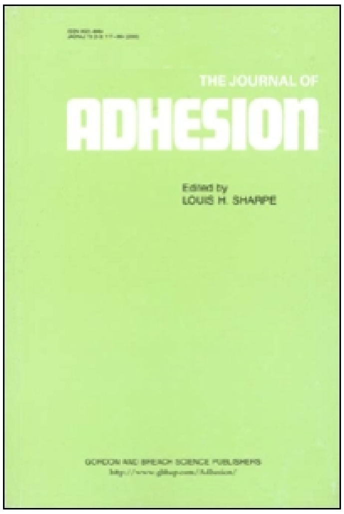

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Calorimetric Measurements of The Heat Generated by The Peel Adhesion Test

J. L. Goldfarb[a]; R. J. Farris[a]
[a] Polymer Science & Engineering Department, University of Massachusetts, Amherst, MA, U.S.A.

To cite this Article Goldfarb, J. L. and Farris, R. J.(1991) 'Calorimetric Measurements of The Heat Generated by The Peel Adhesion Test', The Journal of Adhesion, 35: 4, 233 — 244
To link to this Article: DOI: 10.1080/00218469108041010
URL: http://dx.doi.org/10.1080/00218469108041010

J. Adhesion, 1991, Vol. 35, pp. 233–244
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United Kingdom

Calorimetric Measurements of The Heat Generated by The Peel Adhesion Test

J. L. GOLDFARB and R. J. FARRIS*

Polymer Science & Engineering Department, University of Massachusetts, Amherst, MA 01003, U.S.A.

(Received March 9, 1991; in final form May 21, 1991)

The peel test is a simple mechanical test commonly used to measure the adhesion of flexible films bonded to rigid substrates. When the film is deformed elastically during peeling, the peel force is a direct measure of the strength of the interface. However, when plastic deformation takes place, the work of detachment is much larger than the thermodynamic work of forming the fracture surfaces. Simultaneous mechanical and calorimetric measurements of the work of detachment and the heat generated during the peeling of polymeric films from metal substrates and metal films from polymeric substrates have been made. An energy balance for peeling has been proposed. Most of the work of peeling was consumed by plastic deformation. The peeled polymer dissipated approximately one half of the work of peeling as heat and most of the remainder was stored in the peeled material. The peeled metal dissipated most of the work of peeling as heat.

KEY WORDS Adhesion; peel energy; calorimetric measurements; thermal dissipation; inelastic deformation; energy balance.

1 INTRODUCTION

The peel test is a simple 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 being 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 thin films which strongly adhere to rigid substrates, the peel force is sufficient to cause inelastic deformation near the point of detachment where the material is subjected to severe curvature.[1] Under these conditions, the work of detachment will significantly exceed the true adhesion. Thus, the peel test is extremely sensitive to energy dissipative mechanisms. Detailed theoretical analysis of plastic deformation during peeling have been presented by Kim[2] and Gent.[3,4]

Interestingly, not all of the energy consumed by plastic deformation and viscous dissipation is dissipated as heat. In this paper, the results of simultaneous mechan-

---

*Corresponding author.

ical and calorimetric measurements of the work and heat of peeling are presented and an energy balance for peeling is proposed.

2 ENERGY BALANCE

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, ΔQ.

$$\Delta W = \Delta U - \Delta Q \tag{1}$$

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

$$\Delta U = \Delta U_{\text{surface}} + \Delta U_{\text{elastic}} + \Delta U_{\text{stored}} \tag{2}$$

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.

$$\Delta U_{\text{surface}} = W_A \tag{3}$$

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

$$\Delta W = W_A + \psi + \Delta U_{\text{elastic}} \tag{4}$$

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.

$$\psi = \Delta U_{\text{stored}} - \Delta Q \tag{5}$$

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.[5] The total elastic strain energy in the film is

$$U_{\text{ELASTIC}} = \frac{1}{2} V_0 (\sigma_{ij} e_{ij}) \tag{6}$$

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.

$$U = \frac{V_0}{2E} [\sigma_{xx}^2 + \sigma_{yy}^2 + \sigma_{zz}^2 - 2\nu(\sigma_{xx}\sigma_{yy} + \sigma_{xx}\sigma_{zz} + \sigma_{yy}\sigma_{zz}) + 2(1+\nu)(\sigma_{xy}^2 + \sigma_{xz}^2 + \sigma_{yz}^2)] \tag{7}$$

