by the reciprocal of the standard deviations squared as expressed in equation 3.10 and the standard deviation of the combined population is given by equation 3.11. The resulting mean work and heat values are tabulated in Table 4.3. The internal energy change and ratio of work to

heat were computed from the mean values for work and heat. The standard deviations of these quantities were computed using the propagation of errors formula

$$\sigma_{mQ}^2 = \left(\frac{\partial Q}{\partial a} \right)^2 \sigma_{ma}^2 + \left(\frac{\partial Q}{\partial b} \right)^2 \sigma_{mb}^2 + \dots \quad (4.1)$$

where Q is a quantity calculated from several measured quantities, a and b are the mean values of the measured quantities and σ_{mQ}^2 is the variance of the mean of Q , σ_{ma}^2 is the variance of the mean of a and so forth.

Table 4.3 The work, W , heat, Q , internal energy change, ΔU , and ratio of heat to work, Q/W , of peeling determined from combining measurements at all peel rates.

Peeled layer	Number of measurements	W J/m ²	Q J/m ²	ΔU J/m ²	Q/W %
Polyimide	18	625+/-9	-302+/-9	323+/-13	48+/-1.3
Aluminum	16	847+/-35	-852+/-42	-5+/-55	100+/-2.7

The peeled polymer dissipates approximately half of the work of peeling as heat. In contrast, the peeled metal dissipates all of the work of peeling as heat. These samples were cut from the same plate and their interface chemistry is identical. If the locus of separation and the surfaces exposed by peeling are the same for both types of peel experiments, the true adhesion strength of the interface should also be equal. The locus of separation was determined by x-ray photo-electron spectroscopy on the surfaces exposed in the peel test. The surfaces exposed by both types of peel experiments were also compared using scanning electron microscopy.

4.4 Surface Compositions and Locus of Failure

X-ray photoelectron spectroscopy, XPS, of the peeled side of the film and substrate surfaces exposed in the polyimide/aluminum peel tests was performed to provide information on the elemental compositions at the surfaces. From this information, the molecular composition of the failure surfaces and locus of failure can be determined. XPS has been widely applied to this type of study and has been used previously by other investigators to determine the elemental composition and interface chemistry of polyimide coatings peeled from metal and semiconductor substrates.^{1,2,3}

Surface composition at the locus of failure was obtained by XPS analysis on a Perkin Elmer PHI 5100 ESCA instrument equipped with an MgK α source. The surfaces examined included a) the top surface of the polyimide film for reference, b) the surface of a chromic acid etched aluminum sheet for reference, c) polyimide peeled from a rigid aluminum substrate, d) rigid polyimide substrate, from which aluminum had been peeled, e) aluminum peeled from a rigid polyimide substrate and f) rigid aluminum substrate, from which polyimide had been peeled. Both survey scans and high resolution spectra of the C(1s), O(1s), N(1s) and Al(2p) regions were performed. The survey spectra were scanned from 0-1000 eV and the high resolution spectra typically had scan widths of 20 eV. Various XPS spectra are shown in Figures 4.5, 4.6, and 4.7. The relative elemental compositions were computed from the peak areas using correction factors for the photo-ionization cross section. For the PHI 5100 instrument, sensitivity factors of 0.203, 0.540, 0.342 and 0.185 were used for C(1s), O(1s), N(1s) and Al(2p) respectively. The

Figure 4.5 XPS spectrum of polyimide surface exposed by peeling polyimide from aluminum.

Figure 4.6 XPS spectrum of aluminum surface exposed when polyimide was peeled from it.

Figure 4.7 XPS spectrum of aluminum substrate surface before coating with polyimide.

elemental composition data is summarized in Table 4.4. Other researchers using this technique on PMDA-ODA have estimated the relative error in the elemental compositions at less than ten percent.¹ Penetration depths are also reported in Table 4.4. These are based on the escape depths of electrons and are functions of the take off angle setting of the instrument. Take off angles of 15° and 75° were used resulting in sampling depths of approximately 15 and 40 nm (nanometers) respectively. According to the literature, the effective sampling depth, z , for electrons is given by $z = 3\lambda \sin\theta$, where θ is the take-off angle and λ is the inelastic mean free path.^{4,5} Accuracy in sampling depth is limited by the error in estimating the inelastic mean free path. Sampling depths should be considered as approximations.

Table 4.4 Atomic compositions, determined from XPS, of the surfaces exposed by peeling polyimide/aluminum in the peel test

Surface	C(1s)	O(1s)	N(1s)	Al(2p)	Sampling Depth nm
PMDA-ODA (C ₂₂ O ₅ N ₂)	75.9%	17.2%	6.9%	0.0%	
Peeled PMDA-ODA	74.3%	18.2%	7.5%	0.0%	1
PMDA-ODA substrate	73.2%	18.7%	8.0%	0.0%	1
Acid etched Al	20.9%	55.8%	0.0%	22.9%	1
Al substrate	66.2%	23.9%	6.4%	3.5%	1
AL substrate	62.9%	28.6%	4.5%	4.8%	4
Peeled Al	65.3%	24.8%	6.0%	3.9%	1
Peeled Al	62.0%	27.4%	5.6%	5.0%	4

The relative compositions of carbon, nitrogen and oxygen in PMDA-ODA polyimide, according to the structure shown in Figure 4.1, are given in the top line of Table 4.4 for reference. The compositions of the peeled polyimide and polyimide substrate surfaces are nearly identical to that of the pure polyimide and no aluminum is found on

either of these surfaces. The acid etched aluminum substrate has carbon, oxygen and aluminum, but no nitrogen. Its composition corresponds to aluminum oxide, Al_2O_3 , with carbon as a contaminant. The peeled aluminum and the aluminum substrate surfaces both contain nitrogen, in contrast to the acid etched aluminum substrate which had not been coated with polyimide. Therefore, aluminum surfaces exposed by peeling must contain polyimide. It is assumed that the aluminum surfaces exposed in the peel test are composed of polyimide and Al_2O_3 in a ratio which can be determined from the relative amounts of nitrogen and aluminum on the surfaces. The relative molecular compositions on each surface are given in Table 4.5.

Table 4.5 Molecular compositions, determined from XPS, of the surfaces exposed by peeling polyimide/aluminum in the peel test.

Surface	$\text{C}_{22}\text{O}_5\text{N}_2$	Al_2O_3	Sampling Depth nm
Peeled PMDA-ODA	100%	0%	1
PMDA-ODA substrate	100%	0%	1
Al substrate	60%	40%	1
Al substrate	47%	53%	4
Peeled Al	64%	36%	1
Peeled Al	48%	51%	4

The locus of failure and surface compositions are nearly identical for the metal and polymer exposed in both types of peel experiments. Separation occurs in the polyimide film close to the interface such that the organic layer retained on the metal may be approximated, from the sampling depths, to be on the order of 10 nm. This thin layer is suggestive of a boundary layer in the film, near the interface, with inferior strength compared to the bulk film. The same conclusion was

reached by Anderson et. al. in their XPS study of PMDA-ODA peel adhesion.¹ While the surfaces exposed by peeling may appear to be smooth, they are actually microscopically rough such that the retention of a uniform layer of polyimide on the aluminum is not realistic. The micrographs in Section 4.5 show that the surface of the peeled aluminum consists of a carpet of broken polyimide fibrils attached to the aluminum surface. Variation in the ratio of aluminum to polyimide with sampling depth may reflect the distribution of the distances that the polyimide fibrils extend normal to the aluminum surface. The projection of the polyimide fibrils, normal to the aluminum surface, is on the order of 10 nm. There is no evidence of any chemical bonding of the polyimide to the aluminum since the peak shapes of the high resolution spectra are identical for the peeled and reference materials.

4.5 Fractography of the Surfaces Exposed by Peeling

The surfaces exposed by peeling polyimide coated aluminum were examined using optical and electron microscopy. A Jeol scanning electron microscope was used to examine the surfaces which were coated with gold. No surface features, other than scratches, were visible using optical microscopy. A comprehensive fractography study was not attempted because the intent was purely to determine if there were any major differences between the surfaces exposed by peeling polyimide from rigid aluminum or aluminum from rigid polyimide. No obvious differences in the peeled surfaces were detected.

The electron micrograph in Figure 4.8 shows a section of the chromic acid etched aluminum substrate at 10,000X magnification. The visible features include the grain in the metal, surface scratches and pits. The electron micrograph in Figure 4.9 shows the top surface of the polyimide coating at a magnification of 10,000X. There are no grains or patterns and the visible features are probably dust particles contaminating the coating near the top surface. The electron micrograph in Figure 4.10 shows the peel bond boundary at a magnification of 600X. The surfaces of the aluminum, on the left, and the polyimide appear smooth and the bond boundary is straight. Striations can be observed running perpendicular to the bond boundary on both surfaces. The orientation of these striations is not fixed with respect to the peeling direction, but corresponds to the grain in the aluminum substrate. The distance between adjacent striations also matches the aluminum grain. Therefore, they probably are the grain of the aluminum. Using XPS, it was determined that a 10 nm or less layer of polyimide is on the peeled aluminum surface. Therefore, it is reasonable for the grain of the metal to be replicated on the peeled polymer surface. The electron micrograph in Figure 4.11 shows the aluminum surface peeled from polyimide at a magnification of 10,000X. The principle features are straight ribs or valleys on the surface which do not appear to be preferentially oriented in any particular direction and are probably scratches. Scratches should extend down into the substrate. From this micrograph, it is difficult to determine if these features extend upward from the surface or down into it. If they are scratches, the lighter lines appear to be edges and the dark sections in the middle are depressed into the material. Ribs on polymer fracture surfaces have

Figure 4.8 SEM micrograph of chromic acid etched aluminum substrate material at 10,000X magnification.

Figure 4.9 SEM micrograph of the top surface of a polyimide coating on aluminum at 10,000X magnification.

Figure 4.10 SEM micrograph of the polyimide/aluminum peel boundary at 600X magnification.

Figure 4.11 SEM micrograph of the aluminum surface exposed by peeling polyimide from it at 10,000X magnification.

also been identified as craze initiation sites.⁶ However, these ribs would have a pattern fixed with respect to the direction of crack propagation and are almost evenly spaced. Therefore, it is highly unlikely that the ribs seen on the surfaces exposed in the peel test are due to crazing. The electron micrographs in Figure 4.12 shows high magnification views, 50,000X, of; the aluminum surface exposed by peeling from polyimide in the vicinity of what may be a scratch and the clean aluminum which had not been coated. Very fine detail can be observed in the micrograph of the aluminum peeled from polyimide. The individual nodules, making up the texture are approximately 40 nm in diameter. For comparison, the length of the repeat unit of PMDA-ODA is 1.5 nm. The diameter of these nodules corresponds to that of broken craze fibrils remaining on the fracture surfaces of polystyrene⁶ and these nodules may be broken craze fibrils of polyimide. Alternatively, the visible surface features may be attributed to a thin layer of polyimide replicating the surface texture of the aluminum underneath, but the high resolution micrograph of the aluminum does not show these features. Therefore these features are due to the polymer. The electron micrograph in Figure 4.13 shows the polyimide surface exposed by peeling at a magnification of 10,000X. The ridge running through the micrograph probably corresponds to the replication of a surface scratch on the aluminum by the polyimide coating. Apart from the ridges, the fracture surface appears smooth and featureless. When viewed at high magnification, 30,000X, as shown in Figure 4.14, the polyimide surface exposed by peeling reveals spherical voids spaced about 500 nm apart. The diameter of the cavities is approximately 50 nm.

Figure 4.12 SEM micrographs of the aluminum surface exposed by peeling polyimide from aluminum (top) and the clean aluminum before coating with polyimide (bottom) at 50,000X magnification.

Figure 4.13 SEM micrograph of the polyimide surface by exposed by peeling from aluminum at 10,000X magnification.

Figure 4.14 SEM micrograph of the polyimide surface exposed by peeling from aluminum at 30,000X magnification.

The aluminum and polyimide surfaces are smooth and relatively featureless. In contrast, typical surfaces of glassy polymers, created by fracturing rigid notched specimens, display a remarkable variety of complex surface features.^{7,8,9} Smooth fracture surfaces are observed for polystyrene when crack growth proceeds through a single craze.¹⁰ A transition to a rough fracture surface is observed as the stress intensity factor increases. For most polymers, the stress intensity factor increases proportionally to the crack growth rate.¹⁰ The crack growth rate in peeling is extremely low, approximately 0.027 m/min, when compared to typical growth rates, 100 to 600 m/min, for single edged notched specimens or compact tension specimens. The low crack growth rate in peeling may lead to crack propagation through a single craze mechanism, thus forming a smooth fracture surface. The smooth fracture surfaces also fit with the steady continuous peeling, in which there was little fluctuation in the peel force further supporting a single craze mechanism. A multiple craze mechanism should lead to slip-stick type peel behavior and jagged fracture surfaces. The exact fracture mechanism cannot be confirmed without further experimentation. Smooth surfaces would also be expected if fracture proceeds through cleavage on a weak plane. For PMDA-ODA coatings, a combination of a large, 30-40%, volume loss during solvent evaporation and curing with good adhesion to the substrate results in an in-plane orientation of the molecules parallel to the surface on which the films are prepared.¹¹ There is evidence that the polyimide chain axes near surfaces are strongly oriented parallel to the surface.¹² Near the polyimide/aluminum interface, lack of chain axis perpendicular to the interface should create a weak boundary layer in the polyimide. Qualitatively, the XPS

and microscopy results are consistent with this conclusion. The smooth surfaces resulting from steady peeling of the polyimide/aluminum samples probably are produced by extension of a single craze through a weak boundary layer inside the polyimide film near the polyimide/aluminum interface. Kinloch and Yuen have conducted peel tests of polyimide in an electron microscope and have taken high magnification video of the propagating peel crack.¹³ In their system, the polyimide film was bonded to a metal substrate with a polymeric adhesive. The adhesion of polyimide to aluminum, for the system studied in this thesis, is purely a consequence of solidification of the polyimide on the aluminum. Despite this significant difference, their results are relevant because they also observed failure through a boundary layer in the polyimide film near the surface of the film which generated smooth fracture surfaces. Unfortunately, the mechanism of crack propagation is not clear from their photographs or those in this thesis.

4.6 Mechanical Work Consumed by Propagating the Bend During Peeling

It has now been shown that the peeled polymer dissipates approximately half of the work of peeling as heat and, in contrast, the peeled metal dissipates nearly all of the work of peeling as heat. The interface chemistry of these samples has been proven to be identical as is the locus of failure and the appearance of the fracture surfaces. If the interface and fracture planes are identical, the true adhesion strength of the interface must also be equal. The true adhesion strength should be considered to be the reversible work of creating the

fracture surfaces, the thermodynamic work of adhesion, and the irreversible work expenditure in the vicinity of the crack tip which is required to propagate the crack through the material for a given set of experimental conditions. Additional work is required in 180° peeling to propagate the bend in the peeling film. For elastic bending, the bending energy is released when the film is unloaded. When the force required to separate the bonded layers is large, the peeled film may exceed its elastic limit curvature during peeling and mechanical energy will be irreversibly consumed by plastic and viscous processes associated with propagating the bend in the peeling film. As a consequence of inelastic bending, the peeled polymer is tightly curled as seen in Figure 4.2. The peeled metal also shows visible evidence of plastic deformation, but it has a higher modulus and lower yield stress resulting in little residual curvature. The reinforced substrate does not inelastically deform. The only difference between peeling polymer from metal and metal from polymer is that inelastic deformation occurs in the bulk of the polymer film in the former and in the bulk of the metal in the latter. In both cases, separation occurs cohesively in the polyimide, so dissipation and irreversible work expenditure will occur in a thin layer in the polyimide, compared to the film thickness, near the fracture surfaces.

The bending strain in a film during peeling is equal to the distance from the center of the film divided by the bending radius assuming that plane sections through the thickness of the film remain plane upon deformation. For a film of thickness t and modulus E , the minimum radius for elastic bending, R_e is

$$R_e = Et/2\sigma_0 \quad (4.2)$$

where σ_0 is the yield stress. For a 63 μm polyimide film with a yield stress of 35 MPa and a Young's Modulus of 3 GPa, $R_e = 2.7$ mm. The actual observed radius approaches the thickness of the film, greatly exceeding its elastic limit curvature. In this case, the maximum tensile strain in the bent film is one half the thickness of the film divided by the radius of the film or 0.5 at the outside edge and the maximum compressive strain in the bent film is -0.5 at the inside edge. The stress strain behavior of PMDA-ODA films cast and cured on aluminum substrates is shown in Figure 4.15. When the stretched polyimide is unloaded, very little of the strain is recovered. The yield strain of polyimide films in tension is approximately 0.01. Thus, inelastic deformation due to bending occurs in 98% of the film volume during peeling. The fracture surfaces are smooth so that the irreversible work associated with the advance of the crack probably occurs in a layer on the order of the height of the retained polyimide fibrils on the aluminum side which is 10 nm. In contrast, irreversible work associated with propagating the bend in the peeling film, when the bending radius approaches the film thickness, will occur throughout the volume of the film. This is approximately 10,000 times greater than the volume of material in which irreversible work associated with the advance of the peel crack occurs.

Figure 4.15 The stress-strain behavior of spun cast polyimide film was determined for tensile drawing at a strain rate of 0.0167 s^{-1} .

4.7 Thermomechanics of Drawing Polyimide Films

Inelastic bending during peeling causes molecular rearrangement in the high strain regions of the polymer film similar to that which occurs when the polymer is subjected to homogeneous tensile or compressive deformation. If the polyimide film exhibited ideal plastic deformation, such as the deformation of a Newtonian fluid, all of the work expended in plastic deformation would be dissipated as heat. When most materials are deformed, they undergo physical changes, storing some of the energy consumed by plastic deformation in the deformed material. When glassy polymers like polyimide are drawn to high extensions, a significant fraction of the energy under the stress strain curve is stored in the deformed material. Table 3.1 in Section 3.6 compares the stored energy of inelastic drawing for several metallic and polymeric materials. The thermodynamic results from peeling are qualitatively consistent with those in the table. The peeled polyimide and drawn polymers store a similar fraction of the mechanical energy of deformation and the peeled and drawn metals are nearly ideally plastic.

Figure 4.16 shows the work, heat and internal energy change measured with the deformation calorimeter during uniaxial drawing of spun cast polyimide films from which the aluminum substrate was peeled. The samples were drawn in the deformation calorimeter at 25°C and a constant strain rate of 0.011s^{-1} to a maximum strain and then retracted immediately until the force on the samples was removed. The loading-unloading cycle is illustrated by the approximate stress strain curve in the inset of the figure. Each set of work, heat and internal energy change points on the graph corresponds to an individual experiment done

Figure 4.16 The work, heat and internal energy change, (ΔU), were measured during uniaxial drawing of spun cast polyimide in the calorimeter at a strain rate of 0.011 s^{-1} . The films were drawn to the maximum strain and then the force on the samples was immediately retracted. The loading-unloading path is illustrated in the inset.

with a different sample. At extensions beyond the yield strain, more than half of the energy under the stress strain curve is stored in the deformed material. At a strain of 0.34, the average ratio of heat to work is 0.4.

When heated, uniaxially drawn polyimide film will recover to its original dimensions. Measurement of dimensional recovery was performed using a thermomechanical analyzer, TMA. The TMA used was a Dupont Instruments 2000. Each end of a ribbon of film, approximately 1.5 cm long and 5 mm wide, was placed in metal clamps and suspended from one end in the TMA chamber. A quartz expansion probe was hung from the bottom of the sample with a small but constant stress, 2.5 MPa, so that it moved in accordance with changes in the sample dimensions during heating. Figure 4.17 compares the dimensional changes of as cast polyimide films, from which the aluminum substrate had been peeled to films which were drawn to 30% strain at room temperature after the aluminum substrate was removed. The as cast film exhibits normal thermal expansion when heated from room temperature to the final cure temperature of the polymer. When the temperature exceeds the final cure temperature, which is also the highest temperature that the sample has previously been exposed to, the sample shrinks. The shrinkage may be due to molecular rearrangements or the occurrence of further chemistry. Thermal degradation may also occur at these temperatures. The behavior of the drawn film is completely different. It begins to shrink upon heating as soon as it is exposed to a temperature slightly higher than the temperature at which it was drawn. By the time it has reached 325°C, it has recovered to nearly its original dimensions. The polyimide is then cooled back to 100°C and reheated to 500°C. Between

Figure 4.17 Dimensional changes occurring with temperature were measured for drawn and undrawn polyimide films held with a small constant force.

100 and 325°C, it exhibits positive thermal expansion, but above 325°C, it shrinks. A drawn glassy polymer will shrink when exposed to a temperature exceeding the highest temperature to which it has been exposed since drawing, even if below its glass transition temperature.¹⁴ Analogously, peeled polyimide which is tightly curled, as shown in Figure 4.2, will uncurl to an almost flat state when it is heated to 300°C and held there for 30 minutes.

The dimensional recovery observed upon heating a drawn polyimide film is related to the latent internal energy change measured when the polyimide was drawn in the deformation calorimeter at room temperature. Inelastic deformation of a sub T_g polymer glass or a highly crystalline polymer will produce structural changes in the material which will be frozen in due to restrictions on molecular mobility in the material. The magnitude of these changes is reflected in the latent internal energy change of deformation. Non-equilibrium polymeric glasses can easily be formed through the application of stress at temperatures where the material system exhibits hindered mobility. When the sample is heated, these frozen in deformations relax, releasing the stored energy and bringing the sample closer to thermodynamic equilibrium. This behavior is analogous to thermal annealing of non-equilibrium polymer glasses formed by rapid quenching through T_g .

4.8 Mechanisms of Deformation and Latent Internal Energy Storage

It was not the intent of this study to conduct a detailed examination of the mechanisms of deformation induced latent internal

energy storage in polymers. The primary goal is to measure the internal energy change of peeling and determine how this energy is consumed. However, it appears that peeling produces a significant mechanical deformation induced latent internal energy storage in the peeled polymer. Therefore, a thorough understanding of the peeling experiments requires some examination of the mechanisms of deformation and energy storage in polymers, particularly those mechanisms which relate to the deformation of PMDA-ODA polyimide.

Studies of non-equilibrium states created by the mechanical deformation of polymers have been pursued by other investigators. Adams and Farris measured significant internal energy changes associated with the sub T_g deformation of several amorphous and semi-crystalline polymers.^{14,15} In their work, it was found that 43-79%, depending on testing rate and temperature, of the mechanical energy of deformation remained in deformed bisphenol A polycarbonates. Figure 4.16 shows that a similar result is obtained for PMDA-ODA polyimide. Measurements of thermal shrinkage on drawn polycarbonates are also qualitatively consistent with the behavior of polyimide. The results of these thermomechanical measurements show that molecular motion in drawn polymer glasses takes place at temperatures well below the T_g . The T_g of PMDA-ODA is approximately 350°C. From Figure 4.17, it is clear that the molecules in the material possess sufficient mobility to create macroscopic length changes in the sample at temperatures 300°C below the T_g .

A number of models have been proposed to explain the deformation and relaxation behavior of glassy polymers. The molecular motion necessary for large scale yielding below T_g has been attributed to the

increase in free volume caused by the dilatational component of the stress tensor.¹⁶ This increase in free volume reduces the T_g until, at the yield point, the deformation temperature and T_g are equivalent. Another theory for the yielding and flow of polymers is proposed by Eyring.¹⁷ This theory considers yielding to be an activated rate process where there is a potential energy barrier to deformation which is reduced in the direction of an applied stress. While neither of these explanations addresses the actual mechanisms of polymer deformation, they do provide a broad framework for interpreting the results of events taking place on a molecular level.

For interpreting thermodynamic data on polymer deformation, it is convenient to classify the molecular events which take place in polymers in response to an applied stress as energy elastic, entropic elastic or pure flow processes. Energy elastic processes result in latent internal energy storage equal to the work which they consume. Isothermal entropy elastic processes result in heat flows equal to the work consumed resulting in no internal energy storage, but the entropy of the system changes. Pure flow processes irreversibly dissipate all of the energy consumed as heat and do not change the internal energy of the system.

Polymer molecules may respond to stress by distortion of covalent bond angles or by changes in covalent bond lengths. These are energetically elastic processes. Rotation about covalent bonds may also occur changing the conformation of the molecules in the chain. Through conformational changes, the end to end dimensions of the molecules may change in response to an applied stress. The extended molecules may also orient in the direction of the applied stress. Conformational changes are entropically elastic processes and do not directly

contribute to the latent internal energy change, but the molecular motions may cause changes in morphology or crystallinity which will cause changes in the intermolecular and intramolecular interactions which are energetically elastic processes. Inelastic volume dilatation during deformation is indicative of structural reorganization which results in changes in the intramolecular and intermolecular interactions within the solid.

The primary forces which act on the macromolecules to keep them frozen are the intermolecular interactions. These include some of the same secondary molecular forces which were discussed in relation to adhesion in Chapter 2, for example, hydrogen bonding, van der Waals forces and dipole-dipole interactions. These forces create secondary bonds which are weak relative to primary covalent bonds. These secondary bonds can also deform in response to an applied stress without breaking, storing energy. Additionally, physical anchorage points between the chains due to entanglements, cross-links or crystal domains may restrict motion. When sufficient stress is applied to cause yielding, the elastic energy in some of the chain segments, between anchorage points, is sufficient to cause breakage of secondary bonds, facilitating motion. These bonds reform when the stress is removed, leaving the polymer frozen in the deformed state. The process of breaking and reforming secondary bonds conserves energy because the broken and reformed bonds have identical energies, but the elastic energy in deformed chain segments is dissipated as heat if the chain segments recoil to statistically more favorable dimensions following the breakage of secondary bonds. The breakage and reformation of secondary bonds allows extensive deformation of the chain segments between

anchorage points. For systems which are not chemically crosslinked, the density of anchorage points is not so high that it prevents extensive molecular reorganization which may be accompanied by breakage and redistribution of the physical anchorage points. If this is extensive, the material may not relax to its original dimensions when heated. The above deformation mechanisms may be accompanied by pure flow, viscous, processes which would consume energy and produce heat, but would not change the thermodynamic state of the deformed solid. Related discussions of molecular mechanisms of deformation and their thermodynamic effects may be found in Section 3.6.

The above-mentioned molecular mechanisms can account for large latent internal energy changes when polymers are deformed. The distortion of primary covalent and secondary bonds are responsible for the latent internal energy changes. These mechanisms do not require viscous flow to produce thermal dissipation during the post-yielding deformation of glassy polymers. Thermal dissipation could be caused by decreasing the entropy of the solid polymer. If viscous flow were minimal, it would suit the exceptional ability of these materials to recover their original shape when heated.¹⁵ Dimensional recovery would be facilitated by the application of thermal energy to the system by increasing the entropically elastic restoring force of stretched molecular chain segments between anchorage points while providing sufficient activation energy to break some of the secondary bonds which are preventing the molecules from returning to their undeformed, thermodynamically more stable, dimensions.

Up to this point, all of the data which has been considered has involved tensile deformations, but the bending strains imposed by

peeling will subject the material to equal amounts of tensile and compressive deformation. The release of stored energy and the recovery of dimension and volume of cold compressed amorphous polymers has been studied.¹⁸ The energy release was observed by DSC showing two peaks, one corresponding to the release of energy associated with volume recovery which was completed below T_g , and the other, centered near the T_g , which is associated with shape recovery. At the molecular level, the mechanisms for volume and shape changes are the same for tension and compression. The existence of two separate relaxation peaks for volume and shape recovery, which is not the case for all deformed polymers, would support the concept of a two stage yielding process where stress induced volume dilatation, step 1, facilitates molecular reorganization in the second step. This explanation is consistent with the phenomenological description of deformation given in the preceding paragraphs because the volume dilatation can be associated with deformation of the weak, secondary bonds and molecular reorganization is the result of breakage and reformation of the deformed secondary bonds. It is interesting that volume dilatation, which is expected for tensile deformation, can also occur during inelastic compressive deformation.¹⁹ During elastic compressive deformation, the volume of amorphous and semi-crystalline polymers decreases as would be expected. After the compressive yield point is exceeded, volume dilatation occurs. For several amorphous polymers, polycarbonate and poly(vinyl chloride), the volume increases slightly from the minimum occurring at the compressive yield point. In contrast, the volume of the semi-crystalline polymers, polypropylene and polyethylene, increases enough after compressive yielding so that the overall volume change is positive at large

compressive strains. This behavior is indicative of changes in intramolecular and intermolecular interactions taking place during compression as in tension. Adams performed deformation calorimetric measurements on polyethylene (terephthalate) fibers in compression.²⁰ At a compressive strain of 10%, approximately 30% of the mechanical energy is stored as latent internal energy in the compressed polymer.

