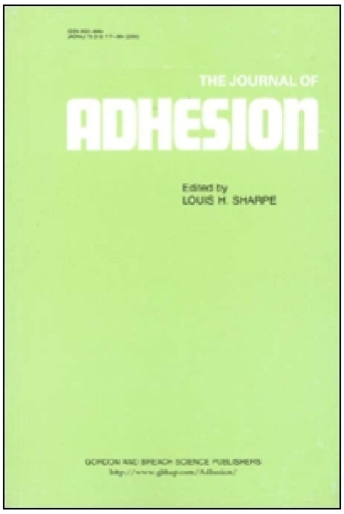

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# Interfacial and Bulk Contributions to Peeling Energy

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# Interfacial and Bulk Contributions to Peeling Energy

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Thin polyurethane films, having low adhesion to dried protein, were developed as candidate materials for non-adhesive surgical dressings. In order to model wound-adhesion, gelatine was cast from solution on to the film and allowed to dry. The film was peeled from the gelatine at 180° peel angle, and the peel force measured as a function of the temperature of test. The dynamic mechanical properties of the films were measured over the range $-90°C$ to $110°C$ and values of $\tan\delta$ were determined at the temperatures employed for peeling. Thus, a correlation was obtained between peeling energy and $\tan\delta$ for each of eight films.

The generalised theory of fracture mechanics states that the adhesive failure energy is given by the product of an interfacial energy term and a "loss function" involving the hysteresis ratio of the material. If the strains are small the hysteresis ratio is proportional to $\tan\delta$. The experimental results show excellent agreement with the theory, but the interfacial term turns out to be much greater than the true interfacial energy (or thermo-dynamic work of adhesion). The reason for this result is discussed.

KEY WORDS: Model for wound-adhesion; model non-adhesive surgical dressing; peeling energy; dynamic mechanical properties; polyurethane films; fracture mechanics; interfacial energy; bulk energy dissipation; work of adhesion; dried gelatine; molecular recoil mechanism.

## INTRODUCTION

This work forms part of a study of the adhesion of surgical dressing to wounds. In a previous paper, a new *in-vitro* test method was described along with results on a variety of commercial wound dressings.[1] Subsequently, a number of solid-film dressing materials were synthesized which exhibited excellent non-stick characteristics to wounds in animal tests.[2] In the current paper, we investigate some of the fundamental adhesive properties of certain of these films, using dried gelatine substrates to mimic dried-out wounds. In particular, we demonstrate the effect of mechanical energy losses on adhesive failure energy and evaluate the interfacial energy term between candidate "non-stick" surgical dressings and the model wound.

There are few published studies on adhesion to wounds, but the reader is referred to Reference 1 for a brief discussion of the relevant literature. Literature relating to the theoretical analysis employed in this paper is cited in the following section.

## THEORETICAL BACKGROUND

It was first proposed by Gent and Schultz,[3] on the basis of experimental findings, that the adhesive failure energy, $\theta$ (per unit area of interface), might be expressed as the product of the true interfacial energy, $\theta_0$, and a term expressing energy dissipation in the system. This proposal was later confirmed theoretically and experimentally by Andrews and Kinloch[4] and Andrews.[5] The results obtained can be written;

$$\theta = \theta_0 \Phi(\dot{c}, T, \varepsilon_0) \tag{1}$$

where $\Phi$ is the "loss function", a dimensionless function depending on debonding rate, $\dot{c}$, temperature, $T$, and strain level, $\varepsilon_0$.

The special value of Equation (1) is that it identifies both the surface energy, $\theta_0$, and the mechanical energy losses as contributing to the adhesive strength. According to generalised fracture mechanics ("GFM"[5]), the loss function, $\Phi$, has an explicit form, which contains the mechanical hysteresis ratio, $\beta$ (the fraction of energy dissipated in a loading-unloading cycle). It is shown that:

$$\theta = \theta_0 \frac{k_1(\varepsilon_0)}{k_1(\varepsilon_0) - \sum_u \{\beta g dx dy\}} \tag{2}$$

where $k_1(\varepsilon_0) = \sum g dx dy$ and $g$ is a distribution function of energy density and $dx$, $dy$ are the dimensions of the "reduced" (dimensionless) 2D element undergoing deformation. The subscript "$u$" indicates that the summation in question is taken only over the unloading regions of the stress field.

Dividing Equation (2) by $k_1(\varepsilon_0)$, and assuming $\beta$ to be independent of position in the stress field,

$$\theta = \theta_0 (1 - \beta \textstyle\sum)^{-1} \tag{3}$$

where,

$$\sum = \frac{\sum_u g dx dy}{\sum g dx dy} \tag{4}$$

Thus $\sum$ is the summation of the energy density distribution function "$g$" for unloading regions of the stress field, as a fraction of the summation for the whole stress field. It must, therefore, be less than unity.