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

$$\Delta U_{\mathrm{ELASTIC}} = -\frac{t\sigma_1^2}{E}(1-\nu) \tag{8}$$

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

$$\Delta W = -\frac{t\sigma_1^2}{E}(1-\nu) + \Delta U_{\mathrm{surface}} + \Delta U_{\mathrm{stored}} - \Delta Q \tag{9}$$

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

3 EXPERIMENTAL

3.1 Materials

The peel test samples used in this study were prepared by spin coating a solution of polyamic acid, polymerized from pyromellitic dianhydride and oxydianiline, onto .004" (.10 mm) aluminum substrates which were bonded to glass plates to prevent curling. The substrates were etched in chromic acid and solvent wiped prior to coating. After coating, the samples were placed in a 150°C oven, driving off the solvent and forming a partially imidized polyamic acid coating. Additional layers were applied on top of the polyamic acid to produce thick coatings. The samples were exposed to a final temperature of 360°C under nitrogen, totally converting the polyamic acid to polyimide. The structure of the fully imidized polymer is shown in Figure 1. After curing, the aluminum was separated from the glass plates and peel test samples were prepared by cutting strips from the polymer/metal sheets.

3.2 Techniques and Equipment

The heat and work of peeling were measured using a deformation calorimeter developed by Farris and Lyon.[6] The instrument operates by measuring pressure changes

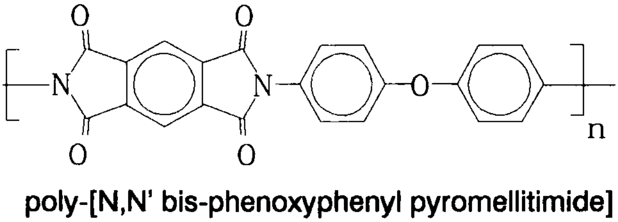

FIGURE 1 Structure of fully cured polyimide coating.

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. The reference chamber is identical to the sample chamber so that no relative pressure change results from volume changes due to motion of the wires. The sample volume is small compared with 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 mechanical tester is equipped with a load cell and displacement transducer. All of the electronic transducers are connected to a computer which collects and analyzes the signals. The work is calculated from the force-displacement data and the heat is calculated from the pressure-time data. The instrument is calibrated using electric resistive heating elements. A minimum heat flow of 84 microwatts is required to produce a pressure deflection equal to twice the signal-to-noise ratio. The minimum detectable heat is about 0.42 millijoules and the precision is ±3%.[6]