Plastic deformation in polyimides, being commercially important polymers, has been extensively studied.^{21,22} PMDA-ODA polyimide is composed of rigid monomer units 18 nm long interconnected by a flexible diphenyl ether linkage.²³ Two different but energetically equivalent structures for the polyimide repeat unit are shown in Figure 4.18. The rigid monomer units have been found to rotate freely around the ether linkage. Bond angle distortions about the imide nitrogens are also possible. However, the long rigid monomer and the limited mobility of the polymer create an unusual structure for the solid polymer. Films of the material are not crystalline but are highly ordered. The structure of PMDA-ODA in the bulk can best be described as smectic ordering where there is lateral alignment of the chain segments with the positions of the phenyl ether linkages correlated.²² For thin polyimide films, prepared on substrates, the polymer chain axes are preferentially aligned parallel to the plane of the substrate. Polyimide is tough and can be elongated 50-70% before break at room temperature. Russell et. al. have studied PMDA-ODA deformation with x-rays.²² The x-ray studies have shown that PMDA-ODA exhibits a conformational change, becoming extended in the direction of stretching and contracting parallel to it. Bundles of chains, ordered in a smectic manner orient as a unit maintaining the lateral alignment of the chain segments. If the

Figure 4.18 Two different structures of the PMDA-ODA repeat unit that are energetically equivalent.

stretching direction is parallel to the chain axis, then the projection of the monomer unit onto the chain axis can increase by bond angle distortions at the imide nitrogens, angles α and β in Figure 4.18, and at the diphenyl linkages, angle θ in Figure 4.18. Before substantial bond angle distortion can occur, PMDA-ODA chains must orient in the stretching direction. X-ray studies provide evidence of such orientation. The observed change in d-spacing, parallel to the stretching direction for elongations of 70% is 1.1 angstroms. From theoretical calculations, the energy required to distort the bond angles α and θ sufficiently to cause this change in length is 3-3.5 kcal/mol or 31.5 to 36.8 J/g.²² The total area under the stress strain curve of PMDA-ODA films at an elongation of approximately 70% is approximately 70 J/g. Upon release of the applied stress, only a small amount of dimensional recovery is observed showing that the internal deformations are frozen into the material. If bond angle distortions were the primary mode of energy storage, the energetic calculations fit the deformation calorimeter data very well. The bond distortional energy is approximately half of the total mechanical work of deformation. Bond angle distortion is an energetically elastic process so that the work consumed by it would remain in the material as stored latent internal energy. The mechanical work expended in changing the conformations of the polymer molecules would produce the majority of the measured heat. Deformation calorimetric measurements show that approximately one half of the mechanical energy input is dissipated as heat and the other half is stored as latent internal energy in the deformed material. The recovery behavior of the stretched PMDA-ODA also fits the deformation mechanism well. Substantial length recovery is observed starting 300°C

below T_g . Elastic energy in covalent bond angle and length distortion would be fully recovered when the thermal energy in the system was sufficient to break the secondary bonds freezing the system in the deformed state. The entropically stretched polymer chains would also retract to statistically more favorable dimensions. The mechanisms of deformation proposed by Russell et. al. are qualitatively and quantitatively consistent with the deformation calorimetric and thermomechanical data for PMDA-ODA films.

4.9 Discussion and Summary of Results

The combination of experimental evidence and theoretical considerations presented in this chapter is sufficient to account for most of the mechanical energy consumed during peeling of polyimide coated aluminum. In this section, the evidence and theories will be re-examined with the goal of constructing a quantitative energy balance.

The fraction of the mechanical energy expended in peeling which was dissipated as heat was directly measured in the calorimeter. When polyimide film was peeled from rigid aluminum, $48 \pm 1.3\%$ of the mechanical energy consumed by peeling was dissipated as heat. In contrast, when aluminum was peeled from rigid polyimide, $100 \pm 2.7\%$ of the mechanical energy was dissipated as heat. Separation occurs cohesively in the polyimide. When polyimide is peeled from aluminum, the aluminum does not inelastically deform and most of the thermal dissipation is caused by inelastic deformation associated with

propagating the bend in the peeling polyimide film or with advancing the crack through the polyimide layer. The mechanisms of heat production during deformation of the polyimide are viscous flow which produces entropy and the deformation induced reductions in the entropy of the polyimide which are frozen into the deformed material. When the aluminum is peeled from polyimide, energy is dissipated due to inelastic deformation caused by propagating the bend in the peeling aluminum and by advancing the crack through the polyimide. The volume of polyimide being inelastically deformed due to advancing the crack when aluminum is peeled is estimated to be 10,000 times smaller than the volume of aluminum film inelastically deformed due to bending. Therefore, the majority of energy dissipation, when aluminum is peeled, occurs in the aluminum. The mechanism of energy dissipation is plasticity which is a flow process and does not change the internal energy. When aluminum is peeled from polyimide, the internal energy of the peeled and bonded samples is identical within experimental error.

When polyimide is peeled from aluminum, 52% of the mechanical energy expended in peeling is consumed by raising the internal energy of the peeled sample. Two of the possible mechanisms for changing the internal energy of the peeled samples appear to be energetically insignificant. These are the creation of the surfaces exposed by peeling and the release of elastic energy from the stressed polyimide film.

The mechanical energy expended in creating the surfaces exposed by peeling would raise the internal energy of the peeled samples. This surface work is thermodynamically reversible and is commonly referred to as the thermodynamic work of adhesion. The locus of failure and the

appearance of the fracture surfaces was shown to be identical for both types of peel experiments so that the work of creating the surfaces exposed by peeling should be the same. The fracture surfaces were found to be smooth and consisted of polyimide. Therefore, the change in internal energy of the peel samples due to surface creation can be estimated to be approximately twice the surface free energy of PMDA-ODA polyimide. The surface free energy of kapton PMDA-ODA has been determined from liquid contact angle measurements to be 0.05 J/m^2 .²⁴ This surface work, 0.1 J/m^2 , is nearly four orders of magnitude smaller than the mechanical energy of peeling and cannot be resolved within the precision of the peeling experiments. While an insignificant amount of the mechanical work expended in peeling is consumed by surface creation, its effect on the total peel energy cannot be ignored. A discussion of the relationship between the thermodynamic work of adhesion and the peel energy may be found in Chapter 2 and this relationship is experimentally investigated in Section 5.10.

The bonded polyimide contains residual tensile stresses which disappear when it is peeled from the aluminum. The elastic energy associated with these stresses is released upon peeling reducing the internal energy of the sample. The stresses become apparent when the samples are removed from the glass plates and they curl into the polyimide side. The stress in a dry PMDA-ODA film cured under the same conditions and remaining on a fully rigid aluminum substrate is estimated from linear elasticity in Section 6.3 to be 11 MPa which would result in an energy release of approximately 2.0 J/m^2 upon peeling of a $63 \text{ }\mu\text{m}$ thick film. However, the aluminum substrate is thin such that it yields easily reducing the stress in PMDA-ODA films. The stress in the

films will also be reduced by swelling due to water absorption under ambient conditions. The estimated elastic energy is really a maximum value and it is still two orders of magnitude smaller than the peel energy. The change in internal energy due to elastic energy in the bonded PMDA-ODA film is insignificant in the overall energy balance and cannot be detected within the precision of the peel experiments.

The key to resolving the cause of the large internal energy change of peeling polyimide is the difference in the thermodynamics of peeling polymer from metal and metal from polymer. Although the mean values for the work and heat of peeling aluminum from polyimide are equal, it is statistically possible and logically probable that the internal energy of the sample increases with peeling. The internal energy could be stored as latent internal energy in the deformed aluminum or in the deformed polymer in the region where cohesive failure occurred and as the free energy of the surfaces exposed by peeling. The capacity of the aluminum to store deformation energy as latent internal energy is minimal when compared to the polymer. Regardless of the mechanism, the value of the internal energy change for peeling aluminum from polyimide is likely to be less than the precision of the measurement or 55 J/m^2 . When the polyimide is peeled, the internal energy change is $323 \pm 13 \text{ J/m}^2$. Since the chemistry of the interface, location of separation and the appearance and composition of the fracture surfaces are identical for both types of samples, the work consumed in breaking the adhesion must be the same. Therefore, no more than 55 J/m^2 can be consumed by thermodynamically reversible processes when the polymer is peeled. Thus, the energy consumed by irreversible processes, when the polymer is peeled, is nearly double the energy actually dissipated as

heat. The remainder must be stored in the peeled polymer as latent internal energy. As a consequence, the peeled polymer is tightly curled. This conclusion is supported by substantial experimental and theoretical evidence presented in this chapter. The volume of polyimide or aluminum being inelastically deformed due to propagating the bend in 180° peeling was estimated to be 4 orders of magnitude larger than that which is inelastically deformed due to propagation of the crack tip through a thin layer in the polyimide near the polyimide/aluminum interface. Most of the mechanical work expended in peeling the polyimide coated aluminum is consumed by bending. The inelastic deformation due to bending is analogous to homogeneous tensile or compressive deformation. Drawn polyimide films were found to store more than 50% of the mechanical energy of drawing as latent internal energy and drawn aluminum films store only 5%, dissipating the rest as heat. As a consequence of the stored latent internal energy, drawn polyimide exhibits remarkable dimensional recovery when heated. Analogously, the tightly curled peeled film recovers to a nearly flat state when heated. The molecular mechanisms of yielding in PMDA-ODA are a combination of entropy and energy elastic processes which are consistent with thermal dissipation, latent internal energy storage and dimensional recovery upon heating.

It is possible that a heat effect results from breaking and reforming covalent chemical bonds near the fracture plane during peeling. The thermodynamic significance of this was discussed in Section 3.6. Changes in chemical energy resulting from the breakage and reformation of primary chemical bonds are unlikely to affect the thermodynamic state of the fractured polymers except for highly

crosslinked materials. Furthermore, it is especially unlikely that significant primary bonds are broken during peeling of PMDA-ODA polyimide because the chain axes of the polymer are oriented parallel to the fracture plane so that fracture would primarily occur through the breakage of weak secondary bonds.

If most of the mechanical energy required to separate polyimide coated aluminum by peeling is consumed by inelastic bending in the bulk of the sample, there must be a way to separate the layers with less energy. In fact, spontaneous delamination driven by residual tensile stresses in the polyimide was observed for 120 μm polyimide films during post-curing cooldown while the aluminum was still attached to the glass plates. The maximum elastic energy in these films, estimated from linear elasticity in Section 6.4, is only 23 J/m^2 compared to the approximate peel energy of 500 J/m^2 for a 120 μm polyimide film estimated by extrapolation of peel energy versus film thickness data in Section 6.4. Less energy is required for spontaneous delamination because relatively little inelastic deformation takes place in the bulk of the polyimide film as compared to peeling.

If the mechanical energy expended in separating polyimide coated aluminum by peeling is almost totally consumed by propagating the bend in the peeling film, as the evidence strongly suggests, then it should be possible to predict the peel force by calculating the energy required to bend the film that is peeled. This has been done for the polyimide film using the data for the work and heat of tensile drawing as shown in Figure 4.16. The loading-unloading path shown in the inset of the figure is a good approximation to that which occurs in peeling. As a section of film traverses the bend during peeling, its elements pass

from an undeformed state in the bonded region through a region of maximum tension or compression where the radius of curvature at the neutral axis is a minimum. The tensile and compressive stresses in the film are partially unloaded when the film is straightened.

Unfortunately, the deformation rates in peeling are too high to be duplicated in tensile drawing. The bending strain rates during peeling can be approximated using equation 2.11 and are two orders of magnitude larger than those used in tensile drawing, a key weakness in this model. The thermodynamic work and heat data is fit to the following power law functions of strain using regression analysis

$$W(e) = ae^b; \quad Q(e) = ce^d; \quad (4.3)$$

where e is the strain and a , b , c and d are the fitting parameters.

These expressions give the approximate work, heat and internal energy change of stretching polyimide film at a constant rate of 0.011s^{-1} to a maximum strain and immediately retracting the sample until the force on it is zero. To calculate the work and heat of bending, the approximate functions are integrated through the half of the film, with thickness t , in tension and the result is multiplied by 2 to account for the half of the film in compression, which assumes compression and tension are equivalent. The result is normalized by the factor $2/t$ which gives the work and heat in units of J/m^2 . The equations used to calculate the work and heat are

$$W(R) = \frac{2}{t} \int_0^{\frac{t}{2}} a \left[\frac{x}{R} \right]^b dx \quad Q(R) = \frac{2}{t} \int_0^{\frac{t}{2}} c \left[\frac{x}{R} \right]^d dx \quad (4.4)$$

where x is the distance from the center of the film and R is the bending radius of the film. The bending strain in the film, as a function of position is given by x/R . The internal energy change is computed by subtracting the heat from the work. The integrals were evaluated numerically with the Mathcad computer program²⁵ for a 63 μm thick film with bending radii ranging from 1 to 2 film thicknesses and the results are plotted in Figure 4.19. For comparison, the work, heat and internal energy change of peeling a 63 μm thick polyimide film from a rigid aluminum substrate at a peel rate of 2.71 cm/min are marked as dashed lines on the figure. An attempt was made to measure the bending radius of the polyimide film near the point of detachment by inserting fine wire-gauge drill bits into the bend in the film. However, the smallest bit, a number 97 with a diameter of 150 μm , was far too large to fit into the bend. During peeling, the bending radius of the 63 μm polyimide film approaches the film thickness such that the propagating bend behaves almost like a plastic hinge. The calculated work, heat and internal energy change of bending appear to match those measured for peeling in the deformation calorimeter quite well. The calculated and measured values are reasonably close at a bending radius of 1.4 times the film thickness which appears to be reasonable based on observations of the peeling process.

The model of plastic bending during peeling which was proposed by Kim is a far more comprehensive treatment of the problem and is reviewed in Section 2.4. However, there is no convincing evidence that such a detailed analysis is more valuable for polymer peeling than the crude analysis presented here. The most significant result of this analysis is to provide further support for the hypothesis that almost all of the

Figure 4.19 Work, (W), heat, (Q), and internal energy change, (ΔU), of bending a $63\ \mu\text{m}$ thick polyimide film calculated from tensile drawing data compared to the work, heat and internal energy change of peeling the same film from a rigid aluminum substrate measured in the deformation calorimeter.

mechanical energy expended in separating polyimide coated aluminum by peeling is consumed by inelastic deformation caused by propagating the bend in the peeling film. Any attempt to use this type of analysis to compute the intrinsic adhesion strength for systems where the peel energy is nearly three orders of magnitude larger than the estimated intrinsic adhesion energy is frivolous since the uncertainty introduced by the limited precision of peel force measurements or the plasticity analysis would totally obscure numbers on the order of the intrinsic adhesion.

4.10 Conclusions

The accumulation of evidence presented in this chapter proves that almost all of the mechanical energy expended in separating polyimide coated aluminum by peeling is consumed by inelastic deformation caused by propagating the bend in the peeling film. When aluminum was peeled from rigid polyimide, all of the mechanical energy expended was dissipated as heat resulting from the limited capacity of the aluminum to store the deformation energy as latent internal energy. In contrast, only 48% of the mechanical energy expended in peeling polyimide from rigid aluminum was dissipated as heat. The separation process was studied and the only difference between peeling polyimide from an aluminum substrate or aluminum from a polyimide substrate was that inelastic deformation due to bending occurs throughout the bulk of the film which is being peeled and is minimal in the substrate. The mechanical peel energy which is not dissipated as heat when the polymer

is peeled was found to be stored as latent internal energy in the peeled polymer. An indistinguishable amount of the mechanical energy expended in peeling is consumed in creating the surfaces exposed in peeling, the thermodynamic work of adhesion, and it is therefore impossible to determine the intrinsic adhesion from peel test data for systems which exhibit strong adhesion.

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CHAPTER 5

PEELING OF FILMS BONDED WITH A PRESSURE SENSITIVE ADHESIVE

5.1 Introduction

Pressure sensitive adhesives (PSAs) are materials which, in the absence of solvent, are aggressively and permanently tacky at room temperature and strongly adhere to a variety of dissimilar surfaces with only the need for finger or hand pressure. They are used in a variety of commercial and consumer applications. The most common and familiar product made with PSAs is adhesive tapes. Thousands of different PSA tapes are available with a tremendous variety of applications, for example, medical bandages, packaging tapes, decorative tapes and labels. In all of these applications, the performance of the tape is evaluated by peel testing, with the adhesion specified by the manufacturer in units of peel force per unit width of tape.

In this chapter, the mechanical energy expended in peeling PSA tapes, the peel energy, is experimentally decomposed to identify the mechanisms which consume the peel energy. The PSA materials are soft rubbery polymers which have very little capacity to support a tensile load. Products utilizing PSAs usually consist of an adhesive coated on a backing or carrier. In this research, several different flexible backing materials were used to support the PSA, producing tapes which could be peeled. Deformation calorimetry was used to measure the mechanical energy consumed by peeling and the resulting heat flux. For polyester backing material, which has a demonstrated capacity to store

deformation energy as latent internal energy, most, but not all, of the peel energy was dissipated as heat. When PSA backed with a perfectly elastic material was peeled, all of the peel energy was dissipated as heat, proving that no latent internal energy is stored in the peeled PSA material and suggesting that the internal energy change of peeling PSA backed with polyester film was stored as latent internal energy in the polyester backing. In Chapter 4, ample evidence was presented to prove that the internal energy change of peeling was stored in the peeled materials, but direct measurement of latent internal energy in the peeled materials was not attempted. In this chapter, direct measurements of the stored latent internal energy in the peeled polyester is accomplished using solution calorimetry. A complimentary study of tensile drawing of polyester films was also performed and the stored latent internal energy in the drawn films was measured by three independent experimental techniques; deformation calorimetry, solution calorimetry and differential scanning calorimetry. The mechanics of the peeling process was also investigated using optical and scanning electron microscopy.

5.2 Pressure Sensitive Adhesives

PSA formulations consist of an elastomer base and various modifiers added to impart good adhesive properties to the mixture. The most commonly used elastomers are natural or synthetic rubbers and block copolymer thermoplastic elastomers. One of the most prevalent block copolymer elastomers used in PSAs is the A-B-A triblock where A is

polystyrene and B is either polyisoprene or polybutadiene. These polymers are trademarked "Kraton" by the Shell Chemical Company, the only domestic producer, and have an overall molecular weight of about 100,000 of which 15-30% by weight is polystyrene.¹ Upon solidification from solvent or the melt, these triblock copolymers develop a domain structure where the high T_g polystyrene endblocks aggregate into domains which function as thermoreversible crosslinks for the lower T_g midblocks. The phase separated solid, in which the low T_g material is the continuous phase, behaves like a crosslinked rubber. The structure and morphology of a styrene-butadiene triblock copolymer is shown in Figure 5.1. For adhesive applications, the midblock fraction of the chains must possess sufficient mobility at the application temperature to permit quick and thorough wetting of the substrate surface. Therefore, most PSAs have a low T_g , -10 to -70°C, component.

The primary function of the modifiers is to increase tack which is defined by ASTM as "the property of a material which enables it to form a bond of measurable strength immediately on contact with another surface."² These modifiers are commonly referred to as tackifier resins and were originally produced from wood rosins. Wood turpentine is a major source of tackifiers. Cationic polymerization of dipentene and α - and β -pinene, the major constituents of turpentine, yields the terpene tackifiers shown in Figure 5.2.³ Tackifiers are all low molecular weight materials, ranging from about 300 to 3000. Some are liquids, but most are brittle solids. For the most effective generation of tack, the tackifier should be close in solubility parameter to the elastomer with which it is blended. For block copolymers, tackifiers are often used which selectively associate with different blocks of the polymer.

Figure 5.1 Morphology of polystyrene-polyisoprene-polystyrene triblock copolymer with phase separated structure.

Figure 5.2 Polyterpene tackifiers.

Terpenes are generally used as midblock tackifiers and α -methylstyrene polymers or coumarone-indene resins are typically used to modify the endblocks.³ Triblock copolymer-tackifying resin interactions were recently studied by Tse⁴ who concluded that: the function of midblock tackifiers is to increase the entanglement molecular weight, thereby reducing the number of trapped entanglements in the rubbery phase, resulting in drastic reductions in the plateau modulus of the rubbery phase. The lower plateau modulus helps establish intimate molecular contact with microscopically rough substrate surfaces. The T_g of the midblock is increased by addition of the resin, in contrast to the effect of regular plasticizers which would decrease both the modulus and the T_g of the polymer due to an increase in free volume associated with the introduction of the chain ends of the small molecules. An additional effect of the resin is to restrict segmental motion of the chains in the midblock resulting in an increase in the viscoelastic loss parameter with increased resin content. This results in increased adhesion energy by increasing the dissipation when the adhesive is removed from its substrate. The endblock modifiers are of high T_g and function to reinforce and stiffen the endblocks. The characteristics of a good PSA are low plateau modulus, high energy dissipation at debonding deformation rates and endblocks which maintain their integrity during deformation so that the material doesn't disintegrate.

5.3 Preparation of Peel Test Samples

All of the peel test samples used in this study were prepared by spin coating a layer of PSA onto substrates using a Headway EC101 photoresist spinner. The pressure sensitive adhesive (Scotch-Grip 4910-NF)⁵ is supplied as a thin syrupy liquid of approximately 300 cps viscosity, consisting of a styrene-isoprene block copolymer and an α -pinene tack agent in 1,1,1-trichloroethane solvent. After coating, the substrates were placed in a 70°C vacuum oven, and dried for 2 hours. For 1200 rpm spin speeds, a dry film of PSA, approximately 25 μ m thick, remained on the substrates after the solvent had been evaporated. Flexible films of differing thicknesses were then bonded to the adhesive coated side of the substrate. The assembly was placed in a press and subjected to a pressure of 15,000 psi for 1 minute at room temperature. Peel test samples were prepared by cutting strips from the bonded sheets and rigid steel wires were bound to the back of the substrate side, prohibiting it from bending while the film was peeled from it. The samples are similar to those shown in Figure 4.2.

The materials bonded with the PSA were; tempered steel tapes bonded to themselves, Mylar⁶ poly(ethylene terephthalate), PET, films of differing thicknesses bonded to aluminum substrates and various polymer films bonded to PET. All materials were solvent wiped with acetone and dried prior to application of the adhesive and bonding. A schematic of several types of peel test samples made with the PSA is shown in Figure 5.3.

Figure 5.3 Peel test samples made by bonding a flexible film to a reinforced substrate coated with a pressure sensitive adhesive.

5.4 Peel Tests in the Deformation Calorimeter

The collection and analysis of the deformation calorimetric data for peeling materials bonded with the PSA was done in a manner consistent with that described in Chapter 4. The form of the force, differential pressure, work and heat responses is almost identical to those obtained when polyimide is peeled from aluminum except that all of the materials bonded with the PSA dissipated a larger fraction of the mechanical work of peeling as heat and the magnitude of the work and heat is approximately twice that of peeling polyimide coated aluminum.

The heat and work of peeling PET films, ranging in thickness from 34-180 μm , from rigid aluminum substrates was measured in the deformation calorimeter. All films were peeled at a constant rate of 2.71 cm/min. After peeling through a distance of 2-4 cm, the peeled film was completely unloaded releasing any elastic energy in the peeled film and negating the thermal effect of thermal expansion. All of the peeled films were tightly curled into a coil, like the peeled polyimide shown in Figure 4.2, which increased in radius with the film thickness. The 34 μm films formed a coil with a radius of approximately 1.5 mm and the 180 μm films formed a coil with a radius of approximately 6 mm. This shows that the PET backing was inelastically bent during peeling. The thermodynamic data is summarized in Table 5.1 and the work, heat and internal energy change of peeling are plotted versus the film thickness in Figure 5.4. 81-86% of the mechanical work expended in peeling is dissipated as heat. The difference between the work and heat, the internal energy change, ΔU , of peeling, is presumed to have raised the energy of the peeled specimen.

Figure 5.4 The work, heat and internal energy change, ΔU , of peeling pressure sensitive adhesive backed with poly(ethylene terephthalate) films at a peel rate of 2.71 cm/min is plotted versus the backing film thickness.

Table 5.1 Measurements of the work, W , heat, Q , internal energy change, ΔU , and ratio of heat to work, Q/W , of peeling PSA backed with PET films of varying thicknesses from rigid aluminum substrates in the deformation calorimeter at a peel rate of 2.71 cm/min.

Film μm	Number of runs	$W \text{ J/m}^2$	$Q \text{ J/m}^2$	$\Delta U \text{ J/m}^2$	$Q/W \%$
34	4	1890+/-210	-1560+/-180	330+/-275	83+/-1.4
45	8	1950+/-140	-1600+/-160	350+/-210	82+/-1.1
72	4	2090+/-110	-1700+/-290	390+/-310	81+/-1.6
120	4	2530+/-350	-2100+/-390	430+/-520	83+/-2.1
180	4	2550+/-340	-2200+/-380	350+/-510	86+/-2.0

The standard deviations of the mean work and heat values are typically 10-20% of the mean. The variability is similar to that observed for the polyimide coated aluminum system in Chapter 4. The principle source of the variability appears to be random errors in the peeling experiments, not systematic errors introduced by the measuring technique. Unfortunately, the variability in the work and heat values, both large numbers compared to ΔU which is derived from their difference, results in extremely poor precision in the mean values for the internal energy change. While the values of the work and heat vary considerably from one peel experiment to another, the ratio of the heat to work appears to be reasonably constant. Therefore the Q/W values are the most precise measurements given in table 5.1. Using the best and worst cases as examples, the precision of the ΔU values for the 180 μm and 45 μm films might lead to the erroneous conclusion that ΔU of peeling could be negative. For the 180 μm film, the worst case, the 95% confidence interval for the mean, μ , is $-250 < \mu < 950$, and the 95% confidence interval for the mean ratio of heat to work is $83.8 < \mu < 88.3$. For the best case, the 45 μm film, the 95% confidence

interval for the mean, μ , is $-40 < \mu < 460$, and the 95% confidence interval for the mean ratio of heat to work is $80.7 < \mu < 83.3$. The most accurate statements that can be made with regard to the data in Table 5.1 is that the ratio of heat to work in all of the peeling experiments falls between 79% and 88% within a 95% confidence interval. While precise values were not obtained, the internal energy change of peeling can be expressed with accuracy as a percentage of the mechanical work of peeling.

The peel rate dependence of the thermodynamic quantities was investigated by peeling PSA backed with 45 μm PET film from rigid aluminum substrates at peel rates ranging from 0.271-13.4 cm/min. The thermodynamic quantities are tabulated in Table 5.2 and plotted in Figure 5.5. The work and heat show a significant increase with

Table 5.2 Measurements of the work, W , heat, Q , internal energy change, ΔU , and ratio of heat to work, Q/W , of peeling PSA backed with 45 μm PET films from rigid aluminum substrates at various peel rates in the deformation calorimeter.

Rate cm/min	Number of runs	$W \text{ J/m}^2$	$Q \text{ J/m}^2$	$\Delta U \text{ J/m}^2$	$Q/W \%$
0.271	4	1370+/-180	-950+/-160	420+/-240	69+/-1.8
0.68	4	1580+/-210	-1150+/-190	430+/-280	73+/-1.8
1.35	4	1840+/-250	-1430+/-310	410+/-400	78+/-4.4
2.71	8	1950+/-140	-1600+/-160	350+/-210	82+/-1.1
6.67	4	2240+/-260	-1650+/-280	590+/-380	74+/-1.8
13.4	4	2440+/-180	-1990+/-220	450+/-280	82+/-1.2

peel rate, but their difference, the internal energy change, remains approximately constant. In contrast, the peel rate did not have as significant an impact on the thermodynamic quantities measured for polyimide coated aluminum. A large part of the peel energy for the PSA tapes is consumed by viscous dissipation in the pressure sensitive

Figure 5.5 The work, heat and internal energy change, ΔU , of peeling pressure sensitive adhesive backed with 45 μm thick poly(ethylene terephthalate) films is plotted versus the peel rate.

adhesive. A soft rubbery polymer, like the pressure sensitive adhesive, is incapable of storing deformation energy and should dissipate all of the mechanical work of deformation as heat. When the PSA is deformed, extensive molecular motion occurs in the midblock segments. Since the midblock material is well above T_g , the material should relax to an equilibrium state following deformation. To verify this, calorimeter peel samples were fabricated using 75 μm thick tempered steel tapes bonded with the PSA. The tempered steel will only deform elastically during peeling. Therefore, it will not store any of the mechanical energy. The thermodynamic data for peeling tempered steel bonded to itself with PSA at a peel rate of 2.71 cm/min is tabulated in Table 5.3. The ratio of heat to work is 100% when the PSA is peeled with the steel backing and all of the peel energy is dissipated as heat proving that the PSA cannot store any deformation energy. Therefore, all mechanical work expended in deforming the PSA will be dissipated as heat.

Table 5.3 Measurements of the work, W , heat, Q , internal energy change, ΔU , and ratio of heat to work, Q/W , of peeling PSA with tempered steel backing in the deformation calorimeter.

Number of runs	$W \text{ J/m}^2$	$Q \text{ J/m}^2$	$\Delta U \text{ J/m}^2$	$Q/W \%$
3	530+/-49	-540+/-53	-10+/-72	100+/-1.3

The ratio of heat to work increases with the peeling rate for the thermodynamic data presented in Table 5.2 while ΔU of peeling remains approximately constant. Therefore, the additional work required for peeling at higher rates is the result of increased thermal dissipation. It is probable that the mechanism of the increased dissipation is

viscous flow in the deforming PSA. Since the PSA can't store deformation energy, all additional energy consumed in deforming it at higher peel rates is dissipated as heat resulting in no change in internal energy. If changes in the deformation rate dependent thermodynamic response of the backing material were a significant contribution to the rate dependent nature of the peel energy, a constant value of ΔU would not necessarily be expected because changes in the amount of energy expended in deforming the backing should result in changes in both the energy dissipated and stored by it resulting in changes in the ΔU of peeling. The amount of energy consumed by deforming the backing and the latent internal energy stored in it probably does change with peel rate, but the changes are insignificant compared to changes in the energy expended in deforming the PSA.

5.5 Solution Calorimetry

The PET film backing was flat before it was bonded to the aluminum with the PSA. The severe residual curvature of the peeled PET films is evidence that they were inelastically deformed to propagate the bend during peeling. Therefore, some fraction of the mechanical energy consumed in peeling PSA is consumed by deforming the backing. A combination of high crystallinity in commercial PET films and amorphous regions with a T_g of 80°C results in hindered molecular mobility in this polymer at room temperature. It is likely that the deformed polymer will contain frozen in deformations leaving it in a non-equilibrium high energy state. Some fraction of the mechanical peel energy, not

dissipated as heat, is stored as latent internal energy in the peeled PET. Direct quantitative measurements of the latent internal energy in stored polymers can be made by solution calorimetry. The heat of solution is a direct measure of the difference between the enthalpy of the solid polymer and its enthalpy in solution. Poly(ethylene terephthalate) is readily dissolved in a solution of phenol in tetrachloroethane making it suitable for solution calorimetry, unlike PMDA-ODA polyimide which is virtually insoluble. In dilute solutions, polymer molecules are able to move freely and quickly come to an equilibrium state which does not depend on their prior deformation or thermal history. Therefore, variations in the heat of solution between polymers of the same chemical structure and molecular weight distribution are equivalent to enthalpy differences of the solid polymers.