From Equation (3) it can be shown that as $\beta$ varies from 0 (perfect elasticity) to 1 (total plasticity or flow) the loss function varies from 1 to infinity. Therefore, if the adhesive displays simple visco-elasticity, and the substrate is rigid, the dissipative terms tend to zero for infinitely slow peeling; as a result $\Phi = 1$ and the measured adhesive energy, $\theta$, equals $\theta_0$. Extrapolation of peeling energies to zero rate has been used by several workers to measure $\theta_0$.[6-8]

Andrews and Kinloch[4] were able to evaluate $\theta_0$ for a cross-linked rubber adhesive bonded to a range of plastic films by determining the shifts of data from different substrates. They showed that $\theta_0$ equalled the calculated thermodynamic work of adhesion, $w_A$, provided that no primary atomic bonds were created at the interface. For a substrate etched to create surface unsaturation (double bonds), the same authors found that $\theta_0 \gg w_A$. This was expected, since curing the adhesive creates covalent bonds across the interface, which raise $\theta_0$ by large amounts without affecting $w_A$, the latter only reflecting van der Waals interactions. In this case, $\theta_0$ remains a valid parameter while $w_A$ is no longer relevant. Later, Andrews and co-workers[9-10] applied similar methods to the evaluation of $\theta_0$ for epoxy-to-metal and epoxy-to-glass adhesive bonds and followed changes in $\theta_0$ due to the hydrolysis of interfacial bonds.

To measure $\theta_0$, the adhesive failure energy, $\theta$ must first be determined. Peel testing provides a useful means of measuring the adhesion between two surfaces, when at least one of the adherends in flexible. For a peel test in which the adhesive is flexible (or supported on a flexible backing which is, at the same time, stiff in tension) the peeling energy is given by [11]

$$\theta = \frac{P}{b}(1 - \cos\phi) \tag{5}$$

where $P$ is the peel force, $b$ is the width of the peeling strip and $\phi$ is the peel angle. For 180° peel angle, as used in this work,

$$\theta = 2P/b \tag{6}$$

The way in which Equations (1) and (5) are used to obtain $\theta_0$ values for solid films used in this study is the subject of this paper.

## EXPERIMENTAL

### Materials

The experimental materials used were elastomeric polyurethanes containing one of two base polymers, referred to as UA2 and UB4, respectively. To these base polymers were added, in solution, a variety of tri-block additive polymers, all having polydimethyl siloxane as the centre block. These additive polymers (denoted S1, S3, S4 and S5, respectively) were incorporated at different percentages before films were cast from solution. The chemical synthesis followed conventional routes and is not discussed here.

The materials code used in this work is such that, for example, UB4(S1)01 denotes that 1% w/w of siloxane additive S1 was incorporated into base film UB4. The films tested were UA2, UA2(S1)05, UB4(S1)05, UB4(S3)10, UB4(S4)20, UB4(S5)01, UB4(S5)05 and UB4(S5)12.

The compositions of the various ingredients were as follows:

*Base polymers*

| Ingredient | Molecular weight | Mole (UA2) | Moles (UB4) |
|---|---|---|---|
| Polyethylene glycol | 1500 | 1 | 1 |
| Polypropylene glycol | 1025 | 3 | 3 |
| Ethane diol | | 6 | |
| Butane diamine | | | 6 |
| Hexamethylene diisocyanate | 262 | 11 | 11 |

Thus, UA2 and UB4 differ only in respect of the type of chain-extender (diol or diamine) employed.

*Siloxane additives*

S1 A triblock polymer by Petrach having a centre block of polydimethyl siloxane of MW 1000 capped by polyether end-blocks of MW 500.
S2 A triblock having a polysiloxane centre block of MW 1049 (Dow-Corning SFD 119) at 49% w/w, chain-extended with butane diol (10%) and Desmodur W (41%). [this additive was not used in the present study].
S3 A triblock having a centre block of S1, MW 1970, at 66% w/w, chain-extended with butane diol (6%) and Desmodur W (28%).
S4 A diblock consisting of monohydroxy PDMS, MW 13000, at 60% w/w, polymerised with polyethylene glycol (10%) and Desmodur W (30%).
S5 A mixture of monohydroxy hexyl PDMS, MW 13000, at 95% w/w, and trifunctional polyether polyols, MW 1025, at 5% w/w (Pluracol TP440 from BASF), which was mixed with and polymerised into the base polymer.

## Test Procedure

### *Adhesion testing*

The adhesion of films to dried gelatine was measured using the "gelatine test" method described in Reference 1. In this test, a concentrated gelatine solution is cast on to the filmic dressing material, using a rectangular window mould, covered to prevent evaporation from the open mould, inverted, and allowed to dry out by moisture loss through the dressing itself. The gelatine is allowed to dry out over a period of two days at ambient temperature.

The dressings were peeled from the gelatine slab, using a 180° peel angle, on an Instron table model testing machine equipped with an environmental chamber and at a convenient cross head speed of 100 mm/min. The peel force was recorded as a function of time, and the average peel force converted to peeling energy, $\theta$, using Equation (5). The peel test was carried out at different temperatures, ranging from 20 to 40°C.