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

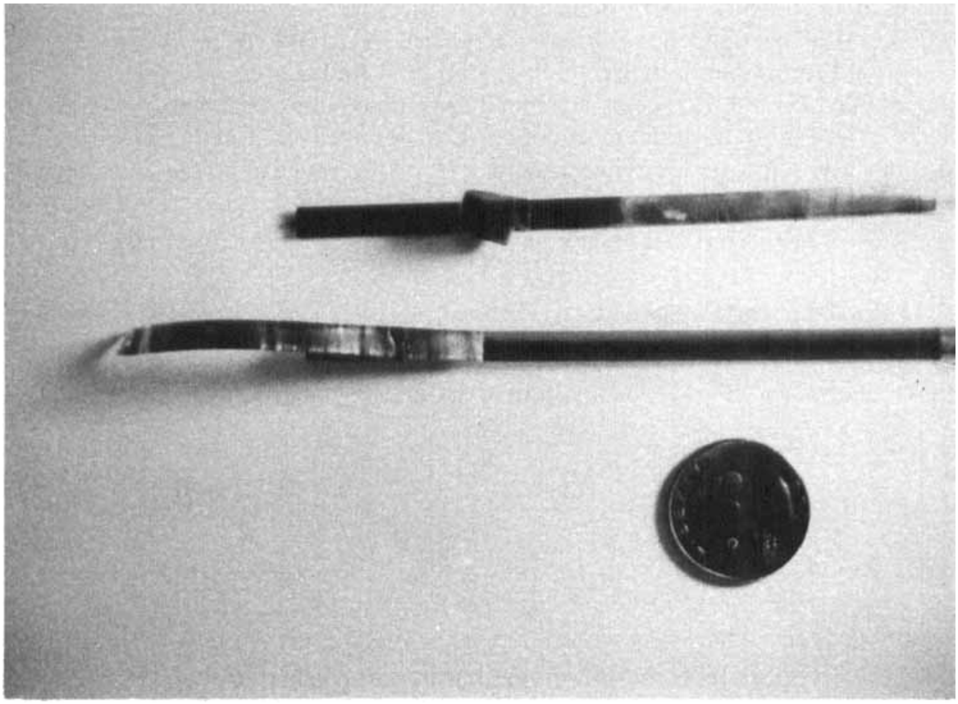

FIGURE 2 Calorimeter peel test samples.

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 RESULTS AND DISCUSSION

In Figure 3, force and differential pressure signals obtained from peeling a polyimide film from aluminum 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 minimum 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. 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 shows the work, heat and internal energy change calculated from the data in Figure 3. The rate of heat dissipation and work expenditure appear to be constant during peeling, increasing proportionally with the peeled area. The total area peeled is .46 (cm^2); the width of the sample multiplied by one-half the crosshead displacement. In 180° peeling, the length of the peeled adherend is one-half the displacement of the testing machine crosshead because the point of

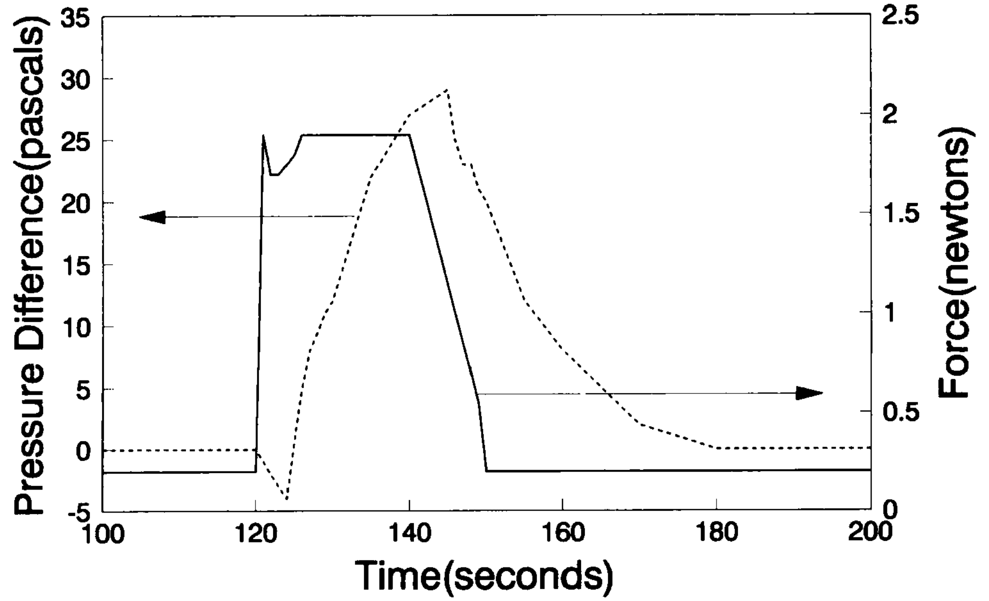

FIGURE 3 Force and pressure signals obtained by peeling polyimide film from aluminum in the calorimeter.