PET films were deformed prior to dissolution by bending during peeling from aluminum or by tensile drawing. The deformed PET films, were placed in the reference cell of a Setaram C.80 double cell Calvet type solution calorimeter, manufactured by Setaram of Lyon, France. Undeformed PET films were placed in the sample cell of the calorimeter. Before placing the peeled samples in the calorimeter, both the peeled and undeformed samples were placed in methylene chloride to remove residual traces of the PSA from the peeled polymer. The undeformed polymer was placed in solvent to insure that the relative heats of solution of the deformed and undeformed polymer were not effected by the solvent. The films were then dried under vacuum at room temperature for one week before being placed in the calorimeter cells. The length of peeled film placed in the reference cell was approximately 7, 19 and

25 cm for the peeled 120, 45 and 34 μm films respectively. The tensile drawn samples were cut from the neck regions of dogbone shaped specimens. They were not washed with solvent and four necked regions were placed in the reference cell for each run. The sample and reference cells are identical, each consisting of two concentric stainless steel cylinders, permanently sealed off at one end, having a total length of approximately 8 cm and a diameter of approximately 1.5 cm. 60 mg of polymer was placed into the inner cylinder of each sample cell and 2.94 g of solvent, a solution of 40% phenol in tetrachloroethane, was placed into the annular region between the inner and outer cylinders. When dissolved, the polymer and solvent in the sample and reference cells will form a 2% solution. A threaded cap with an o-ring seal covers the cells which are kept upright to keep the solvent from mixing with the polymer. The cells are then installed in the calorimeter in an upright position. A typical output for a test is shown in Figure 5.6 where the differential heat flux between the sample and reference cells is plotted versus time for PET film drawn to 50% strain in the reference cell and undeformed PET film in the sample cell. Initially, a few minutes of baseline data is taken to establish a reference point for peak integration. Then, the instrument begins to rotate, causing mixing of the polymer and solvent in the sample and reference cells. As the samples dissolve, a peak forms indicating a differential heat flux between the sample and reference cells. The samples appear to dissolve completely in approximately 30 minutes. After dissolution, data is taken to reestablish the baseline. The thermal peak is then integrated from the baseline which can be seen as a line across the top of the peak in the figure. Figure 5.7 shows the

Figure 5.6 Thermal scan of the differential heat flux for dissolving deformed and undeformed poly(ethylene terephthalate) films in a solution calorimeter.

Figure 5.7 Baseline thermal scan from the solution calorimeter.

baseline response of the instrument, representing the voltage detected by the system at equilibrium, obtained immediately following dissolution of the PET. The instrument baseline is subtracted from the peak area measured during the dissolution run to give the final value the differential heat of solution, ΔH , which is the difference between the heat of solution of the material in the sample cell, ΔH_1 , and the reference cell ΔH_2 . For this polymer solvent combination, the heat of solution is exothermic. In all 17 runs, the heat of solution of the deformed polymer in the reference cell was greater than that of the undeformed polymer in the sample cell, convincingly showing that deformation energy is stored as latent internal energy in the deformed PET and that it can be detected using this technique. Table 5.4 shows the differences in the heats of solution of the deformed and undeformed polymers. A positive value for the differential heat of solution, ΔH , means that the deformed sample had a higher heat of solution than the undeformed sample. ΔH increases as the film thickness decreases for the peeled films and increases with increasing strain for the drawn samples. These trends in ΔH would be expected because the mechanical work of peeling increases as the film thickness decreases when expressed on a per unit mass of peeled film basis and the amount of mechanical work expended per unit mass in drawing increases with the strain.

The stored energy in the deformed PET films is small on a J/g basis and is difficult to measure accurately. The accuracy of the instrument, approximately 0.7 J/g, becomes a significant contributing factor to the appreciable standard deviations. The ΔH values from solution calorimetry of the peeled films are compared to the internal

Table 5.4 Differences in the heat of solution of deformed and undeformed PET films dissolved in a solution of phenol and tetrachloroethane measured by solution calorimetry

Deformed PET film	Number of runs	ΔH J/g
Peeled 34 μm	3	6.6 $\pm$ 1.2
Peeled 45 μm	3	3.3 $\pm$ 1.0
Peeled 120 μm	2	0.5 $\pm$ 0.28
Drawn to strain 0.15	3	2.0 $\pm$ 1.4
Drawn to strain 0.3	3	5.6 $\pm$ 1.2
Drawn to strain 0.5	3	8.3 $\pm$ 0.75

energy changes of peeling measured with the deformation calorimeter in Figure 5.8. To facilitate comparison, the units of the deformation calorimeter data were converted from J/m^2 to J/g of film by dividing by the density times the film thickness. The density of PET is 1.4 g/cm^3 . The conversion factors are tabulated in Table 5.5 for several PET backing thicknesses and the mean internal energy changes of peeling measured in the deformation calorimeter are also listed in the table converted to units of J/g .

Table 5.5 Conversion factors to convert J/m^2 to J/g of PET film and internal energy changes of peeling measured in the deformation calorimeter, ΔU (peeling), converted to units of J/g .

PET film thickness μm	Multiply J/m^2 by	ΔU (peeling) J/g
34	0.0204	6.7
45	0.0159	5.6
72	0.00992	3.9
120	0.00595	2.5
180	0.00397	1.4

With the exception of the 34 μm film, the ΔH values from solution calorimetry are lower than the internal energy changes of peeling measured with deformation calorimetry. The uncertainties in the measured quantities are large enough such that the values for a given film thickness lie within experimental error of one another, but this

Figure 5.8 The internal energy change, ΔU , of peeling pressure sensitive adhesive backed with poly(ethylene terephthalate), PET, films of varying thickness from aluminum measured in the deformation calorimeter and the stored energy in the peeled PET films measured by solution calorimetry are plotted versus the PET film thickness.

certainly doesn't prove that the entire internal energy change of peeling is stored as latent internal energy in the peeled polymer. The results do unequivocally prove that peeled PET contains stored latent internal energy due to peeling induced deformation. The magnitude of the stored latent internal energy is strongly dependent on the film thickness, increasing as the film thickness decreases in agreement with the trend for the internal energy change of peeling measured with the deformation calorimeter.

An argument similar to that used for the polyimide coated aluminum system in Chapter 4 can be used to justify the internal energy change of peeling PET backed PSA. Peeling tempered steel can be compared to peeling PET just as peeling aluminum from polyimide was compared to peeling polyimide from aluminum. For both the PET and steel backing materials, failure occurs at the interface of one or both of the bonded layers and the PSA. In contrast to the polyimide/aluminum system, the bonded materials are different resulting in different thermodynamic works of adhesion for the PET peeled from aluminum and the tempered steel peeled from tempered steel. The thermodynamic work of adhesion must be a very small percentage of the total mechanical work of peeling when the tempered steel is peeled. Assuming that it remains a small contribution when the PET is peeled from aluminum, the logic of Chapter 4 applies and it can be concluded that most of the work not dissipated as heat when the PET is peeled is stored in the peeled PET backing.

Up to this point, the fractions of the mechanical energy which are dissipated as heat and stored in the backing materials have been determined. The peel energy could be further partitioned into energy

consumed in deforming the backing and the PSA layer if the percentage of the energy used to deform the backing which remains in the backing resulting in the internal energy change of peeling were known. The fraction of the mechanical energy consumed by tensile drawing of PET films which remains in the films can be determined using the deformation calorimeter and this result can be used to speculate for peeling. Additionally, the internal energy change of tensile drawing can be compared to the solution calorimeter data for the same process.

5.6 Deformation of Poly(ethylene terephthalate) Films During Peeling

Bending deformation in the PET backing during peeling subjects the film to equal amounts of compressive and tensile deformation. The relationship between bending radius and bending strain in the film was discussed in Chapter 4. The molecular mechanisms responsible for storage of deformation energy as latent internal energy for uniaxial extension or compression of PET should be identical to those responsible for the storage of energy in the films during peeling.

The effect of the PET backing thickness on the peel force and the resulting minimum radius of bending were measured for 180° peeling of PSA backed with PET from rigid aluminum substrates in an Instron tensile testing machine. All peel experiments were done at a constant rate of 2.5 cm/min. The range of film thicknesses studied exceeds that which was possible in the deformation calorimeter. PET films thicker than 180 μm could not be used in the deformation calorimeter because of their large thermal mass. The peel energy and minimum bending radius are

plotted versus the backing thickness in Figure 5.9. During 180° peeling a sharp bend is propagated through the film. As a section of adhesive strip traverses the bend, it passes from an undeformed state in the bonded region through a region of maximum bending deformation where the radius of curvature at the neutral axis is at a minimum. The approximate bending radius was measured by inserting drill bits into the propagating bend in the film. The thinnest films, 22 and 34 μm had bending radii too small to measure and appeared to behave like plastic hinges with the bending radius approaching the film thickness. For the other films, several different bits were tried during peeling until one which consistently slid in and out of the bend with minimal friction was found. For the thinner films, the actual minimum bending radius is believed to be smaller than that measured using this technique because the shape of the bend need not be symmetric. In fact, the peeling film often appears to come off of the substrate with a base angle approaching 90°. Thicker films appeared to exhibit symmetrical bending.

As the film thickness increases, the peel force increases to a maximum followed by a decline. The apparent bending radius increases proportionally to the film thickness. Theory predicts that the bending rigidity of the film increases with the cube of the thickness. The greater rigidity of the thicker films leads to a larger bending radius and less inelastic deformation in the film during peeling. This is opposed by an increase in the volume of film being inelastically deformed resulting in the initial increase in peel energy with film thickness. Changing the film thickness should only change the energy expended in deforming the PET backing. Paradoxically, the peel energy of the thickest films is probably lower than that expended in deforming

Figure 5.9 Mechanical peel energy and minimum bending radius of the peeled film are plotted versus the backing film thickness for peeling pressure sensitive adhesive backed with poly(ethylene terephthalate) films from rigid aluminum substrates.

the PSA when thin films are peeled. Possibly deformation of the PSA is influenced by the bending radius of the backing.

The stress strain behavior of the PET films is illustrated in Figure 5.10. Dogbone shaped tensile specimens conforming to ASTM D638 were cut from 180 μm thick films, placed in the jaws of an Instron tensile tester, drawn to approximately 60% strain at 0.0167 s^{-1} and immediately retracted until the force on the sample reached zero. Mylar PET samples were supplied by Dupont as rectangular 8.5" X 11" plaques. The adhesive backing films and dogbone samples were always cut in a direction parallel to the long edge of the plaques. The yield stress and strain of the PET film at 0.0167 s^{-1} are approximately 70 MPa and 2%. Less than 10% of the strain is recovered upon unloading indicating that the material is plastic. The bending strain rate during peeling of a 45 μm film at 2.71 cm/min, estimated from equation 2.11, is 600 s^{-1} . The data of Gent and Hamed can be used to estimate the yield stress and strain of Mylar at 600 s^{-1} .⁷ The estimated yield stress and strain are 136 MPa and 3%. Presumably the deformation recovered upon loading is also rate dependent. The stress-strain behavior observed in tensile tests is not that different from the behavior at rates associated with peeling. During peeling of thin films, the PET film will be subject to inelastic tensile and compressive deformation throughout most of the film thickness and should therefore retain residual curvature upon unloading.

Figure 5.10 Stress-strain behavior of poly(ethylene terephthalate) films determined for tensile drawing at 25°C and a strain rate of 0.0167 sec⁻¹.

5.7 Thermodynamics of Poly(ethylene terephthalate) Deformation

When heated, uniaxially drawn PET film will shrink. Measurement of dimensional changes was performed using a thermomechanical analyzer. The experimental method is identical to that used for drawn polyimide as described in Chapter 4 except for the temperature profiles. Figure 5.11 compares the dimensional changes of as received PET films to films which were drawn to 30% strain at room temperature. The as received film exhibits normal thermal expansion when heated from room temperature to approximately 100°C where it begins to shrink. PET films are biaxially stretched during manufacturing. After stretching, they are heat set, exposed to high temperature while held at constant dimensions, at a temperature above the T_g (80°C) of the amorphous regions to impart dimensional stability to the films. Since the as received film is already in a stretched state, it will shrink when exposed to a temperature exceeding the heat set temperature. The behavior of the drawn film is completely different. It begins to shrink upon heating at temperatures below T_g . The total dimensional change is 2.5 times greater than that of the as received film. Analogously, peeled PET film which is tightly curled will uncurl to an almost flat state when heated to 150°C and held there for 30 minutes.

The dimensional recovery observed upon heating a drawn PET film is indicative of latent internal energy storage in the deformed film. The stress-strain curve shows that very little of the inelastic tensile deformation is recovered upon unloading. The lack of dimensional recovery could be explained by either of two types of mechanisms. The first type are the frozen in deformations which include energy elastic

Figure 5.11 Thermal shrinkage versus temperature for poly(ethylene terephthalate) films.

deformations resulting in latent internal energy storage in the deformed material and entropically elastic deformations changing the entropy of the deformed material. The second type of mechanism which would result in a lack of strain recovery upon unloading is pure viscous flow which would result in a deformed material identical in its thermodynamic state to the undeformed material. If the latter mechanism predominated, dimensional recovery upon heating would not occur. The fact that PET films deformed under ambient conditions exhibit dimensional recovery upon heating, proves that they must be in a non-equilibrium thermodynamic state. Inelastic deformation of PET, a highly crystalline polymer with glassy amorphous regions at the deformation temperature, should produce structural changes in the material which are frozen in due to restrictions on molecular mobility in the material. Non-equilibrium polymeric glasses can easily be formed through the application of stress at temperatures where the material system exhibits hindered mobility. When the sample is heated, these frozen in deformations relax, bringing the sample closer to thermodynamic equilibrium. The magnitude of the frozen in energy elastic structural changes should be reflected by the stored latent internal energy of drawing which can be measured in the deformation calorimeter. Differentiating between thermal dissipation due to entropically elastic processes and that due to pure dissipation, flow, processes is impossible with the deformation calorimeter alone.

Figure 5.12 shows the work, heat and internal energy change measured with the deformation calorimeter during uniaxial drawing of PET films at 25°C. The samples were drawn in the deformation calorimeter at a constant strain rate of 0.011 s^{-1} to a maximum strain and then

Figure 5.12 The work, heat and internal energy change, ΔU , of drawing poly(ethylene terephthalate) films at 25°C and a strain rate of 0.011s⁻¹ is plotted versus maximum strain. Stored latent internal energy in the deformed films measured by solution calorimetry is also plotted on the figure. The approximate stress strain curve is shown in the schematic in the inset.

retracted immediately until the force on the samples was removed. The loading-unloading cycle is illustrated by the approximate stress strain curve in the inset of the figure. Each set of work, heat and internal energy change points on the graph corresponds to an individual experiment done with a different sample. At extensions beyond the yield strain, a significant fraction of the energy under the stress strain curve is stored in the deformed material. The ratio of heat to work is increasing with strain for inelastic drawing. At strains of 0.23-0.35 and 0.44-0.5, the average ratios of heat to work are 0.50 and 0.72 respectively.

Adams used a deformation calorimeter to measure the stored energy of hollow PET fibers in compression finding that approximately 30% of the mechanical work of deformation was stored in the compressed PET at a compressive strain of 10%.⁸ This result appears to be consistent with that measured for tension. If the ratio of heat to work in homogeneous tensile and compressive deformation is similar, it would be reasonable to assume that the same ratio applies to bending deformation during peeling which is an equal combination of tension and compression. Since the percentage of the peel energy stored in the peeled films is known, the ratio of heat to work could be used to predict the total mechanical work expended in deforming the film during peeling. This prediction would only be an approximation because of the rate and strain dependence of the heat to work ratio.

The stored latent internal energy in drawn PET, determined by solution calorimetry, was listed in Table 5.4 and is plotted on Figure 5.12 as filled triangles to facilitate comparison between the data. At 15 and 30% strain, the stored latent internal energy in the

drawn films measured with deformation and solution calorimetry are equivalent. At 50% strain, the solution calorimeter measurement is slightly lower than that from the deformation calorimeter.

5.8 Differential Scanning Calorimetry of Deformed Poly(ethylene terephthalate) Films

The approach of the internal energy and the enthalpy, equivalent when no pressure-volume work is done, to their equilibrium values can be followed with Differential scanning calorimetry, DSC. DSC has been used extensively to investigate relaxation and recovery processes of polymers in their quenched non-equilibrium states.^{9,10} DSC has been used to a more limited extent to investigate relaxation phenomenon in non-equilibrium states created by mechanical deformation.^{8,11,12,13} Both exothermic and endothermic peaks have been observed which were attributed to the relaxation of frozen in deformation in the materials. Enthalpy relaxation of quenched glasses usually results in endothermic peaks. DSC is an excellent method of observing relaxation in deformed polymers, but caution must be exercised in the measurement of enthalpy changes by DSC because the magnitude of the enthalpy change depends on the heating rate.

In this study, DSC was used to investigate differences in the thermodynamic states of drawn and undrawn PET film. Small pieces were cut from PET films and 8-10 mg of sample was accurately weighed into an aluminum sample pan. The measurements were made in a nitrogen atmosphere to prevent reaction with atmospheric oxygen. The thermograms

were all run on a Dupont 2000 thermal analyzer using the DSC cell. The temperature scale of the instrument was calibrated with the melting transitions of gallium and indium and the energy input was checked with the melting transition of indium. Baseline scans were done before experiments were run and the instrument was not used if the baseline was bad. A heating rate of $20^{\circ}\text{C}/\text{min}$ was used for all scans.

Figure 5.13 compares thermal scans of undeformed PET and PET drawn to 50% strain at 25°C and a strain rate of 0.0167 s^{-1} . The drawn polymer exhibits a heat capacity exotherm, centered near T_g . The T_g determined from the DSC scans is 79.2°C . The exotherm does not appear in the scan of the undrawn material. If the deformed polymer is heated to 150°C and cooled, the exotherm disappears on subsequent heating scans. DSC thermal scans were done for PET films stretched to various maximum strains and immediately unloaded as in the deformation calorimeter and solution calorimeter experiments. The thermal data is summarized in Table 5.6 and the region of the scans where the exotherm appears are plotted for comparison in Figure 5.14.

Table 5.6 Results from DSC thermal scans of PET films drawn to various strains at room temperature. Exotherm refers to the integrated area in the peak centered around the T_g , slope to the slope of the trace below T_g and melting to the area of the melting peak.
Center refers to the melting peaks.

Strain	Exotherm J/g	Slope mW/ $^{\circ}\text{C}$	Melting J/g	Center $^{\circ}\text{C}$
0.0	0.0	0.09	44.5	258
0.2	2.8	0.10	37.6	259
0.3	4.5	0.11	37.9	259
0.4	6.5	0.07	42.4	258
0.5	5.1	0.09	37.9	257
0.55	8.8	0.12	38.7	258

Figure 5.13 DSC thermal scans of undeformed and drawn poly(ethylene terephthalate) films.

Figure 5.14 DSC thermal scans of poly(ethylene terephthalate) films drawn to various strains.

The area of the low temperature exotherms is strongly dependent upon the strain in the film. The slope of the thermal trace after T_g and the enthalpy of the crystal melting peak do not depend upon the deformation history of the sample implying that whatever changes have been imparted to the material by deformation have been erased during the evolution of the exothermic peak. The shape of the crystal melting peaks in Figure 5.13 is different for the drawn and undrawn polymers. The melting peak contains a secondary melting peak centered a few degrees below the main melting peak creating a noticeable shoulder for the film drawn to 50%. Secondary melting peaks are commonly observed with PET and are attributed to melting of less perfect crystals.¹⁴ However, this behavior was not observed for the other deformed samples. Therefore, it cannot be concluded that there is any difference between the melting behavior of the drawn and undrawn polymer. The exothermic peak is definitely associated with the T_g . The peak extends beyond the T_g because the heating rate is high enough such that the sample is not given sufficient time to establish thermodynamic equilibrium at a given temperature causing the relaxation processes to lag behind the temperature. It has been shown that quenched polymer glasses exhibit changes in the slope of the DSC trace, at temperatures below the T_g , which depend on the history of the samples.⁹ No apparent change in slope is observed for drawn PET. Since the relaxation process is associated with the T_g and the thermal behavior after T_g remains unchanged, it seems probable that whatever changes are caused by deformation occur only in the amorphous regions.

If the exotherms are due to relaxation of the changes imparted to the samples by deformation, their magnitudes should be indicative of the

stored latent energy in the deformed materials. A comparison to the values obtained from deformation calorimetry and solution calorimetry shows that the values are consistent, for example, the internal energy change of deforming PET to a strain of 30% is 6.2, 5.6 and 5.1 J/g as measured by deformation calorimetry, solution calorimetry and DSC respectively.

5.9 The Mechanics of Debonding

Optical and electron microscopy were used to investigate the micro-mechanics of 180° peeling of PSA backed with 34 μm PET films from aluminum substrates. A comprehensive study of the micro-mechanics of adhesive failure was not attempted because the focus of this thesis is on a global thermodynamic approach. The optical micrograph in Figure 5.15 shows the surfaces exposed by peeling on both sides of peel front. The PET film is being peeled and it is bent through 180° while the aluminum remains flat. The surface of the metal is clearly visible on the left and the PET surface is covered with deformed PSA. The optical micrograph in Figure 5.16 shows a high magnification view of the peel front when aluminum, left, is peeled from PET as viewed through the PET film. The PSA appears to cavitate forming voids near the peel front with diameters of approximately 25 μm . The stress state near the crack tip in peeling was discussed in Chapter 2. A region of hydrostatic tension exists near the crack tip in peeling facilitating the formation of voids in the material. The micrograph in Figure 5.17 was taken using a Jeol SEM with a gold coated sample. The micrograph shows the peel

front where PET is being peeled from aluminum. Deformation of the PSA is clearly visible. As the material is deformed between the PET and the aluminum, voids are created which expand leading to the formation of filaments which are stretched between the PET and the aluminum. The optical micrograph in Figure 5.18 shows a high magnification view of the base of the filaments attached to the aluminum. The filaments appear to be extended until the base breaks free from the aluminum. After breaking free from the aluminum, the filaments recoil to the PET side, leaving the aluminum virtually clean.

The deformation mechanism of the PSA in peeling resembles craze initiation and development in glassy polymers. Argon and Salama formulated a theory of craze formation and extension based on a meniscus instability mechanism. According to Argon, the initial formation of the cavities which lead to craze material "form by the mechanism of the meniscus instability, in which the yielded polymer at the air-polymer interface at the craze tip, which is basically unstable to perturbations of a well defined wavelength, breaks up, and by repeated convolutions produces the topologically correct form of craze matter in a cyclic but continuous manner."¹⁵ The craze material is formed by the repeated breakup of the concave air-polymer interface at the craze tip as shown schematically in Figure 5.19 which was reproduced from reference 15.

Convolutions of the PSA are clearly visible in the electron micrographs of the peel front. When a crack in a peeling adhesive grows by the meniscus instability mechanism, the convolutions in the separation front will appear as fingers running ahead of the crack from a perspective perpendicular to the plane of the crack. This phenomenon has been observed when scotch tape is peeled from a smooth surface.¹⁶

Figure 5.15 Optical micrograph of the surfaces exposed by peeling of 34 μm poly(ethylene terephthalate) film, right, from pressure sensitive adhesive coated aluminum.

Figure 5.16 Optical micrograph of the peeling of aluminum film, left, from pressure sensitive adhesive coated poly(ethylene terephthalate) film viewed through the polyester film.

Figure 5.17 SEM micrograph of the peel front showing the pressure sensitive adhesive being separated from the aluminum, left, as the polyester film is peeled away.

Figure 5.18 High magnification SEM micrograph of the peel front showing the pressure sensitive adhesive being separated from the aluminum, left, as the polyester film is peeled away.

Figure 5.19 Schematic drawing of craze matter production by the mechanism of interface convolution (meniscus-instability): a) craze tip; b) cross-section in the craze plane; c-d) advance of the craze front by a complete period of interface convolution.

The phenomenon has been analyzed by Field and Ashby who derived conditions for the instability to occur and expressions for the finger spacing at the separation front in non-linear viscous fluids.¹⁷ At low separation rates or for low viscosity fluids, the separation front should be smooth and stable. The microscopic appearance of the peel front for peeling PSA backed with PET from aluminum was compared for the lowest, 0.271 cm/min, and highest, 13.4 cm/min, peel rates and did not appear to be different.

5.10 The Effect of Substrate Surface Energy on the Peel Adhesion

In Chapter 2, a study by Andrews and Kinloch was discussed in which they attempted to relate the thermodynamic work of adhesion to the adhesive failure energy. A similar study is attempted here by peeling PSA backed with 45 μm PET films from several rigid polymeric substrates with differing surface energies. The polymers, their surface energies and the mechanical work of 180° peeling are tabulated in Table 5.7. Liquid contact angles were measured using the sessile drop method with water. The average of the advancing and receding contact angles are listed in the table for comparison to the surface energy values. The surface energy values were tabulated by Kinloch¹⁸ with the exception of the value for Tefcel which represents the opinion of a technical expert working for the Dupont Corporation which manufactures the film.

These experiments are specifically designed so that a correlation between substrate surface energy and peel energy is expected. The backing material is the same for all experiments so that the peel energy

will not vary due to the dissipative characteristics of the backing. The peeled PSA always remains on the peeled PET film so that the failure is adhesive at the substrate surface. The substrates are all low surface energy organic polymers which would be subject to similar surface contamination in the bonding environment. The bonding procedure, identical to that described in section 5.3 was carefully controlled to achieve uniformity. The peel rate was 2.71 cm/min for all of the experiments.

Table 5.7 The mechanical work of peeling, W , PSA backed with 45 μm PET film from rigid polymeric substrates with differing surface energies, γ . The average of the advancing and receding water contact angles, θ° , is also tabulated.

Tradename	Polymer	θ°	$\gamma \text{ J/m}^2$	$W \text{ J/m}^2$
Teflon	poly(tetrafluoroethylene)	89	0.019	186+/-44
Tefcel	poly(ethylene-tetrafluoroethylene copolymer)	80	0.028	1092+/-154
Hercules EK500	polypropylene	85	0.031	2082+/-225
Aclor 33C	poly(chlorotrifluoroethylene)	75	0.033	1633+/-105
Mylar	poly(ethylene terephthalate)	57	0.045	2404+/-246

The peel energy is plotted versus the substrate surface energy in Figure 5.20. A strong correlation between the peel energy and the substrate surface energy exists. It appears that an increase in the substrate surface energy will produce a change in the peel energy approximately 100,000 times greater. Changes in the substrate surface energy should be approximately equal to changes in the thermodynamic work of adhesion because the surface energy of the other surface, the PSA, remains constant. Increasing the substrate surface energy should result in higher elongations of the filaments of PSA spanning the

Figure 5.20 Mechanical energy of peeling pressure sensitive adhesive backed with 45 μm thick poly(ethylene terephthalate) films from rigid substrates with differing surface energies.

backing and substrate because the filament bases will adhere better to the substrates with higher surface energies. The result is more deformation of the PSA material before it breaks free of the substrate which consumes more mechanical peel energy and the higher peel force induces a tighter bend in the peeling backing resulting in increased mechanical work expenditure to deform the backing.

A correlation between thermodynamic work of adhesion and peel energy is not general and applies in very limited situations, for example, when 45 μm PET films were peeled from aluminum substrates, the peel energy was 1950 J/m^2 . If the correlation observed for the polymers was to hold true for aluminum, the peel energy would have to be 65,000 J/m^2 because the surface energy of aluminum oxide is approximately 650 J/m^2 .¹⁸ Obviously, peel strengths of this magnitude are impossible for this system. At some point, the adhesion of the PSA to the bonded layers would be strong enough such that separation would occur within the PSA layer in a manner leaving residual adhesive on the bonded layers. The adhesion which can be achieved by changing the surface chemistry and topology is limited by the cohesive strength of the adhesive and the stress distribution in the joint. Paradoxically, the peel strength of the aluminum substrate was less than that of the PET which has a lower surface energy. The most plausible explanation is the presence of hydrocarbon contaminants on the aluminum which coat exposed metals in most environments reducing the effective surface energy. The XPS spectra of aluminum presented in Chapter 4 shows carbon as a contaminant on the aluminum substrate surface.

5.11 Conclusions

Most of the mechanical energy expended in peeling (peel energy) a pressure sensitive adhesive (PSA) tape is dissipated as heat. The fraction of the peel energy which is dissipated as heat increases with the peel rate and varies with the mechanical properties and thickness of the backing. When PSA backed with PET films was peeled from rigid aluminum substrates, almost all of the peel energy is consumed either by deforming the PET backing or deforming the PSA. Separation is accompanied by extensive inelastic deformation in the PSA layer. The PET backing is also inelastically deformed exhibiting severe residual curvature after peeling. For the range of peel rates and PET backing thicknesses used in this study, the fraction of the peel energy dissipated as heat ranged from 69-86%. When the PSA was peeled with a completely elastic backing material, all of the peel energy was dissipated as heat proving that the PSA is incapable of storing any of the peel energy in the deformed material. The fraction of the peel energy, not dissipated as heat, when PSA backed with PET is peeled must be stored as latent internal energy in the deformed PET backing. Stored latent internal energies of several Joules/gram were measured in the peeled PET backing material using solution calorimetry. Stored latent internal energy was also measured during tensile drawing of PET films by three independent techniques; solution calorimetry, deformation calorimetry and DSC. All three techniques produced consistent results which show that approximately 25-50%, depending on the maximum drawing strain, of the mechanical energy under the stress-strain curve is stored as latent internal energy in inelastically drawn PET film. The energy

stored in the peeled backing is indicative of the total mechanical energy which was consumed to deform it during peeling. Assuming that the thermodynamics of deformation for tensile drawing and bending are similar, the energy expended in deforming the PET backing when the PSA tape is peeled can be estimated to be 2 to 3 times larger than the internal energy change of peeling. For the PET backed tapes peeled at 2.71 cm/min, approximately 17% of the peel energy is stored in the PET backing. The fraction of the peel energy consumed by deforming the PET backing is estimated to be 34-51% with the remainder being consumed by deforming the PSA layer.