## Dynamic Mechanical Thermal Analysis

This established technique was used to measure the shear elastic (storage) modulus ($G'$), the shear loss modulus ($G''$), which is related to the viscous dissipation of energy, and $\tan\delta$, which is the ration of $G''/G'$ and indicates the amount of internal damping or energy dissipation at small strains. The value of $\tan\delta$ passes through a maximum at the glass transition temperature ($T_g$).

Samples in the form of circular discs were tested in shear mode on a Polymer Laboratories Dynamic Mechanical Thermal Analyser (DMTA). The shear sandwich geometry is usually used for measuring the rigidity modulus of rubbers and soft adhesives. The samples were prepared by cutting discs of 8 mm diameter using a circular die. The films used in the present study were too thin to provide adequate specimens, and to overcome this problem they were stacked to a thickness of around

1 mm before cutting and tested. The rubbery nature of the films prevent any inter-layer slippage, especially since they are held under positive clamping pressure.

The mechanical response of the sample was measured at a shear strain of approximately 0.02 (corresponding to a maximum displacement of 16 microns) using temperature sweeps from − 90 to + 110°C, a frequency of 1 Hz and a heating rate of 5°C/min.

## RESULTS

### Effect of Testing Temperature on Adhesive Peeling Energy

The effect of temperature upon the peeling energy for two UB4-based films is shown in Figure 1. Figure 1 is a typical example and shows data for the two films UB4(S1)05 and UB4(S3)10. The results for other UB4-based films were similar, displaying a slight decrease in peeling energy with temperature. The $\theta$ values are different for each film, since the bulk chemical composition (and hence the mechanical loss characteristics) differ from film to film. The effect of temperature upon the peeling energy for films UA2 and UA2(S1)05 is shown in Figure 2, where an increase with temperature is revealed, in

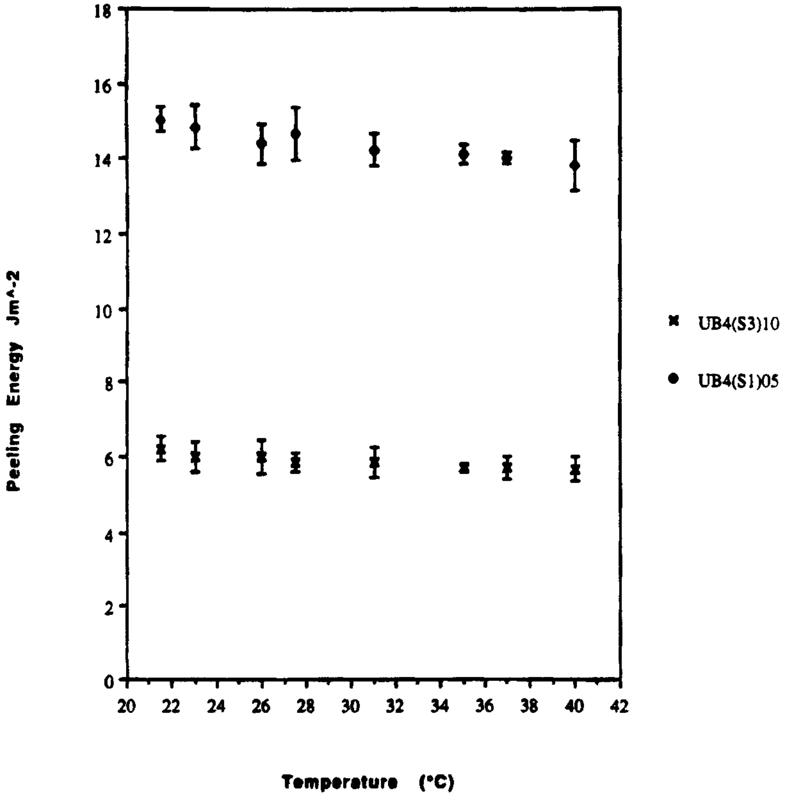

FIGURE 1 Peeling energy as a function of temperature for films UB4(S3)10 and UB4(S1)05.