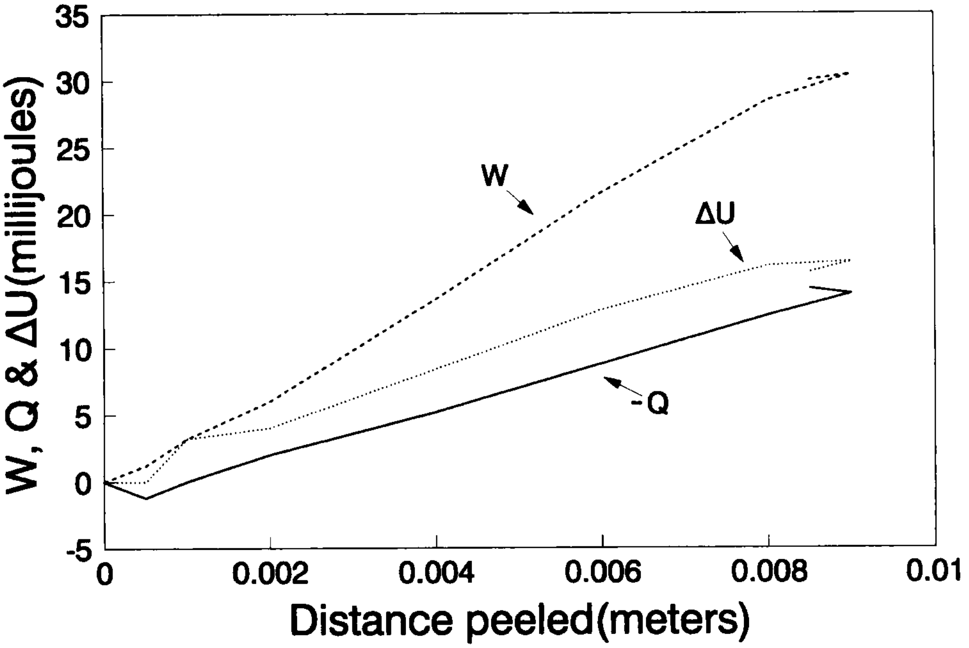

FIGURE 4 Work, (W), heat, (Q), and internal energy change, (ΔU) *versus* distance peeled calculated from the data in Figure 3.

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, conservation of energy requires that the internal energy change has raised the energy of the peeled specimen.

Some of the work expended in peeling may be consumed in breaking chemical bonds. Bond rupture would generate a radical which would then react with another species forming a new chemical bond. There could be a heat effect and an internal energy change associated with bond rupture and reformation. The heat effect and internal energy change due to bond rupture should be small when compared with that due to plasticity or viscoelasticity, particularly for an uncrosslinked polymer where the rupture of a significant quantity of primary chemical bonds is highly unlikely. The polyimide is not highly crosslinked. It is a rigid molecule and thin films exhibit anisotropy due to preferential orientation of the polymer chains in the plane of the film. Furthermore, a very strong preferential orientation of the polymer chains parallel to the interface probably exists near the interface. The lack of a large number of chain axes perpendicular to the interface would favor fracture of the polymer through the rupture of weaker secondary bonds.

It is unlikely that more than 1 (J/M^2) of the measured internal energy change went into creation of the surfaces exposed by peeling. The surface energies of solid polymers can be estimated from liquid contact angle measurements.[7,8] The free surface energy of most polymers is less than .05 (J/M^2) and the free surface energy of most metal oxides is less than 1 (J/M^2).[7]

The peeled material is bent through 180° and exceeds its elastic limit curvature near the point of detachment. The reinforced substrate does not inelastically deform. It is the bending strains that are predominantly responsible for plastic deformation during peeling.[2] As a consequence of inelastic bending, the peeled polymer is tightly curled as seen in Figure 2. The peeled metal also shows visible evidence of plastic deformation. The minimum radius for elastic bending is

$$r_e = Et/2\sigma_o \tag{10}$$

where σ_o is the yield stress. For a 63μm 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 yield strain of polyimide films in tension is approximately .01. Thus, extensive plastic deformation occurs in the bulk of the film during peeling. 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.[9] The ratio of heat to work for drawing of several materials is shown in Table I. The drawing of metals is almost ideally plastic. In contrast, more than half of the energy used to draw thermoplastics is stored in the deformed material. Figure 5 shows the work, heat and internal energy change measured during uniaxial drawing of spun cast polyimide films from which the aluminum substrate was peeled. The samples were drawn in the deformation calorimeter at a constant strain rate to a maximum strain and then retracted immediately until the force on the samples was removed. At extensions beyond the yield strain, more than half of the energy under the stress strain curve is stored in the deformed material. Peeling probably causes molecular rearrangement in the high strain regions of the peeled film similar to that which occurs when the polyimide is subjected to homogeneous tensile or compressive deformation. Thus, it should be expected that the peeled polyimide film contains stored energy.

TABLE I
Ratio of heat to work for plastically drawn materials

Material	ΔQ/ΔW (%)
Copper	92
Lead	98
Aluminum	95
PMMA	45
Polycarbonate	48

Source: Refs. 1, 2.