An indeterminately small fraction of the peel energy is expended in overcoming the thermodynamic work of adhesion. However, a strong relationship does exist between the chemistry and physics of the interface and the peel energy because the peeled material can only be subject to stress, resulting in deformation and energy consumption, if the interface is strong. Under carefully controlled conditions, changing the thermodynamic work of adhesion can produce changes in the peel energy 100,000 times greater. A correlation between the thermodynamic work of adhesion and the peel energy is not general and only applies to carefully controlled experiments. The adhesion which can be achieved by changing the chemistry and topology of the interface is limited by the cohesive strength of the adhesively bonded materials and the stress distribution in the joint.

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CHAPTER 6

THE EFFECT OF RESIDUAL TENSILE STRESSES ON THE ADHESION AND PEEL ENERGY OF COATINGS

6.1 Introduction

Residual tensile stresses can cause cracking or delamination of polymeric coatings. When a liquid coating solidifies on a rigid substrate, and can no longer flow, further shrinkage results in internal tensile stresses in the plane of the coating. If the internal tensile stresses exceed the cohesive strength of the solid coating, cracking may occur which can result in coating-substrate delamination propagating from the crack because a shear stress, acting to bend the coating away from the substrate, is concentrated near the intersection of the crack and the interface. Stressed coatings are particularly vulnerable to stress cracking and delamination in the vicinity of substrate surface features where stress concentrations may exist. Structures containing stressed coatings are also vulnerable to failure by delamination near the edges created when they are cut or punched. The elastic energy stored in stressed coatings will be partially released by delamination having a detrimental effect on the adhesion of the coating. The detrimental effects of residual stress are especially important to the electronics industry where polymers are often coated on metals to take advantage of the high dielectric strength of the former and the excellent conductivity of the latter. High processing temperatures and differing thermal expansion coefficients between coatings and substrates

result in large tensile stresses in the polymer as the laminates are cooled to room temperature. Thus, residual stresses are a significant limitation to the manufacture of electronic devices and assemblies.

The detrimental effect of residual tensile stresses on coating performance is simply illustrated by polyimide coatings exceeding a critical thickness which spontaneously delaminate from aluminum during cooling from elevated cure temperatures. Paradoxically, coatings with thicknesses slightly smaller than the critical thickness had a high peel strength. Thus, the peel test is insufficient for evaluating the adhesion performance of stressed coatings. Evaluation of the stored elastic energy in coatings and of the resistance of the interface to failure by residual stress driven delamination are critical to assessing coating performance.

This chapter will discuss the nature and magnitude of the stresses developed during the processing of polyimide coatings based on PMDA-ODA. The effect of stored elastic energy upon peel adhesion has been investigated for a system where known stresses were applied during bonding and for a polyimide coating with residual shrinkage stresses. The stress distribution in a coating was modeled using finite element analysis. Residual stress driven delamination was observed for polyimide coatings exceeding a critical thickness and surrounding cuts in polyimide coatings.

6.2 Origin of Residual Tensile Stresses in Polymeric Coatings

Residual stresses in polymers arise from volumetric changes due to thermal expansion mismatches, swelling or solidification processes including solvent removal, crystallization or polymerization. For a linear, isotropic, homogeneous material whose elastic properties are changing with time, the relation between volumetric effects and stress may be expressed as¹

$$E \left[de_{ij} - \delta_{ij} (\alpha dT + \beta dc + \tau dt) \right] = (1 + \nu) d\sigma_{ij} - \nu \delta_{ij} d\sigma_{kk} \quad (6.1)$$

Where

E	Elastic modulus
e_{ij}	Strain tensor
δ_{ij}	Kronecker delta
α	Difference between the linear thermal expansion coefficients of the coating and substrate
T	Temperature
β	Linear swelling coefficient
c	Concentration
τ	Linear rate of shrinkage due to polymerization
t	Time
ν	Poisson's ratio
σ_{ij}	Stress tensor

The material properties can change with time, but not with strain or stress, and are incrementally linear. For a one dimensional constraint, $de_{xx} = 0$, $d\sigma_{yy} = d\sigma_{zz} = 0$ and all shear stresses are zero, the stress in the material is given by

$$d\sigma_{xx} = -E(\alpha dT + \beta dc + \tau dt) \quad (6.2)$$

A coating applied to a rigid substrate is free to change in thickness and is thus biaxially constrained, $de_{xx} = de_{yy} = 0$, $d\sigma_{zz} = 0$. The shear

stresses are zero. The stresses in the layer are approximately double those in a one dimensionally constrained material.

$$d\sigma_{xx} = d\sigma_{yy} = \frac{-E (\alpha dT + \beta dc + \tau dt)}{1 - \nu} \quad (6.3)$$

For a volumetrically constrained material, $de_{xx} = de_{yy} = de_{zz} = 0$. The stresses become infinite as the Poisson's ratio approaches 0.5.

$$d\sigma_{xx} = d\sigma_{yy} = d\sigma_{zz} = \frac{-E (\alpha dT + \beta dc + \tau dt)}{1 - 2\nu} \quad (6.4)$$

The in-plane stresses in a coating, σ_{xx} and σ_{yy} are equal and uniform in all regions except near the edges where they disappear. The static equilibrium equations,

$$\frac{\partial \sigma_{ij}}{\partial x_j} = 0 \quad (6.5)$$

can be applied to the two dimensional case illustrated in Figure 6.1.

$$\frac{\partial \sigma_{xx}}{\partial x} + \frac{\partial \sigma_{xz}}{\partial z} = 0 \quad (6.6)$$

$$\frac{\partial \sigma_{xz}}{\partial x} + \frac{\partial \sigma_{zz}}{\partial z} = 0 \quad (6.7)$$

with the boundary conditions:

$$\sigma_{xx} = 0 \text{ at } x = 0$$

$$\sigma_{xx} = \sigma_o \text{ for } x \gg h$$

$$\sigma_{xz} = 0 \text{ at } z = h$$

Away from the immediate vicinity of the edges;

$$\sigma_{xx} = \sigma_o$$

$$\sigma_{xz} = 0$$

where h is the thickness of the coating and σ_0 is the residual stress. The resulting stress distribution is illustrated graphically in Figure 6.1.

The stress distribution of a three dimensional coating resulting from uniform shrinkage was determined from the finite element model shown in Figures 6.2 and 6.3. The finite element program COSMOS/M was used for all of the analysis presented in this thesis.² The thickness of the coating is small compared to its in plane dimensions. The model coating was meshed using three dimensional isoparametric solid elements having three translational and no rotational degrees of freedom. The element density in the X coordinate direction is greatest at $x = 0$ to provide maximum accuracy in the stress calculations at this end of the model. The bottom surface, $z = 0$, represents the side of the coating which is bound to a rigid substrate and zero displacements are specified for all nodes on this surface. Internal tensile stress was imparted to the model by specifying a positive thermal expansion coefficient and applying a uniform negative temperature to the entire structure.

The shear and normal stresses, σ_{xz} and σ_{xx} , near the edge of an isotropic coating, generated by finite element analysis, are shown in Figures 6.4 and 6.5. The stresses are shown on a cut through the thickness of the coating, in the X coordinate direction, going through the middle of the coating. The end where the element density is highest, $X = 0$, is shown in both figures. The stress state away from the edges is equal biaxial tension. Thus, the σ_{yy} and σ_{yz} stresses on a cut through the thickness of the coating in the Y coordinate direction would appear identical to the σ_{xx} and σ_{xz} stresses shown in the figures. In Figure 6.6, the σ_{xx} stress, averaged through the coating thickness

Figure 6.1 The shear, σ_{xz} , stress at the coating-substrate interface and the average normal stress in the coating, σ_{xx} , are plotted as a function of distance from the coating edge.

Figure 6.2 Three dimensional finite element model of a coating lying in the X-Y plane viewed from the side, the Y direction. The coating is constrained by a substrate which is not modeled, but zero displacements are specified for all nodes on the bottom surface, $z = 0$, of the coating as if they were bound to a rigid substrate.

Figure 6.3 Three dimensional finite element model of a coating lying in the X-Y plane viewed from the top surface of the coating, the Z direction.

σ_{xz}	MPa
10	26.4
9	22.6
8	18.9
7	15.1
6	11.3
5	7.55
4	3.78
3	0.00
2	-3.77
1	-7.54

Figure 6.4 The σ_{xz} shear stress near the coating edge is shown on a cut through the thickness of the coating going through the center of the model in the X coordinate direction.

σ_{xx}	MPa
10	66.1
9	57.0
8	47.9
7	38.9
6	29.8
5	20.7
4	11.6
3	2.50
2	-6.59
1	-15.7

Figure 6.5 The σ_{xx} stress near the coating edge is shown at a cut through the thickness of the coating going through the center of the model in the X coordinate direction.

Figure 6.6 The in-plane stress, σ_{xx} , on the cut shown in Figure 6.5, averaged through the coating thickness and divided by the maximum σ_{xx} stress, is plotted versus the distance from the coating edge divided by the coating thickness.

and divided by the maximum σ_{xx} stress, is plotted versus the distance from the coating edge divided by the coating thickness. The average σ_{xx} stress increases from a minimum at the coating edge, reaching a constant value approximately five thicknesses in from the edge. In the three dimensional model, the average value of σ_{xx} does not equal zero at the edge as it does in the two dimensional model shown in Figure 6.1. A stress singularity in the σ_{xx} stress exists where the coating-substrate interface intersects the coating edge. The finite element calculated stress value at this point is approximately twice the far-field tensile stress in the coating. At the point where the top surface of the coating intersects the coating edge, σ_{xx} is zero. The σ_{xx} stress should approach zero at all points on the coating edge, except for the coating-substrate interface, thereby satisfying the equilibrium requirements which dictate that the stress components perpendicular to a free surface must vanish as the surface is approached. This error in the finite element solution appears to be caused by an insufficient number of elements through the film thickness. It appears that the calculated σ_{xx} stress at the edge, near the coating-substrate interface, is influenced by the large σ_{xx} stress at the intersection of the edge and the coating-substrate interface. As the number of elements through the film thickness was increased, the solution improves and non-zero σ_{xx} stresses at the edge nodes become confined to a smaller area near the coating-substrate interface. The σ_{xx} and σ_{yy} thermal stresses, away from the edges can be calculated from

$$\sigma_{xx} = \sigma_{yy} = \frac{-E\alpha\Delta T}{1-\nu} \quad (6.8)$$

Using the material properties, $E = 2.5 \text{ GPa}$, $\nu = .34$, $\Delta\alpha = 23 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ and $\Delta T = -380^{\circ}\text{C}$, the calculated stresses are 34 MPa which are in exact agreement with the stresses calculated by finite element.

The shear stresses, σ_{xz} and σ_{yz} , reach a maximum value near the coating edge and decrease to zero away from the edge. In Figure 6.7, the σ_{xz} shear stress at the coating substrate interface, normalized by the maximum interfacial σ_{xz} stress is plotted versus the distance from the coating edge normalized by the coating thickness. The same stress distribution is observed for the σ_{yz} stress on a cut through the coating in the Y coordinate direction. The σ_{xz} stress decays to zero within approximately five coating thicknesses from the edge. The stress normal to the coating plane, σ_{zz} , and the shear stress, σ_{xy} were negligible throughout the coating.

The in-plane stresses act parallel to the interface. Therefore, they do not exert stress on the interface. In Figure 6.8, the ratio of σ_{xx} at the top of the film to σ_{xx} at the coating-substrate interface is plotted versus the distance from the coating edge divided by the coating thickness. Within one film thickness of an edge, the variation in tensile stresses through the film thickness is significant producing a large shear stress, σ_{xz} , which acts to bend the film away from the substrate. Away from the coating edges, the coating-substrate interface is stress free and there are no forces which would act to delaminate the coating from its substrate regardless of the magnitude of the tensile stresses in the coating. It is the shear stresses, which increase with the magnitude of the in plane tensile stresses, acting on the interface near an edge that can lead to delamination. The effect is clearly seen when an edge is introduced by cutting a stressed coating. The bottom

Figure 6.7 The shear stress, σ_{xz} , at the coating-substrate interface, on the cut shown in Figure 6.4, divided by the maximum interfacial σ_{xz} stress, is plotted versus the distance from the coating edge divided by the coating thickness.

Figure 6.8 The ratio of the in-plane stress, σ_{xx} , at the top surface of the coating to σ_{xx} at the coating-substrate interface is plotted versus the distance from the coating edge divided by the coating thickness.

photograph of Figure 6.9 shows delamination surrounding a cut in a polyimide coating on glass. The introduction of the cut induces shear stresses at the edge which cause delamination to propagate into the coating.

6.3 Residual Tensile Stresses in Polyimide Coatings

The polyimide used in this study, PMDA-ODA, is not soluble and is thus applied as a poly(amic acid) precursor, Dupont Pyralin 2540, which is soluble in N-methyl-2-pyrrolidone, NMP. The polyamic acid was applied to glass or metal plates using a Headway Research EC101 photoresist spinner. The spun-on films are then thermally imidized by baking in several steps as described in Section 4.2. The initial thermal treatment results in a loss of film volume and produces intrinsic tensile stresses in the film. However, researchers have shown that the intrinsic stress in polyimide films fully cured at high temperatures is zero.³ The stress in the fully cured film arises from a mismatch of the coefficient of thermal expansion between the film and substrate. For polyimide imidized at 360°C, the T_g is approximately 360°C. Thus, cooling from this temperature will generate substantial tensile stresses in the film providing that its thermal expansion coefficient is larger than that of the substrate. The stress in PMDA-ODA films has been determined as a function of final bake temperature by Elsner who measured the curvature of a substrate with and without the PMDA-ODA coating.⁴ He found that upon initial heating, the stress increases in a steplike shape with increasing bake temperature.

Figure 6.9 The top optical micrograph shows a cut through a polyimide coating on a glass substrate at 300°C. The coating was cut on a hot stage at 300°C. The bottom micrograph shows an area of delamination surrounding the cut after it has been cooled to 25°C.

Above 200°C, the stress increases linearly with final bake temperature. When the temperature of fully cured coatings was cycled from room temperature to the cure temperature or vice versa, the stress changed linearly and reversibly with temperature and was always approximately zero at the cure temperature. This behavior indicates that the origin of the residual stress in the fully cured film is entirely thermal. Thus, the film stress can be estimated from equation 6.8. The top photograph of Figure 6.9 shows polyimide coating on glass at 300°C with a cut through the film introduced at that temperature. At 300°C, the stresses in the film are small since the cure temperature was 360°C and delamination does not propagate from the cut. As the sample is cooled to 25°C, stresses in the coating build and the film delaminates surrounding the cut.

The accuracy of polyimide residual stresses estimated from the sample thermal history depend on many factors including the accuracy and temperature dependence of the material properties used in the calculations, effects of anisotropy, variations in the moisture content of the film and the effect of multiple layer coating application. The tensile modulus at 23°C, 2.5 ± 0.3 Gpa, was obtained from tensile tests using dogbone shaped ASTM type D638 samples cut from films which had been removed from aluminum substrates. The Poisson's ratio of fully cured PMDA-ODA, 0.34, was determined by Bauer using a high pressure gas dilatometer.¹ The thermal expansion coefficient was determined by measuring dimensional changes of a ribbon of polyimide, cut from a film which had been removed from an aluminum substrate, held at constant force in a thermo-mechanical analyzer while the temperature was ramped from 30°C to 400°C. A plot of the dimensional change versus temperature

is shown in Figure 6.10. The thermal expansion coefficient is temperature dependent over this range increasing with temperature. A linear regression line through the data gives an average value of $43 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ which is comparable to other values reported in the literature. The measured expansion coefficient of the peeled film for 50-100°C is $30 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. In its technical literature, Dupont reports thermal expansion coefficients for Kapton commercial PMDA-ODA films of $18 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ for 23-100°C, $31 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ for 100-200°C, $48 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ for 200-300°C and $78 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ for 300-400°C.⁵ Based on the Dupont values, the computed average expansion coefficient over the range 23-360°C is $41 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. The modulus is also temperature dependent. Bauer measured a 40% decrease in the modulus of Kapton film over the temperature range 23-380°C.¹ The modulus and thermal expansion coefficient of a material are related. When the modulus drops, the thermal expansion coefficient increases and vice-versa. For a ribbon of film held at constant length, the stress, σ , in the film is $\sigma = E\alpha\Delta T$. The stress-temperature plots which show the stress changing linearly with temperature indicate that the product, $E\alpha$, does not change significantly with temperature.

Cast polyimide films exhibit a preferential orientation of the molecules, parallel to the surface on which the films are prepared.⁶ Thus, the thermal expansion coefficients and moduli will be dependent upon the material direction in which they are measured. Differences in the degree of in-plane orientation resulting from variations in film preparation procedures may cause variation in the film properties. Additional variability results from axial orientation induced by the spinning which would result in different molecular orientation in

Figure 6.10 The dimensional change of a ribbon of polyimide film, cast and cured on a substrate, is plotted versus temperature for a sample which was held under constant tension.

samples cut from the edges and the center of a plate. The equilibrium moisture absorption of polyimide films is 1.8% when exposed to 50% relative humidity at 23°C.⁵ Films exposed to ambient conditions after cure would absorb water and swell, decreasing the stress in the film.⁷ Moisture in the films is capable of producing significant variations in the coating stress. The hygroscopic coefficient of expansion for Kapton PMDA-ODA films is 22 ppm/%RH.⁵ The polymer exposed to 50% RH would expand by 0.001% reducing the stress in the film by 4 MPa. The influence of multiple coating layers on the film stress was investigated by Elsner who applied initial layers and prebaked them at 85°C before applying additional layers.⁴ The effect of film thickness on the residual stress is small. However, double layers had slightly lower residual stresses than single layers of equal thickness.

The thermal properties used to estimate residual thermal stresses are summarized in Table 6.1. The thermal stresses in polyimide coatings can be estimated using values of the mechanical and thermal properties measured at any one temperature, because the product, $E\alpha$, remains relatively constant with temperature. The thermal stress is estimated using the modulus and thermal expansion coefficients of spun cast polyimide film experimentally measured near room temperature, 2500 MPa and $30 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. The thermal stress, estimated from equation 6.8, at 20°C in a polyimide film cast on silicon and imidized at 400°C is 38 MPa. Maden and Farris have found that the residual stresses in spin coated polyimide films can be measured to a high degree of precision using the holographic technique. For PMDA-ODA samples cured to 400°C on silicon, the measured residual stress was $25 \pm 0.5 \text{ MPa}$.⁸ Geldermans et. al. also measured the residual stress in PMDA-ODA films cast and

cured on silicon at 400°C using x-ray equipment to measure the lattice curvature of the substrate.⁹ The measured stress in the film at 20°C is 30 +/-5 MPa. The residual stresses measured by both methods are reasonably consistent and it is highly probable that the true stress at 20°C lies between 25 and 30 MPa. The stress estimated from elasticity using equation 6.8 is 25-50% larger than the measured stresses. Stresses estimated from elasticity are crude and can only predict the magnitude, tens of MPa, of the film stress with certainty.

Table 6.1 Thermal expansion coefficients of polyimide films and substrates

Material	$\alpha \times 10^6 \text{ } ^\circ\text{C}^{-1}$
Polyimide	30
Aluminum	20
Silicon	3
Glass	5

Where values are required for residual stress in PMDA-ODA films, it is best to estimate the stress from reliable experimental data. The data of Geldermans et. al. for PMDA-ODA on silicon can be used to accurately estimate the stress in PMDA-ODA films cast and cured on other substrates at 360°C. When PMDA-ODA film was heated to 400°C on silicon, the stress reached zero and became compressive at 375°C. Upon cooling, the stress increases linearly with temperature reaching 30 MPa at 20°C. The residual stress at 20°C in a film cured on silicon at 360°C is estimated to be $(360 - 20)/(375 - 20)$ or 0.96 times the stress in a film cured at 400°C. The residual stress in films cured on substrates other than silicon should be proportional to the ratio of the differences

between the thermal expansion coefficients of the film and substrate. The stress in films cured on glass should be $(30 - 5)/(30 - 3)$ or 92% of those in films cured on silicon and the stress in films cured on aluminum should be $(30 - 20)/(30 - 3)$ or 37% of those in films cured on silicon. Correcting for final cure temperature and substrate thermal expansion, the stress at 20°C in PMDA-ODA cast on glass and aluminum and cured at 360°C is estimated to be 27 MPa and 11 MPa respectively.

6.4 The effect of Residual Tensile Stress on the Peel Energy

Residual tensile stresses in adhesive layers reduce the effective adhesion.¹⁰ Residual stress imparts elastic energy to the bonded layer which is released upon delamination. Thus, the elastic energy reduces the external work required to remove an adhesive from a substrate. The total elastic energy in the adhesive layer is

$$U = \frac{1}{2} V_0 \left(\sigma_{ij} e_{ij} \right) \quad (6.9)$$

Where σ_{ij} is the stress tensor and e_{ij} is the Cauchy strain tensor, V_0 is the volume of the adhesive layer and $i, j = x, y, z$.

To investigate the effect of stored elastic energy in a bonded layer on the peel strength, pressure sensitive tapes were bound to rigid substrates while under tension. Scotch No. 5423 industrial tape was used for this study. This tape consists of a block copolymer type pressure sensitive adhesive backed with 0.25 mm thick ultra-high molecular weight polyethylene, UHMWPE. The tensile properties of the film were determined in an Instron tensile testing machine using

dogbone shaped samples conforming to ASTM standard test D638. The Stress-strain curve is shown in Figure 6.11. The Tensile modulus is 400 ± 20 MPa and the apparent yield strength is 15 MPa. The low modulus and reasonable yield strength make this backing material ideal for storing elastic energy. To bond the tapes under tension, one end of a UHMWPE backed tape is attached to an 8" diameter wheel equipped with a low friction bearing such that it rotates freely about an axle. A weight is attached to the free end of the tape with a clamp and the wheel is rotated such that the free tape is wound around the wheel. The weight is then removed leaving a tape which is held in tension due to its adhesion to the wheel. $1/2$ " wide tapes were loaded with 3, 6, 9, 15 and 18 MPa. The tapes were peeled from wheels at 90° in an Instron tensile tester. The grips of the tensile tester were separated at 1.0 cm/min for all peel tests. The bonded tape has a tensile stress in the direction of its length. All other stresses are zero. The elastic energy, per unit area, in a tape of thickness t is thus

$$U = \frac{t\sigma^2}{2E} \quad (6.10)$$

The peel energy per unit area, in J/m^2 , is equal to the average peel force per unit width of tape in Newtons/meter. In Figure 6.12, the peel energy of UHMWPE backed tapes is plotted versus the elastic energy stored in the tapes. The decrease in the peel energy is comparable in magnitude to the strain energy in the tapes. Kendall observed similar behavior for stretched rubber strips pressed onto glass.¹¹ For the UHMWPE tapes and the rubber strips used by Kendall, the elastic energy in the bonded layers is comparable in magnitude to the peel energy.

Figure 6.11 Stress versus strain for drawing of UHMWPE tape at $.0067 \text{ sec}^{-1}$.

Figure 6.12 The peel energy of UHMWPE backed pressure sensitive tapes is plotted versus the stored elastic energy in the bound tapes. The tapes were peeled from rotating wheels at 1 cm/min.

The possibility exists that the applied loads influenced the peel energy by changing the application pressure of the pressure sensitive adhesive, PSA. When the tape backing is in tension, the PSA is pressed against the wheel with a pressure which can be calculated using the formula for thin walled cylindrical pressure vessels. The internal pressure, p , acting on the walls of a cylindrical pressure vessel with radius r can be related to the hoop stress in the wall, $\sigma_{\phi\phi}$, by

$$\sigma_{\phi\phi} = \frac{pr}{t} \quad (6.11)$$

where t is the wall thickness. Using this formula, the interfacial pressure exerted on the wheel by the loaded tapes varies from 0.05 to 0.3 MPa. The adhesion of a PSA is a function of application pressure if the bonding to the substrate is incomplete. PSA materials are readily deformable so that they can easily conform to a substrate surface. Once the application pressure reaches a level sufficient to cause complete bonding to the substrate, the adhesion should be independent of further increases in application pressure. A minimum load of 9.8 Newtons was used during windup to ensure complete bonding. If the level of bonding were increasing with the applied load, an increase in peel energy with applied tension would be expected. This is clearly not the case and thus one could assume that the effect is negligible. However, it is possible that an increase in bonding with applied tension is counteracting the apparent decrease in peel energy, thus causing the observation of a decrease in peel energy which is slightly less than the applied strain energy in the tape. Another possible source of error is that the yield stress of the UHMWPE was exceeded by the highest applied load. A 1/2" tape loaded with 59 Newtons experiences 18 MPa of tensile

stress. The actual strain energy in the tape will be slightly lower than that calculated assuming linear elastic behavior.

Figure 6.13 shows the peel energy for polyimide films of varying thickness peeled from rigid aluminum substrates at 180°. The films were prepared as described in Chapter 4. The estimated elastic energy in the film per unit area is

$$U = \frac{t\sigma^2}{E}(1-\nu) \quad (6.12)$$

The bonded polyimide contains residual tensile stresses which disappear when it is peeled from the aluminum. The elastic energy associated with these stresses is released upon peeling reducing the external work input required to peel the sample. The stresses become apparent when the polyimide coated aluminum is removed from the glass plates and it curls into the polyimide side. The stress in a dry PMDA-ODA film cured under the same conditions on an aluminum substrate which is bonded to a glass plate is estimated from the data of Geldermans et. al. to be 27 MPa. The aluminum is 0.004" thick and the glass is 0.25" thick. As long as the polyimide coated aluminum is bonded to the glass, it is appropriate to use the difference between the thermal expansion coefficient of polyimide and glass to estimate the stress in the polyimide. When the peel sample is detached from the glass plate, the stress in the polyimide should decrease because the difference between the thermal expansion coefficients of polyimide and aluminum, $10 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, is less than that of polyimide and glass, $25 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. The stress in the polyimide on aluminum is estimated to be 11 MPa. The elastic energy stored in the film per unit area can be calculated using equation 6.12. However, the estimated stress is really a maximum value

Figure 6.13 The peel energy of polyimide films peeled from rigid aluminum substrates at 180° is plotted versus the film thickness. Polyimide films exceeding 120 μm spontaneously delaminate from aluminum substrates during post-curing cooldown.

because the aluminum substrate is thin such that it yields easily reducing the stress in PMDA-ODA films. The stress in the films will also be reduced by swelling due to water absorption under ambient conditions.

Using equation 6.12, the calculated maximum strain energy in dry 30 μm and 95 μm thick polyimide films cured on aluminum at 360°C is 0.96 J/m² and 3.0 J/m². The decrease in work with increasing film thickness displayed in Figure 6.13 is two orders of magnitude greater than the increase in internal elastic energy with film thickness. The elastic energy stored in the polyimide film represents a small fraction of the peel energy. Even in the 95 μm film, the stored elastic energy is only 1% of the peel energy. The comparisons of peel and stored elastic energies remain valid when the precision of the elastic energies calculated from estimated thermal stresses are considered. This variability is insignificant when compared to the large difference between the stored elastic and peel energies.

It was determined in Chapters 4 and 5 that most of the peel energy is consumed by plastic deformation. The volume of film being plastically deformed during peeling increases proportionally with the film thickness. However, the bending rigidity of the film increases with the cube of thickness.¹⁰ Thus, the greater bending rigidity of thicker films leads to a larger bend radius and lower strains in the film near the point of detachment in peeling, reducing plastic deformation and lowering the peel energy. Croll¹⁰ and Kendall¹¹ observed a decrease in the peel energy of bonded films, with film thickness, equal to the change in internal elastic energy. In both cases the adhesion was extremely weak. Croll measured energies less

than 3 J/m^2 when peeling polystyrene from steel and Kendall measured energies less than 6 J/m^2 when peeling rubber from glass. In practice, decohesion due to residual stress will be of primary concern in systems where the adhesion is strong. For coatings which strongly adhere to rigid substrates, the effect of film thickness upon the peel energy is dominated by plastic deformation, not stored elastic energy. In this case, the peel test is not sensitive enough to detect the loss of adhesion due to residual stress.

While the stored elastic energy is small compared to the peel energy, it is large compared to the work required to reversibly create the surfaces exposed by delamination. Polyimide coatings thicker than $120 \text{ }\mu\text{m}$ spontaneously delaminated from the aluminum which was still bonded to the glass plate during post-cure cooldown while slightly thinner coatings had high peel strengths. The maximum strain energy in these films is estimated to be 23 J/m^2 . Extrapolating the peel energy to the thickness at which spontaneous delamination occurs on Figure 6.13 predicts a peel energy of approximately 500 J/m^2 . Residual stress driven delamination requires less energy than peeling because there is much less plastic deformation. The resistance of the interface to residual stress induced delamination is far less than that predicted by peel testing. Thus, predicting the performance of coatings containing stored elastic energy requires knowledge of the stresses in the coating and of the true delamination resistance of the interface.