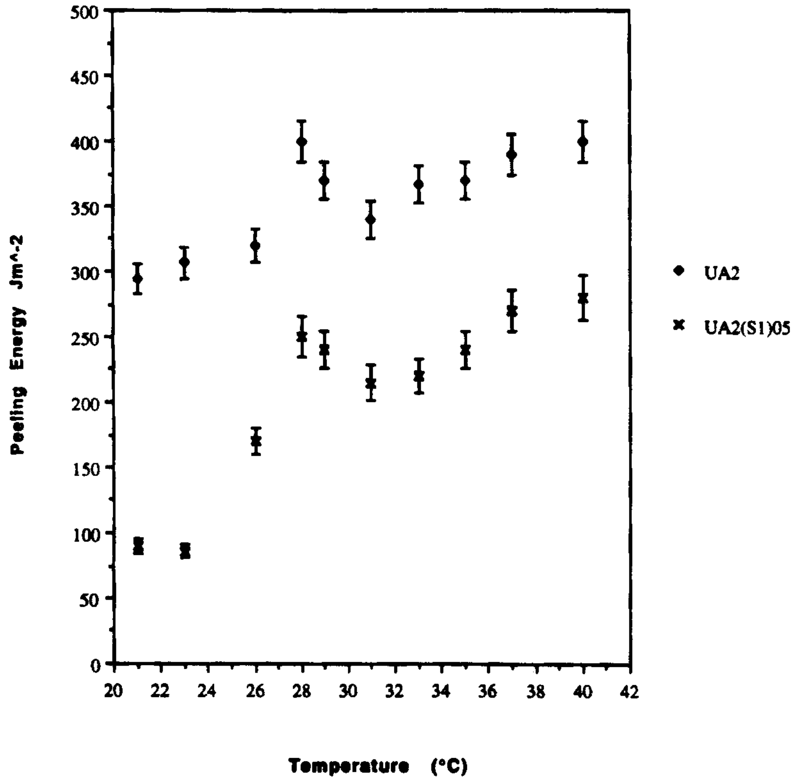

FIGURE 2 Peeling energy as a function of temperature for films UA2 and UA2(S1)05.

contrast to UB4-based films. The effect of raising temperature from 21°C to 40°C is quite marked, more than doubling $\theta$ for the lower adherency film.

Figure 2 also demonstrates the effect of siloxane addition. The $\theta$ values are dependent on the percentage of siloxane used, since this affects both the bulk properties and, more significantly, the surface chemistry. High percentages of siloxane cause a decrease in $\theta_0$ and, hence, give a lower value of $\theta$. The two films in Figure 2 were very similar in bulk composition (so that $\Phi$ should be similar for both) but differed with respect to their surface energy. Thus, both films show similar plots of peeling energy against temperature, with a suggestion of a peak in the curves around 28°C. However, UA2(S1)05 displays significantly lower $\theta$ values than the base-film UA2 over the whole temperature range, due to a decrease in $\theta_0$ caused by the presence of siloxane at the surface.

### Dynamic Mechanical Testing

Typical plots of $G''$ and $\tan\delta$ *versus* temperature for films UA2 and UB4(S1)05 are shown in Figure 3. The results show that $\tan\delta$ and $G''$ go through a maximum (at $T_g$) and then a minimum as the temperature is raised. The "runaway" rise of $\tan\delta$ above $T_g$ is due to the onset of flow following melting of the hard domains in these low-melting, phase-mixed polyurethane systems. The dynamic mechanical response of the other

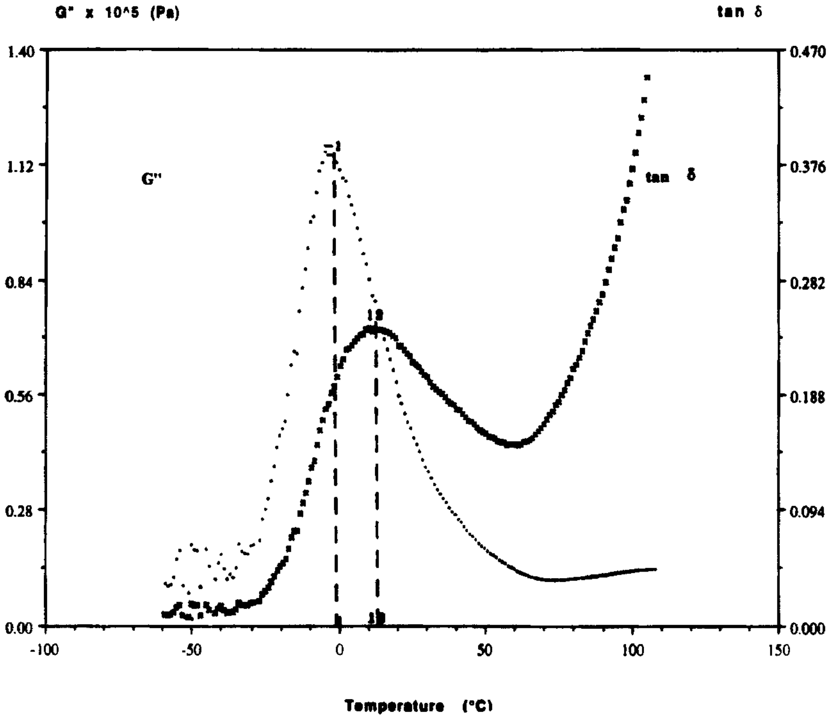

FIGURE 3(a) DMTA traces giving $G''$ and tan $\delta$ as functions of temperature for film UA2.

films resembles the plots shown in Figure 3. The only difference is that $T_g$ differs from film to film due to the different composition and percentages of siloxane used.

## Effect of Hysteresis on Peeling Energy

Figures 4 to 6, respectively, show plots of peeling energy $\theta$ *versus* tan $\delta$ for the following films;

UA2, UA2(S1)05

UB4(S1)05, UB4(S3)10, UB4(S4)20,

UB4(S5)01, UB4(S5)05, UB4(S5)12.