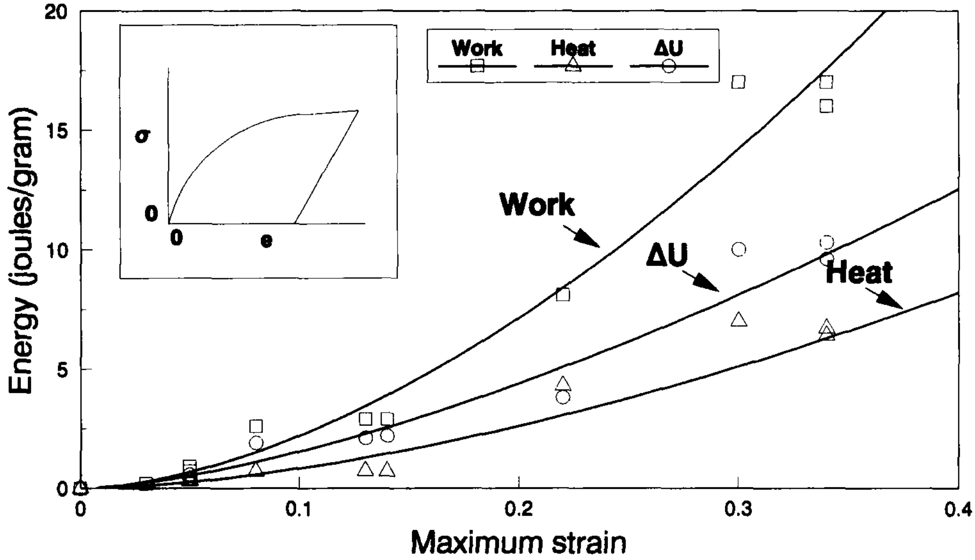

FIGURE 5 The work, heat, and internal energy change, ΔU, were measured during uniaxial drawing of spun cast polyimide films in the calorimeter. The samples were drawn at a strain rate of .011 s^{-1} to the maximum strain and then immediately retracted until the force on the samples was removed.

The heat and work of peeling were measured for samples identical to those shown in Figure 2. Figure 6 compares the ratio of heat to work for both types of peel experiments. The peeled polymer dissipates approximately half of the work of peeling as heat. In contrast, the peeled metal dissipates nearly all of the work of peeling as heat.

The interface chemistry of these samples is identical. If the location and mode of separation are the same, the true adhesion strength of the interface should also be equal. The locus of separation is the same and the surfaces exposed by peeling are similar for both types of peel experiments. The locus of separation was determined by X-ray photoelectron spectroscopy on the surfaces exposed in the peel test. Separation occurs in the polyimide film close to the interface. The same spectra were observed for the metal and polymer exposed in both types of experiments. SEM micrographs were taken of the surfaces exposed by both types of experiments and there were no differences. Therefore, 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.

When aluminum is the substrate, there is no inelastic deformation in the substrate and very little energy is dissipated within the metal. When polyimide is the substrate, there is very little dissipation in the bulk of the film due to bending strains. However, separation occurs cohesively within the polyimide. Thus, some energy is dissipated in the region of the polyimide film close to the interface whether it is the substrate or the peeled film. Dissipation due to separation occurs very close to the interface. The polyimide layer on the aluminum is not visible under an optical microscope and XPS indicates that it is less than 100 angstroms. Deformation and dissipation due