Spontaneous delamination, driven by residual stress has been used to measure adhesion.¹² Since spontaneous delamination occurs with little energy dissipation, tests based on the phenomena should give values of adhesion closer to the intrinsic energy required to reversibly

separate the interface. Development of an adhesion test based on spontaneous delamination is the subject of Chapter 7.

6.5 Summary

Residual tensile stresses in thermally cured polyimide coatings are caused by the mismatch in thermal expansion coefficients of the coating and substrate. The residual stress level at a given temperature can be estimated if the thermal and mechanical properties of the coating and substrate are known. Residual stress estimates from elasticity can contain considerable uncertainty so direct stress measurements are desirable. Fortunately, previous investigators have made careful measurements of the residual stresses in PMDA-ODA polyimide film cured on silicon. Their results, obtained by different methods, are in excellent agreement and provide the basis for accurately estimating the stress in PMDA-ODA films cured on substrates other than silicon.

The reduction in the peel strength of stressed tapes clearly shows the effect of internal stresses on the adhesion of bonded layers. In this case, the stored elastic energy was comparable in magnitude to the peel energy. In most cases where the adhesion is good, the elastic energy associated with the residual stresses will be small compared to the peel energy. This was true for polyimide coated aluminum and the detrimental effect of residual stress is not reflected in its peel behavior. Residual stress driven delamination of polyimide from aluminum bonded to glass was observed for coatings exceeding a critical thickness while slightly thinner coatings had high peel strengths.

Residual stress driven delamination of polyimide from aluminum required less than 23 J/m^2 , while the energy needed for peeling varied from 500 to 900 J/m^2 depending on the film thickness. Stress driven delamination requires less energy because it occurs with much less plastic deformation than peeling. Delamination is a likely mode of failure in coating applications. While the peel test is acceptable for tapes, it is totally insufficient for evaluating the adhesion of stressed coatings.

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CHAPTER 7

MODELING OF RESIDUAL TENSILE STRESS DRIVEN DELAMINATION OF A CUT-THROUGH COATING BY FINITE ELEMENT ANALYSIS

7.1 Introduction

A thin film or coating bonded to a substrate and under a state of residual biaxial tensile stress will delaminate from a cut-through if the elastic energy from the residual stress is high compared to the adhesion. Strong, high modulus films are often used as coatings and these can develop high residual stresses during processing. Interfacial delamination is one of the most significant failure modes of these films. Delamination is likely to initiate from a crack in the film because shear stresses are concentrated near the intersection of the interface and the crack. Thus, tests to determine the interfacial resistance to delamination provide important data for design and performance prediction. There is a significant need for quantitative measurement of the interfacial resistance to delamination at a cut-through for use in the failure prediction of complex multi-layer structures manufactured by the electronics industry.

Standard adhesion tests such as the peel, pull-off, blister and scratch tests may be poor at predicting interfacial resistance to delamination. The cut test uses spontaneous delamination caused by residual tensile stresses in the film to measure the adhesion energy. Farris and Bauer used the spontaneous delamination of a coating from a circular cut to measure adhesion energy.^{1,2} For this simple case, there

is an analytical solution for the stresses in the delaminated film, but circular cuts are difficult to make. In this chapter, a cut test is developed using a straight cut, through the coating to the substrate, of a length which is very long compared to the coating thickness. A linear elastic finite element analysis is used to compute the approximate difference between the elastic energy of the cut coating before and after delamination. The difference in the elastic energy divided by the delaminated area, A , not the surface area, $2A$, will be referred to in this chapter as the adhesion energy. All interfacial toughness values will also be reported based on A , not $2A$.

7.2 Analysis of Spontaneous Interfacial Delamination of a Thin Coating Caused by a Cut

Delamination propagating from a cut in a stressed coating on a rigid substrate has been modeled using concepts from interfacial fracture mechanics. The shape and extent of the area of delamination are predictable and the toughness of polyimide/glass interface has been estimated. The analysis provides insight into the mechanics of the process which is essential for interpretation of the numerical results presented later in this chapter.

7.2.1 Growth of a Plane Strain Interface Crack

The energy release rate, G , of a two dimensional plane strain crack propagating from a cut-through, as shown in Figure 7.1, was computed by Thouless et al. using finite element techniques for the case where the elastic properties of the film coincide with those of the substrate.³ He found that the energy release rate approaches steady-state conditions becoming length independent when the crack exceeds 3 to 5 film thicknesses. For this case, the energy release rate is given by

$$G = \frac{1-\nu^2}{2E} \sigma^2 t \quad (7.1)$$

where ν is the film's Poisson's ratio, E is the film's elastic modulus, t is the film thickness and σ is the residual stress which is assumed to be equal biaxial.

In fracture mechanics, a parameter K is defined as the stress intensity factor which relates the magnitude of the stress near the crack tip to the applied loadings and geometry of the structure in which the crack is initiated. For convenience, crack tip loading is separated into three modes which are characterized by the stress intensity factors K_1 , K_2 and K_3 . Mode 1 refers to tensile loads acting normal to the crack plane. Mode 2 refers to shear loads acting parallel to the crack plane in the direction of crack propagation, often referred to as in-plane shear. Mode 3 refers to shear loads acting parallel to the crack plane perpendicular to the direction of crack propagation, often referred to as antiplane shear. The plane strain interface crack can be characterized by the stress intensity factors, K_1 and K_2 . At

Figure 7.1 Variation of the energy release rate, G , for a plane strain interface crack growing from a cut in a film with residual biaxial tension.

steady-state, the mode mixity is constant. The steady state plane strain problem for delamination driven by residual tensile stress has $K_1 > 0$, so the crack is open, but, it is a mixed mode problem with the phase of the stress intensity factors, $\Psi = \tan^{-1} (K_1/K_2)$, dependent on the Dundurs parameter, Ω , which measures the elastic mismatch between the film and substrate.⁴

$$\Omega = \frac{E/(1-\nu^2) - E_s/(1-\nu_s^2)}{E/(1-\nu^2) + E_s(1-\nu_s^2)} \quad (7.2)$$

The subscript, s, refers to properties of the substrate. When $\Omega = -1$, the substrate is stiffer than the film and Ψ approaches 45° indicating that modes 1 and 2 contribute equally to crack growth. As the film becomes stiffer, Ψ increases, reaching 70° for $\Omega = 1$. In this case, mode 2 is dominant. The energy release rate under combined mode 1 and 2 is⁴

$$G = \frac{1}{2} \left[\frac{1-\nu^2}{E} + \frac{1-\nu_s^2}{E_s} \right] \left[K_I^2 + K_{II}^2 \right] \quad (7.3)$$

The interface toughness is generally strongly mode-dependent with the energy release rate needed to drive the crack increasing as the ratio of mode 2 to mode 1 increases. The general condition for delamination of a plane strain crack can be written as

$$G = G_c(\Psi) \quad (7.4)$$

where G_c is the mode-dependent interface toughness which must be determined by test. There are two limiting cases of the condition expressed by equation 7.4. At one extreme, the interface is ideally brittle and has a mode-independent toughness. At the other extreme, the interface crack is fully shielded from any effect of K_2 and the

condition for crack advance is independent of K_2 . Experimental data for an epoxy glass interface obtained by Cao and Evans over a range of modes 1 and 2 fell between the two extremes, but closer to the fully shielded criterion.⁵

7.2.2 Modeling the Cut Test

In the cut test, a straight cut, which is very long compared to the film thickness, is made through to the substrate. If substrate cracking does not occur, three decohesion shapes have been observed for a single straight cut.⁴ Those shapes are shown in Figure 7.2. If the stress in the film is lower than the critical value needed to initiate delamination at the intersection of the cut-through and the interface, σ_i , no delamination is observed. At stress levels larger than the σ_i , but less than a critical stress value σ_c , delamination limited to several film thicknesses from the cut occurs. When the film stress exceeds σ_c , extensive delamination will propagate 20 to 100 film thicknesses from the cut depending on the cut length.

The extensive delamination case of the cut test has been modeled and criterion governing the advance of the interface crack have been proposed.^{4,5,6,7,8} Using these criterion, the shapes of the delaminated regions surrounding a cut-through have been calculated.⁴ Energy release rates can't be calculated from experimentally measurable quantities, but the calculated shapes are in agreement with experimental observation. The results provide valuable insight into the mechanics of interface crack propagation from a cut-through.

No delamination

$$a = 0$$

Limited delamination

$$a \approx t$$

Extensive delamination

$$a \approx L$$

Figure 7.2 Three regimes of behavior for the cut test.

For extensive delamination, the change in strain energy associated with deformation is primarily due to in-plane deformation of the delaminated film.⁴ Thus, the stress distribution of the cut delaminated film is analyzed as a two-dimensional plane stress problem. The predominate deformation mode changes very rapidly from in-plane to bending and crack tip loading as the distance from the delamination boundary approaches the film thickness.⁶ The stress distribution within the delaminated region can be determined from the sum of two plane stress problems. The first problem is uniform equal biaxial tension and the second is the plane stress distribution for a film clamped along the edges of the delamination boundary, C , and subject to a normal traction on the cut face. The boundary conditions are no displacements on the boundary C and a normal stress and no shear stresses on the cut face. Locally, along the crack front, C , the stresses in the film resolve into two components which are normal, σ_{nn} , and tangential, σ_{nt} to the crack boundary. Along the crack front, σ_{nn} induces mode 1 and mode 2 with K_1 and K_2 in fixed proportion characterized by Ψ . σ_{nt} induces mode 3. The steady state energy release rate is used because the radius of curvature of the boundary, C , and the length scale over which the stresses change are assumed to be large compared to the film thickness. Since the relative ratio of K_2 to K_1 is fixed along the front, the shape of the delaminated region does not depend on Ψ , but the shape is strongly dependent on K_3 . The boundary, C , was found by numerical iteration, for differing values of film stress, such that it satisfies an equation for the estimated critical energy release rate. The results provide the following insights. When mode 3 has no influence on the delamination, the boundary of the delaminated region remains attached to

the edge of the cut. When the residual stress level is high, the crack is subject to mode 3 near the ends of the cut and the delamination boundary stands off the ends of the cut. For a given residual stress level, the delamination is always more extensive when mode 3 is present. The shape of the delaminated region is very sensitive to the extent which mode 3 enters the process. Experimental observations for the polyimide/glass interface suggest that mode three has a relatively small influence on the fracture process and that the interface is far from brittle, with significant shielding of the crack tip from the influence of mode 3.⁴ When the delamination boundary stands off the ends of the cut, singular stress fields are produced near the cut ends. Kim has calculated the stress intensity factor at the end of the cut using a modified J-integral.⁶ Experiments performed by Kim on PMDA-ODA polyimide cured on glass at 400°C show the combined mode I and mode II toughness to be 4.1-4.5 J/m² and the mode III toughness to be 15 J/m².⁶

For the axisymmetric delamination induced by a circular cut, mode 3 is not present. The plane stress problem for this case was solved by Farris and Bauer.² When a circle of radius a is cut in a film in uniform biaxial tension, the center chip will delaminate completely and the film surrounding the cut will delaminate to a radius b . The stress state in the delaminated film was found using the plane stress solution for a hollow cylinder under pressure. In cylindrical coordinates

$$\sigma_{rr} = \frac{-E\alpha\Delta T b^2(1-a^2/r^2)}{b^2(1-\nu)+a^2(1+\nu)} \quad \text{For } a \leq r \leq b \quad (7.5)$$

$$\sigma_{\theta\theta} = \frac{-E\alpha\Delta T b^2(1+a^2/r^2)}{b^2(1-\nu)+a^2(1+\nu)} \quad \text{For } a \leq r \leq b \quad (7.6)$$

where E is the film elastic modulus, α is the difference between the thermal expansion coefficients of the film and substrate, ΔT is the temperature difference from the temperature at which the film is stress free, and ν is the Poisson's ratio of the film. The elastic energy for the bonded case in the region from radius, $r_1 = a$ to $r_2 = b$ is

$$U = \frac{tE\pi(b^2 - a^2)(\alpha\Delta T)^2}{1 - \nu} \quad (7.7)$$

For the film delaminated between $a \leq r \leq b$, the elastic energy is

$$U = \frac{tE\pi(b^2 - a^2)(\alpha\Delta T)^2 b^2}{b^2(1 - \nu) + a^2(1 + \nu)} \quad (7.8)$$

Farris and Bauer performed experiments on the polyimide/glass interface using PI5878, a PMDA-ODA polyimide. They measured an interfacial toughness of 1.68 J/m^2 for a coating with a delaminated radius of 1.05 cm and a cut of radius 0.7 cm. The film thickness was $35 \text{ }\mu\text{m}$, the modulus was 3 GPa, the Poisson's ratio was 0.25 and the residual stress in the film was estimated at 30 MPa for the coating cured at 220°C .

7.3 Finite Element Modeling of the Cut Test

The purpose of this investigation is to determine the resistance to delamination by estimating the elastic energy released when a stressed coating delaminates surrounding a cut. There is no need for complex three dimensional analysis of the stresses in the coating because the change in elastic energy is primarily associated with in-plane deformation of the cut film. Knowledge of the stresses at the

crack tip is also unnecessary because the debond shape is determined from experimental measurements.

An approximate model of the cut test was constructed using two-dimensional, 4-node, quadrilateral, plane stress, thick shell elements having six degrees of freedom per node. The aspect ratio of elements used in the analysis is approximately 1. The finite element program COSMOS/M was used for all of the analysis presented in this thesis.⁹ Linear elasticity and small strains were assumed for all calculations. Internal tensile stress was imparted to the model by specifying a positive thermal expansion coefficient and applying a uniform negative temperature to the entire structure. The estimated residual stress in a polyimide cured on glass at 360°C is 27 MPa. The material properties of polyimide used in the analysis are $\Delta\alpha = 21 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, $E = 2500 \text{ MPa}$ and $\nu = 0.34$. The temperature applied to the structure is -340°C.

7.3.1 Elastic Energy and Thermodynamics

The first law of thermodynamics gives the complete energy balance for a deformation process per unit volume of material.

$$dU = dq + dW \tag{7.9}$$

U is the internal energy, q is the heat flow and W is the work done on or by the system. For a solid, the incremental work done during deformation per unit volume is

$$dW = \sigma_{ij} de_{ij} \tag{7.10}$$

Where σ_{ij} is the stress tensor and e_{ij} is the Cauchy strain tensor. The first law of thermodynamics for solid deformation is

$$dU = dq + \sigma_{ij} de_{ij} \quad (7.11)$$

For reversible deformation processes, the second law of thermodynamics can be combined with the first law to yield

$$dU = TdS + \sigma_{ij} de_{ij} \quad (7.12)$$

where S is the entropy per unit volume and T is the temperature of the system. The Helmholtz function, A , giving the maximum work which can be done by a system,

$$A = U - TS \quad (7.13)$$

can be combined with equation 7.12 to yield

$$dA = \sigma_{ij} de_{ij} - SdT \quad (7.14)$$

From equation 7.14, it follows that

$$\left[\frac{\partial A}{\partial e_{ij}} \right]_T = \sigma_{ij} \quad \left[\frac{\partial A}{\partial T} \right]_{e_{ij}} = -S \quad (7.15)$$

from which:

$$\left[\frac{\partial \sigma_{ij}}{\partial T} \right]_{e_{pq}} = - \left[\frac{\partial S}{\partial e_{ij}} \right]_T \quad (7.16)$$

From these relations, it can be seen that the Helmholtz free energy and the stress can change with temperature at constant strain. Thus, temperature induced changes in the state of stress and strain in a solid are fundamentally different from changes induced by distortional mechanical loads. For a body subject to thermal loading only, it is possible to have non-zero strains and zero stresses or zero strains and

non-zero stresses. Thermal loads result in volume dilatation only, while most mechanical loads, except for uniform pressure, produce volume dilatation and distortional strain. For an isotropic elastic material with thermal expansion coefficient α , the stress-strain-temperature relations in Cartesian coordinates are

$$e_{ij} = \frac{1}{E} \left[(1+\nu)\sigma_{ij} - \nu\delta_{ij}\sigma_{kk} \right] - \delta_{ij}\alpha\Delta T \quad (7.17)$$

Where δ_{ij} is the Kroneker delta. In its most general form, the strain energy of an isotropic elastic solid can be expressed as a function of the first two invariants of the strain tensor, J_1 and J_2 , and the temperature change, ΔT .¹⁰

$$U = V \left[\frac{1}{2}(\lambda + \mu)J_1^2 - 2\mu J_2^2 - \frac{E\alpha}{1-2\nu}J_1\Delta T + \frac{3E\alpha^2}{2(1-2\nu)}\Delta T^2 \right] \quad (7.18)$$

λ and μ are the Lamé constants and V is volume. Computation of the strain energy in the body subject to thermal loads from $1/2V\sigma_{ij}e_{ij}$ will result in erroneous strain energy. For temperature changes, the strain energy is modified by two temperature dependent terms describing the entropy changes due to volume dilatation and temperature changes. The strain energy, in terms of the stress components, does not explicitly contain T . For isotropic linear elastic materials, equation 6.9 can be written in terms of the first two stress invariants, I_1 and I_2 .

$$U = \frac{V}{2E} \left[I_1^2 - 2(1+\nu)I_2 \right] \quad (7.19)$$

Strain energies calculated from equation 7.19 will be correct for thermal, mechanical or combined loading.

Version 1.65 of COSMOS/M finite element software computes strain energy from the stresses and strains using the formula $1/2V\sigma_{ij}e_{ij}$ which

yields the correct result for mechanical loads but not for thermal loads due to omission of the entropy terms. Thus, it was necessary to write a computer program to calculate the strain energy from equation 7.19 using the stresses output by COSMOS/M. Only node or element stresses and displacements were available in the output file. Lack of nodal positions required to calculate element volumes made the program inappropriate for calculating the strain energy of models with differing element volumes. The "c" source code of the computer program, specifically written for shell elements, may be found in Appendix B. The program results were compared with analytical solutions for two cases shown in Figure 7.3. In the first test, a negative temperature change was applied to a plate with a positive thermal expansion coefficient where the plate is clamped along the edges. The resulting stress state is equal biaxial tension and the energy can be calculated from

$$U = \frac{VE(\alpha\Delta T)^2}{1-\nu} \quad (7.20)$$

The elastic energy calculated by the program was identical to the analytical solution for the thermally loaded plate. A coating on a rigid and zero thermal expansion substrate cannot develop strains in the plane of the coating, but will change in thickness when subject to thermal shrinkage. A finite element model using shell elements neglects the strain perpendicular to the plane of the coating. COSMOS/M, using the incorrect strain energy formula for thermal stress, calculated a strain energy 10^{-30} smaller than the correct value, for this case. In the second test, pure shear was applied to a plate by specifying zero x displacement on the bottom edge and a non-zero x displacement, u_x , on

Figure 7.3 Models used to test the strain energy program. The top model is a plate, clamped along its edges and subject to a negative temperature change. The bottom model is a plate subject to pure shear.

the top edge. Zero y displacement was specified for all nodes. The displacement boundary conditions result in a shear strain, γ , equal to u_x divided by the y dimension of the plate and a shear stress, $\tau = \gamma\mu$, where μ is the shear modulus, throughout the plate. Pure shear is an excellent test of the program because it generates all of the in-plane stress components. For pure shear the elastic energy is

$$U = \frac{V\tau^2}{2\mu} \quad (7.21)$$

For pure shear, the program result is identical to the energy calculated by COSMOS/M and differs from the value calculated from equation 7.21 by 3%.

7.3.2 Circular Cuts

Circular cuts were made through 68 μm thick PMDA-ODA films cast on 1/4" thick glass substrates. A surgical scalpel was used to cut around dimes which were glued to the top of the film. The radius of the cut was 8.5 mm. The radius of the delaminated region, 14.5 mm $\pm$.5 mm, was determined from 18 measurements made on three cuts in differing locations on the same film.

An illustration of the delamination surrounding a circular cut is shown in Figure 7.4. Equations 7.7 and 7.8 can be used to calculate the elastic energy in the annular region between the cut radius and the delamination radius for the cut coating before and after delamination. Using the material properties listed at the beginning of this section,

Figure 7.4 An axial section showing delamination in a film surrounding a circular cut.

an energy of 0.00567 J is calculated for the bonded state and 0.00335 J is calculated for the delaminated film.

Figure 7.5 shows the finite element model of a circular cut. The annular region was meshed with 12 rings of 48 4-node, quadrilateral shell elements for a total of 576 elements. The model of the cut and bonded film has zero displacements set for all nodes lying on the curves $r_1 = a$, the cut boundary, and $r_2 = b$, the delaminated radius. The calculated stress in the annular region is uniform equal biaxial tension, consistent with equation 6.8, which predicts $\sigma_{xx} = \sigma_{yy} = 27 \text{ MPa}$. The Figure shows the model of the cut delaminated film in which the displacements of all nodes lying on the curve $r_2 = b$, are set to zero, but no force or displacement conditions are placed on nodes lying on the curve $r_1 = a$. When boundary conditions on a curve in a two dimensional model, or on a surface in a three dimensional model are not specified, that geometric entity is assumed to be free and stresses normal to the tangent of the curve or the plane of the surface will be zero for a properly designed finite element model. Bending shear stresses, or all shear stresses not acting in the plane of the surface, should also disappear at a free surface.

The resultant displacements, the magnitude of the displacement vector, of the delaminated film are shown in Figure 7.6. The resultant displacements are radially symmetric with maximum values reaching 70% of the film thickness at the center of the annulus. The total radius of the delamination boundary, r_2 , is 213 film thicknesses. The stresses acting in the plane of the coating in the delaminated region, calculated by Finite element analysis are shown in Figures 7.7, 7.8 and 7.9. The stresses are highest in the center of the annulus. The strain energy

Figure 7.5 Finite element model of delamination in a film surrounding a circular cut.

u_{res}	microns
1	47.6
2	42.3
3	37.0
4	31.7
5	26.4
6	21.1
7	15.9
8	10.6
9	5.28
10	1.0E-16

Figure 7.6 Resultant displacement of the delaminated film surrounding a circular cut.

σ_{xx}	MPa
10	31.4
9	28.0
8	24.7
7	21.3
6	18.0
5	14.6
4	11.2
3	7.88
2	4.52
1	1.16

Figure 7.7 Tensile stress, σ_{xx} , acting on the cut film after delamination.

σ_{yy}	MPa
10	31.4
9	28.0
8	24.7
7	21.3
6	18.0
5	14.6
4	11.2
3	7.88
2	4.52
1	1.16

Figure 7.8 Tensile stress, σ_{yy} , acting on the cut film after delamination.

σ_{xy}	MPa
10	15.3
9	11.9
8	8.51
7	5.11
6	1.70
5	-1.70
4	-5.11
3	-8.51
2	-11.9
1	-15.3

Figure 7.9 Shear stress, σ_{xy} , acting on the cut film after delamination.

was calculated from the stresses in the output files. The program listed in Appendix B could not be used due to the variation of element volume with radial position. Fortunately, symmetry dictates that the strain energy in an element is only a function of radial position. The same holds true for the stresses in cylindrical, but not Cartesian, coordinates. Thus, the strain energies of one radial section of 12 elements could be computed using equation 7.19. Multiplying the energy in each element by 48 results in the elastic energy of the entire ring of elements. The stress output for a radial section of elements is listed in Table 7.1. The σ_{xz} and σ_{yz} shear stress components are all zero. The element radial positions, volumes, and the strain energy in the ring of elements between the radii, r_1 and r_2 are also listed in Table 7.1. The elastic energies calculated from the element stresses agree with those calculated from equations 7.7 and 7.8 to 3 significant figures. This verifies the validity of the finite element model. The difference between the elastic energies of the bonded and delaminated states is 0.00232 J. When divided by the area of the annular region, .000433 m², the adhesion energy is 5.36 J/m². All of the adhesion energies reported in this thesis are on a per unit area of interface basis and should not be confused with fracture energy which is usually reported on a surface area basis and is thus equal to one-half the adhesion energy. The value is higher than that reported by Farris and Bauer² because the films used in this study were cured at higher temperatures.

The accuracy of the adhesion determined from a circular cut will depend on the deviation of the delaminated radius, variations in the film thickness and the accuracy to which the residual stress is known.

The variation of the adhesion with delamination radius can be determined from equations 7.7 and 7.8. The adhesion for $r_2 = 13.5$ mm is equal to 5.19 J/m^2 and the adhesion for $r_2 = 15$ mm is equal to 5.85 J/m^2 . The energy in the film is proportional to the film thickness. The calculated adhesion energy is also proportional to film thickness and will vary accordingly. Film thickness was measured with a Mitutoyo electronic micrometer having a resolution of $\pm 0.1 \text{ }\mu\text{m}$. The deviation in measured thickness with position was approximately $\pm 5\%$ of the film thickness. The most significant source of uncertainty in these measurements is the estimated value for the residual stress. Conservatively, the true stress in the bonded polyimide films on glass will be within $\pm 25\%$ of the stress estimated from experimental measurements of the stress in polyimide films cured on various substrates, see Chapter 6. However, the adhesion energy is proportional to the square of the stresses. For an accuracy of $\pm 25\%$, the reported adhesion energies could vary from 0.75^2 , 0.56 , to 1.25^2 , 1.56 , times the reported values.

Table 7.1 Calculation of elastic energy for concentric rings of elements based on the stresses in one radial section.

Ring	r_1 mm	r_2 mm	$V \text{ m}^3 \times 10^{-9}$	σ_{xx} MPa	σ_{yy} MPa	σ_{xy} MPa	$U \text{ J} \times 10^{-4}$
1	8.5	9.0	1.868	30.95	1.022	1.305	3.519
2	9.0	9.5	1.975	29.40	2.593	1.676	3.266
3	9.5	10.0	2.082	28.07	3.905	1.472	3.040
4	10.0	10.5	2.189	26.93	5.021	1.004	2.890
5	10.5	11.0	2.295	25.94	5.999	0.4795	2.762
6	11.0	11.5	2.402	25.05	6.874	0.01515	2.678
7	11.5	12.0	2.509	24.26	7.657	-0.3314	2.616
8	12.0	12.5	2.616	23.56	8.350	-0.5399	2.570
9	12.5	13.0	2.722	22.96	8.955	-0.6090	2.549
10	13.0	13.5	2.829	22.44	9.476	-0.5435	2.534
11	13.5	14.0	2.936	22.00	9.927	-0.3462	2.550
12	14.0	14.5	3.043	21.61	10.33	-0.0129	2.565

7.3.3 Finite Element Analysis of Straight Cuts

Polyimide, PMDA-ODA, films were cast and thermally imidized on a glass microscope slide according to the procedure delineated in Section 4.2. Several Cuts, ranging in length from slightly less than 1 mm to almost 5 mm were made through the film to the glass substrate using a surgical scalpel. When films were cut at room temperature, a delaminated region appeared instantaneously. Films were also cut on a microscope hot stage at a temperature of 300°C. At this temperature, the stress in the films is relatively small and no delamination was observed. The film was cooled in several steps and was observed for 1/2 hour at each temperature. At temperatures as low as 80°C, no

delamination was observed. When the film was cooled from 80°C to 30°C, extensive delamination occurred. Photographs of the cut film at 300°C and 30°C are shown in Figure 6.9.

The cut film was exposed to ambient conditions for several hours before photographs of the delaminated areas surrounding each cut were made using an optical microscope. Figure 7.10 shows a photograph of a 1450 μm long cut in an 80 μm thick film. The image in the photograph is approximately 23 times the actual size. The image was taken using polarized and reflected light. Under these lighting conditions, there is a black area surround the cut which is approximately 2 film thicknesses wide. The black region is a reflection from the coating edge and nearly disappears when viewed with transmitted light. Examination under transmitted light also reveals that the length of the cut extends to the edges of the black regions. Photographs used to model the cut regions were taken with reflected light since delamination is readily apparent under these conditions. Figure 7.11 shows the finite element model of the cut delaminated film corresponding to the photograph shown in Figure 7.10. One-half of the film is modeled and an axis of symmetry is assumed on a line running through the film coincident with the cut. 600 4-node, quadrilateral shell elements are used. The bonded film is modeled by specifying zero displacements for all nodes around the perimeter of the model. The delaminated film is modeled by specifying zero displacements for all nodes in regions where the film is bonded to the substrate. Nodes lying on the cut or in delaminated regions of the film have complete translational freedom. When the boundary of the delaminated area extends beyond the ends of the cut, the nodes lying in this region which are collinear with the cut are

Figure 7.10 Optical micrograph of a cut in a polyimide film on a glass microscope slide viewed under polarized reflected light.

Figure 7.11 Finite element model of cut delaminated film.

constrained to have zero displacements perpendicular to the cut. The stress state of the bonded film is equal biaxial tension with $\sigma_{xx} = \sigma_{yy} = 27$ MPa and the displacements are zero. For the cut and delaminated film, Figure 7.12 shows the magnitude of the resultant displacement vector and Figures 7.13 and 7.14 show the components in the x and y directions. The units of displacement are microns and the maximum displacement is approximately 1/10 of the film thickness. The maximum extent of delamination is 23 film thicknesses from the cut. Most of the displacement is perpendicular to the cut with the maximum at the cut edge. The y component, parallel to the cut, of the displacement reaches a maximum value on the cut edge between the center and the ends of the cut. The displacements in the delaminated region extending beyond the cut ends are nearly zero. The finite element stress output is displayed graphically in Figures 7.15, 7.16, and 7.17. The state of stress in the bonded regions is equal biaxial tension with $\sigma_{xx} = \sigma_{yy} = 27$ MPa. The tensile stresses attain minimum values at the cut edge and increase with the distance from the cut. A stress concentration develops at the ends of the cuts. The maximum calculated tensile stresses, approximately twice the stresses in the bonded film, occur near the cut tip. Large in-plane shear stresses are also developed near the cut tip with maximum magnitudes equal to one-half of the in-plane stresses in the bonded film. Elastic energy in the delaminated film was calculated from the nodal stress outputs using the computer program listed in Appendix A. The elastic energy in the bonded film can be calculated from equation 7.20. The adhesion energy is computed by dividing the difference between the elastic energy in the cut film before and after delamination by the area of delamination.