These figures show the values of $\theta$ obtained at any temperature, $T$, plotted against tan $\delta$ obtained by DMTA at the same temperature. The results indicate a linear relationship as follows:

$$\theta_T = \theta_0 + R(\tan\delta)_T \tag{7}$$

where $\theta_0$ and $R$ are constants which vary from one film to the next.

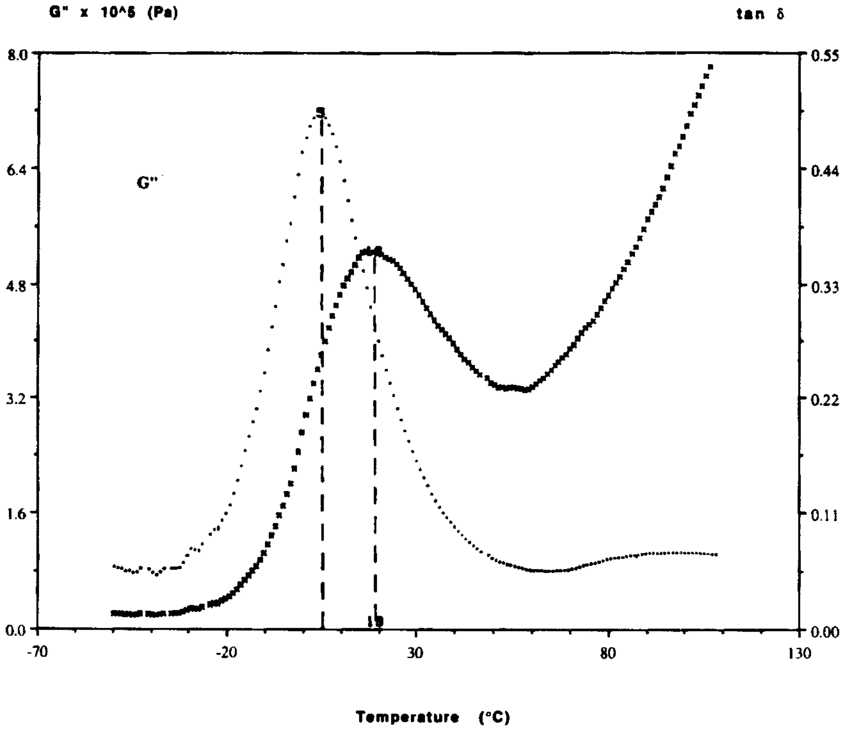

FIGURE 3(b) DMTA traces giving $G''$ and $\tan\delta$ as functions of temperature for film UB4(S1)05.

In order to establish the theoretical significance of the results, and of Equation (7) in particular, we revert to Equation (3):

$$\theta = \theta_0(1 - \beta\textstyle\sum)^{-1} \tag{3}$$

which can be expanded to give:

$$\theta = \theta_0(1 + \beta\textstyle\sum + (\beta\sum)^2 + \cdots) \tag{8}$$

If the term $\beta\sum$ is small, this can be further reduced to:

$$\theta = \theta_0(1 + \beta\textstyle\sum) \tag{9}$$

which is identical in form to Equation (7) provided:

$$R\tan\delta = \theta_0\beta\textstyle\sum \tag{10}$$

Consider now the energy losses around the peeling point (Fig. 7) in a normal, highly adhesive situation. Because the local stresses are high, the energy losses in this vicinity can best be described by $\beta$, since this parameter includes high-strain dissipation processes, such as plastic deformation. Further from the peeling point, however, the

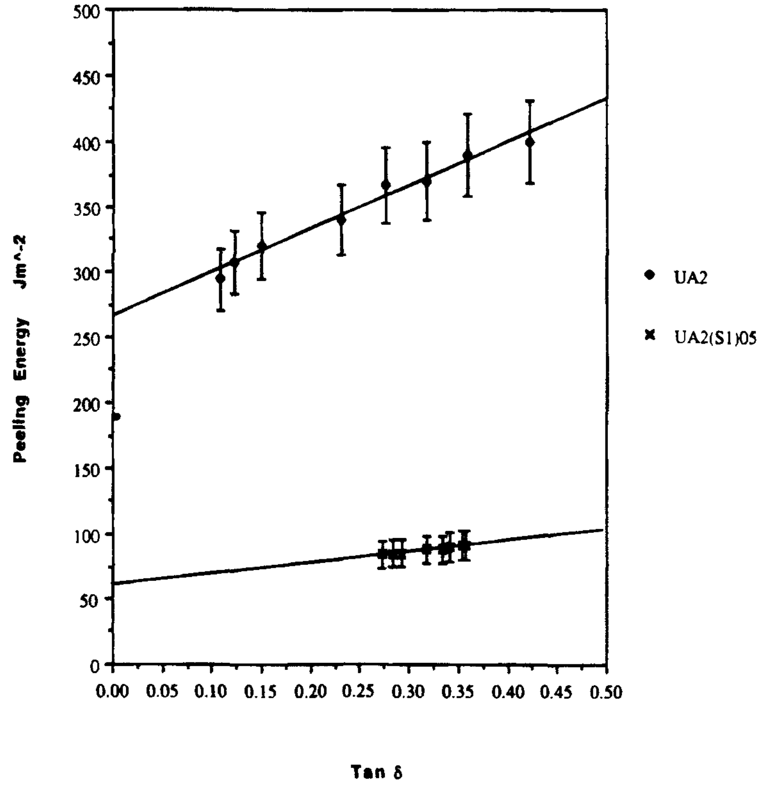

FIGURE 4 Peeling energy *versus* tan $\delta$ for films UA2 and UA2(S1)05.