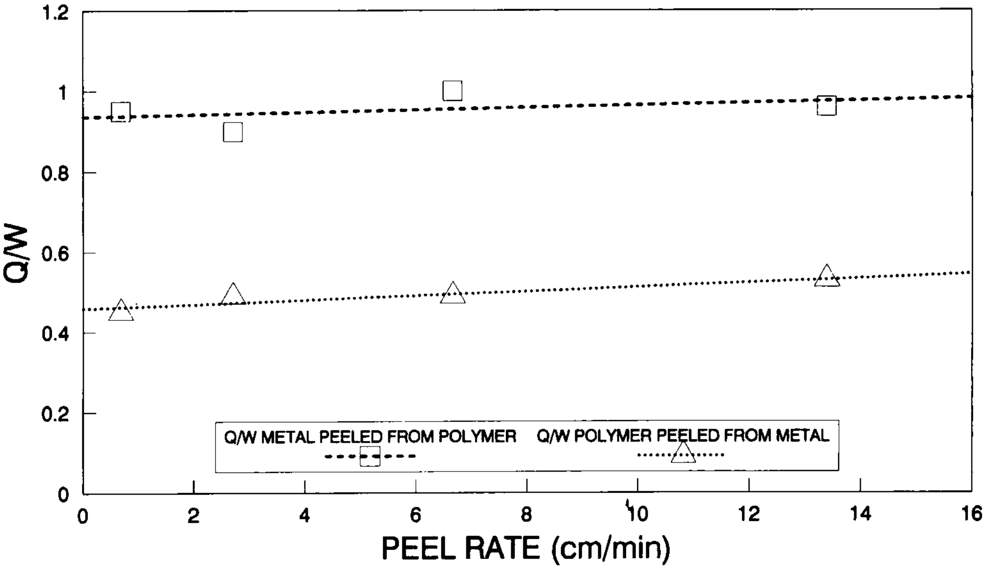

FIGURE 6 The work, (W), and Heat, (Q), were measured in the calorimeter during the peeling of polyimide from an aluminum substrate and aluminum from a polyimide substrate. The peeled material is bent through 180° near the point of detachment exceeding its elastic limit curvature. The substrate is reinforced and does not deform during peeling.

to separation should be confined to a very small zone, compared with the film thickness, near the interface in contrast to the bending deformation which takes place in the bulk of the film during peeling.

Table II compares the work, heat and internal energy change of peeling polyimide and aluminum measured at the same peel rate in the calorimeter. When the aluminum was peeled from polyimide, all but 50 (J/m^2) of the peel energy was dissipated as heat. When the polyimide was peeled from aluminum, 350 (J/m^2) of the peel energy was not dissipated as heat. 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 50 (J/M^2) can be consumed by processes other than plastic deformation or viscous dissipation when the polymer is peeled.

TABLE II
Thermodynamic data from peeling a 63 μm polyimide film from aluminum and peeling 0.004" (0.10 mm) aluminum from polyimide at a peel rate of 2.71 (cm/min)

Thermodynamic quantity	Energy expended (J/M^2) Polymer peeled	Metal peeled
ΔW	660	800
ΔQ	−310	−750
ΔU	350	50

Thus, the energy consumed by dissipative 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 a consequence, the peeled polymer is tightly curled. Some of the 50 (J/m^2) internal energy change measured when the aluminum was peeled may have been stored in the peeled aluminum or in the region of the polyimide where cohesive failure occurred.

Thermodynamically, changes in the structure of the polymer due to peeling induce a non-equilibrium high energy state. At high temperatures or over time periods which are long compared with the duration of experimental observation, these changes may relax out of the material due to molecular rearrangement. When the peeled polymer is placed in an oven at 300°C for 30 minutes, relaxation occurs and it uncurls to a flat state, releasing its stored energy.

Direct quantitative measurements of differences in the enthalpic states of solids can be made using solution calorimetry. In solution, a polymer is able to move freely and quickly comes to an equilibrium state which does not depend on its prior history. Thus, the enthalpy of the polymer in solution should be the same regardless of whether or not the polymer was deformed prior to dissolution. 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. The technique is not well suited to polyimides which are insoluble. 34μm Poly(ethylene terephalate) film, PET, which was bonded to aluminum using a pressure sensitive adhesive, was removed by peeling in the deformation calorimeter resulting in the expenditure of 47.3 (J/g) of work, the production of 40.5 (J/g) of heat and an internal energy change of 6.8 (J/g). The peeled polymer film was placed in one cell of a Setaram C.80 double cell Calvet type solution calorimeter, manufactured by Setaram of Lyon, France. The peeled films were tightly curled showing visible evidence of extensive plastic deformation. Films, from which the aluminum substrate had been peeled, were placed in the other cell of the calorimeter. These films were flat and showed no visible signs of plastic deformation. Before placing the samples in the calorimeter, both the peeled and undeformed samples were placed in methylene chloride, to remove residual traces of the pressure sensitive adhesive. The films were then dried under vacuum at room temperature for several days before being dissolved in the calorimeter using a solution of phenol and tetrachloroethane. The enthalpy of the peeled film was greater than that of the undeformed film. The enthalpy difference between the peeled and undeformed polymer is equal to the energy stored in the peeled polymer. The stored energy in the peeled PET film was 6.6 (J/g) which is almost equal to the internal energy change of peeling measured in the deformation calorimeter. The precision of the solution calorimetry measurements is ±1 (J/g). Thus, the peel energy was almost entirely consumed by dissipative mechanisms accompanying deformation of the peel sample and a significant amount of this energy is stored in the deformed polymer.