U_{res}	microns
10	9.88
9	8.79
8	7.69
7	6.59
6	5.49
5	4.39
4	3.29
3	2.20
2	1.10
1	1.0E-16

Figure 7.12 Resultant displacement of the delaminated film.

U_x	microns
10	0.0187
9	-1.08
8	-2.18
7	-3.28
6	-4.38
5	-5.48
4	-6.58
3	-7.68
2	-8.78
1	-9.88

Figure 7.13 Displacement component, u_x , of the delaminated film perpendicular to the cut.

Figure 7.14 Displacement component, u_y , of the delaminated film parallel to the cut.

σ_{xx}	MPa
10	63.4
9	55.7
8	48.0
7	40.3
6	32.6
5	24.8
4	17.1
3	9.44
2	1.74
1	-5.97

Figure 7.15 Stress component, σ_{xx} , of the delaminated film perpendicular to the cut.

Figure 7.16 Stress component, σ_{yy} , of the delaminated film parallel to the cut.

σ_{xy}	MPa
10	14.1
9	11.0
8	7.85
7	4.17
6	1.57
5	-1.57
4	-4.71
3	-7.85
2	-11.0
1	-14.1

Figure 7.17 Shear stress, σ_{xy} , the delaminated film acting in the plane of the film.

Adhesion energies calculated for 5 cuts of varying lengths in the same film are tabulated in Table 7.2.

Table 7.2 Interfacial adhesion computed from finite element analysis of straight cuts in coatings.

Cut length μm	$\Delta E \text{ J/m}^2$
572	3.9
748	5.4
1450	5.3
3111	7.0
4735	5.0
Mean	5.3
Standard Deviation	1.1

The measured adhesion energy is an average value representative of contributions from all three modes of crack loading. The mode mixity changes as the delamination boundary advances away from the cut, eventually reaching steady state after the crack has advanced several film thicknesses. Thus, it would be reasonable if the adhesion energy were dependent on cut length when the length is on the order of a film thickness. The data is insufficient to verify this, but the adhesion energy does not appear to exhibit any strong dependence on cut-length over the range of lengths used in this study. The possibility that the adhesion energy is strongly cut-length dependent is a limitation to the usefulness of the data since actual coating failure may initiate from cracks of any length.

The measured adhesion energy does not appear to contain a significant contribution from mode 3. If mode 3 were significant, the adhesion energy determined from straight cuts should be larger than that

determined from circular cuts which have no mode 3 contribution. The average adhesion energies determined from straight and circular cuts are identical. The same material property and stress values were used in all calculations. The agreement may be coincidental, but the statistical deviations are not large enough to cast doubt upon their equality. The adhesion energy, 5.3 J/m^2 , is much closer to Kim's value for the combined mode 1 and mode 2 toughness of polyimide/glass, $4.1\text{-}4.5 \text{ J/m}^2$, than it is to Kim's value for the mode 3 toughness, 15 J/m^2 .⁶ Comparison with Kim's data is particularly appropriate because he used similar substrate material, a similar polymer precursor, based on PMDA-ODA in NMP, a similar curing procedure and he used the same data to estimate the film residual stress.

Statistical deviations in the calculated adhesion energy reflect actual variations in the toughness of the interface and the mode of crack propagation as well as dimensional errors in modeling the delamination boundary, cut and stand off regions. Errors in the estimated stress and film thickness do not factor into the statistical deviation since the same values were used for all of the straight cuts.

The accuracy of the adhesion energy determined from straight cuts suffers from the same limitations as that determined from circular cuts. If the residual stress and film thickness are known accurately, an absolute upper limit on the adhesion energy, of films which delaminate, is established by the total strain energy in the film. For the $80 \text{ }\mu\text{m}$ thick films on glass, this value is 15.5 J/m^2 . Adhesion energy determined from circular cuts is relatively insensitive to small deviations in the radius of delamination boundary. However, the energy determined from straight cuts shows extreme sensitivity to the length of

the delaminated region beyond the edge of the cut, the stand-off, while it remains relatively insensitive to small deviations in the shape of the delamination boundary elsewhere. For the cut shown in Figure 7.10, releasing displacement conditions for all nodes, collinear with the cut, except for the node at each end of the delaminated region, would change the calculated energy release from 5.3 to 7.3 J/m². Theoretical modeling has established that mode 3 controls the shape and extent of the stand-off region. According to the theory, in the absence of mode 3, the boundaries of the delaminated regions should be attached to the cut ends. The existence of the stand-off region at the ends of the straight cuts and the sensitivity of the adhesion energy to the size of the stand-off region appear to contradict the evidence for mode 3 having little influence on the adhesion energy.

Modeling a delaminated film with finite elements is only an approximation of the actual physical problem. The use of shell elements neglects out of plane bending and assumes constant stresses through the thickness of the film. Both of these conditions break down within a few film thicknesses of the delamination boundary. The analysis in Chapter 6 show tremendous variation in the stresses, through the coating thickness, near an edge. Similar variation would be expected near the delamination boundary. However, the stresses are nearly uniform beyond several film thickness from an edge. The ratio of tensile stresses at the top of the film to those at the film/substrate interface is plotted in Figure 6.8 which shows that the stresses become nearly uniform through the film thickness within 2-3 coating thickness from an edge. Theoretical analysis of the cut test by Choi and Kim⁶ produces a similar conclusion showing that bending is only important within 1 film

thickness from the edge. The cut lengths in this study varied from 7-60 film thicknesses and the extent of delamination varied from 8-73 film thicknesses from the cut. Shell elements may be a poor approximation of the physical problem for the shortest cuts but should provide excellent accuracy for the longer cuts. For the longer cuts, the change in strain energy with delamination is primarily associated with in-plane deformation of the film.

The accuracy of the finite element solution near the cut-tip may be limited due to a stress singularity near the cut-tip and an insufficient element density in this region. However, the calculated adhesion energy will not be significantly affected because the region of stress concentration is a small fraction of the model.

7.4 Summary

A new adhesion test has been developed for coatings with residual biaxial tension. When these coatings are cut through to the substrate, delamination will propagate from the cut-through if the stress in the film is high. Finite element analysis was used to calculate the elastic energy in the cut, delaminated films. The difference between the elastic energy in the cut film, before and after delamination, divided by the area of delamination is a measure of the adhesion energy. Previous investigators found an analytical solution for a circular cut-through in a stressed film. This problem was used to check the accuracy of the finite element solution. The adhesion energy of polyimide/glass was calculated for several straight and circular cuts. The same

adhesion energy, 5.3 J/m^2 , was obtained for straight and circular cuts. The calculated adhesion energy is an average value because the energy release rate varies as the delamination boundary advances from the cut. The adhesion energy contains contributions from all three modes of crack propagation. However, the results indicate that mode 3, dominant near the ends of the cut, does not significantly alter the measured adhesion energy. The accuracy of the test is limited by knowledge of the residual stress in the film because the adhesion energy is dependent on the residual stress squared.

The cut-through test is an excellent test to obtain the adhesion energies of stressed coatings for use in engineering design. In engineering applications, adhesive failure of these coatings by delamination, initiating from a crack in the film, is a likely mode of failure.

References

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CHAPTER 8

SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK

8.1 Summary

The goal of this dissertation was to analyze adhesion in terms of a global thermodynamic energy balance. From a global thermodynamic perspective, a complete detailed analysis of the micro-mechanisms and fracture mechanics of separating adhesively bonded materials is unnecessary because the intent is purely to determine how the energy expended in separating the bonded materials, the adhesion energy, is consumed. Globally partitioning the adhesion energy shows which aspects of adhesively bonded structures are most important in determining the total adhesion energy. Hopefully, this work can serve as a guide to micro-mechanics modelers showing them which aspects of the structures deserve emphasis.

An energy balance was proposed which is applicable to the separation of adhesive bonds between coatings or tapes and substrates. Adhesive bonds were separated by peeling which is used extensively to characterize the adhesion strength of flexible tapes and coatings. The experimental approach to decomposing the adhesion energy was to simultaneously measure the mechanical work expended and heat dissipated during peeling of adhesively bonded materials. This accomplished partitioning of the mechanical work into heat and an internal energy change which is the difference between the internal energy of the peeled and bonded materials. Additional experiments were done on the peeled

materials to determine the mechanisms responsible for changing the internal energy.

Peeling of two commercially important classes of adhesive systems was studied; pressure sensitive adhesive (PSA) tapes and polymeric coatings. In the peel test, most of the mechanical energy expended is dissipated as heat. Almost all of the work which is not dissipated as heat is stored as latent internal energy in the peeled materials.

During 180° peeling, the peeled material must be bent through 180° to bring stress to bear on the interface. When polyimide coatings were peeled from aluminum substrates, almost all of the mechanical energy was consumed by propagating the bend in the peeling coating. The fraction of the peel energy dissipated as heat was $48 \pm 1.3\%$ and nearly all of the remainder was stored as latent internal energy in the peeled polyimide. When the bend was propagated through aluminum, which has a limited capacity to store latent internal energy, $100 \pm 2.7\%$ of the mechanical energy was dissipated as heat. This means that it is unlikely that more than 2.7% of the peel energy could have been consumed by other mechanisms of energy consumption, such as surface formation, which could not be detected within experimental precision.

When a stiff coating which strongly adheres to a rigid substrate is peeled, most of the mechanical energy is consumed by deforming the bulk of the peeling film. For a proper characterization of the adhesion energy, it is necessary that inelastic deformation and dissipation be caused directly by the crack tip stresses associated with the propagating peel crack, not bending stress in the film. If separation occurs cohesively within one or both of the bonded layers, it is impossible to separate the bonded materials without crack tip specific

deformation and dissipation. When the majority of the mechanical work is consumed by bending, the peel energy outrageously overestimates the adhesion energy which is therefore totally useless for predicting failure of adhesive bonds under loading conditions other than peeling.

When PSA tapes were peeled, the mechanical work was consumed by propagating the bend in the peeled backing and by deforming the PSA adhesive layer. The fraction of the mechanical work which was dissipated as heat depended on the peel rate and the backing thickness. For the limited range of peel rates and PET backing thicknesses used in this study, 69-86% of the peel energy was dissipated as heat. It was found that elastomeric PSA materials were incapable of storing any of the energy of deformation as latent internal energy. All of the energy expended in deforming a PSA will be dissipated as heat. The fraction of the peel energy, not dissipated as heat, is stored in the backing. The energy stored in the backing is indicative of the total mechanical energy expended in deforming it. Studies of PET deformation showed that 25-50% of the energy under the stress-strain curve is stored in deformed PET. From this result, it is estimated that 34-51% of the energy used to peel PET backed PSA tapes from aluminum at 2.71 cm/min is used to deform the PET backing and the remainder is used to deform the PSA layer. The relative fractions of the energy expended in deforming the PSA and the backing will be strongly dependent on the peel rate and backing thickness. The energy expended in deforming the PSA is the direct result of separation, not bending, and it is part of the true adhesion energy. In the vicinity of the peel front, the entire PSA layer behaves similar to craze matter. The peel test is not a bad test for measuring the adhesion of PSA tapes because a large fraction of the

energy is consumed by deformation the PSA layer and it is impossible to separate materials bonded with a PSA without causing extensive deformation of the adhesive layer. It should be possible to compare the adhesion of different PSA tapes by peeling providing that the backing materials exhibit similar dissipative characteristics.

From an energetics point of view, the energy consumed to create the surfaces exposed by peeling is insignificant since it accounts for an indeterminately small fraction of the total peel energy. However, the peel energy does depend on the chemistry and physics of the interface because the peeled material can only be subject to stress, resulting in dissipation, if the interface is strong. A correlation between the surface energies of the materials exposed by peeling and the peel energy was observed using carefully controlled conditions, but it is not generally applicable to all systems. In systems like the polyimide coated aluminum where separation occurs cohesively within the polyimide, the adhesion energy should be independent of the surface properties at the interface providing that sufficient attractive forces exist at the interface to produce cohesive failure. The adhesion which can be achieved by changing the surfaces at the interface is limited by the cohesive strength of the bonded materials and the stress distribution in the joint.

The fact that most of the peel energy of stiff coatings is consumed by bending creates a serious deficiency of the test for use on coatings containing tensile stresses. When a crack is introduced in the coating, a shear stress, which acts to delaminate the coating, is concentrated near the intersection of the crack and the coating-substrate interface. This process occurs with little bending

deformation as compared to peeling and requires considerably less energy. As a result, spontaneous delamination was observed for coatings exceeding a critical thickness while slightly thinner coatings had high peel strengths. The spontaneous delamination energy of a 120 μm thick polyimide coating from aluminum is estimated to be less than 23 J/m^2 while the extrapolated value of the peel energy at that film thickness is 500 J/m^2 . The peel test is not capable of detecting detrimental effect of tensile stresses on the adhesion of coatings.

For coatings with residual tensile stresses, a superior adhesion test was developed based on calculating the stored elastic energy released when the stressed coating delaminates surrounding a cut-through. Photographs of delamination in cut coatings were taken and the coatings were modeled using linear elastic finite element analysis to calculate the stored elastic energy released in the delaminated region surrounding the cut-through. Detailed modeling of the stresses at the crack tip and near the cut ends was unnecessary to determine the approximate energy release. In the cut-through test, the stored elastic energy in the coating released by delamination is predominately consumed by crack tip specific dissipation and creation of the delamination surfaces.

8.2 Recommendations for Future Work

This work has only been a first attempt at directly measuring the heat of a fracture process. A more comprehensive study of fracture processes, involving both bi-material interfaces and homogenous materials could be done with the deformation calorimeter.

The peel behavior of the systems studied in this thesis should be studied over a wider range of viscoelastic behavior for the bonded materials. Since the accessible deformation rates are limited, this could be done by changing the testing temperature. It would also be interesting to compare the work and heat of peeling materials from substrates with identical compositions but different surface roughnesses.

Fracture experiments other than peeling should be investigated with the calorimeter. Double trouser tearing of rubbers can be done within the calorimeter sample chamber. Fracture energy samples, such as compact tension samples, could be broken in the calorimeter. The samples would have to be small enough to fit within the calorimeter cell and have a small thermal mass.

Cut tests should be done on polyimide coatings of differing thicknesses bound to glass. It would be interesting to measure the delamination resistance of polyimide coated on glass plates which had been previously coated with different vapor deposited metals to see if there is any correlation between the adhesion energy and the metal surface energy.

APPENDIX A

DEFORMATION CALORIMETER SOFTWARE

This appendix contains commented source listings of the deformation calorimeter software written in Microsoft C version 5.0. The software consists of the following main programs;

- ANALYZE The main program for analyzing peel test data,
- ATENSILE The main program for analyzing tensile test data,
and the following subroutines;
- PLOT Plotting routines developed with the Graphic 3.02 library of
c functions from Scientific Endeavors Corporation,
Kingston, TN,
- SUBS Subroutines for data smoothing, decimation of data points
prior to plotting, linear regression and conversion of
elapsed time to array vectors and
- VIDEO A library of c functions which use the DOS interrupts to
control input from the keyboard and output to the
video display.

The following input files, all stored in the directory c:\caldata, are required by the software:

- *****.HDR Sample geometry and calibration constants stored in ASCII
text format. The first line of the file contains the
following; load cell calibration in kg/volt, lvd
calibration in m/volt, calorimeter constant in
joule/volt*sec and calorimeter time constant in seconds.
The second line of this file contains; Initial grip
separation in meters, initial strain, sample width in mm and
sample thickness in mm. The third and final line of this
file contains the sample description, experiment description
and run date.
- *****.PRS This file contains differential pressure data stored in 4
byte single precision IEEE format.
- *****.TIM This file contains the elapsed time from the beginning of
data collection corresponding to the data points in the
other data files stored in 4 byte single precision IEEE
format.
- *****.FOR This file contains the force data stored in 4 byte single
precision IEEE format.
- *****.DIS This file contains the displacement data stored in 4
byte single precision IEEE format.

MAIN PROGRAM ANALYZE

```

#include <stdio.h>
#include <conio.h>
#include <math.h>
#include <string.h>
#include <ctype.h>
#include <malloc.h>
#include <io.h>
#include <types.h>
#include <stat.h>
#include <fcntl.h>

/* plot field selection and label index*/
int fildx1,fildx2,fildx3;
char filnam[8];
char filnam2[8];

/* plot labeling */
extern char xlb[40];
extern char yllb[40];
extern char y2lb[40];
extern char tplb[80];
extern char tplb2[70];
extern char infol[70];
extern char info2[70];
extern char info3[70];
extern char info4[70];

/* plot vectors */

extern float cx[500],cyl[500],cy2[500];

char l1[40] = "FILE: ";
char l2[40] = "Time (seconds)";
char l3[40] = "-Pressure Difference(volts)";
char l4[80] = "DIFFERENTIAL PRESSURE AND FORCE VS. TIME";
char l5[40] = "Integrated pressure (v*sec)";
char l6[70] = "180 PEEL IN THE DEFORMATION CALORIMETER";

/* pointers to allocated arrays and file streams*/
FILE *file_ptr;
FILE *header, *prsfile, *forfile, *timfile,*disfile;
float *tim, *disp, *force, *heat, *work;
float prs[2500];

main()
{
    short a;
    int l,i,j;
    float sum1,sum2,sum3;
    double scr;
    char char1[60];
    char char2[60];
    char *string, *result;
    char xc[40];
    char baselabel[60];
/* data loading and decimation */
int datcrs;
int inc,npts, point,npts_in_file;
/* calibrations */
float lc, lvdt, c, tau;

```

```

/* sample dimensions */
float init_sep, length, width, thickness;
/* baseline calculation */
float basel, base2, base;
float slope, intcpt;
/* integration variables */
float start, end, dur;
float int0p, int1p, qatt, power;
int dx1, dx2, dx3, ppts;
float datum, datum1, datum2;
float idisp, incdisp;
double sumdisp;
double deltal;
float deltax, avprs, avforce, avtim, intwk;
int bytesread, bytes;
float shift;
char material[70];
char experiment[70];
char date[10];
char ex1[3], ex2[3], ex3[3];
unsigned int max_bytes;
int ppasses, dpasses, tim_flag, area_flag;
float area;
/* initialize pointers*/
string = &char1[0];
result = &char2[0];

/* get filename and open files */

new_file:
    vinit();
    vclear(0,0,24,79,2);
    setpos(0,0);

getname:
    say(0,0,"Filename: ");
    rstr(&filnam[0]);
    strcpy(filnam2, filnam);
    l = strlen(filnam);

    if ( l > 8 ) {
        say(2,0,"Maximum filename length is 8 characters.");
        goto getname;
    }

reanalyze:
    free((void *)tim);
    free((void *)heat);
    free((void *)work);
    free((void *)disp);
    free((void *)force);

    strcpy(xc, "c:\\caldata\\");
    result = strcat(xc, filnam);
    result = strcat(xc, ".prs");
    if ((prsfile = fopen(xc, "r+b")) == NULL) goto nofile;

    strcpy(xc, "c:\\caldata\\");
    result = strcat(xc, filnam);
    result = strcat(xc, ".tim");
    if ((timfile = fopen(xc, "r+b")) == NULL) goto nofile;

    strcpy(xc, "c:\\caldata\\");

```

```

        result = strcat(xc,filnam);
        result = strcat(xc,".for");
        if ((forfile = fopen(xc,"r+b")) == NULL ) goto nofile;

        strcpy(xc,"c:\\caldata\\");
        result = strcat(xc,filnam);
        result = strcat(xc,".dis");
        if ((disfile = fopen(xc,"r+b")) == NULL ) goto nofile;

        strcpy(xc,"c:\\caldata\\");
        result = strcat(xc,filnam);
        result = strcat(xc,".hdr");
        if ((header = fopen(xc,"r")) == NULL ) goto nofile;

        goto files_loaded;

nofile:
        say(4,0,"This file is not present, reenter: ");
        clearerr(timfile);
        clearerr(prsfile);
        clearerr(forfile);
        clearerr(disfile);
        clearerr(header);
        goto getname;

files_loaded:

npts = fread((char *)prs,sizeof(float),2500,prsfile);
npts_in_file = npts;
bytes = npts*4;

/* allocate memory for data vectors based on number of data points */
if((    tim = (float far *) _fmalloc(bytes)) == NULL)
    (printf("allocation failed\n"); exit(0);)
    max_bytes = _fmsize(tim);

if((    heat = (float far *) _fmalloc(bytes)) == NULL)
    (printf("allocation failed\n"); exit(0);)
    max_bytes = _fmsize(heat);

if((    work = (float far *) _fmalloc(bytes)) == NULL)
    (printf("allocation failed\n"); exit(0);)
    max_bytes = _fmsize(work);

if((    disp = (float far *) _fmalloc(bytes)) == NULL)
    (printf("allocation failed\n"); exit(0);)
    max_bytes = _fmsize(disp);

if((    force = (float far *) _fmalloc(bytes)) == NULL)
    (printf("allocation failed\n"); exit(0);)
    max_bytes = _fmsize(force);

/* read raw data */

datcrs = 1;
read_files:

npts = fread((char *)tim,sizeof(float),npts,timfile);
npts = fread((char *)force,sizeof(float),npts,forfile);
npts = fread((char *)disp,sizeof(float),npts,disfile);

files_read:
    fclose(timfile);

```

```

        fclose(prsfile);
        fclose(forfile);
        fclose(disfile);

        /* load header file */

fscanf(header,"%f %f %f %f \n",&lc, &lvdt, &c, &tau);
fscanf(header,"%f %f %f %f \n",&init_sep, &length, &width,
        &thickness);
fscanf(header,"%[^!\\"] %s %[^!\\"] %s %[^!\\"]
\n",material,xc,experiment,xc,date);

/* start analysis*/
/*****
/* smooth data */

say (6,0,"Do you want to smooth the raw data(Y/N)?");
rstr(xc);

if ( tolower(xc[0]) == 'y' )
{

say(8,0, "Number of passes for displacement:");
rint(&dpasses);
say(9,0, "Number of passes for pressure:");
rint(&ppasses);

if( dpasses > 0)
    { smooth(dis, npts, dpasses);}

if( ppasses > 0)
    { smooth(prs, npts, ppasses);}
}

npts = npts_in_file;

/* plot pressure data vs. time */

decimate(npts, &ppts, &inc);

    datcrs = 0;
    point = 0;
load_vectors:
    cx[point] = tim[datcrs];
    cyl[point] = prs[datcrs];
    datcrs = datcrs + inc;
    point = point + 1;
    if (point < ppts ) goto load_vectors;

/* set up plot */
/* fildx3 = 0 for a 2 axis plot */

    fildx1 = 2;
    fildx2 = 3;
    fildx3 = 0;
    strcpy(xlb,12);
    strcpy(ylb,13);
    strcpy(tplb,"PRESSURE VS. TIME");
    strcpy(infol,11);
    result = strcat(infol,filnam);
    strcpy(info2,"EXPERIMENT: ");
    result = strcat(info2,experiment);
    strcpy(info3,"SAMPLE: ");
    result = strcat(info3,material);

```



```

        strcpy(tplb2, 16);
        vclear(0,0,24,79,2);
        setpos(0,0);

    a = plot(fildx1,fildx2,fildx3,ppts);

/* set extensions for ASCII output files of plot vectors */
strcpy(ex1,"ttx");
strcpy(ex2,"ptx");
strcpy(ex3," ");

/* call subroutine which produces output ASCII files */
output(filnam, ppts, 2,ex1,ex2,ex3);

        vclear(0,0,24,79,2);

/*****
/* baseline correction */

        say(1,0," baseline origin (seconds):");
        rfl(&basel);
        say(3,0," baseline end (seconds):");
        rfl(&base2);

/* find datacount for both times*/
datcrs_time(basel, base2, &dx1, &dx2, tim);

/* calculate mean values for both ends */
sum2 = 0;
sum3 = 0;
for (datcrs = dx1-10; datcrs <= dx1+10; datcrs++)
{
    sum1 = prs[datcrs];
    sum2 = sum2+sum1;
}
sum2 = sum2/21;

for (datcrs = dx2-10; datcrs <= dx2+10; datcrs++)
{
    sum1 = prs[datcrs];
    sum3 = sum3+sum1;
}
sum3 = sum3/21;

/* calculate slope in volts/second */
slope = (sum3 - sum2) / (base2-basel);
intcpt = prs[dx1] - slope * basel;

/* put basel and base2 on the plot by putting in tplb2 */
/* subtract baseline from prs data*/

for ( j = 0; j <= npts; j++)
    prs[j] = prs[j] - intcpt - tim[j] * slope;

/* plot corrected pressure and force data vs. time */

    datcrs = 0;
    point = 0;
    while( datcrs < npts)
    {
        cyl[point] = prs[datcrs];

```

```

        cy2[point] = force[datcrs] * 9.81 * lc;
        datcrs = datcrs + inc;
        point = point + 1;
    }

    fildx1 = 2;
    fildx2 = 4;
    fildx3 = 1;
    strcpy(xlb,12);
    strcpy(tplb,14);
    strcpy(y2lb,"--Force(Newtons)");

    vclear(0,0,24,79,2);
    a = plot(fildx1,fildx2,fildx3,ppts);

    strcpy(ex1,"ttx");
    strcpy(ex2,"ptx");
    strcpy(ex3,"ftx");
    output(filnam, ppts, 3,ex1,ex2,ex3);
    vclear(0,0,24,79,2);

/* compute displacements */
/* for initial length use an average of first 30 points */

    suml = 0.0;
    for ( datcrs = 0; datcrs <= 29; datcrs++)
        {suml = suml + disp[datcrs];}
    idisp = suml/30;

    for( datcrs = 0; datcrs < npts; datcrs++)
    {   incdisp = disp[datcrs] - idisp;
        sumdisp = lvdtt* fabs(incdisp);
        disp[datcrs] = sumdisp;
    }

/*****
/* plot force displacement and displacement time */

say (1,0,"Do you want to plot force vs. displacement(Y/N)?");
rstr(xc);
if ( tolower(xc[0]) == 'y' )
{
    datcrs = 0;
    point = 0;
    do
    {
        cx[point] = disp[datcrs];
        cyl[point] = force[datcrs] * lc;
        datcrs = datcrs + inc;
        point = point + 1;
    }
    while(point <= ppts );

/* fildx3 = 0 for a 2 axis plot */
    fildx1 = 2;
    fildx2 = 3;
    fildx3 = 0;
    strcpy(xlb,"Displacement(meters)");
    strcpy(yllb,"Force(kg)");
    strcpy(tplb,"FORCE VS. DISPLACEMENT");
    vclear(0,0,24,79,2);
    setpos(0,0);

```

```

    a = plot(fildx1,fildx2,fildx3,ppts);
    strcpy(ex1,"dtx");
    strcpy(ex2,"ftx");
    strcpy(ex3," ");
    output(filnam, ppts, 2,ex1,ex2,ex3);
    vclear(0,0,24,79,2);
}
/*****
say (2,0,"Do you want to plot displacement vs time(Y/N)?");
rstr(xc);
if ( tolower(xc[0]) == 'y' )
{
    datcrs = 0;
    point = 0;
do
{
    cx[point] = tim[datcrs];
    cyl[point] = disp[datcrs];
    datcrs = datcrs + inc;
    point = point + 1;
}
while(point <= ppts );

/* fildx3 = 0 for a 2 axis plot */
    fildx1 = 2;
    fildx2 = 3;
    fildx3 = 0;
    strcpy(xlb,"Time(seconds)");
    strcpy(ylb,"Displacement(meters)");
    strcpy(tplb,"DISPLACEMENT VS. TIME");
    vclear(0,0,24,79,2);
    setpos(0,0);

    a = plot(fildx1,fildx2,fildx3,ppts);
    strcpy(ex1,"ttx");
    strcpy(ex2,"dtx");
    strcpy(ex3," ");
    output(filnam, ppts, 2,ex1,ex2,ex3);

    vclear(0,0,24,79,2);
}
/*****
/* integrate work and heat */

    vclear(0,0,24,79,2);

    say(5,0," starting integration boundary(seconds):");
    rfl(&start);
    say(7,0," ending integration boundary(seconds):");
    rfl(&end);

tim_flag = 0;
say (9,0,"Do you want to plot vs time instead of displacement(Y/N)?");
rstr(xc);
if ( tolower(xc[0]) == 'y' ){ tim_flag = 1;}

area_flag = 0;
say (12,0,"Do you want to display Q & W divided by the area
peeled(Y/N)?");
rstr(xc);
if ( tolower(xc[0]) == 'y' ){ area_flag = 1;}