strains are lower, and the energy losses can equally well be expressed in terms of tan $\delta$. However, in the present work, the adhesive forces are low, so that all the energy losses may, plausibly, be described in terms of tan $\delta$.

McCrum *et al.*[11] have shown that for small strains, $\beta = 2\pi \tan\delta$, and since $\sum < 1$ by definition, and $\beta$ is everywhere less than 0.4, the approximation of Equation (8) and (9) is likely to be valid, with:

$$R = 2\pi\theta_0\sum \tag{11}$$

Thus, theory provides an approximate relationship between $\theta$ and tan $\delta$ which accords with the results of Figures 4 to 6. Specifically, the intercept on the ordinate is identified with $\theta_0$, which is normally considered to be the threshold peeling energy for a perfectly elastic system and equal to the thermodynamic work of adhesion. We shall see presently that this is not necessarily so, and is certainly not the case here. The slope of the experimental curve is identified with $2\pi\theta_0\sum$ and this means, of course, that for a fixed value of the stress-field parameter, the slopes in Figures 4–6 should be proportional to the intercepts.

Figure 8 shows the slopes from Figures 4–6 plotted against their respective intercepts, $\theta_0$. Two straight lines are obtained, one with a slope of 4.07, corresponding to all

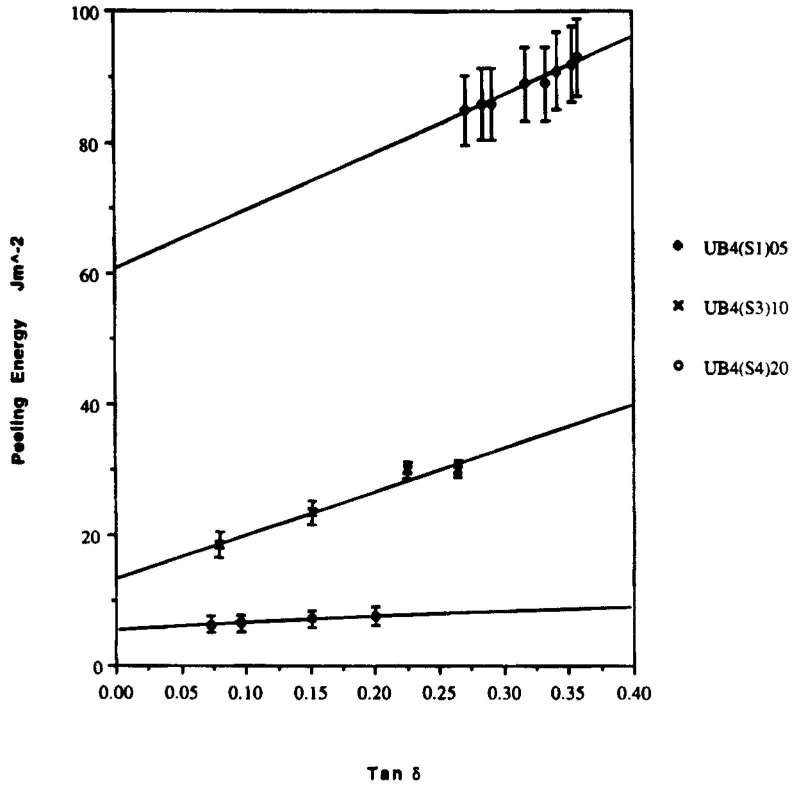

FIGURE 5 Peeling energy *versus* tan $\delta$ for films (UB4)(S1)05, UB4(S3)10 and UB4(S4)20.

films having UB4 as their base polymer, and the other with a slope of 1.31, for the two films based upon polymer UA2. The reason why a single relationship is not obtained for both film-types can plausibly be explained by different energy-density distribution functions ($g$) for UB4 and UA2. The term can be calculated and takes the value 0.21 for UA2 and 0.65 for UB4. These values fully justify the approximation made in Equation (9).

## The Significance of $\theta_0$

It is evident that the $\theta_0$ found (as intercepts in Figures 4–6) can not correspond to a simple interfacial energy, since it is too large (from 5 to 250 $\mathrm{Jm}^{-2}$) even for the hydrogen bonding expected between gelatine and a urethane elastomer. This is not a new observation, Ahagon and Gent[8] having measured rate-independent $\theta_0$ values around 1.4 $\mathrm{J/m^2}$ in the absence of primary or hydrogen bonding, which is still some 25 times too large for a simple Van der Waals interaction energy.