We have found that most of the energy required to peel the polyimide/aluminum laminates is consumed by processes other than breaking the bonds which join the materials. As a consequence, it should be possible to separate these materials with far less energy. The elastic energy in a stressed coating increases with coating thickness. Stressed coatings exceeding a critical thickness will spontaneously delaminate when the elastic energy in the coating is greater than the energy required for debonding.[10] The elastic energy in the coating per unit area at the critical thickness is a measure of the adhesion.[11,5] The residual stresses in spun cast polyimide films can be measured using a holographic interferometry technique to a high degree of precision.[12] The elastic energy in a 63μm polyimide film corresponding to the measured stresses is 12 (J/m^2). While this may be small compared with the peel energy, spontaneous delamination was observed for polyimide coatings exceeding 120μm. The strain energy in a 120μm film corresponding to the measured stresses is 23 (J/M^2). Spontaneous delamination requires less energy than peeling because it occurs with less energy dissipation.

5 CONCLUSIONS

The work of peeling a thin flexible material, strongly bonded to a rigid substrate, greatly exceeds the thermodynamic work of adhesion. Most of the work of peeling is consumed by dissipative processes which accompany deformation of the peeled materials. Polymeric adherends are capable of storing a large portion of the peel energy in the peeled material. Metals dissipate most of the peel energy as heat. The peel test measures deformation of the test specimen. It does not measure the true interfacial strength. However, a strong relationship does exist between the nature of the interface and the peel energy because the peeled material can only be subjected to stress (and thus to energy losses) if the interface is strong.[13,14] Thus, the peel test can provide a qualitative measure of adhesion, providing that comparisons are not made between systems which would exhibit dramatically differing amounts of energy dissipation. If no irreversible deformation occurs in the bulk of the test sample when two materials are separated, there will still be dissipation in the region of separation regardless of whether separation occurs interfacially or cohesively within one or both of the layers. The energy required to separate bonded layers when irreversible deformation is confined to the region of the interface would be a useful measure of adhesion.

Acknowledgment

The authors gratefully acknowledge the support of the Materials Research Laboratory at The University of Massachusetts.

References

1. K. S. Kim, *J. Adhesion Sci. Technol.* **3,** 175 (1989).
2. K. S. Kim, *J. Eng. Mat. & Tech.* **110,** 266 (1988).
3. A. N. Gent and G. R. Hamed, *Polym. Eng. Sci.* **17,** 462 (1977).
4. A. N. Gent and G. R. Hamed, *J. Appl. Polym. Sci.* **21,** 2817 (1977).
5. S. G. Croll, *J. Coat. Tech.* **52,** 35 (1980).
6. R. E. Lyon and R. J. Farris, *Rev. Sci. Instrum.* **57,** 8 (1986).
7. A. J. Kinloch, *Adhesion and Adhesives* (Chapman and Hall, New York, 1987), pp. 24–30.
8. T. Hata, Y. Kitazaki and T. Saito, *J. Adhesion* **21,** 177 (1987).

9. G. W. Adams, *The Thermodynamics of Deformation for Thermoplastic Polymers*, Ph.D. Thesis, The University of Massachusetts (1987).
10. H. M. Jensen, J. W. Hutchinson and K. S. Kim, *Int. J. Solids Structures* **26,** 1099 (1990).
11. C. L. Bauer, *The Determination of The Mechanical Behavior of Polyamic Acid/Polyimide Coatings*, Ph.D. Thesis, The University of Massachusetts (1988).
12. R. J. Farris, M. A. Maden, J. L. Goldfarb and K. Tong, *Proc. of The 14th Meeting of The Adhesion Soc.* (1991).
13. C. A. Dahlquist, **ASTM STP 360,** 46 (1963).
14. E. H. Andrews and A. J. Kinloch, *Proc. Royal Soc. Lond. A.* **332,** 385 (1973).