```

```

/* find the indices of start and end */
datcrs_time(start, end, &dx1, &dx2, tim);
/* integrate */
    j = 0;
    datcrs = dx1;
    int0p = 0.0;
    intwk = 0.0;
    intlpl = 0.0;

    while( datcrs <= dx2 )
    {
/* integrate pressure-time */

        avprs = (prs[datcrs] + prs[datcrs+1])/2; /*trap rule*/
        deltax = tim[datcrs+1] - tim[datcrs];
        int0p = int0p + ( avprs * deltax);
        avtim = (tim[datcrs]+tim[datcrs+1])/2 -tim[dx1];
        intlpl = intlpl+(avtim*avprs*deltax);

        heat[datcrs] = (c * int0p) + (avprs * tau);

/* work */
        avforce = 9.81*lc*((force[datcrs]+force[datcrs+1])/2);
        linear_reg(&slope, (datcrs - 10), (datcrs + 10), tim, disp);
        intwk += avforce * deltax * slope;
        work[datcrs] = 1000 * intwk; /*millijoules*/
        datcrs++;
        j++;
    }

    strcpy(tplb,"WORK AND HEAT OF PEELING");
    strcpy(tplb2,"Work =");
    scr = work[ (datcrs -1)];

if (area_flag == 1)
{
    scr = (2.0 * scr)/(sumdisp*width); /*j/m^2*/
    gcvt(scr,4,string); /*2 for 180 peel*/
    result = strcat(tplb2,string);
    result = strcat(tplb2,"(J/m^2) Heat =");
    scr = (2.0 * heat[datcrs - 1]) / (sumdisp*width);
    gcvt(scr,4,string);
    result = strcat(tplb2,string);
    result = strcat(tplb2,"(J/m^2)");
}
else{
    gcvt(scr,4,string);
    result = strcat(tplb2,string);
    result = strcat(tplb2,"(mj) Heat =");
    scr = heat[datcrs - 1];
    gcvt(scr,4,string);
    result = strcat(tplb2,string);
    result = strcat(tplb2,"(mj)");
}

if (tim_flag == 1){
    strcpy(xlb,"Time(seconds)");
}
else

```



```

        {strcpy(xlb,"Displacement(M)");}
        strcpy(yllb,"-Work(mj) and --Heat(mj)");
        strcpy(y2lb,"Work(mj)");

/* decimate data */
        npts = dx2 - dx1;
        decimate(npts, &ppts, &inc);

        datcrs = 0;
        point = 0;
        do
        {
            if (tim_flag == 1)
                { cx[point] = tim[dx1 + datcrs];}
            else
                { cx[point] = disp[dx1 + datcrs];}

            cy2[point] = heat[ dx1 + datcrs];
            cyl[point] = work[dx1 + datcrs];
            datcrs = datcrs + inc;
            point = point + 1;
        }
        while(point <= ppts );

/* plot the curves */

        fildx1 = 0;
        fildx2 = 9; /*two plots on one scale*/
        fildx3 = 0; /*single axis pair*/

        vclear(0,0,24,79,2);
        setpos(0,0);
        a = plot(fildx1,fildx2,fildx3,ppts);
        strcpy(ex1,"dtx");
        strcpy(ex2,"wtx");
        strcpy(ex3,"qtx");
        output(filnam, ppts,3,ex1,ex2,ex3);

        vclear(0,0,24,79,2);
        setpos(0,0);

        strcpy(tplb2," ");

        say (10,0,"Do you want to repeat the analysis(Y/N)?");
        rstr(xc);

        if ( tolower(xc[0]) == 'y' ) {
            goto reanalyze; }

        say (12,0,"Do you want to analyze another file(Y/N)?");
        rstr(xc);
        vclear(0,0,24,79,2);
        if ( tolower(xc[0]) == 'y' ) {
            strcat(tplb2," ");
            goto new_file; }

    }

```

MAIN PROGRAM ATENSILE

```

#include <stdio.h>
#include <conio.h>
#include <math.h>
#include <string.h>
#include <ctype.h>
#include <malloc.h>
#include <io.h>
#include <types.h>
#include <stat.h>
#include <fcntl.h>

/* plot field selection and label index*/
int fildx1,fildx2,fildx3;
char filnam[8];
char filnam2[8];
/* plot labeling */
extern char xlb[40];
extern char ylb[40];
extern char y2lb[40];
extern char tplb[80];
extern char tplb2[70];
extern char infol[70];
extern char info2[70];
extern char info3[70];
extern char info4[70];

/* plot vectors */
extern float cx[500],cyl[500],cy2[500];

/*plot labels */
char l1[40] = "FILE: ";
char l2[40] = "Time (seconds)";
char l3[40] = "-Pressure Difference(volts)";
char l4[80] = "DIFFERENTIAL PRESSURE AND FORCE VS. TIME";
char l5[40] = "Integrated pressure (v*sec)";
char l6[70] = "UNIAXIAL EXTENSION IN THE DEFORMATION CALORIMETER";

/* pointers to allocated arrays and file streams*/
FILE *file_ptr;
FILE *header, *prsfile, *forfile, *timfile,*disfile;
float *tim, *disp, *force, *heat, *work;
float prs[2500];

main()
{
    short a;
    int l,i,j;
    float sum1,sum2,sum3;
    double scr;
    char charl[60];
    char char2[60];
    char *string, *result;
    char xc[40];
    char baselabel[60];
    char ex1[3], ex2[3], ex3[3];

/* data loading and decimation */
int datcrs;
int inc,npts, point,npts_in_file;

```

```

/*  calibrations */
float lc, lvdt, c, tau;
/*  sample dimensions */
float init_sep, length, width, thickness;
/*  baseline calculation */
float base1, base2, base;
float slope, intercpt;
/*  integration variables */
float start, end, dur;
float int0p, int1p, qatt, power;
int dx1, dx2, dx3, ppts;
float datum, datum1, datum2;
float idisp, incdisp;
double sumdisp;
double delta1;
float deltax, avprs, avforce, intwk;
int bytesread, bytes;
float shift;
char material[70];
char experiment[70];
char date[10];
unsigned int max_bytes;
int ppasses, dpasses, tim_flag, area_flag;
float area;
string = &char1[0];
result = &char2[0];

/* get filename and open files */

new_file:
    vinit();
    vclear(0,0,24,79,2);
    setpos(0,0);

getname:
    say(0,0,"Filename: ");
    rstr(&filnam[0]);
    strcpy(filnam2, filnam);
    l = strlen(filnam);

    if ( l > 8 ) {
        say(2,0,"Maximum filename length is 8 characters.");
        goto getname;
    }

reanalyze:
    free((void *)tim);
    free((void *)heat);
    free((void *)work);
    free((void *)disp);
    free((void *)force);

    strcpy(xc, "c:\\caldata\\");
    result = strcat(xc, filnam);
    result = strcat(xc, ".prs");
    if ((prsfile = fopen(xc, "r+b")) == NULL) goto nofile;

    strcpy(xc, "c:\\caldata\\");
    result = strcat(xc, filnam);
    result = strcat(xc, ".tim");
    if ((timfile = fopen(xc, "r+b")) == NULL) goto nofile;

```

```

strcpy(xc,"c:\\caldata\\");
result = strcat(xc,filnam);
result = strcat(xc,".for");
if ((forfile = fopen(xc,"r+b")) == NULL ) goto nofile;

strcpy(xc,"c:\\caldata\\");
result = strcat(xc,filnam);
result = strcat(xc,".dis");
if ((disfile = fopen(xc,"r+b")) == NULL ) goto nofile;

strcpy(xc,"c:\\caldata\\");
result = strcat(xc,filnam);
result = strcat(xc,".hdr");
if ((header = fopen(xc,"r")) == NULL ) goto nofile;

goto files_loaded;

nofile:
    say(4,0,"This file is not present, reenter: ");
    clearerr(timfile);
    clearerr(prsfile);
    clearerr(forfile);
    clearerr(disfile);
    clearerr(header);
    goto getname;

files_loaded:

    npts = fread((char *)prs,sizeof(float),2500,prsfile);
    npts_in_file = npts;
    bytes = npts*4;

/* allocate memory for data vectors based on the number of data points*/
if(( tim = (float far *) _fmalloc(bytes)) == NULL)
    {printf("allocation failed\n"); exit(0);}
max_bytes = _fmsize(tim);

if(( heat = (float far *) _fmalloc(bytes)) == NULL)
    {printf("allocation failed\n"); exit(0);}
max_bytes = _fmsize(heat);

if(( work = (float far *) _fmalloc(bytes)) == NULL)
    {printf("allocation failed\n"); exit(0);}
max_bytes = _fmsize(work);

if(( disp = (float far *) _fmalloc(bytes)) == NULL)
    {printf("allocation failed\n"); exit(0);}
max_bytes = _fmsize(disp);

if(( force = (float far *) _fmalloc(bytes)) == NULL)
    {printf("allocation failed\n"); exit(0);}
max_bytes = _fmsize(force);

/* read raw data */

    datcrs = 1;
read_files:

    npts = fread((char *)tim,sizeof(float),npts,timfile);

```



```

npts = fread((char *)force,sizeof(float),npts,forfile);
npts = fread((char *)disp,sizeof(float),npts,disfile);

files_read:
    fclose(timfile);
    fclose(prsfile);
    fclose(forfile);
    fclose(disfile);

/* load header */
fscanf(header,"%f %f %f %f \n",&lc, &lvdt, &c, &tau);
fscanf(header,"%f %f %f %f \n",&init_sep, &length, &width,
    &thickness);
fscanf(header,"%[^!\\"] %s %[^!\\"] %s %[^!\\"]
\n",material,xc,experiment,xc,date);

/* start analysis */
/*****
/* smooth data */

say (6,0,"Do you want to smooth the raw data(Y/N)?");
rstr(xc);

if ( tolower(xc[0]) == 'y' )
{

say(8,0, "Number of passes for displacement:");
rint(&dpasses);
say(9,0, "Number of passes for pressure:");
rint(&ppasses);

if( dpasses > 0)
    { smooth(disp, npts, dpasses);}

if( ppasses > 0)
    { smooth(prs, npts, ppasses);}
}

npts = npts_in_file;
/* plot pressure data vs. time */

decimate(npts, &ppts, &inc);

    datcrs = 0;
    point = 0;
load_vectors:
    cx[point] = tim[datcrs];
    cyl[point] = prs[datcrs];
    datcrs = datcrs + inc;
    point = point + 1;
    if (point < ppts ) goto load_vectors;

/* fildx3 = 0 for a 2 axis plot */
    fildx1 = 2;
    fildx2 = 3;
    fildx3 = 0;
    strcpy(xlb,12);
    strcpy(ylb,13);
    strcpy(tp1b,"PRESSURE VS. TIME");
    strcpy(infol,11);

```

```

    result = strcat(info1,filnam);
    strcpy(info2,"EXPERIMENT: ");
    result = strcat(info2,experiment);
    strcpy(info3,"SAMPLE: ");
    result = strcat(info3,material);
    strcpy(tplb2, 16);
    vclear(0,0,24,79,2);
    setpos(0,0);

    a = plot(fildx1,fildx2,fildx3,ppts);

/* create ASCII output files of plot data */
strcpy(ex1,"ttx");
strcpy(ex2,"ptx");
strcpy(ex3," ");
output(filnam, ppts,2,ex1,ex2,ex3);

    vclear(0,0,24,79,2);

/*****
/* baseline correction */

    say(1,0," baseline origin (seconds):");
    rfl(&basel);
    say(3,0," baseline end (seconds):");
    rfl(&base2);

/* find datacount for both times*/
datcrs_time(basel, base2, &dx1, &dx2, tim);

/* calculate mean values for both ends */
sum2 = 0;
sum3 = 0;
for (datcrs = dx1-10; datcrs <= dx1+10; datcrs++)
{
    sum1 = prs[datcrs];
    sum2 = sum2+sum1;
}
sum2 = sum2/21;

for (datcrs = dx2-10; datcrs <= dx2+10; datcrs++)
{
    sum1 = prs[datcrs];
    sum3 = sum3+sum1;
}

sum3 = sum3/21;

/* calculate slope in volts/second */
slope = (sum3 - sum2) / (base2-basel);
intcpt = prs[dx1] - slope * basel;

/* put basel and base2 on the plot by putting in */
/* tplb2 */
/* subtaract baseline from prs data*/

for ( j = 0; j <= npts; j++)
    prs[j] = prs[j] - intcpt - tim[j] * slope;

/* plot corrected pressure data vs. time */

datcrs = 0;
point = 0;

```

```

    while( datercs < npts)
    {
        cyl[point] = prs[datercs];
        cy2[point] = force[datercs] * 9.81 * lc;
        datercs = datercs + inc;
        point = point + 1;
    }

    fildx1 = 2;
    fildx2 = 4;
    fildx3 = 1;
    strcpy(xlb,12);
    strcpy(tplb,14);
    strcpy(y2lb,"--Force(Newtons)");

    vclear(0,0,24,79,2);
    a = plot(fildx1,fildx2,fildx3,ppts);
    strcpy(ex1,"ttx");
    strcpy(ex2,"ptx");
    strcpy(ex3,"ftx");
    output(filnam, ppts,3,ex1,ex2,ex3);

    vclear(0,0,24,79,2);

/* compute displacements */
/* for start use an average of first 30 points */

    suml = 0.0;
    for ( datercs = 0; datercs <= 29; datercs++)
        {suml = suml + disp[datercs];}
    idisp = suml/30;

    for( datercs = 0; datercs < npts; datercs++)
    {
        incdisp = disp[datercs] - idisp;
        sumdisp = lvd* fabs(incdisp);
        disp[datercs] = (sumdisp/init_sep) + length;
    }

/*****
/* plot force displacement and displacement time */

say (1,0,"Do you want to plot stress vs. strain(Y/N)?");
rstr(xc);
if ( tolower(xc[0]) == 'y' )
{
    datercs = 0;
    point = 0;
    do
    {
        cx[point] = disp[datercs];
        cyl[point] = (force[datercs] *9.81*lc) / (width*thickness*1.0e+6);
        datercs = datercs + inc;
        point = point + 1;
    }
    while(point <= ppts - 1 );

/* fildx3 = 0 for a 2 axis plot */
    fildx1 = 2;
    fildx2 = 3;
    fildx3 = 0;
    strcpy(xlb,"Strain");
    strcpy(yllb,"Stress(MPa)");

```

```

        strcpy(tplb,"STRESS VS. STRAIN");
        vclear(0,0,24,79,2);
        setpos(0,0);

        a = plot(fildx1,fildx2,fildx3,ppts);
        strcpy(ex1,"etx");
        strcpy(ex2,"stx");
        strcpy(ex3," ");
        output(filnam, ppts,2,ex1,ex2,ex3);

        vclear(0,0,24,79,2);
    }

    /*****
say (2,0,"Do you want to plot displacement vs time(Y/N)?");
rstr(xc);
if ( tolower(xc[0]) == 'y' )
{
    daters = 0;
    point = 0;
do
{
    cx[point] = tim[datcrs];
    cyl[point] = disp[datcrs];
    daters = daters + inc;
    point = point + 1;
}
while(point <= ppts );

/* fildx3 = 0 for a 2 axis plot */
    fildx1 = 2;
    fildx2 = 3;
    fildx3 = 0;
    strcpy(xlb,"Time(seconds)");
    strcpy(ylb,"Displacement(meters)");
    strcpy(tplb,"DISPLACEMENT VS. TIME");
    vclear(0,0,24,79,2);
    setpos(0,0);

    a = plot(fildx1,fildx2,fildx3,ppts);
    vclear(0,0,24,79,2);
}

/* *****/

/* integrate work and heat */

    vclear(0,0,24,79,2);

    say(5,0," starting integration boundary(seconds):");
    rfl(&start);
    say(7,0," ending integration boundary(seconds):");
    rfl(&end);

tim_flag = 0;
say (9,0,"Do you want to plot vs time instead of displacement(Y/N)?");
rstr(xc);
if ( tolower(xc[0]) == 'y' ){ tim_flag = 1;}

area_flag = 0;

```



```

say (12,0,"Do you want to display Q & W divided by the area
peeled(Y/N)?");
rstr(xc);
if ( tolower(xc[0]) == 'y' ){ area_flag = 1;}

/*    find the indices of start and end */
datcrs_time(start, end, &dx1, &dx2, tim);

/*    integrate */

    j = 0;
    datcrs = dx1;
    int0p = 0.0;
    intwk = 0.0;

    while( datcrs <= dx2 )
    {
        avprs = (prs[datcrs] + prs[datcrs+1])/2; /*trap rule*/
        deltax = tim[datcrs+1] - tim[datcrs];
        int0p = int0p + ( avprs * deltax);
        heat[datcrs] = (c * int0p) + (avprs * tau);
/* work */
        avforce = 9.81*lc*((force[datcrs]+force[datcrs+1])/2);
        linear_reg(&slope, (datcrs - 10), (datcrs + 10), tim, disp);
        intwk += avforce * deltax * slope*init_sep;
        work[datcrs] = 1000 * intwk; /*millijoules*/
        datcrs++;
        j++;
    }

    strcpy(tplb,"WORK AND HEAT VS. STRAIN");
    strcpy(tplb2,"Work =");
    scr = work[ (datcrs - 1)];

if (area_flag == 1)
{
    scr = (2.0 * scr)/(sumdisp*width); /*j/m^2*/
    gcvt(scr,4,string); /*2 for 180 peel*/
    result = strcat(tplb2,string);
    result = strcat(tplb2,"(J/m^2) Heat =");
    scr = (2.0 * heat[datcrs - 1]) / (sumdisp*width);
    gcvt(scr,4,string);
    result = strcat(tplb2,string);
    result = strcat(tplb2,"(J/m^2)");
}
else{
    gcvt(scr,4,string);
    result = strcat(tplb2,string);
    result = strcat(tplb2,"(mj) Heat =.");
    scr = heat[datcrs - 1];
    gcvt(scr,4,string);
    result = strcat(tplb2,string);
    result = strcat(tplb2,"(mj)");
}

if (tim_flag == 1){
    strcpy(xlb,"Time(seconds)");
}
else
{
    strcpy(xlb,"Strain");
}
strcpy(y1lb,"-Work(mj) and --Heat(mj)");
strcpy(y2lb,"Work(mj)");

```

```

/* decimate data */
  npts = dx2 - dx1;
  decimate(npts, &ppts, &inc);

  datercs = 0;
  point = 0;
  do
  {
    if (tim_flag == 1)
      { cx[point] = tim[dx1 + datercs]; }
    else
      { cx[point] = disp[dx1 + datercs]; }

    cy2[point] = heat[ dx1 + datercs];
    cyl[point] = work[dx1 + datercs];
    datercs = datercs + inc;
    point = point + 1;
  }
  while(point <= ppts );

/* plot the curves */

  fildx1 = 0;
  fildx2 = 9; /*two plots on one scale*/
  fildx3 = 0; /*single axis pair*/

  vclear(0,0,24,79,2);
  setpos(0,0);
  a = plot(fildx1,fildx2,fildx3,ppts);
  strcpy(ex1,"dtx");
  strcpy(ex2,"wtx");
  strcpy(ex3,"qtx");
  output(filnam, ppts,3,ex1,ex2,ex3);

  strcpy(tplb2," ");

  say (6,0,"Do you want to repeat the analysis(Y/N)?");
  rstr(xc);

  if ( tolower(xc[0]) == 'y' ) {
    goto reanalyze; }

  say (6,0,"Do you want to analyze another file(Y/N)?");
  rstr(xc);

  if ( tolower(xc[0]) == 'y' ) {
    strcat(tplb2," ");
    goto new_file; }

}

```

PLOTTING SUBROUTINE (PLOT)

```

#include <stdio.h>
#include <conio.h>
#include <math.h>

int hp_flag;
int sym;
float cx[500],cyl[500],cy2[500];
char xlb[40];
char y1lb[40];
char y2lb[40];
char tplb[80];
char tplb2[70];
char info1[70];
char info2[70];
char info3[70];
char info4[70];
char m2[10] = " * 10 E-2";
char m3[10] = " * 10 E-3";
char m6[10] = " * 10 E-6";
char m9[10] = " * 10 E-9";
char mn3[10] = " * 10 E+3";
char mn6[10] = " * 10 E+6";
char mn9[10] = " * 10 E+9";
float xmin,xmax,ylmin,ylmax,y2min,y2max,xinc,ylinc,y2inc;

extern short plot(dx1,dx2,dx3,npts)

int dx1;
int dx2;
int dx3; /* plot with one or two y axes */
int npts;
{
    int nxdiv,nyldiv,ny2div,i,il,i2;
    float xstep;
    float cxswp,cylswp,cy2swp;
    char *pxlb,*py1lb,*py2lb,*ptplb,*ptplb2;
    char ans,xc[5];
    float strwidth();
    float hwidth;
    float mult;
    int auto_flag = 0;
    int constx_flag=0;
    int constyl_flag=0;
    int consty2_flag=0;
    pxlb = &xlb[0];
    py1lb = &y1lb[0];
    py2lb = &y2lb[0];
    ptplb = &tplb[0];
    ptplb2 = &tplb2[0];
    il = npts-1;

    nxdiv=5;
    nyldiv=5;
    ny2div=5;
    sym =0;

    say(1,0,"Do you want a plot on the plotter(Y/N or c to continue)?: ");
    rstr(xc);

```

```

        if ( xc[0] == 'Y' || xc[0] == 'y' )
        {
            hp_flag = 2;
        }

        if ( xc[0] == 'c' || xc[0] == 'C' ) goto end;
/* allows quick run through the program by entering c */
say(3,0,"Do you wish to select the plot scales(Y/N)?: ");
rstr(xc);

        if ( xc[0] == 'Y' || xc[0] == 'y' ) auto_flag = 1;

        ylmin = cyl[0];
        ylmax = cyl[0];
        y2min = cy2[0];
        y2max = cy2[0];
        xmin = cx[0];
        xmax = cx[0];

/* plot with two scales */

        if( dx3 == 0 )
        {
            /* determine maximum and minimum values */
            for (i2=0; i2 < npts; i2++)
            {
                if ( cx[i2] < xmin ) xmin = cx[i2];
                if ( cx[i2] > xmax ) xmax = cx[i2];
                if ( cyl[i2] < ylmin ) ylmin = cyl[i2];
                if ( cyl[i2] > ylmax ) ylmax = cyl[i2];
            }

            if ( auto_flag == 1 ) scale(i1); /* automatic scale */
            else /* manual scale */
            {
                if ( xmax == xmin ) { /* constant x vector */
                    constx_flag = 1;
                    cxswp = cx[1];
                    cx[1] = xmin - ( xmin / 2.0 );
                }

                if ( ylmax == ylmin ) { /* constant y vector */
                    constyl_flag = 1;
                    cylswp = cyl[1];
                    ylmin = ylmin - ( ylmin / 2.0 );
                    cyl[1] = ylmin;
                }
            }

/* determine exponents for very small or very large numbers */
/* so that plot labels consist of easy numbers */

            if ( ylmin > -0.00000001 && ylmax < 0.00000001 ){

                mult = 1000000.0;
                for (i2=0; i2<=i1; i2++)
                { cyl[i2] = cyl[i2] * mult;}

                strcat(yl1b,m9);
                goto contyl;
            }

            if ( ylmin > -0.00001 && ylmax < 0.00001 ){

                mult = 1000000.0;

```



```

        for (i2=0; i2<=i1; i2++)
            { cyl[i2] = cyl[i2] * mult;}

        strcat(yllb,m6);
        goto contyl;
    }

    if ( ylmin > -.001 && ylmax < .001 ){
        mult = 1000.0;
        for (i2=0; i2<=i1; i2++)
            { cyl[i2] = cyl[i2] * mult;}
        strcat(yllb,m3);
        goto contyl;
    }

    if ( ylmin > -.01 && ylmax < .01 ){
        mult = 100.0;
        for (i2=0; i2<=i1; i2++)
            { cyl[i2] = cyl[i2] * mult;}
        strcat(yllb,m2);
        goto contyl;
    }

    if ( ylmin < -100.0 || ylmax > 100.0 ){
        mult = .001;
        for (i2=0; i2<=i1; i2++)
            { cyl[i2] = cyl[i2] * mult;}
        strcat(yllb,mn3);
        goto contyl;
    }

    if ( ylmin < -10000.0 || ylmax > 10000.0 ){
        mult = .000001;
        for (i2=0; i2<=i1; i2++)
            { cyl[i2] = cyl[i2] * mult;}
        strcat(yllb,mn6);
        goto contyl;
    }

contyl:

    if ( xmin > -.001 && xmax < .001 ){
        mult = 1000.0;
        for (i2=0; i2<=i1; i2++)
            { cx[i2] = cx[i2] * mult;}
        strcat(xlb,m3);
        goto contxl;
    }

    if ( xmin > -.01 && xmax < .01 ){
        mult = 100.0;
        for (i2=0; i2<=i1; i2++)
            { cx[i2] = cx[i2] * mult;}
        strcat(xlb,m2);
        goto contxl;
    }

}

contxl:

/* commence plotting with calls to graphics package */

bgnplot(1,'g',"curv.tkf");
startplot(0);
font(4,"simplex.fnt",'\\310',"triplex.fnt",'\\311',

```

```

        "complex.fnt", '\312', "simgrma.fnt", '\313');
    page(9.0,6.855);
/*    pbox(); */
    cross(0);
    physor(1.0,1.5);
    area2d(6.5,4.5);
    color(2);
    if(auto_flag == 1)
        graf("%-3.3f",xmin,xinc,xmax,"%-3.3f",ylmin,ylinc,ylmax,0);
        else scales(nxdiv,nyldiv,cx,cyl,npts,0);
    xname(px1b);
    yname(py1b);

    hwidth = strwidth(ptplb,0.2);
    prtfmt(4.0 - hwidth,6.5,ptplb,0.2,0);
    hwidth = strwidth(ptplb2,0.16);
    prtfmt(4.0 - hwidth,6.2,ptplb2,0.16,0);
    prtfmt(1.0,0.1,info1,0.12,0);
    prtfmt(1.0,0.35,info2,0.12,0);
    prtfmt(1.0,0.6,info3,0.12,0);
    if ( constyl_flag == 1 ) cyl[1] = cylswp;
    if ( constx_flag == 1 ) cx[1] = cxswp;
    acrop(1);
    sympick(3);
if(dx2 == 9) solid();
    curve(cx,cyl,npts,sym);
color(7);
if(dx2 == 9){ dash(); curve(cx,cy2,npts,sym);}

    endplot();
    stopplot();
    hp_flag = 0;
    auto_flag = 0;
}

/* plot with three scales */
if( dx3 != 0 )
{
    for (i2=0; i2 < npts; i2++)
    {
        if ( cx[i2] < xmin ) xmin = cx[i2];
        if ( cx[i2] > xmax ) xmax = cx[i2];
        if ( cyl[i2] < ylmin ) ylmin = cyl[i2];
        if ( cyl[i2] > ymax ) ymax = cyl[i2];
        if ( cy2[i2] < y2min ) y2min = cy2[i2];
        if ( cy2[i2] > y2max ) y2max = cy2[i2];
    }

    if (auto_flag == 1 ) scale(i1);
    else
    {
        if ( xmax == xmin )
        {
            constx_flag = 1;
            cxswp = cx[0];
            cx[0] = xmin - ( xmin / 2.0);
        }
        if ( ymax == ylmin )

```

```

        {
            constyl_flag = 1;
            cylswp = cyl[0];
            cyl[0] = ylmin - ( ylmin / 2.0 );
        }

        if ( y2max == y2min )
        {
            consty2_flag = 1;
            cy2swp = cy2[0];
            cy2[0] = y2min - ( y2min / 2.0 );
        }

        if ( ylmin > -0.00000001 && ylmax < 0.00000001 ){
            mult = 1000000.0;
            for (i2=0; i2<=i1; i2++)
                { cyl[i2] = cyl[i2] * mult;}

            strcat(yl1b,m9);
            goto ylend;
        }

        if ( ylmin > -0.00001 && ylmax < 0.00001 ){
            mult = 1000000.0;
            for (i2=0; i2<=i1; i2++)
                { cyl[i2] = cyl[i2] * mult;}

            strcat(yl1b,m6);
            goto ylend;
        }

        if ( ylmin > -.001 && ylmax < .001 ){
            mult = 1000.0;
            for (i2=0; i2<=i1; i2++)
                { cyl[i2] = cyl[i2] * mult;}
            strcat(yl1b,m3);
            goto ylend;
        }

        if ( ylmin > -.01 && ylmax < .01 ){
            mult = 100.0;
            for (i2=0; i2<=i1; i2++)
                { cyl[i2] = cyl[i2] * mult;}
            strcat(yl1b,m2);
            goto ylend;
        }

        if ( ylmin < -100.0 || ylmax > 100.0 ){
            mult = .001;
            for (i2=0; i2<=i1; i2++)
                { cyl[i2] = cyl[i2] * mult;}
            strcat(yl1b,mn3);
            goto ylend;
        }

        if ( ylmin < -10000.0 || ylmax > 10000.0 ){
            mult = .000001;
            for (i2=0; i2<=i1; i2++)
                { cyl[i2] = cyl[i2] * mult;}
            strcat(yl1b,mn6);
            goto ylend;
        }

```

ylend:

```

if ( xmin > -.001 && xmax < .001 ){
    mult = 1000.0;
    for (i2=0; i2<=i1; i2++)
        { cx[i2] = cx[i2] * mult;}
    strcat(xlb,m3);
    goto x2end;
}
if ( xmin > -.01 && xmax < .01 ){
    mult = 100.0;
    for (i2=0; i2<=i1; i2++)
        { cx[i2] = cx[i2] * mult;}
    strcat(xlb,m2);
    goto x2end;
}

```

x2end:

```

if ( y2min > -0.00000001 && y2max < 0.00000001 ){
    mult = 1000000.0;
    for (i2=0; i2<=i1; i2++)
        { cy2[i2] = cy2[i2] * mult;}

    strcat(y2lb,m9);
    goto endy2;
}

if ( y2min > -0.00001 && y2max < 0.00001 ){
    mult = 1000000.0;
    for (i2=0; i2<=i1; i2++)
        { cy2[i2] = cy2[i2] * mult;}

    strcat(y2lb,m6);
    goto endy2;
}

if ( y2min > -.001 && y2max < .001 ){
    mult = 1000.0;
    for (i2=0; i2<=i1; i2++)
        { cy2[i2] = cy2[i2] * mult;}
    strcat(y2lb,m3);
    goto endy2;
}

if ( y2min > -.01 && y2max < .01 ){
    mult = 100.0;
    for (i2=0; i2<=i1; i2++)
        { cy2[i2] = cy2[i2] * mult;}
    strcat(y2lb,m2);
    goto endy2;
}

if ( y2min < -100.0 || y2max > 100.0 ){
    mult = .001;
    for (i2=0; i2<=i1; i2++)
        { cy2[i2] = cy2[i2] * mult;}
    strcat(y2lb,mn3);
    goto endy2;
}

if ( y2min < -10000.0 || y2max > 10000.0 ){
    mult = .000001;
    for (i2=0; i2<=i1; i2++)
        { cy2[i2] = cy2[i2] * mult;}
}