Andrews[12] has pointed out that $\theta_0$ in GFM does not have to be regarded as the thermodynamic work of adhesion, but may rather be seen as the energy consumed (per unit area of crack surface) in a volume of material contained within an arbitrary

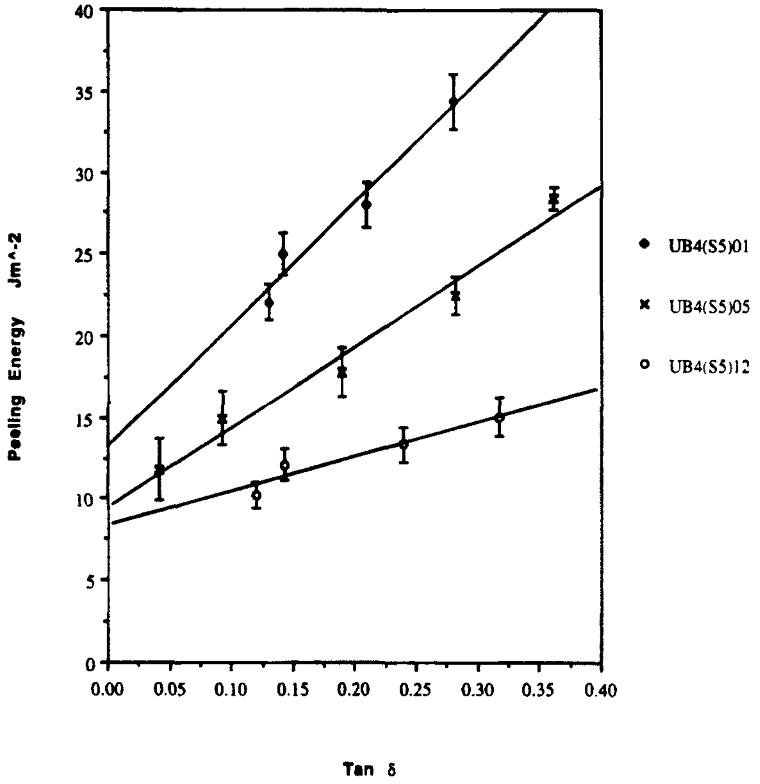

FIGURE 6 Peeling energy *versus* tan $\delta$ for film UB4(S5)01, UB4(S5)05 and UB4(S5)12.

boundary (see Fig. 9). For convenience we call the region within the boundary a "process zone". Only if the boundary is chosen to coincide precisely with the physical surface of the crack is $\theta_0$ equal to $w_A$. Thus, for example, if crack propagation in a glassy plastic is preceded by crazing, the work done within the craze zone can be assigned to $\theta_0$, and the stress-field integration carried out only over the solid polymer, excluding this zone.

This approach can be used here to explain the high values of $\theta_0$. The assumption made earlier that energy losses *everywhere* in the specimen can be characterised by tan $\delta$ is clearly incorrect. By assuming that energy dissipation can be respresented by tan $\delta$, we automatically exclude from the stress-field integration (represented by $\sum$) any "process zone", so that energy losses occurring in such a zone, and exceeding those represented by tan $\delta$, must of necessity appear in $\theta_0$. Even though the adhesion is weak, so that low strains prevail throughout most of the peeling film, there must be a small region around the peeling point where high deformations, and thus the potential for higher energy losses, are to be found.

What is the nature of this localised energy dissipation process? One answer is that given by Ahagon and Gent to explain their results.[8] When a rubberlike network breaks, the energy stored in the broken network chains is dissipated by recoil of the severed