```



```

        strcat(y2lb,mn6);
        goto endy2;
    }
}

endy2:
    .
    bgnplot(1,'g',"curv.tkf");
    startplot(0);
    font(4,"simplex.fnt",'\\310',"triplex.fnt",'\\311',
        "complex.fnt",'\\312',"simgrma.fnt",'\\313');

    page(9.0,6.855);
/*    pbox();    */
    cross(0);
    grid(0);
    physor(0.6,1.5);
    area2d(6.5,4.5);
    numht(0.12);
/* draw outer y axis */
    color(7);
    if(auto_flag == 1)

    graf("%-3.3f",xmin,xinc,xmax,"%-3.3f",y2min,y2inc,y2max,1);
        else scales(nxdiv,ny2div,cx,cy2,npts,1);

    yname(py2lb);

/* draw the plot */

    physor(1.6,1.5);
    area2d(6.5,4.5);
/* draw inner y axis and x-axis*/
    color(2);
    if(auto_flag == 1)

    graf("%-3.3f",xmin,xinc,xmax,"%-3.3f",ylmin,ylinc,ylmax,0);
        else scales(nxdiv,nyldiv,cx,cyl,npts,0);
    xname(px1b);
    color(2);
    yname(py1lb);
    hwidth = strwidth(ptplb,0.2);
    prtfmt(4.5 - hwidth,6.5,ptplb,0.2,0);
    hwidth = strwidth(ptplb2,0.16);
    prtfmt(4.5 - hwidth,6.2,ptplb2,0.16,0);
    prtfmt(0.6,0.1,info1,0.12,0);
    prtfmt(0.6,0.35,info2,0.12,0);
    prtfmt(0.6,0.6,info3,0.12,0);
    acrop(1);
    if ( constx_flag == 1 ) cx[0] = cxswp;
    if ( constyl_flag == 1 ) cyl[0] = cylswp;
    sympick(3);
    solid();
    curve(cx,cyl,npts,sym);
    color(7);
    axesoff(1);

    if(auto_flag == 1)

    {graf("%-3.2f",xmin,xinc,xmax,"%-3.2f",y2min,y2inc,y2max,0);}

    else {
        if ( constx_flag == 1 ) {cx[0] = 0.0;}

```

```

        scales(nxdiv,ny2div,cx,cy2,npts,0); }

        if ( consty2_flag == 1 ) cy2[0] = cy2swp;
        if ( constx_flag == 1 ) cx[0] = cxswp;
sympick(4);
        dash();
curve(cx,cy2,npts,sym);

endplot();
stopplot();
end:
    hp_flag = 0;
    auto_flag = 0;
/*    i2 = system("c:\\MODE 80"); */
    vinit();
}

)

```

SUBROUTINES

```

#include <stdio.h>
#include <conio.h>
#include <math.h>
#include <string.h>
#include <ctype.h>
#include <malloc.h>
#include <fcntl.h>

extern float cx[500],cyl[500],cy2[500];

datcrs_time(base1, base2, dx1, dx2, tim)
/* returns the indices of the data vector corresponding to the */
/* ends of a time interval */
float base1; /* beggining of time interval */
float base2; /* end of time interval */
int *dx1; /* pointer to index corresponding to beggining */
int *dx2; /* pointer to index corresponding to the end */
float *tim; /* pointer to time vector */
{
    int datcrs;
    float base;

    datcrs = 0;
    base = 0.0;
    while( base < base1)
    {
        datcrs = datcrs + 1;
        base = *(tim + datcrs);
    }
    *dx1 = datcrs;

    while( base < base2 )
    {
        datcrs = datcrs + 1;
        base = *(tim + datcrs);
    }
    *dx2 = datcrs;
}

decimate(npts, ppts, inc)
/* decimates data points to yield 500 or less for plotting */
int npts; /* total number of points */
int *ppts; /* number of points to plot */
int *inc; /* number of points to skip */
{
    /* decimate data */

    if (npts > 500) {
        *inc = (npts/500 + 1);
        *ppts = (npts/ *inc);
    }
}

```

```

        else
            {
                *ppts = npts;
                *inc = 1;
            }
    }

smooth(vector, points, passes)
/* smooths data by moving average */
    float *vector; /* pointer to data vector to be smoothed */
    int points; /* number of points in moving average */
    int passes; /* number of times to repeat the process */
{
    int pass;
    int dater;
    float dat1, dat2, dat3;
    int start, skip;
    float datum;
    float scr;

    for(pass = 1; pass <= passes; pass++)
    {
        dater = 0;
        dat1 = *(vector + dater);
        dater = 1;
        dat2 = *(vector + dater);

        for(dater = 2; dater <= (points - 1); dater++)
        {
            dat3 = *(vector + dater);
            *(vector + dater) = ((dat1 + dat2 + dat3) / 3.0);
            dat1 = dat2;
            dat2 = dat3;
        }
    }
}

```

```

linear_reg(slope, first, last, xvector, yvector)

```

```

/* determines the slope of the best line through the points */
/* by the method of least squares */

```

```

float *slope; /* computed slope of the best line */
int first; /* index of first data point */
int last; /* index of last data point */
float *xvector; /* pointer to first included x data point */
float *yvector; /* pointer to corresponding y data point */

```

```

{
    float sumx;
    float sumy;
    float sumx2;

```



```

float sumxy;
register int x;

sumx = 0.0;
sumxy = 0.0;
sumy = 0.0;
sumx2 = 0.0;

for( x = first; x < last; x++)
{
    sumx += *(xvector + x);
    sumy += *(yvector + x);
    sumxy += *(yvector + x) * *(xvector + x);
    sumx2 += *(xvector + x) * *(xvector + x);
}

x = last - first;

*slope = (sumxy - (x * (sumx/x) * (sumy/x))) / (sumx2 - (x *
(sumx/x)*(sumx/x)));
}

output(filnam, npts, nfiles, ext1, ext2, ext3)

/* create ASCII text output files of plot data */

char *filnam; /* root name of text file */
int npts; /* number of data */
int nfiles; /* number of files using the same root name */
char *ext1; /* file name extensions */
char *ext2;
char *ext3;

{
    FILE *out1, *out2, *out3;
    char xc[50];
    int dx1;
    char *result;

    vclear(0,0,24,79,2);

    say(3,0,"Do you wish to output the data to a file(Y/N)?: ");
    rstr(xc);

    if ( xc[0] == 'Y' || xc[0] == 'y')
    {
        strcpy(xc,"c:\\caldata\\");
        result = strcat(xc,filnam);
        result = strcat(xc,".");
        result = strcat(xc,ext1);
        out1 = fopen(xc,"w");

        strcpy(xc,"c:\\caldata\\");
        result = strcat(xc,filnam);
        result = strcat(xc,".");
        result = strcat(xc,ext2);
        out2 = fopen(xc,"w");
    }
}

```

```
if (nfiles == 3)
{
    strcpy(xc,"c:\\caldata\\");
    result = strcat(xc,filnam);
    result = strcat(xc,".");
    result = strcat(xc,ext3);
    out3 = fopen(xc,"w");
}

dx1 = 0;
while(dx1 <= npts)
{
    fprintf(out1,"%f \n",cx[dx1]);
    fprintf(out2,"%f \n",cyl[dx1]);
    if (nfiles == 3) fprintf(out3,"%f \n",cy2[dx1]);
    dx1 = dx1 + 2;
}

fclose(out1);
fclose(out2);
fclose(out3);

}

)
```

VIDEO AND KEYBOARD FUNCTIONS

Note: For functions and options of DOS interrupts, see a DOS reference manual

INITIALIZE THE VIDEO MODE

```
#include <dos.h>
vinit()
{
    union REGS regset;
    struct SREGS segregs;
    unsigned int ax,bx,dx,si,di,cflag;
    unsigned int cs, ds, es, ss;
    segread(&segregs);
    cs = segregs.cs;
    ds = segregs.ds;
    es = segregs.es;
    ss = segregs.ss;
    ax = regset.x.ax;
    bx = regset.x.bx;
    dx = regset.x.dx;
    si = regset.x.si;
    di = regset.x.di;
    cflag = regset.x.cflag;
    regset.h.ah = 5;
    regset.h.al = 0;

    int86x( 0x10, &regset, &regset, &segregs );

    regset.h.ah = 0;
    regset.h.al = 3;

    int86x( 0x10, &regset, &regset, &segregs );
    segregs.cs = cs;
    segregs.ds = ds;
    segregs.es = es;
    segregs.ss = ss;
    regset.x.ax = ax;
    regset.x.bx = bx;
    regset.x.dx = dx;
    regset.x.si = si;
    regset.x.di = di;
    regset.x.cflag = cflag;
}
```

CLEAR A PORTION OF THE SCREEN AND SET THE COLORS

```
#include <dos.h>
#include <\video\video.h>

vclear( top, lft, bot, rht, attrib )
{
    int top;
    int lft;
    int bot;
    int rht;
    int attrib;
    {

    union REGS regset;
    struct SREGS segregs;
    unsigned int ax,bx,dx,si,di,cflag;
```

```

unsigned int cs, ds, es, ss;
segread(&segregs);
cs = segregs.cs;
ds = segregs.ds;
es = segregs.es;
ss = segregs.ss;
ax = regset.x.ax;
bx = regset.x.bx;
dx = regset.x.dx;
si = regset.x.si;
di = regset.x.di;
cflag = regset.x.cflag;

regset.h.ah = 6;
regset.h.al = 0;
regset.h.bh = attrib;
regset.h.bl = 0;
regset.h.ch = top;
regset.h.cl = lft;
regset.h.dh = bot;
regset.h.dl = rht;

int86x( 0x10, &regset, &regset, &segregs );

segregs.cs = cs;
segregs.ds = ds;
segregs.es = es;
segregs.ss = ss;
regset.x.ax  = ax;
regset.x.bx  = bx;
regset.x.dx  = dx;
regset.x.si  = si;
regset.x.di  = di;
regset.x.cflag = cflag;

)

```

SET THE FORGROUND AND BACKGROUND COLORS OF A PORTION OF THE SCREEN

```

#include <dos.h>

vattrib( row, col )
int row;
int col;
{
int attrib;
union REGS regset;
struct SREGS segregs;
unsigned int ax,bx,dx,si,di,cflag;
unsigned int cs, ds, es, ss;
segread(&segregs);
cs = segregs.cs;
ds = segregs.ds;
es = segregs.es;
ss = segregs.ss;
ax = regset.x.ax;
bx = regset.x.bx;
dx = regset.x.dx;
si = regset.x.si;
di = regset.x.di;
cflag = regset.x.cflag;

```



```

    regset.h.ah = 2;
    regset.h.dh = row;
    regset.h.dl = col;
    regset.h.bh = 0;
    int86x( 0x10, &regset, &regset, &segregs );

    regset.h.ah = 8;
    regset.h.bh = 0;
    int86x( 0x10, &regset, &regset, &segregs );
    attrib = regset.h.ah;

    segregs.cs = cs;
    segregs.ds = ds;
    segregs.es = es;
    segregs.ss = ss;
    regset.x.ax = ax;
    regset.x.bx = bx;
    regset.x.dx = dx;
    regset.x.si = si;
    regset.x.di = di;
    regset.x.cflag = cflag;
    return(attrib);

}

```

SET THE CURSOR TO A SCREEN POSITION

```

#include <dos.h>

```

```

setpos( row, col )
    int row;
    int col;
    {
        union REGS regset;
        struct SREGS segregs;
        unsigned int ax,bx,dx,si,di,cflag;
        unsigned int cs, ds, es, ss;
        segread(&segregs);
        cs = segregs.cs;
        ds = segregs.ds;
        es = segregs.es;
        ss = segregs.ss;
        ax = regset.x.ax;
        bx = regset.x.bx;
        dx = regset.x.dx;
        si = regset.x.si;
        di = regset.x.di;
        cflag = regset.x.cflag;

        regset.h.ah = 2;
        regset.x.bx = 0;
        regset.x.cx = 0;
        regset.h.dh = row;
        regset.h.dl = col;
        regset.h.bh = 0;
        int86x( 0x10, &regset, &regset, &segregs );

        segregs.cs = cs;
        segregs.ds = ds;
    }

```

```

segregs.es = es;
segregs.ss = ss;
regset.x.ax  = ax;
regset.x.bx  = bx;
regset.x.dx  = dx;
regset.x.si  = si;
regset.x.di  = di;
regset.x.cflag = cflag;
}

```

PLACE A TEXT STRING AT A SPECIFIED SCREEN LOCATION

```

#include <dos.h>
#include <stdio.h>
say( row, col, text )
    int row, col;
    char *text;

{
    int intno = 0x10;
    int attrib;
    /* without declaring a var here, prog won't always run? */
    float mystery;
    union REGS regset;
        struct SREGS segregs;
        unsigned int ax,bx,dx,si,di,cflag;
        unsigned int cs, ds, es, ss;
        segread(&segregs);
        cs = segregs.cs;
        ds = segregs.ds;
        es = segregs.es;
        ss = segregs.ss;
        ax = regset.x.ax;
        bx = regset.x.bx;
        dx = regset.x.dx;
        si = regset.x.si;
        di = regset.x.di;
        cflag = regset.x.cflag;

    attrib = vattrib(row,col);
    setpos(row,col);
    while (*text != '\0' )
    {
        regset.h.bl = attrib;
        regset.h.al = *text;
        regset.h.ah = 0x9;
        regset.h.bh = 0;
        regset.x.cx = 1;
        int86x(intno, &regset, &regset, &segregs);
        text++;
        col++;
        setpos(row,col);
    }

    segregs.cs = cs;
    segregs.ds = ds;
    segregs.es = es;
    segregs.ss = ss;
    regset.x.ax  = ax;
    regset.x.bx  = bx;
    regset.x.dx  = dx;
    regset.x.si  = si;
    regset.x.di  = di;
}

```

```
    regset.x.cflag = cflag;
```

```
)
```

READ TEXT FROM KEYBOARD AND ECHO TO THE SCREEN AT CURRENT CURSOR POSITION

```
#include <dos.h>
#include <stdio.h>
#include <ctype.h>
#define video 0x10
#define key 0x21
```

```
rstr( text )
```

```
    char *text;
```

```
{
```

```
int attrib;
int row,col;
char *rm;
```

```
union REGS regset;
    struct SREGS segregs;
    unsigned int ax,bx,dx,si,di,cflag;
    unsigned int cs, ds, es, ss;
    segread(&segregs);
    cs = segregs.cs;
    ds = segregs.ds;
    es = segregs.es;
    ss = segregs.ss;
    ax = regset.x.ax;
    bx = regset.x.bx;
    dx = regset.x.dx;
    si = regset.x.si;
    di = regset.x.di;
    cflag = regset.x.cflag;
```

```
regset.h.ah = 0x9;
regset.h.bh = 0;
regset.h.bl = 0;
regset.x.cx = 1;
regset.h.al = 0;
```

```
rm = text;
```

```
/* get current cursor position and attribute */
    regset.h.ah = 3;
```

```
    int86x(video, &regset, &regset,&segregs);
    row = regset.h.dh;
    col = regset.h.dl;
```

```
attrib = vattrib(row,col);
```

```
/* read a char from keyboard and check in */
getmore:
```

```
    regset.h.ah = 7;
    int86x(key, &regset, &regset,&segregs);
    *text = regset.h.al;
    if ( toascii(*text) == 13) goto done;
```

```

    if ( toascii(*text) == 8 )
    { if (text <= rm) goto rt_margin;
      text--; col--;
      setpos(row,col);
      regset.h.ah = 0x9;
      regset.h.bh = 0;
      regset.x.cx = 1;
      regset.h.bl = attrib;
      regset.h.al = 0x20;
      int86x(video, &regset, &regset,&segregs);
rt_margin:
      goto getmore;}

    if ( isalnum(*text) == 0 && isspace(*text) == 0
        && ispunct(*text) == 0) goto getmore;

/* echo character to crt */

    regset.h.ah = 0x9;
    regset.h.bh = 0;
    regset.x.cx = 1;
    regset.h.bl = attrib;
    regset.h.al = *text;
    int86x(video, &regset, &regset,&segregs);
    text++;
    col++;
    setpos(row,col);
    if (col >79 ) goto done;
    goto getmore;

done:
*text = '\0';

segregs.cs = cs;
segregs.ds = ds;
segregs.es = es;
segregs.ss = ss;
regset.x.ax  = ax;
regset.x.bx  = bx;
regset.x.dx  = dx;
regset.x.si  = si;
regset.x.di  = di;
regset.x.cflag = cflag;
}

```

READ AN INTEGER VALUE FROM KEYBOARD AND ECHO TO THE SCREEN AT CURRENT CURSOR POSITION

```

#include <dos.h>
#include <stdio.h>
#include <ctype.h>
#include <stdlib.h>
#include <math.h>

```

```

#define video 0x10
#define key 0x21

```

```

rint(pint)
int *pint;

```



```

{
char *text;
char *tocon;
char safe[30];
int attrib;
int row,col;
int sign_flag = 0;
int radix_flag = 0;

union REGS regset;

    struct SREGS segregs;
    unsigned int ax,bx,dx,si,di,cflag;
    unsigned int cs, ds, es, ss;
    segread(&segregs);
    cs = segregs.cs;
    ds = segregs.ds;
    es = segregs.es;
    ss = segregs.ss;
    ax = regset.x.ax;
    bx = regset.x.bx;
    dx = regset.x.dx;
    si = regset.x.si;
    di = regset.x.di;
    cflag = regset.x.cflag;

tocon = &safe[0];
text = tocon;

/* get current cursor position and attribute */
    regset.h.ah = 3;
    regset.h.bh = 0;
    int86x(video, &regset, &regset, &segregs);
    row = regset.h.dh;
    col = regset.h.dl;

attrib = vattrib(row,col);

/* read a char from keyboard and check in */
getmore:

    regset.h.ah = 7;
    int86x(key, &regset, &regset, &segregs);
    *text = regset.h.al;
    if ( toascii(*text) == 13) goto done;
    if ( toascii(*text) == 8 )
        { if (text <= tocon) goto rt_margin;
          text--; col--;
          setpos(row,col);
          regset.h.ah = 0x9;
          regset.h.bh = 0;
          regset.x.cx = 1;
          regset.h.bl = attrib;
          regset.h.al = 0x20;
          int86x(video, &regset, &regset, &segregs);
rt_margin:
          goto getmore;}

    if ( isdigit(*text) != 0 ) goto echo;
    if ( *text == '+' || *text == '-' && sign_flag == 0)
        {sign_flag = 1; goto echo;}

    goto getmore;

```

```

/* echo character to crt */
echo:
    regset.h.ah = 0x9;
    regset.h.bh = 0;
    regset.x.cx = 1;
    regset.h.bl = attrib;
    regset.h.al = *text;
    int86x(video, &regset, &regset, &segregs);
    text++;
    col++;
    setpos(row,col);
    if (col > 79 ) goto done;
    goto getmore;

```

```

done:
    *text = '\0';
    *pint = atoi(tocon);
    segregs.cs = cs;
    segregs.ds = ds;
    segregs.es = es;
    segregs.ss = ss;
    regset.x.ax = ax;
    regset.x.bx = bx;
    regset.x.dx = dx;
    regset.x.si = si;
    regset.x.di = di;
    regset.x.cflag = cflag;

```

```

}

```

READ A REAL NUMBER FROM KEYBOARD AND ECHO TO THE SCREEN AT CURRENT CURSOR POSITION

```

#include <dos.h>
#include <stdio.h>
#include <ctype.h>
#include <math.h>

#define video 0x10
#define key 0x21

rfl(pnum)
float *pnum;
{
    char *text;
    char *tocon;
    char safe[30];
    int attrib;
    int row,col;
    int first_flag = 0;

    union REGS regset;

    struct SREGS segregs;
    unsigned int ax,bx,dx,si,di,cflag;
    unsigned int cs, ds, es, ss;
    segread(&segregs);
    cs = segregs.cs;

```

```

ds = segregs.ds;
es = segregs.es;
ss = segregs.ss;
ax = regset.x.ax;
bx = regset.x.bx;
dx = regset.x.dx;
si = regset.x.si;
di = regset.x.di;
cflag = regset.x.cflag;

regset.h.ah = 0x9;
regset.h.bh = 0;
regset.h.bl = 0;
regset.x.cx = 1;
regset.h.al = 0;

text = &safe[0];
tocon = text;

/* get current cursor position and attribute */
regset.h.ah = 3;

int86x(video, &regset, &regset, &segregs);
row = regset.h.dh;
col = regset.h.dl;

attrib = vattrib(row,col);

/* read a char from keyboard and check in */
getmore:
    regset.h.ah = 7;
    int86x(key, &regset, &regset, &segregs);
    *text = regset.h.al;
    if ( toascii(*text) == 13) goto done;

    if ( toascii(*text) == 8 )
    { if (text <= tocon) goto rt_margin;
      text--; col--;
      setpos(row,col);
      regset.h.ah = 0x9;
      regset.h.bh = 0;
      regset.x.cx = 1;
      regset.h.bl = attrib;
      regset.h.al = 0x20;
      int86x(video, &regset, &regset, &segregs);
rt_margin:
      goto getmore;}

    if ( isdigit(*text) != 0 )
        {first_flag = 1 ; goto echo;}

    if ( *text == '+' || *text == '-' ) goto echo;
    if ( *text == '.' ) goto echo;
    if (*text == 'e' || *text == 'E' && first_flag == 1)
        goto echo;

        goto getmore;

/* echo character to crt */
echo:

    regset.h.ah = 0x9;
    regset.h.bh = 0;

```

```

    regset.x.cx = 1;
    regset.h.bl = attrib;
    regset.h.al = *text;
    int86x(video, &regset, &regset, &segregs);
    text++;
    col++;
    setpos(row,col);
    if (col > 79 ) goto done;
    goto getmore;

```

```

done:
*text = '\0';
*pnum = atof(tocon);

```

```

    segregcs.cs = cs;
    segregcs.ds = ds;
    segregcs.es = es;
    segregcs.ss = ss;
    regset.x.ax = ax;
    regset.x.bx = bx;
    regset.x.dx = dx;
    regset.x.si = si;
    regset.x.di = di;
    regset.x.cflag = cflag;

```

```

)

```

WRITE AN INTEGER VALUE ON THE SCREEN AT THE CURRENT CURSOR LOCATION

```

#include <dos.h>
#include <math.h>

```

```

pint( integ )

```

```

int *integ;

```

```

{
int intno = 0x10;
int attrib;
char *text;
char strng[20];
int row,col;
union REGS regset;
    struct SREGS segregcs;
    unsigned int ax,bx,dx,si,di,cflag;
    unsigned int cs, ds, es, ss;
    segread(&segregcs);
    cs = segregcs.cs;
    ds = segregcs.ds;
    es = segregcs.es;
    ss = segregcs.ss;
    ax = regset.x.ax;
    bx = regset.x.bx;
    dx = regset.x.dx;
    si = regset.x.si;
    di = regset.x.di;
    cflag = regset.x.cflag;

```

```

    regset.h.ah = 0x9;
    regset.h.bh = 0;
    regset.h.bl = 0;
    regset.x.cx = 1;

```



```

regset.h.al = 0;
regset.h.ah = 3;
int86x(intno, &regset, &regset, &segregs);
row = regset.h.dh;
col = regset.h.dl;

text = &strng[0];
attrib = vattrib(row,col);

itoa(*integ,strng,10);

while (*text != '\0' )
{
    regset.h.bl = attrib;
    regset.h.ah = 0x9;
    regset.h.bh = 0;
    regset.x.cx = 1;
    regset.h.al = *text;
    int86x(intno, &regset, &regset, &segregs);
    text++;
    col++;
    setpos(row,col);
}

segregs.cs = cs;
segregs.ds = ds;
segregs.es = es;
segregs.ss = ss;
regset.x.ax = ax;
regset.x.bx = bx;
regset.x.dx = dx;
regset.x.si = si;
regset.x.di = di;
regset.x.cflag = cflag;
}

```

WRITE AN REAL VALUE ON THE SCREEN AT THE CURRENT CURSOR LOCATION WITH A SPECIFIED NUMBER OF DECIMAL PLACES

```

#include <dos.h>
#include<stdlib.h>

pfl( floater, precision )

float *floater;
int precision;

{
    int intno = 0x10;
    int attrib;
    char *text;
    char strng[20];
    int row,col;
    union REGS regset;
    struct SREGS segreg;
    unsigned int ax,bx,dx,si,di,cflag;
    unsigned int cs, ds, es, ss;
    segread(&segreg);
    cs = segreg.cs;
    ds = segreg.ds;
    es = segreg.es;
    ss = segreg.ss;
}

```

```

ax = regset.x.ax;
bx = regset.x.bx;
dx = regset.x.dx;
si = regset.x.si;
di = regset.x.di;
cflag = regset.x.cflag;

```

```

regset.h.ah = 0x9;
regset.h.bh = 0;
regset.h.bl = 0;
regset.x.cx = 1;
regset.h.al = 0;
regset.h.ah = 3;
int86x(intno, &regset, &regset, &segregs);
row = regset.h.dh;
col = regset.h.dl;

```

```

text = &strng[0];
attrib = vattrib(row,col);

```

```

gcvt(*floater,precision,strng);

```

```

while (*text != '\0' )
{
    regset.h.bl = attrib;
    regset.h.ah = 0x9;
    regset.h.bh = 0;
    regset.x.cx = 1;
    regset.h.al = *text;
    int86x(intno, &regset, &regset, &segregs);
    text++;
    col++;
    setpos(row,col);
}

```

```

segregs.cs = cs;
segregs.ds = ds;
segregs.es = es;
segregs.ss = ss;
regset.x.ax = ax;
regset.x.bx = bx;
regset.x.dx = dx;
regset.x.si = si;
regset.x.di = di;
regset.x.cflag = cflag;

```

```

)

```

APPENDIX B

PROGRAM TO CALCULATE THE ELASTIC ENERGY FROM THE ELEMENTAL STRESS OUTPUT FILE OF COSMOS M FOR SHELL ELEMENTS

Coded in Microsoft "C" version 5.0

```
#include <stdio.h>
#include <conio.h>
#include <math.h>
#include <string.h>
#include <ctype.h>
#include <io.h>
#include <types.h>
float stress[6][1600];

main()
{
    float d1,d2,d3,d4,d5,d6,d7,d8;
    float ex,nuxy,vol;
    float sum1,sum2;
    char filnam[60];
    char xc[60];
    char str1[60];
    char str2[60];
    char str3[60];
    char str4[60];
    char str5[60];
    char str6[60];
    char str7[60];
    char str8[60];
    char str9[60];
    char str10[60];
    FILE *input, *output;
    char *result;
    int i,j,l,elems;
    vclear(0,0,24,79,2);
    setpos(0,0);

    /* Initialize pointers */
    result = &str1[0];

    /* Retrieve file */
    say(0,0,"Enter complete filename with path and extension: ");
    rstr(&filnam[0]);

    l = strlen(filnam);
    strcpy(xc, filnam);
    input = fopen(xc,"r");
    output = fopen("stresses","r+w");

    vclear(0,0,24,79,2);
    setpos(0,0);

    printf("How many elements? ");
    scanf("%d",&elems);
    printf("total volume? ");
```

```

scanf("%f",&vol);

/* read output file stresses */
i = 0;

for(j=0; j<elems; j++)
{
fscanf(input,"%s %s %d \n",str1,str2,&l);
fscanf(input,"%s %s %s %s %s %s %s %s %s \n", /* element number */
str1,str2,str3,str4,str5,str6,str7,str8,str9,str10);
/*moment labels */
fscanf(input,"%s %s %s %s %s %s %s %s %s \n",
str1,str2,str3,str4,str5,str6,str7,str8,str9);
/*moments and velocities */
fscanf(input,"%s %s %s %s %s %s %s %s %s \n",
str1,str2,str3,str4,str5,str6,str7,str8,str9);
/*stress labels */
fscanf(input,"%s %e %e %e %e %e %e
\n",str1,&stress[0][i],&stress[1][i],&stress[2][i],&stress[3][i],&stress
[4][i],&d2);
i++; /* top stresses */
fscanf(input,"%s %e %e %e %e %e %e
\n",str1,&stress[0][i],&stress[1][i],&stress[2][i],&stress[3][i],&stress
[4][i],&d2);
i++; /*bottom stresses*/
}

vclear(0,0,24,79,2);
setpos(0,0);

/* print stresses on screen */
for(j=0; j<i; j++)
{
printf("%d %e %e %e %e %e
\n",j, stress[0][j], stress[1][j], stress[2][j], stress[3][j], stress[4][j]);
}

fclose(input);
fclose(output);

/* calculate elastic energy */
ex = 2500.0;
nuxy = 0.34;
sum1 = 0.0;

for(j=0; j<=i; j++)
{
sum1 = sum1 + pow(stress[0][j],2.0) + pow(stress[1][j],2.0);
sum1 = sum1 - 2.0*nuxy*stress[0][j]*stress[1][j];
sum1 = sum1 +
2.0*(1+nuxy)*((pow(stress[2][j],2.0))+(pow(stress[3][j],2.0))+(pow(stres
s[4][j],2.0)));
}
sum2 = (sum1*vol)/(2.0*ex*elems*2.0);

printf(" total strain energy = %e \n", sum2);

} /* end brace */

```


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