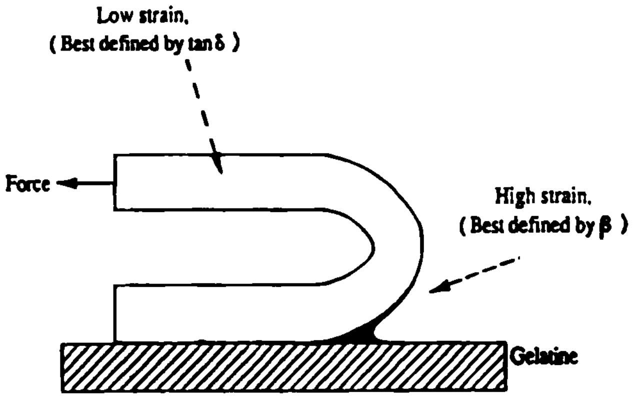

FIGURE 7 Schematic representation of peel test showing region of high strain

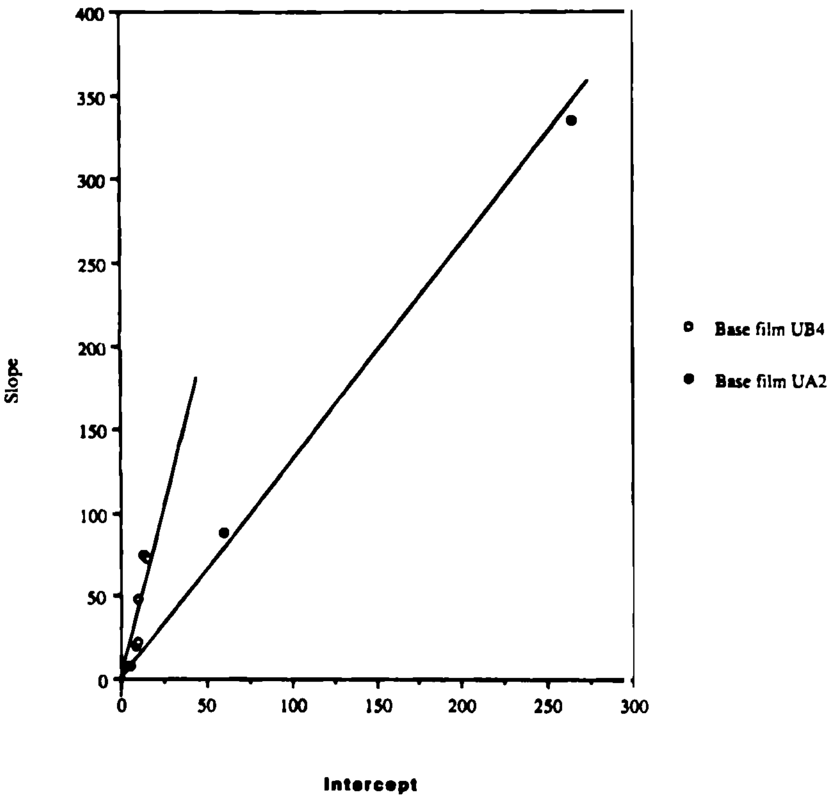

FIGURE 8 A plot of the slopes from Figures 4–6 *versus* the corresponding intercepts.

molecular segments. This stored energy, which is many times larger than the energy required to break a single interatomic bond, must then appear in $\theta_0$. The advantage of this explanation is that the "molecular recoil" process would be insensitive to rate and temperature, as is observed in our case.

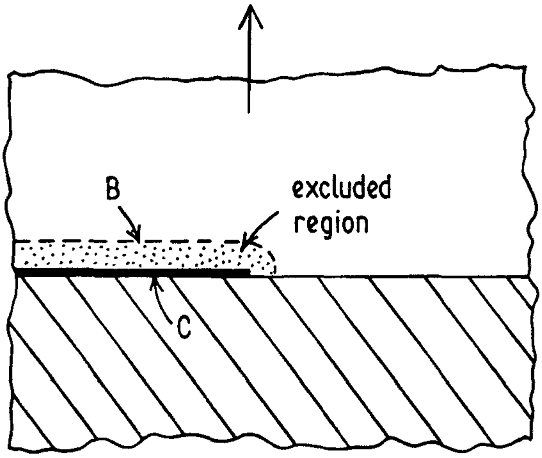

FIGURE 9 Schematic showing region excluded from stress-field integration by assigning an arbitrary boundary, B, around crack C. Energy consumed within the boundary (that is, in the "process zone") appears in $\theta_0$.

An alternative answer is that in phase-mixed polyurethane elastomers, such as used here, the rubberlike network is poor, and the hard domains are small and relatively unstable. They are, thus, prone to plastic deformation with its accompanying energy dissipation. Because the peeling forces are low, such dissipations would be limited to a small "process zone" at the peeling point in which the stresses exceed those required to disrupt the weak rubberlike network. However, because our $\theta_0$ values are independent of temperature, the Ahagon and Gent explanation is more consistent with the facts.

Furthermore, although $\theta_0$ greatly exceeds the true thermodynamic work of adhesion, it remains true under GFM that $\theta_0$ (*measured*) is proportional to $w_A$. This is because Equation (1) can be applied to the process zone itself, as well as to the specimen as a whole. Thus:

$$\theta_0(\text{measured}) = w_A \Phi_2 \tag{12}$$

where $\Phi_2$ is a loss function evaluated only over the process zone and involving the appropriate parameters for the loss process concerned. The effects upon $\theta_0$ of adding siloxane to the system are, therefore, a direct consequence of a reduction in $w_A$ brought about by the presence of siloxane additives at the surface of the film.

## CONCLUSION

The peeling energy of low-adhesion polyurethane films from dried gelatine (representing a dried-out wound) can be separated into an "interfacial" term and a bulk energy dissipation term, using the theory of Generalized Fracture Mechanics (GFM). The bulk dissipation term is governed by $\tan\delta$ for the polymer in the predicted manner. However, the interfacial adhesive energy term turns out to be much greater than the thermodynamic work of adhesion, and must contain energy dissipated by some non-visco-elastic mechanism in a "process zone" around the peeling point. The most likely origin of this energy dissipation is the "molecular recoil" mechanism proposed by Ahagon and Gent.

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